UNITED STATES DEPARTMENT OF COMMERCE • MAURICE H. STANS, *Secretary*
NATIONAL BUREAU OF STANDARDS • LEWIS M. BRANSCOMB, *Director*

JANAF Thermochemical Tables

SECOND EDITION

D. R. Stull and H. Prophet

Project Directors

Office of Standard Reference Data
National Bureau of Standards
Washington, D.C. 20234

NSRDS—NBS 37

Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37, 1141 pages (June 1971)
CODEN: NSRDA

Issued June 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 (Order by Catalog No. C 13.48:37) - Price $9.75
Stock Number 0303-0872

JANAF THERMOCHEMICAL TABLES

Second Edition

Superseding PB 168-370 and addenda 1, 2 and 3.

Prepared under
Air Force Contracts
F04611-67-C-0009
F04611-70-0028

by

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Technically Assisted by
The Thermochemical Working Group
Interagency Chemical Rocket Propulsion Group

July 1970

Foreword

The National Standard Reference Data System provides effective access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, with responsibility to administer it assigned to the National Bureau of Standards.

The System now comprises a complex of data centers and other activities, carried on in academic institutions and other laboratories both in and out of government. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. In addition, the centers and projects establish criteria for evaluation and compilation of data and make recommendations on needed improvements in experimental techniques. They are nornally closely associated with active research in the relevant field.

The technical scope of the NSRDS is indicated by the principal categories of data compilation projects now active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

The NSDRS receives advice and planning assistance from the National Research Council of the National Academy of Sciences-National Academy of Engineering. An overall Review Committee considers the program as a whole and makes recommendations on policy, long-term planning, and international collaboration. Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The NSRDS–NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

The JANAF Thermochemical Tables Project, sponsored and monitored by agencies of the Defense Department, has been considered an important part of the National Standard Reference Data System. The tables have found wide utility in technical areas far removed from those for which the work was initiated. Consequently, when plans for a Second Edition of the JANAF Thermochemical Tables were under discussion, a suggestion was made that they be incorporated into the NSRDS–NBS publication series. This suggestion was accepted, and the present volume, NSRDS–NBS 37, is the outcome. It is hoped that this publication channel will lead to even wider distribution and greater use of these very valuable tables.

LEWIS M. BRANSCOMB, *Director*

PREFACE TO THE FIRST EDITION

Beginning in the mid-1950's, when elements other than the conventional carbon, hydrogen, oxygen, nitrogen, chlorine, and fluorine came into consideration as rocket propellant ingredients, formidable difficulties were encountered in conducting rigorous theoretical performance calculations for these new propellants. The first major problem was calculational techniques. The second was the lack of accurate thermodynamic data.

By the end of 1959, the calculational technique problem had been substantially resolved by applying the method of minimization of free energy to large, high-speed digital computers. At this point the calculations became as accurate as the thermodynamic data upon which they were based. However, serious gaps were present in the available data. For propellant ingredients, only the standard heat of formation is required to conduct a performance calculation. However, this must be known to a high degree of accuracy. For combustion products, the enthalpy and entropy must be known, as a function of temperature, in addition to the standard heat of formation.

In order to resolve the problem, a substantial experimental thermodynamic research program was initiated under the sponsorship and technical direction of Project PRINCIPIA of the Advanced Research Projects Agency. Simultaneously, a project was initiated to critically evaluate and compile consistent tables of thermodynamic properties of propellant combustion products for use by the aerospace industry. This project, known as the "JANAF Thermochemical Tables," was undertaken by the Dow Chemical Company. Since the objective of the project was to have one single source of "best available data" prepared for use by the entire industry, the JANAF Thermochemical Panel undertook the task of furnishing a critical review of the Tables prior to their publication and distribution. This approach was designed to insure that the Tables be of the highest possible quality.

Washington, D.C.
July 1964

G. V. MOCK
Advanced Research Project Agency

PREFACE TO THE SECOND EDITION

It is appropriate to call attention to some of the reasons for the phenomenal success of the JANAF Thermochemical Tables in achieving, first, the initial limited objective of providing the standard data for the chemical rocket propulsion industry, and later, upon publication, world-wide recognition as thermodynamic reference data of the highest quality and timeliness.

First, and most obvious, there was the selection and continued support of a highly competent evaluation team, themselves engaged in a broad specturm of thermodynamic research. The personnel of the Thermal Research Laboratory of the Dow Chemical Company, under the direction of Dr. D. R. Stull and Dr. H. Prophet, have filled this role to a degree of excellence not likely to be exceeded anywhere. Moreover, the group has heroically remained productive in spite of many battles to retain continuing support, and the actual sharp reduction of funding over the past two years to a less-than-viable level.

A second important factor is the unusual approach to format, evaluation, and distribution of the Tables, as it has been followed since their inception. The primary distribution is in frequently issued loose-leaf supplements. Each previously issued table may thus be revised as often as necessary to take account of improved data. Each loose-leaf table is accompanied on its reverse side by a complete explanation of the selection of the key data, together with all references.

The third vital distinction of these Tables has been the existence of a continuing cognizant working group composed of technological users of data, thermodynamicists, and government sponsors of both research and development. Independent prepublication review of the Tables has been an important contribution of some of the members of this group; but its annual technical meetings have resulted in even more far-reaching benefits. Together, the users and generators of data have been able to establish realistic priorities for the species to be included in the Tables; at the same time the course of experimental research has been guided by the demonstration of absence or inadequacy of needed data. Although the working group no longer enjoys official recognition, the members and participants have enthusiastically volunteered to continue meeting in this important work.

Special words of appreciation are due to Dr. Charles W. Beckett, who has lined up all the technical presentations at the last six annual meetings of the working group; and to Mr. Curtis C. Selph who has served with wisdom and insight as the Air Force project monitor for the JANAF Thermochemical Tables contracts.

JOSEPH F. MASI
Air Force Office of Scientific Research

Arlington, Virginia
October, 1970

Members of the JANAF Thermochemical Panel (1959-1961) and the JANAF Thermochemical Working Group (1961-1964) were:

- T. O. Dobbins, Advanced Research Projects Agency (Past Chairman)
- W. H. Jones, Institute for Defense Analysis; Aerospace Corporation (Past Chairman)
- W. G. May, Institute for Defense Analyses; Esso Research and Engineering Company (Past Chairman)
- C. W. Beckett, National Bureau of Standards (Vice Chairman)
- G. W. Avery, Chemical Propulsion Information Agency (Past Secretary)
- B. K. Farris, Chemical Propulsion Information Agency (Past Secretary)
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- B. J. Alley, Army Materiel Command
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- L. J. Gordon, Aerojet-General Corporation
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- D. L. Hildenbrand, Philco Corporation
- J. L. Margrave, University of Wisconsin
- J. P. McCullough, U.S. Bureau of Mines
- P. L. Nichols, Jr., Jet Propulsion Laboratory
- C. C. Selph, Air Force Systems Command
- D. R. Stull, Dow Chemical Company

The Thermochemical Working Group of the Interagency Chemical Rocket Propulsion Group (ICRPG) has consisted of the following at various times during its existence (1964-1969).

Members

- J. F. Masi, Air Force Office of Scientific Research (Chairman)
- C. W. Beckett, National Bureau of Standards (Vice Chairman)
- T. O. Dobbins, Advanced Research Projects Agency
- S. Gordon, National Aeronautics and Space Administration
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- C. E. Selph, Air Force Rocket Propulsion Laboratory
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T. L. Reedy

Project Personnel

The Tables began under the direction of Daniel R. Stull in 1959. Major contributions in the first two years were made by Thomas E. Dergazarian, Samuel Levine and Louis A. DuPlessis. In the years from 1961 to 1969 the major contributors were Jing Chao, Harold Prophet, Alan N. Syverud and Andrew T. Hu. In 1969 Harold Prophet succeeded Daniel R. Stull as project director. At present Alan N. Syverud, Andrew T. Hu and Jerry L. Curnutt are the principal contributors.

Special mention must be made of Alan N. Syverud for his help in the technical editing of the Tables. Also G. C. Sinke has aided the project on numerous occasions with criticism, advice and tables.

We also wish to acknowledge the valuable asssistance of Norma Dumont 1959-64, Viola E. Harrington 1964-66, Carol S. Scheffler 1966-67, Wildene B. Harris 1967-68 and Mary J. Walter since 1968 in the typing of these Tables. Isabel Carr has provided valuable services to the group in abstracting, searching and ordering documents, and proof reading the Tables.

We also wish to thank the staff of the Computation Research Laboratory for their assistance in the many facets of the production of these Tables.

DANIEL R. STULL
HAROLD PROPHET

Contents

Library of Congress Catalog Card Number: 77-611423

CONSTANTS USED

The fundamental constants are those recommended by the International Union of Pure and Applied Chemistry as reported by F. D. Rossini, Pure and Applied Chemistry, 9, 453 (1964). The physical scale based on the atomic mass of $^{12}C = 12$ reported by A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962) is employed. The temperature scale is nominally the 1948 International Practical Temperature Scale for measured quantities and nominally the thermodynamic temperature scale for calculated gaseous quantities. The probable errors between these scales and the 1968 International Practical Temperature Scale are given by T. B. Douglas, J. Research Natl. Bur. Std. 73A, 451 (1969).

Fundamental Constants

Name	Symbol	Value	Units
Velocity of Light	c	2.997925×10^{10}	cm s^{-1}
Planck Constant	h	6.6256×10^{-27}	erg s
Avogadro Constant	N	6.02252×10^{23}	mol^{-1}
Faraday Constant	$\mathcal{F}$	96,487.0	C mol^{-1}
Absolute temperature of the "ice point", 0°C	$T_{0°C}$	273.1500	K
Molar volume of ideal gas	$V_{0°C}$ (1 atm)	22,413.6	cm^3 mol^{-1}
Pressure-Volume product for a mole of gas at 0°C and zero pressure	$(PV)^{P=0}_{T_{0°C}}$	2271.06	J mol^{-1}
Electronic Charge	e	1.60210×10^{-19}	C
Gas constant	R	8.3143 1.987165	J deg^{-1} mol^{-1} cal deg^{-1} mol^{-1}
Boltzmann Constant	k	1.38054×10^{-16}	erg deg^{-1} $molecule^{-1}$
Second radiation constant	c_2	1.43879	cm deg
Constant relating wave number and energy per mole E, in the relation $(\Delta E)=Nhc(\Delta\nu)=Z(\Delta\nu)$	Z	11.96255	J cm mol^{-1}

Defined Constants

Name	Symbol	Value	Units
Standard gravity	g	980.665	cm s^{-2}
Standard atmosphere	atm	101 325	N m^{-2}
Standard millimeter of mercury pressure	mmHg	1/760	atm
Thermochemical calorie	cal	4.1840	J

SYMBOLS AND TERMINOLOGY

Throughout these tables, the symbols used are defined as follows:

amorph.	Amorphous state
B	The rotational constant for diatomic or linear molecules
C_p	Molar heat capacity at constant pressure
c	Crystalline state
D	Centrifugal distortion constant
D_0	Dissociation energy required to break a bond at 0°K
E	Internal or intrinsic energy
G or F	Gibbs energy = E + PV - TS = H - TS
g_i	Quantum weight of electronic states
( )	Parentheses following a vibrational frequency are used to indicate the degeneracy
g	Gaseous state, or statistical weight
GFW	Gram Formula Mass
gls	Glassy state
H	Enthalpy (or heat content) = E + PV
I_A, I_B, I_C	Principal moments of inertia of a molecule
$I_AI_BI_C$	Product of the principal moments of inertia of a molecule
K	Equilibrium constant
k	Hooke's Law force constant
liq. or ℓ	Liquid state
ln	Logarithm to the base e (e = 2.7182818)
log	Logarithm to the base 10
n	Number of potential maxima in an internal rotation
P	Pressure in atmospheres
r	Internuclear distance
S	Entropy
T	Temperature in degrees Kelvin (T° = t° + 273.15°)
t	Temperature in degrees Celsius
V	Volume
V_o	Potential barrier
x	First order vibrational anharmonicity constant
y	Second order vibrational anharmonicity constant
α	Vibrational-rotational interaction constant
ε	Electronic energy level
μ	Reduced mass of the molecule
ρ	Density
σ	Symmetry number
ω	Vibrational frequency
[ ]	Square brackets enclose estimated quantities

Subscripts

a	Atomization
b	Boiling point at one atmosphere pressure
c	Combustion, or critical state
d	Dissociation
e	Equilibrium position
f	Formation from elements in their standard states
i	The i th quantity
m	Melting
p	Constant pressure
r	Reaction
s	Sublimation
t	Transition
v	Vaporization

In addition to the above symbols, the spectroscopic symbols and terminology employed by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., and "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, are adopted.

Circular superscript, °, indicates the thermodynamic standard state.

Numerical subscript, as $_{298.15}$, denotes temperature in Kelvins.

Δ indicates the increment in a given property for a given process or reaction, taken as the value for the final state (or sum for the products) less that for the initial state (or sum for reactants).

ΔH, ΔG, ΔS, ΔC_p equal the increment in enthalpy, Gibbs energy, entropy and heat capacity, respectively, for a process or reaction.

ΔH_f° represents the standard enthalpy of formation, which is the increment in enthalpy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\Delta H^\circ_{c\ 298.15}$ symbolizes the enthalpy of combustion of a given substance, in gaseous oxygen to completely oxidized products at 25°C. and constant pressure, with all reactants and products in their appropriate standard states.

SYMBOLS AND TERMINOLOGY

$\Delta H^\circ_{r\ 298.15}$ represents the enthalpy change in a given reaction at 25°C and constant pressure with all the reactants and products in their appropriate standard states.

When the reaction or process evolves heat, the sign of the change in enthalpy is negative. Conversely, when the reaction or process absorbs heat, the sign of the change in enthalpy is positive.

ΔG°_f or ΔF°_f denotes the standard Gibbs energy of formation, which is the increment in Gibbs energy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\mathrm{Log}_{10}K_p$ stands for the logarithm (to the base 10) of the thermodynamic equilibrium constant of formation for the reaction of forming the given compound from its elements at the indicated temperature.

$(H^\circ_T - H^\circ_{298.15})$ indicates the enthalpy (or heat content) in the standard state at the temperature T less the enthalpy in the standard state at 298.15 K.

$(G^\circ_T - H^\circ_{298.15})/T$ or $(F^\circ_T - H^\circ_{298.15})/T$ denotes the Gibbs energy function in the standard state at temperature T, and is defined as $-S^\circ_T + (H^\circ_T - H^\circ_{298.15})/T$.

S°_T represents the absolute entropy of the thermodynamic standard state at the absolute temperature T, omitting contributions from nuclear spins.

The Standard State is taken as the state at one atmosphere pressure and the temperature under consideration for the solid, liquid, and ideal gas. Only homogeneous substances are considered here.

The Reference State applies to elements in their stable standard state. Consequently the Reference State tables presented here are either single phase or polyphase tables.

CHANGES IN SYMBOLS ON TABLES DATED 6-30-66 OR LATER

The following symbols are used, without periods, to indicate units as follows:

Symbol	Unit	Symbol	Unit
Å	angstrom	eu	calories per degree-mole
atm	atmosphere	g	gram
cal	calorie	J	joule
deg	degree (temperature)	kcal	kilocalorie
°C	degree Celsius	mm	millimeter
°K	degree Kelvin	mol	mole
eV	electron volt	gibbs	calories per degree

Subscripts as defined earlier are used as symbol modifiers but are placed on the same line, thus, heat capacity is abbreviated as Cp°, enthalpy of formation as ΔHf°, etc.

RELATIONSHIP TO SI UNITS

The symbols cal. $\mathrm{mole}^{-1}\ \mathrm{deg}^{-1}$ and gibbs/mol are identical and refer to units of calories per degree-mole. These units can be converted to SI units of joules per degree-mole by multiplying the tabulated values by 4.184. Similarly values in kilocalories per mole can be converted to joules per mole by multiplying with the factor 4184. For further discussions of the SI system and for conversions from other units the reader should consult Pure and Applied Chemistry, 21, 1 (1970).

EVALUATION OF THERMODYNAMIC DATA

A. Interconsistency

The basic aim of these thermodynamic property tables is to provide a related and consistent set of enthalpies and Gibbs energies of formation. This allows the prediction of the enthalpy and gibbs energy changes of any reaction among the constituent of the tables. Since the enthalpy and Gibbs energy of formation are related to each other by the entropy of formation we may choose to make consistent any two of these quantities. The entropy, which is an absolute quantity in thermochemical calculations is ideal for this purpose. Since the enthalpy of reaction is the most common link between different materials, we adopt it as the other consistent quantity. Unfortunately enthalpies are not absolute quantities and in order to achieve consistency it is necessary to provide a consistent base. This is done by referring all enthalpies of formation to the elements in their reference states. By convention the enthalpy of formation of an element in its reference state is zero at all temperatures.

The reference state may be single phase or multiphase and examples of both kinds are found in this compilation. In these tables we have generally chosen the ideal diatomic gas for the reference state of permanent gases such as O_2, N_2, Cl_2 etc. For elements which are solid at room temperature we adopt the solid state up to the melting point, then the liquid up to the boiling point, and then the gas phase. These choices are arbitrary and vary in different compilations. Enthalpies or Gibbs energies of formation taken from different sources should be checked to ensure that the reference states are the same.

The choice of reference states is the first step in any scheme for interconsistency, and is the relation of all quantities to comparable bases. The next step in obtaining an interconsistent set of values, ideally, would be to take all the measured values of enthalpies, Gibbs energies and entropies of reaction and, after adjustment to the proper reference states, to solve the whole set simultaneously. This would provide values for enthalpies, Gibbs energies and entropies which when combined would yield the minimum overall deviations from the measured values. We have already taken this approach in a limited sense by treating grou of interrelated fluorides simultaneously. Hopefully with even larger memories in computers we shall be able to move towards the ultimate goal. As an interim solution it is necessary to fix, simultaneously when possible, certain key values for common reactants such as water, hydrochloric acid, etc., these can then be used to help fix smaller groups of interrelated compounds.

Because of the several revisions of these tables we do not claim to maintain perfect interconsistency. However, the consistency of the tables is a prime concern and a cause for revision if the effects are of the same order of magnitude as the stated uncertainties. As an example, over 100 fluoride tables have been revised since a new HF gas table was adopted in December 1968.

Another type of consistency is involved in systems where properties must be estimated. For example the estimation of certai properties of a series of halides must be done so that the proper graduation in properties occurs from fluoride to iodide and from polyhalide to monohalide. Similarly the evaluation of experimental data must be done in a consistent manner, and this is discussed in the next section.

B. General Evaluation Techniques

1. The Second-Law Method

Starting from the equation $\Delta G° = -T\ell nK$, by differentiation with respect to T and substitution of $d(\Delta G°)/dT = -\Delta S°$, we obtain $\Delta H° = RT^2 d(\ell nK)/dT$, the well known van't Hoff equation. By substituting $dT = -T^2 d(1/T)$ one obtains $\Delta H° = -Rd(\ell nK)/d(1/T)$, thus, the slope of a ℓnK versus $1/T$ plot is $-\Delta H°/R$. If $\Delta H°$ is constant then the slope is constant and the plot is a straight line. Since the variation of $\Delta H°$ with temperature is often quite small it is customary to assume a straight line relationship. This method of obtaining heats of reaction from equilibrium measurements is known as a "second-law" calculation. However, it should be noted that for greatest accuracy the equilibrium measurements should extend over a wide range of temperature, and in this case $\Delta H°$ is probably not constant. Curvature corrections can be applied by assuming a specific form for the variation of $\Delta H°$ with temperature, however, the effects of such corrections are of significance only with very precise measurements. It should be noted that the second law cannot be applied to a single observation, but the third-law method, which is described below, can be used. The second-law method can be applied when only relative values of the equilibrium constant are available, for example, from mass-spectroscopic intensity measurements.

2. The Third-Law Method

The third-law method is based on a knowledge of the absolute entropy of the reactants and products. It allows the calculatio of a reaction enthalpy from each data point when the change in the Gibbs-energy function for the reaction is known. The Gibbs-energy function is defined as $gef_T = (G°_T - H°_{ref})/T$ and is easily calculated from the relation

$$S°_T = -(G°_T - H°_T)/T = (H°_T - H°_{ref})/T - (G°_T - H°_{ref})/T$$

thus,

$$gef_T = -S°_T + (H°_T - H°_{ref})/T.$$

From the definition we can write for the change in a reaction

$$\Delta G°/T = \Delta gef_T + \Delta H°_{ref}/T = -R\ell nKp$$

thus,

$$\Delta H°_{ref}/T = -R\ell nKp - \Delta gef_T$$

where Δ signifies Σ products $-\Sigma$ reactants.

In the JANAF Thermochemical Tables, Gibbs-energy functions are based on 298 K and, thus, yield enthalpies at 298 K regardless of the temperature of the reaction. It should be noted that, since most of these tables are single phase tables, the Gibbs-energy functions of liquids are based on liquid at 298 K even though it may not exist at 298 K. This differs from the usual convention of combining all condensed phases into one table; in this case the enthalpy of reaction refers to the state stable at the base temperature. In these tables the functions always refer to the state of the table at 298 K regardless of its stability. For example, if the vapor pressure over liquid copper is analysed using Cu(ℓ) Gibbs-energy functions the enthalpy of vaporization at 298 K will result. To calculate the enthalpy of sublimation of Cu it is necessary to add the heat of melting at 298 K, which is the difference in the heat of formation of Cu(ℓ) and Cu(c) at 298 K. It should also be noted that Gibbs-energy functions are always negative, thus the function $-(G^\circ_T-H^\circ_T)/T$ is usually tabulated and the proper sign must be remembered when using these functions.

The analysis of data by the third law is generally considered superior to the second-law analysis. It is definitely superior if the Gibbs-energy functions are measured, because each data point is independent of the others. Thus, third-law analysis will often reveal trends in the equilibrium constants of a set of data that indicate nonequilibrium or erroneous values. We have found a combination of the two methods to be so valuable that a third-law calculation is always accompanied by a second-law treatment of the same data. The calculation is done in ascending temperature order to give ΔH_{298} and its deviation from the mean, δ, and the calculated log K_p and its deviation from the least-squares line. Third-law analyses enables bad points to be seen as deviations from the general trend of the differences; thus the method can be used even when the Gibbs-energy functions are estimated. If these bad points are located on the ends of the data set, the second-law line often fits quite well through them and by itself does not arouse suspicion. Moreover, the dropping of such points can bring widely discordant slopes into agreement with each other and often with the third-law values. The data sets given in Table 1 illustrate these comments. The first set of data contains all the reported points and is in disagreement with earlier values around 54 kcal/mole. The third-law analysis indicates the first two points are poor, and the effect of dropping these two is shown in the second set of data. This latter second-law slope has changed considerably; the heat is in good agreement with the earlier data and with the third law. The size of the third-law deviations in the second set indicates that the data are not very reproducible. A deviation of 0.5 kcal at 1000°K represents an uncertainty of 30% in the measured equilibrium constants.

If measured Gibbs-energy functions are available, third-law analysis is preferred; however, if the data are good, the second-law value should agree. When the Gibbs-energy functions are estimated, the third-law values derived from them must be handled carefully. Values that are constant and that agree with the second-law enthalpy indicate that the Gibbs-energy functions and equilibrium data are mutually consistent. A drift with temperature of the third-law values indicates errors in either the data or the functions. The magnitude of such drifts is often given in the table write-up and represents the entropy change required to bring the second- and third-law values into agreement. If the drift is within the experimental entropy uncertainty then the data are acceptable. Drifts which are much larger than reasonable entropy errors generally indicate failure to attain equilibrium.

Table 1. Analysis of Equilibrium Data

$PbF_2(c) \rightarrow PbF_2(g)$, data of Nesmeyanov and Iofa, Russ. J. Inorg. Chem. 4, 219 (1959)

Analysis I

Third Law			Second Law		
T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference
792.0*	54.276	-1.105	-5.959	-6.016	0.057
806.0*	54.004	-1.377	-5.653	-5.816	0.163
852.0	54.980	-0.401	-5.222	-5.207	-0.015
884.0	55.552	0.171	-4.925	-4.820	-0.105
884.0	55.700	0.319	-4.962	-4.820	-0.142
900.0	55.720	0.339	-4.754	-4.637	-0.117
907.0	55.561	0.180	-4.621	-4.559	-0.062
911.0	55.824	0.444	-4.630	-4.515	-0.115
921.0	54.998	-0.383	-4.301	-4.407	0.106
936.0	55.988	0.607	-4.339	-4.248	-0.091
941.0	55.757	0.376	-4.221	-4.197	-0.024
950.0	54.957	-0.423	-3.923	-4.105	0.182
958.0	56.122	0.741	-4.090	-4.025	-0.065
984.0	55.661	0.280	-3.671	-3.774	0.103
988.0	55.611	0.230	-3.614	-3.737	0.123
Average = 55.381			Standard deviation =		0.029
ΔH_{298} = 55.38				ΔH_{298} =	47.29

Analysis II

Third Law			Second Law		
T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference
852.0	54.980	-0.592	-5.222	-5.344	0.122
884.0	55.552	-0.020	-4.925	-4.900	-0.025
884.0	55.700	0.128	-4.962	-4.900	-0.061
900.0	55.720	0.148	-4.754	-4.691	-0.063
907.0	55.561	-0.011	-4.621	-4.601	-0.020
911.0	55.824	0.253	-4.630	-4.551	-0.080
921.0	54.998	-0.574	-4.301	-4.426	0.125
936.0	55.988	0.416	-4.339	-4.245	-0.094
941.0	55.757	0.185	-4.221	-4.186	-0.035
950.0	54.957	-0.614	-3.923	-4.081	0.158
958.0	56.122	0.550	-4.090	-3.989	-0.101
984.0	55.661	0.089	-3.671	-3.701	0.030
988.0	55.611	0.039	-3.614	-3.658	0.045
Average = 55.572			Standard deviation =		0.025
ΔH_{298} = 55.57				ΔH_{298} =	53.79

* Deleted in Analysis II

3. Heat Capacities

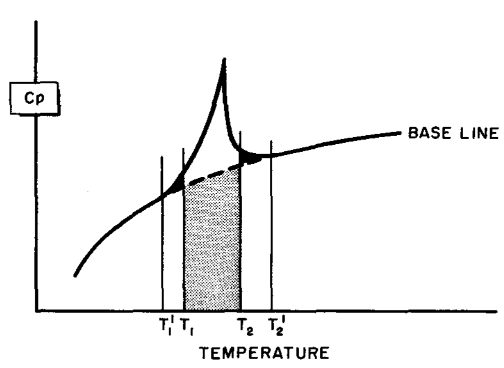
The evaluation of reported values is a relatively subjective procedure, but the analysis should be as objective as possible and therefore certain ground rules must be laid. The first step is the fitting by orthogonal polynomials and the computer-generated plotting of all information so that a general idea of the agreement can be visually obtained. If certain data sets differ from the majority, they are examined for possible causes of the difference. Calibration data, sample purity, and experimental scatter are checked. If the source of error can be located, the data are given appropriately less weight. Otherwise all data of equal reliability are considered equal, even if they disagree. Such data are then smoothed by a weighted orthogonal polynomial curvefit. Enthalpy data are smoothed similarly and heat capacities are derived directly from the differentiated polynomial. The smoothing of enthalpy data requires constraining the fit so that it passes through zero at the reference temperature. Additional constraints are often used to fix the heat capacity at 298 K, or to join enthalpy data smoothly with low-temperature heat capacities.

4. Transitions

The evaluation of solid state transitions involves first the recognition of the type of transition, which may not always be obvious. A first-order transition such as fusion involves a change of enthalpy and entropy at the transition point, whereas second-order transitions involve only discontinuities in heat capacity. Because of impurities and other factors, all first-orde transitions do not occur at one temperature; rather, they spread a little on either side and are sometimes difficult to distinquish from λ-type second-order transitions. In order to evaluate the enthalpy of a first-order transition from heat-capacity data, an enthalpy change $(H_{T_2} - H_{T_1})$ from T_1 to T_2°K must be reported on either side of the transition. The normal heat-capacit curve is extended forward and backward to the temperature of the transition-heat-capacity maximum to form a base line. If T_1' a T_2' are the temperatures at which the transitional heat capacity curve leaves and rejoins the base line, and ubl and obl designa under and over the base line, the heat of transition given by

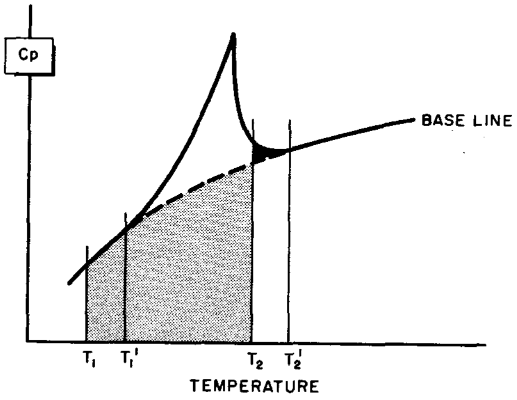
$$\Delta H_t = (H_{T_2} - H_{T_1}) - (H_{T_2} - H_{T_1})_{ubl} + (H_{T_1'} - H_{T_1})_{obl} + (H_{T_2} - H_{T_2'})_{obl}$$

Figures 1 and 2 show two possible cases. The shaded areas represent the enthalpy over the base line and cross-hatched areas the enthalpy under the base line.



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 1



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 2

Many enthalpies of fusion and enthalpies of solid-state transitions are obtained from enthalpy measurements and therefore require different treatment. Here the heats are given directly by the difference in enthalpy at the transition temperature. Normally, the enthalpy above and below can be smoothly extended to the temperature of transition, although the transition temperature may not be clearly obtainable from the enthalpy data.

The heats of the remaining transitions, vaporization and sublimation, are evaluated from equilibrium data by the second- and third-law methods just described except when calorimetric measurements are available.

5. Equilibrium

Perhaps the most significant factors to be established in evaluating equilibrium data are that equilibrium was attained and that the process was properly described. For example, in a sublimation process the most accurate measurements are valueless if the vapor phase is not uniquely defined. If polymerization or breakdown might have occurred, the first order of business is to establish the exact reaction. Because mass spectroscopy has shown that vapor phases are often extremely complex, it is almost a requirement that before equilibrium data can be accepted the vapor phases must be examined by a mass spectrometer to ensure their composition. Some methods of measurement are less accurate than others and should be given less weight. For example, equilibria determined in a mass spectrometer are usually quite rough because many approximations and uncertainties are involved in obtaining an absolute pressure measurement. On the other hand, measurements of the electromotive force of reversible cells can have great accuracy. Once the system is defined and equilibrium data are available, the data are analyzed by the second- and third-law methods.

CONSTRUCTION OF THE TABLES

1. Solid Phase

To produce a final table after all of the data have been evaluated or estimated, the enthalpy of formation, the entropy at 298 K, and the heat capacity at reasonable intervals through the temperature range of interest are needed. The enthalpy is obtained from the heat capacity by evaluating $\int_{298}^{T} C_p dT$. The entropy is similarly obtained from the heat capacity by evaluating $\int_{298}^{T} (C_p/T)dT$. The Gibbs energy function is then obtained from the relation $(G^\circ_T - H^\circ_{ref})/T = -S^\circ_T + (H^\circ_T - H^\circ_{ref})/T$. Enthalpies of formation at temperatures other than 298 K require a knowledge of the enthalpies of the reference elements:

$$\Delta Hf^\circ_T = \Delta Hf^\circ_{298} + (H_T - H_{298})_{compd} - \Sigma(H_T - H_{298})_{elements}$$

The Gibbs energy of formation is readily calculated from the heat of formation when the entropies of the elements are known. Thus

$$\Delta Gf^\circ_T = \Delta Hf^\circ_T - T[S_T(compd) - \Sigma S_T(elements)]$$

The logarithm of the equilibrium constant of formation is then found from the relation $\Delta Gf^\circ_T = -4.5756T \log K_p$.

Until now, we have only considered the calculation of values above 298 K; however, it is desirable to have data all the way to absolute zero. The temperature 0 K is a natural base for measurements involving gases in their lowest energy state, and values are needed in order to convert to the thermochemical reference temperature of 298 K. There is no basic difference in evaluating low-temperature data, but many more heat-capacity points are needed because of the large curvature. It is also necessary to evaluate the starting entropy at some temperature above 0 K because data rarely extend to below 5 K. In order to evaluate enthalpy it is necessary to start with a value above zero and integrate up to 298 K; then the value at 298 K is subtracted from the intermediate values, giving negative values below 298 K.

The tables extend to well above the normal melting point to facilitate the use of the tables by computers which can then interpolate values accurately right at the melting point. Dotted and solid lines indicate the end of the phase stability and solid-state transitions respectively.

2. Liquid Phase

The construction is identical with that used for the solid phase; however, the required data at 298 K are not usually readily available. The data are obtained by calculating a preliminary table using the chosen heat capacities with zero values for ΔHf°_{298} and S°_{298}. The correct starting values are then determined by comparing the values from the tables of crystal and liquid, using the following equations:

$$\Delta Hm^\circ = \Delta Hf^\circ_{Tm}(\ell) - \Delta Hf^\circ_{Tm}(c)$$

$$\Delta Sm^\circ = \frac{\Delta Hm^\circ}{Tm} = S^\circ_{Tm}(\ell) - S^\circ_{Tm}(c)$$

The correct values at 298 K may be obtained from the above relations. A typical liquid table is extrapolated both below the melting point and above the boiling point to facilitate interpolation near the phase boundaries.

3. Gas Phase

The data required for the various types of molecules are summarized below. The equations used are given in the section on Calculational Methods. All molecules require the gram formula mass and enthalpy of formation at 298 K.

Additionally, monatomic species require: $\varepsilon_0, \varepsilon_1 \ldots \varepsilon_n$ and $g_0, g_1 \ldots g_n$

Diatomic species require: $B_e, \sigma, x_e, \omega_e, \alpha_e, \varepsilon_i, g_i$ (i = 0,... n)

Linear polyatomic species require: B_e, σ, ω_i (i = 1,... 3N-5), ε_i, g_i (i = 0,... n)

Nonlinear polyatomic species require: σ, $\log I_A I_B I_C$, ω_i (i = 1,... 3N-6), ε_i, g_i (i = 0,... n)

ε_i is the energy of the i th electronic level
g_i is the statistical weight of the i th electronic level
B_e is the rotational constant
σ is the symmetry number
x_e is the anharmonicity correction = $\omega_e x_e/\omega_e$
ω_e is the fundamental frequency of a diatomic molecule
ω_i is a fundamental frequency of a polyatomic molecule
α_e is the rotational vibrational interaction constant
N is the number of atoms in the molecule
$I_A I_B I_C$ is the product of the moments of inertia

Monatomic species often have a large number of electronic levels; it is usual to average the higher levels taking account of the individual multiplicities. Diatomic and polyatomic species sometimes have several excited states which are low enough to make appreciable contributions. These states are treated by direct summation over the individual partition functions using anharmonic-oscillator approximations for each state. If vibrational and rotational constants for the higher states are not available the calculations are simplified by assuming the ground state values for each state.

4. Multiphase Tables

Tables which show only values for the real phases at one atmosphere pressure are multiphase tables. In this compilation they are generally reference state tables, though some solid phase tables include more than one phase. Multiphase tables can always be recognized by the presence of solid lines, indicating phase transitions, on the table. They are prepared in a manner similar to tables for condensed phases. The functions are evaluated in the same manner as for a solid up to the first transition point; then the heat and entropy of transition are added and the integration is continued using the second-phase heat capacities. At each phase boundary the above process is repeated.

USE OF TABLES

The rapid proliferation of thermodynamic tabulations in recent years brings with it the possibility of serious abuse of th information in them. First, as we explained earlier, not all tabulations are based on the same reference states. To avoid thi pitfall it is helpful to write down the reaction and check the value and state of each component. It is even better to utilize only a single compilation whenever possible, because values from different compilations may not be consistent or compatible. Second, the base temperatures of compilations differ between 0 and 298 K. Only enthalpies and Gibbs-energy functions are affected, but they can result in serious errors if used indiscriminately.

A different type of error is caused by misunderstanding the significance of negative Gibbs-energy changes. For example, m species in the JANAF Thermochemical Tables have large negative Gibbs energies of formation at 6000 K. This does not necessaril imply that the species are stable, but only that the Gibbs-energy change from the elemental reference state is negative. In fa nearly all the elements are monatomic gases at 6000 K, and the reference states are generally unstable with respect to the atom Similarly, a negative Gibbs-energy change does not mean a reaction will occur, but means only that the reaction is favorable as written. For example, at 298 K

$$C + O_2 \rightarrow CO + 1/2\ O_2 \qquad \Delta G_{298} = -32.8 \text{ kcal/mole}$$

However, at normal pressures this reaction would generally be recognized as unlikely in view of

$$C + O_2 \rightarrow CO_2 \qquad \Delta G_{298} = -94.3 \text{ kcal/mole}$$

Similarly, in combining free energies of reaction, one should be careful not to combine impossible reactions with possible ones to obtain an over-all favorability:

$$4C + H_2 + O_2 \rightarrow C_2H_2 + 2CO \qquad \Delta G = -15.6 \text{ kcal/mole}$$

This equation is impossible because we cannot combine the reactions

$$2C + H_2 \rightarrow C_2H_2 \qquad \Delta G = +50.0 \text{ kcal/mole}$$

and

$$2C + O_2 \rightarrow 2CO \qquad \Delta G = -65.5 \text{ kcal/mole}$$

by simple addition. Both reactions must be written so that they are possible. They then become

$$C_2H_2 \rightarrow 2C + H_2 \qquad \Delta G = -50.0 \text{ kcal/mole}$$

$$2C + O_2 \rightarrow 2CO \qquad \Delta G = -65.6 \text{ kcal/mole}$$

Then by simple addition

$$C_2H_2 + O_2 \rightarrow 2CO + H_2 \qquad \Delta G = -115.6 \text{ kcal/mole}$$

Although these tables have been continuously revised it is not possible to keep all the tables fully revised with the latest da Thus, each table indicates the dates of each revision at the foot of the tabular values. The latest date is most important sin information generated after that date has not been incorporated. The frequency of revisions often indicates the level of resea activity on the compound and may indicate further changes in the future.

CALCULATIONAL METHODS

The presentation of Mayer and Mayer "Statistical Mechanics", John Wiley & Sons, Inc., New York, (1940) forms the basis for the expressions given below for the ideal gas state. The calculations have been carried out by a Burroughs B5500 electronic computer.

I. Ideal Monatomic gas

(a) Translation

$(H^\circ - H_0^\circ)/T = C_p^\circ = 4.967913$ cal deg^{-1} mol^{-1}.

$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 11.439043 \log T - 7.282868$ cal deg^{-1} mol^{-1}.

$S^\circ = 6.863426 \log M + 11.439043 \log T - 2.314954$ cal deg^{-1} mol^{-1}.

(b) Electronic

$$C_p^\circ = \frac{4.113664}{T^2}\left[\frac{\sum \varepsilon_i^2 g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}} - \left(\frac{\sum \varepsilon_i g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}}\right)^2\right] \text{cal deg}^{-1}\text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = \frac{2.859114}{T}\,\frac{\sum \varepsilon_i g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}} \quad \text{cal deg}^{-1}\text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 4.575617 \log \sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}} \quad \text{cal deg}^{-1}\text{ mol}^{-1}.$$

$$S^\circ = \frac{2.859114}{T}\,\frac{\sum \varepsilon_i g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}}} + 4.575617 \log \sum g_i e^{-\frac{1.438790\,\varepsilon_i}{T}} \quad \text{cal deg}^{-1}\text{ mol}^{-1}.$$

II. Ideal Diatomic Gas

(a) Translation and Rotation

$C_p^\circ = 6.955079 + 0.0914148\,(B/T)^2$ cal deg^{-1} mol^{-1}.

$(H^\circ - H_0^\circ)/T = 6.955079 - 0.953038\,(B/T) - 0.0914148\,(B/T)^2$ cal deg^{-1} mol^{-1}.

$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) + 0.953038\,(B/T) + 0.0457074\,(B/T)^2 - 8.005804$ cal deg^{-1} mol^{-1}.

$S^\circ = 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) - 0.0457074\,(B/T)^2 - 1.050725$ cal deg^{-1} mol^{-1}.

where $B = (B_e - \alpha_e/2)$ when spectroscopic constants are available.

$B = \frac{2.799076 \times 10^{-39}}{I}$ when calculated from a molecular model, (I in g cm^2)

(b) Vibration

$C_p^\circ = 1.987165\, u^2 e^{-u}/(1-e^{-u})^2$ cal deg^{-1} mol^{-1}.

$(H - H_0^\circ)/T = 1.987165\, u e^{-u}/(1-e^{-u})$ cal deg^{-1} mol^{-1}.

$-(G^\circ - H_0^\circ)/T = -4.575617 \log (1-e^{-u})$ cal deg^{-1} mol^{-1}.

$S^\circ = 1.987165\, u e^{-u}/(1-e^{-u}) - 4.575617 \log (1-e^{-u})$ cal deg^{-1} mol^{-1}.

where $u = (1.438790/T) \cdot (\omega_e - 2\omega_e x_e)$ when spectroscopic constants are available.

$u = (1.438790/T)\omega$ where ω is the fundamental wave number of a harmonic oscillator.

(c) Electronic

Same as I(b) when the i th-state vibrational partition function, Q_v^i and the i th-state rotational partition function, Q_r^i, are equal to the respective ground state partition functions. In this case the partition function $Q = Q_t Q_v Q_r \sum_i Q_e^i$, otherwise all the thermodynamic functions are derived from $Q = Q_t \sum_i Q_e^i Q_v^i Q_r^i$, where Q_t is the translational partition function and $Q_e^i = g_i \exp(\varepsilon_i/kT)$.

(d) Anharmonicity Corrections

$$C_p{}^\circ = 1.987615 \left[\frac{16\gamma}{u} - \frac{\delta u^2 e^u}{(e^u - 1)^2} + \frac{u^2 e^u (2\delta e^u - 4Xu - 8X)}{(e^u - 1)^3} + \frac{12Xu^3 e^{2u}}{(e^u - 1)^4}\right] \text{cal deg}^{-1} \text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{u(\delta e^u - 2X)}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3}\right] \text{cal deg}^{-1} \text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{2Xu}{(e^u - 1)^2}\right] \text{cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 1.987165 \left[\frac{16\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{\delta u e^u}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3}\right] \text{cal deg}^{-1} \text{ mol}^{-1}.$$

where u is $(\omega_e - 2\omega_e x_e) \cdot 1.438790/T$

$X = (\omega_e x_e)/\omega_e$; $\delta = \alpha_e/B_e$; $\gamma = B_e/\omega_e$.

III. Linear Polyatomic Molecule

(a) Translation and rotation same as for II (a).

(b) Vibration same as II (b) for 3N-5 vibrational degrees of freedom.

(c) Electronic same as II (c) where levels and quantum weight are known.

(d) Anharmonic corrections neglected.

IV. Nonlinear Polyatomic Molecule (Rigid Rotator, Harmonic Oscillator).

(a) Translation and Rotation

$C_p{}^\circ = 7.948662$ cal deg^{-1} mol^{-1}.

$(H^\circ - H_0^\circ)/T = 7.948662$ cal deg^{-1} mol^{-1}.

$$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 10.297926 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 2.349265 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

(b) Vibration same as II (b) for 3N-6 vibrational degrees of freedom.

(c) Electronic same as II (c) where levels and quantum weight are known.

(d) Anharmonic corrections neglected.

V. Condensed States

Evaluation of thermodynamic data for condensed states rests upon either measured or estimated information. Heat-capacity data are plotted, smoothed, and data for calculations read back at regular temperature intervals. Integration of this smoothed heat capacity data is carried out with the relations

$$H_T^\circ - H_{298.15}^\circ = \int_{298.15}^{T} C_p^\circ \, dT \qquad S_T^\circ = \int_0^T \frac{C_p^\circ}{T} \, dT$$

by machine, three points at a time. The computer calculates the constants for a parabolic equation through the three points, and employs the constants to integrate the first temperature interval. The lowest point is discarded; the next higher point is combined with the two retained points; and a new set of parabolic constants calculated and used for integrating the next higher temperature interval. This recurrent procedure is well suited to this type of calculation. At the appropriate temperatures, transition enthalpies are added to the enthalpy total, while the quotient of the transition enthalpy divided by the absolute temperature is added to the entropy total.

NOTES

1. Indexing

The modified Hill indexing system, J. Am. Chem. Soc. 22, 478-94 (1900), for Chemical Compounds as used by Chemical Abstracts and the Classification Division of the U. S. Patent Office is used to index the chemical compounds in this data collection. The arrangement of atomic symbols in chemical formulas is alphabetical except for carbon compounds. Thus, the indexing of chemical compounds is as follows: Ac (actinium compounds), Ag (silver compounds), Al (aluminum compounds), Am (americium compounds), Ar (argon), As (arsenic compounds), Au (gold compounds), B (boron compounds), Ba (barium compounds), Be (beryllium compounds), and so on throughout the alphabet. Once the correct order of the elements in the formula is deduced, the location of a compound within the group is easily accomplished. This obviates the need for pagination, and the index page indicates the correct order.

Organic (carbon) compounds represent a gigantic group, so that for convenience this one class of compounds presents the exceptions to the alphabetical rule. In carbon compounds the C always comes first, followed immediately by H if hydrogen is present, and then followed by any other elements present in their normal alphabetical order. The number of atoms of the element indexed first also influences the order of indexing the compound; e.g., all formulas with C (one carbon atom only) come before those with C_2 (two carbon atoms), followed by C_3 compounds, and so on. Thus: $CHBF_4O$ (formyl fluoride, compound with BF_3), $CHCl_3$ (chloroform), CH_2F_3P (trifluoromethylphosphine), CH_3NO_3 (methyl nitrate), CH_4Cl_2Si (dichloromethylsilane), $CH_{10}N_4O_3$ (hydrazine carbonate), CO (carbon monoxide), CO_2 (carbon dioxide), CO_3Zn (zinc carbonate), CZr (zirconium carbide), C_2Ba (barium acetylide), C_2BrClF_2 (bromochlorodifluoroethylene), C_2Ca (calcium carbide), and so on. See any formula index of Chemical Abstracts for further details and examples.

2. Selection of Enthalpy Reference Temperature

Since no enthalpy measurements can be made in the sense of an absolute quantity, and since all enthalpy measurements are made as a difference between an initial and a final state, it is necessary to select the thermodynamic state to which all other thermodynamic states will be referred. For these tables, the thermodynamic state selected is chosen as the state at one atmosphere total pressure tabulated at 298.15 K. Note that the temperature 298 K listed in the table actually refers to 298.15 K., but decimals have been omitted in the temperature column. Usage in theoretical work indicates the selection of the state existing at absolute zero, which is a hypothetical state that is even approached by relatively few measurements. Values of the difference in heat between 298.15 and 0 K will permit theoretical workers to use these tables, so it was decided to tabulate values at 0 K. Modern usage of thermodynamic data sometimes requires application to conditions below ambient, so the decision was made to tabulate values at 0, 100, and 200 K where the information is available.

3. Limitations of Calculated Quantities

Calculation of the contributions of rotation and translation involves the use of quantum statistics, but to obtain a numerical solution the quantum statistics are usually replaced by classical statistics at temperatures above about 100 K. Attempts to employ these methods below 100 K lead into a temperature range where the approximation afforded by classical statistics no longer holds. For this reason the equations presented under "Calculational Methods" fail in the vicinity of 0 K. In agreement with the third law concept, C_p° and S° are zero at 0 K. For a reference element, log K_p is zero at 0 K, while for compounds the absolute values of the free energy function and log K_p become infinite at 0 K.

4. Reference State of an Element

A related set of thermodynamic property tables requires that there be a reference table of the thermodynamic properties for each element to which all other forms of that element or any compound involving that element may be referred. If the temperature range of interest (6000 K here) can be represented by a single phase for that material (say hydrogen) the tabulated values in the reference table will be smooth and regular. If the temperature range of interest includes more than one phase (say magnesium) there will be a solid phase (from 0 to 922 K, the melting point), a liquid phase (922 to 1378 K, where the vapor pressure reaches one atmosphere), and a gas phase (1378 to 6000 K), the tabulated values in the reference table will be discontinuous at these phase boundaries. Practical usage dictates that in so far as possible the phase most stable at one atmosphere pressure (that is, the form most easily worked with) be selected. This practice is followed in these tables, and does lead to discontinuities in the thermodynamic functions. Attention is called to these discontinuities in the polyphase reference-state tables by insertion of a solid line at the temperature of a phase transition. The phase transitions considered are: first-order solid-state transformations from one crystal type to some other, solid to liquid, and solid or liquid to gas at one atmosphere.

5. Single-Phase Table

It is expected that these tables will be employed on various problems solved by automatic machine computation. Such calculations are carried out in numerous ways, and vary from one installation to another. Programs to perform these calculations are simplified if the thermodynamic functions are smooth and extend beyond the actual range of use permitting a wide latitude in iterative procedures. For this reason, most tables other than elemental reference states are tabulated as single-phase tables. Thus, tables for the solid state are extrapolated well past the melting point; those for the liquid state are extrapolated below the melting point (into the supercooled-liquid range to 298.15 K) and well above the atmospheric boiling point, while gas tables are tabulated from 0 K to 6000 K. Care has been taken to preserve the correct free energy relationships between the extrapolated-phase functions and the functions of the real phase. Attention is called to these extrapolations by insertion of a dotted line at the temperature where the indicated phase meets an adjacent more stable phase, but for reasons mentioned above the indicated phase is extrapolated into a temperature range where it is thermodynamically unstable.

NOTES

6. Mole

With each table and text there is listed either the atomic, molecular, or gram formula mass. It is generally understood that this mass in grams refers to Avogadro's number of atoms or molecules, and will be referred to simply as a "mole".

7. Point Groups and Ground-State Configurations

Throughout these tables the nomenclature and definition of the ground-state configurations and point groups are those in use by C. E. Moore, U. S. National Bureau of Standards Circular 467, (1949), and G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, (1950), and "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra", D. Van Nostrand Co., New York, (1945).

8. Decimal Places

Three decimal places have been arbitrarily carried in the tables even though *in numerous cases the data do not warrant* this accuracy. This has been done to preserve the proper relationship of the thermodynamic functions, and to facilitate machine interpolation of these values.

9. Higher Electronic Terms

A single electronic term of 30,000 cm^{-1} and above contributes a negligible amount to the thermodynamic functions at temperatures of 6000 K and below. On the other hand, a number of such terms cannot be neglected. In these cases, the number of terms and their values have been summed and their contribution included.

10. Estimated Vibrational Frequencies

Some vibrational frequencies have been estimated by analogy with related molecules. Occasionally, more than one frequency has been averaged at the same value. This is not to be confused with a true degeneracy which is indicated by placing the degeneracy value in parentheses following the frequency. However, when the information has been taken from another compilation, the degeneracies indicated by the compiler have been retained.

11. Quantum Weight

The term quantum weight is also referred to as statistical weight by many authors. The quantity is the product of the spin multiplicity and state degeneracy of the electronic level under consideration.

12. Isotope Effects

The functions calculated for gases from molecular constants are, in general, obtained from constants which have been corrected to the natural isotopic abundance.

INDEX TO TABLES

Filing Order	Table Title
$BClF$	Boron Chloride Fluoride (g)
$BClF_2$	Boron Chloride Difluoride (g)
$BClO$	Boron Oxide Chloride (g)
BCl_2	Boron Dichloride (g)
BCl_2^+	Boron Dichloride Unipositive Ion (g)
BCl_2^-	Boron Dichloride Uninegative Ion (g)
BCl_2F	Boron Dichloride Fluoride (g)
BCl_2H	Boron Dichloride Hydride (g)
BCl_3	Boron Trichloride (g)
BF	Boron Monofluoride (g)
BFO	Boron Oxide Fluoride (g)
BF_2	Boron Difluoride (g)
BF_2^+	Boron Difluoride Unipositive Ion (g)
BF_2^-	Boron Difluoride Uninegative Ion (g)
BF_2H	Difluoroborane (g)
BF_2HO	Boron Hydroxide Difluoride (g)
BF_2O	Boron Oxide Difluoride (g)
BF_3	Boron Trifluoride (g)
BF_4K	Potassium Tetrafluoroborate (c)
BF_4K	Potassium Tetrafluoroborate (ℓ)
BF_4K	Potassium Tetrafluoroborate (g)
BH	Boron Monohydride (g)
BHO	Boron Oxide Hydride (g)
BHO^+	Boron Oxide Hydride Unipositive Ion (g)
BHO_2	Metaboric Acid (c)
BHO_2	Metaboric Acid (g)
BH_2	Boron Dihydride (g)
BH_2O_2	Boron Dihydroxide (g)
BH_3	Boron Trihydride (g)
BH_3O_3	Boric Acid (c)
BH_3O_3	Boric Acid (g)
BH_4K	Potassium Tetrahydroborate (c)
BH_4Li	Lithium Tetrahydroborate (c)
BH_4Na	Sodium Tetrahydroborate (c)
BI	Boron Iodide (g)
BI_2	Boron Diiodide (g)
BI_3	Boron Triiodide (g)
$BLiO_2$	Lithium Metaborate (c)
$BLiO_2$	Lithium Metaborate (ℓ)
$BLiO_2$	Lithium Metaborate (g)
BN	Boron Nitride (c)
BN	Boron Nitride (g)
$BNaO_2$	Sodium Metaborate (c)
$BNaO_2$	Sodium Metaborate (ℓ)
$BNaO_2$	Sodium Metaborate (g)
BO	Boron Monoxide (g)
BO_2	Boron Dioxide (g)
BO_2^-	Boron Dioxide Uninegative Ion (g)
BS	Boron Monosulfide (g)
BTi	Titanium Monoboride (c)

Filing Order	Table Title
B_2	Boron, Diatomic (g)
B_2BeO_4	Beryllium Diborate (g)
$B_2Be_3O_6$	Triberyllium Diborate (c)
B_2Cl_4	Boron Dichloride, Dimeric (g)
B_2F_4	Boron Difluoride, Dimeric (g)
$B_2H_4O_4$	Boron Dihydroxide, Dimeric (c)
$B_2H_4O_4$	Boron Dihydroxide, Dimeric (g)
B_2H_6	Diborane (g)
B_2Mg	Magnesium Diboride (c)
B_2O	Diboron Monoxide (g)
B_2O_2	Boron Monoxide, Dimeric (g)
B_2O_3	Boron Oxide (c)
B_2O_3	Boron Oxide (ℓ)
B_2O_3	Boron Oxide (g)
B_2O_4Pb	Lead Diborate (c)
B_2Ti	Titanium Diboride (c)
B_2Ti	Titanium Diboride (ℓ)
B_2Zr	Zirconium Diboride (c)
B_2Zr	Zirconium Diboride (ℓ)
$B_3Cl_3O_3$	Boron Oxide Chloride, Trimeric (g)
$B_3FH_2O_3$	Monofluoroboroxin (g)
$B_3F_2HO_3$	Difluoroboroxin (g)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (c)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (g)
$B_3H_3O_3$	Boroxin (c)
$B_3H_3O_3$	Boroxin (g)
$B_3H_3O_6$	Metaboric Acid, Trimeric (g)
$B_3H_6N_3$	Borazine (g)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (c)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (ℓ)
$B_4Li_2O_7$	Dilithium Tetraborate (c)
$B_4Li_2O_7$	Dilithium Tetraborate (ℓ)
B_4Mg	Magnesium Tetraboride (c)
$B_4Na_2O_7$	Disodium Tetraborate (c)
$B_4Na_2O_7$	Disodium Tetraborate (ℓ)
B_4O_7Pb	Lead Tetraborate (c)
B_5H_9	Pentaborane (ℓ)
B_5H_9	Pentaborane (g)
$B_6K_2O_{10}$	Dipotassium Hexaborate (c)
$B_6Li_2O_{10}$	Dilithium Hexaborate (c)
$B_6Na_2O_{10}$	Disodium Hexaborate (c)
$B_6O_{10}Pb$	Lead Hexaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (ℓ)
$B_8Li_2O_{13}$	Dilithium Octaborate (c)
$B_{10}H_{14}$	Decaborane (c)
$B_{10}H_{14}$	Decaborane (ℓ)
$B_{10}H_{14}$	Decaborane (g)

ng r	Table Title
$_{17}$Pb$_2$	Dilead Decaborate (c)
	Beryllium (ref. st.)
	Beryllium (c)
	Beryllium (ℓ)
	Beryllium (g)
	Beryllium Unipositive Ion (g)
	Beryllium Monobromide (g)
$_2$	Beryllium Dibromide (c)
$_2$	Beryllium Dibromide (ℓ)
$_2$	Beryllium Dibromide (g)
l	Beryllium Monochloride (g)
l$^+$	Beryllium Monochloride Unipositive Ion (g)
lF	Beryllium Chloride Fluoride (g)
l$_2$	Beryllium Dichloride (c,α)
l$_2$	Beryllium Dichloride (c,β)
l$_2$	Beryllium Dichloride (ℓ)
l$_2$	Beryllium Dichloride (g)
	Beryllium Monofluoride (g)
$_2$	Beryllium Difluoride (c)
$_2$	Beryllium Difluoride (ℓ)
$_2$	Beryllium Difluoride (g)
$_3$Li	Lithium Trifluoroberyllate (c)
$_3$Li	Lithium Beryllium Fluoride (g)
$_4$Li$_2$	Dilithium Tetrafluoroberyllate (c)
$_4$Li$_2$	Dilithium Tetrafluoroberyllate (ℓ)
	Beryllium Monohydride (g)
$^+$	Beryllium Monohydride Unipositive Ion (g)
	Beryllium Monohydroxide (g)
$^+$	Beryllium Monohydroxide Unipositive Ion (g)
$_2$	Beryllium Dihydride (g)
$_2$O$_2$	Beryllium Hydroxide (c,α)
$_2$O$_2$	Beryllium Hydroxide (c,β)
$_2$O$_2$	Beryllium Hydroxide (g)
	Beryllium Monoiodide (g)
$_2$	Beryllium Diiodide (c)
$_2$	Beryllium Diiodide (ℓ)
$_2$	Beryllium Diiodide (g)
	Beryllium Nitride (g)
	Beryllium Oxide (c)
	Beryllium Oxide (ℓ)
	Beryllium Oxide (g)
$_4$S	Beryllium Sulfate (c,α)
$_4$S	Beryllium Sulfate (c,β)
$_4$S	Beryllium Sulfate (c,γ)
$_4$W	Beryllium Tungstate (c)
Cl$_4$	Beryllium Dichloride, Dimeric (g)
F$_2$O	Dilithium Oxide Difluoride (g)
O	Diberyllium Oxide (g)
O$_2$	Beryllium Oxide, Dimeric (g)
O$_4$Si	Beryllium Orthosilicate (c)

Filing Order	Table Title
Be_3N_2	Beryllium Nitride (c,α)
Be_3N_2	Beryllium Nitride (ℓ)
Be_3O_3	Beryllium Oxide, Trimeric (g)
Be_4O_4	Beryllium Oxide, Tetrameric (g)
Be_5O_5	Beryllium Oxide, Pentameric (g)
Be_6O_6	Beryllium Oxide, Hexameric (g)
Br	Bromine, Monatomic (g)
BrCl	Bromine Monochloride (g)
BrF	Bromine Monofluoride (g)
BrF_3	Bromine Trifluoride (g)
BrF_5	Bromine Pentafluoride (g)
BrH	Hydrogen Bromide (g)
BrH_4N	Ammonium Bromide (c)
BrHg	Mercurous Bromide (g)
BrI	Iodine Monobromide (g)
BrK	Potassium Bromide (c)
BrK	Potassium Bromide (ℓ)
BrK	Potassium Bromide (g)
BrLi	Lithium Bromide (c)
BrLi	Lithium Bromide (ℓ)
BrLi	Lithium Bromide (g)
BrMg	Magnesium Monobromide (g)
BrN	Nitrogen Bromide (g)
BrNO	Nitrosyl Bromide (g)
BrNa	Sodium Bromide (c)
BrNa	Sodium Bromide (ℓ)
BrNa	Sodium Bromide (g)
BrP	Phosphorus Monobromide (g)
BrPb	Lead Monobromide (g)
BrTi	Titanium Monobromide (g)
BrW	Tungsten Monobromide (g)
BrZr	Zirconium Monobromide (g)
Br_2	Bromine (ref. st.)
Br_2	Bromine (ℓ)
Br_2	Bromine, Diatomic (g)
Br_2Fe	Iron Dibromide (c)
Br_2Fe	Iron Dibromide (ℓ)
Br_2Fe	Iron Dibromide (g)
Br_2Hg	Mercuric Bromide (c)
Br_2Hg	Mercuric Bromide (ℓ)
Br_2Hg	Mercuric Bromide (g)
Br_2Hg_2	Mercurous Bromide (c)
Br_2K_2	Potassium Bromide, Dimeric (g)
Br_2Li_2	Lithium Bromide, Dimeric (g)
Br_2Mg	Magnesium Dibromide (c)
Br_2Mg	Magnesium Dibromide (ℓ)
Br_2Mg	Magnesium Dibromide (g)
Br_2Na_2	Sodium Bromide, Dimeric (g)
Br_2Pb	Lead Dibromide (c)

Filing Order	Table Title
Br_2Pb	Lead Dibromide (ℓ)
Br_2Pb	Lead Dibromide (g)
Br_2Ti	Titanium Dibromide (c)
Br_2Ti	Titanium Dibromide (g)
Br_2Zr	Zirconium Dibromide (c)
Br_2Zr	Zirconium Dibromide (ℓ)
Br_2Zr	Zirconium Dibromide (g)
Br_3OP	Phosphoryl Bromide (g)
Br_3P	Phosphorus Tribromide (g)
Br_3PS	Thiophosphoryl Bromide (g)
Br_3Ti	Titanium Tribromide (c)
Br_3Ti	Titanium Tribromide (g)
Br_3Zr	Zirconium Tribromide (c)
Br_3Zr	Zirconium Tribromide (g)
Br_4Fe_2	Iron Dibromide, Dimeric (g)
Br_4Pb	Lead Tetrabromide (g)
Br_4Ti	Titanium Tetrabromide (c)
Br_4Ti	Titanium Tetrabromide (ℓ)
Br_4Ti	Titanium Tetrabromide (g)
Br_4Zr	Zirconium Tetrabromide (c)
Br_4Zr	Zirconium Tetrabromide (g)
Br_5W	Tungsten Pentabromide (c)
Br_5W	Tungsten Pentabromide (ℓ)
Br_5W	Tungsten Pentabromide (g)
Br_6W	Tungsten Hexabromide (c)
Br_6W	Tungsten Hexabromide (g)
C	Carbon (ref. st., Graphite)
C	Carbon, Monatomic (g)
C^-	Carbon Uninegative Ion (g)
CAl	Aluminum Carbide (g)
CB	Boron Carbide (g)
CB_4	Boron Carbide (c)
CB_4	Boron Carbide (ℓ)
CBe_2	Beryllium Carbide (c)
CBe_2	Beryllium Carbide (ℓ)
CBr	Carbon Monobromide (g)
$CBrF_3$	Bromotrifluoromethane (g)
CBrN	Cyanogen Bromide (g)
CBr_4	Carbon Tetrabromide (g)
CCl	Carbon Monochloride (g)
CClFO	Carbonyl Chlorofluoride (g)
$CClF_3$	Chlorotrifluoromethane (g)
CClN	Cyanogen Chloride (g)
CClO	Carbonyl Monochloride (g)
CCl_2	Carbon Dichloride (g)
CCl_2F_2	Dichlorodifluoromethane (g)
CCl_2O	Carbonyl Chloride (g)
CCl_3	Trichloromethyl (g)
CCl_3F	Trichlorofluoromethane (g)
CCl_4	Carbon Tetrachloride (g)

Filing Order	Table Title
CF	Carbon Monofluoride (g)
CFN	Cyanogen Fluoride (g)
CFO	Carbonyl Monofluoride (g)
CF_2	Carbon Difluoride (g)
CF_2O	Carbonyl Fluoride (g)
CF_3	Trifluoromethyl (g)
CF_3I	Trifluoroiodomethane (g)
CF_4	Carbon Tetrafluoride (g)
CF_4O	Trifluoromethyl Hypofluorite (g)
CH	Methylidyne (g)
CHCl	Monochloromethylene (g)
$CHClF_2$	Chlorodifluoromethane (g)
$CHCl_2F$	Dichlorofluoromethane (g)
$CHCl_3$	Chloroform (g)
CHF	Monofluoromethylene (g)
CHFO	Formyl Fluoride (g)
CHF_3	Trifluoromethane (g)
CHN	Hydrogen Cyanide (g)
CHNO	Hydrogen Isocyanate (g)
CHO	Formyl (g)
CHO^+	Formyl Unipositive Ion (g)
CHP	Methinophosphide (g)
CH_2	Methylene (g)
CH_2ClF	Chlorofluoromethane (g)
CH_2Cl_2	Dichloromethane (g)
CH_2F_2	Difluoromethane (g)
CH_2O	Formaldehyde (g)
CH_3	Methyl (g)
CH_3Cl	Methyl Chloride (g)
CH_3Cl_3Si	Trichloromethylsilane (g)
CH_3F	Fluoromethane (g)
CH_3F_3Si	Trifluoromethylsilane (g)
CH_4	Methane (g)
CIN	Cyanogen Iodide (g)
CKN	Potassium Cyanide (c)
CKN	Potassium Cyanide (ℓ)
CKN	Potassium Cyanide (g)
CK_2O_3	Potassium Carbonate (c)
CK_2O_3	Potassium Carbonate (ℓ)
CLi_2O_3	Lithium Carbonate (c)
CLi_2O_3	Lithium Carbonate (ℓ)
$CMgO_3$	Magnesium Carbonate (c)
CN	Cyano (g)
CN^+	Cyano Unipositive Ion (g)
CN^-	Cyano Uninegative Ion (g)
CNNa	Sodium Cyanide (c)
CNNa	Sodium Cyanide (ℓ)
CNNa	Sodium Cyanide (g)
CN_2	CNN Radical (g)
CN_2	NCN Radical (g)

Filing Order	Table Title
CNa_2O_3	Sodium Carbonate (c)
CNa_2O_3	Sodium Carbonate (ℓ)
CO	Carbon Monoxide (g)
COS	Carbon Oxysulfide (g)
CO_2	Carbon Dioxide (g)
CO_2^-	Carbon Dioxide Uninegative Ion (g)
CP	Carbon Phosphide (g)
CS	Carbon Monosulfide (g)
CS_2	Carbon Disulfide (g)
CSi	Silicon Carbide (c,α)
CSi	Silicon Carbide (c,β)
CSi	Silicon Carbide (g)
CSi_2	Disilicon Carbide (g)
CTi	Titanium Carbide (c)
CTi	Titanium Carbide (ℓ)
CZr	Zirconium Carbide (c)
CZr	Zirconium Carbide (ℓ)
C_2	Carbon, Diatomic (g)
C_2^-	Dimeric Carbon Uninegative Ion (g)
C_2Be	Beryllium Carbide (g)
C_2Cl_2	Dichloroacetylene (g)
C_2Cl_4	Tetrachloroethylene (g)
C_2Cl_6	Hexachloroethane (g)
C_2F_2	Difluoroacetylene (g)
C_2F_3N	Trifluoroacetonitrile (g)
C_2F_4	Tetrafluoroethylene (g)
C_2F_6	Hexafluoroethane (g)
C_2H	CCH Radical (g)
C_2HCl	Chloroacetylene (g)
C_2HF	Monofluorocetylene (g)
C_2H_2	Acetylene (g)
C_2H_4	Ethylene (g)
C_2H_4O	Ethylene Oxide (g)
$C_2K_2N_2$	Potassium Cyanide, Dimeric (g)
C_2Li_2	Lithium Carbide (c)
C_2Mg	Magnesium Carbide (c)
C_2N	CNC Radical (g)
C_2N_2	Cyanogen (g)
$C_2N_2Na_2$	Sodium Cyanide, Dimeric (g)
C_2O	CCO Radical (g)
C_2Si	Silicon Dicarbide (g)
C_3	Carbon, Trimeric (g)
C_3Al_4	Aluminum Carbide (c)
C_3Mg_2	Magnesium Carbide (c)
C_3O_2	Carbon Suboxide (g)
C_4	Carbon, Tetratomic (g)
$C_4H_{12}Si$	Tetramethylsilane (g)
C_4N_2	Carbon Subnitride (g)
C_5	Carbon, Pentatomic (g)
Ca	Calcium (ref. st.)
Ca	Calcium (α)
Ca	Calcium (β)
Ca	Calcium (ℓ)
Ca	Calcium (g)
$CaCl$	Calcium Monochloride (g)
$CaCl_2$	Calcium Chloride (c)
$CaCl_2$	Calcium Chloride (ℓ)
$CaCl_2$	Calcium Chloride (g)
CaF	Calcium Monofluoride (g)
CaF_2	Calcium Difluoride (c)
CaF_2	Calcium Difluoride (ℓ)
CaF_2	Calcium Difluoride (g)
$CaHO$	Calcium Monohydroxide (g)
$CaHO^+$	Calcium Monohydroxide Unipositive Ion (g)
Cl	Chlorine, Monatomic (g)
Cl^+	Chlorine Unipositive Ion (g)
Cl^-	Chlorine Uninegative Ion (g)
$ClCs$	Cesium Monochloride (c)
$ClCs$	Cesium Monochloride (ℓ)
$ClCs$	Cesium Monochloride (g)
$ClCu$	Copper Monochloride (c)
$ClCu$	Copper Monochloride (ℓ)
$ClCu$	Copper Monochloride (g)
ClF	Chlorine Monofluoride (g)
$ClFLi_2$	Lithium Chlorofluoride (g)
$ClFMg$	Magnesium Chloride Fluoride (g)
$ClFO_3$	Perchloryl Fluoride (g)
ClF_2OP	Phosphoryl Difluorochloride (g)
ClF_3	Chlorine Trifluoride (g)
ClF_3Si	Chlorotrifluorosilane (g)
ClF_5	Chlorine Pentafluoride (g)
$ClFe$	Iron Monochloride (g)
ClH	Hydrogen Chloride (g)
$ClHO$	Hydrogen Oxychloride (g)
ClH_3Si	Chlorosilane (g)
ClH_4N	Ammonium Chloride (c)
ClH_4NO_4	Ammonium Perchlorate (c)
$ClHg$	Mercurous Chloride (g)
ClI	Iodine Monochloride (c)
ClI	Iodine Monochloride (ℓ)
ClI	Iodine Monochloride (g)
ClK	Potassium Chloride (c)
ClK	Potassium Chloride (ℓ)
ClK	Potassium Chloride (g)
$ClKO_4$	Potassium Perchlorate (c)
$ClLi$	Lithium Chloride (c)
$ClLi$	Lithium Chloride (ℓ)
$ClLi$	Lithium Chloride (g)
$ClLiO$	Lithium Oxychloride (g)

Filing Order	Table Title
$ClLiO_4$	Lithium Perchlorate (c)
$ClLiO_4$	Lithium Perchlorate (ℓ)
$ClMg$	Magnesium Monochloride (g)
$ClMg^+$	Magnesium Monochloride Unipositive Ion (g)
$ClNO$	Nitrosyl Chloride (g)
$ClNO_2$	Nitryl Chloride (g)
$ClNa$	Sodium Chloride (c)
$ClNa$	Sodium Chloride (ℓ)
$ClNa$	Sodium Chloride (g)
$ClNaO_4$	Sodium Perchlorate (c)
ClO	Chlorine Monoxide (g)
$ClOTi$	Titanium Oxychloride (g)
ClO_2	Chlorine Dioxide (g)
ClP	Phosphorus Monochloride (g)
$ClPb$	Lead Monochloride (g)
$ClSi$	Silicon Monochloride (g)
$ClTi$	Titanium Monochloride (g)
ClW	Tungsten Monochloride (g)
$ClZr$	Zirconium Monochloride (g)
Cl_2	Chlorine, Diatomic (ref. st.,g)
Cl_2Cs_2	Cesium Monochloride, Dimeric (g)
Cl_2Cu	Copper Dichloride (c)
Cl_2FOP	Phosphoryl Fluorodichloride (g)
Cl_2Fe	Iron Dichloride (c)
Cl_2Fe	Iron Dichloride (ℓ)
Cl_2Fe	Iron Dichloride (g)
Cl_2H_2Si	Dichlorosilane (g)
Cl_2Hg	Mercuric Chloride (c)
Cl_2Hg	Mercuric Chloride (ℓ)
Cl_2Hg	Mercuric Chloride (g)
Cl_2Hg_2	Mercurous Chloride (c)
Cl_2K_2	Potassium Chloride, Dimeric (g)
Cl_2Li_2	Lithium Chloride, Dimeric (g)
Cl_2Mg	Magnesium Dichloride (c)
Cl_2Mg	Magnesium Dichloride (ℓ)
Cl_2Mg	Magnesium Dichloride (g)
Cl_2MoO_2	Molybdenum Dioxydichloride (g)
Cl_2Na_2	Sodium Chloride, Dimeric (g)
Cl_2O	Chlorine Monoxide (g)
Cl_2OTi	Titanium Oxydichloride (g)
Cl_2O_2W	Tungsten Dioxydichloride (c)
Cl_2O_2W	Tungsten Dioxydichloride (g)
Cl_2Pb	Lead Dichloride (c)
Cl_2Pb	Lead Dichloride (ℓ)
Cl_2Pb	Lead Dichloride (g)
Cl_2Si	Silicon Dichloride (g)
Cl_2Ti	Titanium Dichloride (c)
Cl_2Ti	Titanium Dichloride (g)
Cl_2W	Tungsten Dichloride (c)

Filing Order	Table Title
Cl_2W	Tungsten Dichloride (g)
Cl_2Zr	Zirconium Dichloride (c)
Cl_2Zr	Zirconium Dichloride (ℓ)
Cl_2Zr	Zirconium Dichloride (g)
Cl_3Cu_3	Copper Monochloride, Trimeric (g)
Cl_3FSi	Trichlorofluorosilane (g)
Cl_3Fe	Iron Trichloride (c)
Cl_3Fe	Iron Trichloride (ℓ)
Cl_3Fe	Iron Trichloride (g)
Cl_3HSi	Trichlorosilane (g)
Cl_3Li_3	Lithium Chloride, Trimeric (g)
Cl_3OP	Phosphoryl Chloride (g)
Cl_3P	Phosphorus Trichloride (g)
Cl_3PS	Thiophosphoryl Chloride (g)
Cl_3Si	Silicon Trichloride (g)
Cl_3Ti	Titanium Trichloride (c)
Cl_3Ti	Titanium Trichloride (g)
Cl_3Zr	Zirconium Trichloride (c)
Cl_3Zr	Zirconium Trichloride (g)
Cl_4Mg_2	Magnesium Dichloride, Dimeric (g)
Cl_4Mo	Molybdenum Tetrachloride (c)
Cl_4Mo	Molybdenum Tetrachloride (ℓ)
Cl_4Mo	Molybdenum Tetrachloride (g)
Cl_4OW	Tungsten Oxytetrachloride (c)
Cl_4OW	Tungsten Oxytetrachloride (ℓ)
Cl_4OW	Tungsten Oxytetrachloride (g)
Cl_4Pb	Lead Tetrachloride (g)
Cl_4Si	Silicon Tetrachloride (g)
Cl_4Ti	Titanium Tetrachloride (c)
Cl_4Ti	Titanium Tetrachloride (ℓ)
Cl_4Ti	Titanium Tetrachloride (g)
Cl_4W	Tungsten Tetrachloride (c)
Cl_4W	Tungsten Tetrachloride (g)
Cl_4Zr	Zirconium Tetrachloride (c)
Cl_4Zr	Zirconium Tetrachloride (g)
Cl_5Mo	Molybdenum Pentachloride (c)
Cl_5Mo	Molybdenum Pentachloride (ℓ)
Cl_5Mo	Molybdenum Pentachloride (g)
Cl_5P	Phosphorus Pentachloride (g)
Cl_5W	Tungsten Pentachloride (c)
Cl_5W	Tungsten Pentachloride (ℓ)
Cl_5W	Tungsten Pentachloride (g)
Cl_6Fe_2	Iron Trichloride, Dimeric (g)
Cl_6Mo	Molybdenum Hexachloride (c)
Cl_6Mo	Molybdenum Hexachloride (g)
Cl_6W	Tungsten Hexachloride (c,α)
Cl_6W	Tungsten Hexachloride (c,β)
Cl_6W	Tungsten Hexachloride (ℓ)
Cl_6W	Tungsten Hexachloride (g)

ling der	Table Title
$_{10}W_2$	Tungsten Pentachloride, Dimeric (g)
	Cobalt (ref. st.)
	Cobalt (c)
	Cobalt (ℓ)
	Cobalt (g)
$^+$	Cobalt Unipositive Ion (g)
F_2	Cobalt Difluoride (c)
F_2	Cobalt Difluoride (ℓ)
F_2	Cobalt Difluoride (g)
	Cesium (ref. st.)
	Cesium (c)
	Cesium (ℓ)
	Cesium (g)
$^+$	Cesium Unipositive Ion (g)
F	Cesium Monofluoride (c)
F	Cesium Monofluoride (ℓ)
F	Cesium Monofluoride (g)
O	Cesium Monoxide (g)
$_2$	Cesium, Dimeric (g)
$_2F_2$	Cesium Monofluoride, Dimeric (g)
$_2O$	Dicesium Monoxide (g)
	Copper (ref. st.)
	Copper (c)
	Copper (ℓ)
	Copper (g)
$^+$	Copper Unipositive Ion (g)
F	Copper Monofluoride (c)
F	Copper Monofluoride (g)
F_2	Copper Difluoride (c)
F_2	Copper Difluoride (ℓ)
F_2	Copper Difluoride (g)
H_2O_2	Copper Dihydroxide (c)
O	Copper Monoxide (c)
O	Copper Monoxide (g)
O_4S	Copper Sulfate (c)
$_2$	Copper, Diatomic (g)
$_2O$	Dicopper Monoxide (c)
$_2O$	Dicopper Monoxide (ℓ)
$_2O_5S$	Copper Oxide Sulfate (c)
	Fluorine, Monatomic (g)
$^-$	Fluorine Uninegative Ion (g)
Fe	Iron Monofluoride (g)
H	Hydrogen Fluoride (g)
HO	Hydrogen Oxyfluoride (g)
H_3Si	Fluorosilane (g)
Hg	Mercurous Fluoride (g)
I	Iodine Monofluoride (g)

Filing Order	Table Title
FK	Potassium Fluoride (c)
FK	Potassium Fluoride (ℓ)
FK	Potassium Fluoride (g)
FLi	Lithium Fluoride (c)
FLi	Lithium Fluoride (ℓ)
FLi	Lithium Fluoride (g)
FLiO	Lithium Oxyfluoride (g)
FMg	Magnesium Monofluoride (g)
FN	Nitrogen Monofluoride (g)
FNO	Nitrosyl Fluoride (g)
FNO_2	Nitryl Fluoride (g)
FNO_3	Fluorine Nitrate (g)
FNa	Sodium Fluoride (c)
FNa	Sodium Fluoride (ℓ)
FNa	Sodium Fluoride (g)
FO	Fluorine Monoxide (g)
FOTi	Titanium Oxyfluoride (g)
FO_2	Monofluorine Dioxide (g)
FP	Phosphorus Monofluoride (g)
FPS	Phosphorus Thiofluoride (g)
FPb	Lead Monofluoride (g)
FSi	Silicon Monofluoride (g)
FTi	Titanium Monofluoride (g)
FW	Tungsten Monofluoride (g)
FZr	Zirconium Monofluoride (g)
F_2	Fluorine, Diatomic (ref.st.,g)
F_2Fe	Iron Difluoride (c)
F_2Fe	Iron Difluoride (ℓ)
F_2Fe	Iron Difluoride (g)
F_2HK	Potassium Bifluoride (c)
F_2HK	Potassium Bifluoride (ℓ)
F_2H_2Si	Difluorosilane (g)
F_2Hg	Mercuric Fluoride (c)
F_2Hg	Mercuric Fluoride (ℓ)
F_2Hg	Mercuric Fluoride (g)
F_2Hg_2	Mercurous Fluoride (c)
F_2K^-	Potassium Difluoride Uninegative Ion (g)
F_2K_2	Potassium Fluoride, Dimeric (g)
F_2Li^-	Lithium Difluoride Uninegative Ion (g)
F_2Li_2	Lithium Fluoride, Dimeric (g)
F_2Mg	Magnesium Fluoride (c)
F_2Mg	Magnesium Fluoride (ℓ)
F_2Mg	Magnesium Fluoride (g)
F_2N	Nitrogen Difluoride (g)
F_2N_2	Difluorodiazine, cis- (g)
F_2N_2	Difluorodiazine, trans- (g)
F_2Na^-	Sodium Difluoride Uninegative Ion (g)
F_2Na_2	Sodium Fluoride, Dimeric (g)
F_2O	Oxygen Difluoride (g)
F_2OS	Thionyl Fluoride (g)

Filing Order	Table Title
F_2OSi	Silicon Oxydifluoride (g)
F_2OTi	Titanium Oxydifluoride (g)
F_2O_2S	Sulfuryl Fluoride (g)
F_2P	Phosphorus Difluoride (g)
F_2Pb	Lead Difluoride (c)
F_2Pb	Lead Difluoride (ℓ)
F_2Pb	Lead Difluoride (g)
F_2Si	Silicon Difluoride (g)
F_2Ti	Titanium Difluoride (g)
F_2Zr	Zirconium Difluoride (c)
F_2Zr	Zirconium Difluoride (ℓ)
F_2Zr	Zirconium Difluoride (g)
F_3Fe	Iron Trifluoride (c)
F_3Fe	Iron Trifluoride (g)
F_3HSi	Trifluorosilane (g)
F_3Li_3	Lithium Fluoride, Trimeric (g)
F_3N	Nitrogen Trifluoride (g)
F_3NO	Trifluoramine Oxide (g)
F_3OP	Phosphoryl Fluoride (g)
F_3P	Phosphorus Trifluoride (g)
F_3PS	Thiophosphoryl Fluoride (g)
F_3Si	Silicon Trifluoride (g)
F_3Ti	Titanium Trifluoride (c)
F_3Ti	Titanium Trifluoride (g)
F_3Zr	Zirconium Trifluoride (c)
F_3Zr	Zirconium Trifluoride (g)
F_4Mg_2	Magnesium Difluoride, Dimeric (g)
F_4MoO	Molybdenum Oxytetrafluoride (g)
F_4N_2	Tetrafluorohydrazine (g)
F_4OW	Tungsten Oxytetrafluoride (c)
F_4OW	Tungsten Oxytetrafluoride (ℓ)
F_4OW	Tungsten Oxytetrafluoride (g)
F_4Pb	Lead Tetrafluoride (g)
F_4S	Sulfur Tetrafluoride (g)
F_4Si	Silicon Tetrafluoride (g)
F_4Ti	Titanium Tetrafluoride (c)
F_4Ti	Titanium Tetrafluoride (g)
F_4Zr	Zirconium Tetrafluoride (c)
F_4Zr	Zirconium Tetrafluoride (g)
F_5I	Iodine Pentafluoride (g)
F_5P	Phosphorus Pentafluoride (g)
F_6Mo	Molybdenum Hexafluoride (ℓ)
F_6Mo	Molybdenum Hexafluoride (g)
F_6S	Sulfur Hexafluoride (g)
F_6W	Tungsten Hexafluoride (ℓ)
F_6W	Tungsten Hexafluoride (g)
F_7I	Iodine Heptafluoride (g)
Fe	Iron (ref. st.)
Fe	Iron (c)

Filing Order	Table Title
Fe	Iron (ℓ)
Fe	Iron (g)
FeH_2O_2	Iron Dihydroxide (c)
FeH_2O_2	Iron Dihydroxide (g)
FeH_3O_3	Iron Trihydroxide (c)
FeI_2	Iron Diiodide (c)
FeI_2	Iron Diiodide (ℓ)
FeI_2	Iron Diiodide (g)
$Fe_{0.947}O$	Wüstite (c)
FeO	Iron Oxide (c)
FeO	Iron Oxide (ℓ)
FeO	Iron Oxide (g)
FeO_4S	Iron Sulfate (c)
Fe_2I_4	Iron Diiodide, Dimeric (g)
Fe_2O_3	Hematite (c)
$Fe_2O_{12}S_3$	Diiron Trisulfate (c)
Fe_3O_4	Magnetite (c)
H	Hydrogen, Monatomic (g)
H^+	Proton (g)
H^-	Hydrogen Uninegative Ion (g)
HHg	Mercury Monohydride (g)
HI	Hydrogen Iodide (g)
HK	Potassium Hydride (c)
HK	Potassium Hydride (g)
HKO	Potassium Hydroxide (c)
HKO	Potassium Hydroxide (ℓ)
HKO	Potassium Hydroxide (g)
HLi	Lithium Hydride (c)
HLi	Lithium Hydride (ℓ)
HLi	Lithium Hydride (g)
HLiO	Lithium Hydroxide (c)
HLiO	Lithium Hydroxide (ℓ)
HLiO	Lithium Hydroxide (g)
HMg	Magnesium Monohydride (g)
HMgO	Magnesium Monohydroxide (g)
$HMgO^+$	Magnesium Monohydroxide Unipositive Ion (g)
HN	Imidogen (g)
HNO	Nitroxyl (g)
HNO_2	Nitrous Acid, cis- (g)
HNO_2	Nitrous Acid, trans- (g)
HNO_3	Nitric Acid (g)
HNa	Sodium Hydride (c)
HNa	Sodium Hydride (g)
HNaO	Sodium Hydroxide (c)
HNaO	Sodium Hydroxide (ℓ)
HNaO	Sodium Hydroxide (g)
HO	Hydroxyl (g)
HO^+	Hydroxyl Unipositive Ion (g)
HO^-	Hydroxyl Uninegative Ion (g)
HO_2	Hydroperoxyl (g)

ing ler	Table Title
	Phosphorus Monohydride (g)
	Lead Monohydride (g)
	Sulfur Monohydride (g)
	Silicon Monohydride (g)
	Zirconium Hydride (g)
	Hydrogen, Diatomic (ref. st., g)
$_2O_2$	Potassium Hydroxide, Dimeric (g)
i_2O_2	Lithium Hydroxide, Dimeric (g)
g	Magnesium Hydride (c)
gO_2	Magnesium Dihydroxide (c)
gO_2	Magnesium Dihydroxide (g)
O_4	Molybdic Acid (g)
	Amidogen (g)
$_2$	Diimide (g)
a_2O_2	Sodium Hydroxide, Dimeric (g)
	Water (g)
$_2$	Hydrogen Peroxide (g)
$_4S$	Sulfuric Acid (ℓ)
$_4S$	Sulfuric Acid (g)
$_4W$	Tungstic Acid (c)
$_4W$	Tungstic Acid (g)
P	Phophorus Hydride (g)
S	Hydrogen Sulfide (g)
Ti	Titanium Hydride (c)
N	Ammonia (g)
$^+$	Hydronium Unipositive Ion (g)
$_4P$	Orthophosphoric Acid (c)
$_4P$	Orthophosphoric Acid (ℓ)
P	Phosphine (g)
IN	Ammonium Iodide (c)
N_2	Hydrazine (ℓ)
N_2	Hydrazine (g)
Si	Silane (g)
	Mercury (ref. st.)
	Mercury (ℓ)
	Mercury, Monatomic (g)
I	Mercurous Iodide (g)
I_2	Mercuric Iodide (c)
I_2	Mercuric Iodide (ℓ)
I_2	Mercuric Iodide (g)
O	Mercuric Oxide (c)
O	Mercury Monoxide (g)
$_2I_2$	Mercurous Iodide (c)
$_2I_2$	Mercurous Iodide (ℓ)
	Iodine, Monatomic (g)
	Potassium Iodide (c)
	Potassium Iodide (ℓ)
	Potassium Iodide (g)

Filing Order	Table Title
ILi	Lithium Iodide (c)
ILi	Lithium Iodide (ℓ)
ILi	Lithium Iodide (g)
INO	Nitrosyl Iodide (g)
INa	Sodium Iodide (c)
INa	Sodium Iodide (ℓ)
IPb	Lead Monoiodide (g)
ITi	Titanium Monoiodide (g)
IZr	Zirconium Monoiodide (g)
I_2	Iodine (ref. st.)
I_2	Iodine (ℓ)
I_2	Iodine, Diatomic (g)
I_2K_2	Potassium Iodide, Dimeric (g)
I_2Li_2	Lithium Iodide, Dimeric (g)
I_2Pb	Lead Diiodide (c)
I_2Pb	Lead Diiodide (ℓ)
I_2Pb	Lead Diiodide (g)
I_2Ti	Titanium Diiodide (c)
I_2Ti	Titanium Diiodide (g)
I_2Zr	Zirconium Diiodide (c)
I_2Zr	Zirconium Diiodide (ℓ)
I_2Zr	Zirconium Diiodide (g)
I_3Ti	Titanium Triiodide (c)
I_3Ti	Titanium Triiodide (g)
I_3Zr	Zirconium Triiodide (c)
I_3Zr	Zirconium Triiodide (g)
I_4Pb	Lead Tetraiodide (g)
I_4Ti	Titanium Tetraiodide (c)
I_4Ti	Titanium Tetraiodide (ℓ)
I_4Ti	Titanium Tetraiodide (g)
I_4Zr	Zirconium Tetraiodide (c)
I_4Zr	Zirconium Tetraiodide (g)
K	Potassium (ref. st.)
K	Potassium (ℓ)
K	Potassium, Monatomic (g)
K^+	Potassium Unipositive Ion (g)
KO	Potassium Monoxide (g)
KO^-	Potassium Monoxide Uninegative Ion (g)
K_2	Potassium, Diatomic (g)
K_2O	Potassium Oxide (c)
K_2O_2	Potassium Peroxide (c)
Li	Lithium (ref. st.)
Li	Lithium (c)
Li	Lithium (ℓ)
Li	Lithium, Monatomic (g)
Li^+	Lithium Unipositive Ion (g)
LiN	Lithium Nitride (g)

Filing Order	Table Title
LiNO	Lithium Nitroxide (g)
LiNaO	Lithium Sodium Oxide (g)
LiO	Lithium Monoxide (g)
LiO^-	Lithium Monoxide Uninegative Ion (g)
Li_2	Lithium, Diatomic (g)
Li_2O	Lithium Oxide (c)
Li_2O	Lithium Oxide (ℓ)
Li_2O	Lithium Oxide (g)
Li_2O_2	Lithium Peroxide (c)
Li_2O_2	Lithium Monoxide, Dimeric (g)
Li_2O_3Si	Lithium Metasilicate (c)
Li_2O_3Si	Lithium Metasilicate (ℓ)
Li_2O_3Ti	Lithium Metatitanate (c)
Li_2O_3Ti	Lithium Metatitanate (ℓ)
$Li_2O_5Si_2$	Lithium Disilicate (c)
$Li_2O_5Si_2$	Lithium Disilicate (ℓ)
Li_3N	Lithium Nitride (c)
Mg	Magnesium (ref. st.)
Mg	Magnesium (c)
Mg	Magnesium (ℓ)
Mg	Magnesium, Monatomic (g)
Mg^+	Magnesium Unipositive Ion (g)
MgN	Magnesium Nitride (g)
MgO	Magnesium Oxide (c)
MgO	Magnesium Oxide (ℓ)
MgO	Magnesium Oxide (g)
MgO_3Si	Magnesium Metasilicate (c)
MgO_3Si	Magnesium Metasilicate (ℓ)
MgO_3Ti	Magnesium Metatitanate (c)
MgO_3Ti	Magnesium Metatitanate (ℓ)
MgO_4S	Magnesium Sulfate (c)
MgO_4S	Magnesium Sulfate (ℓ)
MgO_4W	Magnesium Tungstate (c)
MgO_5Ti_2	Magnesium Dititanate (c)
MgO_5Ti_2	Magnesium Dititanate (ℓ)
MgS	Magnesium Sulfide (c)
MgS	Magnesium Sulfide (g)
Mg_2O_4Si	Magnesium Orthosilicate (c)
Mg_2O_4Si	Magnesium Orthosilicate (ℓ)
Mg_2O_4Ti	Magnesium Orthotitanate (c)
Mg_2O_4Ti	Magnesium Orthotitanate (ℓ)
Mg_2Si	Magnesium Silicide (c)
Mg_2Si	Magnesium Silicide (ℓ)
Mg_3N_2	Magnesium Nitride (c)
$Mg_3O_8P_2$	Magnesium Orthophosphate (c)
$Mg_3O_8P_2$	Magnesium Orthophosphate (ℓ)
Mo	Molybdenum (ref. st.)

Filing Order	Table Title
Mo	Molybdenum (c)
Mo	Molybdenum (ℓ)
Mo	Molybdenum, Monatomic (g)
Mo^+	Molybdenum Unipositive Ion (g)
MoO	Molybdenum Monoxide (g)
MoO_2	Molybdenum Dioxide (c)
MoO_2	Molybdenum Dioxide (g)
MoO_3	Molybdenum Trioxide (c)
MoO_3	Molybdenum Trioxide (ℓ)
MoO_3	Molybdenum Trioxide (g)
N	Nitrogen, Monatomic (g)
NO	Nitric Oxide (g)
NO^+	Nitric Oxide Unipositive Ion (g)
NO_2	Nitrogen Dioxide (g)
NO_2^-	Nitrogen Dioxide Negative Ion (g)
NO_3	Nitrogen Trioxide (g)
NP	Phosphorus Nitride (g)
NS	Sulfur Nitride (g)
NSi	Silicon Nitride (g)
NSi_2	Disilicon Nitride (g)
NTi	Titanium Nitride (c)
NTi	Titanium Nitride (ℓ)
NZr	Zirconium Nitride (c)
NZr	Zirconium Nitride (ℓ)
NZr	Zirconium Nitride (g)
N_2	Nitrogen (ref. st., g)
N_2O	Dinitrogen Monoxide (g)
N_2O_3	Dinitrogen Trioxide (g)
N_2O_4	Nitrogen Tetroxide (c)
N_2O_4	Dinitrogen Tetroxide (ℓ)
N_2O_4	Nitrogen Tetroxide (g)
N_2O_5	Dinitrogen Pentoxide (g)
N_4Si_3	Silicon Nitride (c,α)
N_5P_3	Triphosphorus Pentanitride (c)
Na	Sodium (ref. st.)
Na	Sodium (c)
Na	Sodium (ℓ)
Na	Sodium Monatomic (g)
Na^+	Sodium Unipositive Ion (g)
NaO	Sodium Monoxide (g)
NaO^-	Sodium Monoxide Uninegative Ion (g)
NaO_2	Sodium Superoxide (c)
Na_2	Sodium Diatomic (g)
Na_2O	Disodium Monoxide (c)
Na_2O	Disodium Monoxide (ℓ)
Na_2O_2	Disodium Dioxide (c)
Na_2O_3Si	Sodium Metasilicate (c)
Na_2O_3Si	Sodium Metasilicate (ℓ)

Filing Order	Table Title
Na_2O_4S	Sodium Sulfate (c,V)
Na_2O_4S	Sodium Sulfate (c,III)
Na_2O_4S	Sodium Sulfate (c,I)
Na_2O_4S	Sodium Sulfate (c,δ)
Na_2O_4S	Sodium Sulfate (ℓ)
Na_2O_4W	Sodium Tungstate (c)
$Na_2O_5Si_2$	Sodium Disilicate (c)
$Na_2O_5Si_2$	Sodium Disilicate (ℓ)
Na_2S	Sodium Sulfide (c)
Na_2S	Sodium Sulfide (ℓ)
O	Oxygen, Monatomic (g)
O^-	Oxygen Uninegative Ion (g)
OP	Phosphorus Monoxide (g)
OPb	Lead Monoxide (c, Red)
OPb	Lead Monoxide (c, Yellow)
OPb	Lead Monoxide (ℓ)
OPb	Lead Monoxide (g)
OS	Sulfur Monoxide (g)
OS_2	Disulfur Monoxide (g)
OSi	Silicon Monoxide (g)
OTi	Titanium Monoxide (c,α)
OTi	Titanium Monoxide (c,β)
OTi	Titanium Monoxide (ℓ)
OTi	Titanium Monoxide (g)
OW	Tungsten Monoxide (g)
OZr	Zirconium Monoxide (g)
O_2	Oxygen, Diatomic (ref. st., g)
O_2^-	Diatomic Oxygen Uninegative Ion (g)
O_2P	Phosphorus Dioxide (g)
O_2Pb	Lead Dioxide (c)
O_2S	Sulfur Dioxide (g)
O_2Si	Quartz (c)
O_2Si	Cristobalite (c,low)
O_2Si	Cristobalite (c,high)
O_2Si	Silicon Dioxide (ℓ)
O_2Si	Silicon Dioxide (g)
O_2Ti	Anatase (c)
O_2Ti	Rutile (c)
O_2Ti	Titanium Dioxide (ℓ)
O_2Ti	Titanium Dioxide (g)
O_2W	Tungsten Dioxide (c)
O_2W	Tungsten Dioxide (g)
$O_{2.72}W$	Tungsten Oxide (c)
$O_{2.90}W$	Tungsten Oxide (c)
$O_{2.96}W$	Tungsten Oxide (c)
O_2Zr	Zirconium Dioxide (c)
O_2Zr	Zirconium Dioxide (ℓ)
O_2Zr	Zirconium Dioxide (g)

Filing Order	Table Title
O_3	Ozone (g)
O_3PbSi	Lead Metasilicate (c)
O_3S	Sulfur Trioxide (g)
O_3Ti_2	Dititanium Trioxide (c)
O_3Ti_2	Dititanium Trioxide (ℓ)
O_3W	Tungsten Trioxide (c)
O_3W	Tungsten Trioxide (ℓ)
O_3W	Tungsten Trioxide (g)
O_4Pb_2Si	Lead Orthosilicate (c)
O_4Pb_3	Lead Orthoplumbate (c)
O_4SiZr	Zirconium Orthosilicate (c)
O_5Ti_3	Trititanium Pentoxide (c,α)
O_5Ti_3	Trititanium Pentoxide (c,β)
O_5Ti_3	Trititanium Pentoxide (ℓ)
O_6P_4	Phosphorus Trioxide, Dimeric (g)
O_6W_2	Tungsten Trioxide, Dimeric (g)
O_8W_3	Tritungsten Octaoxide (g)
O_9W_3	Tungsten Trioxide, Trimeric (g)
$O_{10}P_4$	Phosphorus Pentoxide, Dimeric (c)
$O_{10}P_4$	Phosphorus Pentoxide, Dimeric (g)
$O_{12}W_4$	Tungsten Trioxide, Tetrameric (g)
P	Phosphorus (ref. st.)
P	Phosphorus (c, Red, V)
P	Phosphorus (c, White)
P	Phosphorus (ℓ)
P	Phosphorus (g)
PS	Phosphorus Sulfide (g)
P_2	Phosphorus, Diatomic (g)
P_4	Phosphorus, Tetratomic (g)
P_4S_3	Phosphorus Sulfide (c)
P_4S_3	Phosphorus Sulfide (ℓ)
P_4S_3	Phosphorus Sulfide (g)
Pb	Lead (ref. st.)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
Pb_2	Lead, Diatomic (g)
S	Sulfur (ref. st.)
S	Sulfur (c)
S	Sulfur (ℓ)
S	Sulfur, Monatomic (g)
SSi	Silicon Monosulfide (g)
S_2	Sulfur, Diatomic (g)
S_2Si	Silicon Disulfide (c)
S_2Si	Silicon Disulfide (ℓ)
S_8	Sulfur Octatomic (g)

Filing Order	Table Title
Si	Silicon (ref. st.)
Si	Silicon (c)
Si	Silicon (ℓ)
Si	Silicon, Monatomic (g)
Si_2	Silicon, Diatomic (g)
Si_3	Silicon, Triatomic (g)
Ti	Titanium (ref. st.)
Ti	Titanium (c,α)
Ti	Titanium (c,β)
Ti	Titanium (ℓ)
Ti	Titanium, Monatomic (g)
Ti^+	Titanium Unipositive Ion (g)

Filing Order	Table Title
W	Tungsten (ref. st.)
W	Tungsten (c)
W	Tungsten (ℓ)
W	Tungsten, Monatomic (g)
W^+	Tungsten Unipositive Ion
Zr	Zirconium (ref. st.)
Zr	Zirconium (c,α)
Zr	Zirconium (c,β)
Zr	Zirconium (ℓ)
Zr	Zirconium (g)
Zr^+	Zirconium Unipositive Ion (g)
e^-	Electron Gas (ref. st.)

(Reference State)   At. Wt. = 26.9815

ALUMINUM (Al)   (REFERENCE STATE)   AT. WT. = 26.9815

0	to 933°K.	Crystal
933	to 2766.8°K.	Liquid
2766.8	to 6000°K.	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.094	.000	.000	.000
100	3.116	1.650	11.530	-.986	.000	.000	.000
200	5.158	4.572	7.302	-.546	.000	.000	.000
298	5.806	6.769	6.769	.000	.000	.000	.000
300	5.814	6.805	6.769	.011	.000	.000	.000
400	6.163	8.528	7.002	.610	.000	.000	.000
500	6.450	9.934	7.452	1.241	.000	.000	.000
600	6.717	11.134	7.968	1.900	.000	.000	.000
700	6.999	12.190	8.497	2.585	.000	.000	.000
800	7.370	13.147	9.019	3.302	.000	.000	.000
900	7.901	14.044	9.528	4.064	.000	.000	.000
1000	7.588	17.603	10.205	7.397	.000	.000	.000
1100	7.588	18.326	10.911	8.156	.000	.000	.000
1200	7.588	18.986	11.557	8.915	.000	.000	.000
1300	7.588	19.593	12.152	9.673	.000	.000	.000
1400	7.588	20.156	12.704	10.432	.000	.000	.000
1500	7.588	20.679	13.218	11.191	.000	.000	.000
1600	7.588	21.169	13.700	11.950	.000	.000	.000
1700	7.588	21.629	14.153	12.709	.000	.000	.000
1800	7.588	22.063	14.581	13.467	.000	.000	.000
1900	7.588	22.473	14.985	14.226	.000	.000	.000
2000	7.588	22.862	15.370	14.985	.000	.000	.000
2100	7.588	23.232	15.735	15.744	.000	.000	.000
2200	7.588	23.585	16.084	16.503	.000	.000	.000
2300	7.588	23.923	16.418	17.261	.000	.000	.000
2400	7.588	24.246	16.737	18.020	.000	.000	.000
2500	7.588	24.555	17.044	18.779	.000	.000	.000
2600	7.588	24.853	17.338	19.538	.000	.000	.000
2700	7.588	25.139	17.622	20.297	.000	.000	.000
2800	4.970	50.501	18.192	90.466	.000	.000	.000
2900	4.971	50.675	19.309	90.963	.000	.000	.000
3000	4.971	50.844	20.357	91.460	.000	.000	.000
3100	4.971	51.007	21.343	91.957	.000	.000	.000
3200	4.972	51.165	22.273	92.454	.000	.000	.000
3300	4.973	51.318	23.151	92.951	.000	.000	.000
3400	4.975	51.466	23.981	93.449	.000	.000	.000
3500	4.977	51.610	24.769	93.946	.000	.000	.000
3600	4.979	51.751	25.516	94.444	.000	.000	.000
3700	4.982	51.887	26.227	94.942	.000	.000	.000
3800	4.986	52.020	26.904	95.441	.000	.000	.000
3900	4.991	52.150	27.550	95.939	.000	.000	.000
4000	4.996	52.276	28.166	96.439	.000	.000	.000
4100	5.002	52.399	28.756	96.939	.000	.000	.000
4200	5.010	52.520	29.320	97.439	.000	.000	.000
4300	5.019	52.638	29.861	97.941	.000	.000	.000
4400	5.029	52.754	30.380	98.443	.000	.000	.000
4500	5.041	52.867	30.879	98.947	.000	.000	.000
4600	5.055	52.978	31.358	99.451	.000	.000	.000
4700	5.071	53.086	31.819	99.958	.000	.000	.000
4800	5.088	53.193	32.263	100.466	.000	.000	.000
4900	5.108	53.299	32.691	100.975	.000	.000	.000
5000	5.130	53.402	33.105	101.487	.000	.000	.000
5100	5.154	53.504	33.503	102.001	.000	.000	.000
5200	5.181	53.604	33.889	102.518	.000	.000	.000
5300	5.211	53.703	34.262	103.038	.000	.000	.000
5400	5.244	53.801	34.623	103.560	.000	.000	.000
5500	5.280	53.897	34.972	104.087	.000	.000	.000
5600	5.319	53.993	35.311	104.617	.000	.000	.000
5700	5.361	54.087	35.640	105.150	.000	.000	.000
5800	5.406	54.181	35.959	105.689	.000	.000	.000
5900	5.456	54.274	36.268	106.232	.000	.000	.000
6000	5.508	54.366	36.569	106.780	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1965

Al

Aluminum (Al)

(Liquid) At. Wt. = 26.9815

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	7.588	8.420	8.420	.000	2.072	1.580	-1.158
300	7.588	8.467	8.420	.014	2.075	1.576	-1.148
400	7.588	10.650	8.718	.773	2.235	1.386	-.757
500	7.588	12.343	9.280	1.532	2.363	1.158	-.506
600	7.588	13.727	9.909	2.290	2.462	.907	-.330
700	7.588	14.896	10.540	3.049	2.536	.642	-.200
800	7.588	15.909	11.149	3.808	2.579	.368	-.101
900	7.588	16.803	11.729	4.567	2.575	.092	-.022
1000	7.588	17.603	12.277	5.326	.000	.000	.000
1100	7.588	18.326	12.795	6.084	.000	.000	.000
1200	7.588	18.986	13.283	6.843	.000	.000	.000
1300	7.588	19.594	13.746	7.602	.000	.000	.000
1400	7.588	20.156	14.184	8.361	.000	.000	.000
1500	7.588	20.679	14.600	9.120	.000	.000	.000
1600	7.588	21.169	14.995	9.878	.000	.000	.000
1700	7.588	21.629	15.372	10.637	.000	.000	.000
1800	7.588	22.063	15.732	11.396	.000	.000	.000
1900	7.588	22.473	16.076	12.155	.000	.000	.000
2000	7.588	22.862	16.405	12.914	.000	.000	.000
2100	7.588	23.233	16.722	13.672	.000	.000	.000
2200	7.588	23.585	17.026	14.431	.000	.000	.000
2300	7.588	23.923	17.318	15.190	.000	.000	.000
2400	7.588	24.246	17.600	15.949	.000	.000	.000
2500	7.588	24.555	17.872	16.708	.000	.000	.000
2600	7.588	24.853	18.135	17.466	.000	.000	.000
2700	7.588	25.139	18.389	18.225	.000	.000	.000
2800	7.588	25.415	18.635	18.984	-69.410	.831	-.065
2900	7.588	25.682	18.874	19.743	-69.148	3.332	-.251
3000	7.588	25.939	19.105	20.502	-68.886	5.829	-.425
3100	7.588	26.188	19.330	21.260	-68.625	8.314	-.586
3200	7.588	26.429	19.548	22.019	-68.363	10.792	-.737
3300	7.588	26.662	19.760	22.778	-68.101	13.264	-.878
3400	7.588	26.889	19.966	23.537	-67.840	15.722	-1.011
3500	7.588	27.109	20.167	24.296	-67.578	18.175	-1.135
3600	7.588	27.322	20.363	25.054	-67.318	20.627	-1.252
3700	7.588	27.530	20.554	25.813	-67.057	23.064	-1.362
3800	7.588	27.733	20.740	26.572	-66.797	25.494	-1.466
3900	7.588	27.930	20.922	27.331	-66.536	27.922	-1.565
4000	7.588	28.122	21.099	28.090	-66.277	30.339	-1.658

Dec. 31, 1960; Dec. 31, 1965; June 30, 1967

ALUMINUM (Al) (LIQUID) AT. WT. = 26.9815

$S°_{298.15}$ = 8.42 gibbs/mol

Tm° = 933°K

Tb° = 2766.8°K

$\Delta Hf°_{298.15}$ = 2.072 kcal/mol

ΔHm° = 2.56 ± 0.05 kcal/mol

ΔHv° = 69.497 kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between $H°_{933} - H°_{298}$ for (c) and (ℓ).

Heat Capacity and Entropy

The heat capacity is adopted from the enthalpy measurements of R. A. McDonald, private communication, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan, Oct. 1965. The liquid enthalpies were determined in crucibles of BN and TiB_2 sealed in a platinum-rhodium capsule. The liquid enthalpies are in agreement with the determination of J. W. Awberry and E. Griffiths, Proc. Phys. Soc. (London) 38, 378 (1926) and higher, by as much as 12 percent, than those of F. Wust, A. Meuthen and R. Dorrer, Forsch. Arb. Ver. Deut. Ing. No 204 (1918) and S. Umino, Sci. Repts. Tohoku. Imp. Univ. Ser 1, 15, 597 (1926). The enthalpy data is adequately represented by a constant heat capacity. The entropy is calculated from that of the crystal in a manner analogous to the heat of formation.

Melting Data

See Al(c) for details.

Vaporization Data

The temperature of boiling and the heat of vaporization are derived from the adopted functions and the heat of sublimation in order to maintain thermodynamic consistency.

Aluminum (Al)
(Ideal Gas) At. Wt. = 26.9815

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.654	77.440	77.440	INFINITE
100	6.020	33.345	43.998	-1.065	77.923	74.753	-163.365
200	5.290	37.231	39.775	-.509	78.037	71.505	-78.134
298	5.112	39.304	39.304	.000	78.000	68.300	-50.063
300	5.111	39.335	39.304	.009	77.998	68.239	-49.710
400	5.047	40.795	39.503	.517	77.907	65.000	-35.513
500	5.018	41.918	39.878	1.020	77.779	61.787	-27.006
600	5.002	42.832	40.297	1.521	77.621	58.602	-21.345
700	4.993	43.602	40.715	2.021	77.436	55.447	-17.311
800	4.987	44.268	41.119	2.520	77.218	52.321	-14.293
900	4.983	44.855	41.502	3.018	76.954	49.224	-11.953
1000	4.980	45.380	41.864	3.516	74.119	46.342	-10.128
1100	4.978	45.855	42.206	4.014	73.658	43.576	-8.657
1200	4.976	46.288	42.528	4.512	73.597	40.835	-7.437
1300	4.975	46.686	42.833	5.010	73.337	38.116	-6.408
1400	4.974	47.055	43.121	5.507	73.075	35.416	-5.528
1500	4.973	47.398	43.395	6.004	72.813	32.735	-4.769
1600	4.973	47.719	43.655	6.502	72.552	30.072	-4.107
1700	4.972	48.020	43.903	6.999	72.290	27.425	-3.526
1800	4.972	48.305	44.140	7.496	72.029	24.794	-3.010
1900	4.971	48.573	44.366	7.993	71.767	22.177	-2.551
2000	4.971	48.828	44.583	8.490	71.505	19.573	-2.139
2100	4.971	49.071	44.791	8.988	71.244	16.982	-1.767
2200	4.971	49.302	44.991	9.485	70.982	14.404	-1.431
2300	4.970	49.523	45.183	9.982	70.721	11.841	-1.125
2400	4.970	49.735	45.369	10.479	70.459	9.285	-.845
2500	4.970	49.938	45.547	10.976	70.197	6.739	-.589
2600	4.970	50.132	45.720	11.473	69.935	4.209	-.354
2700	4.970	50.320	45.887	11.970	69.673	1.684	-.136
2800	4.970	50.501	46.048	12.467	.000	.000	.000
2900	4.971	50.675	46.205	12.964	.000	.000	.000
3000	4.971	50.844	46.357	13.461	.000	.000	.000
3100	4.971	51.007	46.504	13.958	.000	.000	.000
3200	4.972	51.165	46.647	14.455	.000	.000	.000
3300	4.973	51.318	46.787	14.952	.000	.000	.000
3400	4.975	51.466	46.922	15.450	.000	.000	.000
3500	4.977	51.610	47.054	15.947	.000	.000	.000
3600	4.979	51.751	47.182	16.445	.000	.000	.000
3700	4.982	51.887	47.306	16.943	.000	.000	.000
3800	4.986	52.020	47.430	17.442	.000	.000	.000
3900	4.991	52.150	47.549	17.941	.000	.000	.000
4000	4.996	52.276	47.666	18.440	.000	.000	.000
4100	5.002	52.399	47.780	18.940	.000	.000	.000
4200	5.010	52.520	47.891	19.440	.000	.000	.000
4300	5.019	52.638	48.000	19.942	.000	.000	.000
4400	5.029	52.754	48.107	20.444	.000	.000	.000
4500	5.041	52.867	48.212	20.948	.000	.000	.000
4600	5.055	52.978	48.314	21.453	.000	.000	.000
4700	5.071	53.086	48.414	21.959	.000	.000	.000
4800	5.088	53.193	48.513	22.467	.000	.000	.000
4900	5.106	53.299	48.609	22.977	.000	.000	.000
5000	5.130	53.402	48.704	23.488	.000	.000	.000
5100	5.154	53.504	48.797	24.003	.000	.000	.000
5200	5.181	53.604	48.889	24.519	.000	.000	.000
5300	5.211	53.703	48.979	25.039	.000	.000	.000
5400	5.244	53.801	49.067	25.562	.000	.000	.000
5500	5.280	53.897	49.154	26.088	.000	.000	.000
5600	5.319	53.993	49.240	26.618	.000	.000	.000
5700	5.361	54.087	49.324	27.152	.000	.000	.000
5800	5.406	54.181	49.407	27.690	.000	.000	.000
5900	5.456	54.274	49.489	28.233	.000	.000	.000
6000	5.508	54.366	49.569	28.781	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

ALUMINUM (Al) (IDEAL GAS) AT. WT. = 26.9815

Ground State Configuration $^2P^\circ_{1/2}$

$S^\circ_{298.15}$ = 39.304 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 77.44 ± 0.9 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 78.0 ± 0.9 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i
0	2	32700	18	42200	12
112	4	37689	2	43600	20
25348	2	38930	10	44430	18
29100	12	40275	6	46130	84
		41319	14		

Heat of Formation.

The heat of sublimation of aluminum has been derived from a second and third law analysis of the vapor pressure data of several investigators; the results are tabulated below.

				ΔH_{298} subl. kcal. mole^{-1}		Drift
Ref.	Range °K.	Method	Points	2nd law	3rd law	cal. deg.$^{-1}$ mole^{-1}
1	1273-1473	Knudsen	10*	76.3 ± 2.3	75.32 ± 0.7	-0.8 ± 1.7
2	1734-2237	Boiling	4	83.1 ± 0.3	74.58 ± 1.8	-4.3 ± 0.2
3	1383-1468	Knudsen	10	89.8 ± 32.9	77.29 ± 3.7	-9.0 ± 23.3
4	1410-1468	Knudsen	6	71.9 ± 19.2	78.4 ± 1.3	4.5 ± 13.2
5	1511-1723	Mass Spec	11	77.2 ± 2		
6	2473	Boiling	1		70.5	
7	1476	Knudsen	1		77.35	
8	1400-1611	Torsion	104	80.3 ± 1.2	79.5 ± 0.3	-0.3 ± 0.8

*1 point rejected due to failure of statistical test.

References:

1. Yu. A. Priselkov, Yu. A. Sapozhnikov and A. V. Tseplyaeva, Izv. Akad. Nauk. SSR, Otd. Tech. Nauk. No. 1, 106 (1959)
2. E. Baur and R. Brunner, Helv. Chim. Acta, 17, 958 (1934).
3. L. Brewer and A. W. Searcy, J. Am. Chem. Soc. 73, 5308 (1951).
4. Ref. 3 omitting data from TaC cells.
5. R. F. Porter, P. Schissel and M. G. Inghram, J. Chem Phys. 23, 339 (1955).
6. H. von Wartenberg, Z. Elektrochem. 19, 482 (1913).
7. L. Farkas, Z. Physik, 7, 735 (1931).
8. N. D. Potter, Philco Corporation, Newport Beach, California. Private communication Jan. 11, 1966.

It is apparent that there is little real agreement in the data; in Ref. 3 some of this is due to diffusion of liquid Al through the TaC crucibles, while Ref. 8 reports surface oxidation of the sample. The data for Ref. 5 have been reworked since they corrected their data using ΔC_p between (l) and (g) of -2 cal. deg.$^{-1}$ mole^{-1}, where our tables give a value of -2.62 cal. deg.$^{-1}$ mole^{-1}. Ref. 8 has obtained by far the largest number of data points all of which are in good agreement, show no trend and little scatter. Ref. 1 has gone to a great deal of trouble to ensure uniform heating, total collection of effusate and good Knudsen conditions and also has no trend. It is difficult to imagine why these two series differ by a factor of 3 in the pressure. An intermediate value of the heat of sublimation has been adopted at 78 ± 2 kcal. mole^{-1}. This choice is also indicated by the decomposition of AlN(c) to Al(g) and 1/2 N_2(g), which has been well established as 153.7 ± 0.8 kcal. mole^{-1}, combined with the heat of formation of AlN(c) = -76 ± 0.3 kcal. mole^{-1}, to yield ΔH°_{sub} Al = 77.7 ± 0.9 kcal. mole^{-1}.

Heat Capacity and Entropy.

The electronic ground state configuration and the higher electronic levels are taken from C. E. Moore, Natl. Bur. Stds. Circular 467, "Atomic Energy Levels" Washington 1949.

Aluminum Unipositive Ion (Al^+)

(Ideal Gas) Mol. Wt. = 26.98095

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	4.968	35.813	35.813	.000	217.300	207.153	-151.840
300	4.968	35.844	35.813	.009	217.307	207.090	-150.858
400	4.968	37.273	36.008	.506	217.704	203.624	-111.250
500	4.968	38.382	36.376	1.003	218.071	200.061	-87.442
600	4.968	39.288	36.788	1.500	218.409	196.426	-71.545
700	4.968	40.053	37.201	1.996	218.714	192.737	-60.172
800	4.968	40.717	37.600	2.493	218.992	189.007	-51.632
900	4.968	41.302	37.980	2.990	219.239	185.245	-44.982
1000	4.968	41.825	38.339	3.487	216.961	181.641	-39.696
1100	4.968	42.299	38.677	3.984	217.255	178.095	-35.382
1200	4.968	42.731	38.998	4.481	217.549	174.523	-31.783
1300	4.968	43.129	39.300	4.977	217.841	170.923	-28.733
1400	4.968	43.497	39.587	5.474	218.135	167.304	-26.116
1500	4.968	43.840	39.859	5.971	218.429	163.662	-23.844
1600	4.968	44.161	40.118	6.468	218.723	160.001	-21.854
1700	4.968	44.462	40.365	6.965	219.017	156.322	-20.096
1800	4.968	44.746	40.600	7.461	219.309	152.625	-18.530
1900	4.968	45.014	40.826	7.958	219.603	148.916	-17.128
2000	4.968	45.269	41.042	8.455	219.897	145.187	-15.865
2100	4.968	45.512	41.249	8.952	220.191	141.441	-14.719
2200	4.968	45.743	41.448	9.449	220.485	137.685	-13.677
2300	4.968	45.964	41.639	9.945	220.777	133.913	-12.724
2400	4.968	46.175	41.824	10.442	221.071	130.133	-11.850
2500	4.968	46.378	42.002	10.939	221.365	126.338	-11.044
2600	4.968	46.573	42.174	11.436	221.659	122.529	-10.299
2700	4.968	46.760	42.341	11.933	221.953	118.713	-9.609
2800	4.968	46.941	42.502	12.430	151.693	116.536	-9.096
2900	4.968	47.115	42.658	12.926	152.188	115.271	-8.687
3000	4.968	47.284	42.809	13.423	152.685	113.988	-8.304
3100	4.968	47.446	42.956	13.920	153.182	112.693	-7.944
3200	4.968	47.604	43.099	14.417	153.678	111.380	-7.607
3300	4.969	47.757	43.238	14.914	154.175	110.050	-7.288
3400	4.969	47.905	43.373	15.411	154.671	108.706	-6.987
3500	4.969	48.049	43.504	15.907	155.166	107.346	-6.703
3600	4.969	48.189	43.633	16.404	155.662	105.975	-6.433
3700	4.970	48.326	43.758	16.901	156.158	104.580	-6.177
3800	4.971	48.458	43.880	17.398	156.654	103.185	-5.934
3900	4.971	48.587	43.999	17.895	157.149	101.773	-5.703
4000	4.973	48.713	44.115	18.393	157.644	100.344	-5.482
4100	4.974	48.836	44.229	18.890	158.138	98.901	-5.272
4200	4.976	48.956	44.340	19.388	158.632	97.454	-5.071
4300	4.978	49.073	44.449	19.885	159.125	95.993	-4.879
4400	4.981	49.187	44.555	20.383	159.617	94.519	-4.695
4500	4.984	49.299	44.659	20.881	160.108	93.036	-4.518
4600	4.988	49.409	44.761	21.380	160.599	91.539	-4.349
4700	4.992	49.516	44.861	21.879	161.089	90.030	-4.186
4800	4.998	49.621	44.959	22.378	161.577	88.512	-4.030
4900	5.004	49.725	45.055	22.879	162.065	86.987	-3.880
5000	5.011	49.826	45.150	23.379	162.549	85.449	-3.735
5100	5.019	49.925	45.243	23.881	163.034	83.902	-3.595
5200	5.028	50.023	45.334	24.383	163.516	82.344	-3.461
5300	5.038	50.118	45.423	24.886	163.997	80.782	-3.331
5400	5.050	50.213	45.511	25.391	164.476	79.204	-3.205
5500	5.062	50.306	45.597	25.896	164.952	77.618	-3.084
5600	5.077	50.397	45.682	26.403	165.425	76.027	-2.967
5700	5.092	50.487	45.765	26.912	165.897	74.429	-2.854
5800	5.109	50.576	45.848	27.422	166.366	72.818	-2.744
5900	5.128	50.663	45.929	27.934	166.832	71.204	-2.637
6000	5.148	50.749	46.008	28.447	167.293	69.583	-2.534

June 30, 1965

ALUMINUM UNIPOSITIVE ION (Al^+) (IDEAL GAS) MOL. WT. = 26.98095

Ground State Configuration $^1S_0$

$\Delta H^\circ_{f\ 0}$ = 215.4 ± .5 kcal/mole

$S^\circ_{298.15}$ = 35.813 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 217.3 ± .5 kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_i$, cm.$^{-1}$	g_i	$\mathcal{E}_i$, cm.$^{-1}$	g_i
0.0	1	94084.5	1
37392.0	1	94146.8	3
37453.8	3	94267.7	5
37579.3	5	95348.2	1
59849.7	3	95546.8	7
85479.0	5	95547.9	5
91271.2	3	95548.8	3

Heat of Formation.

The heat of formation was calculated from the equation: $Al(g) - e^- \rightarrow Al^+(g)$ with the JANAF auxiliary value for Al(g); using an I.P. = 4.827916 X 10^4 cm^{-1} (138.047 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.481 kcal./mole.

Aluminum Boron Dioxide ($AlBO_2$)

(Ideal Gas)   GFW = 69.7913

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.870	- 128.809	- 128.809	INFINITE
100	8.336	53.455	74.134	- 2.068	- 128.832	- 129.852	283.792
200	10.453	59.825	65.508	- 1.137	- 129.103	- 130.789	142.920
298	12.627	64.420	64.420	.000	- 129.400	- 131.560	96.436
300	12.663	64.498	64.420	.023	- 129.406	- 131.574	95.851
400	14.289	68.377	64.938	1.376	- 129.685	- 132.253	72.260
500	15.445	71.697	65.966	2.866	- 129.970	- 132.862	58.074
600	16.294	74.592	67.168	4.454	- 130.271	- 133.413	48.596
700	16.936	77.154	68.415	6.117	- 130.587	- 133.912	41.809
800	17.432	79.449	69.653	7.837	- 130.927	- 134.365	36.707
900	17.821	81.526	70.859	9.600	- 131.306	- 134.773	32.727
1000	18.129	83.420	72.021	11.398	- 134.253	- 134.951	29.493
1100	18.377	85.160	73.138	13.224	- 134.629	- 135.004	26.823
1200	18.578	86.768	74.207	15.072	- 135.007	- 135.021	24.591
1300	18.743	88.261	75.232	16.938	- 135.390	- 135.006	22.697
1400	18.879	89.655	76.213	18.820	- 135.778	- 134.961	21.068
1500	18.993	90.962	77.153	20.713	- 136.176	- 134.892	19.654
1600	19.089	92.191	78.055	22.618	- 136.580	- 134.792	18.412
1700	19.171	93.351	78.921	24.531	- 136.993	- 134.668	17.313
1800	19.240	94.448	79.753	26.451	- 137.415	- 134.517	16.333
1900	19.300	95.490	80.554	28.379	- 137.844	- 134.345	15.453
2000	19.353	96.482	81.326	30.311	- 138.280	- 134.152	14.659
2100	19.398	97.427	82.070	32.249	- 138.721	- 133.933	13.939
2200	19.438	98.330	82.789	34.191	- 139.170	- 133.695	13.281
2300	19.473	99.195	83.484	36.136	- 139.624	- 133.434	12.679
2400	19.504	100.025	84.156	38.085	- 140.086	- 133.155	12.125
2500	19.531	100.821	84.807	40.037	- 145.942	- 132.750	11.605
2600	19.556	101.588	85.437	41.991	- 146.409	- 132.213	11.113
2700	19.578	102.326	86.049	43.948	- 146.879	- 131.656	10.657
2800	19.598	103.039	86.643	45.907	- 216.762	- 130.256	10.167
2900	19.616	103.727	87.221	47.868	- 216.976	- 127.161	9.583
3000	19.632	104.392	87.782	49.830	- 217.194	- 124.059	9.038
3100	19.647	105.036	88.328	51.794	- 217.414	- 120.951	8.527
3200	19.660	105.660	88.860	53.759	- 217.638	- 117.836	8.048
3300	19.673	106.265	89.379	55.726	- 217.864	- 114.713	7.597
3400	19.684	106.853	89.884	57.694	- 218.095	- 111.587	7.173
3500	19.694	107.423	90.377	59.663	- 218.327	- 108.452	6.772
3600	19.704	107.978	90.858	61.633	- 218.563	- 105.304	6.393
3700	19.713	108.518	91.328	63.603	- 218.803	- 102.156	6.034
3800	19.721	109.044	91.788	65.575	- 219.045	- 98.999	5.694
3900	19.728	109.557	92.237	67.548	- 219.288	- 95.842	5.371
4000	19.735	110.056	92.676	69.521	- 340.716	- 90.528	4.946
4100	19.742	110.544	93.106	71.495	- 340.736	- 84.277	4.492
4200	19.748	111.019	93.527	73.469	- 340.757	- 78.013	4.059
4300	19.753	111.484	93.939	75.444	- 340.783	- 71.758	3.647
4400	19.759	111.938	94.343	77.420	- 340.812	- 65.500	3.253
4500	19.763	112.382	94.739	79.396	- 340.845	- 59.244	2.877
4600	19.768	112.817	95.127	81.372	- 340.880	- 52.984	2.517
4700	19.772	113.242	95.508	83.349	- 340.921	- 46.729	2.173
4800	19.776	113.658	95.882	85.327	- 340.964	- 40.465	1.842
4900	19.780	114.066	96.249	87.305	- 341.011	- 34.208	1.526
5000	19.784	114.466	96.609	89.283	- 341.063	- 27.948	1.222
5100	19.787	114.858	96.963	91.261	- 341.121	- 21.682	.929
5200	19.790	115.242	97.311	93.240	- 341.182	- 15.422	.648
5300	19.793	115.619	97.653	95.220	- 341.247	- 9.155	.378
5400	19.796	115.989	97.989	97.199	- 341.319	- 2.890	.117
5500	19.799	116.352	98.320	99.179	- 341.395	3.383	- .134
5600	19.801	116.709	98.645	101.159	- 341.479	9.646	- .376
5700	19.804	117.059	98.965	103.139	- 341.568	15.919	- .610
5800	19.806	117.404	99.280	105.120	- 341.664	22.193	- .836
5900	19.808	117.742	99.590	107.100	- 341.767	28.470	- 1.055
6000	19.810	118.075	99.895	109.081	- 341.877	34.749	- 1.266

June 30, 1966

ALUMINUM BORON DIOXIDE ($AlBO_2$)   (IDEAL GAS)   GFW = 69.7913

Point Group [C_s] ΔHf°_0 = -128.8 ± 4 kcal/mol

$S^\circ_{298.15}$ = [64.4] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -129.4 ± 4 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Bond Distance: Al-O = [1.66] Å   O-B = [1.36] Å   B=O = [1.20] Å

Bond Angle: Al-O-B = [145]°   O-B=O = [180]° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.65357] X 10^{-115} g^3 cm^6

Heat of Formation.

The heat of formation, ΔHf°_{298} ($AlBO_2$, g) = -129.4 ± 4 kcal/mol, was calculated from the heat of reaction, ΔHr°_{1500} = -14.7 ± 3.2 kcal/mol for 1/2 Al_2O(g) + 1/2 B_2O_3(g) = $AlBO_2$(g), with all JANAF auxiliary data. The value of ΔHr°_{1500} was obtained from the mass spectrometric determination of ion intensity ratios by A. Büchler, P. E. Blackburn and J. L. Stauffer, "Thermodynamics of Vaporization in the Aluminum Oxide-Boron Oxide System," ARPA Order No 315-62, Arthur D. Little, Inc., Cambridge, Mass.

Heat Capacity and Entropy.

The bent molecular structure, the bond distances O-B and B=O, and the bond angle O-B-O were assumed to be the same as those in $LiBO_2$(g). The bond distance Al-O and the bond angle Al-O-(BO) were estimated to be the same as those in Al_2O(g). The three principal moments of inertia are I_A = 0.7255 X 10^{-39}, I_B = 29.9238 X 10^{-39}, and I_C = 30.6493 X 10^{-39} g cm^2.

The vibrational frequencies were estimated by comparison with those in $LiBO_2$(g), Al_2O(g), B_2O_3(g), and AlCl(g).

Aluminum Monobromide (AlBr)

(Ideal Gas) Mol. Wt. = 106.896

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.287	5.337	5.337	INFINITE
100	7.225	48.631	64.496	-1.586	5.597	1.542	-3.371
200	8.092	53.926	58.013	-.817	5.339	-2.442	2.669
298	8.509	57.246	57.246	.000	3.600	-6.026	4.417
300	8.514	57.299	57.246	.016	3.588	-6.086	4.433
400	8.710	59.778	57.583	.878	-.266	-8.528	4.659
500	8.816	61.734	58.224	1.755	-.458	-10.573	4.621
600	8.881	63.347	58.948	2.640	-.673	-12.576	4.580
700	8.926	64.720	59.677	3.530	-.916	-14.541	4.540
800	8.959	65.914	60.383	4.425	-1.186	-16.469	4.499
900	8.986	66.971	61.058	5.322	-1.485	-18.362	4.459
1000	9.009	67.919	61.697	6.222	-4.307	-20.035	4.378
1100	9.028	68.778	62.302	7.124	-4.556	-21.596	4.290
1200	9.046	69.565	62.875	8.027	-4.804	-23.134	4.213
1300	9.062	70.289	63.418	8.933	-5.051	-24.651	4.144
1400	9.078	70.962	63.933	9.840	-5.297	-26.151	4.082
1500	9.092	71.588	64.423	10.748	-5.542	-27.631	4.026
1600	9.106	72.176	64.889	11.658	-5.787	-29.096	3.974
1700	9.120	72.728	65.334	12.569	-6.031	-30.545	3.927
1800	9.133	73.250	65.760	13.482	-6.274	-31.981	3.883
1900	9.146	73.744	66.167	14.396	-6.516	-33.401	3.842
2000	9.158	74.213	66.558	15.311	-6.757	-34.809	3.804
2100	9.171	74.660	66.933	16.228	-6.998	-36.207	3.768
2200	9.183	75.087	67.294	17.145	-7.238	-37.592	3.734
2300	9.196	75.496	67.642	18.064	-7.478	-38.967	3.703
2400	9.208	75.887	67.977	18.984	-7.717	-40.329	3.672
2500	9.220	76.264	68.301	19.906	-7.955	-41.685	3.644
2600	9.232	76.625	68.615	20.828	-8.192	-43.028	3.617
2700	9.244	76.974	68.918	21.752	-8.429	-44.366	3.591
2800	9.256	77.310	69.211	22.677	-79.219	-44.037	3.437
2900	9.267	77.635	69.496	23.603	-79.252	-42.781	3.224
3000	9.279	77.950	69.773	24.531	-79.283	-41.524	3.025
3100	9.291	78.254	70.042	25.459	-79.315	-40.263	2.838
3200	9.303	78.549	70.303	26.389	-79.346	-39.002	2.664
3300	9.314	78.836	70.557	27.320	-79.376	-37.744	2.500
3400	9.326	79.114	70.805	28.252	-79.405	-36.482	2.345
3500	9.338	79.385	71.046	29.185	-79.435	-35.221	2.199
3600	9.349	79.648	71.281	30.119	-79.464	-33.955	2.061
3700	9.361	79.904	71.511	31.055	-79.492	-32.691	1.931
3800	9.372	80.154	71.735	31.991	-79.520	-31.425	1.807
3900	9.384	80.398	71.954	32.929	-79.548	-30.159	1.690
4000	9.396	80.635	72.168	33.868	-79.576	-28.892	1.578
4100	9.407	80.867	72.378	34.808	-79.604	-27.626	1.473
4200	9.419	81.094	72.582	35.750	-79.632	-26.357	1.371
4300	9.430	81.316	72.783	36.692	-79.659	-25.088	1.275
4400	9.442	81.533	72.979	37.636	-79.688	-23.822	1.183
4500	9.453	81.745	73.172	38.580	-79.717	-22.546	1.095
4600	9.465	81.953	73.360	39.526	-79.746	-21.276	1.011
4700	9.476	82.157	73.545	40.473	-79.776	-20.009	.930
4800	9.488	82.356	73.727	41.422	-79.808	-18.735	.853
4900	9.499	82.552	73.905	42.371	-79.841	-17.459	.779
5000	9.511	82.744	74.080	43.321	-79.875	-16.187	.708
5100	9.522	82.933	74.252	44.273	-79.910	-14.916	.639
5200	9.534	83.118	74.420	45.226	-79.948	-13.643	.573
5300	9.545	83.299	74.586	46.180	-79.987	-12.362	.510
5400	9.557	83.478	74.749	47.135	-80.030	-11.088	.449
5500	9.568	83.653	74.910	48.091	-80.075	-9.810	.390
5600	9.579	83.826	75.067	49.048	-80.124	-8.533	.333
5700	9.591	83.996	75.222	50.007	-80.176	-7.258	.278
5800	9.602	84.162	75.375	50.967	-80.230	-5.970	.225
5900	9.614	84.327	75.525	51.927	-80.290	-4.693	.174
6000	9.625	84.488	75.673	52.889	-80.355	-3.411	.124

Dec. 31, 1961; Sept. 30, 1964

ALUMINUM MONOBROMIDE (AlBr)　　(IDEAL GAS)　　MOL. WT. = 106.896

Ground State Configuration $^1\Sigma^+$

$\Delta H_{f\ 0}^\circ = 5.3 \pm 5.0$ kcal. mole^{-1}

$S_{298.15}^\circ = 57.246$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 3.6 \pm 5.0$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	1

$\omega_e = 377.40$ cm.$^{-1}$　　$\omega_e x_e = 1.276$ cm.$^{-1}$　　$\sigma = 1$

$B_e = 0.1586$ cm.$^{-1}$　　$\alpha_e = 0.000849$ cm.$^{-1}$　　$r_e = 2.295$ Å

Heat of Formation.

S. A. Semenkovich, Zh. Prikl, Khim. 30, 933 (1957) measured the vapor pressure of the reaction $Al(l) + NaBr(l) \rightarrow Na(g) + AlBr(g)$ at 1175°K. By the third law method the heat of reaction ($\Delta H_{r\ 298.15}^\circ$) was evaluated to be 108.31 kcal. mole^{-1}. The value of $\Delta H_{f\ 298.15}^\circ$ for AlBr(g) was calculated as 3.6 ± 5.0 kcal. mole^{-1}. Based on this value the dissociation energy (D_0°) was derived to be 4.3 ± 0.2 e.v. which is in excellent agreement with the value, $D_0^\circ = 4.3 \pm 0.2$ e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The dissociation energy (D_0°) of AlBr(g) was reported to be 2.4 e.v. and 105 kcal. mole^{-1} (4.55 e.v.) by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950 and R. F. Barrow, Trans, Faraday Soc. 56, 952 (1960), respectively. However, using these D_0° values, the corresponding values of $\Delta H_{f\ 298.15}^\circ$ for AlBr(g) were found to be 48.55 and -1.11 kcal. mole^{-1}. The adopted value was calculated from the vapor pressure data reported by S. A. Semenkovich, loc. cit.

Heat Capacity and Entropy.

The spectroscopic constants were taken from G. Herzberg, loc. cit. and corrected to the average isotopic species.

Aluminum Tribromide ($AlBr_3$)

(Crystal) GFW = 266.7085

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-5.238	-121.355	-121.355	INFINITE
100	16.927	20.655	62.555	-4.190	-121.416	-121.386	265.288
200	21.499	33.990	45.185	-2.239	-121.663	-121.277	132.526
298	24.040	43.075	43.075	.000	-126.000	-120.553	88.368
300	24.097	43.224	43.075	.045	-126.016	-120.518	87.798
400	28.150	50.702	44.067	2.654	-136.365	-116.513	63.660
500	29.600	57.190	46.061	5.565	-135.410	-111.659	48.806
600	29.700	62.597	48.380	8.530	-134.436	-107.002	38.975
700	29.720	67.177	50.747	11.501	-133.489	-102.505	32.003
800	29.740	71.147	53.054	14.474	-132.577	-99.142	26.811
900	29.760	74.651	55.263	17.449	-131.711	-93.889	22.799
1000	29.780	77.787	57.361	20.426	-133.417	-89.546	19.570
1100	29.800	80.627	59.349	23.405	-132.550	-85.203	16.928
1200	29.820	83.220	61.232	26.386	-131.683	-80.937	14.741
1300	29.840	85.608	63.016	29.369	-130.815	-76.742	12.901
1400	29.860	87.820	64.710	32.354	-129.948	-72.615	11.336
1500	29.880	89.881	66.320	35.341	-129.082	-68.552	9.988

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRIBROMIDE ($AlBr_3$) (CRYSTAL) GFW = 266.7085

ΔHf°_0 = -121.4 ± 3 kcal/mol

$S^\circ_{298.15}$ = 43.08 ± 0.25 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -126.0 ± 3 kcal/mol

Tm = 370.6°K

ΔHm° = 2.89 kcal/mol

Heat of Formation

The value of ΔHf°_{298} for $AlBr_3(c)$ is that selected by the National Bureau of Standards (1). The methods and auxiliary data used to obtain their value are not given. Their result is apparently based on the heats of reaction of aqueous solutions of $AlBr_3$ measured by Berthelot (2).

Heat Capacity and Entropy

The heat capacity of $AlBr_3(c)$ has been measured from 11.6° to 308.1°K by Justice (3) and the enthalpy from 337° to 367°K by Fischer (4). The heat capacities used are deirved from curve fits of these data. The Cp values above 370.6°K are obtained by graphical extrapolation. Justice (3) reported the value of S°_{298}, based on S°_{12} = 0.951 eu.

Melting Data

Fischer (4) determined the melting temperature (Tm) of $AlBr_3(c)$. The heat of melting (ΔHm°) is calculated from the enthalpies of $AlBr_3(c)$ and $AlBr_3(\ell)$ at the melting temperature. The enthalpy of the crystal at the melting point was determined from the curve used for the heat capacity calculations. The enthalpy of the liquid at the melting point was determined from a linear least squares fit to the enthalpy data for $AlBr_3(\ell)$ reported by Fischer (4).

References

1. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
2. M. P. E. Berthelot, Ann. Chim. Phys. (5) 15, 185 (1878).
3. B. H. Justice, The Dow Chemical Co., Midland, Michigan, Quarterly Progress Report AFRPL-TR-66, 175, October, 1966, Contract AF04611-11201.
4. W. Fischer, Z. Anorg. Chem. 200, 332 (1931).

Aluminum Tribromide ($AlBr_3$)
(Liquid)   GFW = 266.7085

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	29.869	49.352	49.352	.000	- 123.633	- 120.057	88.004
300	29.869	49.537	49.353	.055	- 123.638	- 120.035	87.445
400	29.869	58.130	50.524	3.042	- 133.610	- 116.729	63.778
500	29.869	64.795	52.736	6.029	- 132.579	- 112.630	49.231
600	29.869	70.240	55.214	9.016	- 131.583	- 108.735	39.607
700	29.869	74.845	57.698	12.003	- 130.621	- 105.004	32.784
800	29.869	78.833	60.096	14.990	- 129.695	- 101.405	27.703
900	29.869	82.351	62.377	17.977	- 128.817	- 97.925	23.779
1000	29.869	85.498	64.535	20.964	- 130.513	- 94.353	20.621
1100	29.869	88.345	66.572	23.950	- 129.638	- 90.781	18.037
1200	29.869	90.944	68.496	26.937	- 128.765	- 87.287	15.897
1300	29.869	93.335	70.316	29.924	- 127.893	- 83.865	14.099
1400	29.869	95.548	72.040	32.911	- 127.024	- 80.510	12.568
1500	29.869	97.609	73.677	35.898	- 126.158	- 77.220	11.251

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRIBROMIDE ($AlBr_3$)   (LIQUID)   GFW = 266.7085

$S^\circ_{298.15}$ = 49.352 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -123.633 ± 3 kcal/mol

Tm = 370.6°K   ΔHm° = 2.69 kcal/mol

Tb = 529°K (to dimer gas)   ΔHv° = 5.92 kcal/mol (to dimer gas)

Heat of Formation

The heat of formation (ΔHf°_{298}) of $AlBr_3(\ell)$ is calculated from ΔHf°_{298} of $AlBr_3(c)$ plus the heat of melting (ΔHm°) and the enthalpy differences ($H_{370.6} - H_{298}$) of the crystal and liquid.

Heat Capacity and Entropy

Fischer (1) has measured the enthalpy of $AlBr_3(\ell)$ from 371° to 406°K. The heat capacity used is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 406°K. The entropy (S°_{298}) of $AlBr_3(2)$ was determined in a manner analogous to that for the heat of formation.

Melting Data

See $AlBr_3(c)$ table for details.

Vaporization Data

The heat of vaporization (ΔHv°) of $AlBr_3(\ell)$ is determined from the work of Fischer et al. (2). The boiling temperature (Tb) was calculated from their vapor pressure data. See $Al_2Br_6(g)$ table for details.

References

1. W. Fischer, Z. Anorg. Chem., 200, 332 (1931).
2. W. Fischer, O. Rahlfs and R. B. Benze, Z. Anorg. Chem., 205, 1, (1932).

Aluminum Tribromide (AlBr$_3$)
(Ideal Gas) GFW = 266.7085

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.446	-95.664	-95.664	INFINITE
100	14.228	66.428	99.992	-3.356	-95.682	-100.229	219.051
200	17.245	77.365	86.171	-1.761	-96.285	-104.574	114.273
298	18.469	84.513	84.513	.000	-101.100	-108.008	79.172
300	18.484	84.627	84.514	.034	-101.126	-108.050	78.714
400	19.037	90.030	85.246	1.914	-112.206	-108.085	59.055
500	19.320	94.312	86.646	3.833	-112.242	-107.052	46.792
600	19.481	97.850	88.227	5.773	-112.293	-106.010	38.614
700	19.582	100.861	89.822	7.727	-112.364	-104.958	32.769
800	19.648	103.480	91.369	9.689	-112.463	-103.894	28.382
900	19.694	105.797	92.846	11.656	-112.605	-102.814	24.967
1000	19.727	107.874	94.247	13.627	-115.316	-101.532	22.190
1100	19.752	109.755	95.573	15.601	-115.454	-100.148	19.898
1200	19.771	111.475	96.827	17.577	-115.592	-98.752	17.985
1300	19.786	113.058	98.016	19.555	-115.729	-97.341	16.364
1400	19.797	114.525	99.143	21.534	-115.868	-95.922	14.974
1500	19.807	115.891	100.215	23.515	-116.009	-94.494	13.768
1600	19.815	117.170	101.235	25.496	-116.150	-93.054	12.711
1700	19.821	118.371	102.208	27.477	-116.293	-91.605	11.777
1800	19.827	119.504	103.137	29.460	-116.435	-90.149	10.946
1900	19.931	120.576	104.027	31.443	-116.579	-88.683	10.201
2000	19.835	121.593	104.880	33.426	-116.725	-87.213	9.530
2100	19.839	122.561	105.700	35.410	-116.872	-85.735	8.923
2200	19.841	123.484	106.487	37.394	-117.021	-84.250	8.369
2300	19.844	124.366	107.245	39.378	-117.170	-82.753	7.863
2400	19.846	125.211	107.977	41.363	-117.321	-81.253	7.399
2500	19.848	126.021	108.682	43.347	-117.474	-79.749	6.972
2600	19.850	126.800	109.364	45.332	-117.628	-78.237	6.576
2700	19.852	127.549	110.024	47.317	-117.784	-76.722	6.210
2800	19.853	128.271	110.663	49.303	-187.352	-74.366	5.805
2900	19.854	128.968	111.282	51.288	-187.249	-70.335	5.301
3000	19.855	129.641	111.883	53.273	-187.146	-66.304	4.830
3100	19.856	130.292	112.466	55.259	-187.046	-62.276	4.390
3200	19.857	130.922	113.033	57.245	-186.946	-58.250	3.978
3300	19.858	131.533	113.585	59.230	-186.850	-54.232	3.592
3400	19.859	132.126	114.121	61.216	-186.754	-50.218	3.228
3500	19.960	132.702	114.644	63.202	-186.660	-46.203	2.885
3600	19.860	133.261	115.153	65.188	-186.569	-42.189	2.561
3700	19.861	133.805	115.650	67.174	-186.477	-38.181	2.255
3800	19.862	134.335	116.135	69.160	-186.389	-34.174	1.965
3900	19.862	134.851	116.608	71.147	-186.302	-30.165	1.690
4000	19.863	135.354	117.071	73.133	-186.218	-26.170	1.430
4100	19.863	135.844	117.522	75.119	-186.136	-22.171	1.182
4200	19.863	136.323	117.964	77.105	-186.055	-18.171	.946
4300	19.864	136.790	118.397	79.092	-185.978	-14.171	.720
4400	19.864	137.247	118.820	81.078	-185.902	-10.175	.505
4500	19.864	137.693	119.235	83.065	-185.829	-6.183	.300
4600	19.865	138.130	119.641	85.051	-185.758	-2.191	.104
4700	19.865	138.557	120.039	87.038	-185.692	1.798	-.084
4800	19.865	138.975	120.429	89.024	-185.629	5.783	-.263
4900	19.866	139.385	120.811	91.011	-185.565	9.776	-.436
5000	19.866	139.786	121.187	92.997	-185.511	13.762	-.602
5100	19.866	140.180	121.555	94.984	-185.459	17.741	-.760
5200	19.866	140.566	121.917	96.970	-185.410	21.722	-.913
5300	19.866	140.944	122.273	98.957	-185.365	25.710	-1.060
5400	19.867	141.315	122.622	100.944	-185.325	29.692	-1.202
5500	19.867	141.680	122.965	102.930	-185.291	33.673	-1.338
5600	19.867	142.038	123.303	104.917	-185.262	37.652	-1.469
5700	19.867	142.389	123.634	106.904	-185.238	41.636	-1.596
5800	19.867	142.735	123.961	108.890	-185.220	45.618	-1.719
5900	19.867	143.075	124.282	110.877	-185.208	49.594	-1.837
6000	19.868	143.408	124.598	112.864	-185.204	53.572	-1.951

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRIBROMIDE (AlBr$_3$) (IDEAL GAS) GFW = 266.7085

Point Group [D_{3h}]

$S°_{298.15}$ = 84.5 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -95.7 ± 4 kcal/mol

$\Delta Hf°_{298.15}$ = -101.1 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[215] (1)	[100] (2)
[109] (1)	[418] (2)

Bond Distance: Al-Br = [2.27] Å

Bond Angle: Br-Al-Br = [120°]

σ = [6]

Product of the Moments of Inertia: $I_A I_B I_C$ = 2.16 x 10^{-111} g^3 cm^6

Heat of Formation

Fischer et al. (1) have determined the equilibrium constants for the reaction $2AlBr_3(g) = Al_2Br_6(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both second law and third law methods. The adopted value of $\Delta Hf°_{298}$ is -101.1 ± 4 kcal/mol. The results of the calculations are as follows:

Range T°K	No. Pts.	$\Delta Hr°_{298}$ kcal/mol Second Law	Third Law	Drift, eu	*$Hf°_{298}$ kcal/mol
613-846	4	-29.73	-29.39	0.16 ± 1.33	-98.4
605-854	7	-29.32	-29.35	-0.20 ± 0.67	-98.5

*Calculation based on the third law value of $\Delta Hr°_{298}$.

Heat Capacity and Entropy

The molecular structure of $AlBr_3(g)$ is assumed to be the same as that of $AlF_3(g)$. The bond distance was estimated by Heise and Wieland (2). The vibrational frequencies are estimated from the force constants of $BBr_3(g)$ (3) and then adjusted so that the values of $\Delta Hr°_{298}$ obtained by the second and third law methods are in good agreement. The principal moments of inertia are: $I_A = I_B = 1.03 \times 10^{-37}$, and $I_C = 2.05 \times 10^{-37}$ g cm^2.

References

1. W. Fischer, O. Rahlfs and B. Benze, Z. Anorg. Chem. 205, 1 (1932).
2. M. Heise and K. Weiland, Helv. Chim. Acta 34, 2182 (1951).
3. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.

Aluminum Monochloride (AlCl)

(Ideal Gas) GFW = 62.4345

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.228	-12.337	-12.337	INFINITE
100	7.057	46.141	61.455	-1.531	-12.094	-14.286	31.222
200	7.778	51.245	55.199	-.791	-12.159	-16.478	18.006
298	8.283	54.455	54.455	.000	-12.300	-18.574	13.615
300	8.290	54.507	54.455	.015	-12.303	-18.613	13.559
400	8.559	56.932	54.784	.859	-12.473	-20.690	11.305
500	8.709	58.860	55.413	1.723	-12.667	-22.723	9.932
600	8.802	60.456	56.124	2.599	-12.884	-24.714	9.002
700	8.865	61.818	56.843	3.483	-13.125	-26.667	8.326
800	8.910	63.005	57.541	4.371	-13.396	-28.584	7.809
900	8.945	64.057	58.207	5.264	-13.710	-30.463	7.397
1000	8.974	65.001	58.840	6.160	-16.594	-32.123	7.021
1100	8.998	65.857	59.440	7.059	-16.903	-33.662	6.688
1200	9.018	66.641	60.008	7.960	-17.211	-35.172	6.406
1300	9.037	67.363	60.546	8.862	-17.518	-36.656	6.162
1400	9.054	68.034	61.057	9.767	-17.824	-38.116	5.950
1500	9.070	68.659	61.543	10.673	-18.130	-39.556	5.763
1600	9.085	69.245	62.007	11.581	-18.435	-40.974	5.597
1700	9.099	69.796	62.449	12.490	-18.739	-42.373	5.447
1800	9.113	70.317	62.872	13.401	-19.042	-43.753	5.312
1900	9.126	70.810	63.277	14.313	-19.345	-45.118	5.190
2000	9.139	71.278	63.665	15.226	-19.648	-46.467	5.078
2100	9.152	71.724	64.038	16.141	-19.950	-47.802	4.975
2200	9.165	72.150	64.397	17.057	-20.252	-49.122	4.880
2300	9.177	72.558	64.743	17.974	-20.553	-50.424	4.791
2400	9.190	72.949	65.077	18.892	-20.854	-51.716	4.709
2500	9.202	73.324	65.400	19.812	-21.155	-52.998	4.633
2600	9.215	73.685	65.711	20.733	-21.456	-54.265	4.561
2700	9.228	74.033	66.013	21.655	-21.757	-55.523	4.494
2800	9.242	74.369	66.306	22.578	-91.468	-55.937	4.366
2900	9.256	74.694	66.589	23.503	-91.506	-54.669	4.120
3000	9.271	75.008	66.865	24.429	-91.545	-53.397	3.890
3100	9.287	75.312	67.132	25.357	-91.584	-52.124	3.675
3200	9.304	75.607	67.393	26.287	-91.622	-50.850	3.473
3300	9.323	75.894	67.646	27.218	-91.660	-49.575	3.283
3400	9.343	76.173	67.893	28.151	-91.699	-48.301	3.105
3500	9.364	76.444	68.133	29.087	-91.736	-47.025	2.936
3600	9.388	76.708	68.368	30.024	-91.773	-45.744	2.777
3700	9.414	76.965	68.597	30.964	-91.809	-44.466	2.627
3800	9.441	77.217	68.820	31.907	-91.844	-43.187	2.484
3900	9.472	77.462	69.039	32.853	-91.877	-41.903	2.348
4000	9.504	77.703	69.252	33.802	-91.910	-40.624	2.220
4100	9.539	77.938	69.461	34.754	-91.940	-39.344	2.097
4200	9.577	78.168	69.666	35.710	-91.968	-38.059	1.980
4300	9.618	78.394	69.866	36.669	-91.995	-36.776	1.869
4400	9.661	78.615	70.062	37.633	-92.019	-35.487	1.763
4500	9.707	78.833	70.255	38.602	-92.041	-34.205	1.661
4600	9.756	79.047	70.444	39.575	-92.058	-32.918	1.564
4700	9.807	79.257	70.629	40.553	-92.075	-31.636	1.471
4800	9.862	79.464	70.811	41.536	-92.087	-30.351	1.382
4900	9.919	79.668	70.990	42.525	-92.096	-29.058	1.296
5000	9.978	79.869	71.165	43.520	-92.101	-27.775	1.214
5100	10.040	80.067	71.338	44.521	-92.103	-26.486	1.135
5200	10.105	80.263	71.508	45.528	-92.102	-25.201	1.059
5300	10.171	80.456	71.675	46.542	-92.097	-23.916	.986
5400	10.240	80.647	71.839	47.563	-92.088	-22.627	.916
5500	10.311	80.835	72.001	48.590	-92.077	-21.344	.848
5600	10.384	81.022	72.160	49.625	-92.062	-20.056	.783
5700	10.458	81.206	72.317	50.667	-92.043	-18.774	.720
5800	10.534	81.389	72.472	51.716	-92.022	-17.485	.659
5900	10.611	81.570	72.625	52.774	-91.998	-16.201	.600
6000	10.689	81.749	72.775	53.839	-91.971	-14.916	.543

June 30, 1961; Sept. 30, 1964; June 30, 1970

ALUMINUM MONOCHLORIDE (AlCl) (IDEAL GAS) GFW = 62.4345

Ground State Configuration $^1\Sigma^+$ $\Delta Hf^\circ_0 = -12.34 \pm 1.0$ kcal/mol

$S^\circ_{298.15} = 54.455 \pm 0.02$ gibbs/mol $\Delta Hf^\circ_{298.15} = -12.30 \pm 1.0$ kcal/mol

Electronic Levels and Quantum Weight

ε_i, cm^{-1}	0	24541	24615	24680
g_i	1	2	2	2

$\omega_e = 480.0$ cm^{-1} $\omega_e x_e = 1.94$ cm^{-1} $\sigma = 1$

$B_e = 0.24262$ cm^{-1} $\alpha_e = 0.00159$ cm^{-1} $r_e = 2.1298$ Å

Heat of Formation

Equilibrium constants as a function of temperature for the reaction $2Al(\ell) + AlCl_3(g) \rightarrow 3AlCl(g)$ have been reported by many investigators. The data were subjected to second and third law analyses with results as follows [ΔHr at 298.15°K refers to $2Al(c) + AlCl_3(g) \rightarrow 3AlCl(g)$]:

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta Hr^\circ_{298.15}$ kcal/mol $AlCl_3$ 2nd Law	3rd Law	Drift eu
Rao and Dadape (1)	1125-1425	11	102.3±1.6	102.8±0.8	0.3±1.3
Frisch et al. (2)	931-1034	9	99.7±1.1	106.7±0.5	7.2±1.0
Gross et al. (3)	1225-1278	7	a	109.7±2.8	
Ginsberg et al. (4)	1423-1500	8	91.4±1.8	104.7±0.8	9.1±1.2
Semenkovich (5)	1223-1473	6	89.2±0.4	98.5±1.3	6.8±0.3
Heimgartner (6)	978-1383	13	58.8±2.5	100.0±9.5	33.0±2.2
Weiss (7)	1273-1473	3	93.1±3.4	86.3±1.2	-5.2±2.7
Pinchuk et al. (8)	1173-1373	3	86.0±7.5	95.0±1.9	7.6±5.8
Mitani et al. (9)	1273-1473	b	88.9	99.1±2.1	7.4
Kikuchi et al. (10)	1273-1523	b	78.7	98.7±5.0	14.3
Tanabe et al. (11)	1173-1573	b	93.3	94.6±0.5	0.9
Russell et al. (12)	1388	1		103.8	

[a] Temperature range too small for significant second law calculation.

[b] These data available only as equations as given in Chemical Abstracts.

Unfortunately, most of the data are very discordant and of no help in defining ΔHf(AlCl, g). The results of Rao and Dadape (1) cover a temperature range of 300°K, show good compatibility with the thermodynamic functions, are near an average of all the data, and are judged most acceptable. The third-law heat of reaction derived from their data is adopted and combined with the heat of formation of $AlCl_3(g)$ to give $\Delta Hf^\circ_{298.15}(AlCl, g) = -12.30 \pm 1.0$ kcal/mol.

Gross et al. (3) reported equilibrium constants for the reaction of aluminum with sodium chloride and potassium chloride and Pinchuk et al. (8) determined equilibrium constants for reaction of aluminum with sodium chloride and magnesium chloride. The results of Pinchuk et al. (8) are suspect in that the partial pressures of sodium and magnesium chlorides they calculate from their data exceed the saturation pressures calculated from JANAF data. The data of Gross et al. (3) were recalculated to allow for effects of dimer in sodium chloride and potassium chloride vapors (JANAF data):

Reaction	T, °K	Kp(atm^2)	$\Delta Hr_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$(AlCl, g) kcal/mol
$NaCl(s) + Al(\ell) \rightarrow AlCl(g) + Na(g)$	1043	4.178×10^{-10}	109.24	-12.7 ± 1.0
$NaCl(\ell) + Al(\ell) \rightarrow AlCl(g) + Na(g)$	1243	1.138×10^{-6}	102.31	-13.6 ± 1.5
$KCl(s) + Al(\ell) \rightarrow AlCl(g) + K(g)$	1023	5.141×10^{-11}	110.47	-13.1 ± 1.5

The result for NaCl(s) is the average of 12 experiments whereas the NaCl(ℓ) and KCl(s) are based on 5 and 3 experiments, respectively, and the NaCl(s) value is considered the most reliable. The derived heat of formation is in good agreement with the value selected on the basis of the Rao and Dadape data.

Barrow (13) has compared thermochemical and spectroscopic dissociation energies for monohalides of B, Al, Ga, In, and Tl. A short extrapolation of vibrational levels gives $D_0'' = 124.1$ kcal/mol for AlCl while predissociation indicates $D_0'' \leq 120.1$ kcal/mol. The maximum predissociation value gives $\Delta Hf^\circ_{298.15}(AlCl, g) = -14.1$ kcal/mol, in reasonable agreement with the selected value. Barrow (13) speculates that a potential maximum occurs in the $A^1\Pi$ state of AlF and AlCl which causes extrapolation of vibrational levels to give erroneous heats of dissociation.

Heat Capacity and Entropy

The vibrational frequency and anharmonicity constants were taken from Herzberg (14) and the structural constants are based on microwave spectroscopy by Lide (15). The electronic levels were reported by Sharma (16).

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Aluminum Monochloride Unipositive Ion ($AlCl^+$)

(Ideal Gas) GFW = 62.4339

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	8.317	56.004	56.004	.000	205.000	196.777	-144.242
300	8.324	56.056	56.004	.015	205.006	196.726	-143.315
400	8.582	58.489	56.334	.862	205.336	193.917	-105.951
500	8.726	60.421	56.965	1.728	205.641	191.026	-83.497
600	8.815	62.021	57.678	2.605	205.922	188.076	-68.507
700	8.874	63.384	58.398	3.490	206.179	185.080	-57.785
800	8.918	64.572	59.097	4.380	206.405	182.050	-49.734
900	8.952	65.625	59.765	5.273	206.589	178.995	-43.466
1000	8.979	66.569	60.399	6.170	204.202	176.104	-38.487
1100	9.002	67.426	61.000	7.069	204.391	173.285	-34.429
1200	9.023	68.210	61.568	7.970	204.580	170.449	-31.043
1300	9.041	68.933	62.107	8.873	204.770	167.596	-28.175
1400	9.058	69.604	62.619	9.778	204.961	164.731	-25.716
1500	9.074	70.229	63.106	10.685	205.153	161.849	-23.581
1600	9.088	70.815	63.570	11.593	205.345	158.956	-21.712
1700	9.103	71.367	64.012	12.503	205.538	156.052	-20.062
1800	9.116	71.887	64.435	13.414	205.732	153.135	-18.593
1900	9.129	72.381	64.841	14.326	205.926	150.209	-17.278
2000	9.142	72.849	65.230	15.239	206.120	147.270	-16.093
2100	9.155	73.296	65.603	16.154	206.315	144.321	-15.020
2200	9.167	73.722	65.963	17.070	206.510	141.364	-14.043
2300	9.180	74.130	66.309	17.988	206.706	138.401	-13.151
2400	9.192	74.521	66.643	18.906	206.902	135.428	-12.332
2500	9.204	74.896	66.966	19.826	207.098	132.443	-11.578
2600	9.216	75.257	67.278	20.747	207.295	129.454	-10.882
2700	9.228	75.605	67.580	21.669	207.491	126.456	-10.236
2800	9.240	75.941	67.872	22.593	138.277	124.282	-9.701
2900	9.252	76.266	68.156	23.517	138.734	123.773	-9.328
3000	9.264	76.579	68.432	24.443	139.192	123.248	-8.979
3100	9.277	76.883	68.699	25.370	139.649	122.710	-8.651
3200	9.289	77.178	68.960	26.298	140.106	122.159	-8.343
3300	9.302	77.464	69.213	27.228	140.563	121.591	-8.053
3400	9.315	77.742	69.460	28.159	141.019	121.008	-7.778
3500	9.329	78.012	69.701	29.091	141.476	120.412	-7.519
3600	9.343	78.275	69.935	30.025	141.932	119.807	-7.273
3700	9.358	78.531	70.164	30.960	142.388	119.182	-7.040
3800	9.373	78.781	70.387	31.896	142.843	118.549	-6.818
3900	9.388	79.025	70.606	32.834	143.300	117.907	-6.607
4000	9.405	79.263	70.819	33.774	143.753	117.246	-6.406
4100	9.422	79.495	71.028	34.715	144.209	116.575	-6.214
4200	9.440	79.722	71.232	35.658	144.665	115.900	-6.031
4300	9.458	79.945	71.432	36.603	145.121	115.209	-5.856
4400	9.477	80.162	71.628	37.550	145.577	114.513	-5.688
4500	9.497	80.376	71.820	38.499	146.031	113.797	-5.527
4600	9.518	80.585	72.009	39.449	146.488	113.078	-5.372
4700	9.540	80.790	72.193	40.402	146.944	112.342	-5.224
4800	9.563	80.991	72.374	41.357	147.400	111.599	-5.081
4900	9.586	81.188	72.552	42.315	147.857	110.857	-4.944
5000	9.611	81.382	72.727	43.275	148.312	110.095	-4.812
5100	9.636	81.573	72.899	44.237	148.769	109.326	-4.685
5200	9.662	81.760	73.067	45.202	149.225	108.549	-4.562
5300	9.688	81.944	73.233	46.169	149.680	107.759	-4.444
5400	9.716	82.126	73.396	47.140	150.136	106.965	-4.329
5500	9.744	82.304	73.556	48.113	150.589	106.160	-4.218
5600	9.773	82.480	73.714	49.088	151.041	105.346	-4.111
5700	9.803	82.653	73.869	50.067	151.494	104.529	-4.008
5800	9.833	82.824	74.022	51.049	151.945	103.701	-3.908
5900	9.864	82.992	74.173	52.034	152.393	102.865	-3.810
6000	9.896	83.158	74.321	53.022	152.840	102.025	-3.716

June 30, 1968; June 30, 1970

ALUMINUM MONOCHLORIDE UNIPOSITIVE ION ($AlCl^+$) (IDEAL GAS) GFW = 62.4339

Ground State Configuration $[^2\Sigma]$

ΔHf°_0 = 205 ± 10 kcal/mol

$S^\circ_{298.15}$ = [56.0 ± 0.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 205 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[26000]	[4]

ω_e = [465] cm^{-1}

B_e = [0.2273] cm^{-1}

$\omega_e x_e$ = [2] cm^{-1}

α_e = [0.0013] cm^{-1}

σ = 1

r_e = [2.2] Å

Heat of Formation

D. L. Hildenbrand, E. Murad, L. P. Theard and F. Ju, Aeronutronic Report No. U-3197, July 30, 1965, under contract AF 04(611)-10743, reported an appearance potential of 9.4 ± 0.4eV for $AlCl^+$. They suggested that the magnitude of the value indicated formation by direct ionization of AlCl(g).

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), obtained an appearance potential of 19.7 ± 0.5eV for $AlCl^+$ which they attributed to formation from $AlCl_3(g)$. Assuming the process to be $AlCl_3(g) + e^- \rightarrow AlCl^+(g) + 2Cl(g) + 2e^-$ ΔH = 454 kcal, one obtains $\Delta Hf^\circ_{298}(AlCl^+)$ = 257 kcal/mol, or an ionization potential of 11.6eV. This would almost certainly represent an upper limit, since the fragments could easily contain excess kinetic energy.

We adopt the ionization potential of 9.4 ± 0.4eV obtained by Hildenbrand et al., which yields $\Delta Hf^\circ_{298}(AlCl^+, g)$ = 205 ± 10 kcal/mol.

Heat Capacity and Entropy

$AlCl^+$ is isoelectronic with MgCl, and the electronic configuration of the ground state and first excited state are estimated to be those for MgCl. The vibrational frequency, anharmonicity constant and bond length are estimated by comparison with those for MgCl and AlCl. The rotational constant is calculated from the bond length and atomic masses, and α_e is calculated from the other constants assuming a Morse potential function.

The enthalpy at 0°K is -2.236 kcal/mol.

Aluminum Chloride Fluoride (AlClF)

(Ideal Gas) Mol. Wt. = 81.437

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.870	-119.624	-119.624	INFINITE
100	8.900	56.373	76.843	-2.047	-119.605	-120.783	263.958
200	10.387	63.003	68.413	-1.082	-119.793	-121.909	133.209
298	11.586	67.388	67.388	.000	-120.000	-122.907	90.089
300	11.604	67.460	67.388	.021	-120.004	-122.926	89.547
400	12.372	70.913	67.854	1.223	-120.199	-123.869	67.676
500	12.836	73.727	68.756	2.486	-120.394	-124.765	54.532
600	13.126	76.095	69.787	3.785	-120.601	-125.619	45.755
700	13.316	78.134	70.837	5.108	-120.830	-126.439	39.474
800	13.446	79.921	71.863	6.446	-121.083	-127.223	34.754
900	13.538	81.510	72.849	7.796	-121.364	-127.973	31.075
1000	13.606	82.941	73.787	9.153	-124.168	-128.508	28.084
1100	13.657	84.240	74.679	10.516	-124.399	-128.931	25.615
1200	13.696	85.430	75.526	11.884	-124.630	-129.332	23.553
1300	13.727	86.527	76.331	13.255	-124.861	-129.714	21.806
1400	13.752	87.546	77.096	14.629	-125.093	-130.079	20.305
1500	13.772	88.495	77.825	16.006	-125.325	-130.426	19.002
1600	13.789	89.385	78.520	17.384	-125.558	-130.760	17.860
1700	13.802	90.221	79.184	18.763	-125.792	-131.077	16.850
1800	13.814	91.010	79.819	20.144	-126.028	-131.382	15.951
1900	13.824	91.757	80.428	21.526	-126.264	-131.671	15.145
2000	13.832	92.467	81.012	22.909	-126.502	-131.950	14.418
2100	13.839	93.142	81.574	24.292	-126.741	-132.219	13.760
2200	13.846	93.786	82.114	25.677	-126.982	-132.474	13.159
2300	13.851	94.401	82.635	27.061	-127.225	-132.716	12.610
2400	13.856	94.991	83.138	28.447	-127.469	-132.950	12.106
2500	13.860	95.556	83.623	29.833	-127.715	-133.172	11.641
2600	13.864	96.100	84.093	31.219	-127.963	-133.387	11.212
2700	13.867	96.623	84.547	32.605	-128.213	-133.590	10.813
2800	13.870	97.128	84.988	33.992	-199.019	-132.133	10.313
2900	13.873	97.615	85.415	35.379	-199.071	-129.745	9.777
3000	13.876	98.085	85.829	36.767	-199.125	-127.353	9.277
3100	13.878	98.540	86.232	38.154	-199.181	-124.959	8.809
3200	13.880	98.981	86.624	39.542	-199.240	-122.565	8.370
3300	13.882	99.408	87.005	40.930	-199.301	-120.167	7.958
3400	13.883	99.822	87.376	42.319	-199.364	-117.767	7.570
3500	13.885	100.225	87.737	43.707	-199.431	-115.370	7.204
3600	13.886	100.616	88.089	45.096	-199.499	-112.963	6.857
3700	13.888	100.996	88.433	46.484	-199.571	-110.558	6.530
3800	13.889	101.367	88.768	47.873	-199.644	-108.153	6.220
3900	13.890	101.727	89.096	49.262	-199.721	-105.741	5.925
4000	13.891	102.079	89.416	50.651	-199.800	-103.332	5.646
4100	13.892	102.422	89.729	52.040	-199.882	-100.922	5.379
4200	13.893	102.757	90.036	53.430	-199.967	-98.508	5.126
4300	13.894	103.084	90.335	54.819	-200.053	-96.090	4.884
4400	13.894	103.403	90.629	56.208	-200.144	-93.671	4.652
4500	13.895	103.716	90.916	57.598	-200.237	-91.251	4.432
4600	13.896	104.021	91.198	58.987	-200.332	-88.826	4.220
4700	13.896	104.320	91.474	60.377	-200.431	-86.404	4.018
4800	13.897	104.612	91.744	61.767	-200.533	-83.974	3.823
4900	13.898	104.899	92.010	63.156	-200.639	-81.542	3.637
5000	13.898	105.180	92.270	64.546	-200.747	-79.115	3.458
5100	13.899	105.455	92.526	65.936	-200.859	-76.679	3.286
5200	13.899	105.725	92.778	67.326	-200.975	-74.243	3.120
5300	13.899	105.990	93.024	68.716	-201.095	-71.807	2.961
5400	13.900	106.249	93.267	70.106	-201.220	-69.363	2.807
5500	13.900	106.504	93.505	71.496	-201.348	-66.920	2.659
5600	13.901	106.755	93.740	72.886	-201.482	-64.475	2.516
5700	13.901	107.001	93.970	74.276	-201.622	-62.031	2.378
5800	13.901	107.243	94.197	75.666	-201.765	-59.578	2.245
5900	13.902	107.480	94.420	77.056	-201.915	-57.123	2.116
6000	13.902	107.714	94.640	78.446	-202.073	-54.671	1.991

Dec. 31, 1960; Sept. 30, 1964

ALUMINUM CHLORIDE FLUORIDE (AlClF) (IDEAL GAS) MOL. WT. = 81.437

Point Group C_s

$\Delta H_{f\ 0}^\circ = [-120 \pm 20]$ kcal. mole⁻¹

$S_{298.15}^\circ = [67.388]$ cal. deg.⁻¹ mole⁻¹

$\Delta H_{f\ 298.15}^\circ = [-120 \pm 20]$ kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[590] (1)
[220] (1)
[730] (1)

Bond Distance: Al-F = [1.63] Å Al-Cl = [2.14] Å

Bond Angle: Cl-Al-F = [120]°

$\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = [1.48427 \times 10^{-114}]$ g.³ cm.⁶

Heat of Formation.

The value of $\Delta H_{f\ 298.15}^\circ$ for AlClF(g) was calculated based on an assumption that $\Delta H_r^\circ = 0$ for the reaction $AlF_2(g) + AlCl_2(g) = 2AlClF(g)$. The $\Delta H_{f\ 298.15}^\circ$ values for $AlF_2(g)$ and $AlCl_2(g)$ used for calculation are -165.0 and -75.0 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated to be consistent with those for $AlF_2(g)$ and $AlCl_2(g)$. The bond distances of Al-F and Al-Cl were estimated to be the same as those in $AlF_3(g)$ and $AlCl_3(g)$, respectively. The bond angle and ground state quantum weight were estimated to be consistent with those for $AlF_2(g)$ molecule. The three principal moments of inertia are: $I_A = 2.41078 \times 10^{-38}$, $I_B = 2.3289 \times 10^{-39}$ and $I_C = 2.64367 \times 10^{-38}$ g. cm.²

Aluminum Chloride Difluoride ($AlClF_2$)

(Ideal Gas) Mol Wt. = 100.437

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.531	- 236.830	- 236.830	INFINITE
100	10.409	57.062	83.720	- 2.666	- 237.116	- 236.329	516.471
200	13.670	65.385	72.616	- 1.446	- 237.399	- 235.437	257.262
298	15.663	71.242	71.242	.000	- 237.600	- 234.434	171.837
300	15.693	71.339	71.242	.029	- 237.603	- 234.415	170.763
400	16.993	76.046	71.875	1.668	- 237.746	- 233.328	127.479
500	17.816	79.933	73.109	3.412	- 237.863	- 232.211	101.494
600	18.349	83.232	74.529	5.222	- 237.976	- 231.070	84.163
700	18.707	86.089	75.980	7.076	- 238.099	- 229.909	71.777
800	18.955	88.604	77.404	8.960	- 238.240	- 228.731	62.483
900	19.134	90.847	78.776	10.865	- 238.403	- 227.531	55.249
1000	19.266	92.871	80.086	12.785	- 241.087	- 226.130	49.418
1100	19.366	94.712	81.333	14.717	- 241.195	- 224.629	44.628
1200	19.444	96.400	82.519	16.657	- 241.302	- 223.117	40.633
1300	19.505	97.959	83.648	18.605	- 241.408	- 221.598	37.252
1400	19.554	99.406	84.722	20.558	- 241.514	- 220.070	34.353
1500	19.594	100.757	85.747	22.515	- 241.621	- 218.534	31.839
1600	19.627	102.023	86.725	24.476	- 241.729	- 216.993	29.638
1700	19.654	103.213	87.660	26.441	- 241.837	- 215.441	27.695
1800	19.677	104.337	88.556	28.407	- 241.948	- 213.888	25.968
1900	19.697	105.402	89.414	30.376	- 242.059	- 212.324	24.422
2000	19.714	106.413	90.239	32.346	- 242.173	- 210.756	23.029
2100	19.728	107.375	91.033	34.319	- 242.288	- 209.185	21.769
2200	19.741	108.293	91.796	36.292	- 242.407	- 207.605	20.623
2300	19.752	109.171	92.533	38.267	- 242.527	- 206.020	19.575
2400	19.762	110.011	93.244	40.242	- 242.650	- 204.428	18.615
2500	19.770	110.818	93.931	42.219	- 242.776	- 202.833	17.731
2600	19.778	111.594	94.595	44.197	- 242.904	- 201.235	16.915
2700	19.785	112.340	95.239	46.175	- 243.035	- 199.628	16.158
2800	19.791	113.060	95.862	48.153	- 313.723	- 196.366	15.326
2900	19.796	113.755	96.467	50.133	- 313.657	- 192.177	14.482
3000	19.801	114.426	97.055	52.113	- 313.595	- 187.991	13.694
3100	19.806	115.075	97.626	54.093	- 313.535	- 183.803	12.957
3200	19.810	115.704	98.181	56.074	- 313.480	- 179.619	12.267
3300	19.814	116.314	98.721	58.055	- 313.427	- 175.438	11.618
3400	19.817	116.905	99.247	60.037	- 313.377	- 171.256	11.008
3500	19.820	117.480	99.760	62.019	- 313.333	- 167.078	10.432
3600	19.823	118.038	100.260	64.001	- 313.290	- 162.895	9.889
3700	19.826	118.581	100.748	65.983	- 313.252	- 158.720	9.375
3800	19.828	119.110	101.224	67.966	- 313.216	- 154.543	8.888
3900	19.830	119.625	101.690	69.949	- 313.186	- 150.369	8.426
4000	19.832	120.127	102.144	71.932	- 313.158	- 146.194	7.987
4100	19.834	120.617	102.589	73.915	- 313.134	- 142.024	7.570
4200	19.836	121.095	103.024	75.899	- 313.114	- 137.850	7.173
4300	19.838	121.562	103.450	77.882	- 313.096	- 133.676	6.794
4400	19.839	122.018	103.866	79.866	- 313.085	- 129.506	6.432
4500	19.841	122.464	104.275	81.850	- 313.075	- 125.333	6.087
4600	19.842	122.900	104.675	83.835	- 313.069	- 121.160	5.756
4700	19.843	123.327	105.067	85.819	- 313.069	- 116.992	5.440
4800	19.845	123.744	105.452	87.803	- 313.071	- 112.815	5.136
4900	19.846	124.154	105.830	89.788	- 313.079	- 108.641	4.845
5000	19.847	124.554	106.200	91.772	- 313.091	- 104.469	4.566
5100	19.848	124.948	106.564	93.757	- 313.107	- 100.302	4.298
5200	19.849	125.333	106.921	95.742	- 313.128	- 96.124	4.040
5300	19.850	125.711	107.272	97.727	- 313.154	- 91.950	3.791
5400	19.851	126.082	107.617	99.712	- 313.186	- 87.779	3.552
5500	19.851	126.446	107.956	101.697	- 313.223	- 83.603	3.322
5600	19.852	126.804	108.289	103.682	- 313.266	- 79.427	3.100
5700	19.853	127.155	108.617	105.667	- 313.316	- 75.252	2.885
5800	19.853	127.501	108.940	107.653	- 313.370	- 71.075	2.678
5900	19.854	127.840	109.257	109.638	- 313.432	- 66.898	2.478
6000	19.855	128.174	109.570	111.624	- 313.503	- 62.721	2.285

Dec. 31, 1960; Sept. 30, 1964

ALUMINUM CHLORIDE DIFLUORIDE ($AlClF_2$) (IDEAL GAS) MOL. WT. = 100.437

Point Group C_{2v}

$\Delta H^\circ_{f\ 0} = [-236.8 \pm 20]$ kcal. mole^{-1}

$S^\circ_{298.15} = [71.242]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = [-237.6 \pm 20]$ kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[500] (1)	[250] (1)
[280] (1)	[800] (1)
[200] (1)	[900] (1)

Bond Distance: Al-F = [1.65]Å Al-Cl = [2.14]Å

Bond Angle: Cl-Al-F = [120]° F-Al-F = [120]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 1.47245 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ was calculated based on an assumption that $\Delta H^\circ_r = 0$ for the reaction $AlCl_3(g) + 2AlF_3(g) = 3AlClF_2(g)$. The values of $\Delta H^\circ_{f\ 298.15}$ for $AlF_3(g)$ and $AlCl_3(g)$ used for calculation are -286.5 and -139.7 kcal. mole^{-1}, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for $AlF_3(g)$ and $AlCl_3(g)$. The bond distances of Al-F and Al-Cl atoms were assumed to be the same as those in $AlF_3(g)$ and $AlCl_3(g)$, respectively. The bond angles and ground state quantum weight were estimated by comparison with those for $AlF_3(g)$. The three principal moments of inertia are 1.28827×10^{-38}, 2.79746×10^{-38} and 4.08573×10^{-38} g. cm.^{2}

Aluminum Oxide Chloride (AlOCl)

(Crystal) Mol. Wt. = 78.437

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	13.600	13.000	13.000	.000	- 189.600	- 176.208	129.158
300	13.650	13.084	13.000	.025	- 189.600	- 176.126	128.301
400	15.370	17.293	13.562	1.492	- 189.500	- 171.646	93.778
500	16.540	20.858	14.674	3.092	- 189.319	- 167.201	73.080
600	17.360	23.952	15.968	4.790	- 189.089	- 162.799	59.297
700	17.970	26.676	17.307	6.559	- 188.836	- 158.437	49.464
800	18.370	29.104	18.633	8.377	- 188.575	- 154.113	42.100
900	18.710	31.289	19.920	10.232	- 188.319	- 149.820	36.379
1000	18.940	33.273	21.157	12.116	- 190.568	- 145.371	31.769
1100	19.143	35.088	22.342	14.020	- 190.232	- 140.868	27.986
1200	19.290	36.760	23.475	15.942	- 189.884	- 136.395	24.840
1300	19.420	38.310	24.557	17.878	- 189.527	- 131.953	22.182
1400	19.520	39.753	25.592	19.825	- 189.164	- 127.537	19.909
1500	19.598	41.102	26.581	21.781	- 188.797	- 123.148	17.942
1600	19.650	42.369	27.529	23.744	- 188.427	- 118.783	16.224
1700	19.703	43.562	28.437	25.712	- 188.054	- 114.441	14.712
1800	19.747	44.689	29.309	27.684	- 187.682	- 110.123	13.370
1900	19.783	45.758	30.147	29.661	- 187.309	- 105.822	12.172
2000	19.810	46.773	30.953	31.640	- 186.937	- 101.544	11.096
2100	19.829	47.740	31.730	33.622	- 186.565	- 97.285	10.124
2200	19.840	48.663	32.479	35.606	- 186.196	- 93.042	9.242
2300	19.848	49.545	33.202	37.590	- 185.829	- 88.816	8.439
2400	19.850	50.390	33.900	39.575	- 185.466	- 84.605	7.704
2500	19.852	51.200	34.576	41.560	- 185.107	- 80.410	7.029
2600	19.852	51.979	35.231	43.546	- 184.750	- 76.230	6.407
2700	19.850	52.728	35.865	45.531	- 184.398	- 72.063	5.833
2800	19.850	53.450	36.480	47.516	- 254.604	- 66.255	5.171
2900	19.850	54.147	37.077	49.501	- 254.056	- 59.539	4.487
3000	19.850	54.820	37.658	51.486	- 253.513	- 52.840	3.849

Mar. 31, 1964

ALUMINUM OXIDE CHLORIDE (AlOCl) (CRYSTAL) MOL. WT. = 78.437

$S^\circ_{298.15}$ = [13 ± 1] cal. deg.$^{-1}$ mole^{-1}

T_m = Unknown

T_d = [500]°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -189.6 ± 0.3 kcal. mole^{-1}

ΔH°_m = Unknown

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for AlOCl(c) was calculated from $\Delta H^\circ_{r\ 298}$ = 21.05 kcal. mole^{-1} for the reaction $AlOCl(c) + Cl_2(g) = AlCl_3(c) + 1/2\ O_2(g)$ reported by H. Schafer, F. E. Wittig, and W. Wilborn, Z. anorg. allgem. Chem. 297, 48 (1958). This reaction is the overall reaction of the following four separate reactions.

Chemical Reaction	$\Delta H^\circ_{r\ 298}$, kcal. mole^{-1}
$AlOCl(c) + 2(HCl\cdot 299.5\ H_2O) = AlCl_3\cdot 600\ H_2O(l)$	-46.9
$AlCl_3\cdot 600\ H_2O(l) = AlCl_3(c) + 600\ H_2O(l)$	+79.3
$H_2(g) + Cl_2(g) + 599\ H_2O(l) = 2(HCl\cdot 299.5\ H_2O)$	-79.67
$H_2O(l) = H_2(g) + 1/2\ O_2(g)$	+68.32
$AlOCl(c) + Cl_2(g) = AlCl_3(c) + 1/2\ O_2(g)$	+21.05

Heat Capacity and Entropy.

The heat capacities for AlOCl(c) were estimated based on the assumption that ΔC_p = 0 for the reaction $AlCl_3(c) + Al_2O_3(c) = 3AlOCl(c)$. $S^\circ_{298.15}$ was estimated by H. Schafer, F. E. Wittig, and W. Wilborn, loc. cit.

Temperature of Decomposition.

T_d is estimated as the temperature at which the free energy change of the reaction $6AlOCl(c) \rightarrow 3Al_2O_3(c) + Al_2Cl_6(g)$ approaches zero.

Aluminum Oxide Chloride (AlOCl)

(Ideal Gas) Mol. Wt. = 78.437

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.726	-82.698	-82.698	INFINITE
100	7.749	48.785	68.944	-2.016	-82.800	-83.178	181.778
200	10.374	55.003	60.520	-1.103	-83.030	-83.478	91.216
298	11.967	59.471	59.471	.000	-83.200	-83.664	61.324
300	11.989	59.545	59.471	.022	-83.203	-83.667	60.948
400	12.935	63.135	59.954	1.272	-83.320	-83.802	45.785
500	13.511	66.089	60.895	2.597	-83.415	-83.912	36.676
600	13.877	68.587	61.974	3.968	-83.512	-84.003	30.596
700	14.120	70.745	63.076	5.368	-83.626	-84.076	26.248
800	14.288	72.642	64.156	6.789	-83.763	-84.131	22.983
900	14.409	74.333	65.194	8.224	-83.927	-84.167	20.438
1000	14.498	75.855	66.186	9.670	-86.614	-83.999	18.357
1100	14.565	77.241	67.129	11.123	-86.729	-83.733	16.635
1200	14.617	78.510	68.025	12.582	-86.844	-83.455	15.198
1300	14.658	79.682	68.877	14.046	-86.959	-83.169	13.981
1400	14.691	80.769	69.688	15.514	-87.076	-82.872	12.936
1500	14.718	81.784	70.461	16.984	-87.194	-82.568	12.030
1600	14.740	82.734	71.199	18.457	-87.313	-82.254	11.235
1700	14.758	83.629	71.904	19.932	-87.434	-81.935	10.533
1800	14.774	84.473	72.579	21.409	-87.557	-81.609	9.908
1900	14.787	85.272	73.226	22.887	-87.683	-81.273	9.348
2000	14.798	86.031	73.848	24.366	-87.811	-80.934	8.844
2100	14.808	86.753	74.445	25.846	-87.941	-80.588	8.386
2200	14.816	87.442	75.020	27.328	-88.074	-80.234	7.970
2300	14.824	88.101	75.575	28.810	-88.210	-79.875	7.589
2400	14.830	88.732	76.110	30.292	-88.349	-79.508	7.240
2500	14.836	89.337	76.627	31.776	-88.491	-79.136	6.918
2600	14.841	89.919	77.127	33.259	-88.636	-78.760	6.620
2700	14.846	90.479	77.611	34.744	-88.785	-78.378	6.344
2800	14.850	91.019	78.081	36.229	-159.491	-76.335	5.958
2900	14.854	91.541	78.536	37.714	-159.443	-73.370	5.529
3000	14.857	92.044	78.978	39.199	-159.399	-70.400	5.128
3100	14.860	92.531	79.407	40.685	-159.358	-67.432	4.754
3200	14.863	93.003	79.825	42.171	-159.322	-64.469	4.403
3300	14.865	93.461	80.231	43.658	-159.288	-61.508	4.073
3400	14.867	93.904	80.627	45.144	-159.258	-58.543	3.763
3500	14.869	94.335	81.012	46.631	-159.231	-55.584	3.471
3600	14.871	94.754	81.388	48.118	-159.208	-52.619	3.194
3700	14.873	95.162	81.755	49.605	-159.188	-49.662	2.933
3800	14.875	95.558	82.113	51.093	-159.170	-46.699	2.686
3900	14.876	95.945	82.463	52.580	-159.156	-43.741	2.451
4000	14.878	96.321	82.804	54.068	-159.145	-40.781	2.228
4100	14.879	96.689	83.139	55.556	-159.137	-37.826	2.016
4200	14.880	97.047	83.466	57.044	-159.133	-34.865	1.814
4300	14.881	97.398	83.786	58.532	-159.130	-31.908	1.622
4400	14.882	97.740	84.099	60.020	-159.132	-28.951	1.438
4500	14.883	98.074	84.406	61.508	-159.136	-25.987	1.262
4600	14.884	98.401	84.706	62.997	-159.142	-23.026	1.094
4700	14.885	98.721	85.001	64.485	-159.152	-20.070	.933
4800	14.886	99.035	85.290	65.974	-159.165	-17.114	.779
4900	14.887	99.342	85.574	67.462	-159.182	-14.152	.631
5000	14.887	99.642	85.852	68.951	-159.201	-11.191	.489
5100	14.888	99.937	86.126	70.440	-159.223	-8.228	.353
5200	14.889	100.226	86.394	71.929	-159.249	-5.270	.221
5300	14.889	100.510	86.658	73.417	-159.279	-2.308	.095
5400	14.890	100.788	86.917	74.906	-159.313	.654	-.026
5500	14.890	101.062	87.171	76.395	-159.350	3.613	-.144
5600	14.891	101.330	87.422	77.884	-159.392	6.578	-.257
5700	14.891	101.593	87.668	79.374	-159.439	9.540	-.366
5800	14.892	101.852	87.911	80.863	-159.490	12.512	-.471
5900	14.892	102.107	88.149	82.352	-159.547	15.474	-.573
6000	14.892	102.357	88.384	83.841	-159.610	18.443	-.672

Dec. 31, 1960; Sept. 30, 1964

ALUMINUM OXIDE CHLORIDE (AlOCl) (IDEAL GAS) MOL. WT. = 78.437

Point Group $C_{\infty v}$

$\Delta H_f^\circ{}_0$ = [-82.7 ± 5.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [59.471] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [-83.2 ± 5.0] kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[450] (1)
[350] (2)
[900] (1)

Bond Distance: O = Al = [1.62]Å   Al-Cl = [2.14]Å

Bond Angle: O-Al-Cl = 180°

σ = 1

Rotational Constant: B_o = [0.097703] cm.$^{-1}$

Heat of Formation.

The free energy change of the reaction 1/3 Al_2O_3(l) + 1/3 $AlCl_3$(g) = AlOCl(g), $\Delta F_r^\circ{}_{2400^\circ K.}$ = 28 ± 3 kcal. mole^{-1}, has been determined by M. A. Greenbaum, et al., Maremont Corporation, California, private communication, August 26, 1964. Incorporating appropriate auxiliary data the heat of reaction was derived to be 82.9 kcal. mole^{-1}, yielding $\Delta H_f^\circ{}_{298.15}$ = -83.2 ± 5 kcal. mole^{-1} for AlOCl(g).

Heat Capacity and Entropy.

Point group, ground state quantum weight and vibrational frequencies were obtained from J. Hilsenrath, W. H. Evans and H. W. Woolley, National Bureau of Standards Report 6484, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine", July 1, 1959. The bond distances of r_{O-Al} and r_{Al-Cl} were assumed to be the same as those in AlO(g) and AlCl(g) molecules, respectively. The three principal moments of inertia are: I_A = 0 and $I_B = I_C$ = 2.86467 X 10^{-38} g. cm.^{2}

Aluminum Dichloride (AlCl$_2$)

(Ideal Gas) Mol. Wt. = 97.894

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.012	-74.724	-74.724	INFINITE
100	9.134	57.108	78.936	-2.183	-74.702	-75.729	165.497
200	11.186	64.107	69.913	-1.161	-74.843	-76.719	83.830
298	12.341	68.815	68.815	.000	-75.000	-77.611	56.888
300	12.356	68.892	68.815	.023	-75.003	-77.628	56.549
400	12.943	72.536	69.308	1.291	-75.162	-78.478	42.876
500	13.260	75.461	70.256	2.603	-75.330	-79.287	34.655
600	13.446	77.897	71.332	3.939	-75.519	-80.062	29.161
700	13.564	79.979	72.422	5.290	-75.733	-80.803	25.227
800	13.642	81.796	73.483	6.650	-75.975	-81.512	22.267
900	13.697	83.406	74.498	8.017	-76.245	-82.186	19.957
1000	13.737	84.851	75.462	9.389	-79.039	-82.647	18.062
1100	13.766	86.162	76.376	10.764	-79.261	-82.997	16.489
1200	13.789	87.361	77.242	12.142	-79.483	-83.328	15.175
1300	13.807	88.465	78.064	13.522	-79.705	-83.639	14.060
1400	13.821	89.489	78.844	14.903	-79.928	-83.933	13.102
1500	13.832	90.443	79.585	16.286	-80.151	-84.211	12.269
1600	13.842	91.336	80.292	17.670	-80.375	-84.474	11.538
1700	13.850	92.175	80.967	19.054	-80.600	-84.722	10.891
1800	13.856	92.967	81.612	20.440	-80.825	-84.960	10.315
1900	13.862	93.716	82.229	21.826	-81.051	-85.180	9.797
2000	13.866	94.428	82.822	23.212	-81.280	-85.394	9.331
2100	13.871	95.104	83.390	24.599	-81.508	-85.595	8.908
2200	13.874	95.750	83.938	25.986	-81.739	-85.785	8.522
2300	13.877	96.366	84.465	27.374	-81.970	-85.961	8.168
2400	13.880	96.957	84.973	28.761	-82.204	-86.130	7.843
2500	13.882	97.524	85.464	30.150	-82.439	-86.289	7.543
2600	13.885	98.068	85.938	31.538	-82.676	-86.438	7.265
2700	13.886	98.592	86.397	32.926	-82.916	-86.579	7.008
2800	13.888	99.097	86.842	34.315	-153.712	-85.056	6.639
2900	13.890	99.585	87.273	35.704	-153.753	-82.607	6.225
3000	13.891	100.056	87.691	37.093	-153.797	-80.153	5.839
3100	13.892	100.511	88.097	38.482	-153.844	-77.695	5.477
3200	13.893	100.952	88.492	39.872	-153.894	-75.238	5.138
3300	13.894	101.380	88.876	41.261	-153.947	-72.780	4.820
3400	13.895	101.794	89.250	42.650	-154.002	-70.317	4.520
3500	13.896	102.197	89.614	44.040	-154.061	-67.859	4.237
3600	13.897	102.589	89.969	45.430	-154.122	-65.393	3.970
3700	13.898	102.970	90.316	46.819	-154.187	-62.930	3.717
3800	13.898	103.340	90.653	48.209	-154.253	-60.461	3.477
3900	13.899	103.701	90.983	49.599	-154.323	-57.989	3.249
4000	13.900	104.053	91.306	50.989	-154.396	-55.520	3.033
4100	13.900	104.396	91.621	52.379	-154.471	-53.049	2.828
4200	13.901	104.731	91.929	53.769	-154.550	-50.575	2.632
4300	13.901	105.058	92.231	55.159	-154.630	-48.097	2.444
4400	13.902	105.378	92.526	56.549	-154.714	-45.620	2.266
4500	13.902	105.690	92.815	57.940	-154.799	-43.136	2.095
4600	13.902	105.996	93.098	59.330	-154.887	-40.655	1.931
4700	13.903	106.295	93.376	60.720	-154.978	-38.174	1.775
4800	13.903	106.588	93.648	62.110	-155.072	-35.691	1.625
4900	13.903	106.874	93.915	63.501	-155.168	-33.193	1.480
5000	13.904	107.155	94.177	64.891	-155.267	-30.707	1.342
5100	13.904	107.431	94.434	66.281	-155.368	-28.214	1.209
5200	13.904	107.701	94.687	67.672	-155.472	-25.722	1.081
5300	13.904	107.965	94.935	69.062	-155.580	-23.223	.958
5400	13.905	108.225	95.178	70.453	-155.691	-20.724	.839
5500	13.905	108.480	95.418	71.843	-155.806	-18.223	.724
5600	13.905	108.731	95.654	73.234	-155.924	-15.723	.614
5700	13.905	108.977	95.885	74.624	-156.048	-13.223	.507
5800	13.906	109.219	96.113	76.015	-156.174	-10.710	.404
5900	13.906	109.457	96.337	77.405	-156.307	-8.205	.304
6000	13.906	109.690	96.558	78.796	-156.445	-5.689	.207

June 30, 1961; Sept. 30, 1964

ALUMINUM DICHLORIDE (AlCl$_2$) (IDEAL GAS) MOL. WT. = 97.894

Point Group C_{2v}

$\Delta H^\circ_{f\ 0}$ = [-75 ± 20] kcal. mole^{-1}

$S^\circ_{298.15}$ = [68.815] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-75 ± 20] kcal. mole^{-1}

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[430] (1)
[210] (1)
[540] (1)

Bond Distance: Al-Cl = [2.14]Å

Bond Angle: Cl-Al-Cl = [120]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.62845 X 10^{-114}] g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for AlCl$_2$(g) was calculated based on an assumption that $\Delta H^\circ_r = 0$ for the reaction AlCl(g) + AlCl$_3$(g) = 2AlCl$_2$(g). The values of $\Delta H^\circ_{f\ 298.15}$ for AlCl(g) and AlCl$_3$(g) used for calculation are -11.2 and -139.7 kcal. mole^{-1}, respectively.

Heat Capacity and Entropies.

The vibrational frequencies were calculated by valence force field method described by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, using force constants , k_1 = 2.05 X 10^5 and k_δ/l^2 = 0.25 X 10^5 dynes/cm., estimated from those for AlCl(g) and other similar compounds. The bond distance was assumed to be the same as that for AlCl(g). The bond angle and ground state quantum weight were estimated to be consistent with those for AlF$_2$(g). The three principal moments of inertia are I_A = 4.04243 X 10^{-38}, I_B = 3.7149 X 10^{-39} and I_C = 4.41392 X 10^{-38} g. cm.^{2}

Aluminum Dichloride Unipositive Ion ($AlCl_2^+$)

(Ideal Gas) GFW = 97.887

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	13.255	62.959	62.959	.000	110.000	107.648	- 78.908
300	13.270	63.041	62.959	.025	110.008	107.633	- 78.410
400	13.882	66.951	63.488	1.385	110.436	106.777	- 58.340
500	14.214	70.088	64.505	2.792	110.856	105.814	- 46.251
600	14.410	72.698	65.659	4.224	111.257	104.767	- 38.162
700	14.534	74.930	66.828	5.671	111.637	103.655	- 32.362
800	14.617	76.876	67.965	7.129	111.989	102.490	- 27.999
900	14.675	78.601	69.053	8.594	112.299	101.284	- 24.595
1000	14.718	80.150	70.086	10.064	110.039	100.228	- 21.905
1100	14.749	81.554	71.066	11.537	110.353	99.232	- 19.716
1200	14.773	82.839	71.994	13.013	110.667	98.207	- 17.886
1300	14.792	84.022	72.874	14.492	110.982	97.155	- 16.333
1400	14.808	85.119	73.710	15.972	111.296	96.081	- 14.999
1500	14.820	86.141	74.505	17.453	111.609	94.982	- 13.839
1600	14.830	87.098	75.263	18.936	111.922	93.863	- 12.821
1700	14.838	87.997	75.986	20.419	112.234	92.727	- 11.921
1800	14.845	88.845	76.677	21.903	112.545	91.569	- 11.118
1900	14.851	89.648	77.339	23.388	112.856	90.398	- 10.398
2000	14.856	90.410	77.973	24.873	113.164	89.207	- 9.748
2100	14.861	91.135	78.583	26.359	113.473	87.998	- 9.158
2200	14.864	91.826	79.169	27.846	113.780	86.778	- 8.621
2300	14.868	92.487	79.734	29.332	114.085	85.546	- 8.129
2400	14.871	93.120	80.279	30.819	114.389	84.300	- 7.677
2500	14.873	93.727	80.805	32.306	114.690	83.038	- 7.259
2600	14.876	94.310	81.313	33.794	114.991	81.767	- 6.873
2700	14.878	94.872	81.805	35.281	115.288	80.483	- 6.515
2800	14.879	95.413	82.281	36.769	46.173	80.020	- 6.246
2500	14.881	95.935	82.743	38.257	46.727	81.217	- 6.121
3000	14.883	96.440	83.191	39.745	47.279	82.395	- 6.003
3100	14.884	96.928	83.626	41.234	47.829	83.557	- 5.891
3200	14.885	97.400	84.050	42.722	48.375	84.704	- 5.785
3300	14.886	97.858	84.461	44.211	48.919	85.832	- 5.684
3400	14.887	98.303	84.862	45.699	49.458	86.941	- 5.589
3500	14.888	98.734	85.252	47.188	49.996	88.033	- 5.497
3600	14.889	99.154	85.632	48.677	50.531	89.117	- 5.410
3700	14.890	99.562	86.003	50.166	51.063	90.177	- 5.327
3800	14.891	99.959	86.365	51.655	51.592	91.227	- 5.247
3900	14.891	100.346	86.719	53.144	52.119	92.268	- 5.171
4000	14.892	100.723	87.064	54.633	52.640	93.286	- 5.097
4100	14.892	101.090	87.402	56.123	53.162	94.292	- 5.026
4200	14.893	101.449	87.732	57.612	53.680	95.293	- 4.959
4300	14.893	101.800	88.055	59.101	54.195	96.277	- 4.893
4400	14.894	102.142	88.371	60.590	54.708	97.256	- 4.831
4500	14.894	102.477	88.681	62.080	55.217	98.211	- 4.770
4600	14.895	102.804	88.985	63.569	55.726	99.164	- 4.711
4700	14.895	103.124	89.282	65.059	56.231	100.099	- 4.655
4800	14.895	103.438	89.574	66.548	56.733	101.023	- 4.600
4900	14.896	103.745	89.860	68.038	57.234	101.951	- 4.547
5000	14.896	104.046	90.141	69.528	57.731	102.855	- 4.496
5100	14.896	104.341	90.416	71.017	58.226	103.753	- 4.446
5200	14.897	104.630	90.687	72.507	58.718	104.642	- 4.398
5300	14.897	104.914	90.953	73.996	59.205	105.516	- 4.351
5400	14.897	105.193	91.214	75.486	59.691	106.387	- 4.306
5500	14.897	105.466	91.470	76.976	60.172	107.247	- 4.262
5600	14.898	105.734	91.723	78.466	60.649	108.096	- 4.219
5700	14.898	105.998	91.971	79.955	61.122	108.940	- 4.177
5800	14.898	106.257	92.215	81.445	61.591	109.777	- 4.137
5900	14.898	106.512	92.455	82.935	62.055	110.601	- 4.097
6000	14.898	106.762	92.691	84.425	62.514	111.425	- 4.059

June 30, 1968

ALUMINUM DICHLORIDE UNIPOSITIVE ION ($AlCl_2^+$) (IDEAL GAS) GFW = 97.887

Point Group [$D_{\infty h}$]

ΔHf_0° = [110 ± 40] kcal/mol

$S^\circ_{298.15}$ = [63 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [110 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[590] (1)
[180] (2)
[380] (1)

Bond Distance: Al-Cl = [2.17] Å

Bond Angle: Cl-Al-Cl = [180°]

Rotational Constant: B_0 = [0.0505] cm^{-1}

σ = 2

Heat of Formation

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), reported an appearance potential of 13.4 ± 0.5eV (309 ± 12 kcal) for $AlCl_2^+$; they indicated that $AlCl_3(g)$ was the probable parent molecule. Assuming the formation reaction to be $AlCl_3 + e^- \rightarrow AlCl_2^+ + Cl + 2\ e^-$, we obtain $\Delta Hf^\circ_{298}(AlCl_2^+, g)$ = 140 kcal/mol or an ionization potential of 215 kcal or 9.3eV. Since there is a possibility of the fragments containing excess kinetic energy, the ionization potential represents an upper limit to the true value. A comparison of the ionization potentials of BF_x and BCl_x indicates that the chloride is lower by ~1eV per atom; on this basis we would obtain an ionization potential of 7eV using the value for AlF_2 of 9eV.

The National Bureau of Standards Report No. 8628, Jan. 1, 1965, gives an estimate of 8 ± 1eV (185 ± 25 kcal); we adopt this value as being representative of the probable range of values. The adopted ionization potential yields $\Delta Hf^\circ_{298.15}(AlCl_2^+, g)$ = 110 ± 40 kcal/mol in conjunction with $\Delta Hf^\circ_{298}(AlCl_2, g)$ = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

$AlCl_2^+$ is isoelectronic with $MgCl_2$ and on this basis we assume the ground state to be singlet and linear in accordance with the predictions of A. D. Walsh, J. Chem. Soc. 2266 (1953). The vibrational frequencies are estimated to lie between those for $AlCl_2$ and $MgCl_2$. The bond length is estimated as the sum of the covalent radii of the atoms.

The enthalpy at 0°K is -3.128 kcal/mol.

Aluminum Dichloride Uninegative Ion ($AlCl_2^-$)

(Ideal Gas) GFW = 97.888

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	12.289	67.441	67.441	.000	-80.000	-80.714	59.165
300	12.304	67.517	67.442	.023	-80.012	-80.719	58.803
400	12.906	71.149	67.933	1.286	-80.675	-80.854	44.177
500	13.233	74.067	68.877	2.595	-81.347	-80.821	35.327
600	13.426	76.498	69.950	3.929	-82.038	-80.652	29.377
700	13.548	78.578	71.038	5.278	-82.748	-80.364	25.091
800	13.629	80.392	72.096	6.637	-83.489	-79.974	21.848
900	13.687	82.001	73.109	8.003	-84.272	-79.488	19.302
1000	13.728	83.445	74.072	9.374	-87.625	-78.730	17.206
1100	13.759	84.755	74.984	10.748	-88.404	-77.804	15.458
1200	13.783	85.954	75.849	12.125	-89.183	-76.807	13.988
1300	13.801	87.058	76.670	13.504	-89.960	-75.742	12.733
1400	13.816	88.081	77.449	14.885	-90.739	-74.619	11.649
1500	13.828	89.035	78.190	16.208	-91.518	-73.441	10.700
1600	13.838	89.927	78.896	17.651	-92.299	-72.210	9.863
1700	13.846	90.767	79.569	19.035	-93.080	-70.930	9.119
1800	13.853	91.558	80.214	20.420	-93.860	-69.603	8.451
1900	13.859	92.307	80.831	21.806	-94.642	-68.235	7.849
2000	13.864	93.018	81.422	23.192	-95.427	-66.826	7.302
2100	13.868	93.695	81.991	24.578	-96.212	-65.377	6.804
2200	13.872	94.340	82.538	25.965	-96.999	-63.891	6.347
2300	13.875	94.957	83.064	27.353	-97.784	-62.364	5.926
2400	13.878	95.547	83.572	28.740	-98.574	-60.808	5.537
2500	13.880	96.114	84.063	30.128	-99.366	-59.220	5.177
2600	13.883	96.658	84.537	31.516	-100.159	-57.597	4.841
2700	13.885	97.182	84.995	32.905	-100.954	-55.949	4.529
2800	13.886	97.687	85.440	34.293	-171.163	-53.435	4.171
2900	13.888	98.175	85.870	35.682	-171.700	-49.223	3.710
3000	13.889	98.645	86.288	37.071	-172.241	-44.988	3.277
3100	13.891	99.101	86.694	38.460	-172.785	-40.737	2.872
3200	13.892	99.542	87.089	39.849	-173.332	-36.471	2.491
3300	13.893	99.969	87.473	41.238	-173.882	-32.184	2.131
3400	13.894	100.384	87.847	42.628	-174.433	-27.884	1.792
3500	13.895	100.787	88.211	44.017	-174.989	-23.568	1.472
3600	13.896	101.178	88.565	45.407	-175.547	-19.230	1.167
3700	13.897	101.559	88.911	46.796	-176.109	-14.878	.879
3800	13.897	101.930	89.249	48.186	-176.673	-10.517	.605
3900	13.898	102.291	89.579	49.576	-177.239	-6.134	.344
4000	13.898	102.643	89.901	50.966	-177.809	-1.740	.095
4100	13.899	102.986	90.216	52.355	-178.382	2.667	-.142
4200	13.900	103.321	90.524	53.745	-178.957	7.088	-.369
4300	13.900	103.648	90.826	55.135	-179.535	11.524	-.586
4400	13.901	103.967	91.121	56.525	-180.115	15.979	-.794
4500	13.901	104.280	91.410	57.915	-180.698	20.440	-.993
4600	13.901	104.585	91.693	59.306	-181.281	24.917	-1.184
4700	13.902	104.884	91.970	60.696	-181.870	29.403	-1.367
4800	13.902	105.177	92.242	62.086	-182.461	33.904	-1.544
4900	13.902	105.464	92.509	63.476	-183.054	38.423	-1.714
5000	13.903	105.745	92.771	64.866	-183.649	42.944	-1.877
5100	13.903	106.020	93.028	66.257	-184.246	47.489	-2.035
5200	13.903	106.290	93.281	67.647	-184.848	52.034	-2.187
5300	13.904	106.555	93.529	69.037	-185.454	56.594	-2.334
5400	13.904	106.815	93.772	70.428	-186.061	61.170	-2.476
5500	13.904	107.070	94.012	71.818	-186.674	65.751	-2.613
5600	13.904	107.320	94.247	73.208	-187.289	70.350	-2.746
5700	13.904	107.566	94.479	74.599	-187.908	74.946	-2.874
5800	13.905	107.808	94.706	75.989	-188.533	79.572	-2.998
5900	13.905	108.046	94.931	77.380	-189.162	84.198	-3.119
6000	13.905	108.279	95.151	78.770	-189.797	88.835	-3.236

June 30, 1968

ALUMINUM DICHLORIDE UNINEGATIVE ION ($AlCl_2^-$) (IDEAL GAS) GFW = 97.888

Point Group [C_{2v}]

ΔHf°_0 = [-80 ± 40] kcal/mol

$S^\circ_{298.15}$ = [67.4 ± 0.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-80 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[550] (1)
[200] (1)
[450] (1)

Bond Distance: Al-Cl = [2.14] Å

Bond Angle: Cl-Al-Cl = [120°]

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.634 x 100^{-114}] g^3 cm^6

Heat of Formation

$AlCl_2^-$ is isoelectronic with $SiCl_2$, and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same in the two molecules. This leads to $\Delta Hf^\circ_{298}(AlCl_2^-, g)$ = -80 kcal/mol or an electron affinity of 5 kcal. An alternative route assumes that the heat of reaction is identical for the processes $AlCl_3(g) \rightarrow AlCl_2^-(g) + Cl^+(g)$ and $AlCl(g) \rightarrow Al^-(g) + Cl^+(g)$. Using the electron affinity of Al(g) given in National Bureau of Standards Report No. 8628, Jan. 1, 1965, we obtain $\Delta Hf^\circ_{298}(AlCl_2^-, g)$ = -63 kcal/mol or an electron affinity of -12 kcal. In addition, using the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953), the electron must go into a non-bonding orbital; thus the binding energy should be close to that of $AlCl_2$. The dissociation energy of $AlCl_2$ is 211 kcal which leads to $\Delta Hf^\circ_{298}(AlCl_2^-, g)$ = -87 kcal/mol, or an electron affinity of 12 kcal. We adopt an intermediate value for the electron affinity of 5 ± 20 kcal/mol, or $\Delta Hf^\circ_{298}(AlCl_2^-, g)$ = -80 ± 40 kcal/mol using $\Delta Hf^\circ_{298}(AlCl_2, g)$ = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

As noted earlier, $AlCl_2^-$ is isoelectronic with $SiCl_2$ and, with 18 valence electrons, should be definitely bent according to the correlation scheme of A. D. Walsh, loc. cit. The vibrational frequencies are estimated to lie between those of $SiCl_2$ and $AlCl_2$. The bond length and angle are estimated as equal to those for $AlCl_2(g)$. By analogy with SiF_2 (see G. Herzberg "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Company Inc., New York, 1966) we do not expect any low lying electronic levels.

The enthalpy at 0°K is -3.006 kcal/mol. The three principal moments of inertia are: $I_A = 3.7155 \times 10^{-39}$, $I_B = 4.0438 \times 10^{-38}$, and $I_C = 4.4154 \times 10^{-38}$ g cm^2.

Aluminum Dichloride Fluoride ($AlCl_2F$)

(Ideal Gas) Mol. Wt. = 116.894

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.734	- 187.991	- 187.991	INFINITE
100	11.238	59.274	87.557	- 2.828	- 188.240	- 187.449	409.649
200	14.508	68.177	75.802	- 1.525	- 188.450	- 186.585	203.881
298	16.410	74.356	74.356	.000	- 188.600	- 185.641	136.072
300	16.438	74.457	74.356	.030	- 188.603	- 185.623	135.219
400	17.582	79.357	75.016	1.736	- 188.709	- 184.612	100.862
500	18.269	83.361	76.297	3.532	- 188.797	- 183.577	80.238
600	18.700	86.732	77.763	5.382	- 188.888	- 182.525	66.481
700	18.982	89.638	79.256	7.267	- 188.993	- 181.457	56.651
800	19.176	92.186	80.717	9.175	- 189.120	- 180.373	49.273
900	19.314	94.453	82.119	11.100	- 189.270	- 179.270	43.530
1000	19.415	96.493	83.456	13.037	- 191.942	- 177.965	38.892
1100	19.491	98.347	84.727	14.982	- 192.039	- 176.563	35.078
1200	19.550	100.046	85.934	16.934	- 192.136	- 175.152	31.898
1300	19.596	101.613	87.080	18.892	- 192.232	- 173.733	29.206
1400	19.633	103.066	88.171	20.853	- 192.328	- 172.306	26.897
1500	19.664	104.422	89.210	22.818	- 192.424	- 170.872	24.895
1600	19.688	105.692	90.201	24.786	- 192.522	- 169.432	23.142
1700	19.709	106.886	91.147	26.756	- 192.620	- 167.985	21.595
1800	19.727	108.013	92.053	28.728	- 192.720	- 166.535	20.219
1900	19.741	109.080	92.922	30.701	- 192.821	- 165.074	18.987
2000	19.754	110.093	93.755	32.676	- 192.925	- 163.612	17.878
2100	19.765	111.057	94.556	34.652	- 193.029	- 162.146	16.874
2200	19.774	111.977	95.327	36.629	- 193.136	- 160.673	15.961
2300	19.783	112.856	96.070	38.607	- 193.245	- 159.193	15.126
2400	19.790	113.698	96.787	40.585	- 193.356	- 157.710	14.361
2500	19.796	114.506	97.480	42.565	- 193.471	- 156.223	13.656
2600	19.802	115.282	98.150	44.545	- 193.588	- 154.730	13.006
2700	19.807	116.030	98.798	46.525	- 193.708	- 153.235	12.403
2800	19.812	116.750	99.427	48.506	- 264.386	- 150.078	11.714
2900	19.816	117.446	100.036	50.487	- 264.309	- 146.001	11.002
3000	19.820	118.117	100.628	52.469	- 264.237	- 141.921	10.338
3100	19.823	118.767	101.203	54.451	- 264.168	- 137.844	9.718
3200	19.826	119.397	101.761	56.434	- 264.104	- 133.773	9.136
3300	19.829	120.007	102.305	58.416	- 264.043	- 129.700	8.589
3400	19.831	120.599	102.834	60.399	- 263.984	- 125.630	8.075
3500	19.834	121.174	103.350	62.383	- 263.932	- 121.564	7.590
3600	19.836	121.733	103.853	64.366	- 263.882	- 117.493	7.132
3700	19.838	122.276	104.344	66.350	- 263.836	- 113.428	6.700
3800	19.839	122.805	104.823	68.334	- 263.793	- 109.363	6.290
3900	19.841	123.320	105.290	70.318	- 263.756	- 105.297	5.900
4000	19.843	123.823	105.747	72.302	- 263.722	- 101.238	5.531
4100	19.844	124.313	106.194	74.286	- 263.691	- 97.180	5.180
4200	19.845	124.791	106.631	76.271	- 263.665	- 93.118	4.845
4300	19.847	125.258	107.059	78.255	- 263.640	- 89.056	4.526
4400	19.848	125.714	107.478	80.240	- 263.622	- 84.995	4.222
4500	19.849	126.160	107.888	82.225	- 263.605	- 80.934	3.931
4600	19.850	126.597	108.290	84.210	- 263.592	- 76.878	3.652
4700	19.851	127.024	108.684	86.195	- 263.583	- 72.821	3.386
4800	19.852	127.441	109.071	88.180	- 263.577	- 68.759	3.131
4900	19.853	127.851	109.450	90.165	- 263.576	- 64.697	2.885
5000	19.853	128.252	109.822	92.150	- 263.578	- 60.643	2.651
5100	19.854	128.645	110.187	94.136	- 263.582	- 56.581	2.425
5200	19.855	129.031	110.546	96.121	- 263.592	- 52.524	2.207
5300	19.856	129.409	110.898	98.107	- 263.605	- 48.465	1.998
5400	19.856	129.780	111.244	100.092	- 263.624	- 44.406	1.797
5500	19.857	130.144	111.585	102.078	- 263.646	- 40.344	1.603
5600	19.857	130.502	111.919	104.064	- 263.674	- 36.283	1.416
5700	19.858	130.854	112.248	106.049	- 263.708	- 32.231	1.236
5800	19.858	131.199	112.572	108.035	- 263.745	- 28.161	1.061
5900	19.859	131.538	112.891	110.021	- 263.790	- 24.099	.893
6000	19.859	131.872	113.204	112.007	- 263.841	- 20.037	.730

Dec. 31, 1960; Sept. 30, 1964

ALUMINUM DICHLORIDE FLUORIDE ($AlCl_2F$) (IDEAL GAS) MOL. WT. = 116.894

Point Group C_{2v}

$\Delta H^\circ_{f\ 0}$ = [-188.0 ± 20] kcal. mole^{-1}

$S^\circ_{298.15}$ = [74.356] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-188.6 ± 20] kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[420] (1)	[200] (1)
[260] (1)	[650] (1)
[150] (1)	[820] (1)

Bond Distance: Al-F = [1.65]Å Al-Cl = [2.14]Å

Bond Angle: F-Al-Cl = [120]° Cl-Al-Cl = [120]° $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.64645 X 10^{-113}] g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ was calculated based on an assumption the $\Delta H^\circ_r = 0$ for the reaction $AlF_3(g) + 2AlCl_3(g) = 3AlCl_2F(g)$. The values of $\Delta H^\circ_{f\ 298.15}$ for $AlF_3(g)$ and $AlCl_3(g)$ used for calculation are -286.5 and -139.7 kcal. mole^{-1}, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for $AlF_3(g)$ and $AlCl_3(g)$. The bond distances of Al-F and Al-Cl atoms were assumed to be the same as those in $AlF_3(g)$ and $AlCl_3(g)$, respectively. The bond angles and ground state quantum weight were estimated by comparison with those for $AlF_3(g)$. The three principal moments of inertia are 4.04374 X 10^{-38}, 1.92508 X 10^{-38} and 5.96882 X 10^{-38} g.^{3} cm.^{6}

Aluminum Trichloride ($AlCl_3$)
(Crystal) GFW = 133.341

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 4.058	- 168.323	- 168.323	INFINITE
100	11.260	7.361	43.251	- 3.589	- 169.004	- 162.803	355.805
200	16.930	17.960	28.035	- 2.015	- 168.961	- 156.592	171.115
298	21.780	26.120	26.120	.000	- 168.650	- 150.587	110.383
300	21.820	26.255	26.120	.040	- 168.643	- 150.476	109.621
400	23.920	32.820	27.001	2.327	- 168.200	- 144.482	78.942
500	26.020	38.383	28.734	4.824	- 167.614	- 138.617	60.589
600	28.120	43.313	30.760	7.531	- 166.869	- 132.885	48.403
700	30.220	47.805	32.879	10.448	- 165.954	- 127.291	39.742
800	32.320	51.977	35.008	13.575	- 164.873	- 121.841	33.285
900	34.420	55.905	37.114	16.912	- 163.633	- 116.534	28.298
1000	36.520	59.641	39.181	20.459	- 164.760	- 111.192	24.301
1100	38.620	63.220	41.205	24.216	- 163.108	- 105.914	21.043
1200	40.720	66.670	43.184	28.183	- 161.250	- 100.796	18.357
1300	42.820	70.012	45.120	32.360	- 159.184	- 95.840	16.112
1400	44.920	73.263	47.014	36.747	- 156.912	- 91.050	14.214
1500	47.020	76.433	48.870	41.344	- 154.433	- 86.432	12.593

Dec. 31, 1960; June 30, 1961; June 30, 1963; Mar. 31, 1964; June 30, 1970

ALUMINUM TRICHLORIDE ($AlCl_3$) (CRYSTAL) GFW = 133.341

$S^\circ_{298.15}$ = 26.12 ± 0.10 gibbs/mol

Tm = 465.7 ± 0.2°K

Ts (to dimer) = 454.3°K

ΔHf°_0 = -168.32 ± 0.20 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -168.65 ± 0.20 kcal/mol

ΔHm° = 8.45 ± 0.2 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to dimer) = 27.66 kcal/mol dimer

Heat of Formation

Gross and Hayman (1) measured the enthalpy of direct combination of "spectrographically pure" aluminum and carefully purified chlorine and derived $\Delta Hf^\circ_{298.15}$ = -168.80 ± 0.16 kcal/mol. Siemonsen (2) also reported the enthalpy of direct combination and is in agreement at -167.5 kcal/mol within his relatively large uncertainty interval of ±1.1 kcal/mol.

Coughlin (3) determined the enthalpy of solution of 99.99+% pure Al in 4.360 m HCl and also (4) the enthalpy of solution of anhydrous $AlCl_3$ in the same solvent. Enthalpies of mixing were measured to close a thermochemical cycle at 303.15°K (adjusted to 1961 at. wts.):

	Reaction	$\Delta H^\circ_{303.15}$, cal.
(1)	$Al(c) + 3H^+(sol) = Al^{+++}(sol) + 3/2\ H_2(g)$	-127,057 ± 120
(2)	$3(HCl\cdot 12.731\ H_2O)(\ell) = 3H^+(sol) + 3Cl^-(sol) + 38.193\ H_2O(sol)$	0 ± 10
(3)	$AlCl_3(c) = Al^{+++}(sol) + 3Cl^-(sol)$	-72,504 ± 50
(4)	$38.193\ H_2O(\ell) = 38.193\ H_2O(sol)$	-3,050 ± 20
(5)	$Al(c) + 3(HCl\cdot 12.731\ H_2O)(\ell) = AlCl_3(c) + 38.193\ H_2O(\ell) + 3/2\ H_2(g)$	-51,503 ± 140

With heat capacity data for Al, $AlCl_3$, and H_2 from the JANAF tables and for $HCl[12.731\ H_2O]$ from Parker (5), the enthalpy of reaction 5 at 298.15°K is -51,910 ± 140 cal/mol $AlCl_3$. Interpolation of data for $\Delta Hf^\circ_{298.15}$(HCl, aq) selected by Wagman et al. (6) yields $\Delta Hf^\circ_{298.15}(AlCl_3, c)$ = -168.37 kcal/mol. The overall uncertainty is estimated as 300 cal/mol.

Earlier investigations on the enthalpies of solution of Al were adjusted to the conditions of Coughlin's experiments by means of the data of Smith and Bass (7) for the effects of HCl concentration and H_2O dilution on $\Delta Hf(AlCl_3, aq)$ and estimates of ΔCp of solution of Al of +20 gibbs/mol.

Investigator(s)	ΔH(soln) as reported kcal/mol Al	ΔHsoln adjusted kcal/mol Al
Young (8)	-126.83	-126.79
Roth and Wolf (9)	-124.01	-127.29
Canneri and Rossi (10)	-125.40	-126.80
Somermeier (11)	-128.36	-126.42
Richards and Burgess (12)	-126.00	-124.06

Only Richards and Burgess deviate more than expected; they report a value for Mg in good agreement with modern values and it seems likely their sample of Al was impure.

Several values for the enthalpy of solution of $AlCl_3(c)$ in water have also been published and are listed here along with Coughlin's value recalculated to solution in pure water at 20°C.

Investigator(s)	ΔH(soln) in H_2O at 20°C (kcal/mol $AlCl_3$)
Coughlin (3)	-78.22 (adjusted)
Thomsen (13)	-76.85
Berthelot (13)	-76.3
Baud (13)	-77.6
Sabatier (13)	-78.
Roth and Büchner (14)	-77.9
Roth and Börger (15)	-79.3
Klemm and Tanke (16)	-77.7 (adjusted)

Klemm and Tanke (16) measured the enthalpy of solution of $AlCl_3$ in $HCl\cdot 20\ H_2O$ at 0°C. A weighted average of the values of Gross and Hayman (1) and of Coughlin (4) is adopted for $\Delta Hf^\circ_{298.15}(AlCl_3, c)$ = -168.65 ± 0.20 kcal/mol.

Heat Capacity and Entropy

Justice (17) reported low temperature heat capacity data (13° to 310°K) and presented smoothed thermodynamic functions, including $S^\circ_{298.15}$ = 26.12 gibbs/mol, of which 0.086 gibbs/mol is extrapolation below 13°K. Heat content relative to 273.15°K was measured by Fischer (18) from 298°K to 504°K and heat content relative to 298.15°K was measured by McDonald (19) from 310° to 493°K. The heat content data for the crystal can be fit within about 2% by integration of Cp(c) (gibbs/mol) = 15.52 + 0.021T, which is an extrapolation of Cp data reported by Justice (17).

Melting Data

See table for $AlCl_3(\ell)$.

Sublimation Data

See table for $Al_2Cl_6(g)$.

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Aluminum Trichloride ($AlCl_3$)

(Liquid) GFW = 133.341

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0							
100							
200							
298	30.000	41.326	41.326	- .000	- 161.280	- 147.751	108.304
300	30.000	41.512	41.327	.055	- 161.258	- 147.667	107.576
400	30.000	50.142	42.503	3.056	- 160.102	- 143.313	78.303
500	30.000	56.836	44.725	6.056	- 159.013	- 139.243	60.863
600	30.000	62.306	47.213	9.056	- 157.975	- 135.387	49.315
700	30.000	66.931	49.708	12.056	- 156.977	- 131.702	41.119
800	30.000	70.937	52.117	15.055	- 156.023	- 128.158	35.011
900	30.000	74.470	54.408	18.055	- 155.120	- 124.729	30.288
1000	30.000	77.631	56.575	21.055	- 156.794	- 121.216	26.492
1100	30.000	80.490	58.621	24.056	- 155.899	- 117.702	23.385
1200	30.000	83.100	60.554	27.056	- 155.008	- 114.270	20.811
1300	30.000	85.502	62.382	30.056	- 154.119	- 110.911	18.646
1400	30.000	87.725	64.114	33.056	- 153.234	- 107.619	16.800
1500	30.000	89.795	65.758	36.056	- 152.352	- 104.393	15.210

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

ALUMINUM TRICHLORIDE ($AlCl_3$) (LIQUID) GFW = 133.341

$S^\circ_{298.15}$ = 41.326 ± 0.5 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -161.28 ± 0.40 kcal/mol

Tm = 465.7 ± 0.2°K ΔHm = 8.45 ± 0.20 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298.15}(\ell)$ was obtained from $\Delta Hf^\circ_{298.15}(c)$ by adding ΔHm and the difference between $(H_{465.7}-H_{298.15})$ for crystal and liquid.

Melting Point

Kendall et al. (1) observed $AlCl_3$ to melt "sharply" at 463.4°K, Foster (2) noted that $AlCl_3$ began melting and melted completely in the range 465.7 ± 0.2°K, Nisel'son et al. (3) reported Tm = 467.2°K, and Ostrikova et al. (4) reported Tm = 466°K. Smits and Meijering (5) and Treadwell and Terebesi (6) derived triple point temperatures of 465.8°K and 466.5°K, respectively, from intersection of vapor pressure curves for crystal and liquid. The value of Foster is adopted as most accurate. The vapor pressure at the triple point is 2.3 atm.

Heat of Fusion and Heat Capacity

Fischer (7) and McDonald (8) measured heat content data for the liquid over a short range (473°-504°K) of temperature. Their data can be represented within 2% by the heat capacity equation derived for the crystal [see $AlCl_3$(c) table], a heat of fusion of 8.45 kcal/mol, and a liquid heat capacity of 30.0 gibbs/mol. Fischer's data are high, while McDonald's points lie below the selected values.

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Aluminum Trichloride ($AlCl_3$)

(Ideal Gas) GFW = 133.341

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.959	-139.274	-139.274	INFINITE
100	12.193	59.060	89.084	-3.003	-139.468	-138.436	302.552
200	15.403	68.602	76.640	-1.608	-139.604	-137.363	150.103
298	17.176	75.118	75.118	.000	-139.700	-136.246	99.871
300	17.200	75.224	75.118	.032	-139.702	-136.225	99.240
400	18.166	80.319	75.806	1.805	-139.773	-135.054	73.790
500	18.708	84.436	77.139	3.651	-139.837	-133.867	58.513
600	19.034	87.878	78.646	5.540	-139.911	-132.667	48.324
700	19.242	90.829	80.180	7.454	-139.998	-131.452	41.041
800	19.383	93.408	81.676	9.386	-140.113	-130.225	35.576
900	19.481	95.697	83.109	11.329	-140.266	-128.980	31.320
1000	19.553	97.754	84.473	13.281	-142.988	-127.534	27.872
1100	19.607	99.620	85.766	15.239	-143.135	-125.981	25.030
1200	19.648	101.328	86.993	17.202	-143.281	-124.416	22.659
1300	19.681	102.902	88.157	19.169	-143.425	-122.838	20.651
1400	19.707	104.361	89.263	21.138	-143.571	-121.248	18.928
1500	19.728	105.722	90.315	23.110	-143.717	-119.649	17.433
1600	19.745	106.996	91.318	25.084	-143.864	-118.040	16.123
1700	19.759	108.193	92.276	27.059	-144.012	-116.419	14.967
1800	19.771	109.323	93.192	29.035	-144.160	-114.792	13.938
1900	19.781	110.392	94.069	31.013	-144.309	-113.155	13.016
2000	19.790	111.407	94.911	32.992	-144.462	-111.513	12.186
2100	19.798	112.373	95.720	34.971	-144.614	-109.864	11.434
2200	19.804	113.294	96.498	36.951	-144.770	-108.205	10.749
2300	19.810	114.174	97.247	38.932	-144.926	-106.536	10.123
2400	19.815	115.018	97.970	40.913	-145.085	-104.863	9.549
2500	19.819	115.826	98.669	42.895	-145.248	-103.187	9.021
2600	19.823	116.604	99.344	44.877	-145.413	-101.500	8.532
2700	19.827	117.352	99.997	46.859	-145.581	-99.810	8.079
2800	19.830	118.073	100.630	48.842	-215.164	-97.279	7.593
2900	19.833	118.769	101.243	50.825	-215.077	-93.073	7.014
3000	19.835	119.442	101.839	52.809	-214.995	-88.867	6.474
3100	19.838	120.092	102.417	54.792	-214.917	-84.664	5.969
3200	19.840	120.722	102.979	56.776	-214.843	-80.463	5.495
3300	19.842	121.332	103.526	58.760	-214.773	-76.263	5.051
3400	19.843	121.925	104.059	60.745	-214.707	-72.068	4.632
3500	19.845	122.500	104.577	62.729	-214.647	-67.877	4.238
3600	19.846	123.059	105.083	64.714	-214.589	-63.679	3.866
3700	19.848	123.603	105.576	66.698	-214.537	-59.489	3.514
3800	19.849	124.132	106.058	68.683	-214.488	-55.302	3.181
3900	19.850	124.648	106.528	70.668	-214.442	-51.109	2.864
4000	19.851	125.150	106.987	72.653	-214.403	-46.924	2.564
4100	19.852	125.640	107.436	74.638	-214.366	-42.741	2.278
4200	19.853	126.119	107.875	76.624	-214.332	-38.555	2.006
4300	19.854	126.586	108.305	78.609	-214.303	-34.371	1.747
4400	19.855	127.042	108.726	80.594	-214.276	-30.179	1.499
4500	19.855	127.489	109.138	82.580	-214.254	-26.001	1.263
4600	19.856	127.925	109.541	84.565	-214.232	-21.816	1.036
4700	19.857	128.352	109.937	86.551	-214.215	-17.636	.820
4800	19.857	128.770	110.325	88.537	-214.202	-13.457	.613
4900	19.858	129.180	110.706	90.523	-214.190	-9.266	.413
5000	19.859	129.581	111.079	92.508	-214.182	-5.088	.222
5100	19.859	129.974	111.446	94.494	-214.176	-.902	.039
5200	19.860	130.360	111.806	96.480	-214.174	3.279	-.138
5300	19.860	130.738	112.159	98.466	-214.176	7.457	-.307
5400	19.860	131.109	112.507	100.452	-214.181	11.641	-.471
5500	19.861	131.474	112.848	102.438	-214.190	15.822	-.629
5600	19.861	131.832	113.184	104.424	-214.203	20.004	-.781
5700	19.862	132.183	113.515	106.410	-214.220	24.180	-.927
5800	19.862	132.528	113.839	108.397	-214.241	28.371	-1.069
5900	19.862	132.868	114.159	110.383	-214.268	32.550	-1.206
6000	19.863	133.202	114.474	112.369	-214.299	36.736	-1.338

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

ALUMINUM TRICHLORIDE ($AlCl_3$) (IDEAL GAS) GFW = 133.341

Point Group D_{3h}

$\Delta Hf^\circ_0 = -139.27 \pm 0.70$ kcal/mol

$S^\circ_{298.15} = 75.118 \pm 1.0$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -139.70 \pm 0.70$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
371 (1)	146 (2)
[185] (1)	610 (2)

Bond Distance: Al-Cl = 2.06 Å

Bond Angle: Cl-Al-Cl = 120° $\sigma = 6$

Product of the Moments of Inertia: $I_AI_BI_C = 1.0518 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The heat of formation is calculated from the value adopted for Al_2Cl_6(g) and the heat of dissociation of Al_2Cl_6, derived from equilibrium P-V-T data on aluminum chloride vapor as listed below.

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta Hr_{298.15}$(kcal/mol Al_2Cl_6) 2nd Law	3rd Law
Smits and Meijering (1)	669-816	6	29.28	30.12
Fischer et al. (2)	647-869	16[a]	30.82	30.35
Vrieland and Stull (3)	669-825	19[b]	30.22	30.40

[a] Twenty three points reported, points at 938, 881, 944, 734, 805, 605, and 688°K rejected by statistical test.

[b] Twenty six points reported, points at 627.9, 643.1, 671.3, 638.4, 671.6, 722.5, and 686.9°K rejected by statistical test.

The three investigations are in reasonable agreement. Giving consideration also to equilibrium data on the reaction of $AlCl_3$(g) and Al(ℓ) to form AlCl(g) [see AlCl(g) table], there is selected as a best value $\Delta Hr^\circ_{298.15}$ = 30.24 kcal/mol Al_2Cl_6, which yields $\Delta Hf^\circ_{298.15}(AlCl_3, g) = -139.70$ kcal/mol.

Heat Capacity and Entropy

Zasorin and Rambidi (4) carried out electron diffraction experiments on aluminum chloride vapor at 800°K where the monomer should predominate. They found a planar symmetrical structure with Al-Cl = 2.06 ± 0.01 Å and Cl-Al-Cl angles of 120°. The individual moments of inertia are $I_A = I_B = 3.7466 \times 10^{-38}$ g cm^2 and $I_C = 7.4932 \times 10^{-38}$ g cm^2. For aluminum chloride vapor at high temperatures (monomer predominant), Klemperer (5) observed a band at 610 cm^{-1} in the infrared spectrum and Beattie and Horder (6) reported Raman bands at 371 cm^{-1} and 146 cm^{-1}. The remaining frequency should be infrared active but presumably was beyond the range of Klemperer's measurements. Zasorin and Rambidi (7) give 95 ± 15 cm^{-1} based on amplitudes of vibration observed in electron diffraction measurements. However, this frequency gives thermodynamic functions clearly not compatible with the equilibrium P-V-T data. Force constant ratios in the boron halides also suggest a higher wavenumber. An estimate of 185 cm^{-1} was therefore adopted as an optimum value for fitting both the Al_2Cl_6 dissociation data and the equilibrium data for $AlCl_3(g) + 2Al(\ell) \rightarrow 3AlCl(g)$ [see AlCl(g) table].

References

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Potassium Tetrachloroaluminate ($KAlCl_4$)

(Crystal) Mol. Wt. = 207.908

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	37.400	47.000	47.000	.000	- 286.000	- 261.610	191.756
300	37.440	47.231	47.001	.069	- 285.985	- 261.459	190.464
400	39.550	58.294	48.495	3.920	- 285.705	- 253.302	138.391
500	41.660	67.346	51.386	7.980	- 284.721	- 245.311	107.220
600	43.780	75.128	54.708	12.252	- 283.569	- 237.534	86.518
700	45.600	82.019	58.127	16.724	- 282.256	- 229.964	71.795
800	47.000	88.204	61.507	21.358	- 280.822	- 222.593	60.807
900	47.800	93.789	64.789	26.100	- 279.319	- 215.402	52.304
1000	48.300	98.854	67.946	30.908	- 280.292	- 208.199	45.500
1100	48.407	103.462	70.969	35.743	- 297.588	- 200.043	39.743
1200	48.500	107.678	73.854	40.589	- 295.739	- 191.257	34.831
1300	48.580	111.564	76.608	45.443	- 293.886	- 182.627	30.701
1400	48.647	115.166	79.235	50.304	- 292.030	- 174.136	27.183
1500	48.700	118.525	81.743	55.172	- 290.171	- 165.780	24.153
1600	48.763	121.670	84.142	60.045	- 288.311	- 157.547	21.519
1700	48.825	124.628	86.437	64.924	- 286.448	- 149.431	19.210
1800	48.885	127.420	88.637	69.810	- 284.582	- 141.427	17.171
1900	48.943	130.065	90.748	74.701	- 282.715	- 133.521	15.358
2000	49.000	132.577	92.777	79.599	- 280.847	- 125.717	13.737

June 30, 1962; June 30, 1963

POTASSIUM TETRACHLOROALUMINATE ($KAlCl_4$) (CRYSTAL) MOL. WT. = 207.908

$S^\circ_{298.15}$ = [47 ± 2] cal. deg.$^{-1}$ mole^{-1}

T_m = 529°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -286.0 ± 2.5 kcal. mole^{-1}

ΔH°_m = Unknown

Heat of Formation.

The heat of reaction of aluminum chloride and potassium chloride was measured by E. Baud, Ann. Chim. Phys. 1, 8 (1904). From ΔH°_r = -26.38 kcal. mole^{-1} for the reaction: $Al_2Cl_6(c) + 2KCl(c) = 2KAlCl_4(c)$, the value of $\Delta H^\circ_{f\ 298.15}$ for $KAlCl_4(c)$ was calculated to be -286 kcal. mole^{-1}.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for $KMgCl_3(c)$, reported by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). $S^\circ_{298.15}$ was estimated according to the methods suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by W. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. 306, 1 (1960).

Sodium Tetrachloroaluminate ($NaAlCl_4$)

(Crystal) Mol. Wt. = 191.799

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	37.040	45.000	45.000	.000	- 273.000	- 248.956	182.481
300	37.080	45.229	45.001	.069	- 272.984	- 248.806	181.247
400	39.390	56.206	46.482	3.890	- 272.764	- 240.824	131.574
500	41.600	65.237	49.355	7.941	- 271.787	- 232.948	101.816
600	43.600	73.001	52.664	12.203	- 270.640	- 225.285	82.056
700	45.200	79.850	56.068	16.647	- 269.345	- 217.828	68.006
800	46.250	85.960	59.430	21.224	- 267.951	- 210.563	57.520
900	47.150	91.464	62.688	25.898	- 266.494	- 203.475	49.408
1000	47.600	96.459	65.819	30.639	- 267.503	- 196.369	42.914
1100	47.869	101.008	68.815	35.413	- 265.919	- 189.334	37.615
1200	48.100	105.184	71.674	40.212	- 287.560	- 181.985	33.142
1300	48.294	109.042	74.402	45.032	- 285.741	- 173.261	29.126
1400	48.450	112.627	77.006	49.869	- 283.909	- 164.677	25.706
1500	48.594	115.974	79.493	54.722	- 282.065	- 156.225	22.761
1600	48.700	119.114	81.872	59.587	- 280.213	- 147.895	20.201
1700	48.769	122.069	84.151	64.461	- 278.353	- 139.679	17.956
1800	48.800	124.857	86.335	69.339	- 276.494	- 131.578	15.975
1900	48.850	127.497	88.433	74.222	- 274.632	- 123.573	14.213
2000	48.900	130.904	90.449	79.109	- 272.773	- 115.673	12.640

SODIUM TETRACHLOROALUMINATE ($NaAlCl_4$) (CRYSTAL) MOL. WT. = 191.799

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [45 ± 2] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -273 ± 1 kcal. mole^{-1}

T_m = 424°K.

ΔH_m° = Unknown

Heat of Formation.

The heat of formation at 298.15°K. was calculated from ΔH_r° = -11.9 kcal. mole^{-1} for the reaction Al_2Cl_6 (c) + 2NaCl(c) = $2NaAlCl_4$(c) measured by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those of $KAlCl_4$(c). $S^\circ_{298.15}$ was estimated according to the methods suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by W. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. 306, 1 (1960).

Tripotassium Hexachloroaluminate (K_3AlCl_6)

(Crystal) Mol. Wt. = 357.022

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	59.490	90.000	90.000	.000	- 500.000	- 463.325	339.610
300	59.580	90.368	90.001	.110	- 499.985	- 463.098	337.350
400	61.940	107.949	92.381	6.227	- 500.897	- 450.601	246.185
500	64.450	122.043	96.947	12.548	- 499.991	- 438.126	191.496
600	66.800	134.004	102.151	19.112	- 498.868	- 425.854	155.110
700	68.800	144.453	107.463	25.893	- 497.556	- 413.787	129.184
800	70.700	153.765	112.679	32.868	- 496.091	- 401.922	109.795
900	72.390	162.193	117.720	40.025	- 494.487	- 390.242	94.759
1000	73.800	169.895	122.558	47.337	- 495.292	- 378.569	82.732
1100	75.175	176.995	127.188	54.787	- 550.144	- 363.913	72.299
1200	76.400	183.589	131.617	62.367	- 547.455	- 347.100	63.212
1300	77.475	189.748	135.854	70.062	- 544.657	- 330.519	55.563
1400	78.400	195.524	139.912	77.857	- 541.765	- 314.152	49.039
1500	79.188	200.961	143.802	85.737	- 538.794	- 297.997	43.416
1600	79.900	206.094	147.537	93.692	- 535.754	- 282.041	38.523
1700	80.538	210.958	151.126	101.715	- 532.652	- 266.279	34.231
1800	81.100	215.577	154.579	109.797	- 529.497	- 250.703	30.438
1900	81.588	219.976	157.906	117.932	- 526.298	- 235.297	27.064
2000	82.000	224.171	161.115	126.112	- 523.063	- 220.063	24.046

June 30, 1962; Sept. 30, 1963

TRIPOTASSIUM HEXACHLOROALUMINATE (K_3AlCl_6) (CRYSTAL) MOL. WT. = 357.022

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [90 ± 2] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -500 ± 1 kcal. mole^{-1}

T_m = [800]°K.

ΔH_m° = Unknown

Heat of Formation.

The heat of formation at 298.15°K. was recalculated from the same quantity given in National Bureau of Standards (U. S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952. The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(c) + 6KCl(c) = 2K_3AlCl_6(c)$ measured by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by comparison with the corresponding values of the sum of the constituent halides for $Na_3AlF_6(c)$.

Temperature of Melting.

T_m was estimated by comparison with that for $K_3AlF_6(c)$.

Trisodium Hexachloroaluminate (Na_3AlCl_6)

(Crystal) Mol. Wt. = 308.695

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	58.350	83.000	83.000	.000	- 473.000	- 437.064	320.361
300	58.440	83.361	83.001	.108	- 472.984	- 436.840	318.222
400	60.800	100.614	85.337	6.111	- 474.100	- 424.765	232.070
500	63.100	114.431	89.817	12.307	- 473.313	- 412.515	180.302
600	65.250	126.128	94.918	18.726	- 472.320	- 400.446	145.855
700	67.200	136.335	100.121	25.350	- 471.135	- 388.562	121.309
800	69.000	145.427	105.226	32.161	- 469.783	- 376.857	102.948
900	70.500	153.642	110.156	39.137	- 468.294	- 365.326	88.709
1000	71.850	161.141	114.885	46.256	- 469.199	- 353.787	77.316
1100	73.069	168.047	119.408	53.503	- 467.431	- 342.335	68.012
1200	74.200	174.454	123.732	60.867	- 535.287	- 329.672	60.039
1300	75.244	180.435	127.866	68.340	- 532.711	- 312.641	52.557
1400	76.200	186.047	131.823	75.913	- 530.041	- 295.813	46.176
1500	77.150	191.337	135.616	83.581	- 527.282	- 279.178	40.674
1600	78.000	196.344	139.257	91.339	- 524.439	- 262.728	35.885
1700	78.750	201.096	142.756	99.178	- 521.515	- 246.455	31.682
1800	79.400	205.616	146.123	107.086	- 518.531	- 230.365	27.969
1900	80.025	209.926	149.369	115.058	- 515.486	- 214.430	24.664
2000	80.600	214.045	152.500	123.089	- 512.394	- 198.670	21.709

Sept. 30, 1963

TRISODIUM HEXACHLOROALUMINATE (Na_3AlCl_6) (CRYSTAL) MOL. WT. = 308.695

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [83 ± 2] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -473 ± 1 kcal. mole^{-1}

T_m = [780]°K.

ΔH°_m = Unknown

Heat of Formation.

The heat of formation at 298.15°K. was recalculated from the same quantity given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952. The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(c) + 6NaCl(c) = 2Na_3AlCl_6(c)$ measured by E. Baud, Ann. Chim. Phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities and $S^\circ_{298.15}$ were estimated by comparison with the corresponding values of the sum of the constituent halides for $Na_3AlF_6(c)$.

Temperature of Melting.

T_m was estimated by comparison with that for $Na_3AlF_6(c)$.

Aluminum Monofluoride (AlF)

(Ideal Gas) GFW = 45.9799

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.125	-63.376	-63.376	INFINITE
100	6.960	43.580	57.880	-1.430	-63.134	-65.293	142.697
200	7.178	48.448	52.081	-.727	-63.223	-67.444	73.699
298	7.632	51.397	51.397	.000	-63.400	-69.484	50.933
300	7.640	51.445	51.397	.014	-63.404	-69.522	50.647
400	8.031	53.699	51.702	.799	-63.603	-71.530	39.082
500	8.301	55.522	52.290	1.616	-63.820	-73.488	32.122
600	8.485	57.053	52.959	2.456	-64.055	-75.400	27.464
700	8.612	58.371	53.641	3.311	-64.311	-77.270	24.125
800	8.704	59.527	54.306	4.177	-64.595	-79.103	21.610
900	8.773	60.557	54.944	5.051	-64.921	-80.898	19.645
1000	8.827	61.484	55.552	5.932	-67.816	-82.470	18.024
1100	8.870	62.327	56.131	6.816	-68.136	-83.921	16.674
1200	8.905	63.101	56.680	7.705	-68.455	-85.342	15.543
1300	8.935	63.815	57.201	8.597	-68.772	-86.736	14.582
1400	8.960	64.478	57.698	9.492	-69.090	-88.105	13.754
1500	8.983	65.097	58.171	10.389	-69.407	-89.453	13.033
1600	9.003	65.677	58.622	11.289	-69.724	-90.779	12.400
1700	9.022	66.224	59.053	12.190	-70.041	-92.085	11.838
1800	9.039	66.740	59.466	13.093	-70.357	-93.372	11.337
1900	9.054	67.229	59.862	13.998	-70.673	-94.642	10.886
2000	9.069	67.694	60.242	14.904	-70.990	-95.896	10.479
2100	9.083	68.136	60.607	15.811	-71.306	-97.135	10.109
2200	9.097	68.559	60.959	16.720	-71.623	-98.358	9.771
2300	9.109	68.964	61.298	17.631	-71.938	-99.563	9.461
2400	9.122	69.352	61.626	18.542	-72.254	-100.758	9.175
2500	9.134	69.725	61.942	19.455	-72.571	-101.941	8.912
2600	9.145	70.083	62.249	20.369	-72.888	-103.108	8.667
2700	9.157	70.428	62.545	21.284	-73.204	-104.266	8.440
2800	9.168	70.762	62.833	22.200	-142.930	-104.580	8.163
2900	9.179	71.083	63.112	23.118	-142.985	-103.210	7.778
3000	9.190	71.395	63.383	24.036	-143.040	-101.837	7.419
3100	9.200	71.696	63.646	24.956	-143.094	-100.463	7.083
3200	9.211	71.989	63.902	25.876	-143.149	-99.086	6.767
3300	9.221	72.272	64.152	26.798	-143.204	-97.708	6.471
3400	9.231	72.548	64.395	27.720	-143.260	-96.330	6.192
3500	9.241	72.815	64.631	28.644	-143.316	-94.948	5.929
3600	9.251	73.076	64.862	29.569	-143.371	-93.563	5.680
3700	9.261	73.329	65.088	30.494	-143.428	-92.181	5.445
3800	9.271	73.577	65.308	31.421	-143.485	-90.794	5.222
3900	9.281	73.817	65.523	32.348	-143.542	-89.406	5.010
4000	9.291	74.053	65.733	33.277	-143.601	-88.019	4.809
4100	9.301	74.282	65.939	34.207	-143.659	-86.631	4.618
4200	9.310	74.506	66.140	35.137	-143.718	-85.237	4.435
4300	9.320	74.726	66.337	36.069	-143.779	-83.843	4.261
4400	9.330	74.940	66.531	37.001	-143.840	-82.447	4.095
4500	9.339	75.150	66.720	37.935	-143.903	-81.053	3.936
4600	9.349	75.355	66.905	38.869	-143.967	-79.654	3.784
4700	9.359	75.556	67.087	39.804	-144.033	-78.260	3.639
4800	9.369	75.753	67.266	40.741	-144.100	-76.859	3.499
4900	9.378	75.947	67.441	41.678	-144.169	-75.452	3.365
5000	9.388	76.136	67.613	42.616	-144.241	-74.051	3.237
5100	9.398	76.322	67.782	43.556	-144.314	-72.647	3.113
5200	9.408	76.505	67.948	44.496	-144.391	-71.241	2.994
5300	9.418	76.684	68.111	45.437	-144.471	-69.834	2.880
5400	9.428	76.860	68.271	46.380	-144.553	-68.425	2.769
5500	9.439	77.033	68.429	47.323	-144.639	-67.017	2.663
5600	9.449	77.204	68.584	48.267	-144.730	-65.601	2.560
5700	9.459	77.371	68.737	49.213	-144.823	-64.189	2.461
5800	9.470	77.535	68.887	50.159	-144.921	-62.772	2.365
5900	9.481	77.697	69.035	51.107	-145.024	-61.356	2.273
6000	9.492	77.857	69.181	52.055	-145.132	-59.937	2.183

Dec. 31, 1960; Sept. 30, 1964; June 30, 1969

ALUMINUM MONOFLUORIDE (AlF)   (IDEAL GAS)   GFW = 45.9799

Ground State Configuration $^1\Sigma^+$

$\Delta Hf^\circ_0 = -63.4 \pm 0.8$ kcal/mol

$S^\circ_{298.15} = 51.40 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -63.4 \pm 0.8$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
43935	2
54251	1

$\omega_e = 801.95$ cm^{-1} $\omega_e x_e = 4.70$ cm^{-1} $\sigma = 1$

$B_e = 0.55228$ cm^{-1} $\alpha_e = 0.00483$ cm^{-1} $r_e = 1.6547$ Å

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce AlF(g) and the results of 2nd and 3rd law analyses are given below.

Ref.		Range °K	Reaction	Points	$\Delta Hr^\circ_{298.15}$ kcal/mol 2nd law	$\Delta Hr^\circ_{298.15}$ kcal/mol 3rd law	Drift eu	$\Delta Hf^\circ_{298.15}$(AlF, g) kcal/mol
1.	[cell 7]	882-931	A	8	162.7 ± 5.8	169.75 ± 0.6	7.9 ± 6.4	-63.68 ± 0.8
1.	[cell 9]	856-932	A	8	171.6 ± 4.1	170.66 ± 0.6	-1.4 ± 4.6	-63.38 ± 0.8
1.	[cell 15x]	866-931	A	8	173.4 ± 1.5	170.49 ± 0.2	-3.3 ± 1.7	-63.44 ± 0.6
1.	[cell 16x]	867-929	A	7*	171.6 ± 3.7	170.31 ± 0.4	-1.8 ± 4.2	-63.50 ± 0.7
2.			A		58.4	172.8 ± 1.8**		-62.67 ± 1.1
3.		1170-1373	B	5	166.1 ± 1.0	166.50 ± 0.2	0.3 ± 0.7	-63.39 ± 0.6
4.		1287-1349	B	5	519.5 ± 14.2	176.0 ± 12.8	-261 ± 11	-60.2 ± 4
5.		1199-1348	C	10	100.8 ± 1.8	98.02 ± 0.5	-2.2 ± 1.4	-62.48 ± 0.9

* 1 point rejected due to statistical test. ** Value given by original author.

A) $AlF_3(c) + 2\ Al(c) = 3\ AlF(g)$ B) $AlF_3(c) + 2\ Al(\ell) = 3\ AlF(g)$ C) $AlF_3(g) + 2\ Al(\ell) = 3\ AlF(g)$

It is apparent that the runs with least drift are in close agreement at -63.4 kcal/mol and we adopt this value.

This value is confirmed by Gross et al. (6) who report the heat of reaction A as 172.9 kcal/mol or ΔHf°_{298}(AlF, g) = -62.96 kcal/mol. Also the data of Hildenbrand et al. (7) on the reaction $BeF_2(g) + Al(c) = Be(c) + 2\ AlF(g)$ yield ΔHr°_{298} = 59.25 ± 0.5 kcal/mol which gives ΔHf°_{298}(AlF, g) = -64.12 ± 1.7 kcal/mol. The highest observed levels in the $A^1\Pi$ state of AlF correspond to an absolute minimum of 156.4 kcal for the dissociation energy of AlF. Barrow et al. (8) indicate that normal extrapolation of the levels would yield a dissociation energy of 167.0 kcal. The dissociation energy corresponding to the adopted heat of formation is 159.2 kcal which may indicate a potential hump in the $A^1\Pi$ state.

Heat Capacity and Entropy

The rotational, vibrational constants and electronic levels are from the analyses of Naude and Hugo (9), Barrow et al. (8) and Lide (10).

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Aluminum Monofluoride Unipositive Ion (AlF^+)

(Ideal Gas) GFW = 45.9794

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.751	52.947	52.947	.000	161.000	152.967	-112.128
300	7.759	52.995	52.947	.014	161.005	152.917	-111.400
400	8.144	55.283	53.256	.811	161.315	150.175	-82.052
500	8.399	57.130	53.852	1.639	161.605	147.355	-64.409
600	8.569	58.677	54.531	2.488	161.876	144.479	-52.626
700	8.686	60.008	55.221	3.351	162.125	141.559	-44.197
800	8.772	61.173	55.893	4.224	162.345	138.606	-37.865
900	8.836	62.210	56.539	5.105	162.523	135.628	-32.935
1000	8.887	63.144	57.153	5.991	160.130	132.815	-29.027
1100	8.928	63.993	57.737	6.882	160.313	130.075	-25.843
1200	8.963	64.772	58.291	7.776	160.497	127.318	-23.188
1300	8.993	65.490	58.818	8.674	160.682	124.545	-20.938
1400	9.019	66.158	59.318	9.575	160.867	121.759	-19.007
1500	9.043	66.781	59.795	10.478	161.052	118.958	-17.332
1600	9.065	67.365	60.250	11.383	161.238	116.145	-15.865
1700	9.085	67.915	60.685	12.291	161.425	113.322	-14.569
1800	9.104	68.435	61.102	13.200	161.611	110.487	-13.415
1900	9.122	68.928	61.501	14.112	161.799	107.642	-12.382
2000	9.139	69.396	61.884	15.025	161.986	104.787	-11.451
2100	9.155	69.842	62.252	15.939	162.174	101.920	-10.607
2200	9.171	70.269	62.607	16.856	162.362	99.047	-9.839
2300	9.187	70.677	62.949	17.774	162.550	96.166	-9.138
2400	9.202	71.068	63.279	18.693	162.738	93.277	-8.494
2500	9.216	71.444	63.598	19.614	162.927	90.376	-7.901
2600	9.231	71.806	63.907	20.536	163.116	87.471	-7.353
2700	9.245	72.154	64.206	21.460	163.305	84.559	-6.845
2800	9.259	72.491	64.496	22.385	94.085	82.468	-6.437
2900	9.273	72.816	64.777	23.312	94.535	82.045	-6.183
3000	9.287	73.131	65.051	24.240	94.987	81.605	-5.945
3100	9.301	73.435	65.316	25.169	95.439	81.152	-5.721
3200	9.315	73.731	65.574	26.100	95.891	80.688	-5.511
3300	9.329	74.018	65.826	27.032	96.344	80.205	-5.312
3400	9.343	74.296	66.071	27.966	96.795	79.708	-5.124
3500	9.357	74.567	66.310	28.901	97.248	79.199	-4.945
3600	9.372	74.831	66.543	29.837	97.701	78.680	-4.777
3700	9.387	75.088	66.771	30.775	98.154	78.140	-4.616
3800	9.402	75.339	66.993	31.715	98.607	77.596	-4.463
3900	9.418	75.583	67.210	32.656	99.060	77.038	-4.317
4000	9.434	75.822	67.422	33.598	99.512	76.465	-4.178
4100	9.451	76.055	67.630	34.542	99.964	75.880	-4.045
4200	9.468	76.283	67.833	35.488	100.418	75.292	-3.918
4300	9.486	76.506	68.032	36.436	100.871	74.689	-3.796
4400	9.504	76.724	68.227	37.386	101.323	74.078	-3.679
4500	9.523	76.938	68.419	38.337	101.774	73.449	-3.567
4600	9.543	77.147	68.606	39.290	102.227	72.817	-3.460
4700	9.564	77.353	68.790	40.245	102.677	72.168	-3.356
4800	9.585	77.554	68.970	41.203	103.128	71.513	-3.256
4900	9.607	77.752	69.148	42.163	103.579	70.857	-3.160
5000	9.630	77.947	69.322	43.124	104.026	70.183	-3.068
5100	9.654	78.138	69.493	44.089	104.475	69.499	-2.978
5200	9.679	78.325	69.661	45.055	104.921	68.811	-2.892
5300	9.705	78.510	69.826	46.024	105.366	68.111	-2.809
5400	9.732	78.692	69.989	46.996	105.811	67.403	-2.728
5500	9.759	78.870	70.148	47.971	106.252	66.686	-2.650
5600	9.788	79.047	70.306	48.948	106.691	65.963	-2.574
5700	9.817	79.220	70.461	49.928	107.130	65.235	-2.501
5800	9.848	79.391	70.613	50.912	107.565	64.495	-2.430
5900	9.879	79.560	70.763	51.898	107.998	63.748	-2.361
6000	9.911	79.726	70.911	52.888	108.428	62.997	-2.295

June 30, 1968

ALUMINUM MONOFLUORIDE UNIPOSITIVE ION (AlF^+) (IDEAL GAS) GFW = 45.9794

Ground State Configuration [$^2\Sigma$]

ΔHf°_0 = 161 ± 12 kcal/mol

$S^\circ_{298.15}$ = [52.95 ± 0.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 161 ± 12 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[28000]	[4]
[37000]	[2]
[45000]	[2]

ω_e = [740] cm^{-1}

$\omega_e x_e$ = [6] cm^{-1}

σ = 1

B_e = [0.5232] cm^{-1}

α_e = [0.0053] cm^{-1}

r_e = [1.7] Å

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) reported the ionization potential of AlF as 9.7 ± 0.5eV (224 ± 12 kcal). The magnitude of the value has been confirmed by R. F. Porter, J. Chem. Phys. 33, 951 (1960) who found it between 9 and 10eV. Using the above value in conjunction with ΔHf°_{298}(AlF, g) = -62.5 kcal/mol, and the equation $AlF(g) \rightarrow AlF^+(g) + e^-$ yields $\Delta Hf^\circ_{298}(AlF^+, g)$ = 161 ± 12 kcal/mol.

Heat Capacity and Entropy

AlF^+ is isoelectronic with MgF, and the electronic configuration of the ground and excited states we estimate to be those for MgF(g). The vibrational frequency, anharmonicity constant and bond length we estimate by comparison with those for MgF and AlF. The rotational constant is calculated from the bond length and atomic masses, and α_e is calculated from the other constants assuming a Morse potential function.

The enthalpy at 0°K is -2.139 kcal.

Aluminum Oxide Fluoride (AlOF)

(Ideal Gas) Mol. Wt. = 61.98

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.448	- 139.461	- 139.461	INFINITE
100	7.116	46.705	64.207	- 1.750	- 139.574	- 139.968	305.886
200	8.839	52.095	56.908	- .963	- 139.918	- 140.245	153.245
298	10.692	55.986	55.986	.000	- 140.200	- 140.347	102.872
300	10.722	56.052	55.986	.020	- 140.205	- 140.348	102.238
400	12.018	59.328	56.424	1.162	- 140.400	- 140.363	76.687
500	12.846	62.105	57.290	2.408	- 140.550	- 140.337	61.338
600	13.381	64.498	58.296	3.721	- 140.687	- 140.281	51.095
700	13.740	66.590	59.335	5.078	- 140.831	- 140.202	43.771
800	13.989	68.441	60.360	6.465	- 140.992	- 140.102	38.272
900	14.167	70.100	61.351	7.874	- 141.175	- 139.980	33.990
1000	14.299	71.600	62.303	9.297	- 143.880	- 139.651	30.519
1100	14.399	72.968	63.211	10.732	- 144.010	- 139.222	27.660
1200	14.477	74.224	64.077	12.176	- 144.139	- 138.781	25.274
1300	14.538	75.385	64.903	13.627	- 144.268	- 138.330	23.254
1400	14.587	76.464	65.690	15.084	- 144.397	- 137.868	21.521
1500	14.627	77.472	66.443	16.544	- 144.527	- 137.397	20.018
1600	14.659	78.417	67.162	18.009	- 144.659	- 136.917	18.701
1700	14.687	79.307	67.850	19.476	- 144.791	- 136.429	17.538
1800	14.710	80.147	68.510	20.946	- 144.927	- 135.934	16.504
1900	14.730	80.943	69.144	22.418	- 145.065	- 135.429	15.577
2000	14.746	81.699	69.753	23.892	- 145.204	- 134.919	14.743
2100	14.761	82.419	70.339	25.367	- 145.346	- 134.403	13.987
2200	14.773	83.106	70.904	26.844	- 145.492	- 133.878	13.299
2300	14.784	83.763	71.449	28.322	- 145.640	- 133.347	12.670
2400	14.794	84.392	71.975	29.801	- 145.791	- 132.808	12.093
2500	14.803	84.996	72.484	31.281	- 145.945	- 132.265	11.562
2600	14.810	85.577	72.976	32.761	- 146.102	- 131.715	11.071
2700	14.817	86.136	73.454	34.243	- 146.262	- 131.159	10.616
2800	14.823	86.675	73.916	35.725	- 216.979	- 128.943	10.064
2900	14.829	87.195	74.365	37.207	- 216.943	- 125.799	9.480
3000	14.834	87.698	74.801	38.690	- 216.910	- 122.657	8.935
3100	14.838	88.184	75.225	40.174	- 216.879	- 119.515	8.425
3200	14.842	88.656	75.638	41.658	- 216.852	- 116.376	7.948
3300	14.846	89.112	76.039	43.142	- 216.827	- 113.237	7.499
3400	14.849	89.556	76.430	44.627	- 216.805	- 110.099	7.077
3500	14.852	89.986	76.811	46.112	- 215.787	- 106.961	6.679
3600	14.855	90.405	77.183	47.598	- 216.771	- 103.820	6.302
3700	14.858	90.812	77.546	49.083	- 216.759	- 100.685	5.947
3800	14.860	91.208	77.900	50.569	- 216.748	- 97.546	5.610
3900	14.862	91.594	78.246	52.055	- 216.742	- 94.410	5.290
4000	14.864	91.970	78.585	53.542	- 216.737	- 91.274	4.987
4100	14.866	92.337	78.916	55.028	- 216.737	- 88.140	4.698
4200	14.868	92.696	79.240	56.515	- 216.739	- 85.002	4.423
4300	14.870	93.045	79.557	58.002	- 216.743	- 81.863	4.161
4400	14.871	93.387	79.867	59.489	- 216.753	- 78.730	3.910
4500	14.873	93.722	80.171	60.976	- 216.764	- 75.590	3.671
4600	14.874	94.048	80.469	62.463	- 216.778	- 72.450	3.442
4700	14.875	94.368	80.762	63.951	- 216.797	- 69.317	3.223
4800	14.877	94.682	81.048	65.438	- 216.818	- 66.177	3.013
4900	14.878	94.988	81.330	66.926	- 216.844	- 63.037	2.811
5000	14.879	95.289	81.606	68.414	- 216.874	- 59.900	2.618
5100	14.880	95.583	81.877	69.902	- 216.907	- 56.759	2.432
5200	14.881	95.872	82.144	71.390	- 216.945	- 53.621	2.253
5300	14.882	96.156	82.405	72.878	- 216.986	- 50.476	2.081
5400	14.882	96.434	82.663	74.366	- 217.034	- 47.337	1.916
5500	14.883	96.707	82.915	75.855	- 217.085	- 44.194	1.756
5600	14.884	96.975	83.164	77.343	- 217.144	- 41.048	1.602
5700	14.885	97.239	83.409	78.831	- 217.207	- 37.906	1.453
5800	14.885	97.498	83.649	80.320	- 217.275	- 34.755	1.310
5900	14.886	97.752	83.886	81.808	- 217.350	- 31.609	1.171
6000	14.887	98.002	84.119	83.297	- 217.432	- 28.461	1.037

Dec. 31, 1960; Mar. 31, 1964

ALUMINUM OXIDE FLUORIDE (AlOF) (IDEAL GAS) MOL. WT. = 61.98

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [55.986] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -139.5 ± 2.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -140.2 ± 2.6 kcal. mole^{-1}

<u>Vibrational Frequencies and Degeneracies</u>

<u>ω, cm.$^{-1}$</u>

[900](1)
[500](2)
[750](1)

Bond Distance: O=Al = [1.62] Å   Al-F = [1.65] Å

Bond Angle: O-Al-F = [180]° σ = 1

Rotational Constant: B_0 = [0.180806] cm.$^{-1}$

Heat of Formation.

The equilibrium constants (2200-2225°K.) of the chemical reaction Al_2O_3 (c) + AlF_3 (g) = 3AlOF (g) were measured by M. Farber and H. L. Petersen, Trans. Faraday Soc. 59, 836 (1963). Using this data, the heat of reaction at 298.15°K. was calculated by the third law method to be 266.2 ± 1.7 kcal. mole^{-1}. The value of $\Delta H^\circ_{f\ 298.15}$ for AlOF (g) was then derived.

Heat Capacity and Entropy.

The bond distances of Al-O and Al-F were estimated to be the same as those for AlO (g) and AlF (g), respectively. The point group, ground state quantum weight and vibrational frequencies were obtained from W. H. Evans, J. Hilsenrath and H. W. Woolley, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds," National Bureau of Standards Report 6928, July 1, 1960. The moment of inertia is 1.54800 x 10^{-38} g. cm.^{2}

Aluminum Difluoride (AlF_2)

(Ideal Gas) Mol. Wt. = 64.98

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.779	- 164.575	- 164.575	INFINITE
100	8.777	52.784	72.387	- 1.960	- 164.557	- 165.601	361.904
200	9.904	59.228	64.349	- 1.024	- 164.763	- 166.586	182.028
298	10.949	63.381	63.381	.000	- 165.000	- 167.434	122.727
300	10.967	63.449	63.381	.020	- 165.005	- 167.450	121.981
400	11.802	66.725	63.822	1.161	- 165.231	- 168.229	91.912
500	12.375	69.424	64.680	2.372	- 165.454	- 168.954	73.846
600	12.761	71.717	65.667	3.630	- 165.684	- 169.633	61.786
700	13.024	73.705	66.676	4.920	- 165.932	- 170.271	53.159
800	13.210	75.457	67.667	6.232	- 166.202	- 170.874	46.678
900	13.345	77.021	68.621	7.560	- 166.497	- 171.439	41.629
1000	13.445	78.432	69.532	8.900	- 169.314	- 171.787	37.542
1100	13.521	79.718	70.401	10.249	- 169.557	- 172.024	34.176
1200	13.580	80.897	71.227	11.604	- 169.799	- 172.236	31.367
1300	13.627	81.986	72.013	12.964	- 170.042	- 172.430	28.987
1400	13.665	82.997	72.762	14.329	- 170.284	- 172.604	26.943
1500	13.695	83.941	73.476	15.697	- 170.527	- 172.761	25.170
1600	13.721	84.825	74.158	17.068	- 170.771	- 172.901	23.616
1700	13.742	85.658	74.810	18.441	- 171.016	- 173.027	22.243
1800	13.760	86.444	75.435	19.816	- 171.263	- 173.140	21.021
1900	13.775	87.188	76.034	21.193	- 171.510	- 173.235	19.926
2000	13.788	87.895	76.610	22.571	- 171.759	- 173.319	18.939
2100	13.799	88.568	77.163	23.950	- 172.010	- 173.394	18.044
2200	13.809	89.210	77.696	25.331	- 172.262	- 173.452	17.230
2300	13.818	89.824	78.210	26.712	- 172.516	- 173.500	16.485
2400	13.825	90.413	78.707	28.094	- 172.772	- 173.540	15.802
2500	13.832	90.977	79.186	29.477	- 173.030	- 173.565	15.172
2600	13.838	91.520	79.650	30.861	- 173.289	- 173.583	14.590
2700	13.843	92.042	80.100	32.245	- 173.550	- 173.588	14.050
2800	13.848	92.546	80.535	33.629	- 244.367	- 171.934	13.419
2900	13.852	93.032	80.958	35.014	- 244.429	- 169.345	12.762
3000	13.856	93.501	81.368	36.399	- 244.494	- 166.755	12.147
3100	13.859	93.956	81.767	37.785	- 244.559	- 164.163	11.573
3200	13.862	94.396	82.155	39.171	- 244.628	- 161.569	11.034
3300	13.865	94.822	82.532	40.558	- 244.697	- 158.970	10.528
3400	13.868	95.236	82.900	41.944	- 244.769	- 156.372	10.051
3500	13.870	95.638	83.258	43.331	- 244.844	- 153.770	9.601
3600	13.872	96.029	83.607	44.718	- 244.920	- 151.165	9.177
3700	13.874	96.409	83.948	46.106	- 244.998	- 148.562	8.775
3800	13.876	96.779	84.281	47.493	- 245.079	- 145.952	8.394
3900	13.878	97.140	84.606	48.881	- 245.163	- 143.346	8.032
4000	13.880	97.491	84.924	50.269	- 245.248	- 140.732	7.689
4100	13.881	97.834	85.235	51.657	- 245.337	- 138.122	7.362
4200	13.883	98.168	85.539	53.045	- 245.429	- 135.502	7.051
4300	13.884	98.495	85.836	54.433	- 245.522	- 132.883	6.754
4400	13.885	98.814	86.127	55.822	- 245.620	- 130.265	6.470
4500	13.886	99.126	86.413	57.210	- 245.720	- 127.640	6.199
4600	13.887	99.431	86.693	58.599	- 245.823	- 125.013	5.939
4700	13.888	99.730	86.967	59.988	- 245.930	- 122.391	5.691
4800	13.889	100.023	87.236	61.377	- 246.040	- 119.762	5.453
4900	13.890	100.309	87.500	62.766	- 246.155	- 117.124	5.224
5000	13.891	100.590	87.759	64.155	- 246.274	- 114.494	5.004
5100	13.892	100.865	88.013	65.544	- 246.397	- 111.859	4.793
5200	13.892	101.134	88.263	66.933	- 246.525	- 109.214	4.590
5300	13.893	101.399	88.508	68.322	- 246.657	- 106.572	4.394
5400	13.894	101.659	88.749	69.712	- 246.795	- 103.933	4.206
5500	13.894	101.914	88.986	71.101	- 246.938	- 101.287	4.025
5600	13.895	102.164	89.219	72.491	- 247.087	- 98.631	3.849
5700	13.895	102.410	89.449	73.880	- 247.243	- 95.982	3.680
5800	13.896	102.652	89.674	75.270	- 247.403	- 93.326	3.516
5900	13.896	102.889	89.896	76.659	- 247.572	- 90.667	3.358
6000	13.897	103.123	90.115	78.049	- 247.748	- 88.010	3.206

Dec. 31, 1960; Sept. 30, 1964

ALUMINUM DIFLUORIDE (AlF_2) (IDEAL GAS) MOL. WT. = 64.98

Point Group [C_{2v}]

$S^\circ_{298.15}$=[63.381]cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight =[2]

$\Delta H^\circ_{f\ 0}$ = -[-165 ± 20] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-165 ± 20] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[917](1)
[236](1)
[750](1)

Bond Distance: Al-F = [1.65]Å

Bond Angle: F-Al-F =[120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ =[3.367909 X 10^{-115}]g.^{3} cm.^{6}

Heat of Formation.

The selected heat of formation, -165 ± 20 kcal. mole^{-1} is the weighted average of two estimates (a) [-163 ± 20 kcal. mole^{-1}] and (b) [-175 ± 30 kcal. mole^{-1}]. The first estimate (a) is based upon appearance potentials reported by T. C. Ehlert and J. L. Margrave, J. Am. Chem. Soc. 86, 3901 (1964).

(1) $AlF_3(g) \rightarrow AlF_2^+(ion) + F(g)$ 15.2 ± 0.3 e.v.

(2) $AlF_2^+(ion) \rightarrow AlF_2(g)$ -9 ± 1 e.v.

(3) (1) + (2) or $AlF_3(g) \rightarrow AlF_2(g) + F(g)$ 6.2 ± 1.3 e.v.

The second estimate (b) is based upon the average Al-F bond strength of $AlF_3(g)$ and AlF(g). i.e.

(4) $AlF_3(g) + AlF(g) \rightarrow 2\ AlF_2(g)$ $\Delta H_{r\ 298} = 0$

Heat Capacity and Entropy.

The bond distance, 1.65Å, was estimated from a consideration of the Al-F distance 1.63 and 1.655Å in $AlF_3(g)$ and AlF(g). The bent configuration and bond angle estimates were based on the correlations of A. D. Walsh, J. Chem. Soc., 2266, (1953). From the molecular constants the principal moments of inertia were found to be I_A = 1.7829 X 10^{-39}, I_B = 12.8817 X 10^{-39}, and I_C = 14.6646 X 10^{-39} g. cm.^{2}. The vibrational frequencies were calculated assuming valence forces, [G. Herzberg, "Molecular Spectra and Molecular Structure II", D. Van Nostrand Co., 1945] and using force constants calculated from $AlF_3(g)$.

Aluminum Difluoride Unipositive Ion (AlF_2^+)

(Ideal Gas) GFW = 64.9778

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°₂₉₈)/T (gibbs/mol)	H°−H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	12.335	57.799	57.799	.000	42.000	39.743	-29.132
300	12.355	57.875	57.799	.023	42.007	39.728	-28.942
400	13.181	61.553	58.295	1.303	42.415	38.909	-21.259
500	13.687	64.553	59.256	2.648	42.819	37.984	-16.603
600	14.008	67.079	60.355	4.034	43.211	36.980	-13.470
700	14.221	69.255	61.474	5.447	43.584	35.911	-11.212
800	14.368	71.164	62.569	6.876	43.927	34.791	-9.505
900	14.473	72.863	63.620	8.319	44.229	33.631	-8.167
1000	14.551	74.392	64.622	9.770	41.959	32.622	-7.130
1100	14.609	75.782	65.574	11.228	42.263	31.674	-6.293
1200	14.655	77.055	66.479	12.692	42.568	30.698	-5.591
1300	14.690	78.230	67.338	14.159	42.870	29.696	-4.992
1400	14.719	79.319	68.155	15.629	43.171	28.673	-4.476
1500	14.742	80.336	68.934	17.103	43.472	27.626	-4.025
1600	14.761	81.288	69.677	18.578	43.770	26.559	-3.628
1700	14.777	82.183	70.386	20.055	44.067	25.475	-3.275
1800	14.791	83.028	71.065	21.533	44.361	24.372	-2.959
1900	14.802	83.828	71.716	23.013	44.655	23.255	-2.675
2000	14.812	84.588	72.341	24.493	44.946	22.121	-2.417
2100	14.820	85.310	72.941	25.975	45.236	20.970	-2.182
2200	14.828	86.000	73.519	27.457	45.523	19.808	-1.968
2300	14.834	86.659	74.076	28.941	45.810	18.634	-1.771
2400	14.840	87.291	74.614	30.424	46.093	17.447	-1.589
2500	14.845	87.897	75.133	31.908	46.374	16.245	-1.420
2600	14.849	88.479	75.635	33.393	46.654	15.036	-1.264
2700	14.853	89.039	76.122	34.878	46.932	13.816	-1.118
2800	14.857	89.580	76.593	36.364	-22.201	13.413	-1.047
2900	14.860	90.101	77.049	37.850	-21.666	14.676	-1.106
3000	14.863	90.605	77.493	39.336	-21.133	15.917	-1.160
3100	14.865	91.092	77.924	40.822	-20.601	17.144	-1.209
3200	14.868	91.564	78.343	42.309	-20.071	18.357	-1.254
3300	14.870	92.022	78.750	43.796	-19.543	19.549	-1.295
3400	14.872	92.466	79.147	45.283	-19.019	20.724	-1.332
3500	14.873	92.897	79.534	46.770	-18.496	21.887	-1.367
3600	14.875	93.316	79.911	48.257	-17.975	23.037	-1.399
3700	14.877	93.723	80.279	49.745	-17.456	24.164	-1.427
3800	14.878	94.120	80.638	51.233	-16.940	25.284	-1.454
3900	14.879	94.507	80.989	52.720	-16.427	26.389	-1.479
4000	14.881	94.883	81.331	54.208	-15.917	27.478	-1.501
4100	14.882	95.251	81.666	55.697	-15.408	28.552	-1.522
4200	14.883	95.610	81.994	57.185	-14.902	29.624	-1.542
4300	14.884	95.960	82.315	58.673	-14.399	30.679	-1.559
4400	14.885	96.302	82.629	60.162	-13.899	31.725	-1.576
4500	14.885	96.636	82.936	61.650	-13.404	32.751	-1.591
4600	14.886	96.964	83.238	63.139	-12.909	33.774	-1.605
4700	14.887	97.284	83.533	64.627	-12.421	34.778	-1.617
4800	14.888	97.597	83.823	66.116	-11.934	35.777	-1.629
4900	14.888	97.904	84.107	67.605	-11.451	36.774	-1.640
5000	14.889	98.205	84.386	69.094	-10.974	37.751	-1.650
5100	14.889	98.500	84.660	70.583	-10.500	38.716	-1.659
5200	14.890	98.789	84.929	72.072	-10.031	39.681	-1.668
5300	14.890	99.073	85.193	73.561	-9.567	40.632	-1.675
5400	14.891	99.351	85.453	75.050	-9.108	41.571	-1.682
5500	14.891	99.624	85.708	76.539	-8.655	42.505	-1.689
5600	14.892	99.892	85.959	78.028	-8.209	43.432	-1.695
5700	14.892	100.156	86.206	79.517	-7.767	44.354	-1.701
5800	14.893	100.415	86.448	81.006	-7.332	45.263	-1.706
5900	14.893	100.670	86.687	82.496	-6.903	46.164	-1.710
6000	14.893	100.920	86.922	83.985	-6.482	47.063	-1.714

June 30, 1968

ALUMINUM DIFLUORIDE UNIPOSITIVE ION (AlF_2^+) (IDEAL GAS) GFW = 64.9778

Point Group [$D_{\infty h}$]

ΔHf°_0 = [42.3 ± 10] kcal/mol

$S^\circ_{298.15}$ = [57.8 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [42 ± 10] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[850] (1)
[240] (2)
[500] (1)

Bond Distance: Al-F = [1.7] Å

Bond Angle: F-Al-F = [180°]

σ = 2

Rotational Constant: B_0 = [0.1535] cm^{-1}

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) report the appearance potential of AlF_2^+ from AlF_3 as 15.2 ± 0.3eV. Assuming the reaction to be $AlF_3(g) + e^- \rightarrow AlF_2^+ + F + 2e^-$ ΔH = 350.5 ± 7 kcal we calculate $\Delta Hf^\circ_{298}(AlF_2^+, g)$ = 42 ± 10 kcal/mol, or an ionization potential for AlF_2 of 9eV. Due to the neglect of any kinetic energy of the fragments this probably is an upper limit.

Heat Capacity and Entropy

The linear configuration is estimated from the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953), however, it should be noted that the isoelectronic MgF_2 is considered to be bent. The vibrational frequencies are estimated to lie between those for AlF_2 and MgF_2. The bond distance is estimated by comparison with AlF and AlF_3.

The enthalpy at 0°K is -2.883 kcal/mol.

Aluminum Difluoride Uninegative Ion (AlF_2^-)

(Ideal Gas) GFW = 64.9788

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.702	61.427	61.427	.000	-175.000	-175.365	128.546
300	10.722	61.493	61.427	.020	-175.014	-175.367	127.755
400	11.624	64.709	61.859	1.140	-175.760	-175.371	95.818
500	12.245	67.374	62.703	2.335	-176.500	-175.189	76.575
600	12.662	69.646	63.676	3.582	-177.241	-174.857	63.692
700	12.948	71.620	64.673	4.863	-177.992	-174.399	54.450
800	13.150	73.363	65.652	6.169	-178.766	-173.834	47.489
900	13.296	74.921	66.597	7.491	-179.579	-173.170	42.051
1000	13.404	76.328	67.501	8.827	-182.958	-172.229	37.641
1100	13.487	77.609	68.362	10.171	-183.762	-171.118	33.998
1200	13.551	78.786	69.183	11.523	-184.563	-169.934	30.949
1300	13.602	79.872	69.964	12.881	-185.362	-168.681	28.358
1400	13.643	80.882	70.708	14.243	-186.163	-167.367	26.127
1500	13.676	81.824	71.418	15.609	-186.964	-165.997	24.186
1600	13.704	82.708	72.096	16.979	-187.765	-164.573	22.480
1700	13.727	83.539	72.745	18.350	-188.568	-163.099	20.968
1800	13.746	84.325	73.367	19.724	-189.370	-161.577	19.618
1900	13.763	85.068	73.963	21.099	-190.175	-160.013	18.406
2000	13.777	85.775	74.536	22.476	-190.981	-158.404	17.310
2100	13.789	86.447	75.088	23.855	-191.788	-156.756	16.314
2200	13.800	87.089	75.619	25.234	-192.598	-155.070	15.405
2300	13.809	87.702	76.131	26.614	-193.407	-153.341	14.571
2400	13.817	88.290	76.625	27.996	-194.219	-151.584	13.804
2500	13.824	88.854	77.103	29.378	-195.034	-149.793	13.095
2600	13.831	89.397	77.566	30.761	-195.850	-147.966	12.438
2700	13.836	89.919	78.014	32.144	-196.668	-146.110	11.827
2800	13.842	90.422	78.448	33.528	-266.897	-143.392	11.192
2900	13.846	90.908	78.869	34.912	-267.456	-138.971	10.473
3000	13.850	91.377	79.278	36.297	-268.018	-134.531	9.801
3100	13.854	91.832	79.676	37.682	-268.581	-130.071	9.170
3200	13.857	92.272	80.063	39.068	-269.146	-125.596	8.578
3300	13.861	92.698	80.439	40.454	-269.713	-121.101	8.020
3400	13.863	93.112	80.806	41.840	-270.282	-116.591	7.494
3500	13.866	93.514	81.163	43.226	-270.854	-112.061	6.997
3600	13.868	93.904	81.512	44.613	-271.427	-107.513	6.527
3700	13.871	94.284	81.852	46.000	-272.003	-102.951	6.081
3800	13.873	94.654	82.184	47.387	-272.582	-98.376	5.658
3900	13.875	95.015	82.508	48.775	-273.162	-93.784	5.256
4000	13.876	95.366	82.825	50.162	-273.745	-89.177	4.872
4100	13.878	95.709	83.135	51.550	-274.331	-84.557	4.507
4200	13.879	96.043	83.439	52.938	-274.919	-79.922	4.159
4300	13.881	96.370	83.736	54.326	-275.510	-75.271	3.826
4400	13.882	96.689	84.027	55.714	-276.105	-70.607	3.507
4500	13.883	97.001	84.311	57.102	-276.702	-65.930	3.202
4600	13.885	97.306	84.591	58.491	-277.301	-61.239	2.910
4700	13.886	97.605	84.864	59.879	-277.907	-56.539	2.629
4800	13.887	97.897	85.133	61.268	-278.514	-51.819	2.359
4900	13.888	98.183	85.396	62.656	-279.126	-47.087	2.100
5000	13.888	98.464	85.655	64.045	-279.741	-42.350	1.851
5100	13.889	98.739	85.909	65.434	-280.361	-37.595	1.611
5200	13.890	99.009	86.158	66.823	-280.986	-32.829	1.380
5300	13.891	99.273	86.403	68.212	-281.616	-28.049	1.157
5400	13.892	99.533	86.644	69.601	-282.251	-23.260	.941
5500	13.892	99.788	86.880	70.990	-282.892	-18.461	.734
5600	13.893	100.038	87.113	72.380	-283.537	-13.640	.532
5700	13.893	100.284	87.342	73.769	-284.189	-8.822	.338
5800	13.894	100.526	87.567	75.158	-284.848	-3.980	.150
5900	13.895	100.763	87.789	76.548	-285.513	.866	-.032
6000	13.895	100.997	88.007	77.937	-286.186	5.723	-.208

June 30, 1968

ALUMINUM DIFLUORIDE UNINEGATIVE ION (AlF_2^-) (IDEAL GAS) GFW = 64.9788

Point Group [C_{2v}] ΔHf_0° = [-174.5 ± 40] kcal/mol

$S^\circ_{298.15}$ = [61.4 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-175 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
ω, cm^{-1}
[820] (1)
[320] (1)
[900] (1)

Bond Distance: [1.65] Å

Bond Angle: F-Al-F = [120°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.368 x 10^{-115}] g^3 cm^6

Heat of Formation

AlF_2^- is isoelectronic with SiF_2 and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same; this yields $\Delta Hf^\circ_{298}(AlF_2^-, g)$ = -191 kcal/mol, or an electron affinity for AlF_2 of 26 kcal/mol.

The binding energy should be close to that of AlF_2 since the extra electron should go into a non-bonding orbital according to the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953); using this approach yields $\Delta Hf^\circ_{298}(AlF_2^-, g)$ = -177 kcal/mol or an electron affinity for AlF_2 of 12 kcal. Another method of estimation assumes that the heats are identical for the two reactions $AlF_3 \rightarrow AlF_2^- + F^+$ and $AlF \rightarrow Al^- + F^+$ which yields $\Delta Hf^\circ_{298}(AlF_2^-, g)$ = -161 kcal/mol or an electron affinity for AlF_2 of -4 kcal.

We adopt a median value for the electron affinity for AlF_2 of 10 ± 20 kcal, which leads to $\Delta Hf^\circ_{298}(AlF_2^-, g)$ = -175 ± 40 kcal/mol when combined with $\Delta Hf^\circ_{298}(AlF_2, g)$ = -165 ± 20 kcal/mol.

Heat Capacity and Entropy

According to the predictions of A. D. Walsh, loc. cit., there is no doubt that the molecule is bent; the bond length is assumed to lie between those of AlF and AlF_3, the angle is that in AlF_3. The vibrational frequencies are estimated between those for SiF_2 and AlF_2. By analogy with SiF_2 no low electronic levels are expected (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York 1966).

The enthalpy at 0°K is -2.698 kcal/mol.

The individual principal moments of inertia are $I_A = 1.783 \times 10^{-39}$ g cm^2, $I_B = 12.882 \times 10^{-39}$ g cm^2 and $I_C = 14.665 \times 10^{-39}$ g cm^2.

Aluminum Trifluoride (AlF_3)

(Crystal) GFW = 83.9767

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.778	-359.519	-359.519	INFINITE
100	5.959	2.882	28.642	-2.576	-360.465	-354.484	774.725
200	13.594	9.558	17.403	-1.569	-360.951	-348.285	380.587
298	17.957	15.890	15.890	.000	-361.000	-342.053	250.731
300	18.021	16.001	15.890	.033	-360.999	-341.936	249.100
400	20.623	21.581	16.633	1.979	-360.807	-335.604	183.365
500	22.054	26.349	18.112	4.119	-360.509	-329.338	143.953
600	23.258	30.472	19.836	6.382	-360.153	-323.136	117.702
700	25.181	34.186	21.624	8.793	-359.703	-316.999	98.972
800	23.546	37.583	23.419	11.331	-359.181	-310.943	84.946
900	23.833	40.373	25.151	13.700	-358.888	-304.931	74.047
1000	24.099	42.898	26.801	16.097	-361.152	-298.767	65.296
1100	24.353	45.207	28.371	18.520	-360.826	-292.545	58.123
1200	24.598	47.337	29.864	20.967	-360.483	-286.352	52.152
1300	24.837	49.315	31.285	23.439	-360.124	-280.189	47.104
1400	25.071	51.164	32.640	25.934	-359.748	-274.053	42.782
1500	25.302	52.902	33.933	28.453	-359.354	-267.946	39.040
1600	25.531	54.542	35.170	30.995	-358.944	-261.866	35.769
1700	25.758	56.097	36.356	33.559	-358.516	-255.811	32.887
1800	25.984	57.576	37.494	36.146	-358.070	-249.783	30.328
1900	26.210	58.986	38.588	38.756	-357.605	-243.780	28.041
2000	26.435	60.337	39.642	41.388	-357.122	-237.800	25.986
2100	26.660	61.632	40.659	44.043	-356.621	-231.849	24.129
2200	26.885	62.877	41.641	46.720	-356.103	-225.920	22.443
2300	27.110	64.077	42.590	49.420	-355.563	-220.011	20.906
2400	27.335	65.236	43.510	52.142	-355.007	-214.130	19.499
2500	27.560	66.356	44.401	54.887	-354.433	-208.275	18.207

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1965; June 30, 1970

ALUMINUM TRIFLUORIDE (AlF_3) (CRYSTAL) GFW = 83.9767

$\Delta Hf^\circ_0 = -359.5 \pm 0.3$ kcal/mol

$S^\circ_{298.15} = 15.89 \pm 0.1$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -361.0 \pm 0.3$ kcal/mol

Tt = 728°K

$\Delta Ht^\circ = 0.1346$ kcal/mol

Ts = [1549]°K

$\Delta Hs^\circ_{298.15} = 71.965 \pm 0.5$ kcal/mol monomer

$\Delta Hs^\circ_{298.15} = 92.55 \pm 4$ kcal/mol dimer

Heat of Formation

The adopted value is from separate calorimetric studies of combustion in fluorine of aluminum (1) and aluminum-Teflon mixtures (2). More extensive auxiliary data (2) for Teflon bring the aluminum-Teflon study into exact agreement with the aluminum study (1). Calorimetric data relating AlF_3 to PbF_2 (1, 3) tend to confirm this value, but PbF_2 is probably more uncertain than is AlF_3.

Solid-state emf data (4) relating AlF_3 to MgF_2 via ThF_4 gave $\Delta Gf^\circ = -305.7$ kcal/mol for AlF_3(c) at 600°C. The adopted ΔHf° yields $\Delta Gf^\circ = -306.5$ kcal/mol; this is more negative by 0.8 kcal/mol. The adopted ΔHf° is also 2.4 kcal/mol more negative than indicated by entrainment data (5) for $2/3\ AlF_3(c) + H_2O(g) \rightarrow 1/3\ Al_2O_3(\alpha, c) + 2HF(g)$ in the range from 849° to 1312°K. Analysis of the equilibrium constants yields $\Delta Hr^\circ_{298.15} = 33.11 \pm 0.2$ kcal/mol (3rd law) and 33.33 ± 0.22 kcal/mol (2nd law) with an insignificant entropy difference, $\Delta Sr^\circ(\text{2nd law}) - \Delta Sr^\circ(\text{3rd law}) = 0.2 \pm 0.2$ gibbs/mol. It has been suggested (1) that interaction of the condensed phases caused the equilibria to deviate from the standard-state reaction assumed above. An alternative may be that the reaction with water vapor produced Al_2O_3 in a metastable form; such forms require ignition temperatures greater than 1400°K for complete conversion to α-Al_2O_3 (6).

Heat Capacity and Entropy

Cp° and S°_{298} are taken from Douglas and Ditmars (7), whose tables are based on heat capacity measurements from 54° to 298°K (8) and relative enthalpy measurements from 323° to 1173°K (7). The enthalpy data confirm earlier data (401°-1401°K) of O'Brien and Kelley (9) rather than the adjusted values proposed by Frank (10). Douglas and Ditmars (7) gave a detailed comparison with other data. The entropy is derived from Cp° using the extrapolation $S^\circ_{50} = 0.53 \pm 0.06$ gibbs/mol.

Transition Data

Tt and ΔHt° are from Douglas and Ditmars (7). The values were obtained from extensive enthalpy data for the transition region assuming the presence of a very small amount of impurity in solid solution.

Sublimation Data

Ts is the temperature at which the calculated total pressure (monomer plus dimer) reaches one atm; the mole fraction of dimer is calculated as 0.109 at Ts. Sublimation temperatures of 1533° and 1566°K were obtained in two sublimation-pressure studies (11, 12) at the Technische Hochschule, Breslau. The selected enthalpies of sublimation to $AlF_3(g)$ and $Al_2F_6(g)$ reproduce closely the entrainment data of Krause and Douglas (13). Selection of these values of ΔHs° and comparisons with other vapor-pressure data are discussed on the gas-phase tables.

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Aluminum Trifluoride (AlF_3)

(Ideal Gas) GFW = 83.9767

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.368	-288.144	-288.144	INFINITE
100	9.839	52.727	77.982	-2.526	-288.450	-287.453	628.229
200	12.928	60.591	67.457	-1.373	-288.790	-286.330	312.887
298	14.945	66.150	66.150	.000	-289.035	-285.073	208.964
300	14.977	66.243	66.151	.028	-289.039	-285.049	207.658
400	16.402	70.760	66.757	1.601	-289.220	-283.688	155.000
500	17.352	74.530	67.945	3.292	-289.370	-282.289	123.388
600	17.985	77.753	69.318	5.061	-289.508	-280.860	102.303
700	18.418	80.560	70.727	6.883	-289.648	-279.407	87.235
800	18.723	83.040	72.115	8.741	-289.806	-277.934	75.928
900	18.943	85.259	73.454	10.624	-289.999	-276.439	67.128
1000	19.107	87.264	74.736	12.527	-292.756	-274.737	60.044
1100	19.232	89.091	75.960	14.445	-292.936	-272.927	54.226
1200	19.329	90.769	77.125	16.373	-293.112	-271.100	49.374
1300	19.406	92.319	78.235	18.310	-293.288	-269.258	45.266
1400	19.468	93.760	79.293	20.254	-293.463	-267.402	41.743
1500	19.518	95.104	80.302	22.203	-293.640	-265.535	38.688
1600	19.560	96.365	81.267	24.157	-293.817	-263.656	36.014
1700	19.594	97.552	82.191	26.115	-293.995	-261.765	33.652
1800	19.624	98.673	83.076	28.076	-294.175	-259.865	31.552
1900	19.649	99.735	83.925	30.039	-294.357	-257.953	29.671
2000	19.670	100.743	84.741	32.005	-294.540	-256.032	27.978
2100	19.688	101.703	85.526	33.973	-294.726	-254.105	26.445
2200	19.704	102.620	86.282	35.943	-294.915	-252.166	25.050
2300	19.718	103.496	87.012	37.914	-295.105	-250.215	23.776
2400	19.731	104.335	87.716	39.886	-295.298	-248.260	22.607
2500	19.742	105.141	88.397	41.860	-295.495	-246.299	21.531
2600	19.751	105.916	89.056	43.835	-295.694	-244.326	20.537
2700	19.760	106.661	89.694	45.810	-295.895	-242.346	19.617
2800	19.768	107.380	90.313	47.787	-365.508	-239.530	18.696
2900	19.775	108.074	90.914	49.764	-365.453	-235.030	17.712
3000	19.781	108.744	91.497	51.742	-365.401	-230.537	16.795
3100	19.787	109.393	92.064	53.720	-365.351	-226.041	15.936
3200	19.792	110.021	92.615	55.699	-365.305	-221.547	15.131
3300	19.797	110.630	93.152	57.678	-365.261	-217.055	14.375
3400	19.801	111.221	93.675	59.658	-365.220	-212.566	13.664
3500	19.805	111.795	94.184	61.639	-365.183	-208.074	12.993
3600	19.809	112.353	94.681	63.619	-365.148	-203.583	12.359
3700	19.812	112.896	95.166	65.600	-365.117	-199.098	11.760
3800	19.815	113.425	95.640	67.582	-365.089	-194.610	11.193
3900	19.818	113.939	96.103	69.563	-365.065	-190.126	10.654
4000	19.821	114.441	96.555	71.545	-365.044	-185.640	10.143
4100	19.823	114.931	96.997	73.527	-365.028	-181.159	9.657
4200	19.825	115.408	97.430	75.510	-365.014	-176.672	9.193
4300	19.827	115.875	97.853	77.492	-365.003	-172.186	8.751
4400	19.829	116.331	98.268	79.475	-364.998	-167.700	8.330
4500	19.831	116.776	98.674	81.458	-364.997	-163.220	7.927
4600	19.833	117.212	99.073	83.442	-364.998	-158.734	7.542
4700	19.835	117.639	99.463	85.425	-365.007	-154.255	7.173
4800	19.836	118.056	99.846	87.408	-365.018	-149.768	6.819
4900	19.838	118.465	100.222	89.392	-365.034	-145.278	6.480
5000	19.839	118.866	100.591	91.376	-365.056	-140.796	6.154
5100	19.840	119.259	100.953	93.360	-365.083	-136.315	5.841
5200	19.841	119.644	101.309	95.344	-365.116	-131.824	5.540
5300	19.842	120.022	101.658	97.328	-365.155	-127.337	5.251
5400	19.844	120.393	102.002	99.312	-365.200	-122.854	4.972
5500	19.845	120.757	102.340	101.297	-365.252	-118.366	4.703
5600	19.846	121.115	102.672	103.281	-365.311	-113.872	4.444
5700	19.846	121.466	102.998	105.266	-365.376	-109.383	4.194
5800	19.847	121.811	103.320	107.251	-365.448	-104.890	3.952
5900	19.848	122.151	103.636	109.235	-365.529	-100.400	3.719
6000	19.849	122.484	103.947	111.220	-365.617	-95.906	3.493

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1965; June 30, 1970

ALUMINUM TRIFLUORIDE (AlF_3) (IDEAL GAS) GFW = 83.9767

Point Group D_{3h}

$S°_{298.15}$ = 66.15 ± 0.2 gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0 = -288.14 \pm 0.6$ kcal/mol

$\Delta Hf°_{298.15} = -289.035 \pm 0.6$ kcal/mol

Vibrational Frequencies and Degeneracies, ω, cm^{-1}

[650] (1) 297 (1) 935 (2) 263 (2)

Bond Distance: Al-F = 1.63 ± 0.01 Å

Bond Angle: F-Al-F = 120° σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 3.9742 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

ΔHf° is calculated from that of the crystal by use of $\Delta Hs°_{298.15}$ = 71.965 ± 0.5 kcal/mol. Sublimation studies by mass-spectrometric and entrainment techniques suggest the presence of a small amount of dimer in the saturated vapor. These studies are reviewed on the table for $Al_2F_6(g)$. ΔHs(monomer) and ΔHs(dimer) are selected by adopting (a) the JANAF entropies for crystal, monomer and dimer, (b) the mass spectrometric value of 2 ΔHs(monomer) - ΔHs(dimer) = -49 kcal/mol at 1000°K, and (c) the entrainment data of Krause and Douglas (1). The resulting calculated pressures deviate by <0.5% from the entrainment data (1), by <10% from the mass-spectrometric equation (3) and by <3% from the mass-effusion equation (4).

Further comparisons with experimental data are given below. The adopted values favor the later (11) of two sublimation-point studies (11, 12); both show considerable scatter and similar deviations from the calculated dP/dT. Torsion-effusion data suggest the possibility of more serious discrepancy. Although data of Witt and Barrow (9) are consistent with the JANAF pressures, Hildenbrand et al. (7, 8) noted a trend toward increasing pressure with decreasing orifice area. They concluded (7) that the condensation coefficient <0.06, based on **eightfold** variation in the product of Clausing factor x orifice area. JANAF predictions for the pressure are 60 to 80% of the adjusted torsion values (7) and the discrepancy corresponds roughly to the ratios used in the adjustment. In contrast, the JANAF predictions agree closely with mass-effusion data of Ko et al. (4), who reported no significant effect from a **twelvefold** variation in orifice area.

Comparison of Calculated and Observed Total Pressures over $AlF_3(c)$

Source		Method	T, °K Range	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range	Difference[a] in dP/dT
(1) Krause (1968)		Entrainment	1194-1258	0.019-0.029	1.004-0.996	Very small (-)
(2) Naryshkin (1939)		Entrainment	1108-1273	0.010-0.032	0.73 -2.22	Uncertain (?)
(3) Erokhin (1967)		Mass Spec.[b]	983-1165	0.003-0.016	1.09 -0.91	Small (-)
(4) Ko (1965)		Mass Effusion	1027-1184	0.005-0.018	0.994-0.972	Very small (-)
(5) Blackburn (1965)		Mass Effusion	889-1006	0.001-0.004	1.42 -1.66	Uncertain (+)
(6) Evseev (1959)		Mass Effusion	980-1123	0.003-0.012	1.64 -0.88	Large (-)
(7) Hildenbrand (1963)		Torsion Effusion[c]				
	P=Pt/0.901	Cell Gr-22	1004-1114	0.004-0.011	0.67 -0.74	Very Small (?)
	P=Pt/0.847	Cell Gr-7	989-1102	0.004-0.010	0.60 -0.81	Medium (+)
	P=Pt/0.689	Cell Gr-9	977-1088	0.003-0.009	0.63 -0.73	Small (+)
	P=Pt/0.806	Cell Pt-9	963-1053	0.003-0.007	0.60 -0.72	Small (+)
	P=Pt/0.699	Cell Pt-12	949-1067	0.002-0.007	0.49 -0.74	Medium (+)
(8) Hildenbrand (1961)		Torsion Effusion				
		Cell Gr-7	992-1101	0.004-0.010	0.89 -1.01	Small (+)
		Cell Gr-9	938-1080	0.002-0.008	0.94 -1.34	Medium (+)
(9) Witt (1959)		Torsion Effusion	955-1063	0.003-0.007	1.11 -1.07	Small (-)
(10) Vetyukov (1959)		Dynamic B. P.	1335-1453	0.044-0.076	0.84 -1.64	Large (+)
(11) Ruff (1934)		Dynamic B. P.	1367-1524	0.052-0.100	1.33 -0.79	Large (-)
(12) Olbrich (1928)		Dynamic B. P.	1371-1567	0.053-0.116	2.70 -1.28	Large (-)

[a] Magnitude and sign of the difference, calculated minus observed, in dP/dT. [b] Absolute pressures of monomer were obtained by integration of the ion intensity during total sublimation. [c] Based on P calculated from the torsion pressure Pt by the equation given.

Heat Capacity and Entropy

The molecular structure is that derived from electron-diffraction data by Akishin et al. (13). Observed vibrational frequencies are those reported by Büchler et al. (14) from infrared spectra of the vapor at 1000-1200°K. These frequencies are confirmed by infrared spectra of AlF_3 isolated in matrices of neon, argon and krypton (15). The Raman-active fundamental ν_1 is estimated as 650 ± 50 cm^{-1} by three methods: (a) calculation of the force constant k_1 from ν_3 and ν_4; (b) comparison of $k_1(XY_3)/k(XY)$ for X = B, Al and Y = F, Cl and Br; and (c) extrapolation of $\nu_1(BY_3)/\nu_1(AlY_3)$ to Y = F from Y = Cl, Br and I, using recent gas-phase Raman data (16) for AlY_3. Principal moments of inertia are $I_A=I_B=12.572\times10^{-39}$ and $I_C=25.144\times10^{-39}$ g cm^2.

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Lithium Tetrafluoroaluminate ($LiAlF_4$)

(Ideal Gas) GFW = 109.9141

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.755	-441.336	-441.336	INFINITE
100	12.693	58.525	96.759	-3.823	-442.019	-439.392	960.290
200	19.801	69.682	80.545	-2.173	-442.651	-436.507	476.992
298	24.102	78.463	78.463	.000	-443.000	-433.413	317.700
300	24.163	78.612	78.464	.045	-443.005	-433.355	315.699
400	26.718	85.946	79.446	2.600	-443.210	-430.102	234.997
500	28.243	92.086	81.377	5.354	-444.119	-426.732	186.524
600	29.196	97.326	83.610	8.230	-444.279	-423.238	154.164
700	29.822	101.877	85.901	11.183	-444.413	-419.720	131.043
800	30.251	105.889	88.154	14.188	-444.549	-416.186	113.697
900	30.556	109.470	90.327	17.229	-444.713	-412.630	100.200
1000	30.780	112.702	92.406	20.296	-447.439	-408.873	89.359
1100	30.949	115.644	94.386	23.383	-447.583	-405.009	80.468
1200	31.080	118.343	96.272	26.485	-447.722	-401.133	73.056
1300	31.183	120.835	98.067	29.598	-447.859	-397.244	66.783
1400	31.265	123.149	99.777	32.721	-447.994	-393.345	61.404
1500	31.332	125.308	101.407	35.851	-448.128	-389.436	56.741
1600	31.387	127.332	102.965	38.987	-448.262	-385.520	52.660
1700	31.432	129.236	104.455	42.128	-483.443	-380.265	48.886
1800	31.471	131.034	105.882	45.273	-483.397	-374.198	45.434
1900	31.504	132.736	107.251	48.422	-483.352	-368.131	42.345
2000	31.532	134.353	108.566	51.573	-483.312	-362.067	39.565
2100	31.556	135.892	109.831	54.728	-483.275	-356.011	37.050
2200	31.577	137.360	111.049	57.885	-483.243	-349.951	34.764
2300	31.595	138.764	112.224	61.043	-483.213	-343.889	32.677
2400	31.611	140.109	113.358	64.203	-483.191	-337.833	30.764
2500	31.626	141.400	114.454	67.365	-483.174	-331.779	29.004
2600	31.638	142.641	115.514	70.529	-483.161	-325.723	27.380
2700	31.650	143.835	116.541	73.693	-483.155	-319.668	25.875
2800	31.660	144.986	117.537	76.858	-552.564	-312.784	24.414
2900	31.669	146.097	118.503	80.025	-552.310	-304.222	22.927
3000	31.677	147.171	119.440	83.192	-552.064	-295.675	21.540
3100	31.684	148.210	120.352	86.360	-551.825	-287.131	20.243
3200	31.691	149.216	121.238	89.529	-551.594	-278.596	19.027
3300	31.697	150.191	122.101	92.698	-551.373	-270.068	17.886
3400	31.703	151.138	122.941	95.868	-551.161	-261.547	16.812
3500	31.708	152.057	123.760	99.039	-550.958	-253.030	15.800
3600	31.713	152.950	124.558	102.210	-550.765	-244.517	14.844
3700	31.717	153.819	125.337	105.382	-550.583	-236.017	13.941
3800	31.721	154.665	126.098	108.553	-550.414	-227.512	13.085
3900	31.725	155.489	126.841	111.726	-550.255	-219.020	12.274
4000	31.728	156.292	127.568	114.898	-550.109	-210.529	11.503
4100	31.731	157.076	128.278	118.071	-549.976	-202.044	10.770
4200	31.734	157.840	128.973	121.245	-549.855	-193.558	10.072
4300	31.737	158.587	129.653	124.418	-549.747	-185.073	9.406
4400	31.740	159.317	130.319	127.592	-549.655	-176.591	8.771
4500	31.742	160.030	130.971	130.766	-549.578	-168.117	8.165
4600	31.744	160.728	131.610	133.941	-549.514	-159.640	7.585
4700	31.747	161.411	132.237	137.115	-549.471	-151.172	7.029
4800	31.749	162.079	132.852	140.290	-549.442	-142.694	6.497
4900	31.750	162.734	133.455	143.465	-549.433	-134.215	5.986
5000	31.752	163.375	134.047	146.640	-549.443	-125.743	5.496
5100	31.754	164.004	134.628	149.815	-549.474	-117.273	5.025
5200	31.755	164.620	135.199	152.991	-549.526	-108.792	4.572
5300	31.757	165.225	135.760	156.166	-549.602	-100.317	4.137
5400	31.758	165.819	136.311	159.342	-549.701	-91.845	3.717
5500	31.759	166.402	136.853	162.518	-549.826	-83.363	3.313
5600	31.761	166.974	137.386	165.694	-549.978	-74.879	2.922
5700	31.762	167.536	137.910	168.870	-550.157	-66.393	2.546
5800	31.763	168.089	138.425	172.046	-550.366	-57.902	2.182
5900	31.764	168.631	138.933	175.223	-550.605	-49.415	1.830
6000	31.765	169.165	139.432	178.399	-550.878	-40.916	1.490

Sept. 30, 1962; Sept. 30, 1963; Dec. 31, 1963; Mar. 31, 1964; June 30, 1970

LITHIUM TETRAFLUOROALUMINATE ($LiAlF_4$) (IDEAL GAS) GFW = 109.9141

Point Group [C_{2v}]

ΔHf°_0 = -441.3 ± 2 kcal/mol

$S^\circ_{298.15}$ = [78.46] ± 2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -443.0 ± 2 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
800 (1)	[300] (1)	555 (1)	890 (1)
665 (1)	[195] (1)	450 (1)	330 (1)
[560] (1)	[180] (1)	240 (1)	285 (1)

Bond Distance: Al-F = [1.69] Å LiF = [1.8] Å

Bond Angle: F-Al-F = [109.47°] σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.0109 x 10^{-113}] g^3 cm^6

Heat of Formation

Mass spectrometric studies (1) of the two-phase systems LiF + Li_3AlF_6 and Li_3AlF_6 + AlF_3 suggested that the vapor contains small amounts of Li_2AlF_5 and $Li_2(AlF_4)_2$ but that $LiAlF_4$(g) constitutes of the order of 90%. Hildenbrand et al. (2) reported torsion effusion pressures for the compositions 3LiF·AlF_3 and LiF·AlF_3; as a first approximation, these total pressures should correspond to the reactions (A) Li_3AlF_6(c) → $LiAlF_4$(g) + 2LiF(c), and (B) 1/3 Li_3AlF_6(c) + 2/3 AlF_3(c) → $LiAlF_4$(g). Porter and Zeller (3) reported mass spectrometric equilibrium constants for the reaction (C) Li_2F_2 + AlF_3(g) → LiF(g) + $LiAlF_4$(g). Second- and third-law analyses of these data are summarized below. Kuxmann and Tillessen (4) reported total vapor pressures over molten nLiF·AlF_3 (0.81 ≤ n ≤ 3), but we have made no attempt to establish the liquid phase activities necessary for use of these data.

The adopted ΔHf° is derived from reaction (B) which exhibits entropy deviations (δS) and orifice area effects which are relatively minor. Data for reaction (A) yield a ΔHf° that is more negative by 1.5 kcal/mol, but the very large entropy deviation suggests the presence of systematic uncertainties. Combination of (B) and (A) into the reaction 3LiF(c) + AlF_3(c) → Li_3AlF_6(c) gives ΔHr_{298} = -3.3 kcal/mol, which is fairly consistent with the calorimetric value (5) of ΔHr°_{298} = -5.4 ± 0.5 kcal/mol. Sidorov and Kolosov (6) suggested that the equilibrium constants for reaction (C) should be considered as lower limits since AlF_3 and $LiAlF_4$ are probably both precursors of AlF_2^+.

Source	Reaction	Method	Range T, °K	δS gibbs/mol	$\Delta Hr^\circ_{298.15}$, kcal/mol 2nd Law	$\Delta Hr^\circ_{298.15}$, kcal/mol 3rd Law	$\Delta Hf^\circ_{298.15}$ kcal/mol
(2) Hildenbrand (1963)	A	Torsion effusion, Cell 7	987-1058	33 ±1	103.3±1.5	69.33	-444.5±2.3
(2) Hildenbrand (1963)	B	Torsion effusion, Cell 7	899-980	7.6±1.9	74.3±1.8	67.14	-443.1±2
		Torsion effusion, Cell 9	873-976	2.7±0.5	69.9±0.5	67.35	-442.9±2
		Torsion effusion, Cell 15X	854-980	2.3±1.0	69.6±0.9	67.48	-442.8±2
(3) Porter (1960)	C	Mass spectrometry	1000-1100	4 ±5	-1 ±5	<-5.5	<-438.4±6

Heat Capacity and Entropy

The point group and molecular structure are assumed to be similar to those adopted for $NaAlF_4$. A discussion of the incomplete structural evidence is given on the table for $NaAlF_4$(g). The adopted structure consists of tetrahedral AlF_4 combined with Li to form a planar ring, AlF_2Li, through coordination with two fluorines. The Al-F distance is assumed to be equal to that observed in $NaAlF_4$, while the Li-F distance is estimated by comparison of the M-F distances in MF(g), M_2F_2(g), M_3AlF_6(c) (M = Li and Na) with that in $NaAlF_4$(g). The principal moments of inertia are I_A = 24.026 x 10^{-39} and I_B = I_C = 28.930 x 10^{-39} g cm^2.

Snelson (7) observed eight fundamentals in the infrared spectra of $LiAlF_4$ isolated in rare gas matrices. He estimated gas phase fundamentals by assuming a constant shift of about 15 cm^{-1} from the value in a neon matrix to the value in the gas. McCory et al. (8) found absorptions near 778 and 866 cm^{-1} in the infrared spectra of the vapor at high temperatures. We adopt average values of 800 and 890 cm^{-1} for these two fundamentals and Snelson's values for the other six. The four additional fundamentals necessary for C_{2v} symmetry are estimated by comparison with Li_2F_2, Al_2F_6, AlF_3 and $AlCl_4^-$. Sidorov and Kolosov (6), using somewhat different estimates for fundamental frequencies and structural parameters, calculated S°_{1000} = 114 ± 2 gibbs/mol. The JANAF value is 112.7 ± 2 gibbs/mol.

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Sodium Tetrafluoroaluminate ($NaAlF_4$)

(Ideal Gas) GFW = 125.9649

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.158	-444.903	-444.903	INFINITE
100	14.348	60.704	102.324	-4.162	-445.723	-442.920	968.001
200	21.613	73.172	84.778	-2.321	-446.311	-439.869	480.666
298	25.331	82.566	82.566	.000	-446.600	-436.643	320.068
300	25.383	82.723	82.566	.047	-446.604	-436.582	318.049
400	27.524	90.346	83.591	2.702	-447.432	-433.159	236.667
500	28.801	96.636	85.590	5.523	-447.597	-429.572	187.766
600	29.601	101.963	87.886	8.446	-447.718	-425.955	155.154
700	30.127	106.569	90.234	11.434	-447.823	-422.320	131.854
800	30.489	110.616	92.534	14.466	-447.935	-418.670	114.375
900	30.746	114.223	94.747	17.529	-448.076	-415.003	100.776
1000	30.936	117.473	96.860	20.613	-450.785	-411.137	89.854
1100	31.079	120.428	98.870	23.714	-450.923	-407.167	80.897
1200	31.189	123.138	100.781	26.828	-474.302	-402.725	73.346
1300	31.276	125.638	102.598	29.951	-474.240	-396.762	66.702
1400	31.345	127.958	104.328	33.083	-474.178	-390.804	61.007
1500	31.402	130.123	105.976	36.220	-474.119	-384.850	56.073
1600	31.449	132.151	107.549	39.363	-474.062	-378.902	51.756
1700	31.487	134.058	109.053	42.509	-474.007	-372.954	47.947
1800	31.520	135.859	110.493	45.660	-473.955	-367.014	44.562
1900	31.548	137.564	111.873	48.813	-473.906	-361.073	41.533
2000	31.572	139.183	113.198	51.969	-473.861	-355.135	38.807
2100	31.592	140.724	114.473	55.127	-473.819	-349.204	36.342
2200	31.610	142.194	115.700	58.288	-473.781	-343.271	34.101
2300	31.625	143.599	116.882	61.449	-473.746	-337.336	32.054
2400	31.639	144.946	118.024	64.613	-473.716	-331.405	30.179
2500	31.651	146.238	119.127	67.777	-473.692	-325.481	28.453
2600	31.662	147.479	120.193	70.943	-473.672	-319.550	26.861
2700	31.672	148.674	121.226	74.110	-473.656	-313.623	25.386
2800	31.680	149.826	122.227	77.277	-543.056	-306.868	23.952
2900	31.688	150.938	123.198	80.446	-542.789	-298.433	22.490
3000	31.695	152.012	124.141	83.615	-542.531	-290.016	21.128
3100	31.701	153.052	125.057	86.784	-542.277	-281.603	19.853
3200	31.707	154.058	125.947	89.955	-542.030	-273.196	18.658
3300	31.712	155.034	126.814	93.126	-541.791	-264.799	17.537
3400	31.717	155.981	127.658	96.297	-541.560	-256.411	16.482
3500	31.721	156.900	128.481	99.469	-541.338	-248.021	15.487
3600	31.725	157.794	129.282	102.641	-541.124	-239.641	14.548
3700	31.729	158.663	130.065	105.814	-540.920	-231.275	13.661
3800	31.732	159.509	130.829	108.987	-540.727	-222.904	12.820
3900	31.735	160.334	131.575	112.161	-540.546	-214.548	12.023
4000	31.738	161.137	132.304	115.334	-540.377	-206.190	11.266
4100	31.741	161.921	133.017	118.508	-540.222	-197.839	10.546
4200	31.744	162.686	133.714	121.683	-540.080	-189.489	9.860
4300	31.746	163.433	134.396	124.857	-539.953	-181.139	9.206
4400	31.748	164.163	135.065	128.032	-539.846	-172.797	8.583
4500	31.750	164.876	135.719	131.207	-539.756	-164.457	7.987
4600	31.752	165.574	136.361	134.382	-539.685	-156.119	7.417
4700	31.754	166.257	136.990	137.557	-539.639	-147.786	6.872
4800	31.756	166.926	137.606	140.732	-539.615	-139.446	6.349
4900	31.757	167.580	138.211	143.908	-539.617	-131.100	5.847
5000	31.759	168.222	138.805	147.084	-539.648	-122.768	5.366
5100	31.760	168.851	139.388	150.260	-539.709	-114.434	4.904
5200	31.761	169.468	139.961	153.436	-539.803	-106.090	4.459
5300	31.763	170.073	140.523	156.612	-539.933	-97.746	4.031
5400	31.764	170.666	141.076	159.788	-540.102	-89.408	3.619
5500	31.765	171.249	141.619	162.965	-540.311	-81.062	3.221
5600	31.766	171.822	142.153	166.141	-540.565	-72.704	2.837
5700	31.767	172.384	142.679	169.318	-540.863	-64.347	2.467
5800	31.768	172.936	143.196	172.495	-541.210	-55.984	2.110
5900	31.769	173.479	143.704	175.672	-541.610	-47.617	1.764
6000	31.770	174.013	144.205	178.848	-542.064	-39.241	1.429

June 30, 1970

SODIUM TETRAFLUOROALUMINATE ($NaAlF_4$) (IDEAL GAS) GFW = 125.9649

Point Group [C_{2v}]

ΔHf°_0 = -444.9 ± 2.3 kcal/mol

$S^\circ_{298.15}$ = [82.57] ± 2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -446.6 ± 2.3 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
800 (1)	[300] (1)	385 (1)	890 (1)
680 (1)	[160] (1)	340 (1)	320 (1)
[390] (1)	[180] (1)	[190] (1)	[200] (1)

Bond Distance: Al-F = 1.69 ± 0.02 Å Na-F = 2.11 ± 0.02 Å

Bond Angle: F-Al-F = 109.47° σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C = 4.79396 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

ΔHf° is based on $\Delta Hr^\circ_{298.15}$ = 69.36 kcal/mol for the reaction $Na_3AlF_6(c) \rightarrow NaAlF_4(g) + 2NaF(c)$. ΔHr° is calculated by third law analysis of the pressure equation reported for this reaction by Sidorov and Kolosov (1). The second law ΔHr° = 70.5 kcal/mol and the entropy deviation is 1.1 gibbs/mol. Sidorov and Kolosov obtained their pressure equation by combination of the temperature variation of ion intensities with integration of intensities during total sublimation at 931°K (2).

Sidorov et al. (2) concluded that the pressure of the dimer $(NaAlF_4)_2$ at 931°K is almost half of the monomer pressure over the two-phase system $Na_5Al_3F_{14}$-AlF_3. In contrast, Büchler et al. (3) reported the approximate vapor composition of 97% monomer, 1% dimer, 1% Na_2AlF_5, and 1% AlF_3 over the same condensed phases at 833°K. The latter composition was obtained from a mass spectrometric study by the twin crucible method.

Vapor pressures over melts in the NaF-AlF_3 system have been measured by the entrainment and boiling point techniques (4-7). We have made no attempt to establish the liquid phase activities necessary for use of these data.

Heat Capacity and Entropy

The adopted structure (C_{2v} symmetry) consists of tetrahedral AlF_4 combined with Na to form a planar ring, AlF_2Na, through coordination with two fluorines. Experimental evidence available for $NaAlF_4$ and $LiAlF_4$ does not distinguish conclusively between this structure and the alternatives which have been seriously considered. Alternatives include a C_s structure, in which the ring is non-planar, and two C_{3v} structures, in which Na (or Li) is coordinated to one or three fluorines instead of two.

Electron diffraction data (8) for the vapor gave the adopted bond distances and showed that the AlF_4 group is essentially tetrahedral. Wave error at small scattering angles precluded the calculation of accurate non-bonded distances for Na.

Snelson (9) observed the infrared spectra of $LiAlF_4$ and $NaAlF_4$ isolated in matrices of neon and argon. Eight fundamentals were found above 200 cm^{-1} for $LiAlF_4$ and six for $NaAlF_4$. Snelson chose a C_{3v} structure for $LiAlF_4$ on the basis of Redlich-Teller product-rule calculations for istopic shifts due to Li.

Neither the infrared data nor the electron-diffraction data are conclusive so we apply these qualitative arguments. Coordination of Na to three fluorines seems less likely, since there are no known examples of this behavior. The C_{2v} structure, as suggested by Büchler and Berkowitz-Mattuck (3), is likely because it is a hybrid between the accepted structures of Na_2F_2 and Al_2F_6. C_{2v} symmetry (σ = 2) is a compromise which has an entropy effect intermediate between the other alternatives. The principal moments of inertia of the C_{2v} structure are $I_A = 24.026 \times 10^{-39}$ and $I_B = I_C = 44.669 \times 10^{-39}$ g cm^2.

The fundamental vibrations of 800 and 890 cm^{-1} are average values from gas phase (10) and matrix (9) spectra. Four other observed values are from the matrix data. Six fundamentals are estimated by comparisons similar to those used for $LiAlF_4(g)$.

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Tripotassium Hexafluoroaluminate (K_3AlF_6)

(Crystal) Mol. Wt. = 258.28

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	53.250	68.000	68.000	.000	- 795.000	- 756.097	554.208
300	53.390	68.330	68.001	.099	- 794.993	- 755.856	550.614
400	57.620	84.425	70.166	5.704	- 796.237	- 742.552	405.692
500	61.020	97.657	74.377	11.640	- 795.578	- 729.205	318.720
600	63.910	109.046	79.228	17.891	- 794.657	- 716.010	260.794
700	66.660	119.105	84.220	24.420	- 793.516	- 702.988	219.472
800	69.330	128.182	89.157	31.220	- 792.166	- 690.150	188.531
900	71.400	136.472	93.960	38.261	- 790.637	- 677.485	164.508
1000	73.000	144.081	98.597	45.484	- 791.503	- 664.818	145.289
1100	74.400	151.106	103.055	52.856	- 846.418	- 649.164	128.971
1200	75.600	157.633	107.335	60.358	- 843.798	- 631.343	114.978
1300	76.600	163.725	111.441	67.969	- 841.087	- 613.750	103.176
1400	77.400	169.432	115.381	75.671	- 838.297	- 596.364	93.092
1500	78.038	174.794	119.165	83.444	- 835.448	- 579.180	84.382
1600	78.600	179.849	122.801	91.276	- 832.552	- 562.190	76.788
1700	79.088	184.629	126.299	99.161	- 829.615	- 545.385	70.111
1800	79.500	189.161	129.666	107.091	- 826.645	- 528.755	64.197
1900	79.800	193.468	132.912	115.057	- 823.651	- 512.285	58.923
2000	80.000	197.567	136.043	123.048	- 820.641	- 495.969	54.194

June 30, 1962; Sept. 30, 1963; Dec. 31, 1963

TRIPOTASSIUM HEXAFLUOROALUMINATE (K_3AlF_6) (CRYSTAL) MOL. WT. = 258.28

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [68.0 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-795 ± 5] kcal. mole^{-1}

T_m = 1293°K.

ΔH°_m = Unknown

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ adopted was calculated based upon $\Delta H^\circ_r = -30.2$ kcal. mole^{-1} for the reaction, $AlF_3(c) + 3KF(c) = K_3AlF_6(c)$, which was estimated by comparison with the values of ΔH°_r of the similar reactions for $Na_3AlF_6(c)$, $Na_3AlCl_6(c)$ and $K_3AlCl_6(c)$.

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by the addition of a correction term, $3(M_{KF}-M_{NaF})$, to the corresponding values for $Na_3AlF_6(c)$, where M denotes either C_p or $S^\circ_{298.15}$.

Temperature of Melting.

T_m was obtained from F. P. Hall and H. Insley, J. Am. Ceram. Soc. 21, 113 (1938).

Trilithium Hexafluoroaluminate (Li_3AlF_6)

(Crystal) GFW = 161.7889

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 7.683	- 805.644	- 805.644	INFINITE
100	16.965	9.136	79.746	- 7.061	- 807.570	- 795.583	1738.744
200	37.338	27.715	49.025	- 4.262	- 808.633	- 783.090	855.721
298	48.400	44.907	44.907	.000	- 808.700	- 770.517	564.804
300	48.550	45.207	44.908	.090	- 808.696	- 770.282	561.150
400	54.940	60.122	46.898	5.289	- 808.269	- 757.529	413.894
500	59.300	72.874	50.849	11.012	- 809.852	- 744.692	325.504
600	62.690	83.996	55.466	17.118	- 809.040	- 731.729	266.532
700	65.500	93.876	60.261	23.531	- 807.965	- 718.927	224.459
800	68.000	103.457	65.072	30.708	- 806.179	- 706.330	192.960
900	70.500	111.964	69.817	37.933	- 804.417	- 693.952	168.515
1000	73.000	119.624	74.416	45.208	- 805.200	- 681.585	148.960
1100	75.500	126.699	78.851	52.633	- 803.274	- 669.315	132.981
1200	78.000	133.375	83.119	60.308	- 801.113	- 657.231	119.698
1300	80.500	139.717	87.231	68.233	- 798.713	- 645.336	108.491
1400	83.000	145.775	91.198	76.408	- 796.073	- 633.633	98.915
1500	85.500	151.586	95.031	84.833	- 793.189	- 622.130	90.644

Sept. 30, 1963; Dec. 31, 1963; June 30, 1970

TRILITHIUM HEXAFLUOROALUMINATE (Li_3AlF_6) (CRYSTAL) GFW = 161.7889

ΔHf°_0 = -805.6 ± 1.1 kcal/mol

$S^\circ_{298.15}$ = 44.907 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -808.7 ± 1.1 kcal/mol

Tt_1 = 748 K ($\beta \rightarrow \gamma$)

ΔHt°_1 = [0.5] kcal/mol

Tt_2 = 848 K ($\gamma \rightarrow \delta$)

ΔHt°_2 = [0.3] kcal/mol

Tt_3 = 978 K ($\delta \rightarrow \epsilon$)

ΔHt°_3 = [0.1] kcal/mol

Tm = 1058 ± 3 K

ΔHm° = 20.6 ± 1.0 kcal/mol

Heat of Formation

ΔHf° is derived from ΔHr° = -5.4 ± 0.5 kcal/mol at 298.15 K for the reaction 3 LiF(c) + AlF_3(c) → Li_3AlF_6 (α, β mixture). Greene et al. (1) obtained this result by heating the fluorides under standardized conditions in a small electrical furnace contained in their calorimeter at 25°C. ΔHr° includes a small endothermic effect observed during heating of the reaction product. The authors suggest that the enthalpy of conversion between the α- and β-forms is small and thus their result should apply to both forms.

Heat Capacity and Entropy

Furukawa et al. (2) measured Cp°(15-370 K) using a sample prepared by fusion of stoichiometric proportions of LiF and AlF_3 in graphite. X-ray diffraction and petrographic examination of separate portions of the sample indicated a single phase identified as β-Li_3AlF_6. The authors tabulated values of Cp° and S° based on their data and the extrapolation S°_{15} = 0.042 gibbs/mol. These values are adopted.

Douglas and Neufer (3) reported relative enthalpy data (323-973 K) for part of the same sample used in measurement of Cp° (2). Their study was made prior to discovery of the five crystalline phases, and their drop-calorimetric data reveal only the transition near 748 K. Reinterpretation of the data above 748 K is complicated by the proximity of the furnace temperatures to the transition temperatures and by the tendency of high-temperature forms to revert to both α- and β-forms under different conditions of cooling. Björge and Jenssen (4) and Rolin et al. (5) also reported crystalline enthalpy data, but these are relatively imprecise and include similar uncertainties in the final state after the drop. These difficulties preclude the derivation of accurate heat capacities for the high-temperature forms.

Cp° for the β-form is adopted from (2, 3), since the two methods are in good agreement. The curve is extrapolated linearly above 748 K to obtain Cp° for the high-temperature forms. Obvious differences in Cp° are not apparent in the observed data for the different forms, so this should be an adequate approximation.

Transition Data

Existence of five polymorphic forms was shown by high-temperature X-ray diffraction (1, 6, 7) and differential thermal analysis (6, 7). Both α- and β-forms persisted at room temperature, but the α-form appeared only on quenching of high-temperature forms (1). The α-form transformed to β near 490 K (1, 6), but the reverse transformation was not observed. Single-crystal X-ray diffraction showed the α-form to be orthorhombic (8).

The adopted values of Tt are the lowest temperatures at which the high-temperature form was observed growing at the expense of the low-temperature form (1). DTA data (6, 7) were higher by roughly 30° for Tt_1 and 25° for Tt_2. Combination of the observed enthalpies (3) with the adopted Cp° yields ΔHt°_1 = 0.76 and ΔHt°_2 = 0.03 or 0.15 kcal/mol; however, we prefer to adopt ΔHt° values (0.5 and 0.3 kcal/mol) which are more consistent with the areas of peaks in the DTA curve (7). Evidence suggests that ΔHt°_3 is small, so we estimate 0.1 kcal/mol.

Melting Data

See the table for the liquid.

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Trilithium Hexafluoroaluminate (Li_3AlF_6)

(Liquid) GFW = 161.7889

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	48.400	58.759	58.759	.000	- 792.935	- 758.882	556.275
300	48.550	59.058	58.759	.090	- 792.931	- 758.673	552.692
400	54.940	73.973	60.750	5.289	- 792.504	- 747.304	408.308
500	59.300	86.725	64.701	11.012	- 794.087	- 735.852	321.641
600	62.690	97.848	69.318	17.118	- 793.275	- 724.275	263.817
700	65.500	107.728	74.112	23.531	- 792.200	- 712.858	222.564
800	86.000	119.212	79.048	32.131	- 788.991	- 701.746	191.708
900	86.000	129.341	84.084	40.731	- 785.854	- 691.028	167.805
1000	86.000	138.402	89.071	49.331	- 785.312	- 680.475	148.718
1100	86.000	146.599	93.934	57.931	- 782.211	- 670.142	133.145
1200	86.000	154.082	98.639	66.531	- 779.125	- 660.091	120.219
1300	86.000	160.966	103.172	75.131	- 776.050	- 650.295	109.324
1400	86.000	167.339	107.531	83.731	- 772.985	- 640.735	100.023
1500	86.000	173.272	111.718	92.331	- 769.926	- 631.395	91.994
1600	86.000	178.823	115.741	100.931	- 766.873	- 622.259	84.997
1700	86.000	184.036	119.606	109.531	- 868.967	- 609.330	78.335
1800	86.000	188.952	123.323	118.131	- 865.382	- 594.159	72.141
1900	86.000	193.602	126.901	126.731	- 861.804	- 579.186	66.622
2000	86.000	198.013	130.347	135.331	- 858.238	- 564.404	61.675
2100	86.000	202.209	133.670	143.931	- 854.684	- 549.808	57.219
2200	86.000	206.210	136.877	152.531	- 851.142	- 535.370	53.184
2300	86.000	210.032	139.975	161.131	- 847.605	- 521.093	49.515
2400	86.000	213.693	142.971	169.731	- 844.087	- 506.975	46.166
2500	86.000	217.203	145.871	178.331	- 840.581	- 493.001	43.098
2600	86.000	220.576	148.680	186.931	- 837.087	- 479.169	40.278
2700	86.000	223.822	151.403	195.531	- 833.608	- 465.468	37.677
2800	86.000	226.949	154.045	204.131	- 899.551	- 451.068	35.207
2900	86.000	229.967	156.612	212.731	- 895.846	- 435.112	32.791
3000	86.000	232.883	159.106	221.331	- 892.156	- 419.292	30.545

TRILITHIUM HEXAFLUOROALUMINATE (Li_3AlF_6) (LIQUID) GFW = 161.7889

$S^\circ_{298.15}$ = 58.758 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -792.935 kcal/mol

Tm = 1058 ± 3 K

ΔHm° = 20.6 ± 1.0 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298.15}$ is calculated from that of the crystal by addition of ΔHm° and the difference of ($H^\circ_{1058}-H^\circ_{298.15}$) for the crystal and liquid.

Heat Capacity and Entropy

Relative enthalpy data were measured by Björge and Jenssen (1) from 1065 to 1088 K and by Rolin et al. (2) from about 1075 to 1145 K. The data are consistent with liquid heat capacities in the range from roughly 82 to 92 gibbs/mol. We adopt the mean value of 86 gibbs/mol and extrapolate this to higher and lower temperatures. A glass transition is assumed at 700 K and Cp° at lower temperatures is taken to be the same as that of β-Li_3AlF_6. S°_{298} is calculated in a manner analogous to that of the heat of formation.

Melting Data

Tm was observed at 780°C (3), 782°C (2, 4), 783°C (5, 8) and 785°C (1). The last and highest value is adopted for this table. Combination of the observed liquid enthalpies with the adopted crystal enthalpies yields values for ΔHm° of 19.7 kcal/mol (1, authors gave 20.2 ± 1.0) and 21.5 ± 0.3 kcal/mol (2, authors gave 21.5). We adopt the mean value of 20.6 kcal/mol which is confirmed by values of 20.7 (8), 20.8 (4), 22.2 (4), 20.1 (4) and 22.0 (2) derived from crystal-liquid phase data for binary systems. The agreement among values for ΔHm° seemingly excludes the possibility of large dicrepancies in the enthalpies due to formation of the α-phase instead of β during drop-calorimetry from high temperatures.

Vaporization Data

Li_3AlF_6 vaporizes mainly to $LiAlF_4$(g) with small contributions from species such as Li_2AlF_5(g), Li_2F_2(g) and LiF(g) (6, 7).

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Cryolite (Na_3AlF_6)

(Crystal) GFW = 209.9413

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 9.105	- 788.058	- 788.058	INFINITE
100	23.910	14.887	96.217	- 8.133	- 790.237	- 777.645	1699.542
200	42.790	38.074	61.464	- 4.678	- 791.085	- 764.624	835.542
298	51.559	56.990	56.990	.000	- 791.000	- 751.640	550.967
300	51.674	57.309	56.991	.095	- 790.994	- 751.395	547.391
400	56.077	72.846	59.079	5.507	- 792.523	- 738.099	403.278
500	59.191	85.697	63.154	11.271	- 792.034	- 724.546	316.699
600	62.577	96.779	67.854	17.355	- 791.268	- 711.115	259.023
700	66.519	106.715	72.707	23.805	- 790.174	- 697.839	217.875
800	70.941	115.882	77.538	30.675	- 788.704	- 684.745	187.064
900	67.400	126.378	82.428	39.555	- 785.284	- 671.988	163.181
1000	67.400	133.479	87.184	46.295	- 786.602	- 659.283	144.086
1100	67.400	139.903	91.689	53.035	- 785.385	- 646.616	128.471
1200	85.000	146.548	95.972	60.691	- 852.999	- 632.699	115.230
1300	85.000	153.351	100.128	69.191	- 849.457	- 614.483	103.304
1400	85.000	159.651	104.157	77.691	- 845.928	- 596.541	93.124
1500	85.000	165.515	108.054	86.191	- 842.411	- 578.849	84.338
1600	85.000	171.001	111.819	94.691	- 838.906	- 561.394	76.683
1700	85.000	176.154	115.453	103.191	- 835.407	- 544.153	69.956
1800	85.000	181.012	118.962	111.691	- 831.922	- 527.125	64.002
1900	85.000	185.608	122.350	120.191	- 828.444	- 510.283	58.696
2000	85.000	189.968	125.622	128.691	- 824.978	- 493.628	53.941

Sept. 30, 1961; Sept. 30, 1963; Dec. 31, 1963; Dec. 31, 1965; Dec. 31, 1968

CRYOLITE (Na_3AlF_6) (CRYSTAL) GFW = 209.9413

$S°_{298.15}$ = 56.99 ± 0.40 gibbs/mol
Tt ($\alpha \rightarrow \beta$) = 838°K
Tt ($\beta \rightarrow \gamma$) = 1153°K
Tm = 1285°K

$\Delta Hf°_0$ = -788 ± 1 kcal/mol
$\Delta Hf°_{298.15}$ = -791 ± 1 kcal/mol
$\Delta Ht°(\alpha \rightarrow \beta)$ = 1.97 ± 0.40 kcal/mol
$\Delta Ht°(\beta \rightarrow \gamma)$ = 0.09 ± 0.10 kcal/mol
$\Delta Hm°$ = 25.64 kcal/mol

Heat of Formation

The heats of solution of Al(c), NaCl(c), and Na_3AlF_6(c) in 4.36 M HCl acid solution were determined at 303.15°K by Coughlin (1). The enthalpy change for the reaction Al(c) + 2.96 NaCl(c) + 5.96 (HF·5.716 H_2O) + 3.617 $H_2O(\ell)$ = $Na_{2.96}AlF_{5.96}$(c) + 2.96 (HCl·12.731 H_2O) + 3/2 H_2(g) was derived as $\Delta Hr°_{298.15}$ = -153.22 ± 0.14 kcal/mol. Using the $\Delta Hf°_{298}$ data on $H_2O(\ell)$, HCl and HF solution from (2, 3) and NaCl from JANAF Table (4), we calculate the value $\Delta Hf°_{298}$ = -791.2 ± 0.7 kcal/mol for Na_3AlF_6(c).

Baud (5) reported ΔHr° = -40.7 kcal/mol for the reaction $2AlF_3(c) + 6NaF(c) = 2Na_3AlF_6(c)$. Based on JANAF $\Delta Hf°_{298}$ values for AlF_3(c) and NaF(c), we obtain $\Delta Hf°_{298}(Na_3AlF_6, c)$ = -793.7 ± 2 kcal/mol.

Mashovets and Yudin (6) determined the equilibrium constants in the temperature range 1101-1239°K for the reaction $2/3\ Na_3AlF_6(c) + H_2O(g) = 1/3\ Al_2O_3(c) + 2HF(g) + 2NaF(c)$, using the transpiration method. Based on the reported Kp values, we evaluate $\Delta Hr°_{298}$ = 48.1 ± 0.8 and 46.6 kcal/mol by the second and third law methods, respectively. From the third law $\Delta Hr°_{298}$ value, we calculate $\Delta Hf°_{298}(Na_3AlF_6, c)$ = -791.3 kcal/mol.

The equilibrium pressures of sodium vapor in the reaction $2NaF(c) + 1/3\ Al(\ell) = Na(g) + 1/3\ Na_3AlF_6(c)$ at temperatures 1020 - 1150°K were determined by Ono et al. (7), employing differential thermal analysis and X-ray analysis. Since the reported vapor pressures are the total pressures of Na(g) and Na_2(g), we calculate the partial pressures of Na(g) by use of the equilibrium constants for the reaction $Na_2(g) = 2Na(g)$ derived from JANAF functions for Na_2(g) and Na(g). Based on the calculated Na(g) pressures we evaluate the enthalpy change of the above reaction by the third law method to be 109.2 kcal/mol, yielding $\Delta Hf°_{298}(Na_3AlF_6, c)$ = -791.1 kcal/mol.

The amounts of sodium over the mixtures of cryolite and aluminum were measured in the temperature range 1023 - 1373°K by the ultraviolet absorption method by Stokes and Frank (8). The enthalpy change for the reaction $6NaF(\ell) + Al(\ell) = 3Na(g) + Na_3AlF_6(\ell)$ is not evaluated due to lack of appropriate data on the activities of $NaF(\ell)$ and $Na_3AlF_6(\ell)$.

The heat of formation (298°K) for cryolite(c) is adopted as -791 ± 1 kcal/mol.

Heat Capacity and Entropy

The low temperature heat capacities, 53.66 - 296.00°K, were measured by King (9). The values of Cp below 53.66°K are extrapolated using the Cp equation given by King. $S°_{298}$ is derived based on the adopted low temperature heat capacities.

The high temperature enthalpies, 401.3 - 1370.5°K, determined by O'Brien and Kelley (10), are adopted to derive the heat capacities which join smoothly at 298°K with the low temperature Cp's. The heat capacity of $Na_3AlF_6(\gamma)$ is estimated such that the calculated enthalpy at 1200.5°K is consistent with the measured value reported by O'Brien and Kelley. The heat capacity above the melting point is obtained by linear extrapolation.

Frank (21) commented that the enthalpies reported by O'Brien and Kelley were incorrect due to an apparent error in temperature measurement. However, his reported corrected enthalpy values are not used here (see NaF(c) table for details). The high temperature enthalpies have also been measured by the following investigators: Joly, 284.5 - 373.3°K (11); Baud, 289 - 328°K (12); Roth and Bertram, 369 - 1371°K(13); Krestovnikov and Karetnikov, 573 - 1273°K (14); Lyshenko, 290 - 1217°K (15); and Albright, 350.0 - 1311.8°K (16). Their data are not used for evaluation due to inconsistencies among the reported values.

Transition Data

Landon and Ubbelohde (17) determined the electrical conductance (σ) of crystals and melt of cryolite, and observed two transition temperatures from a plot of log σ vs 1/T, i.e. Tt($\alpha \rightarrow \beta$) = 838°K and Tt($\beta \rightarrow \gamma$) = 1153°K, which are adopted here. Other values of Tt($\alpha \rightarrow \beta$) reported are (°K): 823 (16), 833 (18), 834 (19), 835 (20), and 838 (13).

The values of $\Delta Ht°(\alpha \rightarrow \beta)$ and $\Delta Ht°(\beta \rightarrow \gamma)$ are calculated as the difference between the adopted enthalpies for α and β at 838°K and β and γ at 1153°K, respectively. The value of $\Delta Ht°(\alpha \rightarrow \beta)$ has also been reported as (kcal/mol): 1.24 (13), 2.16 (10), 2.24 (20), and 2.38 (16). Landon and Ubbelohde (17) estimated that $\Delta Ht°(\beta \rightarrow \gamma)$ = 0.01 x ΔHm = 0.2 kcal/mol.

The cause of the discrepancies among the reported values for Tt, ΔHt° and the high temperature enthalpies may be due to differences in the sample composition.

Melting Data

See the $Na_3AlF_6(\ell)$ table for details.

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Cryolite (Na_3AlF_6)

(Liquid) GFW = 209.9413

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	51.559	68.544	68.544	.000	- 774.052	- 738.137	541.069
300	51.674	68.863	68.545	.095	- 774.046	- 737.913	537.569
400	56.077	84.400	70.633	5.507	- 775.575	- 725.773	396.544
500	59.191	97.250	74.708	11.271	- 775.086	- 713.375	311.816
600	62.577	108.333	79.408	17.355	- 774.320	- 701.099	255.375
700	66.519	118.269	84.261	23.805	- 773.226	- 688.979	215.109
800	94.700	127.436	89.091	30.676	- 771.755	- 677.040	184.959
900	94.700	138.590	93.984	40.146	- 767.745	- 665.441	161.591
1000	94.700	148.568	98.952	49.616	- 766.333	- 654.103	142.954
1100	94.700	157.593	103.879	59.086	- 762.386	- 643.077	127.767
1200	94.700	165.833	108.704	68.556	- 828.186	- 631.029	114.926
1300	94.700	173.414	113.394	78.026	- 823.674	- 614.781	103.354
1400	94.700	180.432	117.935	87.496	- 819.175	- 598.882	93.490
1500	94.700	186.965	122.321	96.966	- 814.688	- 583.302	84.987
1600	94.700	193.077	126.555	106.436	- 810.213	- 568.023	77.588
1700	94.700	198.818	130.638	115.906	- 805.744	- 553.019	71.095
1800	94.700	204.231	134.578	125.376	- 801.289	- 538.286	65.357
1900	94.700	209.351	138.380	134.846	- 796.841	- 523.793	60.250
2000	94.700	214.209	142.051	144.316	- 792.405	- 509.537	55.680
2100	94.700	218.829	145.598	153.786	- 787.975	- 495.511	51.568
2200	94.700	223.235	149.027	163.256	- 783.557	- 481.686	47.851
2300	94.700	227.444	152.346	172.726	- 779.144	- 468.060	44.476
2400	94.700	231.475	155.560	182.196	- 774.744	- 454.626	41.399
2500	94.700	235.340	158.674	191.666	- 770.353	- 441.387	38.586
2600	94.700	239.055	161.695	201.136	- 765.974	- 428.309	36.003
2700	94.700	242.629	164.626	210.606	- 761.604	- 415.406	33.625
2800	94.700	246.073	167.474	220.076	- 826.656	- 401.839	31.365
2900	94.700	249.396	170.242	229.546	- 822.048	- 386.737	29.145
3000	94.700	252.606	172.934	239.016	- 817.458	- 371.815	27.087

Dec. 31, 1968

CRYOLITE (Na_3AlF_6) (LIQUID) GFW = 209.9413

$S^\circ_{298.15}$ = 68.544 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -774.052 kcal/mol

Tm = 1285°K ΔHm° = 25.64 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1285} - H^\circ_{298}$ for crystal and liquid.

Yudin and Mashovets (1) studied the dissociation of cryolite and reported $K_{1300} = 2.23\times10^{-5}$ for the reaction $Na_3AlF_6(\ell) = 3NaF(\ell) + AlF_3(c)$. Based on this K_{1300} value, we evaluated the enthalpy change by the third law method as 24.3 kcal/mol. Using ΔHf°_{298} = -360.8 and -130.6 kcal/mol for $AlF_3(c)$ and $NaF(\ell)$, respectively, we obtain $\Delta Hf^\circ_{298} = -776.7 \pm 3$ kcal/mol for $Na_3AlF_6(\ell)$.

Heat Capacity and Entropy

The high temperature enthalpies, 1285.5 - 1370.5°K, were measured by O'Brien and Kelley (2). Using their data we derive a constant Cp, 94.7 gibbs/mol, for $Na_3AlF_6(\ell)$. A glass transition temperature is assumed at 800°K., and the heat capacities below 800°K are taken to be the same as those of the $Na_3AlF_6(c)$. The Cp values above 1370.5°K are obtained by linear extrapolation. The entropy, S°_{298}, is calculated in a manner analogous to that of the heat of formation.

Albright (3) measured the high temperature enthalpies of $Na_3AlF_6(\ell)$ in the temperature range 1298.1 - 1311.8°K. However, his data are systematically higher (about 4.9%) than the values determined by O'Brien and Kelley (2), which is also true for the other sets of enthalpy data measured using this calorimeter. Therefore Albright's enthalpy data is not used for evaluation.

Melting Data

The melting point of cryolite has been reported as (°K): 1273 (4), 1279 (3), 1281 (5), 1282 (6, 7), 1293 (9), and 1300 (2). The value of Tm adopted is that determined by Landon and Ubbelohde (8). This value is corrected from the original measured value 1286°K, due to the thermocouple standardization against the freezing points of assay gold giving a gold point of 1064.2 ± 0.15°C compared with the fixed value of 1063.0°C.

The value of ΔHm° is calculated as the difference between the enthalpies at Tm for crystal and liquid. Other reported values of ΔHm° are (in kcal/mol): 16.64 (4), 26.6 (10), 27.64 (2), and 27.91 (3).

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Aluminum Monohydride (AlH)

(Ideal Gas) Mol. Wt. = 27.988

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.071	62.034	62.034	INFINITE
100	6.961	37.259	51.081	- 1.382	62.238	59.897	- 130.898
200	6.968	42.086	45.515	- .686	62.191	57.540	- 62.874
298	7.020	44.875	44.875	.000	62.000	55.291	- 40.527
300	7.022	44.918	44.875	.013	61.995	55.249	- 40.247
400	7.180	46.958	45.152	.722	61.761	53.036	- 28.976
500	7.408	48.584	45.681	1.451	61.513	50.882	- 22.240
600	7.650	49.956	46.282	2.204	61.260	48.780	- 17.767
700	7.874	51.152	46.894	2.981	60.999	46.720	- 14.586
800	8.068	52.217	47.494	3.778	60.727	44.699	- 12.211
900	8.232	53.177	48.073	4.593	60.439	42.713	- 10.372
1000	8.370	54.051	48.628	5.424	57.639	40.944	- 8.948
1100	8.486	54.855	49.158	6.267	57.419	39.285	- 7.805
1200	8.585	55.598	49.664	7.120	57.205	37.646	- 6.856
1300	8.669	56.288	50.147	7.983	56.996	36.024	- 6.056
1400	8.742	56.933	50.609	8.854	56.790	34.419	- 5.373
1500	8.806	57.539	51.051	9.731	56.584	32.829	- 4.783
1600	8.863	58.109	51.475	10.615	56.379	31.252	- 4.269
1700	8.913	58.648	51.881	11.504	56.174	29.688	- 3.816
1800	8.959	59.158	52.271	12.397	55.969	28.135	- 3.416
1900	9.001	59.644	52.647	13.295	55.764	26.595	- 3.059
2000	9.039	60.107	53.008	14.197	55.559	25.065	- 2.739
2100	9.074	60.549	53.357	15.103	55.352	23.545	- 2.450
2200	9.107	60.971	53.693	16.012	55.146	22.036	- 2.189
2300	9.138	61.377	54.019	16.924	54.938	20.535	- 1.951
2400	9.168	61.767	54.333	17.840	54.730	19.044	- 1.734
2500	9.196	62.141	54.638	18.758	54.521	17.561	- 1.535
2600	9.222	62.503	54.934	19.679	54.312	16.086	- 1.352
2700	9.248	62.851	55.221	20.602	54.102	14.619	- 1.183
2800	9.272	63.188	55.499	21.528	- 16.663	14.814	- 1.156
2900	9.296	63.514	55.770	22.457	- 16.670	15.938	- 1.201
3000	9.319	63.829	56.033	23.387	- 16.679	17.063	- 1.243
3100	9.341	64.135	56.290	24.320	- 16.687	18.188	- 1.282
3200	9.363	64.432	56.540	25.256	- 16.696	19.313	- 1.319
3300	9.384	64.720	56.783	26.193	- 16.706	20.440	- 1.354
3400	9.405	65.001	57.021	27.132	- 16.715	21.563	- 1.386
3500	9.426	65.274	57.253	28.074	- 16.726	22.689	- 1.417
3600	9.446	65.540	57.479	29.018	- 16.736	23.817	- 1.446
3700	9.465	65.799	57.701	29.963	- 16.748	24.942	- 1.473
3800	9.485	66.051	57.917	30.911	- 16.760	26.070	- 1.499
3900	9.504	66.298	58.129	31.860	- 16.773	27.199	- 1.524
4000	9.523	66.539	58.336	32.811	- 16.787	28.325	- 1.548
4100	9.542	66.774	58.539	33.765	- 16.802	29.451	- 1.570
4200	9.561	67.004	58.738	34.720	- 16.818	30.581	- 1.591
4300	9.579	67.230	58.933	35.677	- 16.835	31.710	- 1.612
4400	9.597	67.450	59.124	36.636	- 16.853	32.836	- 1.631
4500	9.615	67.666	59.311	37.596	- 16.873	33.969	- 1.650
4600	9.633	67.877	59.495	38.559	- 16.894	35.100	- 1.668
4700	9.651	68.085	59.676	39.523	- 16.917	36.227	- 1.684
4800	9.669	68.288	59.853	40.489	- 16.941	37.358	- 1.701
4900	9.687	68.488	60.027	41.457	- 16.968	38.494	- 1.717
5000	9.704	68.684	60.198	42.426	- 16.997	39.623	- 1.732
5100	9.722	68.876	60.367	43.398	- 17.028	40.758	- 1.747
5200	9.739	69.065	60.532	44.371	- 17.062	41.889	- 1.760
5300	9.756	69.251	60.695	45.345	- 17.098	43.025	- 1.774
5400	9.773	69.433	60.855	46.322	- 17.139	44.159	- 1.787
5500	9.791	69.613	61.013	47.300	- 17.182	45.292	- 1.800
5600	9.808	69.789	61.168	48.280	- 17.230	46.430	- 1.812
5700	9.825	69.963	61.321	49.262	- 17.281	47.566	- 1.824
5800	9.842	70.134	61.471	50.245	- 17.337	48.706	- 1.835
5900	9.859	70.302	61.619	51.230	- 17.397	49.847	- 1.846
6000	9.876	70.468	61.765	52.217	- 17.463	50.984	- 1.857

Dec. 31, 1960; June 30, 1963

ALUMINUM MONOHYDRIDE (AlH) (IDEAL GAS) MOL. WT. = 27.988

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0}$ = 62.0 ± 5.0 kcal mole^{-1}

$S^\circ_{298.15}$ = 44.875 cal deg^{-1} mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 62.0 ± 5.0 kcal mole^{-1}

Electronic Levels and Multiplicities

ε, cm^{-1}	g_i
0	1

ω_e = 1682.56 cm^{-1}

$\omega_e x_e$ = 28.09 cm^{-1}

σ = 1

B_e = 6.3907 cm^{-1}

α_e = 0.1858 cm^{-1}

r_e = 1.6477 Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies", 2nd Ed., Chapman Hall, Ltd., London (1953), extrapolated the available $X^1\Sigma$ vibrational levels and also considered predissociation in the $A^1\Pi$ state and concluded that the best value of D_0° was 2.9 ± 0.2 e.v. The linear Birge-Sponer extrapolation gave a value of 3.05 e.v. while the predissociation limit was 3.07 e.v. Gaydon's recommended value is adopted here and leads to a vlaue of $\Delta H^\circ_{f\ 298.15}$ = 62.16 ± 5.0 kcal mole^{-1} using JANAF auxiliary data.

Heat Capacity and Entropy

P. B. Zeeman and G. J. Ritter, Can. J. Phys. 32, 555 (1954) examined the UV band system of AlH under high resolution and reported the molecular constants adopted above.

Aluminum Oxide Hydride (HAlO)

(Ideal Gas) Mol. Wt. = 43.988

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.155	8.988	8.988	INFINITE
100	6.957	43.532	58.135	-1.460	8.841	7.948	-17.370
200	7.242	48.400	52.183	-.756	8.462	7.171	-7.836
298	8.262	51.464	51.464	.000	8.000	6.632	-4.861
300	8.285	51.515	51.464	.015	7.991	6.623	-4.825
400	9.541	54.072	51.804	.907	7.584	6.231	-3.404
500	10.634	56.323	52.487	1.918	7.252	5.932	-2.593
600	11.495	58.341	53.298	3.026	6.977	5.695	-2.074
700	12.154	60.165	54.151	4.210	6.734	5.501	-1.717
800	12.656	61.822	55.008	5.452	6.508	5.340	-1.459
900	13.042	63.336	55.850	6.737	6.283	5.208	-1.265
1000	13.342	64.726	56.669	8.057	3.559	5.285	-1.155
1100	13.578	66.009	57.461	9.404	3.423	5.464	-1.086
1200	13.767	67.199	58.223	10.771	3.299	5.656	-1.030
1300	13.919	68.307	58.957	12.156	3.183	5.856	-.984
1400	14.043	69.344	59.662	13.554	3.073	6.066	-.947
1500	14.146	70.316	60.340	14.964	2.964	6.285	-.916
1600	14.232	71.232	60.993	16.383	2.855	6.509	-.889
1700	14.304	72.097	61.621	17.810	2.748	6.741	-.867
1800	14.366	72.916	62.226	19.243	2.638	6.978	-.847
1900	14.418	73.695	62.809	20.683	2.527	7.224	-.831
2000	14.464	74.435	63.372	22.127	2.414	7.473	-.817
2100	14.503	75.142	63.916	23.575	2.298	7.728	-.804
2200	14.538	75.817	64.441	25.027	2.178	7.990	-.794
2300	14.568	76.464	64.950	26.482	2.055	8.257	-.785
2400	14.594	77.085	65.443	27.941	1.929	8.530	-.777
2500	14.618	77.681	65.921	29.401	1.798	8.807	-.770
2600	14.639	78.255	66.384	30.864	1.665	9.090	-.764
2700	14.658	78.808	66.834	32.329	1.528	9.377	-.759
2800	14.675	79.341	67.271	33.796	-69.168	11.323	-.884
2900	14.690	79.856	67.696	35.264	-69.110	14.198	-1.070
3000	14.704	80.355	68.110	36.734	-69.055	17.070	-1.243
3100	14.716	80.837	68.513	38.205	-69.004	19.940	-1.406
3200	14.728	81.304	68.905	39.677	-68.958	22.807	-1.558
3300	14.738	81.758	69.288	41.150	-68.914	25.675	-1.700
3400	14.748	82.198	69.661	42.624	-68.874	28.539	-1.834
3500	14.756	82.626	70.026	44.100	-68.838	31.402	-1.961
3600	14.764	83.041	70.381	45.576	-68.805	34.269	-2.080
3700	14.772	83.446	70.729	47.052	-68.777	37.130	-2.193
3800	14.779	83.840	71.069	48.530	-68.751	39.994	-2.300
3900	14.785	84.224	71.401	50.008	-68.730	42.855	-2.401
4000	14.791	84.598	71.727	51.487	-68.712	45.715	-2.498
4100	14.796	84.964	72.045	52.966	-68.698	48.574	-2.589
4200	14.801	85.320	72.357	54.446	-68.688	51.435	-2.676
4300	14.806	85.669	72.662	55.927	-68.681	54.296	-2.759
4400	14.810	86.009	72.962	57.407	-68.680	57.152	-2.839
4500	14.814	86.342	73.256	58.889	-68.681	60.015	-2.915
4600	14.818	86.668	73.544	60.370	-68.686	62.878	-2.987
4700	14.822	86.986	73.826	61.852	-68.696	65.734	-3.056
4800	14.825	87.298	74.104	63.335	-68.710	68.595	-3.123
4900	14.828	87.604	74.376	64.817	-68.728	71.458	-3.187
5000	14.831	87.904	74.644	66.300	-68.751	74.315	-3.248
5100	14.834	88.197	74.906	67.783	-68.779	77.181	-3.307
5200	14.837	88.485	75.165	69.267	-68.812	80.039	-3.364
5300	14.839	88.768	75.419	70.751	-68.848	82.906	-3.419
5400	14.842	89.045	75.669	72.235	-68.892	85.767	-3.471
5500	14.844	89.318	75.914	73.719	-68.939	88.631	-3.522
5600	14.846	89.585	76.156	75.204	-68.994	91.497	-3.571
5700	14.848	89.848	76.394	76.688	-69.055	94.361	-3.618
5800	14.850	90.106	76.628	78.173	-69.121	97.232	-3.664
5900	14.852	90.360	76.859	79.658	-69.195	100.102	-3.708
6000	14.854	90.610	77.086	81.144	-69.276	102.970	-3.750

Dec. 31, 1960; Mar. 31, 1964

ALUMINUM OXIDE HYDRIDE (HAlO) (IDEAL GAS) MOL. WT. = 43.988

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [51.464] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = [9 ± 20] kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [8 ± 20] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[900] (1)
[1000] (2)
[1600] (1)

Bond Distance: Al=O = [1.62] Å Al-H = [1.64] Å

Bond Angle: H-Al-O = [180°]

σ = 1

B_0 = [0.5271] cm.$^{-1}$

Heat of Formation.

The heat of formation was estimated by summing the constituent bond energies. The Al=O was taken as that in AlO(g) and the Al-H bond was taken as that in AlH(g), this gave a heat of atomization of 182 kcal.

Heat Capacity and Entropy.

Vibrational frequencies, bond lengths and angles and point group were taken from National Bureau of Standards Report 6297, Jan. 1, 1959, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine".

Aluminum Monohydroxide (AlOH)

(Ideal Gas) GFW = 43.9889

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.110	-41.967	-41.967	INFINITE
100	6.955	43.955	58.108	-1.415	-42.104	-43.046	94.076
200	7.063	48.792	52.377	-.717	-42.498	-43.868	47.936
298	7.628	51.701	51.701	.000	-43.000	-44.439	32.575
300	7.643	51.748	51.701	.014	-43.010	-44.448	32.380
400	8.526	54.065	52.011	.822	-43.504	-44.851	24.506
500	9.386	56.062	52.626	1.718	-43.953	-45.135	19.729
600	10.110	57.840	53.349	2.694	-44.364	-45.333	16.513
700	10.699	59.444	54.107	3.736	-44.747	-45.464	14.194
800	11.181	60.905	54.867	4.830	-45.122	-45.541	12.441
900	11.585	62.246	55.614	5.969	-45.508	-45.570	11.066
1000	11.929	63.485	56.340	7.145	-48.437	-45.372	9.916
1100	12.227	64.636	57.042	8.354	-48.770	-45.050	8.951
1200	12.487	65.712	57.720	9.590	-49.084	-44.698	8.141
1300	12.715	66.720	58.374	10.850	-49.383	-44.320	7.451
1400	12.916	67.670	59.005	12.132	-49.669	-43.919	6.856
1500	13.093	68.567	59.612	13.432	-49.946	-43.499	6.338
1600	13.251	69.418	60.199	14.750	-50.215	-43.061	5.882
1700	13.390	70.225	60.765	16.082	-50.476	-42.605	5.477
1800	13.515	70.994	61.312	17.427	-50.732	-42.134	5.116
1900	13.625	71.728	61.841	18.784	-50.984	-41.650	4.791
2000	13.725	72.429	62.353	20.152	-51.233	-41.154	4.497
2100	13.813	73.101	62.849	21.529	-51.480	-40.644	4.230
2200	13.893	73.746	63.330	22.914	-51.725	-40.122	3.986
2300	13.965	74.365	63.796	24.307	-51.968	-39.587	3.762
2400	14.030	74.960	64.249	25.707	-52.211	-39.043	3.555
2500	14.089	75.534	64.689	27.113	-52.456	-38.493	3.365
2600	14.142	76.088	65.117	28.525	-52.699	-37.928	3.188
2700	14.190	76.623	65.533	29.941	-52.944	-37.356	3.024
2800	14.235	77.140	65.939	31.363	-122.600	-35.944	2.806
2900	14.275	77.640	66.334	32.788	-122.584	-32.849	2.476
3000	14.312	78.124	66.719	34.217	-122.571	-29.755	2.168
3100	14.346	78.594	67.094	35.650	-122.557	-26.661	1.880
3200	14.377	79.050	67.461	37.086	-122.546	-23.567	1.610
3300	14.406	79.493	67.819	38.526	-122.536	-20.474	1.356
3400	14.432	79.923	68.168	39.967	-122.530	-17.384	1.117
3500	14.457	80.342	68.510	41.412	-122.524	-14.292	.892
3600	14.479	80.750	68.844	42.859	-122.520	-11.196	.680
3700	14.500	81.147	69.172	44.308	-122.520	-8.105	.479
3800	14.520	81.534	69.492	45.759	-122.521	-5.013	.288
3900	14.538	81.911	69.806	47.212	-122.524	-1.919	.108
4000	14.555	82.279	70.113	48.666	-122.532	1.171	-.064
4100	14.571	82.639	70.414	50.123	-122.541	4.262	-.227
4200	14.586	82.990	70.709	51.580	-122.552	7.357	-.383
4300	14.599	83.334	70.999	53.040	-122.567	10.451	-.531
4400	14.612	83.669	71.283	54.500	-122.585	13.545	-.673
4500	14.625	83.998	71.562	55.962	-122.606	16.638	-.808
4600	14.636	84.320	71.836	57.425	-122.629	19.736	-.938
4700	14.647	84.634	72.105	58.889	-122.658	22.826	-1.061
4800	14.657	84.943	72.369	60.355	-122.689	25.922	-1.180
4900	14.666	85.245	72.629	61.821	-122.723	29.022	-1.294
5000	14.675	85.542	72.884	63.288	-122.762	32.116	-1.404
5100	14.684	85.832	73.135	64.756	-122.805	35.218	-1.509
5200	14.692	86.118	73.382	66.225	-122.852	38.312	-1.610
5300	14.700	86.397	73.625	67.694	-122.904	41.415	-1.708
5400	14.707	86.672	73.864	69.165	-122.960	44.514	-1.802
5500	14.714	86.942	74.099	70.636	-123.022	47.615	-1.892
5600	14.720	87.207	74.331	72.107	-123.090	50.718	-1.979
5700	14.726	87.468	74.559	73.580	-123.161	53.821	-2.064
5800	14.732	87.724	74.784	75.053	-123.241	56.930	-2.145
5900	14.738	87.976	75.005	76.526	-123.326	60.037	-2.224
6000	14.743	88.224	75.224	78.000	-123.417	63.145	-2.300

Mar. 31, 1964; Dec. 31, 1967

ALUMINUM MONOHYDROXIDE (AlOH) (IDEAL GAS) GFW = 43.9889

Point Group [$C_{\infty v}$] ΔHf°_0 = [-42 ± 3] kcal/mol

$S^\circ_{298.15}$ = [51.7 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-43 ± 3] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1000] (1)
[1300] (2)
[3600] (1)

Bond Distance: Al-O = [1.87] Å O-H = [0.96] Å
Bond Angle: Al-O-H = [180°] σ = 1
Rotational Constant: B_0 = [0.4256] cm^{-1}

Heat of Formation

From a mass-spectrometric investigation of the equilibrium

$$1/3Al_2O_3(c) + 1/3Al(g) + 1/2D_2(g) = AlOD(g)$$

M. Farber et al. (1) report second law heats of reaction of 56.7 ± 0.6 kcal at 1980°K, 57.1 ± 2.8 kcal at 2060°K and 62.7 ± 1.4 kcal at 2000°K. Using JANAF auxilliary data, assuming AlOD to be AlOH, we obtain ΔHf°_{298}(AlOD, g) = -44.6 ± 1, -44.0 ± 3.2 and -38.6 ± 1.8 kcal/mol. A second equilibrium in the same investigation was

$$Al_2O(g) + D_2O(g) = 2AlOD(g)$$

for which second law heats of reaction of 6.3 ± 2.1 kcal at 2060°K and 5.7 ± 0.8 kcal at 2000°K were reported. Farber et al. also measured the heat of reaction

$$1/3Al_2O_3(c) + 4/3\ Al(g) = Al_2O(g)$$

at the same temperatures as -10.7 ± 2.8 kcal at 2060° and -10.3 ± 10.2 kcal at 2000°K. Combining these reactions and eliminating $Al_2O(g)$ yields ΔHr_{2060} = -4.4 ± 5.0 kcal and ΔH_{2000} = -5 ± 11 kcal for the reaction

$$1/3Al_2O_3(c) + 4/3Al(g) + D_2O(g) = 2AlOD(g).$$

Using auxiliary JANAF values for $Al_2O_3(c)$ and Al(g), $\Delta Hf^\circ_{298}(D_2O, g)$ = -59.56 kcal/mol (2), and functions for $D_2O(g)$ from Friedman and Haar (3) we obtain ΔHf°_{298}(AlOD, g) = -43.9 ± 6 kcal/mol and -43.4 ± 3 kcal/mol. From all the above results we adopt a value of ΔHf°_{298}(AlOD, g) = -44 ± 3 kcal/mol, assuming that AlOH is less stable than AlOD by 1 kcal/mol as is the case for H_2O, HDO and D_2O, we obtain ΔHf°_{298}(AlOH, g) = -43 ± 3 kcal/mol.

Farber et al. (1) also performed weight loss experiments under molecular flow conditions by allowing hydrogen to flow over $Al_2O_3(c)$. The products assumed were AlOH(g), Al(g), $Al_2O(g)$, H(g) and $H_2O(g)$ and the equilibrium amounts of H(g), Al(g) and $Al_2O(g)$ were assumed to be those predicted by the free energies from the JANAF tables. A 3rd law analysis of the equilibrium constants given by Farber for the reaction $2H_2(g) + Al_2O_3(c) = 2AlOH(g) + H_2O(g)$ yields ΔHr°_{298} = 238 ± 12 kcal/mol and ΔHf°_{298}(AlOH, g) = -52 ± 6 kcal/mol. However, the assumed equilibria involving $Al_2O(g)$ and Al(g) may be significantly in error and thus the ΔHf°_{298} should be considered as simply confirming the magnitude determined mass-spectrometrically.

References

1. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Final Report, under USAF contract F04611-67-C-0010, AFRPL-TR-67-244, November 1967.
2. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
3. A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).

Heat Capacity and Entropy

The vibrational frequencies are estimated by using the AlO(g) fundamental as approximately the Al-O stretch; the O-H stretch is that in $H_2O(g)$; and the bending frequency is approximately the OH bend in $CD_3OH(g)$ reported by T. Shimanouchi, U. S. Natl. Bur. Std. NSRDS-NBS 6, 1967.

The AlO bond length was taken from U. S. Natl. Bur. Std. Report No. 6297, Jan. 1, 1959, and the OH bond length is assumed to be that in $H_2O(g)$. The bond angle is assumed to be 180° using the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAB" molecules with less than 11 valence electrons. Confirmation of this prediction is scanty for molecules having A more electronegative than B; however, R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966), have confirmed the linearity of KOH and CsOH which have 8 valence electrons.

Aluminum Monohydroxide Unipositive Ion ($AlOH^+$)

(Ideal Gas) GFW = 43.98832

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	8.015	54.632	54.632	.000	130.000	126.200	-92.507
300	8.034	54.682	54.632	.015	130.000	126.176	-91.919
400	9.079	57.138	54.960	.871	130.052	124.896	-68.240
500	9.962	59.262	55.613	1.825	130.156	123.596	-54.024
600	10.643	61.142	56.381	2.857	130.299	122.270	-44.537
700	11.167	62.823	57.183	3.948	130.461	120.919	-37.753
800	11.586	64.343	57.984	5.087	130.628	119.545	-32.658
900	11.933	65.728	58.769	6.263	130.776	118.151	-28.691
1000	12.229	67.001	59.529	7.472	128.376	116.924	-25.554
1100	12.487	68.179	60.263	8.708	128.568	115.770	-23.001
1200	12.713	69.275	60.969	9.968	128.775	114.598	-20.871
1300	12.913	70.301	61.648	11.249	128.994	113.406	-19.065
1400	13.090	71.264	62.300	12.550	129.223	112.200	-17.515
1500	13.248	72.173	62.929	13.867	129.460	110.975	-16.169
1600	13.389	73.033	63.533	15.199	129.702	109.734	-14.989
1700	13.514	73.848	64.116	16.544	129.951	108.480	-13.946
1800	13.626	74.624	64.679	17.901	130.203	107.209	-13.017
1900	13.726	75.363	65.222	19.269	130.458	105.926	-12.184
2000	13.816	76.070	65.747	20.646	130.716	104.627	-11.433
2100	13.897	76.746	66.255	22.032	130.975	103.314	-10.752
2200	13.970	77.394	66.746	23.425	131.235	101.991	-10.132
2300	14.036	78.017	67.223	24.826	131.496	100.657	-9.565
2400	14.095	78.615	67.685	26.232	131.756	99.313	-9.044
2500	14.149	79.192	68.134	27.644	132.014	97.952	-8.563
2600	14.198	79.748	68.570	29.062	132.274	96.586	-8.119
2700	14.242	80.284	68.994	30.484	132.531	95.209	-7.707
2800	14.283	80.803	69.406	31.910	63.378	94.651	-7.388
2900	14.320	81.305	69.808	33.340	63.894	95.760	-7.217
3000	14.354	81.791	70.200	34.774	64.409	96.848	-7.055
3100	14.386	82.262	70.581	36.211	64.924	97.921	-6.903
3200	14.414	82.719	70.953	37.651	65.436	98.980	-6.760
3300	14.441	83.163	71.317	39.094	65.946	100.021	-6.624
3400	14.465	83.595	71.671	40.539	66.452	101.043	-6.495
3500	14.488	84.014	72.018	41.987	66.958	102.053	-6.373
3600	14.509	84.423	72.357	43.437	67.462	103.052	-6.256
3700	14.528	84.821	72.689	44.889	67.962	104.029	-6.145
3800	14.547	85.208	73.013	46.342	68.460	105.000	-6.039
3900	14.563	85.586	73.330	47.798	68.957	105.957	-5.938
4000	14.579	85.955	73.641	49.255	69.448	106.895	-5.840
4100	14.594	86.315	73.946	50.714	69.938	107.823	-5.747
4200	14.608	86.667	74.245	52.174	70.426	108.746	-5.659
4300	14.620	87.011	74.538	53.635	70.910	109.653	-5.573
4400	14.632	87.347	74.825	55.098	71.392	110.550	-5.491
4500	14.644	87.676	75.107	56.562	71.868	111.431	-5.412
4600	14.654	87.998	75.384	58.027	72.344	112.310	-5.336
4700	14.664	88.314	75.656	59.493	72.814	113.168	-5.262
4800	14.674	88.623	75.923	60.959	73.282	114.020	-5.191
4900	14.683	88.925	76.185	62.427	73.747	114.870	-5.123
5000	14.691	89.222	76.443	63.896	74.206	115.701	-5.057
5100	14.699	89.513	76.696	65.366	74.661	116.528	-4.994
5200	14.707	89.798	76.945	66.836	75.112	117.342	-4.932
5300	14.714	90.079	77.190	68.307	75.559	118.152	-4.872
5400	14.720	90.354	77.432	69.779	76.001	118.949	-4.814
5500	14.727	90.624	77.669	71.251	76.437	119.740	-4.758
5600	14.733	90.889	77.903	72.724	76.867	120.521	-4.704
5700	14.739	91.150	78.133	74.197	77.293	121.300	-4.651
5800	14.744	91.406	78.360	75.672	77.712	122.068	-4.600
5900	14.749	91.659	78.583	77.146	78.125	122.830	-4.550
6000	14.754	91.906	78.803	78.621	78.532	123.586	-4.502

Dec. 31, 1967

ALUMINUM MONOHYDROXIDE UNIPOSITIVE ION ($AlOH^+$) (IDEAL GAS) GFW = 43.98832

Point Group [$C_{\infty v}$] ΔHf°_0 = [131 ± 26] kcal/mol

$S^\circ_{298.15}$ = [54.6 ± 0.5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [130 ± 26] kcal/mol

Ground State Quantum Weight = [4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[900] (1)
[1100] (2)
[3600] (1)

Bond Distance: Al-O = [1.90] Å O-H = [0.96] Å

Bond Angle: Al-O-H = [180°] σ = 1

Rotational Constant: B_0 = [0.413] cm^{-1}

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(AlOH, g) and its ionization potential, which is estimated to be 7.5 ± 1 eV (173 ± 23 kcal). The ionization potential is estimated from a reported value of 7.5 eV for the appearance potential of $AlOD^+$, presumably from the parent AlOD, by M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, Space Sciences, Inc., Final Report under USAF contract F04611-67-C-0010, AFRPL-TR-67-244, November, 1967.

Heat Capacity and Entropy

According to the correlation diagram given by A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAB" molecules, a compound with 9 valence electrons would have the three outermost electrons in an unfilled Π orbital. Thus, it would be a $^2\Pi$ state since the molecule ought to be linear if it has less than 11 valence electrons. The outermost orbital is a bonding orbital and thus the loss of an electron from it would weaken the bonding. The vibrational frequencies are estimated from those for AlOH(g) with somewhat lower frequencies due to the weaker bonding. Similarly, the Al-O bond length is slightly increased over that in AlOH(g). The enthalpy at 0°K is -2.138 kcal/mol.

Aluminum Monohydroxide Uninegative Ion ($AlOH^-$)

(Ideal Gas) GFW = 43.98942

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	8.729	57.304	57.304	.000	-55.000	-56.622	41.505
300	8.742	57.358	57.304	.016	-55.017	-56.632	41.257
400	9.454	59.972	57.655	.927	-55.905	-57.036	31.163
500	10.040	62.147	58.342	1.903	-56.772	-57.218	25.010
600	10.489	64.019	59.136	2.930	-57.628	-57.227	20.845
700	10.841	65.664	59.953	3.997	-58.482	-57.091	17.825
800	11.131	67.131	60.761	5.096	-59.349	-56.835	15.527
900	11.381	68.456	61.543	6.222	-60.245	-56.467	13.712
1000	11.603	69.667	62.296	7.371	-63.698	-55.814	12.198
1100	11.803	70.783	63.017	8.542	-64.566	-54.985	10.925
1200	11.984	71.818	63.708	9.731	-65.424	-54.077	9.849
1300	12.148	72.783	64.369	10.938	-66.271	-53.096	8.926
1400	12.296	73.689	65.003	12.160	-67.114	-52.050	8.125
1500	12.429	74.542	65.611	13.397	-67.952	-50.945	7.423
1600	12.550	75.348	66.195	14.646	-68.787	-49.785	6.800
1700	12.658	76.112	66.756	15.906	-69.617	-48.571	6.244
1800	12.756	76.839	67.296	17.177	-70.443	-47.308	5.744
1900	12.844	77.531	67.816	18.457	-71.269	-46.002	5.291
2000	12.923	78.192	68.319	19.746	-72.094	-44.652	4.879
2100	12.995	78.824	68.804	21.042	-72.919	-43.258	4.502
2200	13.060	79.430	69.273	22.344	-73.744	-41.827	4.155
2300	13.119	80.012	69.728	23.653	-74.567	-40.355	3.835
2400	13.172	80.571	70.168	24.968	-75.393	-38.850	3.538
2500	13.220	81.110	70.595	26.288	-76.220	-37.314	3.262
2600	13.265	81.629	71.009	27.612	-77.048	-35.739	3.004
2700	13.305	82.131	71.412	28.940	-77.878	-34.137	2.763
2800	13.342	82.615	71.804	30.273	-148.120	-31.671	2.472
2900	13.375	83.084	72.185	31.609	-148.690	-27.502	2.073
3000	13.406	83.538	72.555	32.948	-149.263	-23.311	1.698
3100	13.435	83.978	72.917	34.290	-149.838	-19.103	1.347
3200	13.461	84.405	73.269	35.634	-150.415	-14.879	1.016
3300	13.485	84.820	73.613	36.982	-150.994	-10.634	.704
3400	13.507	85.223	73.949	38.331	-151.576	-6.375	.410
3500	13.528	85.614	74.276	39.683	-152.159	-2.096	.131
3600	13.547	85.996	74.597	41.037	-152.746	2.203	-.134
3700	13.565	86.367	74.910	42.393	-153.336	6.517	-.385
3800	13.581	86.729	75.216	43.750	-153.928	10.843	-.624
3900	13.597	87.082	75.516	45.109	-154.522	15.188	-.851
4000	13.611	87.427	75.809	46.469	-155.120	19.546	-1.068
4100	13.625	87.763	76.097	47.831	-155.720	23.920	-1.275
4200	13.637	88.091	76.378	49.194	-156.323	28.308	-1.473
4300	13.649	88.412	76.654	50.559	-156.930	32.711	-1.663
4400	13.660	88.726	76.925	51.924	-157.540	37.128	-1.844
4500	13.671	89.033	77.191	53.291	-158.153	41.560	-2.018
4600	13.680	89.334	77.452	54.658	-158.768	46.008	-2.186
4700	13.689	89.628	77.708	56.027	-159.390	50.462	-2.346
4800	13.698	89.917	77.959	57.396	-160.014	54.935	-2.501
4900	13.706	90.199	78.206	58.766	-160.640	59.421	-2.650
5000	13.714	90.476	78.449	60.137	-161.271	63.914	-2.794
5100	13.721	90.748	78.687	61.509	-161.908	68.431	-2.932
5200	13.728	91.014	78.922	62.881	-162.548	72.946	-3.066
5300	13.735	91.276	79.152	64.255	-163.193	77.487	-3.195
5400	13.741	91.533	79.379	65.628	-163.843	82.032	-3.320
5500	13.747	91.785	79.602	67.003	-164.499	86.589	-3.441
5600	13.752	92.032	79.822	68.378	-165.159	91.164	-3.558
5700	13.758	92.276	80.038	69.753	-165.825	95.740	-3.671
5800	13.763	92.515	80.252	71.129	-166.498	100.341	-3.781
5900	13.767	92.751	80.461	72.506	-167.177	104.948	-3.888
6000	13.772	92.982	80.668	73.883	-167.863	109.563	-3.991

Dec. 31, 1967

ALUMINUM MONOHYDROXIDE UNINEGATIVE ION ($AlOH^-$) (IDEAL GAS) GFW = 43.98942

Point Group [C_s]

ΔHf°_0 = [-54.33 ± 23] kcal/mol

$S^\circ_{298.15}$ = [57.3 ± 0.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-55 ± 23] kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[900] (1)
[1100] (1)
[3600] (1)

Bond Distance: Al-O = [1.90] Å O-H = [0.96] Å

Bond Angle: Al-O-H = [120°] σ = 1

Product of the moments of Inertia: $I_A I_B I_C$ = [4.554×10^{-117}] g^3 cm^6

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(AlOH, g) and its electron affinity, which is estimated to be 0.5 ± 0.9 eV (12 ± 20 kcal). The electron affinity is estimated to be small, or even negative, since the additional electron must go into an antibonding orbital, according to the correlation diagram of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

Heat Capacity and Entropy

Since the molecule now has 11 valence electrons, the Walsh correlation diagram predicts a bent molecule. The extra electron is antibonding thus making the bonds weaker than in AlOH(g). Thus the vibrational frequencies and bond lengths are taken to be the same as in $AlOH^+$(g), which is also less strongly bound than AlOH(g). The bond angle is arbitrarily chosen as 120°. The principal moments of inertia are $I_A = 6.536 \times 10^{-39}$ g cm^2, $I_B = 0.105 \times 10^{-39}$ g cm^2 and $I_C = 6.641 \times 10^{-39}$ g cm^2. The enthalpy at 0°K is -2.419 kcal/mol.

Aluminum Dioxyhdride (AlO_2H)

(Ideal Gas) GFW = 59.98827

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.801	-108.620	-108.620	INFINITE
100	8.244	50.112	70.130	-2.002	-109.000	-108.488	237.100
200	10.137	56.367	61.809	-1.088	-109.526	-107.790	117.787
298	11.983	60.770	60.770	.000	-110.000	-106.838	78.314
300	12.014	60.844	60.770	.022	-110.008	-106.818	77.817
400	13.483	64.512	61.260	1.301	-110.387	-105.695	57.749
500	14.566	67.643	62.231	2.706	-110.693	-104.485	45.670
600	15.360	70.373	63.366	4.204	-110.959	-103.219	37.597
700	15.961	72.788	64.543	5.771	-111.206	-101.908	31.817
800	16.436	74.951	65.711	7.392	-111.453	-100.564	27.473
900	16.825	76.910	66.848	9.056	-111.721	-99.187	24.086
1000	17.154	78.700	67.945	10.755	-114.541	-97.595	21.329
1100	17.436	80.349	68.999	12.485	-114.772	-95.890	19.052
1200	17.681	81.877	70.009	14.241	-114.990	-94.164	17.150
1300	17.894	83.300	70.977	16.020	-115.198	-92.420	15.537
1400	18.081	84.634	71.906	17.819	-115.399	-90.660	14.153
1500	18.246	85.887	72.796	19.636	-115.595	-88.886	12.951
1600	18.391	87.069	73.652	21.468	-115.788	-87.100	11.897
1700	18.519	88.188	74.474	23.313	-115.977	-85.300	10.966
1800	18.632	89.250	75.266	25.171	-116.165	-83.489	10.137
1900	18.733	90.260	76.029	27.039	-116.354	-81.669	9.394
2000	18.823	91.223	76.764	28.917	-116.542	-79.840	8.725
2100	18.904	92.143	77.475	30.804	-116.732	-78.000	8.118
2200	18.976	93.025	78.162	32.698	-116.925	-76.152	7.565
2300	19.041	93.870	78.827	34.599	-117.117	-74.293	7.059
2400	19.099	94.681	79.470	36.506	-117.315	-72.424	6.595
2500	19.151	95.462	80.095	38.418	-117.517	-70.555	6.168
2600	19.199	96.214	80.700	40.336	-117.720	-68.670	5.772
2700	19.242	96.939	81.288	42.258	-117.929	-66.781	5.406
2800	19.282	97.640	81.860	44.184	-187.551	-64.052	5.000
2900	19.318	98.317	82.416	46.114	-187.505	-59.641	4.495
3000	19.351	98.973	82.957	48.048	-187.463	-55.233	4.024
3100	19.381	99.608	83.484	49.984	-187.425	-50.825	3.583
3200	19.408	100.223	83.997	51.924	-187.391	-46.420	3.170
3300	19.434	100.821	84.498	53.866	-187.362	-42.015	2.783
3400	19.457	101.402	84.987	55.810	-187.338	-37.613	2.418
3500	19.479	101.966	85.464	57.757	-187.316	-33.211	2.074
3600	19.499	102.515	85.930	59.706	-187.300	-28.804	1.749
3700	19.518	103.049	86.385	61.657	-187.289	-24.403	1.441
3800	19.535	103.570	86.831	63.610	-187.281	-20.000	1.150
3900	19.551	104.078	87.266	65.564	-187.277	-15.598	.874
4000	19.566	104.573	87.693	67.520	-187.279	-11.198	.612
4100	19.580	105.056	88.111	69.477	-187.284	-6.797	.362
4200	19.593	105.528	88.520	71.436	-187.293	-2.393	.125
4300	19.605	105.989	88.921	73.396	-187.308	2.011	-.102
4400	19.617	106.440	89.314	75.357	-187.326	6.414	-.319
4500	19.627	106.881	89.699	77.319	-187.350	10.816	-.525
4600	19.637	107.313	90.077	79.282	-187.376	15.225	-.723
4700	19.647	107.735	90.449	81.246	-187.410	19.624	-.913
4800	19.656	108.149	90.813	83.211	-187.447	24.030	-1.094
4900	19.664	108.554	91.171	85.177	-187.487	28.438	-1.268
5000	19.672	108.952	91.523	87.144	-187.534	32.841	-1.435
5100	19.679	109.341	91.868	89.112	-187.586	37.255	-1.596
5200	19.687	109.723	92.208	91.080	-187.642	41.657	-1.751
5300	19.693	110.098	92.542	93.049	-187.704	46.074	-1.900
5400	19.700	110.467	92.871	95.019	-187.772	50.481	-2.043
5500	19.706	110.828	93.194	96.989	-187.845	54.894	-2.181
5600	19.711	111.183	93.512	98.960	-187.926	59.307	-2.315
5700	19.717	111.532	93.825	100.931	-188.010	63.721	-2.443
5800	19.722	111.875	94.133	102.903	-188.103	68.143	-2.568
5900	19.727	112.212	94.437	104.876	-188.202	72.561	-2.688
6000	19.731	112.544	94.736	106.849	-188.308	76.982	-2.804

Dec. 31, 1960; Mar. 31, 1964; Dec. 31, 1968

ALUMINUM DIOXYHDRIDE (AlO_2H) (IDEAL GAS) GFW = 59.98827

Point Group $[C_s]$

$\Delta Hf°_0 = [-109 \pm 15]$ kcal/mol

$S°_{298.15}$ $[60.8 \pm 1.5]$ gibbs/mol

$\Delta Hf°_{298.15} = [-110 \pm 15]$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[3400] (1)	[700] (1)
[1200] (1)	[500] (1)
[1100] (1)	[400] (1)

Bond Distances: Al=O = [1.62] Å Al-O = [1.87] Å O-H = [0.94] Å

Bond Angles: O-Al-O = [180°] Al-O-H = [105°]

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = [37.349 \times 10^{-117}]\ g^3\ cm^6$

Heat of Formation

The hydroxyl group can often be considered as intermediate between F and Cl as is illustrated by the following examples of bond energies from these tables.

D(F-H) = 136 kcal, D(Cl-H) = 103 kcal and D(HO-H) = 119 kcal; also

D(F-BO) = 163 kcal, D(Cl-BO) = 105 kcal and D(HO-BO) = 143 kcal. Thus from

D(F-AlO) = 181 kcal and D(Cl-AlO) = 134 kcal we estimate D(HO-AlO) = 158 ± 20 kcal. This yields $\Delta Hf°_{298}$(HOAlO, g) = -127 ± 20 kcal/mol.

Consider also D(FB-O) = 175 kcal and D(ClB-O) = 169 kcal; and D(FAl-O) = 138 kcal and D(ClAl-O) = 132 kcal; it is evident that the substituent F or Cl has little effect on the B-O and Al-O bonds. Thus, we assume that D(HOAl-O) = 135 ± 10 kcal/mol which leads to $\Delta Hf°_{298}$(HOAlO, g) = -119 ± 10 kcal/mol.

M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, "Investigation of the Thermodynamic Properties of Rocket Combustion Products," AFRPL-TR-67-244, Nov. 1967, found no evidence for the ion $DOAlO^+$ when reacting $D_2O(g) + Al_2O_3(c)$. From estimates of the pressure needed to ensure detection of DOAlO and a knowledge of the D_2O pressure, they calculated the most negative value of $\Delta Hf°_{298}$(HOAlO, g) = -104 ± 10 kcal/mol. The absence of $DOAlO^+$ may be caused by fragmentation by the ionizing electrons and thus the value quoted may not be a real limit.

We adopt $\Delta Hf°_{298}$(HOAlO, g) = -110 ± 15 kcal/mol which encompasses all the values.

Heat Capacity and Entropy

Vibrational frequencies, bond distances, bond angles, and the product of the moments of inertia were taken from "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine," National Bureau of Standards Report No. 6297, January 1, 1959. The individual moments of inertia are : $I_A = 0.13 \times 10^{-39}\ g\ cm^2$, $I_B = 16.9 \times 10^{-39}\ g\ cm^2$, and $I_C = 17.0 \times 10^{-39}\ g\ cm^2$.

Lithium Tetrahydroaluminate ($LiAlH_4$)

(Crystal) Mol. Wt. = 37.952

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	20.650	21.000	21.000	.000	-28.000	-11.560	8.474
300	20.780	21.128	21.000	.038	-28.010	-11.459	8.347
400	22.400	27.582	21.867	2.286	-28.368	-5.885	3.215
500	24.200	32.770	23.542	4.614	-29.483	-.145	.063
600	25.550	37.309	25.466	7.106	-29.760	5.751	-2.095
700	26.600	41.330	27.451	9.716	-29.941	11.685	-3.648
800	27.300	44.931	29.415	12.413	-30.064	17.639	-4.819
900	27.817	48.179	31.322	15.171	-30.168	23.610	-5.733
1000	28.150	51.128	33.157	17.971	-32.766	29.775	-6.507
1100	28.432	53.825	34.916	20.801	-32.776	36.030	-7.158
1200	28.620	56.308	36.596	23.654	-32.779	42.285	-7.701
1300	28.795	58.606	38.202	26.525	-32.782	48.539	-8.160
1400	28.930	60.745	39.737	29.412	-32.788	54.796	-8.554
1500	29.070	62.746	41.205	32.312	-32.803	61.054	-8.895
1600	29.200	64.626	42.610	35.225	-32.827	67.309	-9.194
1700	29.330	66.400	43.958	38.152	-67.001	74.898	-9.628
1800	29.457	68.080	45.252	41.091	-67.753	83.294	-10.113
1900	29.580	69.676	46.496	44.043	-67.610	91.684	-10.546
2000	29.700	71.197	47.693	47.007	-67.474	100.063	-10.934

June 30, 1963; Mar. 31, 1964

LITHIUM TETRAHYDROALUMINATE ($LiAlH_4$) (CRYSTAL) MOL. WT. = 37.952

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [21.0 ± 2.0] $\Delta H_f^\circ{}_{298.15}$ = -28.0 ± 2.0 kcal. mole^{-1}

T_d = [410 ± 10]°K.

Heat of Formation.

The heats of solution of $LiAlH_4(c)$ in HCl(aq.) were measured calorimetrically by the following investigators: W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. 71, 2775 (1949), L. G. Fasolino, et al., "Heat of Formation of Lithium Aluminum Hydride," Special Report, National Research Corporation, Ma., April 26, 1963, and M. B. Smith and G. E. Bass, Jr., J. Chem. Eng. Data, 8, 342 (1963). The results are given in the following table.

Investigator		Chemical Reaction	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1}
Davis, et al.	(1)	$LiAlH_4(c) + 10(HCl\cdot 50H_2O) \rightarrow (LiCl + AlCl_3 + 6HCl)\cdot 500H_2O + 4H_2(g)$	-165.87
	(2)	$(AlCl_3 + LiCl + 6HCl)\cdot 500\ H_2O + 41020\ H_2O(l) \rightarrow (AlCl_3 + LiCl + 6HCl)\cdot 41520\ H_2O$	-4.43
	(3)	$(AlCl_3 + LiCl + 6HCl)\cdot 41520\ H_2O \rightarrow AlCl_3\cdot 5190\ H_2O + LiCl\cdot 5190\ H_2O + 6(HCl\cdot 5190\ H_2O)$	0.00(assumed)
		(1) + (2) + (3)	-170.30
Fasolino, et al.	(4)	$Al + 60(HCl\cdot 14H_2O) \rightarrow (AlCl_3 + 57\ HCl)\cdot 840\ H_2O + 3/2\ H_2$	-128.14
	(5)	$Li + 60(HCl\cdot 14H_2O) \rightarrow (LiCl + 59\ HCl)\cdot 840\ H_2O + 1/2\ H_2$	-67.05
	(6)	$LiAlH_4 + 60(HCl\cdot 14\ H_2O) \rightarrow (LiCl + AlCl_3 + 56\ HCl)\cdot 840\ H_2O + 4H_2$	-170.52
		(4) + (5) - (6)	-24.67
Smith and Bass	(7)	$LiAlH_4(c) + 39.715(HCl\cdot 11.624\ H_2O) \rightarrow [LiCl + AlCl_3 + 35.715\ (HCl\cdot 12.926\ H_2O)] + 4H_2(g)$	-164.6
	(8)	$LiCl(c) + [AlCl_3 + 35.715(HCl\cdot 12.926\ H_2O)] \rightarrow [LiCl + AlCl_3 + 35.715\ (HCl\cdot 12.926\ H_2O)]$	-6.75
		(7) - (8)	-157.85

Incorporating appropriate auxiliary thermal data, the heats of formation ($\Delta H_f^\circ{}_{298.15}$) for $LiAlH_4(c)$ were derived as -28.51 (recalculated value, by Smith and Bass, loc. cit.), -24.67 ± 1.31 and -28.4 ± 1.5 kcal. mole^{-1}, resp. The adopted value, -28.0 ± 2.0 kcal. mole^{-1}, is the weighted average of the above three values.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for $LiBH_4(c)$, $LiBO_2(c)$ and $LiAlO_2(c)$. The entropy value ($S^\circ_{298.15}$) was calculated from that for $LiBH_4(c)$ by the substitution of the entropy contribution of B atom by that of Al atom in the $LiAlH_4(c)$ molecule. The entropy values of the constituent B and Al atoms in crystalline compounds were taken from O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.

Temperature of Decomposition.

T_d was reported by A. E. Finholt, A. C. Bond, Jr. and H. I. Schlesinger, J. Am. Chem. Soc. 69, 1199 (1947). The decomposition products are aluminum, hydrogen, and lithium hydride. This reaction is apparently kinetically controlled since the free energy for the decomposition is negative even at room temperature.

Aluminum Monoiodide (AlI)

(Ideal Gas) Mol. Wt. = 153.89

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.330	14.641	14.641	INFINITE
100	7.412	50.408	66.655	-1.625	14.876	10.729	-23.447
200	8.294	55.858	60.024	-.833	14.636	6.649	-7.265
298	8.634	59.243	59.243	.000	14.300	2.793	-2.047
300	8.638	59.297	59.243	.016	14.293	2.721	-1.982
400	8.789	61.805	59.584	.888	11.982	-1.011	.552
500	8.870	63.776	60.233	1.772	6.477	-3.732	1.631
600	8.921	65.398	60.962	2.661	6.262	-5.755	2.096
700	8.957	66.776	61.697	3.555	6.020	-7.739	2.416
800	8.985	67.974	62.408	4.452	5.750	-9.686	2.646
900	9.007	69.033	63.087	5.352	5.451	-11.597	2.816
1000	9.027	69.983	63.730	6.254	2.628	-13.289	2.904
1100	9.045	70.845	64.338	7.157	2.378	-14.870	2.954
1200	9.061	71.632	64.913	8.063	2.129	-16.426	2.991
1300	9.076	72.358	65.459	8.970	1.882	-17.963	3.020
1400	9.091	73.031	65.976	9.878	1.634	-19.479	3.041
1500	9.105	73.659	66.467	10.788	1.387	-20.980	3.057
1600	9.119	74.247	66.935	11.699	1.141	-22.462	3.068
1700	9.132	74.800	67.382	12.612	.896	-23.930	3.076
1800	9.145	75.323	67.809	13.525	.651	-25.385	3.082
1900	9.158	75.817	68.217	14.441	.407	-26.822	3.085
2000	9.171	76.288	68.609	15.357	.163	-28.252	3.087
2100	9.183	76.735	68.985	16.275	-.079	-29.665	3.087
2200	9.196	77.163	69.348	17.194	-.322	-31.069	3.086
2300	9.208	77.572	69.696	18.114	-.564	-32.461	3.084
2400	9.221	77.964	70.033	19.035	-.805	-33.842	3.082
2500	9.233	78.341	70.357	19.958	-1.046	-35.214	3.078
2600	9.245	78.703	70.672	20.882	-1.286	-36.577	3.074
2700	9.257	79.052	70.976	21.807	-1.526	-37.930	3.070
2800	9.270	79.389	71.270	22.733	-72.319	-37.620	2.936
2900	9.282	79.715.	71.556	23.661	-72.354	-36.383	2.742
3000	9.294	80.029	71.833	24.590	-72.389	-35.138	2.560
3100	9.306	80.334	72.102	25.520	-72.424	-33.896	2.390
3200	9.318	80.630	72.364	26.451	-72.459	-32.654	2.230
3300	9.330	80.917	72.619	27.383	-72.492	-31.409	2.080
3400	9.342	81.196	72.867	28.317	-72.525	-30.166	1.939
3500	9.354	81.467	73.109	29.252	-72.558	-28.920	1.806
3600	9.366	81.730	73.345	30.188	-72.591	-27.669	1.680
3700	9.378	81.987	73.575	31.125	-72.624	-26.424	1.561
3800	9.390	82.237	73.800	32.063	-72.655	-25.173	1.448
3900	9.402	82.481	74.019	33.003	-72.688	-23.920	1.340
4000	9.414	82.720	74.234	33.943	-72.720	-22.676	1.239
4100	9.426	82.952	74.443	34.885	-72.752	-21.422	1.142
4200	9.438	83.179	74.649	35.829	-72.784	-20.167	1.049
4300	9.449	83.402	74.850	36.773	-72.817	-18.918	.961
4400	9.461	83.619	75.047	37.718	-72.851	-17.666	.877
4500	9.473	83.832	75.239	38.665	-72.884	-16.407	.797
4600	9.485	84.040	75.429	39.613	-72.918	-15.149	.720
4700	9.497	84.244	75.614	40.562	-72.953	-13.898	.646
4800	9.509	84.444	75.796	41.513	-72.990	-12.640	.575
4900	9.521	84.640	75.974	42.464	-73.028	-11.376	.507
5000	9.533	84.833	76.150	43.417	-73.068	-10.123	.442
5100	9.545	85.022	76.322	44.371	-73.108	-8.864	.380
5200	9.556	85.207	76.491	45.326	-73.152	-7.604	.320
5300	9.568	85.389	76.657	46.282	-73.197	-6.340	.261
5400	9.580	85.568	76.820	47.239	-73.246	-5.076	.205
5500	9.592	85.744	76.981	48.198	-73.297	-3.818	.152
5600	9.604	85.917	77.139	49.158	-73.351	-2.553	.100
5700	9.616	86.087	77.295	50.119	-73.409	-1.290	.049
5800	9.628	86.255	77.448	51.081	-73.471	-.025	.001
5900	9.640	86.419	77.598	52.044	-73.536	1.246	-.046
6000	9.651	86.581	77.747	53.009	-73.608	2.514	-.092

Dec. 31, 1961; Sept. 30, 1964

ALUMINUM MONOIODIDE (AlI) (IDEAL GAS) MOL. WT. = 153.89

Ground State Configuration $^1\Sigma^+$

$\Delta H_{f\ 0}^\circ = 14.6 \pm 2.0$ kcal. mole⁻¹

$S^\circ_{298.15} = [59.243]$ cal. deg.⁻¹ mole⁻¹

$\Delta H^\circ_{f\ 298.15} = 14.3 \pm 2.0$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ_1, cm.⁻¹	g_1
0	1

$\omega_e = 316.1$ cm.⁻¹

$\omega_e x_e = 1.0$ cm.⁻¹

$\sigma = 1$

$B_e = [0.1156]$ cm.⁻¹

$\alpha_e = [0.000492]$ cm.⁻¹

$r_e = [2.56]$ Å

Heat of Formation.

The dissociation energy (D_0°) of AlI(g) was reported by A. G. Gaydon [1], R. F. Barrow [2], and G. Herzberg [3], respectively. Hence the corresponding values of $\Delta H^\circ_{f\ 298.15}$ for AlI(g) were derived. The results are given as follows.

Investigator	D_0° e.v.	D_0° kcal. mole⁻¹	$\Delta H^\circ_{f\ 298.15}$ kcal. mole⁻¹
Gaydon [1]	3.92	90.4	12.7
Barrow [2]	—	87.0	16.0
Herzberg [3]	2.9	66.9	36.2

[1] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall Ltd., London, 1953.
[2] R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960).
[3] G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

The adopted value of $\Delta H^\circ_{f\ 298.15}$ for AlI(g) is the average of the first two $\Delta H^\circ_{f\ 298.15}$ values listed in the above table.

Heat Capacity and Entropy.

The spectroscopic constants, ω_e and $\omega_e x_e$, and ground state configuration were taken from G. Herzberg, loc. cit. The values of B_e and α_e were estimated. The bond length (r_e) was estimated by comparison with those for Al_2I_6(g) reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 60, 1852 (1938).

Aluminum Triiodide (AlI_3)

(Crystal) Mol. Wt. = 407.71

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	23.640	45.300	45.300	.000	-73.900	-72.974	53.489
300	23.680	45.446	45.300	.044	-73.903	-72.968	53.155
400	25.940	52.564	46.256	2.523	-79.779	-72.434	39.574
500	27.940	58.587	48.134	5.226	-94.987	-69.163	30.230
600	29.158	63.797	50.321	8.086	-94.129	-64.079	23.340
700	29.899	68.353	52.578	11.042	-93.208	-59.143	18.464
800	30.335	72.376	54.806	14.055	-92.263	-54.340	14.844
900	30.574	75.964	56.962	17.102	-91.319	-49.656	12.058
1000	30.700	79.192	59.026	20.166	-92.884	-44.892	9.811
1100	30.799	82.123	60.995	23.242	-91.869	-40.143	7.975
1200	30.870	84.806	62.869	26.325	-90.849	-35.485	6.462
1300	30.908	87.279	64.653	29.414	-89.824	-30.913	5.197
1400	30.951	89.571	66.352	32.507	-88.799	-26.419	4.124
1500	31.000	91.708	67.972	35.605	-87.771	-22.001	3.205

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE (AlI_3) (CRYSTAL) MOL. WT. = 407.71

$S^\circ_{298.15}$ = [45.3 ± 2.0] cal. deg.$^{-1}$ mole^{-1}

T_m = 464.15°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -73.9 ± 1.5 kcal. mole^{-1}

ΔH°_m = 3.8 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ (to dimer) = 28.8 ± 1.8 kcal. mole^{-1}

Heat of Formation.

J. D. Corbett and N. W. Gregory, J. Am. Chem. Soc. 76, 1446 (1954) reported the free energy change, $\Delta F^\circ_{298.15}$ = -8.7 ± 0.2 kcal. mole^{-1}, for the reaction $AlI_3(c) + 3HCl(g) \rightarrow AlCl_3(c) + 3HI(g)$. By the relationship $\Delta H = \Delta F + T\Delta S$ the value of $\Delta H^\circ_{r\ 298.15}$ was derived as -10.1 ± 0.2 kcal. mole^{-1}. The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $AlI_3(c)$ was evaluated to be -73.66 ± 0.30 kcal. mole^{-1}. The heat of solution of $AlI_3(c)$ in water was measured by D. J. A. Dear and D. D. Eley, J. Chem. Soc., 4684 (1954). From the value, $\Delta H^\circ_{r\ 298.15}$ = -91.4 ± 1.5 kcal. mole^{-1} for the reaction $AlI_3(c) \rightarrow Al^{+++}(aq.) + 3I^-(aq.)$, the heat of formation for $AlI_3(c)$ was calculated to be -74.1 ± 1.5 kcal. mole^{-1}. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $AlI_3(c)$ is the average of the above two values.

Heat Capacity and Entropy.

The heat capacities, 298.15-464°K., were taken from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). They were derived from the enthalpy data measured by W. Fischer, Z. anorg. Chem. 200, 332 (1931). Above 464°K. the C_p values were obtained by graphical extrapolation. The entropy, $S^\circ_{298.15}$, for $AlI_3(c)$ was calculated from $S^\circ_{298.15}$ for $AlI_3(l)$ by subtracting ΔS°_m and the difference between $S^\circ_{464.15}-S^\circ_{298.15}$ for crystal and liquid.

Melting Data.

Temperature and heat of melting were reported by W. Fischer, loc. cit.

Heat of Sublimation.

Heat of sublimation was calculated from vapor pressure data reported by W. Fischer, O. Rahlfs, and B. Benze, Z. anorg. allgem. Chemie, 205, 1 (1932), by both the second and third law methods. See $Al_2I_6(g)$ table for details.

Aluminum Triiodide (AlI_3)

(Liquid) Mol. Wt. = 407.71

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	29.000	52.450	52.450	.000	-70.770	-71.976	52.757
300	29.000	52.629	52.451	.054	-70.763	-71.983	52.437
400	29.000	60.972	53.588	2.954	-76.218	-72.237	39.467
500	29.000	67.443	55.736	5.854	-91.230	-69.834	30.523
600	29.000	72.731	58.141	8.754	-90.331	-65.641	23.909
700	29.000	77.201	60.553	11.654	-89.467	-61.595	19.230
800	29.000	81.073	62.881	14.554	-88.634	-57.669	15.754
900	29.000	84.489	65.096	17.454	-87.837	-53.848	13.075
1000	29.000	87.545	67.191	20.354	-89.567	-49.927	10.911
1100	29.000	90.309	69.169	23.254	-88.727	-46.005	9.140
1200	29.000	92.832	71.037	26.154	-87.891	-42.158	7.678
1300	29.000	95.153	72.804	29.054	-87.054	-38.380	6.452
1400	29.000	97.302	74.478	31.954	-86.222	-34.666	5.411
1500	29.000	99.303	76.067	34.854	-85.392	-31.015	4.519
1600	29.000	101.175	77.579	37.754	-84.563	-27.414	3.744
1700	29.000	102.933	79.019	40.654	-83.737	-23.868	3.068
1800	29.000	104.590	80.394	43.554	-82.912	-20.371	2.473
1900	29.000	106.158	81.709	46.454	-82.091	-16.918	1.946
2000	29.000	107.646	82.969	49.354	-81.271	-13.512	1.476

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AlI_3

ALUMINUM TRIIODIDE (AlI_3) (LIQUID) MOL. WT. = 407.71

$S^\circ_{298.15}$ = [52.45] cal. deg.$^{-1}$ mole^{-1} ΔH_f° 298.15 = -70.77 ± 1.5 kcal. mole^{-1}

T_m = 464.15°K. ΔH_m° = 3.8 kcal. mole^{-1}

Heat of Formation.

ΔH_f° 298.15(l) was obtained from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{464.15}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity, 464-500°K., was obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). It was derived based on the enthalpy data measured by W. Fischer, Z. anorg. Chem. 200, 332 (1931). The C_p values above 500°K. were assumed to be the same as that at 500°K. The entropy, $S^\circ_{298.15}$, was estimated so that the values of ΔH_v° calculated from vapor pressure data by the second and third law methods were in reasonable agreement.

Melting Data.

T_m and ΔH_m° were reported by W. Fischer, loc. cit.

Aluminum Triiodide (AlI_3)

(Ideal Gas) Mol. Wt. = 407.71

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 4.360	- 47.535	- 47.535	INFINITE
100	13.828	69.035	102.015	- 3.298	- 47.672	- 52.224	114.130
200	16.950	79.725	88.414	- 1.738	- 48.321	- 56.543	61.784
298	18.281	86.776	86.776	.000	- 49.000	- 60.440	44.302
300	18.298	86.890	86.777	.034	- 49.013	- 60.511	44.080
400	18.917	92.249	87.503	1.898	- 55.504	- 64.033	34.984
500	19.238	96.508	88.893	3.807	- 71.506	- 64.643	28.254
600	19.422	100.033	90.464	5.741	- 71.574	- 63.265	23.043
700	19.538	103.036	92.051	7.690	- 71.661	- 61.874	19.317
800	19.614	105.651	93.591	9.648	- 71.770	- 60.467	16.518
900	19.667	107.964	95.062	11.612	- 71.909	- 59.047	14.338
1000	19.705	110.038	96.458	13.580	- 74.570	- 57.424	12.549
1100	19.734	111.918	97.779	15.553	- 74.658	- 55.706	11.067
1200	19.756	113.636	99.030	17.527	- 74.747	- 53.979	9.830
1300	19.773	115.218	100.215	19.504	- 74.834	- 52.244	8.783
1400	19.787	116.684	101.340	21.482	- 74.924	- 50.502	7.883
1500	19.798	118.049	102.409	23.461	- 75.015	- 48.757	7.104
1600	19.807	119.327	103.427	25.441	- 75.106	- 47.000	6.420
1700	19.814	120.528	104.398	27.422	- 75.198	- 45.242	5.816
1800	19.820	121.661	105.325	29.404	- 75.292	- 43.478	5.279
1900	19.826	122.733	106.214	31.386	- 75.388	- 41.707	4.797
2000	19.830	123.750	107.065	33.369	- 75.486	- 39.934	4.364
2100	19.834	124.717	107.883	35.352	- 75.584	- 38.153	3.970
2200	19.838	125.640	108.669	37.336	- 75.685	- 36.369	3.613
2300	19.841	126.522	109.427	39.320	- 75.787	- 34.579	3.286
2400	19.843	127.366	110.157	41.304	- 75.890	- 32.784	2.985
2500	19.845	128.177	110.861	43.288	- 75.996	- 30.986	2.709
2600	19.848	128.955	111.542	45.273	- 76.104	- 29.185	2.453
2700	19.849	129.704	112.201	47.258	- 76.214	- 27.379	2.216
2800	19.851	130.426	112.839	49.243	- 146.879	- 23.913	1.866
2900	19.852	131.123	113.458	51.228	- 146.789	- 19.524	1.471
3000	19.854	131.796	114.058	53.213	- 146.702	- 15.139	1.103
3100	19.855	132.447	114.641	55.199	- 146.616	- 10.753	.758
3200	19.856	133.077	115.207	57.184	- 146.532	- 6.372	.435
3300	19.857	133.688	115.758	59.170	- 146.451	- 1.992	.132
3400	19.858	134.281	116.294	61.156	- 146.370	2.382	- .153
3500	19.859	134.856	116.816	63.141	- 146.293	6.757	- .422
3600	19.859	135.416	117.325	65.127	- 146.218	11.130	- .676
3700	19.860	135.960	117.821	67.113	- 146.144	15.496	- .915
3800	19.861	136.490	118.306	69.099	- 146.072	19.865	- 1.142
3900	19.861	137.006	118.779	71.086	- 146.004	24.234	- 1.358
4000	19.862	137.508	119.241	73.072	- 145.937	28.593	- 1.562
4100	19.862	137.999	119.692	75.058	- 145.873	32.959	- 1.757
4200	19.863	138.478	120.134	77.044	- 145.813	37.322	- 1.942
4300	19.863	138.945	120.566	79.031	- 145.754	41.677	- 2.118
4400	19.864	139.402	120.989	81.017	- 145.700	46.032	- 2.286
4500	19.864	139.848	121.403	83.003	- 145.648	50.397	- 2.447
4600	19.865	140.285	121.809	84.990	- 145.599	54.754	- 2.601
4700	19.865	140.712	122.206	86.976	- 145.552	59.101	- 2.748
4800	19.865	141.130	122.596	88.963	- 145.511	63.457	- 2.889
4900	19.866	141.540	122.979	90.949	- 145.473	67.816	- 3.025
5000	19.866	141.941	123.354	92.936	- 145.440	72.165	- 3.154
5100	19.866	142.334	123.722	94.922	- 145.409	76.516	- 3.279
5200	19.866	142.720	124.084	96.909	- 145.385	80.864	- 3.398
5300	19.867	143.099	124.439	98.896	- 145.363	85.218	- 3.514
5400	19.867	143.470	124.788	100.882	- 145.349	89.573	- 3.625
5500	19.867	143.834	125.131	102.869	- 145.338	93.917	- 3.732
5600	19.867	144.192	125.468	104.856	- 145.335	98.265	- 3.835
5700	19.867	144.544	125.800	106.842	- 145.338	102.615	- 3.934
5800	19.868	144.890	126.126	108.829	- 145.345	106.968	- 4.030
5900	19.868	145.229	126.447	110.816	- 145.360	111.318	- 4.123
6000	19.868	145.563	126.763	112.803	- 145.383	115.670	- 4.213

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ALUMINUM TRIIODIDE (AlI_3) (IDEAL GAS) MOL. WT. = 407.71

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [86.776] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -47.5 ± 1.8 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -49.0 ± 1.8 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[210] (1)	[95] (1)
[170] (1)	[450] (2)

Bond Distance: Al-I = 2.44 ± 0.02 Å

Bond Angle: I-Al-I = [120]°K.

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 1.33213 \times 10^{-110}$ g.^{3} cm.^{6}

Heat of Formation.

The equilibrium pressures of the reaction $Al_2I_6(g) \rightarrow 2AlI_3(g)$ at several temperatures were determined by W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932). The heats of dissociation of $Al_2I_6(g)$ were calculated by both second and third law methods. The heats of vaporization, i.e. $AlI_3(l) \rightarrow AlI_3(g)$, were also evaluated using the calculated partial pressure of $AlI_3(g)$ over $AlI_3(l)$. See $Al_2I_6(g)$ table for detail. The results obtained are summarized as follows:

Chemical Reaction or Process	Temperature Range (°K.)	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H^\circ_{f\ 298.15}(AlI_3, g)$ Kcal. Mole^{-1}
$Al_2I_6(g) \rightarrow 2AlI_3(g)$	614 - 744	25.18	23.34	-47.9
$Al_2I_6(g) \rightarrow 2AlI_3(g)$	482.8 - 578.0	23.07	23.34	-49.0
$AlI_3(l) \rightarrow AlI_3(g)$	493.8 - 645.2	21.45	22.69	-49.2

The three $\Delta H^\circ_{f\ 298.15}(AlI_3, g)$ values were calculated using the respective second law values of $\Delta H^\circ_{r\ 298.15}$. The adopted value, $\Delta H^\circ_{f\ 298.15}$ = -49.0 ± 1.8 kcal. mole^{-1}, is the weighted average of the above three values.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were obtained from P. A. Akishin, N. G. Rambidi, and E. L. Zosorin, Kristallografiya, 4, 186 (1959). The vibrational frequencies were estimated such that the values of ΔH°_r obtained by the third law method are in reasonable agreement with the corresponding values calculated by the second law method. The three principal moments of inertia are: $I_A = I_B = 1.8815 \times 10^{-37}$ and $I_C = 3.7630 \times 10^{-37}$ g. cm.^{2}.

Lithium Aluminate ($LiAlO_2$)

(Crystal) Mol. Wt. = 65.92

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.723	- 282.779	- 282.779	INFINITE
100	4.293	1.932	23.727	- 2.179	- 283.173	- 278.874	609.449
200	11.461	7.215	14.093	- 1.376	- 283.932	- 274.265	299.689
298	16.208	12.751	12.749	.001	- 284.329	- 269.429	197.487
300	16.283	12.851	12.749	.031	- 284.334	- 269.337	196.203
400	19.490	18.012	13.432	1.832	- 284.462	- 264.312	144.406
500	21.130	22.567	14.814	3.876	- 285.194	- 259.199	113.290
600	22.153	26.514	16.442	6.043	- 285.151	- 254.003	92.516
700	22.885	29.988	18.134	8.297	- 285.062	- 248.819	77.681
800	23.462	33.082	19.813	10.615	- 284.950	- 243.650	66.559
900	23.949	35.875	21.445	12.987	- 284.830	- 238.493	57.911
1000	24.380	38.421	23.017	15.403	- 287.203	- 233.166	50.956
1100	24.774	40.763	24.525	17.861	- 286.972	- 227.774	45.252
1200	25.143	42.935	25.970	20.357	- 286.712	- 222.404	40.503
1300	25.495	44.961	27.354	22.889	- 286.423	- 217.057	36.489
1400	25.834	46.883	28.680	25.456	- 286.105	- 211.733	33.051
1500	26.163	48.657	29.953	28.056	- 285.759	- 206.432	30.076
1600	26.485	50.355	31.175	30.688	- 285.385	- 201.155	27.475
1700	26.802	51.971	32.351	33.353	- 320.029	- 194.575	25.013
1800	27.115	53.511	33.484	36.049	- 319.419	- 187.242	22.730
1900	27.425	54.986	34.577	38.776	- 318.764	- 179.882	20.690
2000	27.733	56.400	35.633	41.534	- 318.124	- 172.591	18.859
2100	28.040	57.761	36.655	44.322	- 317.440	- 165.332	17.206
2200	28.040	59.065	37.644	47.126	- 316.748	- 158.104	15.705
2300	28.040	60.312	38.603	49.930	- 316.060	- 150.910	14.339
2400	28.040	61.505	39.532	52.734	- 315.381	- 143.742	13.089
2500	28.040	62.650	40.434	55.538	- 314.709	- 136.605	11.941
2600	28.040	63.749	41.310	58.342	- 314.043	- 129.496	10.885
2700	28.040	64.808	42.161	61.146	- 313.386	- 122.411	9.908
2800	28.040	65.827	42.988	63.950	- 383.290	- 113.696	8.874
2900	28.040	66.811	43.793	66.754	- 382.447	- 104.082	7.843
3000	28.040	67.762	44.576	69.558	- 381.611	- 94.495	6.884

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LITHIUM ALUMINATE ($LiAlO_2$) (CRYSTAL) MOL. WT. = 65.92

ΔH_{f0}° = -282.78 kcal. mole^{-1}

T_m = 1883°K

ΔH_f° 298.15 = -284.33 ± .20 kcal. mole^{-1}

$S^\circ_{298.15}$ = 12.75 cal. deg.$^{-1}$ mole^{-1}

ΔH_m = [6000] cal. mole^{-1}

Heat of Formation.

ΔH_f° 298.15 was measured by J. P. Coughlin, J. Am. Chem. Soc. 79, 2397 (1957).

Heat Capacity and Extrapolation.

Thermodynamic functions are based on the low temperature heat capacity data of E. G. King, J. Am. Chem. Soc. 77, 3189 (1955), and on the high temperature heat content results of A. O. Christensen, K. O. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960).

Melting.

R. Ballo and E. Dittler, Z. anorg. u allgem. Chem. 76, 39 (1912), list the melting point as between 1900° to 2000°K. More recently, K. H. Kim and F. A. Hummel, J. Am. Ceram. Soc. 43, 611 (1960), determined the melting point as 1883° ± 15°K. by rapidly heating a small sample on a Pt-Rh strip furnace. The value, which was used in this report, was derived from an average of ten measurements by Kim and Hummel.

H. Prophet, The Dow Chemical Company, private communication March 9, 1961, using an arc-image furnace reports the melting point to be about 1975°K. After seven successive runs on the same sample the melting point approached that of Al_2O_3 at 2308°K. The sample, therefore is decomposed upon fusion to Li_2O vapor and Al_2O_3(c). See O. N. Salmon and L. Marcus J. Am. Ceram. Soc. 43, 549 (1960), and F. A. Hummel, B. S. R. Sastry and D. Watring, Ibid, 41, 88 (1958).

Lithium Aluminate ($LiAlO_2$)

(Liquid) Mol. Wt. = 65.92

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	21.000	19.200	19.200	.000	- 273.301	- 260.323	190.813
300	21.000	19.330	19.200	.039	- 273.297	- 260.244	189.578
400	21.000	25.371	20.024	2.139	- 273.126	- 255.920	139.821
500	21.000	30.057	21.580	4.239	- 273.802	- 251.553	109.948
600	21.000	33.886	23.321	6.339	- 273.826	- 247.101	90.002
700	21.000	37.123	25.068	8.439	- 273.891	- 242.643	75.753
800	21.000	39.927	26.754	10.539	- 273.997	- 238.173	65.063
900	21.000	42.401	28.358	12.639	- 274.149	- 233.686	56.744
1000	21.000	44.613	29.875	14.739	- 276.838	- 228.995	50.044
1100	21.000	46.615	31.307	16.839	- 276.965	- 224.205	44.543
1200	21.000	48.442	32.660	18.939	- 277.101	- 219.403	39.957
1300	21.000	50.123	33.939	21.039	- 277.244	- 214.589	36.074
1400	21.000	51.679	35.151	23.139	- 277.393	- 209.764	32.744
1500	21.000	53.128	36.302	25.239	- 277.547	- 204.928	29.857
1600	21.000	54.483	37.397	27.339	- 277.705	- 200.080	27.328
1700	21.000	55.757	38.440	29.439	- 312.914	- 193.896	24.926
1800	21.000	56.987	39.435	31.539	- 312.900	- 186.894	22.691
1900	21.000	58.092	40.388	33.639	- 312.892	- 179.893	20.691
2000	21.000	59.169	41.300	35.739	- 312.890	- 172.895	18.892
2100	21.000	60.194	42.175	37.839	- 312.894	- 165.896	17.264
2200	21.000	61.171	43.017	39.939	- 312.906	- 158.895	15.784
2300	21.000	62.104	43.827	42.039	- 312.922	- 151.895	14.433
2400	21.000	62.998	44.607	44.139	- 312.947	- 144.892	13.194
2500	21.000	63.855	45.360	46.239	- 312.979	- 137.890	12.054
2600	21.000	64.679	46.087	48.339	- 313.017	- 130.887	11.002
2700	21.000	65.472	46.790	50.439	- 313.064	- 123.882	10.027
2800	21.000	66.235	47.471	52.539	- 383.672	- 115.220	8.993
2900	21.000	66.972	48.131	54.639	- 383.533	- 105.635	7.961
3000	21.000	67.684	48.771	56.739	- 383.401	- 96.052	6.997

September 30, 1961

Lithium Aluminate ($LiAlO_2$) (Liquid)

Mol. Wt. = 65.92

ΔH_f° $_{298.15}$ = [-273.3] kcal. mole^{-1}

$S^\circ_{298.15}$ = [19.2] cal. deg.$^{-1}$ mole^{-1}

T_m = 1883°K

ΔH_m = [6000] cal. mole^{-1}

Heat capacity, entropy, and ΔH_m are all estimated.

Aluminum Nitride (AlN)

(Crystal) Mol. Wt. = 40.988

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-.925	-74.795	-74.795	INFINITE
100	1.360	.519	9.388	-.887	-75.205	-73.187	159.942
200	4.613	2.455	5.399	-.589	-75.701	-70.979	77.558
298	7.201	4.816	4.816	.000	-76.000	-68.595	50.279
300	7.225	4.861	4.816	.013	-76.004	-68.549	49.935
400	8.700	7.155	5.119	.814	-76.149	-66.038	36.080
500	9.701	9.210	5.736	1.737	-76.204	-63.503	27.756
600	10.439	11.048	6.471	2.747	-76.207	-60.962	22.204
700	10.915	12.696	7.245	3.816	-76.188	-58.423	18.240
800	11.255	14.177	8.020	4.926	-76.166	-55.887	15.267
900	11.495	15.518	8.780	6.064	-76.155	-53.352	12.955
1000	11.660	16.738	9.516	7.222	-78.655	-50.634	11.065
1100	11.769	17.855	10.224	8.394	-78.577	-47.835	9.504
1200	11.836	18.882	10.903	9.575	-78.497	-45.044	8.203
1300	11.876	19.831	11.554	10.760	-78.417	-42.260	7.104
1400	11.901	20.712	12.177	11.949	-78.339	-39.482	6.163
1500	11.923	21.534	12.774	13.140	-78.262	-36.709	5.348
1600	11.955	22.304	13.345	14.334	-78.186	-33.940	4.636
1700	12.000	23.030	13.894	15.532	-78.110	-31.178	4.008
1800	12.023	23.717	14.421	16.733	-78.033	-28.420	3.450
1900	12.035	24.367	14.927	17.936	-77.957	-25.664	2.952
2000	12.065	24.985	15.415	19.141	-77.881	-22.914	2.504
2100	12.092	25.575	15.885	20.349	-77.804	-20.169	2.099
2200	12.115	26.138	16.338	21.559	-77.727	-17.425	1.731
2300	12.135	26.677	16.776	22.772	-77.649	-14.687	1.396
2400	12.152	27.194	17.199	23.986	-77.570	-11.951	1.088
2500	12.165	27.690	17.609	25.202	-77.491	-9.218	.806
2600	12.183	28.167	18.006	26.420	-77.412	-6.490	.545
2700	12.199	28.628	18.391	27.639	-77.333	-3.763	.305
2800	12.215	29.072	18.765	28.859	-147.807	.613	-.048
2900	12.231	29.500	19.127	30.082	-147.522	5.908	-.445
3000	12.245	29.915	19.480	31.305	-147.238	11.196	-.816

Dec. 31, 1960; Dec. 31, 1961; Dec. 31, 1962

ALUMINUM NITRIDE (AlN) (CRYSTAL) MOL. WT. = 40.988

$\Delta H_{f\ 0}^\circ = -74.8 \pm 0.3$ kcal. mole^{-1}

$T_d = [2790°K]$

$\Delta H_{f\ 298.15}^\circ = -76.0 \pm 0.3$ kcal. mole^{-1}

$S_{298.15}^\circ = 4.816$ cal. deg.$^{-1}$ mole^{-1}

Heat of Formation.

The selected heat of formation is the average of two independent calorimetric determinations. The heat of formation was reported to be -76.5 ± 0.2 kcal. mole^{-1} and -75.6 ± 0.4 kcal. mole^{-1}. The former value was reported by C. A. Neugebauer and J. L. Margrave, Z. Anorg. Allgem. Chem. 290, 82 (1957). The later value was reported by A. D. Mah, E. G. King, W. W. Weller, and A. V. Christensen, U. S. Bureau of Mines Report of Investigations 5716 (1961).

Vapor pressure measurements agree with the selected heat of formation. For instance $\Delta H_{f\ 298.15} = -75.5$ kcal. mole^{-1} for AlN(c) was calculated from the heat for the reaction $2AlN(c) \rightarrow 2Al(g) + N_2(g)$ and the heat of sublimation, 78.0 kcal. mole^{-1}, for Al(c). This heat of reaction was obtained from a third law calculation using JANAF values for the free energy functions and torsion effusion pressures measured by D. L. Hildenbrand and L. P. Theard, Aeronutronic Technical Report U-1497 (1961). Vapor pressure measurements with a microbalance in a vacuum system by L. H. Dreger, V. V. Dadape, and J. L. Margrave, J. Phys. Chem. 66, 1556 (1962) agree with the selected $\Delta H_{f\ 298.15}^\circ$. When recalculated with the sublimation coefficient ($\alpha \approx 2.2 \times 10^{-3}$) reported by Hildenbrand and Theard, some of the Knudsen cell measurements by M. Hoch and D. White, "The Vaporization of Boron Nitride and Aluminum Nitride," ASTIA Unclassified Report 142616, October 29, 1956, agree with the selected heat of formation.

Earlier determinations of the heat of formation which apparently are in error are summarized by C. A. Neugebauer and J. L. Margrave (loc. cit.) and by L. H. Dreger et al. (loc. cit.).

Heat Capacity and Entropy.

The heat capacity and entropy were reported by A. D. Mah et al. (loc. cit.). They measured the low temperature (51-298.15°K) and high temperature (298.15-1800°K) heat capacities and extrapolated the heat capacity from 0 to 51°K using the T^3 law. A smooth extrapolation of the heat capacity was made from 1800° to 3000°K. The heat content of AlN(c) was recently determined from 300 to 1200°K by R. Mezaki, "Heat Contents of Inorganic Substances at High Temperatures," M. S. Thesis, University of Wisconsin (1961). The enthalpies reported by Mezaki are about 1% greater than those of Mah et al.

Decomposition Data.

P. O. Schissel and W. S. Williams, Bull. Am. Phys. Soc. II, 4, 139 (1959) studied the vaporization of AlN with the mass spectrometer and detected only the gaseous species Al and N_2. The temperature at which the ΔF_f° of AlN(c) and Al(g) were equal, 2788.9°K, was taken as the temperature of decomposition.

Aluminum Nitride (AlN)

(Ideal Gas)   GFW = 40.9882

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.106	104.024	104.024	INFINITE
100	6.957	42.840	56.950	-1.411	104.266	102.056	-223.043
200	7.079	47.683	51.242	-.712	104.176	99.853	-109.114
298	7.444	50.573	50.573	.000	104.000	97.763	-71.662
300	7.452	50.620	50.574	.014	103.996	97.724	-71.192
400	7.938	52.818	50.871	.779	103.814	95.661	-52.267
500	8.134	54.601	51.444	1.578	103.631	93.644	-40.932
600	8.347	56.104	52.099	2.403	103.440	91.664	-33.389
700	8.500	57.402	52.766	3.246	103.234	89.718	-28.011
800	8.612	58.545	53.418	4.102	103.002	87.802	-23.986
900	8.697	59.564	54.045	4.967	102.726	85.919	-20.864
1000	8.763	60.484	54.644	5.840	99.879	84.251	-18.413
1100	8.815	61.322	55.214	6.719	99.605	82.701	-16.431
1200	8.858	62.091	55.755	7.603	99.329	81.176	-14.784
1300	8.894	62.801	56.270	8.491	99.053	79.675	-13.395
1400	8.925	63.462	56.760	9.382	98.775	78.195	-12.207
1500	8.952	64.078	57.228	10.276	98.495	76.735	-11.180
1600	8.976	64.657	57.674	11.172	98.214	75.293	-10.285
1700	8.997	65.202	58.101	12.071	97.933	73.868	-9.496
1800	9.017	65.717	58.510	12.971	97.651	72.462	-8.798
1900	9.035	66.205	58.902	13.874	97.368	71.070	-8.175
2000	9.052	66.668	59.279	14.778	97.084	69.694	-7.616
2100	9.067	67.110	59.642	15.684	96.800	68.331	-7.111
2200	9.082	67.533	59.991	16.592	96.516	66.980	-6.654
2300	9.096	67.937	60.328	17.501	96.232	65.646	-6.238
2400	9.110	68.324	60.653	18.411	95.948	64.323	-5.857
2500	9.123	68.696	60.967	19.323	95.663	63.009	-5.508
2600	9.135	69.054	61.271	20.236	95.379	61.710	-5.187
2700	9.147	69.399	61.566	21.150	95.094	60.419	-4.891
2800	9.159	69.732	61.852	22.065	25.400	59.970	-4.681
2900	9.171	70.054	62.129	22.982	25.379	61.204	-4.612
3000	9.182	70.365	62.398	23.899	25.357	62.441	-4.549
3100	9.193	70.666	62.660	24.818	25.335	63.675	-4.489
3200	9.204	70.958	62.915	25.738	25.314	64.916	-4.434
3300	9.215	71.242	63.163	26.659	25.293	66.152	-4.381
3400	9.226	71.517	63.405	27.581	25.272	67.390	-4.332
3500	9.236	71.784	63.640	28.504	25.252	68.630	-4.285
3600	9.247	72.045	63.870	29.428	25.232	69.870	-4.242
3700	9.257	72.298	64.095	30.353	25.212	71.110	-4.200
3800	9.267	72.545	64.314	31.279	25.191	72.351	-4.161
3900	9.277	72.786	64.528	32.207	25.172	73.595	-4.124
4000	9.287	73.021	64.737	33.135	25.151	74.833	-4.089
4100	9.297	73.251	64.942	34.064	25.131	76.072	-4.055
4200	9.307	73.475	65.143	34.994	25.111	77.317	-4.023
4300	9.317	73.694	65.339	35.925	25.090	78.561	-3.993
4400	9.327	73.908	65.531	36.858	25.070	79.808	-3.964
4500	9.336	74.118	65.720	37.791	25.047	81.050	-3.936
4600	9.346	74.323	65.905	38.725	25.026	82.298	-3.910
4700	9.356	74.524	66.086	39.660	25.002	83.538	-3.885
4800	9.365	74.721	66.264	40.596	24.977	84.785	-3.860
4900	9.375	74.915	66.438	41.533	24.952	86.031	-3.837
5000	9.385	75.104	66.610	42.471	24.925	87.280	-3.815
5100	9.394	75.290	66.778	43.410	24.896	88.526	-3.794
5200	9.404	75.472	66.944	44.350	24.864	89.776	-3.773
5300	9.413	75.652	67.106	45.291	24.830	91.019	-3.753
5400	9.423	75.828	67.266	46.233	24.795	92.271	-3.734
5500	9.432	76.001	67.423	47.175	24.755	93.519	-3.716
5600	9.441	76.171	67.578	48.119	24.712	94.771	-3.699
5700	9.451	76.338	67.730	49.064	24.668	96.023	-3.682
5800	9.460	76.502	67.880	50.009	24.617	97.280	-3.666
5900	9.470	76.664	68.028	50.956	24.563	98.531	-3.650
6000	9.479	76.823	68.173	51.903	24.505	99.787	-3.635

Dec. 31, 1960; Mar. 31, 1964; Mar. 31, 1967

ALUMINUM NITRIDE (AlN)   (IDEAL GAS)   GFW = 40.9882

Ground State Configuration $[^1\Sigma^+]$

$\Delta Hf^\circ_0 = 104 \pm 20$ kcal/mol

$S^\circ_{298.15} = [50.573]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 104 \pm 20$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

$\omega_e = [930]$ cm^{-1}

$\omega_e x_e = [6.9]$ cm^{-1}

$\sigma = 1$

$B_e = [0.6748]$ cm^{-1}

$\alpha_e = [0.0064]$ cm^{-1}

$r_e = [1.65]$ Å

Heat of Formation.

The heat of formation is calculated from the estimated ω_e and $\omega_e x_e$, using $D_0 = \omega_e{}^2/4\omega_e x_e$, as 89 kcal/mol. J. L. Margrave and P. Staphitanonda, J. Phys. Chem. 59, 1231 (1955) estimated values of the bond length as 1.23 - 1.65 Å and calculated from an ionic model D_0 values of 137 - 82 kcal/mol. Using an estimated bond length of 1.65 Å and a D_0 = 87 kcal/mol leads to ΔHf°_{298} = 104 kcal/mol.

Heat Capacity and Entropy.

The bond length is estimated as 1.65 Å from a comparison with the bond lengths of SO, PO, SiO, AlO, MgO, S_2, SiS, AlS, PN, SiN, and the sums of covalent radii. This bond length is then used with Guggenheimer's Relation [K. M. Guggenheimer, Proc. Phys. Soc. (London), 58, 456 (1946)] to calculate a value for ω_e. By analogy with SiN(g) it is taken to closely approach the multiple bonding case, which gives ω_e = 960 cm^{-1}. The anharmonicity correction x_e is calculated by assuming the product $x_e\mu^{1/2}$ equal to that for AlO(g). The value of α_e is calculated using the relation:

$$\alpha_e = 6[(\omega_e x_e B_e{}^3)^{1/2} - B_e{}^2]/\omega_e$$

Sodium Aluminate ($NaAlO_2$)

(Crystal) Mol. Wt. = 81.971

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.844	- 268.974	- 268.974	INFINITE
100	6.754	3.586	29.556	- 2.597	- 269.866	- 265.338	579.869
200	13.601	10.583	18.323	- 1.548	- 270.526	- 260.537	284.687
298	17.610	16.826	16.826	.000	- 270.840	- 255.561	187.322
300	17.660	16.935	16.826	.033	- 270.843	- 255.466	186.098
400	19.936	22.347	17.549	1.919	- 271.609	- 250.268	136.733
500	21.406	26.968	18.982	3.993	- 271.634	- 244.927	107.052
600	22.531	30.973	20.654	6.191	- 271.568	- 239.591	87.267
700	23.492	34.520	22.386	8.494	- 271.436	- 234.272	73.140
800	23.602	38.085	24.136	11.159	- 270.980	- 228.999	62.557
900	24.026	40.889	25.844	13.540	- 270.850	- 223.758	54.333
1000	24.450	43.442	27.478	15.964	- 273.215	- 218.347	47.717
1100	24.874	45.792	29.037	18.430	- 272.984	- 212.873	42.292
1200	25.298	47.975	30.526	20.939	- 295.963	- 206.962	37.691
1300	25.722	50.017	31.947	23.490	- 295.466	- 199.566	33.548
1400	26.146	51.938	33.307	26.083	- 294.934	- 192.209	30.004
1500	26.570	53.757	34.610	28.719	- 294.366	- 184.891	26.937
1600	26.994	55.485	35.862	31.397	- 293.762	- 177.611	24.259
1700	27.426	57.135	37.065	34.119	- 293.118	- 170.371	21.902
1800	27.842	58.714	38.224	36.882	- 292.441	- 163.170	19.811
1900	28.241	60.230	39.342	39.686	- 291.729	- 156.006	17.944
2000	28.624	61.688	40.424	42.530	- 290.983	- 148.884	16.269
2100	28.990	63.094	41.470	45.411	- 290.204	- 141.799	14.757
2200	29.340	64.451	42.484	48.327	- 289.398	- 134.750	13.386
2300	29.604	65.761	43.467	51.275	- 288.564	- 127.741	12.138
2400	29.853	67.026	44.423	54.248	- 287.712	- 120.764	10.997
2500	30.084	68.249	45.352	57.245	- 286.842	- 113.828	9.950
2600	30.300	69.434	46.255	60.264	- 285.956	- 106.924	8.987
2700	30.499	70.581	47.135	63.304	- 285.056	- 100.057	8.099
2800	30.683	71.693	47.992	66.363	- 354.698	- 91.569	7.147
2900	30.849	72.773	48.828	69.440	- 353.571	- 82.189	6.194
3000	31.000	73.822	49.644	72.533	- 352.436	- 72.850	5.307

Dec. 31, 1960; Mar. 31, 1963

SODIUM ALUMINATE ($NaAlO_2$) (CRYSTAL) MOL. WT. = 81.971

$\Delta H_{f\ 0}^\circ = -268.97 \pm 0.17$ kcal. mole^{-1}

$S_{298.15}^\circ = 16.826$ cal. deg.$^{-1}$ mole^{-1} $\Delta H_{f\ 298.15}^\circ = -270.84 \pm 0.17$ kcal. mole^{-1}

$T_t = 740$°K. $\Delta H_t = 0.310$ kcal. mole^{-1}

T_m = above 1923°K. ΔH_m° = Unknown

Heat of Formation.

$\Delta H_{f\ 298.15}^\circ$ was reported by J. P. Coughlin, J. Am. Chem. Soc. 79, 2397 (1957). The value was calculated from the measured heat of solution of $NaAlO_2$(c) at 303.15°K. in 4.360m hydrochloric acid solution.

Heat Capacity and Entropy.

The low temperature heat capacities, below 350°K., were measured by E. F. Westrum, University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. Heat capacities above 350°K, 399.4 — 1698.6°K., were measured by A. U. Christensen, K. C. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960). These two sets of C_p data were plotted graphically and joined smoothly at 350°K. Low temperature heat capacities 51°-298°K., were also determined by E. G. King, J. Am. Chem. Soc. 77, 3189 (1955), which agree very well with those reported by E. F. Westrum, loc. cit. $S_{298.15}^\circ$ was reported by E. F. Westrum, loc. cit., using S_{10}°(extrap.) = 0.01 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_t and ΔH_t° were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.

Temperature of Melting.

T_m was taken from K. Kammermeyer and A. B. Peck, J. Am. Ceram. Soc. 16, 363 (1933).

Aluminum Monoxide (AlO)

(Ideal Gas) GFW = 42.9809

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.100	20.031	20.031	INFINITE
100	6.957	44.459	58.513	-1.405	20.273	18.062	-39.474
200	7.052	49.297	52.832	-.707	20.181	15.858	-17.329
298	7.381	52.169	52.169	.000	20.000	13.769	-10.093
300	7.388	52.214	52.169	.014	19.996	13.730	-10.003
400	7.765	54.392	52.463	.772	19.800	11.672	-6.377
500	8.066	56.159	53.031	1.564	19.596	9.663	-4.224
600	8.290	57.651	53.680	2.382	19.377	7.697	-2.804
700	8.459	58.942	54.341	3.220	19.141	5.769	-1.801
800	8.601	60.081	54.989	4.073	18.878	3.876	-1.059
900	8.738	61.102	55.612	4.940	18.576	2.018	-.490
1000	8.882	62.030	56.208	5.821	15.711	.380	-.083
1100	9.044	62.884	56.777	6.717	15.428	-1.140	.226
1200	9.224	63.678	57.319	7.631	15.159	-2.635	.480
1300	9.420	64.424	57.837	8.563	14.904	-4.106	.690
1400	9.628	65.130	58.333	9.515	14.665	-5.559	.868
1500	9.840	65.801	58.809	10.488	14.444	-6.997	1.019
1600	10.051	66.443	59.266	11.483	14.241	-8.419	1.150
1700	10.254	67.058	59.707	12.498	14.057	-9.830	1.264
1800	10.445	67.650	60.132	13.533	13.889	-11.229	1.363
1900	10.619	68.220	60.542	14.587	13.736	-12.621	1.452
2000	10.774	68.768	60.940	15.656	13.597	-14.005	1.530
2100	10.909	69.297	61.325	16.741	13.470	-15.383	1.601
2200	11.022	69.807	61.699	17.837	13.351	-16.754	1.664
2300	11.116	70.299	62.063	18.944	13.242	-18.118	1.722
2400	11.190	70.774	62.416	20.060	13.138	-19.478	1.774
2500	11.246	71.232	62.759	21.182	13.037	-20.839	1.822
2600	11.286	71.674	63.094	22.309	12.939	-22.190	1.865
2700	11.311	72.101	63.420	23.439	12.841	-23.541	1.905
2800	11.323	72.512	63.737	24.570	-56.668	-24.055	1.878
2900	11.325	72.910	64.046	25.703	-56.507	-22.894	1.725
3000	11.317	73.293	64.348	26.835	-56.348	-21.737	1.584
3100	11.302	73.664	64.643	27.966	-56.192	-20.585	1.451
3200	11.281	74.023	64.930	29.095	-56.041	-19.439	1.328
3300	11.255	74.370	65.211	30.222	-55.894	-18.297	1.212
3400	11.225	74.705	65.486	31.346	-55.754	-17.162	1.103
3500	11.193	75.030	65.754	32.467	-55.617	-16.030	1.001
3600	11.158	75.345	66.016	33.585	-55.486	-14.897	.904
3700	11.123	75.650	66.272	34.699	-55.361	-13.773	.814
3800	11.086	75.946	66.523	35.809	-55.242	-12.651	.728
3900	11.050	76.234	66.768	36.916	-55.128	-11.530	.646
4000	11.014	76.513	67.008	38.019	-55.020	-10.416	.569
4100	10.979	76.785	67.243	39.119	-54.918	-9.304	.496
4200	10.945	77.049	67.474	40.215	-54.820	-8.191	.426
4300	10.912	77.306	67.699	41.308	-54.730	-7.081	.360
4400	10.880	77.556	67.921	42.398	-54.643	-5.972	.297
4500	10.850	77.801	68.137	43.484	-54.563	-4.868	.236
4600	10.822	78.039	68.350	44.568	-54.487	-3.762	.179
4700	10.795	78.271	68.559	45.648	-54.419	-2.665	.124
4800	10.770	78.498	68.763	46.727	-54.354	-1.564	.071
4900	10.746	78.720	68.964	47.802	-54.294	-.462	.021
5000	10.724	78.937	69.162	48.876	-54.240	.634	-.028
5100	10.704	79.149	69.355	49.947	-54.191	1.733	-.074
5200	10.685	79.357	69.546	51.017	-54.147	2.826	-.119
5300	10.669	79.560	69.733	52.084	-54.109	3.923	-.162
5400	10.653	79.759	69.917	53.151	-54.075	5.018	-.203
5500	10.640	79.955	70.097	54.215	-54.048	6.110	-.243
5600	10.628	80.146	70.275	55.279	-54.027	7.205	-.281
5700	10.617	80.334	70.450	56.341	-54.010	8.295	-.318
5800	10.608	80.519	70.622	57.402	-54.000	9.392	-.354
5900	10.601	80.700	70.791	58.462	-53.996	10.485	-.388
6000	10.594	80.878	70.958	59.522	-53.997	11.578	-.422

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1962; Sept. 30, 1965; June 30, 1970

ALUMINUM MONOXIDE (AlO) (IDEAL GAS) GFW = 42.9809

Symmetry Number = 1

ΔHf°_0 = 20 ± 4 kcal/mol

$S^\circ_{298.15}$ = 52.169 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 20 ± 4 kcal/mol

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^2\Sigma^+$	0	2	1.6176	0.64136	0.0058	979.23	6.97
$A^2\Pi$	5282	2	1.7748	0.5328	[0.0050]	728.5	4.15
	5411	2					
$B^2\Sigma^+$	20635.2	2	1.6668	0.60408	0.00447	870.05	3.52
$C^2\Pi$	33092.5	4	[1.73]	[0.5605]	[0.0056]	855.4	6.0
$D^2\Sigma^+$	40187.2	2	1.7304	0.5605	[0.0056]	819.6	5.8
$E^2\Delta$	45260	4	1.849	0.4910	[0.0050]	[520]	[2.5]

Heat of Formation

The vibrational quanta of the ground and first excited states can be linearly extrapolated to obtain approximate dissociation energies of 98.3 and 106.5 kcal/mol. Both these states can correlate with ground state atoms and we assume, with a high degree of confidence, that these are the products of the dissociation. Hildenbrand (1) has shown that improved values from ground state extrapolations can be obtained by correcting the extrapolation for the ionicity of the state. The corrected value is obtained from D°_0 = D(linear extrapolation)[0.365(r_x/r_e)+0.448] eV where r_x = 14.4/(IP-EA) and IP-EA is the difference, in eV, between the ionization potential of the electropositive element and EA is the electron affinity of the more electronegative element. This approach yields a corrected value of 114.7 kcal for the ground state dissociation energy. The second and higher excited states all have extrapolations of the same magnitude as the ground state but involve excited products, thus, they do not add materially to the knowledge of the dissociation energy.

Drowart et al. (2) have determined the partial pressures of Al(g), O(g) and AlO(g) over Al_2O_3, by mass-spectrometry in the temperature range 2000-2500°K. A similar experiment has also been reported by Efimenko (3) over a mixture of Be and Al_2O_3. An analysis of this data for the reaction AlO(g) → Al(g) + O(g) by the 2nd and 3rd law methods is given below.

Reference	Points	Range °K	ΔHr_{298}, kcal/mol		Drift	ΔHf°_{298}(AlO, g)
			2nd law	3rd law	eu	kcal/mol
2. Mo cell	15	2036-2466	114.7 ± 7.0	116.0 ± 2.6	0.4 ± 3.1	21.6
2. W cell	15*	2188-2514	122.1 ± 5.0	114.7 ± 1.9	-3.2 ± 2.2	22.9
3. W cell	10*	1511-1743	68.4 ± 7.3	75.2 ± 1.9	3.7 ± 4.4	62.4

*2 or 3 points rejected due to failure of a statistical test.

In addition Tyte (4) has obtained a value for the onset of continuous absorption, which he interprets as the dissociation of AlO, of 36630 cm^{-1} or 104.73 kcal. However, McDonald and Innes (5) conclude that Tyte was seeing continuous absorption from the $A^2\Pi$ state, since bands of two systems terminating in this state were seen by Tyte. On this basis they conclude that the best value of the dissociation energy should be 41912 cm^{-1} or 119.83 kcal/mol, which corresponds to ΔHf°_{298}(AlO, g) = 16.57 kcal/mol. Many other values have been reported for ΔHf°_{298}(AlO, g), including 9.3 kcal/mol (6), -0.7 kcal/mol (7), 48.7 kcal/mol (8) and 20.3 ± 3 kcal/mol (9).

The situation is not clearly resolved, and so a median value of D°_0 = 116.3 ± 4 kcal is adopted which corresponds to ΔHf°_{298}(AlO, g) = 20 ± 4 kcal/mol.

Heat Capacity and Entropy

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states. The ground and B state constants were obtained from Lagerqvist et al. (10), the A and E state constants from McDonald and Innes (5), the C state constants from McDonald et al. (11), and the D state constants are from Krishnamachari et al. (12). Estimated quantities are obtained by comparison with other states and from combination of references (5) and (13) for ω_e of the E state. Several other sets of data exist but are no longer considered significant to the analysis. References to them may be found in the adopted studies.

References

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Aluminum Monoxide Unipositive Ion (AlO$^+$)

(Ideal Gas) GFW = 42.9804

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.591	51.064	51.064	.000	239.000	231.612	-169.776
300	7.601	51.111	51.064	.014	239.006	231.565	-168.695
400	8.271	53.382	51.369	.805	239.339	229.037	-125.140
500	9.275	55.330	51.970	1.680	239.714	226.419	-98.967
600	10.523	57.129	52.681	2.669	240.164	223.718	-81.489
700	11.716	58.844	53.440	3.783	240.700	220.936	-68.979
800	12.590	60.470	54.218	5.001	241.299	218.072	-59.574
900	13.048	61.983	54.998	6.287	241.913	215.132	-52.241
1000	13.141	63.365	55.767	7.599	239.975	212.308	-46.400
1100	12.984	64.612	56.515	8.906	240.601	209.510	-41.626
1200	12.689	65.730	57.237	10.191	241.200	206.658	-37.637
1300	12.339	66.732	57.930	11.443	241.761	203.755	-34.254
1400	11.984	67.633	58.591	12.659	242.283	200.813	-31.348
1500	11.650	68.448	59.222	13.840	242.767	197.832	-28.824
1600	11.351	69.191	59.822	14.990	243.216	194.822	-26.611
1700	11.089	69.871	60.393	16.111	243.635	191.785	-24.656
1800	10.863	70.498	60.938	17.209	244.026	188.724	-22.914
1900	10.669	71.080	61.456	18.285	244.393	185.642	-21.354
2000	10.504	71.623	61.951	19.344	244.739	182.539	-19.947
2100	10.363	72.132	62.424	20.387	245.068	179.420	-18.672
2200	10.243	72.611	62.876	21.417	245.380	176.286	-17.512
2300	10.141	73.064	63.309	22.436	245.679	173.140	-16.452
2400	10.054	73.494	63.725	23.446	245.966	169.982	-15.479
2500	9.979	73.903	64.124	24.447	246.241	166.807	-14.582
2600	9.915	74.293	64.508	25.442	246.508	163.625	-13.754
2700	9.861	74.666	64.877	26.431	246.766	160.433	-12.986
2800	9.814	75.024	65.233	27.414	177.606	158.061	-12.337
2900	9.774	75.368	65.577	28.394	178.110	157.354	-11.858
3000	9.740	75.698	65.908	29.369	178.609	156.629	-11.410
3100	9.710	76.017	66.229	30.342	179.103	155.889	-10.990
3200	9.685	76.325	66.540	31.311	179.592	155.135	-10.595
3300	9.664	76.623	66.841	32.279	180.076	154.362	-10.223
3400	9.646	76.911	67.133	33.244	180.554	153.574	-9.872
3500	9.630	77.190	67.416	34.208	181.031	152.773	-9.540
3600	9.618	77.461	67.692	35.170	181.503	151.962	-9.225
3700	9.607	77.725	67.959	36.132	181.973	151.131	-8.927
3800	9.599	77.981	68.220	37.092	182.438	150.293	-8.644
3900	9.592	78.230	68.473	38.051	182.903	149.443	-8.375
4000	9.587	78.473	68.720	39.010	183.362	148.575	-8.118
4100	9.583	78.710	68.961	39.969	183.820	147.697	-7.873
4200	9.580	78.940	69.196	40.927	184.276	146.815	-7.640
4300	9.579	79.166	69.425	41.885	184.729	145.919	-7.416
4400	9.578	79.386	69.649	42.843	185.181	145.013	-7.203
4500	9.579	79.601	69.868	43.801	185.628	144.092	-6.998
4600	9.580	79.812	70.082	44.759	186.076	143.168	-6.802
4700	9.582	80.018	70.291	45.717	186.519	142.224	-6.613
4800	9.585	80.220	70.496	46.675	186.961	141.276	-6.432
4900	9.588	80.417	70.696	47.634	187.401	140.325	-6.259
5000	9.592	80.611	70.892	48.593	187.836	139.359	-6.091
5100	9.596	80.801	71.085	49.552	188.270	138.384	-5.930
5200	9.601	80.987	71.274	50.512	188.701	137.401	-5.775
5300	9.606	81.170	71.459	51.472	189.129	136.411	-5.625
5400	9.612	81.350	71.640	52.433	189.554	135.412	-5.480
5500	9.618	81.526	71.818	53.395	189.975	134.404	-5.341
5600	9.624	81.700	71.993	54.357	190.391	133.388	-5.206
5700	9.631	81.870	72.165	55.320	190.806	132.369	-5.075
5800	9.637	82.038	72.334	56.283	191.215	131.341	-4.949
5900	9.644	82.203	72.500	57.247	191.620	130.304	-4.827
6000	9.652	82.365	72.663	58.212	192.020	129.266	-4.708

June 30, 1968; June 30, 1970

ALUMINUM MONOXIDE UNIPOSITIVE ION (AlO$^+$) (IDEAL GAS) GFW = 42.9804

Ground State Configuration [$^1\Sigma$] ΔHf_0° = 239 ± 15 kcal/mol

$S^\circ_{298.15}$ = [51.1 ± 3] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 239 ± 15 kcal/mol

Electronic Levels and Degeneracies

ε_i, cm^{-1}	g_i
0	[1]
[2300]	[6]
[2300]	[3]
[3600]	[2]
[20000]	[1]

ω_e = [850] cm^{-1} $\omega_e x_e$ = [6.0] cm^{-1} σ = 1

B_e = [0.581] cm^{-1} α_e = [0.0053] cm^{-1} r_e = [1.7] Å

Heat of Formation

The ionization potential of AlO has been reported as 9.5 ± 0.5eV(219 kcal) by J. Drowart, G. DeMaria, R. P. Burns, and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960), and by G. DeMaria, J. Drowart and M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value in conjunction with ΔHf°_{298}(AlO, g) = 20 ± 4 kcal/mol, we obtain ΔHf°_{298}(AlO$^+$) = 239 ± 15 kcal/mol.

Heat Capacity and Entropy

AlO$^+$ is isoelectronic with MgO and we estimated the electronic ground state and excited states by comparison with those for MgO as reported by W. G. Richards, G. Verhaegen and C. M. Moser, J. Chem. Phys. 45, 3226 (1966). The bond length is estimated to be longer than that in AlO, since the dissociation energy of AlO$^+$ is less than that of AlO. The vibrational frequency and anharmonicity are estimated between those for MgO and AlO and the rotational constant, α_e, is derived from the above quantities assuming a Morse potential function.

The enthalpy at 0°K is -2.118 kcal/mol.

Aluminum Dioxide (AlO_2)

(Ideal Gas) GFW = 58.9803

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-2.707	-43.538	-43.538	INFINITE
100	8.023	48.101	67.973	-1.987	-43.618	-44.124	96.433
200	10.160	54.373	59.723	-1.070	-43.839	-44.556	48.688
298	11.561	58.707	58.707	.000	-44.000	-44.875	32.894
300	11.583	58.779	58.708	.021	-44.003	-44.881	32.696
400	12.550	62.253	59.175	1.231	-44.103	-45.156	24.672
500	13.191	65.127	60.086	2.520	-44.176	-45.411	19.849
600	13.619	67.572	61.135	3.862	-44.248	-45.652	16.629
700	13.912	69.695	62.210	5.240	-44.333	-45.879	14.324
800	14.119	71.567	63.265	6.642	-44.446	-46.093	12.592
900	14.269	73.239	64.282	8.062	-44.602	-46.290	11.241
1000	14.381	74.748	65.254	9.494	-47.330	-46.283	10.115
1100	14.466	76.123	66.181	10.937	-47.485	-46.172	9.174
1200	14.532	77.385	67.062	12.387	-47.642	-46.046	8.386
1300	14.585	78.550	67.902	13.843	-47.801	-45.906	7.718
1400	14.627	79.633	68.702	15.303	-47.964	-45.754	7.142
1500	14.661	80.643	69.464	16.768	-48.129	-45.591	6.643
1600	14.690	81.590	70.193	18.236	-48.297	-45.416	6.204
1700	14.714	82.482	70.890	19.706	-48.468	-45.231	5.815
1800	14.734	83.323	71.557	21.178	-48.643	-45.034	5.468
1900	14.751	84.120	72.198	22.652	-48.823	-44.829	5.157
2000	14.766	84.877	72.813	24.128	-49.006	-44.616	4.875
2100	14.778	85.598	73.405	25.605	-49.193	-44.392	4.620
2200	14.790	86.286	73.975	27.084	-49.385	-44.159	4.387
2300	14.800	86.943	74.524	28.563	-49.580	-43.915	4.173
2400	14.809	87.573	75.055	30.044	-49.780	-43.663	3.976
2500	14.817	88.178	75.568	31.525	-49.986	-43.409	3.795
2600	14.825	88.759	76.064	33.007	-50.195	-43.139	3.626
2700	14.833	89.319	76.545	34.490	-50.409	-42.865	3.470
2800	14.840	89.859	77.011	35.974	-120.037	-41.751	3.259
2900	14.847	90.380	77.463	37.458	-119.998	-38.956	2.936
3000	14.855	90.883	77.902	38.943	-119.963	-36.161	2.634
3100	14.863	91.370	78.329	40.429	-119.931	-33.367	2.352
3200	14.871	91.842	78.743	41.916	-119.903	-30.576	2.088
3300	14.879	92.300	79.147	43.403	-119.879	-27.785	1.840
3400	14.888	92.744	79.541	44.892	-119.859	-24.997	1.607
3500	14.898	93.176	79.924	46.381	-119.841	-22.208	1.387
3600	14.908	93.596	80.298	47.871	-119.827	-19.415	1.179
3700	14.919	94.004	80.663	49.363	-119.815	-16.627	.982
3800	14.930	94.402	81.019	50.855	-119.807	-13.838	.796
3900	14.943	94.790	81.368	52.349	-119.799	-11.049	.619
4000	14.956	95.169	81.708	53.844	-119.796	-8.264	.452
4100	14.970	95.538	82.041	55.340	-119.795	-5.476	.292
4200	14.984	95.899	82.366	56.837	-119.795	-2.687	.140
4300	15.000	96.252	82.685	58.337	-119.797	.104	-.005
4400	15.016	96.597	82.998	59.837	-119.802	2.893	-.144
4500	15.033	96.935	83.304	61.340	-119.808	5.681	-.276
4600	15.050	97.265	83.603	62.844	-119.815	8.474	-.403
4700	15.068	97.589	83.898	64.350	-119.826	11.257	-.523
4800	15.087	97.907	84.186	65.858	-119.837	14.047	-.640
4900	15.107	98.218	84.469	67.367	-119.850	16.837	-.751
5000	15.127	98.523	84.747	68.879	-119.865	19.624	-.858
5100	15.147	98.823	85.020	70.393	-119.882	22.418	-.961
5200	15.168	99.117	85.289	71.908	-119.902	25.203	-1.059
5300	15.189	99.406	85.552	73.426	-119.923	27.998	-1.155
5400	15.211	99.691	85.812	74.946	-119.946	30.787	-1.246
5500	15.233	99.970	86.066	76.468	-119.972	33.579	-1.334
5600	15.255	100.245	86.317	77.993	-120.001	36.371	-1.419
5700	15.278	100.515	86.564	79.520	-120.031	39.160	-1.508
5800	15.300	100.781	86.807	81.048	-120.067	41.959	-1.581
5900	15.323	101.042	87.046	82.580	-120.104	44.752	-1.658
6000	15.346	101.300	87.281	84.113	-120.146	47.548	-1.732

June 30, 1968; Dec. 31, 1968

ALUMINUM DIOXIDE (AlO_2) (IDEAL GAS) GFW = 58.9803

Point Group [$D_{\infty h}$]

ΔHf°_0 = [-44 ± 20] kcal/mol

$S^\circ_{298.15}$ = [58.7 ± 4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-44 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]
[20000]	[4]
[25000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[680] (1)
[295] (2)
[1005] (1)

Bond Distance: Al-O = [1.66] Å

σ = 2

Bond Angle: O-Al-O = [180°]

Rotational Constant: B_0 = [0.1912] cm^{-1}

Heat of Formation

The OH bond strength in H_2O is 119 kcal and in HOBO it is 118 kcal. Thus, it appears very reasonable to assume 118 kcal for the value in HOAlO. This assumption leads to $\Delta Hf^\circ_{298}(AlO_2, g)$ = -44 ± 20 kcal/mol, using the JANAF ΔHf°_{298}(HOAlO, g) = -110 kcal/mol. This value is consistent with the independently estimated $\Delta Hf^\circ_{298}(AlO_2^-, g)$ = -130 ± 15 kcal/mol, since it yields an electron affinity for AlO_2 of 86 kcal in good agreement with the value 98 kcal for BO_2.

Heat Capacity and Entropy

The electronic ground and excited states and molecular configuration are estimated to be similar to those for BO_2. The AlO bond length is assumed to be equal to that in Al_2O. The vibrational frequencies are estimated from a valence force field treatment using k_1 from BO_2 modified by the ratio k(AlO)/k(BO) and using the same ratio of bending to stretch force constants as in BO_2.

The adopted molecular configuration and electronic ground state are in accord with the predictions of A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

Aluminum Dioxide Uninegative Ion (AlO_2^-)

(Ideal Gas) GFW = 58.9809

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.081	55.509	55.509	.000	-145.000	-143.434	105.140
300	11.102	55.578	55.509	.021	-145.012	-143.424	104.485
400	12.066	58.910	55.957	1.181	-145.659	-142.796	78.020
500	12.761	61.682	56.833	2.425	-146.274	-142.009	62.072
600	13.255	64.055	57.843	3.727	-146.883	-141.099	51.395
700	13.609	66.126	58.882	5.071	-147.498	-140.085	43.736
800	13.866	67.961	59.904	6.445	-148.136	-138.984	37.969
900	14.056	69.606	60.892	7.842	-148.812	-137.800	33.462
1000	14.201	71.094	61.839	9.255	-152.056	-136.354	29.800
1100	14.312	72.453	62.743	10.681	-152.725	-134.753	26.773
1200	14.400	73.702	63.605	12.117	-153.393	-133.091	24.239
1300	14.470	74.858	64.427	13.560	-154.061	-131.370	22.085
1400	14.526	75.932	65.211	15.010	-154.731	-129.600	20.231
1500	14.572	76.936	65.959	16.465	-155.403	-127.782	18.618
1600	14.611	77.878	66.675	17.924	-156.077	-125.918	17.200
1700	14.643	78.765	67.360	19.387	-156.752	-124.013	15.943
1800	14.670	79.602	68.017	20.853	-157.429	-122.065	14.821
1900	14.693	80.396	68.648	22.321	-158.112	-120.084	13.813
2000	14.713	81.150	69.255	23.791	-158.798	-118.066	12.902
2100	14.731	81.869	69.838	25.264	-159.486	-116.012	12.073
2200	14.746	82.554	70.401	26.737	-160.181	-113.926	11.318
2300	14.759	83.210	70.944	28.213	-160.875	-111.805	10.624
2400	14.770	83.839	71.468	29.689	-161.577	-109.656	9.986
2500	14.781	84.442	71.975	31.167	-162.283	-107.482	9.396
2600	14.790	85.022	72.466	32.645	-162.993	-105.274	8.849
2700	14.798	85.580	72.941	34.125	-163.707	-103.043	8.341
2800	14.805	86.118	73.402	35.605	-233.836	-99.952	7.802
2900	14.812	86.638	73.850	37.086	-234.296	-95.162	7.172
3000	14.818	87.140	74.284	38.567	-234.762	-90.354	6.582
3100	14.823	87.626	74.707	40.049	-235.231	-85.532	6.030
3200	14.828	88.097	75.118	41.532	-235.704	-80.698	5.511
3300	14.833	88.553	75.518	43.015	-236.181	-75.848	5.023
3400	14.837	88.996	75.908	44.498	-236.663	-70.984	4.563
3500	14.840	89.426	76.288	45.982	-237.147	-66.106	4.128
3600	14.844	89.844	76.659	47.466	-237.636	-61.207	3.716
3700	14.847	90.251	77.021	48.951	-238.128	-56.299	3.325
3800	14.850	90.647	77.374	50.436	-238.624	-51.379	2.955
3900	14.853	91.033	77.720	51.921	-239.122	-46.445	2.603
4000	14.855	91.409	78.057	53.406	-239.625	-41.500	2.267
4100	14.857	91.776	78.387	54.892	-240.131	-36.540	1.948
4200	14.860	92.134	78.710	56.378	-240.639	-31.570	1.643
4300	14.862	92.483	79.027	57.864	-241.152	-26.584	1.351
4400	14.864	92.825	79.336	59.350	-241.668	-21.589	1.072
4500	14.865	93.159	79.640	60.837	-242.186	-16.579	.805
4600	14.867	93.486	79.937	62.323	-242.708	-11.557	.549
4700	14.868	93.806	80.229	63.810	-243.235	-6.532	.304
4800	14.870	94.119	80.515	65.297	-243.764	-1.487	.068
4900	14.871	94.425	80.796	66.784	-244.296	3.564	-.159
5000	14.873	94.726	81.071	68.271	-244.832	8.625	-.377
5100	14.874	95.020	81.342	69.758	-245.373	13.706	-.587
5200	14.875	95.309	81.608	71.246	-245.917	18.784	-.789
5300	14.876	95.592	81.869	72.733	-246.466	23.885	-.985
5400	14.877	95.870	82.126	74.221	-247.018	28.990	-1.173
5500	14.878	96.143	82.378	75.709	-247.575	34.105	-1.355
5600	14.879	96.412	82.626	77.197	-248.137	39.235	-1.531
5700	14.880	96.675	82.871	78.685	-248.703	44.363	-1.701
5800	14.881	96.934	83.111	80.173	-249.276	49.518	-1.866
5900	14.881	97.188	83.347	81.661	-249.854	54.674	-2.025
6000	14.882	97.438	83.580	83.149	-250.438	59.839	-2.180

June 30, 1968; Dec. 31, 1968

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO_2^-) (IDEAL GAS) GFW = 58.9809

Point Group $[D_{\infty h}]$ ΔHf°_0 = [-144.5 ± 15] kcal/mol

$S^\circ_{298.15}$ = [55.5 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-145 ± 15] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[800] (1)
[320] (2)
[1200] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: O-Al-O = [180°] σ = 2

Rotational Constant: B_0 = [0.1912] cm^{-1}

Heat of Formation

The heat of formation of AlO_2^- is estimated from the following considerations. The heats of the following reactions are calculated from the tables:

$BO_2^- \rightarrow B^- + 2O$ ΔH = 411 kcal
$CO_2 \rightarrow C + 2O$ ΔH = 384 kcal
$BO_2^- \rightarrow B + O + O^-$ ΔH = 382 kcal
$BOF \rightarrow B + O + F$ ΔH = 355 kcal

It is apparent that the heat of dissociation of BO_2^- is closely predicted by use of the corresponding isoelectronic decomposition. Thus using

$SiO_2 \rightarrow Si + 2O$ ΔH = 299
we predict $AlO_2^- \rightarrow Al^- + 2O$ ΔH = [320]
and using $AlOF \rightarrow Al + O + F$ ΔH = 297
we predict $AlO_2^- \rightarrow Al + O + O^-$ ΔH = [320]

From these two reactions we estimate ΔHf(AlO_2^-, g) = -158 and -135 kcal/mol and we adopt the value -145 ± 15 kcal/mol. From the value adopted for AlO_2(g) we obtain an electron affinity of 4.38 ev (101 kcal) which is comparable to that for BO_2(g).

Heat Capacity and Entropy

The configuration of the molecule is assumed to be linear using the correlations of Walsh, (1) for 16 electron XY_2 molecules; the ground state is assumed to be $^1\Sigma$ from the same correlation diagrams. The bond length is taken to be that in Al_2O and the vibrational frequencies are estimated between those for AlO_2 and SiO_2.

The enthalpy at 0°K is -2.630 kcal/mol.

Reference

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

Aluminum Sulfide (AlS)

(Ideal Gas) Mol. Wt. = 59.046

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.172	47.975	47.975	INFINITE
100	6.981	47.055	61.819	-1.476	48.401	44.157	-96.500
200	7.449	52.010	55.804	-.759	48.283	39.920	-43.620
298	7.982	55.090	55.090	.000	48.000	35.868	-26.291
300	7.991	55.139	55.090	.015	47.994	35.793	-26.074
400	8.334	57.489	55.408	.832	47.115	31.798	-17.373
500	8.542	59.373	56.019	1.677	46.395	28.052	-12.261
600	8.674	60.943	56.713	2.538	45.743	24.446	-8.904
700	8.763	62.288	57.415	3.411	45.129	20.968	-6.546
800	8.827	63.462	58.099	4.290	31.467	16.290	-4.450
900	8.874	64.505	58.754	5.175	31.167	14.412	-3.499
1000	8.912	65.442	59.377	6.065	28.344	12.752	-2.787
1100	8.942	66.293	59.968	6.957	28.093	11.204	-2.226
1200	8.968	67.072	60.528	7.853	27.845	9.680	-1.763
1300	8.990	67.790	61.059	8.751	27.598	8.177	-1.375
1400	9.010	68.457	61.564	9.651	27.351	6.692	-1.045
1500	9.027	69.080	62.044	10.553	27.105	5.223	-.761
1600	9.043	69.663	62.502	11.456	26.860	3.774	-.516
1700	9.059	70.211	62.940	12.361	26.616	2.338	-.301
1800	9.073	70.730	63.358	13.268	26.373	.916	-.111
1900	9.086	71.221	63.759	14.176	26.131	-.489	. 56
2000	9.099	71.687	64.144	15.085	25.889	-1.885	.206
2100	9.112	72.131	64.514	15.996	25.648	-3.270	.340
2200	9.124	72.555	64.870	16.908	25.408	-4.638	.461
2300	9.135	72.961	65.213	17.820	25.167	-6.000	.570
2400	9.147	73.350	65.544	18.735	24.929	-7.349	.669
2500	9.158	73.724	65.864	19.650	24.691	-8.689	.760
2600	9.169	74.083	66.173	20.566	24.453	-10.021	.842
2700	9.180	74.429	66.473	21.484	24.217	-11.343	.918
2800	9.190	74.763	66.763	22.402	-46.574	-11.004	.859
2900	9.201	75.086	67.044	23.322	-46.606	-9.733	.733
3000	9.211	75.398	67.317	24.242	-46.639	-8.458	.616
3100	9.222	75.700	67.583	25.164	-46.669	-7.186	.507
3200	9.232	75.993	67.841	26.087	-46.701	-5.912	.404
3300	9.242	76.278	68.093	27.010	-46.731	-4.638	.307
3400	9.252	76.554	68.337	27.935	-46.760	-3.361	.216
3500	9.262	76.822	68.576	28.861	-46.790	-2.088	.130
3600	9.272	77.083	68.809	29.787	-46.819	-.807	.049
3700	9.282	77.337	69.036	30.715	-46.848	.471	-.028
3800	9.292	77.585	69.258	31.644	-46.875	1.750	-.101
3900	9.302	77.826	69.474	32.574	-46.903	3.031	-.170
4000	9.312	78.062	69.686	33.504	-46.931	4.313	-.236
4100	9.322	78.292	69.893	34.436	-46.958	5.591	-.298
4200	9.332	78.517	70.096	35.369	-46.986	6.875	-.358
4300	9.341	78.737	70.294	36.302	-47.014	8.157	-.415
4400	9.351	78.951	70.488	37.237	-47.043	9.438	-.469
4500	9.361	79.162	70.679	38.173	-47.071	10.728	-.521
4600	9.371	79.368	70.866	39.109	-47.101	12.011	-.571
4700	9.380	79.569	71.049	40.047	-47.130	13.292	-.618
4800	9.390	79.767	71.228	40.985	-47.162	14.577	-.664
4900	9.400	79.960	71.404	41.925	-47.194	15.871	-.708
5000	9.409	80.150	71.577	42.865	-47.229	17.154	-.750
5100	9.419	80.337	71.747	43.806	-47.265	18.445	-.790
5200	9.428	80.520	71.914	44.749	-47.302	19.732	-.829
5300	9.438	80.700	72.078	45.692	-47.341	21.021	-.867
5400	9.448	80.876	72.240	46.636	-47.384	22.314	-.903
5500	9.457	81.049	72.398	47.582	-47.428	23.602	-.938
5600	9.467	81.220	72.554	48.528	-47.477	24.897	-.972
5700	9.476	81.388	72.708	49.475	-47.529	26.186	-1.004
5800	9.486	81.553	72.859	50.423	-47.584	27.483	-1.036
5900	9.496	81.715	73.008	51.372	-47.643	28.776	-1.066
6000	9.505	81.874	73.154	52.322	-47.708	30.074	-1.095

Dec. 31, 1960; Mar. 31, 1964

ALUMINUM SULFIDE (AlS) (IDEAL GAS) MOL. WT. = 59.046

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 55.09 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 48 ± 20 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 48 ± 20 kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_1, cm.$^{-1}$	g_1
0	2

ω_e = 617.12 cm.$^{-1}$

B_e = 0.2799 cm.$^{-1}$

$\omega_e x_e$ = 3.33 cm.$^{-1}$

α_e = 0.0018 cm.$^{-1}$

σ = 1

r_e = 2.03 Å

Heat of Formation.

The dissociation energy of 4.1 e.v. was calculated by adding 17% to the dissociation energy obtained from a linear extrapolation of the vibrational levels, 3.5 e.v. This was done by analogy with the molecule AlO(g) whose observed D_0 is 17% larger than the linear extrapolation. The adopted value of 4.1 e.v. corresponds to a heat of formation of 48 kcal. mole^{-1}.

Heat Capacity and Entropy.

The vibrational and rotational constants were reported by C. N. McKinney and K. K. Innes, J. Mol. Spect. 3, 235 (1959) from an analysis of 6 bands of the $A^2\Sigma^+$-$X^2\Sigma^+$ system.

Beryllium Aluminate ($BeAl_2O_4$)
(Crystal) Mol. Wt. = 126.973

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.128	- 541.322	- 541.322	INFINITE
100	3.911	1.320	31.600	- 3.028	- 542.870	- 534.355	1167.775
200	15.876	7.643	17.873	- 2.046	- 544.270	- 525.275	573.966
298	25.177	15.843	15.843	.000	- 545.000	- 515.786	378.063
300	25.316	15.999	15.843	.047	- 545.008	- 515.606	375.600
400	31.340	24.174	16.917	2.903	- 545.207	- 505.762	276.322
500	34.589	31.545	19.120	6.212	- 545.118	- 495.907	216.750
600	36.721	38.050	21.744	9.784	- 544.910	- 486.083	177.047
700	38.324	43.835	24.494	13.538	- 544.658	- 476.299	148.700
800	39.644	49.040	27.243	17.438	- 544.381	- 466.554	127.450
900	40.799	53.777	29.932	21.461	- 544.097	- 456.840	110.931
1000	41.853	58.131	32.537	25.594	- 548.802	- 446.790	97.641
1100	42.840	62.167	35.049	29.829	- 548.309	- 436.614	86.743
1200	43.782	65.935	37.468	34.161	- 547.762	- 426.483	77.669
1300	44.692	69.476	39.795	38.584	- 547.165	- 416.401	70.000
1400	45.578	72.821	42.036	43.098	- 546.515	- 406.368	63.434
1500	46.447	75.995	44.196	47.699	- 545.816	- 396.381	57.750
1600	47.304	79.020	46.278	52.387	- 547.821	- 386.363	52.772
1700	48.150	81.913	48.290	57.160	- 546.905	- 376.300	48.374
1800	48.988	84.689	50.235	62.017	- 545.924	- 366.293	44.472
1900	49.820	87.360	52.119	66.957	- 544.877	- 356.340	40.986
2000	50.647	89.936	53.946	71.981	- 543.761	- 346.447	37.856
2100	51.470	92.427	55.719	77.087	- 542.578	- 336.610	35.030
2200	52.274	94.840	57.443	82.274	- 541.333	- 326.831	32.466
2300	53.058	97.181	59.120	87.541	- 540.021	- 317.110	30.131
2400	53.822	99.455	60.753	92.885	- 538.649	- 307.443	27.995
2500	54.567	101.667	62.346	98.304	- 537.220	- 297.842	26.036
2600	55.293	103.821	63.899	103.798	- 535.728	- 288.294	24.232
2700	55.999	105.921	65.416	109.362	- 534.182	- 278.808	22.567
2800	56.685	107.970	66.900	114.997	- 744.718	- 264.964	20.680
2900	57.352	109.971	68.351	120.699	- 742.406	- 247.869	18.679
3000	58.000	111.926	69.771	126.467	- 740.040	- 230.853	16.817

Mar. 31, 1962; Sept. 30, 1964

BERYLLIUM ALUMINATE ($BeAl_2O_4$) (CRYSTAL) MOL. WT. = 126.973

$\Delta H_{f\ 0}^\circ = -541 \pm 5$ kcal. mole⁻¹

$S_{298.15}^\circ = 15.84$ cal. deg.⁻¹ mole⁻¹

$\Delta H_{f\ 298.15}^\circ = -545 \pm 5$ kcal. mole⁻¹

$T_m^\circ = 2143$°K.

$\Delta H_m^\circ = [42]$ kcal. mole⁻¹

Heat of Formation.

W. A. Young, J. Phys. Chem. 64, 1003 (1960) studied the equilibria

$$BeO(c) + H_2O(g) \rightarrow Be(OH)_2(g)$$

$$1.5\ BeAl_2O_4 + H_2O(g) \rightarrow 0.5\ BeAl_6O_{10}(c) + Be(OH)_2(g)$$

$$BeAl_6O_{10}(c) + H_2O(g) \rightarrow 3Al_2O_3(c) + Be(OH)_2(g)$$

from his results one obtains $\Delta F_{f\ 1673}^\circ = -379$ kcal. mole⁻¹, which corresponds to $\Delta H_{f\ 298}^\circ = -545$ kcal. mole⁻¹.

Heat Capacity and Entropy.

G. T. Furawaka and W. G. Saba, and T. B. Douglas and W. H. Payne, National Bureau of Standards Report 8186, Jan. 1964 have measured the low temperature heat capacities and the high temperature enthalpy in the range 15 - 1173°K.

Melting Data.

The temperature of melting was taken from National Bureau of Standards Circular 500, Washington (1952).

The heat of melting was estimated as the sum of the ΔH_{fusion}° of the constituent oxides at 2100°K.

Aluminum Tribromide, Dimeric (Al_2Br_6)

(Ideal Gas) GFW = 533.417

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 9.301	- 221.036	- 221.036	INFINITE
100	30.114	91.799	164.263	- 7.246	- 221.197	- 226.186	494.330
200	37.284	115.238	134.356	- 3.824	- 222.172	- 230.852	252.263
298	40.226	130.754	130.754	.000	- 231.500	- 233.904	171.456
300	40.262	131.003	130.754	.074	- 231.547	- 233.919	170.409
400	41.621	142.795	132.353	4.177	- 253.362	- 230.214	125.783
500	42.325	152.165	135.411	8.377	- 253.073	- 224.463	98.113
600	42.730	159.921	138.868	12.632	- 252.800	- 218.768	79.686
700	42.983	166.528	142.359	16.918	- 252.563	- 213.115	66.538
800	43.151	172.280	145.748	21.226	- 252.377	- 207.495	56.685
900	43.267	177.369	148.984	25.547	- 252.274	- 201.890	49.026
1000	43.351	181.932	152.054	29.879	- 257.309	- 195.925	42.819
1100	43.414	186.067	154.961	34.216	- 257.195	- 189.795	37.709
1200	43.462	189.847	157.713	38.560	- 257.078	- 183.674	33.452
1300	43.499	193.327	160.321	42.908	- 256.961	- 177.558	29.850
1400	43.529	196.552	162.795	47.260	- 256.845	- 171.455	26.765
1500	43.553	199.556	165.147	51.614	- 256.733	- 165.363	24.093
1600	43.573	202.368	167.386	55.970	- 256.622	- 159.274	21.756
1700	43.589	205.010	169.522	60.328	- 256.512	- 153.192	19.694
1800	43.603	207.502	171.564	64.688	- 256.401	- 147.119	17.863
1900	43.615	209.859	173.518	69.049	- 256.294	- 141.046	16.224
2000	43.625	212.097	175.391	73.411	- 256.192	- 134.990	14.751
2100	43.633	214.225	177.190	77.774	- 256.089	- 128.932	13.418
2200	43.641	216.255	178.920	82.138	- 255.991	- 122.880	12.207
2300	43.647	218.195	180.586	86.502	- 255.894	- 116.824	11.101
2400	43.653	220.053	182.192	90.867	- 255.801	- 110.778	10.088
2500	43.658	221.835	183.742	95.233	- 255.710	- 104.743	9.157
2600	43.663	223.548	185.241	99.599	- 255.622	- 98.704	8.297
2700	43.667	225.196	186.690	103.965	- 255.537	- 92.678	7.502
2800	43.670	226.784	188.094	108.332	- 394.277	- 84.983	6.633
2900	43.673	228.316	189.454	112.699	- 393.673	- 73.948	5.573
3000	43.676	229.797	190.775	117.067	- 393.071	- 62.933	4.585
3100	43.679	231.229	192.057	121.434	- 392.476	- 51.934	3.661
3200	43.681	232.616	193.303	125.802	- 391.880	- 40.958	2.797
3300	43.683	233.960	194.514	130.171	- 391.289	- 30.005	1.987
3400	43.685	235.264	195.694	134.539	- 390.701	- 19.071	1.226
3500	43.687	236.531	196.843	138.908	- 390.116	- 8.147	.509
3600	43.689	237.761	197.962	143.277	- 389.536	2.763	- .168
3700	43.690	238.958	199.054	147.646	- 388.956	13.648	- .806
3800	43.692	240.123	200.120	152.015	- 388.384	24.524	- 1.410
3900	43.693	241.258	201.160	156.384	- 387.813	35.392	- 1.983
4000	43.694	242.365	202.176	160.753	- 387.249	46.219	- 2.525
4100	43.695	243.444	203.170	165.123	- 386.687	57.043	- 3.041
4200	43.697	244.497	204.141	169.492	- 386.129	67.866	- 3.531
4300	43.697	245.525	205.092	173.862	- 385.577	78.673	- 3.999
4400	43.698	246.529	206.022	178.232	- 385.028	89.472	- 4.444
4500	43.699	247.511	206.933	182.602	- 384.486	100.245	- 4.869
4600	43.700	248.472	207.826	186.972	- 383.947	111.013	- 5.274
4700	43.701	249.412	208.701	191.342	- 383.417	121.762	- 5.662
4800	43.701	250.332	209.558	195.712	- 382.895	132.495	- 6.033
4900	43.702	251.233	210.400	200.082	- 382.375	143.243	- 6.389
5000	43.703	252.116	211.225	204.452	- 381.864	153.961	- 6.730
5100	43.703	252.981	212.036	208.823	- 381.362	164.669	- 7.057
5200	43.704	253.830	212.831	213.193	- 380.867	175.367	- 7.370
5300	43.704	254.662	213.613	217.563	- 380.381	186.067	- 7.673
5400	43.705	255.479	214.380	221.934	- 379.904	196.746	- 7.963
5500	43.705	256.281	215.135	226.304	- 379.438	207.423	- 8.242
5600	43.706	257.069	215.877	230.675	- 378.983	218.083	- 8.511
5700	43.706	257.842	216.606	235.045	- 378.538	228.746	- 8.771
5800	43.707	258.602	217.324	239.416	- 378.104	239.405	- 9.021
5900	43.707	259.350	218.030	243.787	- 377.684	250.040	- 9.262
6000	43.707	260.084	218.725	248.157	- 377.278	260.666	- 9.495

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRIBROMIDE, DIMERIC [$(AlBr_3)_2$] (IDEAL GAS) GFW = 533.417

Point Group D_{2h}

ΔHf°_0 = -221.0 ± 7 kcal/mol

$S^\circ_{298.15}$ = 130.8 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -231.5 ± 7 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
407 (1)	56 (1)	[110] (1)	[20] (1)	342 (1)	377 (1)
192 (1)	[33](1)	504 (1)	491 (1)	63 (1)	186 (1)
122 (1)	162 (1)	93 (1)	92 (1)	[116](1)	68 (1)

Bond Distances: Al-Br = 2.21 ± 0.4 Å $Al\text{-}Br_{bridge}$ = 2.33 ± 0.4 Å

Bond Angles: Br-Al-Br = 114° 38' $Br_{bridge}\text{-}Al\text{-}Br_{bridge}$ = 86° 44' σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 8.80123 \times 10^{-110}\ g^3\ cm^6$

Heat of Formation

The vapor pressures of $AlBr_3$(c) and $AlBr_3$(ℓ) have been measured by Dunne and Gregory (1) and Fischer et al. (2), respectively. Using these data, the heats of vaporization were calculated by both second and third law methods. The adopted value of ΔHf°_{298} for Al_2Br_6(g) is -231.5 ± 7 kcal/mol. The results of these calculations are as follows with reaction (A) corresponding to $2AlBr_3(c) = Al_2Br_6(c)$ and reaction (B) corresponding to $2AlBr_3(\ell) = Al_2Br_6(g)$:

Source	Reac.	Method	No. Pts.	Range T°K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift, eu	*ΔHf°_{298}
1	A	Effusion	3	273-310	19.7±0.7	20.25	2.2±2.4	-231.7
2	B	Weight Loss	18**	413-523	15.6±0.1	15.61	0.1±0.1	-231.5
2	B	Transport	4	396-471	16.1±0.2	15.60	-1.0±0.3	-231.5

*Calculation based on third law ΔHr°_{298}.

**One point rejected due to failure of a statistical test.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from the electron diffraction work of Palmer and Elliott (3). The bond distances and angles have also been reported by Akishin et al. (4), and these values are in good agreement with those given by Palmer and Elliott (3). The principal moments of inertia are $I_A = 5.36492 \times 10^{-37}$, $I_B = 2.51547 \times 10^{-37}$, and $I_C = 6.52171 \times 10^{-37}$ g cm^2. It has been established that the condensed phases of $AlBr_3$ are dimeric (5), (6), thus spectroscopic studies of the crystal and liquid pertain to the structure of Al_2Br_6(g). Gerding and Smit (7) have studied the Raman spectra of Al_2Br_6(ℓ). The eighteen fundamental vibrational frequencies of Al_2Br_6(g) have been predicted by Miller (8) based on seven of the frequencies reported by Gerding and Smit (7). Webb (9) has measured the infrared spectra of Al_2Br_6(c) in the 40-600 cm^{-1} region, the results being in general accord with the predictions of Miller (8). The vibrational frequencies used are adjusted so that the values of ΔHv°_{298} obtained by the third law method are in agreement with the corresponding second law values. These adjustments are based on the assumption that vibrations with a wave number below 300 cm^{-1} have a lower wave number in the gas phase than they have in the condensed phases.

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Aluminum Trichloride, Dimer (Al_2Cl_6)

(Ideal Gas) GFW = 266.681

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-8.083	-308.953	-308.953	INFINITE
100	24.278	79.485	143.885	-6.440	-309.610	-303.684	663.700
200	33.306	99.420	116.979	-3.512	-309.744	-297.705	325.317
298	37.732	113.647	113.647	.000	-309.640	-291.823	213.912
300	37.789	113.881	113.648	.070	-309.637	-291.713	212.513
400	40.019	125.093	115.162	3.972	-309.423	-285.768	156.137
500	41.225	134.165	118.084	8.040	-309.176	-279.882	122.336
600	41.935	141.749	121.414	12.201	-308.940	-274.047	99.821
700	42.384	148.250	124.794	16.419	-308.726	-268.248	83.751
800	42.685	153.930	128.089	20.673	-308.564	-262.480	71.706
900	42.895	158.970	131.245	24.953	-308.478	-256.723	62.341
1000	43.047	163.498	134.248	29.250	-313.529	-250.610	54.771
1100	43.161	167.607	137.097	33.561	-313.427	-244.324	48.543
1200	43.248	171.366	139.798	37.881	-313.325	-238.047	43.354
1300	43.317	174.831	142.361	42.210	-313.218	-231.778	38.965
1400	43.371	178.043	144.797	46.544	-313.114	-225.515	35.204
1500	43.415	181.037	147.114	50.884	-313.010	-219.264	31.947
1600	43.452	183.840	149.323	55.227	-312.909	-213.017	29.097
1700	43.482	186.475	151.431	59.574	-312.807	-206.773	26.582
1800	43.507	188.961	153.448	63.923	-312.707	-200.540	24.349
1900	43.528	191.314	155.380	68.275	-312.609	-194.307	22.350
2000	43.547	193.547	157.233	72.629	-312.518	-188.086	20.553
2100	43.563	195.672	159.013	76.984	-312.426	-181.871	18.928
2200	43.576	197.699	160.726	81.341	-312.341	-175.657	17.450
2300	43.588	199.636	162.376	85.700	-312.255	-169.437	16.100
2400	43.599	201.492	163.967	90.059	-312.177	-163.230	14.864
2500	43.608	203.272	165.504	94.419	-312.107	-157.030	13.728
2600	43.616	204.982	166.990	98.781	-312.038	-150.826	12.678
2700	43.624	206.628	168.427	103.143	-311.978	-144.630	11.707
2800	43.630	208.215	169.820	107.505	-450.747	-136.768	10.675
2900	43.636	209.746	171.171	111.869	-450.176	-125.571	9.463
3000	43.641	211.225	172.481	116.232	-449.615	-114.387	8.333
3100	43.646	212.657	173.754	120.597	-449.061	-103.221	7.277
3200	43.651	214.042	174.992	124.962	-448.516	-92.072	6.288
3300	43.655	215.386	176.196	129.327	-447.980	-80.939	5.360
3400	43.658	216.689	177.367	133.693	-447.451	-69.826	4.488
3500	43.662	217.954	178.509	138.059	-446.932	-58.735	3.668
3600	43.665	219.185	179.622	142.425	-446.421	-47.640	2.892
3700	43.667	220.381	180.707	146.792	-445.918	-36.572	2.160
3800	43.670	221.545	181.767	151.158	-445.424	-25.521	1.468
3900	43.672	222.680	182.801	155.526	-444.935	-14.468	.811
4000	43.675	223.786	183.812	159.893	-444.460	-3.442	.188
4100	43.677	224.864	184.800	164.260	-443.988	7.570	-.404
4200	43.679	225.917	185.767	168.628	-443.524	18.579	-.967
4300	43.680	226.944	186.713	172.996	-443.067	29.575	-1.503
4400	43.682	227.949	187.638	177.364	-442.616	40.577	-2.015
4500	43.684	228.930	188.545	181.733	-442.174	51.542	-2.503
4600	43.685	229.890	189.434	186.101	-441.733	62.513	-2.970
4700	43.687	230.830	190.304	190.470	-441.303	73.465	-3.416
4800	43.688	231.750	191.158	194.838	-440.879	84.406	-3.843
4900	43.689	232.651	191.996	199.207	-440.459	95.364	-4.253
5000	43.690	233.533	192.818	203.576	-440.045	106.285	-4.646
5100	43.691	234.398	193.625	207.945	-439.635	117.217	-5.023
5200	43.692	235.247	194.417	212.314	-439.234	128.129	-5.385
5300	43.693	236.079	195.195	216.684	-438.841	139.028	-5.733
5400	43.694	236.896	195.960	221.053	-438.453	149.933	-6.068
5500	43.695	237.698	196.712	225.422	-438.075	160.823	-6.391
5600	43.696	238.485	197.450	229.792	-437.702	171.708	-6.701
5700	43.696	239.258	198.177	234.162	-437.338	182.575	-7.000
5800	43.697	240.018	198.892	238.531	-436.984	193.464	-7.290
5900	43.698	240.765	199.595	242.901	-436.640	204.323	-7.569
6000	43.699	241.500	200.288	247.271	-436.306	215.188	-7.838

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

ALUMINUM TRICHLORIDE, DIMER (Al_2Cl_6) (IDEAL GAS) GFW = 266.681

Point Group D_{2h}

$S°_{298.15}$ = 113.647 ± 1.0 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -308.95 ± 0.8 kcal/mol

$\Delta Hf°_{298.15}$ = -309.64 ± 0.8 kcal/mol

Vibrational Frequencies (all singly degenerate), cm^{-1}

A_g	A_u	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}
501	36	438	625	610	420	77	484
336		116	[219]	166	[130]		[280]
217			19				[170]
99							

Bond Lengths: Al-Cl = 2.05 Å, $Al\text{-}Cl_{bridge}$ = 2.23 Å

Bond Angles: Cl-Al-Cl = 120°, $Cl_{bridge}\text{-}Al\text{-}Cl_{bridge}$ = 83° σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 5.986 \times 10^{-111}\ g^3\ cm^6$

Heat of Formation

The heat of formation is calculated from the value adopted for $AlCl_3$(c) and the heat of sublimation as derived from vapor pressure data. Vapor pressures were corrected for vapor non-ideality by means of the equation $\Delta G°/T = -R\ell nP - BP/T$. The Berthelot equation of state and critical constants T_c = 625.7°K and P_c = 26.1 atm reported by Denisova and Baskova (1) were used to calculate B. Boston et al. (2) and Nisel'son and Sokolova (3) confirm T_c within ±2°K. The corrected vapor pressures were used to derive $\Delta Hs°_{298.15}$ by both second law and third law methods.

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta Hs°_{298.15}$ (kcal/mol Al_2Cl_6) 2nd Law	3rd Law	Drift eu
Smits and Meijering (4)	444.7-464.6	7[a]	27.53	27.64	0.2±0.2
Smits and Meijering (4)	462.4-481.8	10	27.25	27.66	0.8±0.5
Treadwell and Terebesi (5)	388.7-461.7	11	28.33	27.60	-1.7±0.3
Treadwell and Terebesi (5)	466.5-476.2	3	27.43	27.65	0.4±0.2
Fischer et al. (6)	392.8-428.3	9	27.68	27.67	0.0±1.1
Fischer et al. (6)	403.8-450.4	12[b]	27.74	27.65	-0.2±0.3
Nisel'son et al. (7)	471.2-506.5	18[c]	27.31	27.70	0.7±0.1
Friedel and Crafts (8)	441.0-455.9	5	29.81	27.86	-4.5±3.5
Friedel and Crafts (8)	477.4-486.2	3	30.00	27.82	-4.6±2.9
Maier (9)	392.8-454.5	8[d]	25.87	27.44	3.6±1.7
Dunne and Gregory (10)	294.2-322.2	12[e]	29.96	27.83	-6.9
Denisova and Baskova (1)	467.8-511.6	8	26.34	27.61	2.5±0.3

[a] Nine points reported, points at 420.8° and 433.5°K rejected by statistical test.
[b] Fourteen points reported, points at 395.2 and 441.3°K rejected by statistical test.
[c] Thirteen points reported, point at 472.2°K rejected by statistical test.
[d] Nine points reported, point at 342.0°K rejected by statistical test.
[e] Individual points not reported; their vapor pressure equation was used to calculate 2 points at extremes of temperature range covered.

The first seven data sets show good agreement between second and third law values and an average of $\Delta Hs°_{298.15}$ = 27.66 ± 0.55 kcal/mol Al_2Cl_6 is adopted. The remaining data sets show serious discrepancies between second and third law values, indicating temperature dependent errors in measurement, and are given no weight.

Heat Capacity and Entropy

Electron diffraction data by Palmer and Elliott (11) and by Akishin et al. (12) are in agreement within experimental error and average values for bond angles and distances as given above are selected. The principal moments of inertia are: $I_A = 2.2172 \times 10^{-37}$, $I_B = 9.991 \times 10^{-38}$, and $I_C = 2.7023 \times 10^{-37}\ g\ cm^2$. Klemperer (13) observed three frequencies in the infrared spectrum of Al_2Cl_6 vapor, Beattie and Horder (14) and Maroni et al. (15) reported gas phase Raman spectra, and Gerding and Smit (16) and Pershina and Raskin (17) measured liquid phase Raman frequencies. With previous vibrational assignments and normal coordinate calculations by Onishi and Shimanouchi (18), Miller (19), and Maroni et al. (15) as a starting point, a new assignment was made (see above) which incorporates additional frequencies observed by Beattie and Horder (14) and Pershina and Raskin (17). Raman and infrared spectra of Al_2Br_6 and Al_2I_6 determined by Beattie, et al. (20) were very helpful. The new assignment differs with earlier calculations primarily in the assumption that the frequencies at 36 cm^{-1} and 19 cm^{-1} observed by Pershina and Raskin in the liquid can be assigned to modes not ordinarily Raman active. This assumption is supported by the compatibility of thermodynamic functions based on the new assignment with vapor pressure data as listed above. Use of the frequencies 88 cm^{-1} and 56 cm^{-1} of Miller (19) gives 3rd law heats of sublimation nearly 2 kcal/mol Al_2Cl_6 higher than the average of 2nd law values.

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Tripotassium Nonachloroaluminate ($K_3Al_2Cl_9$)
(Crystal) Mol. Wt. = 490.373

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	80.600	112.000	112.000	.000	- 683.600	- 627.634	460.046
300	80.750	112.499	112.002	.149	- 683.579	- 627.287	456.957
400	84.400	136.236	115.213	8.409	- 684.191	- 608.366	332.380
500	87.780	155.440	121.397	17.021	- 682.900	- 589.553	257.681
600	90.760	171.712	128.461	25.951	- 681.371	- 571.022	207.984
700	93.405	185.905	135.674	35.162	- 679.633	- 552.766	172.573
800	95.760	198.534	142.757	44.622	- 677.727	- 534.775	146.087
900	97.500	209.910	149.596	54.282	- 675.702	- 517.021	125.544
1000	99.600	220.288	156.154	64.134	- 678.580	- 499.139	109.081
1100	102.060	229.893	162.426	74.214	- 732.848	- 478.238	95.013
1200	104.880	238.892	168.426	84.558	- 729.445	- 455.239	82.906
1300	108.060	247.410	174.177	95.202	- 725.751	- 432.540	72.713
1400	111.600	255.545	179.701	106.182	- 721.730	- 410.130	64.021
1500	115.500	263.376	185.019	117.534	- 717.346	- 388.024	56.532

June 30, 1962; Sept. 30, 1964

TRIPOTASSIUM NONACHLOROALUMINATE ($K_3Al_2Cl_9$) (CRYSTAL) MOL. WT. = 490.373

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [112] cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = -683.6 ± 3 kcal. mole^{-1}

T_m = Unknown ΔH°_m = Unknown

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for $K_3Al_2Cl_9$(c) was calculated from the heat of solution, ΔH°_r = -112.07 kcal. mole^{-1}, of $K_3Al_2Cl_9$(c) in water (one mole of solute in 36 l. of water) determined by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities and $S^\circ_{298.15}$ were estimated based on an assumption that the property of the mixed chloride ($2AlCl_3 \cdot 3KCl$) is the sum of the corresponding values for its component chlorides, i.e. $AlCl_3$(c) and KCl(c).

Aluminum Trifluoride, Dimer (Al_2F_6)

(Ideal Gas) GFW = 167.9534

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 6.326	- 627.258	- 627.258	INFINITE
100	17.740	65.661	116.853	- 5.119	- 628.348	- 622.376	1360.201
200	26.367	80.828	95.235	- 2.882	- 629.095	- 616.105	673.248
298	31.964	92.476	92.476	.000	- 629.450	- 609.652	446.887
300	32.048	92.674	92.476	.059	- 629.455	- 609.530	444.042
400	35.684	102.431	93.782	3.460	- 629.562	- 602.864	329.389
500	37.980	110.660	96.357	7.152	- 629.553	- 596.192	260.595
600	39.466	117.725	99.343	11.029	- 629.490	- 589.525	214.734
700	40.462	123.889	102.419	15.029	- 629.413	- 582.868	181.980
800	41.155	129.340	105.450	19.111	- 629.363	- 576.225	157.417
900	41.653	134.217	108.380	23.253	- 629.373	- 569.582	138.313
1000	42.022	138.626	111.188	27.438	- 634.509	- 562.570	122.950
1100	42.301	142.645	113.868	31.655	- 634.486	- 555.378	110.343
1200	42.518	146.335	116.422	35.896	- 634.454	- 548.187	99.838
1300	42.689	149.745	118.855	40.157	- 634.418	- 540.998	90.950
1400	42.826	152.914	121.176	44.432	- 634.382	- 533.812	83.332
1500	42.938	155.873	123.392	48.721	- 634.344	- 526.630	76.730
1600	43.030	158.647	125.510	53.019	- 634.309	- 519.452	70.954
1700	43.107	161.258	127.536	57.326	- 634.274	- 512.273	65.857
1800	43.171	163.723	129.479	61.640	- 634.242	- 505.100	61.327
1900	43.226	166.059	131.343	65.960	- 634.212	- 497.925	57.274
2000	43.273	168.278	133.135	70.285	- 634.186	- 490.751	53.627
2100	43.314	170.390	134.859	74.615	- 634.164	- 483.586	50.327
2200	43.349	172.406	136.520	78.948	- 634.148	- 476.416	47.328
2300	43.380	174.333	138.123	83.284	- 634.133	- 469.239	44.588
2400	43.408	176.180	139.670	87.624	- 634.125	- 462.072	42.077
2500	43.432	177.953	141.166	91.966	- 634.124	- 454.908	39.768
2600	43.453	179.657	142.614	96.310	- 634.127	- 447.737	37.636
2700	43.472	181.297	144.017	100.656	- 634.134	- 440.567	35.661
2800	43.489	182.878	145.377	105.004	- 772.965	- 431.740	33.699
2900	43.505	184.405	146.696	109.354	- 772.459	- 419.559	31.619
3000	43.518	185.880	147.978	113.705	- 771.961	- 407.405	29.679
3100	43.531	187.307	149.224	118.058	- 771.464	- 395.260	27.866
3200	43.542	188.689	150.435	122.411	- 770.976	- 383.129	26.166
3300	43.553	190.029	151.615	126.766	- 770.492	- 371.017	24.571
3400	43.562	191.329	152.764	131.122	- 770.015	- 358.922	23.071
3500	43.571	192.592	153.884	135.479	- 769.544	- 346.833	21.657
3600	43.579	193.820	154.976	139.836	- 769.078	- 334.755	20.322
3700	43.586	195.014	156.042	144.194	- 768.620	- 322.703	19.061
3800	43.593	196.176	157.083	148.553	- 768.169	- 310.654	17.867
3900	43.599	197.309	158.100	152.913	- 767.724	- 298.623	16.734
4000	43.605	198.413	159.094	157.273	- 767.286	- 286.601	15.659
4100	43.611	199.490	160.067	161.634	- 766.856	- 274.596	14.637
4200	43.616	200.541	161.018	165.995	- 766.432	- 262.589	13.664
4300	43.620	201.567	161.949	170.357	- 766.014	- 250.594	12.737
4400	43.625	202.570	162.861	174.719	- 765.608	- 238.609	11.852
4500	43.629	203.550	163.754	179.082	- 765.208	- 226.644	11.007
4600	43.633	204.509	164.630	183.445	- 764.814	- 214.677	10.199
4700	43.636	205.448	165.488	187.809	- 764.434	- 202.730	9.427
4800	43.639	206.366	166.330	192.172	- 764.060	- 190.777	8.686
4900	43.643	207.266	167.157	196.537	- 763.695	- 178.827	7.976
5000	43.646	208.148	167.968	200.901	- 763.343	- 166.902	7.295
5100	43.648	209.012	168.764	205.266	- 763.000	- 154.984	6.642
5200	43.651	209.860	169.546	209.631	- 762.669	- 143.057	6.012
5300	43.654	210.691	170.315	213.996	- 762.350	- 131.142	5.408
5400	43.656	211.507	171.070	218.361	- 762.044	- 119.245	4.826
5500	43.658	212.308	171.812	222.727	- 761.750	- 107.345	4.265
5600	43.660	213.095	172.543	227.093	- 761.471	- 95.440	3.725
5700	43.662	213.868	173.261	231.459	- 761.204	- 83.552	3.204
5800	43.664	214.627	173.968	235.825	- 760.952	- 71.663	2.700
5900	43.666	215.374	174.663	240.192	- 760.716	- 59.787	2.215
6000	43.668	216.107	175.348	244.559	- 760.496	- 47.909	1.745

June 30, 1970

ALUMINUM TRIFLUORIDE, DIMER (Al_2F_6) (IDEAL GAS) GFW = 167.9534

Point Group [D_{2h}]

$S^{\circ}_{298.15}$ = 92.5 ± 3 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -627.3 ± 4 kcal/mol

$\Delta Hf^{\circ}_{298.15}$ = -629.45 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[830] (1)	[200] (1)	[210] (1)	[60] (1)	600 (1)	805 (1)
[600] (1)	[90] (1)	980 (1)	[970] (1)	[230] (1)	575 (1)
[370] (1)	[630] (1)	340 (1)	[260] (1)	[150] (1)	300 (1)

Bond Distance: Al-F [1.63] Å Al-F' = [1.80] Å (F is external, F' is in the bridge)
Bond Angle: F-Al-F = [120°] F'-Al-F' = [90°] σ = [4]
Angle between F'-Al-F' plane and F-Al-F plane = [90°]
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.669 x 10^{-112}] g^3 cm^6

Heat of Formation

The existence of small amounts of dimer in the saturated vapor was inferred from the intensities of AlF_2^+, AlF_3^+ and $Al_2F_5^+$ observed by mass spectrometry (1, 2, 3). Büchler et al. (1) concluded that the precursor of the first two ions was mainly AlF_3, while the dimer was the precursor of $Al_2F_5^+$. Intensities of $Al_2F_5^+$ relative to those of AlF_2^+ were observed as 0.0057 (1), 0.007 (2) and 0.025 (3) at ionizing energies of 60, 90 and 100 V for vapor at 1025, 1100 and 1025°K, respectively.

The temperature dependence of ion intensities was used to derive 2nd-law values of ΔHs° for monomer and dimer (1, 2) and a value of ΔH(dimerization) based on an estimate for the entropy of dimerization (3). The absolute pressure of the monomer was obtained (2) from integration of the intensity of AlF_2^+ during total sublimation at 1100°K, then the pressure of dimer was estimated from the relative ion intensity assuming a relative ionization cross section equal to two and neglecting other effects. Krause and Douglas (4) reported ΔHs°(monomer) plus ΔH° and ΔS° for dimerization; these were derived by combination of ΔHs°(dimer) (1) with precise sublimation pressures from entrainment data near 1200°K, where the dimer is more abundant. After reduction to 1000 K with JANAF functions, these results may be summarized as follows:

Source	Method	ΔHr°, kcal/mol*			ΔSr°, gibbs/mol*		
		c → m	2c → d	2m → d	c → m	2c → d	2m → d
Krause (4)	Entrainment	68.1 ± 0.4	[86]	-50 ± 3	[44.04]	---	-35 ± 3
Büchler (1)	Ion Intensities	67.3 ± 3	85.8 ± 3	-48.8 ± 3	---	---	---
Erokhin (2)	Ion Intensities	70.5	92.1	-49.0	46.4	55.1	-37.7
Porter (3)	Ion Intensities	---	---	-48.0 ± 4	---	---	[-32 ± 3]
JANAF	Adopted	68.4	87.8	[-49]	[44.37]	[52.83]	[-35.9]

* Reactions are abbreviated by c = crystal, d = dimer gas and m = monomer gas. Brackets enclose those values assumed in deriving the other values.

JANAF values are given in the last line. These are based on JANAF entropies, on ΔH°(dimerization) = -49 kcal/mol for which there is close agreement, and on the entrainment pressures of Krause and Douglas (4). Reduction of the dimer value to 298.15°K gives ΔHs° = 92.55 ± 4 and ΔHf° = -629.45 ± 4 kcal/mol. The table for AlF_3(g) gives a detailed comparison of observed and predicted total pressures along with predictions of the mole fraction of dimer in the saturated vapor. The latter are reasonably consistent with the relative ion intensities.

Heat Capacity and Entropy

The molecular structure is assumed to be similar to that of Al_2Cl_6. Bond distances and bond angles are estimated by comparison with AlF_3 (5), $AlCl_3$ (6) and Al_2Cl_6 (5, 6). Principal moments of inertia are I_A = 35.36 x 10^{-39}, I_B = 79.74 x 10^{-39} and I_C = 94.66 x 10^{-39} g cm^2.

Six observed vibrational frequencies are from infrared spectra of the dimer isolated in rare-gas matrices (7). Unobserved fundamentals (2 in infrared, 9 in Raman and 1 inactive) are estimated such that the entropy is consistent with the result of Krause and Douglas (4) as given above. The estimated fundamentals are based on comparisons with Al_2Cl_6, Al_2Br_6 and Al_2I_6 which have been restudied extensively (8-11) since the calculations of Miller (12). Assignments used in the comparisons are minor modifications of those given by Beattie et al. (8).

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Aluminum Triiodide, Dimeric $(AlI_3)_2$

(Ideal Gas) Mol. Wt. = 815.42

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-9.679	-119.029	-119.029	INFINITE
100	31.382	99.508	173.942	-7.443	-119.192	-124.439	271.948
200	38.295	123.756	143.282	-3.905	-120.072	-129.377	141.370
298	40.892	139.608	139.608	.000	-121.000	-133.760	98.044
300	40.922	139.861	139.609	.076	-121.018	-133.839	97.497
400	42.054	151.809	141.230	4.232	-133.572	-137.556	75.154
500	42.624	161.261	144.324	8.468	-165.159	-135.554	59.248
600	42.947	169.063	147.816	12.748	-164.882	-129.663	47.227
700	43.147	175.699	151.337	17.054	-164.647	-123.812	38.654
800	43.278	181.470	154.751	21.375	-164.461	-117.989	32.232
900	43.370	186.573	158.009	25.708	-164.334	-112.190	27.242
1000	43.435	191.146	161.098	30.048	-169.253	-106.030	23.172
1100	43.484	195.288	164.021	34.394	-169.028	-99.720	19.812
1200	43.521	199.074	166.786	38.745	-168.804	-93.429	17.015
1300	43.551	202.558	169.406	43.098	-168.578	-87.156	14.652
1400	43.574	205.787	171.890	47.455	-168.357	-80.900	12.628
1500	43.592	208.794	174.251	51.813	-168.138	-74.665	10.878
1600	43.608	211.607	176.499	56.173	-167.920	-68.434	9.347
1700	43.620	214.252	178.643	60.535	-167.706	-62.226	7.999
1800	43.631	216.745	180.691	64.897	-167.495	-56.028	6.802
1900	43.640	219.104	182.651	69.261	-167.288	-49.839	5.732
2000	43.648	221.343	184.530	73.625	-167.084	-43.668	4.772
2100	43.655	223.473	186.335	77.990	-166.882	-37.500	3.903
2200	43.660	225.504	188.069	82.356	-166.685	-31.345	3.114
2300	43.665	227.445	189.739	86.722	-166.491	-25.196	2.394
2400	43.670	229.303	191.349	91.089	-166.299	-19.054	1.735
2500	43.674	231.086	192.903	95.456	-166.113	-12.925	1.130
2600	43.677	232.799	194.405	99.824	-165.929	-6.804	.572
2700	43.680	234.447	195.858	104.192	-165.751	-.688	.056
2800	43.683	236.036	197.265	108.560	-306.684	8.733	-.682
2900	43.686	237.569	198.628	112.928	-306.106	19.985	-1.506
3000	43.688	239.050	199.951	117.297	-305.533	31.217	-2.274
3100	43.690	240.482	201.235	121.666	-304.963	42.437	-2.992
3200	43.692	241.870	202.484	126.035	-304.398	53.632	-3.663
3300	43.693	243.214	203.698	130.404	-303.837	64.816	-4.292
3400	43.695	244.518	204.879	134.774	-303.278	75.973	-4.883
3500	43.696	245.785	206.030	139.143	-302.725	87.122	-5.440
3600	43.698	247.016	207.151	143.513	-302.177	98.254	-5.965
3700	43.699	248.213	208.245	147.883	-301.632	109.362	-6.459
3800	43.700	249.379	209.312	152.253	-301.090	120.467	-6.928
3900	43.701	250.514	210.354	156.623	-300.556	131.560	-7.372
4000	43.702	251.620	211.372	160.993	-300.025	142.622	-7.792
4100	43.703	252.699	212.367	165.363	-299.499	153.689	-8.192
4200	43.703	253.753	213.340	169.733	-298.981	164.739	-8.572
4300	43.704	254.781	214.292	174.104	-298.465	175.765	-8.933
4400	43.705	255.786	215.223	178.474	-297.960	186.781	-9.277
4500	43.705	256.768	216.136	182.845	-297.457	197.809	-9.606
4600	43.706	257.728	217.029	187.215	-296.962	208.811	-9.920
4700	43.707	258.668	217.905	191.586	-296.471	219.784	-10.219
4800	43.707	259.589	218.764	195.956	-295.991	230.768	-10.507
4900	43.708	260.490	219.607	200.327	-295.517	241.750	-10.782
5000	43.708	261.373	220.433	204.698	-295.053	252.703	-11.045
5100	43.709	262.238	221.244	209.069	-294.593	263.651	-11.298
5200	43.709	263.087	222.041	213.440	-294.148	274.586	-11.540
5300	43.709	263.920	222.823	217.811	-293.707	285.526	-11.773
5400	43.710	264.737	223.592	222.182	-293.280	296.461	-11.998
5500	43.710	265.539	224.347	226.553	-292.862	307.365	-12.213
5600	43.711	266.326	225.090	230.924	-292.458	318.270	-12.420
5700	43.711	267.100	225.820	235.295	-292.065	329.172	-12.621
5800	43.711	267.860	226.538	239.666	-291.683	340.075	-12.814
5900	43.711	268.607	227.245	244.037	-291.314	350.964	-13.000
6000	43.712	269.342	227.941	248.408	-290.963	361.849	-13.180

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE, DIMERIC $((AlI_3)_2)$ (IDEAL GAS) MOL. WT. = 815.42

Point Group D_{2h}

$S^\circ_{298.15}$ = [139.608] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -119.0 ± 3.0 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -121.0 ± 3.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
344 (1)	[53] (1)	[290] (1)
146 (1)	[430] (1)	[53] (1)
94 (1)	[130] (1)	[50] (1)
53 (1)	[20] (1)	[330] (1)
[30] (1)	410 (1)	[140] (1)
[300] (1)	[65] (1)	[55] (1)

Bond Distance: Al-I = 2.53 Å Al-I_{bridge} = 2.58 Å

Bond Angle: I-Al-I = 112 ± 1° I_{bridge}-Al-I_{bridge} = 68 ± 1° σ = 4

Product of the Moments of Inertia: $I_AI_BI_C$ = 5.21725 X 10^{-109} g.^{3} cm.^{6}

Heat of Formation.

W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932) measured the vapor pressure of $AlI_3(l)$. The vapor consists of both $Al_2I_6(g)$ and $AlI_3(g)$ species. The partial pressures of $Al_2I_6(g)$ and $AlI_3(g)$ at different temperatures for the equilibrium $Al_2I_6(g) \rightarrow 2AlI_3(g)$ were determined by W. Fischer, O. Rahlfs and B. Benze, loc. cit. From these partial pressures the mole ratios of $Al_2I_6(g)$ and $AlI_3(g)$ at other temperatures were estimated. The partial pressures of $Al_2I_6(g)$ over $AlI_3(l)$ were calculated from the total pressure using the estimated mole ratio values. The heat of vaporization, $\Delta H^\circ_{v\ 298.15}$ = 20.5 ± 1.0 kcal. mole^{-1}, was evaluated employing the vapor pressures obtained by second law method. The corresponding third law value is 22.4 kcal. mole^{-1}. It was not used due to the uncertainties involved in the estimation of the vibrational frequencies. The heat of formation for $Al_2I_6(g)$ was calculated from $\Delta H_f^\circ(l)$ and ΔH_v° obtained.

Heat Capacity and Entropy.

Molecular structure, bond distances and angles were reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 60, 1852 (1938). Five vibrational frequencies (344, 146, 94, 53 and 410 cm.$^{-1}$) were adopted from the Raman spectrum of $Al_2I_6(l)$ measured by H. Gerding and E. Smit, Z. physik. Chem. 50B, 171 (1941). The remaining ones were estimated by comparison with those for $Al_2Cl_6(g)$ and $Al_2Br_6(g)$ and adjusted so that the value of $\Delta H_{s\ 298.15}$ obtained by the third law method is in reasonable agreement with the corresponding second law value. The three principal moments of inertia are: I_A = 9.32506 X 10^{-37}, I_B = 4.60265 X 10^{-37}, and I_C = 1.21558 X 10^{-36} g. cm.^{2}.

Magnesium Aluminate ($MgAl_2O_4$)

(Crystal) Mol. Wt. = 142.28

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	- 3,683	- 547,349	- 547,349	INFINITE
100	5,418	2,075	37,385	- 3,531	- 548,989	- 540,335	1180,844
200	18,659	9,977	21,547	- 2,314	- 550,578	- 531,145	580,380
298	27,771	19,268	19,268	,000	- 551,200	- 521,358	382,147
300	27,905	19,440	19,269	,052	- 551,208	- 521,173	379,656
400	33,247	28,289	20,438	3,140	- 551,349	- 511,129	279,254
500	36,088	36,040	22,802	6,619	- 551,228	- 501,083	219,013
600	37,923	42,789	25,583	10,324	- 551,014	- 491,075	178,865
700	39,284	48,743	28,475	14,188	- 550,773	- 481,104	150,200
800	40,392	54,063	31,347	18,173	- 550,541	- 471,169	128,711
900	41,353	58,877	34,142	22,262	- 550,335	- 461,258	112,003
1000	42,222	63,280	36,839	26,441	- 557,273	- 450,818	98,522
1100	43,038	67,343	39,430	30,704	- 556,890	- 440,194	87,454
1200	43,801	71,121	41,915	35,047	- 556,470	- 429,604	78,238
1300	44,539	74,656	44,299	39,464	- 556,020	- 419,049	70,445
1400	45,261	77,983	46,587	43,954	- 585,902	- 408,052	63,697
1500	45,967	81,130	48,786	48,515	- 584,980	- 395,379	57,604
1600	46,658	84,119	50,902	53,147	- 583,999	- 382,771	52,282
1700	47,341	86,968	52,940	57,847	- 582,960	- 370,225	47,593
1800	48,018	89,693	54,907	62,615	- 581,867	- 357,744	43,434
1900	48,690	92,307	56,807	67,450	- 580,718	- 345,321	39,719
2000	49,356	94,822	58,645	72,352	- 579,513	- 332,966	36,383
2100	49,932	97,244	60,426	77,317	- 578,255	- 320,670	33,371
2200	50,475	99,579	62,153	82,338	- 576,955	- 308,432	30,638
2300	50,984	101,834	63,829	87,411	- 575,611	- 296,258	28,150
2400	51,459	104,014	65,459	92,533	- 574,230	- 284,140	25,873
2500	51,900	106,124	67,043	97,702	- 572,815	- 272,065	23,785
2600	52,308	108,167	68,586	102,912	- 571,367	- 260,083	21,861
2700	52,681	110,149	70,089	108,162	- 569,892	- 248,140	20,085
2800	53,021	112,071	71,554	113,447	- 709,500	- 232,945	18,181
2900	53,328	113,937	72,983	118,765	- 707,572	- 215,958	16,274
3000	53,600	115,749	74,379	124,112	- 705,627	- 199,036	14,499

Dec. 31, 1960; Mar. 31, 1963

MAGNESIUM ALUMINATE ($MgAl_2O_4$) (CRYSTAL) MOL. WT. = 142.28

$\Delta H_{f\ 0}^\circ = -547.3 \pm 1.9$ kcal. mole^{-1}

$S_{298.15}^\circ = 19.27 \pm 0.10$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -551.2 \pm 1.9$ kcal. mole^{-1}

$T_m = 2408$°K.

ΔH_m° = Unknown

Heat of Formation.

The value of $\Delta H_{f\ 298.15}^\circ$ was calculated from $\Delta H_{r\ 298.15}^\circ = 124.6 \pm 1.5$ kcal. mole^{-1} for the reaction: $4MgO(c) + 2Al(l) = MgAl_2O_4(c) + 3Mg(g)$. The value of $\Delta H_{r\ 298.15}^\circ$ was obtained by the third-law method, using vapor pressure data reported by K. Grjotheim, O. Herstad, and J. M. Toguri, Can. J. Chem. 39, 443 (1961). From the Knudsen experiments with $MgAl_2O_4(c)$, R. L. Altman, J. Phys. Chem., 67, 366 (1963) calculated the value of $\Delta H_{f\ 298.15}^\circ$ as -552 kcal. mole^{-1} which agrees with the value used.

Heat Capacity and Entropy.

The low temperature heat capacity, 53-296°K., was measured by E. G. King, J. Phys. Chem. 59, 218 (1955). The high temperature heat capacity, 400°-1800°K., was reported by K. R. Bonnickson, J. Phys. Chem. 59, 220 (1955). These two sets of data were joined smoothly and extrapolated to 3000°K. $S_{298.15}^\circ$ was reported by E. G. King, loc. cit., based on S_{51}°(extrap.) = 0.32 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Melting.

T_m was taken from "Data on Chemicals for Ceramic Use," U. S. National Research Council Bulletin 118, 1949.

Aluminum Suboxide (Al_2O)

(Ideal Gas) Mol. Wt. = 69.9624

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.777	-30.951	-30.951	INFINITE
100	8.767	51.375	70.963	-1.959	-30.702	-33.433	73.065
200	9.905	57.818	62.932	-1.023	-30.990	-36.101	39.448
298	10.916	61.966	61.966	.000	-31.400	-38.534	28.244
300	10.934	62.033	61.966	.020	-31.408	-38.578	28.103
400	11.749	65.297	62.405	1.157	-31.821	-40.904	22.348
500	12.321	67.984	63.260	2.362	-32.236	-43.128	18.850
600	12.711	70.267	64.242	3.615	-32.672	-45.266	16.487
700	12.982	72.248	65.248	4.900	-33.150	-47.329	14.776
800	13.174	73.994	66.234	6.208	-33.673	-49.319	13.473
900	13.314	75.555	67.184	7.533	-34.249	-51.240	12.442
1000	13.418	76.963	68.093	8.870	-39.870	-52.725	11.522
1100	13.498	78.246	68.959	10.216	-40.343	-53.988	10.726
1200	13.561	79.423	69.782	11.569	-40.814	-55.207	10.054
1300	13.610	80.511	70.566	12.928	-41.284	-56.389	9.479
1400	13.650	81.521	71.313	14.291	-41.753	-57.533	8.981
1500	13.682	82.464	72.025	15.657	-42.222	-58.644	8.544
1600	13.709	83.347	72.706	17.027	-42.691	-59.721	8.157
1700	13.731	84.179	73.356	18.399	-43.159	-60.772	7.812
1800	13.750	84.965	73.980	19.773	-43.630	-61.796	7.503
1900	13.766	85.709	74.578	21.149	-44.102	-62.791	7.222
2000	13.780	86.415	75.152	22.526	-44.574	-63.762	6.967
2100	13.792	87.088	75.704	23.905	-45.048	-64.712	6.734
2200	13.802	87.730	76.236	25.285	-45.524	-65.637	6.520
2300	13.812	88.343	76.750	26.665	-46.002	-66.539	6.322
2400	13.820	88.931	77.245	28.047	-46.481	-67.421	6.139
2500	13.827	89.496	77.724	29.429	-46.963	-68.285	5.969
2600	13.833	90.038	78.187	30.812	-47.446	-69.130	5.811
2700	13.838	90.560	78.636	32.196	-47.931	-69.955	5.662
2800	13.843	91.063	79.071	33.580	-189.527	-67.454	5.265
2900	13.848	91.549	79.493	34.965	-189.610	-63.095	4.755
3000	13.852	92.019	79.902	36.350	-189.695	-58.729	4.278
3100	13.856	92.473	80.301	37.735	-189.783	-54.361	3.832
3200	13.859	92.913	80.688	39.121	-189.874	-49.992	3.414
3300	13.862	93.340	81.065	40.507	-189.965	-45.621	3.021
3400	13.865	93.754	81.432	41.893	-190.058	-41.248	2.651
3500	13.868	94.155	81.790	43.280	-190.154	-36.870	2.302
3600	13.870	94.546	82.139	44.667	-190.252	-32.484	1.972
3700	13.872	94.926	82.479	46.054	-190.352	-28.104	1.660
3800	13.874	95.296	82.812	47.441	-190.453	-23.715	1.364
3900	13.876	95.657	83.136	48.829	-190.558	-19.327	1.083
4000	13.878	96.008	83.454	50.216	-190.664	-14.936	.816
4100	13.879	96.351	83.764	51.604	-190.774	-10.546	.562
4200	13.881	96.685	84.068	52.992	-190.886	-6.145	.320
4300	13.882	97.012	84.365	54.380	-191.000	-1.744	.089
4400	13.883	97.331	84.656	55.768	-191.120	2.652	-.132
4500	13.885	97.643	84.941	57.157	-191.240	7.066	-.343
4600	13.886	97.948	85.221	58.545	-191.365	11.477	-.545
4700	13.887	98.247	85.495	59.934	-191.493	15.878	-.738
4800	13.888	98.539	85.764	61.323	-191.626	20.294	-.924
4900	13.889	98.825	86.027	62.712	-191.763	24.719	-1.102
5000	13.890	99.106	86.286	64.100	-191.906	29.131	-1.273
5100	13.890	99.381	86.540	65.489	-192.054	33.558	-1.438
5200	13.891	99.651	86.790	66.879	-192.207	37.976	-1.596
5300	13.892	99.915	87.035	68.268	-192.366	42.411	-1.749
5400	13.893	100.175	87.276	69.657	-192.533	46.841	-1.896
5500	13.893	100.430	87.513	71.046	-192.706	51.271	-2.037
5600	13.894	100.680	87.745	72.436	-192.889	55.715	-2.174
5700	13.894	100.926	87.975	73.825	-193.080	60.149	-2.306
5800	13.895	101.168	88.200	75.214	-193.279	64.598	-2.434
5900	13.896	101.405	88.422	76.604	-193.488	69.050	-2.558
6000	13.896	101.639	88.640	77.994	-193.710	73.497	-2.677

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1965

ALUMINUM SUBOXIDE (Al_2O) (IDEAL GAS) MOL. WT. = 69.9624

Point Group C_{2v}

$S^\circ_{298.15}$ = 62.0 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -31.0 ± 7 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -31.4 ± 7 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
715 (1)
[238] (1)
994 (1)

Bond Distance: Al-O = 1.66 Å

Bond Angle: Al-O-Al = 145°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 263.2477 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H_f^\circ{}_{298}$ = -31.4 ± 7 kcal. mole^{-1} for $Al_2O(g)$ was calculated from $\Delta H_r^\circ{}_{298}$ = 247 ± 7 kcal. mole^{-1} for the reaction $Al_2O(g) = 2Al(g) + O(g)$; and $\Delta H_r^\circ{}_{298}$ = 131 ± 7 kcal. mole^{-1} for the reaction $Al_2O(g) = AlO(g) + Al(g)$. The values of $\Delta H_r^\circ{}_{298}$ were obtained by the third law method, using the partial pressure data reported by J. Drowart, G. DeMaria, R. Burns and M. Inghram, J. Chem. Phys. 32, 1366 (1960). (The second law values which are in poor agreement with the third law values, are $\Delta H_r^\circ{}_{298}$ = 271 ± 10 kcal. mole^{-1} and ΔH_r° = 154 ± 10 kcal. mole^{-1}, respectively.) L. Brewer and A. Searcy, J. Am. Chem. Soc., 73, 5308 (1951), reported that under reducing condition, Al_2O_3 vaporizes mostly to $Al_2O(g)$, but under neutral condition $AlO(g)$ and $O(g)$ are the major products. Brewer and Searcy also measured the vapor pressures of the $Al-Al_2O_3$ system by Knudsen effusion method, and obtained the heat of formation of $Al_2O(g)$ from gaseous atoms as ΔH°_{298} = -248 kcal. mole^{-1}. This value leads the heat of formation for $Al_2O(g)$, $\Delta H_f^\circ{}_{298}$ = -32.4 ± 7, which agrees with the value selected.

Other references appearing in the recent literature were:

1. Leo Brewer, AEC Report UCRL-8356 (1958).
2. G. DeMaria, J. Drowart, M. Inghram, J. Chem. Phys., 30, 318 (1959).
3. R. Porter, P. Shissel and M. Inghram, J. Chem. Phys. 23, 339 (1955).
4. R. J. Ackerman and R. J. Thorn, J. Am. Chem. Soc., 78, 4169 (1956).
5. C. N. Cochran, J. Am. Chem. Soc., 77, 2190 (1955).
6. M. Cook, A. Filler, R. Keyes, W. Partridge and W. Ursenbach, J. Phys. Chem., 61, 189 (1957)

Heat Capacity and Entropy.

The matrix isolation of high temperature vapors for the investigation of the infrared spectrum of Al_2O has been used to determined the bond distance, angle and vibrational frequencies by M. Linevsky, D. White and D. Mann, J. Chem. Phys., 41, 542 (1964). These reported data have been adopted in this table. The symmetric structure Al-O-Al instead of Al-Al-O for $Al_2O(g)$ was chosen for two reasons: (1) The dissociation energy of $Al_2O(g)$, D°_{298} = 247 ± 7 kcal/mole, is approximately twice the dissociation energy of $AlO(g)$, D°_{298} = 115 ± 5 kcal. mole^{-1}, which implies that the symmetric structure is more reasonable. (2) The dissociation energy of $Al_2(g)$ has been estimated to be only 39 kcal. mole^{-1} by J. Drowart and R. Honig, J. Phys. Chem., 61, 980 (1957). This implies that the Al-O bond energy in "Al-Al-O" structure would be as large as 208 kcal. mole^{-1} if D°Al-Al = 39 kcal. mole^{-1}. Therefore $Al_2O(g)$ must have a symmetric structure. Linevsky et al., loc. cit., have also concluded the bent symmetric structure (instead of a linear one) and the calculated ω_2 from the observed infrared spectra and the reanalysis of the ultraviolet spectra. The three principal moments of inertia are I_A = 0.5105 X 10^{-39}, I_B = 22.4539 X 10^{-39} and I_C = 22.9644 X 10^{-39} g. cm.^{2}

Drowart, et al. (loc. cit.), also postulated a bent symmetric molecule for $Al_2O(g)$, and estimated the bond distance Al-O = [1.0176] Å and angle Al-O-Al = [110]° and the vibrational frequencies as [1079] cm.$^{-1}$, [351] cm.$^{-1}$ and [921] cm.$^{-1}$

The National Bureau of Standards Report No. 6484 "Preliminary Report on the Thermodynamic Properties of Li, Be, Mg, Al and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine" July, 1959, has proposed a trigonal structure for $Al_2O(g)$ with bond distance Al-O = [1.87] Å, and Al-Al = [2.0] Å. Its vibration frequencies were estimated as [450] cm.$^{-1}$, [1000] cm.$^{-1}$ and [1000] cm.$^{-1}$.

Dialuminum Monoxide Unipositive Ion (Al_2O^+)

(Ideal Gas) GFW = 69.9618

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.918	62.697	62.697	.000	146.000	137.161	-100.542
300	10.935	62.765	62.698	.020	146.001	137.106	-99.881
400	11.754	66.029	63.137	1.157	146.081	134.131	-73.286
500	12.324	68.718	63.992	2.363	146.156	131.133	-57.318
600	12.714	71.001	64.975	3.616	146.211	128.122	-46.669
700	12.984	72.983	65.980	4.901	146.233	125.105	-39.060
800	13.175	74.729	66.967	6.210	146.206	122.088	-33.353
900	13.315	76.290	67.918	7.535	146.097	119.080	-28.917
1000	13.419	77.698	68.827	8.872	140.851	116.454	-25.451
1100	13.499	78.981	69.692	10.218	140.757	114.018	-22.653
1200	13.561	80.158	70.516	11.571	140.665	111.591	-20.324
1300	13.610	81.246	71.300	12.929	140.575	109.172	-18.353
1400	13.650	82.256	72.047	14.293	140.485	106.761	-16.666
1500	13.682	83.199	72.759	15.659	140.395	104.353	-15.204
1600	13.709	84.083	73.440	17.029	140.305	101.954	-13.926
1700	13.731	84.915	74.091	18.401	140.215	99.560	-12.799
1800	13.750	85.700	74.714	19.775	140.125	97.173	-11.798
1900	13.766	86.444	75.312	21.151	140.032	94.789	-10.903
2000	13.780	87.150	75.886	22.528	139.939	92.408	-10.098
2100	13.792	87.823	76.439	23.907	139.844	90.032	-9.370
2200	13.802	88.465	76.971	25.286	139.746	87.662	-8.708
2300	13.811	89.078	77.484	26.667	139.649	85.300	-8.105
2400	13.819	89.666	77.980	28.048	139.548	82.941	-7.553
2500	13.826	90.231	78.458	29.431	139.446	80.579	-7.044
2600	13.832	90.773	78.922	30.814	139.342	78.229	-6.576
2700	13.838	91.295	79.370	32.197	139.235	75.879	-6.142
2800	13.843	91.799	79.805	33.581	.307	75.195	-5.869
2900	13.847	92.284	80.227	34.966	.719	77.861	-5.868
3000	13.852	92.754	80.637	36.351	1.131	80.515	-5.866
3100	13.855	93.208	81.035	37.736	1.541	83.155	-5.862
3200	13.859	93.648	81.423	39.122	1.948	85.785	-5.859
3300	13.862	94.075	81.800	40.508	2.354	88.398	-5.854
3400	13.864	94.489	82.167	41.894	2.755	90.995	-5.849
3500	13.867	94.890	82.524	43.281	3.158	93.584	-5.844
3600	13.869	95.281	82.873	44.667	3.556	96.168	-5.838
3700	13.872	95.661	83.214	46.055	3.954	98.729	-5.832
3800	13.874	96.031	83.546	47.442	4.347	101.287	-5.825
3900	13.875	96.392	83.871	48.829	4.742	103.837	-5.819
4000	13.877	96.743	84.189	50.217	5.129	106.366	-5.812
4100	13.879	97.086	84.499	51.605	5.517	108.888	-5.804
4200	13.880	97.420	84.803	52.993	5.903	111.412	-5.797
4300	13.882	97.747	85.100	54.381	6.284	113.919	-5.790
4400	13.883	98.066	85.391	55.769	6.664	116.423	-5.783
4500	13.884	98.378	85.676	57.157	7.038	118.909	-5.775
4600	13.885	98.683	85.956	58.546	7.412	121.396	-5.768
4700	13.886	98.982	86.230	59.934	7.778	123.859	-5.759
4800	13.887	99.274	86.498	61.323	8.142	126.324	-5.752
4900	13.888	99.560	86.762	62.712	8.504	128.793	-5.744
5000	13.889	99.841	87.021	64.101	8.857	131.241	-5.737
5100	13.890	100.116	87.275	65.489	9.206	133.686	-5.729
5200	13.891	100.386	87.524	66.878	9.549	136.120	-5.721
5300	13.891	100.650	87.769	68.268	9.886	138.551	-5.713
5400	13.892	100.910	88.010	69.657	10.218	140.977	-5.706
5500	13.893	101.165	88.247	71.046	10.539	143.391	-5.698
5600	13.893	101.415	88.480	72.435	10.853	145.804	-5.690
5700	13.894	101.661	88.709	73.825	11.161	148.212	-5.683
5800	13.894	101.903	88.935	75.214	11.457	150.616	-5.675
5900	13.895	102.140	89.156	76.603	11.744	153.013	-5.668
6000	13.895	102.374	89.375	77.993	12.021	155.409	-5.661

June 30, 1968

DIALUMINUM MONOXIDE UNIPOSITIVE ION (Al_2O^+) (IDEAL GAS) GFW = 69.9618

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [62.7 ± 2] gibbs/mol

Ground State Quantum Weight = [2]

ΔHf°_0 = 146.5 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 146 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[700] (1)
[250] (1)
[1000] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: Al-O-Al = [155°]

σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [1.481 x 10^{-115}] g^3 cm^6

Heat of Formation

The ionization potential of Al_2O has been reported as 7.7 ± 0.2eV (177.6 kcal) by R. F. Porter, P. Schissel, and M. G. Inghram, J. Chem. Phys. 23, 339 (1955), and has been confirmed as 7.7 ± 0.5eV by G. DeMaria, J. Drowart, M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value with $\Delta Hf^\circ_{298}(Al_2O, g)$ = -31.4 kcal/mol, we obtain $\Delta Hf^\circ_{298}(Al_2O^+, g)$ = 146 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecule is assumed to be bent by analogy with Al_2O, although both these molecules are predicted to be linear according to A. D. Walsh, J. Chem. Soc. 2266 (1953). The electronic ground state is doublet, since there is an odd number of electrons. The bond length is estimated to be the same as that in Al_2O and the vibrational frequencies are also assumed to be close to those for Al_2O. Since normally the molecule Al_2O ought to be linear, the bending must occur due to the occupancy of an outermost orbital with strong angular variation. Presumably this orbital is occupied by a pair of electrons, one of which will be removed in Al_2O^+, thus causing an opening of the bond angle. On this basis the angle is estimated to be greater than that in Al_2O. The individual moments of inertia are: $I_A = 2.645 \times 10^{-40}$ g cm^2, $I_B = 2.353 \times 10^{-38}$ g cm^2 and $I_C = 2.380 \times 10^{-38}$ g cm^2.

The enthalpy at 0°K is -2.769 kcal/mol.

Aluminum Monoxide, Dimeric (Al_2O_2)

(Ideal Gas) Mol. Wt. = 85.9618

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.929	-95.666	-95.666	INFINITE
100	9.017	52.453	73.450	-2.100	-95.762	-96.525	210.945
200	10.510	59.136	64.772	-1.127	-96.353	-97.105	106.106
298	12.496	63.695	63.695	.000	-97.000	-97.344	71.351
300	12.534	63.772	63.695	.023	-97.012	-97.346	70.913
400	14.394	67.643	64.210	1.373	-97.567	-97.370	53.198
500	15.780	71.013	65.241	2.886	-98.039	-97.266	42.513
600	16.758	73.982	66.456	4.516	-98.476	-97.070	35.356
700	17.447	76.620	67.723	6.228	-98.916	-96.802	30.221
800	17.941	78.983	68.985	7.998	-99.376	-96.468	26.353
900	18.304	81.118	70.217	9.812	-99.870	-96.074	23.329
1000	18.576	83.062	71.405	11.656	-105.397	-95.255	20.817
1100	18.785	84.842	72.547	13.525	-105.767	-94.223	18.719
1200	18.948	86.484	73.641	15.412	-106.128	-93.157	16.965
1300	19.078	88.006	74.688	17.313	-106.484	-92.063	15.476
1400	19.182	89.424	75.691	19.226	-106.835	-90.940	14.196
1500	19.268	90.750	76.651	21.149	-107.183	-89.792	13.082
1600	19.339	91.996	77.572	23.080	-107.529	-88.621	12.104
1700	19.398	93.171	78.455	25.016	-107.875	-87.430	11.239
1800	19.448	94.281	79.304	26.959	-108.221	-86.218	10.468
1900	19.490	95.333	80.120	28.906	-108.569	-84.983	9.775
2000	19.527	96.334	80.906	30.857	-108.918	-83.734	9.150
2100	19.558	97.287	81.663	32.811	-109.269	-82.467	8.582
2200	19.585	98.198	82.394	34.768	-109.624	-81.182	8.064
2300	19.609	99.069	83.100	36.728	-109.980	-79.882	7.590
2400	19.631	99.904	83.783	38.690	-110.340	-78.564	7.154
2500	19.649	100.706	84.444	40.654	-110.704	-77.234	6.751
2600	19.666	101.477	85.085	42.620	-111.070	-75.890	6.379
2700	19.681	102.219	85.706	44.587	-111.441	-74.529	6.032
2800	19.694	102.935	86.308	46.556	-252.923	-69.848	5.452
2900	19.706	103.627	86.894	48.526	-252.895	-63.313	4.771
3000	19.717	104.295	87.463	50.497	-252.871	-56.773	4.136
3100	19.727	104.942	88.016	52.469	-252.850	-50.237	3.542
3200	19.736	105.568	88.555	54.442	-252.835	-43.702	2.985
3300	19.744	106.175	89.080	56.416	-252.821	-37.166	2.461
3400	19.751	106.765	89.591	58.391	-252.811	-30.635	1.969
3500	19.758	107.338	90.090	60.366	-252.806	-24.105	1.505
3600	19.764	107.894	90.577	62.343	-252.803	-17.561	1.066
3700	19.770	108.436	91.052	64.319	-252.805	-11.032	.652
3800	19.775	108.963	91.517	66.296	-252.809	-4.494	.258
3900	19.780	109.477	91.971	68.274	-252.817	2.040	-.114
4000	19.785	109.978	92.415	70.252	-252.829	8.571	-.468
4100	19.789	110.466	92.849	72.231	-252.845	15.107	-.805
4200	19.793	110.943	93.274	74.210	-252.865	21.643	-1.126
4300	19.796	111.409	93.691	76.190	-252.887	28.182	-1.432
4400	19.800	111.864	94.098	78.170	-252.916	34.712	-1.724
4500	19.803	112.309	94.498	80.150	-252.947	41.258	-2.004
4600	19.806	112.744	94.890	82.130	-252.984	47.801	-2.271
4700	19.809	113.170	95.275	84.111	-253.025	54.331	-2.526
4800	19.811	113.588	95.652	86.092	-253.071	60.868	-2.771
4900	19.814	113.996	96.022	88.073	-253.123	67.416	-3.007
5000	19.816	114.396	96.385	90.055	-253.180	73.955	-3.232
5100	19.818	114.789	96.742	92.036	-253.244	80.500	-3.450
5200	19.820	115.174	97.093	94.018	-253.314	87.037	-3.658
5300	19.822	115.551	97.438	96.000	-253.389	93.592	-3.859
5400	19.824	115.922	97.777	97.983	-253.473	100.135	-4.052
5500	19.826	116.286	98.110	99.965	-253.564	106.681	-4.239
5600	19.828	116.643	98.438	101.948	-253.665	113.236	-4.419
5700	19.829	116.994	98.760	103.931	-253.774	119.781	-4.592
5800	19.831	117.339	99.078	105.914	-253.892	126.344	-4.761
5900	19.832	117.678	99.390	107.897	-254.021	132.901	-4.929
6000	19.833	118.011	99.698	109.880	-254.163	139.461	-5.040

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1961; Sept. 30, 1965

ALUMINUM MONOXIDE, DIMERIC $((AlO)_2)$ (IDEAL GAS) MOL. WT. = 85.9618

Point Group $[V_h]$

$\Delta H^\circ_{f\ 0} = -95.7 \pm 7$ kcal. mole^{-1}

$S^\circ_{298.15} = [63.7]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -97.0 \pm 7$ kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[200] [1]	[930] [1]
[600] [1]	[1000] [1]
[930] [1]	[1000] [1]

Bond Distance: Al-O = [1.60] Å

Bond Angle: Al-O-Al = [90]°, O-Al-O = [90]°

$\sigma = [4]$

Products of the Moments of Inertia: $I_AI_BI_C = [1.4246 \times 10^{-114}]$ g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298} = -97 \pm 7$ kcal. mole^{-1} for $Al_2O_2(g)$ was calculated from $\Delta H^\circ_{r\ 298} = 372 \pm 7$ kcal. mole^{-1} for the reaction $Al_2O_2(g) = 2Al(g) + 2O(g)$. The value of $\Delta H^\circ_{r\ 298}$ was obtained by the third law method, using the partial pressure data reported by J. Drowart, G. DeMaria, R. Burns and M. Inghram, J. Chem. Phys. 32, 1366 (1960). (The second law value for ΔH°_r, which is in poor agreement with the third law value, is 451 ± 25 kcal. mole.)

Heat Capacity and Entropy.

The molecular structure (plane cyclic model) and vibrational frequencies of $Al_2O_2(g)$ were obtained from Drowart, et al., J. Chem. Phys., 32, 1366 (1960). The bond distance Al-O in Al_2O_2 was assumed to be the same as that in AlO (g). The three principal moments of inertia are $I_A = 6.8005 \times 10^{-39}$, $I_B = 11.4674 \times 10^{-39}$ and $I_C = 18.2679 \times 10^{-39}$ g. cm.^{2}

The configuration was proposed by Drowart, et al., instead of the alternate linear structure OAl-AlO for the reason discussed below. The OB-BO bond ^{1,2} compares to the B_2 dissociation energy ^{3,4} in the same way as the NC-CN bond compares to the C-C single bond. However, for $Al_2O_2(g)$, the relationship between OAl-AlO and Al_2 would be quite different.

References (1) M. Inghram, R. Porter and W. Chupka, J. Chem. Phys., 25, 498 (1956).

(2) D. White, P. Walsh and D. Mann, J. Chem. Phys., 28, 508 (1958).

(3) T. L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publications, London (1958).

(4) G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., (1950).

Dialuminum Dioxide Unipositive Ion ($Al_2O_2^+$)

(Ideal Gas) GFW = 85.9612

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	13.099	64.387	64.387	.000	131.000	128.963	-94.532
300	13.139	64.468	64.387	.024	130.998	128.949	-93.939
400	15.011	68.519	64.927	1.437	130.999	128.271	-70.084
500	16.319	72.018	66.003	3.007	131.073	127.581	-55.765
600	17.205	75.077	67.266	4.686	131.176	126.872	-46.213
700	17.814	77.778	68.579	6.439	131.277	126.146	-39.385
800	18.244	80.186	69.882	8.243	131.346	125.408	-34.260
900	18.556	82.354	71.149	10.084	131.346	124.665	-30.273
1000	18.788	84.322	72.370	11.952	126.218	124.293	-27.164
1100	18.965	86.121	73.539	13.840	126.246	124.099	-24.656
1200	19.102	87.777	74.658	15.744	126.281	123.902	-22.566
1300	19.211	89.311	75.727	17.659	126.319	123.702	-20.796
1400	19.299	90.738	76.748	19.585	126.360	123.500	-19.279
1500	19.370	92.072	77.726	21.519	126.402	123.292	-17.964
1600	19.429	93.324	78.662	23.459	126.444	123.084	-16.812
1700	19.479	94.503	79.560	25.404	126.486	122.873	-15.796
1800	19.520	95.618	80.421	27.354	126.527	122.661	-14.893
1900	19.555	96.674	81.249	29.308	126.565	122.445	-14.084
2000	19.586	97.678	82.046	31.265	126.601	122.225	-13.356
2100	19.612	98.634	82.813	33.225	126.635	122.004	-12.697
2200	19.635	99.547	83.553	35.187	126.664	121.782	-12.098
2300	19.654	100.420	84.267	37.152	126.693	121.563	-11.551
2400	19.672	101.257	84.958	39.118	126.716	121.342	-11.050
2500	19.687	102.061	85.626	41.086	126.735	121.111	-10.588
2600	19.701	102.833	86.273	43.056	126.752	120.888	-10.162
2700	19.713	103.577	86.900	45.026	126.763	120.662	-9.767
2800	19.724	104.294	87.509	46.998	-12.049	122.097	-9.530
2900	19.734	104.986	88.100	48.971	-11.522	126.877	-9.562
3000	19.743	105.656	88.674	50.945	-10.998	131.642	-9.590
3100	19.751	106.303	89.232	52.920	-10.477	136.388	-9.615
3200	19.759	106.930	89.775	54.895	-9.961	141.120	-9.638
3300	19.765	107.538	90.305	56.871	-9.448	145.833	-9.658
3400	19.771	108.128	90.820	58.848	-8.942	150.527	-9.676
3500	19.777	108.702	91.323	60.826	-8.435	155.209	-9.692
3600	19.782	109.259	91.813	62.804	-7.934	159.884	-9.706
3700	19.787	109.801	92.292	64.782	-7.437	164.532	-9.718
3800	19.791	110.329	92.760	66.761	-6.944	169.176	-9.730
3900	19.795	110.843	93.217	68.740	-6.452	173.807	-9.740
4000	19.799	111.344	93.664	70.720	-5.968	178.416	-9.748
4100	19.803	111.833	94.101	72.700	-5.486	183.016	-9.756
4200	19.806	112.310	94.529	74.681	-5.005	187.614	-9.763
4300	19.809	112.776	94.948	76.661	-4.532	192.197	-9.768
4400	19.812	113.232	95.358	78.642	-4.061	196.770	-9.774
4500	19.814	113.677	95.761	80.624	-3.596	201.325	-9.778
4600	19.817	114.113	96.155	82.605	-3.133	205.880	-9.782
4700	19.819	114.539	96.541	84.587	-2.678	210.407	-9.784
4800	19.821	114.956	96.921	86.569	-2.226	214.936	-9.786
4900	19.823	115.365	97.293	88.551	-1.778	219.464	-9.789
5000	19.825	115.765	97.658	90.534	-1.338	223.971	-9.790
5100	19.827	116.158	98.017	92.516	-.904	228.475	-9.791
5200	19.829	116.543	98.370	94.499	-.476	232.963	-9.791
5300	19.830	116.921	98.716	96.482	-.055	237.451	-9.791
5400	19.832	117.291	99.057	98.465	.360	241.928	-9.791
5500	19.833	117.655	99.392	100.448	.765	246.395	-9.791
5600	19.835	118.013	99.721	102.432	1.161	250.856	-9.790
5700	19.836	118.364	100.045	104.415	1.551	255.312	-9.789
5800	19.837	118.709	100.364	106.399	1.929	259.765	-9.788
5900	19.838	119.048	100.678	108.383	2.298	264.206	-9.787
6000	19.839	119.381	100.987	110.367	2.656	268.647	-9.785

June 30, 1968

DIALUMINUM DIOXIDE UNIPOSITIVE ION ($Al_2O_2^+$) (IDEAL GAS) GFW = 85.9612

Point Group [D_{2h}]

ΔHf°_0 = 132.3 ± 20 kcal/mol

$S^\circ_{298.15}$ = [64.4 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 131 ± 20 kcal/mol

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[180] (1)	[850] (1)
[550] (1)	[900] (1)
[850] (1)	[900] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: O-Al-O = [90°] Al-O-Al = [90°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.777 x 10^{-114}] g^3 cm^6

Heat of Formation

G. DeMaria, J. Drowart, and M. G. Inghram, J. Chem. Phys. 30, 318 (1959), have reported an ionization potential for Al_2O_2 of 9.9 ± 0.5eV(228 kcal). Using this value in conjunction with $\Delta Hf^\circ_{298}(Al_2O_2, g)$ = -97 kcal/mol, we obtain $\Delta Hf^\circ_{298}(Al_2O_2^+, g)$ = 131 ± 20 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be the same as that used for Al_2O_2. The bond length is assumed to be longer than that in Al_2O_2 and is made equal to that reported for Al_2O. The bond angle is arbitrarily estimated to be the same as that in Al_2O_2. The vibrational frequencies are estimated to be slightly lower than those for Al_2O_2, since the $Al_2O_2^+$ molecule should be less rigidly bound. The ground state is assumed to be doublet, since there is an odd number of electrons.

The individual moments of inertia are $I_A = 7.32 \times 10^{-39}$ g cm^2, $I_B = 1.234 \times 10^{-38}$ g cm^2, and $I_C = 1.966 \times 10^{-38}$ g cm^2.

The enthalpy at 0°K is -3.010 kcal/mole.

Aluminum Oxide (alpha Al_2O_3)

(Crystal) Mol. Wt. = 101.960

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H_{298}^\circ$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.394	- 397.494	- 397.494	INFINITE
100	3.069	1.024	24.184	- 2.316	- 398.697	- 392.241	857.201
200	12.223	5.946	13.711	- 1.553	- 399.838	- 385.329	421.047
298	18.889	12.174	12.174	.000	- 400.400	- 378.078	277.125
300	18.979	12.291	12.174	.035	- 400.406	- 377.940	275.316
400	22.986	18.339	12.972	2.147	- 400.555	- 370.418	202.378
500	25.345	23.752	14.598	4.577	- 400.475	- 362.891	158.612
600	26.889	28.517	16.529	7.193	- 400.304	- 355.389	129.444
700	27.969	32.749	18.549	9.940	- 400.098	- 347.920	108.620
800	28.758	36.537	20.565	12.778	- 399.889	- 340.481	93.011
900	29.354	39.961	22.533	15.685	- 399.697	- 333.066	80.875
1000	29.814	43.078	24.434	18.644	- 404.522	- 325.301	71.091
1100	30.176	45.938	26.261	21.644	- 404.181	- 317.396	63.058
1200	30.464	48.574	28.012	24.674	- 403.823	- 309.522	56.369
1300	30.995	51.032	29.689	27.745	- 403.437	- 301.680	50.715
1400	31.290	53.339	31.297	30.859	- 403.019	- 293.868	45.873
1500	31.620	55.509	32.839	34.004	- 402.581	- 286.086	41.681
1600	31.920	57.559	34.321	37.181	- 402.119	- 278.334	38.017
1700	32.220	59.503	35.745	40.388	- 401.635	- 270.612	34.788
1800	32.490	61.353	37.117	43.624	- 401.133	- 262.920	31.921
1900	32.760	63.116	38.439	46.886	- 400.613	- 255.254	29.359
2000	33.000	64.803	39.716	50.175	- 400.075	- 247.619	27.057
2100	33.220	66.419	40.949	53.486	- 399.521	- 240.011	24.977
2200	33.450	67.969	42.142	56.819	- 398.956	- 232.427	23.088
2300	33.670	69.461	43.298	60.175	- 398.374	- 224.872	21.367
2400	33.880	70.898	44.418	63.553	- 397.779	- 217.339	19.790
2500	34.100	72.286	45.505	66.952	- 397.172	- 209.834	18.343
2600	34.310	73.627	46.561	70.372	- 396.550	- 202.354	17.009
2700	34.520	74.926	47.588	73.814	- 395.915	- 194.898	15.775
2800	34.735	76.186	48.587	77.277	- 536.375	- 184.157	14.373
2900	34.940	77.408	49.560	80.760	- 535.307	- 171.598	12.931
3000	35.140	78.596	50.508	84.264	- 534.227	- 159.072	11.588
3100	35.340	79.751	51.433	87.788	- 533.132	- 146.584	10.334
3200	35.530	80.876	52.335	91.332	- 532.028	- 134.135	9.161
3300	35.720	81.973	53.217	94.894	- 530.908	- 121.718	8.061
3400	35.906	83.042	54.078	98.476	- 529.777	- 109.338	7.028
3500	36.095	84.085	54.921	102.076	- 528.634	- 96.992	6.056

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1964

ALUMINUM OXIDE (ALPHA Al_2O_3) (CRYSTAL) MOL. WT. = 101.960

$S^\circ_{298.15}$ = 12.174 cal. deg.$^{-1}$ mole^{-1}

T_m = 2315°K.

$\Delta H^\circ_{f\ 0}$ = -397.5 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -400.4 ± 0.3 kcal. mole^{-1}

ΔH_m = 28.30 ± 0.55 kcal. mole^{-1}

Heat of Formation.

The value of ΔH_f derived from the direct combustion of pure aluminum in oxygen was taken from A. D. Mah, J. Phys. Chem. 61, 1572 (1957). Other values for ΔH_f obtained in the same way are: -399.04 ± .24 kcal. mole^{-1} reported by P. E. Snyder and H. Seltz, J. Am. Chem. Soc. 67, 683 (1945); -400.4 ± .3 kcal. mole^{-1} reported by C. E. Holley, Jr., and E. J. Huber, Jr., J. Am. Chem. Soc. 73, 5577 (1951); and -402 ± 2 kcal. mole^{-1} reported by A. Schneider and G. Gattow, Z. anorg. u. allgem. Chem. 277, 41 (1954).

Heat Capacity and Entropy.

The heat capacity measurements reported by G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, (15° to 1200°K.), J. Research Natl. Bur. Standards 57, 67 (1956), were employed in this table. Low temperature measurements were also made by F. Simon and R. C. Swain (30-280°K.), Z. Physik. Chem. 28B, 189 (1935); E. C. Kerr, H. L. Johnston, and N. C. Hallett (20° to 295°K.), J. Am. Chem. Soc. 72, 4740 (1950); J. W. Edwards and G. L. Kingston (53-291°K.), Trans. Faraday Soc. 58, 1313-22 (1962); E. N. Rodigina and K. Z. Gomel'skii, (100-900°K.), Zhur. Fiz. Khim. 32, 1859-62 (1958); B. E. Walker, J. A. Grand, and R. R. Miller (300-900°K.), J. Phys. Chem. 60, 231-3 (1956); R. Dawson, E. B. Brackett, and T. E. Brackett (700-1400°K.), J. Phys. Chem. 67, 1669 (1963), and L. Terebesi (0-1300°K.), Helv. Chim. Acta. 17, 804 (1934). All of the above low temperature data are in good agreement with Furukawa's work.

The heat capacities above 1200°K. (1200-2500°K.) were taken from the enthalpy measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Fomichov, Ukr. Fiz. Zh. 7, 205-10 (1962). The heat capacity values above 2500°K. were extrapolated. High temperature measurements were also made by the following investigators: V. Ya. Chekhovskoi (500-2000°K.), Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR 5, 62-5 (1962); A. Ferrier and M. Olette (1100-2300°K.), Compt. Rend. 254, 4293-95 (1962); C. H. Shomate and B. F. Naylor (500-1800°K.), J. Am. Chem. Soc. 67, 72 (1945) and H. L Johnston and M. Hoch (1000-2000°K.), J. Phys. Chem. 65, 1184-5 (1961); and V. A. Kirillin, A. E. Sheidlin, and V. Ya. Chekhovskii (500-2000°K.), Doklady Akad. Nauk. SSSR 135, 125-8 (1960). Numerical values were not available from Kirillin, et al., but graphical values were in close agreement with an extrapolation of Furukawa's data. The entropy at 298.15 was reported by T. Furukawa, et al., loc. cit., using S°_{15} = 0.0105 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The melting data were obtained from the measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Fomichov, loc. cit. S. J. Schneider "Compilation of the Melting Points of the Metal Oxides," NBS Monograph 68, p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Aluminum Oxide, Gamma (γ - Al_2O_3)

(Crystal)   Mol. Wt. = 101.9612

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH°_f (kcal. mole^{-1})	ΔF°_f (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	19.833	12.550	12.550	.000	- 396.000	- 373.790	273.982
300	19.928	12.673	12.550	.037	- 396.005	- 373.652	272.193
400	24.135	19.023	13.388	2.254	- 396.052	- 366.184	200.064
500	26.612	24.691	15.093	4.799	- 395.866	- 358.736	156.796
600	28.233	29.694	17.118	7.545	- 395.570	- 351.337	127.968
700	29.367	34.135	19.238	10.428	- 395.224	- 343.991	107.394
800	30.196	38.112	21.353	13.407	- 394.876	- 336.697	91.977
900	30.804	41.705	23.418	16.458	- 394.570	- 329.443	79.996
1000	31.305	44.977	25.413	19.565	- 399.370	- 321.853	70.338
1100	31.623	47.976	27.330	22.711	- 399.000	- 314.122	62.407
1200	31.987	50.743	29.167	25.891	- 398.610	- 306.423	55.805
1300	32.447	53.321	30.927	29.113	- 398.190	- 298.756	50.223
1400	32.855	55.741	32.614	32.378	- 397.738	- 291.123	45.444
1500	33.193	58.020	34.232	35.681	- 397.260	- 283.527	41.308
1600	33.516	60.172	35.787	39.016	- 396.758	- 275.960	37.693
1700	33.824	62.213	37.282	42.384	- 396.232	- 268.425	34.507
1800	34.115	64.155	38.721	45.781	- 395.684	- 260.921	31.679
1900	34.390	66.007	40.109	49.206	- 395.119	- 253.451	29.152
2000	34.650	67.778	41.449	52.658	- 394.535	- 246.013	26.882
2100	34.889	69.474	42.743	56.135	- 393.934	- 238.601	24.830
2200	35.123	71.102	43.995	59.636	- 393.319	- 231.219	22.968
2300	35.348	72.669	45.208	63.159	- 392.686	- 223.862	21.271
2400	35.574	74.178	46.384	66.706	- 392.040	- 216.533	19.717
2500	35.801	75.635	47.525	70.274	- 391.382	- 209.242	18.291
2600	36.026	77.043	48.633	73.866	- 390.706	- 201.965	16.976
2700	36.252	78.407	49.711	77.480	- 390.017	- 194.721	15.761
2800	36.472	79.730	50.760	81.116	- 528.134	- 185.841	14.505
2900	36.687	81.013	51.781	84.774	- 526.892	- 173.637	13.085
3000	36.897	82.260	52.776	88.453	- 525.636	- 161.473	11.763

Dec. 31, 1965

ALUMINUM OXIDE, GAMMA (γ- Al_2O_3)   (CRYSTAL)   MOL. WT. = 101.9612

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [12.55] cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = [-396.0 ± 0.5] kcal. mole^{-1}

T_m = 2323°K. ΔH°_m = [20.9] kcal. mole^{-1}

Heat of Formation.

The enthalpy change (ΔH°_t) for the transition $Al_2O_3(\gamma, c) \rightarrow Al_2O_3(\alpha, c)$ has been determined by (1) V. Kostomaroff and M. Rey, Silicates Ind. 28, 9 (1963); and (2) T. Yokokawa and O. J. Kleppa, J. Phys. Chem. 68, 3246 (1964). The results obtained are presented in the table. The enthalpies of solution for $Al_2O_3(\gamma, c)$ and Al(c) in 2N KOH(aq.) have been measured by (3) K. K. Kelley, C. H. Shomate, F. E. Young, B. F. Naylor, A. E. Salo and E. H. Huffman, U. S. Bur. Mines Tech. Rept. 688 (1946). Based on their reported values, -16.13 ± 1.0 and -196.02 ± 0.25 kcal. mole^{-1}, respectively, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $Al_2O_3(\gamma, c)$ was evaluated to be -384.84 ± 1.1 kcal. mole^{-1}. Hence, the enthalpy of transition ($\gamma \rightarrow \alpha$) was calculated as -15.6 ± 1.1 kcal. mole^{-1}, using $\Delta H^\circ_{f\ 298.15}$ (Al_2O_3, α, c) = -400.4 kcal. mole^{-1}.

Source	Method	Temperature, °K.	ΔH°_t, kcal. mole^{-1}	$\Delta H^\circ_{t\ 298.15}$, kcal. mole^{-1}
(2)	solution calorimetry	978	-5.3	-4.4
(1)	differential thermal analysis	1473	-11.0	-9.4
(3)	solution calorimetry	298.15	-15.6	-15.6

The heat of formation for $Al_2O_3(\gamma, c)$ was calculated from that for $Al_2O_3(\alpha, c)$ and the ΔH°_t value reported by Yokokawa and Kleppa, loc. cit., which was arbitrarily selected.

Heat Capacity and Entropy.

The heat capacities were assumed to be larger than those for $Al_2O_3(\alpha, c)$ by 5% at each temperature. The value of $S^\circ_{298.15}$ was estimated such that at T_m, ΔF°_f (Al_2O_3, γ, c) > ΔF°_f (Al_2O_3, α, c).

Melting Data.

T_m was reported by M. Plummer, J. Appl. Chem. 8, 35 (1958). The difference between ΔH°_f for Al_2O_3 (γ, c) and Al_2O_3 (l) at T_m is ΔH°_m.

Aluminum Oxide (Al_2O_3)
(Liquid) Mol. Wt. = 101.96

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	18.889	23.728	23.728	.000	- 373.356	- 354.478	259.827
300	18.979	23.845	23.728	.035	- 373.362	- 354.362	258.140
400	22.986	29.894	24.526	2.147	- 373.511	- 347.996	190.127
500	25.345	35.292	26.150	4.571	- 373.438	- 341.623	149.316
600	26.889	40.062	28.080	7.189	- 373.264	- 335.276	122.118
700	27.969	44.291	30.099	9.934	- 373.060	- 328.961	102.701
800	28.758	48.081	32.114	12.773	- 372.850	- 322.676	88.147
900	29.354	51.504	34.082	15.680	- 372.658	- 316.415	76.832
1000	29.814	54.622	35.982	18.640	- 377.483	- 309.805	67.704
1100	30.176	57.481	37.808	21.640	- 377.141	- 303.054	60.208
1200	30.464	60.119	39.559	24.672	- 376.781	- 296.335	53.967
1300	30.995	62.580	41.236	27.747	- 376.391	- 289.647	48.692
1400	31.290	64.889	42.844	30.863	- 375.971	- 282.990	44.175
1500	31.620	67.060	44.387	34.009	- 375.432	- 276.363	40.264
1600	34.623	69.110	45.869	37.186	- 375.070	- 269.766	36.847
1700	34.623	71.209	47.298	40.649	- 374.331	- 263.208	33.836
1800	34.623	73.188	48.682	44.111	- 373.602	- 256.693	31.165
1900	34.623	75.060	50.021	47.573	- 372.882	- 250.215	28.780
2000	34.623	76.836	51.318	51.036	- 372.170	- 243.780	26.638
2100	34.623	78.525	52.574	54.498	- 371.465	- 237.378	24.703
2200	34.623	80.136	53.790	57.960	- 370.771	- 231.009	22.948
2300	34.623	81.675	54.969	61.422	- 370.083	- 224.673	21.348
2400	34.623	83.148	56.113	64.885	- 369.403	- 218.363	19.884
2500	34.623	84.562	57.223	68.347	- 368.733	- 212.085	18.540
2600	34.623	85.920	58.301	71.809	- 368.069	- 205.833	17.301
2700	34.623	87.226	59.348	75.272	- 367.413	- 199.607	16.156
2800	34.623	88.486	60.366	78.734	- 507.874	- 190.096	14.837
2900	34.623	89.701	61.357	82.196	- 506.827	- 178.766	13.472
3000	34.623	90.874	62.321	85.659	- 505.788	- 167.469	12.200
3100	34.623	92.010	63.261	89.121	- 504.756	- 156.207	11.012
3200	34.623	93.109	64.177	92.583	- 503.732	- 144.983	9.901
3300	34.623	94.174	65.069	96.045	- 502.713	- 133.788	8.860
3400	34.623	95.208	65.941	99.508	- 501.701	- 122.626	7.882
3500	34.623	96.211	66.791	102.970	- 500.696	- 111.496	6.962

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1964

ALUMINUM OXIDE (Al_2O_3) (LIQUID) MOL. WT. = 101.96

$S^\circ_{298.15}$ = [23.728] cal. deg.$^{-1}$ mole^{-1}

T_m = 2315°K.

$\Delta H^\circ_{f\ 298.15}$ = [373.356] kcal. mole^{-1}

ΔH°_m = 28.30 ± 0.55 kcal. mole^{-1}

Heat of Formation.

The heat of formation for the liquid was obtained from $\Delta H_{f\ 298.15}$ for α crystal by adding on ΔH_m plus the difference between $H_{2315}-H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacities of the liquid alpha-Al_2O_3 was taken from the crystal heat capacities up to 1600°K. where a glass transition was assumed. From 1600°K. to 3500°K. the heat capacities were assumed to be the constant value of 34.623 measured by P. B. Kantor, L. S. Lazareva, V. V. Kandyba and E. M. Fomichov (2300-2500°K.) Ukr. Fiz. Zh. 7, 205-10 (1962).

The entropy at 298.15°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting data was taken from the measurements of P. B. Kantor, et al., loc. cit. S. J. Schneider, "Compilation of the Melting Points of the Metal Oxides," NBS Monograph 68 p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Sillimanite (Al_2SiO_5)

(Crystal) GFW = 162.046

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.164	- 614.830	- 614.830	INFINITE
100	7.714	3.609	42.687	- 3.908	- 616.584	- 606.175	1324.794
200	20.500	13.048	25.407	- 2.472	- 618.053	- 595.168	650.369
298	29.210	22.987	22.987	.000	- 618.810	- 583.760	427.907
300	29.342	23.169	22.988	.054	- 618.819	- 583.543	425.111
400	35.248	32.474	24.217	3.303	- 619.053	- 571.736	312.382
500	39.005	40.769	26.714	7.027	- 618.962	- 559.912	244.737
600	41.354	48.099	29.680	11.051	- 618.712	- 548.125	199.654
700	42.963	54.400	32.785	15.270	- 618.393	- 536.384	167.467
800	44.215	60.420	35.882	19.631	- 618.061	- 524.694	143.340
900	45.294	65.691	38.906	24.107	- 617.756	- 513.039	124.583
1000	46.256	70.514	41.829	28.685	- 622.535	- 501.051	109.505
1100	47.122	74.964	44.641	33.354	- 622.117	- 488.926	97.141
1200	47.984	79.101	47.343	38.110	- 621.644	- 476.838	86.844
1300	48.827	82.975	49.936	42.951	- 621.117	- 464.791	78.138
1400	49.612	86.623	52.428	47.873	- 620.538	- 452.788	70.683
1500	50.377	90.072	54.823	52.872	- 619.909	- 440.828	64.229
1600	51.126	93.347	57.129	57.948	- 619.229	- 428.910	58.586
1700	51.864	96.469	59.352	63.097	- 630.490	- 416.932	53.600
1800	52.592	99.454	61.498	68.320	- 629.656	- 404.390	49.100
1900	53.313	102.316	63.571	73.615	- 628.766	- 391.900	45.079
2000	54.028	105.069	65.578	78.983	- 627.817	- 379.461	41.466
2100	54.735	107.722	67.522	84.421	- 626.809	- 367.067	38.201
2200	55.441	110.285	69.408	89.930	- 625.748	- 354.726	35.239
2300	56.144	112.765	71.239	95.509	- 624.625	- 342.428	32.538
2400	56.845	115.169	73.020	101.158	- 623.449	- 330.178	30.067
2500	57.544	117.504	74.753	106.878	- 622.217	- 317.995	27.799
2600	58.241	119.774	76.441	112.667	- 620.926	- 305.845	25.709
2700	58.936	121.986	78.087	118.526	- 619.580	- 293.758	23.778
2800	59.628	124.141	79.694	124.454	- 756.997	- 280.050	21.859
2900	60.319	126.246	81.263	130.451	- 755.014	- 263.052	19.824
3000	61.007	128.302	82.796	136.518	- 752.974	- 246.120	17.930

Dec. 31, 1960; Sept. 30, 1964; Sept. 30, 1966; Sept. 30, 1967

SILLIMANITE (Al_2SiO_5) (CRYSTAL) GFW = 162.046

ΔHf°_0 = -614.83 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 22.987 ±0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -618.81 ± 0.5 kcal/mol

Heat of Formation

The heat of the reaction $Al_2O_3(\alpha) + SiO_2$ (quartz) $\rightarrow Al_2SiO_5$ (sillimanite) has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -1.51 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHr°_{298} = -0.71 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 145, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957) suggested that ΔHr° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHr° should lie between 0 and -6 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔHr° = -0.356 kcal/mol from high temperature - high pressure equilibria. These later values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.4° to 296.5°K by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S°_{51} = 0.73 gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1964)]. The crystal structure of sillimanite, L. Bragg and G. F. Claringbull, "Crystal Structure of Minerals," Vol. IV, G. Bell and Sons Ltd., London, 1965, indicates that there is no mixing of the tetra-coordinated aluminum and silicon atoms. Thus there should be no residual entropy at 0°K.

Andalusite (Al_2SiO_5)

(Crystal) GFW = 162.046

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.085	- 615.461	- 615.461	INFINITE
100	7.247	3.242	41.802	- 3.856	- 617.243	- 606.796	1326.152
200	20.221	12.391	24.695	- 2.461	- 618.752	- 595.735	650.989
298	29.339	22.280	22.280	.000	- 619.520	- 584.259	428.273
300	29.474	22.462	22.281	.054	- 619.529	- 584.041	425.473
400	35.747	31.854	23.519	3.334	- 619.732	- 572.167	312.617
500	39.524	40.266	26.044	7.111	- 619.589	- 560.287	244.901
600	41.710	47.675	29.045	11.178	- 619.295	- 548.454	199.774
700	43.276	54.227	32.183	15.430	- 618.943	- 536.673	167.557
800	44.484	60.086	35.312	19.820	- 618.582	- 524.947	143.409
900	45.495	65.385	38.363	24.320	- 618.253	- 513.261	124.637
1000	46.377	70.225	41.311	28.914	- 623.016	- 501.243	109.547
1100	47.175	74.683	44.145	33.592	- 622.589	- 489.089	97.173
1200	47.916	78.820	46.864	38.347	- 622.117	- 476.974	86.869
1300	48.617	82.683	49.472	43.174	- 621.604	- 464.898	78.156
1400	49.289	86.311	51.976	48.069	- 621.051	- 452.864	70.695
1500	49.940	89.734	54.380	53.031	- 620.460	- 440.872	64.235
1600	50.574	92.977	56.692	58.057	- 619.830	- 428.919	58.588
1700	51.195	96.062	58.917	63.145	- 631.152	- 416.902	53.596
1800	51.806	99.005	61.063	68.295	- 630.391	- 404.317	49.091
1900	52.410	101.823	63.135	73.506	- 629.585	- 391.782	45.065
2000	53.007	104.526	65.137	78.777	- 628.732	- 379.290	41.447
2100	53.599	107.127	67.075	84.108	- 627.832	- 366.840	38.178
2200	54.186	109.634	68.953	89.497	- 626.891	- 354.437	35.210
2300	54.768	112.055	70.775	94.945	- 625.899	- 342.069	32.504
2400	55.345	114.398	72.544	100.450	- 624.867	- 329.746	30.027
2500	55.917	116.669	74.264	106.013	- 623.792	- 317.482	27.754
2600	56.484	118.873	75.937	111.634	- 622.669	- 305.246	25.658
2700	57.046	121.016	77.567	117.310	- 621.506	- 293.064	23.722
2800	57.603	123.100	79.157	123.043	- 759.119	- 279.256	21.797
2900	58.155	125.131	80.707	128.830	- 757.345	- 262.150	19.756
3000	58.702	127.112	82.221	134.673	- 755.529	- 245.104	17.856

Sept. 30, 1966; Sept. 30, 1967

ANDALUSITE (Al_2SiO_5) (CRYSTAL) GFW = 162.046

ΔHf°_0 = -615.46 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 22.28 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -619.52 ± 0.5 kcal/mol

Heat of Formation

The heat of the reaction $Al_2O_3(\alpha) + SiO_2(\text{quartz}) \rightarrow Al_2SiO_5(\text{andalusite})$ has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -1.99 ± 0.17 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHr°_{298} = -1.42 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 145, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957), suggested that ΔHr° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHr° should lie between 0 and -6 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔHr° = -1.108 kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.9° to 296.2°K by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S°_{51} = 0.62 gibbs/mol. The high temperature enthalpy has been measured to 1600°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1954)]. Since all the aluminum and silicon atoms occupy differently coordinated sites, there is no possibility of any residual entropy of mixing in this polymorph.

Kyanite (Al_2SiO_5)

(Crystal) GFW = 162.046

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-3.835	-615.750	-615.750	INFINITE
100	5.663	2.135	38.912	-3.678	-617.604	-607.047	1326.700
200	19.354	10.343	22.411	-2.414	-619.245	-595.818	651.080
298	29.099	20.032	20.032	.000	-620.060	-584.129	428.178
300	29.232	20.213	20.033	.054	-620.070	-583.907	425.376
400	35.439	29.519	21.259	3.304	-620.302	-571.803	312.419
500	39.555	37.898	23.765	7.067	-620.173	-559.687	244.639
600	42.120	45.350	26.754	11.158	-619.855	-547.619	199.470
700	43.795	51.975	29.893	15.457	-619.456	-535.609	167.225
800	45.000	57.904	33.030	19.899	-619.043	-523.663	143.058
900	45.975	63.261	36.096	24.448	-618.665	-511.761	124.272
1000	46.896	68.153	39.061	29.092	-623.378	-499.533	109.173
1100	47.744	72.663	41.913	33.825	-622.896	-487.174	96.793
1200	48.558	76.853	44.652	38.641	-622.363	-474.860	86.484
1300	49.259	80.768	47.282	43.532	-621.786	-462.591	77.769
1400	49.919	84.443	49.806	48.491	-621.169	-450.367	70.305
1500	50.538	87.908	52.232	53.514	-620.517	-438.191	63.844
1600	51.178	91.190	54.565	58.600	-619.827	-426.057	58.197
1700	51.799	94.311	56.812	63.749	-631.089	-413.862	53.206
1800	52.414	97.289	58.979	68.959	-630.267	-401.104	48.701
1900	53.024	100.140	61.071	74.231	-629.400	-388.399	44.676
2000	53.628	102.875	63.093	79.564	-628.485	-375.741	41.059
2100	54.220	105.506	65.050	84.956	-627.524	-363.127	37.791
2200	54.809	108.042	66.947	90.408	-626.520	-350.563	34.825
2300	55.396	110.491	68.787	95.918	-625.466	-338.038	32.121
2400	55.980	112.861	70.575	101.487	-624.370	-325.560	29.646
2500	56.562	115.158	72.312	107.114	-623.231	-313.143	27.375
2600	57.141	117.388	74.003	112.799	-622.044	-300.759	25.281
2700	57.718	119.555	75.650	118.542	-620.814	-288.428	23.347
2800	58.293	121.664	77.256	124.343	-758.359	-274.475	21.424
2900	58.865	123.720	78.823	130.201	-756.515	-257.228	19.385
3000	59.434	125.725	80.353	136.116	-754.626	-240.041	17.487

Sept. 30, 1966; Sept. 30, 1967

KYANITE (Al_2SiO_5) (CRYSTAL) GFW = 162.046

ΔHf_0° = -615.75 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 20.032 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -620.06 ± 0.5 kcal/mol

Heat of Formation

The heat of the reaction $Al_2O_3(\alpha) + SiO_2(\text{quartz}) \rightarrow Al_2SiO_5(\text{kyanite})$ has been determined at 968° by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -2.37 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHr°_{298} = -1.96 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 145, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957), suggested that ΔHr° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHr° should lie between 0 and -6 kcal/mol. R. W. Haskell and R. C. DeVries, J. Am. Ceram. Soc. 47, 202 (1964), from phase equilibria obtained ΔHr° = -2 ± 7 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔHr° = -0.622 kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.8° to 296.3° by S. S. Todd, J. Am. Chem. Soc. 724742 (1950). The entropy is based on S°_{51} = 0.33 gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1954)]. The high temperature heat capacity has been measured between 100° and 1200°C by V. Ya. Leonidov, Yu. P. Barskii and N. I. Khitarov, Geochemistry (English Transl.) 1964, 409 (1964). The values reported are in excellent agreement with the adopted functions. Since the aluminum atoms and the silicon atoms occupy different types of sites there is no possibility of any residual entropy of mixing in this polymorph.

Mullite ($Al_6Si_2O_{13}$)

(Crystal) GFW = 426.0532

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 11.011	-1619.252	-1619.252	INFINITE
100	20.379	14.508	117.851	- 10.334	-1623.850	-1597.221	3490.722
200	54.005	39.355	72.126	- 6.554	-1627.808	-1568.994	1714.516
298	77.830	65.700	65.700	.000	-1629.830	-1539.659	1128.600
300	78.162	66.183	65.701	.144	-1629.854	-1539.101	1121.234
400	93.390	90.882	68.966	8.767	-1630.461	-1508.724	824.328
500	103.250	112.840	75.590	18.625	-1630.228	-1478.303	646.165
600	109.900	132.283	83.451	29.299	-1629.552	-1447.980	527.426
700	114.600	149.592	91.686	40.534	-1628.654	-1417.783	442.652
800	118.100	165.134	99.912	52.177	-1627.700	-1387.731	379.110
900	120.650	179.196	107.953	64.119	-1626.845	-1357.783	329.715
1000	122.700	192.016	115.728	76.288	-1641.297	-1326.823	289.977
1100	124.212	203.782	123.205	88.635	-1640.228	-1295.434	257.379
1200	125.626	214.652	130.379	101.127	-1639.092	-1264.141	230.231
1300	126.940	224.760	137.254	113.757	-1637.891	-1232.941	207.276
1400	128.154	234.212	143.846	126.512	-1636.635	-1201.835	187.615
1500	129.270	243.092	150.169	139.384	-1635.329	-1170.827	170.589
1600	130.097	251.461	156.241	152.352	-1633.985	-1139.903	155.703
1700	130.919	259.373	162.077	165.403	-1656.597	-1108.852	142.552
1800	131.737	266.880	167.693	178.536	-1655.091	-1076.666	130.725
1900	132.551	274.024	173.103	191.751	-1653.548	-1044.578	120.154
2000	133.360	280.844	178.320	205.046	-1651.956	-1012.577	110.649
2100	134.106	287.368	183.359	218.419	-1650.320	- 980.647	102.057
2200	134.876	293.624	188.230	231.868	-1648.653	- 948.803	94.255
2300	135.672	299.637	192.944	245.395	-1646.928	- 917.018	87.137
2400	136.494	305.429	197.511	259.003	-1645.167	- 885.309	80.618
2500	137.340	311.018	201.940	272.695	-1643.361	- 853.713	74.632
2600	138.212	316.421	206.240	286.472	-1641.496	- 822.151	69.108
2700	139.108	321.654	210.418	300.338	-1639.581	- 790.683	64.001
2800	140.030	326.730	214.482	314.295	-2054.068	- 754.289	58.875
2900	140.978	331.660	218.438	328.345	-2050.461	- 707.933	53.351
3000	141.950	336.456	222.292	342.491	-2046.792	- 661.696	48.204

Sept. 30, 1966; Sept. 30, 1967

MULLITE ($Al_6Si_2O_{13}$) (CRYSTAL) GFW = 426.053

$\Delta Hf^\circ_0 = -1619.25 \pm 1.5$ kcal/mol

$S^\circ_{298.15} = 65.7 \pm 3$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -1629.83 \pm 1.5$ kcal/mol

$Tm = 2023°K$

Heat of Formation

The heat of the reaction $3Al_2O_3(\alpha) + 2SiO_2(\text{quartz}) \rightarrow Al_6Si_2O_{13}$ has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be +5.44 ± 0.35 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta Hr^\circ_{298} = +4.11$ kcal/mol, which is used to calculate the adopted value.

Heat Capacity and Entropy

The low temperature heat capacity and high temperature enthalpy of mullite have been measured by L. B. Pankratz, W. W. Weller and K. K. Kelley, U. S. Bur. Mines RI 6287, 1963. The low temperature investigations extended from 53.5°K to 296.4°K; the Debye-Einstein equation 3D(182/T) + 15E(350/T) + 10E(502/T) + 15E(897/T) represented the data from 53.5° to 114.6°K within 1.4 percent and gave a smooth extrapolation to zero. From this equation the entropy at 51°K was found to be 2.17 gibbs/mol as opposed to the value 1.96 gibbs/mol found by Pankratz et al. However, since it is known that mullite has some of its Al atoms on Si sites, there will be configurational entropy remaining at 0°K. This is borne out by the free energy determinations of R. H. Rein and J. Chipman, Trans. Met. Soc. AIME 233, 415 (1965), and D. A. R. Kay and J. Taylor, Trans. Faraday Soc. 56, 1372 (1960), who obtain $\Delta Gr^\circ_{1823} = -5.7 \pm 0.1$ kcal/mol for the formation from oxide. If the entropies and enthalpies reported by Pankratz et al. are used with the heat of formation, they yield $\Delta Gr^\circ_{1823} = +2.9$ kcal/mol. Holm and Kleppa, loc. cit., calculate that random mixing of tetra-coordinated aluminum and silicon atoms could produce 7 eu residual entropy. We have added 4.7 eu in order to match the measured ΔGr°_{1823}.

A review of the enthalpy determination indicated that the values might easily be 2 percent low if as little as 4 percent of kyanite remained unchanged in the sample used for measurement. Since X-ray could not detect this amount, it is not an unreasonable assumption. Accordingly we have checked the effect of increasing the heat capacity above 298°K by 2 percent; this then gives $\Delta Gr^\circ_{1823} = -2.10$ kcal/mol. In order to bring this within reasonable agreement with the observations a residual configurational entropy of 2 gibbs/mol would be needed. Thus the uncertainty in the residual entropy is of the order of 2 eu due to possible uncertainty in the high temperature heat capacity.

Melting Data

The congruent melting point of mullite was reported by S. Aramaki and R. Roy, Nature 184, 631 (1959).

Boron (B)

(Reference State) At. Wt. = 10.82

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- .292	.000	.000	INFINITE
100	.256	.081	2.941	- .286	.000	.000	.000
200	1.447	.588	1.618	- .206	.000	.000	.000
298	2.650	1.403	1.403	.000	.000	.000	.000
300	2.666	1.419	1.403	.005	.000	.000	.000
400	3.720	2.339	1.521	.327	.000	.000	.000
500	4.490	3.257	1.777	.740	.000	.000	.000
600	4.990	4.122	2.097	1.215	.000	.000	.000
700	5.320	4.917	2.444	1.731	.000	.000	.000
800	5.560	5.644	2.799	2.276	.000	.000	.000
900	5.760	6.310	3.153	2.842	.000	.000	.000
1000	5.950	6.927	3.500	3.427	.000	.000	.000
1100	6.120	7.502	3.838	4.031	.000	.000	.000
1200	6.260	8.041	4.166	4.650	.000	.000	.000
1300	6.410	8.548	4.483	5.284	.000	.000	.000
1400	6.540	9.028	4.791	5.931	.000	.000	.000
1500	6.670	9.483	5.089	6.592	.000	.000	.000
1600	6.790	9.918	5.377	7.265	.000	.000	.000
1700	6.900	10.333	5.657	7.950	.000	.000	.000
1800	7.000	10.730	5.927	8.645	.000	.000	.000
1900	7.062	11.110	6.190	9.348	.000	.000	.000
2000	7.120	11.474	6.445	10.057	.000	.000	.000
2100	7.177	11.823	6.693	10.772	.000	.000	.000
2200	7.228	12.158	6.934	11.492	.000	.000	.000
2300	7.274	12.480	7.168	12.217	.000	.000	.000
2400	7.315	12.791	7.396	12.947	.000	.000	.000
2500	7.300	15.289	7.662	19.068	.000	.000	.000
2600	7.300	15.575	7.961	19.798	.000	.000	.000
2700	7.300	15.851	8.248	20.528	.000	.000	.000
2800	7.300	16.116	8.524	21.258	.000	.000	.000
2900	7.300	16.373	8.790	21.988	.000	.000	.000
3000	7.300	16.620	9.047	22.718	.000	.000	.000
3100	7.300	16.859	9.296	23.448	.000	.000	.000
3200	7.300	17.091	9.536	24.178	.000	.000	.000
3300	7.300	17.316	9.768	24.908	.000	.000	.000
3400	7.300	17.534	9.993	25.638	.000	.000	.000
3500	7.300	17.745	10.212	26.368	.000	.000	.000
3600	7.300	17.951	10.424	27.098	.000	.000	.000
3700	7.300	18.151	10.630	27.828	.000	.000	.000
3800	7.300	18.346	10.830	28.558	.000	.000	.000
3900	7.300	18.535	11.026	29.288	.000	.000	.000
4000	4.982	49.551	11.752	151.197	.000	.000	.000
4100	4.985	49.674	12.675	151.696	.000	.000	.000
4200	4.988	49.795	13.558	152.194	.000	.000	.000
4300	4.993	49.912	14.402	152.693	.000	.000	.000
4400	4.997	50.027	15.210	153.193	.000	.000	.000
4500	5.002	50.139	15.985	153.693	.000	.000	.000
4600	5.008	50.249	16.729	154.193	.000	.000	.000
4700	5.015	50.357	17.443	154.694	.000	.000	.000
4800	5.022	50.463	18.130	155.196	.000	.000	.000
4900	5.030	50.566	18.791	155.699	.000	.000	.000
5000	5.039	50.668	19.427	156.202	.000	.000	.000
5100	5.048	50.768	20.041	156.707	.000	.000	.000
5200	5.058	50.866	20.633	157.212	.000	.000	.000
5300	5.069	50.962	21.204	157.718	.000	.000	.000
5400	5.081	51.057	21.756	158.226	.000	.000	.000
5500	5.093	51.151	22.290	158.734	.000	.000	.000
5600	5.107	51.242	22.806	159.244	.000	.000	.000
5700	5.121	51.333	23.306	159.756	.000	.000	.000
5800	5.136	51.422	23.790	160.269	.000	.000	.000
5900	5.152	51.510	24.259	160.783	.000	.000	.000
6000	5.168	51.597	24.714	161.299	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1964

BORON (B) (REFERENCE STATE) AT. WT. = 10.82

0	to	2450°K.	Crystal
2450	to	3931°K.	Liquid
3931	to	6000°K.	Ideal Monatomic Gas

See crystal, liquid and ideal monatomic gas for details.

Boron, Beta-Rhombohedral (B)
(Crystal) At. Wt. = 10.82

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-.292	.000	.000	INFINITE
100	.256	.081	2.941	-.286	.000	.000	.000
200	1.447	.588	1.618	-.206	.000	.000	.000
298	2.650	1.403	1.403	.000	.000	.000	.000
300	2.667	1.419	1.403	.005	.000	.000	.000
400	3.720	2.339	1.521	.327	.000	.000	.000
500	4.490	3.257	1.777	.740	.000	.000	.000
600	4.990	4.122	2.097	1.215	.000	.000	.000
700	5.320	4.917	2.444	1.731	.000	.000	.000
800	5.560	5.644	2.799	2.276	.000	.000	.000
900	5.760	6.310	3.153	2.842	.000	.000	.000
1000	5.950	6.927	3.500	3.427	.000	.000	.000
1100	6.120	7.502	3.838	4.031	.000	.000	.000
1200	6.260	8.041	4.166	4.650	.000	.000	.000
1300	6.410	8.548	4.483	5.284	.000	.000	.000
1400	6.540	9.028	4.791	5.931	.000	.000	.000
1500	6.670	9.483	5.089	6.592	.000	.000	.000
1600	6.790	9.918	5.377	7.265	.000	.000	.000
1700	6.900	10.333	5.657	7.950	.000	.000	.000
1800	7.000	10.730	5.927	8.645	.000	.000	.000
1900	7.062	11.110	6.190	9.348	.000	.000	.000
2000	7.120	11.474	6.445	10.057	.000	.000	.000
2100	7.176	11.823	6.693	10.772	.000	.000	.000
2200	7.228	12.158	6.934	11.492	.000	.000	.000
2300	7.274	12.480	7.168	12.217	.000	.000	.000
2400	7.314	12.791	7.396	12.947	.000	.000	.000
2500	7.350	13.090	7.618	13.680	-5.388	.109	-.010
2600	7.374	13.379	7.834	14.416	-5.382	.328	-.028
2700	7.396	13.657	8.044	15.155	-5.373	.551	-.045
2800	7.416	13.927	8.250	15.895	-5.363	.767	-.060
2900	7.434	14.187	8.450	16.638	-5.350	.989	-.075
3000	7.450	14.440	8.646	17.382	-5.336	1.204	-.088
3100	7.464	14.684	8.836	18.128	-5.320	1.422	-.100
3200	7.476	14.921	9.023	18.875	-5.303	1.641	-.112
3300	7.486	15.151	9.205	19.623	-5.285	1.859	-.123
3400	7.494	15.375	9.383	20.372	-5.266	2.075	-.133
3500	7.500	15.592	9.558	21.122	-5.246	2.289	-.143

Dec. 31, 1960; Dec. 31, 1964

BORON, BETA-RHOMBOHEDRAL (B) (CRYSTAL) AT. WT. = 10.82

$\Delta H^\circ_{f\ 0}$ = 0 kcal. mole^{-1}

$S^\circ_{298.15}$ = 1.403 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 0 kcal. mole^{-1}

T_m = 2450 ± 20 °K.

ΔH°_m = [5.39] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 132.8 ± 4.0 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities, 16.90 - 303.71°K., were measured by H. L. Johnston, H. N. Hersh and E. C. Kerr, J. Am. Chem. Soc. 73, 1112 (1951). The high temperature heat capacities, 282.8 - 1667.8°K., were measured by R. A. McDonald and D. R. Stull, J. Chem. Eng. Data, 7, 84 (1962). These two sets of data were joined smoothly at 298.15°K. by graphical method. The heat capacity values above 1667.8°K. were estimated by graphical extrapolation. The high temperature C_p, 530 - 800°K., were also determined by S. S. Wise, J. L. Margrave and R. L. Altman, J. Phys. Chem. 64, 915 (1960). The other principal investigators are: (1) J. A. Robertson, Ph. D. Thesis, Cornell University, 1944; (2) A. Magnus and H. Danz, Ann. Phys. [4] 81, 407 (1926); (3) H. Moissan and H. Gautier, Compt. rend. 116, 924 (1893); (4) H. F. Weber, Ann. Phys. [2] 154, 367, 553 (1875); (5) H. Kopp, Trans. Roy. Soc. [London] 155, 71 (1865); and (6) V. Regnault, Ann. chim. et phys. [3] 63, 5 (1861) and Phil. Mag. [4] 23, 103 (1862). The value of $S^\circ_{298.15}$ was obtained from H. L. Johnston, H. N. Hersh and E. C. Kerr, loc. cit., based on S°_{17} = 0.00139 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The melting point (T_m) of B(c) has been measured by many investigators. The values of T_m reported are in the range 2273 - 2673°K. Based on the relationship between the values of T_m determined and the purities of the boron sample used, the value T_m = 2450 ± 20°K. was estimated. The data employed for estimation are those reported by C. F. Cline, J. Electrochem. Soc. 106 (4), 332 (1959), and A. W. Searcy and C. E. Myers, J. Phys. Chem. 61, 957 (1957). The estimated value for T_m is in agreement with the value taken by H. L. Schick, et al., "Thermodynamics of Certain Refractory Compounds", ASD-TR-61-260, Part I, Vol. 1, May 1962, in which the reported melting points of boron were reviewed. The heat of melting was calculated assuming entropy of melting is 2.2 cal. deg.$^{-1}$ mole^{-1} at 2450°K.

Heat of Sublimation.

The adopted value of $\Delta H^\circ_{s\ 298.15}$ is the weighted average of eight $\Delta H^\circ_{s\ 298.15}$ values derived from vapor pressure data. See B(g) table for details.

Boron (B)

(Liquid) At. Wt. = 10.82

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	2.650	3.533	3.533	.000	5.260	4.625	- 3.390
300	2.666	3.549	3.533	.005	5.260	4.621	- 3.366
400	3.720	4.469	3.651	.327	5.260	4.408	- 2.408
500	4.490	5.387	3.907	.740	5.260	4.195	- 1.833
600	4.990	6.252	4.227	1.215	5.260	3.982	- 1.450
700	5.320	7.047	4.574	1.731	5.260	3.769	- 1.177
800	5.560	7.774	4.929	2.276	5.260	3.556	- .971
900	5.760	8.440	5.283	2.842	5.260	3.343	- .812
1000	5.950	9.057	5.630	3.427	5.260	3.130	- .684
1100	6.120	9.632	5.968	4.031	5.260	2.917	- .580
1200	6.260	10.171	6.296	4.650	5.260	2.704	- .492
1300	6.410	10.678	6.613	5.284	5.260	2.491	- .419
1400	6.540	11.158	6.921	5.931	5.260	2.278	- .356
1500	6.670	11.613	7.219	6.592	5.260	2.065	- .301
1600	6.790	12.046	7.507	7.262	5.257	1.852	- .253
1700	7.300	12.474	7.787	7.968	5.278	1.639	- .211
1800	7.300	12.891	8.059	8.698	5.313	1.423	- .173
1900	7.300	13.286	8.324	9.428	5.340	1.206	- .139
2000	7.300	13.660	8.581	10.158	5.361	.989	- .108
2100	7.300	14.016	8.832	10.888	5.376	.771	- .080
2200	7.300	14.356	9.075	11.618	5.386	.551	- .055
2300	7.300	14.681	9.312	12.348	5.391	.329	- .031
2400	7.300	14.991	9.542	13.078	5.391	.111	- .010
2500	7.300	15.289	9.766	13.808	.000	.000	.000
2600	7.300	15.576	9.984	14.538	.000	.000	.000
2700	7.300	15.851	10.196	15.268	.000	.000	.000
2800	7.300	16.116	10.403	15.998	.000	.000	.000
2900	7.300	16.373	10.604	16.728	.000	.000	.000
3000	7.300	16.620	10.801	17.458	.000	.000	.000
3100	7.300	16.860	10.992	18.188	.000	.000	.000
3200	7.300	17.091	11.179	18.918	.000	.000	.000
3300	7.300	17.316	11.362	19.648	.000	.000	.000
3400	7.300	17.534	11.540	20.378	.000	.000	.000
3500	7.300	17.745	11.715	21.108	.000	.000	.000
3600	7.300	17.951	11.885	21.838	.000	.000	.000
3700	7.300	18.151	12.052	22.568	.000	.000	.000
3800	7.300	18.346	12.215	23.298	.000	.000	.000
3900	7.300	18.535	12.374	24.028	.000	.000	.000
4000	7.300	18.720	12.531	24.758	- 121.179	2.145	- .117
4100	7.300	18.900	12.684	25.488	- 120.948	5.226	- .279
4200	7.300	19.076	12.834	26.218	- 120.716	8.304	- .432
4300	7.300	19.248	12.981	26.948	- 120.485	11.370	- .578
4400	7.300	19.416	13.125	27.678	- 120.255	14.434	- .717
4500	7.300	19.580	13.267	28.408	- 120.025	17.491	- .849
4600	7.300	19.740	13.406	29.138	- 119.795	20.547	- .976
4700	7.300	19.897	13.543	29.868	- 119.566	23.596	- 1.097
4800	7.300	20.051	13.677	30.598	- 119.338	26.640	- 1.213
4900	7.300	20.202	13.808	31.328	- 119.111	29.673	- 1.323
5000	7.300	20.349	13.938	32.058	- 118.884	32.711	- 1.430

Dec. 31, 1960; Dec. 31, 1964

BORON (B) (LIQUID) AT. WT. = 10.82

$S^\circ_{298.15}$ = [3.533] cal. deg.$^{-1}$ mole^{-1}

T_m = [2450 ± 20]°K.

T_b = [3931]°K.

$\Delta H^\circ_{f\ 298.15}$ = [5.260] kcal. mole^{-1}

ΔH°_m = [5.39] kcal. mole^{-1}

ΔH°_v = [121.3 ± 4] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ for B(l) was obtained from $\Delta H^\circ_{f\ 298.15}$ for B(c) by adding ΔH°_m and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of liquid was estimated by comparison with the heat capacity of solid at the melting temperature. The value of $S^\circ_{298.15}$ was obtained in a manner analogous to that of the heat of formation. A glass transition temperature at 1600°K. is assumed.

Melting Data.

See B(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF°_f) for both B(l) and B(g) are equal. The difference in heat of formation (ΔH°_f) of B(l) and B(g) at the boiling point is the heat of vaporization (ΔH°_v).

Boron, Monatomic (B)

(Ideal Gas) At. Wt. = 10.82

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.511	131.581	131.581	INFINITE
100	4.993	31.211	41.071	- .986	132.100	128.987	- 281.887
200	4.974	34.664	37.104	- .488	132.518	125.703	- 137.355
298	4.971	36.649	36.649	.000	132.800	122.291	- 89.638
300	4.971	36.680	36.649	.009	132.804	122.226	- 89.037
400	4.970	38.110	36.844	.506	132.979	118.671	- 64.836
500	4.969	39.219	37.212	1.003	133.063	115.083	- 50.300
600	4.969	40.125	37.624	1.500	133.085	111.484	- 40.606
700	4.969	40.891	38.038	1.997	133.066	107.885	- 33.682
800	4.969	41.554	38.437	2.494	133.018	104.290	- 28.489
900	4.968	42.139	38.816	2.991	132.949	100.703	- 24.453
1000	4.968	42.663	39.175	3.487	132.860	97.125	- 21.226
1100	4.968	43.136	39.514	3.984	132.753	93.556	- 18.587
1200	4.968	43.569	39.834	4.481	132.631	89.999	- 16.390
1300	4.968	43.966	40.137	4.978	132.494	86.451	- 14.533
1400	4.968	44.335	40.424	5.475	132.344	82.915	- 12.943
1500	4.968	44.677	40.696	5.972	132.180	79.389	- 11.566
1600	4.968	44.998	40.955	6.468	132.003	75.875	- 10.364
1700	4.968	45.299	41.202	6.965	131.815	72.373	- 9.304
1800	4.968	45.583	41.437	7.462	131.617	68.882	- 8.363
1900	4.968	45.852	41.662	7.959	131.411	65.403	- 7.523
2000	4.968	46.107	41.878	8.456	131.199	61.935	- 6.768
2100	4.968	46.349	42.085	8.953	130.981	58.476	- 6.085
2200	4.968	46.580	42.285	9.449	130.757	55.029	- 5.466
2300	4.968	46.801	42.476	9.946	130.529	51.591	- 4.902
2400	4.968	47.012	42.661	10.443	130.296	48.166	- 4.386
2500	4.968	47.215	42.839	10.940	124.672	44.857	- 3.921
2600	4.968	47.410	43.011	11.437	124.439	41.668	- 3.502
2700	4.968	47.598	43.177	11.933	124.205	38.491	- 3.116
2800	4.969	47.778	43.338	12.430	123.972	35.319	- 2.757
2900	4.969	47.953	43.495	12.927	123.739	32.160	- 2.424
3000	4.969	48.121	43.646	13.424	123.506	29.003	- 2.113
3100	4.969	48.284	43.793	13.921	123.273	25.855	- 1.823
3200	4.970	48.442	43.936	14.418	123.040	22.720	- 1.552
3300	4.970	48.595	44.075	14.915	122.807	19.590	- 1.297
3400	4.971	48.743	44.210	15.412	122.574	16.463	- 1.058
3500	4.972	48.887	44.341	15.909	122.341	13.344	- .833
3600	4.973	49.027	44.470	16.406	122.108	10.235	- .621
3700	4.975	49.164	44.595	16.904	121.876	7.131	- .421
3800	4.977	49.296	44.717	17.401	121.643	4.033	- .232
3900	4.979	49.426	44.836	17.899	121.411	.940	- .053
4000	4.982	49.552	44.952	18.397	.000	.000	- .000
4100	4.985	49.675	45.066	18.896	.000	.000	.000
4200	4.988	49.795	45.177	19.394	.000	.000	.000
4300	4.993	49.912	45.286	19.893	.000	.000	.000
4400	4.997	50.027	45.392	20.393	.000	.000	.000
4500	5.002	50.140	45.496	20.893	.000	.000	.000
4600	5.008	50.250	45.598	21.393	.000	.000	.000
4700	5.015	50.357	45.699	21.894	.000	.000	.000
4800	5.022	50.463	45.797	22.396	.000	.000	.000
4900	5.030	50.567	45.893	22.899	.000	.000	.000
5000	5.039	50.668	45.987	23.402	.000	.000	.000
5100	5.048	50.768	46.080	23.907	.000	.000	.000
5200	5.058	50.866	46.171	24.412	.000	.000	.000
5300	5.069	50.963	46.261	24.918	.000	.000	.000
5400	5.081	51.058	46.349	25.426	.000	.000	.000
5500	5.093	51.151	46.435	25.934	.000	.000	.000
5600	5.107	51.243	46.520	26.444	.000	.000	.000
5700	5.121	51.333	46.604	26.956	.000	.000	.000
5800	5.136	51.423	46.686	27.469	.000	.000	.000
5900	5.152	51.511	46.767	27.983	.000	.000	.000
6000	5.168	51.597	46.847	28.499	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1964

BORON, MONATOMIC (B) (IDEAL GAS) AT. WT. = 10.82

Ground State Configuration $^2P_{1/2}$

$\Delta H^\circ_{f\ 0}$ = 131.6 ± 4 kcal. mole^{-1}

$S^\circ_{298.15}$ = 36.649 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 132.8 ± 4 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	gi	ϵ, cm.$^{-1}$	gi	ϵ, cm.$^{-1}$	gi	ϵ, cm.$^{-1}$	gi
0	2	40040	2	60146	2	64156	2
16	4	47857	10	62098	2	64664	10
[28805]	2	54765	10	62481	10	65195	10
28810	4	55009	2	63561	2	65553	2
28816	6	59989	10	63847	10		

Heat of Formation.

The vapor pressures of B(g) over condensed phases B(c) and $B_4C(c)$, respectively, were determined by many investigators. Using the vapor pressure data reported, the corresponding heats of sublimation and decomposition were evaluated by both the third and second law methods. The values of $\Delta H^\circ_{f\ 298.15}$ for B(g) were then calculated. The results obtained are listed as follows (all calculations were made employing JANAF functions).

Investigator	Process or Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H^\circ_{f\ 298.15}$,* kcal. mole^{-1}
Hildenbrand and Hall[1]	$0.25CB_4(c) \rightarrow 0.25C(c) + B(g)$	138.5	137.6 ± 1.2	135.3 ± 1.3
Hildenbrand[2]	$B(c) \rightarrow B(g)$	136.1	136.3 ± 3	136.1 ± 0.3
Paule and Margrave[3]	$B(c) \rightarrow B(g)$	136.4	135.4 ± 1.6	136.4 ± 1.0
Robson and Gilles[4]	$0.25CB_4(c) \rightarrow 0.25C(c) + B(g)$	137.7	142 ± 4	134.5 ± 1.3
Searcy and Myers[5]	$B(c) \rightarrow B(g)$	139.1	148.4 ± 8.4	139.1 ± 2.5
Schissel and Williams[6]	$B(c) \rightarrow B(g)$	—	129 ± 5	129 ± 5
Chupka[7]	$B(c) \rightarrow B(g)$	129.2	131.7	129.2
Akishin et al.[8]	$B(c) \rightarrow B(g)$	131.7	—	131.7 ± 5
Verhaegen and Drowart[9]	$B(am.) \rightarrow B(g)$	—	129.1 ± 5	130.3 ± 5**
	$0.25CB_4(c) \rightarrow 0.25C(c) + B(g)$	—	134.4 ± 5	131.2 ± 5
Linevsky, et al.[10]	$B(c) \rightarrow B(g)$	—	131.4	131.4
Schissel and Trulson[11]	$B(c) \rightarrow B(g)$	—	132.8 ± 1.4	132.8 ± 1.4

*Calculation based on the third law values available.
**Based on a heat of transition of 1.2 kcal. mole^{-1} for B(c) to B(am.).

1 D. L. Hildenbrand and W. F. Hall, J. Phys. Chem. 68, 989 (1964) - 2374-2615°K. - torsion-effusion.

2 D. L. Hildenbrand, "Thermodynamic Properties of Propellant Combustion Products", QLR-64-10, Philco Corporation, California, 1950-2140°K., torsion-Langmuir method. Listed $\Delta H^\circ_{f\ 298.15}$ value is the average of three reported values.

3 R. G. Paule and J. L. Margrave, J. Phys. Chem 67, 1368 (1963) - 1781-2152°K. - free-evaporation.

4 H. E. Robson and P. W. Gilles, J. Phys. Chem. 68, 983 (1964) - 2184-2522°K. - Knudsen-effusion.

5 A. W. Searcy and C. E. Myers, J. Phys. Chem. 61, 957 (1957) - 2115-2413°K. - Knudsen-effusion.

6 P. O. Schissel and W. S. Williams, Bull, Am. Phys. Soc. 4, 139 (1959). The quoted value of ΔH°_r was derived from vapor pressure data determined by the mass spectrometer-effusion method.

7 The third and second law values of $\Delta H^\circ_{r\ 298.15}$ were calculated from the respective values of $\Delta H^\circ_{r\ 0}$ quoted by G. Verhaegen and J. Drowart, J. Chem. Phys. 37, 1367 (1962). Vapor pressure data obtained by mass spectrometer-effusion method.

8 P. A. Akishin, D. O. Hikitin and L. N. Gorokhov, Proc. Acad. Sci., USSR, 129, 1075 (1959). The vapor pressure data (2024 - 2231°K.) were determined by the mass spectrometric method.

9 The two second law values were recalculated from $\Delta H^\circ_{r\ 2060}$ = 127.4 and $\Delta H^\circ_{r\ 2080}$ = 133.1 kcal. mole^{-1} for the first and second reactions in the above table, respectively. The data were reported by G. Verhaegen and J. Drowart, J. Phys. Chem. 37, 1367 (1962), which were derived from vapor pressures determined by the mass spectrometric method.

10 M. J. Linevsky, G. M. Kibler, T. F. Lyon and V. J. DeSantis, "Refractory materials Research", WADD-TR-60-646, Part IV, August 1964, General Electric Co., Ohio.

11 P. O. Schissel and O. C. Trulson, J. Phys. Chem. 66, 1492 (1962).

The adopted value of $\Delta H^\circ_{f\ 298.15}$ for B(g) is the weighted average of the 12 $\Delta H^\circ_{f\ 298.15}$ values given in the above table.

Heat Capacity and Entropy.

The electronic levels and quantum weights used were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, National Bureau of Standards Circular 467, 1949.

Boron Unipositive Ion (B^+)

(Ideal Gas) GFW = 10.81045

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	4.968	33.086	33.086	.000	324.084	313.151	-229.54
300	4.968	33.117	33.086	.009	324.097	313.082	-228.080
400	4.968	34.546	33.281	.506	324.769	309.307	-168.997
500	4.968	35.654	33.649	1.003	325.350	305.373	-133.478
600	4.968	36.560	34.061	1.500	325.869	301.328	-109.759
700	4.968	37.326	34.474	1.996	326.345	297.199	-92.790
800	4.968	37.989	34.873	2.493	326.794	293.004	-80.045
900	4.968	38.575	35.252	2.990	327.222	288.755	-70.119
1000	4.968	39.098	35.611	3.487	327.631	284.459	-62.168
1100	4.968	39.571	35.950	3.984	328.021	280.123	-55.655
1200	4.968	40.004	36.270	4.480	328.395	275.753	-50.221
1300	4.968	40.401	36.573	4.977	328.754	271.350	-45.618
1400	4.968	40.770	36.860	5.474	329.101	266.922	-41.668
1500	4.968	41.112	37.132	5.971	329.434	262.467	-38.241
1600	4.968	41.433	37.391	6.467	329.754	257.993	-35.240
1700	4.968	41.734	37.637	6.964	330.063	253.499	-32.589
1800	4.968	42.018	37.873	7.461	330.361	248.985	-30.231
1900	4.968	42.287	38.098	7.958	330.652	244.457	-28.119
2000	4.968	42.541	38.314	8.455	330.937	239.914	-26.217
2100	4.968	42.784	38.521	8.951	331.215	235.355	-24.494
2200	4.968	43.015	38.720	9.448	331.489	230.785	-22.926
2300	4.968	43.236	38.912	9.945	331.757	226.199	-21.494
2400	4.968	43.447	39.096	10.442	332.021	221.606	-20.180
2500	4.968	43.650	39.274	10.939	326.894	217.109	-18.980
2600	4.968	43.845	39.447	11.435	327.157	212.711	-17.880
2700	4.968	44.032	39.613	11.932	327.421	208.307	-16.861
2800	4.968	44.213	39.774	12.429	327.685	203.889	-15.914
2900	4.968	44.387	39.930	12.926	327.948	199.465	-15.032
3000	4.968	44.556	40.082	13.423	328.212	195.027	-14.208
3100	4.968	44.719	40.228	13.919	328.475	190.582	-13.436
3200	4.968	44.876	40.371	14.416	328.739	186.133	-12.712
3300	4.968	45.029	40.510	14.913	329.003	181.674	-12.032
3400	4.969	45.178	40.645	15.410	329.266	177.206	-11.391
3500	4.969	45.322	40.777	15.907	329.530	172.728	-10.786
3600	4.969	45.462	40.905	16.404	329.794	168.245	-10.214
3700	4.970	45.598	41.030	16.901	330.058	163.751	-9.672
3800	4.970	45.730	41.152	17.398	330.322	159.256	-9.159
3900	4.971	45.859	41.271	17.895	330.586	154.749	-8.672
4000	4.973	45.985	41.387	18.392	209.670	152.381	-8.326
4100	4.974	46.108	41.501	18.889	210.165	150.940	-8.046
4200	4.976	46.228	41.612	19.387	210.662	149.497	-7.779
4300	4.978	46.345	41.721	19.884	211.157	148.033	-7.524
4400	4.981	46.460	41.827	20.382	211.652	146.561	-7.280
4500	4.985	46.572	41.931	20.881	212.147	145.072	-7.046
4600	4.989	46.681	42.033	21.379	212.642	143.577	-6.821
4700	4.993	46.789	42.133	21.878	213.137	142.071	-6.606
4800	4.999	46.894	42.232	22.378	213.632	140.554	-6.400
4900	5.005	46.997	42.328	22.878	214.126	139.025	-6.201
5000	5.012	47.098	42.422	23.379	214.620	137.490	-6.010
5100	5.021	47.197	42.515	23.881	215.114	135.940	-5.825
5200	5.030	47.295	42.606	24.383	215.608	134.385	-5.648
5300	5.041	47.391	42.695	24.887	216.103	132.814	-5.477
5400	5.052	47.485	42.783	25.391	216.596	131.238	-5.311
5500	5.065	47.578	42.869	25.897	217.091	129.658	-5.152
5600	5.080	47.669	42.954	26.404	217.584	128.055	-4.998
5700	5.096	47.759	43.038	26.913	218.078	126.460	-4.849
5800	5.113	47.848	43.120	27.424	218.573	124.844	-4.704
5900	5.132	47.936	43.201	27.936	219.068	123.224	-4.565
6000	5.153	48.022	43.280	28.450	219.563	121.600	-4.429

Dec. 31, 1967

BORON UNIPOSITIVE ION (B^+) (IDEAL GAS) GFW = 10.81045

Ground State Configuration $^1S_0$

$\Delta Hf^\circ_0 = 322.9 \pm 4.0$ kcal/mol

$S^\circ_{298.15} = 33.086$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 324.1 \pm 4.0$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	1	144019.32	12	184793.57	36
37348.4	9	151658.48	20	189126.6	3
73396.7	3	166741.85	4	194753.14	21
100152.89	14	174212.71	57	197721.0	5
129245.18	4	181473.27	12	200484.6	15
135946.0	1				

Heat of Formation

We calculate the heat of formation at 0°K from the reaction $B(g) - e^-(g) \rightarrow B^+(g)$ using the JANAF auxiliary value for B(g) and an ionization potential of 191.314 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. I, 1949.

Heat Capacity and Entropy

We obtain the electronic levels and quantum weights from C. E. Moore, loc. cit. $H^\circ_0 - H^\circ_{298} = -1.481$ kcal/mol at 0°K.

Beryllium Boron Dioxide ($BeBO_2$)

(Ideal Gas) GFW = 51.8220

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.771	-115.136	-115.136	INFINITE
100	8.188	52.913	72.634	-1.972	-115.066	-116.184	253.920
200	9.912	59.053	64.435	-1.076	-115.068	-117.313	128.193
298	11.990	63.404	63.404	.000	-115.200	-118.395	86.786
300	12.027	63.478	63.404	.022	-115.203	-118.415	86.265
400	13.741	67.185	63.898	1.315	-115.382	-119.460	65.270
500	15.009	70.394	64.884	2.755	-115.590	-120.455	52.651
600	15.951	73.218	66.042	4.306	-115.811	-121.408	44.223
700	16.663	75.733	67.250	5.938	-116.045	-122.322	38.191
800	17.212	77.995	68.454	7.633	-116.288	-123.203	33.658
900	17.641	80.048	69.630	9.376	-116.542	-124.052	30.124
1000	17.980	81.925	70.767	11.158	-116.812	-124.871	27.291
1100	18.251	83.652	71.861	12.970	-117.107	-125.664	24.967
1200	18.471	85.250	72.911	14.807	-117.426	-126.428	23.026
1300	18.650	86.736	73.918	16.663	-117.773	-127.164	21.378
1400	18.799	88.123	74.884	18.536	-118.147	-127.872	19.962
1500	18.922	89.425	75.810	20.422	-118.553	-128.555	18.730
1600	19.027	90.649	76.700	22.319	-121.745	-129.127	17.638
1700	19.115	91.806	77.555	24.227	-122.097	-129.579	16.659
1800	19.191	92.900	78.377	26.142	-122.464	-130.008	15.785
1900	19.256	93.940	79.169	28.064	-122.843	-130.418	15.001
2000	19.312	94.929	79.933	29.993	-123.231	-130.807	14.294
2100	19.361	95.872	80.669	31.926	-123.631	-131.174	13.651
2200	19.404	96.774	81.381	33.865	-124.042	-131.524	13.066
2300	19.442	97.637	82.069	35.807	-124.464	-131.854	12.529
2400	19.475	98.466	82.735	37.753	-124.898	-132.165	12.035
2500	19.505	99.261	83.380	39.702	-130.732	-132.352	11.570
2600	19.532	100.027	84.006	41.654	-131.180	-132.407	11.130
2700	19.556	100.764	84.613	43.608	-131.636	-132.443	10.721
2800	19.577	101.476	85.203	45.565	-203.129	-131.359	10.253
2900	19.596	102.163	85.776	47.524	-203.348	-128.786	9.706
3000	19.614	102.828	86.333	49.484	-203.573	-126.215	9.195
3100	19.630	103.471	86.876	51.446	-203.801	-123.635	8.716
3200	19.644	104.095	87.404	53.410	-204.033	-121.044	8.267
3300	19.658	104.699	87.919	55.375	-204.271	-118.444	7.844
3400	19.670	105.286	88.421	57.342	-204.515	-115.840	7.446
3500	19.681	105.857	88.911	59.309	-204.764	-113.235	7.071
3600	19.691	106.411	89.390	61.278	-205.019	-110.609	6.715
3700	19.700	106.951	89.857	63.247	-205.282	-107.987	6.378
3800	19.709	107.477	90.314	65.218	-205.551	-105.353	6.059
3900	19.717	107.989	90.761	67.189	-205.827	-102.715	5.756
4000	19.725	108.488	91.198	69.161	-327.291	-97.923	5.350
4100	19.732	108.975	91.625	71.134	-327.353	-92.189	4.914
4200	19.738	109.451	92.044	73.108	-327.421	-86.451	4.499
4300	19.744	109.915	92.454	75.082	-327.500	-80.706	4.102
4400	19.750	110.369	92.856	77.056	-327.591	-74.969	3.724
4500	19.755	110.813	93.250	79.032	-327.690	-69.228	3.362
4600	19.760	111.247	93.637	81.007	-327.801	-63.480	3.016
4700	19.765	111.672	94.016	82.984	-327.922	-57.733	2.685
4800	19.769	112.088	94.388	84.960	-328.056	-51.979	2.367
4900	19.773	112.496	94.754	86.937	-328.201	-46.235	2.062
5000	19.777	112.896	95.113	88.915	-328.357	-40.477	1.769
5100	19.781	113.287	95.465	90.893	-328.528	-34.712	1.488
5200	19.784	113.671	95.812	92.871	-328.710	-28.956	1.217
5300	19.787	114.048	96.152	94.850	-328.905	-23.185	.956
5400	19.790	114.418	96.487	96.829	-329.114	-17.421	.705
5500	19.793	114.781	96.816	98.808	-329.335	-11.639	.462
5600	19.796	115.138	97.140	100.787	-329.572	-5.869	.229
5700	19.799	115.488	97.459	102.767	-329.821	-.082	.003
5800	19.801	115.833	97.773	104.747	-330.084	5.707	-.215
5900	19.804	116.171	98.082	106.727	-330.361	11.497	-.426
6000	19.806	116.504	98.386	108.708	-330.651	17.295	-.630

June 30, 1966

BERYLLIUM BORON DIOXIDE ($BeBO_2$) (IDEAL GAS) GFW = 51.8220

Point Group $[C_s]$

$S^\circ_{298.15}$ = [63.4] gibbs/mol

Ground State Quantum Weight = [2]

ΔHf°_0 = [-115.1 ± 8] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-115.2 ± 8] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[2000](1)	[600](1)
[1000](1)	[400](1)
[900](1)	[800](1)

Bond Distance: Be-O = [1.40] Å O-B = [1.36] Å B=O = [1.20] Å

Bond Angle: Be-O-B = [120]° O-B=O = [180]° σ = [1]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.450656] X 10^{-115} g^3 cm^6

Heat of Formation.

Since P. E. Blackburn and A. Büchler, J. Phys. Chem. 69, 4250 (1965), have postulated that the BO_2^- group has the pseudochloride character in bond strength, the heat of formation of $BeBO_2(g)$ is estimated by adding the difference of the heats of formation of BeCl(g) and AlCl(g) to the heat of formation of $AlBO_2(g)$, using all JANAF values ΔHf°_{298} (BeCl, g) = 3.0, ΔHf°_{298} (AlCl, g) = -11.2 and ΔHf°_{298} ($AlBO_2$, g) = -129.4 kcal/mol.

Heat Capacity and Entropy.

All molecular constants are estimated by comparison with those in $LiBO_2(g)$, $AlBO_2(g)$ $B_2O_3(g)$ and BeCl(g). The three principal moments of inertia are I_A = 1.1015 X 10^{-39}, I_B = 14.3751 X 10^{-39} and I_C = 15.4766 X 10^{-39} g cm^2.

Boron Monobromide (BBr)

(Ideal Gas) Mol. Wt. = 90.736

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.150	57.071	57.071	INFINITE
100	6.968	45.817	60.369	-1.455	57.426	53.496	-116.910
200	7.323	50.728	54.451	-.745	57.471	49.533	-54.125
298	7.837	53.750	53.750	.000	56.000	45.817	-33.583
300	7.845	53.799	53.751	.015	55.993	45.753	-33.330
400	8.216	56.111	54.063	.819	52.355	43.087	-23.541
500	8.451	57.971	54.665	1.653	52.335	40.771	-17.820
600	8.604	59.526	55.349	2.506	52.269	38.464	-14.010
700	8.708	60.861	56.043	3.372	52.173	36.171	-11.292
800	8.783	62.029	56.720	4.247	52.055	33.892	-9.258
900	8.839	63.067	57.369	5.128	51.921	31.629	-7.680
1000	8.883	64.000	57.986	6.015	51.772	29.384	-6.422
1100	8.918	64.849	58.572	6.905	51.607	27.151	-5.394
1200	8.947	65.626	59.128	7.798	51.430	24.937	-4.541
1300	8.972	66.343	59.656	8.694	51.239	22.737	-3.822
1400	8.994	67.009	60.157	9.592	51.038	20.552	-3.208
1500	9.014	67.630	60.635	10.493	50.823	18.380	-2.678
1600	9.032	69.212	61.091	11.395	50.598	16.227	-2.216
1700	9.048	68.761	61.526	12.299	50.362	14.084	-1.811
1800	9.064	69.278	61.942	13.205	50.117	11.957	-1.452
1900	9.078	69.769	62.341	14.112	49.865	9.844	-1.132
2000	9.092	70.235	62.725	15.020	49.608	7.744	-.846
2100	9.105	70.679	63.093	15.930	49.346	5.657	-.589
2200	9.118	71.102	63.447	16.841	49.079	3.585	-.356
2300	9.130	71.508	63.789	17.754	48.808	1.522	-.145
2400	9.142	71.897	64.119	18.667	48.532	-.527	.048
2500	9.153	72.270	64.437	19.582	42.866	-2.456	.215
2600	9.165	72.629	64.746	20.498	42.592	-4.264	.358
2700	9.176	72.975	65.044	21.415	42.319	-6.060	.490
2800	9.187	73.309	65.333	22.333	42.045	-7.848	.613
2900	9.198	73.632	65.614	23.252	41.773	-9.623	.725
3000	9.209	73.944	65.886	24.173	41.502	-11.393	.830
3100	9.219	74.246	66.151	25.094	41.230	-13.152	.927
3200	9.230	74.539	66.409	26.016	40.959	-14.901	1.018
3300	9.240	74.823	66.660	26.940	40.689	-16.642	1.102
3400	9.250	75.099	66.904	27.864	40.419	-18.375	1.181
3500	9.261	75.367	67.142	28.790	40.150	-20.101	1.255
3600	9.271	75.628	67.374	29.717	39.881	-21.818	1.324
3700	9.281	75.883	67.600	30.644	39.613	-23.531	1.390
3800	9.291	76.130	67.822	31.573	39.345	-25.230	1.451
3900	9.301	76.372	68.038	32.502	39.078	-26.930	1.509
4000	9.311	76.607	68.249	33.433	-82.368	-26.472	1.446
4100	9.321	76.837	68.456	34.365	-82.403	-25.075	1.337
4200	9.331	77.062	68.658	35.297	-82.437	-23.673	1.232
4300	9.341	77.282	68.856	36.231	-82.472	-22.276	1.132
4400	9.351	77.497	69.050	37.165	-82.507	-20.876	1.037
4500	9.360	77.707	69.240	38.101	-82.541	-19.476	.946
4600	9.370	77.913	69.426	39.037	-82.575	-18.074	.859
4700	9.380	78.114	69.609	39.975	-82.610	-16.666	.775
4800	9.390	78.312	69.788	40.913	-82.645	-15.265	.695
4900	9.400	78.506	69.964	41.853	-82.681	-13.865	.618
5000	9.409	78.696	70.137	42.793	-82.716	-12.458	.545
5100	9.419	78.882	70.307	43.735	-82.753	-11.052	.474
5200	9.429	79.065	70.473	44.677	-82.789	-9.646	.405
5300	9.438	79.245	70.637	45.620	-82.826	-8.241	.340
5400	9.448	79.421	70.798	46.565	-82.864	-6.832	.277
5500	9.458	79.595	70.956	47.510	-82.902	-5.421	.215
5600	9.467	79.765	71.112	48.456	-82.942	-4.015	.157
5700	9.477	79.933	71.266	49.404	-82.983	-2.604	.100
5800	9.487	80.098	71.416	50.352	-83.024	-1.195	.045
5900	9.496	80.260	71.565	51.301	-83.067	.218	-.008
6000	9.506	80.420	71.711	52.251	-83.110	1.628	-.059

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

BORON MONOBROMIDE (BBr) (IDEAL GAS) MOL. WT. = 90.736

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0}$ = 57 ± 10 kcal. mole^{-1}

$S^\circ_{298.15}$ = 53.750 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 56 ± 10 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 689.04 cm.$^{-1}$

$\omega_e x_e$ = 3.57 cm.$^{-1}$

σ = 1

B_e = 0.497 cm.$^{-1}$

α_e = 0.0036 cm.$^{-1}$

r_e = 1.887 Å

Heat of Formation.

G. Herzberg, "Spectra of Diatomic Molecules" D. Van Nostrand Co. New York 1950 reports a D_0° of 4.1 e.v. which corresponds to a heat of formation of 64 kcal. mole^{-1} A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, London 1953, gives essentially the same value, with a rider that the value is unrealiable due to the ionic nature of the bonding. R. F. Barrow, Trans. Farad. Soc. 56, 952 (1960) made a critical evaluation of the bond dissociation energies of the group III halides and concluded D_0 BBr = 103.5 which gives ΔH_f° = 56 kcal. mole^{-1}. An estimate of the dissociation energy by taking the ratio $D(BF)/(\Delta H_a(BF_3)/3) = 1.177$ and applying this to BBr_3 yields D(BBr) = 103 kcal. mole^{-1}, this was the value adopted.

Heat Capacity and Entropy.

The vibrational and rotational constants were all taken from National Bureau Standards Report 7093, Jan. 1, 1962.

Boron Bromide Chloride (BBrCl)

(Ideal Gas) Mol. Wt. = 126.193

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.842	- 1.023	- 1.023	INFINITE
100	9.035	58.183	78.289	- 2.011	- .883	- 3.790	8.282
200	10.161	64.801	70.048	- 1.050	- .948	- 6.685	7.304
298	11.197	69.056	69.056	.000	- 2.500	- 9.303	6.819
300	11.214	69.126	69.057	.021	- 2.508	- 9.345	6.808
400	12.003	72.467	69.507	1.184	- 6.202	- 10.868	5.938
500	12.531	75.206	70.381	2.413	- 6.254	- 12.029	5.258
600	12.882	77.524	71.383	3.684	- 6.336	- 13.176	4.799
700	13.120	79.529	72.407	4.985	- 6.437	- 14.309	4.467
800	13.287	81.292	73.410	6.306	- 6.552	- 15.426	4.214
900	13.407	82.864	74.374	7.641	- 6.677	- 16.528	4.013
1000	13.496	84.282	75.295	8.986	- 6.814	- 17.615	3.850
1100	13.564	85.572	76.172	10.340	- 6.964	- 18.689	3.713
1200	13.617	86.754	77.005	11.699	- 7.125	- 19.747	3.596
1300	13.659	87.846	77.798	13.063	- 7.299	- 20.792	3.495
1400	13.692	88.859	78.552	14.430	- 7.483	- 21.822	3.406
1500	13.720	89.805	79.271	15.801	- 7.681	- 22.842	3.328
1600	13.742	90.691	79.957	17.174	- 7.889	- 23.844	3.257
1700	13.761	91.525	80.614	18.549	- 8.108	- 24.834	3.193
1800	13.777	92.312	81.242	19.926	- 8.337	- 25.813	3.134
1900	13.790	93.057	81.844	21.305	- 8.574	- 26.776	3.080
2000	13.802	93.765	82.423	22.684	- 8.818	- 27.729	3.030
2100	13.812	94.438	82.979	24.065	- 9.067	- 28.667	2.983
2200	13.821	95.081	83.515	25.447	- 9.322	- 29.595	2.940
2300	13.828	95.696	84.031	26.829	- 9.582	- 30.511	2.899
2400	13.835	96.284	84.529	28.212	- 9.849	- 31.413	2.860
2500	13.841	96.849	85.011	29.596	- 15.508	- 32.198	2.815
2600	13.846	97.392	85.477	30.980	- 15.776	- 32.860	2.762
2700	13.851	97.915	85.928	32.365	- 16.045	- 33.513	2.713
2800	13.855	98.419	86.365	33.750	- 16.317	- 34.156	2.666
2900	13.859	98.905	86.789	35.136	- 16.589	- 34.786	2.621
3000	13.862	99.375	87.201	36.522	- 16.863	- 35.411	2.580
3100	13.865	99.829	87.601	37.908	- 17.140	- 36.023	2.540
3200	13.868	100.270	87.990	39.295	- 17.417	- 36.630	2.502
3300	13.870	100.696	88.369	40.682	- 17.697	- 37.223	2.465
3400	13.873	101.110	88.737	42.069	- 17.977	- 37.809	2.430
3500	13.875	101.513	89.097	43.457	- 18.260	- 38.394	2.397
3600	13.877	101.904	89.447	44.844	- 18.544	- 38.964	2.365
3700	13.879	102.284	89.789	46.232	- 18.830	- 39.526	2.335
3800	13.880	102.654	90.122	47.620	- 19.118	- 40.080	2.305
3900	13.882	103.014	90.448	49.008	- 19.407	- 40.627	2.277
4000	13.883	103.366	90.767	50.396	- 140.877	- 39.025	2.132
4100	13.885	103.709	91.078	51.785	- 140.938	- 36.481	1.945
4200	13.886	104.043	91.383	53.173	- 141.000	- 33.926	1.765
4300	13.887	104.370	91.681	54.562	- 141.064	- 31.378	1.595
4400	13.888	104.689	91.973	55.950	- 141.131	- 28.823	1.432
4500	13.889	105.002	92.259	57.339	- 141.198	- 26.277	1.276
4600	13.890	105.307	92.540	58.728	- 141.266	- 23.720	1.127
4700	13.891	105.606	92.815	60.117	- 141.337	- 21.162	.984
4800	13.892	105.898	93.084	61.506	- 141.410	- 18.604	.847
4900	13.892	106.184	93.349	62.896	- 141.484	- 16.044	.716
5000	13.893	106.465	93.608	64.285	- 141.559	- 13.484	.589
5100	13.894	106.740	93.863	65.674	- 141.636	- 10.921	.468
5200	13.894	107.010	94.113	67.064	- 141.714	- 8.358	.351
5300	13.895	107.275	94.359	68.453	- 141.794	- 5.796	.239
5400	13.896	107.534	94.601	69.843	- 141.877	- 3.227	.131
5500	13.896	107.789	94.838	71.232	- 141.960	- .651	.026
5600	13.897	108.040	95.072	72.622	- 142.046	1.908	- .074
5700	13.897	108.286	95.301	74.012	- 142.135	4.481	- .172
5800	13.898	108.527	95.527	75.401	- 142.224	7.059	- .266
5900	13.898	108.765	95.750	76.791	- 142.316	9.630	- .357
6000	13.899	108.999	95.968	78.181	- 142.410	12.204	- .445

Dec. 31, 1962; Dec. 31, 1964

BORON BROMIDE CHLORIDE (BBrCl) (IDEAL GAS) MOL. WT. = 126.193

Point Group C_s

$S^\circ_{298.15}$ = [69.056] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [2]

$\Delta H^\circ_{f\ 0}$ = [-1.0 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-2.5 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[660](1)
[195](1)
[905](1)

Bond Distance: B-Cl = [1.73] Å B-Br = [1.87] Å

Bond Angle: Cl-B-Br = [120°] $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.192176] X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction $BCl_2 + BBr_2 \rightarrow 2BBrCl$.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for BBr_2 and BCl_2. The bond distances, angles, and quantum weight were assumed the same as in the dihalides. The individual moments of inertia were $I_A = 1.2997 \times 10^{-39}$ g. cm.^{2}, $I_B = 40.4239 \times 10^{-39}$ g. cm.^{2} and $I_C = 41.7236 \times 10^{-39}$ g. cm.^{2}

Boron Bromide Dichloride ($BBrCl_2$)

(Ideal Gas) Mol. Wt. = 161.65

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-3.477	-78.561	-78.561	INFINITE
100	10.218	60.250	86.414	-2.616	-78.742	-79.596	173.949
200	13.421	68.410	75.513	-1.421	-78.933	-80.376	87.826
298	15.392	74.163	74.163	.000	-80.500	-80.881	59.285
300	15.422	74.258	74.163	.029	-80.508	-80.884	58.921
400	16.743	78.889	74.786	1.641	-84.167	-80.257	43.848
500	17.607	82.725	76.001	3.362	-84.154	-79.281	34.652
600	18.179	85.989	77.401	5.153	-84.151	-78.307	28.522
700	18.569	88.822	78.834	6.992	-84.153	-77.332	24.143
800	18.842	91.321	80.242	8.863	-84.161	-76.359	20.859
900	19.040	93.552	81.599	10.758	-84.171	-75.383	18.305
1000	19.188	95.566	82.897	12.669	-84.188	-74.405	16.260
1100	19.300	97.400	84.133	14.594	-84.216	-73.426	14.588
1200	19.387	99.084	85.310	16.528	-84.252	-72.444	13.193
1300	19.455	100.638	86.430	18.471	-84.298	-71.458	12.013
1400	19.511	102.082	87.497	20.419	-84.353	-70.468	11.000
1500	19.556	103.430	88.515	22.372	-84.421	-69.476	10.122
1600	19.593	104.693	89.487	24.330	-84.499	-68.475	9.353
1700	19.624	105.882	90.417	26.291	-84.587	-67.470	8.673
1800	19.651	107.004	91.307	28.255	-84.685	-66.462	8.069
1900	19.673	108.067	92.162	30.221	-84.790	-65.444	7.527
2000	19.692	109.077	92.982	32.189	-84.902	-64.424	7.040
2100	19.709	110.038	93.772	34.159	-85.019	-63.398	6.598
2200	19.723	110.955	94.532	36.131	-85.144	-62.365	6.195
2300	19.735	111.832	95.266	38.104	-85.273	-61.326	5.827
2400	19.746	112.673	95.973	40.078	-85.409	-60.282	5.489
2500	19.756	113.479	96.658	42.053	-90.939	-59.124	5.168
2600	19.765	114.254	97.320	44.029	-91.077	-57.848	4.862
2700	19.773	115.000	97.961	46.006	-91.219	-56.567	4.579
2800	19.780	115.719	98.582	47.984	-91.364	-55.280	4.315
2900	19.786	116.413	99.185	49.962	-91.510	-53.987	4.068
3000	19.792	117.084	99.771	51.941	-91.659	-52.694	3.839
3100	19.797	117.733	100.340	53.920	-91.812	-51.393	3.623
3200	19.801	118.362	100.893	55.900	-91.967	-50.087	3.421
3300	19.805	118.971	101.432	57.880	-92.126	-48.774	3.230
3400	19.809	119.563	101.956	59.861	-92.286	-47.459	3.050
3500	19.813	120.137	102.468	61.842	-92.451	-46.141	2.881
3600	19.816	120.695	102.966	63.824	-92.618	-44.812	2.720
3700	19.819	121.238	103.453	65.805	-92.788	-43.481	2.568
3800	19.822	121.767	103.928	67.788	-92.960	-42.148	2.424
3900	19.824	122.282	104.392	69.770	-93.136	-40.809	2.287
4000	19.827	122.783	104.845	71.752	-214.494	-37.318	2.039
4100	19.829	123.273	105.289	73.735	-214.443	-32.893	1.753
4200	19.831	123.751	105.723	75.718	-214.394	-28.462	1.481
4300	19.833	124.218	106.148	77.701	-214.348	-24.039	1.222
4400	19.835	124.674	106.563	79.685	-214.305	-19.610	.974
4500	19.836	125.119	106.971	81.668	-214.265	-15.187	.738
4600	19.838	125.555	107.370	83.652	-214.224	-10.762	.511
4700	19.839	125.982	107.762	85.636	-214.188	-6.337	.295
4800	19.841	126.400	108.146	87.620	-214.154	-1.919	.087
4900	19.842	126.809	108.522	89.604	-214.121	2.503	-.112
5000	19.843	127.210	108.892	91.588	-214.090	6.923	-.303
5100	19.844	127.603	109.255	93.573	-214.061	11.344	-.486
5200	19.845	127.988	109.612	95.557	-214.033	15.766	-.663
5300	19.846	128.366	109.962	97.542	-214.007	20.181	-.832
5400	19.847	128.737	110.306	99.527	-213.984	24.598	-.996
5500	19.848	129.101	110.645	101.511	-213.962	29.026	-1.153
5600	19.849	129.459	110.977	103.496	-213.942	33.433	-1.305
5700	19.850	129.810	111.305	105.481	-213.925	37.852	-1.451
5800	19.851	130.155	111.627	107.466	-213.909	42.274	-1.593
5900	19.852	130.495	111.944	109.451	-213.895	46.684	-1.729
6000	19.852	130.828	112.256	111.436	-213.884	51.106	-1.861

Sept. 30, 1962; Dec. 31, 1964

BORON BROMIDE DICHLORIDE ($BBrCl_2$) (IDEAL GAS) MOL. WT. = 161.65

Point Group C_{2v}

$S^\circ_{298.15}$ = 74.163 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H_f^\circ{}_0$ = -78.5 ± 10 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -80.5 ± 10 kcal. mole^{-1}

<u>Vibrational Frequencies and Degeneracies</u>

ω, cm.$^{-1}$	ω, cm.$^{-1}$
885(1)	959 (1)
406(1)	[208](1)
218(1)	433 (1)

Bond Distance: B-Cl = 1.73 Å B-Br = 1.87 Å

Bond Angle: Cl-B-Cl = [120°] Br-B-Cl = [120°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 9.19303 X 10^{-113} g.^{3} cm.^{6}

<u>Heat of Formation</u>.

The heat of formation was estimated by assuming ΔH_r = 0 for the reaction

$$BBr_3 + 2BCl_3 \rightarrow 3BBrCl_2$$

<u>Heat Capacity and Entropy</u>.

Vibrational frequencies were obtained from L. P. Lindeman and M. K. Wilson, J. Chem. Phys. <u>24</u>, 242 (1956). The b_1 mode was the only unobserved frequency and was calculated from a normal coordinate treatment. Bond distances were reported by T. Wentink and V. H. Tiensuu, J. Chem. Phys. <u>28</u>, 826 (1958). Bond angles were estimated by analogy with the other trihalides of boron. The individual moments of inertia were I_A = 26.4242 X 10^{-39} g. cm.^{2}, I_B = 47.2327 X 10^{-39} g. cm.^{2} and I_C = 73.6569 X 10^{-39} g. cm.^{2}

Boron Bromide Fluoride (BBrF)

(Ideal Gas) Mol. Wt. = 109.736

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	-2.679	-55.902	-55.902	INFINITE
100	8.418	55.751	74.485	-1.873	-55.784	-58.673	128.224
200	9.477	61.928	66.809	-.976	-55.903	-61.526	67.230
298	10.408	65.887	65.887	.000	-57.500	-64.080	46.969
300	10.425	65.951	65.887	.019	-57.509	-64.120	46.709
400	11.261	69.069	66.306	1.105	-61.250	-65.560	35.819
500	11.900	71.654	67.125	2.265	-61.349	-66.628	29.122
600	12.362	73.867	68.069	3.479	-61.469	-67.673	24.649
700	12.694	75.799	69.038	4.733	-61.604	-68.696	21.447
800	12.936	77.511	69.992	6.015	-61.748	-69.700	19.040
900	13.116	79.045	70.914	7.318	-61.898	-70.685	17.164
1000	13.251	80.434	71.798	8.637	-62.056	-71.652	15.659
1100	13.356	81.702	72.641	9.967	-62.227	-72.604	14.424
1200	13.438	82.868	73.446	11.307	-62.406	-73.539	13.393
1300	13.504	83.947	74.213	12.654	-62.597	-74.460	12.517
1400	13.557	84.949	74.944	14.007	-62.797	-75.363	11.764
1500	13.601	85.886	75.643	15.365	-63.010	-76.255	11.110
1600	13.637	86.765	76.311	16.727	-63.233	-77.130	10.535
1700	13.667	87.593	76.950	18.093	-63.466	-77.992	10.026
1800	13.692	88.375	77.563	19.461	-63.710	-78.842	9.572
1900	13.714	89.116	78.152	20.831	-63.961	-79.675	9.164
2000	13.733	89.820	78.718	22.203	-64.218	-80.495	8.796
2100	13.749	90.490	79.263	23.577	-64.481	-81.302	8.461
2200	13.763	91.130	79.788	24.953	-64.750	-82.097	8.155
2300	13.775	91.742	80.294	26.330	-65.024	-82.879	7.875
2400	13.786	92.328	80.784	27.708	-65.304	-83.647	7.617
2500	13.796	92.891	81.257	29.087	-70.975	-84.297	7.369
2600	13.804	93.433	81.715	30.467	-71.257	-84.826	7.130
2700	13.812	93.954	82.158	31.848	-71.539	-85.342	6.908
2800	13.819	94.456	82.589	33.229	-71.823	-85.848	6.700
2900	13.825	94.941	83.006	34.612	-72.107	-86.340	6.506
3000	13.830	95.410	83.412	35.994	-72.393	-86.830	6.325
3100	13.835	95.864	83.806	37.378	-72.679	-87.308	6.155
3200	13.840	96.303	84.190	38.761	-72.967	-87.773	5.994
3300	13.844	96.729	84.564	40.146	-73.256	-88.232	5.843
3400	13.848	97.142	84.927	41.530	-73.546	-88.680	5.700
3500	13.852	97.544	85.282	42.915	-73.838	-89.123	5.565
3600	13.855	97.934	85.628	44.301	-74.131	-89.553	5.436
3700	13.858	98.314	85.966	45.686	-74.425	-89.980	5.315
3800	13.861	98.683	86.296	47.072	-74.720	-90.392	5.198
3900	13.863	99.043	86.618	48.458	-75.018	-90.803	5.088
4000	13.865	99.394	86.933	49.845	-196.495	-89.059	4.866
4100	13.868	99.737	87.241	51.231	-196.564	-86.376	4.604
4200	13.870	100.071	87.543	52.618	-196.633	-83.682	4.354
4300	13.871	100.397	87.838	54.005	-196.704	-80.991	4.116
4400	13.873	100.716	88.127	55.392	-196.778	-78.299	3.889
4500	13.875	101.028	88.410	56.780	-196.853	-75.610	3.672
4600	13.876	101.333	88.688	58.167	-196.930	-72.914	3.464
4700	13.878	101.631	88.960	59.555	-197.009	-70.212	3.265
4800	13.879	101.924	89.227	60.943	-197.090	-67.517	3.074
4900	13.880	102.210	89.489	62.331	-197.174	-64.818	2.891
5000	13.882	102.490	89.746	63.719	-197.260	-62.112	2.715
5100	13.883	102.765	89.999	65.107	-197.349	-59.412	2.546
5200	13.884	103.035	90.247	66.496	-197.439	-56.707	2.383
5300	13.885	103.299	90.491	67.884	-197.532	-53.997	2.227
5400	13.886	103.559	90.730	69.273	-197.629	-51.294	2.076
5500	13.887	103.814	90.966	70.661	-197.726	-48.577	1.930
5600	13.888	104.064	91.198	72.050	-197.828	-45.869	1.790
5700	13.888	104.310	91.426	73.439	-197.933	-43.153	1.654
5800	13.889	104.551	91.650	74.828	-198.040	-40.434	1.524
5900	13.890	104.789	91.870	76.217	-198.150	-37.720	1.397
6000	13.891	105.022	92.088	77.606	-198.263	-34.997	1.275

Dec. 31, 1962; Dec. 31, 1964

BORON BROMIDE FLUORIDE (BBrF) (IDEAL GAS) MOL. WT. = 109.736

Point Group C_s

$S^\circ_{298.15}$ = [65.887] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [2]

$\Delta H^\circ_{f\ 0}$ = [56 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [57.5 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[860](1)
[310](1)
[1140](1)

Bond Distance: B-F = [1.3] Å B-Br = [1.87] Å

Bond Angle: Br-B-F = [120°]

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.13196] X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction $BBr_2 + BF_2 \rightarrow 2BBrF$.

Heat Capacity and Entropy.

The vibrational frequencies, bond lengths, angles and quantum weight were estimated by comparison with the respective dihalides. The individual moments of inertia were $I_A = 0.8407 \times 10^{-39}$ g. cm.^{2}, $I_B = 21.7537 \times 10^{-39}$ g. cm.^{2} and $I_C = 22.5944 \times 10^{-39}$ g. cm.^{2}

Boron Bromide Difluoride ($BBrF_2$)

(Ideal Gas) Mol. Wt. 128,736

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.054	- 193.723	- 193.723	INFINITE
100	8.742	56.536	78.971	- 2.243	- 193.947	- 194.879	425.888
200	11.472	63.443	69.598	- 1.231	- 194.300	- 195.672	213.811
298	13.492	68.424	68.424	.000	- 196.000	- 196.114	143.748
300	13.524	68.508	68.424	.025	- 196.011	- 196.115	142.863
400	14.997	72.611	68.974	1.455	- 199.793	- 195.378	106.745
500	16.088	76.080	70.057	3.012	- 199.897	- 194.263	84.908
600	16.896	79.089	71.317	4.663	- 199.997	- 193.127	70.343
700	17.496	81.741	72.621	6.384	- 200.089	- 191.974	59.934
800	17.944	84.108	73.911	8.157	- 200.175	- 190.810	52.124
900	18.283	86.242	75.165	9.969	- 200.254	- 189.635	46.047
1000	18.545	88.182	76.371	11.811	- 200.332	- 188.449	41.184
1100	18.749	89.959	77.527	13.676	- 200.414	- 187.258	37.203
1200	18.911	91.598	78.632	15.560	- 200.498	- 186.057	33.884
1300	19.041	93.117	79.688	17.457	- 200.590	- 184.850	31.075
1400	19.148	94.532	80.699	19.367	- 200.687	- 183.635	28.665
1500	19.235	95.856	81.665	21.286	- 200.794	- 182.414	26.576
1600	19.308	97.100	82.592	23.214	- 200.909	- 181.185	24.747
1700	19.369	98.273	83.480	25.147	- 201.034	- 179.948	23.133
1800	19.421	99.381	84.333	27.087	- 201.166	- 178.706	21.697
1900	19.465	100.432	85.153	29.031	- 201.305	- 177.452	20.411
2000	19.504	101.432	85.942	30.980	- 201.450	- 176.194	19.253
2100	19.537	102.384	86.702	32.932	- 201.600	- 174.927	18.204
2200	19.566	103.294	87.436	34.887	- 201.755	- 173.655	17.250
2300	19.591	104.164	88.145	36.845	- 201.916	- 172.372	16.378
2400	19.613	104.998	88.830	38.805	- 202.083	- 171.083	15.578
2500	19.633	105.799	89.492	40.768	- 207.642	- 169.679	14.833
2600	19.651	106.570	90.135	42.732	- 207.811	- 168.159	14.134
2700	19.667	107.312	90.757	44.698	- 207.980	- 166.630	13.487
2800	19.681	108.027	91.361	46.665	- 208.151	- 165.096	12.886
2900	19.694	108.718	91.948	48.634	- 208.324	- 163.551	12.325
3000	19.705	109.386	92.518	50.604	- 208.499	- 162.010	11.802
3100	19.716	110.032	93.073	52.575	- 208.675	- 160.456	11.312
3200	19.725	110.658	93.612	54.547	- 208.853	- 158.896	10.852
3300	19.734	111.265	94.138	56.520	- 209.033	- 157.332	10.419
3400	19.742	111.855	94.651	58.494	- 209.214	- 155.765	10.012
3500	19.749	112.427	95.150	60.468	- 209.399	- 154.188	9.627
3600	19.756	112.984	95.638	62.443	- 209.584	- 152.609	9.264
3700	19.762	113.525	96.114	64.419	- 209.772	- 151.023	8.920
3800	19.768	114.052	96.579	66.396	- 209.962	- 149.430	8.594
3900	19.773	114.566	97.034	68.373	- 210.155	- 147.840	8.284
4000	19.778	115.066	97.479	70.350	- 331.528	- 144.092	7.872
4100	19.782	115.555	97.914	72.328	- 331.494	- 139.411	7.431
4200	19.786	116.031	98.339	74.307	- 331.461	- 134.718	7.010
4300	19.790	116.497	98.756	76.286	- 331.430	- 130.035	6.609
4400	19.794	116.952	99.165	78.265	- 331.404	- 125.352	6.226
4500	19.797	117.397	99.565	80.244	- 331.380	- 120.674	5.860
4600	19.801	117.832	99.957	82.224	- 331.357	- 115.990	5.511
4700	19.804	118.258	100.342	84.205	- 331.339	- 111.306	5.175
4800	19.807	118.675	100.720	86.185	- 331.323	- 106.623	4.854
4900	19.809	119.083	101.090	88.166	- 331.312	- 101.943	4.547
5000	19.812	119.484	101.454	90.147	- 331.302	- 97.265	4.251
5100	19.814	119.876	101.812	92.128	- 331.297	- 92.587	3.967
5200	19.816	120.261	102.163	94.110	- 331.294	- 87.903	3.694
5300	19.818	120.638	102.508	96.091	- 331.295	- 83.220	3.431
5400	19.820	121.009	102.847	98.073	- 331.301	- 78.548	3.179
5500	19.822	121.372	103.180	100.056	- 331.307	- 73.855	2.935
5600	19.824	121.729	103.508	102.038	- 331.320	- 69.179	2.700
5700	19.826	122.080	103.831	104.020	- 331.337	- 64.495	2.473
5800	19.827	122.425	104.149	106.003	- 331.356	- 59.815	2.254
5900	19.829	122.764	104.461	107.986	- 331.380	- 55.136	2.042
6000	19.830	123.097	104.769	109.969	- 331.408	- 50.452	1.838

Sept. 30, 1962; Dec. 31, 1964

BORON BROMIDE DIFLUORIDE ($BBrF_2$) (IDEAL GAS) MOL. WT. = 128.736

Point Group C_{2v}

$S^\circ_{298.15}$ = 68.424 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H^\circ_{f\ 0}$ = [-193.7 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-196.0 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1215 (1)	1427 (1)
633 (1)	[346](1)
[330](1)	573 (1)

Bond Distance: B-F = 1.295 Å B-Br = 1.87 Å

Bond Angle: F-B-F = [120°] Br-B-F = [120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 8.46916 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction $2BF_3 + BBr_3 \rightarrow 3BBrF_2$.

Heat Capacity and Entropy.

All but two of the vibrational frequencies have been observed and assigned by L. P. Lindeman and M. K. Wilson J. Chem. Phys. 24, 242 (1956), the two remaining frequencies were calculated by a normal coordinate treatment. The bond distances were reported by T. Wentink and V. H. Tiensuu, J. Chem. Phys. 28, 826 (1958). The bond angles were estimated by analogy with the other boron trihalides. The individual moments of inertia were I_A = 7.9349 X 10^{-39} g. cm.^{2}, I_B = 28.9426 X 10^{-29} X 10^{-29} g. cm.^{2} and I_C = 36.8775 X 10^{-39} g. cm.^{2}

Boron Oxide Bromide (BOBr)

(Ideal Gas) Mol. Wt. = 106.736

T, °K.	cal. mole⁻¹deg.⁻¹ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole⁻¹ $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	- 2.620	- 58.361	- 58.361	INFINITE
100	7.555	49.288	68.422	- 1.913	- 58.351	- 60.552	132.230
200	9.847	55.253	60.450	- 1.039	- 58.482	- 62.702	68.515
298	11.188	59.463	59.463	.000	- 60.000	- 64.581	47.337
300	11.206	59.532	59.463	.021	- 60.007	- 64.610	47.066
400	11.969	62.869	59.913	1.182	- 63.643	- 65.396	35.729
500	12.498	65.600	60.786	2.407	- 63.638	- 65.836	28.776
600	12.909	67.916	61.786	3.678	- 63.664	- 66.274	24.139
700	13.239	69.932	62.809	4.986	- 63.707	- 66.705	20.825
800	13.505	71.718	63.813	6.324	- 63.762	- 67.131	18.339
900	13.720	73.321	64.782	7.686	- 63.822	- 67.548	16.402
1000	13.893	74.776	65.709	9.066	- 63.890	- 67.958	14.851
1100	14.034	76.107	66.595	10.463	- 63.967	- 68.362	13.582
1200	14.149	77.333	67.439	11.872	- 64.053	- 68.757	12.522
1300	14.244	78.470	68.245	13.292	- 64.148	- 69.146	11.624
1400	14.323	79.528	69.013	14.721	- 64.251	- 69.525	10.853
1500	14.390	80.519	69.748	16.156	- 64.366	- 69.900	10.184
1600	14.445	81.449	70.450	17.598	- 64.490	- 70.263	9.597
1700	14.493	82.326	71.123	19.045	- 64.624	- 70.619	9.078
1800	14.534	83.156	71.769	20.497	- 64.768	- 70.970	8.616
1900	14.569	83.943	72.389	21.952	- 64.919	- 71.310	8.202
2000	14.599	84.691	72.986	23.410	- 65.077	- 71.643	7.828
2100	14.626	85.404	73.560	24.872	- 65.240	- 71.966	7.489
2200	14.649	86.085	74.114	26.335	- 65.410	- 72.283	7.180
2300	14.670	86.736	74.649	27.801	- 65.586	- 72.590	6.897
2400	14.688	87.361	75.166	29.269	- 65.768	- 72.890	6.637
2500	14.704	87.961	75.666	30.739	- 71.343	- 73.075	6.388
2600	14.719	88.538	76.150	32.210	- 71.527	- 73.141	6.148
2700	14.732	89.094	76.619	33.683	- 71.714	- 73.199	5.925
2800	14.743	89.630	77.074	35.156	- 71.904	- 73.252	5.717
2900	14.754	90.147	77.516	36.631	- 72.094	- 73.292	5.523
3000	14.764	90.648	77.945	38.107	- 72.287	- 73.334	5.342
3100	14.772	91.132	78.363	39.584	- 72.481	- 73.365	5.172
3200	14.780	91.601	78.769	41.062	- 72.678	- 73.390	5.012
3300	14.787	92.056	79.165	42.540	- 72.876	- 73.409	4.861
3400	14.794	92.498	79.551	44.019	- 73.077	- 73.424	4.719
3500	14.800	92.926	79.927	45.499	- 73.279	- 73.430	4.585
3600	14.806	93.344	80.294	46.979	- 73.483	- 73.433	4.458
3700	14.811	93.749	80.652	48.460	- 73.689	- 73.426	4.337
3800	14.816	94.144	81.002	49.941	- 73.897	- 73.414	4.222
3900	14.820	94.529	81.344	51.423	- 74.106	- 73.402	4.113
4000	14.824	94.904	81.678	52.905	- 195.496	- 71.236	3.892
4100	14.828	95.271	82.005	54.388	- 195.478	- 68.134	3.632
4200	14.831	95.628	82.325	55.871	- 195.460	- 65.023	3.383
4300	14.835	95.977	82.639	57.354	- 195.445	- 61.917	3.147
4400	14.838	96.318	82.946	58.838	- 195.432	- 58.812	2.921
4500	14.841	96.651	83.247	60.322	- 195.421	- 55.707	2.705
4600	14.843	96.978	83.542	61.806	- 195.411	- 52.604	2.499
4700	14.846	97.297	83.831	63.290	- 195.403	- 49.496	2.301
4800	14.848	97.610	84.115	64.775	- 195.398	- 46.394	2.112
4900	14.851	97.916	84.393	66.260	- 195.394	- 43.294	1.931
5000	14.853	98.216	84.667	67.745	- 195.392	- 40.187	1.756
5100	14.855	98.510	84.935	69.231	- 195.394	- 37.082	1.589
5200	14.857	98.798	85.199	70.716	- 195.396	- 33.977	1.428
5300	14.858	99.081	85.458	72.202	- 195.400	- 30.872	1.273
5400	14.860	99.359	85.713	73.688	- 195.407	- 27.772	1.124
5500	14.862	99.632	85.964	75.174	- 195.415	- 24.662	.980
5600	14.863	99.900	86.210	76.660	- 195.426	- 21.566	.842
5700	14.865	100.163	86.453	78.147	- 195.440	- 18.458	.708
5800	14.866	100.421	86.691	79.633	- 195.456	- 15.349	.578
5900	14.867	100.675	86.926	81.120	- 195.474	- 12.243	.454
6000	14.868	100.925	87.157	82.607	- 195.494	- 9.137	.333

Dec. 31, 1962; Mar. 31, 1965

BORON OXIDE BROMIDE (BOBr) (IDEAL GAS) MOL. WT. = 106.736

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [59.46] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-58 ± 7] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-60 ± 7] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[550] (1)
[370] (2)
[1800] (1)

Bond Distance: O=B = [1.20] Å B-Br = [1.87] Å

Bond Angle: O-B-Br = [180]°

Rotation Constant: B_0 = [0.11742] cm.$^{-1}$

σ = 1

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for BOBr (g) was calculated based on an assumption that D(BO-Br) = 92.5 kcal. mole^{-1} which was estimated by comparison with the following related bond energy values: D(BF_2-F) = 159, D(BO-F) = 169, D(BCl_2-Cl) = 105, D(BO-Cl) = 110 and D(BBr_2-Br) = 90.5 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, $k_1 = 4.2 \times 10^5$, $k_2 = 16.9 \times 10^5$ dynes cm.$^{-1}$ and $k_\delta = 0.37 \times 10^{-11}$ dynes cm. rad.$^{-1}$ The B=O and B-F bond distances were assumed to be the same as those in BO(g) and BBr_3(g), respectively. The moment of inertia is 2.38357×10^{-38} g. cm.^{2}

Boron Dibromide (BBr_2)

(Ideal Gas) Mol. Wt. = 170.652

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.918	18.233	18.233	INFINITE
100	9.344	59.220	79.888	-2.067	18.410	13.783	-30.122
200	10.444	66.029	71.420	-1.078	18.148	9.239	-10.096
298	11.486	70.402	70.402	.000	15.000	5.276	-3.867
300	11.503	70.473	70.402	.021	14.983	5.216	-3.800
400	12.248	73.892	70.863	1.211	7.611	3.471	-1.897
500	12.726	76.680	71.756	2.462	7.566	2.440	-1.067
600	13.035	79.030	72.778	3.751	7.492	1.422	-.518
700	13.242	81.056	73.819	5.066	7.398	.417	-.130
800	13.385	82.834	74.837	6.397	7.288	-.573	.157
900	13.488	84.416	75.815	7.741	7.168	-1.548	.376
1000	13.564	85.842	76.748	9.094	7.036	-2.509	.548
1100	13.621	87.137	77.634	10.454	6.890	-3.457	.687
1200	13.666	88.325	78.476	11.818	6.732	-4.391	.800
1300	13.701	89.420	79.276	13.186	6.561	-5.310	.893
1400	13.729	90.436	80.038	14.558	6.380	-6.216	.970
1500	13.752	91.384	80.763	15.932	6.185	-7.111	1.036
1600	13.771	92.272	81.455	17.308	5.979	-7.989	1.091
1700	13.786	93.108	82.116	18.686	5.762	-8.856	1.138
1800	13.799	93.896	82.749	20.065	5.535	-9.711	1.179
1900	13.811	94.642	83.355	21.446	5.301	-10.549	1.213
2000	13.820	95.351	83.937	22.827	5.059	-11.379	1.243
2100	13.829	96.026	84.497	24.210	4.813	-12.195	1.269
2200	13.836	96.669	85.036	25.593	4.560	-12.998	1.291
2300	13.842	97.284	85.555	26.977	4.302	-13.790	1.310
2400	13.848	97.873	86.056	28.362	4.039	-14.569	1.327
2500	13.853	98.439	86.540	29.747	-1.616	-15.231	1.331
2600	13.857	98.982	87.008	31.132	-1.881	-15.770	1.326
2700	13.861	99.505	87.462	32.518	-2.146	-16.299	1.319
2800	13.864	100.009	87.901	33.904	-2.413	-16.819	1.313
2900	13.867	100.496	88.327	35.291	-2.679	-17.327	1.306
3000	13.870	100.966	88.740	36.678	-2.946	-17.829	1.299
3100	13.873	101.421	89.142	38.065	-3.215	-18.321	1.292
3200	13.875	101.862	89.533	39.452	-3.484	-18.805	1.284
3300	13.877	102.288	89.913	40.840	-3.754	-19.277	1.277
3400	13.879	102.703	90.283	42.228	-4.024	-19.746	1.269
3500	13.881	103.105	90.644	43.616	-4.296	-20.204	1.262
3600	13.883	103.496	90.995	45.004	-4.569	-20.654	1.254
3700	13.884	103.877	91.338	46.392	-4.842	-21.100	1.246
3800	13.885	104.247	91.673	47.781	-5.116	-21.532	1.238
3900	13.887	104.608	92.000	49.169	-5.392	-21.963	1.231
4000	13.888	104.959	92.320	50.558	-126.847	-20.239	1.106
4100	13.889	105.302	92.632	51.947	-126.893	-17.575	.937
4200	13.890	105.637	92.938	53.336	-126.939	-14.904	.776
4300	13.891	105.964	93.237	54.725	-126.987	-12.237	.622
4400	13.892	106.283	93.530	56.114	-127.037	-9.566	.475
4500	13.893	106.595	93.817	57.503	-127.088	-6.897	.335
4600	13.894	106.901	94.098	58.893	-127.139	-4.227	.201
4700	13.894	107.199	94.373	60.282	-127.193	-1.548	.072
4800	13.895	107.492	94.644	61.671	-127.250	1.122	-.051
4900	13.896	107.778	94.909	63.061	-127.307	3.797	-.169
5000	13.896	108.059	95.169	64.451	-127.365	6.475	-.283
5100	13.897	108.334	95.425	65.840	-127.428	9.150	-.392
5200	13.897	108.604	95.675	67.230	-127.490	11.828	-.497
5300	13.898	108.869	95.922	68.620	-127.554	14.507	-.598
5400	13.898	109.129	96.164	70.009	-127.623	17.184	-.695
5500	13.899	109.384	96.402	71.399	-127.691	19.874	-.790
5600	13.899	109.634	96.636	72.789	-127.763	22.552	-.880
5700	13.900	109.880	96.866	74.179	-127.838	25.241	-.968
5800	13.900	110.122	97.093	75.569	-127.914	27.926	-1.052
5900	13.900	110.360	97.316	76.959	-127.993	30.611	-1.134
6000	13.901	110.593	97.535	78.349	-128.075	33.301	-1.213

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

BORON DIBROMIDE (BBr_2) (IDEAL GAS) MOL. WT. = 170.652

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [70.402] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [2]

$\Delta H^\circ_{f\ 0}$ = [18.2 ± 15] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [15.0 ± 15] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[600](1)
[150](1)
[830](1)

Bond Distance: [1.87] Å

Bond Angle: [120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 7.26584 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by analogy with BF_3, specifically the ratio

$$\Delta H_r(BX_3 \rightarrow BX_2 + X) / \Delta H_r(BX_3 \rightarrow B + 3X)$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trihalide given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were I_B = 1.4708 X 10^{-39} g. cm.^{2}, I_A = 69.5532 X 10^{-39} g. cm.^{2} and I_C = 71.0240 X 10^{-39} g. cm.^{2}

Boron Dibromide Chloride (BBr_2Cl)

(Ideal Gas) Mol. Wt. = 206.109

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.607	-61.359	-61.359	INFINITE
100	10.827	62.411	89.591	-2.718	-61.495	-64.181	140.261
200	13.932	70.977	78.299	-1.464	-61.852	-66.735	72.921
298	15.781	76.909	76.909	.000	-65.000	-68.720	50.371
300	15.810	77.007	76.910	.029	-65.016	-68.743	50.077
400	17.038	81.736	77.546	1.676	-72.346	-68.479	37.414
500	17.833	85.630	78.785	3.422	-72.323	-67.516	29.510
600	18.354	88.930	80.208	5.234	-72.309	-66.556	24.242
700	18.706	91.788	81.663	7.088	-72.303	-65.598	20.480
800	18.953	94.303	83.089	8.971	-72.303	-64.641	17.658
900	19.131	96.546	84.462	10.876	-72.308	-63.683	15.464
1000	19.262	98.569	85.773	12.796	-72.320	-62.723	13.707
1100	19.363	100.409	87.021	14.727	-72.343	-61.763	12.271
1200	19.440	102.098	88.208	16.668	-72.374	-60.800	11.073
1300	19.502	103.656	89.337	18.615	-72.417	-59.832	10.058
1400	19.551	105.103	90.412	20.568	-72.469	-58.862	9.188
1500	19.591	106.454	91.437	22.525	-72.534	-57.891	8.434
1600	19.624	107.719	92.416	24.486	-72.609	-56.910	7.773
1700	19.652	108.910	93.351	26.449	-72.695	-55.926	7.189
1800	19.675	110.034	94.247	28.416	-72.790	-54.939	6.670
1900	19.695	111.098	95.106	30.384	-72.893	-53.942	6.204
2000	19.712	112.109	95.931	32.355	-73.003	-52.944	5.785
2100	19.727	113.071	96.725	34.327	-73.117	-51.938	5.405
2200	19.740	113.989	97.489	36.300	-73.239	-50.926	5.059
2300	19.751	114.867	98.225	38.275	-73.366	-49.909	4.742
2400	19.761	115.707	98.936	40.250	-73.499	-48.883	4.451
2500	19.769	116.514	99.623	42.227	-79.024	-47.747	4.174
2600	19.777	117.290	100.288	44.204	-79.159	-46.494	3.908
2700	19.784	118.036	100.932	46.182	-79.296	-45.234	3.661
2800	19.790	118.756	101.556	48.161	-79.436	-43.971	3.432
2900	19.796	119.450	102.161	50.140	-79.576	-42.698	3.218
3000	19.801	120.122	102.748	52.120	-79.718	-41.429	3.018
3100	19.805	120.771	103.319	54.100	-79.864	-40.150	2.830
3200	19.809	121.400	103.874	56.081	-80.010	-38.866	2.654
3300	19.813	122.009	104.415	58.062	-80.159	-37.576	2.488
3400	19.817	122.601	104.941	60.044	-80.309	-36.284	2.332
3500	19.820	123.175	105.454	62.026	-80.463	-34.987	2.185
3600	19.823	123.734	105.954	64.008	-80.618	-33.687	2.045
3700	19.825	124.277	106.442	65.990	-80.775	-32.381	1.913
3800	19.828	124.806	106.918	67.973	-80.934	-31.071	1.787
3900	19.830	125.321	107.383	69.956	-81.096	-29.756	1.667
4000	19.832	125.823	107.838	71.939	-202.439	-26.295	1.437
4100	19.834	126.313	108.283	73.922	-202.373	-21.895	1.167
4200	19.836	126.791	108.718	75.905	-202.309	-17.490	.910
4300	19.837	127.257	109.144	77.889	-202.246	-13.087	.665
4400	19.839	127.713	109.560	79.873	-202.187	-8.686	.431
4500	19.841	128.159	109.969	81.857	-202.130	-4.294	.209
4600	19.842	128.595	110.369	83.841	-202.073	.104	-.005
4700	19.843	129.022	110.761	85.825	-202.019	4.501	-.209
4800	19.844	129.440	111.146	87.810	-201.969	8.890	-.405
4900	19.846	129.849	111.524	89.794	-201.920	13.283	-.592
5000	19.847	130.250	111.894	91.779	-201.872	17.676	-.773
5100	19.848	130.643	112.258	93.763	-201.828	22.065	-.946
5200	19.849	131.028	112.615	95.748	-201.784	26.457	-1.112
5300	19.849	131.407	112.966	97.733	-201.742	30.840	-1.272
5400	19.850	131.778	113.311	99.718	-201.705	35.226	-1.426
5500	19.851	132.142	113.650	101.703	-201.667	39.623	-1.574
5600	19.852	132.499	113.984	103.688	-201.634	44.005	-1.717
5700	19.853	132.851	114.312	105.674	-201.603	48.390	-1.855
5800	19.853	133.196	114.634	107.659	-201.574	52.780	-1.989
5900	19.854	133.536	114.952	109.644	-201.547	57.159	-2.117
6000	19.855	133.869	115.264	111.630	-201.524	61.546	-2.242

Sept. 30, 1962; Dec. 31, 1964

BORON DIBROMIDE CHLORIDE (BBr_2Cl) (IDEAL GAS) MOL. WT. = 206.109

Point Group C_{2v}

$S^\circ_{298.15}$ = 76.909 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H^\circ_{f\ 0}$ = [-61.4 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-65 ± 10] kcal. mole^{-1}

Vibrational Levels and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
925(1)	834(1)
344(1)	195(1)
166(1)	409(1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.75 Å

Bond Angle: Br-B-Br = [120°] Cl-B-Br = [120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.55478 X 10^{-112} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction

$$2BBr_3 + BCl_3 \rightarrow 3BBr_2Cl$$

Heat Capacity and Entropy.

The vibrational frequencies have all been observed and assigned by L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956). The bond lengths were reported by T. Wentink and V. H. Tiensuu, J. Chem. Phys., 28, 826 (1958). Bond angles were estimated by analogy with the other trihalides of boron. Individual moments of inertia are I_B = 35.0734 X 10^{-39} g. cm.^{2}, I_A = 69.5934 X 10^{-39} g. cm.^{2} and I_C = 104.6668 X 10^{-39} g. cm.^{2}

Boron Dibromide Fluoride (BBr_2F)

(Ideal Gas) Mol. Wt. = 189.652

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.387	- 119.181	- 119.181	INFINITE
100	9.938	60.594	85.927	- 2.533	- 119.349	- 122.078	266.789
200	12.998	68.496	75.373	- 1.375	- 119.792	- 124.640	136.193
298	14.894	74.066	74.066	.000	- 123.000	- 126.594	92.792
300	14.923	74.159	74.067	.028	- 123.017	- 126.617	92.236
400	16.213	78.640	74.669	1.588	- 130.404	- 126.301	69.005
500	17.110	82.360	75.846	3.257	- 130.434	- 125.274	54.754
600	17.742	85.538	77.203	5.001	- 130.469	- 124.237	45.251
700	18.194	88.309	78.596	6.800	- 130.505	- 123.196	38.462
800	18.524	90.761	79.966	8.636	- 130.543	- 122.150	33.368
900	18.770	92.958	81.290	10.502	- 130.579	- 121.099	29.406
1000	18.956	94.946	82.557	12.388	- 130.620	- 120.043	26.234
1100	19.100	96.759	83.767	14.291	- 130.669	- 118.983	23.639
1200	19.214	98.426	84.920	16.207	- 130.724	- 117.917	21.475
1300	19.305	99.968	86.019	18.133	- 130.788	- 116.848	19.643
1400	19.378	101.401	87.067	20.068	- 130.860	- 115.772	18.072
1500	19.439	102.741	88.068	22.009	- 130.944	- 114.694	16.710
1600	19.489	103.997	89.025	23.955	- 131.037	- 113.607	15.517
1700	19.531	105.180	89.941	25.906	- 131.140	- 112.514	14.464
1800	19.566	106.297	90.819	27.861	- 131.252	- 111.417	13.527
1900	19.597	107.356	91.661	29.819	- 131.371	- 110.310	12.688
2000	19.623	108.362	92.471	31.780	- 131.496	- 109.199	11.932
2100	19.645	109.319	93.251	33.744	- 131.627	- 108.080	11.247
2200	19.665	110.234	94.002	35.709	- 131.764	- 106.957	10.625
2300	19.682	111.108	94.727	37.676	- 131.906	- 105.824	10.055
2400	19.697	111.946	95.427	39.645	- 132.054	- 104.686	9.532
2500	19.711	112.751	96.104	41.616	- 137.594	- 103.435	9.042
2600	19.723	113.524	96.760	43.588	- 137.744	- 102.065	8.579
2700	19.734	114.269	97.394	45.560	- 137.895	- 100.691	8.150
2800	19.743	114.986	98.010	47.534	- 138.047	- 99.309	7.751
2900	19.752	115.679	98.607	49.509	- 138.200	- 97.919	7.379
3000	19.760	116.349	99.188	51.485	- 138.355	- 96.532	7.032
3100	19.767	116.997	99.752	53.461	- 138.512	- 95.135	6.707
3200	19.773	117.625	100.301	55.438	- 138.670	- 93.734	6.401
3300	19.779	118.233	100.835	57.416	- 138.829	- 92.326	6.114
3400	19.784	118.824	101.355	59.394	- 138.990	- 90.915	5.844
3500	19.789	119.398	101.863	61.372	- 139.153	- 89.500	5.588
3600	19.794	119.955	102.357	63.352	- 139.317	- 88.077	5.347
3700	19.798	120.497	102.840	65.331	- 139.483	- 86.650	5.118
3800	19.802	121.026	103.312	67.311	- 139.651	- 85.221	4.901
3900	19.805	121.540	103.773	69.292	- 139.821	- 83.788	4.695
4000	19.809	122.041	104.223	71.272	- 261.171	- 80.203	4.382
4100	19.812	122.531	104.664	73.253	- 261.114	- 75.685	4.034
4200	19.815	123.008	105.095	75.235	- 261.057	- 71.156	3.702
4300	19.817	123.474	105.517	77.216	- 261.002	- 66.634	3.387
4400	19.820	123.930	105.930	79.198	- 260.951	- 62.115	3.085
4500	19.822	124.375	106.335	81.180	- 260.902	- 57.599	2.797
4600	19.824	124.811	106.732	83.162	- 260.854	- 53.081	2.522
4700	19.826	125.237	107.121	85.145	- 260.809	- 48.560	2.258
4800	19.828	125.655	107.503	87.128	- 260.768	- 44.048	2.005
4900	19.830	126.064	107.878	89.111	- 260.729	- 39.536	1.763
5000	19.832	126.464	108.246	91.094	- 260.692	- 35.017	1.531
5100	19.833	126.857	108.607	93.077	- 260.660	- 30.510	1.307
5200	19.835	127.242	108.961	95.060	- 260.629	- 25.994	1.092
5300	19.836	127.620	109.310	97.044	- 260.600	- 21.483	.886
5400	19.837	127.991	109.652	99.028	- 260.577	- 16.978	.687
5500	19.839	128.355	109.989	101.011	- 260.554	- 12.457	.495
5600	19.840	128.712	110.320	102.995	- 260.537	- 7.952	.310
5700	19.841	129.063	110.646	104.979	- 260.523	- 3.436	.132
5800	19.842	129.409	110.967	106.963	- 260.511	1.069	- .040
5900	19.843	129.748	111.282	108.948	- 260.503	5.578	- .207
6000	19.844	130.081	111.593	110.932	- 260.499	10.089	- .367

Sept. 30, 1962; Dec. 31, 1964

BORON DIBROMIDE FLUORIDE (BBr_2F) (IDEAL GAS) MOL. WT. = 189.652

Point Group C_{2v}

$S^\circ_{298.15}$ = [74.066] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H^\circ_{f\ 0}$ = [-119.2 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-123 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1310 (1)	869 (1)
[418](1)	[283](1)
[183](1)	[496](1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.295 Å

Bond Angle: Br-B-Br = [120°] Br-B-F = [120°]

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 8.72359 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction $2BBr_3 + BF_3 \rightarrow 3BBr_2F$.

Heat Capacity and Entropy.

Two of the vibrational frequencies were observed and assigned by L. P. Lindeman and M. K Wilson, J. Chem. Phys. 24, 242 (1956), the remaining frequencies were calculated by a normal coordinate treatment using force constants obtained by comparison with the other mixed trihalides. The bond distances were reported by T. Wentink and V. H. Tiensuu, J. Chem. Phys. 28, 826 (1958). The bond angles were estimated by analogy with the other trihalides. The individual moments of inertia were $I_B = 14.8452 \times 10^{-39}$ g. cm.^{2}, $I_A = 69.5934 \times 10^{-39}$ g. cm.^{2} and $I_C = 84.4386 \times 10^{-39}$ g. cm.^{2}

Boron Dibromide Hydride (BBr_2H)

(Ideal Gas) Mol. Wt. = 171.63697

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.017	-20.854	-20.854	INFINITE
100	9.325	58.192	79.889	-2.170	-21.060	-24.365	53.249
200	10.922	65.114	70.924	-1.162	-21.605	-27.479	30.027
298	12.726	69.817	69.817	.000	-25.000	-29.897	21.915
300	12.757	69.896	69.817	.024	-25.021	-29.928	21.802
400	14.209	73.776	70.337	1.376	-32.578	-30.022	16.403
500	15.247	77.065	71.362	2.852	-32.747	-29.364	12.835
600	16.006	79.915	72.555	4.416	-32.896	-28.673	10.444
700	16.589	82.428	73.790	6.047	-33.025	-27.958	8.729
800	17.054	84.675	75.012	7.730	-33.136	-27.228	7.438
900	17.434	86.706	76.200	9.455	-33.231	-26.483	6.431
1000	17.748	88.560	77.345	11.214	-33.316	-25.728	5.623
1100	18.011	90.264	78.443	13.003	-33.396	-24.966	4.960
1200	18.231	91.841	79.495	14.815	-33.473	-24.195	4.407
1300	18.418	93.308	80.501	16.648	-33.551	-23.419	3.937
1400	18.577	94.678	81.466	18.498	-33.631	-22.635	3.533
1500	18.713	95.965	82.390	20.363	-33.718	-21.849	3.183
1600	18.830	97.176	83.276	22.240	-33.812	-21.053	2.876
1700	18.931	98.321	84.128	24.128	-33.912	-20.252	2.604
1800	19.018	99.406	84.947	26.026	-34.019	-19.448	2.361
1900	19.095	100.436	85.735	27.931	-34.132	-18.633	2.143
2000	19.162	101.417	86.495	29.844	-34.249	-17.815	1.947
2100	19.221	102.354	87.228	31.763	-34.371	-16.992	1.768
2200	19.273	103.249	87.936	33.688	-34.498	-16.160	1.605
2300	19.319	104.107	88.621	35.618	-34.630	-15.324	1.456
2400	19.361	104.930	89.283	37.552	-34.768	-14.479	1.319
2500	19.398	105.721	89.925	39.490	-40.297	-13.524	1.182
2600	19.431	106.482	90.547	41.431	-40.436	-12.448	1.046
2700	19.461	107.216	91.151	43.376	-40.576	-11.370	.920
2800	19.488	107.924	91.738	45.323	-40.718	-10.286	.803
2900	19.512	108.609	92.308	47.273	-40.860	-9.195	.693
3000	19.534	109.271	92.862	49.226	-41.003	-8.104	.590
3100	19.555	109.911	93.402	51.180	-41.149	-7.002	.494
3200	19.573	110.533	93.927	53.136	-41.296	-5.900	.403
3300	19.590	111.135	94.440	55.095	-41.445	-4.790	.317
3400	19.606	111.720	94.939	57.054	-41.595	-3.678	.236
3500	19.620	112.289	95.427	59.016	-41.748	-2.562	.160
3600	19.633	112.842	95.903	60.978	-41.903	-1.440	.087
3700	19.646	113.380	96.368	62.942	-42.059	-.314	.019
3800	19.657	113.904	96.823	64.908	-42.218	.819	-.047
3900	19.668	114.415	97.267	66.874	-42.380	1.952	-.109
4000	19.677	114.913	97.702	68.841	-163.722	5.234	-.286
4100	19.686	115.399	98.128	70.809	-163.657	9.455	-.504
4200	19.695	115.873	98.545	72.778	-163.594	13.684	-.712
4300	19.703	116.337	98.953	74.748	-163.533	17.901	-.910
4400	19.710	116.790	99.354	76.719	-163.476	22.120	-1.099
4500	19.717	117.233	99.746	78.690	-163.422	26.334	-1.279
4600	19.724	117.666	100.131	80.662	-163.369	30.555	-1.452
4700	19.730	118.090	100.508	82.635	-163.321	34.775	-1.617
4800	19.735	118.506	100.879	84.608	-163.276	38.984	-1.775
4900	19.741	118.913	101.243	86.582	-163.234	43.196	-1.927
5000	19.746	119.312	101.600	88.556	-163.194	47.409	-2.072
5100	19.751	119.703	101.952	90.531	-163.159	51.619	-2.212
5200	19.755	120.086	102.297	92.506	-163.126	55.833	-2.347
5300	19.759	120.463	102.636	94.482	-163.096	60.042	-2.476
5400	19.763	120.832	102.969	96.458	-163.072	64.249	-2.600
5500	19.767	121.195	103.297	98.435	-163.049	68.465	-2.721
5600	19.771	121.551	103.620	100.412	-163.032	72.667	-2.836
5700	19.774	121.901	103.938	102.389	-163.019	76.880	-2.948
5800	19.778	122.245	104.251	104.367	-163.008	81.088	-3.055
5900	19.781	122.583	104.558	106.344	-163.002	85.297	-3.160
6000	19.784	122.915	104.862	108.323	-162.999	89.505	-3.260

Mar. 31, 1966

BORON DIBROMIDE HYDRIDE (BBr_2H) (IDEAL GAS) MOL. WT. = 171.63697

Point Group C_{2v}

$\Delta H_f^\circ{}_0$ = [-21 ± 5] kcal. mole^{-1}

$S^\circ_{298.15}$ = [69.82] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [-25 ± 5] kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
2600 (1)	1044 (1)
[532](1)	775 (1)
[158](1)	783 (1)

Bond Distance : B-H = 1.20 Å B-Br = [1.87] Å

Bond Angle: Br-B-Br = 119.3 ± 2° Br-B-H = 120.3 ± 1°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 1.08645 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H_f^\circ{}_{298.15}$ (BBr_2H, g) was derived by assuming the B-H bond strength to be 92 kcal. mole^{-1}, the same as that in BCl_2H(g).

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. 41, 3165 (1964). The B-Br bond distance was taken from that in BBr_3(g) molecule. The vibrational frequencies adopted and corrected to the average isotopic species were assigned by O. Brieux de Mandirola and J. F. Westerkamp, Spectrochim. Acta, 21, 1101 (1965), from infrared spectrum. The values in brackets are calculated by the Wilson's FG-method. Infrared spectrum of BBr_2H(g) was also reported by S. K. Wason and R. F. Porter, J. Phys. Chem. 69, 2461 (1965), and three frequencies, ν_1, ν_4 and ν_5, were assigned. The three principal moments of inertia are: $I_A = 6.87842 \times 10^{-38}$, $I_B = 2.2244 \times 10^{-39}$ and $I_C = 7.10086 \times 10^{-38}$ g. cm.^{2}

Boron Tribromide (BBr_3)

(Liquid) Mol. Wt. = 250.568

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	30.600	54.700	54.700	.000	-57.000	-56.619	41.501
300	30.600	54.889	54.701	.057	-56.998	-56.616	41.243
400	30.600	63.692	55.901	3.117	-66.620	-54.439	29.743
500	30.600	70.520	58.167	6.177	-65.297	-51.550	22.531
600	30.600	76.099	60.705	9.237	-64.044	-48.919	17.818
700	30.600	80.816	63.249	12.297	-62.840	-46.494	14.515
800	30.600	84.902	65.706	15.357	-61.669	-44.240	12.085
900	30.600	88.506	68.043	18.417	-60.522	-42.130	10.230
1000	30.600	91.730	70.253	21.477	-59.397	-40.145	8.773

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

BORON TRIBROMIDE (BBr_3) (LIQUID) MOL. WT. = 250.568

$S^\circ_{298.15}$ = 54.7 cal. deg.$^{-1}$ mole^{-1}

T_m = 227.2°K

T_b = 364.4°K

ΔH_f° 298.15 = -57.0 ± 0.2 kcal. mole^{-1}

ΔH_m° = Unknown

ΔH_v° = 7.30 kcal. mole^{-1}

Heat of Formation.

The heat of formation of boron tribromide liquid has been determined by H. A. Skinner and N. B. Smith, Trans. Farad. Soc. 51, 19 (1955) by hydrolysis to H_3BO_3 and HBr. The adopted heat of formation was calculated from Skinners hydrolysis data using ΔH_f° H_3BO_3(c) from these tables, ΔH_{soln} H_3BO_3 from L. G. Fasilino, National Research Corporation Special Report NONR-3608 (00) June 2, 1964, with the dilution data of J. Smisko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950). The ΔH_f° HBr(aq) was taken from W. H. Evans, Appendix III, Natl. Bureau of Standards Report 8504, 1 July 1964.

Heat Capacity and Entropy.

The heat capacity was estimated from that of the gas by K. K. Kelley USBM Bulletin 383. The entropy was back calculated from that of the gas by adjusting the free energy functions to give the best fit of the vapor pressure data.

Melting Data.

The temperature of melting was reported by J. Goubeau and H. Keller, Z. anorg. allgem. Chem. 267, 1 (1951) and A. Stock and E. Kuss, Ber. 47, 3113 (1914). This value was recently confirmed by the triple point measurement of 227.31°K by W. F. Barber, C. F. Boynton and P. E. Gallagher J. Chem. Eng. Data 9, 137 (1964).

Boiling Data.

The boiling point is from the data of Stock and Kuss, loc. cit. A second and third law analysis of the vapor pressure data of Stock and Kuss (1) and Barber et. al. (2) loc. cit. indicated that the data of Stock gave the best agreement as indicated below.

ΔH_v 298.15 kcal. mole^{-1}

	Second Law	Third Law	
		S°_{298} = 54.7	S°_{298} = 54.26
Ref 1.	8.175 ± 0.03	8.222 (-0.02)	8.361 (0.42)
Ref 2.	8.229 ± 0.03	8.203 (-0.44)	8.347 (0.00)

Ref. 1. had the first eight data points rejected due to a statistical test on the third law values. The values in parentheses are values of the third law drift measured as $\Delta(\Delta H)$ / ΔT. The second law entropy also confirmed the choice of the data of ref. 1 and an entropy of 54.7 cal. deg.$^{-1}$ mole^{-1}.

Boron Tribromide (BBr_3)

(Ideal Gas) Mol. Wt. = 250.568

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.755	- 43.475	- 43.475	INFINITE
100	11.546	62.346	90.633	- 2.829	- 43.556	- 47.852	104.576
200	14.474	71.364	78.918	- 1.511	- 44.075	- 51.961	56.777
298	16.198	77.487	77.487	.000	- 48.800	- 55.213	40.470
300	16.224	77.588	77.488	.030	- 48.825	- 55.252	40.249
400	17.358	82.423	78.139	1.713	- 59.823	- 55.135	30.123
500	18.079	86.380	79.404	3.488	- 59.786	- 53.969	23.589
600	18.545	89.720	80.852	5.321	- 59.760	- 52.807	19.234
700	18.857	92.604	82.329	7.192	- 59.745	- 51.650	16.125
800	19.074	95.137	83.775	9.089	- 59.736	- 50.495	13.794
900	19.230	97.393	85.165	11.005	- 59.734	- 49.340	11.981
1000	19.345	99.425	86.491	12.934	- 59.740	- 48.183	10.530
1100	19.432	101.273	87.752	14.873	- 59.758	- 47.028	9.343
1200	19.499	102.967	88.951	16.819	- 59.785	- 45.869	8.353
1300	19.553	104.530	90.090	18.772	- 59.823	- 44.707	7.516
1400	19.595	105.980	91.174	20.730	- 59.872	- 43.542	6.797
1500	19.630	107.334	92.206	22.691	- 59.934	- 42.377	6.174
1600	19.659	108.602	93.192	24.656	- 60.005	- 41.202	5.628
1700	19.683	109.794	94.134	26.623	- 60.088	- 40.023	5.145
1800	19.703	110.920	95.035	28.592	- 60.181	- 38.843	4.716
1900	19.720	111.985	95.900	30.563	- 60.280	- 37.651	4.331
2000	19.735	112.997	96.729	32.536	- 60.388	- 36.460	3.984
2100	19.747	113.960	97.527	34.510	- 60.500	- 35.260	3.669
2200	19.758	114.879	98.295	36.485	- 60.618	- 34.055	3.383
2300	19.768	115.758	99.035	38.462	- 60.742	- 32.846	3.121
2400	19.776	116.599	99.750	40.439	- 60.872	- 31.627	2.880
2500	19.784	117.407	100.440	42.417	- 66.394	- 30.299	2.649
2600	19.790	118.183	101.108	44.396	- 66.525	- 28.852	2.425
2700	19.796	118.930	101.754	46.375	- 66.657	- 27.402	2.218
2800	19.802	119.650	102.380	48.355	- 66.792	- 25.945	2.025
2900	19.806	120.345	102.988	50.335	- 66.926	- 24.481	1.845
3000	19.811	121.016	103.578	52.316	- 67.061	- 23.016	1.677
3100	19.815	121.666	104.151	54.297	- 67.199	- 21.546	1.519
3200	19.818	122.295	104.708	56.279	- 67.336	- 20.070	1.371
3300	19.821	122.905	105.250	58.261	- 67.476	- 18.593	1.231
3400	19.824	123.497	105.778	60.243	- 67.616	- 17.110	1.100
3500	19.827	124.072	106.293	62.226	- 67.758	- 15.624	.976
3600	19.830	124.630	106.794	64.209	- 67.902	- 14.130	.858
3700	19.832	125.174	107.284	66.192	- 68.045	- 12.638	.746
3800	19.834	125.702	107.762	68.175	- 68.191	- 11.133	.640
3900	19.836	126.218	108.228	70.159	- 68.339	- 9.632	.540
4000	19.838	126.720	108.684	72.142	- 189.667	- 5.983	.327
4100	19.839	127.210	109.130	74.126	- 189.586	- 1.394	.074
4200	19.841	127.688	109.566	76.110	- 189.505	3.201	- .167
4300	19.842	128.155	109.993	78.094	- 189.427	7.788	- .396
4400	19.844	128.611	110.411	80.079	- 189.351	12.375	- .615
4500	19.845	129.057	110.821	82.063	- 189.277	16.956	- .823
4600	19.846	129.493	111.222	84.048	- 189.204	21.541	- 1.023
4700	19.847	129.920	111.615	86.032	- 189.133	26.124	- 1.215
4800	19.848	130.338	112.001	88.017	- 189.066	30.699	- 1.398
4900	19.849	130.747	112.379	90.002	- 189.001	35.277	- 1.573
5000	19.850	131.148	112.751	91.987	- 188.936	39.856	- 1.742
5100	19.851	131.541	113.115	93.972	- 188.876	44.428	- 1.904
5200	19.852	131.927	113.473	95.957	- 188.817	49.000	- 2.059
5300	19.853	132.305	113.825	97.942	- 188.760	53.575	- 2.209
5400	19.853	132.676	114.171	99.928	- 188.707	58.143	- 2.353
5500	19.854	133.040	114.511	101.913	- 188.655	62.725	- 2.492
5600	19.855	133.398	114.845	103.899	- 188.607	67.285	- 2.626
5700	19.855	133.749	115.173	105.884	- 188.563	71.861	- 2.755
5800	19.856	134.095	115.496	107.870	- 188.520	76.426	- 2.880
5900	19.857	134.434	115.815	109.855	- 188.481	80.995	- 3.000
6000	19.857	134.768	116.128	111.841	- 188.446	85.556	- 3.116

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

BORON TRIBROMIDE (BBr_3) (IDEAL GAS) MOL. WT. = 250.568

Point Group D_{3h}

$\Delta H_f^\circ{}_0 = -43.5 \pm 0.22$ kcal. mole^{-1}

$S^\circ_{298.15} = 77.487$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -48.8 \pm 0.22$ kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
278 (1)
379 (1)
827 (2)
150 (2)

Bond Distance: B-Br = 1.87 ± 0.02 Å

Bond Angle: Br-B-Br = 120° ± 6°

$\sigma = 6$

Product of the Moments of Inertia: $I_A I_B I_C = 6.74115 \times 10^{-112}$ g.^{3} cm.^{6}

Heat of Formation.

$\Delta H_f^\circ{}_{298}$ was obtained from the heat of formation of the liquid plus the heat of vaporization at 298°K, taken as 8.20 kcal. mole^{-1} as the average second and third law value derived from the vapor pressures of A. Stock and E. Kuss, Ber. 47, 3113 (1914). See BBr_3(l) for details.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from T. Wentink, Jr., and V. H. Tiensuu, J. Chem. Phys., 28, 825 (1958) modified for the natural isotopic abundances (B^{10} 18.83%, B^{11} 81.17%) given by J. R. Bradford, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., 1956. B-Br bond distance was reported by T. Wentink, Jr., and V. H. Tiensuu, loc. cit. Br-B-Br angle was taken from L. E. Sutton (editor), "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. The individual moments of inertia were $I_A = I_B = 419.187 \times 10^{-39}$ g. cm.^{2}, $I_C = 838.375 \times 10^{-39}$ g. cm.^{2}

Boron Monochloride (BCl)

(Ideal Gas) Mol. Wt. = 46.277

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.118	33.071	33.071	INFINITE
100	6.959	43.155	57.386	- 1.423	33.409	31.362	- 68.537
200	7.140	48.013	51.619	- .721	33.671	29.202	- 31.908
298	7.567	50.942	50.942	.000	33.800	26.974	- 19.772
300	7.575	50.988	50.942	.014	33.802	26.932	- 19.619
400	7.967	53.224	51.244	.792	33.843	24.633	- 13.458
500	8.248	55.034	51.827	1.604	33.815	22.333	- 9.761
600	8.442	56.556	52.491	2.439	33.740	20.043	- 7.300
700	8.579	57.868	53.168	3.290	33.637	17.769	- 5.547
800	8.678	59.020	53.829	4.153	33.512	15.510	- 4.237
900	8.752	60.047	54.464	5.025	33.372	13.267	- 3.222
1000	8.810	60.972	55.069	5.903	33.219	11.042	- 2.413
1100	8.856	61.814	55.645	6.786	33.049	8.832	- 1.755
1200	8.894	62.586	56.191	7.674	32.868	6.639	- 1.209
1300	8.926	63.300	56.711	8.565	32.674	4.460	- .750
1400	8.954	63.962	57.206	9.459	32.469	2.298	- .359
1500	8.978	64.581	57.677	10.356	32.252	.149	- .022
1600	9.000	65.161	58.127	11.255	32.024	- 1.983	.271
1700	9.020	65.707	58.557	12.156	31.785	- 4.100	.527
1800	9.038	66.223	58.968	13.059	31.538	- 6.205	.753
1900	9.054	66.712	59.363	13.963	31.283	- 8.294	.954
2000	9.070	67.177	59.742	14.869	31.023	- 10.370	1.133
2100	9.085	67.620	60.107	15.777	30.758	- 12.434	1.294
2200	9.099	68.043	60.458	16.686	30.488	- 14.484	1.439
2300	9.112	68.448	60.797	17.597	30.214	- 16.523	1.570
2400	9.125	68.836	61.124	18.509	29.936	- 18.548	1.689
2500	9.138	69.209	61.440	19.422	24.266	- 20.454	1.788
2600	9.150	69.567	61.746	20.336	23.988	- 22.236	1.869
2700	9.162	69.913	62.042	21.252	23.710	- 24.009	1.943
2800	9.174	70.246	62.329	22.169	23.431	- 25.771	2.011
2900	9.185	70.568	62.607	23.087	23.152	- 27.521	2.074
3000	9.196	70.880	62.878	24.006	22.873	- 29.267	2.132
3100	9.207	71.182	63.141	24.926	22.594	- 31.002	2.186
3200	9.218	71.474	63.397	25.847	22.314	- 32.724	2.235
3300	9.229	71.758	63.646	26.770	22.034	- 34.439	2.281
3400	9.240	72.034	63.889	27.693	21.754	- 36.146	2.323
3500	9.250	72.302	64.125	28.618	21.473	- 37.848	2.363
3600	9.261	72.562	64.356	29.543	21.192	- 39.534	2.400
3700	9.271	72.816	64.581	30.470	20.911	- 41.218	2.435
3800	9.281	73.064	64.801	31.397	20.629	- 42.895	2.467
3900	9.292	73.305	65.016	32.326	20.348	- 44.564	2.497
4000	9.302	73.540	65.226	33.256	- 101.114	- 44.078	2.408
4100	9.312	73.770	65.432	34.186	- 101.165	- 42.653	2.274
4200	9.322	73.995	65.633	35.118	- 101.215	- 41.224	2.145
4300	9.332	74.214	65.830	36.051	- 101.266	- 39.795	2.023
4400	9.342	74.429	66.023	36.984	- 101.318	- 38.365	1.905
4500	9.352	74.639	66.212	37.919	- 101.369	- 36.936	1.794
4600	9.361	74.844	66.398	38.855	- 101.420	- 35.500	1.687
4700	9.371	75.046	66.579	39.791	- 101.472	- 34.067	1.584
4800	9.381	75.243	66.758	40.729	- 101.524	- 32.630	1.486
4900	9.391	75.437	66.933	41.668	- 101.577	- 31.199	1.391
5000	9.401	75.627	67.105	42.607	- 101.629	- 29.762	1.301
5100	9.410	75.813	67.274	43.548	- 101.682	- 28.321	1.214
5200	9.420	75.996	67.440	44.489	- 101.735	- 26.883	1.130
5300	9.430	76.175	67.603	45.432	- 101.788	- 25.444	1.049
5400	9.439	76.351	67.763	46.375	- 101.842	- 24.001	.971
5500	9.449	76.525	67.921	47.320	- 101.895	- 22.557	.896
5600	9.459	76.695	68.076	48.265	- 101.949	- 21.118	.824
5700	9.468	76.863	68.229	49.211	- 102.005	- 19.677	.754
5800	9.478	77.027	68.379	50.159	- 102.060	- 18.226	.687
5900	9.488	77.189	68.527	51.107	- 102.115	- 16.781	.622
6000	9.497	77.349	68.673	52.056	- 102.172	- 15.334	.559

Mar. 31, 1961; Dec. 31, 1964

BORON MONOCHLORIDE (BCl) (IDEAL GAS) MOL. WT. = 46.277

Ground State Configuration $^1\Sigma$

$S^\circ_{298.15}$ = 50.942 cal deg^{-1} mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 33.1 ± 4.0 kcal mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 33.8 ± 4.0 kcal mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 843.65 cm^{-1}

$\omega_e x_e$ = 5.167 cm^{-1}

σ = 1

B_e = 0.6914 cm^{-1}

α_e = 0.00657 cm^{-1}

r_e = 1.7157 Å

Heat of Formation

The dissociation energy (D_0°) of BCl(g) has been reported by G. Herzberg[1], A. G. Gaydon[2] and R. F. Barrow[3], respectively. Hence the corresponding values of $\Delta H^\circ_{f\ 298.15}$ for BCl(g) were derived. The results are given as follows.

	D_0°		$\Delta H^\circ_{f\ 298.15}$
Investigator	e.v.	kcal mole^{-1}	kcal mole^{-1}
Herzberg[1]	4.2	96.9	62.6
Gaydon[2]	5.1 ± 0.4	117.6 ± 9.2	41.8 ± 9.2
Barrow[3]	---	127	33.8 ± 4

[1] G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

[2] A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953.

[3] R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960).

The last value of $\Delta H^\circ_{f\ 298.15}$ listed in the above table is adopted. Using the bond energy, D°(B-Cl), obtained from BCl_3(g) molecule, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for BCl(g) was calculated as 37.8 kcal mole^{-1} employing the same ratio of D°(B-X)/ average bond energy of BX_3 as found in BF(g) and BF_3(g), which is within the uncertainty of the value evaluated from dissociation energy.

Heat Capacity and Entropy

The spectroscopic constants were obtained from G. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is 4.0514 x 10^{-39} g cm^2.

Boron Monochloride Unipositive Ion (BCl^+)

(Ideal Gas) GFW = 46.2634

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	7.563	52.347	52.346	.000	295.000	286.268	-209.840
300	7.571	52.393	52.347	.014	295.010	286.213	-208.506
400	7.963	54.628	52.649	.792	295.548	283.198	-154.732
500	8.243	56.436	53.231	1.603	296.017	280.056	-122.412
600	8.437	57.958	53.895	2.437	296.439	276.823	-100.833
700	8.573	59.269	54.571	3.288	296.831	273.522	-85.397
800	8.672	60.420	55.232	4.151	297.202	270.166	-73.806
900	8.746	61.446	55.867	5.022	297.559	266.765	-64.779
1000	8.803	62.371	56.472	5.899	297.902	263.325	-57.550
1100	8.849	63.212	57.047	6.782	298.229	259.852	-51.628
1200	8.886	63.984	57.593	7.669	298.544	256.350	-46.688
1300	8.918	64.696	58.112	8.559	298.845	252.820	-42.503
1400	8.945	65.358	58.607	9.452	299.136	249.270	-38.913
1500	8.969	65.976	59.077	10.348	299.415	245.697	-35.798
1600	8.990	66.556	59.527	11.246	299.683	242.108	-33.070
1700	9.009	67.101	59.957	12.146	299.940	238.502	-30.662
1800	9.026	67.617	60.368	13.048	300.188	234.879	-28.518
1900	9.043	68.105	60.762	13.951	300.429	231.246	-26.599
2000	9.058	68.569	61.141	14.856	300.665	227.599	-24.871
2100	9.072	69.012	61.506	15.762	300.895	223.939	-23.306
2200	9.085	69.434	61.856	16.670	301.121	220.269	-21.882
2300	9.098	69.838	62.195	17.580	301.342	216.588	-20.581
2400	9.111	70.226	62.521	18.490	301.559	212.901	-19.387
2500	9.123	70.598	62.837	19.402	296.385	209.310	-18.298
2600	9.135	70.956	63.142	20.315	296.602	205.823	-17.301
2700	9.146	71.301	63.438	21.229	296.819	202.329	-16.377
2800	9.157	71.634	63.725	22.144	297.036	198.824	-15.519
2900	9.168	71.955	64.003	23.060	297.252	195.315	-14.719
3000	9.179	72.266	64.274	23.978	297.468	191.793	-13.972
3100	9.190	72.567	64.536	24.896	297.684	188.266	-13.273
3200	9.201	72.859	64.792	25.816	297.900	184.736	-12.617
3300	9.212	73.143	65.041	26.736	298.115	181.197	-12.000
3400	9.223	73.418	65.283	27.658	298.329	177.652	-11.419
3500	9.235	73.685	65.519	28.581	298.543	174.097	-10.871
3600	9.246	73.946	65.750	29.505	298.758	170.540	-10.353
3700	9.258	74.199	65.975	30.430	298.972	166.973	-9.863
3800	9.270	74.446	66.194	31.357	299.187	163.405	-9.398
3900	9.282	74.687	66.409	32.284	299.401	159.827	-8.956
4000	9.295	74.922	66.619	33.213	178.434	158.390	-8.654
4100	9.308	75.152	66.824	34.143	178.880	157.881	-8.416
4200	9.322	75.376	67.025	35.075	179.327	157.370	-8.189
4300	9.336	75.596	67.222	36.007	179.773	156.840	-7.971
4400	9.351	75.811	67.415	36.942	180.219	156.304	-7.764
4500	9.366	76.021	67.604	37.878	180.664	155.750	-7.564
4600	9.382	76.227	67.789	38.815	181.112	155.194	-7.373
4700	9.399	76.429	67.971	39.754	181.560	154.627	-7.190
4800	9.416	76.627	68.149	40.695	182.007	154.048	-7.014
4900	9.434	76.821	68.324	41.637	182.455	153.461	-6.845
5000	9.453	77.012	68.496	42.582	182.904	152.866	-6.682
5100	9.472	77.199	68.665	43.528	183.354	152.259	-6.525
5200	9.492	77.384	68.830	44.476	183.805	151.648	-6.374
5300	9.513	77.565	68.994	45.426	184.257	151.020	-6.227
5400	9.534	77.743	69.154	46.379	184.709	150.389	-6.087
5500	9.557	77.918	69.312	47.333	185.163	149.755	-5.951
5600	9.580	78.090	69.467	48.290	185.616	149.098	-5.819
5700	9.603	78.260	69.620	49.249	186.070	148.448	-5.692
5800	9.627	78.427	69.770	50.211	186.526	147.782	-5.569
5900	9.652	78.592	69.918	51.175	186.983	147.109	-5.449
6000	9.678	78.754	70.064	52.141	187.441	146.435	-5.334

June 30, 1968

BORON MONOCHLORIDE UNIPOSITIVE ION (BCl^+) (IDEAL GAS) GFW = 42.2634

Ground State Configuration $[^2\Sigma]$

ΔHf°_0 = [294.3 ± 10] kcal/mol

$S^\circ_{298.15}$ = [52.3 ± 0.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [295 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[28000]	[4]

ω_e = [845] cm^{-1}

B_e = [0.68] cm^{-1}

$\omega_e x_e$ = [5] cm^{-1}

α_e = [0.0056] cm^{-1}

σ = 1

r_e = [1.73] Å

Heat of Formation

Several values of the appearance potential of BCl^+ from BCl_3 have been reported. Osberghaus (1) gave 19.2eV, Marriott and Craggs (2) reported 18.54 ± 0.07eV, and Koski et al. (3) obtained two values of 17.2 ± 0.2eV and 20 ± 0.2eV. We make the presumption that the higher values, 19.2 and 20, refer to the reaction $BCl_3(g) + e^- \rightarrow BCl^+ + 2Cl(g) + 2e^-$ and the other values to $BCl_3(g) + e^- \rightarrow BCl^+ + Cl_2(g) + 2e^-$. Using the lower value in each case to help eliminate any excess kinetic energy, we obtain $\Delta Hf^\circ_{298}(BCl^+, g)$ = 289 and 300 kcal/mol, respectively. We adopt an average value of $\Delta Hf^\circ_{298}(BCl^+, g)$ = 295 ± 10 kcal/mol, which corresponds to an ionization potential for BCl(g) of 11.3 ± 0.3eV.

Heat Capacity and Entropy

BCl^+ is isoelectronic with BeCl,and the ground state configuration and electronic levels are estimated by comparison with BeCl. The bond length, frequency and anharmonicity constant are estimated between the values for BCl and BeCl; the rotational constant is calculated from the bond length and atomic masses, and α_e is obtained from the above constants assuming a Morse potential function.

The enthalpy at 0°K is -2.118 kcal/mol.

References

1. O. Osberghaus, Z. Phys. 128, 366 (1950).
2. J. Marriott and J. D. Craggs, J. Electron. Contr. 3, 194 (1957).
3. W. S. Koski, J. J. Kaufman and C. F. Pachuki, J. Am. Chem. Soc. 81, 1326 (1959).

Boron Chloride Fluoride (BClF)

(Ideal Gas) Mol. Wt. = 65.277

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.631	- 75.187	- 75.187	INFINITE
100	8.253	53.326	71.628	- 1.830	- 75.090	- 76.121	166.353
200	9.258	59.362	64.130	- .954	- 75.004	- 77.189	84.344
298	10.169	63.229	63.229	.000	- 75.000	- 78.267	57.369
300	10.186	63.292	63.230	.019	- 75.001	- 78.288	57.030
400	11.025	66.341	63.640	1.081	- 75.061	- 79.375	43.367
500	11.688	68.876	64.440	2.218	- 75.167	- 80.443	35.160
600	12.181	71.053	65.365	3.412	- 75.298	- 81.486	29.680
700	12.542	72.959	66.317	4.650	- 75.441	- 82.506	25.758
800	12.809	74.652	67.255	5.918	- 75.594	- 83.506	22.812
900	13.008	76.173	68.163	7.209	- 75.751	- 84.485	20.515
1000	13.160	77.551	69.034	8.518	- 75.917	- 85.446	18.673
1100	13.278	78.812	69.866	9.840	- 76.094	- 86.392	17.164
1200	13.371	79.971	70.660	11.173	- 76.278	- 87.319	15.902
1300	13.445	81.044	71.418	12.514	- 76.474	- 88.231	14.832
1400	13.506	82.043	72.142	13.861	- 76.679	- 89.128	13.913
1500	13.555	82.977	72.834	15.214	- 76.895	- 90.011	13.114
1600	13.596	83.853	73.495	16.572	- 77.122	- 90.877	12.413
1700	13.631	84.678	74.129	17.933	- 77.359	- 91.728	11.792
1800	13.660	85.458	74.737	19.298	- 77.606	- 92.569	11.239
1900	13.685	86.197	75.321	20.665	- 77.860	- 93.391	10.742
2000	13.706	86.900	75.882	22.035	- 78.120	- 94.202	10.293
2100	13.724	87.569	76.423	23.406	- 78.386	- 95.000	9.886
2200	13.741	88.208	76.944	24.779	- 78.659	- 95.786	9.515
2300	13.755	88.819	77.447	26.154	- 78.936	- 96.557	9.175
2400	13.767	89.404	77.933	27.530	- 79.219	- 97.315	8.861
2500	13.778	89.967	78.404	28.908	- 84.895	- 97.957	8.563
2600	13.788	90.507	78.859	30.286	- 85.181	- 98.472	8.277
2700	13.797	91.028	79.300	31.665	- 85.468	- 98.978	8.011
2800	13.805	91.530	79.728	33.045	- 85.757	- 99.474	7.764
2900	13.812	92.014	80.143	34.426	- 86.048	- 99.955	7.532
3000	13.818	92.483	80.547	35.808	- 86.341	- 100.435	7.316
3100	13.824	92.936	80.939	37.190	- 86.635	- 100.900	7.113
3200	13.829	93.375	81.321	38.572	- 86.932	- 101.354	6.922
3300	13.834	93.800	81.693	39.956	- 87.231	- 101.797	6.741
3400	13.839	94.213	82.055	41.339	- 87.531	- 102.233	6.571
3500	13.843	94.615	82.408	42.723	- 87.835	- 102.666	6.410
3600	13.846	95.005	82.753	44.108	- 88.139	- 103.083	6.258
3700	13.850	95.384	83.089	45.493	- 88.446	- 103.493	6.113
3800	13.853	95.753	83.417	46.878	- 88.755	- 103.893	5.975
3900	13.856	96.113	83.738	48.263	- 89.067	- 104.291	5.844
4000	13.858	96.464	84.052	49.649	- 210.559	- 102.531	5.602
4100	13.861	96.806	84.359	51.035	- 210.643	- 99.830	5.321
4200	13.863	97.140	84.659	52.421	- 210.729	- 97.123	5.054
4300	13.865	97.467	84.953	53.807	- 210.816	- 94.421	4.799
4400	13.867	97.785	85.241	55.194	- 210.906	- 91.708	4.555
4500	13.869	98.097	85.524	56.581	- 210.999	- 89.004	4.322
4600	13.871	98.402	85.800	57.968	- 211.092	- 86.291	4.100
4700	13.873	98.700	86.072	59.355	- 211.188	- 83.573	3.886
4800	13.874	98.992	86.338	60.742	- 211.286	- 80.856	3.681
4900	13.876	99.278	86.599	62.130	- 211.387	- 78.139	3.485
5000	13.877	99.559	86.855	63.518	- 211.489	- 75.421	3.297
5100	13.878	99.834	87.107	64.905	- 211.594	- 72.700	3.115
5200	13.880	100.103	87.354	66.293	- 211.700	- 69.971	2.941
5300	13.881	100.368	87.597	67.681	- 211.808	- 67.251	2.773
5400	13.882	100.627	87.836	69.070	- 211.920	- 64.522	2.611
5500	13.883	100.882	88.071	70.458	- 212.032	- 61.786	2.455
5600	13.884	101.132	88.302	71.846	- 212.148	- 59.058	2.305
5700	13.885	101.378	88.530	73.235	- 212.267	- 56.323	2.159
5800	13.886	101.619	88.753	74.623	- 212.387	- 53.583	2.019
5900	13.887	101.857	88.973	76.012	- 212.510	- 50.850	1.884
6000	13.887	102.090	89.190	77.400	- 212.636	- 48.104	1.752

Mar. 31, 1961; Dec. 31, 1964

BORON CHLORIDE FLUORIDE (BClF) (IDEAL GAS) MOL. WT. = 65.277

Point Group C_s

$S^\circ_{298.15}$ = [63.229] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = [-75.2 ± 7.0] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-75.0 ± 7.0] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[920] (1)
[360] (1)
[1220] (1)

Bond Distance: B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: F-B-Cl = [120]°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.81165 X 10^{-115}] g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for BClF(g) was estimated based on an assumption that ΔH°_r = 0 for the reaction $BCl_2(g)$ + $BF_2(g)$ = 2BClF(g). The values of $\Delta H^\circ_{f\ 298.15}$ of $BCl_2(g)$ and $BF_2(g)$, used for calculation, are -20 and -130 kcal. mole^{-1}, respectively.

Heat Capacity and Entropy.

The ground state quantum weight and bond angle were assumed to be the same as those for $BF_2(g)$. The bond distances of B-Cl and B-F were estimated by comparison with those in $BCl_3(g)$ and $BF_3(g)$ molecules, respectively. The vibrational frequencies were estimated from the corresponding values for $BCl_2(g)$ and $BF_2(g)$. The three principal moments of inertia are: I_A = 1.48569 X 10^{-38}, I_B = 7.7980 X 10^{-40} and I_C = 1.56367 X 10^{-38} g. cm.^{2}

Boron Chloride Difluoride ($BClF_2$)

(Ideal Gas) Mol. Wt. = 84.277

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_P
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	- 2.945	- 211.046	- 211.046	INFINITE
100	8.428	54.323	75.737	- 2.141	- 211.294	- 210.389	459.783
200	10.902	60.893	66.789	- 1.179	- 211.472	- 209.409	228.820
298	13.018	65.662	65.662	.000	- 211.600	- 208.370	152.732
300	13.052	65.742	65.662	.024	- 211.602	- 208.351	151.776
400	14.637	69.726	66.194	1.413	- 211.721	- 207.248	113.230
500	15.814	73.125	67.249	2.938	- 211.842	- 206.116	90.089
600	16.683	76.089	68.480	4.565	- 211.956	- 204.960	74.653
700	17.327	78.711	69.758	6.267	- 212.060	- 203.785	63.621
800	17.807	81.058	71.027	8.025	- 212.157	- 202.598	55.344
900	18.171	83.177	72.261	9.825	- 212.244	- 201.397	48.904
1000	18.451	85.107	73.450	11.656	- 212.329	- 200.188	43.749
1100	18.670	86.876	74.592	13.513	- 212.417	- 198.970	39.530
1200	18.844	88.508	75.684	15.389	- 212.507	- 197.742	36.012
1300	18.983	90.022	76.730	17.281	- 212.603	- 196.507	33.034
1400	19.097	91.433	77.730	19.185	- 212.705	- 195.265	30.481
1500	19.190	92.754	78.688	21.099	- 212.816	- 194.016	28.267
1600	19.268	93.995	79.606	23.022	- 212.935	- 192.759	26.328
1700	19.334	95.166	80.488	24.953	- 213.062	- 191.494	24.617
1800	19.389	96.272	81.334	26.889	- 213.198	- 190.223	23.095
1900	19.437	97.322	82.148	28.830	- 213.340	- 188.942	21.732
2000	19.478	98.320	82.932	30.776	- 213.488	- 187.653	20.505
2100	19.513	99.271	83.688	32.726	- 213.640	- 186.358	19.394
2200	19.544	100.180	84.417	34.679	- 213.799	- 185.056	18.383
2300	19.571	101.049	85.121	36.634	- 213.963	- 183.745	17.459
2400	19.595	101.883	85.802	38.593	- 214.133	- 182.428	16.612
2500	19.617	102.683	86.462	40.553	- 219.697	- 180.994	15.822
2600	19.635	103.453	87.100	42.516	- 219.870	- 179.443	15.083
2700	19.652	104.194	87.720	44.480	- 220.044	- 177.882	14.398
2800	19.668	104.909	88.321	46.446	- 220.221	- 176.319	13.762
2900	19.681	105.599	88.905	48.414	- 220.400	- 174.744	13.168
3000	19.694	106.267	89.473	50.383	- 220.582	- 173.173	12.615
3100	19.705	106.913	90.025	52.352	- 220.766	- 171.590	12.097
3200	19.715	107.539	90.562	54.323	- 220.953	- 170.001	11.610
3300	19.724	108.145	91.086	56.295	- 221.142	- 168.401	11.152
3400	19.733	108.734	91.597	58.268	- 221.334	- 166.799	10.721
3500	19.740	109.306	92.094	60.242	- 221.530	- 165.194	10.315
3600	19.748	109.863	92.580	62.216	- 221.727	- 163.581	9.930
3700	19.754	110.404	93.055	64.191	- 221.928	- 161.964	9.566
3800	19.760	110.931	93.518	66.167	- 222.131	- 160.339	9.221
3900	19.766	111.444	93.971	68.143	- 222.338	- 158.713	8.894
4000	19.771	111.945	94.414	70.120	- 343.726	- 154.934	8.465
4100	19.776	112.433	94.848	72.098	- 343.707	- 150.216	8.007
4200	19.780	112.909	95.272	74.076	- 343.690	- 145.490	7.570
4300	19.785	113.375	95.688	76.054	- 343.676	- 140.774	7.155
4400	19.789	113.830	96.095	78.032	- 343.667	- 136.055	6.758
4500	19.792	114.275	96.494	80.011	- 343.659	- 131.342	6.379
4600	19.796	114.710	96.885	81.991	- 343.653	- 126.623	6.016
4700	19.799	115.135	97.269	83.971	- 343.652	- 121.899	5.668
4800	19.802	115.552	97.646	85.951	- 343.653	- 117.179	5.335
4900	19.805	115.961	98.015	87.931	- 343.658	- 112.466	5.016
5000	19.807	116.361	98.378	89.912	- 343.665	- 107.747	4.709
5100	19.810	116.753	98.735	91.892	- 343.676	- 103.029	4.415
5200	19.812	117.138	99.085	93.874	- 343.688	- 98.308	4.132
5300	19.815	117.515	99.429	95.855	- 343.705	- 93.590	3.859
5400	19.817	117.885	99.768	97.836	- 343.726	- 88.873	3.597
5500	19.819	118.249	100.100	99.818	- 343.747	- 84.147	3.344
5600	19.821	118.606	100.428	101.800	- 343.774	- 79.431	3.100
5700	19.822	118.957	100.750	103.782	- 343.805	- 74.710	2.864
5800	19.824	119.302	101.066	105.765	- 343.837	- 69.990	2.637
5900	19.826	119.641	101.378	107.747	- 343.873	- 65.272	2.418
6000	19.827	119.974	101.686	109.730	- 343.914	- 60.546	2.205

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1964

BORON CHLORIDE DIFLUORIDE ($BClF_2$) (IDEAL GAS) MOL. WT. = 84.277

Point Group = C_{2v}

$S^\circ_{298.15}$ = 65.66 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -211 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -211.6 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1250 (1)	1430 (1)
697 (1)	366 (1)
429 (1)	608 (1)

Bond Distance: B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: F-B-Cl = [120°] F-B-F = [120°]

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 3567.6 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation.

The values for BCl_2F and $BClF_2$ of $\Delta H^\circ_{f\ 298.15} = -154$ and $\Delta H^\circ_{f\ 298.15} = -211.6$ kcal. mole^{-1}, respectively, are obtained from the average bond energies of BF_3 and BCl_3. The calculated values were each made less negative by about 0.8 kcal. mole^{-1} in order to make them consistent with the equilibrium measurements of T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Rossouw, J. Chem. Phys. 23, 1544 (1955) and S. R. Gunn and R. H. Sanborn, J. Chem. Phys. 33, 955 (1960) for the reaction

$$BF_3(g) + BCl_3(g) \rightarrow BClF_2(g) + BCl_2F(g).$$

Values for the heat of reaction are $\Delta H_{298.15} = +1.68$ kcal. mole^{-1} and $\Delta H_{298.15} = 1.1$ (uncertainty of -0.5 to +0.8) kcal. mole^{-1}, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta H_{298.15} = 1.6$ kcal. mole^{-1} fixes the sum of the heats of formation of $BClF_2$ and BCl_2F as -365.6 kcal. mole^{-1}, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 kcal. mole^{-1}.

Heat Capacity and Entropy.

The observed frequencies of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), were adjusted to the normal isotopic composition of 81.2% ^{10}B and 18.8% ^{11}B. The bond angles were assumed to be 120° and the bond lengths were taken to be the same as in the respective trihalides. As a result, the principal moments of inertia are: $I_A = 17.6044 \times 10^{-39}$, $I_B = 7.935 \times 10^{-39}$, and $I_C = 25.5394 \times 10^{-39}$ g. cm.^{2}.

Boron Oxide Chloride (BOCl)

(Ideal Gas) Mol. Wt. = 62.277

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.536	-75.709	-75.709	INFINITE
100	7.384	46.962	65.292	-1.833	-75.720	-76.072	166.247
200	9.382	52.692	57.665	-.995	-75.662	-76.443	83.529
298	10.765	56.720	56.720	.000	-75.600	-76.843	56.325
300	10.785	56.786	56.720	.020	-75.599	-76.851	55.983
400	11.642	60.015	57.154	1.144	-75.567	-77.275	42.219
500	12.241	62.681	58.001	2.340	-75.577	-77.701	33.961
600	12.703	64.955	58.075	3.588	-75.615	-78.122	28.455
700	13.069	66.942	59.074	4.877	-75.670	-78.536	24.519
800	13.363	68.707	60.957	6.199	-75.735	-78.942	21.565
900	13.599	70.295	61.908	7.548	-75.804	-79.339	19.265
1000	13.790	71.738	62.820	8.918	-75.880	-79.727	17.423
1100	13.945	73.060	63.692	10.305	-75.965	-80.108	15.915
1200	14.072	74.279	64.524	11.706	-76.057	-80.480	14.657
1300	14.176	75.409	65.318	13.118	-76.158	-80.845	13.591
1400	14.263	76.463	66.077	14.541	-76.267	-81.201	12.675
1500	14.336	77.450	66.803	15.971	-76.386	-81.551	11.881
1600	14.398	78.377	67.497	17.407	-76.515	-81.889	11.185
1700	14.450	79.251	68.163	18.850	-76.653	-82.220	10.570
1800	14.495	80.079	68.802	20.297	-76.801	-82.545	10.022
1900	14.534	80.864	69.417	21.749	-76.956	-82.860	9.531
2000	14.568	81.610	70.008	23.204	-77.117	-83.166	9.088
2100	14.597	82.321	70.577	24.662	-77.284	-83.463	8.686
2200	14.623	83.001	71.127	26.123	-77.458	-83.754	8.320
2300	14.645	83.652	71.657	27.587	-77.637	-84.038	7.985
2400	14.666	84.275	72.170	29.052	-77.823	-84.309	7.677
2500	14.683	84.874	72.666	30.520	-83.402	-84.467	7.384
2600	14.699	85.451	73.147	31.989	-83.592	-84.508	7.103
2700	14.714	86.006	73.613	33.460	-83.784	-84.539	6.843
2800	14.727	86.541	74.065	34.932	-83.979	-84.563	6.600
2900	14.738	87.058	74.505	36.405	-84.176	-84.578	6.374
3000	14.749	87.558	74.931	37.879	-84.376	-84.591	6.162
3100	14.758	88.042	75.346	39.355	-84.579	-84.596	5.964
3200	14.767	88.510	75.751	40.831	-84.785	-84.591	5.777
3300	14.775	88.965	76.144	42.308	-84.993	-84.582	5.601
3400	14.782	89.406	76.528	43.786	-85.204	-84.565	5.436
3500	14.789	89.835	76.902	45.264	-85.418	-84.548	5.279
3600	14.795	90.251	77.267	46.744	-85.634	-84.515	5.130
3700	14.801	90.657	77.623	48.224	-85.853	-84.483	4.990
3800	14.806	91.052	77.972	49.704	-86.075	-84.442	4.856
3900	14.811	91.436	78.312	51.185	-86.298	-84.397	4.729
4000	14.816	91.811	78.645	52.666	-207.704	-82.200	4.491
4100	14.820	92.177	78.970	54.148	-207.701	-79.064	4.214
4200	14.824	92.534	79.289	55.630	-207.699	-75.922	3.950
4300	14.827	92.883	79.601	57.113	-207.700	-72.786	3.699
4400	14.831	93.224	79.907	58.596	-207.704	-69.648	3.459
4500	14.834	93.557	80.207	60.079	-207.710	-66.511	3.230
4600	14.837	93.883	80.500	61.562	-207.717	-63.371	3.011
4700	14.840	94.203	80.788	63.046	-207.726	-60.236	2.801
4800	14.842	94.515	81.071	64.530	-207.738	-57.094	2.599
4900	14.845	94.821	81.349	66.015	-207.751	-53.960	2.407
5000	14.847	95.121	81.621	67.499	-207.766	-50.821	2.221
5100	14.849	95.415	81.889	68.984	-207.783	-47.679	2.043
5200	14.852	95.703	82.152	70.469	-207.801	-44.539	1.872
5300	14.853	95.986	82.410	71.954	-207.821	-41.401	1.707
5400	14.855	96.264	82.664	73.440	-207.843	-38.264	1.549
5500	14.857	96.537	82.914	74.926	-207.865	-35.119	1.395
5600	14.859	96.804	83.159	76.411	-207.891	-31.981	1.248
5700	14.860	97.067	83.401	77.897	-207.919	-28.839	1.106
5800	14.862	97.326	83.639	79.383	-207.948	-25.698	.968
5900	14.863	97.580	83.873	80.870	-207.979	-22.557	.836
6000	14.865	97.830	84.104	82.356	-208.012	-19.411	.707

Dec. 31, 1960; Sept. 30, 1963; Mar. 31, 1965

BORON OXIDE CHLORIDE (BOCl) (IDEAL GAS) MOL. WT. = 62.277

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [56.72] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -74.8 ± 7.0 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -75.6 ± 7.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[690] (1)

[400] (2)

[1850] (1)

Bond Distance: Cl-B = [1.75] Å B=O [1.20] Å

Bond Angle: Cl-B-O = [180]°

Rotational Constant: B_0 = [0.16504] cm.$^{-1}$

σ = 1

Heat of Formation.

The vapor-phase equilbria existing in the $B_2O_3 + BCl_3$ system were determined by an effusion method in the temperature range 1234-1389°K. by J. Blauer and M. Farber, Trans. Faraday Soc. 60, 301 (1964). Based on the equilibrium constants reported for the reaction $1/3\ B_2O_3(l) + 1/3\ BCl_3(g) = BOCl(g)$, the second and third law values of $\Delta H^\circ_{r\ 298.15}$ were evaluated as 57.7 and 56.3 kcal. mole^{-1}, respectively. The third law value for $\Delta H^\circ_{r\ 298.15}$ was adopted for the calculation of the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for BOCl(g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, $k_1 = 5.2 \times 10^5$, $k_2 = 16.7 \times 10^5$ dynes cm.$^{-1}$ and $k_\delta = 0.40 \times 10^{-11}$ dynes cm. rad.$^{-1}$ The B=O and B-Cl bond distances were assumed to be the same as those in BO(g) and $BCl_3(g)$, respectively. The moment of inertia is 1.6958×10^{-38} g. cm.^{2}

Boron Dichloride (BCl_2)

(Ideal Gas) Mol. Wt. = 81.734

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.775	-20.289	-20.289	INFINITE
100	8.756	54.374	73.950	-1.958	-20.179	-21.089	46.088
200	9.898	60.810	65.923	-1.023	-20.045	-22.058	24.102
298	10.919	64.956	64.956	.000	-20.000	-23.060	16.903
300	10.937	65.024	64.957	.020	-20.000	-23.080	16.813
400	11.758	68.289	65.396	1.157	-20.015	-24.105	13.170
500	12.331	70.979	66.252	2.363	-20.075	-25.122	10.980
600	12.721	73.263	67.235	3.617	-20.165	-26.122	9.515
700	12.990	75.246	68.241	4.904	-20.272	-27.107	8.463
800	13.181	76.993	69.228	6.213	-20.394	-28.076	7.670
900	13.320	78.554	70.179	7.538	-20.525	-29.028	7.049
1000	13.424	79.963	71.088	8.875	-20.667	-29.966	6.549
1100	13.503	81.247	71.954	10.222	-20.821	-30.889	6.137
1200	13.565	82.424	72.778	11.575	-20.987	-31.796	5.791
1300	13.613	83.512	73.562	12.934	-21.164	-32.691	5.496
1400	13.653	84.522	74.310	14.298	-21.351	-33.569	5.240
1500	13.685	85.466	75.022	15.665	-21.551	-34.438	5.017
1600	13.711	86.350	75.703	17.035	-21.762	-35.289	4.820
1700	13.734	87.182	76.354	18.407	-21.984	-36.126	4.644
1800	13.752	87.967	76.977	19.781	-22.216	-36.952	4.486
1900	13.768	88.711	77.576	21.157	-22.455	-37.763	4.344
2000	13.782	89.418	78.150	22.535	-22.701	-38.563	4.214
2100	13.794	90.090	78.703	23.914	-22.952	-39.349	4.095
2200	13.804	90.732	79.235	25.293	-23.211	-40.124	3.986
2300	13.813	91.346	79.749	26.674	-23.474	-40.887	3.885
2400	13.821	91.934	80.244	28.056	-23.743	-41.637	3.791
2500	13.828	92.498	80.723	29.438	-29.406	-42.268	3.695
2600	13.834	93.041	81.186	30.821	-29.678	-42.779	3.596
2700	13.839	93.563	81.635	32.205	-29.952	-43.276	3.503
2800	13.844	94.066	82.070	33.589	-30.229	-43.764	3.416
2900	13.849	94.552	82.492	34.974	-30.507	-44.241	3.334
3000	13.853	95.022	82.902	36.359	-30.788	-44.714	3.257
3100	13.856	95.476	83.301	37.744	-31.072	-45.173	3.185
3200	13.860	95.916	83.688	39.130	-31.358	-45.623	3.116
3300	13.863	96.343	84.065	40.516	-31.647	-46.064	3.051
3400	13.866	96.757	84.432	41.903	-31.937	-46.496	2.989
3500	13.868	97.159	84.790	43.290	-32.231	-46.924	2.930
3600	13.870	97.549	85.139	44.676	-32.528	-47.334	2.873
3700	13.873	97.929	85.480	46.064	-32.826	-47.741	2.820
3800	13.875	98.299	85.812	47.451	-33.127	-48.141	2.769
3900	13.876	98.660	86.137	48.838	-33.431	-48.535	2.720
4000	13.878	99.011	86.454	50.226	-154.916	-46.772	2.555
4100	13.880	99.354	86.765	51.614	-154.992	-44.070	2.349
4200	13.881	99.688	87.069	53.002	-155.070	-41.359	2.152
4300	13.882	100.015	87.366	54.390	-155.150	-38.654	1.965
4400	13.884	100.334	87.657	55.779	-155.232	-35.940	1.785
4500	13.885	100.646	87.942	57.167	-155.317	-33.232	1.614
4600	13.886	100.951	88.222	58.556	-155.401	-30.516	1.450
4700	13.887	101.250	88.496	59.944	-155.489	-27.799	1.293
4800	13.888	101.542	88.765	61.333	-155.578	-25.080	1.142
4900	13.889	101.829	89.028	62.722	-155.669	-22.365	.997
5000	13.890	102.109	89.287	64.111	-155.760	-19.640	.858
5100	13.891	102.384	89.541	65.500	-155.853	-16.914	.725
5200	13.891	102.654	89.791	66.889	-155.947	-14.190	.596
5300	13.892	102.919	90.036	68.278	-156.043	-11.469	.473
5400	13.893	103.178	90.277	69.667	-156.141	-8.737	.354
5500	13.893	103.433	90.514	71.057	-156.238	-6.000	.238
5600	13.894	103.684	90.747	72.446	-156.338	-3.279	.128
5700	13.895	103.930	90.976	73.835	-156.441	-.546	.021
5800	13.895	104.171	91.201	75.225	-156.543	2.197	-.083
5900	13.896	104.409	91.423	76.615	-156.647	4.930	-.183
6000	13.896	104.642	91.642	78.004	-156.754	7.676	-.280

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964

BORON DICHLORIDE (BCl_2) (IDEAL GAS) MOL. WT. = 81.734

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [64.956] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [2]

$\Delta H_f^\circ{}_0$ = [-20.3 ± 15] kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [-20 ± 15] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[720](1)
[240](1)
[980](1)

Bond Distance: B-Cl = [1.73] Å

Bond Angle: Cl-B-Cl = [120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ =[8.49841 X 10^{-115}]g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by analogy with BF_3, specifically the ratio

$$\Delta H_r(BX_3 \rightarrow BX_2 + X) \;/\; \Delta H_r(BX_3 \rightarrow B + 3X)$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trichloride given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trichlorides and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were I_B = 1.1661 X 10^{-39} g. cm.^{2}, I_A = 26.4189 X 10^{-39} g. cm.^{2} and I_C = 27.5851 X 10^{-39} g. cm.^{2}

Boron Dichloride Unipositive Ion (BCl_2^+)

(Ideal Gas) GFW = 81.71645

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	12.661	61.590	61.590	.000	148.000	144.456	-105.889
300	12.678	61.668	61.590	.023	148.012	144.434	-105.220
400	13.402	65.423	62.097	1.330	148.664	143.141	-78.209
500	13.846	68.465	63.076	2.695	149.260	141.691	-61.933
600	14.128	71.017	64.193	4.094	149.812	140.125	-51.040
700	14.313	73.209	65.328	5.517	150.337	138.468	-43.232
800	14.441	75.129	66.435	6.955	150.841	136.737	-37.355
900	14.532	76.836	67.498	8.404	151.331	134.945	-32.769
1000	14.599	78.371	68.510	9.861	151.806	133.098	-29.089
1100	14.650	79.764	69.471	11.323	152.264	131.205	-26.068
1200	14.689	81.041	70.382	12.790	152.709	129.272	-23.544
1300	14.720	82.218	71.248	14.261	153.140	127.300	-21.401
1400	14.745	83.310	72.071	15.734	153.559	125.298	-19.560
1500	14.765	84.328	72.855	17.210	153.965	123.263	-17.959
1600	14.781	85.281	73.602	18.687	154.358	121.204	-16.556
1700	14.795	86.178	74.315	20.166	154.740	119.122	-15.314
1800	14.807	87.024	74.998	21.646	155.110	117.013	-14.207
1900	14.818	87.825	75.652	23.127	155.473	114.890	-13.215
2000	14.827	88.585	76.280	24.609	155.828	112.745	-12.320
2100	14.836	89.309	76.883	26.093	156.179	110.580	-11.508
2200	14.844	89.999	77.464	27.577	156.522	108.401	-10.769
2300	14.853	90.659	78.023	29.061	156.858	106.206	-10.092
2400	14.861	91.291	78.563	30.547	157.190	103.999	-9.470
2500	14.870	91.898	79.085	32.034	152.129	101.884	-8.907
2600	14.879	92.481	79.589	33.521	152.458	99.867	-8.395
2700	14.889	93.043	80.077	35.009	152.785	97.840	-7.920
2800	14.899	93.585	80.549	36.499	153.111	95.798	-7.477
2900	14.911	94.108	81.008	37.989	153.434	93.747	-7.065
3000	14.923	94.614	81.453	39.481	153.757	91.680	-6.679
3100	14.936	95.103	81.886	40.974	154.078	89.604	-6.317
3200	14.950	95.577	82.306	42.468	154.397	87.522	-5.977
3300	14.965	96.038	82.715	43.964	154.715	85.429	-5.658
3400	14.981	96.485	83.114	45.461	155.031	83.326	-5.356
3500	14.997	96.919	83.502	46.960	155.346	81.209	-5.071
3600	15.015	97.342	83.881	48.461	155.661	79.089	-4.801
3700	15.033	97.754	84.250	49.963	155.974	76.955	-4.546
3800	15.052	98.155	84.611	51.467	156.287	74.817	-4.303
3900	15.072	98.546	84.963	52.973	156.599	72.668	-4.072
4000	15.092	98.928	85.307	54.482	35.731	72.656	-3.970
4100	15.113	99.301	85.644	55.992	36.274	73.569	-3.922
4200	15.134	99.665	85.974	57.504	36.817	74.478	-3.876
4300	15.156	100.021	86.296	59.019	37.361	75.367	-3.831
4400	15.178	100.370	86.612	60.535	37.903	76.249	-3.787
4500	15.200	100.711	86.922	62.054	38.445	77.107	-3.745
4600	15.222	101.046	87.225	63.575	38.990	77.963	-3.704
4700	15.245	101.373	87.523	65.099	39.535	78.806	-3.664
4800	15.267	101.695	87.815	66.624	40.079	79.633	-3.626
4900	15.290	102.010	88.101	68.152	40.624	80.453	-3.588
5000	15.313	102.319	88.382	69.682	41.170	81.262	-3.552
5100	15.335	102.622	88.659	71.215	41.718	82.058	-3.516
5200	15.358	102.920	88.930	72.749	42.266	82.846	-3.482
5300	15.380	103.213	89.197	74.286	42.815	83.615	-3.448
5400	15.402	103.501	89.459	75.825	43.364	84.379	-3.415
5500	15.424	103.783	89.717	77.367	43.916	85.141	-3.383
5600	15.446	104.062	89.970	78.910	44.466	85.875	-3.351
5700	15.467	104.335	90.220	80.456	45.017	86.615	-3.321
5800	15.488	104.604	90.466	82.003	45.569	87.339	-3.291
5900	15.509	104.869	90.708	83.553	46.122	88.052	-3.262
6000	15.530	105.130	90.946	85.105	46.675	88.765	-3.233

June 30, 1968

BORON DICHLORIDE UNIPOSITIVE ION (BCl_2^+) (IDEAL GAS) GFW = 81.71645

Point Group [$D_{\infty h}$] ΔHf°_0 = 147.4 ± 5 kcal/mol

$S^\circ_{298.15}$ = [61.6 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 148.0 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[16000]	1
$^1A_1$	[35000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[500] (1)
[150] (2)
[800] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [180°] σ = 2

Rotational Constant: B_0 = [0.0785] cm^{-1}

Heat of Formation

The appearance potential (AP) of the positive ion fragment BCl_2^+(g) from BCl_3(g) was determined mass spectrometrically by Osberghaus (1), Marriott (2), and Koski (3) as 13.2 ± 0.5, 13.01 ± 0.02, and 11.8 ± 0.2 eV, respectively. From the reaction $BCl_3 + e^- = BCl_2^+ + Cl + 2e^-$, the corresponding values of ΔHf°_{298} for BCl_2^+(g) are derived to be 180.4 ± 11.5, 176.0 ± 0.5, and 148.1 ± 4.6 kcal/ mol, using ΔHf°_0 = -96.078 and 28.520 kcal/mol for BCl_3(g) and Cl(g). The value of ΔHf°_{298} for BCl_2^+(g) is adopted as 148 ± 5 kcal/mol, since the lowest value is likely to have the least excess kinetic energy in the fragments.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) predictions for 16 valence electron XY_2 molecules. The electronic states, levels and vibrational frequenceis are estimated by comparison with those for CO_2 (5). The B-Cl bond distance is estimated using the method of Krasnov (6). The moment of inertia is 3.564 x 10^{-38} g cm^2. The enthalpy at 0°K is -3.07 kcal/mol.

References

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3. W. S. Kocki, J. J. Kaufman, and C. F. Pachucki, J. Am. Chem. Soc. 81, 1326 (1959).
4. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
6. K. S. Krasnov, Zh. Strukt, Khim. 1, 209 (1960).

Boron Dichloride Uninegative Ion (BCl_2^-)

(Ideal Gas) GFW = 81.71755

		gibbs/mol			kcal/mol		
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.863	63.549	63.549	.000	-26.000	-27.153	19.904
300	10.880	63.616	63.549	.020	-26.009	-27.161	19.786
400	11.707	66.865	63.986	1.152	-26.526	-27.468	15.008
500	12.296	69.545	64.838	2.354	-27.087	-27.639	12.081
600	12.724	71.826	65.817	3.605	-27.677	-27.694	10.088
700	13.070	73.814	66.820	4.896	-28.276	-27.649	8.632
800	13.389	75.580	67.807	6.219	-28.881	-27.519	7.518
900	13.704	77.176	68.761	7.573	-29.480	-27.313	6.633
1000	14.021	78.636	69.676	8.960	-30.069	-27.040	5.910
1100	14.334	79.987	70.553	10.377	-30.650	-26.710	5.307
1200	14.632	81.247	71.392	11.826	-31.217	-26.327	4.795
1300	14.904	82.429	72.196	13.303	-31.772	-25.896	4.354
1400	15.144	83.543	72.967	14.806	-32.317	-25.423	3.969
1500	15.346	84.595	73.708	16.330	-32.857	-24.914	3.630
1600	15.509	85.591	74.420	17.873	-33.392	-24.365	3.328
1700	15.634	86.535	75.105	19.431	-33.925	-23.784	3.058
1800	15.723	87.431	75.765	20.999	-34.459	-23.173	2.814
1900	15.780	88.283	76.401	22.574	-34.996	-22.531	2.592
2000	15.810	89.093	77.016	24.154	-35.537	-21.861	2.389
2100	15.818	89.865	77.609	25.736	-36.082	-21.163	2.202
2200	15.806	90.600	78.183	27.317	-36.636	-20.440	2.031
2300	15.780	91.302	78.739	28.896	-37.197	-19.690	1.871
2400	15.742	91.973	79.276	30.473	-37.768	-18.917	1.723
2500	15.696	92.615	79.797	32.045	-43.738	-18.010	1.574
2600	15.644	93.229	80.302	33.612	-44.323	-16.970	1.426
2700	15.588	93.819	80.792	35.173	-44.917	-15.907	1.288
2800	15.529	94.385	81.267	36.729	-45.519	-14.822	1.157
2900	15.470	94.929	81.729	38.279	-46.128	-13.713	1.033
3000	15.410	95.452	82.178	39.823	-46.747	-12.586	.917
3100	15.352	95.956	82.614	41.361	-47.375	-11.438	.806
3200	15.294	96.443	83.039	42.893	-48.012	-10.270	.701
3300	15.238	96.913	83.452	44.420	-48.657	-9.079	.601
3400	15.185	97.367	83.855	45.941	-49.309	-7.869	.506
3500	15.133	97.806	84.247	47.457	-49.971	-6.645	.415
3600	15.084	98.232	84.630	48.968	-50.640	-5.394	.327
3700	15.038	98.644	85.003	50.474	-51.317	-4.125	.244
3800	14.994	99.045	85.367	51.976	-52.000	-2.843	.164
3900	14.952	99.434	85.723	53.473	-52.691	-1.542	.086
4000	14.913	99.812	86.070	54.966	-174.567	1.926	-.105
4100	14.876	100.180	86.410	56.456	-175.038	6.343	-.338
4200	14.841	100.538	86.742	57.941	-175.516	10.773	-.561
4300	14.809	100.887	87.067	59.424	-175.998	15.212	-.773
4400	14.778	101.227	87.385	60.903	-176.487	19.667	-.977
4500	14.750	101.558	87.696	62.380	-176.979	24.128	-1.172
4600	14.723	101.882	88.001	63.853	-177.476	28.603	-1.359
4700	14.698	102.199	88.300	65.324	-177.978	33.092	-1.539
4800	14.674	102.508	88.593	66.793	-178.484	37.589	-1.711
4900	14.652	102.810	88.880	68.259	-178.995	42.092	-1.877
5000	14.632	103.106	89.161	69.723	-179.507	46.608	-2.037
5100	14.613	103.396	89.438	71.186	-180.023	51.141	-2.192
5200	14.595	103.679	89.709	72.646	-180.543	55.677	-2.340
5300	14.578	103.957	89.975	74.105	-181.066	60.222	-2.483
5400	14.562	104.229	90.236	75.562	-181.593	64.780	-2.622
5500	14.548	104.496	90.493	77.017	-182.122	69.352	-2.756
5600	14.534	104.758	90.746	78.471	-182.653	73.926	-2.885
5700	14.521	105.016	90.994	79.924	-183.189	78.506	-3.010
5800	14.509	105.268	91.238	81.376	-183.726	83.108	-3.132
5900	14.498	105.516	91.478	82.826	-184.267	87.712	-3.249
6000	14.487	105.760	91.714	84.275	-184.811	92.326	-3.363

June 30, 1968; Dec. 31, 1968

BORON DICHLORIDE UNINEGATIVE ION (BCl_2^-) (IDEAL GAS) GFW = 81.71755

Point Group $[C_{2v}]$

$\Delta Hf_0° = [-26 \pm 30]$ kcal/mol

$S°_{298.15} = [63.5 \pm 2]$ gibbs/mol

$\Delta Hf°_{298.15} = [-26 \pm 30]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[4000]	3
[20000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[740] (1)
[245] (1)
[990] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [120°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = [8.798 \times 10^{-115}]\ g^3\ cm^6$

Heat of Formation

The electron captured by BCl_2 should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus one expects a small electron affinity. In fact one reasonable estimate of the dissociation energy yields a negative electron affinity (EA). Consider the isoelectronic reactions $BCl_2^- \rightarrow B^- + 2Cl$ and $CCl_2 \rightarrow C + 2Cl$, if we make the assumption that these binding energies are the same then $\Delta Hf°_{298}(BCl_2^-, g) = 12$ kcal/mol or $EA(BCl_2) = -32$ kcal. Another possible estimate is obtained from the isoelectronic reactions $BCl_2^- \rightarrow BCl + Cl^-$ and $BClAr \rightarrow BCl + Ar$, although the latter reaction is unknown we expect a zero bond strength; applying this to the first reaction yields $\Delta Hf°_{298}(BCl_2^-, g) = -22$ kcal/mol or $EA(BCl_2) = 2$ kcal.

In consideration of the above arguments we choose $EA(BCl_2) = EA(B, g) = 6$ kcal (2) which gives $\Delta Hf°_{298}(BCl_2^-, g) = -26$ kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be bent using the correlations of A. D. Walsh (1) for 18 valence electron XY_2 molecules. The B-Cl bond distance is estimated using the method of Krasnov (3). The Cl-B-Cl bond angle is taken as 120°. The electronic levels, quantum weights and vibrational frequencies are estimated by comparison with those for CF_2(4) and other related isoelectronic molecules. The three principal moments of inertia are $I_A = 1.179 \times 10^{-39}$, $I_B = 2.673 \times 10^{-38}$ and $I_C = 2.791 \times 10^{-38}$ g cm². The enthalpy at 0°K is -2.76 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
4. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.

Boron Dichloride Fluoride

(Ideal Gas) Mol. Wt. = 100.734

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.171	-153.630	-153.630	INFINITE
100	9.078	56.280	79.785	-2.350	-153.864	-152.930	334.213
200	12.037	63.512	69.962	-1.290	-153.954	-151.953	166.039
298	14.117	68.732	68.732	.000	-154.000	-150.964	110.654
300	14.149	68.819	68.732	.026	-154.001	-150.945	109.958
400	15.616	73.103	69.306	1.519	-154.045	-149.920	81.909
500	16.651	76.705	70.435	3.135	-154.099	-148.882	65.073
600	17.385	79.810	71.745	4.839	-154.155	-147.834	53.846
700	17.912	82.537	73.096	6.605	-154.208	-146.776	45.823
800	18.297	84.950	74.429	8.417	-154.260	-145.712	39.805
900	18.584	87.122	75.721	10.261	-154.310	-144.640	35.122
1000	18.801	89.092	76.961	12.131	-154.362	-143.563	31.374
1100	18.970	90.892	78.147	14.020	-154.420	-142.481	28.307
1200	19.103	92.549	79.279	15.924	-154.483	-141.392	25.750
1300	19.209	94.082	80.359	17.840	-154.555	-140.299	23.585
1400	19.295	95.509	81.391	19.765	-154.634	-139.198	21.729
1500	19.365	96.842	82.377	21.698	-154.724	-138.093	20.119
1600	19.424	98.094	83.321	23.638	-154.822	-136.981	18.710
1700	19.473	99.273	84.225	25.582	-154.931	-135.861	17.465
1800	19.515	100.388	85.092	27.532	-155.048	-134.740	16.359
1900	19.550	101.444	85.925	29.485	-155.172	-133.606	15.367
2000	19.581	102.447	86.726	31.442	-155.303	-132.466	14.474
2100	19.607	103.403	87.498	33.401	-155.438	-131.322	13.666
2200	19.630	104.316	88.242	35.363	-155.581	-130.171	12.931
2300	19.650	105.189	88.960	37.327	-155.729	-129.012	12.258
2400	19.668	106.026	89.653	39.293	-155.883	-127.847	11.641
2500	19.684	106.829	90.325	41.260	-161.431	-126.567	11.064
2600	19.698	107.601	90.974	43.230	-161.588	-125.168	10.521
2700	19.710	108.345	91.604	45.200	-161.748	-123.764	10.018
2800	19.721	109.062	92.215	47.172	-161.911	-122.355	9.550
2900	19.731	109.754	92.808	49.144	-162.076	-120.937	9.114
3000	19.741	110.423	93.384	51.118	-162.245	-119.519	8.707
3100	19.749	111.070	93.944	53.092	-162.417	-118.091	8.325
3200	19.756	111.698	94.489	55.068	-162.592	-116.661	7.967
3300	19.763	112.306	95.020	57.044	-162.770	-115.221	7.630
3400	19.769	112.896	95.537	59.020	-162.951	-113.775	7.313
3500	19.775	113.469	96.041	60.997	-163.137	-112.329	7.014
3600	19.781	114.026	96.533	62.975	-163.325	-110.871	6.730
3700	19.785	114.568	97.013	64.954	-163.516	-109.411	6.462
3800	19.790	115.096	97.482	66.932	-163.711	-107.948	6.208
3900	19.794	115.610	97.940	68.911	-163.909	-106.480	5.967
4000	19.798	116.111	98.388	70.891	-285.289	-102.857	5.620
4100	19.801	116.600	98.826	72.871	-285.262	-98.300	5.240
4200	19.805	117.077	99.255	74.851	-285.237	-93.736	4.877
4300	19.808	117.543	99.675	76.832	-285.215	-89.178	4.532
4400	19.811	117.999	100.087	78.813	-285.197	-84.618	4.203
4500	19.813	118.444	100.490	80.794	-285.181	-80.064	3.888
4600	19.816	118.879	100.885	82.776	-285.166	-75.502	3.587
4700	19.818	119.306	101.272	84.757	-285.155	-70.946	3.299
4800	19.821	119.723	101.652	86.739	-285.147	-66.387	3.023
4900	19.823	120.131	102.025	88.721	-285.142	-61.826	2.757
5000	19.825	120.532	102.391	90.704	-285.137	-57.272	2.503
5100	19.827	120.925	102.751	92.686	-285.136	-52.716	2.259
5200	19.828	121.310	103.104	94.669	-285.136	-48.156	2.024
5300	19.830	121.687	103.451	96.652	-285.139	-43.599	1.798
5400	19.831	122.058	103.792	98.635	-285.145	-39.046	1.580
5500	19.833	122.422	104.128	100.618	-285.152	-34.481	1.370
5600	19.834	122.779	104.458	102.602	-285.162	-29.928	1.168
5700	19.836	123.130	104.782	104.585	-285.176	-25.370	.973
5800	19.837	123.475	105.101	106.569	-285.191	-20.809	.784
5900	19.838	123.814	105.416	108.553	-285.208	-16.254	.602
6000	19.839	124.148	105.725	110.536	-285.229	-11.695	.426

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1964

BORON DICHLORIDE FLUORIDE (BCl_2F) (IDEAL GAS) MOL. WT. = 100.734

Point Group = C_{2v}

$S^\circ_{298.15}$ = 68.73 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -154 ± 5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -154 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1320 (1)	1000 (1)
[554] (1)	[339] (1)
[266] (1)	528 (1)

Bond Distance: B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: Cl-B-Cl = [120°] F-B-Cl = [120°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 12020 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

The values for BCl_2F and $BClF_2$ of $\Delta H_f^\circ{}_{298.15}$ = -154 and $\Delta H_f^\circ{}_{298.15}$ = -211.6 kcal. mole^{-1}, respectively, are obtained from the average bond energies of BF_3 and BCl_3. The calculated values were each made less negative by about 0.8 kcal. mole^{-1} in order to make them consistent with the equilibrium measurements of T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Rossouw, J. Chem. Phys. 23, 1544 (1955) and S. R. Gunn and R. H. Sanborn, J. Chem. Phys. 33, 955 (1960) for the reaction

$$BF_3(g) + BCl_3(g) \rightarrow BClF_2(g) + BCl_2F(g).$$

Values for the heat of reaction are $\Delta H_{298.15}$ = +1.68 kcal. mole^{-1} and $\Delta H_{298.15}$ = 1.1 (uncertainty of -0.5 to +0.8) kcal. mole^{-1}, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta H_{298.15}$ = 1.6 kcal. mole^{-1} fixes the sum of the heats of formation of $BClF_2$ and BCl_2F as -365.6 kcal. mole^{-1}, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 kcal. mole^{-1}.

Heat Capacity and Entropy.

The spectroscopic constants are based on the work of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), who observed ν_1, ν_4, and ν_6 and calculated ν_2, ν_3, and ν_5. The frequencies were adjusted to the normal isotopic composition of 81.2% ^{11}B and 18.8% ^{10}B. The bond angles were taken to be 120° while the bond lengths were assumed to be the same as in the respective trihalides. As a result, the principal moments of inertia are I_A = 11.8748 X 10^{-39}, I_B = 26.4268 X 10^{-39}, and I_C = 38.3016 X 10^{-39} g. cm.^{2}.

Boron Dichloride Hydride (BCl_2H)

(Ideal Gas) Mol. Wt. = 82.72497

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.807	-58.609	-58.609	INFINITE
100	8.521	53.399	73.385	-1.999	-58.887	-58.481	127.809
200	10.035	59.744	65.118	-1.075	-59.066	-58.013	63.394
298	11.865	64.092	64.092	.000	-59.300	-57.450	42.112
300	11.898	64.165	64.092	.022	-59.305	-57.439	41.844
400	13.499	67.818	64.579	1.295	-59.530	-56.783	31.025
500	14.686	70.964	65.549	2.708	-59.733	-56.071	24.509
600	15.564	73.723	66.686	4.222	-59.913	-55.321	20.151
700	16.236	76.175	67.870	5.814	-60.066	-54.544	17.029
800	16.768	78.379	69.048	7.465	-60.199	-53.747	14.683
900	17.198	80.380	70.197	9.164	-60.312	-52.933	12.854
1000	17.551	82.210	71.309	10.902	-60.412	-52.107	11.388
1100	17.843	83.897	72.377	12.672	-60.506	-51.273	10.187
1200	18.088	85.461	73.403	14.469	-60.595	-50.429	9.184
1300	18.294	86.917	74.387	16.288	-60.684	-49.579	8.335
1400	18.469	88.279	75.331	18.127	-60.773	-48.720	7.606
1500	18.617	89.559	76.238	19.981	-60.869	-47.858	6.973
1600	18.745	90.764	77.108	21.849	-60.971	-46.986	6.418
1700	18.855	91.904	77.945	23.730	-61.078	-46.107	5.927
1800	18.950	92.984	78.751	25.620	-61.192	-45.224	5.491
1900	19.033	94.011	79.528	27.519	-61.311	-44.332	5.099
2000	19.106	94.990	80.276	29.426	-61.435	-43.437	4.747
2100	19.170	95.923	80.999	31.340	-61.563	-42.533	4.426
2200	19.226	96.816	81.698	33.260	-61.698	-41.624	4.135
2300	19.277	97.672	82.374	35.185	-61.836	-40.708	3.868
2400	19.321	98.494	83.029	37.115	-61.980	-39.786	3.623
2500	19.361	99.283	83.663	39.049	-67.519	-38.750	3.388
2600	19.397	100.043	84.279	40.987	-67.666	-37.595	3.160
2700	19.429	100.776	84.876	42.929	-67.816	-36.437	2.949
2800	19.459	101.483	85.457	44.873	-67.969	-35.272	2.753
2900	19.485	102.166	86.021	46.820	-68.124	-34.098	2.570
3000	19.509	102.827	86.571	48.770	-68.282	-32.926	2.399
3100	19.531	103.467	87.105	50.722	-68.443	-31.745	2.238
3200	19.551	104.088	87.626	52.676	-68.608	-30.560	2.087
3300	19.569	104.690	88.134	54.632	-68.776	-29.366	1.945
3400	19.586	105.274	88.630	56.590	-68.947	-28.168	1.811
3500	19.601	105.842	89.114	58.549	-69.123	-26.969	1.684
3600	19.616	106.394	89.586	60.510	-69.302	-25.758	1.564
3700	19.629	106.932	90.048	62.472	-69.485	-24.547	1.450
3800	19.641	107.456	90.499	64.436	-69.671	-23.332	1.342
3900	19.652	107.966	90.940	66.400	-69.861	-22.109	1.239
4000	19.663	108.464	91.372	68.366	-191.234	-18.738	1.024
4100	19.673	108.949	91.795	70.333	-191.200	-14.426	.769
4200	19.682	109.424	92.209	72.301	-191.168	-10.115	.526
4300	19.690	109.887	92.615	74.269	-191.140	-5.806	.295
4400	19.698	110.340	93.013	76.239	-191.116	-1.494	.074
4500	19.706	110.782	93.403	78.209	-191.096	2.813	-.137
4600	19.713	111.215	93.785	80.180	-191.077	7.126	-.339
4700	19.719	111.639	94.160	82.151	-191.062	11.437	-.532
4800	19.725	112.055	94.529	84.124	-191.050	15.741	-.717
4900	19.731	112.461	94.891	86.096	-191.042	20.052	-.894
5000	19.737	112.860	95.246	88.070	-191.035	24.357	-1.065
5100	19.742	113.251	95.595	90.044	-191.032	28.669	-1.229
5200	19.747	113.634	95.939	92.018	-191.030	32.978	-1.386
5300	19.751	114.011	96.276	93.993	-191.032	37.278	-1.537
5400	19.755	114.380	96.608	95.968	-191.038	41.586	-1.683
5500	19.760	114.742	96.934	97.944	-191.045	45.903	-1.824
5600	19.763	115.098	97.256	99.920	-191.055	50.204	-1.959
5700	19.767	115.448	97.572	101.897	-191.070	54.512	-2.090
5800	19.771	115.792	97.883	103.874	-191.086	58.822	-2.216
5900	19.774	116.130	98.189	105.851	-191.105	63.129	-2.338
6000	19.777	116.462	98.491	107.829	-191.127	67.443	-2.457

Mar. 31, 1966

BORON DICHLORIDE HYDRIDE (BCl_2H) (IDEAL GAS) MOL. WT. = 82.72497

Point Group C_{2v}

$S^\circ_{298.15}$ = [64.1] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -58.6 ± 1 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -59.3 ± 1 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[2610](1)	1091 (1)
744 (1)	[894](1)
[287](1)	786 (1)

Bond Distance: B-H = 1.13 ± 0.2 Å B-Cl = [1.75] Å

Bond Angle: Cl-B-Cl = 119.7 ± 3° Cl-B-H = 120.15 ± 1.5° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 1.39215 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The chemical equilibria for the following two reactions: (A) $BCl_3(g) + H_2(g) = BHCl_2(g) + HCl(g)$, and (B) $6BHCl_2(g) = B_2H_6(g) + 4BCl_3(l, g)$ were investigated by (1) J. H. Murib, D. Horvitz, and C. A. Bonecutter, Ind. Eng. Chem. Prod. Res. Develop. 4, 273 (1965); (2) P. H. Mook, G. R. Seiler, and E. R. Watson, "Process Development, Prepilot and Pilot Plant Investigations - High Energy Boron Fuels," ASDTR 62-7-558 A, Vol. IV, March 1962; and (3) L. Lynds and C. D. Bass, Inorg. Chem. 3, 1147 (1964). Using the reported equilibrium constants, the corresponding enthalpy changes and the respective $\Delta H_f^\circ{}_{298.15}$ values were evaluated. The results obtained are presented as follows.

Reaction	Temperature, °K.	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1} Third Law Value	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1} Second Law Value	$\Delta H_f^\circ{}_{298.15}$* kcal. mole^{-1}	Reference
A	873 - 973	16.19	15.57 ± 0.8	-58.06 ± 0.5	(1)
A	1073 -1273	13.91	13.50 ± 3.0	-60.3 ± 0.7	(2)
B	273	-17.85	——	-59.6	(1)
B	298	-19.09	——	-59.4	(3)

*Based on the third law value of $\Delta H_r^\circ{}_{298.15}$.

The value of $\Delta H_f^\circ{}_{298.15}$ for $BHCl_2(g)$ is selected as -59.3 ± 1 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and Cl-B-Cl bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. 40, 1590 (1964). The B-Cl bond distance was assumed to be the same as that in $BCl_3(g)$. The vibrational frequencies adopted were reported by C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, J. Chem. Phys. 40, 3611 (1964), and corrected to the average isotopic species. It has been pointed out that the complete assignment of the infrared spectra of $HBCl_2(g)$ is quite difficult due to the unavoidable presence of $BCl_3(g)$. The adopted frequencies were obtained using the Green's function and partitioning techniques, taking $HBCl_2$ as an "isotopic" species of BCl_3. An excellent agreement between the calculated and observed spectra reported by L. Lynds and C. D. Bass, loc. cit. was claimed. Spectra of the mixture of BCl_3, $HBCl_2$ and $DBCl_2$ are quite complex and have been observed by L. Lynds and D. R. Stern, J. Am. Chem. Soc. 81, 5006 (1959), H. G. Nadean and D. M. Oaks, Jr., Anal. Chem. 32, 1481 (1961), and H. W. Mayers and R. F. Putnam, Inorg. Chem. 2, 655 (1963) and only three bands were correlated with $HBCl_2$. Analysis of infrared data from previous works, according to the conventional Wilson's method of symmetry coordinates, has been undertaken by O. B. de Mandirola and J. F. Westerkamp, Spectrochim. Acta, 20, 1633 (1964). Based on four observed frequencies, a set of six frequencies was derived and assigned. The three principal moments of inertia are: $I_A = 2.6960 \times 10^{-38}$, $I_B = 1.7957 \times 10^{-39}$ and $I_C = 2.87557 \times 10^{-38}$ g. cm.^{2}

Boron Trichloride (BCl_3)

(Ideal Gas) Mol. Wt. = 117.191

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.351	-96.078	-96.078	INFINITE
100	9.725	56.006	81.104	-2.510	-96.294	-95.108	207.849
200	12.866	63.783	70.632	-1.370	-96.316	-93.908	102.612
298	14.912	69.328	69.328	.000	-96.310	-92.730	67.969
300	14.944	69.420	69.328	.028	-96.310	-92.708	67.534
400	16.353	73.926	69.933	1.597	-96.307	-91.508	49.995
500	17.298	77.683	71.118	3.283	-96.314	-90.306	39.471
600	17.935	80.897	72.486	5.047	-96.329	-89.103	32.454
700	18.373	83.697	73.892	6.863	-96.345	-87.898	27.442
800	18.684	86.172	75.275	8.717	-96.366	-86.692	23.682
900	18.910	88.386	76.611	10.597	-96.386	-85.480	20.756
1000	19.079	90.388	77.891	12.497	-96.412	-84.268	18.416
1100	19.208	92.212	79.111	14.412	-96.447	-83.051	16.500
1200	19.308	93.888	80.273	16.338	-96.490	-81.832	14.903
1300	19.388	95.437	81.381	18.273	-96.542	-80.609	13.551
1400	19.452	96.876	82.437	20.215	-96.603	-79.380	12.391
1500	19.504	98.220	83.445	22.163	-96.675	-78.149	11.386
1600	19.547	99.480	84.408	24.115	-96.758	-76.910	10.505
1700	19.583	100.666	85.330	26.072	-96.850	-75.664	9.727
1800	19.614	101.787	86.213	28.032	-96.951	-74.419	9.035
1900	19.640	102.848	87.061	29.995	-97.059	-73.161	8.415
2000	19.662	103.856	87.876	31.960	-97.176	-71.901	7.857
2100	19.681	104.815	88.660	33.927	-97.296	-70.634	7.351
2200	19.698	105.731	89.415	35.896	-97.424	-69.361	6.890
2300	19.713	106.607	90.144	37.866	-97.557	-68.081	6.469
2400	19.725	107.447	90.847	39.838	-97.697	-66.798	6.082
2500	19.737	108.252	91.528	41.811	-103.231	-65.398	5.717
2600	19.747	109.026	92.186	43.786	-103.374	-63.881	5.369
2700	19.756	109.772	92.823	45.761	-103.521	-62.361	5.047
2800	19.764	110.490	93.442	47.737	-103.671	-60.831	4.748
2900	19.771	111.184	94.042	49.714	-103.824	-59.299	4.469
3000	19.778	111.855	94.624	51.691	-103.980	-57.765	4.208
3100	19.784	112.503	95.191	53.669	-104.141	-56.221	3.963
3200	19.789	113.131	95.741	55.648	-104.305	-54.672	3.734
3300	19.794	113.740	96.278	57.627	-104.474	-53.116	3.518
3400	19.799	114.331	96.800	59.607	-104.644	-51.555	3.314
3500	19.803	114.905	97.309	61.587	-104.821	-49.997	3.122
3600	19.807	115.463	97.806	63.567	-105.000	-48.424	2.940
3700	19.810	116.006	98.290	65.548	-105.183	-46.851	2.767
3800	19.813	116.534	98.763	67.529	-105.369	-45.272	2.604
3900	19.816	117.049	99.226	69.511	-105.559	-43.689	2.448
4000	19.819	117.551	99.678	71.493	-226.932	-39.956	2.183
4100	19.822	118.040	100.120	73.475	-226.896	-35.283	1.881
4200	19.824	118.518	100.552	75.457	-226.864	-30.609	1.593
4300	19.826	118.984	100.975	77.439	-226.834	-25.936	1.318
4400	19.828	119.440	101.390	79.422	-226.808	-21.260	1.056
4500	19.830	119.886	101.796	81.405	-226.784	-16.596	.806
4600	19.832	120.322	102.194	83.388	-226.761	-11.925	.567
4700	19.834	120.748	102.584	85.371	-226.741	-7.249	.337
4800	19.835	121.166	102.967	87.355	-226.724	-2.583	.118
4900	19.837	121.575	103.342	89.339	-226.708	2.087	-.093
5000	19.838	121.976	103.711	91.322	-226.693	6.754	-.295
5100	19.840	122.368	104.073	93.306	-226.680	11.432	-.490
5200	19.841	122.754	104.429	95.290	-226.668	16.097	-.676
5300	19.842	123.132	104.778	97.274	-226.658	20.759	-.856
5400	19.843	123.503	105.121	99.259	-226.650	25.427	-1.029
5500	19.844	123.867	105.459	101.243	-226.642	30.103	-1.196
5600	19.845	124.224	105.791	103.228	-226.636	34.766	-1.357
5700	19.846	124.575	106.117	105.212	-226.634	39.434	-1.512
5800	19.847	124.921	106.438	107.197	-226.631	44.102	-1.662
5900	19.848	125.260	106.755	109.182	-226.630	48.767	-1.806
6000	19.849	125.594	107.066	111.166	-226.631	53.437	-1.946

Dec. 31, 1960; Dec. 31, 1964

BORON TRICHLORIDE (BCl_3) (IDEAL GAS) MOL. WT. = 117.191

Point Group D_{3h}

$\Delta H_f^\circ{}_{0} = -96.08 \pm 0.50$ kcal. mole^{-1}

$S^\circ_{298.15} = 69.328$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -96.31 \pm 0.50$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
471.0 (1)	986.3 (2)
470.6 (1)	243.0 (2)

Bond Distance: B-Cl = 1.75 Å

Bond Angle: Cl-B-Cl = 120°

$\sigma = 6$

Product of the Moments of Inertia: $I_AI_BI_C = 3.95517 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The enthalpy change ($\Delta H_r^\circ{}_{298.15}$) of the reaction B(amorph) + 3/2 $Cl_2(g) = BCl_3(g)$ has been determined in a calorimeter by W. H. Johnson, R. G. Miller and E. J. Prosen, J. Res. Natl. Bur. Std. 62, 213 (1959). From the reported value, $\Delta H_r^\circ{}_{298.15} = -97.51 \pm 0.32$ kcal. mole^{-1}, the heat of formation ($\Delta H_f^\circ{}_{298.15}$) for $BCl_3(g)$ was derived as -96.31 ± 0.50 kcal. mole^{-1}, using $\Delta H_r^\circ{}_{298.15} = 1.20 \pm 0.40$ kcal. mole^{-1} for the reaction B(c) = B(amorph). Some other related heats of reaction reported by previous investigators are presented as follows.

Investigator	Reaction	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1}	$\Delta H_f^\circ{}_{298.15}$, kcal.mole^{-1}
Gal'chenko, et al.[1]	B(am.) + 3/2 $Cl_2(g) = BCl_3(g)$ B(am.) + 3/2 $Cl_2(g) = BCl_3(l)$	-97.4 ± 0.7 -103.3 ∓ 0.6	-96.2 ± 0.8 -96.5 ∓ 0.7
J. R. Lacher, et al.[2]	$B_2H_6(g) + 6\ Cl_2(g) = 2\ BCl_3(g) + 6\ HCl(g)$	-342.9	-100.4 ± 5.0
Skinner and Smith[3]	$BCl_3(l) + (n+3)H_2O(l) = (H_3BO_3+3HCl)\cdot n\ H_2O$ (Sol.)	-69.2 ± 1.0	-97.2 ± 1.0
Gunn and Green[4]	$BCl_3(l) + 2403\ H_2O(l) = (H_3BO_3+3HCl)\cdot 2400H_2O$ (Sol.)	-68.68 ± 0.06	-96.3 ± 0.2
Fasolino[5]	$BCl_3(l) + 593\ H_2O(l) = (H_3BO_3+3HCl)\cdot 590\ H_2O$ (Sol.)	-69.12 ± 0.11	-95.44 ± 0.39

[1] G. L. Gal'chenko, B. I. Timofeev and S. M. Skuratov, Russ. J. Inorg. Chem. 5,1279 (1960). $\Delta H_f^\circ{}_{298.15}$ were derived from $\Delta H_r^\circ{}_{298.15}$ using $\Delta H_r^\circ = -1.2 \pm 0.4$ kcal. mole^{-1} for B(am.) = B(c) and $\Delta H_v^\circ{}_{298.15}(BCl_3, l) = 5.6$ kcal. mole^{-1}.

[2] J. R. Lacher, R. E. Scruby and J. D. Park, J. Am. Chem. Soc. 74, 5292 (1952). The $\Delta H_f^\circ{}_{298.15}$ value was calculated based on $\Delta H_f^\circ{}_{298.15} = 9.80$ kcal. mole^{-1} for $B_2H_6(g)$.

[3] H. A. Skinner and N. B. Smith, Trans, Faraday Soc. 49, 601 (1953), where n = 4978, average value of seven sets of measurement.

[4] S. R. Gunn and L. G. Green, J. Phys. Chem. 64, 61 (1960).

[5] L. G. Fasolino, "Heat of Formation of Boron Trichloride", NONR-3608(00) National Research Corporation, Massachusetts, July 15, 1964.

The heats of formation for $BCl_3(l)$ derived from the heats of hydrolysis reported by other investigators were reviewed by W. H. Johnson, R. G. Miller and E. J. Prosen, loc. cit.

Heat Capacity and Entropy.

The bond distance of B and Cl atoms has been reported to be 1.73 ± 0.02, 1.76 ± 0.02 and 1.75 Å by H. A. Levy and L. O. Brockway, J. Am. Chem. Soc. 59, 2085 (1937), A. H. Gregg, G. C. Hampson and G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Faraday Soc. 33, 852 (1937), and C. Spencer and W. N. Lipscomb, J. Chem. Phys. 28, 355 (1958), respectively. The last value is adopted. The values of vibrational frequencies used were reported by L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956). The vibrational frequencies were also determined by A. B. D. Cassie, Proc. Roy. Soc. A148, 87 (1935), T. F. Anderson, E. N. Lassettre and D. M. Yost, J. Chem. Phys. 4, 703 (1936), and R. E. Scruby, J. R. Lacher and J. D. Park, J. Chem. Phys. 19, 386 (1951). The molecular structure was given by H. A. Levy, et al., loc. cit. The three principal moments of inertia are: $I_A = I_B = 2.7042 \times 10^{-38}$ and $I_C = 5.4085 \times 10^{-38}$ g. cm.^{2}

Boron Monofluoride (BF)

(Ideal Gas) Mol. Wt. = 29.82

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.078	-28.431	-28.431	INFINITE
100	6.957	40.269	54.108	-1.384	-28.090	-30.074	65.724
200	6.968	45.093	48.533	-.688	-27.824	-32.171	35.153
298	7.073	47.890	47.890	.000	-27.700	-34.338	25.169
300	7.076	47.934	47.891	.013	-27.699	-34.379	25.044
400	7.309	50.000	48.171	.732	-27.687	-36.610	20.002
500	7.581	51.660	48.708	1.476	-27.759	-38.835	16.974
600	7.832	53.065	49.320	2.247	-27.879	-41.039	14.948
700	8.042	54.288	49.944	3.041	-28.027	-43.220	13.493
800	8.211	55.374	50.556	3.854	-28.192	-45.380	12.397
900	8.348	56.349	51.146	4.682	-28.368	-47.518	11.538
1000	8.457	57.234	51.712	5.523	-28.555	-49.635	10.847
1100	8.546	58.045	52.251	6.373	-28.754	-51.735	10.278
1200	8.620	58.792	52.765	7.231	-28.964	-53.814	9.800
1300	8.681	59.484	53.256	8.097	-29.184	-55.876	9.393
1400	8.732	60.129	53.724	8.967	-29.414	-57.920	9.041
1500	8.776	60.733	54.171	9.843	-29.655	-59.949	8.734
1600	8.814	61.301	54.599	10.722	-29.906	-61.960	8.463
1700	8.848	61.836	55.010	11.605	-30.167	-63.955	8.222
1800	8.877	62.343	55.403	12.492	-30.436	-65.937	8.005
1900	8.903	62.824	55.781	13.381	-30.712	-67.902	7.810
2000	8.927	63.281	56.145	14.272	-30.993	-69.850	7.633
2100	8.949	63.717	56.495	15.166	-31.279	-71.786	7.471
2200	8.969	64.134	56.833	16.062	-31.570	-73.709	7.322
2300	8.987	64.533	57.159	16.960	-31.865	-75.618	7.185
2400	9.004	64.916	57.474	17.859	-32.164	-77.513	7.058
2500	9.020	65.283	57.779	18.761	-37.854	-79.286	6.931
2600	9.035	65.638	58.075	19.663	-38.153	-80.940	6.803
2700	9.049	65.979	58.361	20.567	-38.452	-82.578	6.684
2800	9.062	66.308	58.639	21.473	-38.749	-84.207	6.572
2900	9.075	66.626	58.909	22.380	-39.048	-85.822	6.467
3000	9.088	66.934	59.172	23.288	-39.346	-87.433	6.369
3100	9.100	67.232	59.427	24.197	-39.644	-89.031	6.276
3200	9.111	67.521	59.675	25.108	-39.942	-90.618	6.189
3300	9.122	67.802	59.917	26.020	-40.239	-92.198	6.106
3400	9.133	68.075	60.153	26.932	-40.537	-93.769	6.027
3500	9.143	68.339	60.383	27.846	-40.835	-95.329	5.952
3600	9.154	68.597	60.608	28.761	-41.133	-96.881	5.881
3700	9.164	68.848	60.827	29.677	-41.431	-98.426	5.813
3800	9.173	69.093	61.042	30.594	-41.729	-99.962	5.749
3900	9.183	69.331	61.251	31.512	-42.028	-101.493	5.687
4000	9.192	69.564	61.456	32.430	-163.505	-100.869	5.511
4100	9.202	69.791	61.657	33.350	-163.573	-99.303	5.293
4200	9.211	70.013	61.853	34.271	-163.640	-97.731	5.085
4300	9.220	70.229	62.045	35.192	-163.707	-96.159	4.887
4400	9.229	70.441	62.234	36.115	-163.777	-94.587	4.698
4500	9.238	70.649	62.418	37.038	-163.846	-93.018	4.517
4600	9.246	70.852	62.599	37.962	-163.915	-91.442	4.344
4700	9.255	71.051	62.777	38.887	-163.986	-89.865	4.179
4800	9.264	71.246	62.952	39.813	-164.058	-88.285	4.020
4900	9.272	71.437	63.123	40.740	-164.131	-86.709	3.867
5000	9.280	71.624	63.291	41.668	-164.204	-85.124	3.721
5100	9.289	71.808	63.456	42.596	-164.280	-83.544	3.580
5200	9.297	71.989	63.618	43.525	-164.356	-81.962	3.445
5300	9.305	72.166	63.778	44.456	-164.432	-80.377	3.314
5400	9.313	72.340	63.935	45.386	-164.512	-78.792	3.189
5500	9.322	72.511	64.089	46.318	-164.591	-77.199	3.067
5600	9.330	72.679	64.241	47.251	-164.673	-75.614	2.951
5700	9.338	72.844	64.391	48.184	-164.757	-74.019	2.838
5800	9.346	73.007	64.538	49.118	-164.842	-72.431	2.729
5900	9.354	73.166	64.683	50.053	-164.929	-70.833	2.624
6000	9.362	73.324	64.826	50.989	-165.018	-69.240	2.522

Dec. 31, 1960; Dec. 31, 1964

BORON MONOFLUORIDE (BF) (IDEAL GAS) MOL. WT. = 29.82

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0}$ = -28.4 ± 3.3 kcal. mole^{-1}

$S^\circ_{298.15}$ = 47.890 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -27.7 ± 3.3 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 1410.3 cm.$^{-1}$

$\omega_e x_e$ = 11.98 cm.$^{-1}$

σ = 1

B_e = 1.5286 cm.$^{-1}$

α_e = 0.0168 cm.$^{-1}$

r_e = 1.265 Å

Heat of Formation.

The equilibria of the reaction 2/3 B(c) + 1/3 $BF_3(g)$ = BF(g) were studied by J. Blauer, M. A. Greenbaum and M. Farber[1], by means of transpiration at pressures below 300μ. The values of log K_p at 1375 and 1476°K. were reported as -3.99 ± 0.02 and -3.30 ± 0.05, respectively. By the third law method the value of $\Delta H^\circ_{r\ 298.15}$ for the reaction was derived to be 61.38 kcal. mole^{-1}, yielding $\Delta H^\circ_{f\ 298.15}$ = -28.7 ± 2.6 kcal. mole^{-1} for BF(g). The system B + CaF_2 was studied mass spectrometrically in a graphite Knudsen cell by D. L. Hildenbrand. The equilibria involving BF(g) were observed. Intensity measurements were made at temperatures, 1583-1734°K. From the third law value, $\Delta H^\circ_{r\ 298.15}$ = 12.2 ± 0.3 kcal. mole^{-1}, for the reaction $BF_3(g)$ + Ca(g) = BF(g) + $CaF_2(g)$, the value of $\Delta H^\circ_{f\ 298.15}$ for BF(g) was derived as -26.7 ± 2 kcal. mole^{-1}. The dissociation energy (D_0°) of BF(g) molecule has been reported by G. Herzberg[2], A. G. Gaydon[3] and R. F. Barrow[4], respectively. Hence the corresponding values of $\Delta H^\circ_{f\ 298.15}$ for BF(g) were derived. The results are compared with those obtained from equilibrium data as follows.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1}	$\Delta H^\circ_{f\ 298.15}$, kcal. mole^{-1}
Farber, et al.[1]	2/3 B(c) + 1/3 $BF_3(g)$ = BF(g)	61.38	-28.7 ± 2.6
Herzberg[2]	BF(g) = B(g) + F(g)	100.2	+51.5
Gaydon[3]	BF(g) = B(g) + F(g)	197.0	-45.3 ± 11.5
Barrow[4]	BF(g) = B(g) + F(g)	186.0	-34.3
Gross, et al.[5]	2/3 B(c) + 1/3 $BF_3(g)$ = BF(g)	—	-28 ± 3
Hildenbrand[6]	$BF_3(g)$ + Ca(g) = BF(g) + $CaF_2(g)$	12.2	-26.7 ± 2

[1] J. Blauer, M. A. Greenbaum and M. Farber, J. Phys. Chem. 68, 2332 (1964).

[2] G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950. $\Delta H^\circ_{r\ 298.15}$ was calculated based on D_0° = 4.3 e.v.

[3] A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. $\Delta H^\circ_{r\ 298.15}$ was derived from D_0° = 8.5 ± 0.5 e.v.

[4] R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960). $\Delta H^\circ_{r\ 298.15}$ was calculated based on D_0° = 185 kcal. mole^{-1}.

[5] P. Gross, C. Hayman, D. L. Levi and R. H. Lewin, "Stability of Lower Boron Halides", Final Technical Report, August 22, 1963, Fulmer Research Institute Limited, England. The reported value, $\Delta H^\circ_{f\ 298.15}$ = -28 ± 3 kcal. mole^{-1}, is a preliminary estimated one.

[6] D. L. Hildenbrand, "Thermodynamic Properties of Propellant Combustion Products", QLR-65-3, Philco Corporation, California.

The value of $\Delta H^\circ_{f\ 298.15}$ adopted is the average of the first and last $\Delta H^\circ_{f\ 298.15}$ values listed in the above table.

Heat Capacity and Entropy.

The spectroscopic constants used were obtained from R. Onaka, J. Chem. Phys. 27, 374 (1957) and corrected to the average isotopic species. Spectroscopic constants for BF(g) were also reported by G. Herzberg, loc. cit. The moment of inertia (I) is 1.8321 X 10^{-39} g. cm.^{2}

BFO

Boron Oxide Fluoride (BOF)

(Ideal Gas) Mol. Wt. = 45.82

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_P
0	.000	.000	INFINITE	- 2.374	- 143.990	- 143.990	INFINITE
100	7.110	44.736	61.505	- 1.677	- 144.002	- 144.357	315.477
200	8.505	50.055	54.562	- .901	- 143.997	- 144.713	158.127
298	9.798	53.705	53.705	.000	- 144.000	- 145.066	106.331
300	9.819	53.766	53.705	.018	- 144.000	- 145.073	105.681
400	10.792	56.730	54.103	1.051	- 144.030	- 145.427	79.454
500	11.540	59.222	54.884	2.169	- 144.094	- 145.770	63.713
600	12.130	61.380	55.791	3.354	- 144.178	- 146.097	53.213
700	12.600	63.287	56.728	4.591	- 144.271	- 146.409	45.709
800	12.975	64.995	57.656	5.871	- 144.368	- 146.709	40.077
900	13.275	66.541	58.559	7.184	- 144.466	- 146.996	35.694
1000	13.515	67.952	59.429	8.524	- 144.567	- 147.270	32.184
1100	13.710	69.250	60.263	9.885	- 144.675	- 147.536	29.311
1200	13.869	70.450	61.063	11.264	- 144.788	- 147.791	26.915
1300	14.000	71.565	61.828	12.658	- 144.908	- 148.036	24.886
1400	14.109	72.607	62.562	14.064	- 145.035	- 148.272	23.145
1500	14.200	73.584	63.264	15.479	- 145.171	- 148.500	21.635
1600	14.277	74.503	63.938	16.903	- 145.316	- 148.716	20.313
1700	14.342	75.370	64.585	18.334	- 145.470	- 148.923	19.144
1800	14.398	76.192	65.208	19.771	- 145.634	- 149.124	18.105
1900	14.446	76.971	65.806	21.214	- 145.804	- 149.311	17.174
2000	14.487	77.713	66.383	22.660	- 145.980	- 149.491	16.335
2100	14.524	78.421	66.940	24.111	- 146.162	- 149.662	15.575
2200	14.556	79.098	67.477	25.565	- 146.350	- 149.826	14.883
2300	14.584	79.745	67.997	27.022	- 146.544	- 149.979	14.251
2400	14.609	80.366	68.499	28.482	- 146.744	- 150.122	13.670
2500	14.631	80.963	68.986	29.944	- 152.337	- 150.151	13.126
2600	14.651	81.537	69.458	31.408	- 152.541	- 150.059	12.613
2700	14.669	82.091	69.915	32.874	- 152.746	- 149.960	12.138
2800	14.685	82.625	70.360	34.341	- 152.954	- 149.855	11.696
2900	14.699	83.140	70.792	35.810	- 153.164	- 149.736	11.284
3000	14.712	83.639	71.212	37.281	- 153.376	- 149.618	10.899
3100	14.724	84.121	71.620	38.753	- 153.590	- 149.488	10.538
3200	14.735	84.589	72.018	40.226	- 153.806	- 149.353	10.200
3300	14.745	85.042	72.406	41.700	- 154.025	- 149.208	9.881
3400	14.754	85.483	72.784	43.175	- 154.246	- 149.061	9.581
3500	14.762	85.910	73.153	44.650	- 154.469	- 148.904	9.298
3600	14.770	86.326	73.513	46.127	- 154.694	- 148.740	9.029
3700	14.777	86.731	73.865	47.604	- 154.922	- 148.572	8.775
3800	14.783	87.125	74.209	49.082	- 155.151	- 148.395	8.534
3900	14.789	87.509	74.545	50.561	- 155.383	- 148.219	8.306
4000	14.795	87.884	74.874	52.040	- 276.796	- 145.888	7.971
4100	14.800	88.249	75.196	53.520	- 276.801	- 142.614	7.602
4200	14.805	88.606	75.511	55.000	- 276.807	- 139.339	7.250
4300	14.809	88.954	75.819	56.481	- 276.815	- 136.063	6.915
4400	14.813	89.295	76.122	57.962	- 276.828	- 132.794	6.596
4500	14.817	89.628	76.418	59.443	- 276.841	- 129.522	6.290
4600	14.821	89.954	76.709	60.925	- 276.856	- 126.247	5.998
4700	14.825	90.272	76.994	62.408	- 276.875	- 122.969	5.718
4800	14.828	90.585	77.274	63.890	- 276.895	- 119.695	5.450
4900	14.831	90.890	77.549	65.373	- 276.919	- 116.422	5.192
5000	14.834	91.190	77.819	66.857	- 276.944	- 113.146	4.945
5100	14.836	91.484	78.084	68.340	- 276.973	- 109.871	4.708
5200	14.839	91.772	78.344	69.824	- 277.003	- 106.594	4.480
5300	14.841	92.055	78.600	71.308	- 277.036	- 103.318	4.260
5400	14.844	92.332	78.852	72.792	- 277.072	- 100.042	4.049
5500	14.846	92.604	79.100	74.277	- 277.109	- 96.753	3.844
5600	14.848	92.872	79.343	75.761	- 277.151	- 93.482	3.648
5700	14.850	93.135	79.583	77.246	- 277.196	- 90.202	3.458
5800	14.852	93.393	79.819	78.731	- 277.242	- 86.918	3.275
5900	14.854	93.647	80.051	80.217	- 277.291	- 83.639	3.098
6000	14.855	93.897	80.780	81.702	- 277.344	- 80.355	2.927

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965

BORON OXIDE FLUORIDE (BOF) (IDEAL GAS) MOL. WT. = 45.82

Point Group [$C_{\infty v}$]

$\Delta H^\circ_{f\ 0}$ = -144 ± 3 kcal. mole^{-1}

$S^\circ_{298.15}$ = [53.7] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -144 ± 3 kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[1050] (1)
[500] (2)
[1900] (1)

Bond Distance: B-F = [1.30] Å B-O = [1.20] Å

Bond Angle: O-B-F = [180°]

σ = 1

B_0 = [0.30939] cm.$^{-1}$

Heat of Formation.

The equilibrium constants for the reaction $B_2O_3(l) + BF_3(g) = 3BOF(g)$ in the temperature range 1054-1253°K. were determined by M. Farber and J. Blauer, Trans. Faraday Soc. 58, 2090 (1962), using the so-called Molecular Flow Reaction Method. The value of ΔH°_r for this reaction was evaluated by both the second and third law methods, using the equilibrium constants corrected for the trimer and correcting K_p at 1200°K. from 9.6 X 10^{-11} to 9.6 X 10^{-10}. D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. 39, 1973 (1963) analyzed the vapor above mixture of MgF_2 and B_2O_3 contained in a Knudsen cell with a mass spectrometer and found that in the temperature range 980-1230°K. the vapor is composed of $BF_3(g)$, $(BOF)_3(g)$ and $BOF(g)$ species. From the reported temperature dependence of appropriate ion intensities the enthalpy change of the reaction $(BOF)_3(g) = 3BOF(g)$ was derived by the second law method as 127.9 kcal. mole^{-1} at 1115°K. or 129.75 kcal. mole^{-1} at 298.15°K. The results obtained are presented as follows, using JANAF free energy functions and auxiliary data.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second law value	Third law value	$\Delta H^\circ_{f\ 298.15}$ kcal. mole^{-1}
Farber and Blauer	$B_2O_3(l) + BF_3(g) = 3BOF(g)$	150.2 ± 16.6	149.0	-140.1 ± 6*
Hildenbrand, et al.	$(BOF)_3(g) = 3BOF(g)$	129.8 ± 3	——	-145.2 ± 1.5

*Calculation based on the third law value and one point rejected due to statistical test.

The adopted value of $\Delta H^\circ_{f\ 298.15}$ for BOF(g) is the weighted average of the two $\Delta H^\circ_{f\ 298.15}$ values listed above.

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, k_1 = 10 X 10^5, k_2 = 25.6 X 10^5 dynes cm.$^{-1}$ and k_δ = 0.47 X 10^{-11} dynes cm. rad.$^{-1}$. The B-O and B-F bond distances were assumed to be the same as those in BO(g) and $BF_3(g)$ molecules. The moment of inertia is 9.0464 X 10^{-39} g. cm.^{2}

BFO

Boron Difluoride (BF_2)

(Ideal Gas) Mol. Wt. = 48.82

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.543	- 130.141	- 130.141	INFINITE
100	8.054	49.521	66.991	- 1.747	- 130.046	- 130.920	286.113
200	8.824	55.325	59.850	- .905	- 129.984	- 131.823	144.042
298	9.618	58.996	58.996	.000	- 130.000	- 132.727	97.287
300	9.633	59.056	58.997	.018	- 130.001	- 132.744	96.700
400	10.415	61.936	59.384	1.021	- 130.090	- 133.646	73.017
500	11.101	64.336	60.141	2.098	- 130.233	- 134.520	58.796
600	11.654	66.411	61.017	3.236	- 130.402	- 135.362	49.303
700	12.084	68.241	61.920	4.424	- 130.581	- 136.174	42.513
800	12.415	69.877	62.815	5.650	- 130.766	- 136.961	37.414
900	12.671	71.355	63.683	6.905	- 130.953	- 137.725	33.443
1000	12.870	72.701	64.518	8.182	- 131.146	- 138.467	30.260
1100	13.027	73.935	65.319	9.477	- 131.347	- 139.190	27.653
1200	13.152	75.074	66.085	10.787	- 131.553	- 139.892	25.477
1300	13.254	76.131	66.818	12.107	- 131.770	- 140.579	23.632
1400	13.337	77.116	67.518	13.437	- 131.994	- 141.247	22.049
1500	13.405	78.039	68.189	14.774	- 132.229	- 141.901	20.674
1600	13.463	78.906	68.832	16.117	- 132.474	- 142.538	19.469
1700	13.511	79.723	69.449	17.466	- 132.728	- 143.157	18.403
1800	13.552	80.497	70.042	18.819	- 132.992	- 143.766	17.455
1900	13.587	81.231	70.611	20.176	- 133.262	- 144.358	16.604
2000	13.617	81.928	71.160	21.537	- 133.537	- 144.931	15.837
2100	13.643	82.593	71.689	22.900	- 133.819	- 145.495	15.141
2200	13.666	83.228	72.199	24.265	- 134.107	- 146.044	14.507
2300	13.686	83.836	72.692	25.633	- 134.399	- 146.580	13.928
2400	13.704	84.419	73.168	27.002	- 134.698	- 147.103	13.395
2500	13.720	84.979	73.630	28.374	- 140.388	- 147.506	12.894
2600	13.734	85.517	74.077	29.746	- 140.689	- 147.784	12.422
2700	13.747	86.036	74.510	31.120	- 140.990	- 148.050	11.983
2800	13.758	86.536	74.931	32.496	- 141.291	- 148.308	11.575
2900	13.768	87.019	75.339	33.872	- 141.595	- 148.549	11.194
3000	13.777	87.486	75.736	35.249	- 141.901	- 148.789	10.839
3100	13.785	87.938	76.123	36.627	- 142.207	- 149.014	10.505
3200	13.793	88.376	76.499	38.006	- 142.515	- 149.228	10.191
3300	13.800	88.800	76.865	39.386	- 142.824	- 149.431	9.896
3400	13.806	89.212	77.222	40.766	- 143.135	- 149.625	9.617
3500	13.812	89.613	77.571	42.147	- 143.448	- 149.814	9.354
3600	13.817	90.002	77.911	43.529	- 143.761	- 149.989	9.105
3700	13.822	90.380	78.242	44.911	- 144.077	- 150.157	8.869
3800	13.827	90.749	78.567	46.293	- 144.395	- 150.315	8.645
3900	13.831	91.108	78.884	47.676	- 144.715	- 150.471	8.432
4000	13.835	91.459	79.194	49.059	- 266.215	- 148.471	8.112
4100	13.839	91.800	79.497	50.443	- 266.307	- 145.525	7.757
4200	13.842	92.134	79.794	51.827	- 266.400	- 142.576	7.419
4300	13.845	92.459	80.085	53.211	- 266.495	- 139.623	7.096
4400	13.848	92.778	80.370	54.596	- 266.594	- 136.675	6.788
4500	13.851	93.089	80.649	55.981	- 266.694	- 133.724	6.494
4600	13.853	93.393	80.923	57.366	- 266.796	- 130.765	6.212
4700	13.856	93.691	81.191	58.752	- 266.901	- 127.805	5.943
4800	13.858	93.983	81.455	60.137	- 267.009	- 124.842	5.684
4900	13.860	94.269	81.713	61.523	- 267.120	- 121.884	5.436
5000	13.862	94.549	81.967	62.909	- 267.233	- 118.918	5.198
5100	13.864	94.823	82.217	64.296	- 267.349	- 115.951	4.969
5200	13.866	95.093	82.462	65.682	- 267.468	- 112.981	4.748
5300	13.867	95.357	82.702	67.069	- 267.589	- 110.010	4.536
5400	13.869	95.616	82.939	68.456	- 267.715	- 107.038	4.332
5500	13.871	95.871	83.172	69.842	- 267.843	- 104.058	4.135
5600	13.872	96.121	83.401	71.230	- 267.974	- 101.083	3.945
5700	13.873	96.366	83.626	72.617	- 268.110	- 98.096	3.761
5800	13.875	96.607	83.848	74.004	- 268.248	- 95.112	3.584
5900	13.876	96.845	84.066	75.392	- 268.389	- 92.133	3.413
6000	13.877	97.078	84.281	76.779	- 268.535	- 89.141	3.247

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1964

BORON DIFLUORIDE (BF_2) (IDEAL GAS) MOL. WT. = 48.82

Point Group C_{2v}

$\Delta H_f^\circ{}_0 = -130 \pm 6$ kcal. mole^{-1}

$S^\circ_{298.15}$ = [58.996] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -130 \pm 6$ kcal. mole^{-1}

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[1120] (1)
[470] (1)
[1450] (1)

Bond Distance: B-F = [1.295] Å

Bond Angle: F-B-F = [120]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 3.96332 \times 10^{-116}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation ($\Delta H_f^\circ{}_{298.15}$) was obtained from J. L. Margrave, J. Phys. Chem. 66, 1209 (1962), from appearance potentials.

Heat Capacity and Entropy.

The bond distance and angle were assumed to be the same as those in BF_3(g) molecule. The vibrational frequencies were calculated using force constants transferred from those for BF_3(g) given by G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., 1945. The three principal moments of inertia are: $I_A = 7.9278 \times 10^{-39}$, $I_B = 5.8710 \times 10^{-40}$ and $I_C = 8.5149 \times 10^{-39}$ g. cm.^{2}

Boron Difluoride Unipositive Ion (BF_2^+)

(Ideal Gas) GFW = 48.80725

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.586	53.785	53.785	.000	84.000	81.340	-59.624
300	10.605	53.850	53.785	.020	84.010	81.322	-59.243
400	11.513	57.032	54.213	1.128	84.523	80.349	-43.901
500	12.211	59.679	55.048	2.315	84.987	79.250	-34.640
600	12.747	61.955	56.014	3.564	85.426	78.062	-28.434
700	13.156	63.952	57.008	4.860	85.851	76.800	-23.978
800	13.470	65.730	57.990	6.192	86.269	75.478	-20.620
900	13.713	67.331	58.940	7.552	86.684	74.105	-17.995
1000	13.902	68.786	59.853	8.933	87.092	72.685	-15.885
1100	14.052	70.119	60.727	10.331	87.491	71.225	-14.151
1200	14.172	71.347	61.561	11.743	87.884	69.730	-12.700
1300	14.269	72.485	62.358	13.165	88.265	68.201	-11.466
1400	14.349	73.545	63.120	14.596	88.639	66.644	-10.404
1500	14.414	74.538	63.848	16.034	89.002	65.060	-9.479
1600	14.470	75.470	64.546	17.478	89.355	63.452	-8.667
1700	14.516	76.348	65.214	18.928	89.699	61.823	-7.948
1800	14.556	77.179	65.856	20.381	90.031	60.171	-7.306
1900	14.589	77.967	66.473	21.839	90.359	58.505	-6.730
2000	14.619	78.716	67.067	23.299	90.680	56.821	-6.209
2100	14.644	79.430	67.639	24.762	90.995	55.118	-5.736
2200	14.666	80.112	68.190	26.228	91.305	53.403	-5.305
2300	14.686	80.764	68.723	27.695	91.608	51.673	-4.910
2400	14.703	81.390	69.238	29.165	91.907	49.932	-4.547
2500	14.718	81.990	69.736	30.636	86.813	48.285	-4.221
2600	14.732	82.568	70.218	32.109	87.110	46.737	-3.929
2700	14.745	83.124	70.686	33.582	87.405	45.183	-3.657
2800	14.756	83.660	71.140	35.057	87.700	43.610	-3.404
2900	14.766	84.178	71.581	36.533	87.992	42.035	-3.168
3000	14.775	84.679	72.009	38.011	88.284	40.439	-2.946
3100	14.784	85.164	72.426	39.489	88.575	38.839	-2.738
3200	14.792	85.633	72.831	40.967	88.863	37.234	-2.543
3300	14.800	86.089	73.226	42.447	89.151	35.616	-2.359
3400	14.808	86.531	73.611	43.927	89.436	33.991	-2.185
3500	14.815	86.960	73.986	45.409	89.721	32.356	-2.020
3600	14.822	87.377	74.352	46.890	90.004	30.715	-1.865
3700	14.829	87.784	74.710	48.373	90.286	29.060	-1.716
3800	14.836	88.179	75.059	49.856	90.566	27.406	-1.576
3900	14.843	88.565	75.400	51.340	90.844	25.735	-1.442
4000	14.850	88.941	75.734	52.825	-30.058	26.208	-1.432
4100	14.857	89.307	76.061	54.310	-29.552	27.605	-1.471
4200	14.865	89.665	76.381	55.796	-29.046	29.001	-1.509
4300	14.872	90.015	76.694	57.283	-28.541	30.377	-1.544
4400	14.880	90.357	77.000	58.771	-28.040	31.742	-1.577
4500	14.888	90.692	77.301	60.259	-27.541	33.089	-1.607
4600	14.897	91.019	77.595	61.748	-27.042	34.433	-1.636
4700	14.905	91.340	77.884	63.238	-26.546	35.765	-1.663
4800	14.914	91.653	78.168	64.729	-26.051	37.087	-1.689
4900	14.924	91.961	78.446	66.221	-25.559	38.396	-1.713
5000	14.933	92.263	78.720	67.714	-25.069	39.698	-1.735
5100	14.943	92.558	78.988	69.208	-24.581	40.983	-1.756
5200	14.954	92.849	79.252	70.703	-24.094	42.270	-1.777
5300	14.965	93.134	79.511	72.199	-23.609	43.539	-1.795
5400	14.976	93.413	79.766	73.696	-23.128	44.796	-1.813
5500	14.987	93.688	80.017	75.194	-22.647	46.057	-1.830
5600	14.999	93.959	80.263	76.693	-22.171	47.295	-1.846
5700	15.010	94.224	80.506	78.194	-21.696	48.539	-1.861
5800	15.023	94.485	80.745	79.695	-21.223	49.762	-1.875
5900	15.035	94.742	80.980	81.198	-20.752	50.980	-1.888
6000	15.048	94.995	81.211	82.702	-20.284	52.197	-1.901

June 30, 1968

BORON DIFLUORIDE UNIPOSITIVE ION (BF_2^+) (IDEAL GAS) GFW = 48.80725

Point Group [$D_{\infty h}$] ΔHf_0° = 83.9 ± 2 kcal/mol

$S^\circ_{298.15}$ = [53.8 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 84.0 ± 2 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[25000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[900] (1)
[370] (2)
[1550] (1)

Bonc Distance: B-F = [1.31] Å

Bond Angle: F-B-F = [180°] σ = 2

Rotational Constant: B_0 = [0.2585] cm^{-1}

Heat of Formation

The electron impact reaction at low pressure in BF_3(g) has been studied with a mass spectrometer by Osberghaus (1), Law (2), and Marriott (3). From the reported appearance potentials 17.0 ± 0.5, 16.2 ± 0.2, and 16.7 ± 0.05 eV and assumed process $BF_3 + e^- = BF_2^+ + F + 2e^-$, we calculate the corresponding values of ΔHf°_{298} (BF_2^+, g) as 102.8 ± 11.5, 84.4 ± 4.6, and 83.7 ± 1.2 kcal/mol, using ΔHf_0° = 270.977 and 18.357 kcal/mol for BF_3 (g) and F (g). The adopted value of ΔHf°_{298} for BF_2^+ (g) is 84 ± 2 kcal/mol, since the lower values are likely to have the least excess kinetic energy in the fragments.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) prediction for 16 valence electron XY_2 molecules. The electronic states and levels, and vibrational frequencies are estimated by comparision with those for CO_2(5). The B-F bond distance is calculated by the method recommended by Krasnov (6). The moment of inertia is 1.083×10^{-38} g cm^2. The enthalpy at 0°K is -2.54 kcal/mol.

References

1. O. Osberghaus, Z. Phys. 128, 366 (1950).
2. R. W. Law and J. L. Margrave, J. Chem. Phys. 25, 1086 (1956).
3. J. Marriott and J. D. Craggs, J. Electron. Contr. 3, 194 (1957).
4. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966.
6. K. S. Krasnov, Zh. Strukt, Khim. 1, 209 (1960).

Boron Difluoride Uninegative Ion (BF_2^-)

(Ideal Gas) GFW = 48.80835

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	9.702	57.489	57.489	.000	- 136.000	- 136.790	100.270
300	9.722	57.549	57.489	.018	- 136.010	- 136.796	99.655
400	10.728	60.489	57.883	1.042	- 136.575	- 136.973	74.838
500	11.500	62.970	58.659	2.156	- 137.178	- 137.004	59.884
600	12.058	65.119	59.561	3.335	- 137.803	- 136.910	49.869
700	12.461	67.010	60.492	4.562	- 138.439	- 136.710	42.683
800	12.762	68.694	61.414	5.824	- 139.085	- 136.420	37.268
900	13.000	70.211	62.309	7.112	- 139.736	- 136.049	33.037
1000	13.204	71.592	63.169	8.423	- 140.392	- 135.603	29.636
1100	13.393	72.859	63.993	9.753	- 141.055	- 135.094	26.841
1200	13.579	74.033	64.781	11.101	- 141.720	- 134.522	24.500
1300	13.767	75.127	65.536	12.468	- 142.386	- 133.894	22.510
1400	13.959	76.154	66.258	13.855	- 143.050	- 133.215	20.796
1500	14.155	77.124	66.950	15.260	- 143.714	- 132.490	19.304
1600	14.351	78.044	67.615	16.686	- 144.373	- 131.720	17.992
1700	14.543	78.919	68.254	18.130	- 145.029	- 130.909	16.829
1800	14.729	79.756	68.870	19.594	- 145.678	- 130.061	15.792
1900	14.905	80.557	69.464	21.076	- 146.320	- 129.176	14.859
2000	15.069	81.326	70.038	22.575	- 146.954	- 128.256	14.015
2100	15.218	82.065	70.594	24.089	- 147.582	- 127.306	13.249
2200	15.351	82.776	71.131	25.618	- 148.203	- 126.326	12.549
2300	15.467	83.461	71.653	27.159	- 148.818	- 125.316	11.908
2400	15.567	84.121	72.158	28.711	- 149.431	- 124.282	11.317
2500	15.650	84.759	72.650	30.272	- 155.429	- 123.113	10.763
2600	15.717	85.374	73.127	31.840	- 156.031	- 121.809	10.239
2700	15.769	85.968	73.592	33.415	- 156.628	- 120.480	9.752
2800	15.808	86.542	74.044	34.994	- 157.223	- 119.132	9.299
2900	15.834	87.097	74.485	36.576	- 157.817	- 117.757	8.874
3000	15.848	87.634	74.914	38.160	- 158.413	- 116.369	8.477
3100	15.853	88.154	75.333	39.745	- 159.009	- 114.958	8.105
3200	15.849	88.657	75.742	41.330	- 159.608	- 113.529	7.754
3300	15.838	89.145	76.140	42.915	- 160.209	- 112.078	7.423
3400	15.820	89.618	76.530	44.498	- 160.813	- 110.611	7.110
3500	15.797	90.076	76.910	46.079	- 161.423	- 109.126	6.814
3600	15.770	90.520	77.282	47.657	- 162.037	- 107.621	6.533
3700	15.739	90.952	77.646	49.233	- 162.656	- 106.099	6.267
3800	15.705	91.371	78.002	50.805	- 163.281	- 104.561	6.014
3900	15.669	91.779	78.350	52.373	- 163.913	- 103.013	5.773
4000	15.631	92.175	78.690	53.938	- 285.727	- 99.295	5.425
4100	15.592	92.561	79.024	55.500	- 286.138	- 94.630	5.044
4200	15.552	92.936	79.351	57.057	- 286.555	- 89.952	4.681
4300	15.512	93.301	79.671	58.610	- 286.978	- 85.266	4.334
4400	15.472	93.658	79.985	60.159	- 287.410	- 80.572	4.002
4500	15.432	94.005	80.293	61.705	- 287.845	- 75.867	3.685
4600	15.393	94.344	80.594	63.246	- 288.288	- 71.152	3.380
4700	15.354	94.674	80.890	64.783	- 288.739	- 66.425	3.089
4800	15.316	94.997	81.181	66.317	- 289.195	- 61.685	2.809
4900	15.278	95.312	81.466	67.846	- 289.660	- 56.946	2.540
5000	15.242	95.621	81.746	69.372	- 290.129	- 52.192	2.281
5100	15.207	95.922	82.021	70.895	- 290.606	- 47.429	2.032
5200	15.172	96.217	82.291	72.414	- 291.089	- 42.655	1.793
5300	15.139	96.506	82.557	73.929	- 291.579	- 37.872	1.562
5400	15.107	96.789	82.818	75.442	- 292.076	- 33.084	1.339
5500	15.076	97.065	83.074	76.951	- 292.578	- 28.278	1.124
5600	15.046	97.337	83.327	78.457	- 293.087	- 23.468	.916
5700	15.017	97.603	83.575	79.960	- 293.604	- 18.652	.715
5800	14.989	97.864	83.819	81.460	- 294.126	- 13.822	.521
5900	14.963	98.120	84.059	82.958	- 294.654	- 8.986	.333
6000	14.937	98.371	84.296	84.453	- 295.189	- 4.141	.151

June 30, 1968; Dec. 31, 1968

BORON DIFLUORIDE UNINEGATIVE ION (BF_2^-) (IDEAL GAS) GFW = 48.80835

Point Group [C_{2v}]

ΔHf°_0 = [-136 ± 30] kcal/mol

$S^\circ_{298.15}$ = [57.5 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-136 ± 30] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[6000]	3
[28000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1000] (1)
[570] (1)
[1100] (1)

Bond Distance: B-F = [1.30] Å

Bond Angle: F-B-F = [120°]

σ = 2

Product of the Moments of Inertia: $I_A I_B I_C$ = [4.054 x 10^{-116}] g^3 cm^6

Heat of Formation

The electron captured by BF_2 should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus we would expect a small electron affinity. Two estimates of the dissociation energy of BF_2^- indicate a negative electron affinity (EA); consider the isoelectronic reactions $BF_2^- \rightarrow B^- + 2F$ and $CF_2 \rightarrow C + 2F$ if we make the reasonable assumption that the atomization energies are the same then $\Delta Hf^\circ_{298}(BF_2^-, g)$ = -86 kcal/mol, or $EA(BF_2)$ = -44 kcal. Another approach is to consider the isoelectronic reactions $BF_2^- \rightarrow BF + F^-$ and $BFNe \rightarrow BF + Ne$, although the latter reaction is unknown we would expect zero bond strength, and if used in the first reaction this yields $\Delta Hf^\circ_{298}(BF_2^-, g)$ = -90 kcal/mol, or $EA(BF_2)$ = -40 kcal.

In consideration of the above we choose $EA(BF_2) = EA(B, g)$ = 6 kcal (2), which gives $\Delta Hf^\circ_{298}(BF_2^-, g)$ = -136 kcal/mol.

Heat Capacity and Entropy

The molecular structure and B-F bond distance are assumed to be the same as those for the $BF_2(g)$ molecule. The electronic levels, quantum weights and vibrational frequencies are estimated by comparison with those for CF_2(3) which is isoelectronic with BF_2^-. The three principal moments of inertia are: $I_A = 5.904 \times 10^{-40}$, $I_B = 7.997 \times 10^{-39}$ and $I_C = 8.587 \times 10^{-39}$ g cm^2. The enthalpy at 0°K is -2.52 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. G. Herzberg, "Electronic Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York, 1966.

Difluoroborane (BHF_2)

(Ideal Gas) Mol. Wt. = 49.81577

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.550	- 174.536	- 174.536	INFINITE
100	7.998	48.830	66.379	- 1.755	- 174.821	- 174.408	381.149
200	8.765	54.560	59.179	- .924	- 175.072	- 173.906	190.026
298	10.124	58.300	58.300	.000	- 175.400	- 173.267	127.002
300	10.152	58.363	58.300	.019	- 175.407	- 173.254	126.210
400	11.677	61.494	58.717	1.111	- 175.754	- 172.483	94.236
500	13.027	64.249	59.553	2.348	- 176.086	- 171.628	75.015
600	14.134	66.726	60.546	3.708	- 176.383	- 170.708	62.177
700	15.026	68.974	61.592	5.168	- 176.641	- 169.740	52.993
800	15.746	71.029	62.645	6.708	- 176.865	- 168.739	46.095
900	16.332	72.919	63.683	8.313	- 177.058	- 167.712	40.724
1000	16.812	74.665	64.695	9.970	- 177.230	- 166.664	36.423
1100	17.208	76.287	65.676	11.672	- 177.387	- 165.600	32.900
1200	17.537	77.799	66.624	13.410	- 177.532	- 164.521	29.962
1300	17.813	79.214	67.538	15.178	- 177.673	- 163.432	27.474
1400	18.046	80.543	68.420	16.971	- 177.811	- 162.330	25.340
1500	18.243	81.794	69.271	18.786	- 177.951	- 161.219	23.488
1600	18.411	82.977	70.091	20.619	- 178.095	- 160.099	21.868
1700	18.556	84.098	70.882	22.467	- 178.243	- 158.970	20.436
1800	18.681	85.162	71.646	24.329	- 178.397	- 157.834	19.163
1900	18.790	86.175	72.384	26.203	- 178.553	- 156.686	18.022
2000	18.885	87.141	73.098	28.087	- 178.713	- 155.529	16.995
2100	18.968	88.065	73.789	29.979	- 178.877	- 154.368	16.065
2200	19.042	88.949	74.458	31.880	- 179.046	- 153.197	15.218
2300	19.107	89.797	75.107	33.787	- 179.218	- 152.018	14.444
2400	19.165	90.611	75.736	35.701	- 179.395	- 150.829	13.734
2500	19.216	91.395	76.347	37.620	- 184.966	- 149.530	13.071
2600	19.263	92.149	76.940	39.544	- 185.145	- 148.107	12.449
2700	19.305	92.877	77.517	41.473	- 185.325	- 146.677	11.872
2800	19.342	93.580	78.078	43.405	- 185.506	- 145.246	11.336
2900	19.376	94.259	78.624	45.341	- 185.689	- 143.799	10.836
3000	19.407	94.917	79.157	47.280	- 185.875	- 142.358	10.370
3100	19.435	95.553	79.675	49.222	- 186.061	- 140.903	9.933
3200	19.461	96.171	80.181	51.167	- 186.250	- 139.444	9.523
3300	19.485	96.770	80.675	53.114	- 186.441	- 137.976	9.137
3400	19.506	97.352	81.157	55.064	- 186.634	- 136.504	8.774
3500	19.526	97.918	81.628	57.016	- 186.831	- 135.027	8.431
3600	19.545	98.468	82.088	58.969	- 187.029	- 133.542	8.107
3700	19.562	99.004	82.538	60.924	- 187.231	- 132.055	7.800
3800	19.577	99.526	82.978	62.881	- 187.435	- 130.559	7.508
3900	19.592	100.035	83.409	64.840	- 187.644	- 129.066	7.232
4000	19.605	100.531	83.831	66.800	- 309.033	- 125.413	6.852
4100	19.618	101.015	84.244	68.761	- 309.016	- 120.824	6.440
4200	19.629	101.488	84.649	70.723	- 309.001	- 116.229	6.048
4300	19.640	101.950	85.046	72.687	- 308.989	- 111.640	5.674
4400	19.651	102.402	85.435	74.651	- 308.983	- 107.054	5.317
4500	19.660	102.843	85.817	76.617	- 308.979	- 102.465	4.976
4600	19.669	103.275	86.192	78.583	- 308.978	- 97.873	4.650
4700	19.677	103.699	86.560	80.551	- 308.983	- 93.286	4.338
4800	19.685	104.113	86.921	82.519	- 308.990	- 88.692	4.038
4900	19.693	104.519	87.276	84.488	- 309.003	- 84.105	3.751
5000	19.700	104.917	87.625	86.457	- 309.019	- 79.516	3.475
5100	19.706	105.307	87.968	88.428	- 309.040	- 74.927	3.211
5200	19.713	105.690	88.305	90.399	- 309.064	- 70.335	2.956
5300	19.718	106.065	88.637	92.370	- 309.092	- 65.740	2.711
5400	19.724	106.434	88.963	94.342	- 309.127	- 61.157	2.475
5500	19.729	106.796	89.284	96.315	- 309.164	- 56.557	2.247
5600	19.734	107.151	89.600	98.288	- 309.207	- 51.966	2.028
5700	19.739	107.501	89.911	100.262	- 309.256	- 47.372	1.816
5800	19.744	107.844	90.217	102.236	- 309.308	- 42.777	1.612
5900	19.748	108.182	90.519	104.210	- 309.365	- 38.186	1.414
6000	19.752	108.513	90.816	106.185	- 309.427	- 33.583	1.223

Dec. 31, 1965

DIFLUOROBORANE (BHF_2) (IDEAL GAS) MOL. WT. = 49.81577

Point Group C_{2v}

$S^\circ_{298.15}$ = 58.3 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -174.5 ± 0.8 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -175.4 ± 0.8 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
2640 (1)	1411 (1)
1174 (1)	[1158](1)
544 (1)	928 (1)

Bond Distance: B-H = 1.15 Å B-F = 1.30 ± 0.15 Å

Bond Angle: F-B-F = 120 ± 5° F-B-H = 120 ± 2.5° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 7.5168 X 10^{-116} g.^{3} cm.^{6}

Heat of Formation.

The equilibrium pressures at 296 and 360°K. for the reaction 1/6 $B_2H_6(g)$ + 2/3 $BF_3(g)$ = $HBF_2(g)$ were determined by R. F. Porter and S. K. Wason, J. Phys. Chem. 69, 2208 (1965). By the third law method, the enthalpy change was evaluated to be 3.06 ± 0.33 kcal. mole^{-1}. Based on the values of $\Delta H^\circ_{f\ 298.15}$ for $B_2H_6(g)$ and $BF_3(g)$ as 9.8 and -270.1 kcal. mole^{-1}, respectively, the heat of formation for $BHF_2(g)$ was derived to be -175.4 ± 0.8 kcal. mole^{-1}. The drift in the third law heat of reaction is 3.6 e.u.

Heat Capacity and Entropy.

The infrared spectrum of $BHF_2(g)$ has been observed by the following investigators:

T. D. Coyle, J. J. Ritter and T. C. Farrar, Proc. Chem. Soc. 25 (1964).
M. Perec and L. N. Becka, J. Chem. Phys. 43, 721 (1965).
L Lynds, J. Chem. Phys. 42, 1124 (1965).
R. F. Porter and S. K. Wason, J. Phys. Chem. 69, 2208 (1965).

The vibrational frequencies, except ν_5, were obtained from Porter and Wason, and corrected to the average isotopic species. The value of ν_5 was estimated by comparison with the same value reported by other investigators. The molecular structure, bond distances and angle were obtained from Perec and Becka, loc. cit. The three principal moments of inertia are: I_A = 7.9959 X 10^{-39}, I_B = 1.0404 X 10^{-39} and I_C = 9.0362 X 10^{-39} g. cm.^{2}

The vibrational-rotational spectrum of $BHF_2(g)$ has been studied by L. Lynds and C. D. Bass, J. Chem. Phys. 43, 4357 (1965). The values of ν_1, ν_2, ν_3 and ν_6 were assigned as 1164.2, 2620.8, 541.5 and 923.5 cm.$^{-1}$, respectively, which are in fair agreement with the adopted values reported by Porter and Wason, loc. cit.

Boron Hydroxide Difluoride ($BOHF_2$)

(Ideal Gas) Mol. Wt. = 65.828

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.803	- 257.351	- 257.351	INFINITE
100	8.149	53.684	73.732	- 2.005	- 257.990	- 255.986	559.429
200	10.076	59.849	65.370	- 1.104	- 258.511	- 253.779	277.304
298	12.424	64.310	64.310	.000	- 259.000	- 251.354	184.238
300	12.468	64.387	64.310	.023	- 259.009	- 251.307	183.068
400	14.702	68.286	64.826	1.384	- 259.443	- 248.671	135.861
500	16.581	71.776	65.873	2.951	- 259.810	- 245.935	107.493
600	18.070	74.936	67.125	4.687	- 260.109	- 243.130	88.556
700	19.233	77.813	68.449	6.555	- 260.348	- 240.280	75.015
800	20.150	80.443	69.787	8.526	- 260.540	- 237.401	64.852
900	20.885	82.861	71.107	10.579	- 260.692	- 234.500	56.942
1000	21.486	85.093	72.395	12.698	- 260.816	- 231.582	50.610
1100	21.985	87.165	73.645	14.872	- 260.920	- 228.654	45.427
1200	22.406	89.097	74.853	17.092	- 261.007	- 225.716	41.106
1300	22.764	90.905	76.019	19.351	- 261.085	- 222.772	37.450
1400	23.072	92.603	77.143	21.644	- 261.156	- 219.821	34.314
1500	23.339	94.204	78.228	23.965	- 261.225	- 216.866	31.596
1600	23.571	95.718	79.274	26.310	- 261.295	- 213.907	29.217
1700	23.773	97.153	80.284	28.678	- 261.365	- 210.942	27.117
1800	23.952	98.517	81.259	31.064	- 261.439	- 207.976	25.251
1900	24.109	99.817	82.202	33.467	- 261.513	- 205.004	23.580
2000	24.248	101.057	83.114	35.885	- 261.589	- 202.027	22.075
2100	24.372	102.243	83.997	38.316	- 261.667	- 199.047	20.714
2200	24.483	103.379	84.852	40.759	- 261.749	- 196.063	19.476
2300	24.582	104.470	85.682	43.213	- 261.833	- 193.076	18.346
2400	24.671	105.518	86.487	45.675	- 261.923	- 190.083	17.309
2500	24.751	106.527	87.268	48.146	- 267.406	- 186.982	16.345
2600	24.823	107.499	88.028	50.625	- 267.496	- 183.762	15.446
2700	24.889	108.437	88.766	53.111	- 267.588	- 180.537	14.613
2800	24.949	109.343	89.485	55.603	- 267.681	- 177.314	13.839
2900	25.003	110.220	90.185	58.100	- 267.776	- 174.080	13.118
3000	25.053	111.068	90.867	60.603	- 267.875	- 170.852	12.446
3100	25.098	111.890	91.532	63.111	- 267.974	- 167.616	11.816
3200	25.140	112.688	92.181	65.623	- 268.077	- 164.378	11.226
3300	25.178	113.462	92.814	68.139	- 268.182	- 161.134	10.671
3400	25.214	114.214	93.432	70.658	- 268.291	- 157.888	10.148
3500	25.246	114.946	94.037	73.181	- 268.403	- 154.641	9.656
3600	25.276	115.657	94.627	75.707	- 268.518	- 151.384	9.190
3700	25.304	116.350	95.205	78.236	- 268.637	- 148.130	8.749
3800	25.330	117.025	95.771	80.768	- 268.759	- 144.867	8.331
3900	25.354	117.684	96.324	83.302	- 268.886	- 141.615	7.935
4000	25.377	118.326	96.866	85.839	- 390.194	- 136.202	7.441
4100	25.398	118.953	97.397	88.378	- 390.097	- 129.855	6.922
4200	25.417	119.565	97.918	90.918	- 390.002	- 123.504	6.426
4300	25.436	120.163	98.428	93.461	- 389.911	- 117.158	5.954
4400	25.453	120.748	98.929	96.006	- 389.826	- 110.818	5.504
4500	25.469	121.320	99.420	98.552	- 389.745	- 104.481	5.074
4600	25.484	121.880	99.902	101.099	- 389.666	- 98.139	4.662
4700	25.498	122.429	100.376	103.648	- 389.594	- 91.805	4.269
4800	25.511	122.965	100.841	106.199	- 389.525	- 85.461	3.891
4900	25.524	123.492	101.298	108.751	- 389.461	- 79.137	3.529
5000	25.536	124.007	101.747	111.304	- 389.401	- 72.801	3.182
5100	25.547	124.513	102.188	113.858	- 389.347	- 66.471	2.848
5200	25.558	125.009	102.622	116.413	- 389.296	- 60.138	2.527
5300	25.568	125.496	103.049	118.969	- 389.249	- 53.806	2.219
5400	25.577	125.974	103.469	121.526	- 389.209	- 47.486	1.922
5500	25.586	126.444	103.883	124.085	- 389.171	- 41.153	1.635
5600	25.595	126.905	104.290	126.644	- 389.140	- 34.831	1.359
5700	25.603	127.358	104.691	129.204	- 389.114	- 28.501	1.093
5800	25.610	127.803	105.085	131.764	- 389.092	- 22.173	.835
5900	25.618	128.241	105.474	134.326	- 389.075	- 15.850	.587
6000	25.625	128.672	105.857	136.888	- 389.064	- 9.525	.347

Dec. 31, 1962; Mar. 31, 1965

BORON HYDROXIDE DIFLUORIDE ($BOHF_2$) (IDEAL GAS) MOL. WT. = 65.828

Point Group C_s

$S^\circ_{298.15}$ = [64.31] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-257 ± 5] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-259 ± 5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[3680](1)	[888](1)
[1463](1)	[696](1)
[1420](1)	[480](1)
[1250](1)	[480](1)
[1250](1)	

Bond Distance: B-F = [1.30] Å B-O = [1.36] Å O-H = [0.96] Å

Bond Angle: F-B-F = [120]° F-B-O = [120]° B-O-H = [105]° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.05094 X 10^{-114}] g.^{3} cm.^{6}

Heat of Formation.

The value of heat of formation ($\Delta H^\circ_{f\ 298.15}$) was calculated based on an assumption that $\Delta H^\circ_{r\ 298.15}$ = 0 for the reaction 2/3 $BF_3(g)$ + 1/3 $B(OH)_3(g)$ = $BOHF_2(g)$.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from J. S. Gordon, Astrosystems International, Inc., private communication, November 2, 1962. The B-F and O-H bond distances were assumed to be the same as those in $BF_3(g)$ and $H_2O(g)$ molecules, respectively. The B-O bond distance and the bond angles were estimated from related molecules. The three principal moments of inertia are: I_A = 7.8114 X 10^{-39}, I_B = 8.3333 X 10^{-39} and I_C = 1.61447 X 10^{-38} g. cm.^{2}

Boron Oxide Difluoride (BOF_2)

(Ideal Gas)   GFW = 64.8072

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.757	- 199.317	- 199.317	INFINITE
100	8.114	53.574	73.172	- 1.960	- 199.568	- 198.778	434.430
200	9.843	59.653	65.017	- 1.073	- 199.809	- 197.892	216.246
298	11.998	63.989	63.989	.000	- 200.000	- 196.910	144.339
300	12.036	64.063	63.989	.022	- 200.003	- 196.892	143.435
400	13.900	67.792	64.485	1.323	- 200.150	- 195.830	106.997
500	15.307	71.053	65.479	2.787	- 200.272	- 194.737	85.119
600	16.330	73.939	66.653	4.371	- 200.372	- 193.619	70.526
700	17.072	76.515	67.882	6.044	- 200.455	- 192.486	60.097
800	17.618	78.832	69.108	7.779	- 200.530	- 191.344	52.273
900	18.026	80.932	70.307	9.563	- 200.595	- 190.192	46.185
1000	18.337	82.848	71.467	11.381	- 200.660	- 189.032	41.313
1100	18.577	84.608	72.582	13.228	- 200.729	- 187.868	37.326
1200	18.767	86.232	73.653	15.095	- 200.802	- 186.693	34.001
1300	18.919	87.741	74.679	16.980	- 200.883	- 185.515	31.188
1400	19.042	89.148	75.663	18.878	- 200.970	- 184.329	28.775
1500	19.143	90.465	76.607	20.787	- 201.069	- 183.138	26.683
1600	19.227	91.703	77.512	22.706	- 201.176	- 181.938	24.852
1700	19.298	92.871	78.381	24.632	- 201.294	- 180.732	23.235
1800	19.358	93.976	79.217	26.565	- 201.423	- 179.521	21.797
1900	19.409	95.024	80.022	28.504	- 201.559	- 178.300	20.509
2000	19.453	96.020	80.797	30.447	- 201.702	- 177.070	19.349
2100	19.492	96.971	81.545	32.394	- 201.852	- 175.837	18.300
2200	19.527	97.878	82.267	34.345	- 202.010	- 174.593	17.344
2300	19.557	98.747	82.964	36.299	- 202.174	- 173.344	16.471
2400	19.585	99.580	83.640	38.257	- 202.345	- 172.086	15.671
2500	19.611	100.380	84.293	40.216	- 207.912	- 170.714	14.924
2600	19.635	101.149	84.927	42.179	- 208.088	- 169.221	14.224
2700	19.658	101.891	85.542	44.143	- 208.268	- 167.722	13.576
2800	19.680	102.606	86.138	46.110	- 208.449	- 166.218	12.974
2900	19.701	103.297	86.718	48.079	- 208.634	- 164.702	12.412
3000	19.723	103.965	87.282	50.050	- 208.823	- 163.188	11.888
3100	19.744	104.612	87.831	52.024	- 209.012	- 161.664	11.397
3200	19.766	105.240	88.365	53.999	- 209.204	- 160.135	10.937
3300	19.788	105.848	88.886	55.977	- 209.399	- 158.597	10.503
3400	19.810	106.439	89.393	57.957	- 209.595	- 157.053	10.095
3500	19.834	107.014	89.888	59.939	- 209.794	- 155.507	9.710
3600	19.858	107.573	90.372	61.924	- 209.993	- 153.950	9.346
3700	19.882	108.117	90.844	63.911	- 210.195	- 152.390	9.001
3800	19.908	108.648	91.306	65.900	- 210.398	- 150.824	8.674
3900	19.935	109.165	91.757	67.892	- 210.603	- 149.258	8.364
4000	19.962	109.670	92.199	69.887	- 331.987	- 145.535	7.952
4100	19.990	110.164	92.631	71.885	- 331.963	- 140.879	7.510
4200	20.019	110.646	93.054	73.885	- 331.938	- 136.214	7.088
4300	20.049	111.117	93.469	75.888	- 331.914	- 131.551	6.686
4400	20.079	111.578	93.875	77.895	- 331.893	- 126.893	6.303
4500	20.110	112.030	94.273	79.904	- 331.871	- 122.239	5.937
4600	20.142	112.472	94.664	81.917	- 331.849	- 117.577	5.586
4700	20.174	112.906	95.048	83.933	- 331.829	- 112.920	5.251
4800	20.206	113.331	95.424	85.952	- 331.809	- 108.259	4.929
4900	20.239	113.748	95.794	87.974	- 331.790	- 103.607	4.621
5000	20.273	114.157	96.157	89.999	- 331.771	- 98.949	4.325
5100	20.306	114.559	96.514	92.028	- 331.754	- 94.295	4.041
5200	20.340	114.953	96.865	94.061	- 331.735	- 89.634	3.767
5300	20.374	115.341	97.210	96.096	- 331.717	- 84.978	3.504
5400	20.407	115.722	97.549	98.135	- 331.702	- 80.329	3.251
5500	20.441	116.097	97.883	100.178	- 331.684	- 75.667	3.007
5600	20.475	116.466	98.212	102.224	- 331.669	- 71.020	2.772
5700	20.508	116.828	98.535	104.273	- 331.655	- 66.360	2.544
5800	20.541	117.185	98.853	106.325	- 331.640	- 61.705	2.325
5900	20.574	117.537	99.167	108.381	- 331.626	- 57.058	2.114
6000	20.606	117.883	99.476	110.440	- 331.614	- 52.401	1.909

Dec. 31, 1965; Dec. 31, 1966

BORON OXIDE DIFLUORIDE (BOF_2)   (IDEAL GAS)   GFW = 64.8072

Point Group C_{2v}

$S^\circ_{298.15}$ = [64] gibbs/mol

ΔHf°_0 = [-199 ± 15] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-200 ± 15] kcal/mol

Electronic Levels and Quantum Weights

ϵ, cm^{-1}	gi
0	[2]
17171	[2]
22390	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1377 (1)	[850] (1)
856 (1)	[1100] (1)
491 (1)	[500] (1)

Bond Distance : B-F = 1.30 ± 0.05 Å   B-O = 1.40 ± 0.05 Å

Bond Angle: F-B-O = 117 ± 5°   F-B-F = 126 ± 5° $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 9.9464 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation.

The molecule $BF_2O(g)$ is similar to $BO_2(g)$ in that both have an extra electron. Based on an assumption that $D^\circ_0(F_2B\text{-}O) = D^\circ_0(OB\text{-}O) - 10 = 134.3$ kcal/mol, where the quantity -10 kcal/mol is estimated as the resonance stabilization energy in $BO_2(g)$, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $BF_2O(g)$ is calculated to be -206 kcal/mol.

Assuming $D^\circ_0(F_2BO\text{-}H) = D^\circ_0(HO\text{-}H) = 118$ kcal/mol, the value of $\Delta Hf^\circ_{298.15}(F_2BO,g)$ is evaluated as -191.6 kcal/mol, using $\Delta Hf^\circ_0 = 51.63$ and -257.35 kcal/mol for H(g) and $F_2BOH(g)$, respectively.

The value of $\Delta Hf^\circ_{298.15}$ for $BOF_2(g)$ is tentatively adopted as -200 ± 15 kcal/mol.

Heat Capacity and Entropy.

The 4465-Å emission spectrum was observed in a discharge through BF_3 and O_2 by C. W. Mathews, J. Mol. Spectry. 19, 203 (1966). The emitter of the discharge was shown to be either the planar BOF_2 molecule or molecule-ion BOF_2^+. No experimental evidence has been found to distinguish between them. The molecular structure, bond distances and angles were reported by Mathews, based on a rotational analysis of the emission spectrum. These values are adopted here.

Three vibrational frequencies for both $^{11}B^{16}OF_2$ and $^{10}B^{16}OF_2$ molecules (or ions) were determined by vibrational analysis of the 5800 - Å bands of the emission spectrum by C. W. Mathews and K. K. Innes, J. Mol. Spectry. 15, 199 (1965). These values are corrected to the average isotopic species and adopted. The last three frequencies are estimated from values calculated by the valence-force method, using force constants transferred from $COF_2(g)$.

The ground state quantum weight is taken as 2 because of the extra electron. The other two electronic levels are estimated from the band systems at 5800 and 4465 Å, assuming that two systems have a common lower state, i.e. the ground state.

The three principal moments of inertia are: $I_A = 8.4647 \times 10^{-39}$, $I_B = 7.4045 \times 10^{-39}$ and $I_C = 1.5869 \times 10^{-38}\ g\ cm^2$.

Boron Trifluoride (BF_3)

(Ideal Gas) GFW = 67.8062

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.784	- 270.747	- 270.747	INFINITE
100	8.147	50.215	70.075	- 1.986	- 270.998	- 269.907	589.880
200	10.030	56.372	61.806	- 1.087	- 271.228	- 268.722	293.646
298	12.057	60.766	60.766	.000	- 271.420	- 267.452	196.048
300	12.092	60.841	60.766	.022	- 271.424	- 267.428	194.821
400	13.753	64.556	61.262	1.318	- 271.605	- 266.068	145.373
500	15.044	67.770	62.249	2.761	- 271.786	- 264.664	115.684
600	16.030	70.605	63.410	4.317	- 271.953	- 263.223	95.879
700	16.777	73.134	64.622	5.959	- 272.103	- 261.755	81.723
800	17.344	75.413	65.831	7.666	- 272.240	- 260.269	71.102
900	17.779	77.483	67.012	9.423	- 272.363	- 258.765	62.837
1000	18.117	79.374	68.155	11.219	- 272.480	- 257.247	56.221
1100	18.383	81.114	69.255	13.044	- 272.596	- 255.719	50.807
1200	18.595	82.723	70.311	14.893	- 272.712	- 254.178	46.292
1300	18.766	84.218	71.324	16.762	- 272.832	- 252.629	42.471
1400	18.905	85.614	72.296	18.646	- 272.955	- 251.070	39.194
1500	19.021	86.922	73.228	20.542	- 273.086	- 249.502	36.352
1600	19.117	88.153	74.122	22.449	- 273.225	- 247.926	33.865
1700	19.199	89.315	74.982	24.365	- 273.371	- 246.339	31.669
1800	19.268	90.414	75.809	26.288	- 273.526	- 244.748	29.716
1900	19.327	91.457	76.606	28.218	- 273.685	- 243.144	27.968
2000	19.378	92.450	77.373	30.153	- 273.849	- 241.530	26.393
2100	19.422	93.396	78.114	32.093	- 274.019	- 239.912	24.968
2200	19.460	94.301	78.829	34.038	- 274.194	- 238.283	23.671
2300	19.494	95.167	79.521	35.985	- 274.374	- 236.646	22.487
2400	19.524	95.997	80.190	37.936	- 274.560	- 235.002	21.400
2500	19.551	96.795	80.838	39.890	- 280.139	- 233.241	20.390
2600	19.574	97.562	81.467	41.846	- 280.327	- 231.362	19.448
2700	19.595	98.301	82.077	43.805	- 280.516	- 229.472	18.574
2800	19.614	99.014	82.669	45.765	- 280.706	- 227.581	17.764
2900	19.631	99.703	83.245	47.728	- 280.899	- 225.676	17.007
3000	19.647	100.368	83.804	49.691	- 281.095	- 223.774	16.302
3100	19.661	101.013	84.349	51.657	- 281.290	- 221.861	15.641
3200	19.674	101.637	84.880	53.624	- 281.489	- 219.939	15.021
3300	19.685	102.243	85.397	55.592	- 281.689	- 218.012	14.438
3400	19.696	102.831	85.901	57.561	- 281.892	- 216.078	13.889
3500	19.706	103.402	86.393	59.531	- 282.098	- 214.139	13.371
3600	19.715	103.957	86.873	61.502	- 282.304	- 212.192	12.882
3700	19.723	104.497	87.342	63.474	- 282.514	- 210.243	12.419
3800	19.730	105.023	87.800	65.446	- 282.727	- 208.284	11.979
3900	19.738	105.536	88.249	67.420	- 282.943	- 206.328	11.562
4000	19.744	106.036	88.687	69.394	- 404.339	- 202.213	11.048
4100	19.750	106.523	89.116	71.368	- 404.329	- 197.162	10.510
4200	19.756	106.999	89.536	73.344	- 404.320	- 192.105	9.996
4300	19.761	107.464	89.948	75.320	- 404.313	- 187.052	9.507
4400	19.766	107.919	90.351	77.296	- 404.313	- 182.000	9.040
4500	19.771	108.363	90.747	79.273	- 404.313	- 176.952	8.594
4600	19.775	108.797	91.134	81.250	- 404.316	- 171.898	8.167
4700	19.779	109.223	91.515	83.228	- 404.325	- 166.844	7.758
4800	19.783	109.639	91.888	85.206	- 404.335	- 161.787	7.366
4900	19.786	110.047	92.254	87.184	- 404.351	- 156.737	6.991
5000	19.790	110.447	92.614	89.163	- 404.369	- 151.683	6.630
5100	19.793	110.839	92.968	91.142	- 404.392	- 146.634	6.284
5200	19.796	111.223	93.315	93.122	- 404.417	- 141.573	5.950
5300	19.799	111.600	93.657	95.101	- 404.447	- 136.519	5.629
5400	19.801	111.970	93.992	97.081	- 404.482	- 131.471	5.321
5500	19.804	112.334	94.322	99.062	- 404.519	- 126.407	5.023
5600	19.806	112.691	94.647	101.042	- 404.562	- 121.353	4.736
5700	19.808	113.041	94.967	103.023	- 404.610	- 116.293	4.459
5800	19.811	113.386	95.282	105.004	- 404.660	- 111.235	4.191
5900	19.813	113.724	95.591	106.985	- 404.715	- 106.180	3.933
6000	19.815	114.057	95.896	108.966	- 404.775	- 101.117	3.683

Dec. 31, 1960: Dec. 31, 1963; Dec. 31, 1964; Sept. 30, 1965; June 30, 1969

BORON TRIFLUORIDE (BF_3) (IDEAL GAS) GFW = 67.8062

Point Group D_{3h}

ΔHf_0° = -270.7 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 60.77 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -271.42 ± 0.4 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
888	(1)
696.7	(1)
1463.3	(2)
480.7	(2)

Bond Distance: B-F = 1.307 ± 0.002 Å

Bond Angle: F-B-F = 120°

σ = 6

Products of the Moments of Inertia: $I_AI_BI_C = 1.0563 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The adopted heat of formation was selected by a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12-31-68). The data which were considered relating directly to BF_3 were as follows.

A. $NF_3(g) + B(c, \beta) \rightarrow BF_3(g) + 0.5\ N_2$ $\Delta Hr^\circ_{298} = -239.46 \pm 1.2$ kcal/mol

Ludwig and Cooper (1) report the above value after correction for 0.44 percent impurities in the boron. As much as 5 percent unburned boron was determined by analysis.

B. $1.5\ F_2(g) + B(c, \beta) \rightarrow BF_3(g)$

Wise et al. (2) originally reported $\Delta Hr^\circ_{298} = -270.1 \pm 0.24$ kcal/mol but later reanalysis (3) of the impurities and due allowance for their effect changed this to -271.6 ± 0.9 kcal/mol. Johnson et al. (3) using zone refined boron obtained $\Delta Hr^\circ_{298} = -271.65 \pm 0.22$ kcal/mol after correction for 0.12 percent impurities. Domalski and Armstrong (4) obtained $\Delta Hr^\circ_{298} = -271.03 \pm 0.51$ kcal/mol from a combustion in the presence of Teflon, the boron contained 0.32 percent impurities and corrections were included. The above reaction constituted about 0.35 of the total energy measured. The measurements of Gross et al. (5), although on a zone refined sample, did not include a complete purity analysis and their data were not included since probable impurities could introduce serious errors.

C. $3HF(50\ H_2O) + B(c, \beta) + 0.75\ O_2(g) \rightarrow BF_3(g) + 1.5\ H_2O(\ell)$

From the measurements of Gunn (6) on the reaction of $BF_3(g) + 15.67\ HF(3.747\ H_2O) \rightarrow$ [solution] and Good and Mänsson (7) for the reaction $B(c, \beta) + 0.75\ O_2(g) + 18.57\ HF(3.065\ H_2O) \rightarrow$ [solution] $+ 1.5\ H_2O(\ell)$, where the resulting solutions have the same composition, we obtain $\Delta Hr^\circ_{298} = -142.77 \pm 0.5$ kcal/mol. Further details of the simultaneous solution are given by Syverud (8).

Heat Capacity and Entropy

The fundamental frequencies were selected from the measurements of Lindeman and Wilson (9), McKean (10), Nielsen (11), Anderson et al. (12) and Yost et al. (13). The bond lengths and structure are those reported by Gin et al. (14) which are in agreement with those of Kuchitsu and Konaka (15) from gas phase electron diffraction. These measurements disagree with the earlier determinations of Nielson (11) and Levy and Brockway (16) but are considerably more precise and are adopted.

The individual moments of inertia are $I_A = I_B = 8.083 \times 10^{-39}\ g\ cm^2$ and $I_C = 16.166 \times 10^{-39}\ g\ cm^2$.

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Potassium Tetrafluoroborate (KBF_4)

(Crystal) GFW = 125.907

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	27.362	32.000	32.000	.000	-451.000	-426.625	312.724
300	27.433	32.170	32.001	.051	-450.995	-426.474	310.686
400	31.266	40.585	33.122	2.985	-451.237	-418.237	228.514
500	35.125	47.977	35.367	6.305	-450.687	-410.047	179.231
600	33.962	60.430	38.469	13.176	-446.681	-402.250	146.519
700	35.019	65.748	41.994	16.626	-446.165	-394.884	123.288
800	36.075	70.490	45.265	20.180	-445.600	-387.599	105.887
900	37.131	74.800	48.310	23.841	-444.969	-380.385	92.370
1000	38.188	78.767	51.160	27.606	-444.280	-373.246	81.573
1100	39.244	82.456	53.840	31.478	-462.433	-365.155	72.550
1200	40.301	85.916	56.370	35.455	-461.366	-356.356	64.901
1300	41.357	89.183	58.769	39.538	-460.220	-347.652	58.446
1400	42.413	92.287	61.054	43.727	-458.989	-339.037	52.926
1500	43.470	95.249	63.235	48.021	-457.675	-330.514	48.156

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

POTASSIUM TETRAFLUOROBORATE (KBF_4) (CRYSTAL) GFW = 125.907

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = 32.00 ± 4.0 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -451.0 ± 1 kcal/mol

Tt = 556°K

ΔHt° = 3.36 ± 0.04 kcal/mol

Tm = 843°K

ΔHm° = 4.22 ± 0.04 kcal/mol

$\Delta Hs^\circ_{298.15}$ = [80] kcal/mol

Heat of Formation

Bills and Cotton (1) measured the enthalpies of several reactions at 25°C which led to the following result:

$$H_3BO_3(c) + 4(HF\cdot 23\ H_2O) + KNO_3(c) \rightarrow KBF_4(c) + HNO_3\cdot 92\ H_2O + 3H_2O.$$
$$\Delta Hr = -19.26 \pm 0.6 \text{ kcal/mol}$$

Combining this result with the following heat of formation data,

$\Delta Hf^\circ(H_3BO_3, c) = -261.47 \pm 0.2$ kcal/mol (2)
$\Delta Hf^\circ(HF\cdot 23\ H_2O) = -76.75 \pm 0.1$ kcal/mol (3)
$\Delta Hf^\circ(KNO_3, c) = -118.22$ kcal/mol (4)
$\Delta Hf^\circ(HNO_3\cdot 92\ H_2O) = -49.44$ kcal/mol (5)
$\Delta Hf^\circ(H_2O, \ell) = -68.315$ kcal/mol (5)

we derive, $\Delta Hf^\circ(KBF_4, c) = -451.6 \pm 1.2$ kcal/mol.

Gross, Hayman, and Joël (6) recently measured the following heats of reaction:

$NaF(c) + BF_3(g) \rightarrow NaBF_4(c)$ $\Delta Hr = -32.04 \pm 0.12$ kcal/mol

$\left\{\begin{matrix} KBF_4 \\ + \\ NaF \end{matrix}\right\}_c + HF(aq.) \rightarrow \text{Soln A}$ $\Delta Hs = +8.14 \pm 0.18$ kcal/mol

$\left\{\begin{matrix} NaBF_4 \\ + \\ KF \end{matrix}\right\}_c + HF(aq.) \rightarrow \text{Soln A}$ $\Delta Hs = -2.94 \pm 0.13$ kcal/mol.

These data combine to give, $\Delta Hr = -43.13 \pm 0.22$ kcal/mol, for the reaction

$KF(c) + BF_3(g) \rightarrow KBF_4(c)$.

Combining this result with the following heats of formation,

$\Delta Hf^\circ(KF, c) = -135.9 \pm 0.1$ kcal/mol (7)
$\Delta Hf^\circ(BF_3, g) = -271.42 \pm 0.4$ kcal/mol (7)

we derive, $\Delta Hf^\circ(KBF_4, c) = -450.5 \pm 0.7$ kcal/mol. An average value, $\Delta Hf^\circ(KBF_4, c) = -451.0 \pm 1$ kcal/mol, of these two results is adopted here.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig (8). S°_{298} is chosen such that a third-law analysis of the equilibrium data for the reaction

$$KBF_4(c, \ell) \rightleftarrows KF(c, \ell) + BF_3(g)$$

reported by de Boer and van Liempt (9) gives the experimentally determined heat of reaction at 25°C (6).

Transition Data

Tt is from the high temperature studies of Dworkin and Bredig (8). ΔHt° is calculated from their high temperature enthalpy data.

Melting Data

Tm has been reported as 803°K by de Boer and van Liempt (9) and 843°K by Dworkin and Bredig (8). Dworkin and Bredig's value is adopted here. ΔHm° is calculated from their high temperature enthalpy data.

Sublimation Data

ΔHs°_{298} is estimated by comparison with data for $LiAlF_4(c)$ reported by Hildenbrand and Theard (10).

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Potassium Tetrafluoroborate (KBF_4)

(Liquid) GFW = 125.907

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	39.942	35.882	35.882	- .000	- 446.801	- 423.584	310.495
300	39.942	36.129	35.883	.074	- 446.773	- 423.440	308.476
400	39.942	47.620	37.449	4.068	- 445.955	- 415.769	277.165
500	39.942	56.532	40.408	8.062	- 444.731	- 408.369	178.498
600	39.942	63.815	43.720	12.056	- 443.602	- 401.202	146.138
700	39.942	69.972	47.042	16.051	- 442.542	- 394.219	123.081
800	39.942	75.305	50.249	20.045	- 441.536	- 387.388	105.829
900	39.942	80.010	53.300	24.039	- 440.572	- 380.677	92.441
1000	39.942	84.218	56.185	28.033	- 439.654	- 374.072	81.753
1100	39.942	88.025	58.909	32.027	- 457.685	- 366.533	72.823
1200	39.942	91.508	61.482	36.022	- 456.601	- 358.292	65.254
1300	39.942	94.697	63.916	40.016	- 455.543	- 350.144	58.864
1400	39.942	97.657	66.222	44.010	- 454.507	- 342.074	53.400
1500	39.942	100.413	68.410	48.004	- 453.493	- 334.078	48.675

Dec. 31, 1969

POTASSIUM TETRAFLUOROBORATE (KBF_4) (LIQUID) GFW = 125.907

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = 35.88 ± 4.0 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -446.8 ± 1.5 kcal/mol

Tm = 843°K

ΔHm° = 4.22 ± 0.04 kcal/mol

Heat of Formation

$\Delta Hf^\circ(\ell)$ is calculated from $\Delta Hf^\circ(c)$ by adding the heat of melting and the difference in $H_{843}-H_{298}$ between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig (1). S°_{298} is calculated in a manner analogous to the heat of formation.

Melting Data

Tm has been reported as 803°K by de Boer and van Liempt (2) and 843°K by Dworkin and Bredig (1). Dworkin and Bredig's value is adopted here. ΔHm° is calculated from their high temperature enthalpy data.

References

1. A. S. Dworkin and M. A. Bredig, private communication, Oak Ridge Natl. Lab., Sept. 23, 1969.
2. J. H. de Boer and J. A. M. van Liempt, Rec. Trav. Chim., 46, 124 (1927).

Potassium Tetrafluoroborate (KBF_4)

(Ideal Gas) GFW = 125.907

T, °K	$Cp°$ (gibbs/mol)	$S°$ (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	$\Delta Hf°$ (kcal/mol)	$\Delta Gf°$ (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.206	-369.001	-369.001	INFINITE
100	10.833	57.949	91.403	-3.345	-369.950	-366.747	801.525
200	17.379	67.628	77.182	-1.911	-370.616	-363.249	396.940
298	21.257	75.350	75.350	.000	-371.000	-359.550	263.557
300	21.315	75.481	75.350	.039	-371.007	-359.479	261.880
400	23.922	81.993	76.220	2.309	-371.913	-355.476	194.223
500	25.768	87.541	77.943	4.799	-372.193	-351.335	153.568
600	27.097	92.363	79.954	7.446	-372.411	-347.141	126.446
700	28.065	96.617	82.036	10.206	-372.585	-342.914	107.062
800	28.780	100.413	84.100	13.050	-372.730	-338.668	92.520
900	29.318	103.836	86.106	15.956	-372.854	-334.402	81.204
1000	29.730	106.947	88.037	18.910	-372.976	-330.123	72.148
1100	30.050	109.796	89.887	21.899	-392.012	-324.808	64.533
1200	30.304	112.422	91.657	24.917	-391.904	-318.701	58.043
1300	30.507	114.856	93.349	27.958	-391.800	-312.606	52.554
1400	30.672	117.123	94.967	31.018	-391.698	-306.517	47.849
1500	30.808	119.244	96.516	34.092	-391.604	-300.435	43.773
1600	30.921	121.236	97.999	37.178	-391.518	-294.360	40.208
1700	31.016	123.113	99.422	40.275	-391.440	-288.291	37.062
1800	31.097	124.889	100.788	43.381	-391.371	-282.229	34.267
1900	31.166	126.572	102.101	46.494	-391.309	-276.166	31.766
2000	31.225	128.172	103.365	49.614	-391.252	-270.104	29.516
2100	31.276	129.697	104.583	52.739	-391.204	-264.050	27.480
2200	31.321	131.153	105.758	55.869	-391.165	-257.996	25.630
2300	31.360	132.546	106.892	59.003	-391.133	-251.943	23.940
2400	31.395	133.881	107.989	62.141	-391.111	-245.892	22.392
2500	31.425	135.163	109.051	65.282	-396.488	-239.734	20.958
2600	31.453	136.397	110.079	68.426	-396.478	-233.462	19.624
2700	31.477	137.584	111.076	71.572	-396.476	-227.191	18.390
2800	31.499	138.729	112.043	74.721	-396.482	-220.925	17.244
2900	31.519	139.835	112.982	77.872	-396.498	-214.647	16.176
3000	31.536	140.904	113.895	81.025	-396.525	-208.385	15.181
3100	31.553	141.938	114.783	84.179	-396.563	-202.112	14.249
3200	31.567	142.940	115.648	87.335	-396.614	-195.836	13.375
3300	31.581	143.912	116.490	90.493	-396.678	-189.562	12.554
3400	31.593	144.855	117.310	93.651	-396.759	-183.285	11.781
3500	31.604	145.771	118.110	96.811	-396.857	-177.002	11.053
3600	31.614	146.661	118.891	99.972	-396.972	-170.715	10.364
3700	31.624	147.527	119.653	103.134	-397.109	-164.432	9.713
3800	31.633	148.371	120.398	106.297	-397.269	-158.138	9.095
3900	31.641	149.193	121.126	109.461	-397.455	-151.851	8.509
4000	31.648	149.994	121.837	112.625	-518.846	-143.401	7.835
4100	31.655	150.775	122.534	115.790	-518.859	-134.017	7.144
4200	31.662	151.538	123.215	118.956	-518.904	-124.625	6.485
4300	31.668	152.283	123.883	122.123	-518.982	-115.235	5.857
4400	31.674	153.011	124.536	125.290	-519.106	-105.847	5.257
4500	31.679	153.723	125.177	128.457	-519.270	-96.455	4.684
4600	31.684	154.420	125.805	131.625	-519.479	-87.058	4.136
4700	31.688	155.101	126.421	134.794	-519.739	-77.652	3.611
4800	31.693	155.768	127.026	137.963	-520.050	-68.236	3.107
4900	31.697	156.422	127.619	141.133	-520.419	-58.823	2.624
5000	31.701	157.062	128.202	144.303	-520.845	-49.401	2.159
5100	31.704	157.690	128.774	147.473	-521.334	-39.970	1.713
5200	31.708	158.306	129.336	150.643	-521.886	-30.520	1.283
5300	31.711	158.910	129.888	153.814	-522.502	-21.066	.869
5400	31.714	159.502	130.431	156.986	-523.187	-11.609	.470
5500	31.717	160.084	130.965	160.157	-523.938	-2.121	.084
5600	31.720	160.656	131.490	163.329	-524.758	7.372	-.288
5700	31.722	161.217	132.007	166.501	-525.646	16.884	-.647
5800	31.725	161.769	132.515	169.673	-526.599	26.408	-.995
5900	31.727	162.311	133.015	172.846	-527.617	35.949	-1.332
6000	31.729	162.845	133.508	176.019	-528.699	45.515	-1.658

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

POTASSIUM TETRAFLUOROBORATE (KBF_4) (IDEAL GAS) GFW = 125.907

Point Group [C_{3v}]

$\Delta Hf°_0$ = [-369.0 ± 5] kcal/mol

$S°_{298.15}$ = [75.35 ± 3] gibbs/mol

$\Delta Hf°_{298.15}$ = [-371.0 ± 5] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[900] (1)	[1000] (1)	[300] (2)
[450] (1)	[300] (1)	[500] (2)
[350] (1)	[250] (1)	[1400] (2)

Bond Distance: B-F = 1.380 Å K-F = 2.752 Å B-K = [2.863] Å

Bond Angle: F-B-F = 109°28' $F_{ax.}$-B-K = [180°]

σ = [3]

Product of Moments of Inertia: $I_AI_BI_C = [4.529 \times 10^{-113}]\ g^3\ cm^6$

Heat of Formation

ΔHf°(g) is calculated from ΔHf°(c) and the estimated heat of sublimation.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with data for BF_4^-, BF_3, KF, and K_2F_2. The infrared and Raman spectra of BF_4^- in various phases have been reported by (1, 2, 3, 4). The molecular structure is assumed to be the same as for $LiAlF_4$ as discussed by Porter and Zeller (5). The B-F and K-F bond lengths and F-B-F bond angle are average values of the crystallographic data recently reported by Clark and Lynton (6). The B-K bond length is calculated from the above structural data according to the assumed molecular model. The individual moments of inertia are $I_A = I_B = 5.292 \times 10^{-38}\ g\ cm^2$ and $I_C = 1.617 \times 10^{-38}\ g\ cm^2$.

References

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4. J. A. A. Ketelaar and R. L. Fulton, Z. Elektrochem., 64, 641 (1960).
5. R. F. Porter and E. E. Zeller, J. Chem. Phys., 33, 858 (1960).
6. M. J. R. Clark and H. Lynton, Can. J. Chem., 47, 2579 (1969).

Boron Monohydride (BH)

(Ideal Gas) Mol. Wt. = 11.828

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.065	105.039	105.039	INFINITE
100	6.962	33.438	47.242	- 1.380	105.338	103.222	- 225.580
200	6.966	38.265	41.685	- .684	105.653	100.970	- 110.329
298	6.975	41.047	41.047	.000	105.800	98.632	- 72.296
300	6.975	41.090	41.047	.013	105.801	98.588	- 71.818
400	7.014	43.101	41.321	.712	105.831	96.176	- 52.546
500	7.108	44.676	41.840	1.418	105.775	93.767	- 40.983
600	7.252	45.984	42.425	2.135	105.667	91.375	- 33.282
700	7.422	47.114	43.016	2.869	105.534	89.004	- 27.787
800	7.599	48.117	43.592	3.620	105.387	86.651	- 23.671
900	7.769	49.022	44.146	4.388	105.233	84.318	- 20.474
1000	7.926	49.848	44.675	5.173	105.074	82.004	- 17.921
1100	8.067	50.611	45.181	5.973	104.907	79.704	- 15.835
1200	8.193	51.318	45.663	6.786	104.734	77.422	- 14.100
1300	8.305	51.978	46.124	7.611	104.553	75.152	- 12.634
1400	8.404	52.597	46.564	8.447	104.365	72.899	- 11.380
1500	8.492	53.180	46.986	9.292	104.166	70.657	- 10.294
1600	8.571	53.731	47.390	10.145	103.957	68.430	- 9.347
1700	8.641	54.253	47.779	11.005	103.739	66.216	- 8.512
1800	8.704	54.748	48.152	11.873	103.513	64.015	- 7.772
1900	8.761	55.221	48.512	12.746	103.280	61.826	- 7.111
2000	8.814	55.671	48.859	13.625	103.042	59.652	- 6.518
2100	8.861	56.103	49.194	14.509	102.799	57.487	- 5.983
2200	8.905	56.516	49.517	15.397	102.552	55.336	- 5.497
2300	8.946	56.913	49.830	16.290	102.300	53.195	- 5.054
2400	8.984	57.294	50.133	17.186	102.043	51.068	- 4.650
2500	9.019	57.662	50.427	18.086	96.394	49.056	- 4.288
2600	9.053	58.016	50.712	18.990	96.138	47.168	- 3.965
2700	9.084	58.358	50.989	19.897	95.881	45.291	- 3.666
2800	9.114	58.689	51.258	20.807	95.625	43.420	- 3.389
2900	9.142	59.009	51.520	21.720	95.369	41.565	- 3.132
3000	9.169	59.320	51.775	22.635	95.112	39.710	- 2.893
3100	9.195	59.621	52.023	23.553	94.856	37.866	- 2.669
3200	9.220	59.913	52.265	24.474	94.600	36.034	- 2.461
3300	9.244	60.197	52.501	25.397	94.344	34.210	- 2.266
3400	9.268	60.474	52.732	26.323	94.088	32.388	- 2.082
3500	9.290	60.743	52.957	27.251	93.831	30.576	- 1.909
3600	9.312	61.005	53.177	28.181	93.575	28.773	- 1.747
3700	9.333	61.260	53.392	29.113	93.318	26.979	- 1.593
3800	9.354	61.509	53.602	30.048	93.061	25.191	- 1.449
3900	9.375	61.753	53.808	30.984	92.804	23.403	- 1.311
4000	9.394	61.990	54.010	31.923	- 28.633	23.775	- 1.299
4100	9.414	62.222	54.207	32.863	- 28.659	25.085	- 1.337
4200	9.433	62.449	54.401	33.805	- 28.686	26.402	- 1.374
4300	9.452	62.672	54.590	34.750	- 28.713	27.707	- 1.408
4400	9.470	62.889	54.776	35.696	- 28.741	29.022	- 1.441
4500	9.489	63.102	54.959	36.644	- 28.770	30.333	- 1.473
4600	9.507	63.311	55.138	37.593	- 28.799	31.647	- 1.504
4700	9.524	63.516	55.315	38.545	- 28.830	32.961	- 1.533
4800	9.542	63.716	55.487	39.498	- 28.861	34.281	- 1.561
4900	9.559	63.913	55.657	40.453	- 28.893	35.593	- 1.587
5000	9.576	64.106	55.824	41.410	- 28.926	36.912	- 1.613
5100	9.593	64.296	55.989	42.369	- 28.961	38.229	- 1.638
5200	9.610	64.483	56.150	43.329	- 28.996	39.543	- 1.662
5300	9.627	64.666	56.309	44.291	- 29.032	40.862	- 1.685
5400	9.643	64.846	56.466	45.254	- 29.070	42.180	- 1.707
5500	9.660	65.023	56.620	46.219	- 29.109	43.505	- 1.729
5600	9.676	65.197	56.771	47.186	- 29.149	44.821	- 1.749
5700	9.692	65.369	56.921	48.154	- 29.192	46.142	- 1.769
5800	9.708	65.537	57.068	49.124	- 29.236	47.466	- 1.788
5900	9.724	65.704	57.213	50.096	- 29.281	48.785	- 1.807
6000	9.740	65.867	57.356	51.069	- 29.328	50.112	- 1.825

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964

BORON MONOHYDRIDE (BH) (IDEAL GAS) MOL. WT. = 11.828

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0}$ = 105.0 ± 2.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = [41.047] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 105.8 ± 2.0 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	1

ω_e = [2368] cm.$^{-1}$ $\omega_e x_e$ = [49] cm.$^{-1}$ σ = 1

B_e = 12.036 cm.$^{-1}$ α_e = .413 cm.$^{-1}$ r_e = 1.2325 Å

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was calculated from D_0 (BH) = 3.39 ± 0.04 e.v. reported by A. C. Hurley, Proc. Royal Soc. (London), A261, 237 (1961). Hurley stated "by combining an analysis of the spectroscopic data with theoretical calculations we obtain a greatly improved estimate of D_0 (BH)". This value and the other D_0 (BH) values which are tabulated below are based on the same spectroscopic data but differ due to different methods of analysis.

D_0 (BH)	Method	Reference
3.0 ± 0.4 e.v.	Birge-Sponer extrapolations	A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1953.
3.5 e.v.	Observed predissociation by rotation in BH, A$^1\Pi$ and deduced D_0(BH).	G. M. Almy and R. B. Horsfall Jr., Phys. Rev., 51, 491 (1937).
< 3.51 e.v.	Pre-dissociation limit. This is only an upper limit due to a maximum in the potential Curve of the A$^1\Pi$ state.	G. Herzberg and L. G. Mundie, J. Chem. Phys. 8, 263 (1940) and G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950.
3.38 ± 0.04 e.v.	The potential energy curve of the A$^1\Pi$ state was determined and was found to have a maximum and a minimum in agreement with Herzberg and Mundie (loc. cit.)	The selected D_0 (BH) value as reported by Hurley (loc. cit.).

Heat Capacity and Entropy.

The molecular constants from G. Herzberg (loc. cit.) were adjusted for the natural abundance of B^{10} and B^{11}. Because the constants ω_e and $\omega_e x_e$ could not be determined directly from the spectrum, Almy and Horsfall (loc. cit.) obtained estimates for the ground state X $^1\Sigma^+$ from the rotational constants for this state and the relations $D_e = 4 B_e^3/\omega_e^2$ and $\omega_e x_e/\omega_e = 0.6\ \alpha_e/B_e$.

Boron Oxide Hydride (HBO)

(Ideal Gas) Mol. Wt. = 27.828

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.215	- 19.873	- 19.873	INFINITE
100	6.972	40.373	55.574	- 1.520	- 19.921	- 20.654	45.138
200	7.620	45.349	49.342	- .799	- 19.921	- 21.397	23.381
298	8.635	48.584	48.584	.000	- 20.000	- 22.109	16.206
300	8.652	48.637	48.584	.016	- 20.002	- 22.123	16.116
400	9.494	51.246	48.934	.925	- 20.118	- 22.813	12.464
500	10.190	53.442	49.622	1.910	- 20.261	- 23.471	10.259
600	10.802	55.355	50.421	2.960	- 20.413	- 24.099	8.777
700	11.345	57.061	51.250	4.068	- 20.561	- 24.700	7.711
800	11.819	58.608	52.074	5.227	- 20.699	- 25.283	6.907
900	12.225	60.024	52.880	6.430	- 20.825	- 25.848	6.277
1000	12.571	61.331	53.661	7.670	- 20.943	- 26.400	5.769
1100	12.863	62.543	54.414	8.942	- 21.057	- 26.940	5.352
1200	13.110	63.673	55.139	10.241	- 21.168	- 27.469	5.003
1300	13.318	64.731	55.836	11.563	- 21.281	- 27.991	4.705
1400	13.496	65.724	56.508	12.904	- 21.396	- 28.501	4.449
1500	13.647	66.661	57.154	14.261	- 21.518	- 29.006	4.226
1600	13.776	67.546	57.776	15.632	- 21.647	- 29.501	4.029
1700	13.888	68.384	58.375	17.016	- 21.783	- 29.986	3.855
1800	13.984	69.181	58.954	18.409	- 21.928	- 30.466	3.699
1900	14.068	69.939	59.512	19.812	- 22.078	- 30.935	3.558
2000	14.141	70.663	60.052	21.223	- 22.234	- 31.398	3.431
2100	14.206	71.354	60.574	22.640	- 22.396	- 31.851	3.315
2200	14.263	72.017	61.079	24.064	- 22.565	- 32.299	3.208
2300	14.313	72.652	61.568	25.492	- 22.739	- 32.738	3.111
2400	14.358	73.262	62.043	26.926	- 22.920	- 33.166	3.020
2500	14.398	73.849	62.503	28.364	- 28.494	- 33.483	2.927
2600	14.434	74.414	62.951	29.805	- 28.679	- 33.677	2.831
2700	14.466	74.960	63.385	31.250	- 28.866	- 33.866	2.741
2800	14.495	75.486	63.808	32.699	- 29.056	- 34.048	2.657
2900	14.522	75.995	64.220	34.149	- 29.248	- 34.219	2.579
3000	14.546	76.488	64.621	35.603	- 29.443	- 34.390	2.505
3100	14.567	76.965	65.011	37.058	- 29.640	- 34.552	2.436
3200	14.587	77.428	65.392	38.516	- 29.840	- 34.708	2.370
3300	14.605	77.877	65.764	39.976	- 30.043	- 34.855	2.308
3400	14.622	78.314	66.126	41.437	- 30.249	- 35.000	2.250
3500	14.637	78.738	66.481	42.900	- 30.457	- 35.139	2.194
3600	14.652	79.150	66.827	44.365	- 30.668	- 35.266	2.141
3700	14.665	79.552	67.165	45.830	- 30.883	- 35.391	2.090
3800	14.677	79.943	67.496	47.298	- 31.099	- 35.507	2.042
3900	14.688	80.325	67.821	48.766	- 31.319	- 35.627	1.996
4000	14.698	80.697	68.138	50.235	- 152.721	- 33.589	1.835
4100	14.708	81.060	68.449	51.705	- 152.715	- 30.611	1.632
4200	14.717	81.414	68.753	53.177	- 152.711	- 27.626	1.437
4300	14.725	81.761	69.052	54.649	- 152.710	- 24.652	1.253
4400	14.733	82.099	69.344	56.122	- 152.713	- 21.672	1.076
4500	14.741	82.430	69.631	57.595	- 152.719	- 18.696	.908
4600	14.748	82.754	69.913	59.070	- 152.727	- 15.713	.747
4700	14.754	83.072	70.190	60.545	- 152.739	- 12.737	.592
4800	14.760	83.382	70.461	62.021	- 152.753	- 9.754	.444
4900	14.766	83.687	70.728	63.497	- 152.771	- 6.782	.302
5000	14.771	83.985	70.990	64.974	- 152.791	- 3.801	.166
5100	14.776	84.278	71.248	66.451	- 152.815	- .820	.035
5200	14.781	84.565	71.501	67.929	- 152.841	2.158	- .091
5300	14.786	84.846	71.750	69.407	- 152.871	5.144	- .212
5400	14.790	85.123	71.996	70.886	- 152.904	8.118	- .329
5500	14.794	85.394	72.237	72.365	- 152.939	11.109	- .441
5600	14.798	85.661	72.474	73.845	- 152.979	14.083	- .550
5700	14.802	85.923	72.708	75.325	- 153.022	17.069	- .654
5800	14.805	86.180	72.938	76.805	- 153.068	20.056	- .756
5900	14.808	86.433	73.164	78.286	- 153.117	23.042	- .853
6000	14.811	86.682	73.388	79.767	- 153.169	26.030	- .948

Dec. 31, 1960; Dec. 31, 1964

BORON OXIDE HYDRIDE (HBO) (IDEAL GAS) MOL. Wt. = 27.828

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [50.236] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-20 ± 20] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-20 ± 20] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[1900](1)
[700](2)
[2300](1)

Bond Distance: H-B = [1.23] Å B=O = [1.20] Å

Bond Angle: H-B-O = [180]°

Rotational Constants: B_0 = [1.3011] cm.$^{-1}$

σ = 1

Heat of Formation.

The heat of formation of the hypothetical species HBO(g) is controversial. Using $\Delta H^\circ_{r\ 298.15}$ = [255] kcal. mole^{-1} for the reaction HBO(g) = H(g) + B(g) + O(g), the value of $\Delta H^\circ_{f\ 298.15}$ for HBO(g) is calculated as [-13] kcal. mole^{-1}. The value of $\Delta H^\circ_{r\ 298.15}$ is the sum of the constituent bond energies, i.e. D(H-B) = 87 and D(B=O) = 168 kcal. mole^{-1}. The D(H-B) value is derived from the dissociation of BH_3(g) and D(B=O) value is calculated as the average value of the B=O bond energies, 175 and 161 kcal. mole^{-1}, in BO(g) and BO_2(g) molecules, respectively.

However, by comparison with the following dissociation reactions:

$(FBO)_3$ (g) → 3 FBO (g) $\Delta H^\circ_{r\ 298.15}$ = 135 kcal. mole^{-1} or 45 kcal. mole^{-1} per mole of FBO(g)

$(HOBO)_3$(g) → 3 HOBO(g) $\Delta H^\circ_{r\ 298.15}$ = 141.8 kcal. mole^{-1} or 47 kcal. mole^{-1} per mole of HOBO(g)

$(ClBO)_3$(g) → 3 ClBO(g) $\Delta H^\circ_{r\ 298.15}$ = 170.6 kcal. mole^{-1} or 57 kcal. mole^{-1} per mole of ClBO(g)

it is estimated $\Delta H^\circ_{r\ 298.15}$ = [70] kcal. mole^{-1} for the reaction 1/3$(HBO)_3$(g) → HBO(g), based on the electronegativity difference among the F, Cl and H atoms. Hence the value of $\Delta H^\circ_{f\ 298.15}$ for HBO(g) is calculated to be -27 kcal. mole^{-1}. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for HBO(g) is 1/2(-13 -27) = -20 kcal. mole^{-1}. The uncertainty is given as ± 20 kcal. mole^{-1}. Other methods of estimation have been tried such as the comparison of the difference in $\Delta H^\circ_{f\ 298.15}$ between H-CH_3 and HO-CH_3 with the corresponding difference between H-BO and HO-BO, etc. They lead to very large negative values for $H^\circ_{f\ 298.15}$(HBO, g). However, a value of 260 ± 15 kcal. mole^{-1} for the atomization of HBO(g) was used by L. V. Gurveech, et al., "Thermodynamic Properties of Individual Substances," Vol. I, Academy of Science, USSR, Moscow, 1962, which was obtained by comparison with the dissociation energies for BO, BH, CN, CH and HCN molecules.

Heat Capacity and Entropy.

The vibrational frequencies and molecular structure were obtained from W. H. Evans, private communication, October 6, 1960. The bond lengths of H-B and B=O in the HBO(g) molecule were assumed to be the same as those in the BH(g) and BO(g) molecules, respectively. The moment of inertia (I) is calculated as 2.1561 X 10^{-39} g. cm.^{2}

Boron Oxide Hydride Unipositive Ion (HBO^+)

(Ideal Gas) GFW = 27.81782

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	9.067	51.774	51.774	.000	335.000	330.452	-242.228
300	9.085	51.831	51.775	.017	335.008	330.423	-240.713
400	9.931	54.565	52.142	.969	335.433	328.831	-179.665
500	10.646	56.859	52.862	1.999	335.831	327.134	-142.990
600	11.273	58.857	53.698	3.095	336.222	325.358	-118.511
700	11.815	60.636	54.564	4.251	336.618	323.515	-101.006
800	12.272	62.245	55.425	5.456	337.023	321.616	-87.861
900	12.652	63.713	56.266	6.702	337.437	319.665	-77.625
1000	12.966	65.063	57.079	7.984	337.858	317.669	-69.426
1100	13.226	66.311	57.862	9.294	338.279	315.629	-62.710
1200	13.441	67.471	58.615	10.627	338.699	313.553	-57.106
1300	13.620	68.554	59.338	11.981	339.114	311.439	-52.358
1400	13.770	69.569	60.033	13.350	339.525	309.296	-48.283
1500	13.897	70.524	60.701	14.734	339.926	307.121	-44.747
1600	14.004	71.424	61.344	16.129	340.318	304.921	-41.650
1700	14.096	72.276	61.962	17.534	340.700	302.698	-38.914
1800	14.175	73.084	62.557	18.948	341.072	300.450	-36.480
1900	14.243	73.852	63.132	20.369	341.436	298.185	-34.299
2000	14.302	74.584	63.686	21.796	341.794	295.899	-32.334
2100	14.354	75.284	64.222	23.229	342.144	293.596	-30.555
2200	14.400	75.952	64.740	24.667	342.487	291.276	-28.936
2300	14.441	76.593	65.242	26.109	342.823	288.939	-27.455
2400	14.477	77.209	65.728	27.555	343.151	286.592	-26.098
2500	14.509	77.800	66.199	29.004	338.085	284.335	-24.857
2600	14.538	78.370	66.656	30.456	338.408	282.180	-23.719
2700	14.564	78.919	67.100	31.912	338.728	280.013	-22.666
2800	14.588	79.449	67.532	33.369	339.045	277.830	-21.686
2900	14.610	79.962	67.952	34.829	339.358	275.643	-20.773
3000	14.631	80.457	68.360	36.291	339.668	273.436	-19.920
3100	14.649	80.937	68.758	37.755	339.977	271.222	-19.121
3200	14.667	81.403	69.146	39.221	340.282	269.003	-18.372
3300	14.684	81.854	69.524	40.689	340.584	266.772	-17.668
3400	14.699	82.293	69.894	42.158	340.882	264.530	-17.004
3500	14.715	82.719	70.254	43.629	341.178	262.279	-16.377
3600	14.729	83.134	70.606	45.101	341.472	260.022	-15.785
3700	14.743	83.538	70.950	46.574	341.762	257.753	-15.225
3800	14.756	83.931	71.286	48.049	342.050	255.482	-14.694
3900	14.770	84.315	71.616	49.526	342.336	253.197	-14.189
4000	14.783	84.689	71.938	51.003	221.438	253.052	-13.826
4100	14.795	85.054	72.253	52.482	221.950	253.834	-13.531
4200	14.808	85.410	72.562	53.962	222.460	254.613	-13.249
4300	14.820	85.759	72.865	55.444	222.967	255.371	-12.979
4400	14.833	86.100	73.162	56.926	223.470	256.119	-12.722
4500	14.845	86.433	73.453	58.410	223.971	256.851	-12.474
4600	14.857	86.760	73.739	59.895	224.471	257.580	-12.238
4700	14.869	87.079	74.019	61.382	224.967	258.295	-12.011
4800	14.881	87.393	74.295	62.869	225.462	258.999	-11.793
4900	14.893	87.700	74.565	64.358	225.953	259.690	-11.583
5000	14.905	88.001	74.831	65.848	226.442	260.375	-11.381
5100	14.916	88.296	75.092	67.339	226.928	261.048	-11.187
5200	14.928	88.586	75.349	68.831	227.413	261.712	-10.999
5300	14.940	88.870	75.601	70.324	227.896	262.367	-18.819
5400	14.951	89.149	75.850	71.819	228.375	263.009	-10.645
5500	14.963	89.424	76.094	73.315	228.854	263.654	-10.477
5600	14.974	89.694	76.334	74.811	229.327	264.271	-10.314
5700	14.986	89.959	76.571	76.309	229.799	264.899	-10.157
5800	14.997	90.219	76.804	77.809	230.269	265.508	-10.005
5900	15.008	90.476	77.034	79.309	230.737	266.111	-9.857
6000	15.019	90.728	77.260	90.810	231.202	266.712	-9.715

June 30, 1968

BORON OXIDE HYDRIDE UNIPOSITIVE ION (HBO^+) (IDEAL GAS) GFW = 27.81782

Point Group [$C_{\infty v}$]

ΔHf°_0 = [335 ± 20] kcal/mol

$S^\circ_{298.15}$ = [51.8 ± 1.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [335 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[20000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1700] (1)
[600] (2)
[2000] (1)

Bond Distance: B-H = [1.25] Å   B-O = [1.25] Å

Bond Angle: H-B-O = [180°]   σ = 1

Rotational Constant: B_0 = [1.208] cm^{-1}

Heat of Formation

Using the correlations developed by A. D. Walsh, J. Chem. Soc. 2288 (1953) for HAB molecules the electron removed by ionization ought to be a bonding electron. This indicates a high ionization potential and also the bond dissociation energy of $BO\text{-}H^+$ should be significantly less than BO-H. Assuming a decrease of 40 kcal we obtain $\Delta Hf^\circ_{298}(HBO^+, g)$ = 335 ± 20 kcal/mol which corresponds to an ionization potential of 355 kcal or 15.4 ± 1eV. This is in accord with the ionization potential of BO, 12.8eV, from National Bureau of Standards Report 8628, Jan. 1, 1965, which should be less than HBO since the electron in BO is unpaired.

Heat Capacity and Entropy

According to the correlations of Walsh loc.cit., the molecule should be linear and since the unpaired electron is in a pi orbital, the ground state should be $^2\Pi$. A first excited state is estimated at 20000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecule CO^+. Since HBO^+ is lacking a bonding electron compared to HBO, we assume that the bond lengths will be slightly longer than in HBO. The vibrational frequencies are also estimated from those in HBO by assuming all values to be 10 per cent lower due to the weaker bonding.

The enthalpy at 0°K is -2.275 kcal/mol.

Metaboric Acid (HBO_2)

(Crystal) Mol. Wt. = 43.828

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T. °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	13.000	11.700	11.700	.000	- 191.870	- 175.677	128.769
300	13.100	11.781	11.700	.024	- 191.870	- 175.577	127.902
400	14.700	15.778	12.234	1.417	- 191.857	- 170.147	92.959
500	15.900	19.187	13.292	2.947	- 191.821	- 164.723	71.997
600	17.100	22.188	14.529	4.595	- 191.753	- 159.309	58.025
700	18.863	24.961	15.823	6.396	- 191.597	- 153.912	48.051
800	20.300	27.577	17.131	8.357	- 191.332	- 148.547	40.579
900	21.425	30.036	18.429	10.446	- 190.979	- 143.219	34.777
1000	22.200	32.337	19.706	12.630	- 190.566	- 137.933	30.144
1100	22.480	34.466	20.953	14.865	- 190.137	- 132.691	26.362
1200	22.700	36.432	22.162	17.124	- 189.712	- 127.486	23.217
1300	22.860	38.256	23.331	19.403	- 189.296	- 122.319	20.563
1400	22.960	39.954	24.458	21.694	- 188.893	- 117.181	18.292
1500	23.000	41.540	25.545	23.993	- 188.509	- 112.074	16.328

Sept 30, 1962; Dec. 31, 1964

METABORIC ACID (HBO_2) (CRYSTAL) MOL. WT. = 43.828

$S^\circ_{298.15}$ = [11.7 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

T_m = 509 ± 1°K

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -191.87 ± 0.20 kcal. mole^{-1}

ΔH°_m = Unknown

$\Delta H^\circ_{s\ 298.15}$ = 57.9 ± 1.0 kcal. mole^{-1}

Heat of Formation.

The enthalpy change (ΔH°_r) of the reaction HBO_2 (c, I) + H_2O(l) = H_3BO_3(c) has been determined by M. V. Kilday and E. J. Prosen, J. Am. Chem. Soc. 82, 5508 (1960). From the value, $\Delta H^\circ_{r\ 298.15}$ = -1.28 kcal. mole^{-1}, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for HBO_2 (c, I) is derived to be -191.87 ± 0.20 kcal. mole^{-1} which is adopted. The heats of solution of HBO_2 (c, I) in H_2O(l) was measured by N. D. Sokolova, S. M. Skuratov, A. M. Shemonaeva and V. M. Yuldasheva, Russ. J. Inorg. Chem. 6, 395 (1961). Based on the reported value, $\Delta H^\circ_{r\ 298.15}$ = 1.76 ± 0.01 kcal. mole^{-1} for the reaction HBO_2(c, I) + 501 H_2O(l) = $H_3BO_3 \cdot 500\ H_2O$(Sol.), the heat of formation for HBO_2(c, I) was derived as -189.46 ± 0.20 kcal. mole^{-1}, using $\Delta H^\circ_{f\ 298.15}$($H_2O$, l) = -68.317 and $\Delta H^\circ_{f\ 298.15}$($H_3BO_3 \cdot 500\ H_2O$, Sol.) = -256.02 ± 0.20 kcal. mole^{-1}.

Heat Capacity and Entropy.

The values of heat capacity for HBO_2(c, I) were estimated by comparison with those of its constituent oxides. $S^\circ_{298.15}$ was calculated as the sum of the entropy contributions from H^+ and BO_2^- in HBO_2(c) suggested by K. K. Kelley, private communication, June 1960, and O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958.

Melting Data.

F. C. Kracek, G. W. Morey and H. E. Merwin, Am. J. Sci. [5] 35A, 143 (1938) reported the existence of three crystal forms of HBO_2(c), namely HBO_2(c, I), m.p. 509 ± 1°K; HBO_2(c, II), m.p. 474.1 ± 0.5°K; and HBO_2(c, III), m.p. 449.2 ± 0.2°K. However, there was no solid phase equilibrium found among these three crystals. N. D. Sokolova, S. M. Skuratov, A. M. Shemonaeva and V. M. Yuldasheva, loc. cit., measured the heats of solution in water of HBO_2(c, I) and HBO_2(c, II) and derived the heat of transition as $\Delta H^\circ_{t\ 298.15}$(II → I) = 1.29 kcal. mole^{-1}.

Heat of Sublimation.

The value of $\Delta H^\circ_{s\ 298.15}$ was calculated as the difference between the $\Delta H^\circ_{f\ 298.15}$ values for HBO_2(g) and HBO_2(c).

Metaboric Acid (HBO_2)

(Ideal Gas) Mol. Wt. = 43.828

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.554	- 133.175	- 133.175	INFINITE
100	7.984	47.787	65.377	- 1.759	- 133.478	- 132.878	290.390
200	8.816	53.517	58.155	- .928	- 133.709	- 132.196	144.450
298	10.094	57.273	57.273	.000	- 134.000	- 131.395	96.310
300	10.118	57.336	57.273	.019	- 134.006	- 131.379	95.705
400	11.366	60.420	57.686	1.094	- 134.311	- 130.457	71.275
500	12.466	63.078	58.504	2.287	- 134.611	- 129.459	56.584
600	13.402	65.436	59.466	3.582	- 134.896	- 128.401	46.768
700	14.189	67.562	60.474	4.962	- 135.161	- 127.297	39.742
800	14.851	69.502	61.483	6.415	- 135.404	- 126.159	34.463
900	15.414	71.284	62.474	7.929	- 135.626	- 124.989	30.350
1000	15.895	72.934	63.438	9.495	- 135.831	- 123.795	27.054
1100	16.311	74.469	64.372	11.106	- 136.026	- 122.583	24.354
1200	16.671	75.904	65.274	12.756	- 136.210	- 121.351	22.100
1300	16.986	77.251	66.144	14.439	- 136.390	- 120.106	20.191
1400	17.260	78.520	66.983	16.151	- 136.566	- 118.847	18.552
1500	17.501	79.719	67.793	17.890	- 136.742	- 117.575	17.130
1600	17.713	80.856	68.574	19.651	- 136.920	- 116.292	15.884
1700	17.901	81.935	69.328	21.432	- 137.100	- 114.996	14.783
1800	18.066	82.963	70.057	23.230	- 137.284	- 113.691	13.803
1900	18.214	83.944	70.763	25.044	- 137.471	- 112.376	12.926
2000	18.345	84.882	71.445	26.872	- 137.659	- 111.051	12.135
2100	18.462	85.779	72.107	28.713	- 137.851	- 109.713	11.417
2200	18.567	86.641	72.748	30.564	- 138.047	- 108.370	10.765
2300	18.661	87.468	73.370	32.426	- 138.246	- 107.017	10.168
2400	18.746	88.264	73.974	34.296	- 138.451	- 105.652	9.620
2500	18.822	89.031	74.561	36.175	- 144.049	- 104.176	9.107
2600	18.892	89.771	75.132	38.060	- 144.256	- 102.576	8.622
2700	18.955	90.485	75.688	39.953	- 144.465	- 100.968	8.172
2800	19.012	91.175	76.228	41.851	- 144.676	- 99.354	7.755
2900	19.065	91.843	76.755	43.755	- 144.889	- 97.726	7.364
3000	19.113	92.490	77.269	45.664	- 145.105	- 96.099	7.000
3100	19.156	93.118	77.770	47.577	- 145.323	- 94.464	6.659
3200	19.197	93.727	78.260	49.495	- 145.544	- 92.821	6.339
3300	19.234	94.318	78.737	51.417	- 145.768	- 91.168	6.037
3400	19.268	94.893	79.204	53.342	- 145.995	- 89.511	5.753
3500	19.300	95.452	79.660	55.270	- 146.225	- 87.849	5.485
3600	19.329	95.996	80.107	57.202	- 146.458	- 86.175	5.231
3700	19.356	96.526	80.543	59.136	- 146.696	- 84.497	4.991
3800	19.381	97.042	80.971	61.073	- 146.935	- 82.808	4.762
3900	19.404	97.546	81.389	63.012	- 147.178	- 81.123	4.546
4000	19.426	98.038	81.799	64.954	- 268.603	- 77.283	4.222
4100	19.447	98.518	82.201	66.897	- 268.621	- 72.500	3.864
4200	19.466	98.986	82.595	68.843	- 268.641	- 67.709	3.523
4300	19.483	99.445	82.982	70.790	- 268.665	- 62.927	3.198
4400	19.500	99.893	83.361	72.739	- 268.694	- 58.145	2.888
4500	19.516	100.331	83.733	74.690	- 268.725	- 53.359	2.591
4600	19.530	100.760	84.099	76.643	- 268.758	- 48.567	2.307
4700	19.544	101.180	84.458	78.596	- 268.796	- 43.779	2.036
4800	19.557	101.592	84.810	80.551	- 268.837	- 38.991	1.775
4900	19.569	101.995	85.157	82.508	- 268.881	- 34.208	1.526
5000	19.581	102.391	85.498	84.465	- 268.928	- 29.420	1.286
5100	19.592	102.779	85.833	86.424	- 268.980	- 24.626	1.055
5200	19.602	103.159	86.162	88.384	- 269.033	- 19.836	.834
5300	19.612	103.533	86.487	90.344	- 269.089	- 15.042	.620
5400	19.621	103.899	86.806	92.306	- 269.151	- 10.250	.415
5500	19.630	104.260	87.120	94.268	- 269.213	- 5.452	.217
5600	19.638	104.613	87.429	96.232	- 269.281	- .660	.026
5700	19.646	104.961	87.734	98.196	- 269.351	4.137	- .159
5800	19.654	105.303	88.034	100.161	- 269.425	8.937	- .337
5900	19.661	105.639	88.329	102.127	- 269.502	13.736	- .509
6000	19.668	105.969	88.620	104.093	- 269.583	18.543	- .675

Dec. 31, 1960; Mar. 31, 1961; June 30, 1963; Dec. 31, 1964

METABORIC ACID (HBO_2) (IDEAL GAS) MOL. WT. = 43.828

Point Group [C_s]

$S^\circ_{298.15}$ = [57.273] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -133.2 ± 1.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -134.0 ± 1.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
3680(1)	[1250](1)
2030(1)	[600](1)
1420(1)	[700](1)

Bond Distance: H-O = [1.0] Å O-B = [1.34] Å B=O = [1.20] Å

Bond Angle: H-O-B = [120]° O-B-O = [180]° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 9.6951 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation.

The equilibrium pressures of the reaction $1/2\ B_2O_3(l) + 1/2\ H_2O(g) = HBO_2(g)$ have been measured by several investigators. Using the equilibrium data reported, the heats of reaction ($\Delta H^\circ_{r\ 298.15}$) were evaluated by both the second and third law methods. The corresponding heats of formation for $HBO_2(g)$ were derived based on the $\Delta H^\circ_{r\ 298.15}$ values obtained by the third law method. The results obtained are presented as follows.

Investigator	Temperature, °K.	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H^\circ_{f\ 298.15}$ kcal. mole^{-1}
Meschi, et al.[1]	1061 - 1451	45.4 ± 0.6	45.16	-133.38 ± 0.50
	1323 - 1451	0.25 ± 6.0	-5.15	-133.62 ± 0.50
White, et al.[2]	1250 - 1450	39.7 ± 2.5	——	-138.87 ± 2.50*
Randall and Margrave[3]	1273	——	44.12	-134.42 ± 1.0
Farber, et al.[4]	1070 - 1323	31.0 ± 10.0	44.07	-134.47 ± 3.20
	1143	——	40.9	-137.64 ± 0.70*
	1071 - 1325	44.2 ± 1.8	39.3	-139.3 ± 1.0*
	1148	——	43.2	-135.3 ± 0.4

*The value not used for the calculation of the weighted average of $\Delta H^\circ_{f\ 298.15}$ for $HBO_2(g)$

[1] D. J. Meschi, W. A. Chupka and J. Berkowitz, J. Chem. Phys. 33, 530 (1960). The $\Delta H^\circ_{r\ 298.15}$ values, 0.25 ± 6.0 and -5.15 kcal. mole^{-1}, were obtained based on the reaction $1/2\ B_2O_3(g) + 1/2\ H_2O(g) = HBO_2(g)$.

[2] D. White, D. E. Mann, P. N. Walsh and A. Sommer, J. Chem. Phys. 32, 488 (1960). The $\Delta H^\circ_{f\ 298.15}$ value was derived using $\Delta H^\circ_{r\ 298.15}$ obtained by the second law method.

[3] S. P. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. 16, 29 (1960). The partial pressure of $HBO_2(g)$, $P_{HBO_2} = 3.813 \times 10^{-4}$ atm., was calculated from the total pressure by the relation $P_{HBO_2} = P_{total} - 3\ P_{H_3BO_3} - 3\ P_{H_3B_3O_6}$ where $P_{H_3BO_3} = 3.030 \times 10^{-5}$ and $P_{H_3B_3O_6} = 2.1466 \times 10^{-5}$ atm.

[4] M. Farber, et al., "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases", QR-1987-5, May 9 - Aug 9, 1961; QR-1987-7, Nov. 9 - Feb. 9, 1962 and Final Report, May 9, 1960 through June 30, 1962, Rocket Power, Inc., California. The first and last sets of data were determined by the Molecular Flow Method and the rest, by Effusion Method.

The value of $\Delta H^\circ_{f\ 298.15}$ for $HBO_2(g)$ adopted is the weighted average of the $\Delta H^\circ_{f\ 298.15}$ value listed above.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were taken from D. White, D. E. Mann, P. N. Walsh and A. Sommer, loc. cit. The three principal moments of inertia are: $I_A = 1.155 \times 10^{-40}$, $I_B = 9.1050 \times 10^{-39}$ and $I_C = 9.2205 \times 10^{-39}$ g. cm.^{2}

Boron Dihydride (BH_2)

(Ideal Gas) Mol. Wt. = 12.836

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.153	48.163	48.163	INFINITE
100	6.959	35.093	49.724	-1.463	48.088	47.025	-102.769
200	7.302	39.980	43.761	-.756	48.112	45.937	-50.196
298	8.133	43.045	43.045	.000	48.000	44.889	-32.903
300	8.149	43.096	43.046	.015	47.997	44.869	-32.686
400	8.947	45.553	43.375	.871	47.837	43.850	-23.958
500	9.597	47.622	44.023	1.799	47.653	42.874	-18.739
600	10.160	49.422	44.776	2.788	47.467	41.936	-15.274
700	10.671	51.027	45.556	3.830	47.291	41.029	-12.809
800	11.136	52.483	46.333	4.920	47.130	40.145	-10.967
900	11.556	53.819	47.091	6.055	46.987	39.281	-9.538
1000	11.930	55.057	47.827	7.230	46.859	38.431	-8.399
1100	12.258	56.210	48.537	8.440	46.739	37.593	-7.469
1200	12.545	57.289	49.222	9.680	46.626	36.768	-6.696
1300	12.795	58.303	49.882	10.948	46.516	35.951	-6.044
1400	13.012	59.259	50.518	12.238	46.405	35.144	-5.486
1500	13.200	60.164	51.131	13.549	46.289	34.341	-5.003
1600	13.365	61.021	51.722	14.877	46.166	33.549	-4.582
1700	13.508	61.835	52.294	16.221	46.038	32.766	-4.212
1800	13.634	62.611	52.845	17.578	45.903	31.988	-3.884
1900	13.744	63.351	53.379	18.947	45.763	31.219	-3.591
2000	13.842	64.059	53.895	20.327	45.619	30.457	-3.328
2100	13.928	64.736	54.396	21.716	45.469	29.704	-3.091
2200	14.005	65.386	54.881	23.112	45.313	28.956	-2.876
2300	14.073	66.010	55.351	24.516	45.153	28.216	-2.681
2400	14.134	66.610	55.808	25.927	44.987	27.486	-2.503
2500	14.189	67.189	56.251	27.343	39.427	26.864	-2.348
2600	14.239	67.746	56.683	28.764	39.258	26.367	-2.216
2700	14.283	68.284	57.103	30.190	39.087	25.876	-2.094
2800	14.323	68.805	57.511	31.621	38.915	25.385	-1.981
2900	14.360	69.308	57.910	33.055	38.741	24.911	-1.877
3000	14.393	69.795	58.298	34.493	38.565	24.435	-1.780
3100	14.424	70.268	58.676	35.934	38.388	23.963	-1.689
3200	14.452	70.726	59.046	37.377	38.207	23.503	-1.605
3300	14.477	71.171	59.406	38.824	38.025	23.049	-1.526
3400	14.501	71.604	59.759	40.273	37.841	22.595	-1.452
3500	14.522	72.024	60.103	41.724	37.653	22.151	-1.383
3600	14.542	72.434	60.440	43.177	37.463	21.710	-1.318
3700	14.561	72.832	60.770	44.632	37.269	21.278	-1.257
3800	14.578	73.221	61.092	46.089	37.074	20.848	-1.199
3900	14.594	73.600	61.408	47.548	36.875	20.421	-1.144
4000	14.609	73.970	61.718	49.008	-84.506	22.146	-1.210
4100	14.622	74.330	62.021	50.470	-84.479	24.814	-1.323
4200	14.635	74.683	62.318	51.933	-84.455	27.483	-1.430
4300	14.647	75.027	62.610	53.397	-84.435	30.147	-1.532
4400	14.658	75.364	62.896	54.862	-84.419	32.810	-1.630
4500	14.669	75.694	63.176	56.328	-84.407	35.469	-1.723
4600	14.679	76.016	63.452	57.796	-84.396	38.138	-1.812
4700	14.688	76.332	63.723	59.264	-84.391	40.803	-1.897
4800	14.697	76.641	63.989	60.733	-84.389	43.469	-1.979
4900	14.705	76.945	64.250	62.203	-84.391	46.126	-2.057
5000	14.713	77.242	64.507	63.674	-84.396	48.789	-2.132
5100	14.720	77.533	64.759	65.146	-84.406	51.458	-2.205
5200	14.727	77.819	65.008	66.618	-84.419	54.120	-2.274
5300	14.733	78.100	65.252	68.091	-84.436	56.783	-2.341
5400	14.739	78.375	65.493	69.565	-84.458	59.446	-2.406
5500	14.745	78.646	65.729	71.039	-84.483	62.114	-2.468
5600	14.751	78.911	65.962	72.514	-84.513	64.777	-2.528
5700	14.756	79.172	66.192	73.989	-84.548	67.448	-2.586
5800	14.761	79.429	66.418	75.465	-84.587	70.111	-2.642
5900	14.766	79.682	66.641	76.941	-84.630	72.776	-2.696
6000	14.770	79.930	66.860	78.418	-84.677	75.445	-2.748

Dec. 31, 1960; Dec. 31, 1964

BORON DIHYDRIDE (BH_2) (IDEAL GAS) MOL. WT. = 12.836

Point Group [$D_{\infty h}$]

$S_{298.15}$ = [43.045] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

$\Delta H_f^\circ{}_0$ = 48 ± 15 kcal. mole⁻¹

$\Delta H_f^\circ{}_{298.15}$ = 48 ± 15 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹	ω, cm.⁻¹	ω, cm.⁻¹
[2430](1)	[840](2)	[2650](1)

Bond Distance: B-H = [1.20 Å]

Bond Angle: H-B-H = [180°]

Rotational Constant: B_0 = 5.80683 cm.⁻¹

σ = 2

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc. 86, 2733 (1964) and the JANAF ($B_2H_6(g)$) $\Delta H_f{}_{298.15}$ = +9.8 kcal. mole⁻¹. For example

	$\Delta H_r^\circ{}_0$
$B_2H_6(g) \rightarrow BH_2^+(ion) + BH_2(g) + H_2(g)$	13.4 e.v.
$BH_2(g) \rightarrow BH_2^+(ion)$	9.8 e.v.
$B_2H_6(g) \rightarrow 2BH_2(g) + H_2(g)$	3.6 e.v.

The ΔH_f data is summarized below.

Investigator	Method	$\Delta H_f^\circ{}_{298.15}$ kcal. mole⁻¹
T. P. Fehlner and W. S. Koski (loc. cit.)	Appearance Potentials	48
C. J. O'Brien and J. R. Perrin, Marquardt Corp., Van Nuys, Calif. and J. Perine, Olin Mathieson Chemical Corp., New York 22, N.Y., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules", October 1959.	Estimate	66
P. C. H. Jordan and H. C. Longuet-Higgins, Mol. Phys. 5, 121 (1962).	Estimate	93

Heat Capacity and Entropy.

The bond distance B-H = 1.20 Å was estimated from a consideration of BH(g), $BH_3(g)$ and other molecules. The bond angle H-B-H = 180° and the electronic configuration of the ground state [$^2A_2$] were estimated by P. C. H. Jordan and H. C. Longuet-Higgins (loc. cit.). The frequencies were estimated assuming valance forces [G. Herzberg, "Molecular Spectra and Molecular Structure II Infrared and Raman Spectra of Polyatomic Molecules" D. Van Nostrand Co. Inc., N. Y. (1945) page 172] and using force constants, $k_1 = 3.5 \times 10^5$ dynes cm.⁻¹ and $k_\delta l^{-1} = 0.35 \times 10^5$ dynes cm.⁻¹, estimated from BH_3, (see A. Shepp and S. H. Bauer, J. Am. Chem. Soc. 76, 265 (1954)).

Boron Dihydroxide ($B(OH)_2$)

(Ideal Gas) Mol. Wt. = 44.836

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.814	- 112.423	- 112.423	INFINITE
100	8.200	47.428	67.576	- 2.015	- 113.102	- 111.246	243.115
200	10.129	53.643	59.178	- 1.107	- 113.557	- 109.217	119.342
298	12.432	58.116	58.116	.000	- 114.000	- 106.994	78.425
300	12.475	58.193	58.116	.023	- 114.008	- 106.951	77.910
400	14.625	62.085	58.632	1.381	- 114.377	- 104.540	57.115
500	16.377	65.544	59.675	2.934	- 114.667	- 102.046	44.602
600	17.769	68.658	60.917	4.644	- 114.887	- 99.500	36.241
700	18.891	71.484	62.228	6.479	- 115.048	- 96.921	30.259
800	19.813	74.069	63.549	8.416	- 115.160	- 94.326	25.767
900	20.580	76.448	64.852	10.437	- 115.231	- 91.716	22.271
1000	21.226	78.651	66.123	12.528	- 115.270	- 89.100	19.472
1100	21.771	80.700	67.356	14.679	- 115.288	- 86.483	17.182
1200	22.235	82.615	68.549	16.879	- 115.289	- 83.863	15.273
1300	22.630	84.410	69.700	19.123	- 115.280	- 81.245	13.658
1400	22.970	86.100	70.812	21.404	- 115.264	- 78.626	12.274
1500	23.262	87.695	71.885	23.716	- 115.250	- 76.010	11.074
1600	23.514	89.205	72.921	26.055	- 115.239	- 73.396	10.025
1700	23.733	90.637	73.921	28.417	- 115.231	- 70.779	9.099
1800	23.925	91.999	74.888	30.800	- 115.229	- 68.166	8.276
1900	24.092	93.297	75.823	33.201	- 115.232	- 65.550	7.540
2000	24.240	94.537	76.728	35.618	- 115.239	- 62.937	6.877
2100	24.370	95.723	77.604	38.049	- 115.252	- 60.320	6.277
2200	24.486	96.859	78.454	40.492	- 115.273	- 57.704	5.732
2300	24.589	97.950	79.278	42.946	- 115.299	- 55.088	5.234
2400	24.681	98.998	80.078	45.409	- 115.335	- 52.464	4.777
2500	24.763	100.008	80.855	47.881	- 120.767	- 49.742	4.348
2600	24.837	100.980	81.611	50.361	- 120.809	- 46.896	3.942
2700	24.904	101.919	82.345	52.849	- 120.856	- 44.052	3.566
2800	24.965	102.826	83.061	55.342	- 120.909	- 41.210	3.216
2900	25.019	103.703	83.757	57.841	- 120.966	- 38.356	2.890
3000	25.069	104.552	84.437	60.346	- 121.028	- 35.510	2.587
3100	25.115	105.375	85.099	62.855	- 121.094	- 32.660	2.302
3200	25.157	106.173	85.745	65.369	- 121.166	- 29.806	2.036
3300	25.195	106.947	86.376	67.886	- 121.244	- 26.946	1.784
3400	25.230	107.700	86.992	70.408	- 121.326	- 24.090	1.548
3500	25.263	108.432	87.594	72.932	- 121.415	- 21.231	1.326
3600	25.293	109.144	88.183	75.460	- 121.508	- 18.364	1.115
3700	25.320	109.837	88.759	77.991	- 121.608	- 15.496	.915
3800	25.346	110.513	89.322	80.524	- 121.712	- 12.625	.726
3900	25.370	111.172	89.874	83.060	- 121.822	- 9.760	.547
4000	25.392	111.814	90.415	85.598	- 243.117	- 4.737	.259
4100	25.412	112.441	90.944	88.138	- 243.007	1.222	- .065
4200	25.432	113.054	91.463	90.680	- 242.901	7.180	- .374
4300	25.449	113.653	91.973	93.224	- 242.801	13.131	- .667
4400	25.466	114.238	92.472	95.770	- 242.707	19.080	- .948
4500	25.482	114.810	92.962	98.318	- 242.618	25.028	- 1.215
4600	25.497	115.371	93.443	100.867	- 242.533	30.978	- 1.472
4700	25.510	115.919	93.916	103.417	- 242.456	36.926	- 1.717
4800	25.524	116.456	94.380	105.969	- 242.382	42.872	- 1.952
4900	25.536	116.983	94.835	108.522	- 242.314	48.804	- 2.177
5000	25.547	117.499	95.284	111.076	- 242.251	54.744	- 2.393
5100	25.558	118.005	95.724	113.631	- 242.195	60.689	- 2.601
5200	25.568	118.501	96.157	116.187	- 242.142	66.624	- 2.800
5300	25.578	118.988	96.584	118.745	- 242.093	72.568	- 2.992
5400	25.587	119.466	97.003	121.303	- 242.052	78.497	- 3.177
5500	25.596	119.936	97.416	123.862	- 242.013	84.440	- 3.355
5600	25.604	120.397	97.822	126.422	- 241.982	90.367	- 3.527
5700	25.612	120.851	98.222	128.983	- 241.955	96.300	- 3.692
5800	25.620	121.296	98.616	131.545	- 241.933	102.239	- 3.852
5900	25.627	121.734	99.004	134.107	- 241.916	108.172	- 4.007
6000	25.634	122.165	99.387	136.670	- 241.904	114.106	- 4.156

Dec. 31, 1960; Dec. 31, 1964

BORON DIHYDROXIDE ($B(OH)_2$) (IDEAL GAS) MOL. WT. = 44.836

Point Group [C_{2h}]

$S^\circ_{298.15}$ = [58.116] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = [-112 ± 15] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-114 ± 15] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[2500](1)	[750](1)	[1300](1)
[1150](1)	[460](1)	[1000](1)
[1100](1)	[3000](1)	[450](1)

Bond Distance: B-O = [1.27] Å O-H = [0.97] Å

Bond Angle: H-O-B = [105]° O-B-O = [180]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.42627 X 10^{-116}] g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for $B(OH)_2(g)$ was calculated by using the bond energy, D°(B-OH) = 132.7 kcal. mole^{-1}, and the heats of formation for B(g) and OH(g) as 132.80 and 9.33 kcal. mole^{-1}, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for $BO_2(g)$, $B(OH)_3(g)$ and other related molecules. The bond distances and angles were estimated by comparison with those for $BO_2(g)$ and $H_2O_2(g)$ molecules. The molecular configuration is assumed to be trans which is considered as more stable than the cis-form. The three principal moments of inertia are: I_A = 2.6870 X 10^{-40}, I_B = 9.3682 X 10^{-39} and I_C = 9.6369 X 10^{-39} g. cm.^{2}

Boron Trihydride (BH_3)

(Ideal Gas) Mol. Wt. = 13.844

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.421	26.407	26.407	INFINITE
100	7.952	35.983	52.243	-1.626	26.057	26.125	-57.094
200	8.159	41.535	45.655	-.824	25.875	26.242	-28.674
298	8.657	44.880	44.880	.000	25.500	26.494	-19.420
300	8.668	44.934	44.880	.016	25.492	26.500	-19.304
400	9.304	47.512	45.227	.914	25.026	26.905	-14.700
500	10.048	49.666	45.905	1.881	24.532	27.432	-11.990
600	10.863	51.569	46.693	2.926	24.052	28.057	-10.219
700	11.698	53.307	47.516	4.054	23.611	28.761	-8.979
800	12.509	54.922	48.341	5.264	23.217	29.523	-8.065
900	13.267	56.440	49.158	6.554	22.873	30.333	-7.365
1000	13.957	57.874	49.958	7.916	22.573	31.179	-6.814
1100	14.575	59.234	50.740	9.343	22.307	32.052	-6.368
1200	15.122	60.526	51.502	10.828	22.072	32.950	-6.001
1300	15.603	61.756	52.244	12.365	21.859	33.863	-5.693
1400	16.026	62.928	52.966	13.947	21.663	34.796	-5.432
1500	16.396	64.046	53.668	15.568	21.474	35.741	-5.207
1600	16.721	65.115	54.350	17.225	21.291	36.696	-5.012
1700	17.007	66.138	55.013	18.911	21.112	37.666	-4.842
1800	17.258	67.117	55.659	20.625	20.935	38.643	-4.692
1900	17.480	68.056	56.287	22.362	20.760	39.633	-4.559
2000	17.677	68.958	56.898	24.120	20.587	40.631	-4.440
2100	17.852	69.825	57.493	25.897	20.412	41.637	-4.333
2200	18.008	70.659	58.073	27.690	20.237	42.652	-4.237
2300	18.147	71.462	58.637	29.498	20.062	43.676	-4.150
2400	18.272	72.237	59.188	31.319	19.882	44.709	-4.071
2500	18.384	72.986	59.725	33.152	14.312	45.850	-4.008
2600	18.486	73.709	60.249	34.995	14.135	47.117	-3.960
2700	18.577	74.408	60.761	36.848	13.958	48.391	-3.917
2800	18.660	75.085	61.260	38.710	13.780	49.666	-3.876
2900	18.736	75.741	61.748	40.580	13.603	50.958	-3.840
3000	18.805	76.378	62.225	42.457	13.424	52.243	-3.806
3100	18.868	76.995	62.692	44.341	13.246	53.540	-3.774
3200	18.926	77.595	63.148	46.231	13.065	54.844	-3.745
3300	18.979	78.179	63.595	48.126	12.881	56.153	-3.719
3400	19.027	78.746	64.032	50.026	12.697	57.465	-3.694
3500	19.072	79.298	64.461	51.931	12.509	58.786	-3.671
3600	19.114	79.836	64.880	53.841	12.319	60.110	-3.649
3700	19.152	80.360	65.292	55.754	12.123	61.443	-3.629
3800	19.188	80.871	65.695	57.671	11.927	62.781	-3.611
3900	19.221	81.370	66.090	59.591	11.726	64.119	-3.593
4000	19.252	81.857	66.479	61.515	-109.657	67.611	-3.694
4100	19.281	82.333	66.859	63.442	-109.634	72.039	-3.840
4200	19.307	82.798	67.233	65.371	-109.614	76.476	-3.979
4300	19.332	83.253	67.601	67.303	-109.598	80.900	-4.112
4400	19.356	83.697	67.961	69.238	-109.587	85.333	-4.238
4500	19.378	84.133	68.316	71.174	-109.582	89.755	-4.359
4600	19.398	84.559	68.664	73.113	-109.578	94.190	-4.475
4700	19.418	84.976	69.007	75.054	-109.582	98.624	-4.586
4800	19.436	85.385	69.344	76.997	-109.588	103.054	-4.692
4900	19.453	85.786	69.676	78.941	-109.601	107.482	-4.794
5000	19.469	86.179	70.002	80.887	-109.617	111.911	-4.891
5100	19.484	86.565	70.323	82.835	-109.640	116.344	-4.985
5200	19.499	86.943	70.639	84.784	-109.666	120.775	-5.076
5300	19.512	87.315	70.950	86.734	-109.697	125.207	-5.163
5400	19.525	87.680	71.256	88.686	-109.735	129.633	-5.246
5500	19.537	88.038	71.558	90.639	-109.777	134.074	-5.327
5600	19.549	88.390	71.856	92.594	-109.825	138.502	-5.405
5700	19.560	88.736	72.149	94.549	-109.878	142.942	-5.480
5800	19.571	89.077	72.438	96.506	-109.938	147.371	-5.553
5900	19.580	89.411	72.723	98.463	-110.002	151.814	-5.623
6000	19.590	89.740	73.003	100.422	-110.071	156.251	-5.691

Dec. 31, 1960; Dec. 31, 1964

BORON TRIHYDRIDE (BH_3) (IDEAL GAS) MOL. WT. = 13.844

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [44.880] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = 26.4 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 25.5 ± 10 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[2384](1)	[802](1)
[1765](2)	[2976](2)

Bond Distance: B-H = [1.16 Å]

Bond Angle: H-B-H = [120°]

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C$ =[7.71 X 10^{-119}]g.^{3} cm.^{6}

Heat of Formation:

$\Delta H^\circ_{f\ 298.15}$ was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski J. Am. Chem. Soc. 86, 2733 (1964). For example

$B_2H_6(g) \rightarrow BH_3^+(ion) + BH_3(g)$	13.1 e.v.
BH_3 +(ion) $\rightarrow BH_3(g)$	-11.4 e.v.
$B_2H_6(g) \rightarrow 2BH_3(g)$	1.7 e.v.

The heat of formation data is summarized below.

Reaction: $B_2H_6(g) \rightarrow 2BH_3(g)$*

*The auxiliary $\Delta H^\circ_{f\ 298.15}(B_2H_6)$ was from the JANAF Table dated Dec. 31, 1964

Investigators	Method	$\Delta H^\circ_{r\ 0}$	$\Delta H^\circ_{f\ 298.15}$*
P. C. H. Jordan and H. C. Longuet-Higgins Mol. Phys. 5, 121 (1962)	Bond energy parameters obtained by linear extrapolation from NH and CH bonds	69.9 kcal. mole^{-1}	41.7 kcal. mole^{-1}
E. J. Sinke, G. A. Pressley Jr., A.B. Bayles, and F. E. Stafford, J. Chem. Phys. 41, 2207(1964)	Apparent equilibrium constants	55 ± 8 kcal. mole^{-1}	33 kcal. mole^{-1}
E. J. Sinke, et al. (loc. cit.)	A recalculation by JANAF using estimated α values and P = 10^{-7}atm (α= degree of dissociation)	49 ± 8 kcal. mole^{-1}	30 kcal. mole^{-1}
W. C. Price, T. R. Passmore and D. M. Roessler, Disscusions Faraday Soc. 35, 201 (1963)	Correlations of ionization and dissociation energies of hydrides and fluorides in relation to electronic structure.	41.5 kcal. mole^{-1}	26.6 kcal. mole^{-1}
T. P. Fehlner and W. S. Koski (loc. cit.)	Appearance Potentials	39.2 kcal. mole^{-1}	25.5 kcal. mole^{-1}
M. E. Garabedian and S. W. Benson, J. Am. Chem. Soc. 86, 176 (1964).	From kinetic data for the decomposition of BH_3CO	32-38 kcal. mole^{-1}	22-25 kcal. mole^{-1}
R. E. McCoy and S. H. Bauer J. Am. Chem. Soc. 78, 2061 (1956)	From calorimetric measurements of analogous compounds	28.4 ± 2 kcal. mole^{-1}	20.1 kcal. mole^{-1}
L. Pauling, "The Nature of the Chemical Bond" Cornell University Press, Ithica, N.Y. (1960) 3rd Ed.	From electronegativities	23.9 kcal. mole^{-1}	18 kcal. mole^{-1}

Heat Capacity and Entropy.

The molecular comfiguration, [planar, H-B-H angle = 120°], was estimated by A. Shepp and S. H. Bauer, J. Am. Chem. Soc. 76, 265 (1954) as well as by P. C. H. Jordan and H. C. Longuet-Higgins, (loc. cit.). In addition Shepp and Bauer estimated the bond distance and the vibrational frequencies. Jordan and Longuet-Higgins estimated the electronic configuration [$^1A_1'$]. The principal moments of inertia calculated from these molecular constants are, $I_A = I_B$ = 3.378 X 10^{-40} and I_C = 6.756 X 10^{-40} g. cm.^{2}

Boric Acid (H_3BO_3)

(Crystal) Mol. Wt. = 61.844

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	,000	,000	INFINITE	- 3,201	- 258,231	- 258,231	INFINITE
100	8,585	6,927	34,737	- 2,781	- 260,025	- 250,823	548,146
200	14,040	14,610	22,815	- 1,641	- 260,889	- 241,267	263,632
298	19,440	21,210	21,210	,000	- 261,470	- 231,503	169,688
300	19,540	21,331	21,210	,036	- 261,478	- 231,317	168,507
400	23,950	27,579	22,033	2,219	- 261,725	- 221,218	120,862
500	27,400	33,302	23,723	4,790	- 261,712	- 211,088	92,262
600	30,400	38,569	25,764	7,683	- 261,476	- 200,982	73,204
700	32,963	43,452	27,946	10,854	- 261,041	- 190,930	59,608
800	35,200	48,003	30,172	14,265	- 260,431	- 180,957	49,433
900	37,050	52,258	32,392	17,879	- 259,672	- 171,066	41,539
1000	38,700	56,249	34,581	21,668	- 258,785	- 161,266	35,243
1100	40,147	60,007	36,723	25,612	- 257,793	- 151,563	30,111
1200	41,400	63,555	38,813	29,691	- 256,706	- 141,951	25,852
1300	42,460	66,912	40,846	33,886	- 255,547	- 132,436	22,263
1400	43,327	70,092	42,823	38,177	- 254,330	- 123,011	19,202
1500	44,000	73,105	44,742	42,545	- 253,078	- 113,674	16,562

Sept. 30, 1962; Dec. 31, 1964

BORIC ACID (H_3BO_3) (CRYSTAL) MOL. WT. = 61.844

$\Delta H^\circ_{f\ 0} = -258.23 \pm 0.20$ kcal mole^{-1}

$S^\circ_{298.15} = 21.21 \pm 0.1$ cal deg^{-1} mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -261.47 \pm 0.20$ kcal mole^{-1}

$T_m = 444.1 \pm 0.2$°K

ΔH°_m = Unknown

$T_d = [330]$°K

$\Delta H^\circ_{s\ 298.15} = 24.3 \pm 0.7$ kcal mole^{-1}

Heat of Formation

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) of $H_3BO_3(c)$ was taken from W. D. Good, M. Mansson and J. P. McCullough, Quarterly Technical Report No. 9, Nov. 4, 1963, U. S. Bur. Mines, Bartlesville, Oklahoma. The value was derived based on the following measurements

	$\Delta H^\circ_{r\ 298.15}$, kcal mole^{-1}
$B(c) + 0.75\ O_2(g) + 18.674\ HF\cdot 57.219\ H_2O(\ell) = HBF_4\cdot 14.674\ HF\cdot 58.719\ H_2O(\ell)$	-173.4 ± 0.2
$H_3BO_3(c) + 18.674\ HF\cdot 55.719\ H_2O(\ell) = HBF_4\cdot 14.675\ HF\cdot 58.719\ H_2O(\ell)$	$+14.6 \pm 0.1$

The heats of solution of $H_3BO_3(c)$ in water have been measured by many investigators. L. G. Fasolino, "Heat of Formation of $B_2O_3(c)$ and B_2O_3(am.)," NONR-3608 (00), June 2, 1964, National Research Corporation, Massachusetts, obtained the value, $\Delta H^\circ_{r\ 298.15} = 5.45 \pm 0.01$ kcal mole^{-1} for the reaction $H_3BO_3(c) + 504\ H_2O(\ell) = H_3BO_3\cdot 504\ H_2O$(sol.) which leads to $\Delta H^\circ_{f\ 298.15}$ ($H_3BO_3\cdot 504\ H_2O$, sol.) = -256.02 kcal mole^{-1}. The $\Delta H^\circ_{r\ 298.15}$ value is in reasonable agreement with the value reported by J. Smisko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950) in which the heats of solution and dilution of $H_3BO_3(c)$ were given. The heats of solution of $H_3BO_3(c)$ in water measured by other previous investigators were reviewed by L. G. Fasolino, loc. cit.

Heat Capacity and Entropy

The low temperature (16-296°K) heat capacities were reported by H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc. 72, 4733 (1950). The heat capacities above 300°K were estimated by comparison with those of its constituent oxides. $S^\circ_{298.15}$ was obtained from H. L. Johnston and E. C. Kerr. loc. cit., using $S^\circ_{17} = 0.18$ cal deg^{-1} mole^{-1}.

Melting Data

The value of T_m was taken from F. C. Kracek, G. W. Morey and H. E. Merwin, Am. J. Sci. [5] 35A, 143 (1938). However, $H_3BO_3(c)$ is in a metastable state at T_m. Measurements of the decomposition pressure of $H_3BO_3(c)$ to form HBO_2(c, II or III) and $H_2O(g)$ have been made by H. Menzel, H. Schulz and H. Deckert, Z. anorg. allgem. Chem 220, 49 (1934); A. Thiel and H. Siebeneck, Z. anorg. allgem. Chem. 220, 236 (1934); M. V. Stackelberg. F. Quatram and J. Dressel, Z. Elektrochem. 43, 14 (1937); S. Bezzi, Gass. chim. ital. 65, 766 (1935); and H. Tazaki, J. Sci. Hiroshima Univ. Ser. A 10, 37, 55, 63, 109, 113 (1939). The decomposition pressures of the system $H_3BO_3(c) = H_2O(g) + HBO_2$(c, I), at the temperatures of 312 to 352°K, have been reported by E. D. West, "The properties of Boron Compounds", ARL Technical Report 60-276, May 1960, National Bureau of Standards.

Temperature of Decomposition

The decomposition temperature (T_d) is calculated as the temperature at which the free energy change of the reaction $H_3BO_3(c) \rightarrow HBO_2(c) + H_2O(g)$ approaches zero.

Heat of Sublimation

The heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) is derived as the difference between the $\Delta H^\circ_{f\ 298.15}$ values for $H_3BO_3(g)$ and $H_3BO_3(c)$.

Boric Acid (H_3BO_3)

(Ideal Gas) Mol. Wt. = 61.844

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100	11,043	56,791	82,550	- 2,576	- 235,509	- 231,294	505,469
200	12,873	64,896	71,877	- 1,396	- 236,334	- 226,770	247,791
298	15,616	70,539	70,539	,000	- 237,160	- 221,900	162,649
300	15,669	70,636	70,539	,029	- 237,175	- 221,806	161,578
400	18,371	75,522	71,187	1,734	- 237,900	- 216,570	118,323
500	20,640	79,874	72,497	3,688	- 238,503	- 211,166	92,296
600	22,471	83,805	74,059	5,847	- 239,002	- 205,650	74,904
700	23,966	87,384	75,711	8,171	- 239,414	- 200,055	62,457
800	25,215	90,668	77,378	10,632	- 239,754	- 194,411	53,108
900	26,280	93,701	79,026	13,208	- 240,033	- 188,726	45,827
1000	27,199	96,519	80,636	15,883	- 240,260	- 183,011	39,995
1100	27,997	99,150	82,201	18,644	- 240,451	- 177,279	35,220
1200	28,693	101,616	83,717	21,479	- 240,608	- 171,526	31,238
1300	29,300	103,937	85,184	24,380	- 240,743	- 165,765	27,866
1400	29,832	106,129	86,602	27,337	- 240,860	- 159,993	24,975
1500	30,298	108,203	87,974	30,344	- 240,969	- 154,212	22,468
1600	30,708	110,172	89,300	33,395	- 241,074	- 148,427	20,273
1700	31,069	112,045	90,584	36,484	- 241,173	- 142,631	18,336
1800	31,387	113,830	91,826	39,607	- 241,274	- 136,834	16,613
1900	31,669	115,534	93,029	42,760	- 241,375	- 131,026	15,071
2000	31,920	117,165	94,195	45,940	- 241,477	- 125,217	13,682
2100	32,143	118,728	95,327	49,143	- 241,582	- 119,400	12,426
2200	32,343	120,228	96,425	52,368	- 241,694	- 113,580	11,283
2300	32,522	121,670	97,491	55,611	- 241,808	- 107,756	10,239
2400	32,683	123,058	98,528	58,871	- 241,931	- 101,921	9,281
2500	32,827	124,395	99,536	62,147	- 247,451	- 95,982	8,390
2600	32,958	125,685	100,517	65,436	- 247,580	- 89,917	7,558
2700	33,077	126,931	101,472	68,738	- 247,715	- 83,850	6,787
2800	33,185	128,136	102,403	72,051	- 247,856	- 77,781	6,071
2900	33,283	129,302	103,311	75,375	- 248,002	- 71,696	5,403
3000	33,373	130,432	104,196	78,708	- 248,154	- 65,619	4,780
3100	33,455	131,528	105,060	82,049	- 248,310	- 59,534	4,197
3200	33,530	132,591	105,904	85,398	- 248,475	- 53,441	3,650
3300	33,599	133,624	106,728	88,755	- 248,646	- 47,343	3,135
3400	33,663	134,628	107,534	92,118	- 248,824	- 41,242	2,651
3500	33,721	135,604	108,322	95,487	- 249,009	- 35,133	2,194
3600	33,776	136,555	109,093	98,862	- 249,201	- 29,018	1,762
3700	33,826	137,481	109,848	102,242	- 249,402	- 22,897	1,352
3800	33,873	138,384	110,587	105,627	- 249,608	- 16,770	,964
3900	33,916	139,264	111,311	109,017	- 249,822	- 10,645	,596
4000	33,957	140,124	112,021	112,410	- 371,224	- 2,368	,129
4100	33,994	140,963	112,717	115,808	- 371,221	6,854	- ,365
4200	34,029	141,782	113,399	119,209	- 371,225	16,082	- ,837
4300	34,062	142,583	114,068	122,614	- 371,237	25,305	- 1,286
4400	34,093	143,367	114,725	126,022	- 371,257	34,519	- 1,715
4500	34,122	144,133	115,370	129,432	- 371,285	43,741	- 2,124
4600	34,149	144,883	116,004	132,846	- 371,318	52,975	- 2,517
4700	34,175	145,618	116,626	136,262	- 371,360	62,198	- 2,892
4800	34,199	146,338	117,238	139,681	- 371,408	71,424	- 3,252
4900	34,221	147,043	117,839	143,102	- 371,463	80,643	- 3,597
5000	34,242	147,735	118,430	146,525	- 371,524	89,866	- 3,928
5100	34,263	148,413	119,011	149,950	- 371,595	99,104	- 4,247
5200	34,282	149,079	119,583	153,377	- 371,670	108,324	- 4,553
5300	34,300	149,732	120,146	156,807	- 371,751	117,566	- 4,848
5400	34,317	150,373	120,700	160,237	- 371,842	126,788	- 5,131
5500	34,333	151,003	121,245	163,670	- 371,936	136,033	- 5,405
5600	34,348	151,622	121,782	167,104	- 372,040	145,257	- 5,669
5700	34,363	152,230	122,311	170,539	- 372,150	154,499	- 5,924
5800	34,376	152,828	122,832	173,976	- 372,266	163,741	- 6,170
5900	34,390	153,415	123,345	177,415	- 372,388	172,987	- 6,408
6000	34,402	153,993	123,851	180,854	- 372,517	182,234	- 6,638

Mar. 31, 1961; Dec. 31, 1964

BORIC ACID (H_3BO_3) (IDEAL GAS) MOL. WT. = 61.844

Point Group C_{3h}

$S^\circ_{298.15}$ = [70.539] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -237.16 ± 0.60 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
3250(1)	Rotation	1185(2)
1060(1)	3150(2)	Rotation
881(1)	1440(2)	Rotation
652(1)	544(2)	

Bond Distance: B-O = [1.36] Å O-H = [0.96] Å

Bond Angle: H-O-B = [114]° O-B-O = [120]° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.15684 X 10^{-114}] g.^{3} cm.^{6}

Heat of Formation.

The vapor pressures of H_3BO_3(c), 109 - 140°C, were measured by M. V. Stackelberg, F. Quatram and J. Dressel, Z. Elecktrochem. 43, 14 (1937). Using the vapor pressures reported, the heats of sublimation of H_3BO_3(c) were evaluated to be 24.4 ± 0.6 and 24.22 kcal. mole^{-1} by the second and third law methods, respectively. The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for H_3BO_3(g) was calculated from the $\Delta H^\circ_{f\ 298.15}$ and $\Delta H^\circ_{s\ 298.15}$ for H_3BO_3(c). The $\Delta H^\circ_{s\ 298.15}$ value adopted is the average of the second and third law values mentioned previously.

Heat Capacity and Entropy.

The molecular structure and constants were taken from C. W. F. T. Pistorius, J. Chem. Phys. 31, 1454 (1959) based on an X-ray diffraction study on H_3BO_3(c) by W. H. Zachariasen, Acta Cryst. 7, 305 (1954). The O-H bond distance was reestimated as 0.96 Å instead of 0.88 Å reported. From the existing infrared and Raman spectra data on H_3BO_3(c) and its aqueous solution C. W. F. T. Pistorius, loc. cit., carried out a normal coordinate treatment by means of Wilson's F-G matrix method and calculated the fifteeen fundamental frequencies for H_3BO_3(c). For H_3BO_3(g) twelve reported frequencies were used and corrected to the average isotopic species. The three torsional frequencies, 824(1) and 209(2) cm.$^{-1}$, were not used based on an assumption that there are three internal rotations, i.e. three OH groups, each rotates about its own B-O bond. Employing the model of having three free rotating OH tops, the value of S°_{400} was evaluated statistically as 75.522 cal. deg.$^{-1}$ mole^{-1}. The corresponding value obtained by using the second law value of ΔS°_{400}, 48.39 ± 1.42 cal. deg.$^{-1}$ mole^{-1}, for the reaction H_3BO_3(c) = H_3BO_3(g), is 75.97 ± 1.42 cal. deg.$^{-1}$ mole^{-1} which is in good agreement with the S°_{400} value based on a model having three free rotating groups. Thus the assumed model is adopted to evaluate the thermodynamic functions. The three principal moments of inertia are: $I_A = I_C$ = 8.3320 X 10^{-39} g. cm.^{2} and I_B = 1.6664 X 10^{-38} g. cm.^{2} The reduced moment of inertia for OH top is I_r = 1.15321 X 10^{-40} g. cm.^{2} The infrared absorption spectrum of H_3BO_3(g) was observed under conditions where one atmosphere of water vapor with a path length of approximately one meter as background, by F. T. Greene, G. E. Leroi, S. P. Randall, J. R. Soulen, L. H. Spinar and J. L. Margrave, "Spectra and Thermodynamic Properties of Light-Element Oxides and Hydroxides", Proceedings of the Conference on Propellant Thermodynamics and Handling, Columbus, Ohio, July, 1959. The following fundamentals were obtained: 3220 cm.$^{-1}$ S., 1490 cm.$^{-1}$ S., 1199 cm.$^{-1}$ S., 881 cm.$^{-1}$ W., and 669 cm.$^{-1}$ W.

Potassium Tetrahydroborate (KBH_4)

(Crystal) Mol. Wt. = 53.952

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.949	- 52.146	- 52.146	INFINITE
100	10.370	7.782	42.192	- 3.441	- 53.576	- 48.618	106.249
200	17.586	17.335	27.440	- 2.021	- 54.062	- 43.446	47.474
298	23.081	25.480	25.480	.000	- 54.230	- 38.191	27.993
300	23.120	25.623	25.480	.043	- 54.231	- 38.092	27.748
400	24.120	32.456	26.405	2.420	- 54.878	- 32.594	17.808
500	24.410	37.866	28.175	4.845	- 55.007	- 27.010	11.806
600	25.343	42.383	30.176	7.324	- 55.129	- 21.398	7.794
700	27.540	46.440	32.213	9.959	- 55.130	- 15.772	4.924
800	28.300	50.169	34.229	12.752	- 55.006	- 10.159	2.775
900	28.830	53.534	36.190	15.610	- 54.850	- 4.562	1.108
1000	29.240	56.594	38.079	18.514	- 54.688	1.016	- .222
1100	29.490	59.393	39.892	21.451	- 73.444	7.603	- 1.511
1200	29.700	61.968	41.626	24.411	- 73.068	14.957	- 2.724
1300	29.856	64.352	43.283	27.389	- 72.709	22.274	- 3.744
1400	30.000	66.570	44.869	30.382	- 72.368	29.570	- 4.616
1500	30.129	68.644	46.385	33.388	- 72.052	36.841	- 5.367
1600	30.250	70.592	47.838	36.407	- 71.759	44.089	- 6.022
1700	30.363	72.429	49.230	39.438	- 71.485	51.323	- 6.598
1800	30.467	74.167	50.568	42.480	- 71.230	58.539	- 7.107
1900	30.563	75.817	51.853	45.531	- 70.994	65.742	- 7.562
2000	30.650	77.387	53.091	48.592	- 70.772	72.934	- 7.969

Mar. 31, 1963; Dec. 31, 1964

POTASSIUM TETRAHYDROBORATE (KBH_4) (CRYSTAL) MOL. WT. = 53.952

$\Delta H^\circ_{f\ 0} = -52.15 \pm .55$ kcal. mole^{-1}

$S^\circ_{298.15} = 25.48$ cal. deg.$^{-1}$ mole $\Delta H^\circ_{f\ 298.15} = -54.23 \pm .55$ kcal. mole^{-1}

$T_d = [770]^\circ K$

Heat of Formation.

The heat of reaction of $KBH_4(c)$ with hydrochloric acid has been measured by solution calorimetry and reported by W. H. Johnson, R. H. Schumm, I. H. Wilson, and E. J. Prosen, J. Res. Nat'l. Bur. Std. 65A, 97 (1961)

$$KBH_4(c) + HCl(g) + 3H_2O(liq) \rightarrow KCl(c) + H_3BO_3(c) + 4H_2(g) \qquad \Delta Hr = -84.62 \pm .44 \text{ kcal. mole}$$

The $\Delta H_{f\ 298.15}$ values for HCl(g) and $H_3BO_3(c)$ were obtained from the JANAF Tables. The $\Delta H_{f\ 298.15}$ value for KCl(c) was calculated from $\Delta H_{f\ 298.15}\ K^+ = -60.32$ kcal. mole^{-1}, $\Delta H_{f\ 298.15}\ Cl^- = -39.952$ kcal. mole^{-1} and ΔH dilution = 4.12 kcal. mole^{-1} obtained from NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. $\Delta H_{f\ 298.15}$ for $H_2O(liq)$ was obtained from W. H. Evans, loc. cit. Unpublished data of The Dow Chemical Company Thermal Laboratory give a value of $\Delta H_{f\ 298.15} = -55.0 \pm 1.0$ kcal. mole^{-1} by solution calorimetry.

Heat Capacity and Entropy.

C_p and S° at temperatures below 298.15°K were reported by G. T. Furukawa, M. L. Reilly, and J. H. Piccirelli, J. Res. Nat'l. Bur Std. 68A, 651 (1964). The values of C_p in the range from 298.15 to 700°K were obtained from T. B. Douglas and A. W. Harman, J. Res. Nat'l. Bur. Std. 60, 117 (1958). These two sets of C_p data were plotted and joined smoothly at 298.15°K. The values of C_p above 700°K were estimated by graphical extrapolation.

Temperature of Decomposition.

The temperature of decomposition (into constituent elements) was estimated according to a report by T. B. Douglas and A. W. Harman, loc. cit.

Lithium Tetrahydroborate ($LiBH_4$)
(Crystal) Mol. Wt. = 21.792

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.028	-43.105	-43.105	INFINITE
100	7.175	4.084	31.660	-2.758	-44.478	-39.825	87.033
200	14.239	11.470	19.727	-1.651	-45.097	-34.917	38.154
298	19.727	18.120	18.120	-.000	-45.522	-29.824	21.860
300	19.835	18.242	18.120	.037	-45.527	-29.727	21.655
400	21.750	24.231	18.924	2.123	-45.772	-24.422	13.343
500	23.490	29.273	20.502	4.385	-46.739	-18.983	8.297
600	25.130	33.708	22.341	6.821	-46.891	-13.415	4.886
700	26.270	37.672	24.253	9.394	-46.938	-7.830	2.444
800	27.020	41.234	26.156	12.062	-46.919	-2.245	.613
900	27.330	44.435	28.013	14.780	-46.882	3.337	-.810
1000	27.570	47.327	29.802	17.525	-46.848	8.915	-1.948
1100	27.818	49.967	31.517	20.295	-46.822	14.490	-2.879
1200	28.040	52.397	33.157	23.088	-46.804	20.064	-3.654
1300	28.207	54.648	34.725	25.900	-46.800	25.634	-4.309
1400	28.366	56.744	36.223	28.729	-46.811	31.208	-4.872
1500	28.517	58.706	37.657	31.573	-46.843	36.782	-5.359
1600	28.660	60.551	39.031	34.432	-46.894	42.357	-5.785
1700	28.795	62.293	40.348	37.305	-82.007	49.267	-6.333
1800	28.921	63.942	41.614	40.191	-81.907	56.986	-6.919
1900	29.040	65.509	42.830	43.089	-81.821	64.701	-7.442
2000	29.150	67.001	44.002	45.999	-81.748	72.412	-7.912

Mar. 31, 1963; Dec. 31, 1964

LITHIUM TETRAHYDROBORATE ($LiBH_4$) (CRYSTAL) MOL. WT. = 21.792

$S^\circ_{298.15}$ = 18.120 cal. deg.$^{-1}$ mole^{-1}

T_m = [750°K.]

$\Delta H_f^\circ{}_0$ = -43.105 ± 0.05 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -45.522 ± 0.05 kcal. mole^{-1}

ΔH_m° = Unknown

Heat of Formation.

The heat of formation of $LiBH_4(c)$ was calculated from the solution calorimetry of W. D. Davis, L. S. Mason, and G. Stegeman J. Am. Chem. Soc. 71, 2775 (1949). The heats of reaction were measured for the following reactions:

$LiBH_4(c) + 1.25(HCl\cdot 200\ H_2O) + 3\ H_2O(l) \rightarrow (NaCl + H_3BO_3 + 0.25\ HCl)\cdot 247\ H_2O + 4\ H_2(g)$ $\quad \Delta H_{1\,298.15}$ = -72.14 kcal.

$LiCl\cdot 60\ H_2O + H_3BO_3\cdot 60\ H_2O + 0.25(HCl\cdot 508\ H_2O) \rightarrow (LiCl + H_3BO_3 + 0.25\ HCl)\cdot 247\ H_2O$ $\quad \Delta H_{2\,298.15}$ = 0.00 kcal. (assumed)

$H_3BO_3\cdot 60\ H_2O + \infty\ H_2O \rightarrow H_3BO_3\cdot\infty H_2O$ $\quad {}^*\Delta H_{3\,298.15}$ = 0.200 kcal.

The summation of the above reactions yields:

$LiBH_4(c) + 1.25(HCl\cdot 200\ H_2O) + 3\ H_2O(l) + \infty\ H_2O \rightarrow LiCl\cdot 60\ H_2O + H_3BO_3\cdot\infty H_2O$
$+ 0.25(HCl\cdot 508\ H_2O) + 4\ H_2(g)$ $\quad \Delta H_{298}$ = -71.94

The heat of formation of Lithium Borohydride crystal was calculated to be -45.522 kcal. mole^{-1} with the following auxiliary data:

Compound	Heat of Formation at 298.15	Reference
HCl (508 H_2O)	-39.815	HCl(g) JANAF; Dilution data from NBS. Rept. 8504, 1 July 1964 Appendix III by W. H. Evans
HCl (200 H_2O)	-39.696	HCl(g) JANAF; Dilution data from W. H. Evans, loc. cit.
LiCl (60 H_2O)	-106.023	Li^+ see $NaBH_4$ table; Cl^- and dilution data W. H. Evans, loc. cit.
H_3BO_3 (∞H_2O)	-256.05	JANAF $H_3BO_3(c)$ and dilution data from J. Smisko and L. S. Mason. J. of Am. Chem. Soc. 72, 3679 (1950)

*This $\Delta H_{r\ 298.15}$ value was obtained from J. Smisko and L. S. Mason loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, 15.72 - 302.88 °K were obtained from the measurements by N.C. Hallett and H. L. Johnston, J. Am. Chem. Soc., 75, 1496 (1953). The C_p values above 298.15°K were estimated by comparison with the C_p's for $NaBH_4$.

The entropy was based on S°_{15} (extrap) = 0.0874 reported by N. C. Hallett and H. L. Johnston loc. cit.

Melting Data.

T_m was estimated by comparison with the T_m for $NaBH_4$.

Sodium Tetrahydroborate ($NaBH_4$)

(Crystal) Mol. Wt. = 37.84

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.893	-43.862	-43.862	INFINITE
100	9.598	6.288	41.128	-3.484	-45.297	-40.471	88.446
200	17.076	16.676	26.021	-1.869	-45.555	-35.420	38.703
298	20.670	24.232	24.232	.000	-45.850	-30.380	22.268
300	20.708	24.360	24.232	.038	-45.855	-30.284	22.061
400	22.600	30.583	25.068	2.206	-46.741	-25.007	13.662
500	24.330	35.814	26.707	4.553	-46.946	-19.548	8.544
600	25.960	40.395	28.614	7.068	-47.027	-14.058	5.120
700	27.550	44.517	30.596	9.744	-46.977	-8.565	2.674
800	28.740	48.276	32.575	12.561	-46.812	-3.089	.844
900	29.700	51.720	34.513	15.486	-46.567	2.363	-.574
1000	30.460	54.889	36.395	18.494	-46.270	7.784	-1.701
1100	31.080	57.821	38.211	21.571	-45.945	13.172	-2.617
1200	31.490	60.544	39.960	24.700	-68.843	18.990	-3.458
1300	31.710	63.074	41.642	27.862	-68.300	26.287	-4.419
1400	31.820	65.429	43.258	31.039	-67.775	33.543	-5.236
1500	31.860	67.626	44.810	34.223	-67.281	40.763	-5.939
1600	31.890	69.683	46.301	37.411	-66.819	47.949	-6.549
1700	31.910	71.617	47.734	40.601	-66.384	55.112	-7.085
1800	31.920	73.441	49.112	43.792	-65.979	62.244	-7.557
1900	31.950	75.167	50.438	46.986	-65.597	69.360	-7.978
2000	32.000	76.807	51.716	50.183	-65.237	76.453	-8.354

Dec. 31, 1960; Dec. 31, 1964

SODIUM TETRAHYDROBORATE ($NaBH_4$) (CRYSTAL) MOL. WT. = 37.84

$S^\circ_{298.15}$ = 24.232 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 189.9°K

T_m = 770°K

$\Delta H^\circ_{f\ 0}$ = -43.86 ± .07 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -45.85 ± .07 kcal. mole^{-1}

$\Delta H^\circ_{t_1}$ = 0.2388 kcal. mole^{-1}

ΔH°_m = Unknown

Heat of Formation.

The heat of formation was calculated from the solution calorimetry of W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. 71, 2775 (1949). The heats of reaction and mixing were measured for the following reactions:

$NaBH_4 + 1.25(HCl\cdot 200H_2O) \rightarrow (NaCl + H_3BO_3 + 0.25HCl)\cdot 247H_2O + 4H_2$ ΔHr = -63.880 kcal. mole^{-1}

$NaCl\cdot 60H_2O + H_3BO_3\cdot 60H_2O \rightarrow (NaCl + H_3BO_3)\ 120H_2O$ ΔHr = -0.026 kcal. mole^{-1}

$NaCl + (H_3BO_3)\cdot 120H_2O + 0.25(HCl\cdot 508H_2O) \rightarrow (NaCl + H_3BO_3 + 0.25HCl)\cdot 247H_2O$ ΔHr = +0.083 kcal. mole^{-1}

$H_3BO_3\cdot 60H_2O + \infty H_2O \rightarrow H_3BO_3\cdot \infty H_2O$ ΔHr = +0.068 kcal. mole^{-1}

The summation of the above equations yields:

$NaBH_4(c) + 1.25(HCl\cdot 200H_2O) + 3H_2O(l) + \infty H_2O \rightarrow NaCl\cdot 60H_2O + H_3BO_3\cdot \infty H_2O + 0.25(HCl\cdot 508H_2O) + 4H_2(g)$

ΔHr = -63.869 kcal. mole^{-1}

The $\Delta H_{f\ 298.15}$ values for HCl were obtained from JANAF value for HCl(g) and heat of dilution data of NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. The $\Delta H_{f\ 298.15}$ $H_2O(l)$ value was obtained from W. H. Evans loc. cit. The $\Delta H_{f\ 298.15}$ value for NaCl was obtained from JANAF value of NaCl(c) together with dilution data from W. H. Evans, loc. cit. The $\Delta H_{f\ 298.15}$ value for H_3BO_3 was obtained from JANAF value for $H_3BO_3(c)$ together with dilution data of J. Smisko and L. S. Mason, J. of Am. Chem. Soc. 72, 3679 (1950).

Heat Capacity and Entropy.

The low temperature heat capacity (15.76 - 301.26) was obtained from H. L. Johnston and N. C. Hallett, J. Am. Chem. Soc. 75, 1467 (1953). In the area of transition (169-193.5°K) the average ΔH = 635.3 cal./mole and the average ΔS = 3.35 cal./mole °K were adopted from H. L. Johnston and N. C. Hallett, loc. cit. Using the present base line these ΔH and ΔS values yield a heat of transition of 0.2388 kcal. mole^{-1}. The low temperature heat capacity was fitted with the smoothed heat capacity data (298.15 - 700°K) of T. B. Douglas and A. W. Harman, J. Research Natl. Bur. Standards 60, 117 (1958). The heat capacity above 700°K was extrapolated from the plot of both sets of data.

Transition Data.

The temperature and heat of transition were obtained from H. L. Johnston and N. C. Hallett loc. cit.

Melting Data.

The melting data was obtained from T. B. Douglas and A. W. Harman loc. cit.

Boron Iodide (BI)

(Ideal Gas) Mol. Wt. = 137.73

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.178	72.691	72.691	INFINITE
100	6.986	47.539	62.363	- 1.482	73.016	68.999	- 150.791
200	7.485	52.508	56.322	- .763	73.067	64.952	- 70.973
298	8.021	55.604	55.604	.000	73.000	60.978	- 44.696
300	8.029	55.653	55.604	.015	72.998	60.903	- 44.366
400	8.366	58.013	55.923	.836	70.911	56.962	- 31.121
500	8.568	59.904	56.537	1.684	65.584	53.980	- 23.593
600	8.696	61.478	57.233	2.547	65.524	51.664	- 18.818
700	8.782	62.825	57.938	3.421	65.433	49.361	- 15.411
800	8.844	64.002	58.624	4.303	65.319	47.073	- 12.859
900	8.891	65.047	59.280	5.190	65.188	44.799	- 10.878
1000	8.927	65.985	59.905	6.081	65.041	42.543	- 9.297
1100	8.958	66.838	60.497	6.975	64.878	40.299	- 8.006
1200	8.983	67.618	61.058	7.872	64.701	38.073	- 6.934
1300	9.006	68.338	61.591	8.771	64.512	35.862	- 6.029
1400	9.026	69.006	62.097	9.673	64.311	33.666	- 5.255
1500	9.044	69.630	62.579	10.577	64.097	31.482	- 4.587
1600	9.061	70.214	63.038	11.482	63.872	29.317	- 4.004
1700	9.076	70.764	63.476	12.389	63.636	27.163	- 3.492
1800	9.091	71.283	63.896	13.297	63.391	25.025	- 3.038
1900	9.105	71.775	64.298	14.207	63.138	22.900	- 2.634
2000	9.119	72.242	64.683	15.118	62.881	20.790	- 2.272
2100	9.132	72.687	65.054	16.031	62.618	18.693	- 1.945
2200	9.145	73.113	65.411	16.945	62.350	16.605	- 1.650
2300	9.158	73.519	65.754	17.860	62.078	14.534	- 1.381
2400	9.170	73.909	66.086	18.776	61.802	12.474	- 1.136
2500	9.182	74.284	66.407	19.694	56.135	10.531	- .921
2600	9.194	74.644	66.716	20.612	55.860	8.713	- .732
2700	9.205	74.992	67.017	21.532	55.585	6.904	- .559
2800	9.217	75.326	67.307	22.453	55.310	5.108	- .399
2900	9.228	75.650	67.590	23.376	55.037	3.321	- .250
3000	9.239	75.963	67.863	24.299	54.763	1.540	- .112
3100	9.251	76.266	68.130	25.224	54.490	- .230	.016
3200	9.262	76.560	68.389	26.149	54.218	- 1.990	.136
3300	9.273	76.845	68.641	27.076	53.945	- 3.740	.248
3400	9.284	77.122	68.886	28.004	53.674	- 5.485	.353
3500	9.295	77.392	69.125	28.933	53.403	- 7.224	.451
3600	9.306	77.654	69.358	29.863	53.132	- 8.952	.543
3700	9.317	77.909	69.586	30.794	52.861	- 10.673	.630
3800	9.327	78.157	69.808	31.726	52.592	- 12.383	.712
3900	9.338	78.400	70.026	32.659	52.322	- 14.093	.790
4000	9.349	78.636	70.238	33.594	- 69.126	- 13.646	.746
4100	9.360	78.867	70.446	34.529	- 69.164	- 12.258	.653
4200	9.370	79.093	70.649	35.466	- 69.200	- 10.867	.565
4300	9.381	79.314	70.848	36.403	- 69.237	- 9.482	.482
4400	9.392	79.529	71.043	37.342	- 69.275	- 8.089	.402
4500	9.402	79.741	71.234	38.281	- 69.313	- 6.702	.325
4600	9.413	79.947	71.421	39.222	- 69.349	- 5.306	.252
4700	9.423	80.150	71.604	40.164	- 69.386	- 3.915	.182
4800	9.434	80.348	71.784	41.107	- 69.425	- 2.517	.115
4900	9.445	80.543	71.961	42.051	- 69.463	- 1.128	.050
5000	9.455	80.734	72.135	42.996	- 69.502	.268	- .012
5100	9.466	80.921	72.305	43.942	- 69.541	1.665	- .071
5200	9.476	81.105	72.473	44.889	- 69.581	3.060	- .129
5300	9.487	81.286	72.637	45.837	- 69.621	4.455	- .184
5400	9.497	81.463	72.799	46.786	- 69.663	5.856	- .237
5500	9.508	81.638	72.958	47.737	- 69.704	7.255	- .288
5600	9.518	81.809	73.115	48.688	- 69.747	8.650	- .338
5700	9.529	81.977	73.269	49.640	- 69.792	10.057	- .386
5800	9.539	82.143	73.420	50.594	- 69.837	11.456	- .432
5900	9.550	82.306	73.570	51.548	- 69.883	12.859	- .476
6000	9.560	82.467	73.716	52.503	- 69.930	14.262	- .519

June 30, 1963; Dec. 31, 1963; Dec. 31, 1964

BORON MONOIODIDE (BI) (IDEAL GAS) MOL. WT. = 137.73

Ground State Configuration [$^1\Sigma^+$]

$\Delta H^\circ_{f\ 0}$ = [72.7 ± 10] kcal. mole^{-1}

$S^\circ_{298.15}$ = [55.604] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [73.0 ± 10] kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	[1]

ω_e = [600] cm.$^{-1}$

$\omega_e x_e$ = [3.04] cm.$^{-1}$

σ = 1

B_e = [0.3912] cm.$^{-1}$

α_e = [0.0027] cm.$^{-1}$

r_e = [2.08] Å

Heat of Formation.

The ratio D(BF) / ($\Delta H_a(BF_3)/3$) = 1.177, where ΔH_a signifies the heat of atomization, was applied to BI_3 giving D(BI) = 84.4 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298}$ = 73 ± 10 kcal. mole^{-1}.

Heat Capacity and Entropy.

The bond length was first estimated by comparison with the ratio of the bond lengths in the other boron trihalides and monohalides. The vibrational frquency was then calculated using Guggenheimer's Relation [Proc. Phys. Soc. (London) 58, 456 (1946)] which was checked using BBr and shown to give an excellent fit. The quantity $x_e\mu^{1/2}$, where μ is the reduced mass, has been shown to be constant for similar molecules and its value was transferred from BBr to give x_e and $\omega_e x_e$ for BI. α_e was then calculated using the Morse potential function and B_e was determined from the bond length. The ground state configuration was assumed to be the same as that in BBr.

Boron Diiodide (BI_2)

(Ideal Gas) Mol. Wt. = 264.64

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.993	58.453	58.453	INFINITE
100	9.618	62.511	83.673	-2.116	58.595	53.810	-117.596
200	10.696	69.490	75.006	-1.103	58.350	49.109	-53.661
298	11.731	73.964	73.964	.000	58.000	44.642	-32.722
300	11.748	74.037	73.964	.022	57.993	44.560	-32.460
400	12.447	77.520	74.434	1.234	53.711	40.280	-22.007
500	12.880	80.348	75.343	2.502	43.043	37.937	-16.581
600	13.155	82.722	76.380	3.805	42.974	36.921	-13.448
700	13.336	84.765	77.435	5.130	42.884	35.920	-11.214
800	13.461	86.554	78.466	6.470	42.778	34.932	-9.542
900	13.549	88.145	79.454	7.821	42.659	33.957	-8.245
1000	13.615	89.576	80.396	9.179	42.527	32.999	-7.211
1100	13.664	90.876	81.290	10.543	42.380	32.052	-6.368
1200	13.702	92.067	82.140	11.912	42.221	31.120	-5.667
1300	13.732	93.165	82.946	13.284	42.050	30.202	-5.077
1400	13.756	94.183	83.713	14.658	41.865	29.298	-4.573
1500	13.776	95.133	84.443	16.035	41.668	28.405	-4.138
1600	13.792	96.022	85.139	17.413	41.459	27.530	-3.760
1700	13.805	96.859	85.804	18.793	41.238	26.666	-3.428
1800	13.816	97.648	86.440	20.174	41.007	25.814	-3.134
1900	13.826	98.396	87.050	21.556	40.767	24.977	-2.873
2000	13.834	99.105	87.635	22.939	40.521	24.150	-2.639
2100	13.841	99.780	88.197	24.323	40.269	23.339	-2.429
2200	13.847	100.424	88.739	25.707	40.010	22.538	-2.239
2300	13.853	101.040	89.260	27.092	39.746	21.752	-2.067
2400	13.857	101.630	89.763	28.478	39.477	20.976	-1.910
2500	13.861	102.195	90.249	29.864	33.815	20.318	-1.776
2600	13.865	102.739	90.719	31.250	33.543	19.782	-1.663
2700	13.868	103.262	91.174	32.637	33.270	19.260	-1.559
2800	13.871	103.767	91.615	34.024	32.996	18.747	-1.463
2900	13.874	104.254	92.042	35.411	32.721	18.245	-1.375
3000	13.876	104.724	92.457	36.799	32.445	17.748	-1.293
3100	13.879	105.179	92.860	38.186	32.167	17.260	-1.217
3200	13.881	105.620	93.252	39.574	31.889	16.786	-1.146
3300	13.882	106.047	93.633	40.962	31.609	16.321	-1.081
3400	13.884	106.461	94.005	42.351	31.329	15.859	-1.019
3500	13.886	106.864	94.366	43.739	31.047	15.410	-.962
3600	13.887	107.255	94.719	45.128	30.764	14.968	-.909
3700	13.888	107.635	95.063	46.517	30.480	14.529	-.858
3800	13.889	108.006	95.399	47.905	30.194	14.106	-.811
3900	13.890	108.367	95.727	49.294	29.907	13.684	-.767
4000	13.891	108.718	96.047	50.684	-91.559	15.413	-.842
4100	13.892	109.061	96.360	52.073	-91.617	18.091	-.964
4200	13.893	109.396	96.667	53.462	-91.676	20.771	-1.081
4300	13.894	109.723	96.966	54.851	-91.737	23.444	-1.191
4400	13.895	110.042	97.260	56.241	-91.800	26.125	-1.298
4500	13.895	110.355	97.548	57.630	-91.865	28.808	-1.399
4600	13.896	110.660	97.829	59.020	-91.930	31.488	-1.496
4700	13.897	110.959	98.105	60.410	-91.997	34.170	-1.589
4800	13.897	111.252	98.376	61.799	-92.068	36.861	-1.678
4900	13.898	111.538	98.642	63.189	-92.140	39.543	-1.764
5000	13.898	111.819	98.903	64.579	-92.214	42.236	-1.846
5100	13.899	112.094	99.159	65.969	-92.290	44.921	-1.925
5200	13.899	112.364	99.410	67.359	-92.369	47.610	-2.001
5300	13.900	112.629	99.657	68.749	-92.449	50.307	-2.074
5400	13.900	112.889	99.900	70.139	-92.533	53.002	-2.145
5500	13.901	113.144	100.138	71.529	-92.618	55.701	-2.213
5600	13.901	113.394	100.372	72.919	-92.707	58.387	-2.279
5700	13.901	113.640	100.603	74.309	-92.799	61.090	-2.342
5800	13.902	113.882	100.830	75.699	-92.893	63.794	-2.404
5900	13.902	114.120	101.053	77.089	-92.989	66.494	-2.463
6000	13.902	114.353	101.273	78.479	-93.089	69.200	-2.520

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

BORON DIIODIDE (BI_2) (IDEAL GAS) MOL. WT. = 264.64

Point Group [C_{2v}]

$\Delta H_{f\ 0}^\circ$ = [58.5 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = [73.964] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = [58.0 ± 15] kcal. mole^{-1}

Ground State Quantum Weight [2]

Vibrational Levels and Degeneracies

ω, cm.$^{-1}$
[550](1)
[110](1)
[770](1)

Bond Distance: B-I = [2.06] Å

Bond Angle: I-B-I = [120°]

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 3.33503 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was estimated by analogy with BF_3, specifically the ratio

$$\Delta H_r(BX_3 \rightarrow BX_2 + X) \ / \ \Delta H_r(BX_3 \rightarrow B + 3X)$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trihalide given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were $I_B = 1.8278 \times 10^{-39}$ g. cm.^{2}, $I_A = 134.1670 \times 10^{-39}$ g. cm.^{2} and $I_C = 135.9948 \times 10^{-39}$ g. cm.^{2}

Boron Triiodide (BI_3)

(Ideal Gas) Mol. Wt. = 391.55

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.025	17.998	17.998	INFINITE
100	12.788	67.153	97.219	-3.007	17.917	13.397	-29.277
200	15.334	76.880	84.824	-1.589	17.488	9.038	-9.876
298	16.919	83.322	83.322	.000	17.000	4.990	-3.658
300	16.942	83.427	83.322	.031	16.990	4.915	-3.581
400	17.922	88.447	84.000	1.779	10.658	1.176	-.642
500	18.510	92.515	85.309	3.603	-5.216	.313	-.137
600	18.878	95.924	86.802	5.474	-5.165	1.413	-.515
700	19.119	98.854	88.319	7.374	-5.129	2.507	-.783
800	19.283	101.418	89.800	9.295	-5.105	3.597	-.983
900	19.400	103.697	91.220	11.229	-5.093	4.682	-1.137
1000	19.486	105.745	92.572	13.174	-5.091	5.770	-1.261
1100	19.551	107.606	93.855	15.126	-5.103	6.854	-1.362
1200	19.601	109.309	95.073	17.083	-5.128	7.944	-1.447
1300	19.640	110.880	96.229	19.046	-5.163	9.034	-1.519
1400	19.671	112.336	97.328	21.011	-5.213	10.130	-1.581
1500	19.697	113.694	98.375	22.980	-5.275	11.224	-1.635
1600	19.717	114.966	99.372	24.950	-5.348	12.330	-1.684
1700	19.735	116.162	100.325	26.923	-5.435	13.436	-1.727
1800	19.750	117.291	101.236	28.897	-5.531	14.547	-1.766
1900	19.762	118.359	102.110	30.873	-5.637	15.666	-1.802
2000	19.773	119.373	102.948	32.850	-5.749	16.788	-1.834
2100	19.782	120.338	103.753	34.827	-5.868	17.920	-1.865
2200	19.790	121.258	104.528	36.806	-5.994	19.056	-1.893
2300	19.797	122.138	105.275	38.785	-6.125	20.197	-1.919
2400	19.803	122.980	105.995	40.765	-6.263	21.348	-1.944
2500	19.808	123.789	106.691	42.746	-11.794	22.608	-1.976
2600	19.813	124.566	107.363	44.727	-11.935	23.986	-2.016
2700	19.817	125.314	108.014	46.708	-12.078	25.371	-2.054
2800	19.821	126.035	108.645	48.690	-12.223	26.760	-2.089
2900	19.825	126.730	109.257	50.673	-12.368	28.159	-2.122
3000	19.828	127.402	109.851	52.655	-12.517	29.555	-2.153
3100	19.831	128.053	110.427	54.638	-12.666	30.959	-2.182
3200	19.833	128.682	110.988	56.621	-12.817	32.370	-2.211
3300	19.836	129.293	111.534	58.605	-12.971	33.785	-2.237
3400	19.838	129.885	112.065	60.589	-13.125	35.204	-2.263
3500	19.840	130.460	112.582	62.572	-13.282	36.628	-2.287
3600	19.842	131.019	113.086	64.557	-13.440	38.056	-2.310
3700	19.843	131.562	113.578	66.541	-13.601	39.489	-2.332
3800	19.845	132.092	114.059	68.525	-13.762	40.925	-2.354
3900	19.846	132.607	114.528	70.510	-13.927	42.368	-2.374
4000	19.847	133.110	114.986	72.494	-135.272	45.952	-2.511
4100	19.849	133.600	115.434	74.479	-135.208	50.487	-2.691
4200	19.850	134.078	115.872	76.464	-135.146	55.022	-2.863
4300	19.851	134.545	116.301	78.449	-135.086	59.542	-3.026
4400	19.852	135.001	116.721	80.434	-135.031	64.069	-3.182
4500	19.853	135.448	117.132	82.419	-134.977	68.592	-3.331
4600	19.854	135.884	117.535	84.405	-134.924	73.118	-3.474
4700	19.854	136.311	117.930	86.390	-134.873	77.637	-3.610
4800	19.855	136.729	118.317	88.376	-134.827	82.162	-3.741
4900	19.856	137.138	118.697	90.361	-134.783	86.682	-3.866
5000	19.856	137.539	119.070	92.347	-134.742	91.203	-3.986
5100	19.857	137.933	119.436	94.332	-134.703	95.715	-4.101
5200	19.858	138.318	119.796	96.318	-134.668	100.234	-4.213
5300	19.858	138.697	120.149	98.304	-134.634	104.748	-4.319
5400	19.859	139.068	120.496	100.290	-134.605	109.270	-4.422
5500	19.859	139.432	120.837	102.276	-134.578	113.789	-4.521
5600	19.860	139.790	121.172	104.262	-134.555	118.293	-4.616
5700	19.860	140.141	121.502	106.248	-134.536	122.816	-4.709
5800	19.861	140.487	121.826	108.234	-134.520	127.327	-4.798
5900	19.861	140.826	122.145	110.220	-134.506	131.844	-4.884
6000	19.861	141.160	122.459	112.206	-134.497	136.361	-4.967

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

BORON TRIIODIDE (BI_3) (IDEAL GAS) MOL. WT. = 391.55

Point Group D_{3h}

$S^\circ_{298.15}$ = 83.322 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H^\circ_{f\ 0}$ = 18.0 ± 12 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 17.0 ± 12 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
190(1)
339(1)
710(2)
100(2)

Bond Distance: B-I = [2.03 ± 0.03] Å

Bond Angle: I-B-I = [120°]

$\sigma = 6$

Product of the Moments of Inertia = [4.418202] X 10^{-111} g.^{3} cm.^{6}

Heat of Formation.

W. S. Koski, J. J. Kaufman and C. F. Pachuki, J. Am. Chem. Soc. 81, 1326 (1959) measured the appearance potential of the B^+ ion from BI_3. Assuming the reaction

$$BI_3 + e \rightarrow B^+ + 3I + 2e$$

one can calculate the heat of atomization of BI_3 as 8.31 ± 0.5 e.v. The analagous reaction for BBr_3 can be checked independently and shows the process to be valid. This value leads to a $\Delta H^\circ_{f\ 298}$ = 17.0 ± 12 kcal. mole^{-1}, if the process is assumed to occur at 298°K.

Heat Capacity and Entropy.

Vibrational frequencies were taken from T. Wentink and V. H. Tiensuu, J. Chem. Phys. 28, 826 (1958) modified according to the natural abundance of boron. The B-I distance was estimated by Koski et al., loc. cit., and the angle was estimated by analogy with the other boron trihalides. The three principal moments of inertia are: $I_A = I_B$ = 1.30238 X 10^{-37} and I_C = 2.60476 X 10^{-37} g. cm.^{2}

Lithium Metaborate ($LiBO_2$)

(Crystal) Mol. Wt. = 49.76

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.142	- 241.960	- 241.960	INFINITE
100	4.501	2.434	22.204	- 1.977	- 242.633	- 238.540	521.304
200	10.311	7.429	13.544	- 1.223	- 243.079	- 234.252	255.967
298	14.291	12.351	12.351	.000	- 243.290	- 229.870	168.491
300	14.354	12.440	12.351	.026	- 243.293	- 229.788	167.392
400	16.992	16.960	12.950	1.604	- 243.369	- 225.271	123.077
500	18.854	20.960	14.160	3.400	- 244.135	- 220.668	96.449
600	20.411	24.538	15.596	5.365	- 244.113	- 215.974	78.665
700	21.823	27.792	17.109	7.478	- 243.994	- 211.293	65.966
800	23.157	30.794	18.635	9.727	- 243.780	- 206.637	56.448
900	24.448	33.596	20.144	12.108	- 243.470	- 202.011	49.053
1000	25.711	36.237	21.622	14.616	- 243.064	- 197.423	43.145
1100	26.955	38.746	23.065	17.249	- 242.562	- 192.884	38.321
1200	28.187	41.144	24.472	20.006	- 241.960	- 188.393	34.309
1300	29.410	43.448	25.844	22.886	- 241.257	- 183.957	30.924
1400	30.627	45.672	27.181	25.888	- 240.451	- 179.578	28.032
1500	31.840	47.826	28.485	29.011	- 239.543	- 175.262	25.534
1600	33.049	49.920	29.760	32.256	- 238.529	- 171.007	23.357
1700	34.254	51.960	31.006	35.621	- 272.458	- 165.494	21.275
1800	35.458	53.952	32.226	39.107	- 271.053	- 159.241	19.334
1900	36.661	55.901	33.421	42.713	- 269.542	- 153.069	17.606
2000	37.862	57.812	34.593	46.439	- 267.923	- 146.981	16.061
2100	39.062	59.688	35.743	50.285	- 266.196	- 140.975	14.671
2200	40.261	61.533	36.873	54.251	- 264.362	- 135.055	13.416
2300	41.459	63.349	37.985	58.337	- 262.417	- 129.222	12.278
2400	42.656	65.139	39.079	62.543	- 260.366	- 123.472	11.243
2500	43.852	66.905	40.157	66.868	- 263.594	- 117.706	10.289

June 30, 1961; Dec. 31, 1964

LITHIUM METABORATE ($LiBO_2$) (CRYSTAL) MOL. WT. = 49.76

$S^\circ_{298.15}$ = 12.351 cal. deg.$^{-1}$ mole^{-1}

T_m = 1117 ± 1°K.

$\Delta H^\circ_{f\ 0}$ = -241.96 ± .20 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -243.29 ± .20 kcal. mole^{-1}

ΔH_m = 8.093 ± .10 kcal. mole^{-1}

Heat of Formation.

G. C. Sinke, Thermal Research Laboratory, The Dow Chemical Co., private communication, July 1960 has measured $\Delta H_{r\ 298.15}$ for the following reaction:

$$LiBO_2(c) + HNO_3 \cdot 111H_2O(Sol.) + H_2O(l) \rightarrow LiNO_3 \cdot 112H_2O(Sol.) + H_3BO_3 \cdot 112H_2O(Sol.)$$

$\Delta H_{r\ 298.15}$ = -10.93 ± 0.05 kcal. mole^{-1}

From this heat of reaction the $\Delta H_{f\ 298.15}$ for $LiBO_2(c)$ is calculated to be -243.29 kcal. mole^{-1} with the following auxiliary heats of formation:

	$\Delta H_{f\ 298.15}$(Kcal. mole^{-1})	Source
$H_3BO_3 \cdot 112\ H_2O$	-256.23	Dilution data from J. Smisko and L. S. Mason, J. of Am. Chem. Soc. 72, 3679 (1950)
$HNO_3 \cdot 111\ H_2O$	-49.44	NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans
$H_2O(l)$	-68.315	W. H. Evans, loc. cit.
$LiNO_3 \cdot 112\ H_2O$	-115.747	*S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958); correction S. R. Gunn Lawrence Radiation Lab. UCRL-7992, 5, July, (1964).

**Dilution and other auxiliary data from W. H. Evans, loc. cit.

L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27 (1954), measured the heats of solution in nitric acid of various Li_2O-B_2O_3 glasses and crystalline mixtures containing 0 to 48 mole % Li_2O. These results were extrapolated to 50 mole % and yielded $\Delta H_{r\ 298.15}$ = -45.20 kcal. for the following reaction:

$$Li_2O(c) + B_2O_3(c) \rightarrow 2\ LiBO_2(c)$$

With JANAF values for $Li_2O(c)$ and $B_2O_3(c)$ the $\Delta H_{f\ 298.15}$ for $LiBO_2(c)$ was calculated to be -245.97 ± .80 kcal. mole^{-1}. This value is in fair agreement with the value adopted for the table.

*$Li(c) + H_2O(l) \rightarrow LiOH \cdot 1000\ H_2O(Sol.) + 1/2\ H_2$	$\Delta H_{r\ 298.15}$ = -53.115 ± 0.019 kcal. mole^{-1}
**$LiOH \cdot 1000\ H_2O(Sol.) \rightarrow LiOH\ \infty\ H_2O$	$\Delta H_{dilution\ 298.15}$ = +.102 kcal. mole^{-1}
$LiOH(\infty H_2O) \rightarrow Li^+(\infty H_2O) + OH^-(\infty H_2O)$	$\Delta H_{r\ 298.15}$ = 0.00
$LiNO_3(\infty H_2O) \rightarrow Li^+(\infty H_2O) + NO_3^-(\infty H_2O)$	$\Delta H_{r\ 298.15}$ = 0.00
$LiNO_3(\infty H_2O) \rightarrow LiNO_3 \cdot 112\ H_2O$	ΔH_{r} dilution = .171 kcal. mole^{-1}

Heat Capacity and Entropy.

F. L. Oetting and W. E. Hatton, The Dow Chemical Company, private communication, April, 1961, have measured C_p from 13° to 326°K. R. A. McDonald, Thermal Research Laboratory The Dow Chemical Company, private communication, April, 1961 has measured H_T-$H_{298.15}$ from 288° to 1116°K. The above data were adopted for the table. The C_p values above T_m were obtained by graphical extrapolation.

The entropy was based on S° = .013 cal. mole^{-1} deg.$^{-1}$ at 15°K. calculated from the low temperature C_p values of F. L. Oetting and W. E. Hatton loc. cit.

Melting Data.

The T_m and ΔH_m adopted for this table were obtained from R. A. McDonald loc. cit. The following cryoscopic data have been published: C. Petit and M. Jaeger, Compt. rend. 244, 1734 (1957), T_m = 1109°K., ΔH_m = 7.4 kcal. mole^{-1}; G. Zarzychi, colloques intern, centre, nat'l. recherche sci. (Paris) 39, Electrolyse C34-C37 (1952), ΔH_m = 8.3 ± 0.6 kcal. mole^{-1}. C. Sutra, Compt. rend. 234, 1283 (1952), T_m =1113°K. and ΔH_m = 8.3 kcal. mole^{-1}.

Lithium Metaborate $(LiBO_2)$

(Liquid) Mol. Wt. = 49.76

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	14.291	15.591	15.591	.000	- 238.819	- 226.365	165.922
300	14.354	15.680	15.591	.026	- 238.822	- 226.289	164.843
400	16.992	20.200	16.190	1.604	- 238.898	- 222.096	121.342
500	18.854	24.200	17.400	3.400	- 239.664	- 217.817	95.209
600	20.411	27.778	18.836	5.365	- 239.642	- 213.447	77.744
700	21.823	31.032	20.349	7.478	- 239.523	- 209.090	65.278
800	34.558	34.872	21.904	10.374	- 238.662	- 204.781	55.941
900	34.558	38.942	23.576	13.830	- 237.277	- 200.629	48.717
1000	34.558	42.583	25.297	17.286	- 235.923	- 196.628	42.971
1100	34.558	45.877	27.021	20.741	- 234.599	- 192.764	38.297
1200	34.558	48.884	28.720	24.197	- 233.298	- 189.019	34.423
1300	34.558	51.650	30.379	27.653	- 232.019	- 185.381	31.164
1400	34.558	54.211	31.990	31.109	- 230.759	- 181.840	28.385
1500	34.558	56.595	33.552	34.565	- 229.518	- 178.391	25.990
1600	34.558	58.825	35.063	38.020	- 228.294	- 175.020	23.905
1700	34.558	60.920	36.522	41.476	- 262.132	- 170.400	21.905
1800	34.558	62.895	37.933	44.932	- 260.757	- 165.042	20.038
1900	34.558	64.763	39.296	48.388	- 259.396	- 159.760	18.376
2000	34.558	66.536	40.614	51.844	- 258.047	- 154.553	16.888
2100	34.558	68.222	41.889	55.299	- 256.711	- 149.411	15.549
2200	34.558	69.830	43.123	58.755	- 255.387	- 144.333	14.337
2300	34.558	71.366	44.318	62.211	- 254.072	- 139.316	13.237
2400	34.558	72.837	45.476	65.667	- 252.771	- 134.353	12.234
2500	34.558	74.248	46.599	69.123	- 256.868	- 129.338	11.306
2600	34.558	75.603	47.689	72.578	- 255.581	- 124.262	10.445
2700	34.558	76.907	48.746	76.034	- 254.302	- 119.234	9.651
2800	34.558	78.164	49.774	79.490	- 253.030	- 114.256	8.918
2900	34.558	79.377	50.775	82.946	- 251.768	- 109.320	8.238
3000	34.558	80.549	51.748	86.402	- 250.513	- 104.431	7.607
3100	34.558	81.682	52.696	89.857	- 249.269	- 99.582	7.020
3200	34.558	82.779	53.619	93.313	- 248.032	- 94.774	6.472
3300	34.558	83.842	54.518	96.769	- 246.805	- 90.002	5.960
3400	34.558	84.874	55.396	100.225	- 245.588	- 85.268	5.481
3500	34.558	85.876	56.253	103.681	- 244.379	- 80.576	5.031
3600	34.558	86.850	57.089	107.136	- 243.182	- 75.911	4.608
3700	34.558	87.797	57.907	110.592	- 241.994	- 71.283	4.210
3800	34.558	88.719	58.706	114.048	- 240.816	- 66.681	3.835
3900	34.558	89.617	59.487	117.504	- 239.648	- 62.120	3.481
4000	34.558	90.492	60.252	120.960	- 359.671	- 55.439	3.029

June 30, 1961; Dec. 31, 1964

LITHIUM METABORATE $(LiBO_2)$ (LIQUID) MOL. WT. = 49.76

$S^\circ_{298.15}$ = [15.591] cal. deg.$^{-1}$ mole^{-1}

T_m = 1117 ± 1°K.

T_b = [2264]°K.

ΔH°_f 298.15 = [-238.819] kcal. mole^{-1}

ΔH°_m = 8.09 ± .10 kcal. mole^{-1}

ΔH°_v = [50.79] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_f(l)$ was obtained from $\Delta H^\circ_f(c)$ by addition of ΔH°_m and difference between $(H^\circ_{1117} - H^\circ_{298.15})$ for the crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald, Thermal Research Laboratory, The Dow Chemical Company, private communication, April 1961, has measured $H_T - H_{298.15}$ from 1118° to 1707°K. The constant value of C_p measured between 1118° and 1707°K. has been extrapolated above and below this range. Lithium metaborate is assumed to have a glass transformation temperature at 745°K. below which C_p of the glass is assumed equal to that of the cyrstal.

The entropy of the liquid was calculated from the entropy of the crystal in a manner analogous to the heat of formation.

Melting Data.

The ΔH_m and T_m values were obtained from R. A. McDonald loc. cit.

Vaporization Data.

The boiling point was found from graphing the ΔF_f's of the liquid and gas. The heat of vaporization was found from the difference in ΔH_f's of the liquid and gas at T_b.

Lithium Metaborate ($LiBO_2$)
(Ideal Gas) Mol. Wt. = 49.76

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.633	-159.543	-159.543	INFINITE
100	8.053	51.878	70.249	-1.837	-159.585	-160.437	350.618
200	9.260	57.779	62.672	-.979	-159.927	-161.170	176.110
298	10.666	61.742	61.742	.000	-160.382	-161.688	118.515
300	10.691	61.808	61.742	.020	-160.391	-161.697	117.790
400	12.002	65.066	62.177	1.155	-160.910	-162.054	88.538
500	13.185	67.874	63.042	2.416	-162.211	-162.201	70.895
600	14.218	70.371	64.059	3.787	-162.783	-162.144	59.058
700	15.094	72.631	65.125	5.254	-163.310	-161.996	50.575
800	15.820	74.695	66.194	6.801	-163.798	-161.775	44.193
900	16.418	76.594	67.245	8.414	-164.256	-161.495	39.214
1000	16.907	78.350	68.269	10.081	-164.691	-161.163	35.220
1100	17.310	79.981	69.261	11.793	-165.110	-160.791	31.945
1200	17.641	81.502	70.218	13.541	-165.517	-160.380	29.208
1300	17.917	82.925	71.141	15.319	-165.916	-159.936	26.886
1400	18.147	84.262	72.031	17.123	-166.308	-159.461	24.892
1500	18.341	85.521	72.889	18.947	-166.699	-158.960	23.159
1600	18.505	86.710	73.716	20.790	-167.087	-158.430	21.639
1700	18.645	87.836	74.514	22.647	-202.524	-156.549	20.125
1800	18.765	88.905	75.284	24.518	-202.734	-153.837	18.677
1900	18.869	89.923	76.028	26.400	-202.947	-151.115	17.381
2000	18.960	90.893	76.747	28.292	-203.162	-148.382	16.214
2100	19.039	91.820	77.443	30.192	-203.381	-145.638	15.156
2200	19.108	92.707	78.117	32.099	-203.606	-142.882	14.193
2300	19.169	93.558	78.770	34.013	-203.833	-140.118	13.314
2400	19.224	94.375	79.403	35.933	-204.068	-137.341	12.506
2500	19.272	95.161	80.018	37.857	-209.697	-134.449	11.753
2600	19.315	95.917	80.615	39.787	-209.935	-131.433	11.047
2700	19.354	96.647	81.195	41.720	-210.179	-128.409	10.393
2800	19.389	97.352	81.760	43.658	-210.425	-125.378	9.786
2900	19.420	98.032	82.309	45.598	-210.679	-122.330	9.219
3000	19.449	98.691	82.844	47.542	-210.936	-119.280	8.689
3100	19.475	99.330	83.366	49.488	-211.201	-116.223	8.193
3200	19.499	99.948	83.874	51.436	-211.472	-113.155	7.728
3300	19.520	100.549	84.371	53.387	-211.750	-110.080	7.290
3400	19.540	101.132	84.855	55.340	-212.036	-106.993	6.877
3500	19.559	101.698	85.328	57.295	-212.328	-103.901	6.488
3600	19.575	102.249	85.791	59.252	-212.629	-100.795	6.119
3700	19.591	102.786	86.243	61.210	-212.939	-97.687	5.770
3800	19.605	103.309	86.685	63.170	-213.257	-94.564	5.438
3900	19.618	103.818	87.118	65.131	-213.584	-91.439	5.124
4000	19.631	104.315	87.541	67.094	-335.100	-86.160	4.707
4100	19.642	104.800	87.957	69.058	-335.216	-79.934	4.261
4200	19.653	105.273	88.363	71.022	-335.342	-73.703	3.835
4300	19.663	105.736	88.762	72.988	-335.478	-67.472	3.429
4400	19.672	106.188	89.153	74.955	-335.626	-61.238	3.042
4500	19.681	106.630	89.536	76.922	-335.787	-55.000	2.671
4600	19.689	107.063	89.913	78.891	-335.958	-48.757	2.316
4700	19.696	107.486	90.282	80.860	-336.144	-42.511	1.977
4800	19.704	107.901	90.645	82.830	-336.343	-36.261	1.651
4900	19.710	108.307	91.001	84.801	-336.557	-30.013	1.339
5000	19.717	108.706	91.351	86.772	-336.785	-23.755	1.038
5100	19.723	109.096	91.695	88.744	-337.031	-17.485	.749
5200	19.728	109.479	92.034	90.717	-337.292	-11.221	.472
5300	19.734	109.855	92.366	92.690	-337.571	-4.948	.204
5400	19.739	110.224	92.694	94.663	-337.870	1.326	-.054
5500	19.743	110.586	93.016	96.638	-338.186	7.621	-.303
5600	19.748	110.942	93.333	98.612	-338.526	13.899	-.542
5700	19.752	111.292	93.645	100.587	-338.887	20.196	-.774
5800	19.756	111.635	93.952	102.563	-339.271	26.506	-.999
5900	19.760	111.973	94.255	104.538	-339.679	32.812	-1.215
6000	19.764	112.305	94.553	106.515	-340.112	39.136	-1.425

June 30, 1962; Dec. 31, 1964; Mar. 31, 1965

LITHIUM METABORATE ($LiBO_2$) (IDEAL GAS) MOL. WT. = 49.76

Point Group C_s

$S^\circ_{298.15}$ = [61.742] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -159.54 ± 1.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -160.38 ± 1.1 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ν, cm.$^{-1}$	ν, cm.$^{-1}$
[2040](1)	[1100](1)
1935 (1)	[500](1)
[1340](1)	600 (1)

Bond Distances: Li-O = 1.82 Å, O-B = 1.36 Å, B=O = 1.20 Å

Bond Angles: LiOB = 100°, O-B=O = 180°

Product of the Moments of Inertia: $I_AI_BI_C$ = 4.01933 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The adopted heat of formation at 298.15 was evaluated by the third-law method using vapor pressure data reported by D. L. Hildenbrand, W. F. Hall and N. D. Potter, J. Chem. Phys. 39, No. 2, 296 (1963). The heat of reaction at 298.15 was found to be 82.908 kcal. mole^{-1} thus giving the value $\Delta H_{f\ 298.15}$ = -160.382 kcal. mole^{-1}. A second-law method was also used on the data of D. L. Hildenbrand et. al., loc. cit. and yielded a $\Delta H_{r\ 298.15}$ = 81.375 kcal. mole^{-1} thus giving $\Delta H_{f\ 298.15}$ = -161.915 kcal. mole^{-1}. A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. 39, No. 2, 286 (1963), have measured the vaporization of lithium metaborate mass spectrometrically in an effusion cell. The second law value reported by A. Büchler and J. B. Berkowitz-Mattuck, loc. cit. for $\Delta H_{r\ 1060}$ was 79 ± 3 kcal. mole^{-1} which yields $\Delta H_{r\ 298.15}$ = 84.078 kcal. mole^{-1} thus giving $\Delta H_{f\ 298.15}$ = -159.212 kcal. mole^{-1} with JANAF auxiliary values.

Heat Capacity and Entropy.

A. Büchler and E. P. Marram, J. Chem Phys. 39, No. 2, 292, (1963), observed and assigned two vibrational frequencies to lithium metaborate which were adopted for this table. The other vibrational frequencies were estimated by comparison with similar molecules. D. White, Ohio State University, in a private communication quoted in D. L. Hildenbrand et. al. loc. cit. assigned vibrational frequencies from matrix-isolation experiments. When these frequencies were used in a third and second law analysis of Hildenbrand's data, the drift in the third law was much larger and the agreement between the second and third law was also much poorer than that using the frequencies employed in this table. The molecular constants were obtained from P. A. Akishin and V. P. Spiridonov, Zhur. Strukt. Khim. 2, 63 (1961). The individual moments of inertia are: I_A = 1.22164 X 10^{-38} g. cm.^{2}, I_B = 2.2710 X 10^{-39} g. cm.^{2}, and I_C = 1.44875 X 10^{-38} g. cm.^{2}.

Boron Nitride (BN)

(Crystal) GFW = 24.8177

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-.628	-59.270	-59.270	INFINITE
100	1.183	.667	6.497	-.583	-59.578	-57.728	126.164
200	2.967	2.025	3.910	-.377	-59.800	-55.788	60.962
298	4.713	3.536	3.536	.000	-59.970	-53.783	39.424
300	4.744	3.565	3.536	.009	-59.973	-53.745	39.153
400	6.280	5.148	3.741	.563	-60.089	-51.649	28.220
500	7.500	6.686	4.178	1.254	-60.162	-49.530	21.650
600	8.420	8.138	4.718	2.052	-60.195	-47.400	17.265
700	9.100	9.489	5.304	2.929	-60.199	-45.267	14.133
800	9.670	10.742	5.907	3.868	-60.176	-43.135	11.784
900	10.180	11.911	6.510	4.861	-60.128	-41.008	9.958
1000	10.600	13.006	7.105	5.901	-60.061	-38.886	8.499
1100	10.950	14.033	7.689	6.979	-59.980	-36.773	7.306
1200	11.200	14.997	8.258	8.087	-59.892	-34.666	6.314
1300	11.400	15.902	8.812	9.218	-59.801	-32.569	5.475
1400	11.540	16.752	9.349	10.365	-59.711	-30.476	4.758
1500	11.640	17.552	9.869	11.524	-59.627	-28.393	4.137
1600	11.690	18.305	10.373	12.691	-59.551	-26.311	3.594
1700	11.697	19.014	10.861	13.860	-59.489	-24.237	3.116
1800	11.700	19.683	11.333	15.030	-59.438	-22.166	2.691
1900	11.700	20.315	11.789	16.200	-59.398	-20.094	2.311
2000	11.700	20.915	12.230	17.370	-59.366	-18.026	1.970
2100	11.700	21.486	12.658	18.540	-59.342	-15.960	1.661
2200	11.700	22.031	13.071	19.710	-59.325	-13.896	1.380
2300	11.700	22.551	13.472	20.880	-59.314	-11.832	1.124
2400	11.700	23.049	13.861	22.050	-59.310	-9.766	.889
2500	11.700	23.526	14.238	23.220	-64.698	-7.592	.664
2600	11.700	23.985	14.604	24.390	-64.697	-5.309	.446
2700	11.700	24.427	14.960	25.560	-64.696	-3.024	.245
2800	11.700	24.852	15.306	26.730	-64.697	-.740	.058
2900	11.700	25.263	15.642	27.900	-64.698	1.546	-.116
3000	11.700	25.659	15.969	29.070	-64.700	3.830	-.279
3100	11.700	26.043	16.288	30.240	-64.703	6.112	-.431
3200	11.700	26.414	16.599	31.410	-64.707	8.398	-.574
3300	11.700	26.774	16.902	32.580	-64.712	10.685	-.708
3400	11.700	27.124	17.197	33.750	-64.717	12.968	-.834
3500	11.700	27.463	17.486	34.920	-64.723	15.250	-.952

Dec. 31, 1960; Sept. 30, 1963; Mar. 31, 1964; June 30, 1966

BORON NITRIDE (BN) (CRYSTAL) GFW = 24.8177

$\Delta Hf^\circ_0 = -59.27 \pm 0.37$ kcal/mol

$S^\circ_{298.15} = 3.536$ gibbs/mol

$\Delta Hf^\circ_{298} = -59.97 \pm 0.37$ kcal/mol

Td = 2600 ± 100°K

Heat of Formation.

The adopted heat of formation was determined by Wise et al. using combustion in fluorine. Other recent calorimetric values are in good agreement as summarized below. Torsion-effusion studies of the decomposition $BN(c) \rightarrow B(am) + 0.5\ N_2(g)$ by D. L.Hildenbrand and W. F. Hall, J. Phys. Chem. 67, 888 (1963), yield essentially the same ΔHf° and indicate that the condensation coefficient, α, is $< 6\times10^{-3}$ for $N_2(g)$ on the surface of the sample. Use of $\alpha = 6 \times 10^{-3}$ brings the following decomposition studies into reasonable agreement: Langmuir studies by L. H. Dreger, V. V. Dadape and J. L. Margrave, J. Phys. Chem 66, 1556 (1962); mass spectrometric studies by P. O. Schissel and W. S. Williams, Bull. Am. Phys. Soc., II, 4, 139 (1959); and Knudsen effusion studies by M. Hoch and D. White, Technical Research Report MCC-1023-TR-214, Ohio State University Research Foundation, Columbus, Ohio, October, 1956.

Source	Reaction	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
1. Dworkin et al. (1954)	$BN(c) + 3/4\ O_2(g) \rightarrow 0.5\ B_2O_3(am) + 0.5\ N_2$	-90.1 ± 0.5	-59.7 ± 0.7
2. Gal'chenko et al. (1959)	$B(am) + 0.5\ N_2(g) \rightarrow BN(c)$	-60.8 ± 0.3	-59.6 ± 0.8
3. Gross (1961)	$BN(c) + 1.5\ F_2(g) \rightarrow BF_3(g) + 0.5\ N_2$	-211.2 ± 0.1	
	$B(c) + 1.5\ F_2(g) \rightarrow BF_3(g)$	-271.4	-60.2
4. Thompson et al. (1961)	$BN(c) + NF_3(g) \rightarrow BF_3(g) + N_2$	-177.63 ± 0.3	
	$B(c) + NF_3(g) \rightarrow BF_3(g) + 0.5\ N_2$	-237.77 ± 0.5	-60.1 ± 2
5. Keavney (1962)	Combustion in O_2- H_2O	-	-59.9 ± 1.5
6. Wise et al. (1966)	$BN(c) + 1.5\ F_2(g) \rightarrow BF_3(g) + 0.5\ N_2$	-211.68 ± 0.3	-59.97 ± 0.37

References

1. A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, J. Chem. Phys. 22, 837 (1954).
2. G. L. Gal'chenko, A. N. Kornilov, and S. M. Skuratov, Russ. J. Inorg. Chem. 5, 1282 (1960).
3. P. Gross, Fulmer Research Institute, Report R. 163/6/15 December 1961, Stoke Poges, England.
4. C. J. Thompson and G. C. Sinke, Dow Chemical Co., Report ARPA 1-164, Jan. 1961.
5. J. J. Keavney, Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., private communication to Wise et al., loc. cit.
6. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 70, 7 (1966).

Heat Capacity and Entropy.

The low temperature heat capacity was taken from E. F. Westrum, Jr., private communication, May 19, 1960. The intermediate heat capacity (300-1650°C) was obtained from R. A. McDonald and D. R. Stull, J. Phys. Chem. 65, 1918 (1961). The high temperature Cp was taken from H. Prophet and D. R. Stull, J. Chem. Eng. Data 8, No. 1, 78, January 1963. The heat capacities in the three temperature ranges were plotted and then graphically smoothed. A. S. Dworkin, D. J. Sasmor, and A. R. Van Artsdalen, loc cit., also reported heat capacity (50-300°K) not employed in this table.

The entropy was obtained by integration of the heat capacity data from E. F. Westrum, Jr., loc. cit., based upon $S^\circ_{10} = 0.0028$ eu.

Temperature of Decomposition.

Observations by The Dow Chemical Company under Contract No. AF 33(616)-6149 show decomposition to elements at 1 atm total pressure at 2600 ± 100°K. The decomposition temperature calculated from these tables is 2832°K; presumably this discrepancy is associated with uncertainties in the high temperature enthalpies of BN(c), B(c) and B(l) and the enthalpy of melting of B(c).

Boron Nitride (BN)

(Ideal Gas) GFW = 24.8177

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.076	113.252	113.252	INFINITE
100	6.957	43.114	56.935	- 1.382	113.593	111.199	- 243.024
200	6.963	47.937	51.368	- .686	113.861	108.691	- 118.772
298	7.039	50.728	50.728	.000	114.000	106.117	- 77.786
300	7.041	50.771	50.728	.013	114.002	106.068	- 77.270
400	7.237	52.822	51.006	.726	114.044	103.415	- 56.503
500	7.489	54.463	51.539	1.462	114.016	100.759	- 44.042
600	7.735	55.851	52.145	2.224	113.946	98.114	- 35.738
700	7.949	57.059	52.762	3.008	113.851	95.483	- 29.811
800	8.126	58.133	53.368	3.812	113.738	92.866	- 25.370
900	8.272	59.099	53.952	4.632	113.613	90.264	- 21.919
1000	8.390	59.976	54.511	5.466	113.474	87.679	- 19.162
1100	8.488	60.781	55.045	6.310	113.320	85.105	- 16.909
1200	8.570	61.523	55.554	7.163	113.154	82.548	- 15.034
1300	8.640	62.212	56.040	8.023	112.975	80.004	- 13.450
1400	8.701	62.854	56.504	8.890	112.784	77.476	- 12.095
1500	8.755	63.457	56.948	9.763	112.582	74.959	- 10.921
1600	8.805	64.023	57.373	10.641	112.369	72.460	- 9.898
1700	8.851	64.558	57.780	11.524	112.145	69.972	- 8.996
1800	8.895	65.066	58.170	12.411	111.913	67.496	- 8.195
1900	8.937	65.548	58.546	13.303	111.675	65.036	- 7.481
2000	8.978	66.007	58.908	14.199	111.433	62.589	- 6.839
2100	9.018	66.446	59.256	15.099	111.187	60.152	- 6.260
2200	9.057	66.867	59.593	16.002	110.937	57.727	- 5.735
2300	9.095	67.270	59.918	16.910	110.686	55.314	- 5.256
2400	9.133	67.658	60.232	17.821	110.431	52.913	- 4.818
2500	9.169	68.032	60.537	18.737	104.788	50.629	- 4.426
2600	9.205	68.392	60.832	19.655	104.538	48.468	- 4.074
2700	9.240	68.740	61.119	20.577	104.291	46.318	- 3.749
2800	9.274	69.077	61.397	21.503	104.046	44.172	- 3.448
2900	9.307	69.403	61.667	22.432	103.804	42.042	- 3.168
3000	9.339	69.719	61.930	23.365	103.564	39.915	- 2.908
3100	9.370	70.025	62.187	24.300	103.327	37.797	- 2.665
3200	9.400	70.323	62.436	25.239	103.091	35.688	- 2.437
3300	9.429	70.613	62.680	26.180	102.858	33.586	- 2.224
3400	9.457	70.895	62.917	27.124	102.627	31.490	- 2.024
3500	9.484	71.169	63.149	28.071	102.398	29.400	- 1.836
3600	9.510	71.437	63.376	29.021	102.171	27.318	- 1.658
3700	9.535	71.698	63.597	29.973	101.946	25.241	- 1.491
3800	9.559	71.952	63.814	30.928	101.723	23.175	- 1.333
3900	9.582	72.201	64.025	31.885	101.502	21.107	- 1.183
4000	9.604	72.444	64.233	32.844	- 19.897	21.193	- 1.158
4100	9.625	72.681	64.436	33.806	- 19.884	22.221	- 1.184
4200	9.646	72.914	64.635	34.769	- 19.869	23.249	- 1.210
4300	9.666	73.141	64.830	35.735	- 19.852	24.275	- 1.234
4400	9.685	73.363	65.022	36.702	- 19.836	25.302	- 1.257
4500	9.704	73.581	65.210	37.672	- 19.818	26.325	- 1.279
4600	9.722	73.795	65.394	38.643	- 19.798	27.350	- 1.299
4700	9.740	74.004	65.575	39.616	- 19.778	28.376	- 1.319
4800	9.757	74.209	65.753	40.591	- 19.758	29.404	- 1.339
4900	9.774	74.410	65.927	41.568	- 19.737	30.424	- 1.357
5000	9.790	74.608	66.099	42.546	- 19.716	31.449	- 1.375
5100	9.806	74.802	66.268	43.526	- 19.695	32.471	- 1.391
5200	9.822	74.993	66.434	44.507	- 19.672	33.493	- 1.408
5300	9.838	75.180	66.597	45.490	- 19.650	34.513	- 1.423
5400	9.853	75.364	66.757	46.475	- 19.629	35.535	- 1.438
5500	9.869	75.545	66.916	47.461	- 19.607	36.562	- 1.453
5600	9.884	75.723	67.071	48.448	- 19.585	37.577	- 1.467
5700	9.898	75.898	67.225	49.438	- 19.564	38.601	- 1.480
5800	9.913	76.070	67.376	50.428	- 19.544	39.622	- 1.493
5900	9.928	76.240	67.524	51.420	- 19.523	40.639	- 1.505
6000	9.942	76.407	67.671	52.414	- 19.504	41.660	- 1.517

Dec. 31, 1960; Sept. 30, 1963; June 30, 1966

BORON NITRIDE (BN) (IDEAL GAS) GFW = 24.8177

Ground State Configuration $^3\Pi$

$S^\circ_{298.15}$ = 50.73 gibbs/mol

ΔHf°_0 = 113 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 114 ± 30 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	6
[8500]	1
[8900]	2
27877	6

ω_e = 1514.6 cm^{-1}

$\omega_e x_e$ = 12.3 cm^{-1}

σ = 1

B_e = 1.666 cm^{-1}

α_e = 0.025 cm^{-1}

r_e = 1.281 Å

Heat of Formation.

The heat of formation is based on D_o = 5.7 eV which was calculated from ω_e and $\omega_e x_e$ observed by A. E. Douglas and G. Herzberg, Can. J. Research 18A, 179 (1940). An uncertainty of ± 1.3 eV was assigned from consideration of other information, which places the dissociation energy between 4 and 7 eV. The value D_o = 4.0 ± 0.5 eV was selected by A. G. Gaydon, "Dissociation Energies," second edition, Chapman and Hall Ltd, London, 1953, from his own extrapolation of the spectroscopic data. An upper limit of $D_0 \leqslant$ 7.0 eV results from the upper limit for the pressure of BN(c) → BN(g) obtained from the B^+ ion intensity at 1600°C observed by P.A.Akishin and Yu. S. Klodeev, Zh. Neorgan. Khim. 7, 941 (1962). It is likely that the BN(g) pressure is even smaller, since it is known that BN(c) → B(s) + 0.5 N_2(g) and Akishin's pressure limit are the same magnitude as that of B(s) → B(g). V. V. Fesenko, Poroshkovaya Met., Akad. Nauk Ukr. S. S. R. 1, No. 4, 80-5 (1961) [cf. Chem. Abs. 56, 10997 (1962)], reports a standard heat of sublimation of 160 kcal/mol for BN(c) → BN(g) and also gives pressures for BN(g) at 2500 and 3000°K which are stated to be two orders less than the equilibrium pressure of nitrogen. Fesenko's original article is not yet available to us and it is not clear from the abstract whether the values are based on new data or are mere calculations. The reported pressures yield D_o = 6.2 eV, but here again the BN(g) pressures are of the same magnitude as the JANAF values for B(s) → B(g).

Some estimated values for D_o (ranging from 5.4 to 6.4 eV) are summarized below along with the experimental evidence.

Source	D_o (eV)	ΔHs°_{298} (kcal/mol)	ΔHf°_{298} (kcal/mol)
Gaydon's extrapolation of spectroscopic data	4.0 ± 0.5	213	153
Linear Birge-Sponer extrapolation	5.7	174	114
Fesenko's "BN(g) pressures"	6.2	161	101
Akishin's upper limit for BN(g) pressure	7.0	145	85
Estimate from geometric mean of D_o for B_2 and N_2	5.4	180	120
Estimate from D_o for series N_2, CN, BN, BeN	5.6	177	117
Estimate $M_2 + N_2$ = 2 MN for M=B from M=C	6.0	166	106
Estimate from arithmetic mean of D_o for B_2 and N_2	6.4	158	98

Heat Capacity and Entropy.

The molecular constants are based on emission spectra of the $^3\Pi$ - $^3\Pi$ transition obtained by Douglas and Herzberg, loc. cit. Observation of the same triplet in absorption by B. A. Thrush, Nature 160, 1044 (1960), strongly suggests that the ground state of BN is $^3\Pi$ in contrast to $^1\Sigma$, as observed for the isoelectronic molecules BeO and C_2. Electronic levels for the $^3\Pi$ states are taken from Douglas and Herzberg, while values for $^1\Sigma+$ and $^1\Pi$ have been estimated from the SCF calculations of J. L. Masse and M. Bärlocher, Helv. Chim. Acta 47, 314 (1964).

Sodium Metaborate ($NaBO_2$)

(Crystal) Mol. Wt. = 65.811

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.782	- 232.874	- 232.874	INFINITE
100	7.751	4.780	29.394	- 2.461	- 233.592	- 229.341	501.201
200	12.740	11.890	18.924	- 1.407	- 233.885	- 224.954	245.806
298	15.760	17.573	17.573	.000	- 234.000	- 220.544	161.655
300	15.780	17.670	17.573	.029	- 234.001	- 220.460	160.597
400	17.370	22.434	18.212	1.689	- 234.718	- 215.885	117.949
500	18.700	26.458	19.469	3.495	- 234.797	- 211.166	92.296
600	19.880	29.972	20.933	5.424	- 234.819	- 206.437	75.191
700	21.050	33.124	22.453	7.470	- 234.773	- 201.710	62.974
800	22.300	36.017	23.970	9.638	- 234.643	- 196.995	53.814
900	23.590	38.718	25.460	11.933	- 234.418	- 192.301	46.695
1000	24.900	41.272	26.914	14.357	- 234.096	- 187.637	41.006
1100	26.190	43.705	28.331	16.912	- 233.680	- 183.012	36.359
1200	27.490	46.040	29.710	19.596	- 256.403	- 177.970	32.411
1300	28.790	48.292	31.053	22.410	- 255.577	- 171.467	28.825
1400	30.090	50.473	32.363	25.354	- 254.641	- 165.032	25.761
1500	31.400	52.594	33.641	28.428	- 253.596	- 158.668	23.117
1600	32.700	54.662	34.891	31.633	- 252.438	- 152.375	20.813
1700	34.000	56.683	36.113	34.968	- 251.166	- 146.158	18.789
1800	35.300	58.663	37.311	38.433	- 249.782	- 140.021	17.000
1900	36.600	60.607	38.486	42.028	- 248.282	- 133.964	15.409
2000	37.900	62.517	39.640	45.753	- 246.664	- 127.990	13-985

Dec. 31, 1960; Mar. 31, 1965

SODIUM METABORATE ($NaBO_2$) (CRYSTAL) MOL. WT. = 65.811

$\Delta H_f^\circ{}_0 = -232.9$ kcal. mole⁻¹

$S^\circ_{298.15} = 17.573$ cal. deg.⁻¹ mole⁻¹

$\Delta H^\circ_{f\ 298.15} = -234 \pm 2$ kcal. mole⁻¹

$T_m = 1239°K.$

$\Delta H_m^\circ = 8.66$ kcal. mole⁻¹

$\Delta H^\circ_{s\ 298.15} = 77.00$ kcal. mole⁻¹

Heat of Formation.

W. H. Evans, D. D. Wagman and E. J. Prosen in NBS Report No. 4943, "Thermodynamic Properties of Some Boron Compounds", August, 1956, extrapolated from the graph of L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27 (1954) the heat of solution to be -25.4 kcal. mole⁻¹ for the first reaction in 2N nitric acid. G. Grenier and D. White, J. Chem. Phys. 61, 1681 (1957) measured the heat of solution at 273.15°K. in 2N nitric acid for the first reaction and found a value of -20.43 kcal. mole⁻¹. The heats of solution for the second and third reactions were obtained from L. Shartsis and W. Capps, loc. cit.

1. $Na_2O \cdot B_2O_3(c)$ + Solvent I = end Solution 1
2. $B_2O_3(c)$ + Solvent II = end Solution 1 $\Delta H_2 = -3.64$ kcal./mole
3. $Na_2O(c)$ + Solvent I = Solvent II $\Delta H_3 = -83.9$ kcal./mole

The combination of the above reactions yields:

$Na_2O(c) + B_2O_3(c) = Na_2O \cdot B_2O_3(c)$

$1/2\ Na_2O(c) + 1/2\ B_2O_3(c) = NaBO_2(c)$

The $\Delta H^\circ_{f\ 298.15}$'s for Na_2O and B_2O_3 are JANAF values. The $\Delta H^\circ_{f\ 298.15}$ value of -234.000 kcal. mole⁻¹ employed in this table was obtained by taking the average of the values given above for reaction 1. Since there were uncertainties in the extrapolation and in assuming no correction for the measurements at 273.15°K., an average value was considered preferable.

Heat Capacity and Entropy.

The low temperature heat capacities (5-298.15°K.) and $S^\circ_{298.15}$ were obtained from G. Grenier and E. F. Westrum, J. Am. Chem. Soc. 78, 6226 (1956). The heat capacities at the higher temperatures were altered slightly from the estimate of K. K. Kelley, U. S. Bureau of Mines Bulletin 393 (1936).

Melting Data.

The T_m was obtained from H. S. Van Klooster, Z. Anorg. Chem. 69, 122 (1911). The adopted ΔH_m° was calculated by K. K. Kelley loc. cit. from H. S. Van Klooster's work. K. K. Kelley also calculated a ΔH_m° of 9.3 kcal. mole⁻¹ from M. H. LeChatelier, Compt. rend. 118, 800 (1894).

Sublimation Data.

The ΔH_s was obtained from the mass spectrometric investigations of A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. 39, 286 (1963).

Sodium Metaborate (NaBO$_2$)

(Liquid) Mol. Wt. = 65.811

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	15.760	20.560	20.560	.000	- 229.339	- 216.773	158.892
300	15.780	20.658	20.560	.029	- 229.340	- 216.695	157.855
400	17.370	25.421	21.199	1.689	- 230.057	- 212.419	116.055
500	18.700	29.443	22.456	3.494	- 230.137	- 207.999	90.912
600	19.880	32.957	23.919	5.423	- 230.159	- 203.568	74.146
700	21.050	36.108	25.439	7.469	- 230.113	- 199.139	62.171
800	22.300	39.001	26.955	9.636	- 229.984	- 194.723	53.193
900	35.000	42.723	28.489	12.811	- 228.879	- 190.366	46.225
1000	35.000	46.411	30.100	16.311	- 227.481	- 186.161	40.683
1100	35.000	49.747	31.737	19.811	- 226.120	- 182.098	36.178
1200	35.000	52.792	33.366	23.311	- 248.027	- 177.696	32.361
1300	35.000	55.594	34.970	26.811	- 246.515	- 171.897	28.897
1400	35.000	58.187	36.537	30.311	- 245.023	- 166.213	25.946
1500	35.000	60.602	38.061	33.811	- 243.552	- 160.636	23.404
1600	35.000	62.861	39.542	37.311	- 242.099	- 155.155	21.192
1700	35.000	64.983	40.976	40.811	- 240.662	- 149.765	19.253
1800	35.000	66.983	42.366	44.311	- 239.243	- 144.458	17.539
1900	35.000	68.876	43.712	47.811	- 237.838	- 139.232	16.015
2000	35.000	70.671	45.015	51.311	- 236.445	- 134.079	14.651
2100	35.000	72.379	46.278	54.811	- 235.062	- 128.995	13.424
2200	35.000	74.007	47.502	58.311	- 233.692	- 123.976	12.315
2300	35.000	75.563	48.688	61.811	- 232.331	- 119.021	11.309
2400	35.000	77.052	49.839	65.311	- 230.982	- 114.119	10.391
2500	35.000	78.481	50.957	68.811	- 235.030	- 109.172	9.543
2600	35.000	79.854	52.042	72.311	- 233.693	- 104.163	8.755
2700	35.000	81.175	53.096	75.811	- 232.363	- 99.207	8.030
2800	35.000	82.448	54.122	79.311	- 231.040	- 94.302	7.360
2900	35.000	83.676	55.120	82.811	- 229.723	- 89.435	6.740
3000	35.000	84.862	56.092	86.311	- 228.414	- 84.621	6.164

Dec. 31, 1960; Mar. 31, 1965

SODIUM METABORATE (NaBO$_2$) (LIQUID) MOL. WT. = 65.811

$S^\circ_{298.15}$ = 20.560 cal. deg.$^{-1}$ mole^{-1}

ΔH°_f 298.15 = [-229.339] kcal. mole^{-1}

T_m = 1239°K.

ΔH°_m = 8.66 kcal. mole^{-1}

Heat of Formation.

ΔH°_f 298.15(l) was obtained from ΔH°_f(c) by addition of ΔH°_m and difference between $(H^\circ_{1239}-H^\circ_{298.15})$ for the crystal and liquid.

Heat Capacity and Entropy.

Sodium metaborate is assumed to have a glass transformation at 826°K. below which C_p of the glass is assumed equal to that of the crystal. Above 826°K. the heat capacity was estimated as a constant value by assuming 8.75 calories contribution from each atom. The $S^\circ_{298.15}$ was obtained in a manner analogous with ΔH°_f 298.15.

Melting Data.

See crystal table.

Sodium Metaborate $(NaBO_2)$
(Ideal Gas) Mol. Wt. = 65.811

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.738	-155.830	-155.830	INFINITE
100	8.188	54.584	73.971	-1.939	-156.070	-156.799	342.667
200	9.784	60.701	65.936	-1.047	-156.525	-157.356	171.942
298	11.504	64.937	64.937	.000	-157.000	-157.665	115.586
300	11.534	65.008	64.937	.021	-157.009	-157.669	114.856
400	12.939	68.527	65.408	1.248	-158.159	-157.764	86.194
500	14.062	71.539	66.340	2.600	-158.692	-157.602	68.884
600	14.984	74.187	67.431	4.053	-159.190	-157.336	57.307
700	15.745	76.556	68.569	5.591	-159.652	-156.991	49.012
800	16.371	78.701	69.703	7.198	-160.083	-156.582	42.774
900	16.884	80.660	70.813	8.862	-160.489	-156.120	37.909
1000	17.305	82.461	71.889	10.572	-160.881	-155.611	34.007
1100	17.651	84.127	72.927	12.320	-161.272	-155.068	30.808
1200	17.937	85.676	73.926	14.100	-184.899	-154.029	28.051
1300	18.174	87.121	74.886	15.906	-185.081	-151.449	25.460
1400	18.373	88.475	75.808	17.734	-185.261	-148.854	23.236
1500	18.541	89.749	76.696	19.579	-185.445	-146.250	21.308
1600	18.683	90.950	77.550	21.441	-185.630	-143.629	19.618
1700	18.804	92.086	78.372	23.315	-185.819	-140.996	18.125
1800	18.909	93.164	79.164	25.201	-186.014	-138.355	16.798
1900	18.999	94.189	79.928	27.097	-186.213	-135.702	15.609
2000	19.077	95.166	80.665	29.001	-186.416	-133.040	14.537
2100	19.146	96.098	81.378	30.912	-186.622	-130.365	13.567
2200	19.206	96.990	82.068	32.830	-186.834	-127.681	12.683
2300	19.260	97.845	82.735	34.753	-187.050	-124.989	11.876
2400	19.307	98.666	83.382	36.681	-187.273	-122.283	11.135
2500	19.349	99.455	84.009	38.614	-192.888	-119.465	10.443
2600	19.387	100.215	84.618	40.551	-193.114	-116.523	9.794
2700	19.420	100.947	85.209	42.491	-193.344	-113.572	9.193
2800	19.451	101.654	85.784	44.435	-193.577	-110.616	8.634
2900	19.478	102.337	86.343	46.381	-193.814	-107.643	8.112
3000	19.503	102.997	86.887	48.330	-194.056	-104.668	7.625
3100	19.526	103.637	87.417	50.282	-194.301	-101.686	7.168
3200	19.546	104.258	87.934	52.235	-194.553	-98.697	6.740
3300	19.565	104.859	88.438	54.191	-194.810	-95.694	6.337
3400	19.583	105.444	88.929	56.148	-195.074	-92.689	5.958
3500	19.598	106.012	89.409	58.108	-195.343	-89.675	5.599
3600	19.613	106.564	89.878	60.068	-195.621	-86.649	5.260
3700	19.627	107.101	90.337	62.030	-195.906	-83.618	4.939
3800	19.639	107.625	90.785	63.993	-196.199	-80.576	4.634
3900	19.651	108.135	91.223	65.958	-196.501	-77.536	4.345
4000	19.661	108.633	91.652	67.924	-317.992	-72.336	3.952
4100	19.671	109.119	92.072	69.890	-318.085	-66.193	3.528
4200	19.681	109.593	92.484	71.858	-318.187	-60.047	3.124
4300	19.689	110.056	92.887	73.826	-318.303	-53.896	2.739
4400	19.697	110.509	93.282	75.796	-318.434	-47.751	2.372
4500	19.705	110.951	93.670	77.766	-318.580	-41.592	2.020
4600	19.712	111.385	94.051	79.737	-318.742	-35.438	1.684
4700	19.719	111.809	94.424	81.708	-318.924	-29.277	1.361
4800	19.725	112.224	94.790	83.680	-319.126	-23.110	1.052
4900	19.731	112.631	95.150	85.653	-319.350	-16.946	.756
5000	19.736	113.029	95.504	87.626	-319.598	-10.768	.471
5100	19.742	113.420	95.851	89.600	-319.873	-4.586	.196
5200	19.747	113.804	96.193	91.575	-320.174	1.591	-.067
5300	19.751	114.180	96.529	93.550	-320.506	7.786	-.321
5400	19.756	114.549	96.859	95.525	-320.873	13.981	-.566
5500	19.760	114.911	97.184	97.501	-321.273	20.194	-.802
5600	19.764	115.268	97.504	99.477	-321.713	26.394	-1.030
5700	19.767	115.617	97.819	101.454	-322.192	32.621	-1.251
5800	19.771	115.961	98.128	103.430	-322.715	38.852	-1.464
5900	19.774	116.299	98.434	105.408	-323.281	45.091	-1.670
6000	19.778	116.632	98.734	107.385	-323.895	51.339	-1.870

Mar. 31, 1965

SODIUM METABORATE $(NaBO_2)$ (IDEAL GAS) MOL. WT. = 65.811

Point Group C_s

$S^\circ_{298.15}$ = [64.937] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-156 ± 3] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-157 ± 3] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ν, cm.$^{-1}$	ν, cm.$^{-1}$
[800] (1)	[400] (1)
1935 (1)	600 (1)
[2040] (1)	[1000] (1)

Bond Distance: Na-O = 2.14 Å, O-B = 1.36 Å, B=O = 1.20 Å

Bond Angle: NaOB = 100°, O-B=O = 180°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 2.566657 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was calculated from the heat of sublimation of 73 ± 3 kcal. mole^{-1} measured mass spectrometrically at 1070°K. by A. Büchler and J. B. Berkowitz - Mattuck, J. of Chem. Phys. 39, 286 (1963) by addition of the difference between $(H^\circ_{1070} - H^\circ_{298.15})$ for the crystal and gas.

Heat Capacity and Entropy.

A. Büchler and E. P. Marram, J. Chem. Phys. 39, No. 2, 292, (1963), observed and assigned two vibrational metaborate frequencies, which were adopted for this table. The other vibrational frequencies were estimated by comparison with lithium metaborate. The molecular constants were obtained from P. A. Akishin and V. P. Spiridonov, Zhur. Strukt. Khim. 2, 63 (1961). The individual moments of inertia are: $I_A = 4.2923 \times 10^{-39}$, $I_B = 22.4009 \times 10^{-39}$, and $I_C = 26.6933 \times 10^{-39}$ g. cm.^{2}

Boron Monoxide (BO)

(Ideal Gas) GFW = 26.8104

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.073	- .744	- .744	INFINITE
100	6.956	41.001	54.794	- 1.379	- .403	- 2.425	5.300
200	6.958	45.824	49.241	- .684	- .135	- 4.560	4.983
298	6.978	48.604	48.604	.000	.000	- 6.768	4.961
300	6.979	48.647	48.604	.013	.001	- 6.810	4.961
400	7.068	50.665	48.879	.715	.026	- 9.087	4.965
500	7.230	52.259	49.401	1.429	- .038	- 11.359	4.965
600	7.427	53.594	49.991	2.162	- .158	- 13.612	4.958
700	7.627	54.754	50.590	2.914	- .311	- 15.842	4.946
800	7.810	55.785	51.176	3.687	- .482	- 18.051	4.931
900	7.971	56.714	51.741	4.476	- .666	- 20.236	4.914
1000	8.108	57.561	52.281	5.280	- .861	- 22.399	4.895
1100	8.225	58.340	52.797	6.097	- 1.067	- 24.544	4.876
1200	8.324	59.060	53.289	6.924	- 1.283	- 26.668	4.857
1300	8.408	59.729	53.759	7.761	- 1.508	- 28.774	4.837
1400	8.480	60.355	54.208	8.606	- 1.743	- 30.862	4.818
1500	8.542	60.942	54.638	9.457	- 1.988	- 32.935	4.799
1600	8.595	61.495	55.049	10.314	- 2.243	- 34.989	4.779
1700	8.641	62.018	55.444	11.175	- 2.507	- 37.028	4.760
1800	8.682	62.513	55.823	12.042	- 2.780	- 39.051	4.741
1900	8.717	62.983	56.188	12.912	- 3.061	- 41.058	4.723
2000	8.749	63.431	56.539	13.785	- 3.347	- 43.051	4.704
2100	8.777	63.859	56.877	14.661	- 3.638	- 45.028	4.686
2200	8.803	64.268	57.204	15.540	- 3.935	- 46.992	4.668
2300	8.826	64.660	57.520	16.422	- 4.236	- 48.944	4.651
2400	8.847	65.036	57.825	17.305	- 4.544	- 50.879	4.633
2500	8.866	65.397	58.121	18.191	- 10.243	- 52.696	4.607
2600	8.884	65.745	58.407	19.079	- 10.551	- 54.388	4.572
2700	8.901	66.081	58.685	19.968	- 10.861	- 56.067	4.538
2800	8.917	66.405	58.955	20.859	- 11.172	- 57.737	4.507
2900	8.932	66.718	59.218	21.751	- 11.483	- 59.391	4.476
3000	8.947	67.021	59.473	22.645	- 11.796	- 61.039	4.447
3100	8.961	67.315	59.721	23.541	- 12.109	- 62.677	4.419
3200	8.976	67.599	59.963	24.438	- 12.423	- 64.303	4.392
3300	8.990	67.876	60.198	25.336	- 12.738	- 65.918	4.366
3400	9.004	68.144	60.428	26.236	- 13.053	- 67.525	4.340
3500	9.018	68.406	60.652	27.137	- 13.369	- 69.125	4.316
3600	9.032	68.660	60.871	28.039	- 13.686	- 70.711	4.293
3700	9.047	68.908	61.085	28.943	- 14.003	- 72.291	4.270
3800	9.063	69.149	61.294	29.849	- 14.320	- 73.860	4.248
3900	9.079	69.385	61.499	30.756	- 14.637	- 75.427	4.227
4000	9.096	69.615	61.699	31.664	- 136.133	- 74.836	4.089
4100	9.113	69.840	61.894	32.575	- 136.219	- 73.303	3.907
4200	9.131	70.059	62.086	33.487	- 136.303	- 71.763	3.734
4300	9.150	70.274	62.274	34.401	- 136.388	- 70.226	3.569
4400	9.170	70.485	62.458	35.317	- 136.474	- 68.688	3.412
4500	9.191	70.691	62.639	36.235	- 136.558	- 67.147	3.261
4600	9.212	70.894	62.816	37.155	- 136.642	- 65.602	3.117
4700	9.235	71.092	62.990	38.078	- 136.725	- 64.056	2.979
4800	9.258	71.287	63.161	39.002	- 136.808	- 62.507	2.846
4900	9.283	71.478	63.329	39.929	- 136.891	- 60.964	2.719
5000	9.308	71.666	63.494	40.859	- 136.971	- 59.412	2.597
5100	9.334	71.850	63.656	41.791	- 137.053	- 57.858	2.479
5200	9.361	72.032	63.815	42.726	- 137.132	- 56.307	2.367
5300	9.389	72.210	63.972	43.663	- 137.210	- 54.751	2.258
5400	9.418	72.386	64.126	44.604	- 137.288	- 53.197	2.153
5500	9.448	72.559	64.278	45.547	- 137.363	- 51.633	2.052
5600	9.478	72.730	64.427	46.493	- 137.439	- 50.080	1.954
5700	9.509	72.898	64.574	47.443	- 137.514	- 48.518	1.860
5800	9.541	73.063	64.719	48.395	- 137.587	- 46.955	1.769
5900	9.573	73.227	64.862	49.351	- 137.658	- 45.392	1.681
6000	9.606	73.388	65.003	50.310	- 137.729	- 43.825	1.596

Dec. 31, 1960; June 30, 1962; Mar. 31, 1965; June 30, 1968

BORON MONOXIDE (BO) (IDEAL GAS) GFW = 26.8104

Ground State Configuration $^2\Sigma^+$

$\Delta Hf_0^\circ = -0.7 \pm 2$ kcal/mol

$S^\circ_{298.15} = 48.60 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 0 \pm 2$ kcal/mol

Electronic Levels and Quantum Weights

	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	23836	2
$A^2\Pi$	23959	2
$B'^2\Sigma$	39957	2
$B^2\Sigma^+$	43175	2

$\omega_e = 1895.66$ cm^{-1} $\omega_e x_e = 11.90$ cm^{-1} $\sigma = 1$

$B_e = 1.800$ cm^{-1} $\alpha_e = 0.01676$ cm^{-1} $r_e = 1.2049$ Å

Heat of Formation

The heat of formation has recently been determined by several workers whose values are in close agreement. P. E. Blackburn, A. Buchler, and J. L. Stauffer, J. Phys. Chem. 70, 2469 (1966), measured the ion currents corresponding to BO^+ and $B_2O_2^+$ as a function of temperature in a mass spectrometer. From a least squares fit of the data they report $\Delta H = 56.6 \pm 1.8$ kcal for the reaction $1/2B_2O_2(g) \rightarrow BO(g)$; this yields $\Delta Hf^\circ_{298}(BO, g) = 2.1 \pm 2.8$ kcal/mol using $\Delta Hf^\circ_{298}(B_2O_2, g) = -109 \pm 2$ kcal/mol.

L. De Galan, Physica, 31, 1286 (1965), from flame photometric measurements reports $D_0^\circ(BO) = 8.3$eV(191.4 kcal), which corresponds to $\Delta Hf^\circ_{298}(BO, g) = -0.1$ kcal/mol.

P. Coppens, S. Smoes and J. Drowart, Trans. Faraday Soc. 64, 630 (1968), from a mass spectrometric study of several isomolecular exchange reactions, conclude that $D_0^\circ(BO) = 8.29 \pm 0.1$eV(191.2 ± 2.3 kcal) or $\Delta Hf^\circ_{298}(BO, g) = 0.1 \pm 2.3$ kcal/mol.

M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Rocket Power, Inc., Report No. AFRPL-TR-67-244, Final Report under Contract F04611-67-C-0010, Nov. 1967 (available as AD830237), investigated the same reaction as Blackburn et al. and report $\Delta Hr^\circ_{1800} = 53.8 \pm 1.9$ kcal, which yields $\Delta Hf^\circ_{298}(BO, g) = 0.9 \pm 2.9$ kcal/mol.

We adopt a median value of 0 ± 2 kcal/mol which includes all the determinations.

Heat Capacity and Entropy

The molecular and vibrational constants for the ground state are from G. Herzberg "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The electronic levels are also given by Herzberg with the exception of the level at 39957, a $^2\Sigma$ level designated B' by A. A. Mal'tsev and D. I. Kataev, Vestn. Mosk, Univ. Serv. II 22, 2 (1967). The molecular constants were all adjusted to reflect normal isotopic abundancies.

Boron Dioxide (BO_2)

(Ideal Gas) GFW = 42.8098

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.565	-68.198	-68.198	INFINITE
100	8.060	45.089	63.300	-1.821	-68.154	-68.515	149.740
200	9.208	51.007	55.810	-.961	-68.070	-68.910	75.301
298	10.343	54.900	54.900	.000	-68.000	-69.339	50.827
300	10.363	54.964	54.900	.019	-67.999	-69.348	50.520
400	11.351	58.085	55.319	1.106	-67.945	-69.806	38.140
500	12.137	60.706	56.141	2.283	-67.912	-70.276	30.718
600	12.730	62.974	57.095	3.527	-67.898	-70.750	25.771
700	13.171	64.971	58.080	4.824	-67.895	-71.225	22.238
800	13.501	66.752	59.055	6.158	-67.904	-71.702	19.588
900	13.750	68.358	60.001	7.521	-67.921	-72.176	17.527
1000	13.942	69.817	60.911	8.906	-67.948	-72.646	15.877
1100	14.091	71.153	61.782	10.308	-67.989	-73.115	14.527
1200	14.209	72.384	62.615	11.723	-68.041	-73.578	13.400
1300	14.304	73.525	63.411	13.149	-68.106	-74.037	12.447
1400	14.381	74.588	64.172	14.583	-68.183	-74.490	11.628
1500	14.444	75.583	64.899	16.025	-68.273	-74.939	10.919
1600	14.497	76.517	65.597	17.472	-68.376	-75.379	10.296
1700	14.541	77.397	66.265	18.924	-68.491	-75.813	9.746
1800	14.579	78.229	66.907	20.380	-68.619	-76.240	9.257
1900	14.611	79.018	67.524	21.839	-68.758	-76.660	8.818
2000	14.639	79.768	68.117	23.302	-68.904	-77.073	8.422
2100	14.663	80.483	68.689	24.767	-69.059	-77.476	8.063
2200	14.685	81.166	69.241	26.234	-69.224	-77.873	7.736
2300	14.704	81.819	69.774	27.704	-69.395	-78.264	7.437
2400	14.722	82.445	70.289	29.175	-69.576	-78.643	7.161
2500	14.738	83.047	70.787	30.648	-75.152	-78.910	6.898
2600	14.753	83.625	71.270	32.123	-75.339	-79.057	6.645
2700	14.768	84.182	71.738	33.599	-75.531	-79.195	6.410
2800	14.781	84.719	72.192	35.076	-75.727	-79.328	6.192
2900	14.795	85.238	72.633	36.555	-75.926	-79.450	5.987
3000	14.809	85.740	73.061	38.035	-76.129	-79.569	5.797
3100	14.823	86.226	73.478	39.517	-76.334	-79.681	5.618
3200	14.837	86.697	73.884	41.000	-76.543	-79.786	5.449
3300	14.851	87.153	74.279	42.484	-76.755	-79.884	5.291
3400	14.866	87.597	74.665	43.970	-76.970	-79.975	5.141
3500	14.882	88.028	75.040	45.458	-77.186	-80.064	4.999
3600	14.898	88.448	75.407	46.946	-77.406	-80.140	4.865
3700	14.914	88.856	75.765	48.437	-77.627	-80.213	4.738
3800	14.932	89.254	76.115	49.929	-77.850	-80.277	4.617
3900	14.950	89.642	76.456	51.423	-78.074	-80.343	4.502
4000	14.969	90.021	76.791	52.919	-199.479	-78.253	4.276
4100	14.988	90.391	77.118	54.417	-199.475	-75.222	4.010
4200	15.008	90.752	77.438	55.917	-199.470	-72.189	3.756
4300	15.029	91.105	77.752	57.419	-199.467	-69.157	3.515
4400	15.050	91.451	78.060	58.923	-199.466	-66.129	3.285
4500	15.072	91.790	78.361	60.429	-199.465	-63.100	3.065
4600	15.095	92.121	78.656	61.937	-199.464	-60.066	2.854
4700	15.117	92.446	78.946	63.448	-199.464	-57.035	2.652
4800	15.141	92.765	79.231	64.961	-199.464	-54.003	2.459
4900	15.164	93.077	79.510	66.476	-199.465	-50.980	2.274
5000	15.188	93.384	79.785	67.994	-199.465	-47.948	2.096
5100	15.213	93.685	80.054	69.514	-199.467	-44.914	1.925
5200	15.237	93.980	80.319	71.036	-199.468	-41.888	1.760
5300	15.262	94.271	80.580	72.561	-199.468	-38.855	1.602
5400	15.287	94.556	80.836	74.089	-199.469	-35.829	1.450
5500	15.312	94.837	81.088	75.618	-199.469	-32.790	1.303
5600	15.337	95.113	81.336	77.151	-199.470	-29.768	1.162
5700	15.361	95.385	81.580	78.686	-199.471	-26.736	1.025
5800	15.386	95.652	81.820	80.223	-199.472	-23.703	.893
5900	15.411	95.915	82.057	81.763	-199.472	-20.674	.766
6000	15.435	96.175	82.290	83.305	-199.473	-17.640	.643

June 30, 1963; Mar. 31, 1965; June 30, 1968

BORON DIOXIDE (BO_2) (IDEAL GAS) GFW = 42.8098

Point Group $D_{\infty h}$

ΔHf_0° = -68 ± 2 kcal/mol

$S^\circ_{298.15}$ = 54.90 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -68 ± 2 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\pi_g$	0	2
$^2\pi_g$	149	2
$^2\pi_u$	18291.6	4
$^2\Sigma_u^+$	24508.0	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1056 (1)
454 (2)
1321.7 (1)

Bond Distance: B-O = 1.263 Å

Bond Angle: O-B-O = 180° σ = 2

Rotational Constant: B_0 = 0.3303 cm^{-1}

Heat of Formation

Greene (1) measured the vapor pressure of B_2O_3 and examined the infrared absorption spectra of B_2O_3, B_2O_2 and BO_2. The isotope shift and oxygen and temperature dependencies of the boric acid fluctuation bands were studied. The enthalpy change, $\Delta Hr^\circ_{2100°K}$ = 76 ± 2 kcal/mol, for the reaction $1/2B_2O_3(\ell) + 1/4\ O_2(g) = BO_2(g)$, was obtained spectroscopically. Based on this data and $\Delta Hf^\circ_{2100°K}(B_2O_3,\ \ell)$ = -291.05 kcal/mol, we derive $\Delta Hf^\circ_{298}(BO_2,\ g)$ = -68.4 ± 2 kcal/mol.

Rusin (2) determined the equilibrium constant of the reaction $HBO_2(g) + OH(g) = BO_2(g) + H_2O(g)$ by simultaneously recording the pressure and spectra at 3000 - 3200°K of HBO_2 and BO_2, which were produced from the combustion in a bomb of mixtures of H, O, CO and a small amount of B_2H_6. Using the experimental value Kp_{3100} = 0.9, and JANAF free energy functions for the reactants and products, we obtain ΔHr°_{298} = 0.53 kcal/mol for that reaction. Employing ΔHf°_{298} = -134.00, 9.43 and -57.80 kcal/mol for $HBO_2(g)$, OH(g) and $H_2O(g)$, respectively, we derive the value $\Delta Hf^\circ_{298}(BO_2,\ g)$ = -66.24 kcal/mol.

In a study of gases from flames containing trimethylborate stabilized on flat porous metal burners, Kaskan (3) obtained data consistent with the bands being due to the molecule $BO_2(g)$. The temperature dependence of the equilibrium constants for the reaction $OH(g) + HBO_2(g) = H_2O(g) + BO_2(g)$ was investigated and the data were reported to be consistent with a value $\Delta Hr^\circ_{1800°K}$ = -16 kcal/mol. Based on this ΔHr°_{1800} value, we calculate the heat of formation at 298°K for $BO_2(g)$ to be -83.62 kcal/mol. Kaskan (4) has studied the effect of oxygen on the intensity of absorption (5470 Å) in the green or "fluctuation" bands of the gas phase in equilibrium with $B_2O_3(\ell)$. At constant temperature the absorptivity was found to depend on the 1/4 power of the oxygen pressure. This is interpreted as evidence that the absorbing species is $BO_2(g)$. The reaction $1/2B_2O_3(\ell) + 1/4\ O_2(g) = BO_2(g)$ was found to be 70 kcal/mol endothermic in the temperature range 1660 - 1950°K, yielding $\Delta Hf^\circ_{298}(BO_2,\ g)$ = -75.28 kcal/mol. Rusin et al. (2) discussed the discrepancy between their results and those of the above two investigations and commented that the results of Kaskan (3, 4) were derived based on the assumption that Beer's law was obeyed over the temperature range 1400 - 2200°K. Actually, the relative population α of the principal electronic state $X^2\pi$ of the BO_2 molecule changes greatly over this temperature range. Therefore the expression for the dependence of the optical density on the concentration of BO_2 must be corrected to allow for the variation of α with temperature.

The heat of formation of $BO_2(g)$ at 298°K is selected as -68 ± 2 kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Johns (5). Vibrational frequencies, bond distance and rotational constant were reported by Johns (5), Sommer (6), and Snowden (7). The values adopted are those determined by Snowden (7). Snowden used a (1:1) mixture of KBF_4 and B_2O_3 placed in a 13 mm Vycor tube. The mixture was heated to produce a vapor which passed through an external electrodeless discharge. The intense emission spectrum of the BO_2 molecule was observed. The fluorescence spectrum obtained by Johns was too weak for a full characterization of the electronic ground state. The moment of inertia is 8.4743×10^{-39} g cm^2.

References

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4. W. E. Kaskan, J. D. Mackenzie, and R. C. Millikan, J. Chem. Phys. 34, 570 (1961).
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6. A. Sommer, D. White, M. J. Linevsky, and D. E. Mann, J. Chem. Phys. 38, 87 (1963).
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Boron Dioxide Uninegative Ion (BO_2^-)

(Ideal Gas) GFW = 42.81035

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	9.349	51.579	51.579	.000	-166.000	-164.862	120.847
300	9.371	51.637	51.580	.017	-166.010	-164.855	120.097
400	10.361	54.475	51.960	1.006	-166.551	-164.390	89.818
500	11.121	56.873	52.709	2.082	-167.116	-163.784	71.590
600	11.725	58.956	53.580	3.225	-167.700	-163.063	59.396
700	12.214	60.801	54.482	4.423	-168.292	-162.242	50.654
800	12.614	62.459	55.377	5.665	-168.890	-161.339	44.076
900	12.942	63.964	56.249	6.944	-169.488	-160.360	38.941
1000	13.212	65.342	57.091	8.252	-170.089	-159.312	34.818
1100	13.435	66.612	57.899	9.584	-170.697	-158.206	31.433
1200	13.620	67.790	58.675	10.938	-171.307	-157.044	28.602
1300	13.775	68.886	59.419	12.307	-171.925	-155.829	26.197
1400	13.905	69.912	60.132	13.692	-172.548	-154.568	24.129
1500	14.015	70.875	60.816	15.088	-173.181	-153.263	22.330
1600	14.108	71.783	61.474	16.494	-173.822	-151.912	20.750
1700	14.188	72.640	62.106	17.909	-174.471	-150.524	19.351
1800	14.257	73.453	62.714	19.331	-175.129	-149.096	18.103
1900	14.317	74.226	63.299	20.760	-175.795	-147.633	16.982
2000	14.369	74.962	63.864	22.195	-176.466	-146.133	15.969
2100	14.415	75.664	64.410	23.634	-177.144	-144.598	15.048
2200	14.455	76.335	64.936	25.077	-177.830	-143.033	14.209
2300	14.491	76.979	65.446	26.525	-178.519	-141.436	13.439
2400	14.522	77.596	65.940	27.975	-179.218	-139.807	12.731
2500	14.551	78.190	66.418	29.429	-185.310	-138.044	12.068
2600	14.576	78.761	66.882	30.885	-186.013	-136.138	11.443
2700	14.598	79.311	67.332	32.344	-186.719	-134.207	10.863
2800	14.619	79.843	67.769	33.805	-187.428	-132.250	10.323
2900	14.637	80.356	68.194	35.268	-188.139	-130.263	9.817
3000	14.654	80.852	68.608	36.732	-188.855	-128.255	9.343
3100	14.669	81.333	69.011	38.199	-189.572	-126.224	8.899
3200	14.683	81.799	69.403	39.666	-190.294	-124.172	8.481
3300	14.696	82.251	69.786	41.135	-191.018	-122.094	8.086
3400	14.708	82.690	70.159	42.605	-191.745	-119.994	7.713
3500	14.719	83.116	70.523	44.077	-192.474	-117.877	7.361
3600	14.728	83.531	70.879	45.549	-193.207	-115.732	7.026
3700	14.738	83.935	71.226	47.022	-193.943	-113.567	6.708
3800	14.746	84.328	71.566	48.497	-194.680	-111.384	6.406
3900	14.754	84.711	71.898	49.972	-195.420	-109.188	6.119
4000	14.762	85.085	72.223	51.448	-317.341	-104.821	5.727
4100	14.769	85.449	72.541	52.924	-317.856	-99.500	5.304
4200	14.776	85.805	72.853	54.401	-318.371	-94.168	4.900
4300	14.782	86.153	73.158	55.879	-318.889	-88.822	4.514
4400	14.788	86.493	73.457	57.358	-319.410	-83.469	4.146
4500	14.794	86.825	73.751	58.837	-319.932	-78.100	3.793
4600	14.799	87.151	74.038	60.316	-320.457	-72.717	3.455
4700	14.805	87.469	74.321	61.797	-320.984	-67.325	3.131
4800	14.810	87.781	74.598	63.277	-321.514	-61.919	2.819
4900	14.815	88.086	74.870	64.759	-322.045	-56.515	2.521
5000	14.820	88.386	75.137	66.240	-322.578	-51.090	2.233
5100	14.825	88.679	75.400	67.722	-323.115	-45.649	1.956
5200	14.830	88.967	75.658	69.205	-323.652	-40.210	1.690
5300	14.835	89.250	75.912	70.688	-324.191	-34.749	1.433
5400	14.840	89.527	76.162	72.172	-324.733	-29.287	1.185
5500	14.845	89.799	76.407	73.656	-325.275	-23.804	.946
5600	14.850	90.067	76.649	75.141	-325.820	-18.322	.715
5700	14.855	90.330	76.886	76.626	-326.368	-12.831	.492
5800	14.860	90.588	77.120	78.112	-326.917	-7.319	.276
5900	14.866	90.842	77.351	79.598	-327.468	-1.805	.067
6000	14.871	91.092	77.578	81.085	-328.021	3.720	-.135

June 30, 1968; Dec. 31, 1968

BORON DIOXIDE UNINEGATIVE ION (BO_2^-) (IDEAL GAS) GFW = 42.81035

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [51.6 ± 2] gibbs/mol

ΔHf°_0 = -166 ± 6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -166 ± 6 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[35000]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1150] (1)
[580] (2)
[2200] (1)

Bond Distance: B-O = [1.25] Å

Bond Angle: O-B-O = [180°]

σ = 2

Rotational Constant: B_0 = [0.3372] cm^{-1}

Heat of Formation

D. E. Jensen, AeroChem TP-187A, Dec. 1968, AeroChem Research Laboratories, Inc., Princeton, N. J., has obtained equilibrium constants for the reaction $HBO_2 + e^- \rightarrow H + BO_2^-$. This involves several assumptions the most basic of which is that boron added to $H_2/N_2/O_2$ flames is converted completely to HBO_2. The free electrons are produced by addition of potassium to the flame, and their concentration is measured directly by a microwave cavity resonance method. The hydrogen atom concentration is taken from previous studies on such flames. The BO_2^- concentration is obtained from the difference between the K^+ concentration and the free electron measurement. The K^+ concentration is measured by an electrostatic probe.

By 2nd and 3rd law analysis of the data, 11 points read back from a plot, we obtain ΔHr_{298}(II) = 27.5 ± 4 kcal and ΔHr_{298}(III) = 20 ± 2 kcal with a drift of -3.7 ± 1.5 eu. The third law value yields $\Delta Hf^\circ_{298}(BO_2^-)$ = -166 ± 6 kcal/mol where the uncertainty includes possible errors in the functions. This corresponds to an electron affinity of BO_2 equal to 98 ± 6 kcal/mol (4.25 eV).

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (1) prediction for 16 valence electron XY_2 molecules. The electronic states are taken from those for $CO_2(g)$ (2), which is isoelectronic with $BO_2^-(g)$. The electronic level 35000 cm^{-1} and vibrational frequencies are estimated by comparison with the corresponding values for CO_2, CO_2^+, and BO_2, and, the data of Vasco and Srb (3) on the BO_2^- ion in alkali halide lattices. The B-O bond distance in $BO_2^-(g)$ is assumed to be smaller than the B-O bond in $BO_2(g)$, because the $BO_2^-(g)$ molecule has one more bonding electron than the $BO_2(g)$ molecule. The moment of inertia is 8.302×10^{-39} g cm^2. The enthalpy at 0°K is -2.30 kcal/mol.

References

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2. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
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Boron Monosulfide (BS)

(Ideal Gas) Mol. Wt. = 42.89

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.085	79.260	79.260	INFINITE
100	6.957	43.998	57.902	-1.390	79.785	75.689	-165.411
200	6.988	48.825	52.295	-.694	80.008	71.485	-78.111
298	7.182	51.645	51.645	.000	80.000	67.296	-49.327
300	7.188	51.690	51.645	.013	79.998	67.216	-48.965
400	7.499	53.799	51.931	.747	79.311	62.997	-34.418
500	7.799	55.506	52.480	1.513	78.726	58.985	-25.781
600	8.044	56.950	53.108	2.305	78.186	55.089	-20.065
700	8.234	58.205	53.749	3.120	77.685	51.304	-16.017
800	8.379	59.314	54.376	3.951	64.146	46.300	-12.648
900	8.491	60.308	54.981	4.794	63.985	44.078	-10.703
1000	8.579	61.207	55.559	5.648	63.813	41.877	-9.152
1100	8.649	62.029	56.111	6.510	63.628	39.689	-7.885
1200	8.706	62.784	56.636	7.377	63.432	37.523	-6.834
1300	8.753	63.482	57.136	8.250	63.226	35.374	-5.947
1400	8.792	64.133	57.613	9.128	63.010	33.239	-5.189
1500	8.825	64.740	58.068	10.009	62.782	31.118	-4.534
1600	8.854	65.311	58.503	10.893	62.545	29.017	-3.963
1700	8.879	65.848	58.919	11.779	62.297	26.929	-3.462
1800	8.901	66.356	59.319	12.668	62.041	24.855	-3.018
1900	8.920	66.838	59.702	13.559	61.779	22.797	-2.622
2000	8.938	67.296	60.070	14.452	61.512	20.752	-2.268
2100	8.954	67.733	60.425	15.347	61.240	18.719	-1.948
2200	8.969	68.150	60.766	16.243	60.964	16.702	-1.659
2300	8.982	68.549	61.096	17.141	60.684	14.695	-1.396
2400	8.995	68.931	61.415	18.039	60.399	12.704	-1.157
2500	9.007	69.299	61.723	18.940	54.726	10.831	-.947
2600	9.018	69.652	62.021	19.841	54.443	9.081	-.763
2700	9.029	69.993	62.310	20.743	54.161	7.340	-.594
2800	9.039	70.321	62.590	21.646	53.879	5.610	-.438
2900	9.048	70.638	62.862	22.551	53.599	3.896	-.294
3000	9.057	70.945	63.127	23.456	53.318	2.186	-.159
3100	9.066	71.242	63.384	24.362	53.039	.485	-.034
3200	9.075	71.530	63.634	25.269	52.759	-1.205	.082
3300	9.083	71.810	63.877	26.177	52.481	-2.889	.191
3400	9.091	72.081	64.115	27.086	52.203	-4.560	.293
3500	9.099	72.345	64.346	27.996	51.925	-6.231	.389
3600	9.107	72.601	64.572	28.906	51.648	-7.885	.479
3700	9.115	72.851	64.792	29.817	51.370	-9.536	.563
3800	9.122	73.094	65.007	30.729	51.094	-11.177	.643
3900	9.129	73.331	65.218	31.641	50.817	-12.815	.718
4000	9.136	73.562	65.424	32.555	-70.637	-12.293	.672
4100	9.143	73.788	65.625	33.469	-70.681	-10.838	.578
4200	9.150	74.008	65.822	34.383	-70.725	-9.371	.488
4300	9.157	74.224	66.015	35.299	-70.768	-7.915	.402
4400	9.164	74.434	66.204	36.215	-70.813	-6.450	.320
4500	9.170	74.640	66.389	37.131	-70.858	-4.987	.242
4600	9.177	74.842	66.571	38.049	-70.901	-3.525	.167
4700	9.184	75.039	66.749	38.967	-70.945	-2.057	.096
4800	9.190	75.233	66.923	39.885	-70.991	-.594	.027
4900	9.196	75.422	67.095	40.805	-71.036	.876	-.039
5000	9.203	75.608	67.263	41.725	-71.082	2.343	-.102
5100	9.209	75.791	67.429	42.645	-71.130	3.810	-.163
5200	9.215	75.969	67.591	43.567	-71.176	5.284	-.222
5300	9.222	76.145	67.751	44.488	-71.224	6.750	-.278
5400	9.228	76.317	67.908	45.411	-71.273	8.226	-.333
5500	9.234	76.487	68.062	46.334	-71.322	9.699	-.385
5600	9.240	76.653	68.214	47.258	-71.373	11.171	-.436
5700	9.246	76.817	68.364	48.182	-71.426	12.643	-.485
5800	9.252	76.978	68.511	49.107	-71.479	14.117	-.532
5900	9.259	77.136	68.656	50.033	-71.532	15.593	-.578
6000	9.265	77.292	68.799	50.959	-71.588	17.074	-.622

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Mar. 31, 1965

BORON MONOSULFIDE (BS) (IDEAL GAS) MOL. WT. = 42.89

Ground State Configuration $^2\Sigma$

$S^\circ_{298.15}$ = 51.645 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 79 ± 18 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 80 ± 18 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	g_i
0	2

ω_e = 1188.23 cm.$^{-1}$

$\omega_e x_e$ = 6.396 cm.$^{-1}$

σ = 1

B_e = 0.80596 cm.$^{-1}$

α_e = 0.00618 cm.$^{-1}$

r_e = 1.609 Å

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for BS(g) was calculated based on D°_0 = 5.1 ± 0.8 e.v. for BS(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy.

The ground state configuration, ω_e, $\omega_e x_e$, B_e, α_e and r_e were reported by P. B. Zeeman, Can. J. Phys. 29, 336 (1951). The molecular constants used for calculation were corrected to the average isotopic species. The moment of inertia is 3.47762 X 10^{-39} g. cm.^{2}

Titanium Monoboride (TiB)

(Crystal) Mol. Wt. = 58.711

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	7.092	8.300	8.300	.000	- 38.300	- 38.171	27.979
300	7.150	8.344	8.300	.013	- 38.303	- 38.170	27.806
400	9.640	10.771	8.614	.863	- 38.395	- 38.109	20.821
500	10.926	13.071	9.279	1.896	- 38.424	- 38.033	16.624
600	11.608	15.128	10.086	3.025	- 38.443	- 37.953	13.824
700	11.980	16.948	10.939	4.206	- 38.472	- 37.870	11.823
800	12.168	18.560	11.793	5.414	- 38.519	- 37.781	10.321
900	12.306	20.002	12.626	6.638	- 38.586	- 37.685	9.151
1000	12.408	21.304	13.430	7.874	- 38.675	- 37.580	8.213
1100	12.474	22.490	14.201	9.118	- 38.789	- 37.466	7.444
1200	12.506	23.577	14.937	10.367	- 39.875	- 37.303	6.793
1300	12.538	24.579	15.641	11.620	- 40.034	- 37.082	6.234
1400	12.570	25.509	16.313	12.875	- 40.216	- 36.848	5.752
1500	12.602	26.378	16.955	14.134	- 40.418	- 36.602	5.333
1600	12.634	27.192	17.570	15.395	- 40.641	- 36.338	4.963
1700	12.666	27.959	18.159	16.660	- 40.882	- 36.064	4.636
1800	12.698	28.684	18.724	17.929	- 41.139	- 35.774	4.343
1900	12.730	29.371	19.266	19.200	- 41.412	- 35.467	4.079
2000	12.762	30.025	19.788	20.475	- 45.371	- 35.053	3.830
2100	12.794	30.649	20.290	21.752	- 45.609	- 34.531	3.594
2200	12.826	31.244	20.775	23.033	- 45.848	- 33.996	3.377
2300	12.858	31.815	21.242	24.318	- 46.088	- 33.452	3.179
2400	12.890	32.363	21.694	25.605	- 46.331	- 32.898	2.996
2500	12.922	32.890	22.132	26.896	- 51.961	- 32.224	2.817
2600	12.954	33.397	22.555	28.189	- 52.198	- 31.431	2.642
2700	12.986	33.887	22.966	29.486	- 52.431	- 30.628	2.479
2800	13.018	34.360	23.365	30.787	- 52.660	- 29.818	2.327
2900	13.050	34.817	23.752	32.090	- 52.887	- 28.994	2.185
3000	13.082	35.260	24.128	33.397	- 53.110	- 28.168	2.052
3100	13.114	35.690	24.494	34.706	- 53.331	- 27.334	1.927
3200	13.146	36.106	24.850	36.019	- 53.548	- 26.492	1.809
3300	13.178	36.512	25.198	37.336	- 53.761	- 25.642	1.698
3400	13.210	36.905	25.536	38.655	- 53.972	- 24.786	1.593
3500	13.242	37.289	25.867	39.978	- 54.179	- 23.929	1.494
3600	13.274	37.662	26.189	41.303	- 156.846	- 21.615	1.312
3700	13.306	38.026	26.504	42.632	- 157.067	- 17.854	1.055
3800	13.338	38.382	26.812	43.965	- 157.298	- 14.088	.810
3900	13.370	38.729	27.113	45.300	- 157.541	- 10.320	.578
4000	13.402	39.067	27.408	46.639	- 278.971	- 4.395	.240

Mar. 31, 1963; June 30, 1965

TITANIUM MONOBORIDE (TiB) (CRYSTAL) MOL. WT. = 58.711

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [8.3 ± 1.5] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -38.3 ± 9 kcal. mole^{-1}

T_d = [2500]°K.

Heat of Formation.

P. O. Schissel and O. C. Trulson, J. Phys. Chem., 66, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system and obtained ΔF°_{2340} = -118.54 kcal. mole^{-1} for the reaction TiB(c) = Ti(g) + B(g). This corresponds to $\Delta F_f^\circ{}_{2340}$(TiB(c)) = -33.266 ± 9 kcal. mole^{-1}, where 4 kcal. mole^{-1} of the uncertainty is due to the heat of sublimation of boron. When this is reduced to 298°K. one obtains $\Delta H_f^\circ{}_{298}$(TiB(c)) = -38.3 ± 9 kcal. mole^{-1}. This value implies a high stability for TiB. This is also indicated by the phase studies of H. Nowotny, F. Benesovsky, C. Brukl and O. Schob, Monatshefte fur Chemie 92, 403 (1961).

Heat Capacity and Entropy.

The heat capacities from 298 to 1200°K. were estimated from that of TiB_2 by assuming the difference to be the same as that between CrB and CrB_2 as determined by R. Mezaki, E. W. Tilleux, D. W. Barnes and J. L. Margrave (Paper presented at the International Symposium on Nuclear Materials, Vienna, May 1962). A linear extrapolation was assumed above 1200°K.

The heat capacities above 298°K. were also estimated from the relationship C_p(Ti) + C_p(2B) - C_p(TiB_2) = 2/3 [C_p(Ti) + C_p(B) - C_p(TiB)]. This estimation agreed with the above to 4% over the temperature range 400 to 1000°K.

S°_{298}(TiB, c) = 8.3 cal. mole^{-1} deg.$^{-1}$ was calculated by the method of W. M. Latimer, J. Am. Chem. Soc., 73, 1480 (1951). Using JANAF S°_{298}(TiB_2, c) = 6.8 cal. mole^{-1} deg.$^{-1}$ and Latimer's value of 9.8 e.u. for the entropy contribution of Ti, an entropy contribution of -1.5 e.u. per Boron atom was calculated.

Decomposition Data.

The phase diagram given in, "The Metallurgy of the Rarer Metals - No. 4 Titanium", by A. D. McQuillan and M. K. McQuillan, Academic Press, New York (1956) was used to estimate the decomposition temperature. This diagram shows the decomposition products are TiB_2 and Ti_2B. However, Nowotny et al. (loc. cit.) have shown Ti_2B to be nonexistent and so the decomposition products are not defined, probably a eutectic of TiB and TiB_2 is involved.

Boron, Diatomic (B_2)

(Ideal Gas) Mol. Wt. = 21.64

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.094	193.490	193.490	INFINITE
100	6.958	40.545	54.536	- 1.399	194.173	190.135	- 415.519
200	7.023	45.378	48.885	- .702	194.710	185.870	- 203.100
298	7.301	48.228	48.228	.000	195.000	181.457	- 133.005
300	7.307	48.273	48.228	.014	195.004	181.373	- 132.124
400	7.667	50.425	48.519	.762	195.108	176.810	- 96.600
500	7.976	52.170	49.080	1.545	195.065	172.237	- 75.281
600	8.212	53.646	49.721	2.355	194.925	167.684	- 61.076
700	8.388	54.926	50.375	3.186	194.724	163.159	- 50.938
800	8.521	56.055	51.016	4.031	194.479	158.666	- 43.343
900	8.623	57.065	51.633	4.889	194.205	154.204	- 37.444
1000	8.703	57.978	52.223	5.755	193.901	149.777	- 32.732
1100	8.767	58.811	52.784	6.629	193.567	145.379	- 28.883
1200	8.820	59.576	53.319	7.508	193.208	141.016	- 25.681
1300	8.865	60.284	53.828	8.393	192.825	136.680	- 22.977
1400	8.902	60.942	54.313	9.281	192.419	132.379	- 20.664
1500	8.935	61.557	54.775	10.173	191.989	128.102	- 18.664
1600	8.964	62.135	55.217	11.068	191.538	123.860	- 16.918
1700	8.991	62.679	55.641	11.966	191.066	119.644	- 15.380
1800	9.014	63.194	56.046	12.866	190.576	115.455	- 14.017
1900	9.036	63.682	56.435	13.769	190.073	111.295	- 12.801
2000	9.056	64.146	56.809	14.673	189.559	107.163	- 11.710
2100	9.075	64.588	57.169	15.580	189.036	103.057	- 10.725
2200	9.092	65.011	57.516	16.488	188.504	98.975	- 9.832
2300	9.109	65.415	57.851	17.398	187.964	94.918	- 9.019
2400	9.125	65.803	58.174	18.310	187.416	90.885	- 8.276
2500	9.141	66.176	58.487	19.223	176.087	87.092	- 7.613
2600	9.155	66.535	58.789	20.138	175.542	83.541	- 7.022
2700	9.170	66.881	59.083	21.054	174.998	80.015	- 6.476
2800	9.184	67.214	59.367	21.972	174.456	76.506	- 5.971
2900	9.197	67.537	59.643	22.891	173.915	73.021	- 5.503
3000	9.210	67.849	59.912	23.811	173.375	69.548	- 5.066
3100	9.223	68.151	60.173	24.733	172.837	66.095	- 4.659
3200	9.236	68.444	60.427	25.656	172.300	62.662	- 4.279
3300	9.249	68.728	60.674	26.580	171.764	59.247	- 3.924
3400	9.261	69.005	60.915	27.506	171.230	55.844	- 3.589
3500	9.273	69.273	61.150	28.432	170.696	52.456	- 3.275
3600	9.285	69.535	61.379	29.360	170.164	49.086	- 2.980
3700	9.297	69.789	61.603	30.289	169.633	45.732	- 2.701
3800	9.309	70.037	61.822	31.220	169.104	42.393	- 2.438
3900	9.321	70.279	62.035	32.151	168.575	39.060	- 2.189
4000	9.332	70.516	62.245	33.084	- 74.310	40.034	- 2.187
4100	9.344	70.746	62.449	34.018	- 74.374	42.894	- 2.286
4200	9.355	70.971	62.649	34.953	- 74.435	45.764	- 2.381
4300	9.366	71.192	62.845	35.889	- 74.497	48.620	- 2.471
4400	9.378	71.407	63.038	36.826	- 74.560	51.487	- 2.557
4500	9.389	71.618	63.226	37.764	- 74.622	54.348	- 2.639
4600	9.400	71.824	63.411	38.704	- 74.682	57.218	- 2.718
4700	9.411	72.027	63.592	39.644	- 74.744	60.085	- 2.794
4800	9.422	72.225	63.770	40.586	- 74.806	62.959	- 2.866
4900	9.433	72.419	63.944	41.528	- 74.870	65.824	- 2.936
5000	9.444	72.610	64.116	42.472	- 74.932	68.698	- 3.003
5100	9.455	72.797	64.284	43.417	- 74.997	71.572	- 3.067
5200	9.466	72.981	64.449	44.363	- 75.061	74.444	- 3.129
5300	9.477	73.161	64.612	45.310	- 75.126	77.318	- 3.188
5400	9.487	73.338	64.772	46.259	- 75.193	80.197	- 3.246
5500	9.498	73.513	64.929	47.208	- 75.260	83.079	- 3.301
5600	9.509	73.684	65.084	48.158	- 75.330	85.950	- 3.354
5700	9.520	73.852	65.237	49.110	- 75.402	88.838	- 3.406
5800	9.531	74.018	65.387	50.062	- 75.476	91.715	- 3.456
5900	9.541	74.181	65.534	51.016	- 75.550	94.600	- 3.504
6000	9.552	74.341	65.680	51.970	- 75.628	97.490	- 3.551

Dec. 31, 1960; Dec. 31, 1964

BORON, DIATOMIC (B_2) (IDEAL GAS) MOL. WT. = 21.64

Ground State Configuration $^3\Sigma_g^-$

$S^\circ_{298.15}$ = 48.228 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 193.5 ± 6.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 195.0 ± 6.4 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	3

ω_e = 1061.0 cm.$^{-1}$

B_e = 1.235 cm.$^{-1}$

$\omega_e x_e$ = 9.58 cm.$^{-1}$

α_e = 0.0144 cm.$^{-1}$

σ = 2

r_e = 1.589 Å

Heat of Formation.

The equilibrium vapor pressure of the reaction $B_2(g) \rightarrow B(g) + B(c)$ was determined by G. Verhaegen and J. Drowart, J. Chem. Phys. 37, 1367 (1962). Using the value, $P_{B_2(g)}/P_{B(g)} = 9 \times 10^{-5}$ at 2330°K. where P is partial pressure, the heat of reaction ($\Delta H^\circ_{r\ 298.15}$) was evaluated to be -62.2 ± 5.0 kcal mole^{-1}. This leads to $\Delta H^\circ_{f\ 298.15}$ = 195.0 ± 6.4 kcal. mole^{-1} for $B_2(g)$ or D_0° = 3.0 e.v. which is in excellent agreement with the value, D_0° = 3.0 ± 0.5 e.v. reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The value, D_0° = 3.6 e.v., estimated by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, yields $\Delta H^\circ_{f\ 298.15}$ = 181.6 kcal. mole^{-1} for $B_2(g)$ which is not used.

Heat Capacity and Entropy.

Molecular and spectroscopic constants were obtained from G. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is 2.26779×10^{-39} g. cm.^{2}

Beryllium Diborate (BeB_2O_4)

(Ideal Gas) Mol. Wt. = 94.6318

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	-4.455	-322.253	-322.253	INFINITE
100	12.591	59.799	94.638	-3.484	-322.730	-320.376	700.148
200	17.793	70.171	79.959	-1.957	-322.861	-317.965	347.440
298	21.932	78.079	78.079	.000	-323.000	-315.542	231.287
300	22.001	78.215	78.080	.041	-323.002	-315.496	229.828
400	25.297	85.016	78.985	2.412	-323.136	-312.974	170.993
500	27.839	90.946	80.797	5.075	-323.265	-310.417	135.677
600	29.782	96.202	82.935	7.960	-323.382	-307.836	112.124
700	31.266	100.909	85.172	11.016	-323.486	-305.236	95.295
800	32.407	105.162	87.409	14.202	-323.581	-302.626	82.670
900	33.294	109.032	89.600	17.489	-323.671	-300.000	72.846
1000	33.989	112.577	91.723	20.854	-323.770	-297.362	64.985
1100	34.543	115.844	93.769	24.282	-323.892	-294.718	58.552
1200	34.988	118.869	95.736	27.759	-324.038	-292.058	53.188
1300	35.350	121.685	97.625	31.277	-324.214	-289.387	48.648
1400	35.647	124.315	99.439	34.827	-324.422	-286.699	44.754
1500	35.895	126.784	101.180	38.405	-324.668	-284.000	41.377
1600	36.102	129.107	102.854	42.005	-327.707	-281.198	38.408
1700	36.278	131.301	104.463	45.624	-327.915	-278.285	35.774
1800	36.427	133.379	106.013	49.259	-328.146	-275.361	33.432
1900	36.555	135.352	107.505	52.909	-328.395	-272.421	31.334
2000	36.666	137.230	108.945	56.570	-328.660	-269.470	29.445
2100	36.763	139.021	110.335	60.242	-328.941	-266.500	27.734
2200	36.847	140.734	111.678	63.922	-329.243	-263.522	26.177
2300	36.922	142.373	112.977	67.611	-329.559	-260.527	24.755
2400	36.987	143.946	114.235	71.306	-329.896	-257.514	23.449
2500	37.046	145.457	115.454	75.008	-341.026	-254.279	22.228
2600	37.098	146.911	116.636	78.715	-341.381	-250.800	21.081
2700	37.144	148.312	117.783	82.427	-341.747	-247.306	20.017
2800	37.186	149.664	118.898	86.144	-413.153	-242.698	18.942
2900	37.224	150.969	119.981	89.864	-413.289	-236.598	17.830
3000	37.258	152.232	121.036	93.588	-413.433	-230.508	16.792
3100	37.289	153.454	122.062	97.316	-413.582	-224.411	15.820
3200	37.317	154.638	123.061	101.046	-413.740	-218.303	14.909
3300	37.343	155.787	124.036	104.779	-413.906	-212.193	14.052
3400	37.366	156.902	124.986	108.515	-414.082	-206.077	13.246
3500	37.388	157.986	125.913	112.252	-414.265	-199.967	12.486
3600	37.408	159.039	126.819	115.992	-414.457	-193.831	11.767
3700	37.426	160.064	127.704	119.734	-414.659	-187.701	11.087
3800	37.443	161.063	128.569	123.477	-414.871	-181.562	10.442
3900	37.459	162.035	129.414	127.223	-415.090	-175.424	9.830
4000	37.474	162.984	130.242	130.969	-657.681	-164.989	9.014
4100	37.487	163.909	131.052	134.717	-657.462	-152.674	8.138
4200	37.500	164.813	131.845	138.467	-657.249	-140.360	7.303
4300	37.511	165.695	132.622	142.217	-657.051	-128.048	6.508
4400	37.522	166.558	133.383	145.969	-656.867	-115.755	5.749
4500	37.533	167.401	134.130	149.722	-656.694	-103.460	5.024
4600	37.542	168.226	134.862	153.475	-656.534	-91.162	4.331
4700	37.551	169.034	135.581	157.230	-656.388	-78.876	3.668
4800	37.560	169.825	136.286	160.986	-656.255	-66.585	3.032
4900	37.568	170.599	136.978	164.742	-656.137	-54.314	2.422
5000	37.575	171.358	137.658	168.499	-656.032	-42.027	1.837
5100	37.582	172.102	138.326	172.257	-655.945	-29.742	1.274
5200	37.589	172.832	138.983	176.015	-655.870	-17.476	.734
5300	37.595	173.548	139.628	179.775	-655.809	-5.192	.214
5400	37.601	174.251	140.263	183.534	-655.767	7.073	-.286
5500	37.607	174.941	140.887	187.295	-655.735	19.362	-.769
5600	37.612	175.619	141.501	191.056	-655.724	31.620	-1.234
5700	37.617	176.284	142.106	194.817	-655.728	43.902	-1.683
5800	37.622	176.939	142.701	198.579	-655.747	56.180	-2.117
5900	37.626	177.582	143.287	202.341	-655.782	68.449	-2.535
6000	37.631	178.214	143.863	206.104	-655.833	80.733	-2.941

Dec. 31, 1962; June 30, 1965

BERYLLIUM DIBORATE (BeB_2O_4) (IDEAL GAS) MOL.WT. = 94.6318

Point Group [C_{2h}]

$S^\circ_{298.15}$ = [78.079] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight [1]

$\Delta H^\circ_{f\ 0} = -322 \pm 10$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -323 \pm 10$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ν, cm.$^{-1}$	ν, cm.$^{-1}$	ν, cm.$^{-1}$
[2000] (1)	[1050] (1)	[400] (1)
[1600] (1)	[650] (1)	[350] (1)
[1200] (1)	[650] (1)	[200] (1)
[1200] (1)	[600] (1)	[150] (1)
[1050] (1)	[500] (1)	[120] (1)

Bond Distance: Be-O = [1.63] Å O-B = [1.34] Å B=O = [1.20] Å

Bond Angle: O=B-O = [180°] O-Be-O = [180°] B-O-Be = [95°]

$\sigma = 2$

Product of Moments of Inertia: $I_AI_BI_C = 5.3801 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was obtained from mass spectrometric studies; the following reactions at 1500°K. were reported by P. E. Blackburn and A. Büchler, Interim Technical Report No. 1, March 1965:

1. $B_2O_3(l) \rightarrow B_2O_3(g)$ ΔH_1 = 92.226 kcal/mole
2. $1/3\ Be_3B_2O_6(c) + 2/3\ B_2O_3(l) \rightarrow Be(BO_2)_2(g)$ $\Delta H_2 = 118 \pm 2$ kcal/mole
3. $Be_3B_2O_6(c) \rightarrow 3BeO(c) + B_2O_3(g)$ $\Delta H_3 = 112 \pm 1$ kcal/mole
4. $Be_3B_2O_6(c) \rightarrow 2BeO(c) + Be(BO_2)_2(g)$ $\Delta H_4 = 137 \pm 3$ kcal/mole
5. $3BeO(c) + B_2O_3(l) \rightarrow Be_3B_2O_6(c)$ ΔH_5 = -23 kcal/mole
6. $BeO(c) + B_2O_3(g) \rightarrow Be(BO_2)_2(g)$ ΔH_6 = 22 kcal/mole

The value of ΔH_1 was obtained from JANAF values for $B_2O_3(l)$ and $B_2O_3(g)$. The values for ΔH_2, ΔH_3 and ΔH_4 were obtained from P. E. Blackburn and A. Büchler loc. cit. The value for ΔH_5 was obtained by taking the average of ΔH_5 = -20 kcal/mole in a weight loss experiment, $\Delta H_5 = \Delta H_1 - \Delta H_3$ = -19.774 kcal/mole, and $\Delta H_5 = 3/2\ (\Delta H_2 - \Delta H_4)$ = -28.5 kcal/mole. The ΔH_6 value was obtained by taking the average of $\Delta H_6 = \Delta H_4 - \Delta H_3$ = 25 kcal/mole and $\Delta H_6 = \Delta H_2 - \Delta H_1 + 1/3\ \Delta H_5$ = 18.107 kcal/mole. The $\Delta H_{f\ 298.15}$ of BeB_2O_4 was calculated from reaction 6 with auxiliary JANAF values.

Heat Capacity and Entropy.

The vibrational frequencies estimated by comparison with B_2O_3, were adjusted to obtain an S°_{1500} = 127 obtained in a manner analogous with ΔH_f from the report of P. E. Blackburn and A. Büchler loc. cit. The frequencies listed are not in point group order. All other molecular constants were estimated by comparison with related boron oxide molecules. The individual moments of inertia are $I_A = 8.5561 \times 10^{-39}$ g. cm.^{2}, $I_B = 75.1345 \times 10^{-39}$ g. cm.^{2} and $I_C = 83.6909 \times 10^{-39}$ g. cm.^{2}

Triberyllium Diborate ($Be_3B_2O_6$)

(Crystal) GFW = 144.655

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	33.400	24.000	24.000	.000	- 741.960	- 702.408	514.879
300	33.560	24.207	24.001	.062	- 741.968	- 702.163	511.525
400	41.830	35.033	25.421	3.845	- 742.279	- 688.839	376.364
500	48.480	45.100	28.362	8.369	- 742.286	- 675.470	295.248
600	54.160	54.451	31.941	13.506	- 741.990	- 662.130	241.181
700	59.170	63.187	35.787	19.180	- 741.398	- 648.862	202.584
800	63.290	71.369	39.729	25.312	- 740.535	- 635.703	173.666
900	66.340	79.009	43.674	31.802	- 739.470	- 622.659	151.202
1000	68.420	86.112	47.567	38.545	- 738.298	- 609.739	133.258
1100	69.840	92.703	51.375	45.462	- 737.098	- 596.943	118.602
1200	70.840	98.825	55.077	52.498	- 735.911	- 584.254	106.407
1300	71.600	104.526	58.664	59.621	- 734.763	- 571.663	96.105
1400	72.230	109.856	62.132	66.813	- 733.665	- 559.160	87.289
1500	72.790	114.858	65.482	74.064	- 732.629	- 546.734	79.659
1600	73.310	119.573	68.717	81.369	- 739.918	- 534.136	72.959
1700	73.830	124.032	71.841	88.726	- 738.656	- 521.311	67.019
1800	74.380	128.268	74.859	96.137	- 737.396	- 508.564	61.748
1900	74.900	132.304	77.777	103.601	- 736.132	- 495.887	57.040
2000	75.400	136.158	80.600	111.116	- 734.859	- 483.277	52.810
2100	75.920	139.850	83.334	118.682	- 733.577	- 470.726	48.989
2200	76.400	143.393	85.984	126.298	- 732.291	- 458.241	45.522
2300	76.860	146.799	88.555	133.961	- 730.995	- 445.811	42.362
2400	77.300	150.079	91.051	141.669	- 729.697	- 433.431	39.469
2500	77.720	153.243	93.475	149.420	- 739.174	- 420.906	36.796
2600	78.180	156.301	95.833	157.215	- 737.849	- 408.197	34.312
2700	78.610	159.259	98.128	165.055	- 736.509	- 395.540	32.017
2800	79.070	162.126	100.363	172.939	- 948.245	- 379.616	29.630
2900	79.530	164.909	102.541	180.868	- 946.120	- 359.334	27.080
3000	80.000	167.613	104.665	188.845	- 943.968	- 339.141	24.706

Sept. 30, 1966

TRIBERYLLIUM DIBORATE ($Be_3B_2O_6$) (CRYSTAL) GFW = 144.655

$S^\circ_{298.15}$ = [24 ± 3] gibbs/mol

Tm = 1768 ± 5°K

ΔHf° = Unknown

$\Delta Hf^\circ_{298.15}$ = -741.96 ± 2 kcal/mol

ΔHm° = Unknown

Heat of Formation.

The adopted $\Delta Hf^\circ_{298.15}$ = -741.96 ± 2 kcal/mol was calculated from $\Delta Hr^\circ_{298.15}$ = -13.38 ± 0.5 kcal/mol for 3 BeO (c) + B_2O_3(gl) = $Be_3B_2O_6$(c) measured calorimetrically by P. Gross, Fulmer Research Institute, Administration Report No. 5, Stoke Poges, England, January - April 1966. From equilibrium data relating to the same reaction at 1500°K, P. E. Blackburn and A. Buchler, J. Phys. Chem. 69, 4250 (1965), report heats of reaction of -21 ± 2 and -28.5 ± 5 kcal/mol, which correspond to -21.7 and -29.2 kcal/mol at 298°K. The discepancy of 8 to 16 kcal is attributed primarily to the equilibrium values. These values result from differences between 2nd law heats of reaction derived from the variation with temperature of intensities for $B_2O_3^+$ and $Be(BO_2)_2^+$, respectively, over the systems B_2O_3(l) - $Be_3B_2O_6$(c) and $Be_3B_2O_6$(c) - BeO(c). The reported reactions and their heats are:

	Reactions	ΔHr°_{1500} (kcal/mol)
(a)	$B_2O_3(l) \rightarrow B_2O_3(g)$	91 ± 0.5
(b)	$Be_3B_2O_6(c) \rightarrow 3\ BeO(c) + B_2O_3(g)$	112 ± 1
(c)	$1/3\ Be_3B_2O_6(c) + 2/3\ B_2O_3(l) \rightarrow Be(BO_2)_2(g)$	118 ± 2
(d)	$Be_3B_2O_6(g) \rightarrow 2\ BeO(c) + Be(BO_2)_2(g)$	137 ± 3

Heat Capacity and Entropy.

The heat capacity was estimated from that for BeO(c) and B_2O_3(c). The adopted $S^\circ_{298.15}$ = 24 ± 3 eu is an average value from the following three estimates. Blackburn and Buchler, loc. cit., report Kp = 2.7×10^{-5} and Kp = 9.3×10^{-6} atm at 1500°K for reactions a and b (see heat of formation) based on vacuum balance data and ion intensities, respectively. These Kp's yield ΔGr°_{1500} = -3.17 kcal/mol for 3 BeO(c) + B_2O_3(l) → $Be_3B_2O_6$(c). Combining this with the JANAF value for ΔHr°_{1500} = -12.64 kcal/mol, we get ΔSr°_{1500} = -6.3 and S°_{298} ($Be_3B_2O_6$,c) = 22.9 eu. This entropy agrees with 23 eu estimated from the sum of entropies for the component oxides; however, the entropy for $Ca_3B_2O_6$(c), observed by K. K. Kelley, S. S. Todd and C. H. Shomate, J. Am. Chem. Soc. 70, 1350 (1948), is larger than that of the component oxides by 2.5 eu. Use of this increment gives 25.5 eu for $Be_3B_2O_6$(c).

Melting Data.

Tm was obtained from P. E. Blackburn and A. Buchler, loc. cit.

Boron Dichloride, Dimeric (B_2Cl_4)

(Ideal Gas) Mol Wt. = 163.468

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100	14.151	65.889	103.472	- 3.758	- 117.100	- 114.635	250.523
200	19.277	77.397	87.739	- 2.069	- 117.013	- 112.194	122.594
298	22.667	85.767	85.767	.000	- 116.900	- 109.859	80.525
300	22.719	85.907	85.767	.042	- 116.898	- 109.815	79.997
400	25.048	92.780	86.688	2.437	- 116.807	- 107.469	58.715
500	26.603	98.546	88.499	5.024	- 116.752	- 105.140	45.955
600	27.649	103.493	90.596	7.739	- 116.725	- 102.820	37.451
700	28.332	107.808	92.753	10.539	- 116.713	- 100.504	31.377
800	28.870	111.628	94.878	13.400	- 116.714	- 98.191	26.823
900	29.217	115.049	96.932	16.305	- 116.721	- 95.874	23.280
1000	29.511	118.143	98.901	19.242	- 116.742	- 93.557	20.446
1100	29.684	120.964	100.781	22.202	- 116.784	- 91.238	18.126
1200	29.840	123.554	102.572	25.178	- 116.846	- 88.912	16.192
1300	29.978	125.948	104.280	28.169	- 116.927	- 86.582	14.555
1400	30.099	128.174	105.908	31.173	- 117.025	- 84.243	13.150
1500	30.203	130.254	107.462	34.188	- 117.144	- 81.900	11.932
1600	30.263	132.205	108.948	37.212	- 117.282	- 79.543	10.865
1700	30.319	134.041	110.370	40.241	- 117.441	- 77.177	9.921
1800	30.370	135.775	111.734	43.275	- 117.619	- 74.806	9.082
1900	30.417	137.418	113.042	46.315	- 117.809	- 72.418	8.330
2000	30.460	138.979	114.300	49.359	- 118.013	- 70.023	7.651
2100	30.485	140.466	115.511	52.406	- 118.226	- 67.620	7.037
2200	30.508	141.885	116.678	55.455	- 118.453	- 65.206	6.477
2300	30.530	143.242	117.804	58.507	- 118.689	- 62.780	5.965
2400	30.551	144.542	118.891	61.561	- 118.937	- 60.343	5.495
2500	30.571	145.790	119.943	64.618	- 129.970	- 57.680	5.042
2600	30.589	146.989	120.960	67.676	- 130.222	- 54.783	4.605
2700	30.606	148.144	121.945	70.735	- 130.479	- 51.876	4.199
2800	30.622	149.257	122.901	73.797	- 130.739	- 48.960	3.821
2900	30.637	150.332	123.828	76.860	- 131.002	- 46.032	3.469
3000	30.650	151.371	124.730	79.924	- 131.270	- 43.103	3.140
3100	30.658	152.376	125.605	82.989	- 131.543	- 40.161	2.831
3200	30.666	153.349	126.457	86.056	- 131.820	- 37.206	2.541
3300	30.673	154.293	127.286	89.123	- 132.103	- 34.242	2.268
3400	30.680	155.209	128.094	92.190	- 132.390	- 31.270	2.010
3500	30.687	156.098	128.882	95.259	- 132.683	- 28.299	1.767
3600	30.693	156.963	129.649	98.328	- 132.980	- 25.308	1.536
3700	30.699	157.804	130.399	101.397	- 133.283	- 22.312	1.318
3800	30.705	158.623	131.131	104.467	- 133.589	- 19.311	1.111
3900	30.710	159.421	131.847	107.538	- 133.900	- 16.303	.914
4000	30.715	160.199	132.546	110.609	- 376.575	- 8.995	.491
4100	30.719	160.957	133.230	113.681	- 376.431	.191	- .010
4200	30.722	161.697	133.899	116.753	- 376.291	9.382	- .488
4300	30.726	162.420	134.554	119.825	- 376.155	18.560	- .943
4400	30.729	163.126	135.195	122.898	- 376.024	27.747	- 1.378
4500	30.733	163.817	135.823	125.971	- 375.897	36.911	- 1.793
4600	30.736	164.493	136.439	129.045	- 375.769	46.083	- 2.189
4700	30.739	165.154	137.044	132.118	- 375.648	55.258	- 2.569
4800	30.742	165.801	137.636	135.192	- 375.530	64.424	- 2.933
4900	30.744	166.435	138.217	138.267	- 375.415	73.586	- 3.282
5000	30.747	167.056	138.788	141.341	- 375.301	82.749	- 3.617
5100	30.749	167.665	139.348	144.416	- 375.190	91.914	- 3.939
5200	30.752	168.262	139.898	147.491	- 375.081	101.073	- 4.248
5300	30.754	168.848	140.439	150.567	- 374.975	110.218	- 4.545
5400	30.756	169.423	140.971	153.642	- 374.874	119.372	- 4.831
5500	30.758	169.987	141.493	156.718	- 374.772	128.538	- 5.107
5600	30.760	170.541	142.007	159.794	- 374.674	137.675	- 5.373
5700	30.762	171.085	142.512	162.870	- 374.582	146.825	- 5.629
5800	30.763	171.620	143.009	165.946	- 374.490	155.978	- 5.877
5900	30.765	172.146	143.498	169.022	- 374.402	165.118	- 6.116
6000	30.766	172.663	143.980	172.099	- 374.317	174.269	- 6.347

Dec. 31, 1960; Dec. 31, 1964

BORON DICHLORIDE, DIMERIC (B_2Cl_4) (IDEAL GAS) MOL. WT. = 163.468

Point Group D_{2d}

$\Delta H_{f\ 0}^\circ$ = Unknown

$S_{298.15}^\circ$ = 85.767 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -116.9 \pm 1.2$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1131(1)	Rotation	917(2)
401(1)	730(1)	617(2)
225(1)	291(1)	180(2)

Bond Distance: B-Cl = 1.73 ± 0.02 Å B-B = 1.75 ± 0.01 Å

$\sigma = 4$

Bond Angle: Cl-B-Cl = 120 ± 2°

Dihedral angle between two BCl_2 planes = 90°

Product of the Moments of Inertia: $I_AI_BI_C = 5.33449 \times 10^{-112}$ g.^{3} cm.^{6}

Heat of Formation.

S. R. Gunn, L. G. Green and A. I. Von Egidy, J. Phys. Chem. 63, 1787 (1959) determined the enthalpy change (ΔH_r°) of the reaction $B_2Cl_4(l) + Cl_2(g) = 2BCl_3(g)$. From the value, $\Delta H_{r\ 298.15}^\circ = -67.3 \pm 0.6$ kcal. mole^{-1}, the heat of formation for $B_2Cl_4(l)$ was calculated as -125.32 ± 1.20 kcal. mole^{-1}. Based on $\Delta H_{v\ 338.7}^\circ = 8.029$ kcal. mole^{-1} reported by G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, J. Am. Chem. Soc. 76, 5293 (1954), the heat of formation for $B_2Cl_4(g)$ was derived to be -116.9 ± 1.2 kcal. mole^{-1}.

Heat Capacity and Entropy.

The vibrational frequencies, molecular structure and constants were taken from D. E. Mann and L. Fano, J. Chem. Phys. 26, 1665 (1957). The barrier restricting internal rotation about the B-B single bond is fixed at 1.53 ± 0.60 kcal. mole^{-1} obtained from E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc. 77, 5808 (1955). The three principal moments of inertia are: $I_A = 1.00465 \times 10^{-37}$, $I_B = 5.28520 \times 10^{-38}$ and $I_C = 1.00465 \times 10^{-37}$ g. cm.^{2} The reduced moment of inertia for BCl_2 top is $I_r = 1.3213 \times 10^{-38}$ g. cm.^{2}

Boron Difluoride, Dimeric (B_2F_4)
(Ideal Gas) Mol. Wt. = 97.64

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100	10.354	60.935	89.891	- 2.896	- 341.694	- 339.632	742.229
200	14.806	69.489	77.666	- 1.637	- 341.995	- 337.438	368.718
298	18.378	76.093	76.093	.000	- 342.200	- 335.162	245.668
300	18.436	76.207	76.093	.034	- 342.204	- 335.119	244.122
400	21.204	81.907	76.852	2.022	- 342.400	- 332.726	181.784
500	23.313	86.876	78.370	4.253	- 342.609	- 330.285	144.361
600	24.896	91.274	80.162	6.667	- 342.809	- 327.800	119.395
700	26.077	95.205	82.035	9.219	- 342.991	- 325.283	101.553
800	26.964	98.747	83.906	11.873	- 343.159	- 322.744	88.165
900	27.638	101.964	85.737	14.605	- 343.311	- 320.183	77.747
1000	28.157	104.904	87.508	17.395	- 343.461	- 317.605	69.409
1100	28.563	107.607	89.214	20.232	- 343.616	- 315.012	62.584
1200	28.886	110.107	90.853	23.105	- 343.775	- 312.403	56.894
1300	29.145	112.430	92.424	26.007	- 343.947	- 309.783	52.077
1400	29.357	114.598	93.931	28.933	- 344.129	- 307.147	47.945
1500	29.531	116.629	95.378	31.877	- 344.329	- 304.499	44.363
1600	29.676	118.540	96.766	34.838	- 344.544	- 301.837	41.227
1700	29.798	120.343	98.100	37.812	- 344.776	- 299.160	38.458
1800	29.902	122.049	99.384	40.797	- 345.025	- 296.474	35.995
1900	29.990	123.668	100.620	43.792	- 345.284	- 293.768	33.789
2000	30.066	125.208	101.811	46.795	- 345.553	- 291.045	31.802
2100	30.132	126.677	102.960	49.805	- 345.833	- 288.317	30.004
2200	30.190	128.080	104.071	52.821	- 346.123	- 285.570	28.367
2300	30.241	129.423	105.144	55.842	- 346.422	- 282.811	26.872
2400	30.285	130.711	106.182	58.869	- 346.731	- 280.038	25.500
2500	30.325	131.948	107.189	61.899	- 357.825	- 277.035	24.217
2600	30.360	133.138	108.164	64.934	- 358.136	- 273.798	23.014
2700	30.392	134.285	109.110	67.971	- 358.449	- 270.545	21.898
2800	30.420	135.391	110.029	71.012	- 358.762	- 267.289	20.862
2900	30.445	136.458	110.922	74.055	- 359.079	- 264.005	19.895
3000	30.468	137.491	111.791	77.101	- 359.399	- 260.732	18.993
3100	30.489	138.490	112.636	80.149	- 359.719	- 257.438	18.148
3200	30.508	139.459	113.459	83.199	- 360.043	- 254.133	17.356
3300	30.526	140.398	114.261	86.250	- 360.370	- 250.816	16.610
3400	30.541	141.309	115.043	89.304	- 360.698	- 247.489	15.908
3500	30.556	142.195	115.807	92.359	- 361.031	- 244.156	15.245
3600	30.569	143.056	116.552	95.415	- 361.365	- 240.808	14.618
3700	30.582	143.893	117.279	98.472	- 361.704	- 237.454	14.025
3800	30.593	144.709	117.991	101.531	- 362.045	- 234.088	13.462
3900	30.603	145.504	118.686	104.591	- 362.391	- 230.727	12.929
4000	30.613	146.279	119.366	107.652	- 605.096	- 223.052	12.186
4100	30.622	147.035	120.032	110.714	- 604.986	- 213.506	11.380
4200	30.631	147.773	120.683	113.776	- 604.878	- 203.950	10.612
4300	30.638	148.494	121.322	116.840	- 604.772	- 194.406	9.880
4400	30.646	149.198	121.947	119.904	- 604.676	- 184.863	9.182
4500	30.653	149.887	122.561	122.969	- 604.581	- 175.331	8.515
4600	30.659	150.561	123.162	126.034	- 604.490	- 165.792	7.877
4700	30.665	151.220	123.752	129.101	- 604.405	- 156.251	7.265
4800	30.671	151.866	124.331	132.167	- 604.325	- 146.712	6.680
4900	30.676	152.498	124.899	135.235	- 604.251	- 137.183	6.118
5000	30.681	153.118	125.458	138.303	- 604.181	- 127.651	5.579
5100	30.686	153.726	126.006	141.371	- 604.119	- 118.130	5.062
5200	30.690	154.322	126.545	144.440	- 604.060	- 108.594	4.564
5300	30.694	154.906	127.074	147.509	- 604.007	- 99.066	4.085
5400	30.698	155.480	127.595	150.578	- 603.964	- 89.549	3.624
5500	30.702	156.043	128.107	153.648	- 603.922	- 80.008	3.179
5600	30.705	156.597	128.611	156.719	- 603.889	- 70.495	2.751
5700	30.709	157.140	129.107	159.790	- 603.864	- 60.962	2.337
5800	30.712	157.674	129.595	162.861	- 603.843	- 51.440	1.938
5900	30.715	158.199	130.075	165.932	- 603.830	- 41.920	1.553
6000	30.718	158.716	130.548	169.004	- 603.824	- 32.396	1.180

Dec. 31, 1964

BORON DIFLUORIDE, DIMERIC (B_2F_4) (IDEAL GAS) MOL. WT. = 97.64

Point Group V_d

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [76.093] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -342.2 ± 1.0 kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1380 (1)	1155 (1)	325 (1)
[630] (1)	542 (1)	1378 (1)
[304] (1)	1386 (1)	662 (1)
Rotation	657 (1)	325 (1)

Bond Distance: B-B = 1.67 Å B-F = 1.32 Å

Bond Angle: F-B-F = 120° F-B-B = 120°

σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 2.50147 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was calculated based on the value, $\Delta H_r^\circ = -82.0 \pm 1.0$ kcal. mole^{-1} for the reaction $B_2F_4(g) + Cl_2(g) = 0.92\ BF_3(g) + 0.46\ BF_2Cl(g) + 0.32\ BFCl_2(g) + 0.30\ BCl_3(g)$ reported by S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 178 (1961).

Heat Capacity and Entropy.

The molecular and spectroscopic constants were obtained from J. N. Gayles and J. Self, J. Chem. Phys. 40, 3530 (1964). The vibrational frequencies were corrected to the average isotopic species. The molecular configuration was reported to be staggered, analogous to that observed for $B_2Cl_4(g)$. The angle between two B-BF_2 planes is approximately 90°. The thermodynamic functions were evaluated based on an assumption that there is free rotation at B-B bond between the two BF_2 rotating tops. The internal moment of inertia is 4.12218×10^{-39} g. cm.^{2} The three principal moments of inertia are: $I_A = 3.89497 \times 10^{-38}$, $I_B = 1.64887 \times 10^{-38}$ and $I_C = 3.89497 \times 10^{-38}$ g. cm.^{2} The reduced moment of inertia for BF_2 top is $I_r = 4.12218 \times 10^{-39}$ g. cm.^{2}

Boron Dihydroxide, Dimeric ($B_2(OH)_4$)

(Crystal)   Mol. Wt. = 89.65148

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	27.770	30.000	30.000	.000	- 337.100	- 297.377	217.983
300	27.910	30.172	30.001	.052	- 337.110	- 297.132	216.460
400	34.210	39.097	31.175	3.169	- 337.447	- 283.744	155.031
500	39.140	47.272	33.589	6.842	- 337.460	- 270.311	118.153
600	43.430	54.797	36.505	10.976	- 337.186	- 256.902	93.577
700	47.090	61.773	39.622	15.505	- 336.649	- 243.559	76.043
800	50.290	68.276	42.802	20.379	- 335.873	- 230.315	62.919
900	52.930	74.354	45.974	25.542	- 334.894	- 217.175	52.737
1000	55.290	80.056	49.100	30.956	- 333.740	- 204.154	44.618
1100	57.360	85.425	52.160	36.591	- 332.443	- 191.259	38.000
1200	59.140	90.494	55.146	42.418	- 331.018	- 178.484	32.506
1300	60.660	95.289	58.051	48.410	- 329.496	- 165.835	27.879
1400	61.900	99.832	60.874	54.541	- 327.895	- 153.304	23.932
1500	62.860	104.137	63.616	60.781	- 326.251	- 140.892	20.528

Mar. 31, 1966

BORON DIHYDROXIDE, DIMERIC ($B_2(OH)_4$)   (CRYSTAL)   MOL. WT. = 89.65148

$S^\circ_{298.15}$ = [30 ± 1] cal. deg.$^{-1}$ mole^{-1}

T_m = Unknown

$\Delta H_f^\circ{}_0$ = Unknown

$\Delta H_f^\circ{}_{298.15}$ = -337.1 ± 2.0 kcal. mole^{-1}

ΔH_m° = Unknown

$\Delta H_s^\circ{}_{298.15}$ = [30.1] kcal. mole^{-1}

Heat of Formation.

The enthalpy change, $\Delta H_r^\circ{}_{298.15}$ = -91.3 ± 1.0 kcal. mole^{-1}, for the reaction $B_2(OH)_4(c) + (m + 2)\cdot AgNO_3(aq.) + (n + 2)\cdot H_2O(l) = 2Ag(c) + [2H_3BO_3 + 2HNO_3 + mAgNO_3]\cdot nH_2O(aq.)$ was determined calorimetrically by A. Finch, P. J. Gardner and I. J. Hyams, Trans. Faraday Soc. 61, 649 (1965). The heat of formation of $B_2(OH)_4(c)$ was reported to be -335.1 kcal. mole^{-1}. This value was corrected to be -337.1 ± 2 kcal. mole^{-1} by use of more recent data on the $\Delta H_f^\circ{}_{298.15}$ values used for calculation.

Heat Capacity and Entropy.

The heat capacity for $B_2(OH)_4(c)$ was estimated by comparison with those for $B(OH)_3(c)$. The value of $S^\circ_{298.15}$ was calculated based on 3 cal. deg.$^{-1}$ mole^{-1} per atom for $B_2(OH)_4(c)$, which was obtained from the corresponding values for $HBO_2(c)$ and $B(OH)_3(c)$.

Heat of Sublimation.

The value, $\Delta H_s^\circ{}_{298.15}$, was calculated as the difference between $\Delta H_f^\circ{}_{298.15}$ for $B_2(OH)_4(g)$ and $B_2(OH)_4(c)$.

Boron Dihydroxide, Dimeric ($B_2(OH)_4$)

(Ideal Gas) Mol. Wt. = 89.65148

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100	12.326	64.168	101.205	-3.704	-304.878	-298.096	651.480
200	18.820	74.732	85.444	-2.142	-306.042	-290.852	317.829
298	24.721	83.369	83.369	.000	-307.000	-283.189	207.583
300	24.824	83.522	83.369	.046	-307.016	-283.043	206.196
400	29.857	91.380	84.407	2.789	-307.727	-274.937	150.218
500	33.765	98.482	86.523	5.979	-308.225	-266.679	116.565
600	36.761	104.915	89.061	9.512	-308.550	-258.337	94.099
700	39.115	110.765	91.750	13.310	-308.744	-249.949	78.037
800	41.023	116.117	94.467	17.320	-308.832	-241.546	65.987
900	42.614	121.043	97.149	21.504	-308.832	-233.134	56.613
1000	43.963	125.605	99.770	25.835	-308.761	-224.724	49.115
1100	45.120	129.850	102.314	30.291	-308.643	-216.327	42.980
1200	46.119	133.820	104.775	34.854	-308.482	-207.939	37.871
1300	46.986	137.547	107.154	39.510	-308.296	-199.570	33.551
1400	47.741	141.057	109.452	44.247	-308.089	-191.213	29.850
1500	48.400	144.374	111.671	49.055	-307.877	-182.873	26.645
1600	48.977	147.516	113.814	53.924	-307.664	-174.547	23.842
1700	49.484	150.501	115.885	58.848	-307.448	-166.231	21.370
1800	49.931	153.342	117.887	63.819	-307.239	-157.932	19.176
1900	50.326	156.053	119.825	68.832	-307.034	-149.643	17.213
2000	50.676	158.643	121.702	73.883	-306.831	-141.365	15.448
2100	50.988	161.123	123.520	78.966	-306.636	-133.094	13.851
2200	51.267	163.502	125.284	84.079	-306.451	-124.836	12.401
2300	51.516	165.786	126.996	89.219	-306.271	-116.586	11.078
2400	51.740	167.984	128.658	94.382	-306.106	-108.337	9.865
2500	51.942	170.190	130.274	99.566	-316.730	-99.890	8.732
2600	52.124	172.141	131.845	104.769	-316.571	-91.216	7.667
2700	52.289	174.111	133.374	109.990	-316.420	-82.549	6.682
2800	52.439	176.016	134.863	115.227	-316.275	-73.896	5.768
2900	52.575	177.858	136.314	120.477	-316.137	-65.229	4.916
3000	52.700	179.643	137.729	125.741	-316.007	-56.588	4.122
3100	52.814	181.373	139.109	131.017	-315.881	-47.945	3.380
3200	52.918	183.051	140.456	136.304	-315.766	-39.302	2.684
3300	53.014	184.681	141.772	141.600	-315.660	-30.662	2.031
3400	53.103	186.265	143.057	146.906	-315.562	-22.030	1.416
3500	53.184	187.805	144.314	152.221	-315.473	-13.399	.837
3600	53.260	189.305	145.543	157.543	-315.393	-4.767	.289
3700	53.329	190.765	146.745	162.872	-315.326	3.862	-.228
3800	53.394	192.188	147.923	168.209	-315.263	12.494	-.719
3900	53.454	193.576	149.075	173.551	-315.213	21.107	-1.183
4000	53.510	194.930	150.205	178.899	-557.531	34.021	-1.859
4100	53.563	196.252	151.312	184.253	-557.037	48.804	-2.601
4200	53.611	197.543	152.397	189.612	-556.550	63.584	-3.309
4300	53.657	198.805	153.462	194.975	-556.075	78.343	-3.982
4400	53.700	200.039	154.507	200.343	-555.611	93.085	-4.624
4500	53.740	201.246	155.532	205.715	-555.157	107.819	-5.236
4600	53.777	202.428	156.539	211.091	-554.709	122.558	-5.823
4700	53.813	203.585	157.527	216.470	-554.276	137.278	-6.383
4800	53.846	204.718	158.499	221.853	-553.849	151.991	-6.920
4900	53.877	205.829	159.453	227.239	-553.433	166.676	-7.434
5000	53.907	206.917	160.392	232.629	-553.025	181.370	-7.928
5100	53.935	207.985	161.314	238.021	-552.631	196.064	-8.402
5200	53.961	209.033	162.222	243.415	-552.243	210.727	-8.857
5300	53.986	210.061	163.115	248.813	-551.863	225.408	-9.295
5400	54.009	211.070	163.994	254.213	-551.497	240.056	-9.716
5500	54.032	212.061	164.859	259.615	-551.135	254.730	-10.122
5600	54.053	213.035	165.710	265.019	-550.789	269.359	-10.512
5700	54.073	213.992	166.549	270.425	-550.451	284.006	-10.889
5800	54.092	214.933	167.375	275.833	-550.123	298.644	-11.253
5900	54.111	215.857	168.189	281.244	-549.802	313.279	-11.605
6000	54.128	216.767	168.991	286.656	-549.492	327.906	-11.944

Mar. 31, 1966

BORON DIHYDROXIDE, DIMERIC ($B_2(OH)_4$) (IDEAL GAS) MOL. WT. = 89.65148

Point Group $[C_2]$

$S^\circ_{298.15}$ = [83.37] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = [-307 ± 5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[1380](1)	[1386](1)	[824](2)
[630](1)	[657](1)	[209](2)
[304](1)	[325](1)	[3200](4)
Rotation (1)	[1378](1)	[1200](2)
[1155](1)	[862](1)	[880](2)
[542](1)	[325](1)	

Bond Distance: B-B = [1.67] Å B-O = [1.36] Å B-H = [0.96] Å

Bond Angle: H-O-B = [114]° O-B-O = [120]° O-B-B = [120]° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = [2.2995 \times 10^{-113}]$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $B_2(OH)_4(g)$ was calculated, using bond energies, D(B-OH) = 132 and D(B-B) = 78 kcal. mole^{-1}. The bond energy D(B-OH) was taken from that in $B(OH)_3(g)$ and D(B-B) was estimated by comparison with that in $B_2F_4(g)$.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that for $B_2F_4(g)$, i.e. the two $B(OH)_2$ units have staggered configuration, and free rotation about B-B bond. The B-B bond distance was taken as that in B_2F_4 molecule. Those for B-O and B-H bond and bond angles were adopted from H_3BO_3 molecule. Eleven vibrational frequencies were assumed to be the same as those for $B_2F_4(g)$. In addition to these were added four OH torsion frequencies, 824(2) and 209(2), four OH stretching, 3200(4), and four B-O-H bending frequencies, 1200(2) and 880(2). The thermodynamic functions were evaluated based on a molecular model having free internal rotation of two $B(OH)_2$ groups about B-B bond. The reduced moment of inertia for the rotation is calculated as 4.10146×10^{-39} g. cm.^{2} The three principal moments of inertia are: $I_A = 1.64037 \times 10^{-38}$ and $I_B = I_C = 3.7441 \times 10^{-38}$ g. cm.^{2}

Diborane (B_2H_6)
(Ideal Gas) Mol. Wt. = 27.688

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.904	13.552	13.552	INFINITE
100	8.268	44.654	65.685	-2.103	12.064	14.931	-32.630
200	10.397	50.934	56.860	-1.185	11.013	18.174	-19.858
298	13.886	55.709	55.709	.000	9.800	21.941	-16.082
300	13.957	55.795	55.709	.026	9.777	22.016	-16.038
400	17.747	60.335	56.302	1.613	8.638	26.272	-14.354
500	21.196	64.673	57.546	3.563	7.665	30.795	-13.460
600	24.219	68.811	59.081	5.838	6.890	35.498	-12.929
700	26.835	72.746	60.755	8.394	6.308	40.316	-12.587
800	29.077	76.480	62.489	11.192	5.898	45.203	-12.348
900	30.984	80.018	64.242	14.198	5.636	50.133	-12.173
1000	32.600	83.368	65.988	17.379	5.493	55.087	-12.038
1100	33.966	86.541	67.714	20.709	5.437	60.048	-11.930
1200	35.123	89.547	69.409	24.165	5.453	65.015	-11.840
1300	36.105	92.399	71.069	27.728	5.516	69.973	-11.763
1400.	36.941	95.106	72.690	31.382	5.614	74.931	-11.697
1500	37.656	97.679	74.271	35.112	5.724	79.877	-11.637
1600	38.271	100.130	75.811	38.909	5.841	84.815	-11.585
1700	38.802	102.466	77.311	42.764	5.965	89.750	-11.537
1800	39.262	104.697	78.771	46.667	6.087	94.671	-11.494
1900	39.664	106.831	80.192	50.614	6.210	99.530	-11.455
2000	40.016	108.875	81.575	54.599	6.332	104.504	-11.419
2100	40.325	110.835	82.922	58.616	6.447	109.410	-11.386
2200	40.599	112.717	84.234	62.662	6.557	114.309	-11.355
2300	40.841	114.527	85.512	66.735	6.663	119.204	-11.326
2400	41.058	116.270	86.757	70.830	6.757	124.101	-11.300
2500	41.251	117.950	87.972	74.945	-3.935	129.198	-11.294
2600	41.425	119.572	89.156	79.079	-3.841	134.527	-11.307
2700	41.581	121.138	90.312	83.230	-3.751	139.849	-11.319
2800	41.722	122.653	91.440	87.395	-3.665	145.158	-11.330
2900	41.850	124.119	92.541	91.574	-3.580	150.483	-11.340
3000	41.966	125.540	93.618	95.765	-3.501	155.787	-11.349
3100	42.072	126.918	94.670	99.967	-3.423	161.091	-11.356
3200	42.169	128.255	95.699	104.179	-3.353	166.401	-11.364
3300	42.257	129.554	96.705	108.400	-3.289	171.711	-11.371
3400	42.338	130.817	97.690	112.630	-3.228	177.006	-11.377
3500	42.413	132.045	98.654	116.868	-3.177	182.306	-11.383
3600	42.482	133.241	99.598	121.112	-3.132	187.608	-11.389
3700	42.546	134.406	100.523	125.364	-3.097	192.907	-11.394
3800	42.605	135.541	101.430	129.621	-3.066	198.206	-11.399
3900	42.660	136.648	102.319	133.885	-3.046	203.498	-11.403
4000	42.710	137.729	103.190	138.155	-245.392	213.085	-11.642
4100	42.758	138.784	104.046	142.427	-244.924	224.538	-11.968
4200	42.802	139.815	104.885	146.705	-244.465	235.994	-12.279
4300	42.843	140.823	105.709	150.987	-244.016	247.423	-12.575
4400	42.881	141.808	106.518	155.273	-243.577	258.842	-12.856
4500	42.917	142.772	107.313	159.563	-243.149	270.247	-13.124
4600	42.951	143.716	108.095	163.856	-242.727	281.665	-13.381
4700	42.983	144.640	108.862	168.153	-242.318	293.060	-13.627
4800	43.012	145.545	109.617	172.453	-241.917	304.448	-13.861
4900	43.040	146.432	110.359	176.755	-241.528	315.823	-14.086
5000	43.067	147.302	111.090	181.061	-241.147	327.188	-14.301
5100	43.092	148.155	111.808	185.369	-240.780	338.560	-14.508
5200	43.115	148.992	112.515	189.679	-240.420	349.911	-14.706
5300	43.137	149.814	113.211	193.992	-240.071	361.267	-14.896
5400	43.158	150.620	113.896	198.306	-239.737	372.597	-15.079
5500	43.178	151.412	114.571	202.623	-239.409	383.945	-15.256
5600	43.197	152.191	115.236	206.942	-239.095	395.262	-15.425
5700	43.215	152.955	115.891	211.263	-238.792	406.596	-15.589
5800	43.232	153.707	116.537	215.585	-238.502	417.908	-15.746
5900	43.248	154.446	117.173	219.909	-238.221	429.229	-15.899
6000	43.264	155.173	117.800	224.235	-237.951	440.535	-16.046

Dec. 31, 1960; Dec. 31, 1964

DIBORANE (B_2H_6) (IDEAL GAS) MOL. WT. = 27.688

Point Group D_{2h}
$S^\circ_{298.15}$ = 55.709 cal. deg. mole^{-1}
Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0 = 13.6 \pm 4.0$ kcal. mole^{-1}
$\Delta H_f^\circ{}_{298.15} = 9.8 \pm 4.0$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
2532(1)	2600(1)	1026(1)	2615(1)
2109(1)	919(1)	584(1)	1601(1)
1184(1)	1755(1)	1905(1)	1174(1)
788(1)	942(1)	973(1)	
2612(1)	950(1)	368(1)	

Bond Distance: B-B = 1.775 ± 0.004 Å B-H_t = 1.196 ± 0.016 Å B-H_b = 1.339 ± 0.013 Å

H_t = terminal hydrogen, H_b = bridge hydrogens.

Bond Angles: H_t - B - H_t = 120.2 ± 1.6°

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 2.46622 \times 10^{-116}$ g.^{3} cm.^{6}

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ is a weighted average of the following data. The older data of W. A. Roth et al.(8) deviates from the rest of the investigations and is not included.

Investigator		Reaction	ΔH_r° 298.15 (kcal. mole^{-1})	ΔH_f° 298.15 (kcal. mole^{-1})
Gunn and Green(1)		$B_2H_6(g) \rightarrow 2B(am) + 3H_2(g)$	-5.0	7.4
E. J. Prosen et al.(2)		$B_2H_6(g) \rightarrow 2B(am) + 3H_2(g)$	-6.73	9.13
J. R. Lacher et al.(3)		$B_2H_6(g) + 6Cl_2 \rightarrow 2BCl_3(g) + 6HCl(g)$	-342.3	17.3
E. J. Prosen et al.(4)		$B_2H_6(g) + 6H_2O(l) + [2000H_2O](l) \rightarrow 2[H_3BO_3 + 1000H_2O](soln.) + 6H_2(g)$	-111.46 ± 0.54	9.32
Gunn and Green(7)	(a)	$B_2H_6(g) + 2006H_2O \rightarrow 2(H_3BO_3 + 1000H_2O) + 6H_2(g)$	-112.22 ± 0.10	10.08
Gunn and Green(7)	(b)	$BCl_3(l) + 130.3H_2O \rightarrow (H_3BO_3 + 1000H_2O) + 3(HCl + 100H_2O)$	-68.14	——
(a) - 2(b) =	(c)	$B_2H_6(g) + 6(HCl\cdot 100H_2O) \rightarrow 2BCl_3(l) + 6H_2(g)$	+24.06	10.06
Gunn (9)		$(CH_3)_3N(g) + 1/2\ B_2H_6(g) \rightarrow (CH_3)_3N{:}BH_3(c)$	-32.33 ± 0.06	8.3
McCoy and Bauer(13)		$(CH_3)_3N(g) + 1/2\ B_2H_6(g) \rightarrow (CH_3)_3N{:}BH_3(c)$	-31.40	6.5

Sources of Auxiliary data: From the JANAF tables, $\Delta H_f^\circ{}_{298.15}$ = 1.2, -96.31, -22.063 kcal. mole^{-1} of B(am), $BCl_3(g)$ and HCl(g) respectively. From F. D. Rossini et al. (11) The $\Delta H_v^\circ{}_{298.15}$ = 5.6 kcal. mole^{-1} of BCl_3. From D. D. Wagman(12) the $\Delta H_f^\circ{}_{298.15}$ of $(HCl + 100H_2O)$ = -39.657 kcal. mole^{-1}. From Good et al.(5) the $\Delta H_f^\circ{}_{298.15}$ of $H_3BO_3(c)$ = -261.47 ± 0.20 kcal. mole^{-1} and the H_3BO_3 solution data of Fasolino(6). $\Delta H_f^\circ{}_{298.15}$ of $(CH_3)_3N(g)$ = -5.9 ± 0.4 kcal. mole^{-1} from I Jaffe(10).

(1) S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 779-83(1961); J. Chem. Phys. 36, 1118 (1962). Explosive decomposition while mixed with stibine.

(2) E. J. Prosen, W. H. Johnson and F. Y. Pergiel, J. Res. N.B.S. 61, 247-250 (1958). Decomposition by heating in a flow-type calorimeter.

(3) J. R. Lacher, R. E. Scruby, and J. D. Park, J. Am. Chem. Soc. 74, 5292-4 (1952). A vapor phase chlorination in a flow-type calorimeter.

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(6) L. G. Fasolino, "Heats of Formation of $B_2O_3(c)$ and $B_2O_3(amp)$" Special Report NONR-360, National Research Corporation, Cambridge, Mass. June 2, 1964.

(7) S. R. Gunn and L. G. Green, J. Phys. Chem. 64, 61-63(1960). Heats of hydrolysis of diborane and boron trichloride in a sealed rocking bomb type calorimeter.

(8) W. A. Roth, E. Borger, and A. Bertram, Ber. 70B, 49 (1937); Ber. 70B, 971 (1937) and W. A. Roth, Z. Naturforsch, 1, 574 (1946). Heat of hydrolysis in a bomb type calorimeter.

(9) S. R. Gunn, abstract (No. 42) of a paper presented at the 19th annual Calorimetry Conference, Washington, D. C., and Bethesda, Maryland, Oct. 13-16, 1964.

(10) I. Jaffe, Thesis University of Maryland, 1958.

(11) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, N.B.S. Circ. 500.

(12) W. H. Evans, Appendix III, National Bureau of Standards Report 8504, July 1, 1964.

(13) R. E. McCoy and S. H. Bauer, J. Am. Chem. Soc. 78, 2061 (1956).

Heat Capacity and Entropy.

The molecular constants reported by B. L. Carroll, "Electron Diffraction Investigation of Diborane and Boron-alkyls", Thesis, Iowa State University of Science and Technology, 1963, were selected. They agree well with those reported by K. Hedberg, and V. Schomaker, J. Chem. Phys. 22, 985 (1954). The principal moments are $I_A = 1.0578 \times 10^{-39}$, $I_B = 4.6416 \times 10^{-39}$, and $I_C = 5.0229 \times 10^{-39}$ g. cm.^{2}

The vibrational frequencies for $B_2^{11}H_6$ were those listed by E. C. Wu, Thesis, University of Minn. 1962, "Assignments and Force Constants of Diborane and Isotopic Derivatives" except for ν_8, ν_{10} and ν_{14} which were taken from the calculated frequency column of table VIII-1 page 55 of the Thesis.

Magnesium Diboride (MgB_2)

(Crystal) Mol. Wt. = 45.96

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.625	-21.825	-21.825	INFINITE
100	2.670	.962	16.482	-1.552	-21.918	-21.771	47.578
200	8.220	4.590	9.590	-1.000	-22.088	-21.664	23.672
298	11.430	8.600	8.600	.000	-21.980	-21.378	15.670
300	11.440	8.671	8.600	.021	-21.980	-21.374	15.571
400	13.000	12.190	9.069	1.248	-22.011	-21.170	11.566
500	13.960	15.198	10.002	2.598	-22.129	-20.947	9.156
600	14.670	17.808	11.090	4.030	-22.316	-20.696	7.538
700	15.300	20.117	12.218	5.529	-22.542	-20.407	6.371
800	15.900	22.199	13.337	7.089	-22.797	-20.086	5.487
900	16.530	24.108	14.429	8.711	-23.068	-19.731	4.791
1000	17.140	25.881	15.487	10.394	-25.474	-19.162	4.188
1100	17.705	27.541	16.508	12.137	-25.741	-18.520	3.679
1200	18.270	29.106	17.493	13.935	-26.008	-17.851	3.251
1300	18.833	30.591	18.444	15.790	-26.274	-17.162	2.885
1400	19.400	32.007	19.363	17.702	-56.900	-15.970	2.493
1500	19.991	33.366	20.251	19.672	-56.749	-13.054	1.902
1600	20.550	34.674	21.112	21.699	-56.565	-10.146	1.386
1700	21.071	35.936	21.947	23.780	-56.351	-7.251	.932
1800	21.570	37.154	22.758	25.913	-56.105	-4.370	.531
1900	22.046	38.333	23.547	28.094	-55.826	-1.503	.173
2000	22.500	39.476	24.315	30.321	-55.514	1.348	-.147

Mar. 31, 1963; Mar. 31, 1965

MAGNESIUM DIBORIDE (MgB_2) (CRYSTAL) MOL. WT. = 45.96

$\Delta H_{f\ 0}^\circ = -21.8 \pm 2.0$ kcal. mole^{-1}

$S^\circ_{298.15} = 8.60 \pm 0.04$ cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15} = -22.0 \pm 2.0$ kcal. mole^{-1}

$T_d = [1320]^\circ K$

Heat of Formation.

The equilibrium constants (993 - 1108°K.) for the reaction $2MgB_2(c) = Mg(g) + MgB_4(c)$ were determined by M. Wright and P. N. Walsh, "The Vaporization of $MgB_4(c)$", Technical Research Report OMCC-HEF-55, Jan. 9, 1958, Ohio State University Research Foundation. The corresponding second and third law values of $\Delta H^\circ_{r\ 298.15}$ for this reaction were derived as 53.1 ± 4.7 and 54.1 kcal. mole^{-1}, respectively. Using the third law value obtained, i.e. $\Delta H^\circ_{r\ 298.15} = 54.1$ kcal. mole^{-1}, for the reaction, the $\Delta H^\circ_{f\ 298.15}$ for $MgB_2(c)$ was evaluated as -22.0 ± 2.0 kcal. mole .

Heat Capacity and Entropy.

The low temperature (21.12 - 304.22°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. 79, 3641 (1957). Above 298.15°K. the values of C_p were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using S°_{20} (extrap.) = 0.005 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Decomposition.

T_d was taken from L. Y. Markovsky, Y. D. Kondrashev, and G. V. Kaputovskaya, Zhur. Obshchei Khim., 25, 409 (1955). On heating to high temperatures $MgB_2(c)$ decomposes into boride phases A, B, and C with the separation of Mg. The composition of phase A is close to MgB_6 and that of C is close to MgB_{12}.

Diboron Monoxide (B_2O)

(Ideal Gas) GFW = 37.6214

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.480	22.142	22.142	INFINITE
100	7.975	45.239	62.085	-1.685	22.578	20.140	-44.016
200	8.477	50.890	55.222	-.866	22.888	17.567	-19.196
298	9.180	54.405	54.405	.000	23.000	14.921	-10.937
300	9.193	54.462	54.406	.017	23.000	14.870	-10.833
400	9.903	57.205	54.775	.972	22.956	12.163	-6.646
500	10.556	59.486	55.495	1.996	22.788	9.483	-4.145
600	11.121	61.462	56.328	3.080	22.545	6.844	-2.493
700	11.588	63.213	57.189	4.217	22.261	4.249	-1.327
800	11.966	64.786	58.042	5.395	21.950	1.696	-.463
900	12.269	66.213	58.872	6.607	21.623	-.817	.198
1000	12.514	67.519	59.672	7.847	21.279	-3.290	.719
1100	12.712	68.721	60.441	9.108	20.913	-5.730	1.138
1200	12.873	69.835	61.178	10.388	20.531	-8.135	1.482
1300	13.005	70.870	61.884	11.682	20.129	-10.508	1.767
1400	13.115	71.838	62.561	12.988	19.709	-12.848	2.006
1500	13.206	72.746	63.210	14.304	19.267	-15.161	2.209
1600	13.284	73.601	63.833	15.629	18.807	-17.439	2.382
1700	13.349	74.409	64.432	16.961	18.328	-19.691	2.532
1800	13.405	75.173	65.007	18.298	17.831	-21.913	2.661
1900	13.45	75.899	65.562	19.641	17.321	-24.108	2.773
2000	13.495	76.590	66.096	20.989	16.800	-26.274	2.871
2100	13.531	77.250	66.612	22.340	16.269	-28.415	2.957
2200	13.563	77.880	67.110	23.695	15.728	-30.529	3.033
2300	13.591	78.484	67.591	25.053	15.178	-32.622	3.100
2400	13.616	79.063	68.057	26.413	14.617	-34.686	3.159
2500	13.638	79.619	68.508	27.776	3.274	-36.511	3.192
2600	13.658	80.154	68.946	29.141	2.713	-38.092	3.202
2700	13.676	80.670	69.371	30.508	2.151	-39.648	3.209
2800	13.692	81.168	69.783	31.876	1.587	-41.190	3.215
2900	13.706	81.648	70.184	33.246	1.023	-42.700	3.218
3000	13.719	82.113	70.574	34.617	.458	-44.201	3.220
3100	13.731	82.563	70.954	35.990	-.108	-45.683	3.221
3200	13.742	82.999	71.323	37.363	-.675	-47.142	3.220
3300	13.751	83.422	71.684	38.738	-1.244	-48.584	3.218
3400	13.760	83.833	72.035	40.114	-1.813	-50.010	3.215
3500	13.769	84.232	72.378	41.490	-2.384	-51.424	3.211
3600	13.776	84.620	72.712	42.867	-2.956	-52.814	3.206
3700	13.783	84.998	73.039	44.245	-3.529	-54.193	3.201
3800	13.790	85.365	73.359	45.624	-4.103	-55.549	3.195
3900	13.796	85.723	73.671	47.003	-4.677	-56.900	3.189
4000	13.801	86.073	73.977	48.383	-247.611	-53.943	2.947
4100	13.806	86.414	74.276	49.763	-247.727	-49.102	2.617
4200	13.811	86.746	74.569	51.144	-247.840	-44.245	2.302
4300	13.816	87.071	74.856	52.526	-247.957	-39.398	2.002
4400	13.820	87.389	75.137	53.907	-248.077	-34.549	1.716
4500	13.824	87.700	75.413	55.290	-248.197	-29.699	1.442
4600	13.828	88.004	75.684	56.672	-248.318	-24.841	1.180
4700	13.831	88.301	75.949	58.055	-248.442	-19.977	.929
4800	13.834	88.592	76.209	59.438	-248.568	-15.110	.688
4900	13.837	88.878	76.465	60.822	-248.697	-10.258	.458
5000	13.840	89.157	76.716	62.206	-248.827	-5.384	.235
5100	13.843	89.431	76.963	63.590	-248.961	-.512	.022
5200	13.845	89.700	77.205	64.974	-249.096	4.358	-.183
5300	13.848	89.964	77.443	66.359	-249.232	9.230	-.381
5400	13.850	90.223	77.678	67.744	-249.374	14.105	-.571
5500	13.852	90.477	77.908	69.129	-249.515	18.997	-.755
5600	13.854	90.726	78.135	70.514	-249.662	23.873	-.932
5700	13.856	90.972	78.358	71.900	-249.813	28.758	-1.103
5800	13.858	91.213	78.577	73.286	-249.965	33.646	-1.268
5900	13.860	91.450	78.793	74.672	-250.120	38.537	-1.428
6000	13.861	91.683	79.006	76.058	-250.280	43.435	-1.582

June 30, 1966

DIBORON MONOXIDE (B_2O) (IDEAL GAS) GFW = 37.6214

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [54.4] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = 22 ± 25 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 23 ± 25 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[1250](1)

[600](1)

[1800](1)

Bond Distance: B-O = [1.26] Å

Bond Angle: B-O-B = [150]°

σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.7324] X 10^{-117} g^3 cm^6

Heat of Formation.

The heat of formation was calculated from the estimated heat of reaction ΔHr°_0 = 300 ± 25 kcal/mol for $B_2O(g) \rightarrow 2B(g) + O(g)$, using the JANAF auxiliary data for B(g) and O(g). The value of ΔHr°_0 was assumed to be the sum of the heats of dissociation, 120 kcal/mol for $B_2O(g) \rightarrow BO(g) + B(g)$ and 180 kcal/mol for $BO(g) \rightarrow B(g) + O(g)$. The former was estimated and the latter was derived from the JANAF values.

The possible existence of $B_2O(g)$ in the burning of boron under reducing conditions was discussed by Gilbert S. Bahn in a paper presented at the Combustion Institute, at University of Denver, Apr. 25-27, 1966. He estimated the heat of formation to lie between -27 and +23 kcal/mol, but favored the value of +23 kcal/mol in the theoretical calculations of boron burning in air.

Heat Capacity and Entropy.

The bent molecular structure and the molecular constants were estimated by comparison with those in BO(g), AlO(g) and $Al_2O(g)$. The three principal moments of inertia are I_A = 0.1624 X 10^{-39}, I_B = 5.318 X 10^{-39} and I_C = 5.4804 X 10^{-39} g cm^2.

Boron Monoxide, Dimeric $((BO)_2)$

(Ideal Gas) Mol. Wt. = 53.64

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.963	-109.304	-109.304	INFINITE
100	8.214	46.175	68.564	-2.239	-109.305	-109.754	239.856
200	11.528	52.912	59.150	-1.248	-109.154	-110.254	120.474
298	13.695	57.958	57.958	.000	-109.000	-110.833	81.239
300	13.725	58.043	57.959	.025	-108.998	-110.845	80.747
400	15.027	62.184	58.514	1.468	-108.910	-111.476	60.905
500	15.947	65.640	59.603	3.018	-108.917	-112.119	49.005
600	16.688	68.615	60.863	4.651	-108.989	-112.752	41.068
700	17.307	71.235	62.161	6.352	-109.098	-113.371	35.394
800	17.824	73.581	63.445	8.109	-109.229	-113.974	31.135
900	18.255	75.706	64.691	9.914	-109.370	-114.559	27.818
1000	18.613	77.649	65.891	11.758	-109.523	-115.126	25.160
1100	18.910	79.437	67.042	13.634	-109.694	-115.680	22.982
1200	19.157	81.093	68.145	15.538	-109.876	-116.214	21.164
1300	19.363	82.635	69.201	17.464	-110.075	-116.736	19.624
1400	19.537	84.077	70.213	19.410	-110.287	-117.240	18.301
1500	19.683	85.430	71.182	21.371	-110.519	-117.731	17.153
1600	19.808	86.704	72.113	23.346	-110.767	-118.201	16.145
1700	19.915	87.908	73.007	25.332	-111.033	-118.658	15.254
1800	20.007	89.049	73.867	27.328	-111.316	-119.099	14.460
1900	20.087	90.133	74.695	29.333	-111.612	-119.524	13.748
2000	20.157	91.165	75.493	31.345	-111.918	-119.932	13.105
2100	20.218	92.150	76.263	33.364	-112.234	-120.323	12.522
2200	20.271	93.092	77.006	35.389	-112.561	-120.701	11.990
2300	20.318	93.994	77.726	37.418	-112.898	-121.065	11.503
2400	20.360	94.860	78.422	39.452	-113.246	-121.411	11.055
2500	20.398	95.692	79.096	41.490	-124.378	-121.528	10.623
2600	20.431	96.493	79.750	43.532	-124.728	-121.408	10.205
2700	20.462	97.264	80.384	45.576	-125.082	-121.269	9.816
2800	20.489	98.009	81.000	47.624	-125.437	-121.125	9.454
2900	20.513	98.728	81.599	49.674	-125.795	-120.958	9.115
3000	20.535	99.424	82.182	51.726	-126.156	-120.789	8.799
3100	20.556	100.098	82.749	53.781	-126.518	-120.606	8.502
3200	20.574	100.751	83.301	55.837	-126.884	-120.410	8.223
3300	20.591	101.384	83.840	57.896	-127.251	-120.199	7.960
3400	20.606	101.999	84.365	59.956	-127.622	-119.979	7.712
3500	20.621	102.596	84.877	62.017	-127.995	-119.753	7.477
3600	20.634	103.178	85.378	64.080	-128.370	-119.511	7.255
3700	20.646	103.743	85.866	66.144	-128.748	-119.258	7.044
3800	20.657	104.294	86.344	68.209	-129.128	-118.994	6.843
3900	20.667	104.831	86.811	70.275	-129.510	-118.730	6.653
4000	20.677	105.354	87.268	72.342	-372.253	-114.157	6.237
4100	20.686	105.865	87.716	74.410	-372.178	-107.707	5.741
4200	20.694	106.363	88.154	76.479	-372.102	-101.248	5.268
4300	20.702	106.850	88.583	78.549	-372.030	-94.800	4.818
4400	20.709	107.326	89.004	80.620	-371.962	-88.356	4.388
4500	20.716	107.792	89.416	82.691	-371.896	-81.916	3.978
4600	20.722	108.247	89.820	84.763	-371.831	-75.467	3.585
4700	20.728	108.693	90.217	86.835	-371.771	-69.025	3.209
4800	20.734	109.129	90.607	88.908	-371.713	-62.578	2.849
4900	20.739	109.557	90.989	90.982	-371.658	-56.152	2.504
5000	20.744	109.976	91.365	93.056	-371.605	-49.710	2.173
5100	20.749	110.387	91.734	95.131	-371.557	-43.270	1.854
5200	20.753	110.790	92.096	97.206	-371.510	-36.838	1.548
5300	20.757	111.185	92.453	99.282	-371.465	-30.400	1.254
5400	20.761	111.573	92.803	101.357	-371.427	-23.969	.970
5500	20.765	111.954	93.148	103.434	-371.387	-17.523	.696
5600	20.769	112.328	93.487	105.510	-371.355	-11.101	.433
5700	20.772	112.696	93.821	107.588	-371.325	-4.667	.179
5800	20.775	113.057	94.149	109.665	-371.299	1.768	-.067
5900	20.778	113.412	94.473	111.743	-371.275	8.201	-.304
6000	20.781	113.761	94.791	113.820	-371.257	14.639	-.533

Mar. 31, 1961; Dec. 31, 1964

BORON MONOXIDE, DIMERIC (B_2O_2) (IDEAL GAS) MOL. WT. = 53.64

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = 57.958 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -109.3 ± 2.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -109.0 ± 2.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
2065(1)	565(2)
570(1)	285(2)
1910(1)	

Bond Distance: O=B = 1.20 Å B-B = 1.70 Å

Bond Angle: O-B-B = 180°

Rotational Constant: B_0 = 0.1123 cm.$^{-1}$

σ = 2

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $B_2O_2(g)$ adopted is the weighted average of three $\Delta H^\circ_{f\ 298.15}$ values derived from two different chemical reactions. The chemical reactions related to the production of $B_2O_2(g)$ have been studied by several investigators. Using the equilibrium vapor pressure data, the respective values of $\Delta H^\circ_{r\ 298.15}$ were evaluated by both the second and third law methods. The results obtained are based on the latter and presented as follows.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	$\Delta H^\circ_{f\ 298.15}$ kcal. mole^{-1}
Inghram, et al.[1]	$2/3\ B(c) + 2/3\ B_2O_3(l) = B_2O_2(g)$	94.0	91.8 ± 2.2	-105.5 ± 0.7*
	$2/3\ B(c) + 2/3\ B_2O_3(g) = B_2O_2(g)$	24.8	25.4 ± 0.2	-108.0 ± 0.5
Searcy and Myers[2]	$2MgO(c) + 2B(c) = 2Mg(g) + B_2O_2(g)$	255.4	—	-102.6 ± 10*
Scheer[3]	$2/3\ B(c) + 2/3\ B_2O_3(l) = B_2O_2(g)$	89.3	77.9 ± 0.2	-110.2 ± 0.9
Rentzepis, et al.[4]	$B_2O_3(l) + 3C(c) = 3CO(g) + 2B(c)$	—	—	-108.5 ± 1.5
	$B_2O_3(l) + C(c) = B_2O_2(g) + CO(g)$	—	—	

*The value not used for the calculation of the weighted average of $\Delta H^\circ_{f\ 298.15}$ for $B_2O_2(g)$.

[1] M. G. Inghram, R. F. Porter and W. A. Chupka, J. Chem. Phys. 25, 498 (1956).

[2] A. W. Searcy and C. E. Myers, J. Phys. Chem. 61, 957 (1957).

[3] M. D. Scheer, J. Phys. Chem. 62, 490 (1958).

[4] P. Rentzepis, D. White and P. N. Walsh, J. Phys. Chem. 64, 1784 (1960). The value of $\Delta H^\circ_{f\ 298.15}$ was obtained from derived log $K_f(B_2O_2,\ g)$ values by the third law method.

Heat Capacity and Entropy.

The molecular structure and constants, and vibrational frequencies, corrected to the average isotopic species, were taken from A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys. 38, 87 (1963). The moment of inertia (I) is 2.4922 X 10^{-38} g. cm.^{2}

Boron Oxide (B_2O_3)

(Crystal) Mol Wt. = 69.64

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.218	- 302.162	- 302.162	INFINITE
100	4.987	2.624	22.994	- 2.037	- 303.062	- 297.080	649.236
200	10.499	7.850	14.105	- 1.251	- 303.456	- 290.921	317.888
298	15.050	12.870	12.870	.000	- 303.640	- 284.725	208.699
300	15.140	12.963	12.870	.028	- 303.642	- 284.608	207.327
400	18.350	17.787	13.506	1.712	- 303.668	- 278.257	152.025
500	20.800	22.148	14.806	3.671	- 303.631	- 271.907	118.845
600	23.250	26.153	16.367	5.872	- 303.513	- 265.571	96.729
700	26.200	29.951	18.038	8.339	- 303.245	- 259.265	80.942
800	29.650	33.673	19.760	11.131	- 302.740	- 253.015	69.117
900	32.050	37.316	21.510	14.226	- 301.998	- 246.843	59.939
1000	33.450	40.769	23.265	17.504	- 301.130	- 240.757	52.615
1100	34.300	44.000	25.005	20.895	- 300.206	- 234.766	46.642
1200	34.700	47.003	26.714	24.347	- 299.264	- 228.857	41.679
1300	34.900	49.789	28.383	27.827	- 298.337	- 223.029	37.493
1400	35.000	52.379	30.006	31.323	- 297.432	- 217.268	33.915
1500	35.000	54.794	31.579	34.823	- 296.560	- 211.576	30.825
1600	35.000	57.053	33.101	38.323	- 295.722	- 205.936	28.128
1700	35.000	59.175	34.573	41.823	- 294.915	- 200.350	25.755
1800	35.000	61.175	35.996	45.323	- 294.138	- 194.810	23.652
1900	35.000	63.068	37.372	48.823	- 293.387	- 189.313	21.775
2000	35.000	64.863	38.702	52.323	- 292.655	- 183.855	20.090

Dec. 31, 1960; Dec. 31, 1964

BORON OXIDE (B_2O_3) (CRYSTAL) MOL. WT. = 69.64

$S^\circ_{298.15}$ = 12.87 ± 0.10 cal. deg.$^{-1}$ mole^{-1}

T_m = 723 ± 2°K.

$\Delta H^\circ_{f\ 0}$ = -302.16 ± 0.40 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -303.64 ± 0.40 kcal. mole^{-1}

ΔH°_m = 5.26 ± 0.02 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 104.5 ± 0.6 kcal. mole^{-1}

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for B_2O_3(c) has been reported by many investigators. However, the values obtained were not in good agreement. The value of $\Delta H^\circ_{f\ 298.15}$ for B_2O_3(c) adopted was taken from L. G. Fasolino, "Heats of Formation of B_2O_3(c) and B_2O_3(am.)". NONR-3608 (00), National Research Corporation, Massachusetts, June 2, 1964. The other derived values of $\Delta H^\circ_{f\ 298.15}$ for B_2O_3(c) are listed in the following table.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1}	$\Delta H^\circ_{f\ 298.15}$, kcal. mole^{-1}
Roth[1]	$B_2O_3(gl) + 3\ H_2O(l) = 2\ H_3BO_3(c)$	-18.15	-304.2 ± 0.4
Eggersgluess et al.[2]	$2B(am.) + 3/2\ O_2(g) = B_2O_3(gl.)$	-281.1 ± 3.1	-283.1 ± 3.1
Artsdalen and Anderson[3]	$1/2\ B_2O_3(am.) + 3/2\ H_2O(l) = H_3BO_3(c)$	-9.13± 0.04	-304.1 ± 0.4
Eckstein and Artsdalen[4]	$2B(c) + 3/2\ O_2(g) = B_2O_3(gl.)$	-304.6 ± 4.2	-309.0 ± 4.2
Gal'chenko et al.[5]	$2B(am.) + 3/2\ O_2(g) = B_2O_3(gl.)$	-298.7 ± 1.8	-300.7 ± 2.0
Fasolino	$B_2O_3(c) + 348\ H_2O(l) = 2\ H_3BO_3 \cdot 345\ H_2O(Sol.)$	-3.45± 0.03	-303.64± 0.40

[1] W. A. Roth, Z. Naturforsch, 1, 574 (1946).

[2] W. Eggersgluess, A. G. Monroe and W. G. Parker, Trans. Faraday Soc. 45, 661 (1949).

[3] E. R. Van Artsdalen and K. P. Anderson, J. Am. Chem. Soc. 73, 579 (1951).

[4] B. H. Eckstein and E. R. Van Artsdalen, J. Am. Chem. Soc. 80, 1352 (1958).

[5] G. L. Gal'chenko, A. N. Kornilov and S. M. Skuratov, Russ. J. Inorg. Chem. 5, 1039 (1960).

In order to evaluate the values of $\Delta H^\circ_{f\ 298.15}$ for B_2O_3(c) from the corresponding $\Delta H^\circ_{r\ 298.15}$ values, the following auxiliary data (298.15°K) were used: ΔH°_f(B,am.) = 1.2 ± 0.4 kcal. mole^{-1}, ΔH°_r = 4.36 kcal. mole^{-1} for the reaction $B_2O_3(c) = B_2O_3(gl.)$, $\Delta H^\circ_f(H_3BO_3, c)$ = -261.47 ± 0.20 kcal. mole^{-1}, $\Delta H^\circ_f(2\ H_3BO_3 \cdot 345\ H_2O, Sol.)$ = -512.04 ± 0.40 kcal. mole^{-1} and $\Delta H^\circ_f(H_2O, l)$ = -68.317 kcal. mole^{-1}.

Heat Capacity and Entropy.

The low temperature (18.08 - 296.60°K.) heat capacities used were reported by E. C. Kerr, H. N. Hersh and H. L. Johnston, J. Am. Chem. Soc. 72, 4738 (1950). The high temperature (350.6 - 718.4°K.) heat capacities were derived from the heat content measurements determined by J. C. Southard, J. Am. Chem. Soc. 63, 3147 (1941). These two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 718.4°K. were estimated by graphical extrapolation. $S^\circ_{298.15}$ was obtained from E. C. Kerr, H. N. Hersh and H. L. Johnston, loc. cit., based on S°_{18} = 0.027 cal. deg.$^{-1}$ mole^{-1}. The specific heats of B_2O_3(c) in the temperature range 51 to 298°K. were also determined by K. K. Kelley, J. Am. Chem. Soc. 63, 1137 (1941). The C_p values reported are in good agreement with the values adopted.

Melting Data.

Melting temperature (T_m) was taken from F. C. Kracek, G. W. Morey and H. E. Merwin, Am. J. Sci. [5] 35A, 143 (1938). The heat of melting (ΔH°_m) was converted from $\Delta H^\circ_{m\ 298.15}$ = 4.36 ± 0.02 kcal. mole^{-1} reported by J. C. Southard, loc. cit.

Heat of Sublimation.

The value of heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) was calculated as the difference in the heats of formation ($\Delta H^\circ_{f\ 298.15}$) for B_2O_3(g) and B_2O_3(c).

Boron Oxide (B_2O_3)

(Liquid) Mol. Wt. = 69.64

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	15.050	18.739	18.739	- .000	- 299.280	- 282.115	206.786
300	15.140	18.832	18.739	.028	- 299.282	- 282.009	205.433
400	18.350	23.656	19.375	1.712	- 299.308	- 276.244	150.926
500	20.800	28.017	20.675	3.671	- 299.271	- 270.481	118.222
600	28.600	32.354	22.248	6.064	- 298.961	- 264.739	96.426
700	31.700	37.060	24.031	9.120	- 298.104	- 259.100	80.891
800	31.930	41.323	25.932	12.313	- 297.198	- 253.593	69.275
900	31.650	45.068	27.854	15.493	- 296.371	- 248.192	60.266
1000	31.400	48.391	29.744	18.646	- 295.628	- 242.877	53.078
1100	31.050	51.367	31.578	21.768	- 294.973	- 237.637	47.212
1200	30.750	54.055	33.341	24.857	- 294.394	- 232.449	42.333
1300	30.600	56.510	35.030	27.924	- 293.881	- 227.310	38.212
1400	30.540	58.775	36.646	30.980	- 293.414	- 222.205	34.686
1500	30.540	60.882	38.193	34.034	- 292.989	- 217.137	31.635
1600	30.540	62.853	39.673	37.088	- 292.596	- 212.091	28.969
1700	30.540	64.705	41.091	40.143	- 292.234	- 207.070	26.619
1800	30.540	66.446	42.452	43.189	- 291.912	- 202.071	24.534
1900	30.540	68.097	43.759	46.243	- 291.606	- 197.088	22.669
2000	30.540	69.663	45.015	49.297	- 291.320	- 192.120	20.993
2100	30.540	71.153	46.224	52.351	- 291.054	- 187.165	19.478
2200	30.540	72.574	47.390	55.405	- 290.808	- 182.225	18.101
2300	30.540	73.932	48.515	58.459	- 290.578	- 177.297	16.846
2400	30.540	75.232	49.601	61.513	- 290.367	- 172.373	15.696
2500	30.540	76.479	50.652	64.567	- 300.947	- 167.247	14.620
2600	30.540	77.677	51.669	67.621	- 300.751	- 161.903	13.609
2700	30.540	78.830	52.654	70.675	- 300.564	- 156.565	12.672
2800	30.540	79.941	53.609	73.729	- 300.384	- 151.238	11.804
2900	30.540	81.013	54.536	76.783	- 300.212	- 145.909	10.995
3000	30.540	82.048	55.436	79.837	- 300.048	- 140.593	10.242
3100	30.540	83.049	56.310	82.891	- 299.889	- 135.281	9.537
3200	30.540	84.019	57.161	85.945	- 299.738	- 129.975	8.876
3300	30.540	84.959	57.989	88.999	- 299.593	- 124.672	8.256
3400	30.540	85.871	58.796	92.053	- 299.456	- 119.373	7.673
3500	30.540	86.756	59.583	95.107	- 299.323	- 114.084	7.123
3600	30.540	87.616	60.349	98.161	- 299.196	- 108.787	6.604
3700	30.540	88.453	61.097	101.215	- 299.075	- 103.500	6.113
3800	30.540	89.267	61.828	104.269	- 298.958	- 98.210	5.648
3900	30.540	90.060	62.542	107.323	- 298.846	- 92.936	5.208
4000	30.540	90.833	63.239	110.377	- 541.098	- 83.366	4.555

Dec. 31, 1960; Dec. 31, 1964

BOROŃ OXIDE (B_2O_3) (LIQUID) MOL. WT. = 69.64

$S^\circ_{298.15}$ = 18.739 cal. deg.$^{-1}$ mole^{-1}

T_m = 723 ± 2°K.

T_b = 2316°K.

$\Delta H^\circ_{f\ 298.15}$ = -299.28 ± 0.40 kcal. mole^{-1}

ΔH°_m = 5.26 ± 0.02 kcal. mole^{-1}

ΔH°_v = 87.55 kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ for $B_2O_3(l)$ was obtained from $\Delta H^\circ_{f\ 298.15}$ for $B_2O_3(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}$ - $H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat content (H°_t - $H^\circ_{298.15}$) measurements on B_2O_3(glass) and $B_2O_3(l)$ were determined, from 381.7 to 1776.8°K., by J. C. Southard, J. Am. Chem. Soc. 63, 3147 (1941) and, from 1015 to 2154°K., by R. M. Krasovitskaya, P. B. Kantor, L. S. Kan, V. V. Kandyba, L. M. Kutsyna and E. N. Fomichev, Russ. J. Phys. Chem. 35, 737 (1961). Based on these data the corresponding heat capacities (C_p) were derived. The C_p values thus obtained were plotted and joined smoothly, assuming a glass transition temperature at 550°K. The heat capacities above 2154°K. were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation. The heat capacities of B_2O_3 glass and liquid have also been measured between 35 and 350°C with a radiation calorimeter by S. B. Thomas and G. S. Parks, J. Phys. Chem. 35, 2091 (1931). The heat capacity curves obtained have been compared and discussed.

Melting Data.

See the $B_2O_3(c)$ table.

Vaporization Data.

The boiling point (T_b) was calculated as the temperature at which the difference in ΔF°_f values for $B_2O_3(g)$ and $B_2O_3(l)$ becomes zero. The corresponding difference in ΔH°_f values at T_b is the heat of vaporization (ΔH°_v).

B_2O_3

Boron Oxide (B_2O_3)

(Ideal Gas) Mol. Wt. = 69.64

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-3,427	-198,870	-198,870	INFINITE
100	9,570	54,227	80,034	-2,581	-199,106	-198,284	433,328
200	13,224	61,965	69,180	-1,443	-199,148	-197,436	215,738
298	15,979	67,798	67,798	,000	-199,140	-196,602	144,106
300	16,020	67,897	67,799	,030	-199,140	-196,586	143,206
400	17,861	72,774	68,451	1,729	-199,151	-195,735	106,939
500	19,207	76,911	69,740	3,586	-199,217	-194,874	85,175
600	20,272	80,510	71,241	5,561	-199,324	-193,995	70,659
700	21,138	83,703	72,798	7,633	-199,451	-193,097	60,285
800	21,846	86,573	74,343	9,784	-199,587	-192,182	52,499
900	22,427	89,181	75,849	11,998	-199,726	-191,248	46,439
1000	22,903	91,569	77,303	14,266	-199,869	-190,296	41,587
1100	23,295	93,771	78,702	16,576	-200,025	-189,333	37,615
1200	23,619	95,812	80,044	18,922	-200,189	-188,352	34,302
1300	23,889	97,714	81,330	21,298	-200,366	-187,360	31,497
1400	24,116	99,493	82,565	23,699	-200,556	-186,352	29,089
1500	24,307	101,163	83,750	26,120	-200,763	-185,332	27,002
1600	24,469	102,737	84,888	28,559	-200,985	-184,294	25,172
1700	24,608	104,225	85,982	31,013	-201,224	-183,244	23,557
1800	24,727	105,635	87,035	33,480	-201,481	-182,181	22,119
1900	24,830	106,975	88,049	35,958	-201,752	-181,101	20,830
2000	24,920	108,251	89,028	38,446	-202,032	-180,008	19,669
2100	24,999	109,468	89,972	40,942	-202,323	-178,896	18,617
2200	25,068	110,633	90,885	43,445	-202,628	-177,775	17,659
2300	25,129	111,749	91,768	45,955	-202,942	-176,640	16,784
2400	25,183	112,819	92,623	48,471	-203,269	-175,485	15,979
2500	25,231	113,848	93,452	50,991	-214,383	-174,105	15,220
2600	25,275	114,839	94,255	53,517	-214,715	-172,489	14,498
2700	25,313	115,793	95,035	56,046	-215,053	-170,854	13,829
2800	25,348	116,715	95,793	58,579	-215,394	-169,215	13,207
2900	25,380	117,605	96,530	61,116	-215,740	-167,553	12,627
3000	25,409	118,466	97,247	63,655	-216,090	-165,889	12,084
3100	25,435	119,299	97,945	66,197	-216,443	-164,210	11,576
3200	25,458	120,107	98,625	68,742	-216,801	-162,520	11,099
3300	25,480	120,891	99,288	71,289	-217,164	-160,818	10,650
3400	25.500	121.652	99,935	73,838	-217.531	-159.104	10.227
3500	25,518	122,391	100,566	76,389	-217,901	-157,384	9,827
3600	25,535	123,110	101,182	78,942	-218,275	-155,644	9,448
3700	25,551	123,810	101,784	81,496	-218,654	-153,900	9,090
3800	25,565	124,492	102,373	84,052	-219,036	-152,142	8,750
3900	25,578	125,156	102,949	86,609	-219,421	-150,385	8,427
4000	25.591	125,804	103,512	89,167	-462,168	-144,320	7,885
4100	25,602	126,436	104,063	91,727	-462,099	-136,374	7,269
4200	25,613	127,053	104,603	94,288	-462,030	-128,424	6,682
4300	25,623	127,656	105,132	96,850	-461,966	-120,481	6,123
4400	25,632	128,245	105,651	99,412	-461,908	-112,543	5,590
4500	25,641	128,821	106,160	101,976	-461,851	-104,605	5,080
4600	25,649	129,385	106,658	104,541	-461,797	-96,663	4,592
4700	25,657	129,936	107,148	107,106	-461,749	-88,722	4,125
4800	25,664	130,477	107,628	109,672	-461,704	-80,785	3,678
4900	25,671	131,006	108,100	112,239	-461,662	-72,862	3,250
5000	25,677	131,524	108,563	114,806	-461,623	-64,921	2,838
5100	25,683	132,033	109,018	117,374	-461,591	-56,985	2,442
5200	25,689	132,532	109,466	119,943	-461,559	-49,059	2,062
5300	25,694	133,021	109,906	122,512	-461,531	-41,121	1,696
5400	25,699	133,501	110,338	125,082	-461,508	-33,194	1,343
5500	25,704	133,973	110,764	127,652	-461,486	-25,250	1,003
5600	25,709	134,436	111,182	130,223	-461,471	-17,332	,676
5700	25,713	134,891	111,594	132,794	-461,460	-9,399	,360
5800	25,717	135,339	112,000	135,365	-461,452	-1,468	,055
5900	25,721	135,778	112,399	137,937	-461,447	6,464	-,239
6000	25,725	136,211	112,792	140,509	-461,447	14,398	-,524

Mar. 31, 1961; Dec. 31, 1964

BORON OXIDE (B_2O_3) (IDEAL GAS) MOL. WT. = 69.64

Point Group C_{2v}

$S^\circ_{298.15}$ = 67.798 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -198.87 ± 0.50 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -199.14 ± 0.50 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
2073(1)	[172](1)	1240(1)
730(1)	[460](1)	457(1)
521(1)	2073 (1)	480(1)

Bond Distance: O-B = 1.36 ± 0.02 Å B=O = 1.20 ± 0.03 Å

Bond Angle: O-B-O = 180° B-O-B = 120° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 3.15283 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation ($\Delta H_f^\circ{}_{298.15}$) for $B_2O_3(g)$ was calculated from the values of $\Delta H_f^\circ{}_{298.15}$ and $\Delta H_v^\circ{}_{298.15}$ for $B_2O_3(l)$. The $\Delta H_v^\circ{}_{298.15}$ value was obtained from the analyses of the vapor pressure data of $B_2O_3(l)$ by both the second and third law methods. Ten sets vapor pressure data were employed for examination. The results obtained are presented as follows.

Investigator	Temperature, °K.	$\Delta H_v^\circ{}_{298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H_f^\circ{}_{298.15}$* kcal. mole^{-1}
Cole and Taylor[1]	1473 - 1673	87.77	72.92 ± 2.3	-211.51
Speiser, et al.[2]	1331 - 1642	99.25	87.10 ± 1.8	-200.03
Soulen, et al.[3]	1567 - 1808	98.49	65.87 ± 7.8	-200.79
Searcy and Myers[4]	1501 - 1566	98.70	101.3 ±12.5	-200.58
Scheer[5]	1414 - 1621	101.89	95.25 ± 0.9	-197.39
Nesmeyanov and Firsova[6]	1299 - 1515	98.86	82.36 ± 2.9	-200.42
White, et al.[7]	1220 - 1641	99.36	90.52 ± 0.6	-199.92
Sommer[8]	1228 - 1641	99.63	93.08 ± 0.7	-199.65
Blackburn[9]	1325 - 1547	99.43	92.78 ± 1.4	-199.85
Hildenbrand, et al.[10]	1436 - 1584	100.14	100.75 ± 1.1	-199.14
Büchler, et al.[11]	1300	—	100.2 ± 3.0	-199.08

*All calculations based on the third law values listed except the last one.

[1] S. S. Cole and N. W. Taylor, J. Am. Ceram. Soc. 18, 82 (1935).

[2] R. Speiser, S. Naiditch and H. L. Johnston, J. Am. Chem. Soc. 72, 2578 (1950).

[3] J. R. Soulen, P. Sthapitanonda and J. L. Margrave, J. Phys. Chem. 59, 132 (1955).

[4] A. W. Searcy and C. E. Myers, J. Phys. Chem. 61, 957 (1957).

[5] M. D. Sheer, J. Phys. Chem. 61, 1184 (1957).

[6] A. N. Nesmeyanov and L. P. Firsova, Russ. J. Phys. Chem. 34, 490 (1960).

[7] D. White, P. N. Walsh, H. W. Goldstein and D. F. Dever, J. Phys. Chem. 65, 1404 (1961).

[8] A. Sommer, Ph. D. Thesis, The Ohio State University, 1962.

[9] P. E. Blackburn, "Research on Thermodynamics of the Al-B-O and Be-B-O Systems, "Quarterly Report No. 4, Mar. 1 - May 31, 1963, Arthur D. Little, Inc.

[10] D. L. Hildenbrand, W. F. Hall and N. D. Potter, J. Chem. Phys. 39, 296 (1963).

[11] A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. 39, 286 (1963).

The free energy functions of $B_2O_3(g)$ used for calculation are obtained using two estimated vibrational frequencies, 172 and 460 cm.$^{-1}$. Similar evaluations were made using 259 and 460 cm.$^{-1}$ instead, each corresponding third law values of ΔH_v° obtained was lower by more than 1 kcal. mole^{-1} than that of the previous ones. The value of $\Delta H_v^\circ{}_{298.15}$ for $B_2O_3(g)$ adopted is the third law value based on the vapor pressures reported by D. L. Hildenbrand, W. F. Hall and N. D. Potter, loc. cit.

Heat Capacity and Entropy.

The bond distances were reported by P. A. Akishin and V. P. Spridinov, Doklady Akad. Nauk. S.S.S.R. 131, 557 (1960). The bond angle was taken from W. Weltner, Jr. and J. R. W. Warn, J. Chem. Phys. 37, 292 (1962). The vibrational frequencies were obtained from A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys. 38, 87 (1963) and corrected to the average isotopic species. The three principal moments of inertia are: I_A = 3.10959 X 10^{-38}, I_B = 2.9758 X 10^{-39} and I_C = 3.40717 X 10^{-38} g. cm.^{2}

B_2O_3

Lead Diborate (PbB_2O_4)

(Crystal) Mol. Wt. = 292.85

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	25.600	31.200	31.200	.000	- 372.000	- 346.628	254.073
300	25.700	31.359	31.200	.047	- 372.001	- 346.471	252.892
400	30.980	39.501	32.275	2.890	- 371.876	- 337.972	184.651
500	35.180	46.875	34.469	6.203	- 371.524	- 329.533	144.032
600	38.830	53.623	37.107	9.909	- 370.968	- 321.183	116.985
700	41.790	59.838	39.916	13.945	- 371.390	- 312.751	97.640
800	44.140	65.578	42.770	18.246	- 370.496	- 304.436	83.164
900	45.970	70.886	45.603	22.755	- 369.461	- 296.239	71.933
1000	47.420	75.807	48.380	27.427	- 368.319	- 288.160	62.974
1100	48.570	80.383	51.084	32.228	- 367.103	- 280.206	55.669
1200	49.480	84.649	53.706	37.132	- 365.824	- 272.359	49.601
1300	50.210	88.639	56.241	42.118	- 364.506	- 264.625	44.485
1400	50.830	92.383	58.690	47.170	- 363.161	- 256.992	40.116
1500	51.420	95.911	61.055	52.283	- 361.796	- 249.458	36.344
1600	51.930	99.246	63.339	57.451	- 360.415	- 242.012	33.056
1700	52.380	102.408	65.545	62.667	- 359.022	- 234.653	30.165
1800	52.800	105.414	67.677	67.926	- 357.625	- 227.380	27.606
1900	53.200	108.279	69.739	73.226	- 356.219	- 220.183	25.326
2000	53.580	111.018	71.735	78.565	- 354.801	- 213.061	23.281

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

LEAD DIBORATE (PbB_2O_4) (CRYSTAL) MOL. WT. = 292.85

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [31.2 ± 3] cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15}$ = -372 ± 1.5 kcal. mole^{-1}

Heat of Formation.

W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system. L. Shartsis and E. Newman, J. Am. Ceram. Soc. 31, 213 (1948) measured heats of solution of the lead borate glasses in 2 N HNO_3. In their phase studies C. Mazzetti and F. De Carli, Gazz. chim. ital. 56, 19 (1926) established that the compounds formed were $PbO\cdot B_2O_3$, $PbO\cdot 2B_2O_3$, $PbO\cdot 3B_2O_3$ and 2 $PbO\cdot 5B_2O_3$. From the Shartsis and Newman paper loc. cit. Evans obtained the following:

$$PbO(c) + B_2O_3(c) \rightarrow PbO\cdot B_2O_3(gls.) \qquad \Delta H_r = -16.2 \text{ kcal. mole}^{-1}$$

and estimated a $\Delta H_{298.15}$ of 7.0 kcal. mole^{-1} for the conversion to the $PbO\cdot B_2O_3$(crystal). With auxiliary JANAF values the $\Delta H_f^\circ{}_{298.15}$ was calculated to be -372 kcal./mole. The results of B. M. Lepinskikh and O. A. Esin, Zhur. Neorg. Khim. 6, 1223 (1961) studying the lead borate system at 1000°K. with cells of the type $Pb(liq.)/PbO,B_2O_3/$ $/Pt/ O_2(g)$ were in fair agreement with the results of Shartsis and Newman.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities for B_2O_3 and PbO.

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the consituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:

$$MO + B_2O_3 \rightarrow MO\cdot B_2O_3$$

that the simple addition of entropies will give values at least 2.7 e.u. too low for the reaction. The reason for this is propably structural, the $B_2O_4^{--}$ ion is a flexible chain. Therefore, the $S^\circ_{298.15}$ for PbB_2O_4 was obtained from the summation of JANAF $S^\circ_{298.15}$ for constituent oxides and the addition of 2.7 e.u.

Titanium Diboride (TiB_2)

(Crystal) Mol. Wt. = 69.522

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.333	-66.399	-66.399	INFINITE
100	1.798	.602	13.472	-1.287	-66.499	-66.347	144.995
200	6.722	3.357	7.662	-.861	-66.691	-66.116	72.245
298	10.583	6.808	6.808	.000	-66.800	-65.808	48.236
300	10.641	6.874	6.808	.020	-66.801	-65.802	47.934
400	13.119	10.310	7.260	1.220	-66.865	-65.459	35.763
500	14.739	13.422	8.187	2.618	-66.942	-65.099	28.453
600	15.814	16.208	9.296	4.147	-67.036	-64.721	23.573
700	16.610	18.708	10.465	5.770	-67.139	-64.328	20.083
800	17.225	20.966	11.639	7.462	-67.247	-63.919	17.461
900	17.814	23.029	12.791	9.214	-67.352	-63.496	15.418
1000	18.377	24.936	13.912	11.024	-67.452	-63.062	13.782
1100	18.914	26.713	14.995	12.889	-67.549	-62.620	12.441
1200	19.427	28.380	16.042	14.806	-68.586	-62.129	11.315
1300	19.914	29.955	17.052	16.773	-68.665	-61.589	10.354
1400	20.375	31.448	18.028	18.788	-68.734	-61.041	9.528
1500	20.810	32.868	18.970	20.848	-68.796	-60.491	8.813
1600	21.219	34.225	19.881	22.949	-68.852	-59.933	8.186
1700	21.602	35.523	20.764	25.090	-68.902	-59.376	7.633
1800	21.959	36.768	21.618	27.269	-68.944	-58.816	7.141
1900	22.290	37.964	22.447	29.481	-68.979	-58.251	6.700
2000	22.595	39.115	23.252	31.726	-72.677	-57.591	6.293
2100	22.874	40.224	24.034	34.000	-72.633	-56.835	5.915
2200	23.127	41.294	24.794	36.300	-72.573	-56.084	5.571
2300	23.354	42.327	25.534	38.624	-72.499	-55.336	5.258
2400	23.555	43.326	26.255	40.969	-72.414	-54.594	4.971
2500	23.755	44.291	26.957	43.335	-83.090	-53.633	4.688
2600	23.955	45.227	27.642	45.720	-82.965	-52.461	4.410
2700	24.155	46.135	28.310	48.126	-82.819	-51.288	4.151
2800	24.355	47.017	28.963	50.551	-82.654	-50.126	3.912
2900	24.555	47.875	29.600	52.997	-82.468	-48.961	3.690
3000	24.755	48.711	30.223	55.462	-82.263	-47.814	3.483
3100	24.955	49.526	30.833	57.948	-82.037	-46.669	3.290
3200	25.155	50.321	31.429	60.453	-81.792	-45.532	3.110
3300	25.355	51.098	32.014	62.979	-81.526	-44.398	2.940
3400	25.555	51.858	32.586	65.524	-81.241	-43.280	2.782
3500	25.755	52.602	33.148	68.090	-80.935	-42.173	2.633
3600	25.955	53.330	33.698	70.675	-183.072	-39.622	2.405
3700	26.155	54.044	34.238	73.281	-182.746	-35.641	2.105
3800	26.355	54.744	34.769	75.906	-182.415	-31.665	1.821
3900	26.555	55.431	35.290	78.552	-182.077	-27.707	1.553
4000	26.755	56.106	35.802	81.217	-424.090	-19.466	1.063

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

TITANIUM DIBORIDE (TiB_2) (CRYSTAL) MOL. WT. = 69.522

$\Delta H^\circ_{f\ 0}$ = -66.4 ± 4.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = 6.808 ± 0.1 cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = -66.8 ± 4.0 kcal. mole^{-1}

T_m = 3193°K. ΔH°_m = [24] kcal. mole^{-1}

Heat of Formation.

G. M. Kibler, T. F. Lyon, M. J. Linevsky, and V. J. DeSantis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vapor pressure of the reaction $TiB_2(c) + 1/2\ C(c) = Ti(g) + 1/2\ B_4C(c)$ by comparing the absorption intensity of the 3371.45Å Ti resonance line of the above reaction at temperature T_1 to Ti (g) over pure titanium metal at temperature T_2. Using JANAF auxiliary data ΔF°_{2475} = 81.612 kcal. mole^{-1} for the above reaction and $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -66.9 kcal. mole^{-1} were calculated.

W. S. Williams, J. Phys. Chem. 65, 2213 (1961) found 2150 ± 25°K. to be the temperature at which $TiB_2(c)$ was formed from a mixture of TiN(c) and BN(c). If ΔF°_{2150} = 0 is assumed for the reaction $TiN(c) + 2BN(c) = TiB_2(c) + 3/2\ N_2(g)$ then $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -70.7 kcal. mole^{-1}. If, however, $N_2(g)$ is 1/2 atm. then ΔF°_{2150} = 4.4 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -66.3 kcal. mole^{-1}. He has also shown by stability comparisons that ΔF and $\Delta H > 0$ for the reaction $TiB_2 + 3/2C = TiC + 1/2B_4C$. Thus $\Delta H^\circ_{f\ 298}\ TiB_2 < -51$ kcal. mole^{-1}.

P. O. Schissel and O. C. Trulson, J. Phys. Chem. 66, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system. Only the set of measurements without excess boron or titanium was used. The value ΔF°_{2261} = 194.9 kcal. mole^{-1} for the reaction $TiB_2(c) = Ti(g) + 2B(g)$ was obtained. This corresponds to $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -62.9 kcal. mole^{-1} using JANAF auxiliary data.

V. A. Epel'baum and M. I. Starostina, Bor Trudy Konf. Khim. Bora i Ego Soedinenii 97 (1955-pub.1958) report $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -66.85 ± 2.7 kcal. mole^{-1} from combustion calorimetry.

C. E. Lowell and W. S. Williams, Rev. Sci. Inst. 32, 1120 (1961) used high temperature calorimetry to obtain the heat of formation of $TiB_2(c)$. From their data and JANAF auxiliary data $\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -48.2 ± 5 kcal. mole^{-1} was calculated. We question the adiabaticity of the experiment and believe their value is an upper limit.

$\Delta H^\circ_{f\ 298}(TiB_2(c))$ = -66.8 ± 4 kcal. mole^{-1} was chosen as representative of the first four investigations.

Heat Capacity and Entropy.

The heat capacity of $TiB_2(c)$ has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum[1]	Adiabatic Calorimetry	5- 850°K.
Walker et al.[2]	Drop calorimeter	373- 977°K.
Southern Research Institute[3]	Drop type ice calorimeter	586-2689°K.
Mezaki[4]	Copper-block drop calorimeter	420-1180°K.
Prophet[5]	Arc-imaging furnace	1300-2150°K.
Barriault et al.[6]	Pulse-method	1733-2417°K.

[1] L. Kaufman and E. V. Clougherty, Technical Documentary Report No. RTD-TDR-63-4096 Part 1 p. 239 (Dec. 1963).

[2] B. E. Walker, C. T. Ewing, and R. R. Miller, J. Phys. Chem. 61, 1682 (1957).

[3] Southern Research Institute, Technical Documentary Report No. ASD-TDR-62-675 p. 253 (Jan. 1963).

[4] R. Mezaki, M. S. Thesis, University of Wisconsin (1961).

[5] H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.

[6] R. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).

The low temperature data of Westrum[1] and the medium range data of Walker et al.[2] were used to obtain the C_p's of this tabulation. Their data were fitted to a Shomate plot and extrapolated to 4000°K.

$S^\circ_{298.15}$ = 6.808 cal. deg.$^{-1}$ mole^{-1} was determined by Westrum[1].

Melting Data.

The melting point has been reported as 3063°, 3193°, and 3203°K. by F. W. Glaser, Trans. AIME 194, 391 (1952), B. Post, F. W. Glaser, and D. Moskowitz, Acta. Met. 2, 20 (1954), and by G. V. Samsonov and G. V. Petrash, Metallovedi Obrabotka Metalov No. 4, 19 (1955) respectively. The heat of melting is derived from an estimated ΔS_m = 2.5 cal. deg.$^{-1}$ g. atom^{-1} at 3193°K. It should be pointed out that an error of 0.5 cal. deg.$^{-1}$ g. atom^{-1} in the estimation of ΔS_m is 5 kcal. mole^{-1} in ΔH°_m.

Titanium Diboride (TiB_2)

(Liquid) Mol. Wt. = 69.522

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	10.583	13.455	13.455	.000	- 44.993	- 45.983	33.705
300	10.641	13.521	13.455	.020	- 44.994	- 45.989	33.501
400	13.119	16.957	13.907	1.220	- 45.058	- 46.311	25.302
500	14.739	20.069	14.834	2.618	- 45.135	- 46.615	20.375
600	15.814	22.855	15.943	4.147	- 45.229	- 46.902	17.083
700	16.610	25.355	17.112	5.770	- 45.332	- 47.174	14.728
800	17.225	27.613	18.286	7.462	- 45.440	- 47.429	12.956
900	17.814	29.676	19.438	9.214	- 45.545	- 47.671	11.576
1000	18.377	31.583	20.559	11.024	- 45.645	- 47.902	10.468
1100	18.914	33.360	21.642	12.889	- 45.742	- 48.125	9.561
1200	19.427	35.027	22.689	14.806	- 46.779	- 48.298	8.796
1300	19.914	36.602	23.699	16.773	- 46.858	- 48.423	8.140
1400	20.375	38.095	24.675	18.788	- 46.927	- 48.540	7.577
1500	20.810	39.515	25.617	20.848	- 46.989	- 48.654	7.089
1600	21.219	40.872	26.528	22.949	- 47.045	- 48.762	6.660
1700	21.602	42.170	27.411	25.090	- 47.095	- 48.869	6.282
1800	21.959	43.415	28.265	27.269	- 47.137	- 48.973	5.946
1900	22.290	44.611	29.094	29.481	- 47.172	- 49.074	5.644
2000	22.595	45.762	29.899	31.726	- 50.870	- 49.078	5.363
2100	26.000	46.871	30.681	34.000	- 50.826	- 48.987	5.098
2200	26.000	48.081	31.445	36.600	- 50.466	- 48.909	4.858
2300	26.000	49.237	32.193	39.200	- 50.116	- 48.847	4.641
2400	26.000	50.343	32.927	41.800	- 49.776	- 48.797	4.443
2500	26.000	51.405	33.645	44.400	- 60.218	- 48.546	4.244
2600	26.000	52.424	34.347	47.000	- 59.878	- 48.087	4.042
2700	26.000	53.406	35.035	49.600	- 59.538	- 47.639	3.856
2800	26.000	54.351	35.708	52.200	- 59.198	- 47.206	3.684
2900	26.000	55.263	36.367	54.800	- 58.858	- 46.777	3.525
3000	26.000	56.145	37.012	57.400	- 58.518	- 46.371	3.378
3100	26.000	56.997	37.643	60.000	- 58.178	- 45.971	3.241
3200	26.000	57.823	38.261	62.600	- 57.838	- 45.586	3.113
3300	26.000	58.623	38.865	65.200	- 57.498	- 45.203	2.993
3400	26.000	59.399	39.458	67.800	- 57.158	- 44.837	2.882
3500	26.000	60.153	40.039	70.400	- 56.818	- 44.484	2.778
3600	26.000	60.885	40.608	73.000	- 158.940	- 42.689	2.591
3700	26.000	61.598	41.165	75.600	- 158.620	- 39.466	2.331
3800	26.000	62.291	41.712	78.200	- 158.314	- 36.243	2.084
3900	26.000	62.966	42.249	80.800	- 158.022	- 33.039	1.851
4000	26.000	63.625	42.775	83.400	- 400.100	- 25.552	1.396
4100	26.000	64.267	43.291	86.000	- 399.371	- 16.198	.863
4200	26.000	64.893	43.798	88.600	- 398.652	- 6.851	.356
4300	26.000	65.505	44.296	91.200	- 397.947	2.464	- .125
4400	26.000	66.103	44.785	93.800	- 397.255	11.769	- .585
4500	26.000	66.687	45.265	96.400	- 396.574	21.057	- 1.023
4600	26.000	67.258	45.737	99.000	- 395.903	30.333	- 1.441
4700	26.000	67.818	46.201	101.600	- 395.245	39.589	- 1.841
4800	26.000	68.365	46.657	104.200	- 394.598	48.840	- 2.224
4900	26.000	68.901	47.105	106.800	- 393.962	58.063	- 2.590
5000	26.000	69.426	47.546	109.400	- 393.334	67.286	- 2.941
5100	26.000	69.941	47.981	112.000	- 392.719	76.491	- 3.278
5200	26.000	70.446	48.408	114.600	- 392.111	85.685	- 3.601
5300	26.000	70.941	48.828	117.200	- 391.512	94.869	- 3.912
5400	26.000	71.427	49.242	119.800	- 390.924	104.040	- 4.211
5500	26.000	71.904	49.650	122.400	- 390.342	113.210	- 4.498
5600	26.000	72.373	50.052	125.000	- 389.770	122.344	- 4.774
5700	26.000	72.833	50.447	127.600	- 389.207	131.488	- 5.041
5800	26.000	73.285	50.837	130.200	- 388.651	140.616	- 5.298
5900	26.000	73.730	51.221	132.800	- 388.101	149.737	- 5.546
6000	26.000	74.167	51.600	135.400	- 387.559	158.855	- 5.786

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

TITANIUM DIBORIDE (TiB_2) (LIQUID) MOL. WT. = 69.522

$S^\circ_{298.15}$ = [13.455] cal. deg.$^{-1}$ mole^{-1}

T_m = 3193°K.

T_d = [4250]°K.

$\Delta H^\circ_{f\ 298.15}$ = [-44.99] kcal. mole^{-1}

ΔH°_m [24] kcal. mole^{-1}

<u>Heat of Formation</u>.

$\Delta H^\circ_{f\ 298.15}(l)$ was calculated from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_{Tm} and the difference between $\Delta H^\circ_{Tm}-H^\circ_{298.15}$ for crystal and liquid.

<u>Heat Capacity and Entropy</u>.

A glass transition is assumed at 2100°K. $C_p(l)$ at and below 2100°K. were assumed to be equal to those of $TiB_2(c)$. Above 2100°K. the heat capacities were estimated to be constant. $S^\circ_{298.15}(l)$ is calculated based on $S^\circ_{298.15}(c)$ and an estimated ΔS°_m = 2.5 cal. deg.$^{-1}$ gm. atom^{-1}.

<u>Melting Data</u>.

See $TiB_2(c)$ table for details.

<u>Decomposition Data</u>.

T_d estimated from ΔF°_{Td} = 0 for the reaction $TiB_2(l) = Ti(g) + 2B(g)$.

Zirconium Diboride (ZrB_2)

(Crystal)   Mol. Wt. = 112.842

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.590	-76.789	-76.789	INFINITE
100	2.870	1.177	16.207	-1.503	-76.926	-76.690	167.599
200	7.840	4.716	9.536	-.964	-77.070	-76.388	83.469
298	11.530	8.590	8.590	.000	-77.100	-76.049	55.743
300	11.589	8.662	8.590	.021	-77.100	-76.042	55.394
400	13.744	12.328	9.076	1.301	-77.099	-75.691	41.354
500	14.970	15.538	10.054	2.742	-77.155	-75.334	32.927
600	15.729	18.338	11.207	4.279	-77.272	-74.959	27.302
700	16.259	20.804	12.405	5.879	-77.429	-74.561	23.278
800	16.661	23.002	13.595	7.526	-77.610	-74.140	20.253
900	16.991	24.984	14.752	9.209	-77.804	-73.695	17.895
1000	17.245	26.788	15.867	10.921	-78.016	-73.225	16.003
1100	17.489	28.443	16.936	12.657	-78.258	-72.737	14.451
1200	17.733	29.975	17.959	14.419	-79.472	-72.174	13.144
1300	17.977	31.404	18.939	16.204	-79.729	-71.557	12.029
1400	18.221	32.745	19.878	18.014	-79.995	-70.917	11.070
1500	18.465	34.011	20.778	19.848	-80.271	-70.263	10.237
1600	18.709	35.210	21.643	21.707	-80.553	-69.582	9.504
1700	18.953	36.352	22.475	23.590	-80.843	-68.890	8.856
1800	19.197	37.442	23.276	25.498	-81.134	-68.178	8.278
1900	19.441	38.486	24.050	27.429	-81.425	-67.450	7.758
2000	19.685	39.490	24.797	29.386	-81.710	-66.708	7.289
2100	19.929	40.456	25.520	31.366	-81.990	-65.950	6.863
2200	20.173	41.389	26.220	33.372	-87.164	-65.015	6.458
2300	20.417	42.291	26.899	35.401	-87.435	-64.003	6.081
2400	20.661	43.165	27.559	37.455	-87.691	-62.976	5.734
2500	20.905	44.013	28.200	39.533	-98.705	-61.722	5.395
2600	21.149	44.838	28.824	41.636	-98.912	-60.242	5.064
2700	21.393	45.641	29.432	43.763	-99.095	-58.749	4.755
2800	21.637	46.423	30.025	45.915	-99.253	-57.253	4.469
2900	21.881	47.187	30.604	48.090	-99.388	-55.745	4.201
3000	22.125	47.933	31.169	50.291	-99.497	-54.242	3.951
3100	22.369	48.662	31.722	52.515	-99.583	-52.735	3.718
3200	22.613	49.376	32.262	54.765	-99.643	-51.221	3.498
3300	22.857	50.076	32.791	57.038	-99.680	-49.705	3.292
3400	23.101	50.762	33.310	59.336	-99.692	-48.189	3.097
3500	23.345	51.435	33.818	61.658	-99.680	-46.679	2.915
3600	23.589	52.096	34.317	64.005	-99.643	-45.164	2.742
3700	23.833	52.745	34.806	66.376	-99.582	-43.649	2.578
3800	24.077	53.384	35.287	68.772	-99.496	-42.135	2.423
3900	24.321	54.013	35.759	71.191	-99.387	-40.633	2.277
4000	24.565	54.632	36.223	73.636	-341.610	-34.838	1.903

Sept. 30, 1962; Mar. 31, 1963; June 30, 1965

ZIRCONIUM DIBORIDE (ZrB_2)   (CRYSTAL)   MOL. Wt. = 112.842

$\Delta H^\circ_{f\ 0}$ = -76.8 ± 1.6 kcal. mole^{-1}

$S^\circ_{298.15}$ = 8.59 ± 0.01 cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = -77.1 ± 1.6 kcal. mole^{-1}

T_m = 3323°K. ΔH°_m = [25] kcal. mole^{-1}

Heat of Formation.

G. K. Johnson, Argonne National Laboratory, private communication, May 1965, reported $\Delta H^\circ_{f\ 298}$ ($ZrB_{1.999\ \pm\ 0.006}$) = -78.7 ± 1.5 kcal. mole^{-1}. Their value was obtained by fluorine bomb calorimetry and was based on their recently redetermined value of $\Delta H^\circ_{f\ 298}(BF_3(g))$ = -271.80 ± 0.20 kcal. mole^{-1}.

G. M. Kibler, T. F. Lyon, M. J. Linevsky, and V. J. De Santis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vaporization of $ZrB_{1.931}$ by the Knudsen effusion method. Over the range 2260 to 2500°K., log K_p = 22.038 - $\frac{10.164 \times 10^4}{T}$ for the reaction $ZrB_{1.931}$ (c) = Zr (g) + 1.931 B (g). JANAF auxiliary data were used to calculate $\Delta H^\circ_{r\ 298}$ = 478.5 ± 1.5 kcal. mole^{-1} by the 3rd law method and $\Delta H^\circ_{f\ 298}$ ($ZrB_{1.931}$(c)) = -76.7 ± 3.2 kcal. mole^{-1}.

O. C. Trulson and H. W. Goldstein, Union Carbide Res. Inst., report No. C-25 (October 1964), investigated the decomposition vapor pressure of the reaction ZrB_2 (c) = Zr (g) + 2B (g) and reported $\Delta H^\circ_{f\ 298}$ (ZrB_2(c)) = -72.1 ± 5.3 kcal. mole^{-1}. They also reported $\Delta H^\circ_{r\ 298}$ = 289.7 kcal. mole^{-1} for the reaction ZrB_2(c) + C (c) = ZrC(c) + 2B (g). Using the JANAF $\Delta H^\circ_{f\ 298}$ (ZrC(c)) = -47.0 ± 3 kcal. mole^{-1}, $\Delta H^\circ_{f\ 298}$ (ZrB_2(c)) = -76.1 ± 3 kcal. mole^{-1} was calculated. JANAF values for $\Delta H^\circ_{v\ 298}$ B (g) and Zr (g) were not used since their independent determinations serve to cancel instrumental constants.

From oxygen bomb calorimetry, E. J. Huber, Jr., E. L. Head, and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) reported $\Delta H^\circ_{f\ 298}$(ZrB_2(c)) = -77.2 ± 1.2 kcal. mole^{-1}.

$\Delta H^\circ_{f\ 298}$(ZrB_2(c)) = -77.1 ± 1.6 was chosen as a value representative of the above.

Heat Capacity and Entropy.

The heat capacity of ZrB_2(c) has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum and Feick[1]	Adiabatic calorimetry	5- 350°K.
Valentine et al.[2]	Copper-block drop calorimeter	410-1125°K.
Mezaki[3]	Copper-block drop calorimeter	430-1170°K.
Prophet[4]	Arc-imaging furnace	1300-2150°K.
Barriault et al.[5]	Pulse-method	1740-2520°K.
Southern Research Institute[6]	Drop type ice calorimeter	500-2500°K.

[1] E. F. Westrum, Jr. and G. Feick, J. Chem. Eng. Data 8(2), 193 (1963).

[2] R. H. Valentine, T. F. Jambois, and J. L. Margrave, J. Chem. Eng. Data 9(2), 182 (1964).

[3] R. Mezaki, M. S. Thesis, University of Wisconsin (1961).

[4] H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.

[5] R. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).

[6] D. Neel, C. Pears, and S. Oglesby, Southern Research Institute, report ASD-TRD-62-675 (August 1962).

Westrum and Feick's[1] C_p values were adopted to 350°K. The disparities in heat capacities above room temperatures seem too great to be errors in measurement and are probably due to sample differences. Since the samples used by Westrum and Feick[1] and by Valentine et al.[2] were from the same batch, Valentine's data were used above 350°K. The two sets of data were fitted to a Shomate plot which was extrapolated to 4000°K. However, in consideration of the results of Mezaki[3], Prophet[4] and Southern Research Institute[6], the C_p extrapolation ran somewhat higher than a direct extrapolation of Valentine's data would yield.

$S^\circ_{298.15}(ZrB_2)$ = 8.59 cal. mole^{-1} °K.$^{-1}$ was determined by Westrum[1].

Melting Data.

The melting point has been reported as 3313°, 3323°, and 3265°K. by F. Glaser and B. Post, J. of Metals, 5, 1117 (1953), B. Post, F. Glaser, and D. W. Moskowitz, Acta. Met. 2, 70 (1954) and H. Greenwood, Engineer 187, 349 (1949) respectively. The heat of melting is derived from an estimated ΔS_m = 2.5 cal. deg.$^{-1}$ g. atom^{-1} at 3323°K. It should be pointed out that an error of 0.5 cal. deg.$^{-1}$ g. atom^{-1} in the estimation of ΔS_m is 5 kcal. mole^{-1} in ΔH°_m.

Zirconium Diboride (ZrB_2)

(Liquid) Mol. Wt. = 112.842

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	11.530	15.448	15.448	.000	-54.194	-55.187	40.452
300	11.589	15.520	15.448	.021	-54.194	-55.194	40.207
400	13.744	19.186	15.934	1.301	-54.193	-55.528	30.338
500	14.970	22.396	16.912	2.742	-54.249	-55.857	24.414
600	15.729	25.196	18.065	4.279	-54.366	-56.168	20.458
700	16.259	27.662	19.263	5.879	-54.523	-56.456	17.625
800	16.661	29.860	20.453	7.526	-54.704	-56.720	15.495
900	16.991	31.842	21.610	9.209	-54.898	-56.961	13.831
1000	17.245	33.646	22.725	10.921	-55.110	-57.177	12.495
1100	17.489	35.301	23.794	12.657	-55.352	-57.374	11.399
1200	17.733	36.833	24.817	14.419	-56.566	-57.498	10.471
1300	17.977	38.262	25.797	16.204	-56.823	-57.567	9.677
1400	18.221	39.603	26.736	18.014	-57.089	-57.613	8.993
1500	18.465	40.869	27.636	19.848	-57.365	-57.644	8.398
1600	18.709	42.068	28.501	21.707	-57.647	-57.649	7.874
1700	18.953	43.210	29.333	23.590	-57.937	-57.643	7.410
1800	19.197	44.300	30.134	25.498	-58.228	-57.616	6.995
1900	19.441	45.344	30.908	27.429	-58.519	-57.574	6.622
2000	19.685	46.348	31.655	29.386	-58.804	-57.518	6.285
2100	19.929	47.314	32.378	31.366	-59.084	-57.446	5.978
2200	23.000	48.247	33.078	33.372	-64.258	-57.196	5.682
2300	23.000	49.269	33.760	35.672	-64.258	-56.875	5.404
2400	23.000	50.248	34.426	37.972	-64.268	-56.552	5.150
2500	23.000	51.187	35.078	40.272	-75.060	-56.013	4.896
2600	23.000	52.089	35.715	42.572	-75.070	-55.253	4.644
2700	23.000	52.957	36.338	44.872	-75.080	-54.487	4.410
2800	23.000	53.793	36.946	47.172	-75.090	-53.726	4.193
2900	23.000	54.601	37.541	49.472	-75.100	-52.959	3.991
3000	23.000	55.380	38.123	51.772	-75.110	-52.196	3.802
3100	23.000	56.134	38.692	54.072	-75.120	-51.436	3.626
3200	23.000	56.865	39.249	56.372	-75.130	-50.673	3.461
3300	23.000	57.572	39.793	58.672	-75.140	-49.902	3.305
3400	23.000	58.259	40.326	60.972	-75.150	-49.137	3.158
3500	23.000	58.926	40.848	63.272	-75.160	-48.378	3.021
3600	23.000	59.574	41.359	65.572	-75.170	-47.612	2.890
3700	23.000	60.204	41.860	67.872	-75.180	-46.846	2.767
3800	23.000	60.817	42.351	70.172	-75.190	-46.075	2.650
3900	23.000	61.415	42.832	72.472	-75.200	-45.315	2.539
4000	23.000	61.997	43.304	74.772	-317.568	-40.256	2.199
4100	23.000	62.565	43.767	77.072	-317.116	-33.331	1.777
4200	23.000	63.119	44.221	79.372	-316.662	-26.405	1.374
4300	23.000	63.660	44.667	81.672	-316.210	-19.502	.991
4400	23.000	64.189	45.105	83.972	-315.760	-12.609	.626
4500	23.000	64.706	45.535	86.272	-315.310	-5.728	.278
4600	23.000	65.212	45.957	88.572	-314.860	1.146	-.054
4700	23.000	65.706	46.372	90.872	-314.412	8.017	-.373
4800	23.000	66.190	46.780	93.172	-450.399	16.401	-.747
4900	23.000	66.665	47.181	95.472	-450.010	26.108	-1.164
5000	23.000	67.129	47.575	97.772	-449.626	35.829	-1.566
5100	23.000	67.585	47.963	100.072	-449.250	45.531	-1.951
5200	23.000	68.031	48.345	102.372	-448.879	55.235	-2.321
5300	23.000	68.470	48.720	104.672	-448.515	64.912	-2.677
5400	23.000	68.899	49.090	106.972	-448.158	74.605	-3.019
5500	23.000	69.321	49.454	109.272	-447.804	84.288	-3.349
5600	23.000	69.736	49.812	111.572	-447.458	93.950	-3.666
5700	23.000	70.143	50.165	113.872	-447.118	103.616	-3.973
5800	23.000	70.543	50.513	116.172	-446.784	113.275	-4.268
5900	23.000	70.936	50.856	118.472	-446.453	122.932	-4.553
6000	23.000	71.323	51.194	120.772	-446.128	132.578	-4.829

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

ZIRCONIUM DIBORIDE (ZrB_2) (LIQUID) MOL. WT. = 112.842

$S^\circ_{298.15}$ = [15.448] cal. deg.$^{-1}$ mole^{-1}

T_m = 3323°K.

T_d = [4466]°K.

$\Delta H^\circ_{f\ 298.15}$ = [-54.194] kcal. mole^{-1}

ΔH°_m = [25] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}(l)$ was calculated from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_{Tm} and the difference between $\Delta H^\circ_{Tm}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2200°K. $C_p(l)$ at and below 2200°K. were assumed to be equal to those of $ZrB_2(c)$. Above 2200°K. the heat capacities were estimated to be constant. $S^\circ_{298.15}$ (c) and an estimated ΔS°_m = 2.5 cal. deg.$^{-1}$ gm. atom^{-1}.

Melting Data.

See $ZrB_2(c)$ table for details.

Decomposition Data.

T_d estimated from ΔF°_{Td} = 0 for the reaction $ZrB_2(l) = Zr(g) + 2B(g)$.

Boron Oxide Chloride, Trimeric $((BOCl)_3)$
(Ideal Gas) Mol. Wt. = 186.831

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-6.057	-388.778	-388.778	INFINITE
100	16.750	65.733	114.858	-4.912	-389.772	-383.314	837.693
200	25.199	80.088	94.052	-2.793	-389.994	-376.742	411.664
298	31.436	91.367	91.367	.000	-390.000	-370.238	271.379
300	31.538	91.562	91.367	.058	-389.999	-370.117	269.617
400	36.260	101.318	92.666	3.461	-389.874	-363.505	198.600
500	39.618	109.792	95.262	7.265	-389.685	-356.933	156.008
600	41.975	117.236	98.317	11.351	-389.459	-350.402	127.628
700	43.646	123.839	101.500	15.637	-389.206	-343.912	107.369
800	44.854	129.750	104.669	20.065	-388.939	-337.463	92.186
900	45.747	135.087	107.757	24.597	-388.660	-331.045	80.385
1000	46.421	139.943	110.736	29.207	-388.387	-324.655	70.950
1100	46.940	144.393	113.597	33.876	-388.134	-318.298	63.237
1200	47.347	148.496	116.336	38.591	-387.898	-311.958	56.813
1300	47.672	152.299	118.958	43.343	-387.687	-305.640	51.380
1400	47.934	155.842	121.468	48.124	-387.499	-299.334	46.726
1500	48.149	159.156	123.871	52.928	-387.343	-293.045	42.695
1600	48.327	162.270	126.174	57.752	-387.215	-286.761	39.168
1700	48.476	165.204	128.385	62.593	-387.116	-280.483	36.057
1800	48.602	167.978	130.508	67.447	-387.047	-274.215	33.293
1900	48.709	170.609	132.550	72.312	-387.001	-267.946	30.819
2000	48.802	173.110	134.516	77.188	-386.975	-261.682	28.594
2100	48.881	175.493	136.411	82.072	-386.966	-255.417	26.580
2200	48.951	177.769	138.240	86.964	-386.979	-249.154	24.750
2300	49.012	179.946	140.006	91.862	-387.008	-242.888	23.079
2400	49.065	182.033	141.714	96.766	-387.059	-236.616	21.546
2500	49.113	184.037	143.367	101.675	-403.291	-230.024	20.108
2600	49.155	185.964	144.968	106.588	-403.353	-223.091	18.752
2700	49.193	187.820	146.521	111.506	-403.425	-216.154	17.496
2800	49.227	189.610	148.028	116.427	-403.505	-209.220	16.330
2900	49.257	191.337	149.492	121.351	-403.592	-202.270	15.243
3000	49.285	193.008	150.915	126.278	-403.688	-195.334	14.229
3100	49.310	194.624	152.299	131.208	-403.793	-188.388	13.281
3200	49.332	196.190	153.646	136.140	-403.906	-181.438	12.391
3300	49.353	197.709	154.959	141.074	-404.029	-174.482	11.555
3400	49.372	199.182	156.238	146.011	-404.159	-167.519	10.768
3500	49.389	200.614	157.485	150.949	-404.299	-160.571	10.026
3600	49.405	202.005	158.703	155.888	-404.446	-153.594	9.324
3700	49.419	203.359	159.892	160.829	-404.602	-146.625	8.660
3800	49.433	204.677	161.053	165.772	-404.763	-139.647	8.031
3900	49.445	205.961	162.188	170.716	-404.933	-132.676	7.435
4000	49.457	207.213	163.298	175.661	-768.649	-119.257	6.516
4100	49.468	208.435	164.384	180.607	-768.140	-103.033	5.492
4200	49.478	209.627	165.447	185.555	-767.634	-86.807	4.517
4300	49.487	210.791	166.488	190.503	-767.136	-70.603	3.588
4400	49.496	211.929	167.508	195.452	-766.648	-54.409	2.702
4500	49.504	213.041	168.508	200.402	-766.165	-38.234	1.857
4600	49.512	214.129	169.488	205.353	-765.684	-22.055	1.048
4700	49.519	215.194	170.449	210.304	-765.213	-5.890	.274
4800	49.525	216.237	171.392	215.257	-764.747	10.261	-.467
4900	49.532	217.258	172.317	220.209	-764.289	26.390	-1.177
5000	49.538	218.259	173.226	225.163	-763.832	42.523	-1.859
5100	49.543	219.240	174.119	230.117	-763.384	58.654	-2.513
5200	49.548	220.202	174.996	235.072	-762.938	74.763	-3.142
5300	49.553	221.146	175.858	240.027	-762.498	90.865	-3.747
5400	49.558	222.072	176.705	244.982	-762.067	106.958	-4.329
5500	49.562	222.982	177.538	249.938	-761.635	123.065	-4.890
5600	49.567	223.875	178.358	254.895	-761.213	139.124	-5.429
5700	49.571	224.752	179.164	259.852	-760.798	155.201	-5.950
5800	49.574	225.614	179.957	264.809	-760.386	171.277	-6.454
5900	49.578	226.462	180.739	269.766	-759.979	187.328	-6.939
6000	49.581	227.295	181.508	274.724	-759.580	203.393	-7.408

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1963; June 30, 1964; Mar. 31, 1965

BORON OXIDE CHLORIDE, TRIMERIC $((BOCl)_3)$ (IDEAL GAS) MOL. WT. = 186.831

Point Group $[D_{3h}]$

$\Delta H_{f\ 0}^\circ = -389 \pm 2$ kcal. mole^{-1}

$S^\circ_{298.15} = [91.367]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -390 \pm 2$ kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[807] (1)	[980] (2)	[600] (1)
[690] (1)	[1300] (2)	[140] (1)
[333] (1)	[920] (2)	[400] (2)
[1037] (1)	[390] (2)	[120] (2)
[400] (1)	[150] (2)	

Bond Distance: B-Cl = [1.75]Å B-O = [1.36]Å

Bond Angle: Cl-B-O = [120°] B-O-B = [120°] $\sigma = 6$

Product of the Moments of Inertia: $I_AI_BI_C = [1.86850 \times 10^{-111}]$ g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constants for the reaction $B_2O_3(l) + BCl_3(g) = (BOCl)_3(g)$ were determined in the temperature range 536-825°K. by a transpiration method by J. Blauer and M. Farber, J. Chem. Phys. 39, 158 (1963); and in the temperature range 1234-1309°K. by an effusion method by the same investigators, Trans. Faraday Soc. 60, 301 (1964). Using the reported equilibrium constants, the enthalpy changes for this reaction were evaluated by both the second and third law methods. The results obtained are given in the following table.

Method Used	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H^\circ_{f\ 298.15}$* kcal. mole^{-1}
Transpiration	5.31	5.07 ± 0.4	-390 ± 2
Effusion	12.57	5.85 ± 3.3	-386 ± 3

*Based on the third law values

By a mass spectroscopic method the enthalpy change, $\Delta H^\circ_{r\ 1000} = 16.6 \pm 2.5$ kcal. mole^{-1}, for the reaction $BCl_3(g) + B_2O_3(l) = (BOCl)_3(g)$ was determined by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964). The $\Delta H^\circ_{f\ 298.15}$ value for $(BOCl)_3(g)$ was derived as -377 ± 3 kcal. mole^{-1}. However, it is possible that the intensity of $B_3O_3Cl_3^+$, employed to plot the ion ratios $I(B_3O_3Cl_3^+)/I(BCl_2^+)$ versus $\frac{1}{T}$, does not fully reflect the concentration of $B_3O_3Cl_3$ especially at the highest temperatures, due to changes in the fragmentation pattern with temperature.

The value of $\Delta H^\circ_{f\ 298.15}$ adopted for $(BOCl)_3(g)$ is -390 ± 2 kcal. mole^{-1} derived from transpiration data. The effusion data were measured in the temperature range where Porter and Gupta, loc. cit. found the presence of $(BOCl)_4(g)$. However, this point was not taken into consideration in the report. Hence, the corresponding $\Delta H^\circ_{f\ 298.15}$ value was not adopted.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with related molecules such as $B_3O_3F_3(g)$ and $(BH_2O)_3(g)$. The B-Cl bond distance was assumed to be the same as that in $BCl_3(g)$. The B-O bond distance and all bond angles were estimated. The three principal moments of inertia are: $I_A = I_B = 9.77585 \times 10^{-38}$ and $I_C = 1.95517 \times 10^{-37}$ g. cm.^{2}

Monofluoroboroxin ($B_3O_3H_2F$)

(Ideal Gas) Mol. Wt. = 101.4554

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 4.273	- 379.205	- 379.205	INFINITE
100	11.162	57.652	91.583	- 3.393	- 380.520	- 375.559	820.744
200	17.234	67.298	77.132	- 1.967	- 381.306	- 370.285	404.609
298	22.764	75.225	75.225	.000	- 382.000	- 364.731	267.342
300	22.863	75.367	75.226	.042	- 382.012	- 364.625	265.616
400	27.749	82.635	76.184	2.580	- 382.586	- 358.738	195.996
500	31.713	89.269	78.147	5.561	- 383.043	- 352.721	154.167
600	34.866	95.341	80.514	8.896	- 383.381	- 346.622	126.251
700	37.367	100.911	83.036	12.512	- 383.608	- 340.475	106.296
800	39.354	106.035	85.595	16.352	- 383.739	- 334.307	91.324
900	40.941	110.766	88.132	20.370	- 383.790	- 328.125	79.676
1000	42.218	115.148	90.617	24.530	- 383.786	- 321.936	70.356
1100	43.254	119.222	93.035	28.806	- 383.753	- 315.755	62.732
1200	44.100	123.023	95.377	33.175	- 383.695	- 309.573	56.378
1300	44.799	126.581	97.642	37.621	- 383.632	- 303.400	51.004
1400	45.380	129.923	99.830	42.131	- 383.567	- 297.229	46.397
1500	45.867	133.071	101.942	46.694	- 383.515	- 291.067	42.406
1600	46.279	136.045	103.981	51.301	- 383.477	- 284.904	38.914
1700	46.630	138.861	105.951	55.947	- 383.455	- 278.742	35.833
1800	46.930	141.535	107.854	60.626	- 383.453	- 272.586	33.095
1900	47.190	144.080	109.694	65.332	- 383.466	- 266.426	30.645
2000	47.415	146.506	111.475	70.063	- 383.491	- 260.264	28.439
2100	47.612	148.824	113.199	74.814	- 383.531	- 254.100	26.443
2200	47.785	151.043	114.869	79.584	- 383.588	- 247.936	24.629
2300	47.937	153.171	116.488	84.370	- 383.657	- 241.771	22.972
2400	48.072	155.214	118.059	89.171	- 383.746	- 235.595	21.453
2500	48.192	157.179	119.585	93.984	- 400.013	- 229.099	20.027
2600	48.299	159.071	121.068	98.809	- 400.108	- 222.259	18.682
2700	48.396	160.896	122.509	103.644	- 400.209	- 215.413	17.436
2800	48.482	162.657	123.912	108.488	- 400.316	- 208.571	16.279
2900	48.561	164.360	125.277	113.340	- 400.429	- 201.709	15.201
3000	48.632	166.008	126.608	118.200	- 400.549	- 194.865	14.195
3100	48.696	167.603	127.905	123.066	- 400.673	- 188.007	13.254
3200	48.755	169.150	129.169	127.939	- 400.806	- 181.144	12.371
3300	48.809	170.651	130.404	132.817	- 400.946	- 174.274	11.541
3400	48.858	172.109	131.609	137.700	- 401.092	- 167.403	10.760
3500	48.903	173.526	132.787	142.588	- 401.246	- 160.534	10.024
3600	48.945	174.904	133.937	147.481	- 401.406	- 153.647	9.327
3700	48.983	176.246	135.063	152.377	- 401.576	- 146.764	8.669
3800	49.019	177.553	136.164	157.277	- 401.750	- 139.869	8.044
3900	49.052	178.826	137.242	162.181	- 401.933	- 132.985	7.452
4000	49.082	180.069	138.297	167.088	- 765.660	- 119.652	6.537
4100	49.110	181.281	139.330	171.997	- 765.165	- 103.509	5.517
4200	49.137	182.465	140.343	176.910	- 764.672	- 87.366	4.546
4300	49.162	183.621	141.337	181.825	- 764.189	- 71.244	3.621
4400	49.184	184.752	142.310	186.742	- 763.718	- 55.142	2.739
4500	49.206	185.857	143.266	191.661	- 763.252	- 39.047	1.896
4600	49.226	186.939	144.204	196.583	- 762.791	- 22.950	1.090
4700	49.245	187.998	145.124	201.507	- 762.343	- 6.870	.319
4800	49.263	189.035	146.028	206.432	- 761.900	9.205	- .419
4900	49.280	190.051	146.916	211.359	- 761.468	25.249	- 1.126
5000	49.295	191.047	147.789	216.288	- 761.042	41.301	- 1.805
5100	49.310	192.023	148.647	221.218	- 760.628	57.351	- 2.458
5200	49.324	192.981	149.490	226.150	- 760.218	73.378	- 3.084
5300	49.337	193.920	150.320	231.083	- 759.817	89.413	- 3.687
5400	49.350	194.843	151.136	236.017	- 759.428	105.417	- 4.266
5500	49.362	195.748	151.939	240.953	- 759.042	121.453	- 4.826
5600	49.373	196.638	152.729	245.890	- 758.671	137.436	- 5.363
5700	49.383	197.512	153.507	250.827	- 758.309	153.441	- 5.883
5800	49.394	198.371	154.273	255.766	- 757.954	169.434	- 6.384
5900	49.403	199.215	155.028	260.706	- 757.608	185.422	- 6.868
6000	49.412	200.045	155.771	265.647	- 757.272	201.411	- 7.336

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965; Dec. 31, 1965

MONOFLUOROBOROXIN ($B_3O_3H_2F$) (IDEAL GAS) MOL. WT. = 101.44554

Point Group $[C_{2v}]$

$S^\circ_{298.15}$ = [75.225] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -379 ± 6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -382 ± 6 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[2100] (1)	[880] (1)	[350] (1)
[870] (1)	[1460] (1)	[225] (1)
[670] (1)	[520] (1)	[800] (1)
[2200] (1)	[2230] (1)	[225] (1)
[1390] (1)	[1390] (1)	[840] (1)
[1200] (1)	[1200] (1)	[800] (1)
[880] (1)	[350] (1)	[260] (1)

Bond Distance: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°] σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.1654] X 10^{-113} g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constants (K), 1246-1326°K, for the two reactions $2B_3O_3F_2H(g) = B_3O_3FH_2(g) + B_3O_3F_3(g)$ and $2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$ were reported by F. R. Porter and W. P. Sholette, J. Chem. Phys. 37, 198 (1962). The $\Delta H^\circ_{f\ 298.15}$ for $B_3O_3H_2F(g)$ adopted was evaluated by use of K values slightly outside the ranges given by Porter and Sholette. See the table for $B_3O_3F_2H(g)$ for details.

Heat Capacity and Entropy.

The structure was assumed to be a planar six membered ring structure of C_{2v} symmetry, which has 21 vibrations of the type $8A_1$, $7B_1$, $2A_2$, and $4B_2$. These frequencies were estimated from the values for boroxin and trifluoroboroxin, the symmetry being reduced from D_{3h} as follows: $3A_1' \rightarrow 3A_1$, $2A_2' \rightarrow 2B_1$, $5E' \rightarrow 5A_1 + 5B_1$, $2A_2 \rightarrow 2B_2$ and $2E'' \rightarrow 2A_2 + 2B_2$.

The B-F distance was taken as approximately equal to that in $(CH_3)_2O\cdot BF_3$ reported by S. H. Bauer, G. R. Findlay and A. W. Laubengayer, J. Am. Chem. Soc. 67, 339 (1945). The other bond lengths and angles were taken equal to those in boroxin. The individual moments of inertia were calculated to be $I_A = 32.995 \times 10^{-39}$, $I_B = 13.973 \times 10^{-39}$, and $I_C = 46.968 \times 10^{-39}$ g. cm.^{2}

Difluoroboroxin ($B_3O_3HF_2$)
(Ideal Gas) Mol. Wt. = 119.43597

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.571	-472.461	-472.461	INFINITE
100	11.771	59.643	96.365	-3.672	-473.724	-468.147	1023.084
200	18.724	69.975	80.684	-2.142	-474.455	-462.266	505.117
298	24.744	78.608	78.608	.000	-475.000	-456.169	334.365
300	24.847	78.761	78.608	.046	-475.009	-456.054	332.219
400	29.837	86.619	79.646	2.789	-475.415	-449.669	245.676
500	33.785	93.719	81.762	5.979	-475.718	-443.196	193.712
600	36.857	100.162	84.301	9.517	-475.919	-436.670	159.049
700	39.230	106.030	86.992	13.327	-476.026	-430.118	134.283
800	41.066	111.394	89.712	17.345	-476.059	-423.561	115.706
900	42.495	116.316	92.398	21.526	-476.029	-417.000	101.256
1000	43.618	120.854	95.020	25.834	-475.960	-410.441	89.698
1100	44.512	125.055	97.562	30.242	-475.878	-403.896	80.243
1200	45.230	128.960	100.018	34.731	-475.782	-397.354	72.365
1300	45.814	132.604	102.386	39.284	-475.692	-390.823	65.700
1400	46.294	136.017	104.667	43.890	-475.607	-384.296	59.988
1500	46.692	139.225	106.865	48.540	-475.540	-377.779	55.040
1600	47.026	142.250	108.983	53.226	-475.492	-371.263	50.710
1700	47.308	145.109	111.025	57.943	-475.465	-364.747	46.889
1800	47.548	147.820	112.994	62.686	-475.461	-358.238	43.494
1900	47.755	150.397	114.896	67.452	-475.474	-351.726	40.456
2000	47.933	152.851	116.733	72.236	-475.501	-345.211	37.721
2100	48.088	155.193	118.509	77.038	-475.544	-338.693	35.247
2200	48.223	157.434	120.228	81.853	-475.605	-332.177	32.997
2300	48.342	159.580	121.892	86.682	-475.680	-325.657	30.943
2400	48.448	161.640	123.506	91.521	-475.775	-319.128	29.059
2500	48.541	163.619	125.071	96.371	-492.049	-312.275	27.298
2600	48.625	165.525	126.590	101.229	-492.152	-305.083	25.643
2700	48.699	167.361	128.067	106.095	-492.261	-297.880	24.111
2800	48.766	169.134	129.502	110.969	-492.376	-290.686	22.688
2900	48.827	170.846	130.898	115.848	-492.497	-283.468	21.362
3000	48.882	172.502	132.257	120.734	-492.626	-276.266	20.125
3100	48.931	174.106	133.582	125.625	-492.759	-269.055	18.967
3200	48.976	175.660	134.872	130.520	-492.900	-261.835	17.882
3300	49.018	177.168	136.131	135.420	-493.048	-254.610	16.861
3400	49.055	178.632	137.360	140.323	-493.204	-247.382	15.901
3500	49.090	180.054	138.560	145.231	-493.366	-240.153	14.995
3600	49.122	181.437	139.732	150.141	-493.534	-232.908	14.139
3700	49.151	182.784	140.877	155.055	-493.710	-225.669	13.329
3800	49.178	184.095	141.997	159.972	-493.892	-218.415	12.561
3900	49.204	185.373	143.093	164.891	-494.082	-211.178	11.834
4000	49.227	186.619	144.166	169.812	-857.816	-197.484	10.789
4100	49.248	187.834	145.216	174.736	-857.327	-180.980	9.647
4200	49.269	189.021	146.245	179.662	-856.840	-164.478	8.558
4300	49.287	190.181	147.253	184.590	-856.361	-148.001	7.522
4400	49.305	191.314	148.242	189.519	-855.895	-131.536	6.533
4500	49.321	192.423	149.211	194.451	-855.433	-115.088	5.589
4600	49.337	193.507	150.162	199.384	-854.976	-98.632	4.686
4700	49.351	194.568	151.096	204.318	-854.531	-82.191	3.822
4800	49.364	195.607	152.013	209.254	-854.091	-65.756	2.994
4900	49.377	196.625	152.913	214.191	-853.661	-49.353	2.201
5000	49.389	197.623	153.797	219.129	-853.236	-32.941	1.440
5100	49.400	198.601	154.666	224.069	-852.824	-16.536	.709
5200	49.411	199.560	155.520	229.009	-852.415	-.143	.006
5300	49.421	200.502	156.360	233.951	-852.014	16.242	-.670
5400	49.431	201.425	157.186	238.893	-851.626	32.613	-1.320
5500	49.439	202.332	157.999	243.837	-851.240	49.006	-1.947
5600	49.448	203.223	158.798	248.781	-850.868	65.351	-2.550
5700	49.456	204.099	159.585	253.726	-850.505	81.710	-3.133
5800	49.464	204.959	160.360	258.672	-850.148	98.065	-3.695
5900	49.471	205.804	161.123	263.619	-849.800	114.411	-4.238
6000	49.478	206.636	161.875	268.567	-849.462	130.755	-4.763

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965; Dec. 31, 1965

DIFLUOROBOROXIN ($B_3O_3HF_2$) (IDEAL GAS) MOL. WT. = 119.43597

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [78.6] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -472 ± 5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -475 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[1650] (1)	[660] (1)	[300] (1)
[830] (1)	[1370] (1)	[220] (1)
[610] (1)	[490] (1)	[710] (1)
[1800] (1)	[1840] (1)	[220] (1)
[1385] (1)	[1385] (1)	[780] (1)
[1080] (1)	[1080] (1)	[700] (1)
[660] (1)	[310] (1)	[230] (1)

Bond Distance: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]

σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [7.5869] X 10^{-113} g.^{3} cm.^{6}

Heat of Formation.

The stabilities of gaseous boroxin ($B_3O_3H_3$) and its fluoro derivatives have been studied by R. F. Porter and W. P. Sholette, J. Chem. Phys. 37, 198 (1962). From the mass spectra of the gaseous reaction products generated by reaction of an H_2-BF_3 mixture on B_2O_3 at 1250°K., the equilibrium constants (K) for the following proposed reactions were reported.

	Reaction	Temperature, °K.	K	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1}
(1)	$H_2(g) + B_3O_3F_3(g) = HF(g) + B_3O_3F_2H\ (g)$	1246 - 1326	4.2 X 10^{-3} - 2.3 X 10^{-2}	20.45 - 17.17
(2)	$2B_3O_3F_2H(g) = B_3O_3FH_2(g) + B_3O_3F_3(g)$	1246 - 1326	0.62 - 0.46	1.28 - 2.15
(3)	$2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$	1246 - 1326	1.0 - 0.63	-2.56 - -1.51

Using these reported K values the corresponding enthalpy changes ($\Delta H_r^\circ{}_{298.15}$) were evaluated by the third law method. The results obtained are listed in the above table. Based on $\Delta H_f^\circ{}_{298.15}$ = -565.3 and -64.8 kcal. mole^{-1} for $B_3O_3F_3(g)$ and HF(g), respectively, the value of $\Delta H_f^\circ{}_{298.15}$ for $B_3O_3F_2H(g)$ was calculated from Reaction (1) as -482 kcal. mole^{-1}. From Reaction (2), the $\Delta H_f^\circ{}_{298.15}$ value for $B_3O_3FH_2(g)$ was calculated as -397 kcal. mole^{-1}. However, employing $\Delta H_f^\circ{}_{298.15}(B_3O_3H_3,\ g)$ = -291 kcal. mole^{-1}, the values of $\Delta H_f^\circ{}_{298.15}$ for $B_3O_3FH_2(g)$ and $B_3O_3F_2H(g)$ thus obtained do not fit properly for Reaction (3). Therefore the $\Delta H_f^\circ{}_{298.15}$ for $B_3O_3FH_2(g)$ and $B_3O_3F_2H(g)$ adopted were evaluated by use of K values slightly outside the ranges given by Porter and Sholette.

Heat Capacity and Entropy.

The vibrational frequencies were obtained by comparison with $B_3O_3F_3(g)$ and $B_3H_3O_3(g)$. The types of vibration and symmetry are identical to those given for $B_3O_3H_2F(g)$. The bond angles and lengths were taken equal to those for $B_3O_3H_2F(g)$. The individual moments of inertia were calculated to be I_A = 22.051 X 10^{-39}, I_B = 48.659 X 10^{-39} and I_C = 70.710 X 10^{-39} g. cm.^{2}

Boron Oxide Fluoride, Trimeric $((BOF)_3)$

(Crystal) Mol. Wt. = 137.46

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	30.000	52.000	52.000	- .000	- 586.500	- 557.166	408.394
300	30.085	52.186	52.001	.056	- 586.500	- 556.986	405.744
400	34.600	61.462	53.235	3.291	- 586.452	- 547.151	298.935
500	39.000	69.666	55.715	6.976	- 586.313	- 537.340	234.860
600	42.725	77.113	58.670	11.066	- 586.029	- 527.569	192.158
700	46.000	83.951	61.800	15.506	- 585.580	- 517.858	161.675
800	48.825	90.283	64.969	20.251	- 584.966	- 508.227	138.835
900	51.200	96.175	68.113	25.256	- 584.194	- 498.679	121.090
1000	53.100	101.671	71.197	30.474	- 583.299	- 489.221	106.914
1100	54.600	106.806	74.204	35.862	- 582.319	- 479.864	95.336
1200	55.650	111.604	77.123	41.377	- 581.279	- 470.592	85.702
1300	56.400	116.090	79.949	46.982	- 580.216	- 461.412	77.567
1400	56.850	120.288	82.682	52.647	- 579.148	- 452.312	70.606
1500	57.000	124.217	85.322	58.342	- 578.109	- 443.292	64.585

Sept. 30, 1962; Mar. 31, 1965

BORON OXIDE FLUORIDE, TRIMERIC $((BOF)_3)$ (CRYSTAL) MOL. WT. = 137.46

$S^\circ_{298.15}$ = [52] cal. deg.$^{-1}$ mole^{-1}

T_m = 353°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -586.5 ± 3.0 kcal. mole^{-1}

ΔH°_m = Unknown

$\Delta H^\circ_{s\ 298.15}$ = 21.2 ± 3.2 kcal. mole^{-1}

Heat of Formation.

The heats of solution of the compounds: $B_2O_3(gl)$, $BF_3(g)$ and $(BOF)_3(c)$ in water and methanol, respectively, were reported by E. M. Magee, J. Inorg. Nucl. Chem. 22, 156 (1961). The corresponding enthalpy changes for the reaction $B_2O_3(gl) + BF_3(g) = (BOF)_3(c)$ were derived as -19.8 and -14.4 kcal. mole^{-1}, yielding $\Delta H^\circ_{f\ 298.15}$ for $(BOF)_3(c)$ -589.18 and -583.78 kcal. mole^{-1}, respectively. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $(BOF)_3(c)$ is the average of these two values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p) for $(BOF)_3(c)$ were estimated from the C_p values for $B_2O_3(c)$ and $BF_3(g)$, according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958. $S^\circ_{298.15}$ for $(BOF)_3(c)$ was estimated by E. M. Magee, loc. cit.

Melting Data.

The value of T_m was reported by E. M. Magee, loc. cit.

Heat of Sublimation.

The heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) for $(BOF)_3(c)$ is calculated as the difference between $\Delta H^\circ_{f\ 298.15}$ for crystal and gas.

Boron Oxide Fluoride, Trimeric $((BOF)_3)$

(Ideal Gas) Mol. Wt. = 137.46

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 5.184	- 563.331	- 563.331	INFINITE
100	13.862	60.014	102.010	- 4.200	- 564.476	- 558.121	1219.713
200	21.508	72.080	84.154	- 2.415	- 565.001	- 551.531	602.657
298	27.489	81.825	81.825	.000	- 565.300	- 544.859	399.373
300	27.590	81.995	81.825	.051	- 565.305	- 544.733	396.819
400	32.456	90.626	82.969	3.063	- 565.480	- 537.845	293.851
500	36.226	98.292	85.281	6.505	- 565.584	- 530.924	232.055
600	39.066	105.161	88.032	10.277	- 565.618	- 523.987	190.853
700	41.189	111.350	90.929	14.295	- 565.591	- 517.048	161.422
800	42.783	116.959	93.838	18.497	- 565.520	- 510.121	139.352
900	43.994	122.071	96.695	22.839	- 565.411	- 503.203	122.188
1000	44.927	126.757	99.470	27.287	- 565.286	- 496.295	108.460
1100	45.657	131.074	102.150	31.817	- 565.164	- 489.404	97.231
1200	46.237	135.073	104.729	36.413	- 565.043	- 482.520	87.875
1300	46.703	138.793	107.208	41.061	- 564.937	- 475.648	79.960
1400	47.083	142.268	109.589	45.751	- 564.845	- 468.781	73.176
1500	47.396	145.528	111.878	50.475	- 564.776	- 461.926	67.299
1600	47.657	148.595	114.077	55.228	- 564.730	- 455.068	62.156
1700	47.876	151.491	116.194	60.005	- 564.708	- 448.214	57.619
1800	48.062	154.233	118.232	64.802	- 564.713	- 441.366	53.587
1900	48.221	156.836	120.196	69.617	- 564.736	- 434.512	49.978
2000	48.358	159.313	122.090	74.446	- 564.774	- 427.655	46.730
2100	48.477	161.675	123.919	79.288	- 564.830	- 420.797	43.791
2200	48.581	163.933	125.687	84.141	- 564.904	- 413.938	41.119
2300	48.672	166.094	127.397	89.003	- 564.993	- 407.074	38.679
2400	48.752	168.168	129.053	93.875	- 565.102	- 400.204	36.442
2500	48.823	170.159	130.658	98.754	- 581.389	- 393.006	34.355
2600	48.886	172.075	132.214	103.639	- 581.506	- 385.468	32.400
2700	48.943	173.921	133.725	108.531	- 581.629	- 377.920	30.589
2800	48.994	175.702	135.192	113.427	- 581.758	- 370.379	28.908
2900	49.040	177.422	136.619	118.329	- 581.893	- 362.815	27.341
3000	49.081	179.086	138.007	123.235	- 582.036	- 355.270	25.880
3100	49.118	180.696	139.358	128.145	- 582.182	- 347.711	24.512
3200	49.153	182.256	140.675	133.059	- 582.337	- 340.144	23.230
3300	49.184	183.769	141.958	137.976	- 582.498	- 332.571	22.024
3400	49.212	185.237	143.209	142.895	- 582.666	- 324.990	20.889
3500	49.238	186.664	144.430	147.818	- 582.840	- 317.414	19.819
3600	49.262	188.052	145.623	152.743	- 583.020	- 309.823	18.808
3700	49.284	189.402	146.788	157.670	- 583.208	- 302.233	17.851
3800	49.305	190.716	147.927	162.600	- 583.401	- 294.627	16.944
3900	49.324	191.997	149.040	167.531	- 583.601	- 287.041	16.085
4000	49.341	193.246	150.130	172.465	- 947.343	- 272.995	14.915
4100	49.357	194.465	151.197	177.400	- 946.863	- 256.147	13.653
4200	49.373	195.654	152.241	182.336	- 946.385	- 239.292	12.451
4300	49.387	196.816	153.264	187.274	- 945.914	- 222.461	11.306
4400	49.400	197.952	154.267	192.213	- 945.455	- 205.648	10.214
4500	49.412	199.062	155.250	197.154	- 945.000	- 188.844	9.171
4600	49.424	200.148	156.214	202.096	- 944.549	- 172.039	8.173
4700	49.434	201.211	157.161	207.039	- 944.109	- 155.247	7.219
4800	49.444	202.252	158.089	211.983	- 943.674	- 138.460	6.304
4900	49.454	203.272	159.001	216.927	- 943.249	- 121.707	5.428
5000	49.463	204.271	159.896	221.873	- 942.828	- 104.941	4.587
5100	49.471	205.251	160.776	226.820	- 942.419	- 88.189	3.779
5200	49.479	206.211	161.641	231.768	- 942.013	- 71.440	3.002
5300	49.487	207.154	162.490	236.716	- 941.615	- 54.702	2.256
5400	49.494	208.079	163.326	241.665	- 941.229	- 37.984	1.537
5500	49.501	208.987	164.148	246.615	- 940.843	- 21.238	.844
5600	49.507	209.879	164.957	251.565	- 940.472	- 4.539	.177
5700	49.513	210.755	165.753	256.516	- 940.110	12.178	- .467
5800	49.519	211.617	166.536	261.468	- 939.753	28.879	- 1.088
5900	49.524	212.463	167.307	266.420	- 939.404	45.574	- 1.688
6000	49.529	213.296	168.067	271.372	- 939.066	62.271	- 2.268

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Sept. 30, 1963; Mar. 31, 1965

BORON OXIDE FLUORIDE, TRIMERIC $((BOF)_3)$ (IDEAL GAS) MOL. WT. = 137.46

Point Group $[D_{3h}]$

$S^\circ_{298.15}$ = [81.8] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -563.3 ± 1.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -565.3 ± 1.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[1233] (1)	1450 (2)	714 (1)
[790] (1)	1381 (2)	[170] (1)
[570] (1)	966 (2)	[630] (2)
[1280] (1)	[420] (2)	[185] (2)
[440] (1)	[220] (2)	

Bond Distance: B-F = [1.3] Å B-O = [1.36] Å

Bond Angle: F-B-O = [120°] B-O-B = [120°] O-B-O = [120°] σ = 6

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.9254 X 10^{-112}]g.^{3} cm.^{6}

Heat of Formation.

The enthalpy changes (ΔH°_r) of the reaction $B_2O_3(l) + BF_3(g) = (BOF)_3(g)$ were derived by both the second and third law methods, using the equilibrium constant data reported by several investigators. The results are given as follows.

Investigator	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H^\circ_{f\ 298.15}$* kcal. mole^{-1}
Hildenbrand, et al.[1]	4.06	4.01 ± 0.3	-565.32 ± 1.0
Fisher, et al.[2]	3.41	6.45 ± 0.6	-565.97 ± 1.5
Smith and Lawrence[3]	4.03	——	-565.35 ± 1.3
Farber[4]	5.25	——	-564.13 ± 2.0
	2.56	7.58 ± 0.2	-565.82 ± 2.0
Porter, et al.[5]	—	4.33 ± 0.30	-565.05 ± 1.0

*Calculation based on the third law values available.

[1] D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. 39, 1973 (1963).

[2] H. D. Fisher, J. Kiehl and A. Cane, Report HTC-61-90, June 1961, Hughes Tool Company, Culver City, California

[3] D. D. Smith and R. W. Lawrence, Aerojet Report No. 1952, February 1961, Aerojet-General Corporation.

[4] M. Farber, J. Chem. Phys. 36, 661 (1962). The first $\Delta H^\circ_{r\ 298.15}$ value was evaluated based on K_{1000} = 11.8. The second $\Delta H^\circ_{r\ 298.15}$ values refer to the reaction $B_2O_3(c) + BF_3(g) = (BOF)_3(g)$.

[5] R. F. Porter, D. R. Bidinosti and K. F. Watterson, J. Chem. Phys. 36, 2104 (1962). The $\Delta H^\circ_{r\ 298.15}$ value was derived from $\Delta H^\circ_{r\ 700}$ = 3.46 ± 0.30 kcal. mole^{-1}.

The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $(BOF)_3(g)$ is the weighted average of the six $\Delta H^\circ_{f\ 298.15}$ values listed above.

Heat Capacity and Entropy.

The infra-red spectrum has been reported by D. D. Smith and R. L. Lawrence, loc. cit., and by H. D. Fisher, W. J. Lehmann, and I. Shapiro, J. Phys. Chem. 65, 1166 (1961) who also made a partial assignment. The unassigned bands at 1280 and 1233 from Fisher, et al., can be assigned to the A_2' and A_1' species which may be observed if the selection rules are not rigorously obeyed in the solid. All the unobserved frequencies were estimated by comparison with $B_3O_3(OH)_3$, $B_3O_3(OD)_3$ from J. L. Parsons, J. Chem. Phys. 33, 1860 (1960) and $B_3O_3H_3$ and $B_3O_3D_3$ from S. K. Gupta and R. F. Porter, J. Phys. Chem. 67, 1286 (1963) and G. H. Lee, W. H. Bauer and S. E. Wiberley, J. Phys. Chem. 67, 1742 (1963). The D_{3h} assumed symmetry has 14 vibrations of the type $3A_1'$, $2A_2'$, 5E', $2A_2''$ and 2E" which are given in order above. The B-F bond distance was assumed to be the same as that in BF_3. The B-O bond distance was estimated by comparison with other related compounds. The three principal moments of inertia are: $I_A = I_B$ = 4.5832 X 10^{-38} and I_C = 9.1664 X 10^{-38} g. cm.^{2}

Boroxin ($B_3O_3H_3$)

(Crystal) Mol. Wt. = 83.484

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	23.500	40.000	40.000	.000	- 301.700	- 276.498	202.669
300	23.600	40.146	40.000	.044	- 301.710	- 276.343	201.306
400	28.700	47.631	40.987	2.658	- 302.170	- 267.813	146.319
500	33.900	54.598	43.019	5.789	- 302.422	- 259.190	113.286
600	38.900	61.234	45.506	9.437	- 302.382	- 250.541	91.255
700	43.000	67.546	48.208	13.537	- 302.050	- 241.921	75.528
800	46.500	73.525	51.002	18.018	- 301.460	- 233.373	63.751
900	49.138	79.160	53.821	22.805	- 300.660	- 224.908	54.612
1000	51.200	84.449	56.622	27.827	- 299.711	- 216.538	47.322
1100	52.517	89.392	59.379	33.014	- 298.683	- 208.272	41.378
1200	53.600	94.010	62.075	38.322	- 297.605	- 200.098	36.441
1300	54.203	98.324	64.699	43.713	- 296.518	- 192.018	32.280
1400	54.738	102.361	67.247	49.161	- 295.438	- 184.018	28.725
1500	55.203	106.154	69.715	54.658	- 294.379	- 176.099	25.656
1600	55.600	109.730	72.105	60.199	- 293.340	- 168.248	22.980
1700	55.928	113.111	74.419	65.776	- 292.321	- 160.459	20.627
1800	56.188	116.315	76.658	71.382	- 291.329	- 152.733	18.543
1900	56.378	119.358	78.826	77.011	- 290.360	- 145.059	16.685
2000	56.500	122.254	80.926	82.656	- 289.415	- 137.437	15.018

Mar. 31, 1965

BOROXIN ($B_3O_3H_3$) **(CRYSTAL)** **MOL. WT. = 83.484**

$S^\circ_{298.15}$ = [40 ± 10] cal. deg.$^{-1}$ mole^{-1}

T_m = Unknown

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -301.7 ± 10 kcal. mole^{-1}

ΔH°_m = Unknown

$\Delta H^\circ_{s\ 298.15}$ = 10.7 ± 0.5 kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for $B_3O_3H_3$(c) was calculated from the $\Delta H^\circ_{f\ 298.15}$ for $B_3O_3H_3$(g) and $\Delta H^\circ_{s\ 298.15}$ for $B_3O_3H_3$(c) reported by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964).

Heat Capacity and Entropy.

The heat capacities (C_p) were estimated from those for B_2O_3(c) and 1/2 B_2H_6(g), according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958. The value of $S^\circ_{298.15}$ for $B_3O_3H_3$(c) was calculated based on $\Delta S^\circ_{r\ 298.15}$ = 6.6 cal. deg.$^{-1}$ mole^{-1} for the reaction $B_3O_3H_3$(c) = B_2O_3(am) + 1/2 B_2H_6(g), which was obtained from the calculated $\Delta H^\circ_{r\ 298.15}$ and measured $\Delta F^\circ_{r\ 298.15}$ evaluated from the vapor pressure reported by W. P. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963).

Heat of Sublimation.

$\Delta H^\circ_{s\ 298.15}$ was taken from R. F. Porter and S. K. Gupta, loc. cit.

Boroxin ($B_3O_3H_3$)

(Ideal Gas) Mol. Wt. = 83.484

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	- 4.026	- 288.002	- 288.002	INFINITE
100	10.643	53.317	84.937	- 3.162	- 289.363	- 284.785	622.366
200	16.060	62.409	71.505	- 1.819	- 290.185	- 279.888	305.833
298	20.992	69.744	69.744	.000	- 291.000	- 274.666	201.326
300	21.084	69.874	69.745	.039	- 291.015	- 274.566	200.012
400	25.753	76.594	70.629	2.386	- 291.742	- 268.970	146.951
500	29.706	82.779	72.449	5.165	- 292.346	- 263.204	115.041
600	32.920	88.490	74.653	8.302	- 292.817	- 257.329	93.728
700	35.514	93.767	77.011	11.729	- 293.158	- 251.385	78.482
800	37.614	98.651	79.415	15.389	- 293.389	- 245.403	67.038
900	39.326	103.183	81.807	19.239	- 293.526	- 239.395	58.130
1000	40.731	107.402	84.158	23.244	- 293.594	- 233.374	51.001
1100	41.891	111.340	86.452	27.377	- 293.620	- 227.353	45.169
1200	42.856	115.028	88.682	31.615	- 293.612	- 221.326	40.307
1300	43.664	118.491	90.843	35.943	- 293.588	- 215.305	36.194
1400	44.345	121.752	92.935	40.344	- 293.554	- 209.281	32.669
1500	44.923	124.832	94.960	44.808	- 293.529	- 203.266	29.614
1600	45.416	127.748	96.919	49.326	- 293.513	- 197.249	26.942
1700	45.839	130.514	98.814	53.889	- 293.508	- 191.231	24.583
1800	46.205	133.145	100.649	58.492	- 293.519	- 185.218	22.487
1900	46.523	135.651	102.426	63.129	- 293.543	- 179.198	20.611
2000	46.800	138.045	104.148	67.795	- 293.576	- 173.180	18.923
2100	47.044	140.334	105.817	72.487	- 293.622	- 167.156	17.395
2200	47.259	142.528	107.436	77.203	- 293.683	- 161.134	16.006
2300	47.449	144.633	109.008	81.938	- 293.755	- 155.109	14.738
2400	47.618	146.656	110.534	86.692	- 293.845	- 149.073	13.574
2500	47.769	148.603	112.018	91.461	- 310.113	- 142.719	12.476
2600	47.905	150.479	113.462	96.245	- 310.207	- 136.018	11.433
2700	48.026	152.290	114.867	101.042	- 310.308	- 129.316	10.467
2800	48.136	154.038	116.235	105.850	- 310.413	- 122.615	9.570
2900	48.236	155.729	117.567	110.669	- 310.524	- 115.893	8.734
3000	48.326	157.366	118.867	115.497	- 310.641	- 109.188	7.954
3100	48.408	158.952	120.135	120.334	- 310.762	- 102.474	7.224
3200	48.483	160.490	121.372	125.178	- 310.891	- 95.752	6.539
3300	48.552	161.983	122.580	130.030	- 311.027	- 89.023	5.895
3400	48.615	163.433	123.760	134.889	- 311.169	- 82.293	5.290
3500	48.673	164.843	124.914	139.753	- 311.319	- 75.565	4.718
3600	48.727	166.215	126.042	144.623	- 311.476	- 68.821	4.178
3700	48.776	167.551	127.146	149.498	- 311.642	- 62.079	3.667
3800	48.821	168.852	128.227	154.378	- 311.813	- 55.324	3.182
3900	48.864	170.121	129.285	159.263	- 311.992	- 48.585	2.722
4000	48.903	171.359	130.321	164.151	- 675.717	- 35.393	1.934
4100	48.940	172.567	131.337	169.043	- 675.218	- 19.393	1.034
4200	48.974	173.747	132.333	173.939	- 674.724	- 3.392	.176
4300	49.005	174.899	133.309	178.838	- 674.239	12.587	- .640
4400	49.035	176.026	134.267	183.740	- 673.765	28.550	- 1.418
4500	49.063	177.129	135.207	188.645	- 673.299	44.496	- 2.161
4600	49.089	178.207	136.131	193.552	- 672.837	60.456	- 2.872
4700	49.113	179.263	137.037	198.462	- 672.388	76.395	- 3.552
4800	49.136	180.297	137.928	203.375	- 671.946	92.327	- 4.204
4900	49.158	181.311	138.803	208.290	- 671.513	108.227	- 4.827
5000	49.178	182.304	139.663	213.206	- 671.087	124.138	- 5.426
5100	49.198	183.278	140.508	218.125	- 670.674	140.047	- 6.001
5200	49.216	184.234	141.340	223.046	- 670.266	155.929	- 6.553
5300	49.233	185.171	142.158	227.968	- 669.866	171.822	- 7.085
5400	49.249	186.092	142.963	232.892	- 669.479	187.685	- 7.596
5500	49.264	186.996	143.756	237.818	- 669.095	203.573	- 8.089
5600	49.279	187.883	144.536	242.745	- 668.727	219.419	- 8.563
5700	49.293	188.756	145.304	247.674	- 668.367	235.280	- 9.021
5800	49.306	189.613	146.061	252.604	- 668.017	251.133	- 9.462
5900	49.318	190.456	146.806	257.535	- 667.674	266.978	- 9.889
6000	49.330	191.285	147.540	262.468	- 667.342	282.821	- 10.301

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965

BOROXIN ($B_3O_3H_3$) (IDEAL GAS) MOL. WT. = 83.484

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [69.7] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -288 ± 10 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -291 ± 10 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
2530 (1)	2620 (2)	903 (1)
[920] (1)	1404 (2)	[300] (1)
[735] (1)	1335 (2)	1115 (2)
[1560] (1)	940 (2)	[230] (2)
[550] (1)	[400] (2)	

Bond Distance: B-O = [1.36] Å B-H = [1.18] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°]

σ = [6]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.4563] X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constants (1290-1481°K.) for the reaction (1) $3/2\ H_2(g) + B(am) + B_2O_3(l) = B_3O_3H_3(g)$ were determined by W. P. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963). The equilibrium pressures of $B_2H_6(g)$ and $B_3O_3H_3(g)$ for the reaction (2) $B_3O_3H_3(g) = 1/2\ B_2H_6(g) + B_2O_3(c)$ were measured at 300°K. by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964). The equilibrium constants (1246-1326°K.) for the reaction (3) $2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$ were reported by R. F. Porter and W. P. Sholette, J. Chem. Phys. 37, 198 (1962). Using these data the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reaction	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H_f^\circ{}_{298.15}$* kcal. mole^{-1}
(1)	-5.90	+6.52 ± 4.5	-304.0 ± 5.0
(2)**	-11.11	——	-287.6 ± 2.0
	-12.21	——	-282.5 ± 2.0
(3)	-2.0	——	-314 ± 12.0

*Calculation based on the third law values.

**The initial system for the first set of measurements was $B_2H_6(g) + B(OH)_3(c)$. That for the second set was $B_2H_6(g) + B_2O_3(gl)$.

The value of $\Delta H_f^\circ{}_{298.15}$ for $B_3O_3H_3(g)$ adopted is a weighted average of these $\Delta H_f^\circ{}_{298.15}$ values listed.

Heat Capacity and Entropy.

The infra-red spectrum of solid boroxin has been determined by S. K. Gupta and R. F. Porter, J. Phys. Chem. 67, 1286 (1963) and a partial assignment was made. The infra-red spectra of the gas has also been reported by G. H. Lee, W. H. Bauer, and S. E. Wiberley, J. Phys. Chem. 67, 1742 (1963) and is in essential agreement with the solid. The assignment of the frequencies has been changed slightly due to the non-appearance of the band at 1115 cm.$^{-1}$ in the gas phase. The assumed D_{3h} symmetry has 14 vibrations of the type $3A_1'$, $2A_2'$, $5E'$, $2A_2''$, and $2E''$, the 7 estimated frequencies were obtained by comparison with $B_3O_6H_3$, by J. L. Parsons, J. Chem. Phys. 33, 1860 (1960).

The point group, bond angles and bond lengths were assumed to be the same as for $(BOF)_3(g)$. The B-H bond length was taken as the sum of the single covalent radii of the atoms. The individual moments of inertia were calculated to be $I_A = I_B = 13.973 \times 10^{-39}$, and $I_C = 27.949 \times 10^{-39}$ g.^{3} cm.^{6}

Metaboric Acid, Trimeric $((HBO_2)_3)$

(Ideal Gas) Mol. Wt. = 131.484

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-5.440	-538.303	-538.303	INFINITE
100	12.319	60.120	105.418	-4.530	-540.688	-530.561	1159.485
200	23.148	71.939	85.750	-2.762	-542.105	-519.844	568.032
298	32.807	83.047	83.047	.000	-543.000	-508.717	372.882
300	32.969	83.250	83.048	.061	-543.013	-508.505	370.428
400	40.477	93.820	84.438	3.753	-543.461	-496.924	271.494
500	45.833	103.463	87.294	8.084	-543.610	-485.268	212.100
600	49.633	112.174	90.727	12.868	-543.566	-473.601	172.501
700	52.405	120.044	94.363	17.977	-543.392	-461.951	144.221
800	54.509	127.185	98.026	23.327	-543.130	-450.338	123.021
900	56.170	133.704	101.633	28.864	-542.801	-438.757	106.540
1000	57.522	139.695	105.144	34.551	-542.427	-427.212	93.363
1100	58.648	145.231	108.540	40.361	-542.035	-415.712	82.590
1200	59.602	150.377	111.815	46.274	-541.624	-404.245	73.619
1300	60.418	155.180	114.968	52.276	-541.211	-392.814	66.035
1400	61.123	159.684	118.002	58.354	-540.797	-381.413	59.538
1500	61.735	163.923	120.924	64.498	-540.398	-370.046	53.913
1600	62.270	167.924	123.738	70.699	-540.014	-358.700	48.994
1700	62.740	171.714	126.449	76.950	-539.645	-347.377	44.656
1800	63.153	175.312	129.065	83.245	-539.297	-336.081	40.804
1900	63.519	178.736	131.590	89.579	-538.966	-324.798	37.359
2000	63.844	182.003	134.029	95.947	-538.647	-313.537	34.260
2100	64.133	185.125	136.389	102.346	-538.344	-302.285	31.458
2200	64.392	188.115	138.672	108.773	-538.062	-291.053	28.912
2300	64.623	190.982	140.885	115.224	-537.792	-279.833	26.589
2400	64.832	193.737	143.030	121.697	-537.546	-268.615	24.460
2500	65.020	196.387	145.112	128.190	-553.482	-257.096	22.474
2600	65.190	198.941	147.133	134.700	-553.248	-245.243	20.614
2700	65.344	201.404	149.098	141.227	-553.025	-233.397	18.891
2800	65.484	203.783	151.009	147.768	-552.813	-221.568	17.293
2900	65.611	206.083	152.868	154.323	-552.609	-209.727	15.805
3000	65.728	208.310	154.679	160.890	-552.417	-197.917	14.418
3100	65.835	210.466	156.444	167.469	-552.231	-186.103	13.120
3200	65.933	212.558	158.165	174.057	-552.060	-174.297	11.903
3300	66.023	214.588	159.845	180.655	-551.899	-162.490	10.761
3400	66.106	216.561	161.484	187.261	-551.750	-150.696	9.686
3500	66.183	218.478	163.085	193.876	-551.611	-138.908	8.673
3600	66.254	220.344	164.650	200.498	-551.482	-127.112	7.716
3700	66.319	222.160	166.180	207.126	-551.368	-115.325	6.812
3800	66.380	223.929	167.676	213.761	-551.261	-103.532	5.954
3900	66.437	225.654	169.141	220.402	-551.166	-91.766	5.142
4000	66.490	227.337	170.575	227.049	-914.621	-73.553	4.019
4100	66.539	228.979	171.979	233.700	-913.855	-52.533	2.800
4200	66.585	230.583	173.356	240.356	-913.096	-31.524	1.640
4300	66.628	232.151	174.705	247.017	-912.349	-10.545	.536
4400	66.668	233.683	176.028	253.682	-911.617	10.412	-.517
4500	66.706	235.181	177.326	260.351	-910.894	31.356	-1.523
4600	66.742	236.648	178.599	267.023	-910.178	52.300	-2.485
4700	66.775	238.084	179.850	273.699	-909.478	73.216	-3.404
4800	66.807	239.490	181.078	280.378	-908.786	94.124	-4.285
4900	66.836	240.868	182.284	287.060	-908.105	114.988	-5.128
5000	66.864	242.218	183.469	293.745	-907.434	135.864	-5.938
5100	66.890	243.543	184.634	300.433	-906.777	156.733	-6.716
5200	66.915	244.842	185.780	307.123	-906.126	177.567	-7.463
5300	66.939	246.117	186.906	313.816	-905.484	198.413	-8.181
5400	66.961	247.368	188.014	320.511	-904.858	219.219	-8.872
5500	66.982	248.597	189.104	327.208	-904.235	240.054	-9.538
5600	67.003	249.804	190.178	333.908	-903.630	260.828	-10.179
5700	67.022	250.990	191.234	340.609	-903.034	281.623	-10.797
5800	67.040	252.156	192.274	347.312	-902.448	302.407	-11.394
5900	67.057	253.302	193.299	354.017	-901.870	323.173	-11.971
6000	67.074	254.429	194.309	360.723	-901.305	343.941	-12.527

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1964

METABORIC ACID, TRIMERIC $((HBO_2)_3)$ (IDEAL GAS) MOL. Wt. = 131.484

Point Group C_{3h}

$\Delta H^\circ_{f\ 0} = [-538 \pm 3]$ kcal. mole^{-1}

$S^\circ_{298.15} = [83.047]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = [-543 \pm 3]$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[550](1)	[250](1)	[600](2)
[1150](1)	[500](1)	[450](2)
[950](1)	[350](1)	[3500](2)
[3500](1)	[750](2)	[350](2)
[1100](1)	[900](2)	[200](2)
[600](1)	[1300](2)	[1000](2)
[500](1)	[1000](2)	

Bond Distance: B-O = [1.36] Å O-H = [1.0] Å

Bond Angle: H-O-B = [120]° O-B-O = [120]° B-O-B = [120]° $\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = [1.77712 \times 10^{-112}]$ g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constant, $K_{p\ 1451} = 0.9$, for the reaction $H_3BO_3(l) + B_2O_3(l) = (HBO_2)_3(g)$ was reported by D. J. Meschi, W. A. Chupka and J. Berkowitz, J. Chem. Phys. 33, 530 (1960), which was determined by means of mass spectrometry. The equilibrium constants of the reactions between water vapor and liquid B_2O_3 were determined at 1147°K. by J. A. Blauer and M. Farber, J. Phys. Chem. 68, 2357 (1964), by use of a transpiration method. From the reported value, $1.5\ K_2 + 0.5\ K_3 = 0.0342 \pm 0.0095$, the equilibrium constant, K_2, for the reaction $1.5\ B_2O_3(l) + 1.5\ H_2O(g) = (HBO_2)_3(g)$ was derived as 0.0168, using $K_3 = 0.0181$ for the reaction $0.5\ B_2O_3(l) + 1.5\ H_2O(g) = H_3BO_3(g)$ evaluated by use of JANAF values of ΔF°_f for $B_2O_3(l)$, $H_2O(g)$ and $H_3BO_3(g)$. Employing the equilibrium constants obtained the respective enthalpy changes ($\Delta H^\circ_{r\ 298.15}$) for the two reactions were calculated by the third law method. The corresponding values of $\Delta H^\circ_{f\ 298.15}$ for $(HBO_2)_3(g)$ were also derived. The results are presented as follows.

Investigator	Chemical Reaction	$\Delta H^\circ_{r\ 298.15}$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298.15}$ kcal. mole^{-1}
Meschi, et al.	$H_3BO_3(l) + B_2O_3(l) = (HBO_2)_3(g)$	-7.31	-543.8
Blauer and Farber	$1.5\ B_2O_3(l) + 1.5\ H_2O(g) = (HBO_2)_3(g)$	-6.67	-542.3

The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $(HBO_2)_3(g)$ is the average of these two listed in the above table. The equilibrium constants for the same reactions between $B_2O_3(l)$ and $H_2O(g)$ were also determined by a transpiration method in the temperature region 1000°-1273°K. by S. P. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. 16, 29 (1960). The reported value, $\Delta H^\circ_{f\ 0} = -537.5 \pm 3$ kcal. mole^{-1} for $(HBO_2)_3(g)$, is in good agreement with the value adopted.

Heat Capacity and Entropy.

All the molecular and spectroscopic constants were estimated by D. White, D. E. Mann, P. N. Walsh and A. Sommer, J. Chem. Phys. 32, 488 (1960). The three principal moments of inertia are: $I_A = I_B = 4.4623 \times 10^{-38}$ and $I_C = 8.9247 \times 10^{-38}$ g. cm.^{2} The infrared absorption spectra for $B_3O_3(OH)_3(c)$ in the 430 to 4000 cm.$^{-1}$ was reported by L. J. Parsons, J. Chem. Phys. 33, 1860 (1960). A partial Raman spectrum was also given.

Borazine ($B_3N_3H_6$)
(Ideal Gas) Mol. Wt. = 80.532

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.947	-115.791	-115.791	INFINITE
100	9.414	53.136	84.341	-3.121	-118.287	-110.543	241.581
200	15.548	61.358	70.855	-1.899	-120.169	-102.080	111.543
298	23.166	68.983	68.983	.000	-121.900	-92.829	68.042
300	23.307	69.127	68.984	.043	-121.931	-92.650	67.492
400	30.302	76.821	69.985	2.734	-123.333	-82.667	45.165
500	35.967	84.215	72.098	6.058	-124.399	-72.373	31.633
600	40.486	91.187	74.705	9.889	-125.161	-61.890	22.542
700	44.137	97.712	77.531	14.127	-125.670	-51.300	16.016
800	47.140	103.808	80.439	18.695	-125.969	-40.655	11.106
900	49.645	109.509	83.356	23.538	-126.098	-29.981	7.280
1000	51.758	114.852	86.241	28.611	-126.095	-19.300	4.218
1100	53.554	119.872	89.072	33.879	-125.999	-8.626	1.714
1200	55.089	124.599	91.838	39.313	-125.826	2.041	-.372
1300	56.407	129.062	94.531	44.890	-125.600	12.684	-2.132
1400	57.545	133.285	97.150	50.589	-125.335	23.314	-3.639
1500	58.531	137.289	99.694	56.394	-125.055	33.921	-4.942
1600	59.389	141.095	102.163	62.291	-124.765	44.509	-6.079
1700	60.138	144.718	104.561	68.268	-124.468	55.083	-7.081
1800	60.795	148.175	106.888	74.315	-124.170	65.631	-7.968
1900	61.373	151.477	109.149	80.424	-123.868	76.172	-8.761
2000	61.885	154.639	111.345	86.588	-123.563	86.693	-9.473
2100	62.338	157.669	113.479	92.799	-123.262	97.198	-10.115
2200	62.742	160.579	115.554	99.053	-122.963	107.689	-10.697
2300	63.102	163.376	117.573	105.346	-122.666	118.164	-11.228
2400	63.425	166.068	119.538	111.673	-122.376	128.637	-11.713
2500	63.716	168.664	121.452	118.030	-138.260	139.407	-12.186
2600	63.978	171.168	123.316	124.415	-137.960	150.511	-12.651
2700	64.215	173.587	125.133	130.825	-137.660	161.604	-13.080
2800	64.430	175.926	126.906	137.257	-137.358	172.673	-13.477
2900	64.625	178.190	128.635	143.710	-137.052	183.759	-13.848
3000	64.803	180.384	130.324	150.181	-136.750	194.805	-14.191
3100	64.966	182.512	131.973	156.670	-136.444	205.844	-14.511
3200	65.115	184.577	133.585	163.174	-136.144	216.884	-14.812
3300	65.252	186.583	135.161	169.693	-135.848	227.919	-15.094
3400	65.378	188.533	136.702	176.224	-135.550	238.934	-15.358
3500	65.494	190.429	138.210	182.768	-135.262	249.943	-15.606
3600	65.602	192.276	139.686	189.323	-134.977	260.946	-15.841
3700	65.701	194.075	141.132	195.888	-134.699	271.942	-16.062
3800	65.793	195.828	142.548	202.463	-134.425	282.935	-16.272
3900	65.879	197.538	143.937	209.046	-134.159	293.909	-16.469
4000	65.958	199.207	145.298	215.638	-497.437	311.317	-17.009
4100	66.033	200.837	146.632	222.238	-496.491	331.518	-17.671
4200	66.102	202.429	147.942	228.845	-495.551	351.719	-18.301
4300	66.167	203.985	149.227	235.458	-494.620	371.873	-18.900
4400	66.227	205.507	150.489	242.078	-493.700	392.009	-19.470
4500	66.284	206.996	151.728	248.704	-492.791	412.119	-20.014
4600	66.337	208.453	152.946	255.335	-491.885	432.234	-20.535
4700	66.387	209.881	154.142	261.971	-490.994	452.312	-21.031
4800	66.434	211.279	155.318	268.612	-490.113	472.378	-21.507
4900	66.479	212.649	156.474	275.258	-489.242	492.409	-21.961
5000	66.521	213.992	157.611	281.908	-488.381	512.439	-22.398
5100	66.560	215.310	158.729	288.562	-487.535	532.447	-22.816
5200	66.597	216.603	159.830	295.220	-486.694	552.438	-23.217
5300	66.633	217.872	160.913	301.881	-485.867	572.413	-23.603
5400	66.666	219.118	161.980	308.546	-485.055	592.361	-23.973
5500	66.698	220.341	163.030	315.214	-484.252	612.330	-24.331
5600	66.728	221.543	164.064	321.886	-483.464	632.238	-24.673
5700	66.756	222.725	165.083	328.560	-482.689	652.167	-25.004
5800	66.784	223.886	166.086	335.237	-481.928	672.063	-25.323
5900	66.809	225.028	167.076	341.917	-481.178	691.954	-25.630
6000	66.834	226.151	168.051	348.599	-480.442	711.830	-25.927

Dec. 31, 1960; Mar. 31, 1965

BORAZINE ($B_3N_3H_6$) (IDEAL GAS) MOL. WT. = 80.532

Point Group D_{3h}

$S^\circ_{298.15}$ = 68.983 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0} = -115.8 \pm 3$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -121.9 \pm 3$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
3450 (1)	3400 (2)
2535 (1)	2519 (2)
938 (1)	1610 (2)
851 (1)	1466 (2)
[1650](1)	917 (2)
[1110](1)	717 (2)
[800](1)	525 (2)
1098 (1)	1070 (2)
622 (1)	798 (2)
415 (1)	288 (2)

Bond Distance: B-N = 1.44 Å B-H = 1.20 Å H-N = 1.02 Å

Bond Angle: N-B-N = 120° B-N-B = 120° N-B-H = 120° $\sigma = 6$

Product of Moments of Inertia: $I_AI_BI_C = 8.3303 \times 10^{-14}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of combustion for the reaction $B_3N_3H_6(l) + 15/4\ O_2(g) + 3/2\ H_2O(l) = 3\ H_3BO_3(c) + 3/2\ N_2(g)$ was reported to be -552.9 ± 3.0 kcal. mole^{-1} by M. V. Kilday, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. 65 A, 101 (1961). $\Delta H^\circ_{f\ 298.15}\ H_2O(l) = -68.317$ kcal. mole^{-1} from Natl. Bur. Std. Circ. 500, "Selected Values of Chemical Thermodynamic Properties", 1952 and $\Delta H^\circ_{f\ 298.15}\ H_3BO_3(c) = -261.47$ kcal. mole^{-1} from JANAF tables were used to calculate $\Delta H^\circ_{f\ 298.15}\ B_3N_3H_6(l) = -129.0 \pm 3.0$ kcal. mole^{-1}. Vapor pressure data on $B_3N_3H_6(l)$ reported by A. Stock and E. Pohland, Ber. 59, 2215 (1926) were fitted to a linear least squares. $\Delta C_p(l\text{-}g)$ for borazine was approximated by benzene to calculate a 2nd law $\Delta H_{v\ 298} = 7.1 \pm 0.1$ kcal. mole^{-1}.

Heat Capacity and Entropy.

The fundamental frequency assignment was made by B. L. Crawford, Jr. and J. T. Edsall, J. Chem. Phys. 7, 223 (1939). The three frequencies enclosed by brackets are calculated values. The moments of inertia were calculated from molecular constants given by S. H. Bauer, J. Am. Chem. Soc. 60, 524 (1938). The three principal moments of inertia are: $I_A = I_B = 16.09 \times 10^{-39}$ and $I_C = 32.18 \times 10^{-39}$ g. cm.^{2}.

Dipotassium Tetraborate $(K_2B_4O_7)$

(Crystal) Mol. Wt. = 233.44

T, °K.	cal. mole⁻¹deg.⁻¹ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole⁻¹ $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	40.750	49.800	49.800	.000	- 796.900	- 749.734	549.543
300	40.950	50.053	49.801	.076	- 796.916	- 749.440	545.940
400	49.300	63.092	51.522	4.628	- 798.828	- 733.276	400.624
500	55.640	74.813	55.028	9.893	- 799.288	- 716.829	313.311
600	59.880	85.364	59.221	15.686	- 799.485	- 700.314	255.077
700	62.710	94.817	63.643	21.822	- 799.568	- 683.776	213.474
800	64.800	103.334	68.081	28.203	- 799.600	- 667.239	182.273
900	66.300	111.059	72.434	34.763	- 799.621	- 650.688	158.001
1000	67.700	118.118	76.654	41.464	- 799.664	- 634.137	138.584
1100	68.901	124.629	80.723	48.296	- 837.535	- 615.533	122.289
1200	69.904	130.669	84.637	55.238	- 837.123	- 595.370	108.426
1300	70.708	136.297	88.397	62.270	- 836.716	- 575.240	96.702
1400	71.313	141.560	92.008	69.373	- 836.320	- 555.140	86.657
1500	71.720	146.495	95.478	76.526	- 835.945	- 535.068	77.956
1600	72.279	151.142	98.813	83.727	- 835.588	- 515.023	70.346
1700	72.757	155.539	102.022	90.979	- 835.234	- 494.999	63.633
1800	73.153	159.709	105.112	98.275	- 834.894	- 474.994	57.669
1900	73.467	163.673	108.090	105.607	- 834.574	- 455.011	52.336
2000	73.700	167.448	110.965	112.966	- 834.265	- 435.043	47.537

March 31, 1963

DIPOTASSIUM TETRABORATE $(K_2B_4O_7)$ (CRYSTAL) MOL. WT. = 233.44

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [49.8 ± 1.5] cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15}$ = -796.9 kcal. mole^{-1}

T_m = 1088°K. ΔH_m = 24.9 ± 1 kcal. mole^{-1}

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was recalculated from the experimental data of L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954). They studied the heat of solution of various alkali borates in 2N nitric acid. Average molecular weights were used for physical mixtures of the oxides B_2O_3 and R_2O (where R is either Li, Na, or K) rather than for the borate compounds $R_2O \cdot nB_2O_3$ present. These incorrect molecular weights led to spurious correlations and faulty conclusions. In reinterpreting the data, the steps followed were: (1) The calculation of the correct molecular weights and molar heats of reaction; (2) The establishment that the heat of formation of the borates from the oxides is linear with the mole fraction of B_2O_3 in the total original moles of oxides for the reactions

$R_2O(c) + nB_2O_3(gl) \rightarrow R_2O \cdot nB_2O_3(gl)$ (I)

and $R_2O(c) + nB_2O_3(gl) \rightarrow R_2O \cdot nB_2O_3(c)$ (II)

with the heat of formation being zero at 100 percent R_2O; (3) The evaluation of the least square fit of the line through the heat of reaction data for reaction I and for reaction II; (4) The use of the proper weighting factors in applying least squares to adjust for both the sample size and the molecular weight of the mixture of borates used in each solution experiment.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic. 59-2916, in the range 298-973°K were smoothed graphically and were used to obtain a smooth set of C_p data. The heat capacity was extrapolated smoothly above this region. The entropy at 298°K was estimated from that of $Na_2B_4O_7(c)$ by using an average entropy change of 4.5 ± 1.5 cal. deg.$^{-1}$ mole^{-1} on substituting Na_2 by K_2.

Melting Data.

T_m was given by A. P. Rollet, Comp. Rend. 200, 1763 (1935). The heat of melting was obtained from the heats of formation of the crystal and glass at 298°K combined with the enthalpy differences between 298 and 1088°K. This involves a slight extrapolation of the crystal data and an uncertainty of about 1.0 kcal. mole^{-1}.

Dipotassium Tetraborate ($K_2B_4O_7$)

(Liquid) Mol. Wt. = 233.44

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	40.750	56.700	56.700	.000	- 786.100	- 740.991	543.135
300	40.950	56.953	56.701	.076	- 786.116	- 740.710	539.581
400	49.300	69.992	58.422	4.628	- 788.028	- 725.236	396.232
500	55.650	81.715	61.928	9.894	- 788.487	- 709.479	310.098
600	59.880	92.267	66.121	15.688	- 788.683	- 693.654	252.651
700	89.680	102.650	70.560	22.463	- 788.127	- 677.818	211.614
800	96.200	115.041	75.354	31.750	- 785.253	- 662.257	180.912
900	101.880	126.708	80.418	41.661	- 781.923	- 647.074	157.124
1000	106.730	137.700	85.602	52.098	- 778.230	- 632.284	138.179
1100	109.790	148.018	90.812	62.926	- 812.105	- 615.831	122.349
1200	112.606	157.693	95.987	74.048	- 807.513	- 598.190	108.940
1300	115.180	166.810	101.087	85.439	- 802.747	- 580.938	97.660
1400	117.512	175.433	106.093	97.076	- 797.817	- 564.059	88.049
1500	119.600	183.613	110.990	108.934	- 792.737	- 547.536	79.772
1600	121.446	191.392	115.774	120.988	- 787.527	- 531.361	72.577
1700	123.048	198.804	120.442	133.215	- 782.199	- 515.513	66.271
1800	124.408	205.876	124.993	145.589	- 776.780	- 499.981	60.703
1900	125.526	212.634	129.430	158.088	- 771.293	- 484.755	55.757
2000	126.400	219.096	133.752	170.686	- 765.745	- 469.818	51.337
2100	127.196	225.282	137.965	183.367	- 760.164	- 455.157	47.366
2200	127.924	231.216	142.069	196.123	- 754.554	- 440.760	43.783
2300	128.584	236.918	146.070	208.949	- 767.312	- 426.629	40.537
2400	129.176	242.403	149.970	221.838	- 761.670	- 411.935	37.510
2500	129.700	247.687	153.774	234.782	- 756.004	- 397.489	34.747
2600	130.156	252.783	157.485	247.776	- 750.308	- 383.253	32.214
2700	130.544	257.703	161.106	260.811	- 744.604	- 369.248	29.887
2800	130.864	262.456	164.641	273.882	- 738.895	- 355.448	27.743
2900	131.116	267.053	168.094	286.982	- 733.188	- 341.850	25.761
3000	131.300	271.501	171.467	300.103	- 727.490	- 328.447	23.926

March 31, 1963

DIPOTASSIUM TETRABORATE ($K_2B_4O_7$) (LIQUID) MOL. WT. = 233.44

$S^\circ_{298.15}$ = [56.7 ± 2.5] cal. deg.$^{-1}$ mole^{-1}

T_m = 1088°K.

ΔH_f° 298.15 = -786.1 kcal. mole^{-1}

ΔH_m = 24.9 ± 1 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from reaction (1) given on the crystal table.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1373°K on the glass and liquid were smoothed graphically and used to determine C_p. There is a discontinuity (glass transition) in the C_p curve at 676°K. Above 1373°K the C_p values were extrapolated smoothly.

The entropy at 298°K was obtained from that of the crystal by adding ΔS_m° and the difference between S_{1088}-S_{298} for crystal and liquid.

Melting Data.

See the crystal table.

Dilithium Tetraborate ($Li_2B_4O_7$)

(Crystal) Mol. Wt. = 169.1178

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	43.750	37.200	37.200	.000	- 803.600	- 757.734	555.408
300	43.761	37.471	37.201	.081	- 803.607	- 757.452	551.777
400	47.239	50.492	38.953	4.616	- 804.090	- 741.998	405.390
500	52.567	61.610	42.394	9.608	- 806.144	- 726.257	317.431
600	57.625	71.653	46.446	15.124	- 806.597	- 710.231	258.689
700	61.950	80.869	50.715	21.108	- 806.800	- 694.151	216.713
800	65.586	89.384	55.023	27.489	- 806.776	- 678.063	185.229
900	68.766	97.294	59.285	34.208	- 806.552	- 661.985	160.744
1000	71.803	104.695	63.460	41.234	- 806.140	- 645.937	141.163
1100	75.052	111.691	67.529	48.578	- 805.525	- 629.948	125.153
1200	78.198	118.357	71.489	56.240	- 804.683	- 614.021	111.823
1300	81.344	124.740	75.342	64.218	- 803.613	- 598.176	100.558
1400	84.490	130.883	79.091	72.509	- 802.303	- 582.417	90.915
1500	87.636	136.820	82.743	81.116	- 800.755	- 566.770	82.574
1600	90.782	142.576	86.303	90.036	- 798.958	- 551.222	75.290
1700	93.928	148.174	89.779	99.272	- 867.004	- 533.145	68.537
1800	97.074	153.632	93.175	108.822	- 864.339	- 513.581	62.354
1900	100.220	158.965	96.498	118.687	- 861.413	- 494.172	56.840
2000	103.366	164.185	99.752	128.866	- 858.215	- 474.927	51.895

Mar. 31, 1962; Dec. 31, 1962; June 30, 1965

DILITHIUM TETRABORATE ($Li_2B_4O_7$) (CRYSTAL) MOL. WT. = 169.1178

$\Delta H_f^\circ{}_0$ = Unknown

$S_{298.15}^\circ = [37.2 \pm 1.0]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -803.6 \pm 1.5$ kcal. mole^{-1}

$T_m = 1190 \pm 2$°K.

$\Delta H_m^\circ = 28.8 \pm 1.5$ kcal. mole^{-1}

Heat of Formation.

The heat of formation was calculated from $\Delta H_r^\circ{}_{298} = -12.2$ kcal. for the reaction $Li_2B_4O_7(c) + 2HNO_3(aq.) + 5H_2O(l) = 4H_3BO_3(aq.) + 2LiNO_3(aq.)$. The heat of solution ($\Delta H_r^\circ$) was interpolated from the heat of solution data of L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27 (1954). Auxilliary data are from National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1190°K. were smoothed graphically and used to determine C_p. A linear extrapolation of C_p was used from 1190 to 2000°K.

S_{298}° was estimated by three routes: (1) S_{298}° ($Li_2B_4O_7$) = 37.3 cal. mole^{-1} deg.$^{-1}$ based on JANAF S_{298}° ($Na_2B_4O_7$) = 45.3 and ΔS_{298}° (2Na-2Li) = 8 cal. deg.$^{-1}$ from W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951); (2) S_{298}° ($Li_2B_4O_7$) = 36.7 cal. mole^{-1} deg.$^{-1}$ in a similar manner based on ΔS_{298}° ($2Na^+-2Li^+$) = 8.6 cal. deg.$^{-1}$ from K. K Kelley, Bureau of Mines, private communication, June 1960; and (3) S_{298}° ($Li_2B_4O_7$) = 37.6 cal. mole^{-1} deg.$^{-1}$ based on addition of the JANAF entropies for $2LiBO_2$ and B_2O_3. The value adopted is an average of these estimates.

Melting Data.

The value for T_m is from B. S. R. Sastry and F. A. Hummel, J. Am. Chem. Soc. 42, 216 (1959). A. P. Rollet and R. Bouaziz, Compt. rend. 240, 2417 (1955) earlier reported T_m = 1188°K. ΔH_m = 28.8 kcal. mole^{-1} is from G. S. Smith loc. cit.

Dilithium Tetraborate ($Li_2B_4O_7$)
(Liquid) Mol. Wt. = 169.1178

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	43.295	41.564	41.564	.000	- 792.790	- 748.226	548.438
300	43.400	41.832	41.565	.080	- 792.797	- 747.951	544.856
400	49.050	55.091	43.335	4.703	- 793.193	- 732.941	400.441
500	54.701	66.644	46.863	9.890	- 795.052	- 717.682	313.683
600	60.352	77.116	51.045	15.643	- 795.268	- 702.180	255.757
700	66.003	86.844	55.472	21.961	- 795.137	- 686.671	214.378
800	109.165	98.205	60.033	30.538	- 792.917	- 671.261	183.371
900	109.835	111.101	65.004	41.488	- 788.462	- 656.322	159.369
1000	110.505	122.708	70.204	52.505	- 784.060	- 641.870	140.274
1100	111.175	133.272	75.464	63.589	- 779.704	- 627.866	124.740
1200	111.845	142.974	80.691	74.740	- 775.373	- 614.252	111.865
1300	112.515	151.953	85.832	85.958	- 771.063	- 601.003	101.033
1400	113.156	160.316	90.857	97.242	- 766.760	- 588.080	91.799
1500	113.728	168.142	95.751	108.586	- 762.475	- 575.473	83.842
1600	114.315	175.500	100.508	119.988	- 758.196	- 563.139	76.917
1700	114.918	182.449	105.125	131.450	- 824.016	- 548.424	70.501
1800	115.537	189.035	109.606	142.972	- 819.379	- 532.346	64.633
1900	116.172	195.298	113.952	154.558	- 814.732	- 516.524	59.411
2000	116.822	201.274	118.170	166.207	- 810.064	- 500.954	54.739
2100	117.488	206.990	122.264	177.923	- 805.374	- 485.611	50.536
2200	118.170	212.471	126.241	189.706	- 800.663	- 470.494	46.737
2300	118.868	217.739	130.105	201.557	- 795.918	- 455.597	43.290
2400	119.581	222.813	133.863	213.480	- 791.148	- 440.895	40.147
2500	120.310	227.709	137.520	225.474	- 807.894	- 425.969	37.236
2600	121.055	232.442	141.080	237.542	- 803.020	- 410.789	34.528
2700	121.816	237.025	144.549	249.686	- 798.097	- 395.792	32.036
2800	122.592	241.469	147.932	261.906	- 793.119	- 380.986	29.736
2900	123.384	245.785	151.232	274.205	- 788.090	- 366.343	27.607
3000	124.115	249.981	154.454	286.581	- 783.006	- 351.893	25.634

Mar. 31, 1962; Dec. 31, 1962; June 30, 1965

DILITHIUM TETRABORATE ($Li_2B_4O_7$) (LIQUID) MOL. WT. = 169.1178

$S^\circ_{298.15}$ = [41.564 ± 1.5] cal. deg.$^{-1}$ mole^{-1}

T_m = 1190 ± 2°K.

$\Delta H^\circ_{f\ 298.15}$ = -792.79 ± 1.5 kcal. mole^{-1}

ΔH°_m = 26.3 ± 1.5 kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}(l)$ was calculated from $\Delta H^\circ_{f\ 298.15}(c)$ by adding $\Delta H^\circ_{T_m}$ and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1373°K. were smoothed graphically and used to determine C_p. The C_p data have a discontinuity at about 756°K. A linear extrapolation of C_p was used from 1373 to 3000°K.

The entropy at 298°K. is set so that ΔF is equal at T_m for the crystal and liquid.

Melting Data.

See crystal table for details.

Magnesium Tetraboride (MgB_4)
(Crystal) Mol. Wt. = 67.60

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.275	- 25.011	- 25.011	INFINITE
100	4.120	1.920	23.300	- 2.138	- 25.052	- 24.984	54.601
200	11.060	6.860	13.775	- 1.383	- 25.179	- 24.974	27.289
298	16.810	12.410	12.410	.000	- 25.100	- 24.797	18.176
300	16.900	12.514	12.410	.031	- 25.100	- 24.796	18.063
400	19.000	17.671	13.099	1.829	- 25.204	- 24.685	13.487
500	20.800	22.106	14.467	3.820	- 25.507	- 24.523	10.718
600	22.500	26.053	16.075	5.987	- 25.909	- 24.290	8.847
700	23.890	29.626	17.759	8.307	- 26.346	- 23.984	7.488
800	25.270	32.907	19.450	10.766	- 26.792	- 23.617	6.452
900	26.540	35.959	21.117	13.357	- 27.226	- 23.196	5.633
1000	27.660	38.814	22.745	16.069	- 29.773	- 22.540	4.926
1100	28.610	41.496	24.329	18.883	- 30.177	- 21.802	4.331
1200	29.450	44.022	25.866	21.787	- 30.576	- 21.020	3.828
1300	30.144	46.407	27.355	24.767	- 30.985	- 20.209	3.397
1400	30.800	48.665	28.798	27.814	- 61.770	- 18.882	2.947
1500	31.450	50.813	30.194	30.928	- 61.797	- 15.824	2.305
1600	32.000	52.861	31.547	34.101	- 61.813	- 12.755	1.742
1700	32.400	54.813	32.859	37.321	- 61.830	- 9.689	1.246
1800	32.800	56.676	34.131	40.581	- 61.847	- 6.623	.804
1900	33.200	58.460	35.365	43.881	- 61.855	- 3.555	.409
2000	33.600	60.173	36.563	47.221	- 61.848	- .484	.053

Mar. 31, 1963; Mar. 31, 1965

B_4Mg

MAGNESIUM TETRABORIDE (MgB_4) (CRYSTAL) MOL. WT. = 67.60

$\Delta H_f^\circ{}_0 = -25.0 \pm 2.0$ kcal. mole^{-1}

$S^\circ_{298.15} = 12.41 \pm 0.06$ cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15} = -25.1 \pm 2.0$ kcal. mole^{-1}

$T_d = [1100]$°K.

Heat of Formation.

The equilibrium pressures (1169-1177°K.) of the reaction $MgB_4(c) \rightarrow Mg(g) + 4B(c)$ were measured by M. Wright and P. N. Walsh, "The Vaporization of $MgB_4(c)$", Technical Research Report OMCC-HEF-55, Jan. 9, 1958, Ohio State University Research Foundation. The third law value of $\Delta H_r^\circ{}_{298.15}$ for this reaction was derived as 60.40 ± 1.5 kcal. mole^{-1}. This leads to a $\Delta H_f^\circ{}_{298.15} = -25.1 \pm 2.0$ kcal. mole^{-1} for $MgB_4(c)$. The unit of equilibrium pressures reported should be in atmosphere not in mm Hg as printed. The diameter of the hole drilled through the center of the lid served as the effusion orifice should be 1/16 inch rather than the reported value 1/6 inch.

Heat Capacity and Entropy.

The low temperature (17.34-299.53°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. 79, 3641 (1957). Above 298.15°K. the C_p values were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using S°_{20}(extrap.) = 0.022 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Decomposition.

T_d was estimated from the decomposition reaction reported by M. Wright and P. N. Walsh, loc. cit.

Disodium Tetraborate ($Na_2B_4O_7$)

(Crystal) Mol. Wt. = 201.262

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 7.262	- 778.909	- 778.909	INFINITE
100	18.290	12.145	76.954	- 6.481	- 781.288	- 766.799	1675.758
200	33.400	29.772	49.027	- 3.851	- 782.532	- 751.763	821.449
298	44.640	45.289	45.289	.000	- 783.160	- 736.520	539.857
300	44.801	45.566	45.290	.083	- 783.167	- 736.230	536.318
400	51.100	59.383	47.131	4.901	- 784.813	- 720.428	393.604
500	54.621	71.172	50.791	10.190	- 785.216	- 704.284	307.827
600	57.720	81.411	55.059	15.811	- 785.580	- 688.061	250.614
700	60.396	90.515	59.486	21.720	- 785.870	- 671.785	209.731
800	62.650	98.728	63.886	27.873	- 786.080	- 655.475	179.059
900	64.822	106.234	68.180	34.248	- 786.198	- 639.141	155.197
1000	66.850	113.170	72.337	40.833	- 786.228	- 622.794	136.105
1100	68.734	119.631	76.346	47.613	- 786.192	- 606.459	120.486
1200	70.474	125.687	80.208	54.575	- 832.554	- 589.205	107.304
1300	72.070	131.392	83.928	61.703	- 831.955	- 568.951	95.645
1400	73.522	136.787	87.512	68.984	- 831.280	- 548.744	85.659
1500	74.830	141.902	90.969	76.399	- 830.552	- 528.593	77.012
1600	76.485	146.784	94.306	83.964	- 829.742	- 508.483	69.452
1700	78.159	151.471	97.532	91.697	- 828.829	- 488.430	62.789
1800	79.853	155.986	100.655	99.597	- 827.814	- 468.438	56.873
1900	81.567	160.350	103.682	107.668	- 826.682	- 448.503	51.587
2000	83.300	164.577	106.622	115.911	- 825.421	- 428.633	46.837

Mar. 31, 1963; Mar. 31, 1965

DISODIUM TETRABORATE ($Na_2B_4O_7$) (CRYSTAL) MOL. WT. = 201.262

$S^\circ_{298.15}$ = 45.289 cal. deg.$^{-1}$ mole^{-1}

T_m = 1015.6°K

$\Delta H^\circ_{f\ 0}$ = -778.91 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -783.16 ± 2.0 kcal. mole^{-1}

ΔH°_m = 19.4 ± 1.5 kcal. mole^{-1}

Heat of Formation.

The heat of the reaction $Na_2O(c) + 2B_2O_3(l) \rightarrow Na_2B_4O_7(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $Na_2O(c)$ (June 30, 1962). The above ΔH°_r = -85.2 kcal. mole^{-1}.

Heat Capacity and Entropy.

In the low temperature region (5-344°K) the C_p values are those determined by E. F. Westrum, Jr., and G. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1015.6°K were smoothed graphically and used to determine C_p; the values did not join smoothly with those of Westrum and Grenier and the low temperature values were given greater weight. Above T_m the heat capacity was extrapolated. $S^\circ_{298.15}$ was derived from low temperature heat capacities.

Melting.

The value for T_m is from G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 58, 2248 (1936). Other reported values for T_m are: 1008 ± 5°K by S. S. Coles, S. R. Scholes, and C. R. Amberg, J. Am. Ceram. Soc. 18, 58 (1935); 1011°K by H. Menzel, Z. anorg. Chem., 224, 1 (1935); 1005°K by J. F. Ponomareff, Z. anorg. Chem. 89, 383 (1924); 1015°K by A. L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars", Carnegie Inst. of Washington, Publ. No. 31 (1905) p. 29; and 1064°K by C. H. Burgess and A. Holt, Proc. Roy. Soc. (London) 74, 285 (1904). ΔH°_m was obtained from the values of ΔH°_f for $Na_2B_4O_7(c)$ and $Na_2B_4O_7(l)$ at 298°K as described above and the difference between $H_{1015}-H_{298}$ for crystal and liquid.

Disodium Tetraborate ($Na_2B_4O_7$)

(Liquid) Mol. Wt. = 201.262

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	44.800	47.513	47.513	.000	- 778.360	- 732.383	536.825
300	44.967	47.791	47.514	.083	- 778.366	- 732.098	533.307
400	53.000	61.873	49.379	4.997	- 779.917	- 716.527	391.473
500	59.100	74.374	53.152	10.611	- 779.996	- 700.664	306.245
600	64.200	85.601	57.640	16.777	- 779.814	- 684.809	249.430
700	69.200	95.874	62.378	23.447	- 779.343	- 669.009	208.864
800	106.330	107.921	67.260	32.529	- 776.624	- 653.374	178.485
900	106.330	120.445	72.487	43.162	- 772.484	- 638.217	154.973
1000	106.330	131.648	77.853	53.795	- 768.465	- 623.509	136.261
1100	106.330	141.783	83.212	64.428	- 764.577	- 609.211	121.033
1200	106.330	151.035	88.484	75.061	- 807.268	- 594.337	108.238
1300	106.330	159.545	93.627	85.694	- 803.164	- 576.760	96.957
1400	106.330	167.425	98.620	96.327	- 799.137	- 559.494	87.337
1500	106.330	174.761	103.455	106.960	- 795.191	- 542.520	79.041
1600	106.330	181.624	108.128	117.593	- 791.313	- 525.798	71.817
1700	106.330	188.070	112.643	128.226	- 787.499	- 509.319	65.474
1800	106.330	194.148	117.004	138.859	- 783.752	- 493.067	59.864
1900	106.330	199.897	121.217	149.492	- 780.057	- 477.018	54.867
2000	106.330	205.351	125.288	160.125	- 776.406	- 461.166	50.391
2100	106.330	210.538	129.225	170.758	- 772.795	- 445.489	46.360
2200	106.330	215.485	133.034	181.391	- 769.230	- 429.988	42.713
2300	106.330	220.212	136.723	192.024	- 765.699	- 414.653	39.399
2400	106.330	224.737	140.296	202.657	- 762.211	- 399.453	36.373
2500	106.330	229.077	143.761	213.290	- 780.308	- 383.983	33.566
2600	106.330	233.248	147.124	223.929	- 776.859	- 368.196	30.948
2700	106.330	237.261	150.388	234.556	- 773.433	- 352.541	28.535
2800	106.330	241.128	153.560	245.189	- 770.028	- 337.021	26.304
2900	106.330	244.859	156.644	255.822	- 766.643	- 321.598	24.235
3000	106.330	248.464	159.645	266.455	- 763.282	- 306.317	22.314

Mar. 31, 1963; Mar. 31, 1965

DISODIUM TETRABORATE ($Na_2B_4O_7$) (LIQUID) MOL. WT. = 201.262

$S^\circ_{298.15}$ = 47.513 ± 1.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 1015.6°K.

ΔH_f° 298.15 = -778.36 ± 2.0 kcal. mole^{-1}

ΔH_m° = 19.4 ± 1.5 kcal. mole^{-1}

Heat of Formation.

The heat of reaction $Na_2O(c) + 2B_2O_3(l) \rightarrow Na_2B_4O_7(l)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $Na_2O(c)$ (June 30, 1962). The above ΔH_r° = -80.4 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916, in the range 298 to 1373°K, were smoothed graphically and used to determine C_p. These were joined smoothly with the low temperature data of E. F. Westrum and G. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). At 743°K a glass transition was observed and above this temperature the C_p adopted as constant.

The entropy at 298°K obtained from that of the crystal by adding ΔS_m° and the difference between $S_{1015}-S_{298}$ for crystal and liquid.

Melting.

See the crystal for details.

Lead Tetraborate (PbB_4O_7)
(Crystal) Mol. Wt. = 362.49

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	40.200	39.900	39.900	- .000	- 683.000	- 637.470	467.255
300	40.400	40.149	39.901	.075	- 683.003	- 637.188	464.169
400	49.360	53.030	41.596	4.573	- 682.933	- 621.915	339.782
500	57.020	64.890	45.085	9.902	- 682.487	- 606.706	265.178
600	63.470	75.875	49.312	15.938	- 681.684	- 591.616	215.486
700	68.630	86.060	53.844	22.551	- 681.728	- 576.499	179.982
800	72.780	95.504	58.468	29.629	- 680.344	- 561.561	153.404
900	76.070	104.271	63.076	37.075	- 678.725	- 546.809	132.777
1000	78.880	112.436	67.609	44.827	- 676.913	- 532.241	116.316
1100	81.140	120.064	72.035	52.832	- 674.960	- 517.873	102.887
1200	82.940	127.205	76.338	61.040	- 672.887	- 503.679	91.728
1300	84.250	133.897	80.511	69.402	- 670.746	- 489.666	82.316
1400	85.290	140.180	84.551	77.880	- 668.565	- 475.818	74.275
1500	86.180	146.096	88.459	86.456	- 666.366	- 462.131	67.329
1600	86.860	151.680	92.237	95.109	- 664.162	- 448.583	61.271
1700	87.400	156.963	95.891	103.823	- 661.964	- 435.176	55.943
1800	87.810	161.970	99.424	112.584	- 659.788	- 421.901	51.223
1900	88.120	166.727	102.842	121.381	- 657.633	- 408.746	47.014
2000	88.370	171.253	106.150	130.206	- 655.497	- 395.701	43.238

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

LEAD TETRABORATE (PbB_4O_7) (CRYSTAL) MOL. WT. = 362.49

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [39.9 ± 3] cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15}$ = -683 ± 1.5 kcal. mole^{-1}

Heat of Formation.

See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$$PbO(c) + 2B_2O_3(c) \rightarrow PbO\cdot 2B_2O_3(gls.) \qquad \Delta H_r = -11.9 \text{ kcal. mole}^{-1}$$

and estimated a ΔH_{298} of 11.4 kcal. mole^{-1} for the conversion to the $PbO\cdot 2B_2O_3$(crystal). With auxiliary JANAF values the $\Delta H_f^\circ{}_{298.15}$ was calculated to be -683.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:

$$MO\cdot B_2O_3 + B_2O_3 \rightarrow MO\cdot 2B_2O_3$$

that the simple addition of entropies will give values at least 2.7 e.u. in the case of Na borates and 5.7 e.u. for Ca borates too high for the reaction. The reason for this is probably structural, the $B_4O_7^{--}$ ion is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the average entropy difference of 4.2 for the reaction was assumed to hold for each additional mole of B_2O_3. Therefore the entropy at 298.15 was obtained from $S^\circ_{298.15}$ for PbB_2O_4 and B_2O_3 and the subtraction of 4.2 e.u.

Pentaborane (B_5H_9)
(Liquid) Mol. Wt. = 63.172

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	36.120	44.056	44.056	.000	10.240	41.067	- 30.102
300	36.400	44.280	44.057	.067	10.224	41.257	- 30.054
400	44.300	55.913	45.589	4.130	9.553	51.710	- 28.252
500	45.500	65.862	48.681	8.590	8.803	62.328	- 27.242
600	50.200	74.520	52.276	13.346	8.034	73.110	- 26.629
700	58.400	82.942	56.056	18.820	7.769	83.989	- 26.221
800	61.300	90.934	59.923	24.809	7.856	94.870	- 25.916
900	63.838	98.307	63.784	31.071	8.084	105.734	- 25.674
1000	65.800	105.139	67.582	37.557	8.414	116.569	- 25.475
1100	66.987	111.468	71.288	44.198	8.768	127.365	- 25.304
1200	68.000	117.341	74.884	50.949	9.121	138.136	- 25.157
1300	68.840	122.818	78.363	57.792	9.446	148.869	- 25.026
1400	69.507	127.945	81.723	64.711	9.737	159.588	- 24.912
1500	70.000	132.759	84.967	71.688	9.962	170.279	- 24.808

Dec. 31, 1962; Mar. 31, 1965

PENTABORANE (B_5H_9) (LIQUID) MOL. WT. = 63.172

$S^\circ_{298.15}$ = 44.056

$\Delta H^\circ_{f\ 298.15}$ = 10.240 ± 1.6 kcal. mole^{-1}

T_m = 226.34°K.

ΔH°_m = 1.466 kcal. mole^{-1}

T_b = 335°K.

ΔH°_v = 6.79 kcal. mole^{-1}

Heat of Formation.

The vapor pressures of B_5H_9(l) were measured by H. E. Wirth and E. D. Palmer, J. Phys. Chem. 60, 914 (1956) and H. L. Johnston, E. C. Kerr, J. T. Clarke and N. C. Hallett, "Calorimetric Investigation with the Condensed Gas Calorimeter. IV. The Heat Capacities, Latent Heats and Entropies of Pentaborane from 13 to 296°K.; Heats of Transition, Fusion and Vaporization; Vapor Pressures of the Liquid", TR-6, July 8, 1949, The Ohio State University. By use of both the second and third law methods, the respective heats of vaporization ($\Delta H^\circ_{v\ 298.15}$) were evaluated. The $\Delta H^\circ_{f\ 298.15}$ values for B_5H_9(l) were calculated from $\Delta H^\circ_{f\ 298.15}$ for B_5H_9(g) and $\Delta H^\circ_{v\ 298.15}$ for B_5H_9(l) obtained previously. The results are presented as follows.

Investigator	$\Delta H^\circ_{v\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H^\circ_{f\ 298.15}$* kcal. mole^{-1}
Wirth and Palmer	7.26 ± 0.02	7.26	10.24 ± 1.6
Johnston, et al.	7.23 ± 0.04	7.25	10.23 ± 1.6

*Calculation based on the third law $\Delta H^\circ_{v\ 298.15}$ values.

The adopted value is the average of the two $\Delta H^\circ_{f\ 298.15}$ values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p), 231.34 - 290.19°K., for B_5H_9(l) were measured by Johnston, Kerr, Clarke and Hallett, loc. cit. The C_p values above 290.19°K. were estimated by graphical extrapolation of the C_p curve plotted using the experimental data. The value of $S^\circ_{298.15}$ was derived based on the low temperature C_p, 13.29 - 221.61°K., and ΔH°_m for B_5H_9(c) reported by Johnston, Kerr, Clarke and Hallett, loc. cit. and C_p values, 226.34 - 298.15°K., for B_5H_9(l), using $S^\circ_{13.29}$ = 0.236 cal. deg.$^{-1}$ mole^{-1} for B_5H_9(c).

Melting Data.

The values of T_m and ΔH°_m were taken from Johnston, Kerr, Clarke and Hallett, loc. cit.

Vaporization Data.

The boiling point (T_b) is calculated as the temperature at which the free energy change of the reaction $B_5H_9(l) \rightarrow B_5H_9(g)$ becomes zero. The enthalpy change of the reaction at T_b is heat of vaporization (ΔH°_v).

B_5H_9

Pentaborane (B_5H_9)
(Ideal Gas) Mol. Wt. = 63.172

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.624	24.444	24.444	INFINITE
100	8.289	51.631	79.877	- 2.825	21.798	27.649	- 60.425
200	13.810	58.709	67.570	- 1.772	19.737	34.251	- 37.426
298	22.423	65.803	65.803	.000	17.500	41.843	- 30.671
300	22.588	65.943	65.804	.042	17.458	41.993	- 30.590
400	31.120	73.631	66.794	2.735	15.418	50.488	- 27.584
500	38.568	81.397	68.939	6.229	13.702	59.459	- 25.988
600	44.841	89.000	71.653	10.409	12.357	68.744	- 25.039
700	50.047	96.316	74.657	15.161	11.370	78.228	- 24.423
800	54.342	103.289	77.804	20.388	10.695	87.825	- 23.991
900	57.882	109.901	81.006	26.005	10.278	97.493	- 23.673
1000	60.805	116.155	84.212	31.944	10.061	107.200	- 23.427
1100	63.227	122.068	87.387	38.149	9.979	116.915	- 23.228
1200	65.245	127.658	90.512	44.576	10.008	126.642	- 23.064
1300	66.936	132.949	93.575	51.187	10.101	136.353	- 22.922
1400	68.361	137.964	96.568	57.954	10.240	146.064	- 22.801
1500	69.569	142.722	99.488	64.852	10.386	155.759	- 22.693
1600	70.600	147.246	102.332	71.862	10.530	165.443	- 22.597
1700	71.486	151.553	105.102	78.967	10.669	175.126	- 22.513
1800	72.250	155.661	107.798	86.155	10.795	184.790	- 22.436
1900	72.914	159.586	110.421	93.414	10.912	194.454	- 22.366
2000	73.494	163.341	112.974	100.735	11.020	204.114	- 22.304
2100	74.002	166.939	115.458	108.110	11.113	213.769	- 22.246
2200	74.450	170.393	117.877	115.533	11.192	223.416	- 22.193
2300	74.847	173.711	120.233	122.999	11.257	233.059	- 22.145
2400	75.199	176.904	122.528	130.501	11.298	242.712	- 22.101
2500	75.514	179.980	124.765	138.037	- 15.619	252.887	- 22.106
2600	75.796	182.948	126.946	145.603	- 15.573	263.629	- 22.159
2700	76.050	185.813	129.074	153.195	- 15.532	274.372	- 22.208
2800	76.279	188.583	131.150	160.812	- 15.494	285.096	- 22.252
2900	76.486	191.263	133.177	168.451	- 15.456	295.856	- 22.295
3000	76.674	193.860	135.157	176.109	- 15.426	306.571	- 22.333
3100	76.845	196.376	137.091	183.785	- 15.396	317.299	- 22.368
3200	77.001	198.819	138.982	191.477	- 15.377	328.034	- 22.403
3300	77.144	201.190	140.831	199.185	- 15.365	338.780	- 22.435
3400	77.275	203.495	142.641	206.906	- 15.357	349.503	- 22.465
3500	77.396	205.737	144.412	214.639	- 15.364	360.231	- 22.493
3600	77.507	207.919	146.146	222.384	- 15.378	370.965	- 22.520
3700	77.609	210.044	147.844	230.140	- 15.407	381.701	- 22.545
3800	77.704	212.115	149.508	237.906	- 15.440	392.442	- 22.569
3900	77.792	214.135	151.139	245.681	- 15.492	403.162	- 22.591
4000	77.874	216.105	152.739	253.464	- 621.447	424.629	- 23.200
4100	77.950	218.029	154.308	261.256	- 620.363	450.760	- 24.027
4200	78.021	219.908	155.848	269.054	- 619.289	476.899	- 24.815
4300	78.087	221.745	157.359	276.860	- 618.231	502.968	- 25.562
4400	78.148	223.541	158.843	284.671	- 617.190	529.028	- 26.276
4500	78.206	225.298	160.300	292.489	- 616.165	555.050	- 26.956
4600	78.260	227.017	161.732	300.312	- 615.148	581.084	- 27.606
4700	78.311	228.701	163.139	308.141	- 614.154	607.085	- 28.228
4800	78.359	230.350	164.522	315.975	- 613.172	633.064	- 28.823
4900	78.404	231.966	165.882	323.813	- 612.210	659.005	- 29.392
5000	78.446	233.551	167.220	331.655	- 611.261	684.932	- 29.937
5100	78.486	235.104	168.535	339.502	- 610.336	710.863	- 30.461
5200	78.524	236.629	169.830	347.352	- 609.420	736.748	- 30.963
5300	78.559	238.125	171.105	355.206	- 608.524	762.631	- 31.446
5400	78.593	239.594	172.360	363.064	- 607.652	788.477	- 31.910
5500	78.625	241.036	173.595	370.925	- 606.791	814.351	- 32.358
5600	78.655	242.453	174.812	378.789	- 605.955	840.150	- 32.787
5700	78.684	243.845	176.011	386.656	- 605.139	865.989	- 33.202
5800	78.711	245.214	177.192	394.526	- 604.343	891.776	- 33.601
5900	78.737	246.560	178.357	402.398	- 603.563	917.572	- 33.987
6000	78.761	247.883	179.505	410.273	- 602.804	943.348	- 34.360

Dec. 31, 1960; Mar. 31, 1965

PENTABORANE (B_5H_9) (IDEAL GAS) MOL. WT. = 63.172

Point Group C_{4v}

$\Delta H_f^\circ{}_0 = 24.4 \pm 1.6$ kcal. mole^{-1}

$S^\circ_{298.15} = 65.803$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 17.5 \pm 1.6$ kcal. mole^{-1}

Ground State Quantum Weight = 1

$\sigma = 4$

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
2600 (1)	[1450](1)	[1500](1)	1449 (2)
2600 (1)	[500](1)	[1100](1)	1034 (2)
1844 (1)	1870 (1)	738 (1)	882 (2)
1413 (1)	1387 (1)	470 (1)	700 (2)
1126 (1)	[900](1)	2598 (2)	605 (2)
985 (1)	782 (1)	1802 (2)	568 (2)
799 (1)	2600 (1)	1621 (2)	

Bond Distance: B-B = 1.800 ± 0.003 Å B-B_{apex} = 1.687 ± 0.005 Å
B-H = B_{apex}-H = 1.22 Å B-H_{bridge} = 1.35 ± 0.02 Å

Bond Angle: B_{apex}-B-H = 136° 10' ± 30' H-B_{apex}-B = 131° Å
B-H_{bridge}-B = 83° 37' B-B-B = 90°
Angle between B_{apex}BB plane and BBH_{bridge} plane = 196 ± 2°

Product of the Moments of Inertia: $I_AI_BI_C = 2.3693 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The enthalpy change ($\Delta H_r^\circ{}_{298.15}$) of the reaction $B_5H_9(g) \rightarrow 5B(am.) + 9/2\ H_2(g)$ was reported to be -12.99 ± 0.39 and -9.9 ± 1 kcal. mole^{-1} by E. J. Prosen, W. H. Johnson and F. Y. Pergiel, J. Res. Natl. Bur. Std. 61, 247 (1958) and S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 2173 (1961), respectively. Using $\Delta H_r^\circ{}_{298.15} = 1.2 \pm 0.4$ kcal. mole^{-1} for the reaction $B(c) \rightarrow B(am.)$, the corresponding $\Delta H_f^\circ{}_{298.15}$ values for $B_5H_9(g)$ were derived as 18.99 and 15.9 kcal. mole^{-1}. The adopted value is the average of these two.

Heat Capacity and Entropy.

The molecular structure, a tetragonal pyramid of boron atoms, and constants were obtained from H. J. Hrostowski and R. J. Myers, J. Chem. Phys. 22, 262 (1954). The vibrational frequencies were reported by H. J. Hrostowski and G. C. Pimentel, J. Am. Chem. Soc. 76, 998 (1954). The earlier models of pentaborane were assumed to have a hydro carbon - like structure of low symmetry by S. H. Bauer and L. Pauling, J. Am. Chem. Soc. 58, 2403 (1936) and K. S. Pitzer, J. Am. Chem. Soc. 67, 1126 (1945). However, the electron diffraction and X-ray data by K. Hedberg, M. E. Jones and V. Schomaker, Proc. Natl. Acad. Sci., U. S. 38, 679 (1952) and W. J. Dulmage and W. N. Lipscomb, Acta Cryst. 5, 260 (1952) revealed an unusual pyramidal structure of C_{4v} symmetry. The Raman spectrum of liquid B_5H_9 and the infrared spectrum of the gas B_5H_9 from 3 to 25 microns have been obtained by W. J. Taylor, C. W. Beckett, J. Y. Tung, R. B. Holden and H. L. Johnston, Phys. Rev. 79, 234 (1950). The near infrared spectrum of $B_5H_9(l)$ have been examined at high resolution by P. R. Pondy and H. C. Beachell, J. Chem. Phys. 25, 238 (1956). Ten bands were observed. The three principal moments of inertia are: $I_A = I_B = 1.18344 \times 10^{-38}$ and $I_C = 1.69172 \times 10^{-38}$ g. cm.^{2}

B_5H_9

Dipotassium Hexaborate ($K_2B_6O_{10}$)

(Crystal) Mol. Wt. = 303.12

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	62.600	60.000	60.000	.000	-1107.440	-1040.549	762.707
300	62.700	60.388	60.001	.116	-1107.445	-1040.136	757.702
400	68.300	79.197	62.528	6.668	-1109.008	-1017.426	555.869
500	73.680	95.019	67.483	13.768	-1109.527	- 994.470	434.662
600	78.900	108.916	73.252	21.398	-1109.974	- 971.412	353.820
700	84.000	121.461	79.257	29.543	-1110.247	- 948.292	296.056
800	89.100	133.013	85.263	38.199	-1110.275	- 925.159	252.730
900	94.040	143.795	91.174	47.359	-1110.005	- 902.032	219.033
1000	98.670	153.962	96.949	57.012	-1109.439	- 878.945	192.084
1100	101.170	163.490	102.571	67.012	-1146.532	- 853.887	169.644
1200	102.790	172.365	108.021	77.212	-1145.280	- 827.333	150.671
1300	104.130	180.646	113.293	87.559	-1144.016	- 800.893	134.636
1400	105.320	188.407	118.384	98.032	-1142.739	- 774.542	120.906
1500	106.450	195.712	123.298	108.621	-1141.465	- 748.294	109.021
1600	107.520	202.616	128.042	119.320	-1140.183	- 722.116	98.632
1700	108.580	209.167	132.623	130.125	-1138.894	- 696.030	89.476
1800	109.613	215.402	137.050	141.035	-1137.595	- 670.018	81.347
1900	110.620	221.356	141.331	152.047	-1136.276	- 644.079	74.082
2000	111.600	227.055	145.476	163.158	-1134.919	- 618.209	67.551

Mar. 31, 1963; Mar. 31, 1965

DIPOTASSIUM HEXABORATE ($K_2B_6O_{10}$) (CRYSTAL) MOL. WT. = 303.12

$S^\circ_{298.15}$ = [60 ± 3] cal. deg.$^{-1}$ mole^{-1}

T_d = 1098°K

$\Delta H_f^\circ{}_0$ = Unknown

$\Delta H_f^\circ{}_{298.15}$ = -1,107.44 ± 2.4 kcal. mole^{-1}

Heat of Formation.

The heat of reaction $K_2O(c) + 3B_2O_3(l) \rightarrow K_2B_6O_{10}(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above ΔH_r° = -122.8 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 973°K were graphically smoothed and used to determine C_p. Above this range C_p was extrapolated.

The entropy at 298°K was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate that for the reactions

$MO + B_2O_3 \rightarrow MO.B_2O_3$ (1)

$MO.B_2O_3 + B_2O_3 \rightarrow MO.2B_2O_3$ (2)

the simple addition of entropies will give values at least 2.7 e.u. too low for reaction (1) and at least 2.7 e.u. too high for reaction (2). The reason for this is probably structural, the $B_2O_4^{--}$ ion being a flexible chain while the $B_4O_7^{--}$ ion probably is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the entropy difference for reaction (2) was assumed to hold for each additional mole of B_2O_3 added. Thus a value for $Na_2B_6O_{10}$ was estimated to be 55.5 ± 1.5 and then using an average value of 4.5 ± 1.5 e.u. for the difference between K_2 and Na_2 gave 60 ± 3 e.u. for the entropy of $K_2B_6O_{10}$.

Decomposition Temperature.

The incongruent melting point was given by A.-P. Rollet, Comp. rend. 200, 1763 (1935), the decomposition products being $K_2B_4O_7(l)$ and $K_2B_8O_{13}(c)$.

Dilithium Hexaborate ($Li_2B_6O_{10}$)

(Crystal) Mol. Wt. = 238.80

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	70.080	45.000	45.000	.000	-1113.740	-1047.448	767.763
300	70.180	45.434	45.001	.130	-1113.727	-1047.039	762.731
400	75.590	66.378	47.820	7.423	-1113.163	-1024.899	559.952
500	80.440	83.779	53.319	15.230	-1114.325	-1002.723	438.269
600	84.610	98.824	59.677	23.489	-1114.117	- 980.419	357.100
700	88.050	112.132	66.238	32.126	-1113.866	- 958.156	299.135
800	90.940	124.083	72.734	41.079	-1113.557	- 935.939	255.674
900	93.390	134.939	79.052	50.299	-1113.185	- 913.759	221.880
1000	95.500	144.890	85.145	59.745	-1112.764	- 891.614	194.853
1100	97.145	154.069	90.999	69.377	-1112.327	- 869.526	172.751
1200	98.747	162.591	96.614	79.172	-1111.862	- 847.470	154.338
1300	100.305	170.557	101.999	89.125	-1111.370	- 825.461	138.766
1400	101.819	178.046	107.166	99.232	-1110.835	- 803.483	125.423
1500	103.290	185.121	112.129	109.488	-1110.266	- 781.558	113.867
1600	104.717	191.833	116.903	119.888	-1109.651	- 759.655	103.759
1700	106.101	198.223	121.500	130.430	-1179.083	- 735.145	94.505
1800	107.441	204.326	125.933	141.107	-1178.015	- 709.063	86.088
1900	108.737	210.170	130.214	151.916	-1176.893	- 683.039	78.564
2000	109.990	215.780	134.353	162.853	-1175.706	- 657.082	71.799

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

DILITHIUM HEXABORATE ($Li_2B_6O_{10}$) (CRYSTAL) MOL. WT. = 238.80

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [45.0 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -1,113.74 ± 2.40 kcal. mole^{-1}

T_d = 1107 ± 4°K.

Heat of Formation.

The heat of reaction $Li_2O(c) + 3B_2O_3(l) \rightarrow Li_2B_6O_{10}(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and $Li_2O(c)$ (March 31, 1964). The above ΔH_r° = -72.80 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurement of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 823°K. were used to determine C_p. Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $LiBO_2(c)$.

Temperature of Decomposition.

The incongruent melting point reported by B. S. R. Sastry and F. A. Hummel, J. Am. Ceram. Soc. 42, 216-8 (1959) is used here.

Disodium Hexaborate ($Na_2B_6O_{10}$)

(Crystal) Mol. Wt. = 270.902

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	58.200	55.500	55.500	.000	-1094.760	-1078.411	753.810
300	58.400	55.861	55.501	.108	-1094.771	-1028.001	748.862
400	67.680	73.944	57.904	6.416	-1096.638	-1005.551	549.381
500	76.480	90.005	62.745	13.630	-1097.039	- 982.725	429.528
600	84.550	104.673	68.527	21.687	-1097.049	- 959.852	349.609
700	91.940	118.271	74.674	30.518	-1096.616	- 937.015	292.535
800	98.560	130.990	80.927	40.051	-1095.733	- 914.275	249.756
900	104.250	142.937	87.160	50.199	-1094.431	- 891.667	216.516
1000	109.000	154.176	93.305	60.871	-1092.784	- 869.214	189.958
1100	112.680	164.745	99.324	71.962	-1090.904	- 846.957	168.267
1200	115.420	174.671	105.194	83.373	-1135.327	- 823.949	150.054
1300	117.530	183.996	110.901	95.024	-1132.759	- 798.106	134.167
1400	119.140	192.768	116.438	106.861	-1130.118	- 772.461	120.581
1500	120.330	201.030	121.805	118.838	-1127.456	- 747.014	108.835
1600	121.180	208.824	127.002	130.915	-1124.796	- 721.731	98.579
1700	121.830	216.191	132.034	143.067	-1122.156	- 696.619	89.552
1800	122.330	223.169	136.905	155.275	-1119.557	- 671.666	81.548
1900	122.740	229.794	141.621	167.529	-1116.990	- 646.852	74.401
2000	123.120	236.100	146.189	179.822	-1114.447	- 622.179	67.985

Mar. 31, 1963; Mar. 31, 1965

DISODIUM HEXABORATE ($Na_2B_6O_{10}$) (CRYSTAL) MOL. WT. = 270.902

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [55.5 ± 1.5] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -1094.76 ± 2.2 kcal. mole^{-1}

T_d = 1039°K.

Heat of Formation.

The heat of reaction $Na_2O(c) + 3B_2O_3(l) \rightarrow Na_2B_6O_{10}(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $Na_2O(c)$ (June 30, 1962). The above ΔH_r° = -97.52 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1039°K were smoothed graphically and used to determine C_p. Above this range C_p was extrapolated. Entropy at 298°K was estimated as described in detail for $K_2B_6O_{10}(c)$.

Decomposition Temperature.

The incongruent melting point was reported by G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 58, 2248 (1936), the products are $Na_2B_4O_7(l)$ and $Na_2B_8O_{13}(c)$.

Lead Hexaborate (PbB_6O_{10})

(Crystal) Mol. Wt. = 432.13

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	55.200	48.600	48.600	.000	-1003.000	- 937.311	687.034
300	55.400	48.942	48.601	.102	-1003.005	- 936.905	682.502
400	68.400	66.696	50.934	6.305	-1002.941	- 914.864	499.835
500	79.880	83.221	55.758	13.732	-1002.320	- 892.906	390.270
600	89.830	98.678	61.637	22.225	-1001.142	- 871.122	317.291
700	98.880	113.227	67.978	31.674	-1000.549	- 849.391	265.179
800	106.230	126.932	74.499	41.946	- 998.258	- 827.954	226.176
900	111.630	139.770	81.046	52.851	- 995.533	- 806.826	195.915
1000	115.590	151.746	87.525	64.222	- 992.513	- 786.009	171.774
1100	118.420	162.904	93.876	75.931	- 989.322	- 765.520	152.087
1200	120.220	173.290	100.066	87.868	- 986.030	- 745.314	135.734
1300	121.370	182.961	106.075	99.952	- 982.721	- 725.390	121.943
1400	121.990	191.980	111.893	112.122	- 979.438	- 705.717	110.162
1500	122.320	200.409	117.516	124.339	- 976.226	- 686.285	99.987
1600	122.540	208.310	122.947	136.582	- 973.093	- 667.051	91.111
1700	122.730	215.745	128.189	148.846	- 970.038	- 648.017	83.304
1800	122.880	222.765	133.250	161.127	- 967.066	- 629.167	76.388
1900	122.990	229.411	138.138	173.420	- 964.164	- 610.473	70.217
2000	123.080	235.722	142.860	185.724	- 961.317	- 591.933	64.680

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

LEAD HEXABORATE (PbB_6O_{10}) (CRYSTAL) MOL. WT. = 432.13

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [48.6 ± 3] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -1003 ± 2.0 kcal mole^{-1}

Heat of Formation.

See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and De Carli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$PbO(c) + 3B_2O_3(c) \rightarrow PbO\cdot 3B_2O_3(gls.)$ ΔH_r = -24.5 kcal./mole

and estimated a ΔH_{298} of 16.0 kcal. mole^{-1} for the conversion to the $PbO\cdot 3B_2O_3$(crystal). With auxiliary JANAF values the $\Delta H^\circ_{f\ 298.15}$ was calculated to be -1003.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the PbB_4O_7 table from $S^\circ_{298.15}$ for PbB_4O_7 and B_2O_3 and the subtraction of 4.2 e.u.

Dipotassium Octaborate ($K_2B_8O_{13}$)

(Crystal) Mol. Wt. = 372.76

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	76.790	70.200	70.200	.000	-1420.920	-1334.318	978.035
300	76.970	70.676	70.201	.142	-1420.928	-1333.783	971.614
400	86.160	94.086	73.331	8.302	-1422.594	-1304.441	712.679
500	94.960	114.253	79.541	17.356	-1423.082	-1274.844	557.207
600	104.000	132.371	86.859	27.307	-1423.290	-1245.167	453.530
700	112.680	149.077	94.569	38.156	-1423.058	-1215.489	379.475
800	119.600	164.587	102.364	49.778	-1422.407	-1185.887	323.954
900	125.500	179.023	110.089	62.041	-1421.387	-1156.380	280.794
1000	130.500	192.518	117.664	74.853	-1420.072	-1126.992	246.292
1100	134.000	205.122	125.049	88.081	-1456.404	-1095.715	217.688
1200	137.200	216.921	132.218	101.643	-1454.300	-1063.009	193.591
1300	140.100	228.019	139.165	115.511	-1452.069	-1030.496	173.234
1400	142.700	238.499	145.890	129.653	-1449.712	- 998.150	155.811
1500	145.000	248.424	152.397	144.041	-1447.268	- 965.990	140.738
1600	147.000	257.848	158.696	158.643	-1444.744	- 933.978	127.569
1700	148.700	266.812	164.794	173.431	-1442.166	- 902.136	115.972
1800	150.100	275.353	170.701	188.373	-1439.558	- 870.449	105.682
1900	151.200	283.499	176.425	203.441	-1436.932	- 838.904	96.491
2000	152.000	291.276	181.975	218.603	-1434.291	- 807.497	88.235

Mar. 31, 1963; Mar. 31, 1965

DIPOTASSIUM OCTABORATE ($K_2B_8O_{13}$) (CRYSTAL) MOL. WT. = 372.76

$S^\circ_{298.15}$ = [70.2 ± 4] cal. deg.$^{-1}$ mole^{-1}

T_m = 1130°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -1,420.92 ± 1.4 kcal. mole^{-1}

ΔH°_m = 29.9 ± 1.0 kcal. mole^{-1}

Heat of Formation.

The heat of reaction $K_2O(c) + 4B_2O_3(l) \rightarrow K_2B_8O_{13}(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above ΔH°_r = -137.00 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1130°K were smoothed graphically and used to determine C_p. Above this range C_p is extrapolated.

The entropy at 298°K was obtained by estimating the entropy of $Na_2B_8O_{13}(c)$ as 65.7 ± 2.5 e.u., as described on the table for $K_2B_6O_{10}(c)$ and then using an average value of 4.5 ± 1.5 e.u., for the replacement of Na_2 by K_2.

Melting Data.

T_m is given by A.-P. Rollet, Comp. rend., 200, 1763 (1935). ΔH°_m was obtained from the values of ΔH°_f for $K_2B_8O_{13}(c)$ and $K_2B_8O_{13}(l)$ at 298°K reported above and the enthalpy of the crystal and liquid at T_m.

Dipotassium Octaborate ($K_2B_8O_{13}$)

(Liquid) Mol. Wt. = 372.76

		cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}		
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	77.220	71.295	71.295	.000	-1403.570	-1317.295	965.557
300	77.560	71.774	71.296	.143	-1403.577	-1316.762	959.214
400	94.120	96.428	74.546	8.753	-1404.793	-1287.577	703.466
500	107.600	119.017	81.215	18.901	-1404.186	-1258.330	549.989
600	113.600	139.279	89.240	30.024	-1403.223	-1229.245	447.731
700	158.100	158.560	97.707	42.597	-1401.267	-1200.336	374.744
800	158.100	179.671	106.662	58.407	-1396.428	-1171.976	320.154
900	158.100	198.292	115.829	74.217	-1391.861	-1144.196	277.835
1000	158.100	214.950	124.923	90.027	-1387.549	-1116.901	244.087
1100	158.100	230.018	133.803	105.837	-1421.298	-1087.994	216.154
1200	158.100	243.775	142.403	121.647	-1416.946	-1057.880	192.657
1300	158.100	256.430	150.694	137.457	-1412.773	-1028.135	172.837
1400	158.100	268.146	158.670	153.267	-1408.749	- 998.692	155.895
1500	158.100	279.054	166.336	169.077	-1404.882	- 969.549	141.256
1600	158.100	289.257	173.703	184.887	-1401.151	- 940.639	128.479
1700	158.100	298.842	180.785	200.697	-1397.550	- 911.971	117.236
1800	158.100	307.879	187.597	216.507	-1394.074	- 883.512	107.268
1900	158.100	316.427	194.155	232.317	-1390.706	- 855.241	98.370
2000	158.100	324.536	200.473	248.127	-1387.418	- 827.144	90.382
2100	158.100	332.250	206.566	263.937	-1384.214	- 799.200	83.170
2200	158.100	339.605	212.447	279.747	-1381.102	- 771.418	76.630
2300	158.100	346.633	218.130	295.557	-1378.060	- 743.784	70.672
2400	158.100	353.361	223.625	311.367	-1375.103	- 716.253	65.221
2500	158.100	359.815	228.945	327.177	-1415.323	- 688.003	60.142
2600	158.100	366.016	234.098	342.987	-1412.447	- 658.962	55.388
2700	158.100	371.983	239.095	358.797	-1409.622	- 630.030	50.995
2800	158.100	377.733	243.945	374.607	-1406.844	- 601.218	46.925
2900	158.100	383.281	248.654	390.417	-1404.110	- 572.465	43.140
3000	158.100	388.640	253.232	406.227	-1401.422	- 543.847	39.617

Mar. 31, 1963; Mar. 31, 1965

DIPOTASSIUM OCTABORATE ($K_2B_8O_{13}$) (LIQUID) MOL. WT. = 372.76

$S^\circ_{298.15}$ = [71.295] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -1,403.57 ± 2.4 kcal. mole^{-1}

T_m = 1130°K.

ΔH_m = 29.9 ± 1.0 kcal. mole^{-1}

Heat of Formation.

The heat of reaction $K_2O(c) + 4B_2O_3(l) \rightarrow K_2B_8O_{13}(l)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above ΔH_r° = -119.65 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1373°K on the glass and liquid were smoothed graphically and used to determine C_p. There is a discontinuity in the C_p curve, a glass transition at about 673°K. Above 673°K the C_p values were estimated to be constant.

The entropy was obtained from that of the crystal by adding ΔS_m° and the difference between $S_{1130}-S_{298}$ for crystal and liquid.

Melting Data.

See the crystal table.

Dilithium Octaborate ($Li_2B_8O_{13}$)

(Crystal) Mol. Wt. = 308.44

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	77.800	63.400	63.400	.000	-1413.570	-1330.011	974.878
300	78.100	63.882	63.401	.144	-1413.572	-1329.496	968.490
400	93.300	88.577	66.665	8.765	-1413.391	-1301.481	711.062
500	102.430	110.437	73.281	18.578	-1414.469	-1273.398	556.575
600	108.320	129.656	81.109	29.128	-1414.053	-1245.219	453.549
700	112.700	146.692	89.284	40.186	-1413.580	-1217.117	379.983
800	116.320	161.986	97.432	51.643	-1413.054	-1189.095	324.830
900	119.200	175.858	105.387	63.423	-1412.475	-1161.135	281.949
1000	121.570	188.542	113.078	75.464	-1411.869	-1133.229	247.655
1100	123.600	200.225	120.476	87.724	-1411.271	-1105.402	219.613
1200	125.388	211.057	127.579	100.174	-1410.661	-1077.619	196.252
1300	127.131	221.162	134.393	112.800	-1410.049	-1049.893	176.495
1400	128.828	230.646	140.933	125.598	-1409.413	-1022.207	159.566
1500	130.480	239.591	147.215	138.564	-1408.763	- 994.584	144.904
1600	132.087	248.063	153.255	151.693	-1408.081	- 966.983	132.077
1700	133.648	256.118	159.071	164.980	-1477.461	- 936.781	120.426
1800	135.164	263.800	164.678	178.421	-1476.352	- 905.010	109.878
1900	136.635	271.148	170.089	192.011	-1475.197	- 873.299	100.447
2000	138.060	278.193	175.320	205.746	-1473.980	- 841.656	91.967

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

DILITHIUM OCTABORATE ($Li_2B_8O_{13}$) (CRYSTAL) MOL. WT. = 308.44

$S^\circ_{298.15}$ = [63.4 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

T_d = 908 ± 10°K.

ΔH_f° = Unknown

ΔH_f° 298.15 = -1413.57 ± 2.50 kcal. mole^{-1}

Heat of Formation.

The heat of the reaction $Li_2O(c) + 4B_2O_3(l) \rightarrow Li_2B_8O_{13}(c)$ was reported by L. Shartsis and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $Li_2O(c)$ (March 31, 1964). The above ΔH_r° = -73.35 kcal. mole^{-1}.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range of 298 to 823°K. were used to determine C_p. Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $LiBO_2(c)$.

Temperature of Decomposition. The incongruent melting point reported by B. S. R. Sastry and F. A. Hummel, J. Am. Ceram. Soc. 42, 216-8 (1959) is used here.

Decaborane ($B_{10}H_{14}$)
(Crystal) Mol. Wt. = 122.312

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 6.762	3.426	3.426	INFINITE
100	13.284	12.718	73.128	- 6.041	- 1.226	14.654	- 32.025
200	29.490	26.225	46.230	- 4.001	- 4.207	31.652	- 34.586
298	52.092	42.200	42.200	.000	- 6.900	49.834	- 36.527
300	52.511	42.524	42.201	.097	- 6.944	50.183	- 36.556
400	72.900	60.807	44.541	6.506	- 8.613	69.512	- 37.978
500	78.000	77.559	49.513	14.023	- 10.119	89.207	- 38.991
600	87.200	92.614	55.456	22.295	- 11.497	109.211	- 39.778
700	95.000	106.660	61.779	31.416	- 12.450	129.416	- 40.403
800	100.750	119.729	68.216	41.210	- 13.048	149.720	- 40.900
900	105.750	131.892	74.624	51.541	- 13.361	170.086	- 41.301
1000	110.000	143.260	80.925	62.335	- 13.443	190.481	- 41.628
1100	113.500	153.914	87.081	73.516	- 13.384	210.867	- 41.893
1200	116.250	163.913	93.072	85.010	- 13.218	231.256	- 42.115
1300	118.250	173.302	98.886	96.741	- 13.035	251.611	- 42.298
1400	119.500	182.116	104.520	108.635	- 12.889	271.973	- 42.455
1500	120.000	190.382	109.971	120.616	- 12.880	292.310	- 42.588

Sept. 30, 1962; Dec. 31, 1964

DECABORANE (B_{10} H_{14}) (CRYSTAL) MOL. WT. = 122.312

$\Delta H^\circ_{f\ 0}$ = 3.4 ± 4.5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 42.20 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -6.9 ± 4.5 kcal. mole^{-1}

T_m = 371.93°K

ΔH°_m = 5.25 ± 0.01 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298}$ = 18.2 ± 0.2 kcal. mole^{-1}

Heat of Formation.

The enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of the reaction $B_{10}H_{14}(c) \rightarrow 10B(am) + 7H_2(g)$ was reported to be 19.8 ± 1.4 and 18.0 ± 1.0 kcal. mole^{-1} by W. H. Johnson, M. V. Kilday and E. J. Prosen, J. Res. Natl. Bur. Std. 64A, 521 (1960) and G. L. Gal'chenko, B. I. Timofeev and S. M. Skuratov, Doklady Akademii Nauk. USSR, 142, 1077 (1962), respectively. Using $\Delta H^\circ_{r\ 298.15}$ = 1.2 ± 0.4 kcal. mole^{-1} for the reaction $B(c) \rightarrow B(am)$, the corresponding $\Delta H^\circ_{f\ 298.15}$ values for $B_{10}H_{14}(c)$ were calculated to be -7.8 and -6.0 kcal. mole^{-1}. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $B_{10}H_{14}(c)$ is the average of these two.

Heat Capacity and Entropy.

C_p (60° to 371.93°K.) was given by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955). The heat capacity above 371.93° was estimated by comparison with that of the liquid decaborane. Heat capacity (14° to 205°K.) was also reported by E. C. Kerr, N. C. Hallett and H. L. Johnston, J. Am. Chem. Soc., 73, 1117 (1951). The value of $S^\circ_{298.15}$ was taken from G. T. Furukawa and R. P. Park, loc. cit.

Melting Data.

T_m and ΔH°_m were obtained from G. T. Furukawa and R. P. Park, loc. cit.

Heat of Sublimation.

$\Delta H^\circ_{s\ 298.15}$ was calculated from free energy functions and vapor pressure reported by G. T. Furukawa and R. P. Park, loc. cit. See $B_{10}H_{14}(g)$ table for details.

Decaborane ($B_{10}H_{14}$)

(Liquid) Mol. Wt. = 122.312

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	52.870	56.299	56.299	.000	- 1.700	50.830	- 37.258
300	53.280	56.627	56.300	.098	- 1.743	51.153	- 37.263
400	77.200	75.385	58.679	6.682	- 3.237	69.057	- 37.729
500	83.000	93.215	63.848	14.684	- 4.258	87.240	- 38.131
600	93.200	109.271	70.095	23.505	- 5.087	105.627	- 38.473
700	102.000	124.316	76.778	33.277	- 5.389	124.117	- 38.749
800	109.000	138.405	83.611	43.835	- 5.223	142.604	- 38.956
900	115.000	151.599	90.440	55.044	- 4.658	161.052	- 39.107
1000	120.000	163.983	97.181	66.802	- 3.776	179.425	- 39.211
1100	124.000	175.616	103.789	79.010	- 2.690	197.688	- 39.275
1200	127.000	186.541	110.234	91.569	- 1.459	215.861	- 39.312
1300	129.000	196.792	116.502	104.377	- .199	233.910	- 39.322
1400	130.000	206.395	122.584	117.335	1.011	251.883	- 39.319
1500	130.000	215.370	128.474	130.344	2.048	269.756	- 39.301

Sept. 30, 1962; Dec. 31, 1964

DECABORANE ($B_{10}H_{14}$) (LIQUID) MOL. WT. = 122.312

$S^\circ_{298.15}$ = 56.299 cal. deg.$^{-1}$ mole^{-1}

T_m = 371.93°K.

T_b = [492]°K.

$\Delta H^\circ_{f\ 298.15}$ = -1.7 ± 2.0 kcal. mole^{-1}

ΔH°_m = 5.25 ± 0.01 kcal. mole^{-1}

ΔH°_v = [10.3] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was calculated from $\Delta H^\circ_{f\ 298.15}$ for $B_{10}H_{14}$(c) and ΔH°_m reported by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955) and the difference $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p (371.93° to 380°K) was measured by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955). Heat capacities below 371.93° and above 380°K. were estimated by comparison with that of the gaseous decaborane. $S^\circ_{298.15}$ was calculated from that of crystal in a manner analogous to that of the heat of formation.

Melting and Vaporization Data.

T_m and ΔH°_m were obtained from G. T. Furukawa and R. P. Park, loc. cit. T_b and ΔH°_v were calculated from functions for $B_{10}H_{14}$(l) and $B_{10}H_{14}$(g), respectively.

Decaborane ($B_{10}H_{14}$)

(Ideal Gas) Mol. Wt. = 122.312

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-5.937	22.451	22.451	INFINITE
100	10.996	59.315	110.076	-5.076	17.939	29.159	-63.725
200	25.128	70.808	87.494	-3.337	14.657	41.599	-45.455
298	42.920	84.147	84.147	.000	11.300	55.527	-40.701
300	43.250	84.414	84.148	.080	11.239	55.799	-40.647
400	59.738	99.182	86.050	5.253	8.334	71.109	-38.850
500	73.238	114.017	90.165	11.926	5.984	87.082	-38.062
600	84.050	128.362	95.345	19.811	4.219	103.478	-37.690
700	92.719	141.994	101.044	28.665	2.999	120.131	-37.505
800	99.711	154.848	106.974	38.299	2.241	136.914	-37.401
900	105.389	166.931	112.972	48.564	1.862	153.773	-37.339
1000	110.031	178.284	118.941	59.342	1.764	170.664	-37.297
1100	113.852	188.956	124.826	70.542	1.842	187.547	-37.260
1200	117.019	199.002	130.593	82.091	2.063	204.430	-37.230
1300	119.663	208.476	136.223	93.929	2.353	221.273	-37.198
1400	121.885	217.428	141.707	106.009	2.685	238.111	-37.169
1500	123.766	225.903	147.040	118.294	2.998	254.907	-37.138
1600	125.369	233.943	152.222	130.753	3.281	271.691	-37.109
1700	126.743	241.586	157.256	143.361	3.530	288.465	-37.083
1800	127.929	248.865	162.145	156.096	3.736	305.209	-37.056
1900	128.957	255.809	166.893	168.941	3.909	321.956	-37.032
2000	129.854	262.447	171.506	181.883	4.056	338.698	-37.009
2100	130.641	268.802	175.989	194.908	4.163	355.430	-36.988
2200	131.334	274.896	180.347	208.008	4.239	372.156	-36.968
2300	131.947	280.748	184.586	221.172	4.280	388.873	-36.950
2400	132.492	286.375	188.711	234.395	4.274	405.611	-36.934
2500	132.978	291.794	192.727	247.669	-49.647	423.405	-37.012
2600	133.414	297.018	196.638	260.989	-49.647	442.333	-37.180
2700	133.805	302.061	200.450	274.350	-49.655	461.263	-37.335
2800	134.158	306.933	204.166	287.748	-49.668	480.165	-37.477
2900	134.478	311.647	207.791	301.181	-49.681	499.129	-37.614
3000	134.768	316.211	211.330	314.643	-49.707	518.025	-37.736
3100	135.032	320.634	214.785	328.133	-49.733	536.936	-37.852
3200	135.273	324.925	218.160	341.649	-49.775	555.873	-37.963
3300	135.493	329.091	221.459	355.187	-49.830	574.821	-38.067
3400	135.696	333.139	224.684	368.747	-49.891	593.739	-38.163
3500	135.881	337.075	227.839	382.326	-49.975	612.662	-38.255
3600	136.053	340.906	230.927	395.923	-50.069	631.601	-38.342
3700	136.211	344.635	233.950	409.536	-50.189	650.547	-38.424
3800	136.357	348.270	236.911	423.164	-50.315	669.500	-38.503
3900	136.493	351.814	239.812	436.807	-50.468	688.418	-38.576
4000	136.618	355.271	242.655	450.463	-1262.426	728.826	-39.819
4100	136.735	358.646	245.443	464.130	-1260.301	778.568	-41.499
4200	136.845	361.942	248.178	477.809	-1258.189	828.321	-43.100
4300	136.946	365.163	250.861	491.499	-1256.104	877.947	-44.620
4400	137.041	368.313	253.495	505.198	-1254.048	927.547	-46.069
4500	137.130	371.394	256.081	518.907	-1252.017	977.076	-47.451
4600	137.214	374.408	258.621	532.624	-1249.999	1026.620	-48.773
4700	137.292	377.360	261.116	546.350	-1248.017	1076.104	-50.036
4800	137.366	380.252	263.568	560.083	-1246.059	1125.539	-51.245
4900	137.435	383.085	265.978	573.823	-1244.132	1174.900	-52.400
5000	137.500	385.862	268.348	587.569	-1242.227	1224.248	-53.509
5100	137.561	388.585	270.679	601.323	-1240.362	1273.581	-54.574
5200	137.619	391.257	272.972	615.082	-1238.513	1322.840	-55.595
5300	137.674	393.879	275.229	628.846	-1236.697	1372.080	-56.576
5400	137.726	396.453	277.450	642.616	-1234.923	1421.262	-57.519
5500	137.775	398.980	279.637	656.391	-1233.165	1470.487	-58.429
5600	137.822	401.463	281.790	670.171	-1231.450	1519.567	-59.301
5700	137.866	403.903	283.911	683.956	-1229.771	1568.712	-60.145
5800	137.908	406.301	286.001	697.744	-1228.127	1617.771	-60.956
5900	137.948	408.659	288.060	711.537	-1226.509	1666.839	-61.741
6000	137.986	410.978	290.089	725.334	-1224.928	1715.864	-62.497

Dec. 31, 1960; Sept. 30, 1962; June 30, 1963; Dec. 31, 1964

DECABORANE ($B_{10}H_{14}$) (IDEAL GAS) MOL. WT. = 122.312

Point Group C_{2v}

$S^\circ_{298.15}$ = 84.147 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity [1]

$\Delta H_f^\circ{}_0$ = 22.5 ± 4.5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 11.3 ± 4.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

230(1)	295(1)	344(1)	350(1)	387(1)	434(1)	446(1)	452(1)
464(1)	508(1)	588(1)	618(1)	635(1)	651(1)	690(1)	701(1)
709(1)	720(1)	747(1)	752(1)	767(1)	773(1)	814(1)	822(1)
832(1)	859(1)	862(1)	903(1)	915(1)	921(1)	924(1)	938(1)
942(1)	960(1)	967(1)	972(1)	1008(1)	1037(1)	1060(1)	1104(1)
1160(1)	1190(1)	1210(1)	1250(1)	1300(1)	1360(1)	1390(1)	1410(1)
1460(1)	1500(1)	1555(1)	1590(1)	1620(1)	1665(1)	1880(2)	1929(2)
2550(2)	2576(2)	2595(2)	2618(2)				

Bond Distance: B-B = 1.762 Å $B\text{-}B_{apex}$ = 1.773 Å

$B\text{-}H_{bridge}$ = 1.394 Å B-H = 1.256 Å

σ = 2

Bond Angle: B-B-B = 108° $B\text{-}B_{apex}\text{-}B$ = 59° 34' $B\text{-}B\text{-}B_{apex}$ = 60° 13'

$B\text{-}H_{bridge}\text{-}B$ = 46° 17' $B_{apex}\text{-}B\text{-}H$ = 87° 42' $B_{center}\text{-}B_{center}\text{-}H$ = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 8.6710 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The vapor pressures of decaborane ($B_{10}H_{14}$) were measured by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Std. 55, 255 (1955) and G. A. Miller, J. Phys. Chem. 67, 1363(1963). The heats of vaporization (ΔH_v°) were derived by both the second and third law methods. Using the average value of ΔH_v°, the respective heats of formation ($\Delta H_f^\circ{}_{298.15}$) for $B_{10}H_{14}$(g) were calculated. The results are presented as follows.

		$\Delta H_v^\circ{}_{298.15}$, kcal. mole^{-1}		$\Delta H_f^\circ{}_{298.15}$
Investigator	Process	Third Law Value	Second Law Value	kcal. mole^{-1}
Furukawa and Park	$B_{10}H_{14}(c) \rightarrow B_{10}H_{14}(g)$	18.20	16.63 ± 0.93	10.52 ± 4.5
	$B_{10}H_{14}(l) \rightarrow B_{10}H_{14}(g)$	13.06	13.28 ± 0.06	11.47 ± 4.5
Miller	$B_{10}H_{14}(c) \rightarrow B_{10}H_{14}(g)$	18.27	17.81 ± 0.01	11.14 ± 4.5

The adopted value of $\Delta H_f^\circ{}_{298.15}$ for $B_{10}H_{14}$(g) is the weighted average of the three $\Delta H_f^\circ{}_{298.15}$ values listed in the above table.

Heat Capacity and Entropy.

The molecular structure of $B_{10}H_{14}$(c) were reported by J. S. Kasper, C. M. Lucht and D. Harker, Acta Cryst. 3, 436 (1950); E. B. Moore, Jr., R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys. 27, 209 (1957) and W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, Inc., New York, 1963. For the calculation of the moments of inertia for $B_{10}H_{14}$(g) a simplified molecular model is adopted. The molecule is assumed to be composed of two regular pentagonal pyramids with a common base edge. The angle between the base planes of those pyramids is 73° 30'. Each of 10 H atoms is attached to a single B atom above the base plane. The remaining 4 H atoms, each bridge two B atoms. The vibrational frequencies were obtained from W. H. Evans, National Bureau of Standards Report 7093 (Jan. 1, 1961), which were derived based on the infrared and Raman spectra reported by J. E. Stewart, National Bureau of Standards, private communication, 1957 and W. E. Keller and H. L. Johnston, J. Chem. Phys. 20, 1749 (1952). The three principal moments of inertia are: $I_A = 4.53825 \times 10^{-38}$, $I_B = 3.51508 \times 10^{-38}$ and $I_C = 5.43559 \times 10^{-38}$ g. cm.^{2}

Dilead Decaborate ($Pb_2B_{10}O_{17}$)

(Crystal) Mol. Wt. = 794.62

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	97.200	84.300	84.300	.000	-1694.000	-1581.528	1159.236
300	97.600	84.902	84.302	.180	-1694.004	-1580.834	1151.581
400	120.200	116.193	88.415	11.111	-1693.641	-1543.134	843.089
500	137.900	144.957	96.888	24.034	-1692.407	-1505.634	658.081
600	153.400	171.511	107.140	38.623	-1690.366	-1468.453	534.858
700	166.100	196.135	118.117	54.613	-1689.889	-1431.296	446.849
800	177.000	219.046	129.318	71.783	-1686.394	-1394.596	380.967
900	186.100	240.437	140.489	89.953	-1682.231	-1358.365	329.840
1000	193.400	260.436	151.495	108.941	-1677.534	-1322.612	289.043
1100	199.100	279.149	162.259	128.579	-1672.466	-1287.375	255.766
1200	203.200	296.660	172.737	148.707	-1667.118	-1252.592	228.117
1300	205.800	313.034	182.907	169.165	-1661.656	-1218.274	204.801
1400	207.400	328.349	192.755	189.832	-1656.174	-1184.370	184.880
1500	208.200	342.685	202.277	210.612	-1650.775	-1150.869	167.673
1600	209.000	356.148	211.478	231.472	-1645.474	-1117.706	152.664
1700	209.800	368.842	220.365	252.412	-1640.259	-1084.878	139.464
1800	210.600	380.857	228.950	273.432	-1635.133	-1052.366	127.769
1900	211.400	392.265	237.248	294.532	-1630.067	-1020.130	117.336
2000	212.200	403.128	245.272	315.712	-1625.033	- 988.159	107.976

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

DILEAD DECABORATE ($Pb_2B_{10}O_{17}$) (CRYSTAL) MOL. WT. = 794.62

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [84.3 ± 3] cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15} = -1694 \pm 3$ kcal. mole^{-1}

Heat of Formation.

See lead diborate for the complete writeup. W. H. Evans in NBS. Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$$2PbO(c) + 5B_2O_3(c) \rightarrow 2PBO\cdot 5B_2O_3(gls.) \qquad \Delta H_r = -45.2 \text{ kcal./mole}$$

and estimated a ΔH_{298} of 26.8 kcal. mole^{-1} for the conversion to the $2PbO\cdot 5B_2O_3$(crystal). With auxiliary JANAF values the $\Delta H_f^\circ{}_{298.15}$ was calculated to be -1694.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the PbB_4O_7 table from $S^\circ_{298.15}$'s of $Pb\cdot 2B_2O_3$ and $Pb\cdot 3B_2O_3$ and the subtraction of 4.2 e.u.

Be

Beryllium (Be)

(Reference State) Mol. Wt. = 9.013

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	- ,468	,000	,000	,000
100	,437	,130	4,712	- ,458	,000	,000	,000
200	2,400	1,010	2,610	- ,320	,000	,000	,000
298	3,932	2,280	2,280	,000	,000	,000	,000
300	3,950	2,304	2,280	,007	,000	,000	,000
400	4,770	3,561	2,446	,446	,000	,000	,000
500	5,254	4,684	2,784	,950	,000	,000	,000
600	5,579	5,671	3,184	1,492	,000	,000	,000
700	5,836	6,552	3,604	2,064	,000	,000	,000
800	6,065	7,346	4,022	2,659	,000	,000	,000
900	6,287	8,073	4,433	3,276	,000	,000	,000
1000	6,517	8,747	4,831	3,916	,000	,000	,000
1100	6,765	9,380	5,216	4,580	,000	,000	,000
1200	7,003	9,979	5,588	5,269	,000	,000	,000
1300	7,242	10,549	5,948	5,981	,000	,000	,000
1400	7,481	11,094	6,296	6,717	,000	,000	,000
1500	7,719	11,618	6,634	7,477	,000	,000	,000
1600	6,901	13,895	7,010	11,016	,000	,000	,000
1700	6,952	14,315	7,428	11,709	,000	,000	,000
1800	7,004	14,714	7,821	12,407	,000	,000	,000
1900	7,055	15,094	8,194	13,110	,000	,000	,000
2000	7,106	15,457	8,548	13,818	,000	,000	,000
2100	7,158	15,805	8,886	14,531	,000	,000	,000
2200	7,209	16,139	9,208	15,249	,000	,000	,000
2300	7,250	16,461	9,516	15,972	,000	,000	,000
2400	7,320	16,771	9,812	16,700	,000	,000	,000
2500	7,360	17,070	10,096	17,434	,000	,000	,000
2600	7,400	17,360	10,370	18,172	,000	,000	,000
2700	7,440	17,640	10,634	18,914	,000	,000	,000
2800	4,997	43,675	11,285	90,691	,000	,000	,000
2900	5,007	43,851	12,405	91,191	,000	,000	,000
3000	5,021	44,021	13,456	91,693	,000	,000	,000
3100	5,037	44,185	14,445	92,196	,000	,000	,000
3200	5,057	44,346	15,377	92,700	,000	,000	,000
3300	5,081	44,502	16,257	93,207	,000	,000	,000
3400	5,109	44,654	17,090	93,717	,000	,000	,000
3500	5,142	44,802	17,880	94,229	,000	,000	,000
3600	5,179	44,948	18,630	94,745	,000	,000	,000
3700	5,221	45,090	19,343	95,265	,000	,000	,000
3800	5,268	45,230	20,022	95,790	,000	,000	,000
3900	5,320	45,368	20,670	96,319	,000	,000	,000
4000	5,378	45,503	21,289	96,854	,000	,000	,000
4100	5,440	45,636	21,882	97,395	,000	,000	,000
4200	5,508	45,768	22,449	97,942	,000	,000	,000
4300	5,581	45,899	22,993	98,496	,000	,000	,000
4400	5,658	46,028	23,515	99,058	,000	,000	,000
4500	5,741	46,156	24,016	99,628	,000	,000	,000
4600	5,828	46,283	24,499	100,207	,000	,000	,000
4700	5,919	46,409	24,964	100,794	,000	,000	,000
4800	6,014	46,535	25,412	101,391	,000	,000	,000
4900	6,113	46,660	25,844	101,997	,000	,000	,000
5000	6,215	46,785	26,262	102,613	,000	,000	,000
5100	6,320	46,909	26,666	103,240	,000	,000	,000
5200	6,428	47,032	27,056	103,877	,000	,000	,000
5300	6,538	47,156	27,434	104,526	,000	,000	,000
5400	6,650	47,279	27,801	105,185	,000	,000	,000
5500	6,763	47,402	28,156	105,856	,000	,000	,000
5600	6,877	47,525	28,501	106,538	,000	,000	,000
5700	6,993	47,648	28,835	107,231	,000	,000	,000
5800	7,109	47,771	29,161	107,936	,000	,000	,000
5900	7,224	47,893	29,477	108,653	,000	,000	,000
6000	7,340	48,015	29,785	109,381	,000	,000	,000

September 30, 1961

BERYLLIUM (Be) (REFERENCE STATE) MOL. WT. = 9.013

Solid state to the melting point 1556°K.

Liquid state from 1556°K. to the boiling point 2757°K.

Ideal monatomic gas state above 2757°K.

See Crystal, Liquid, Ideal Monatomic gas for details.

Be

Beryllium (Be)

(Crystal) Mol. Wt. = 9.013

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-.468	.000	.000	INFINITE
100	.437	.130	4.712	-.458	.000	.000	.000
200	2.400	1.010	2.610	-.320	.000	.000	.000
298	3.932	2.280	2.280	.000	.000	.000	.000
300	3.950	2.304	2.280	.007	.000	.000	.000
400	4.770	3.561	2.446	.446	.000	.000	.000
500	5.254	4.684	2.784	.950	.000	.000	.000
600	5.579	5.671	3.184	1.492	.000	.000	.000
700	5.836	6.552	3.604	2.064	.000	.000	.000
800	6.065	7.346	4.022	2.659	.000	.000	.000
900	6.287	8.073	4.433	3.276	.000	.000	.000
1000	6.517	8.747	4.831	3.916	.000	.000	.000
1100	6.765	9.380	5.216	4.580	.000	.000	.000
1200	7.003	9.979	5.588	5.269	.000	.000	.000
1300	7.242	10.549	5.948	5.981	.000	.000	.000
1400	7.481	11.094	6.296	6.717	.000	.000	.000
1500	7.719	11.618	6.634	7.477	.000	.000	.000
1600	7.958	12.124	6.961	8.261	-2.755	.078	-.011
1700	8.197	12.614	7.279	9.069	-2.640	.252	-.032
1800	8.435	13.089	7.589	9.900	-2.507	.418	-.051
1900	8.674	13.551	7.891	10.756	-2.354	.577	-.066
2000	8.913	14.002	8.185	11.635	-2.183	.726	-.079
2100	9.152	14.443	8.472	12.538	-1.993	.867	-.090
2200	9.391	14.874	8.754	13.466	-1.783	.999	-.099
2300	9.629	15.297	9.029	14.417	-1.555	1.122	-.107
2400	9.868	15.712	9.299	15.391	-1.309	1.233	-.112
2500	10.106	16.120	9.564	16.390	-1.044	1.332	-.116
2600	10.345	16.521	9.823	17.413	-.759	1.423	-.120
2700	10.583	16.915	10.079	18.459	-.455	1.301	-.122
2800	10.822	17.305	10.330	19.529	-71.162	2.675	-.209
2900	11.060	17.689	10.577	20.623	-70.568	5.303	-.400
3000	11.299	18.068	10.820	21.741	-69.952	7.909	-.576

September 30, 1961

BERYLLIUM (Be) (CRYSTAL) MOL. WT. = 9.013

$\Delta H_{f0}^\circ = 0$

$\Delta H_s^\circ = 78.254$ kcal. mole^{-1}

$T_m = 1556$°K.

ΔH_f° $_{298.15} = 0$

$S^\circ_{298.15} = 2.280$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_m = 2800 \pm 500$ cal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Extrapolation.

Heat capacity measurements have been reported by F. Simon and M. Ruheman, (71° to 79°K.), Z. physik. Chem. 129, 321 (1935); S. Cristescu and F. Simon, (10° to 300°K.), Z. physik. Chem. 25B, 273 (1934); E. J. Lewis, (97° to 463°K.), Phys. Rev. 34, 1575 (1929); D. C. Ginnings, T. B. Douglas and A. F. Ball, (0° to 900°C.), J. Am. Chem. Soc. 73, 1236 (1951), and R. W. Hill and P. L. Smith, (4° to 300°K.), Phil. Mag. 44, 636 (1953).

A five constant equation was fit to both sets of data adopted from Ginnings and co-workers by the method of least squares, standard deviation ± 0.017, and joined smoothly with the C_p values of Hill and Smith. C_p from 1200°K. to the melting point was extrapolated.

P. B. Kantor, R. M. Krasovitskaya and A. N. Kisel, Fiz. Metal. i Metalloved., Akad. Nauk. S.S.S.R. 10, 835 (1960), report enthalpy data for pure beryllium, purity not given, from 600° to 1560°K. (crystal) and from 1560° to 2200°K. (liquid). Their values for the crystal are too high.

Entropy.

Third law entropy calculated from C_p.

Melting.

Data from O. Kubaschewski, P. Brizgys, O. Huchler, R. Jauch, and K. Reinartz, Z. Elektrochem. 54, 275 (1950).

Heat of Sublimation.

ΔH_s $_{298.15}$ was derived from a third law analysis of the vapor pressure data of E. A. Gulbransen and K. F. Andrew, J. Electrochem. Soc. 97, 383 (1952), and of R. B. Holden, R. Speiser, and H. L. Johnston, J. Am. Chem. Soc. 70, 3897 (1948) which are in good agreement. The results of R. Schuman and A. B. Garrett, J. Am. Chem. Soc. 66, 442 (1944), are too low, and the values given by E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934), have a wrong temperature dependence.

Beryllium (Be)

(Liquid) Mol. Wt. = 9.013

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H_{298}^\circ$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0							
100							
200							
298	3.805	3.954	3.954	.000	2.881	2.381	- 1.746
300	3.837	3.976	3.954	.007	2.881	2.378	- 1.733
400	5.027	5.270	4.122	.459	2.894	2.210	- 1.207
500	5.667	6.466	4.473	.996	2.927	2.036	- .890
600	6.017	7.534	4.896	1.583	2.971	1.853	- .675
700	6.217	8.476	5.342	2.195	3.012	1.664	- .519
800	6.317	9.316	5.787	2.823	3.044	1.469	- .401
900	6.411	10.065	6.222	3.459	3.064	1.271	- .309
1000	6.499	10.745	6.641	4.105	3.069	1.071	- .234
1100	6.581	11.369	7.042	4.759	3.059	.872	- .173
1200	6.657	11.945	7.427	5.421	3.032	.674	- .123
1300	6.727	12.480	7.796	6.090	2.990	.479	- .081
1400	6.791	12.981	8.148	6.766	2.930	.287	- .045
1500	6.849	13.452	8.486	7.448	2.852	.101	- .015
1600	6.901	13.895	8.811	8.136	.000	.000	.000
1700	6.952	14.315	9.122	8.828	.000	.000	.000
1800	7.004	14.714	9.422	9.526	.000	.000	.000
1900	7.055	15.094	9.711	10.229	.000	.000	.000
2000	7.106	15.457	9.989	10.937	.000	.000	.000
2100	7.158	15.805	10.258	11.650	.000	.000	.000
2200	7.209	16.140	10.517	12.369	.000	.000	.000
2300	7.259	16.461	10.769	13.092	.000	.000	.000
2400	7.309	16.771	11.013	13.821	.000	.000	.000
2500	7.358	17.070	11.249	14.554	.000	.000	.000
2600	7.407	17.360	11.478	15.292	.000	.000	.000
2700	7.455	17.640	11.701	16.035	.000	.000	.000
2800	7.500	17.912	11.918	16.783	- 71.028	1.106	- .086
2900	7.500	18.176	12.130	17.533	- 70.778	3.681	- .277
3000	7.500	18.430	12.336	18.283	- 70.530	6.244	- .455
3100	7.500	18.676	12.536	19.033	- 70.283	8.796	- .620
3200	7.500	18.914	12.732	19.783	- 70.037	11.346	- .775
3300	7.500	19.145	12.923	20.533	- 69.794	13.886	- .920
3400	7.500	19.369	13.109	21.283	- 69.554	16.417	- 1.055
3500	7.500	19.586	13.291	22.033	- 69.316	18.941	- 1.183
3600	7.500	19.797	13.469	22.783	- 69.082	21.461	- 1.303
3700	7.500	20.003	13.642	23.533	- 68.852	23.971	- 1.416
3800	7.500	20.203	13.812	24.283	- 68.627	26.477	- 1.523
3900	7.500	20.398	13.979	25.033	- 68.406	28.979	- 1.624
4000	7.500	20.587	14.142	25.783	- 68.191	31.472	- 1.719
4100	7.500	20.773	14.301	26.533	- 67.982	33.958	- 1.810
4200	7.500	20.953	14.457	27.283	- 67.779	36.443	- 1.896
4300	7.500	21.130	14.611	28.033	- 67.583	38.925	- 1.978
4400	7.500	21.302	14.761	28.783	- 67.395	41.399	- 2.056
4500	7.500	21.471	14.908	29.533	- 67.215	43.869	- 2.130
4600	7.500	21.636	15.052	30.283	- 67.044	46.334	- 2.201
4700	7.500	21.797	15.194	31.033	- 66.881	48.796	- 2.269
4800	7.500	21.955	15.333	31.783	- 66.728	51.257	- 2.334
4900	7.500	22.109	15.470	32.533	- 66.584	53.714	- 2.396
5000	7.500	22.261	15.604	33.283	- 66.450	56.171	- 2.455
5100	7.500	22.410	15.736	34.033	- 66.327	58.621	- 2.512
5200	7.500	22.555	15.866	34.783	- 66.214	61.066	- 2.566
5300	7.500	22.698	15.994	35.533	- 66.113	63.515	- 2.619
5400	7.500	22.838	16.119	36.283	- 66.022	65.959	- 2.669
5500	7.500	22.976	16.243	37.033	- 65.943	68.402	- 2.718
5600	7.500	23.111	16.364	37.783	- 65.875	70.844	- 2.765
5700	7.500	23.244	16.484	38.533	- 65.818	73.287	- 2.810
5800	7.500	23.374	16.601	39.283	- 65.773	75.729	- 2.853
5900	7.500	23.502	16.717	40.033	- 65.740	78.165	- 2.895
6000	7.500	23.628	16.831	40.783	- 65.718	80.602	- 2.936

September 30, 1961

BERYLLIUM (Be) (LIQUID) MOL. WT. = 9.013

$\Delta H_{f\ 298.15}^\circ$ = [2.881] kcal. mole^{-1}

T_m = 1556°K.

T_b = 2757°K.

$S_{298.15}^\circ$ = [3.954] cal. deg.$^{-1}$ mole^{-1}

ΔH_m° = 2800 ± 500 cal. mole^{-1}

ΔH_v = 71.137 kcal. mole^{-1}

Heat of Formation.

Obtained from ΔH_m 1556°K.

Heat Capacity and Extrapolation.

Heat capacity from T_m to 2200°K. taken from P. B. Kantor, R. M. Krasovitskaya and A. N. Kisel, Fiz. Metal. i Metalloved., Akad. Nauk S.S.S.R. 10, 835 (1960). C_p values below T_m and above 2200°K. were extrapolated.

Entropy.

Third law entropies between T_m and T_b extrapolated in both directions by means of extrapolated heat capacities.

Vaporization Phenomena.

T_b and ΔH_v derived from a third law analysis of the vapor pressure data of E. A. Gulbransen and K. F. Andrew, J. Electrochem. Soc. 97, 383 (1952), and of R. B. Holden, R. Speiser, and H. L. Johnston, J. Am. Chem. Soc. 70, 3897 (1948).

A mass spectrometric study and review undertaken by O. T. Nikitin and L. N. Gorokhov, Zhur. Neorg. Khim. 6, 224 (1961), on the composition of beryllium vapor reveals that beryllium vaporizing both below and above the melting point, 1556°K., consists only of monatomic Be.

Beryllium (Be)

(Ideal Gas) Mol. Wt. = 9.013

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	,000	,000	INFINITE	-1,481	77,241	77,241	INFINITE
100	4,968	27,118	36,962	-,984	77,728	75,029	-163,969
200	4,968	30,561	32,999	-,488	78,087	72,177	-78,867
298	4,968	32,545	32,545	,000	78,255	69,231	-50,745
300	4,968	32,576	32,545	,009	78,257	69,175	-50,392
400	4,968	34,005	32,740	,506	78,315	66,137	-36,134
500	4,968	35,114	33,108	1,003	78,307	63,093	-27,576
600	4,968	36,019	33,520	1,500	78,262	60,053	-21,873
700	4,968	36,785	33,933	1,996	78,187	57,024	-17,803
800	4,968	37,449	34,332	2,493	78,089	54,007	-14,753
900	4,968	38,034	34,711	2,990	77,969	51,004	-12,385
1000	4,968	38,557	35,070	3,487	77,825	48,015	-10,493
1100	4,968	39,031	35,409	3,984	77,658	45,042	-8,949
1200	4,968	39,463	35,729	4,481	77,466	42,085	-7,664
1300	4,968	39,861	36,032	4,977	77,251	39,146	-6,581
1400	4,968	40,229	36,319	5,474	77,012	36,223	-5,654
1500	4,968	40,572	36,591	5,971	76,748	33,318	-4,854
1600	4,968	40,892	36,850	6,468	73,706	30,511	-4,167
1700	4,968	41,193	37,097	6.965	73.510	27,817	-3,576
1800	4,968	41,477	37,332	7,461	73,309	25,135	-3,052
1900	4,968	41,746	37,557	7,958	73,103	22,464	-2,584
2000	4,969	42,001	37,773	8.455	72,892	19,804	-2,164
2100	4.969	42,243	37,980	8,952	72,676	17,155	-1,785
2200	4,970	42,474	38,179	9,449	72,454	14,516	-1,442
2300	4,972	42,695	38,371	9,946	72,229	11,889	-1,130
2400	4,974	42,907	38,556	10,443	71,998	9,271	-,844
2500	4,977	43,110	38,734	10,941	71,761	6,661	-,582
2600	4,982	43,306	38,906	11,439	71,521	4,063	-,342
2700	4,988	43,494	39,072	11,937	71,278	1,473	-,119
2800	4,997	43,675	39,234	12,437	.000	.000	,000
2900	5,007	43,851	39,390	12,937	.000	.000	,000
3000	5,021	44,021	39,541	13,438	.000	.000	,000
3100	5,037	44,186	39,688	13,941	.000	.000	,000
3200	5,057	44,346	39,832	14,446	.000	.000	,000
3300	5,081	44,502	39,971	14,953	.000	.000	,000
3400	5,109	44,654	40,106	15,462	.000	.000	,000
3500	5,142	44,802	40,238	15,975	.000	.000	,000
3600	5,179	44,948	40,367	16,491	.000	.000	,000
3700	5,221	45,090	40,493	17,010	.000	.000	,000
3800	5,268	45,230	40,616	17,535	.000	.000	,000
3900	5,320	45,368	40,736	18,064	.000	.000	,000
4000	5,378	45,503	40,853	18,599	.000	.000	,000
4100	5,440	45,637	40,968	19,140	.000	.000	,000
4200	5,508	45,768	41,081	19,687	.000	.000	,000
4300	5,581	45,899	41,192	20,242	.000	.000	,000
4400	5,658	46,028	41,300	20,804	.000	.000	,000
4500	5,741	46,156	41,406	21,374	.000	.000	,000
4600	5,828	46,283	41,511	21,952	.000	.000	,000
4700	5,919	46,410	41,614	22,539	.000	.000	,000
4800	6,014	46,535	41,715	23,136	.000	.000	,000
4900	6,113	46,660	41,815	23,742	.000	.000	,000
5000	6,215	46,785	41,913	24,359	.000	.000	,000
5100	6,320	46,909	42,010	24,985	.000	.000	,000
5200	6,428	47,033	42,105	25,623	.000	.000	,000
5300	6,538	47,156	42,199	26,271	.000	.000	,000
5400	6,650	47,279	42,292	26,930	.000	.000	,000
5500	6,763	47,402	42,384	27,601	.000	.000	,000
5600	6,877	47,525	42,475	28,283	.000	.000	,000
5700	6,993	47,648	42,564	28,976	.000	.000	,000
5800	7,109	47,771	42,653	29,681	.000	.000	,000
5900	7,224	47,893	42,741	30,398	.000	.000	,000
6000	7,340	48,015	42,828	31,126	.000	.000	,000

September 30, 1961

BERYLLIUM (Be) (IDEAL GAS) MOL. WT. = 9.013

ΔH_{f0}° = 77.241 kcal. mole⁻¹

$\Delta H_{f\ 298.15}^\circ$ = 78.25 ± 0.5 kcal. mole⁻¹

Ground State Configuration ^1S.

$S_{298.15}^\circ$ = 32.545 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

ϵ_i, cm.⁻¹	g_i	ϵ_i, cm.⁻¹	g_i	ϵ_i, cm.⁻¹	g_i
0.0	1	67943	15	73089	3
21980	9	68781	5	73141	1
42565	3	69009	3	73520	5
52082	3	69322	1	73608	1
54677	1	69634	9	73803	15
56432	5	70606	15	73867	5
58791	9	71002	5	73930	1
59696	9	71162	3	74071	15
60187	3	71320	1	74117	5
62054	15	71483	9	74163	1
64428	5	71499	1	74269	15
64507	3	72030	15	74301	5
65245	1	72251	5	74416	15
65949	9	72355	3	74443	5
67228	3	72448	1	73430	15
		72882	15		
		73017	5		

Heat of Formation.

Derived from a third law analysis of the vapor pressure data. See Be crystal for references.

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949).

Beryllium Unipositive Ion (Be^+)

(Ideal Gas) Mol. Wt. = 9.01165

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	33.922	33.922	.000	294.700	283.779	- 208.005
300	4.968	33.953	33.922	.009	294.711	283.711	- 206.673
400	4.968	35.382	34.117	.506	295.266	279.958	- 152.955
500	4.968	36.491	34.485	1.003	295.756	276.074	- 120.666
600	4.968	37.397	34.897	1.500	296.208	272.094	- 99.105
700	4.968	38.163	35.311	1.996	296.628	268.040	- 83.682
800	4.968	38.826	35.709	2.493	297.027	263.930	- 72.099
900	4.968	39.411	36.089	2.990	297.404	259.771	- 63.078
1000	4.968	39.935	36.448	3.487	297.758	255.569	- 55.852
1100	4.968	40.408	36.787	3.984	298.088	251.336	- 49.933
1200	4.968	40.840	37.107	4.481	298.393	247.072	- 44.996
1300	4.968	41.238	37.409	4.977	298.673	242.782	- 40.813
1400	4.968	41.606	37.696	5.474	298.931	238.474	- 37.226
1500	4.968	41.949	37.968	5.971	299.165	234.146	- 34.113
1600	4.968	42.270	38.227	6.468	296.620	229.882	- 31.399
1700	4.968	42.571	38.474	6.965	296.921	225.703	- 29.015
1800	4.968	42.855	38.710	7.461	297.215	221.504	- 26.893
1900	4.968	43.123	38.935	7.958	297.506	217.292	- 24.993
2000	4.968	43.378	39.151	8.455	297.792	213.062	- 23.281
2100	4.968	43.621	39.358	8.952	298.073	208.817	- 21.731
2200	4.968	43.852	39.557	9.449	298.349	204.560	- 20.320
2300	4.968	44.073	39.749	9.945	298.618	200.291	- 19.031
2400	4.968	44.284	39.933	10.442	298.884	196.013	- 17.849
2500	4.968	44.487	40.111	10.939	299.144	191.719	- 16.759
2600	4.968	44.682	40.283	11.436	299.400	187.418	- 15.753
2700	4.968	44.869	40.450	11.933	299.652	183.109	- 14.821
2800	4.968	45.050	40.611	12.430	228.869	179.894	- 14.041
2900	4.968	45.224	40.767	12.926	229.361	178.139	- 13.424
3000	4.968	45.393	40.918	13.423	229.853	176.360	- 12.847
3100	4.969	45.556	41.065	13.920	230.344	174.566	- 12.306
3200	4.969	45.713	41.208	14.417	230.834	172.767	- 11.799
3300	4.969	45.866	41.347	14.914	231.321	170.944	- 11.321
3400	4.970	46.015	41.482	15.411	231.804	169.104	- 10.869
3500	4.970	46.159	41.614	15.908	232.286	167.252	- 10.443
3600	4.971	46.299	41.742	16.405	232.764	165.390	- 10.040
3700	4.972	46.435	41.867	16.902	233.238	163.508	- 9.658
3800	4.973	46.568	41.989	17.399	233.707	161.617	- 9.295
3900	4.974	46.697	42.108	17.897	234.173	159.718	- 8.950
4000	4.976	46.823	42.224	18.394	234.631	157.799	- 8.621
4100	4.978	46.946	42.338	18.892	235.085	155.869	- 8.308
4200	4.981	47.066	42.449	19.390	235.533	153.935	- 8.010
4300	4.984	47.183	42.558	19.888	235.974	151.991	- 7.725
4400	4.987	47.297	42.664	20.387	236.408	150.036	- 7.452
4500	4.991	47.410	42.768	20.885	236.832	148.061	- 7.190
4600	4.995	47.519	42.870	21.385	237.250	146.087	- 6.940
4700	5.001	47.627	42.970	21.885	237.660	144.097	- 6.700
4800	5.006	47.732	43.069	22.385	238.060	142.103	- 6.470
4900	5.013	47.835	43.165	22.886	238.452	140.104	- 6.249
5000	5.020	47.937	43.259	23.387	238.833	138.093	- 6.036
5100	5.027	48.036	43.352	23.890	239.206	136.074	- 5.831
5200	5.036	48.134	43.443	24.393	239.569	134.045	- 5.633
5300	5.045	48.230	43.532	24.897	239.921	132.013	- 5.443
5400	5.055	48.324	43.620	25.402	240.264	129.974	- 5.260
5500	5.066	48.417	43.707	25.908	240.596	127.929	- 5.083
5600	5.078	48.509	43.792	26.415	240.917	125.871	- 4.912
5700	5.090	48.599	43.875	26.924	241.230	123.821	- 4.747
5800	5.104	48.687	43.957	27.433	241.531	121.761	- 4.588
5900	5.118	48.775	44.038	27.944	241.822	119.686	- 4.433
6000	5.133	48.861	44.118	28.457	242.104	117.616	- 4.284

June 30, 1965

BERYLLIUM UNIPOSITIVE ION (Be^+) (IDEAL GAS) MOL. WT. = 9.01165

Ground State Configuration $^2S_{1/2}$

$\Delta H_{f\ 0}^\circ = 292.2 \pm .5$ kcal/mole

$S_{298.15}^\circ = 33.922$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 294.7 \pm .5$ kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1
0.0	2
31928.8	2
31935.4	4
88231.2	2
96496.4	2
96498.2	4
98053.2	10

Heat of Formation.

The heat of formation was calculated from the equation: $Be(g) - e^- \rightarrow Be^+(g)$ with the JANAF auxiliary value for Be(g); using an I.P. = 7.519229 X 10^4 cm^{-1} (215.001 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K.. The $H^\circ-H_{298}^\circ$ value at 0°K. is -1.481 kcal./mole.

Beryllium Monobromide (BeBr)

(Ideal Gas) Mol. Wt. = 88.929

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.135	10.062	10.062	INFINITE
100	6.963	46.975	61.377	-1.440	10.413	6.372	-13.926
200	7.235	51.859	55.529	-.734	10.396	2.316	-2.531
298	7.719	54.839	54.839	.000	8.800	-1.447	1.060
300	7.727	54.887	54.839	.014	8.791	-1.510	1.100
400	8.110	57.165	55.147	.807	5.025	-4.176	2.282
500	8.365	59.005	55.741	1.632	4.904	-6.463	2.825
600	8.534	60.546	56.416	2.478	4.764	-8.724	3.178
700	8.650	61.870	57.103	3.337	4.605	-10.960	3.422
800	8.733	63.031	57.773	4.206	4.431	-13.172	3.598
900	8.795	64.064	58.416	5.083	4.242	-15.361	3.730
1000	8.843	64.993	59.028	5.965	4.034	-17.527	3.830
1100	8.882	65.838	59.609	6.851	3.805	-19.673	3.908
1200	8.913	66.612	60.161	7.741	3.554	-21.796	3.969
1300	8.940	67.326	60.685	8.634	3.282	-23.897	4.017
1400	8.963	67.990	61.183	9.529	2.988	-25.978	4.055
1500	8.983	68.609	61.658	10.426	2.672	-28.037	4.085
1600	9.001	69.189	62.111	11.325	-.423	-29.994	4.097
1700	9.017	69.735	62.543	12.226	-.670	-31.834	4.092
1800	9.033	70.251	62.957	13.129	-.921	-33.661	4.087
1900	9.047	70.740	63.354	14.033	-1.176	-35.473	4.080
2000	9.060	71.204	63.735	14.938	-1.435	-37.271	4.073
2100	9.073	71.647	64.101	15.845	-1.699	-39.058	4.065
2200	9.085	72.069	64.454	16.753	-1.967	-40.830	4.056
2300	9.096	72.473	64.794	17.662	-2.239	-42.588	4.047
2400	9.107	72.860	65.122	18.572	-2.516	-44.335	4.037
2500	9.118	73.232	65.439	19.483	-2.798	-46.073	4.028
2600	9.129	73.590	65.746	20.396	-3.084	-47.797	4.018
2700	9.139	73.935	66.043	21.309	-3.373	-49.513	4.008
2800	9.149	74.267	66.330	22.224	-74.697	-50.107	3.911
2900	9.159	74.589	66.610	23.139	-74.743	-49.229	3.710
3000	9.169	74.899	66.881	24.055	-74.791	-48.347	3.522
3100	9.178	75.200	67.144	24.973	-74.839	-47.468	3.346
3200	9.188	75.492	67.401	25.891	-74.888	-46.582	3.181
3300	9.197	75.775	67.650	26.810	-74.940	-45.698	3.026
3400	9.207	76.049	67.893	27.730	-74.994	-44.810	2.880
3500	9.216	76.316	68.130	28.652	-75.049	-43.922	2.742
3600	9.225	76.576	68.361	29.574	-75.109	-43.031	2.612
3700	9.234	76.829	68.587	30.497	-75.171	-42.142	2.489
3800	9.243	77.075	68.807	31.420	-75.239	-41.246	2.372
3900	9.252	77.315	69.022	32.345	-75.310	-40.347	2.261
4000	9.261	77.550	69.232	33.271	-75.387	-39.455	2.156
4100	9.269	77.779	69.438	34.197	-75.470	-38.560	2.055
4200	9.278	78.002	69.639	35.125	-75.558	-37.655	1.959
4300	9.287	78.221	69.836	36.053	-75.653	-36.751	1.868
4400	9.296	78.434	70.029	36.982	-75.755	-35.843	1.780
4500	9.304	78.643	70.218	37.912	-75.865	-34.935	1.697
4600	9.313	78.848	70.404	38.843	-75.984	-34.027	1.617
4700	9.322	79.048	70.585	39.775	-76.110	-33.112	1.540
4800	9.330	79.244	70.764	40.707	-76.246	-32.194	1.466
4900	9.339	79.437	70.939	41.641	-76.391	-31.277	1.395
5000	9.347	79.626	71.111	42.575	-76.545	-30.352	1.327
5100	9.356	79.811	71.279	43.510	-76.710	-29.428	1.261
5200	9.365	79.993	71.445	44.446	-76.885	-28.504	1.198
5300	9.373	80.171	71.608	45.383	-77.071	-27.566	1.137
5400	9.382	80.346	71.768	46.321	-77.267	-26.631	1.078
5500	9.390	80.519	71.926	47.259	-77.475	-25.695	1.021
5600	9.399	80.688	72.081	48.199	-77.693	-24.751	.966
5700	9.407	80.854	72.233	49.139	-77.922	-23.798	.912
5800	9.415	81.018	72.383	50.080	-78.163	-22.845	.861
5900	9.424	81.179	72.531	51.022	-78.415	-21.893	.811
6000	9.432	81.337	72.677	51.965	-78.679	-20.935	.763

Dec. 31, 1961; Sept. 30, 1964

BERYLLIUM MONOBROMIDE (BeBr) (IDEAL GAS) MOL. WT. = 88.929

Ground State Configuration $^2\Sigma^+$

$\Delta H_{f\ 0}^\circ$ = [10.1 ± 5.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [54.84] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = [8.8 ± 5.0] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_1 cm.$^{-1}$	g_1
0	2

ω_e = [743] cm.$^{-1}$

$\omega_e x_e$ = [4.06] cm.$^{-1}$

σ = 1

B_e = [0.53780] cm.$^{-1}$

α_e = [0.00293] cm.$^{-1}$

r_e = [1.97] Å

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g), BeCl(g), and the gaseous lithium halides. The resulting value, 97.1 kcal. mole^{-1}, was combined with JANAF heats of formation for Be(g) and Br(g) in arriving at $\Delta H_{f\ 298.15}^\circ$.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g), BeCl(g), and the gaseous lithium halides. The ground term was assumed to be similar to that of BeCl(g) and BeF(g), tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the interatomic distances for the alkali halides, BeF(g), and BeCl(g) was employed in deriving r_e.

Beryllium Dibromide ($BeBr_2$)

(Crystal) Mol. Wt. = 168.8302

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	16.500	25.400	25.400	.000	- 88.400	- 84.445	61.897
300	16.542	25.502	25.400	.031	- 88.409	- 84.420	61.497
400	18.100	30.506	26.072	1.774	- 95.345	- 81.642	44.605
500	18.850	34.630	27.384	3.623	- 94.883	- 78.270	34.210
600	19.350	38.114	28.889	5.535	- 94.401	- 74.993	27.315
700	19.656	41.120	30.427	7.485	- 93.916	- 71.796	22.415
800	19.900	43.762	31.932	9.464	- 93.428	- 68.671	18.759
900	20.063	46.115	33.380	11.462	- 92.945	- 65.604	15.930
1000	20.200	48.236	34.761	13.475	- 92.472	- 62.591	13.678
1100	20.311	50.167	36.075	15.501	- 92.012	- 59.626	11.846
1200	20.397	51.938	37.324	17.537	- 91.568	- 56.701	10.326
1300	20.457	53.573	38.512	19.580	- 91.142	- 53.811	9.046
1400	20.491	55.091	39.643	21.627	- 90.737	- 50.957	7.954
1500	20.500	56.505	40.720	23.677	- 90.355	- 48.130	7.012

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIBROMIDE ($BeBr_2$) (CRYSTAL) MOL. WT. = 168.8302

$S^\circ_{298.15}$ = [25.4 ± 2.0] cal. mole^{-1} deg.$^{-1}$

T_m = 761°K.

$\Delta H_f^\circ{}_0$ = Unknown

$\Delta H_f^\circ{}_{298.15}$ = [-88.4 ± 8] kcal. mole^{-1}

ΔH_m° = [4.5] kcal. mole^{-1}

$\Delta H_s^\circ{}_{298.15}$ = 29.8 ± 1.5 kcal. mole^{-1}

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messerknecht, Z. Anorg. Chem. 148, 157 (1925) and Biltz, Klatte and Rahlfs, Z. Anorg. Chem. 166, 339 (1927) as reported in N. B. S. Circular 500, Washington, 1952. They measured the heat of solution of $BeBr_2$ in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be^{++} and $2Br^-$ to obtain ΔH_f° of the crystal. However Be^{++} was estimated by N. B. S. An uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with $BeCl_2$ and BeF_2. The entropy was also estimated by comparing with α-$BeCl_2$ and BeF_2 and using additive entropy values for the halide ions.

Melting Data.

The melting point has been reported by O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 351 (1933) and by Lebean, Ann. Chim. Phys. 16, 472 (1899) as reported in N. B. S. Circular 500, Washington, 1952. The heat of melting was estimated by comparison with the sum of the heat of transition and melting for BeF_2 and $BeCl_2$.

Sublimation Data.

The heat of sublimation was obtained from an analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 624-695°K. The 3rd law analysis gave $\Delta H_{sub\ 298}$ = 29.78 with a drift of -2.1 ± 0.8 cal. mole^{-1} deg.$^{-1}$ A 2nd law analysis gave $\Delta H_{sub\ 298}$ = 31.1 ± 0.5 kcal. mole^{-1}. The 2nd law result was adopted in order to yield a real liquid region, no attempt was made to eliminate the drift since this would have caused the liquid region to become unreal.

Beryllium Dibromide ($BeBr_2$)

(Liquid) Mol. Wt. = 168.8302

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. $mole^{-1} deg.^{-1}$			kcal. $mole^{-1}$			
0							
100							
200							
298	16.500	28.070	28.070	.000	- 85.880	- 82.721	60.634
300	16.542	28.172	28.070	.031	- 85.889	- 82.701	60.245
400	18.100	33.176	28.742	1.774	- 92.825	- 80.190	43.812
500	27.000	37.307	30.054	3.626	- 92.360	- 77.085	33.692
600	27.000	42.230	31.686	6.326	- 91.090	- 74.150	27.008
700	27.000	46.392	33.497	9.026	- 89.855	- 71.426	22.299
800	27.000	49.997	35.339	11.726	- 88.646	- 68.876	18.815
900	27.000	53.177	37.148	14.426	- 87.461	- 66.475	16.142
1000	27.000	56.022	38.896	17.126	- 86.301	- 64.206	14.031
1100	27.000	58.596	40.572	19.826	- 85.167	- 62.052	12.328
1200	27.000	60.945	42.173	22.526	- 84.059	- 60.000	10.927
1300	27.000	63.106	43.701	25.226	- 82.976	- 58.038	9.757
1400	27.000	65.107	45.160	27.926	- 81.918	- 56.160	8.767
1500	27.000	66.970	46.552	30.626	- 80.886	- 54.358	7.920
1600	27.000	68.712	47.883	33.326	- 82.634	- 52.542	7.177
1700	27.000	70.349	49.157	36.026	- 81.537	- 50.695	6.517
1800	27.000	71.892	50.378	38.726	- 80.446	- 48.913	5.939
1900	27.000	73.352	51.549	41.426	- 79.361	- 47.190	5.428
2000	27.000	74.737	52.674	44.126	- 78.283	- 45.527	4.975

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIBROMIDE ($BeBr_2$) (LIQUID) MOL. WT. = 168.8302

$S^\circ_{298.15}$ = [28.07] cal. $mole^{-1}$ $deg.^{-1}$

T_m = 761°K.

T_b = [794]°K.

$\Delta H^\circ_{f\ 298.15}$ = [-85.88 ± 3] kcal. $mole^{-1}$

ΔH°_m = [4.5] kcal. $mole^{-1}$

ΔH°_v = [23.9] kcal. $mole^{-1}$

Heat of Formation.

The heat of formation was obtained from that of $BeBr_2$(c) by adding ΔH°_m and the difference between H_{761} H_{298} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for $BeCl_2$. A glass transition was assumed at 500°K. below which the heat capacity is that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See $BeBr_2$(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over between $BeBr_2$(l) and (g).

Beryllium Dibromide ($BeBr_2$)

(Ideal Gas) Mol. Wt. = 168.8302

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.200	-54.173	-54.173	INFINITE
100	10.302	53.488	77.372	-2.388	-54.039	-58.088	126.946
200	12.217	61.357	67.569	-1.242	-54.202	-62.092	67.848
298	13.036	66.400	66.400	.000	-57.300	-65.569	48.061
300	13.048	66.481	66.400	.024	-57.316	-65.620	47.802
400	13.594	70.315	66.919	1.358	-64.661	-66.881	36.540
500	13.955	73.390	67.916	2.737	-64.669	-67.436	29.475
600	14.194	75.957	69.048	4.145	-64.691	-67.988	24.763
700	14.358	78.158	70.196	5.573	-64.728	-68.535	21.397
800	14.473	80.083	71.314	7.015	-64.777	-69.076	18.870
900	14.556	81.792	72.385	8.467	-64.840	-69.609	16.902
1000	14.617	83.329	73.404	9.925	-64.922	-70.134	15.327
1100	14.664	84.725	74.371	11.390	-65.023	-70.651	14.036
1200	14.701	86.002	75.288	12.858	-65.147	-71.157	12.959
1300	14.730	87.180	76.158	14.330	-65.292	-71.651	12.045
1400	14.753	88.273	76.984	15.804	-65.460	-72.136	11.260
1500	14.772	89.291	77.771	17.280	-65.652	-72.606	10.578
1600	14.787	90.245	78.521	18.758	-68.622	-72.984	9.969
1700	14.800	91.142	79.238	20.237	-68.746	-73.252	9.417
1800	14.811	91.988	79.923	21.718	-68.874	-73.514	8.925
1900	14.821	92.789	80.579	23.200	-69.007	-73.767	8.485
2000	14.829	93.550	81.209	24.682	-69.147	-74.017	8.088
2100	14.836	94.274	81.814	26.165	-69.291	-74.257	7.728
2200	14.842	94.964	82.396	27.649	-69.441	-74.490	7.400
2300	14.847	95.624	82.957	29.134	-69.596	-74.714	7.099
2400	14.852	96.256	83.498	30.619	-69.757	-74.932	6.823
2500	14.856	96.862	84.020	32.104	-69.925	-75.145	6.569
2600	14.859	97.445	84.526	33.590	-70.097	-75.349	6.333
2700	14.863	98.006	85.015	35.076	-70.274	-75.550	6.115
2800	14.866	98.546	85.488	36.562	-141.488	-74.632	5.825
2900	14.868	99.068	85.948	38.049	-141.424	-72.245	5.444
3000	14.870	99.572	86.393	39.536	-141.363	-69.861	5.089
3100	14.873	100.060	86.826	41.023	-141.305	-67.482	4.757
3200	14.875	100.532	87.247	42.510	-141.248	-65.097	4.446
3300	14.876	100.990	87.657	43.998	-141.195	-62.721	4.154
3400	14.878	101.434	88.056	45.486	-141.145	-60.344	3.879
3500	14.879	101.865	88.444	46.973	-141.100	-57.968	3.619
3600	14.881	102.284	88.823	48.461	-141.059	-55.591	3.375
3700	14.882	102.692	89.192	49.950	-141.021	-53.220	3.143
3800	14.883	103.089	89.553	51.438	-140.991	-50.848	2.924
3900	14.884	103.475	89.905	52.926	-140.966	-48.469	2.716
4000	14.885	103.852	90.249	54.415	-140.947	-46.103	2.519
4100	14.886	104.220	90.585	55.903	-140.936	-43.737	2.331
4200	14.887	104.579	90.914	57.392	-140.931	-41.366	2.152
4300	14.888	104.929	91.236	58.881	-140.934	-38.990	1.982
4400	14.889	105.271	91.551	60.370	-140.946	-36.618	1.819
4500	14.889	105.606	91.859	61.858	-140.968	-34.250	1.663
4600	14.890	105.933	92.162	63.347	-140.999	-31.877	1.514
4700	14.891	106.253	92.458	64.836	-141.039	-29.503	1.372
4800	14.891	106.567	92.749	66.325	-141.091	-27.134	1.235
4900	14.892	106.874	93.034	67.815	-141.151	-24.757	1.104
5000	14.892	107.175	93.314	69.304	-141.223	-22.378	.978
5100	14.893	107.470	93.589	70.793	-141.308	-20.004	.857
5200	14.893	107.759	93.858	72.282	-141.403	-17.627	.741
5300	14.894	108.042	94.123	73.772	-141.510	-15.238	.628
5400	14.894	108.321	94.384	75.261	-141.630	-12.862	.521
5500	14.894	108.594	94.639	76.750	-141.762	-10.471	.416
5600	14.895	108.862	94.891	78.240	-141.906	-8.083	.315
5700	14.895	109.126	95.139	79.729	-142.063	-5.690	.218
5800	14.895	109.385	95.382	81.219	-142.231	-3.292	.124
5900	14.896	109.640	95.621	82.708	-142.414	-.902	.033
6000	14.896	109.890	95.857	84.198	-142.608	1.494	.054

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIBROMIDE ($BeBr_2$) (IDEAL GAS) MOL. WT. = 168.8302

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = [66.4 ± 2] cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-54.2 ± 9.5] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-57.3 ± 9.5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[205] (1)
[180] (2)
[890] (1)

Bond Distance: Be-Br = 1.90Å

Bond Angle: Br-Be-Br = [180°]

Rotational Constant: B_o = 0.02922 cm.$^{-1}$

σ = 2

Heat of Formation.

The heat of formation was obtained from that of the crystal plus $\Delta H^\circ_{s\ 298.15}$, see $BeBr_2$(c) for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with $BeCl_2$. The bond length was reported by P. A. Akishin, V. P. Spirodinov and G. A. Sobelev, Dokl. Akad. Nauk. SSSR 118, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k_1 for the BeF_2, $BeCl_2$, $BeBr_2$, BeI_2 series and also assuming $k_1/k_\delta/l^2$ = 50 as for BeF_2. The principal moment of inertia is 95.7984 x 10^{-39} g. cm.^{2}

Beryllium Monochloride (BeCl)

(Ideal Gas) GFW = 44.4652

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.118	13.947	13.947	INFINITE
100	6.959	44.200	58.426	- 1.423	14.284	12.135	- 26.521
200	7.138	49.057	52.662	- .721	14.485	9.891	- 10.809
298	7.563	51.984	51.984	.000	14.500	7.625	- 5.589
300	7.571	52.031	51.984	.014	14.499	7.582	- 5.524
400	7.963	54.265	52.286	.792	14.423	5.286	- 2.888
500	8.243	56.074	52.869	1.603	14.304	3.016	- 1.318
600	8.437	57.595	53.533	2.437	14.162	.771	- .281
700	8.573	58.907	54.209	3.288	14.002	- 1.449	.452
800	8.672	60.058	54.870	4.151	13.826	- 3.645	.996
900	8.746	61.084	55.504	5.022	13.635	- 5.816	1.412
1000	8.804	62.009	56.109	5.900	13.426	- 7.967	1.741
1100	8.850	62.850	56.684	6.782	13.196	- 10.095	2.006
1200	8.888	63.622	57.231	7.669	12.944	- 12.202	2.222
1300	8.919	64.335	57.750	8.560	12.672	- 14.287	2.402
1400	8.947	64.997	58.244	9.453	12.377	- 16.350	2.552
1500	8.970	65.615	58.715	10.349	12.060	- 18.392	2.680
1600	8.992	66.194	59.165	11.247	8.965	- 20.331	2.777
1700	9.011	66.740	59.595	12.147	8.718	- 22.154	2.848
1800	9.029	67.256	60.006	13.049	8.466	- 23.964	2.910
1900	9.045	67.744	60.401	13.953	8.211	- 25.757	2.963
2000	9.060	68.208	60.779	14.858	7.951	- 27.538	3.009
2100	9.074	68.651	61.144	15.765	7.687	- 29.308	3.050
2200	9.088	69.073	61.495	16.673	7.418	- 31.062	3.086
2300	9.101	69.478	61.833	17.582	7.145	- 32.805	3.117
2400	9.114	69.865	62.160	18.493	6.867	- 34.534	3.145
2500	9.126	70.238	62.475	19.405	6.583	- 36.257	3.170
2600	9.138	70.596	62.781	20.318	6.296	- 37.963	3.191
2700	9.149	70.941	63.077	21.233	6.004	- 39.660	3.210
2800	9.161	71.274	63.364	22.148	- 65.323	- 40.238	3.141
2900	9.172	71.595	63.642	23.065	- 65.373	- 39.338	2.965
3000	9.183	71.907	63.912	23.983	- 65.425	- 38.443	2.801
3100	9.194	72.208	64.175	24.901	- 65.479	- 37.544	2.647
3200	9.205	72.500	64.431	25.821	- 65.534	- 36.639	2.502
3300	9.216	72.783	64.680	26.743	- 65.592	- 35.734	2.367
3400	9.228	73.059	64.922	27.665	- 65.653	- 34.831	2.239
3500	9.239	73.326	65.158	28.588	- 65.717	- 33.923	2.118
3600	9.251	73.587	65.389	29.513	- 65.785	- 33.013	2.004
3700	9.262	73.840	65.614	30.438	- 65.858	- 32.101	1.896
3800	9.275	74.087	65.834	31.365	- 65.935	- 31.188	1.794
3900	9.287	74.329	66.048	32.293	- 66.016	- 30.273	1.696
4000	9.300	74.564	66.258	33.222	- 66.104	- 29.356	1.604
4100	9.313	74.794	66.464	34.153	- 66.197	- 28.440	1.516
4200	9.327	75.018	66.665	35.085	- 66.296	- 27.515	1.432
4300	9.341	75.238	66.861	36.019	- 66.401	- 26.589	1.351
4400	9.356	75.453	67.054	36.953	- 66.514	- 25.662	1.275
4500	9.372	75.663	67.243	37.890	- 66.634	- 24.732	1.201
4600	9.388	75.869	67.429	38.828	- 66.761	- 23.799	1.131
4700	9.405	76.071	67.610	39.767	- 66.896	- 22.864	1.063
4800	9.422	76.270	67.789	40.709	- 67.040	- 21.929	.998
4900	9.440	76.464	67.964	41.652	- 67.191	- 20.984	.936
5000	9.459	76.655	68.136	42.597	- 67.351	- 20.038	.876
5100	9.479	76.843	68.305	43.544	- 67.519	- 19.092	.818
5200	9.499	77.027	68.471	44.493	- 67.696	- 18.143	.763
5300	9.520	77.208	68.634	45.444	- 67.884	- 17.187	.709
5400	9.542	77.386	68.794	46.397	- 68.079	- 16.228	.657
5500	9.564	77.561	68.952	47.352	- 68.284	- 15.264	.607
5600	9.587	77.734	69.107	48.310	- 68.498	- 14.302	.558
5700	9.611	77.904	69.260	49.270	- 68.721	- 13.332	.511
5800	9.636	78.071	69.411	50.232	- 68.954	- 12.351	.465
5900	9.661	78.236	69.559	51.197	- 69.196	- 11.379	.421
6000	9.686	78.399	69.705	52.164	- 69.447	- 10.401	.379

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1962; Mar. 31, 1964; Sept. 30, 1966

BERYLLIUM MONOCHLORIDE (BeCl) (IDEAL GAS) GFW = 44.4652

Ground State Configuration $^2\Sigma^+$

ΔHf°_0 = 13.9 ± 3.0 kcal/mol

$S^\circ_{298.15}$ = 51.984 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 14.5 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
27970	4

ω_e = 845.29 cm^{-1} $\omega_e x_e$ = 4.831 cm^{-1} σ = 1

B_e = [0.769] cm^{-1} α_e = [0.0063] r_e = [1.75] Å

Heat of Formation.

Novikov[1] measured 39 bands in the ultraviolet spectrum of BeCl(g). A linear extrapolation leads to a ground state dissociation energy of 36,555 cm $^{-1}$. The authors assumed that the non-crossing rule applied and that the ground and first excited states had a common dissociation limit. However, in the analogous case of BeF, treated in the same way by the above authors, it was shown by Mann[2] that these assumptions were not correct. If it is assumed that the excited state dissociates $A^2\pi \rightarrow Be(^3P) + F(^2P)$ and the ground state $X^2\Sigma \rightarrow Be(^1SO) + F(^2P)$, then ν_{oo} + D' should equal D" + excitation energy of Be atom. We find ν_{oo} + D' = 27,960 + 30,390 = 58,350 and D" + E_{Be} = 36,555 + 21,981 = 58,536 which is in excellent agreement. Thus the dissociation energy to ground state atoms is taken as 104.5 kcal/mol, which leads to a heat of formation of 3 kcal/mol using reaction a.

Greenbaum et al.[3] report equilibrium constants for reaction b in the temperature range 1573 - 1724°K using the molecular flow effusion method. Also Hildenbrand et al.[4] report equilibrium constants for reactions c and d which were calculated from mass spectrometric ion intensities. The $\Delta Hr^\circ_{298.15}$ values by second and third law analysis for these data and the corresponding $\Delta Hf^\circ_{298.15}$ values are listed below.

Author	Method	Reaction	T°K	$\Delta Hr^\circ_{298.15}$ kcal/mol Second Law	Third Law	Drift eu	$\Delta Hf^\circ_{298.15}$ Kcal/mol
1. Novikov	Spectroscopic	(a) BeCl(g) → Be(g) + Cl(g)		104.5			2.7
3. Greenbaum	Kp	(b) $BeCl_2$(g) + Be(l) →	1573-1724	93.56 ± 7			5.2
		2 BeCl(g)			85.87	-4.521	1.3
4. Hildenbrand	Kp from Mass	(c) Be(g) + AlCl(g) →	1382-1554	27.5 ± 2			16.5 ± 3
	Spectroscopy	BeCl(g) + Al(g)			26.25	- .779	15.3 ± 2
		(d) Be(g) + $BeCl_2$(g) →	1382-1536	33.41± 8			12.8 ± 5
		2 BeCl(g)			36.08	2.198	14.1 ± 2.5

The equilibrium data of Greenbaum et al.[3] was not weighted, since calculations indicated the possibility of reaction of BeCl(g) with the Al_2O_3 tube at the temperatures and pressures used. The data of Hildenbrand et al.[4], which reflect the true gas phase equilibria and appear consistent with each other, were adopted, yielding $\Delta Hf^\circ_{298.15}$ = 14.5 kcal/mol.

Heat Capacity and Entropy.

The vibrational constants used to calculate the functions were derived by Novikov[1] from a two constant equation $[\omega''_o - (2\nu'' + 1)\,\omega''_o x''_o = \Delta G''_o(\nu'')]$. The electronic levels were obtained from Herzberg[5]. B_e was obtained from the estimated bond length, which was taken to be slightly less than that in $BeCl_2$(g), and α_e was estimated from the Morse potential function.

References

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Beryllium Monochloride Unipositive Ion ($BeCl^+$)

(Ideal Gas) GFW = 44.46465

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	7.826	50.870	50.870	.000	234.000	225.970	-165.640
300	7.834	50.919	50.871	.014	234.009	225.920	-164.582
400	8.211	53.228	51.183	.818	234.456	223.154	-121.926
500	8.454	55.088	51.784	1.652	234.856	220.283	-96.285
600	8.613	56.645	52.468	2.506	235.231	217.332	-79.163
700	8.722	57.981	53.162	3.373	235.583	214.320	-66.914
800	8.802	59.151	53.839	4.250	235.918	211.259	-57.713
900	8.863	60.192	54.488	5.133	236.236	208.159	-50.548
1000	8.912	61.128	55.106	6.022	236.535	205.022	-44.807
1100	8.954	61.979	55.693	6.915	236.813	201.858	-40.105
1200	8.993	62.760	56.250	7.812	237.068	198.669	-36.183
1300	9.034	63.482	56.779	8.714	237.303	195.458	-32.859
1400	9.081	64.153	57.282	9.619	237.517	192.231	-30.009
1500	9.136	64.781	57.761	10.530	237.712	188.989	-27.536
1600	9.202	65.373	58.218	11.447	235.133	185.813	-25.381
1700	9.283	65.933	58.656	12.371	235.407	182.724	-23.491
1800	9.380	66.466	59.075	13.304	235.682	179.615	-21.808
1900	9.494	66.976	59.478	14.248	235.964	176.495	-20.302
2000	9.624	67.467	59.865	15.203	236.251	173.357	-18.944
2100	9.771	67.940	60.238	16.173	236.547	170.204	-17.713
2200	9.932	68.398	60.599	17.158	236.852	167.038	-16.594
2300	10.107	68.843	60.948	18.160	237.167	163.858	-15.570
2400	10.293	69.277	61.286	19.180	237.496	160.665	-14.631
2500	10.488	69.701	61.614	20.219	237.836	157.455	-13.765
2600	10.689	70.117	61.933	21.278	238.191	154.234	-12.965
2700	10.893	70.524	62.244	22.357	238.561	150.999	-12.223
2800	11.097	70.924	62.546	23.456	167.915	148.857	-11.619
2900	11.300	71.317	62.842	24.576	168.565	148.166	-11.166
3000	11.498	71.703	63.131	25.716	169.231	147.448	-10.742
3100	11.690	72.083	63.414	26.875	169.915	146.708	-10.343
3200	11.873	72.457	63.690	28.054	170.616	145.954	-9.968
3300	12.046	72.825	63.962	29.250	171.329	145.173	-9.614
3400	12.209	73.187	64.228	30.462	172.054	144.369	-9.280
3500	12.358	73.543	64.489	31.691	172.792	143.542	-8.963
3600	12.496	73.894	64.745	32.934	173.540	142.699	-8.663
3700	12.620	74.238	64.997	34.190	174.295	141.827	-8.377
3800	12.730	74.576	65.245	35.457	175.055	140.940	-8.106
3900	12.827	74.908	65.488	36.735	175.821	140.036	-7.847
4000	12.911	75.234	65.728	38.022	176.587	139.105	-7.600
4100	12.983	75.553	65.964	39.317	177.355	138.154	-7.364
4200	13.042	75.867	66.196	40.618	178.122	137.192	-7.139
4300	13.090	76.174	66.424	41.925	178.888	136.211	-6.923
4400	13.126	76.476	66.649	43.236	179.648	135.212	-6.716
4500	13.153	76.771	66.871	44.550	180.402	134.189	-6.517
4600	13.171	77.060	67.089	45.866	181.149	133.154	-6.326
4700	13.180	77.344	67.304	47.184	181.890	132.102	-6.143
4800	13.182	77.621	67.516	48.502	182.620	131.034	-5.966
4900	13.177	77.893	67.725	49.820	183.340	129.955	-5.796
5000	13.166	78.159	67.931	51.137	184.049	128.862	-5.633
5100	13.149	78.420	68.135	52.453	184.746	127.748	-5.474
5200	13.128	78.675	68.335	53.767	185.431	126.623	-5.322
5300	13.103	78.925	68.532	55.079	186.101	125.485	-5.174
5400	13.074	79.169	68.727	56.387	186.758	124.334	-5.032
5500	13.043	79.409	68.919	57.693	187.401	123.173	-4.894
5600	13.009	79.644	69.108	58.996	188.028	121.996	-4.761
5700	12.974	79.873	69.295	60.295	188.641	120.817	-4.632
5800	12.937	80.099	69.480	61.591	189.239	119.623	-4.508
5900	12.898	80.320	69.662	62.882	189.821	118.413	-4.386
6000	12.860	80.536	69.841	64.170	190.388	117.200	-4.269

June 30, 1968

BERYLLIUM MONOCHLORIDE UNIPOSITIVE ION ($BeCl^+$) (IDEAL GAS) GFW = 44.46465

Ground State Configuration $[^1\Sigma_g^+]$ ΔHf_0° = [233 ± 20] kcal/mol

$S^\circ_{298.15}$ = [50.9 ± 2] gibbs/mol ΔHf_0° = [234 ± 20] kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^3\pi_u$	[10000]	6
$^1\pi_u$	[15000]	2
$^3\Sigma_g^-$	[30000]	3
$^1\Delta$	[35000]	2
$^1\Sigma^+$	[40000]	1

ω_e = [700] cm^{-1} $\omega_e x_e$ = [4.8] cm^{-1} σ = 1

B_e = [0.7241] cm^{-1} α_e = [0.0071] cm^{-1} r_e = [1.8] Å

Heat of Formation

Krasnov (1) has reported calculations of the ionization potentials(IP) for the monohalides (MX, where X = F, Cl, Br, and I) of Group IIA elements (M = Mg, Ca, Sr, and Ba). Based on his data we obtain graphically the value IP(BeCl, g) = 8.9 ± 0.5 eV. The value of $\Delta Hf^\circ_{298}(BeCl^+, g)$ is derived as 219 ± 15 kcal/mol, using $\Delta Hf^\circ_0(BeCl, g)$ = 13.9 kcal/mol. Beckett (2) reported the ionization potential of BeCl(g) to be approximately 9 ± 1 eV, yielding $\Delta Hf^\circ_{298}(BeCl^+, g)$ = 222 ± 23 kcal/mol. Hildenbrand (9) measured the appearance potential (AP) of $BeCl^+(g)$ to be 9.5 ± 0.7 eV which is on the same order of the above IP values, and assumed that $IP(BeCl^+, g) = AP(BeCl^+, g)$ = 9.5 ± 0.7 eV. Using this IP value, we obtain $\Delta Hf^\circ_{298}(BeCl^+, g)$ = 234 ± 20 kcal/mol which is adopted.

Heat Capacity and Entropy

The six electronic states are obtained from Fougere (3). The electronic levels are estimated by comparison with those of the isoelectronic molecules, BeS (4), BeO (5, 6), and MgO (5, 7). The values of ω_e, $\omega_e x_e$ are estimated by comparison with those for BeCl(g) and LiCl(g). B_e and α_e are calculated using the method suggested by Herzberg (5). The bond distance is estimated (8). The moment of inertia is 3.865×10^{-39} g cm^2. The enthalpy at 0°K is -2.15 kcal/mol.

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Beryllium Chloride Fluoride (BeClF)

(Ideal Gas) Mol. Wt. = 63.4636

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.797	- 137.177	- 137.177	INFINITE
100	8.318	47.830	68.514	- 2.068	- 137.156	- 137.632	300.781
200	10.645	54.397	59.934	- 1.107	- 137.044	- 138.151	150.957
298	11.810	58.887	58.887	.000	- 137.000	- 138.711	101.673
300	11.827	58.960	58.887	.022	- 137.000	- 138.722	101.054
400	12.572	62.471	59.361	1.244	- 137.016	- 139.294	76.103
500	13.106	65.337	60.278	2.529	- 137.065	- 139.858	61.129
600	13.495	67.763	61.328	3.860	- 137.127	- 140.412	51.142
700	13.782	69.865	62.401	5.225	- 137.198	- 140.953	44.005
800	13.996	71.720	63.452	6.614	- 137.280	- 141.485	38.650
900	14.157	73.379	64.465	8.022	- 137.372	- 142.005	34.482
1000	14.281	74.877	65.432	9.445	- 137.479	- 142.514	31.145
1100	14.377	76.243	66.354	10.878	- 137.605	- 143.012	28.412
1200	14.454	77.497	67.231	12.319	- 137.751	- 143.497	26.133
1300	14.515	78.657	68.066	13.768	- 137.917	- 143.969	24.202
1400	14.565	79.734	68.861	15.222	- 138.104	- 144.428	22.545
1500	14.606	80.740	69.620	16.681	- 138.314	- 144.872	21.107
1600	14.640	81.684	70.345	18.143	- 141.302	- 145.224	19.836
1700	14.669	82.573	71.038	19.608	- 141.443	- 145.464	18.700
1800	14.693	83.412	71.703	21.077	- 141.589	- 145.698	17.689
1900	14.714	84.207	72.340	22.547	- 141.740	- 145.921	16.784
2000	14.732	84.962	72.952	24.019	- 141.897	- 146.137	15.968
2100	14.747	85.681	73.542	25.493	- 142.058	- 146.345	15.230
2200	14.761	86.368	74.109	26.969	- 142.226	- 146.547	14.557
2300	14.773	87.024	74.656	28.445	- 142.400	- 146.736	13.942
2400	14.783	87.653	75.185	29.923	- 142.579	- 146.921	13.378
2500	14.793	88.257	75.696	31.402	- 142.767	- 147.101	12.859
2600	14.801	88.837	76.190	32.882	- 142.959	- 147.267	12.378
2700	14.808	89.396	76.669	34.362	- 143.157	- 147.430	11.933
2800	14.815	89.934	77.133	35.843	- 214.392	- 146.475	11.432
2900	14.821	90.454	77.584	37.325	- 214.352	- 144.049	10.855
3000	14.826	90.957	78.021	38.808	- 214.316	- 141.629	10.317
3100	14.831	91.443	78.446	40.290	- 214.283	- 139.208	9.814
3200	14.836	91.914	78.860	41.774	- 214.253	- 136.784	9.341
3300	14.840	92.371	79.262	43.258	- 214.228	- 134.365	8.898
3400	14.843	92.814	79.654	44.742	- 214.208	- 131.945	8.481
3500	14.847	93.244	80.037	46.226	- 214.193	- 129.526	8.088
3600	14.850	93.662	80.409	47.711	- 214.183	- 127.103	7.716
3700	14.853	94.069	80.773	49.196	- 214.180	- 124.686	7.365
3800	14.855	94.465	81.128	50.682	- 214.183	- 122.267	7.032
3900	14.858	94.851	81.475	52.167	- 214.194	- 119.847	6.716
4000	14.860	95.227	81.814	53.653	- 214.212	- 117.428	6.416
4100	14.862	95.594	82.146	55.139	- 214.238	- 115.012	6.130
4200	14.864	95.953	82.470	56.626	- 214.272	- 112.594	5.859
4300	14.866	96.302	82.788	58.112	- 214.314	- 110.166	5.599
4400	14.868	96.644	83.099	59.599	- 214.367	- 107.744	5.351
4500	14.869	96.978	83.404	61.086	- 214.429	- 105.322	5.115
4600	14.871	97.305	83.702	62.573	- 214.501	- 102.898	4.889
4700	14.872	97.625	83.995	64.060	- 214.583	- 100.472	4.672
4800	14.874	97.938	84.282	65.547	- 214.676	- 98.041	4.464
4900	14.875	98.245	84.564	67.035	- 214.780	- 95.610	4.264
5000	14.876	98.545	84.841	68.522	- 214.895	- 93.173	4.072
5100	14.877	98.840	85.112	70.010	- 215.022	- 90.740	3.888
5200	14.878	99.129	85.379	71.498	- 215.160	- 88.304	3.711
5300	14.879	99.412	85.641	72.985	- 215.312	- 85.860	3.540
5400	14.880	99.690	85.899	74.473	- 215.475	- 83.418	3.376
5500	14.881	99.963	86.152	75.961	- 215.651	- 80.969	3.217
5600	14.882	100.231	86.401	77.450	- 215.838	- 78.518	3.064
5700	14.883	100.495	86.646	78.938	- 216.039	- 76.067	2.916
5800	14.883	100.754	86.887	80.426	- 216.251	- 73.606	2.773
5900	14.884	101.008	87.124	81.914	- 216.477	- 71.148	2.635
6000	14.885	101.258	87.358	83.403	- 216.715	- 68.683	2.502

Dec. 31, 1960; June 30, 1965

BERYLLIUM CHLORIDE FLUORIDE (BeClF) **(IDEAL GAS)** **MOL. WT. = 63.4636**

Point Group $[C_{\infty v}]$

$S^\circ_{298.15}$ = [58.89] cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-137.2 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-137 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[500](1)
[270](2)
[1300](1)

Bond Distance: Be-Cl = [1.77]Å

Be-F = [1.43]Å

Bond Angle: Cl-Be-F = [180°]

σ = 1

Rotational Constant: B_o = 0.12970 cm.$^{-1}$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_r = 0$ for the reaction $BeF_2 + BeCl_2 \rightarrow 2BeClF$

Heat Capacity and Entropy.

The structure, bond lengths and frequencies were all estimated from the properties of $BeCl_2$ and BeF_2. The principal moment of inertia is 21.579 x 10^{-39} g. cm.^{2}

Beryllium Dichloride, Alpha (α-$BeCl_2$)

(Crystal)   Mol. Wt. = 79.9182

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.863	- 117.536	- 117.536	INFINITE
100	8.045	6.925	31.535	- 2.461	- 117.845	- 114.006	249.147
200	12.800	14.110	21.095	- 1.397	- 117.640	- 110.229	120.446
298	15.500	19.760	19.760	.000	- 117.335	- 106.659	78.179
300	15.540	19.856	19.760	.029	- 117.328	- 106.592	77.649
400	17.390	24.598	20.394	1.682	- 116.944	- 103.070	56.312
500	18.530	28.612	21.647	3.482	- 116.501	- 99.651	43.555
600	19.140	32.049	23.101	5.369	- 116.025	- 96.325	35.085
700	19.445	35.024	24.597	7.299	- 115.545	- 93.080	29.059
800	19.660	37.635	26.067	9.255	- 115.070	- 89.904	24.559
900	19.843	39.962	27.484	11.230	- 114.602	- 86.786	21.073
1000	20.000	42.061	28.838	13.222	- 114.144	- 83.721	18.296
1100	20.131	43.973	30.129	15.229	- 113.698	- 80.699	16.033
1200	20.237	45.730	31.357	17.248	- 113.268	- 77.719	14.154
1300	20.317	47.353	32.525	19.276	- 112.854	- 74.773	12.570
1400	20.371	48.861	33.639	21.310	- 112.460	- 71.860	11.217
1500	20.400	50.267	34.701	23.349	- 112.087	- 68.972	10.049

BERYLLIUM DICHLORIDE, ALPHA (α-$BeCl_2$)   (CRYSTAL)   MOL. WT. = 79.9182

$S_{298.15}^\circ = 19.76 \pm 0.06$ cal. mole^{-1} deg.$^{-1}$

$T_m = 688$°K.

$\Delta H_{f\ 0}^\circ = -117.5 \pm 0.8$ kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -117.3 \pm 0.8$ kcal. mole^{-1}

$\Delta H_m^\circ = 2.07 \pm 0.06$ kcal. mole^{-1}

$\Delta H_{s\ 298.15}^\circ = 31.3$ kcal. mole^{-1}

Heat of Formation.

W. H. Johnson and A. A. Gilliland, J. Res. Nat'l. Bur. Stand. 65A, 59 (1961) have directly reacted beryllium and chlorine and obtained $\Delta H_f^\circ = -118.03 \pm 0.56$ though the crystal form of the product was unknown. P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, Fulmer Research Institute, Report R. 163/SR.1/Sept. 1964 under Contract AF61(052)-447 also by direct combustion of the elements obtain $\Delta H_f^\circ = -117.1 \pm 0.4$ kcal. mole^{-1}. The crystal form of the sample was deduced to be α' by a comparison experiment, the assumption is made here that α and α' are identical. C. J. Thompson, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962) by solution calorimetry report a $\Delta H_f^\circ = -118.25 \pm 0.5$ kcal. mole^{-1}. Initially this sample was reported to be of unknown crystal form. However, G. C. Sinke, private communication February 1965, reports that an x-ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50% α' and 50% β. Using the heats of transition adopted for these tables heats of formation of -117.3 ± 0.8 kcal. mole^{-1} for α and -118.6 ± 0.8 kcal. mole^{-1} for β have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the Nov. 1965 issue have measured the heat capacity of the α' form from 13° to 304°K. and the enthalpy (relative to the α' form) from 676° to 688°K. The assumption has been made that the α and α' forms are identical and the heat capacity curve between 304° and 676°K. has been estimated graphically. The entropy was obtained by integration of the heat capacity curve assuming $S_{13} = 0.16$ cal. mole^{-1} deg.$^{-1}$. The sample was identified as α' by x-ray diffraction both before and after the experiments.

Melting Data.

The temperature and heat of melting were reported by McDonald and Oetting, loc. cit. Several investigations of the melting point are in disagreement mainly due to the uncertainty of the crystal form of the material and a solid state transition just below the pure α-liquid melting point.

Sublimation Data.

The adopted heat of sublimation was derived from that of the β form and heat of the α-β transition at 298°K.

Beryllium Dichloride, Beta (β-$BeCl_2$)

(Crystal) Mol. Wt. = 79.9182

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.729	-118.667	-118.667	INFINITE
100	7.595	5.761	30.501	-2.474	-119.123	-115.167	251.686
200	12.380	12.650	19.410	-1.352	-118.860	-111.157	121.460
298	14.920	18.120	18.120	.000	-118.600	-107.435	78.748
300	14.960	18.212	18.120	.028	-118.594	-107.365	78.212
400	16.420	22.729	18.726	1.601	-118.290	-103.667	56.639
500	17.400	26.506	19.915	3.295	-117.953	-100.050	43.730
600	18.120	29.744	21.290	5.073	-117.586	-96.503	35.149
700	18.680	32.583	22.704	6.915	-117.194	-93.020	29.041
800	19.110	35.106	24.100	8.805	-116.785	-89.595	24.475
900	19.450	37.377	25.451	10.734	-116.363	-86.220	20.936
1000	19.730	39.442	26.748	12.693	-115.938	-82.896	18.116
1100	19.930	41.332	27.990	14.677	-115.515	-79.611	15.817
1200	20.080	43.073	29.175	16.678	-115.103	-76.366	13.907
1300	20.190	44.685	30.307	18.692	-114.703	-73.154	12.298
1400	20.263	46.184	31.388	20.714	-114.321	-69.973	10.923
1500	20.300	47.583	32.421	22.743	-113.958	-66.818	9.735

June 30, 1965

BERYLLIUM DICHLORIDE, BETA (β-$BeCl_2$) (CRYSTAL) MOL. WT. = 79.9182

$S^\circ_{298.15}$ = 18.12 ± 0.05 cal. mole^{-1} deg.$^{-1}$

T°_m = [682°K.]

T°_t = 676°K ($\beta \rightarrow \alpha$)

$\Delta H^\circ_{f\ 0}$ = -118.7 ± 0.8 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -118.6 ± 0.8 kcal. mole^{-1}

ΔH°_m = [3.65] ± 0.15 kcal. mole^{-1}

ΔH°_t = [1.63]-± 0.15 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 32.5 kcal. mole^{-1}

Heat of Formation.

See table for α-$BeCl_2$ for details.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the heat capacity of the β-form from 13 to 304°K. and the enthalpy of the β-form from 298° to 676°K. The entropy was obtained by integration of the heat capacity curve based on S_{13} = 0.06 cal. mole^{-1} deg.$^{-1}$ The sample was identified as β-$BeCl_2$ both before and after the low temperature experiments.

Melting Data.

The temperature and heat of melting were obtained from cross over point of the tables for β-$BeCl_2$ and liquid $BeCl_2$.

Transition Data.

The temperature of the β to α transition was obtained from McDonald and Oetting, loc. cit. The heat of the transition is a function of the heat capacity curve chosen for α-$BeCl_2$ between 298 and 676°K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 kcal. mole^{-1}) than the curve employed here. It should also be noted that the transitional heat is not included in this table, which is for B-$BeCl_2$ only.

Sublimation Data.

The heat of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for $BeCl_2$ (g).

Beryllium Dichloride ($BeCl_2$)

(Liquid) Mol. Wt. = 79.9182

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	14.920	19.065	19.065	.000	- 117.425	- 106.541	78.093
300	14.960	19.157	19.065	.028	- 117.419	- 106.474	77.562
400	16.420	23.674	19.671	1.601	- 117.115	- 102.870	56.203
500	29.020	28.432	20.900	3.766	- 116.307	- 99.367	43.431
600	29.020	33.723	22.609	6.668	- 114.816	- 96.120	35.010
700	29.020	38.196	24.525	9.570	- 113.364	- 93.119	29.072
800	29.020	42.071	26.481	12.472	- 111.943	- 90.325	24.675
900	29.020	45.489	28.407	15.374	- 110.548	- 87.706	21.297
1000	29.020	48.547	30.271	18.276	- 109.180	- 85.243	18.629
1100	29.020	51.313	32.060	21.178	- 107.839	- 82.914	16.473
1200	29.020	53.838	33.771	24.080	- 106.526	- 80.707	14.698
1300	29.020	56.161	35.405	26.982	- 105.238	- 78.608	13.214
1400	29.020	58.311	36.966	29.884	- 103.976	- 76.606	11.958
1500	29.020	60.313	38.456	32.786	- 102.740	- 74.695	10.882
1600	29.020	62.186	39.881	35.688	- 104.285	- 72.786	9.942
1700	29.020	63.946	41.246	38.590	- 102.985	- 70.857	9.109
1800	29.020	65.604	42.553	41.492	- 101.692	- 69.004	8.378
1900	29.020	67.173	43.808	44.394	- 100.405	- 67.222	7.732
2000	29.020	68.662	45.014	47.296	- 99.126	- 65.510	7.158

Sept. 30, 1961; June 30, 1965

BERYLLIUM DICHLORIDE ($BeCl_2$) (LIQUID) MOL. WT. = 79.9182

$S^\circ_{298.15}$ = 19.065 ± 1 cal. mole^{-1} deg.$^{-1}$

T_m = 688°K.

T_b = 805°K.

$\Delta H^\circ_f\ _{298.15}$ = -117.4 ± 1.5 kcal. mole^{-1}

ΔH°_m = 2.07 ± 0.06 kcal. mole^{-1}

ΔH°_v = 25.0 ± 2 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from that of the α-$BeCl_2$ plus ΔH°_m plus the difference of $H_{688}-H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the enthalpy of the liquid, relative to α-$BeCl_2$, from 688° to 713°K. The heat capacity was assumed constant above this point and also below the melting point to 460°K. where a glass transition was assumed. Below 416°K. the heat capacity was assumed to be that of β-$BeCl_2$. The entropy was calculated in a manner analagous to the heat of formation.

Melting Data.

See the table for α-$BeCl_2$ (c) for details.

Vaporization Data.

The boiling point and heat of vaporization were obtained from the cross over point of the $BeCl_2$ (l) and (g) tables. The analysis of the liquid vapor pressure data is given on the table for $BeCl_2$ (g).

Beryllium Dichloride ($BeCl_2$)

(Ideal Gas) Mol. Wt. = 79.9182

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.945	-86.383	-86.383	INFINITE
100	8.934	48.490	70.438	-2.195	-86.344	-86.661	189.388
200	11.297	55.536	61.359	-1.165	-86.173	-87.046	95.115
298	12.338	60.260	60.260	.000	-86.100	-87.499	64.135
300	12.353	60.337	60.260	.023	-86.099	-87.507	63.746
400	13.025	63.988	60.754	1.294	-86.097	-87.978	48.067
500	13.493	66.948	61.706	2.621	-86.127	-88.445	38.657
600	13.822	69.439	62.793	3.988	-86.171	-88.905	32.382
700	14.056	71.589	63.899	5.382	-86.227	-89.357	27.897
800	14.225	73.477	64.981	6.797	-86.293	-89.800	24.531
900	14.351	75.160	66.020	8.226	-86.371	-90.233	21.910
1000	14.446	76.677	67.011	9.666	-86.465	-90.658	19.812
1100	14.519	78.058	67.954	11.114	-86.578	-91.072	18.093
1200	14.576	79.324	68.849	12.569	-86.712	-91.476	16.659
1300	14.621	80.492	69.700	14.029	-86.866	-91.866	15.443
1400	14.658	81.577	70.510	15.493	-87.042	-92.244	14.399
1500	14.689	82.589	71.282	16.961	-87.240	-92.609	13.492
1600	14.714	83.538	72.019	18.431	-90.217	-92.881	12.686
1700	14.735	84.431	72.723	19.903	-90.347	-93.043	11.961
1800	14.752	85.274	73.397	21.378	-90.481	-93.199	11.315
1900	14.768	86.072	74.043	22.854	-90.620	-93.345	10.737
2000	14.781	86.829	74.664	24.331	-90.766	-93.484	10.215
2100	14.792	87.551	75.261	25.810	-90.915	-93.618	9.742
2200	14.802	88.239	75.835	27.289	-91.072	-93.742	9.312
2300	14.810	88.897	76.389	28.770	-91.233	-93.857	8.918
2400	14.818	89.528	76.923	30.251	-91.401	-93.969	8.557
2500	14.824	90.133	77.439	31.734	-91.576	-94.074	8.224
2600	14.830	90.714	77.939	33.216	-91.757	-94.167	7.915
2700	14.836	91.274	78.423	34.700	-91.943	-94.257	7.629
2800	14.840	91.814	78.891	36.183	-163.168	-93.232	7.277
2900	14.845	92.335	79.346	37.668	-163.116	-90.735	6.838
3000	14.849	92.838	79.787	39.152	-163.070	-88.241	6.428
3100	14.852	93.325	80.216	40.637	-163.027	-85.750	6.045
3200	14.855	93.797	80.633	42.123	-162.987	-83.256	5.686
3300	14.858	94.254	81.039	43.608	-162.954	-80.764	5.349
3400	14.861	94.697	81.434	45.094	-162.925	-78.271	5.031
3500	14.863	95.128	81.819	46.581	-162.901	-75.786	4.732
3600	14.865	95.547	82.195	48.067	-162.884	-73.294	4.449
3700	14.868	95.954	82.561	49.554	-162.873	-70.806	4.182
3800	14.869	96.351	82.919	51.040	-162.870	-68.322	3.929
3900	14.871	96.737	83.268	52.528	-162.872	-65.829	3.689
4000	14.873	97.114	83.610	54.015	-162.884	-63.344	3.461
4100	14.874	97.481	83.944	55.502	-162.903	-60.858	3.244
4200	14.876	97.839	84.270	56.990	-162.930	-58.367	3.037
4300	14.877	98.189	84.590	58.477	-162.966	-55.874	2.840
4400	14.878	98.531	84.903	59.965	-163.011	-53.381	2.651
4500	14.879	98.866	85.209	61.453	-163.066	-50.895	2.472
4600	14.881	99.193	85.510	62.941	-163.130	-48.402	2.299
4700	14.882	99.513	85.804	64.429	-163.204	-45.906	2.135
4800	14.882	99.826	86.093	65.917	-163.289	-43.409	1.976
4900	14.883	100.133	86.377	67.405	-163.384	-40.908	1.824
5000	14.884	100.434	86.655	68.894	-163.488	-38.408	1.679
5100	14.885	100.728	86.928	70.382	-163.604	-35.900	1.538
5200	14.886	101.017	87.196	71.871	-163.730	-33.397	1.404
5300	14.886	101.301	87.460	73.359	-163.870	-30.893	1.274
5400	14.887	101.579	87.718	74.848	-164.019	-28.382	1.149
5500	14.888	101.852	87.973	76.337	-164.180	-25.866	1.028
5600	14.888	102.121	88.223	77.826	-164.352	-23.356	.911
5700	14.889	102.384	88.469	79.314	-164.537	-20.834	.799
5800	14.889	102.643	88.712	80.803	-164.732	-18.305	.690
5900	14.890	102.898	88.950	82.292	-164.940	-15.788	.585
6000	14.890	103.148	89.184	83.781	-165.159	-13.257	.483

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1961; June 30, 1965

BERYLLIUM DICHLORIDE ($BeCl_2$) (IDEAL GAS) MOL. WT. = 79.9182

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = 60 ± 1 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -86.4 ± 2.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -86.1 ± 2.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[375] (1)
[230] (2)
1113 (1)

Bond Distance: Be-Cl = 1.77Å

Bond Angle: Cl-Be-Cl = 180°

Rotational Constant: B_o = 0.0759 cm.$^{-1}$

σ = 2

Heat of Formation.

The vapor pressure data over the crystal was assumed to be for the β-form. The 2nd and 3rd law analyses of the data are summarized below after conversion to a common process. The data were also analyzed using gaseous free energy functions based on a bending frequency of 170 cm.$^{-1}$ but no significant improvement of the results was noted.

Ref.	Temperature Range °D.	ΔH°_{298} sub β-$BeCl_2$ kcal. mole^{-1} 2nd law	3rd law	Drift in 3rd law cal. mole^{-1} deg.$^{-1}$
1	680 - 740*	33.5 ± 0.6	31.38	-3.4 ± 0.7
2	680 - 740	34.3	31.22	-4.7
1	613 - 663	31.6 ± 1.6	30.91	-1.3 ± 2.6
2	638 - 668	35.6	31.07	-7.0
3	441 - 518	31.4 ± 0.8	32.45	2.5 ± 1.7
3	510 - 600*	31.8 ± 0.3	32.07	0.40± 0.5
4	460 - 504*	32.45± 0.4	32.48	0.14± 0.8

*Points rejected due to failure of a statistical test.

References:

1. O. Rahlfs and W. Fischer, Z. Anorg. Allgem. Chem. 211, 349 (1933).
2. W. Fischer, T. Petzel and S. Lauter, Z. Anorg. Allgem. Chem. 333, 226 (1964).
3. M. A. Greenbaum et al., Rocket Power, Inc., 7th Quarterly Report March 31, 1963 under Contract AF 04(611)-7414.
4. D. L. Hildenbrand, L. P. Theard, E. Murad and F. Ju, Ford Motor Co., Aeronutronic Div., Report U-3068 April 1965 under Contract AF (04) 611-8523.

It is obvious that there is no real agreement between the data sets, and some of this is undoubtedly due to the difficulty of keeping a single crystal form throughout a series of measurements. It is also doubtful that water vapor was adequately excluded in some experiments. We have adopted the only piece of work which shows adequate 2nd and 3rd law agreement, and no third law trend, that is ΔH_{sub} = 32.5 ± 1 kcal. mole^{-1} from ref. 4. It is interesting to note that all the other data can be made much more precise and its drift removed if a constant pressure is added to all points. The addition which varied from 20-30% of the lowest pressure in each data set serves to indicate the magnitude of possible systematic errors.

Heat Capacity and Entropy.

The linear structure of $BeCl_2(g)$ has been confirmed by the electric deflection experiments of A. Büchler, A. D. Little, Inc. Progress Report No. 8, 31st Dec. 1963 under contract No. DA-19-020-ORD-5584. The bond length was obtained from the electron diffraction data of P. A. Akishin, V. P. Spirodinov and G. A. Sobelev, Dokl. Akad, Nauk SSSR 118, 1134 (1958). A Büchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958) have reported the infra-red spectrum and assigned 1113 as the asymmetric stretch ν_3 and 482 as the bending frequency ν_2. However, A. Snelson, IIT Research Institute, Report No. IITRI-C6013-4 May 1964 under Contract No. DA-31-124-ARO(D)-111 using matrix isolation experiments has shown this second band to be due to beryllium chloride solid. The unobserved frequencies were estimated from a valence force field treatment by assuming that the ratio of stretching to bending force constant was 50:1 the same as for $BeF_2(g)$. This gives 230 cm.$^{-1}$ for ν_2 and 375 cm.$^{-1}$ for the symmetric stretch. The principal moment of inertia is 36.884 X 10^{-39} g. cm.^{2}

Beryllium Monofluoride (BeF)

(Ideal Gas) Mol. Wt. = 28.013

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.082	- 50.237	- 50.237	INFINITE
100	6.958	41.515	55.394	- 1.388	- 49.900	- 52.004	113.649
200	6.980	46.341	49.799	- .692	- 49.692	- 54.204	59.228
298	7.140	49.152	49.152	.000	- 49.678	- 56.431	41.363
300	7.144	49.196	49.152	.013	- 49.679	- 56.473	41.138
400	7.431	51.289	49.436	.741	- 49.775	- 58.724	32.084
500	7.726	52.980	49.981	1.500	- 49.924	- 60.946	26.638
600	7.977	54.411	50.603	2.285	- 50.096	- 63.134	22.995
700	8.177	55.657	51.238	3.093	- 50.286	- 65.292	20.384
800	8.333	56.759	51.860	3.919	- 50.488	- 67.423	18.418
900	8.456	57.748	52.460	4.759	- 50.703	- 69.526	16.882
1000	8.554	58.644	53.035	5.609	- 50.935	- 71.606	15.649
1100	8.632	59.463	53.582	6.469	- 51.186	- 73.661	14.634
1200	8.696	60.217	54.104	7.335	- 51.457	- 75.692	13.785
1300	8.749	60.915	54.602	8.208	- 51.748	- 77.700	13.062
1400	8.794	61.566	55.076	9.085	- 52.060	- 79.685	12.439
1500	8.833	62.174	55.529	9.966	- 52.394	- 81.646	11.895
1600	8.866	62.745	55.963	10.851	- 55.506	- 83.507	11.406
1700	8.896	63.283	56.378	11.740	- 55.769	- 85.249	10.959
1800	8.922	63.792	56.775	12.630	- 56.038	- 86.976	10.560
1900	8.945	64.275	57.158	13.524	- 56.309	- 88.687	10.201
2000	8.967	64.735	57.525	14.419	- 56.585	- 90.384	9.876
2100	8.986	65.173	57.879	15.317	- 56.865	- 92.067	9.581
2200	9.004	65.591	58.220	16.217	- 57.150	- 93.737	9.311
2300	9.021	65.992	58.549	17.118	- 57.440	- 95.392	9.064
2400	9.037	66.376	58.867	18.021	- 57.734	- 97.035	8.836
2500	9.052	66.745	59.175	18.925	- 58.034	- 98.668	8.625
2600	9.066	67.101	59.473	19.831	- 58.337	- 100.286	8.429
2700	9.079	67.443	59.762	20.738	- 58.645	- 101.893	8.247
2800	9.092	67.773	60.042	21.647	- 129.987	- 102.383	7.991
2900	9.104	68.093	60.315	22.557	- 130.052	- 101.393	7.641
3000	9.116	68.402	60.579	23.468	- 130.119	- 100.406	7.314
3100	9.127	68.701	60.836	24.380	- 130.187	- 99.417	7.009
3200	9.139	68.991	61.086	25.293	- 130.256	- 98.420	6.721
3300	9.149	69.272	61.330	26.208	- 130.328	- 97.424	6.452
3400	9.160	69.545	61.568	27.123	- 130.403	- 96.426	6.198
3500	9.170	69.811	61.800	28.040	- 130.481	- 95.426	5.958
3600	9.181	70.069	62.026	28.957	- 130.562	- 94.421	5.732
3700	9.191	70.321	62.247	29.876	- 130.647	- 93.418	5.518
3800	9.200	70.566	62.462	30.795	- 130.738	- 92.410	5.315
3900	9.210	70.805	62.673	31.716	- 130.833	- 91.400	5.122
4000	9.220	71.039	62.879	32.637	- 130.933	- 90.388	4.938
4100	9.229	71.267	63.081	33.560	- 131.040	- 89.376	4.764
4200	9.238	71.489	63.279	34.483	- 131.153	- 88.358	4.598
4300	9.247	71.707	63.472	35.407	- 131.273	- 87.334	4.439
4400	9.256	71.919	63.662	36.332	- 131.402	- 86.312	4.287
4500	9.265	72.127	63.848	37.259	- 131.538	- 85.287	4.142
4600	9.274	72.331	64.030	38.186	- 131.684	- 84.258	4.003
4700	9.283	72.531	64.209	39.113	- 131.838	- 83.226	3.870
4800	9.292	72.726	64.384	40.042	- 132.002	- 82.188	3.742
4900	9.301	72.918	64.556	40.972	- 132.175	- 81.148	3.619
5000	9.309	73.106	64.725	41.902	- 132.359	- 80.103	3.501
5100	9.318	73.290	64.891	42.834	- 132.553	- 79.058	3.388
5200	9.326	73.471	65.055	43.766	- 132.758	- 78.009	3.278
5300	9.335	73.649	65.215	44.699	- 132.975	- 76.951	3.173
5400	9.343	73.824	65.373	45.633	- 133.203	- 75.895	3.072
5500	9.352	73.995	65.528	46.568	- 133.442	- 74.832	2.973
5600	9.360	74.164	65.681	47.503	- 133.693	- 73.762	2.879
5700	9.369	74.329	65.831	48.440	- 133.955	- 72.688	2.787
5800	9.377	74.492	65.979	49.377	- 134.228	- 71.608	2.698
5900	9.385	74.653	66.125	50.315	- 134.515	- 70.531	2.613
6000	9.394	74.811	66.268	51.254	- 134.812	- 69.446	2.529

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1963

BERYLLIUM MONOFLUORIDE (BeF) (IDEAL GAS) MOL. WT. = 28.013

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 49.152 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -50.2 ± 2.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -49.7 ± 2.0 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_i
0	2

ω_e = 1265.62 cm.$^{-1}$

$\omega_e x_e$ = 9.12 cm.$^{-1}$

σ = 1

B_e = 1.4877 cm.$^{-1}$

α_e = 0.01685 cm.$^{-1}$

r_e = 1.361 Å

Heat of Formation.

The selected $\Delta H^\circ_{f\ 298.15}$ was calculated from the experimental data of M. A. Greenbaum, R. E. Yates, M. L. Arin, M. Arshadi, J. Weiher, and M. Farber, J. Phys. Chem. 67, 703 (1963). A molecular flow effusion method was employed by Farber, et al., for the reaction: $BeF_2(g) + Be(c, l) = 2BeF(g)$ from 1425°-1675°K. Using the data reported by Farber, et al. partial pressures, and equilibrium constants were calculated and used to obtain a third law heat for this reaction. From this third law heat the selected $\Delta H^\circ_{f\ 298.15}$ was calculated. The following auxiliary data was used: $\Delta H^\circ_{f\ 298.15}$ = -188 ± 3 kcal. mole and free energy functions from the JANAF Table for $BeF_2(g)$, dated June 30, 1963.

The vapor pressure of an equal mixture of Be powder and $BeF_2(c)$ was measured in a graphite cell by a torsion-effusion method over the temperature range 800°-900°K by D. L. Hildenbrand, L. P. Theard, and N. D. Potter, Aeronutronic Technical Report U-1606, March 15, 1962. No vapor pressure increase over pure BeF_2 was detected. Assuming a detection limit of 20% of the BeF_2 vapor pressure they calculated that $D_0^\circ < 6.8$ e.v. for BeF. In a similar manner mass spectrometric and effusion pressure measurements on a BeF_2-Al system by D. L. Hildenbrand, L. P. Theard, and F. Ju, Aeronutronic Technical Report U-1988, Jan. 31, 1963, and D. L. Hildenbrand, Aeronutronic, private communication, April 19, 1963 lead to a $D_0^\circ < 6.7$ e.v. for BeF.

J. L. Margrave and co-workers, University of Wisconsin, private communication, Dec. 13, 1962, have mass spectrometrically measured the species formed when a reducing agent (Al) was added to BaF_2, SrF_2, CaF_2, and MgF_2. The D_0° values found for the species, BaF, SrF, CaF, and MgF, suggested to Margrave that the D_0° of BeF was likely to be in the range 5 ± 1 e.v.

V. M. Tatevskii, L. N. Tunitskii, and M. M. Navikov, Optics and Spectroscopy 5, 521 (1958), measured the emission spectra of BeF. On the basis of their analysis of the vibrational structure they gave a rather high value (8.0 ± 0.5 e.v.) for the D_0° of BeF. In a recent report on the dissociation energy of BeF, D. E. Mann, National Bureau of Standards Preliminary Report No. 7587, July 1, 1962, has analyzed the spectral data in the literature including the Russian work and concludes that a $D_0^\circ \simeq 6.2$ e.v. is probable.

A. G. Gaydon, Imperial College, London, private communication, Sept. 5, 1962, and W. C. Price, Kings College, London, private communication, March 1, 1963, suggested the Russians have chosen the wrong dissociation products. Therefore, the D_0° value they reported was about 2.5 e.v. too high.

Heats of formation and D_0° values for BeF(g) are summarized as follows:

D_0°	$\Delta H^\circ_{f\ 298.15}$	Remarks
5 ± 1 e.v.	-19.2 kcal. mole^{-1}	J. L. Margrave (loc. cit.)
5.5 e.v.	-30.7 kcal. mole^{-1}	A. G. Gaydon (loc. cit.) and W. C. Price) (loc. cit.)
6.2 e.v.	-46.8 kcal. mole^{-1}	D. E. Mann (loc. cit.)
6.3 e.v.	-48.3 ± 2.5 kcal. mole^{-1}	Calculated from the 2nd law ΔH_r of Farber, et al.
6.3 e.v.	-49.7 ± 2.0 kcal. mole^{-1}	The selected value.
$<$6.7 e.v.	$>$-58 kcal. mole^{-1}	Vapor Pressure of a BeF_2-Al system. Hildenbrand, et al.
$<$6.8 e.v.	$>$-60 kcal. mole^{-1}	Vapor pressure of a BeF_2-Be system. Hildenbrand, et al.
8.0 ± 0.5 e.v.	-88.3 kcal. mole^{-1}	V. M. Tatenskii et al., (loc. cit.)

Heat Capacity and Entropy.

The molecular constants used for this table were taken from G. Herzberg, "Molecular Spectra and Structure I. Spectra of Diatomic Molecules," D. van Nostrand Co., Inc., New York, 1950. To facilitate a comparison with Herzberg's constants, the molecular constants reported by Tatenskii, et al., were changed to the equilibrium state. The two sets of constants showed very slight differences.

Beryllium Difluoride (BeF_2)

(Crystal) GFW = 47.009

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.024	-244.846	-244.846	INFINITE
100	5.020	3.526	21.571	-1.805	-245.332	-241.602	528.020
200	9.341	8.430	13.791	-1.072	-245.437	-237.812	259.869
298	12.385	12.752	12.752	.000	-245.400	-234.078	171.584
300	12.435	12.829	12.752	.023	-245.398	-234.008	170.474
400	14.943	16.749	13.270	1.392	-245.238	-230.231	125.792
500	15.320	20.514	14.333	3.090	-244.851	-226.513	99.009
600	16.120	23.378	15.607	4.662	-244.653	-222.864	81.178
700	16.920	25.923	16.903	6.314	-244.424	-219.250	68.453
800	17.720	28.235	18.177	8.046	-244.153	-215.672	58.919
900	18.520	30.368	19.414	9.858	-243.834	-212.130	51.512
1000	19.320	32.361	20.610	11.750	-243.467	-208.627	45.595
1100	20.120	34.240	21.765	13.722	-243.051	-205.163	40.762
1200	20.920	36.025	22.879	15.774	-242.585	-201.739	36.742
1300	21.720	37.731	23.957	17.906	-242.068	-198.355	33.346

Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964; June 30, 1970

BERYLLIUM DIFLUORIDE (BeF_2) (CRYSTAL) GFW = 47.009

ΔHf°_0 = -244.8 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 12.752 ± 0.04 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -245.4 ± 1.0 kcal/mol

Tt = 500°K (low quartz → high quartz)

ΔHt° = 0.0526 kcal/mol

Tm = 825°K

ΔHm° = 1.137 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 55.15 kcal/mol

Heat of Formation

ΔHf° is the value selected by Parker (1), based on a thorough review of data for BeF_2(c, vitreous, aqueous) and BeO(c). Parker's analysis remains essentially unchanged for BeO(c) and BeF_2(c), even though the results for BeF_2(HF, aqueous) become more negative by 0.93 kcal/mol due to JANAF selections for HF(aqueous). Three values derived by Parker for BeF_2(c) from PbF_2(c) are changed due to JANAF auxiliary data; these values become -246.9, -246.0 and -247.2 for the three paths used by Parker.

The adopted ΔHf° was derived by combination of calorimetric data for Be(c) + F_2(g) → BeF_2(vitreous) and BeF_2(c) → BeF_2(vitreous). Churney and Armstrong (2) obtained $\Delta Hf^\circ_{298.15}$ = -244.32 ± 0.8 kcal/mol for vitreous BeF_2 by combustion in fluorine of polytetrafluoroethylene and mixtures of Be(c) with polytetrafluoroethylene. $\Delta Hr^\circ_{298.15}$(c → vitreous) = 1.125 ± 0.016 kcal/mol was measured via solution calorimetry by Taylor and Gardner (3).

Heat Capacity and Entropy

Cp° is based on JANAF curve fits of measurements by adiabatic calorimetry (8-300°K) and by ice calorimetry (354-776°K) as reported by Taylor and Gardner (3). The sample was estimated as approximately 99.5% BeF_2. Analyses indicated that the major impurity was about 0.3% oxygen, mainly in the form of absorbed water. Petrographic examination and X-ray diffraction showed the sample to be composed almost completely of quartz-type crystals. The entropy is derived from the smoothed Cp° based on the extrapolation S°_8 = 0.0065 gibbs/mol. The adopted Cp° above 300°K agrees closely with the relative enthalpy data and shows a remarkable similarity to that of SiO_2 (low quartz, high quartz).

Transition Data

Tt is the value selected by Taylor and Gardner (3) from their relative enthalpy data. ΔHt° is the corresponding difference in relative enthalpy from the JANAF curve fits for the two crystalline forms. Levina (4) studied the polymorphism of BeF_2 by observing the peaks in Cp near the transition temperatures. For low quartz → high quartz, Levina's peak began near 438°K, was complete near 503°K, and gave ΔHt = 0.17 kcal/mol. Levina found a second transition attributed to a form analogous to tridymite; this began above 670°K, was complete by 740°K, and gave ΔHt = 0.24 kcal/mol. There is no evidence for this transition in the relative enthalpy data, so we suspect that its occurrence may be due to impurities in Levina's sample. Levina also found that the cristobalite-like phase transformed in the region 380 to 420°K with ΔHt = 1.27 kcal/mol.

Melting Data

See the table for BeF_2(ℓ).

Heat of Sublimation

See the table for BeF_2(g).

References

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Beryllium Difluoride (BeF_2)

(Liquid) GFW = 47.009

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	11.927	14.321	14.321	.000	- 244.275	- 233.421	171.102
300	11.977	14.395	14.321	.022	- 244.274	- 233.353	169.998
400	14.151	18.159	14.820	1.336	- 244.169	- 229.726	125.516
500	15.669	21.488	15.827	2.830	- 243.986	- 226.135	98.844
600	16.862	24.454	17.022	4.459	- 243.731	- 222.588	81.077
700	17.880	27.131	18.278	6.197	- 243.416	- 219.088	68.402
800	18.797	29.579	19.540	8.032	- 243.042	- 215.638	58.910
900	19.653	31.843	20.783	9.954	- 242.613	- 212.237	51.538
1000	20.469	33.956	21.996	11.961	- 242.131	- 208.888	45.652
1100	21.258	35.944	23.174	14.047	- 241.601	- 205.588	40.847
1200	22.028	37.827	24.317	16.211	- 241.023	- 202.339	36.851
1300	22.785	39.620	25.426	18.452	- 240.397	- 199.140	33.478
1400	23.532	41.336	26.502	20.768	- 239.724	- 195.992	30.596
1500	24.271	42.985	27.546	23.158	- 239.005	- 192.893	28.104
1600	25.005	44.575	28.561	25.622	- 240.995	- 189.766	25.921
1700	25.734	46.113	29.548	28.159	- 240.069	- 186.591	23.988
1800	26.460	47.604	30.510	30.769	- 239.079	- 183.475	22.277
1900	27.183	49.054	31.448	33.451	- 238.024	- 180.414	20.752
2000	27.904	50.467	32.364	36.205	- 236.905	- 177.410	19.386

Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964

BERYLLIUM DIFLUORIDE (BeF_2) (LIQUID) GFW = 47.009

$S^\circ_{298.15}$ = 14.321 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -244.275 ± 1.0 kcal/mol

Tm = 825°K ΔHm° = 1.137 kcal/mol

Tb = 1448.2°K ΔHv° = 47.646 kcal/mol

Heat of Formation

ΔHf° is obtained from that of the crystal by means of ΔHr° = 1.125 ± 0.016 kcal/mol for BeF_2(c) → BeF_2(vitreous) at 298.15°K. Further details are given in the section on Melting Data. ΔHf°(ℓ) actually is based on the direct determination of ΔHf°(vitreous) by Churney and Armstrong (1) as discussed on the crystal table.

Heat Capacity and Entropy

Cp° is based on a JANAF curve fit of relative enthalpies of Taylor and Gardner (2) for the liquid (828-1183°K) and vitreous (320-473°K) forms of BeF_2. The combined data yield a normal Cp° curve and reveal no need for a glass transition. Scatter in the data is somewhat larger than for the crystal, presumably due to minor variations in the vitreous state at the conclusion of each drop. $S^\circ_{298.15}(\ell)$ is calculated from that of the crystal by addition of ΔSm° and the difference for crystal and liquid of $(S^\circ_{825}-S^\circ_{298.15})$.

Melting Data

Tm is the value selected by Taylor and Gardner (2) from their relative enthalpy data. These showed premelting starting near 804°K and complete melting above 828°K. Cooling of the liquid produced the vitreous state. Tm has also been reported as 815 (3), 821 (4), 818 (5) and 816 ± 5°K (6).

Solution calorimetry (2) gave ΔHr° = 1.125 ± 0.016 kcal/mol for BeF_2(low quartz) → BeF_2(vitreous) at 298.15°K. Confirmation of this result came from transposed temperature-drop calorimetry (7) and calorimetric conversion (8). These gave 1.1 ± 0.2 and 1.1 ± 0.5 kcal/mol, respectively. Combination of ΔHr° = 1.125 with JANAF enthalpies yields ΔHm° = 1.137 kcal/mol.

Vaporization Data

Tb is the calculated temperature at which ΔGr° = 0 for BeF_2(ℓ) → BeF_2(g). ΔHv° is the corresponding value of ΔHr°. These calculations neglect the presence of dimer, which is assumed to be negligible based on extrapolation of the equations of Belousov (9). Cantor (10) obtained Tb = 1442°K by extrapolation of his vapor pressures (1146-1372°K).

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Beryllium Difluoride (BeF_2)

(Ideal Gas) GFW = 47.009

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.615	-190.287	-190.287	INFINITE
100	7.661	44.198	63.257	-1.906	-190.283	-190.620	416.600
200	9.774	50.192	55.336	-1.029	-190.244	-190.971	208.684
298	11.081	54.360	54.360	.000	-190.250	-191.333	140.251
300	11.100	54.429	54.360	.021	-190.250	-191.340	139.391
400	11.955	57.747	54.807	1.176	-190.304	-191.696	104.738
500	12.573	60.484	55.676	2.404	-190.387	-192.035	83.938
600	13.038	62.819	56.677	3.685	-190.480	-192.355	70.065
700	13.392	64.857	57.703	5.008	-190.580	-192.660	60.151
800	13.663	66.664	58.712	6.361	-190.688	-192.951	52.712
900	13.873	68.286	59.688	7.738	-190.804	-193.226	46.922
1000	14.036	69.756	60.622	9.134	-190.933	-193.489	42.287
1100	14.166	71.100	61.514	10.544	-191.079	-193.737	38.492
1200	14.269	72.337	62.365	11.966	-191.243	-193.972	35.327
1300	14.353	73.483	63.177	13.398	-191.426	-194.191	32.647
1400	14.422	74.549	63.952	14.837	-191.630	-194.397	30.347
1500	14.479	75.546	64.692	16.282	-191.856	-194.567	28.351
1600	14.527	76.482	65.400	17.732	-194.860	-194.683	26.592
1700	14.567	77.364	66.078	19.187	-195.016	-194.666	25.026
1800	14.602	78.198	66.728	20.645	-195.178	-194.643	23.633
1900	14.631	78.988	67.353	22.107	-195.343	-194.608	22.385
2000	14.656	79.739	67.954	23.571	-195.514	-194.564	21.261
2100	14.678	80.455	68.532	25.038	-195.690	-194.514	20.243
2200	14.698	81.138	69.090	26.507	-195.872	-194.454	19.317
2300	14.715	81.792	69.628	27.978	-196.059	-194.383	18.471
2400	14.729	82.419	70.148	29.450	-196.253	-194.306	17.694
2500	14.743	83.020	70.651	30.923	-196.455	-194.222	16.979
2600	14.755	83.599	71.138	32.398	-196.661	-194.127	16.318
2700	14.765	84.156	71.610	33.874	-196.872	-194.025	15.705
2800	14.775	84.693	72.067	35.351	-268.119	-192.809	15.049
2900	14.783	85.211	72.512	36.829	-268.091	-190.117	14.328
3000	14.791	85.713	72.943	38.308	-268.067	-187.432	13.654
3100	14.798	86.198	73.363	39.787	-268.045	-184.747	13.025
3200	14.804	86.668	73.772	41.267	-268.026	-182.056	12.434
3300	14.810	87.123	74.169	42.748	-268.011	-179.371	11.879
3400	14.815	87.566	74.557	44.229	-268.001	-176.685	11.357
3500	14.820	87.995	74.935	45.711	-267.995	-173.999	10.865
3600	14.825	88.413	75.303	47.194	-267.993	-171.311	10.400
3700	14.829	88.819	75.663	48.676	-267.999	-168.627	9.960
3800	14.833	89.214	76.015	50.159	-268.011	-165.940	9.544
3900	14.836	89.600	76.358	51.643	-268.029	-163.255	9.149
4000	14.840	89.975	76.694	53.127	-268.054	-160.568	8.773
4100	14.843	90.342	77.022	54.611	-268.088	-157.884	8.416
4200	14.846	90.700	77.344	56.095	-268.130	-155.194	8.076
4300	14.848	91.049	77.658	57.580	-268.179	-152.500	7.751
4400	14.851	91.390	77.966	59.065	-268.240	-149.811	7.441
4500	14.853	91.724	78.269	60.550	-268.310	-147.121	7.145
4600	14.855	92.051	78.565	62.035	-268.391	-144.428	6.862
4700	14.857	92.370	78.855	63.521	-268.482	-141.733	6.591
4800	14.859	92.683	79.140	65.007	-268.584	-139.032	6.330
4900	14.861	92.989	79.419	66.493	-268.698	-136.331	6.081
5000	14.863	93.290	79.694	67.979	-268.824	-133.627	5.841
5100	14.864	93.584	79.963	69.465	-268.963	-130.925	5.611
5200	14.866	93.873	80.228	70.952	-269.113	-128.217	5.389
5300	14.867	94.156	80.488	72.438	-269.278	-125.503	5.175
5400	14.868	94.434	80.744	73.925	-269.455	-122.794	4.970
5500	14.870	94.706	80.995	75.412	-269.645	-120.075	4.771
5600	14.871	94.974	81.242	76.899	-269.849	-117.352	4.580
5700	14.872	95.238	81.486	78.386	-270.066	-114.624	4.395
5800	14.873	95.496	81.725	79.873	-270.296	-111.893	4.216
5900	14.874	95.751	81.960	81.361	-270.540	-109.166	4.044
6000	14.875	96.001	82.192	82.848	-270.798	-106.431	3.877

Dec. 31, 1960; Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964; June 30, 1970

BERYLLIUM DIFLUORIDE (BeF_2) (IDEAL GAS) GFW = 47.009

Point Group $D_{\infty h}$

ΔHf°_0 = -190.3 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 54.36 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -190.25 ± 1.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[670] (1)	345 (2)	1530 (1)

Bond Distance: Be-F = 1.40 ± 0.03 Å

Bond Angle: F-Be-F = 180°

σ = 2

Rotational Constant: B_0 = 0.22635 cm^{-1}

Heat of Formation

ΔHf° is calculated from that of the crystal by means of $\Delta Hs^\circ_{298.15}$ = 55.15 ± 0.1 kcal/mol. The selected value of ΔHs° is an average of those obtained by third-law analysis of vapor pressures measured by manometry (3), torsion effusion (4) and entrainment (8-10). Mass-spectrometric data (1, 2) are in reasonable agreement and so is the average of two Knudsen-effusion studies (6, 7). Several techniques (2, 4, 6) were used to show that the amount of dimer in the vapor is negligible up to at least 1000°K. JANAF analyses of the vaporization data are summarized as follows:

Source	Method	Range T, °K	δS* gibbs/mol	$\Delta Hs^\circ_{298.15}$, kcal/mol 2nd Law	3rd Law
(1) Efimenko (1968)	Mass Spectrometry	705-819	---	56.14±0.43	---
(2) Belousov (1967)	Mass Spectrometry	815-977	-1.0	54.51	55.44
(3) Cantor (1965)	Manometry	1146-1372	0.65±0.08	55.96±0.10	55.14
(4) Hildenbrand (1965)	Torsion Effusion				
	Cell 13	891-942	4.2 ±0.4	58.87±0.34	54.98
	Cell 27	872-907	0.9 ±0.3	55.82±0.22	54.98
	Cell 12	821-921	0.8 ±0.3	54.42±0.27	55.12
	Cell 14	840-921	3.4 ±0.3	58.13±0.29	55.13
(5) Blauer (1965)	Torsion Effusion				
	Cells A & B	713-795	6.2 ±0.9	58.07±0.66	53.44
(6) Greenbaum (1963)	Effusion	823-1053	2.4 ±0.6	56.75±0.59	54.50
(7) Khandamirova (1959)	Effusion	846-950	3.4 ±2.4	58.82±2.20	55.75
(6) Greenbaum (1963)	Entrainment	1123-1223	1.5 ±3.0	55.88±3.50	54.17
(8) Ozhigov (1961)	Entrainment	1019-1241	1.4 ±0.8	56.64±0.94	55.04
(9) Sense (1958)	Entrainment	1075-1298	-0.06±0.43	55.11±0.51	55.18
(10) Novoselova (1958)	Entrainment	1095-1376	-2.1 ±0.5	52.64±0.56	55.25

*δS = ΔSr°(2nd law) - ΔSr°(3rd law)

Heat Capacity and Entropy

The bond length and angle are those derived by Akishin et al. (11) from electron-diffraction data for the vapor. Linearity of BeF_2 was confirmed by electric-deflection studies (12) of the vapor and by infrared studies (13) of matrix-isolated BeF_2. Infrared absorptions were found near 330 and 1540 cm^{-1} in neon matrices, leading to gas-phase estimates of 345 and 1555 cm^{-1} (13). The latter absorption was observed (14) at 1520 cm^{-1} in the infrared spectra of the vapor at 1000°C. We adopt a compromise of 1530 cm^{-1} and use this value in the valence-force-field approximation to estimate 670 cm^{-1} for the symmetric stretching mode.

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Lithium Trifluoroberyllate ($LiBeF_3$)

(Crystal) GFW = 72.9464

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	22.140	21.300	21.300	.000	- 390.240	- 372.171	272.808
300	22.200	21.437	21.300	.041	- 390.238	- 372.059	271.045
400	25.200	28.244	22.208	2.414	- 390.080	- 366.019	199.983
500	27.800	34.154	24.019	5.068	- 390.559	- 359.958	157.337
600	30.000	39.426	26.155	7.962	- 390.167	- 353.871	128.897
700	31.640	44.180	28.396	11.049	- 389.629	- 347.863	108.608
800	32.770	48.482	30.642	14.271	- 388.993	- 341.940	93.414
900	33.620	52.392	32.845	17.592	- 388.294	- 336.099	81.616
1000	34.330	55.971	34.981	20.990	- 387.554	- 330.339	72.196
1100	35.000	59.275	37.041	24.457	- 386.776	- 324.654	64.503
1200	35.570	62.345	39.024	27.986	- 385.970	- 319.042	58.106
1300	36.100	65.214	40.929	31.570	- 385.138	- 313.498	52.704
1400	36.550	67.906	42.761	35.203	- 384.287	- 308.020	48.084
1500	37.000	70.443	44.523	38.880	- 383.419	- 302.602	44.089

LITHIUM TRIFLUOROBERYLLATE ($LiBeF_3$) (CRYSTAL) GFW = 72.9464

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = (21.3 ± 2) gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -390.2 ± 0.7 kcal/mol

Tm = 633°K

ΔHm° = Unknown

Heat of Formation.

The $\Delta Hf^\circ_{298.15}$ = -390.2 ± 0.7 kcal/mol was calculated from the $\Delta Hr^\circ_{298.15}$ = -2.24 ± 0.08 kcal/mol of the reaction $LiF(c) + LiBeF_3(c) = Li_2BeF_4(c)$ measured (calorimetrically) by P. Gross, Fulmer Research Institute, Administrative Report No. 4, January 1966.

Heat Capacity and Entropy.

The heat capacity (298 - 1100°K) was estimated from the difference of the Cp° values for $Li_2BeF_4(c)$ and LiF(c). Above 1100°K the values were extrapolated graphically. The entropy was estimated by addition of S°_{298} for $BeF_2(c)$ and LiF(c).

Melting Data.

Tm was obtained from the phase diagram of a mixture of LiF(c) and $BeF_2(c)$ reported by A. L. Mathews and C. F. Baes, Jr., ORNL-TM 1129, May 1965.

Lithium Trifluoroberyllate ($LiBeF_3$)

(Ideal Gas) Mol. Wt. = 72.953 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.978	-210.240	-210.240	INFINITE
100	8.150	52.522	74.324	-2.180	-210.614	-209.573	457.999
200	10.867	58.842	65.106	-1.253	-211.314	-208.269	227.575
298	14.601	63.889	63.889	.000	-212.000	-206.629	151.456
300	14.665	63.979	63.889	.027	-212.012	-206.596	150.498
400	17.636	68.629	64.503	1.651	-212.603	-204.697	111.836
500	19.704	72.801	65.753	3.524	-213.862	-202.585	88.545
600	21.137	76.528	67.244	5.570	-214.319	-200.284	72.950
700	22.148	79.867	68.813	7.737	-214.701	-197.914	61.789
800	22.879	82.874	70.386	9.991	-215.033	-195.495	53.404
900	23.420	85.602	71.927	12.307	-215.339	-193.033	46.873
1000	23.830	88.091	73.421	14.670	-215.633	-190.539	41.640
1100	24.146	90.378	74.860	17.070	-215.924	-188.015	37.353
1200	24.395	92.490	76.243	19.497	-216.219	-185.465	33.776
1300	24.593	94.451	77.569	21.947	-216.522	-182.890	30.745
1400	24.754	96.280	78.841	24.415	-216.835	-180.291	28.143
1500	24.886	97.992	80.061	26.897	-217.163	-177.669	25.885
1600	24.996	99.602	81.232	29.391	-220.261	-174.947	23.895
1700	25.088	101.120	82.358	31.895	-255.554	-170.779	21.954
1800	25.165	102.556	83.441	34.408	-255.619	-165.791	20.129
1900	25.232	103.919	84.483	36.928	-255.685	-160.797	18.495
2000	25.289	105.214	85.487	39.454	-255.755	-155.801	17.024
2100	25.338	106.449	86.456	41.986	-255.831	-150.805	15.694
2200	25.381	107.629	87.392	44.522	-255.912	-145.801	14.483
2300	25.419	108.758	88.297	47.062	-255.998	-140.791	13.378
2400	25.452	109.841	89.172	49.605	-256.092	-135.781	12.364
2500	25.481	110.880	90.020	52.152	-256.195	-130.767	11.431
2600	25.507	111.880	90.841	54.701	-256.304	-125.747	10.570
2700	25.531	112.843	91.638	57.253	-256.421	-120.722	9.771
2800	25.552	113.772	92.412	59.807	-327.575	-114.588	8.944
2900	25.571	114.669	93.165	62.363	-327.460	-106.979	8.062
3000	25.588	115.536	93.896	64.921	-327.352	-99.383	7.240
3100	25.603	116.376	94.608	67.481	-327.250	-91.787	6.471
3200	25.617	117.189	95.301	70.042	-327.156	-84.190	5.750
3300	25.630	117.977	95.976	72.604	-327.072	-76.599	5.073
3400	25.642	118.743	96.634	75.168	-326.998	-69.009	4.436
3500	25.652	119.486	97.277	77.733	-326.934	-61.422	3.835
3600	25.662	120.209	97.904	80.298	-325.882	-53.833	3.268
3700	25.671	120.912	98.516	82.865	-326.843	-46.254	2.732
3800	25.680	121.597	99.114	85.433	-326.818	-38.665	2.224
3900	25.688	122.264	99.700	88.001	-326.808	-31.085	1.742
4000	25.695	122.914	100.272	90.570	-325.813	-23.503	1.284
4100	25.701	123.549	100.832	93.140	-325.836	-15.922	.849
4200	25.708	124.168	101.380	95.710	-326.876	-8.339	.434
4300	25.713	124.773	101.917	98.282	-326.932	-.748	.038
4400	25.719	125.365	102.443	100.853	-327.010	6.837	-.340
4500	25.724	125.943	102.959	103.425	-327.109	14.423	-.700
4600	25.729	126.508	103.465	105.998	-327.229	22.013	-1.046
4700	25.733	127.061	103.961	108.571	-327.371	29.604	-1.377
4800	25.737	127.603	104.448	111.145	-327.537	37.204	-1.694
4900	25.741	128.134	104.926	113.718	-327.730	44.806	-1.998
5000	25.745	128.654	105.395	116.293	-327.946	52.414	-2.291
5100	25.748	129.164	105.856	118.867	-328.192	60.019	-2.572
5200	25.752	129.664	106.310	121.442	-328.465	67.636	-2.843
5300	25.755	130.154	106.755	124.018	-328.768	75.257	-3.103
5400	25.758	130.636	107.193	126.593	-329.102	82.876	-3.354
5500	25.760	131.108	107.623	129.169	-329.468	90.512	-3.596
5600	25.763	131.573	108.047	131.745	-329.868	98.151	-3.830
5700	25.765	132.029	108.463	134.322	-330.301	105.802	-4.056
5800	25.768	132.477	108.874	136.898	-330.769	113.460	-4.275
5900	25.770	132.917	109.277	139.475	-331.275	121.115	-4.486
6000	25.772	133.350	109.675	142.052	-331.818	128.787	-4.691

December 31, 1962

LITHIUM TRIFLUOROBERYLLATE ($LiBeF_3$) (Ideal Gas)

Mol. Wt. = 72.953

$\Delta H_{f\ 298.15}^\circ$ = -212 kcal. mole⁻¹

$S_{298.15}^\circ$ = [64] cal. deg.⁻¹ mole⁻¹

Point Group [C_{3v}]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹	ω, cm.⁻¹
[1530] (1)	[485] (2)
[820] (2)	[800] (3)
[700] (1)	

Bond distance: Be-F = [1.40] Å Li-Be = [1.209] Å

Li-F = [1.85] Å

Bond angle: F-Be-F = [120]° Li-Be-F = [90]°

Moment of inertia: $I_AI_BI_C$ = 2.1604 X 10^{-114} g.³ cm.⁶ σ = [3]

Heat of Formation. $\Delta H_{f\ 298.15}^\circ$ was calculated from $\Delta H_{r\ 900}^\circ$ = 53 kcal. mole for the reaction: $LiF(g) + BeF_2(g) = LiBeF_3(g)$ reported by J. Berkowitz and W. A. Chupka, Ann, N. Y. Acad. Sci., 79, 1073 (1960).

Heat Capacity and Entropy. The molecular structure was assumed to be pyramidal with Li atom at the top and BeF_3 located at the bottom. Beryllium atom was taken at the center of the equilaternal triangle formed by the three F atoms. The Be-F distance was estimated from that of BeF(g). The bond distance of Li-F was taken from R. F. Porter and E. E. Zeller, J. Chem. Phys., 33, 858 (1960). Vibrational frequencies were estimated by comparison with related fluorides.

Dilithium Tetrafluoroberyllate (Li_2BeF_4)

(Crystal) GFW = 98.8838

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	
0							
100							
200							
298	32.290	29.800	29.800	.000	− 539.000	− 514.169	376.896
300	32.300	30.000	29.801	.060	− 538.997	− 514.016	374.460
400	35.960	39.794	31.111	3.473	− 538.805	− 505.713	276.309
500	39.590	48.210	33.707	7.251	− 539.981	− 497.324	217.380
600	43.140	55.742	36.762	11.388	− 539.476	− 488.833	178.057
700	46.680	62.661	39.974	15.881	− 538.657	− 480.454	150.005
800	49.760	69.105	43.217	20.711	− 537.538	− 472.214	129.003
900	52.235	75.113	46.431	25.813	− 536.187	− 464.127	112.705
1000	54.360	80.729	49.583	31.146	− 534.644	− 456.202	99.703
1100	56.063	85.992	52.656	36.669	− 532.945	− 448.439	89.097
1200	57.560	90.935	55.642	42.352	− 531.121	− 440.836	80.287
1300	58.800	95.592	58.538	48.170	− 529.193	− 433.389	72.859
1400	59.940	99.992	61.343	54.108	− 527.175	− 426.095	66.516
1500	60.965	104.163	64.060	60.154	− 525.077	− 418.947	61.041
1600	61.920	108.128	66.692	66.299	− 525.663	− 411.863	56.258
1700	62.810	111.909	69.241	72.536	− 593.409	− 402.166	51.702
1800	63.620	115.523	71.713	78.858	− 590.623	− 390.997	47.474
1900	64.350	118.983	74.110	85.257	− 587.769	− 379.983	43.708
2000	65.000	122.300	76.437	91.726	− 584.858	− 369.120	40.336

June 30, 1966

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (CRYSTAL) GFW = 98.8838

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [29.8 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -539.0 ± 1.3 kcal/mol

Tm = 745°K

ΔHm° = 10.606 kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298.15}$ = -539.0 ± 1.3 kcal/mol was calculated from the $\Delta Hr^\circ_{298.15}$ = -5.05 ± 0.06 kcal/mol of the reaction $2LiF(c) + BeF_2(gl) = Li_2BeF_4(c)$ measured (calorimetrically) by P. Gross, Fulmer Research Institute, R.163/23/May 1966. A value of ΔHr°_{298} = 1.17 kcal/mol was used for $BeF_2(c) \rightarrow BeF_2(gl)$.

Heat Capacity and Entropy.

The heat capacity is based on the enthalpy data (323-723°K) of T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 8186, January, 1964. The entropy was estimated by addition of values for the component fluorides.

Melting Data.

Tm and ΔHm° were obtained from Douglas et al., loc. cit., who measured the high temperature enthalpies.

Dilithium Tetrafluoroberyllate (Li_2BeF_4)

(Liquid) GFW = 98.8838

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	32.290	39.304	39.304	.000	− 531.217	− 509.220	373.268
300	32.300	39.504	39.305	.060	− 531.214	− 509.084	370.868
400	35.960	49.298	40.615	3.473	− 531.022	− 501.732	274.134
500	55.500	57.713	43.211	7.251	− 532.198	− 494.293	216.055
600	55.500	67.832	46.497	12.801	− 530.280	− 486.891	177.350
700	55.500	76.387	50.171	18.351	− 528.404	− 479.810	149.803
800	55.500	83.798	53.922	23.901	− 526.565	− 472.996	129.216
900	55.500	90.335	57.612	29.451	− 524.766	− 466.407	113.259
1000	55.500	96.182	61.182	35.001	− 523.006	− 460.017	100.537
1100	55.500	101.472	64.608	40.551	− 521.280	− 453.802	90.162
1200	55.500	106.301	67.884	46.101	− 519.589	− 447.743	81.545
1300	55.500	110.744	71.012	51.651	− 517.929	− 441.823	74.277
1400	55.500	114.857	73.999	57.201	− 516.299	− 436.030	68.067
1500	55.500	118.686	76.852	62.751	− 514.697	− 430.352	62.702
1600	55.500	122.268	79.580	68.301	− 515.878	− 424.702	58.012
1700	55.500	125.632	82.191	73.851	− 584.311	− 416.397	53.531
1800	55.500	128.804	84.693	79.401	− 582.297	− 406.578	49.365
1900	55.500	131.805	87.094	84.951	− 580.292	− 396.868	45.650
2000	55.500	134.652	89.402	90.501	− 578.300	− 387.266	42.318

June 30, 1966

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (LIQUID) GFW = 98.8838

$S^\circ_{298.15}$ = [39.3 ± 2] gibbs/mol

Tm = 745°K

$\Delta Hf^\circ_{298.15}$ = -531.2 ± 1.3 kcal/mol

ΔHm° = 10.606 kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298.15}$ was obtained from $\Delta Hf^\circ_{298.15}$(c) by adding ΔHm° and the difference between $H^\circ_{Tm}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 500°K. The heat capacity below 500°K was obtained from the heat capacity of the crystal. Above 500°K the heat capacity was assumed constant at 55.5 gibbs/mol calculated from the liquid enthalpy equation given by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report No. 8186, Washington, 1964. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See Li_2BeF_4(c) table.

Beryllium Monohydride (BeH)

(Ideal Gas) Mol. Wt. = 10.021

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.066	76.181	76.181	INFINITE
100	6.962	34.625	48.434	- 1.381	76.478	74.247	- 162.260
200	6.967	39.452	42.874	- .684	76.735	71.898	- 78.563
298	6.985	42.236	42.236	.000	76.768	69.507	- 50.948
300	6.986	42.279	42.236	.013	76.767	69.462	- 50.601
400	7.060	44.298	42.511	.715	76.683	67.038	- 36.626
500	7.205	45.887	43.033	1.427	76.542	64.642	- 28.254
600	7.393	47.217	43.622	2.157	76.380	62.277	- 22.683
700	7.593	48.372	44.220	2.906	76.206	59.940	- 18.713
800	7.785	49.398	44.804	3.675	76.027	57.628	- 15.743
900	7.958	50.326	45.367	4.463	75.842	55.340	- 13.438
1000	8.111	51.172	45.906	5.266	75.646	53.072	- 11.598
1100	8.245	51.952	46.421	6.084	75.437	50.825	- 10.098
1200	8.361	52.674	46.912	6.915	75.212	48.597	- 8.850
1300	8.462	53.347	47.381	7.756	74.969	46.389	- 7.798
1400	8.550	53.978	47.830	8.607	74.707	44.200	- 6.900
1500	8.628	54.570	48.260	9.466	74.423	42.031	- 6.124
1600	8.697	55.130	48.672	10.332	71.361	39.959	- 5.458
1700	8.758	55.659	49.068	11.205	71.147	38.004	- 4.885
1800	8.813	56.161	49.448	12.083	70.929	36.060	- 4.378
1900	8.862	56.639	49.814	12.967	70.707	34.129	- 3.926
2000	8.908	57.094	50.167	13.856	70.480	32.209	- 3.520
2100	8.949	57.530	50.507	14.749	70.248	30.302	- 3.153
2200	8.988	57.947	50.836	15.645	70.011	28.405	- 2.822
2300	9.023	58.348	51.154	16.546	69.769	26.521	- 2.520
2400	9.057	58.732	51.461	17.450	69.521	24.647	- 2.244
2500	9.088	59.103	51.760	18.357	69.267	22.779	- 1.991
2600	9.118	59.460	52.049	19.267	69.009	20.927	- 1.759
2700	9.146	59.804	52.330	20.181	68.747	19.083	- 1.545
2800	9.172	60.137	52.603	21.097	- 2.550	18.355	- 1.433
2900	9.198	60.460	52.868	22.015	- 2.571	19.105	- 1.440
3000	9.222	60.772	53.127	22.936	- 2.594	19.851	- 1.446
3100	9.246	61.075	53.378	23.860	- 2.618	20.596	- 1.452
3200	9.269	61.369	53.623	24.785	- 2.643	21.349	- 1.458
3300	9.291	61.654	53.862	25.713	- 2.671	22.100	- 1.464
3400	9.312	61.932	54.096	26.643	- 2.703	22.849	- 1.469
3500	9.333	62.202	54.323	27.576	- 2.737	23.600	- 1.474
3600	9.354	62.465	54.546	28.510	- 2.775	24.355	- 1.478
3700	9.374	62.722	54.763	29.446	- 2.818	25.108	- 1.483
3800	9.393	62.972	54.976	30.385	- 2.866	25.864	- 1.487
3900	9.412	63.216	55.184	31.325	- 2.918	26.623	- 1.492
4000	9.431	63.455	55.388	32.267	- 2.977	27.379	- 1.496
4100	9.450	63.688	55.588	33.211	- 3.042	28.136	- 1.500
4200	9.468	63.916	55.783	34.157	- 3.114	28.899	- 1.504
4300	9.486	64.139	55.975	35.105	- 3.193	29.664	- 1.508
4400	9.504	64.357	56.163	36.054	- 3.280	30.428	- 1.511
4500	9.521	64.571	56.348	37.006	- 3.375	31.194	- 1.515
4600	9.539	64.780	56.529	37.959	- 3.480	31.963	- 1.519
4700	9.556	64.986	56.706	38.913	- 3.593	32.734	- 1.522
4800	9.573	65.187	56.881	39.870	- 3.716	33.509	- 1.526
4900	9.590	65.385	57.052	40.828	- 3.849	34.287	- 1.529
5000	9.606	65.579	57.221	41.788	- 3.991	35.068	- 1.533
5100	9.623	65.769	57.387	42.749	- 4.145	35.851	- 1.536
5200	9.639	65.956	57.550	43.712	- 4.309	36.633	- 1.540
5300	9.656	66.140	57.710	44.677	- 4.486	37.425	- 1.543
5400	9.672	66.320	57.868	45.643	- 4.672	38.215	- 1.547
5500	9.688	66.498	58.023	46.611	- 4.871	39.011	- 1.550
5600	9.704	66.673	58.176	47.581	- 5.081	39.811	- 1.554
5700	9.720	66.845	58.327	48.552	- 5.301	40.617	- 1.557
5800	9.736	67.014	58.475	49.525	- 5.535	41.426	- 1.561
5900	9.752	67.180	58.621	50.499	- 5.780	42.235	- 1.564
6000	9.767	67.344	58.765	51.475	- 6.036	43.048	- 1.568

Dec. 31, 1960; Mar. 31, 1963

BERYLLIUM MONOHYDRIDE (BeH) (IDEAL GAS) MOL. WT. = 10.021

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 42.236 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 76 ± 7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 77 ± 7 kcal. mole^{-1}

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_i
0	2

ω_e = 2058.6 cm.$^{-1}$

$\omega_e x_e$ = 35.5 cm.$^{-1}$

σ = 1

B_e = 10.308 cm.$^{-1}$

α_e = 0.300 cm.$^{-1}$

r_e = 1.3431 Å

Heat of Formation.

Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1953, selected a value of 2.3 ± 0.3 e.v. (53 ± 7 kcal. mole^{-1}) for D_0. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950, estimated D_0 as being 2.2 e.v. (50.7 kcal. mole^{-1}). Gaydon's value was used in this table.

Heat Capacity and Entropy.

Molecular constants were found in Herzberg, op. cit.

Beryllium Monohydride Unipositive Ion (BeH^+)
(Ideal Gas) GFW = 10.01962

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.977	40.760	40.760	.000	276.400	268.092	- 196.517
300	6.978	40.803	40.760	.013	276.408	268.041	- 195.267
400	7.030	42.816	41.034	.713	276.819	265.187	- 144.892
500	7.144	44.396	41.554	1.421	277.171	262.238	- 114.624
600	7.307	45.713	42.141	2.143	277.498	259.220	- 94.421
700	7.490	46.853	42.734	2.883	277.811	256.148	- 79.973
800	7.673	47.865	43.313	3.641	278.118	253.032	- 69.125
900	7.845	48.779	43.871	4.417	278.418	249.879	- 60.679
1000	8.000	49.613	44.404	5.210	278.709	246.693	- 53.915
1100	8.137	50.382	44.913	6.017	278.986	243.479	- 48.375
1200	8.258	51.096	45.399	6.836	279.246	240.239	- 43.753
1300	8.364	51.761	45.863	7.668	279.490	236.977	- 39.839
1400	8.457	52.384	46.306	8.509	279.715	233.699	- 36.482
1500	8.539	52.971	46.731	9.359	279.919	230.404	- 33.570
1600	8.612	53.524	47.139	10.216	277.345	227.175	- 31.031
1700	8.677	54.048	47.530	11.081	277.620	224.032	- 28.801
1800	8.735	54.546	47.906	11.951	277.890	220.870	- 26.817
1900	8.788	55.019	48.268	12.828	278.158	217.698	- 25.041
2000	8.836	55.471	48.617	13.709	278.420	214.508	- 23.440
2100	8.880	55.904	48.954	14.595	278.678	211.304	- 21.991
2200	8.921	56.318	49.279	15.485	278.931	208.090	- 20.672
2300	8.960	56.715	49.594	16.379	279.179	204.866	- 19.467
2400	8.996	57.097	49.899	17.277	279.422	201.632	- 18.361
2500	9.031	57.465	50.194	18.178	279.659	198.383	- 17.343
2600	9.065	57.820	50.480	19.083	279.893	195.129	- 16.402
2700	9.099	58.163	50.759	19.991	280.123	191.865	- 15.530
2800	9.131	58.494	51.029	20.903	209.318	189.700	- 14.807
2900	9.164	58.815	51.292	21.818	209.790	188.994	- 14.243
3000	9.198	59.127	51.548	22.736	210.261	188.263	- 13.715
3100	9.232	59.429	51.797	23.657	210.732	187.519	- 13.220
3200	9.267	59.722	52.041	24.582	211.203	186.771	- 12.756
3300	9.303	60.008	52.278	25.511	211.672	186.000	- 12.318
3400	9.340	60.286	52.509	26.443	212.139	185.214	- 11.905
3500	9.379	60.558	52.735	27.379	212.605	184.413	- 11.515
3600	9.419	60.822	52.956	28.319	213.070	183.605	- 11.146
3700	9.461	61.081	53.172	29.263	213.531	182.775	- 10.796
3800	9.505	61.334	53.384	30.211	213.990	181.939	- 10.464
3900	9.550	61.581	53.591	31.164	214.447	181.094	- 10.148
4000	9.597	61.824	53.794	32.121	214.899	180.227	- 9.847
4100	9.646	62.061	53.992	33.083	215.349	179.354	- 9.560
4200	9.696	62.294	54.187	34.050	215.796	178.475	- 9.287
4300	9.748	62.523	54.379	35.022	216.239	177.582	- 9.026
4400	9.801	62.748	54.566	36.000	216.677	176.676	- 8.776
4500	9.856	62.969	54.750	36.982	217.108	175.758	- 8.536
4600	9.912	63.186	54.931	37.971	217.536	174.837	- 8.307
4700	9.969	63.400	55.109	38.965	217.959	173.902	- 8.086
4800	10.027	63.610	55.284	39.965	218.377	172.961	- 7.875
4900	10.087	63.818	55.456	40.970	218.789	172.011	- 7.672
5000	10.147	64.022	55.626	41.982	219.194	171.057	- 7.477
5100	10.208	64.224	55.792	43.000	219.593	170.085	- 7.289
5200	10.269	64.422	55.956	44.024	219.987	169.113	- 7.108
5300	10.331	64.619	56.118	45.054	220.373	168.128	- 6.933
5400	10.393	64.812	56.277	46.090	220.753	167.139	- 6.764
5500	10.455	65.004	56.434	47.132	221.126	166.140	- 6.602
5600	10.517	65.192	56.589	48.181	221.491	165.138	- 6.445
5700	10.579	65.379	56.741	49.236	221.851	164.136	- 6.293
5800	10.641	65.564	56.892	50.297	222.203	163.116	- 6.146
5900	10.702	65.746	57.040	51.364	222.548	162.093	- 6.004
6000	10.763	65.926	57.187	52.437	222.886	161.068	- 5.867

Sept. 30, 1966

BERYLLIUM MONOHYDRIDE UNIPOSITIVE ION (BeH^+) (IDEAL GAS)

GFW = 10.01962

Ground State Configuration $^1\Sigma$

$S°_{298.15}$ = 40.76 gibbs/mol

$\Delta Hf°_0$ = 274.3 ± 10 kcal/mol

$\Delta Hf°_{298.15}$ = 276.4 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1
0	1
[20000]	[3]

ω_e = 2221.7 cm^{-1}

B_e = 10.7996 cm^{-1}

$\omega_e x_e$ = 39.79 cm^{-1}

α_e = 0.2935 cm^{-1}

σ = 1

r_e = 1.31216 Å

Heat of Formation.

The heat of formation was calculated from the equation $BeH(g) \rightarrow BeH^+(g) + e^-$ with the JANAF auxiliary data for BeH(g), using an ionization potential = 8.6 ± 0.4 eV (198.34 ± 9.23 kcal/mol) obtained from C. W. Beckett, NBS Report 8628, Jan. 1, 1965.

The dissociation energy, D_0 (Be^+-H) = 3.2 ± 0.2 eV (73.8 kcal/mol), has been reported by A. G. Gaydon, "Dissociation Energies," 2nd Ed., Chapman and Hall Ltd., London, 1953. This yields $\Delta Hf°_0$ (BeH^+, g) = 270.0 kcal/mol, which is in agreement with the value adopted.

Heat Capacity and Entropy.

The molecular constants were obtained from the ultraviolet spectroscopic studies by W. W. Watson and R. F. Humphreys, Phys. Rev. 52, 318 (1937).

The ground state configuration was given by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, New York, 1950. The estimated electronic level and quantum weight were obtained by assuming that a $^3\Sigma$ level lies below the first observed excited state ($^1\Sigma$) at 40,000 cm^{-1}.

Beryllium Monohydroxide (BeOH)

(Ideal Gas) Mol. Wt. = 26.021

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.383	-24.866	-24.866	INFINITE
100	7.949	44.549	60.436	-1.589	-24.817	-25.964	56.741
200	7.980	50.062	54.028	-.793	-24.801	-27.136	29.652
298	8.229	53.285	53.285	.000	-25.000	-28.250	20.707
300	8.236	53.336	53.286	.015	-25.005	-28.270	20.594
400	8.722	55.769	53.614	.862	-25.300	-29.315	16.016
500	9.263	57.774	54.251	1.761	-25.619	-30.282	13.236
600	9.760	59.507	54.986	2.713	-25.937	-31.185	11.359
700	10.192	61.045	55.743	3.711	-26.251	-32.034	10.001
800	10.565	62.431	56.494	4.749	-26.560	-32.840	8.971
900	10.891	63.695	57.225	5.823	-26.866	-33.606	8.160
1000	11.179	64.857	57.931	6.926	-27.175	-34.338	7.504
1100	11.434	65.935	58.610	8.057	-27.491	-35.039	6.961
1200	11.662	66.940	59.263	9.212	-27.816	-35.712	6.504
1300	11.865	67.881	59.890	10.389	-28.152	-36.356	6.112
1400	12.046	68.768	60.493	11.585	-28.501	-36.974	5.772
1500	12.208	69.604	61.073	12.797	-28.867	-37.567	5.473
1600	12.352	70.397	61.631	14.026	-32.005	-38.057	5.198
1700	12.480	71.150	62.169	15.267	-32.291	-38.425	4.940
1800	12.596	71.866	62.688	16.521	-32.578	-38.778	4.708
1900	12.699	72.550	63.189	17.786	-32.867	-39.115	4.499
2000	12.791	73.204	63.674	19.061	-33.157	-39.437	4.309
2100	12.875	73.830	64.142	20.344	-33.452	-39.743	4.136
2200	12.950	74.431	64.596	21.635	-33.750	-40.036	3.977
2300	13.017	75.008	65.037	22.934	-34.052	-40.314	3.830
2400	13.078	75.563	65.464	24.238	-34.360	-40.577	3.695
2500	13.134	76.098	65.878	25.549	-34.675	-40.834	3.570
2600	13.184	76.614	66.282	26.865	-34.993	-41.071	3.452
2700	13.230	77.113	66.674	28.186	-35.317	-41.299	3.343
2800	13.272	77.595	67.055	29.511	-106.677	-40.408	3.154
2900	13.310	78.061	67.427	30.840	-106.760	-38.036	2.865
3000	13.345	78.513	67.789	32.173	-106.848	-35.667	2.598
3100	13.378	78.951	68.142	33.509	-106.937	-33.295	2.347
3200	13.407	79.376	68.486	34.848	-107.030	-30.916	2.111
3300	13.434	79.789	68.822	36.190	-107.128	-28.535	1.890
3400	13.460	80.191	69.151	37.535	-107.230	-26.154	1.681
3500	13.483	80.581	69.472	38.882	-107.336	-23.769	1.484
3600	13.505	80.961	69.786	40.232	-107.448	-21.377	1.298
3700	13.525	81.332	70.093	41.583	-107.567	-18.986	1.121
3800	13.543	81.692	70.393	42.937	-107.692	-16.589	.954
3900	13.561	82.044	70.688	44.292	-107.824	-14.189	.795
4000	13.577	82.388	70.976	45.649	-107.964	-11.788	.644
4100	13.592	82.723	71.258	47.007	-108.112	-9.384	.500
4200	13.606	83.051	71.535	48.367	-108.269	-6.973	.363
4300	13.619	83.371	71.807	49.728	-108.434	-4.556	.232
4400	13.632	83.685	72.073	51.091	-108.609	-2.141	.106
4500	13.643	83.991	72.335	52.455	-108.795	.280	-.014
4600	13.654	84.291	72.591	53.819	-108.991	2.708	-.129
4700	13.665	84.585	72.843	55.185	-109.198	5.137	-.239
4800	13.674	84.873	73.091	56.552	-109.416	7.573	-.345
4900	13.683	85.155	73.334	57.920	-109.645	10.011	-.447
5000	13.692	85.431	73.573	59.289	-109.886	12.457	-.544
5100	13.700	85.703	73.809	60.659	-110.141	14.909	-.639
5200	13.708	85.969	74.040	62.029	-110.406	17.357	-.729
5300	13.715	86.230	74.267	63.400	-110.686	19.823	-.817
5400	13.722	86.486	74.491	64.772	-110.977	22.283	-.902
5500	13.729	86.738	74.712	66.145	-111.282	24.755	-.984
5600	13.735	86.986	74.929	67.518	-111.600	27.229	-1.063
5700	13.741	87.229	75.142	68.892	-111.930	29.714	-1.139
5800	13.746	87.468	75.353	70.266	-112.275	32.205	-1.213
5900	13.752	87.703	75.560	71.641	-112.632	34.696	-1.285
6000	13.757	87.934	75.765	73.016	-113.002	37.194	-1.355

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM MONOHYDROXIDE (BeOH) (IDEAL GAS) MOL. WT. = 26.021

Point Group [C_s]

$S^\circ_{298.15}$ = [53.28] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = -25 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -25 ± 10 kcal. mole^{-1}

Vibrational Frequencies and Multiplicities

ω, cm.$^{-1}$
[1500] (1)
[1200] (1)
[3600] (1)

Bond Distance: Be-O = [1.4] Å O-H = [0.96] Å

Bond Angle: Be-O-H = [120°] σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [0.447] X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

D. L. Hildenbrand, L. P. Theard, and F. Ju, Ford Motor Co., Aeronutronic Division, Third Quarterly Report, U-2231, April-June, 1963, studied the equilibrium $Be_2O(g) + H_2O(g) \rightarrow 2BeOH(g)$ in a mass spectrometer. Using the JANAF values for the free energy functions and heats of formation yielded $\Delta H^\circ_{f\ 298}$ BeOH(g) = -24.8 ± 10 kcal. mole^{-1}, which was rounded to -25 ± 10 kcal. mole^{-1}. This value is a minimum one, that is, it is the most negative possible value.

Heat Capacity and Entropy.

The molecule was assumed to be nonlinear, the OH stretch was estimated as 3600 cm.$^{-1}$, the Be-O stretch as 1500 cm.$^{-1}$, from BeO(g), and the bending frequency as 1200 cm.$^{-1}$ The Be-O bond length was taken as a little larger than in BeO(g) while the O-H bond length is that in $H_2O(g)$. The bond angle was taken arbitrarily to be 120° and changes in this will have negligible effect on the functions unless it goes to 180°. The molecule contains one free electron and so was assumed to have a statistical weight of 2.

Beryllium Monohydroxide Unipositive Ion ($BeOH^+$)

(Ideal Gas) GFW = 26.01902

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.663	47.983	47.983	.000	194.000	190.844	-139.893
300	7.679	48.030	47.983	.014	194.003	190.824	-139.015
400	8.605	50.364	48.295	.828	194.172	189.739	-103.669
500	9.488	52.382	48.915	1.733	194.356	188.611	-82.442
600	10.217	54.178	49.645	2.720	194.570	187.442	-68.276
700	10.804	55.799	50.410	3.772	194.806	186.235	-58.145
800	11.283	57.274	51.177	4.877	195.061	184.993	-50.538
900	11.682	58.626	51.931	6.026	195.327	183.719	-44.613
1000	12.023	59.875	52.664	7.212	195.597	182.415	-39.867
1100	12.317	61.035	53.373	8.429	195.865	181.085	-35.978
1200	12.572	62.118	54.057	9.674	196.127	179.730	-32.733
1300	12.796	63.134	54.716	10.942	196.379	178.352	-29.984
1400	12.993	64.089	55.352	12.232	196.621	176.956	-27.624
1500	13.166	64.992	55.965	13.540	196.847	175.543	-25.577
1600	13.320	65.846	56.556	14.865	194.302	174.194	-23.794
1700	13.455	66.658	57.127	16.204	194.611	172.929	-22.231
1800	13.576	67.431	57.678	17.555	194.917	171.643	-20.840
1900	13.683	68.168	58.211	18.918	195.224	170.343	-19.594
2000	13.779	68.872	58.726	20.291	195.528	169.025	-18.470
2100	13.864	69.546	59.225	21.674	195.830	167.692	-17.452
2200	13.941	70.193	59.709	23.064	196.127	166.345	-16.525
2300	14.010	70.814	60.179	24.462	196.421	164.985	-15.677
2400	14.072	71.412	60.634	25.866	196.709	163.615	-14.899
2500	14.129	71.988	61.077	27.276	196.991	162.226	-14.182
2600	14.180	72.543	61.507	28.691	197.269	160.833	-13.519
2700	14.226	73.079	61.926	30.112	197.542	159.427	-12.905
2800	14.268	73.597	62.334	31.536	126.779	159.117	-12.420
2900	14.307	74.098	62.731	32.965	127.291	160.266	-12.078
3000	14.342	74.584	63.118	34.398	127.800	161.391	-11.757
3100	14.374	75.055	63.495	35.834	128.307	162.500	-11.456
3200	14.404	75.512	63.864	37.272	128.811	163.600	-11.173
3300	14.432	75.955	64.224	38.714	129.310	164.679	-10.906
3400	14.457	76.386	64.575	40.159	129.804	165.742	-10.654
3500	14.480	76.806	64.918	41.606	130.294	166.791	-10.415
3600	14.502	77.214	65.254	43.055	130.779	167.830	-10.189
3700	14.522	77.612	65.583	44.506	131.256	168.848	-9.973
3800	14.540	77.999	65.905	45.959	131.728	169.861	-9.769
3900	14.557	78.377	66.220	47.414	132.193	170.859	-9.575
4000	14.574	78.746	66.528	48.870	132.648	171.841	-9.389
4100	14.589	79.106	66.831	50.328	133.097	172.812	-9.212
4200	14.603	79.458	67.127	51.788	133.538	173.780	-9.043
4300	14.616	79.801	67.418	53.249	133.969	174.736	-8.881
4400	14.628	80.137	67.703	54.711	134.390	175.678	-8.726
4500	14.640	80.466	67.983	56.175	134.800	176.608	-8.577
4600	14.651	80.788	68.258	57.639	135.201	177.536	-8.435
4700	14.661	81.103	68.528	59.105	135.590	178.450	-8.298
4800	14.670	81.412	68.793	60.571	135.969	179.358	-8.166
4900	14.679	81.715	69.054	62.039	136.336	180.259	-8.040
5000	14.688	82.011	69.310	63.507	136.691	181.154	-7.918
5100	14.696	82.302	69.562	64.976	137.033	182.039	-7.801
5200	14.704	82.588	69.810	66.446	137.364	182.914	-7.688
5300	14.711	82.868	70.053	67.917	137.681	183.792	-7.579
5400	14.718	83.143	70.293	69.388	137.986	184.653	-7.473
5500	14.724	83.413	70.529	70.861	138.278	185.517	-7.372
5600	14.730	83.678	70.762	72.333	138.555	186.368	-7.273
5700	14.736	83.939	70.991	73.807	138.822	187.228	-7.179
5800	14.742	84.196	71.216	75.280	139.074	188.075	-7.087
5900	14.747	84.448	71.438	76.755	139.313	188.914	-6.998
6000	14.752	84.696	71.657	78.230	139.539	189.754	-6.912

June 30, 1968

BERYLLIUM MONOHYDROXIDE UNIPOSITIVE ION ($BeOH^+$) (IDEAL GAS) GFW = 26.01902

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [48.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [194 ± 30] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [194 ± 30] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1300] (1)
[1100] (2)
[3500] (1)

Bond Distance: Be-O = [1.4] Å O-H = [0.96] Å

Bond Angle: Be-O-H = [180°]

Rotational Constant: B_0 = [1.2602] cm^{-1}

σ = 1

Heat of Formation

The ionization potential (IP) of BeOH(g) is estimated as 9.5 ± 1 eV by comparison with the values IP(BeF, g) = 9.1 ± 0.5, IP(MgF, g) = 7.8 ± 0.3 (1) and IP(MgOH, g) = 8.5 eV. (JANAF value). Based on IP(BeOH, g) = 9.5 eV or 219 kcal/mol and ΔHf°_0(BeOH, g) = -25 ± 10 kcal/mol, we derive the heat of formation at 298°K for $BeOH^+$(g) as 194 ± 30 kcal/mol, which is tentatively adopted.

Heat Capacity and Entropy

The $BeOH^+$(g) molecule has eight valence electrons. Based on the criterion given by Walsh (2) that ABH molecules (H = hydrogen atom) containing ten or less valence electrons will be linear in their ground state, we assume that the structure of $BeOH^+$(g) is linear. The vibrational frequencies are estimated by comparison with those for BeOH(g) and LiOH(g). The Be-O and O-H bond distances are assumed to be the same as those in BeOH and H_2O molecules, respectively. The ground state quantum weight of $BeOH^+$(g) is assumed to be the same as that of the isoelectronic molecule LiOH(g). The moment of inertia is 2.221×10^{-39} g cm^2. The enthalpy at 0°K is -2.11 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

Beryllium Dihydride (BeH_2)

(Ideal Gas) Mol. Wt. = 11.029

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.083	30.409	30.409	INFINITE
100	6.956	33.700	47.616	-1.392	30.331	29.413	-64.279
200	6.980	38.524	42.002	-.696	30.286	28.488	-31.128
298	7.259	41.350	41.350	.000	30.000	27.656	-20.271
300	7.268	41.395	41.350	.013	29.993	27.641	-20.136
400	7.943	43.571	41.642	.771	29.618	26.914	-14.704
500	8.805	45.435	42.218	1.608	29.253	26.279	-11.486
600	9.667	47.117	42.897	2.532	28.934	25.715	-9.366
700	10.439	48.667	43.612	3.539	28.668	25.201	-7.868
800	11.098	50.105	44.335	4.616	28.444	24.721	-6.753
900	11.648	51.445	45.051	5.755	28.254	24.268	-5.893
1000	12.102	52.696	45.754	6.943	28.083	23.834	-5.209
1100	12.477	53.868	46.439	8.172	27.921	23.418	-4.652
1200	12.788	54.967	47.104	9.436	27.763	23.015	-4.191
1300	13.047	56.002	47.749	10.728	27.599	22.626	-3.804
1400	13.264	56.977	48.374	12.044	27.425	22.250	-3.473
1500	13.447	57.898	48.978	13.380	27.236	21.888	-3.189
1600	13.603	58.771	49.563	14.733	24.244	21.615	-2.952
1700	13.735	59.600	50.129	16.100	24.074	21.458	-2.758
1800	13.849	60.388	50.678	17.479	23.906	21.306	-2.587
1900	13.948	61.140	51.209	18.869	23.740	21.168	-2.435
2000	14.034	61.858	51.723	20.268	23.574	21.037	-2.299
2100	14.109	62.544	52.222	21.676	23.408	20.913	-2.176
2200	14.175	63.202	52.707	23.090	23.240	20.798	-2.066
2300	14.233	63.833	53.177	24.510	23.071	20.692	-1.966
2400	14.285	64.440	53.634	25.936	22.900	20.593	-1.875
2500	14.331	65.024	54.078	27.367	22.726	20.498	-1.792
2600	14.372	65.587	54.509	28.802	22.551	20.413	-1.716
2700	14.409	66.130	54.930	30.241	22.373	20.334	-1.646
2800	14.442	66.655	55.339	31.684	-48.123	21.535	-1.681
2900	14.472	67.162	55.738	33.130	-48.055	24.023	-1.810
3000	14.500	67.653	56.127	34.578	-47.992	26.506	-1.931
3100	14.524	68.129	56.507	36.030	-47.931	28.988	-2.044
3200	14.547	68.591	56.877	37.483	-47.877	31.468	-2.149
3300	14.568	69.039	57.239	38.939	-47.827	33.948	-2.248
3400	14.587	69.474	57.593	40.397	-47.781	36.423	-2.341
3500	14.604	69.897	57.938	41.856	-47.744	38.902	-2.429
3600	14.620	70.309	58.276	43.317	-47.712	41.375	-2.512
3700	14.635	70.709	58.607	44.780	-47.688	43.852	-2.590
3800	14.649	71.100	58.930	46.244	-47.670	46.328	-2.664
3900	14.661	71.481	59.247	47.710	-47.662	48.798	-2.734
4000	14.673	71.852	59.558	49.177	-47.661	51.275	-2.801
4100	14.684	72.214	59.862	50.644	-47.671	53.746	-2.865
4200	14.694	72.568	60.160	52.113	-47.691	56.220	-2.925
4300	14.704	72.914	60.453	53.583	-47.720	58.691	-2.983
4400	14.713	73.252	60.740	55.054	-47.760	61.169	-3.038
4500	14.721	73.583	61.022	56.526	-47.812	63.643	-3.091
4600	14.729	73.907	61.298	57.998	-47.875	66.124	-3.141
4700	14.736	74.224	61.570	59.471	-47.952	68.601	-3.190
4800	14.743	74.534	61.837	60.945	-48.039	71.084	-3.236
4900	14.749	74.838	62.099	62.420	-48.140	73.567	-3.281
5000	14.755	75.136	62.357	63.895	-48.254	76.047	-3.324
5100	14.761	75.428	62.610	65.371	-48.382	78.536	-3.365
5200	14.766	75.715	62.860	66.847	-48.523	81.026	-3.405
5300	14.771	75.996	63.105	68.324	-48.678	83.525	-3.444
5400	14.776	76.272	63.346	69.802	-48.848	86.015	-3.481
5500	14.781	76.544	63.584	71.280	-49.032	88.515	-3.517
5600	14.785	76.810	63.817	72.758	-49.230	91.017	-3.552
5700	14.789	77.072	64.048	74.237	-49.443	93.521	-3.586
5800	14.793	77.329	64.274	75.716	-49.671	96.031	-3.618
5900	14.797	77.582	64.498	77.195	-49.913	98.550	-3.650
6000	14.800	77.830	64.718	78.675	-50.169	101.064	-3.681

December 31, 1960.

Beryllium Dihydride (BeH_2) (Ideal Gas)

Mol. Wt. = 11.029

ΔH_f° 298.15 = [30] kcal. mole^{-1}

$S^\circ_{298.15}$ = 41.4 cal. deg.$^{-1}$ mole^{-1}

Point Group [$D_{\infty h}$]

Ground State Multiplicity = 1

Vibrational Levels and Multiplicities

ω cm.$^{-1}$
[2200] (1)
[1500] (2)
[1300] (1)

Moment of Inertia: I = [6.01 X 10^{-40}] g. cm.^{2} σ = 2.

Heat of Formation. Estimated by C. J. O'Brien and J. R. Perrin, Marquardt Corp., Van Nuys, Calif., and J. Perrine, Olin Mathieson Chemical Corp., New York 22, N. Y., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules", October, 1959.

Heat Capacities and Entropies. Molecular and spectroscopic parameters estimated.

Beryllium Dihydroxide, Alpha (α-$Be(OH)_2$)
(Crystal) GFW = 43.02694

	gibbs/mol			kcal/mol			
T, °K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0							
100							
200							
298	15.630	11.800	11.800	.000	- 215.750	- 194.673	142.699
300	15.704	11.897	11.800	.029	- 215.754	- 194.543	141.724
400	19.330	16.931	12.462	1.788	- 215.839	- 187.452	102.419
500	22.136	21.558	13.825	3.867	- 215.694	- 180.367	78.839
600	24.253	25.784	15.472	6.188	- 215.370	- 173.330	63.135
700	26.174	29.669	17.226	8.710	- 214.900	- 166.359	51.939
800	27.976	33.283	19.010	11.418	- 214.291	- 159.466	43.564

Dec. 31, 1966

BERYLLIUM DIHYDROXIDE, ALPHA (α-$Be(OH)_2$) (CRYSTAL) GFW = 43.02694

$\Delta Hf°_0$ = Unknown

$S°_{298.15}$ = [11.8 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = -215.75 ± 0.5 kcal/mol

Td = [407]°K

Heat of Formation.

The heat of formation is based on $\Delta Hr°_{298.15} = -79.16 \pm 0.5$ kcal/mol for the reaction $Be(c) + 2H_2O(l) = Be(OH)_2(\alpha,c) + H_2(g)$. The heat of this reaction is obtained by combination of the calorimetric heats of solution for pure beryllium metal and α-$Be(OH)_2$ in aqueous HF, measured by I. J. Bear and A. G. Turnbull, J. Phys. Chem. 69, 2828-33 (1965).

Heat Capacity and Entropy.

The heat capacity was assumed the same as that of the beta phase. The entropy is calculated from the value of $\Delta G°_{298.15} = -0.50$ kcal/mol for the change $\alpha\text{-}Be(OH)_2 \rightarrow \beta\text{-}Be(OH)_2$ which is obtained from the solubilities in concentrated alkali measured by R. Fricke and H. Humme, Z. Anorg. Allgem. Chem. 178, 400 (1929). This is combined with the $\Delta Hf°_{298.15}$ difference and gives a change in entropy, $\Delta S°_{298.15} = -0.8$ eu and an entropy of α-$Be(OH)_2$, $S°_{298.15} = 11.8 \pm 2$ eu.

Decomposition Data.

Td is calculated as the temperature at which $\Delta Gr°$ equals zero for $Be(OH)_2(\alpha,c) = BeO(c) + H_2O(g)$.

Beryllium Dihydroxide, Beta (β -Be(OH)$_2$)

(Crystal) GFW = 43.02694

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	15.630	11.000	11.000	.000	- 216.500	- 195.185	143.074
300	15.704	11.097	11.000	.029	- 216.504	- 195.053	142.096
400	19.330	16.131	11.662	1.788	- 216.589	- 187.882	102.654
500	22.136	20.758	13.025	3.867	- 216.444	- 180.717	78.992
600	24.253	24.984	14.672	6.188	- 216.120	- 173.600	63.234
700	26.174	28.869	16.426	8.710	- 215.650	- 166.549	51.999
800	27.976	32.483	18.210	11.418	- 215.041	- 159.576	43.594
900	29.684	35.877	19.986	14.302	- 214.300	- 152.684	37.077
1000	31.298	39.089	21.737	17.352	- 213.435	- 145.883	31.883

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1966

BERYLLIUM DIHYDROXIDE, BETA (β-Be(OH)$_2$) (CRYSTAL) GFW = 43.02694

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [11.0 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -216.50 ± 0.5 kcal/mol

Td = [417] °K

Heat of Formation.

The heat of formation is based on $\Delta Hr^\circ_{298.15}$ = -79.89 ± 0.5 kcal/mol for the reaction $Be(c) + 2H_2O(l) = Be(OH)_2(\beta,c) + H_2(g)$. The heat of this reaction is obtained by combination of the calorimetric heats of solution measured by Bear and Turnbull for pure beryllium metal and β-Be(OH)$_2$ in aqueous HF. Third law analyses of two studies of the decomposition pressure of water vapor over the β-phase are in good agreement with the selected heat of formation, as summarized below. Fricke and Severin observed a decomposition temperature of 105°C at a pressure of 100 mm, while Baur and Lecocq found 223°C for equilibrium with saturated water vapor at 24.2 atm. We have reduced the latter data to a standard state value of $\Delta G^\circ_{496.15}$ = -3028 cal/mol for the decomposition reaction given below.

	Source	Method	Reaction	T, °K	$\Delta Hr^\circ_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
1	Bear & Turnbull	Calorimetric	$Be(c) + 2H_2O(l) \rightarrow Be(OH)_2(\beta,c) + H_2(g)$	294	-79.89	-216.52 ± 0.5
2	Fricke & Severin	Kp	$Be(OH)_2(\beta,c) \rightarrow BeO(c) + H_2O(g)$	378	15.68	-216.58
3	Baur & Lecocq	Kp	"	496	15.44	-216.34

Sources.

1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. 69, 2828-33 (1965).
2. R. Fricke and H. Severin, Z. Anorg. Allgem. Chem. 205, 287 (1932).
3. A. Baur and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611, 17 pp. (1964).

Heat Capacity and Entropy.

The heat capacity is estimated from that for Mg(OH)$_2$ by subtracting the values for MgO and adding those for BeO.

The entropy is estimated by extrapolation to beryllium of the differences in S°_{298} between the chlorides and hydroxides of magnesium and calcium. Entropies of Mg(OH)$_2$, $MgCl_2$ and $BeCl_2$ are taken from the JANAF tables, while those of Ca(OH)$_2$ and $CaCl_2$ are taken to be 19.9 ± 0.1 and 25.0 ± 1.0 eu, respectively. [Recent low temperature data for $SrCl_2$ and $BaCl_2$ suggest that the $CaCl_2$ extrapolation should be S°_{50} = 2.4 ± 1.0 eu rather than the original value of S°_{50} = 4.59 eu used by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 782 (1943)]. Confirmation of the adopted entropy is obtained from the good agreement between the calorimetric heat of formation and the third law values derived from the equilibrium data.

Decomposition Data.

Td is calculated as the temperature at which ΔGr° equals zero for $Be(OH)_2(\beta,c) = BeO(c) + H_2O(g)$.

Beryllium Dihydroxide ($Be(OH)_2$)

(Ideal Gas) GFW = 43.02694

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.989	-154.822	-154.822	INFINITE
100	8.576	47.684	69.507	-2.182	-155.478	-153.655	335.814
200	11.072	54.378	60.388	-1.202	-155.935	-151.661	165.727
298	13.359	59.238	59.238	.000	-156.400	-149.467	109.562
300	13.398	59.320	59.238	.025	-156.408	-149.424	108.855
400	15.284	63.444	59.787	1.463	-156.814	-147.032	80.335
500	16.751	67.019	60.884	3.068	-157.143	-144.547	63.181
600	17.899	70.178	62.175	4.802	-157.406	-142.002	51.724
700	18.828	73.010	63.524	6.640	-157.620	-139.417	43.528
800	19.605	75.576	64.873	8.563	-157.796	-136.806	37.374
900	20.272	77.925	66.194	10.557	-157.945	-134.172	32.581
1000	20.852	80.091	67.477	12.614	-158.073	-131.523	28.744
1100	21.360	82.103	68.716	14.725	-158.191	-128.862	25.603
1200	21.805	83.981	69.911	16.884	-158.303	-126.191	22.982
1300	22.197	85.742	71.062	19.085	-158.415	-123.510	20.764
1400	22.542	87.400	72.170	21.322	-158.532	-120.822	18.861
1500	22.846	88.966	73.238	23.592	-158.659	-118.123	17.211
1600	23.114	90.449	74.268	25.890	-161.555	-115.339	15.755
1700	23.351	91.858	75.261	28.214	-161.593	-112.448	14.456
1800	23.561	93.198	76.221	30.559	-161.632	-109.556	13.302
1900	23.748	94.477	77.148	32.925	-161.670	-106.661	12.269
2000	23.914	95.700	78.046	35.308	-161.710	-103.768	11.339
2100	24.063	96.870	78.914	37.707	-161.753	-100.867	10.497
2200	24.195	97.993	79.756	40.120	-161.802	-97.969	9.732
2300	24.314	99.071	80.573	42.546	-161.854	-95.064	9.033
2400	24.422	100.108	81.365	44.983	-161.914	-92.156	8.392
2500	24.519	101.107	82.135	47.430	-161.984	-89.254	7.803
2600	24.606	102.070	82.883	49.886	-162.058	-86.338	7.257
2700	24.686	103.001	83.611	52.351	-162.140	-83.427	6.753
2800	24.758	103.900	84.320	54.823	-233.261	-79.404	6.198
2900	24.824	104.770	85.010	57.302	-233.108	-73.906	5.570
3000	24.884	105.612	85.683	59.788	-232.961	-68.420	4.984
3100	24.939	106.429	86.339	62.279	-232.818	-62.941	4.437
3200	24.990	107.222	86.979	64.775	-232.682	-57.462	3.924
3300	25.036	107.991	87.604	67.277	-232.552	-51.986	3.443
3400	25.079	108.739	88.215	69.783	-232.430	-46.518	2.990
3500	25.119	109.467	88.812	72.293	-232.315	-41.054	2.564
3600	25.155	110.175	89.396	74.806	-232.209	-35.588	2.160
3700	25.189	110.865	89.967	77.324	-232.112	-30.129	1.780
3800	25.221	111.537	90.525	79.844	-232.024	-24.669	1.419
3900	25.250	112.192	91.073	82.368	-231.945	-19.212	1.077
4000	25.277	112.832	91.609	84.894	-231.878	-13.762	.752
4100	25.303	113.457	92.134	87.423	-231.821	-8.314	.443
4200	25.327	114.067	92.649	89.955	-231.774	-2.862	.149
4300	25.349	114.663	93.154	92.488	-231.740	2.593	-.132
4400	25.370	115.246	93.649	95.024	-231.718	8.038	-.399
4500	25.389	115.816	94.136	97.562	-231.709	13.487	-.655
4600	25.407	116.374	94.613	100.102	-231.712	18.942	-.900
4700	25.425	116.921	95.082	102.644	-231.729	24.388	-1.134
4800	25.441	117.456	95.542	105.187	-231.759	29.841	-1.359
4900	25.456	117.981	95.995	107.732	-231.802	35.287	-1.574
5000	25.471	118.496	96.440	110.278	-231.860	40.735	-1.781
5100	25.484	119.000	96.877	112.826	-231.933	46.195	-1.980
5200	25.497	119.495	97.308	115.375	-232.019	51.641	-2.170
5300	25.509	119.981	97.731	117.925	-232.121	57.106	-2.355
5400	25.521	120.458	98.147	120.477	-232.237	62.554	-2.532
5500	25.532	120.926	98.557	123.029	-232.368	68.020	-2.703
5600	25.542	121.386	98.961	125.583	-232.515	73.480	-2.868
5700	25.552	121.839	99.358	128.138	-232.675	78.944	-3.027
5800	25.561	122.283	99.750	130.694	-232.851	84.420	-3.181
5900	25.570	122.720	100.135	133.250	-233.043	89.888	-3.330
6000	25.579	123.150	100.515	135.808	-233.248	95.360	-3.473

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1966; Mar. 31, 1967

BERYLLIUM DIHYDROXIDE ($Be(OH)_2$) (IDEAL GAS) GFW = 43.02694

Point Group [C_2]

ΔHf°_0 = -154.8 ± 5 kcal/mol

$S^\circ_{298.15}$ = [59.2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -156.4 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[3200] (1)	649 (1)	[1200] (1)
[1000] (1)	[750] (1)	[1600] (1)
[360] (1)	[360] (1)	[3300] (1)

Bond Distances: Be-O = [1.35] Å O-H = [0.97] Å

Bond Angles: Be-O-H = [100°] O-B-O = [180°]

σ = 2

Angle between Be-O-H planes = [95°]

Product of the Moments of Inertia: $I_AI_BI_C = [32.26] \times 10^{-117}\ g^3cm^6$

Heat of Formation.

The equilibrium reaction (A) $BeO(c) + H_2O(g) \rightarrow Be(OH)_2(g)$ has been studied by several investigators; all of them inferred that $Be(OH)_2(g)$ was the major product, but there has been no direct proof of this. D. F. Hildenbrand, L. P. Theard and F. Ju, Aeronutronic, 3rd Quarterly Technical Report No. U-2231, Contract AF 04(611)-8523, 31 July 1963, have examined the $BeO-H_2O$ system at 2300°C mass-spectroscopically and report only BeOH and $Be(OH)_2$. They report a maximum value of the equilibrium constant for reaction (B) $BeO(g) + H_2O(g) \rightarrow Be(OH)_2$ of 3.5×10^5 atm^{-1} at 2327°K; this yields $\Delta Hf^\circ_{298.15}\ (Be(OH)_2,g) \geq -157.7 \pm 10$ kcal/mol using JANAF functions.

L. I. Grossweiner and R. L. Seifert, J. Am. Chem. Soc. 74, 2701 (1952); W. A. Young, J. Phys. Chem. 64, 1003 (1960); and W. I. Stuart and G. H. Price, J. Nucl. Mater. 14, 417 (1964), have all studied reaction (A) under similar conditions. Each of these investigators varied and $H_2O(g)$ flow rate without detectable change of K_p values. However, Grossweiner and Seifert used a considerably larger flow rate than the other investigators, and the reaction that they studied may not have been quite at equilibrium. The residence times in all cases were quite comparable. A second and third law analysis of the above data are shown below.

J. Blauer, M. A. Greenbaum and M. Farber, J. Phys. Chem. 70, 973 (1966), have also studied reaction (A) using the molecular flow effusion technique. They obtained a large variation of Kp with surface area, although the sample area and size were comparable to that in the earlier investigations. They operated at 300μ pressure, which is at the upper limits of the molecular flow regime. Also encountered was an unexpected variation of the blank experiments with sample size. All the samples investigated were relatively coarse with surface areas <60 cm^2/g; it seems likely that surface area effects would have been found in the three earlier investigations with up to threefold variation in sample weights. We conclude that the variation observed by Blauer et al. is not wholly caused by sample size. A second and third law analysis of the data are shown below.

G.R.B. Elliott, UCRL 1831 (1952), has also investigated reaction (A), but details of the sample are not available and the results show considerable scatter.

A. Baur and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611, Direction des Materiaux et Combustibles Nucleaires, Nov. 1964, cite the results of Morize, Roudier and Bisson, DM/948, in equation form.

Reference	No. of Points	Range °K	ΔHr°_{298} Kcal/mole 2nd law	3rd law	drift eu	$\Delta Hf^\circ_{298.15}$* kcal/mol
Stuart	15	1338-1653	40.6 ± 0.9	44.53	2.6 ± 0.6	-156.4
Young	7	1576-1839	43.9 ± 1.5	44.51	0.25 ± 0.9	-156.4
Grossweiner	24 11	1472-1873 1673	43.7 ± 1.1	45.22 44.62	0.7 ± 0.7	-155.7 -156.3
Blauer	4	1567-1808	39.6 ± 4.4	38.2	-1.1 ± 2.5	-162.7
Elliott	6	1527-1583		47.0	-19 ± 44	-153.9
Morize	Equation	?	50.8	40.6	-6.2	-160.3

*calculated using the 3rd law ΔHr°_{298}.

$\Delta Hf^\circ_{298}(Be(OH)_2,g) = -156.4 \pm 5$ kcal/mol is adopted, with a large uncertainty to cover errors due to the functions as well as the experimental uncertainty.

Heat Capacity and Entropy.

The structure is that assumed by R. L. Altman, J. Chem. Eng. Data 8, 534 (1963). One vibrational frequency was reported by M. Farber, M. A. Greenbaum, M. A. Frisch et al., Rocket Power, Inc., Final Report AFRPL-TR-66-220, Contract AF 04(611)-10929, September 1966. The remaining frequencies were estimated and adjusted to give reasonable agreement between the second and third law heats of reaction. The three principal moments of inertia are $I_A = 2.865 \times 10^{-40}$, $I_B = 10.60 \times 10^{-39}$, and $I_C = 10.62 \times 10^{-39}$ g cm^2.

Beryllium Monoiodide (BeI)

(Ideal Gas) Mol. Wt. = 135.923

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.157	24.588	24.588	INFINITE
100	6.972	48.738	63.358	-1.462	24.908	20.777	-45.405
200	7.363	53.662	57.409	-.749	24.894	16.633	-18.175
298	7.886	56.703	56.703	.000	24.700	12.612	-9.244
300	7.895	56.752	56.704	.015	24.696	12.537	-9.133
400	8.257	59.077	57.018	.824	22.480	8.594	-4.695
500	8.484	60.946	57.623	1.661	17.052	5.640	-2.465
600	8.630	62.506	58.310	2.518	16.918	3.370	-1.227
700	8.729	63.845	59.008	3.386	16.764	1.123	-.351
800	8.800	65.015	59.687	4.262	16.595	-1.099	.300
900	8.853	66.055	60.338	5.145	16.409	-3.300	.801
1000	8.895	66.990	60.957	6.033	16.204	-5.479	1.197
1100	8.928	67.839	61.545	6.924	15.978	-7.636	1.517
1200	8.956	68.617	62.102	7.818	15.729	-9.773	1.780
1300	8.981	69.335	62.631	8.715	15.459	-11.886	1.998
1400	9.002	70.001	63.134	9.614	15.166	-13.979	2.182
1500	9.021	70.623	63.613	10.515	14.851	-16.051	2.339
1600	9.039	71.206	64.069	11.418	11.758	-18.021	2.461
1700	9.055	71.754	64.505	12.323	11.512	-19.875	2.555
1800	9.070	72.272	64.923	13.229	11.261	-21.714	2.636
1900	9.084	72.763	65.323	14.137	11.007	-23.539	2.708
2000	9.098	73.229	65.706	15.046	10.748	-25.351	2.770
2100	9.111	73.674	66.075	15.957	10.485	-27.151	2.825
2200	9.124	74.098	66.430	16.868	10.217	-28.937	2.874
2300	9.136	74.504	66.773	17.781	9.945	-30.709	2.918
2400	9.148	74.893	67.103	18.695	9.668	-32.470	2.957
2500	9.159	75.266	67.422	19.611	9.386	-34.220	2.991
2600	9.171	75.626	67.731	20.527	9.101	-35.959	3.022
2700	9.182	75.972	68.030	21.445	8.811	-37.685	3.050
2800	9.193	76.306	68.319	22.364	-62.512	-38.294	2.989
2900	9.204	76.629	68.600	23.284	-62.558	-37.427	2.820
3000	9.215	76.941	68.873	24.204	-62.607	-36.561	2.663
3100	9.225	77.244	69.138	25.126	-62.655	-35.696	2.516
3200	9.236	77.537	69.396	26.050	-62.704	-34.822	2.378
3300	9.247	77.821	69.647	26.974	-62.756	-33.948	2.248
3400	9.257	78.097	69.892	27.899	-62.810	-33.075	2.126
3500	9.267	78.366	70.130	28.825	-62.866	-32.202	2.011
3600	9.278	78.627	70.362	29.752	-62.926	-31.323	1.901
3700	9.288	78.881	70.589	30.681	-62.989	-30.446	1.798
3800	9.298	79.129	70.811	31.610	-63.057	-29.565	1.700
3900	9.308	79.371	71.027	32.540	-63.128	-28.682	1.607
4000	9.318	79.606	71.239	33.472	-63.205	-27.797	1.519
4100	9.328	79.837	71.445	34.404	-63.288	-26.915	1.435
4200	9.338	80.062	71.648	35.337	-63.377	-26.026	1.354
4300	9.348	80.281	71.846	36.272	-63.472	-25.131	1.277
4400	9.358	80.496	72.040	37.207	-63.575	-24.239	1.204
4500	9.368	80.707	72.231	38.143	-63.686	-23.345	1.134
4600	9.378	80.913	72.417	39.081	-63.805	-22.449	1.067
4700	9.388	81.115	72.600	40.019	-63.932	-21.552	1.002
4800	9.398	81.312	72.780	40.958	-64.068	-20.643	.940
4900	9.408	81.506	72.956	41.899	-64.213	-19.736	.880
5000	9.418	81.697	73.129	42.840	-64.369	-18.829	.823
5100	9.428	81.883	73.298	43.782	-64.534	-17.915	.768
5200	9.438	82.066	73.465	44.725	-64.710	-17.002	.715
5300	9.448	82.246	73.629	45.670	-64.896	-16.081	.663
5400	9.457	82.423	73.790	46.615	-65.093	-15.159	.613
5500	9.467	82.596	73.949	47.561	-65.301	-14.231	.565
5600	9.477	82.767	74.105	48.508	-65.521	-13.303	.519
5700	9.487	82.935	74.258	49.457	-65.750	-12.367	.474
5800	9.497	83.100	74.409	50.406	-65.992	-11.425	.430
5900	9.506	83.262	74.558	51.356	-66.245	-10.484	.388
6000	9.516	83.422	74.704	52.307	-66.508	-9.538	.347

Dec. 31, 1961; Sept. 30, 1964

BERYLLIUM MONOIODIDE (BeI) (IDEAL GAS) MOL. WT. = 135.923

Ground State Configuration $^2\Sigma^+$

$\Delta H_f^\circ{}_0$ = [24.6 ± 5.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [56.70] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [24.7 ± 5.0] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$	g_i
0	[2]

ω_e = [657] cm.$^{-1}$

$\omega_e x_e$ = [3.90] cm.$^{-1}$

σ = 1

B_e = [0.41894] cm.$^{-1}$

α_e = [0.00248] cm.$^{-1}$

r_e = [2.19] Å

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g), BeCl(g), and the gaseous lithium halides. The resulting value, 79.1 kcal. mole^{-1}, was combined with JANAF heats of formation for Be(g) and I(g) in arriving at $\Delta H_f^\circ{}_{298.15}$.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g), BeCl(g), and the gaseous lithium halides. The ground term was assumed to be similar to that of BeCl(g) and BeF(g), tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the interatomic distances for the alkali halides, BeF(g), and BeCl(g) was employed in deriving r_e.

Beryllium Diiodide (BeI_2)

(Crystal) Mol. Wt. = 262.821

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	17.000	28.800	28.800	.000	- 50.600	- 50.231	36.816
300	17.041	28.905	28.800	.031	- 50.600	- 50.228	36.589
400	18.500	34.039	29.490	1.820	- 54.422	- 49.973	27.303
500	19.200	38.247	30.834	3.707	- 64.562	- 47.905	20.938
600	19.650	41.790	32.373	5.650	- 64.058	- 44.623	16.253
700	19.931	44.841	33.941	7.630	- 63.549	- 41.424	12.932
800	20.150	47.517	35.474	9.634	- 63.041	- 38.297	10.462
900	20.289	49.899	36.947	11.657	- 62.539	- 35.234	8.556
1000	20.400	52.042	38.351	13.691	- 62.050	- 32.226	7.043
1100	20.484	53.991	39.686	15.736	- 61.576	- 29.267	5.815
1200	20.541	55.776	40.953	17.787	- 61.123	- 26.350	4.799
1300	20.571	57.421	42.157	19.843	- 60.688	- 23.469	3.945
1400	20.574	58.946	43.303	21.901	- 60.278	- 20.622	3.219

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIIODIDE (BeI_2) (CRYSTAL) MOL. WT. = 262.821

$S^\circ_{298.15}$ = [28.8 ± 2] cal. mole^{-1} deg.$^{-1}$

T_m° = 753°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = [-50.6 ± 8] kcal. mole^{-1}

ΔH°_m = [5] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 30.3 ± 2.0 kcal. mole^{-1}

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messerknecht, Z. anorg. Chem. 148, 157 (1925) and Biltz, Klatte and Rahlfs, Z. anorg. Chem. 166, 339 (1927) as reported in N.B.S. Circular 500, Washington 1952. They measured the heat of solution of BeI_2 in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be^{++} and $2I^-$ to obtain ΔH_f° of the crystal. However Be^{++} was estimated by the Bureau and a total uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with $BeCl_2$ and BeF_2. The entropy was also estimated by comparing with α-$BeCl_2$ and BeF_2 and using additive entropy values for the halide ions. K. N. Semenenko and T. N. Naumova, Zhur. Strukt. Khim. 4, 67 (1963) have reported that between 563 and 643°C BeI_2 exists in a β' form and above 643°C a β form and an unknown form also exist. No allowance has been made for these modifications in the present table.

Melting Data.

The melting point was reported by O. Rahlfs and W. Fischer, Z. anorg. Chem. 211, 351 (1933). The heat of melting was estimated by comparison with the heats of transition and melting for $BeCl_2$ and BeF_2.

Sublimation Data.

The heat of sublimation was obtained from a third law analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 578-703°K. This gave $\Delta H^\circ_{s\ 298}$ = 30.34 kcal. mole^{-1} with a drift of 3.2 ± 1.1 cal. mole^{-1} deg.$^{-1}$ A second law analysis gave $\Delta H^\circ_{s\ 298}$ = 28.1 ± 0.7 kcal. mole^{-1}. No attempt was made to change the functions to eliminate the drift, since a correlation with $BeCl_2$, $BeBr_2$ and BeI_2 indicated that the drift was probably due to the data rather than the functions.

Beryllium Diiodide (BeI_2)

(Liquid) Mol. Wt. = 262.821

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	kcal. mole^{-1} $H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	17.000	32.397	32.397	.000	- 47.446	- 48.149	35.293
300	17.041	32.502	32.397	.031	- 47.446	- 48.153	35.078
400	18.500	37.636	33.087	1.820	- 51.268	- 48.258	26.365
500	27.000	41.850	34.432	3.709	- 61.406	- 46.550	20.346
600	27.000	46.772	36.091	6.409	- 60.145	- 43.699	15.917
700	27.000	50.935	37.921	9.109	- 58.916	- 41.056	12.818
800	27.000	54.540	39.778	11.809	- 57.712	- 38.586	10.541
900	27.000	57.720	41.599	14.509	- 56.533	- 36.267	8.806
1000	27.000	60.565	43.356	17.209	- 55.378	- 34.077	7.447
1100	27.000	63.138	45.039	19.909	- 54.249	- 32.001	6.358
1200	27.000	65.487	46.646	22.609	- 53.147	- 30.028	5.469
1300	27.000	67.649	48.180	25.309	- 52.068	- 28.145	4.731
1400	27.000	69.649	49.643	28.009	- 51.016	- 26.344	4.112
1500	27.000	71.512	51.040	30.709	- 49.989	- 24.619	3.587
1600	27.000	73.255	52.374	33.409	- 51.742	- 22.881	3.125
1700	27.000	74.892	53.651	36.109	- 50.651	- 21.112	2.714
1800	27.000	76.435	54.874	38.809	- 49.566	- 19.405	2.356
1900	27.000	77.895	56.048	41.509	- 48.488	- 17.759	2.043
2000	27.000	79.280	57.175	44.209	- 47.416	- 16.172	1.767

BERYLLIUM DIIODIDE (BeI_2) (LIQUID) MOL. WT. = 262.821

$S^\circ_{298.15}$ = [32.4] cal. mole^{-1} deg.$^{-1}$

T°_m = 753°K.

T°_b = [755]°K.

ΔH°_f 298.15 = [-47.45 ± 3] kcal. mole^{-1}

ΔH°_m = [5] kcal. mole^{-1}

ΔH°_v = [23] kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH°_m and the difference between H_{753}-H_{298} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for $BeCl_2$. A glass transition was assumed at 500°K. below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeI_2(c) table for details.

Vaporizaton Data.

The temperature and heat of vaporization were calculated from the cross over point BeI_2(l) and (g).

Beryllium Diiodide (BeI_2)

(Ideal Gas) Mol. Wt. = 262.821

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.340	-20.018	-20.018	INFINITE
100	11.060	57.007	81.766	-2.476	-19.893	-24.123	52.717
200	12.611	65.254	71.641	-1.277	-20.010	-28.320	30.945
298	13.364	70.441	70.441	.000	-20.300	-32.346	23.709
300	13.376	70.524	70.441	.025	-20.306	-32.421	23.617
400	13.862	74.444	70.972	1.389	-24.553	-36.266	19.814
500	14.166	77.572	71.990	2.791	-35.178	-38.183	16.689
600	14.360	80.173	73.143	4.218	-35.190	-38.785	14.127
700	14.490	82.397	74.310	5.661	-35.218	-39.382	12.295
800	14.579	84.338	75.445	7.115	-35.260	-39.973	10.920
900	14.643	86.059	76.530	8.576	-35.320	-40.559	9.849
1000	14.690	87.605	77.562	10.043	-35.398	-41.137	8.990
1100	14.726	89.007	78.540	11.514	-35.498	-41.707	8.786
1200	14.753	90.289	79.466	12.988	-35.622	-42.266	7.697
1300	14.775	91.471	80.345	14.464	-35.767	-42.813	7.197
1400	14.792	92.566	81.179	15.942	-35.937	-43.348	6.767
1500	14.806	93.587	81.973	17.422	-36.130	-43.873	6.392
1600	14.818	94.543	82.729	18.904	-39.101	-44.301	6.051
1700	14.828	95.442	83.450	20.386	-39.228	-44.624	5.737
1800	14.836	96.290	84.140	21.869	-39.360	-44.938	5.456
1900	14.843	97.092	84.801	23.353	-39.498	-45.244	5.204
2000	14.849	97.854	85.435	24.837	-39.642	-45.546	4.977
2100	14.854	98.578	86.044	26.323	-39.790	-45.834	4.770
2200	14.858	99.269	86.629	27.808	-39.946	-46.119	4.581
2300	14.862	99.930	87.193	29.294	-40.107	-46.395	4.408
2400	14.866	100.562	87.737	30.781	-40.273	-46.662	4.249
2500	14.869	101.169	88.262	32.267	-40.448	-46.928	4.102
2600	14.871	101.753	88.770	33.754	-40.627	-47.184	3.966
2700	14.874	102.314	89.261	35.242	-40.811	-47.432	3.839
2800	14.876	102.855	89.737	36.729	-112.032	-46.565	3.634
2900	14.878	103.377	90.199	38.217	-111.976	-44.227	3.333
3000	14.879	103.881	90.646	39.705	-111.924	-41.892	3.052
3100	14.881	104.369	91.081	41.193	-111.874	-39.561	2.789
3200	14.882	104.842	91.504	42.681	-111.826	-37.228	2.542
3300	14.884	105.300	91.915	44.169	-111.783	-34.896	2.311
3400	14.885	105.744	92.315	45.657	-111.744	-32.568	2.093
3500	14.886	106.175	92.705	47.146	-111.707	-30.237	1.888
3600	14.887	106.595	93.085	48.635	-111.676	-27.911	1.694
3700	14.888	107.003	93.456	50.123	-111.651	-25.589	1.511
3800	14.889	107.400	93.818	51.612	-111.631	-23.262	1.338
3900	14.890	107.787	94.171	53.101	-111.617	-20.934	1.173
4000	14.890	108.163	94.516	54.590	-111.610	-18.610	1.017
4100	14.891	108.531	94.853	56.079	-111.610	-16.285	.868
4200	14.892	108.890	95.183	57.568	-111.618	-13.959	.726
4300	14.892	109.240	95.506	59.058	-111.633	-11.633	.591
4400	14.893	109.583	95.822	60.547	-111.659	-9.311	.462
4500	14.893	109.917	96.132	62.036	-111.694	-6.979	.339
4600	14.894	110.245	96.435	63.526	-111.738	-4.655	.221
4700	14.894	110.565	96.732	65.015	-111.792	-2.329	.108
4800	14.895	110.879	97.024	66.504	-111.858	.002	-.000
4900	14.895	111.186	97.310	67.994	-111.933	2.335	-.104
5000	14.895	111.487	97.590	69.483	-112.021	4.669	-.204
5100	14.896	111.782	97.865	70.973	-112.119	7.002	-.300
5200	14.896	112.071	98.136	72.463	-112.230	9.335	-.392
5300	14.896	112.355	98.402	73.952	-112.354	11.677	-.481
5400	14.897	112.633	98.662	75.442	-112.489	14.022	-.567
5500	14.897	112.907	98.919	76.931	-112.638	16.359	-.650
5600	14.897	113.175	99.171	78.421	-112.799	18.706	-.730
5700	14.897	113.439	99.419	79.911	-112.972	21.058	-.807
5800	14.898	113.698	99.663	81.401	-113.158	23.414	-.882
5900	14.898	113.952	99.903	82.890	-113.358	25.770	-.955
6000	14.898	114.203	100.139	84.380	-113.570	28.126	-1.024

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIIODIDE (BeI_2) (IDEAL GAS) MOL. WT. = 262.821

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = [70.44 ± 2] cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -20 ± 4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-20.3 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[140](1)
[155](2)
[770](1)

Bond Distance: Be-I = 2.12Å

Bond Angle: I-Be-I = [180°]

σ = 2

Rotational Constant: B_o = 0.01478 cm.$^{-1}$

Heat of Formation.

The heat of formation was obtained from that of the crystal plus $\Delta H_{s\ 298}$, see BeI_2 (c) table for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with $BeCl_2$. The bond length was reported by P. A. Akishin, V. P. Spirodinov and G. A. Sobelev, Dokl. Akad. Nauk SSSR, 118, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k_1, for the BeF_2, $BeCl_2$, $BeBr_2$ and BeI_2 series and also assuming $k_1/k/l^2 = 50$ as for BeF_2. The principal moment of inertia is 189.402 x 10^{-39} g. cm.^{2}

Beryllium Nitride (BeN)

(Ideal Gas) Mol. Wt. = 23.021

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-2.085	101.400	101.400	INFINITE
100	6.958	42.221	56.133	-1.391	101.741	99.438	-217.311
200	6.992	47.049	50.522	-.695	101.948	97.039	-106.035
298	7.192	49.872	49.872	.000	101.981	94.615	-69.351
300	7.197	49.916	49.872	.013	101.981	94.569	-68.890
400	7.514	52.029	50.158	.749	101.929	92.105	-50.321
500	7.820	53.740	50.708	1.516	101.840	89.659	-39.188
600	8.069	55.188	51.337	2.311	101.737	87.232	-31.773
700	8.264	56.447	51.979	3.128	101.618	84.823	-26.482
800	8.414	57.561	52.609	3.962	101.486	82.433	-22.519
900	8.531	58.559	53.215	4.809	101.337	80.061	-19.440
1000	8.624	59.463	53.796	5.667	101.168	77.705	-16.982
1100	8.699	60.289	54.349	6.534	100.976	75.368	-14.974
1200	8.760	61.048	54.876	7.407	100.760	73.050	-13.303
1300	8.812	61.752	55.378	8.285	100.521	70.750	-11.894
1400	8.856	62.406	55.857	9.169	100.258	68.469	-10.688
1500	8.894	63.019	56.314	10.056	99.971	66.208	-9.646
1600	8.927	63.594	56.752	10.947	96.905	64.046	-8.748
1700	8.957	64.136	57.170	11.842	96.685	61.999	-7.970
1800	8.984	64.649	57.571	12.739	96.459	59.965	-7.280
1900	9.008	65.135	57.957	13.638	96.229	57.944	-6.665
2000	9.031	65.598	58.327	14.540	95.994	55.935	-6.112
2100	9.051	66.039	58.684	15.444	95.754	53.938	-5.613
2200	9.071	66.460	59.028	16.351	95.510	51.952	-5.161
2300	9.089	66.864	59.360	17.259	95.260	49.979	-4.749
2400	9.106	67.251	59.681	18.168	95.006	48.017	-4.372
2500	9.123	67.623	59.991	19.080	94.746	46.062	-4.027
2600	9.139	67.981	60.292	19.993	94.483	44.122	-3.709
2700	9.154	68.326	60.583	20.908	94.216	42.190	-3.415
2800	9.169	68.660	60.865	21.824	22.915	41.375	-3.229
2900	9.183	68.982	61.140	22.741	22.891	42.037	-3.168
3000	9.197	69.293	61.406	23.660	22.866	42.697	-3.110
3100	9.211	69.595	61.666	24.581	22.840	43.355	-3.056
3200	9.224	69.888	61.918	25.502	22.814	44.020	-3.006
3300	9.237	70.172	62.164	26.425	22.785	44.683	-2.959
3400	9.250	70.448	62.403	27.350	22.754	45.347	-2.915
3500	9.262	70.716	62.637	28.275	22.722	46.010	-2.873
3600	9.275	70.977	62.865	29.202	22.686	46.678	-2.834
3700	9.287	71.231	63.088	30.130	22.647	47.343	-2.796
3800	9.299	71.479	63.305	31.060	22.603	48.012	-2.761
3900	9.311	71.721	63.518	31.990	22.557	48.684	-2.728
4000	9.323	71.957	63.726	32.922	22.504	49.352	-2.696
4100	9.334	72.187	63.930	33.855	22.447	50.021	-2.666
4200	9.346	72.412	64.129	34.789	22.384	50.696	-2.638
4300	9.358	72.632	64.324	35.724	22.315	51.374	-2.611
4400	9.369	72.847	64.516	36.660	22.238	52.049	-2.585
4500	9.380	73.058	64.703	37.598	22.154	52.727	-2.561
4600	9.392	73.264	64.887	38.536	22.062	53.407	-2.537
4700	9.403	73.466	65.067	39.476	21.963	54.088	-2.515
4800	9.414	73.665	65.244	40.417	21.854	54.774	-2.494
4900	9.425	73.859	65.418	41.359	21.737	55.460	-2.473
5000	9.436	74.049	65.589	42.302	21.610	56.154	-2.454
5100	9.447	74.236	65.757	43.246	21.473	56.843	-2.436
5200	9.458	74.420	65.921	44.191	21.328	57.536	-2.418
5300	9.469	74.600	66.084	45.138	21.170	58.235	-2.401
5400	9.480	74.777	66.243	46.085	21.004	58.935	-2.385
5500	9.491	74.951	66.400	47.034	20.825	59.640	-2.370
5600	9.501	75.122	66.554	47.983	20.637	60.347	-2.355
5700	9.512	75.291	66.706	48.934	20.438	61.061	-2.341
5800	9.523	75.456	66.855	49.886	20.228	61.778	-2.328
5900	9.534	75.619	67.002	50.838	20.006	62.492	-2.315
6000	9.545	75.779	67.147	51.792	19.774	63.212	-2.302

June 30, 1963

BERYLLIUM NITRIDE (BeN) (IDEAL GAS) MOL. WT. = 23.021

Ground State Configuration $[^2\Pi]$

$\Delta H_{f\ 0}^\circ = [101]$ kcal mole^{-1}

$S_{298.15}^\circ = [49.87]$ cal deg^{-1} mole^{-1}

$\Delta H_{f\ 298.15}^\circ = [102]$ kcal mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm^{-1}	g_i
0	[4]

$\omega_e = [1194]$ cm^{-1} $\omega_e x_e = [12.4]$ cm^{-1} $\sigma = 1$

$B_e = [1.555]$ cm^{-1} $\alpha_e = [0.019]$ cm^{-1} $r_e = [1.406]$ Å

Heat of Formation

The heat of formation was estimated by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, April 25, 1963.

Molecular Constants

The molecular constants were taken from J. S. Gordon, loc. cit.

Beryllium Oxide (BeO)

(Crystal) Mol. Wt. = 25.013

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- .669	- 142.282	- 142.282	INFINITE
100	.675	.243	6.933	- .669	- 142.630	- 140.565	307.190
200	3.415	1.486	3.856	- .474	- 142.913	- 138.385	151.213
298	6.100	3.378	3.378	.000	- 143.100	- 136.122	99.775
300	6.144	3.416	3.378	.011	- 143.102	- 136.079	99.128
400	8.022	5.463	3.644	.727	- 143.181	- 133.723	73.059
500	9.244	7.391	4.204	1.594	- 143.184	- 131.357	57.413
600	10.138	9.163	4.885	2.567	- 143.130	- 128.996	46.984
700	10.778	10.776	5.613	3.614	- 143.044	- 126.647	39.539
800	11.232	12.247	6.352	4.716	- 142.936	- 124.312	33.959
900	11.527	13.588	7.082	5.855	- 142.821	- 121.990	29.622
1000	11.730	14.814	7.795	7.019	- 142.711	- 119.682	26.155
1100	11.900	15.940	8.485	8.200	- 142.613	- 117.384	23.321
1200	12.070	16.983	9.150	9.399	- 142.527	- 115.094	20.960
1300	12.242	17.955	9.791	10.614	- 142.452	- 112.811	18.964
1400	12.418	18.869	10.407	11.847	- 142.387	- 110.534	17.254
1500	12.595	19.732	11.000	13.098	- 142.332	- 108.261	15.773
1600	12.770	20.550	11.571	14.366	- 145.041	- 105.912	14.466
1700	12.944	21.330	12.123	15.652	- 144.890	- 103.471	13.301
1800	13.117	22.074	12.655	16.955	- 144.729	- 101.039	12.267
1900	13.291	22.788	13.170	18.275	- 144.559	- 98.617	11.343
2000	13.465	23.474	13.668	19.613	- 144.379	- 96.204	10.512
2100	13.640	24.136	14.151	20.968	- 144.190	- 93.799	9.761
2200	13.814	24.774	14.619	22.341	- 143.991	- 91.405	9.080
2300	13.988	25.392	15.074	23.731	- 143.782	- 89.018	8.458
2400	14.593	26.032	15.518	25.234	- 143.468	- 86.643	7.890
2500	14.672	26.629	15.950	26.697	- 143.203	- 84.283	7.368
2600	14.751	27.206	16.372	28.168	- 142.936	- 81.930	6.886
2700	14.830	27.764	16.784	29.647	- 142.668	- 79.588	6.442
2800	14.910	28.305	17.186	31.134	- 213.429	- 76.150	5.943
2900	14.989	28.830	17.578	32.629	- 212.908	- 71.254	5.370
3000	15.068	29.339	17.962	34.132	- 212.384	- 66.379	4.835
3100	15.145	29.834	18.337	35.643	- 211.855	- 61.523	4.337
3200	15.220	30.316	18.704	37.161	- 211.322	- 56.680	3.871
3300	15.294	30.786	19.063	38.686	- 210.786	- 51.856	3.434
3400	15.366	31.243	19.414	40.219	- 210.249	- 47.048	3.024
3500	15.437	31.690	19.759	41.760	- 209.707	- 42.258	2.639
3600	15.506	32.126	20.096	43.307	- 209.165	- 37.479	2.275
3700	15.575	32.552	20.427	44.861	- 208.622	- 32.719	1.933
3800	15.641	32.968	20.752	46.422	- 208.079	- 27.971	1.609
3900	15.706	33.375	21.070	47.989	- 207.534	- 23.238	1.302
4000	15.770	33.773	21.383	49.563	- 206.992	- 18.521	1.012

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE (BeO) (CRYSTAL) MOL. WT. = 25.013

$S^\circ_{298.15}$ = 3.38 ± 0.05 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 2325°K.

T_m = 2820°K.

$\Delta H^\circ_{f\ 0}$ = -142.3 ± 0.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -143.1 ± 0.1 kcal. mole^{-1}

$\Delta H^\circ_{t_1}$ = 0.06 ± 1.0 kcal. mole^{-1}

ΔH°_m = 15.1 ± 0.4 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 174.1 ± 3.0 kcal. mole^{-1}

Heat of Formation.

L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. 75, 3102 (1953) have reviewed earlier determinations of the heat of formation and have made a very careful oxygen bomb calorimeter determination, their value is adopted here.

Heat Capacity and Entropy.

The high temperature enthalpy of BeO(c) has been reported by A. Magnus and H. Danz, Ann. Physik. [4] 81, 407 (1926) up to 1172°K; E. N. Rodigina and K. Z. Gomel'skii, Zhur. Fiz. Khim. 35, 1828 (1961) up to 1128°K; V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Doklady. Akad. Nauk. S.S.S.R. 131, 566 (1960) up to 2840°K; B. E. Walker, C. T. Ewing, and R. R. Miller, private communication, U. S. Naval Research Laboratory 18th April 1963 up to 1100°K; A. C. Victor and T. B. Douglas, J. Res. Natl. Bureau Standards 67A, 325 (1963) up to 1173°K. A high temperature phase transition has been reported by S. B. Austerman, Bull. Am. Physical Soc. II7 (1), 28 (1962) and has been confirmed using high temperature X-rays by T. W. Baker and P. J. Baldock, Nature 193, 1172 (1962). K. K. Kelley, J. Am. Chem. Soc. 61, 1217 (1939) has reported the low temperature heat capacities from 55.5 to 292.4°K. The heat capacity was assumed to follow the T^3 law below 55.5°K. and this gave $S_{55.5}$ = 0.045 cal. deg.$^{-1}$ mole^{-1}. The high temperature enthalpy data was smoothed using both 18 and 27 point groupings and was assumed to be discontinuous at 2325°K. The heat capacity obtained from the smoothed enthalpy was itself smoothed graphically so as to fit with the low temperature heat capacity. The data of Kandyba, et al., show no effect of the transition at 2325° and a value of 0.06 kcal. mole^{-1} was adopted simply to provide a somewhat improved fit of the data above 2325°K. The data above 2700°K. were not included because of apparent premelting effects and the heat capacity curve from 2700 to 2820°K. is extrapolated.

Transition Data.

See heat capacity and entropy.

Melting Data.

Obtained from the enthalpy measurements of Kandyba, et al., loc. cit.

Heat of Sublimation.

The gas above BeO(c) is complex and the value given is for the reaction BeO(c) → BeO(g) and simply read from the respective tables.

Beryllium Oxide (BeO)

(Liquid) Mol. Wt. = 25.013

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	6.100	8.042	8.042	.000	-129.562	-123.975	90.872
300	6.144	8.080	8.042	.011	-129.564	-123.940	90.286
400	8.022	10.127	8.308	.727	-129.643	-122.051	66.682
500	9.244	12.055	8.868	1.594	-129.646	-120.151	52.515
600	10.138	13.827	9.549	2.567	-129.592	-118.256	43.073
700	10.778	15.439	10.277	3.614	-129.506	-116.373	36.332
800	11.232	16.910	11.015	4.716	-129.398	-114.505	31.280
900	11.527	18.252	11.746	5.855	-129.283	-112.650	27.354
1000	11.730	19.477	12.459	7.018	-129.173	-110.807	24.216
1100	11.900	20.609	13.149	8.200	-129.075	-108.975	21.650
1200	12.070	21.646	13.814	9.398	-128.990	-107.152	19.514
1300	12.242	22.619	14.454	10.614	-128.915	-105.335	17.708
1400	12.418	23.532	15.070	11.847	-128.850	-103.525	16.160
1500	12.595	24.395	15.663	13.098	-128.794	-101.718	14.820
1600	12.769	25.214	16.235	14.366	-131.504	-99.836	13.636
1700	12.943	25.993	16.786	15.651	-131.352	-97.861	12.580
1800	13.117	26.738	17.318	16.954	-131.192	-95.896	11.643
1900	16.000	27.452	17.833	18.275	-131.022	-93.939	10.805
2000	16.000	28.272	18.335	19.875	-130.580	-92.000	10.053
2100	16.000	29.053	18.827	21.475	-130.145	-90.081	9.374
2200	16.000	29.797	19.309	23.075	-129.719	-88.183	8.760
2300	16.000	30.508	19.780	24.675	-129.300	-86.304	8.200
2400	16.000	31.189	20.241	26.275	-128.889	-84.442	7.689
2500	16.000	31.842	20.693	27.875	-128.487	-82.601	7.221
2600	16.000	32.470	21.134	29.475	-128.091	-80.771	6.789
2700	16.000	33.074	21.565	31.075	-127.702	-78.959	6.391
2800	16.000	33.656	21.986	32.675	-198.351	-76.053	5.936
2900	16.000	34.217	22.398	34.275	-197.725	-71.694	5.403
3000	16.000	34.760	22.801	35.875	-197.103	-67.359	4.907
3100	16.000	35.284	23.196	37.475	-196.485	-63.047	4.445
3200	16.000	35.792	23.581	39.075	-195.870	-58.750	4.012
3300	16.000	36.285	23.959	40.675	-195.260	-54.475	3.608
3400	16.000	36.762	24.328	42.275	-194.655	-50.219	3.228
3500	16.000	37.226	24.690	43.875	-194.054	-45.981	2.871
3600	16.000	37.677	25.045	45.475	-193.459	-41.756	2.535
3700	16.000	38.115	25.392	47.075	-192.870	-37.552	2.218
3800	16.000	38.542	25.733	48.675	-192.289	-33.361	1.919
3900	16.000	38.957	26.066	50.275	-191.711	-29.186	1.635
4000	16.000	39.362	26.394	51.875	-191.142	-25.028	1.367
4100	16.000	39.758	26.715	53.475	-190.580	-20.883	1.113
4200	16.000	40.143	27.030	55.075	-190.026	-16.751	.872
4300	16.000	40.520	27.339	56.675	-189.480	-12.628	.642
4400	16.000	40.887	27.643	58.275	-188.943	-8.523	.423
4500	16.000	41.247	27.941	59.875	-188.416	-4.429	.215
4600	16.000	41.599	28.235	61.475	-187.898	-.345	.016
4700	16.000	41.943	28.523	63.075	-187.390	3.725	-.173
4800	16.000	42.280	28.806	64.675	-186.893	7.788	-.355
4900	16.000	42.610	29.084	66.275	-186.405	11.837	-.528
5000	16.000	42.933	29.358	67.875	-185.929	15.880	-.694
5100	16.000	43.250	29.627	69.475	-185.464	19.912	-.853
5200	16.000	43.560	29.892	71.075	-185.010	23.930	-1.006
5300	16.000	43.865	30.153	72.675	-184.569	27.948	-1.152
5400	16.000	44.164	30.410	74.275	-184.138	31.950	-1.293
5500	16.000	44.458	30.662	75.875	-183.720	35.949	-1.428
5600	16.000	44.746	30.911	77.475	-183.314	39.939	-1.559
5700	16.000	45.029	31.156	79.075	-182.919	43.923	-1.684
5800	16.000	45.307	31.398	80.675	-182.536	47.904	-1.805
5900	16.000	45.581	31.636	82.275	-182.166	51.869	-1.921
6000	16.000	45.850	31.871	83.875	-181.808	55.832	-2.034

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE (BeO) (LIQUID) MOL. WT. = 25.013

$S^\circ_{298.15}$ = 8.04 cal. deg.$^{-1}$ mole^{-1}

T_m = 2820°K.

T_b = [4060]°K.

ΔH°_f 298.15 = -129.562 ± 0.5 kcal. mole^{-1}

ΔH°_m = 15.1 ± 0.4 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH°_m and the difference between H_{2820}-H_{298} for crystal and liquid.

Heat Capacity and Entropy.

The enthalpy of three points in the liquid phase was determined by V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Fomichev, Dokl. Akad. Nauk. S.S.S.R. 131, 566 (1960). These values were used to obtain a heat capacity for the liquid which was assumed constant. At 1900°K. a glass transition was assumed below which the heat capacity was that of the solid. The entropy at 298°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

See the table for BeO(c).

Vaporization Data.

The vapor composition over BeO(c) at say 2300°K. is composed of Be(g), O(g), BeO(g), $(BeO)_2(g)$, $(BeO)_3(g)$, $(BeO)_4(g)$, $(BeO)_5(g)$, $(BeO)_6(g)$, $Be_2O(g)$ and other species and thus a boiling point becomes almost meaningless and the value given here is the point at which the total pressure reaches 1 atm.

Beryllium Oxide (BeO)

(Ideal Gas) Mol. Wt. = 25.013

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H_{298}^\circ$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.076	30.429	30.429	INFINITE
100	6.957	39.593	53.418	-1.383	30.756	28.886	-63.128
200	6.965	44.416	47.849	-.687	30.974	26.916	-29.412
298	7.046	47.208	47.208	.000	31.000	24.910	-18.259
300	7.049	47.252	47.209	.013	31.000	24.872	-18.119
400	7.254	49.306	47.487	.727	30.919	22.840	-12.478
500	7.510	50.952	48.021	1.465	30.788	20.835	-9.106
600	7.757	52.343	48.628	2.229	30.632	18.858	-6.869
700	7.969	53.555	49.247	3.016	30.458	16.909	-5.279
800	8.145	54.631	49.854	3.822	30.270	14.986	-4.094
900	8.287	55.599	50.440	4.643	30.068	13.088	-3.178
1000	8.402	56.478	51.000	5.478	29.849	11.213	-2.451
1100	8.497	57.284	51.535	6.323	29.610	9.361	-1.860
1200	8.575	58.026	52.046	7.177	29.351	7.531	-1.372
1300	8.640	58.715	52.533	8.038	29.071	5.725	-.962
1400	8.695	59.358	52.997	8.905	28.770	3.939	-.615
1500	8.741	59.959	53.442	9.776	28.446	2.176	-.317
1600	8.782	60.525	53.867	10.653	25.345	.515	-.070
1700	8.817	61.058	54.274	11.533	25.091	-1.029	.132
1800	8.848	61.563	54.665	12.416	24.832	-2.558	.311
1900	8.876	62.042	55.041	13.302	24.568	-4.073	.468
2000	8.901	62.498	55.403	14.191	24.299	-5.574	.609
2100	8.924	62.933	55.751	15.082	24.024	-7.060	.735
2200	8.944	63.349	56.087	15.976	23.744	-8.534	.848
2300	8.963	63.747	56.411	16.871	23.458	-9.994	.950
2400	8.981	64.129	56.725	17.768	23.166	-11.441	1.042
2500	8.997	64.496	57.029	18.667	22.867	-12.879	1.126
2600	9.013	64.849	57.323	19.568	22.564	-14.301	1.202
2700	9.027	65.189	57.608	20.470	22.255	-15.713	1.272
2800	9.041	65.518	57.884	21.373	-49.090	-16.006	1.249
2900	9.054	65.835	58.153	22.278	-49.160	-14.821	1.117
3000	9.066	66.142	58.414	23.184	-49.232	-13.636	.993
3100	9.078	66.440	58.668	24.091	-49.306	-12.451	.878
3200	9.090	66.728	58.916	25.000	-49.383	-11.259	.769
3300	9.101	67.008	59.157	25.909	-49.463	-10.067	.667
3400	9.111	67.280	59.392	26.820	-49.548	-8.872	.570
3500	9.122	67.544	59.621	27.731	-49.636	-7.676	.479
3600	9.132	67.801	59.845	28.644	-49.728	-6.473	.393
3700	9.142	68.052	60.063	29.558	-49.825	-5.272	.311
3800	9.151	68.296	60.276	30.472	-49.928	-4.066	.234
3900	9.161	68.533	60.485	31.388	-50.036	-2.857	.160
4000	9.170	68.765	60.689	32.305	-50.150	-1.648	.090
4100	9.179	68.992	60.889	33.222	-50.271	-.435	.023
4200	9.188	69.213	61.085	34.140	-50.398	.782	-.041
4300	9.197	69.430	61.276	35.060	-50.533	2.006	-.102
4400	9.205	69.641	61.464	35.980	-50.676	3.228	-.160
4500	9.214	69.848	61.648	36.901	-50.828	4.454	-.216
4600	9.222	70.051	61.828	37.822	-50.989	5.685	-.270
4700	9.231	70.249	62.005	38.745	-51.158	6.917	-.322
4800	9.239	70.443	62.179	39.669	-51.337	8.157	-.371
4900	9.247	70.634	62.350	40.593	-51.525	9.396	-.419
5000	9.255	70.821	62.517	41.518	-51.724	10.644	-.465
5100	9.263	71.004	62.682	42.444	-51.933	11.894	-.510
5200	9.271	71.184	62.844	43.371	-52.152	13.143	-.552
5300	9.279	71.361	63.003	44.298	-52.383	14.405	-.594
5400	9.287	71.534	63.159	45.226	-52.625	15.664	-.634
5500	9.295	71.705	63.313	46.155	-52.877	16.932	-.673
5600	9.302	71.872	63.464	47.085	-53.141	18.203	-.710
5700	9.310	72.037	63.613	48.016	-53.416	19.481	-.747
5800	9.318	72.199	63.760	48.947	-53.702	20.766	-.782
5900	9.325	72.359	63.904	49.879	-54.000	22.048	-.817
6000	9.333	72.515	64.047	50.812	-54.308	23.339	-.850

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE (BeO) (IDEAL GAS) MOL. WT. = 25.013

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 47.2 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0$ = 30 ± 3 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 31 ± 3 kcal. mole^{-1}

<u>Electronic Levels and Quantum Weight</u>

ϵ_i, cm.$^{-1}$	g_i
0	1

ω_e = 1487.323 cm.$^{-1}$

$\omega_e x_e$ = 11.8297 cm.$^{-1}$

σ = 1

B_e = 1.6510 cm.$^{-1}$

α_e = 0.0190 cm.$^{-1}$

r_e = 1.3308 Å

<u>Heat of Formation</u>.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. <u>30</u>, 827 (1959) obtained a value of 106 ± 3 kcal. mole^{-1} for D_0, from the reactions $BeO(g) \rightarrow Be(g) + O(g)$ and $BeO(g) + O(g) \rightarrow Be(g) + O_2(g)$. The reactions were followed mass spectrometrically at low electron energies in order to eliminate fragmentation of higher polymers. A Lagerqvist, Arkiv. Fysik <u>7</u>, 473 (1954) had previously reported a value for D_0 = 110 ± 10 kcal. mole^{-1} based on the dissociation limit of the lowest $^1\Pi$ state which was assumed to dissociate to $Be(^1s)$ and $O(^1D)$. The $\Delta H_f^\circ{}_{298}$ BeO(g) = 31 ± 3 kcal. mole^{-1} from D_0 = 106 ± 3 kcal. mole^{-1} was adopted.

<u>Heat Capacity and Entropy</u>.

The spectroscopic constants are from G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York 1950. The ground state configuration has been confirmed by B. A. Thrush, Proc. Chem. Soc. (London), 339 (1960) using absorption spectroscopy.

Beryllium Sulfate, Alpha (α-$BeSO_4$)

(Crystal) GFW = 105.0738

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.102	- 284.431	- 284.431	INFINITE
100	7.008	4.453	32.600	- 2.815	- 285.706	- 277.563	606.612
200	14.502	11.683	20.326	- 1.728	- 286.542	- 269.065	294.021
298	20.482	18.635	18.635	.000	- 287.000	- 260.380	190.864
300	20.581	18.762	18.636	.038	- 287.005	- 260.215	189.566
400	24.828	25.303	19.499	2.322	- 287.681	- 251.236	137.269
500	27.810	31.180	21.258	4.961	- 287.946	- 242.088	105.817
600	30.310	36.470	23.360	7.866	- 287.950	- 232.912	84.838
700	32.980	41.340	25.584	11.029	- 287.715	- 223.730	69.852
800	35.800	45.927	27.843	14.467	- 300.293	- 215.890	58.978
900	38.730	50.312	30.098	18.193	- 299.250	- 205.398	49.877
1000	41.690	54.552	32.332	22.220	- 297.958	- 195.035	42.625
1100	43.759	58.627	34.539	26.497	- 296.466	- 184.816	36.719
1200	45.222	62.501	36.709	30.950	- 294.842	- 174.737	31.824
1300	46.258	66.163	38.835	35.526	- 293.137	- 164.794	27.704
1400	46.984	69.619	40.912	40.190	- 291.384	- 154.989	24.195
1500	47.480	72.879	42.935	44.915	- 289.609	- 145.310	21.172
1600	47.802	75.954	44.904	49.680	- 290.585	- 135.668	18.531
1700	47.970	78.858	46.817	54.470	- 288.701	- 126.043	16.204
1800	48.000	81.601	48.674	59.269	- 286.828	- 116.530	14.149
1900	48.000	84.196	50.475	64.069	- 284.971	- 107.118	12.321
2000	48.000	86.658	52.224	68.869	- 283.130	- 97.808	10.688
2100	48.000	89.000	53.920	73.669	- 281.305	- 88.586	9.219
2200	48.000	91.233	55.565	78.469	- 279.499	- 79.451	7.893
2300	48.000	93.367	57.163	83.269	- 277.707	- 70.399	6.689

Sept. 30, 1966

BERYLLIUM SULFATE (α - $BeSO_4$) (CRYSTAL) GFW = 105.0738

$S^\circ_{298.15}$ = 18.635 gibbs/mol

Tt_1 = 863°K

Tt_2 = 908°K

ΔHf°_0 = -284.4 ± 0.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -287.0 ± 0.8 kcal/mol

ΔHt°_1 = [0.266] kcal/mol

ΔHt°_2 = [4.673] kcal/mol

Heat of Formation.

Bear et al. measured the heats of solution of Be(c) and $BeSO_4$(α) in concentrated HF and the heat of reaction of H_2SO_4 (aq) with $BeSO_4$ (aq HF). Combination of these yields reaction (a) below. Taylor et al. measured heats of solution of Be(c) and $BeSO_4$(α) in H_2SO_4 (aq) which yields reaction (b). Marchal measured the total vapor pressure of $BeSO_4$(c) in the temperature range 863-1103°K. Partial pressures of SO_3(g) were calculated from Marchal's data using JANAF values for the SO_3 - SO_2 equilibrium. Third law analysis of these data yields ΔHr° for reaction (c) as given below. This was converted to ΔHf° for α- $BeSO_4$ using JANAF heats of transition.

Author	Method	Reaction	T°K	ΔHr_T kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
1. Bear (1966)	Calorimetric	(a) $Be(c) + H_2SO_4(109\ H_2O) = H_2(g) + \alpha\text{-}BeSO_4$	294	-74.47	-286.65 ± 0.5
2. Taylor (1966)	Calorimetric	(b) $Be(c) + H_2SO_4(47.849\ H_2O) = H_2(g) + \alpha\text{-}BeSO_4$	298	-76.38	-287.55 ± 0.13
3. Marchal (1925)	Kp (973-1083°K)	(c) $BeSO_4(\gamma) \rightarrow BeO(c) + SO_3(g)$	298	+43.92	-286.55 ± 0.5

References: 1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. 70, 711-17 (1966).
2. A. R. Taylor, Jr., B. B. Letson and D. F. Smith, U. S. Bureau of Mines, Report No. 6724, 1966.
3. G. Marchal, J. Chim. Phys. 22, 502 (1925).

The adopted $\Delta Hf^\circ_{298.15}$ = -287.0 ± 0.8 is an average value of reactions(a) and (b). This value is for relatively finely divided crystals of $BeSO_4$ as was indicated by Bear et al.

Heat Capacity and Entropy.

Low temperature heat capacities (12-301°K) and high temperature enthalpies (366-864°K) were measured by A. R. Taylor, Jr., T. E. Gardner and D. F. Smith, U. S. Bureau of Mines, Report No. 6240, 1963. These data were joined smoothly at 298°K and extrapolated graphically above 864°K. The entropy was obtained from the heat capacities using $S^\circ_{12.56}$ = 0.034 eu.

Transition Data.

I. I. Bosik, A. V. Novoselova and Yu. P. Simanov, Russ. J. Inorg. Chem. 6, 1295 (1961), observed two endothermic effects at 863-883°K and 908-913°K on the heating and cooling curves of $BeSO_4$(c); thus we have adopted Tt ($\alpha \rightarrow \beta$) = 863°K and Tt ($\beta \rightarrow \gamma$) = 908°K. ΔHt° ($\alpha \rightarrow \beta$) = 0.266 kcal/mol was obtained from the single enthalpy point at 863.9°K observed by Taylor, Gardner and Smith. ΔHt° ($\beta \rightarrow \gamma$) = 4.673 kcal/mol was chosen in order to give good agreement with the equilibrium data of Marchal, loc. cit.

Beryllium Sulfate, Beta (β-$BeSO_4$)
(Crystal) GFW = 105.0738

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	20.482	18.943	18.943	.000	− 286.734	− 260.206	190.736
300	20.581	19.070	18.943	.038	− 286.739	− 260.041	189.440
400	24.828	25.611	19.806	2.322	− 287.415	− 251.093	137.191
500	27.810	31.487	21.566	4.961	− 287.680	− 241.976	105.767
600	30.310	36.778	23.667	7.866	− 287.684	− 232.831	84.808
700	32.980	41.648	25.892	11.029	− 287.449	− 223.680	69.836
800	35.800	46.235	28.151	14.467	− 300.027	− 215.870	58.973
900	38.730	50.620	30.405	18.193	− 298.984	− 205.409	49.880
1000	41.690	54.859	32.640	22.220	− 297.692	− 195.076	42.634
1100	43.759	58.935	34.846	26.497	− 296.200	− 184.889	36.734
1200	45.222	62.808	37.017	30.950	− 294.576	− 174.839	31.843
1300	46.258	66.471	39.143	35.526	− 292.871	− 164.928	27.727
1400	46.984	69.927	41.219	40.190	− 291.118	− 155.154	24.221
1500	47.480	73.186	43.243	44.915	− 289.343	− 145.505	21.200
1600	47.802	76.262	45.211	49.680	− 290.319	− 135.895	18.562
1700	47.970	79.165	47.124	54.470	− 288.435	− 126.299	16.237
1800	48.000	81.908	48.981	59.269	− 286.562	− 116.817	14.183
1900	48.000	84.504	50.783	64.069	− 284.705	− 107.437	12.358
2000	48.000	86.966	52.531	68.869	− 282.864	− 98.158	10.726
2100	48.000	89.308	54.227	73.669	− 281.039	− 88.967	9.259
2200	48.000	91.540	55.873	78.469	− 279.233	− 79.860	7.933
2300	48.000	93.674	57.470	83.269	− 277.441	− 70.839	6.731

Sept. 30, 1966

BERYLLIUM SULFATE, BETA (β-$BeSO_4$) (CRYSTAL) GFW = 105.0738

$S^\circ_{298.15}$ = [18.943] gibbs/mol

Tt_1 = 863°K

Tt_2 = 908°K

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = [-286.734] kcal/mol

ΔHt°_1 = [0.266] kcal/mol

ΔHt°_2 = [4.673] kcal/mol

<u>Heat of Formation</u>.

The heat of formation was calculated from that of the alpha phase by adding ΔHt°_1, since the heat capacities of both phases are assumed the same.

<u>Heat Capacity and Entropy</u>.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

<u>Transition Data</u>.

See alpha phase.

Beryllium Sulfate, Gamma (γ -$BeSO_4$)

(Crystal) GFW = 105.0738

T, °K	gibbs/mol Cp°	 S°	 −(G°−H°298)/T	kcal/mol H°−H°298	 ΔHf°	 ΔGf°	Log Kp
100							
200							
298	20.482	24.088	24.088	.000	− 282.061	− 257.067	188.435
300	20.581	24.215	24.088	.038	− 282.066	− 256.912	187.160
400	24.828	30.756	24.951	2.322	− 282.742	− 248.478	135.762
500	27.810	36.632	26.711	4.961	− 283.007	− 239.875	104.849
600	30.310	41.923	28.812	7.866	− 283.011	− 231.245	84.231
700	32.980	46.793	31.037	11.029	− 282.776	− 222.608	69.501
800	35.800	51.380	33.296	14.467	− 295.354	− 215.313	58.821
900	38.730	55.765	35.550	18.193	− 294.311	− 205.367	49.870
1000	41.690	60.004	37.785	22.220	− 293.019	− 195.548	42.737
1100	43.759	64.080	39.991	26.497	− 291.527	− 185.875	36.930
1200	45.222	67.953	42.162	30.950	− 289.903	− 176.340	32.116
1300	46.258	71.616	44.288	35.526	− 288.198	− 166.944	28.066
1400	46.984	75.072	46.364	40.190	− 286.445	− 157.684	24.616
1500	47.480	78.331	48.388	44.915	− 284.670	− 148.549	21.644
1600	47.802	81.407	50.356	49.680	− 285.646	− 139.454	19.048
1700	47.970	84.310	52.269	54.470	− 283.762	− 130.372	16.761
1800	48.000	87.053	54.126	59.269	− 281.889	− 121.405	14.741
1900	48.000	89.649	55.928	64.069	− 280.032	− 112.539	12.945
2000	48.000	92.111	57.676	68.869	− 278.191	− 103.775	11.340
2100	48.000	94.453	59.372	73.669	− 276.366	− 95.098	9.897
2200	48.000	96.685	61.018	78.469	− 274.560	− 86.506	8.594
2300	48.000	98.819	62.615	83.269	− 272.768	− 77.999	7.412

Sept. 30, 1966

BERYLLIUM SULFATE, GAMMA (γ- $BeSO_4$) (CRYSTAL) GFW = 105.0738

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ =[24.088]gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-282.06] kcal/mol

Tt_1 = 863°K

ΔHt°_1 = [0.266] kcal/mol

Tt_2 = 908°K

ΔHt°_2 = [4.673] kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the beta phase by adding ΔHt°_2, since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

See alpha phase.

Beryllium Tungstate ($BeWO_4$)

(Crystal) GFW = 256.8598

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol -(G°-H°298)/T	kcal/mol H°-H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	23.250	21.120	21.120	.000	-361.700	-335.769	246.125
300	23.350	21.264	21.120	.043	-361.701	-335.608	244.490
400	27.000	28.508	22.083	2.570	-361.624	-326.916	178.619
500	29.520	34.816	24.013	5.401	-361.360	-318.266	139.114
600	31.390	40.370	26.286	8.451	-360.973	-309.682	112.801
700	32.820	45.318	28.658	11.662	-360.511	-301.169	94.029
800	34.150	49.788	31.024	15.011	-359.986	-292.729	79.970
900	35.400	53.883	33.339	18.489	-359.395	-284.355	69.051
1000	36.570	57.674	35.586	22.088	-358.744	-276.050	60.331
1100	37.700	61.213	37.756	25.802	-358.036	-267.816	53.210
1200	38.780	64.539	39.851	29.626	-357.272	-259.646	47.288
1300	39.830	67.685	41.872	33.557	-356.453	-251.543	42.288
1400	40.900	70.676	43.824	37.593	-355.578	-243.508	38.013
1500	41.930	73.533	45.710	41.735	-354.646	-235.534	34.317
1600	43.000	76.273	47.535	45.981	-356.412	-227.546	31.081
1700	44.050	78.911	49.303	50.334	-355.247	-219.526	28.222
1800	45.100	81.459	51.019	54.791	-354.008	-211.579	25.689
1900	46.150	83.926	52.687	59.354	-352.691	-203.703	23.431
2000	47.200	86.319	54.309	64.021	-351.297	-195.897	21.407

June 30, 1963; Mar. 31, 1967

BERYLLIUM TUNGSTATE ($BeWO_4$) (CRYSTAL) GFW = 256.8598

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [21.12 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-361.7 ± 15] kcal/mol

Tm = Unknown

ΔHm° = Unknown

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(BeWO_4,c) = -361.7$ kcal/mol, is calculated from $\Delta Hr^\circ_{298} = -17.1$ kcal/mol for $BeO(c) + WO_3(c) \rightarrow BeWO_4(c)$. The value of ΔHr°_{298} is assumed to be the same as that for $MgO(c) + WO_3(c) \rightarrow MgWO_4(c)$, using -143.7, -143.1, -201.5 and -362.3 kcal/mol for the heats of formation of MgO(c), BeO(c), $WO_3(c)$ and $MgWO_4(c)$, respectively.

Heat Capacity and Entropy.

Heat capacities are estimated by comparison with those of $CaWO_4(c)$[1], BeO(c)[2], and CaO(c)[3].

The entropy, $S^\circ_{298} = 21.12$ eu, is calculated from $\Delta S^\circ_{298} = -0.4$ eu for $BeO(c) + WO_3(c) \rightarrow BeWO_4(c)$. The value of ΔS°_{298} is assumed to be the same as that for $MgO(c) + WO_3(c) \rightarrow MgWO_4(c)$, using 6.44, 3.38, 18.14 and 24.18 eu for MgO(c), BeO(c), $WO_3(c)$ and $MgWO_4(c)$, respectively.

References.

1. R. A. Yakovleva and T. N. Rezukhina, Russ. J. Phys. Chem. (English Transl.) <u>34</u>, 390 (1960).
2. JANAF BeO table (Sept. 30, 1965).
3. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

Beryllium Dichloride, Dimeric $((BeCl_2)_2)$

(Ideal Gas) Mol. Wt. = 159.8364

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 6.048	- 179.724	- 179.724	INFINITE
100	18.636	65.446	113.638	- 4.819	- 179.917	- 177.398	387.684
200	24.903	80.650	93.599	- 2.590	- 179.406	- 175.069	191.297
298	27.574	91.150	91.150	.000	- 179.000	- 173.041	126.836
300	27.610	91.321	91.151	.051	- 178.993	- 173.003	126.027
400	29.054	99.481	92.254	2.891	- 178.691	- 171.055	93.456
500	29.890	106.062	94.379	5.842	- 178.454	- 169.173	73.942
600	30.406	111.561	96.797	8.859	- 178.259	- 167.336	60.949
700	30.743	116.275	99.251	11.917	- 178.101	- 165.529	51.678
800	30.973	120.396	101.642	15.004	- 177.976	- 163.744	44.731
900	31.136	124.054	103.933	18.110	- 177.884	- 161.969	39.329
1000	31.256	127.342	106.112	21.230	- 177.832	- 160.206	35.011
1100	31.346	130.325	108.180	24.360	- 177.824	- 158.443	31.478
1200	31.416	133.056	110.140	27.498	- 177.864	- 156.681	28.534
1300	31.471	135.572	112.001	30.643	- 177.947	- 154.911	26.042
1400	31.514	137.906	113.769	33.792	- 178.078	- 153.136	23.904
1500	31.550	140.082	115.452	36.945	- 178.257	- 151.350	22.051
1600	31.579	142.119	117.055	40.102	- 183.994	- 149.391	20.405
1700	31.604	144.034	118.587	43.261	- 184.039	- 147.224	18.926
1800	31.624	145.841	120.051	46.422	- 184.096	- 145.059	17.612
1900	31.642	147.552	121.454	49.586	- 184.162	- 142.887	16.435
2000	31.656	149.175	122.800	52.751	- 184.243	- 140.713	15.376
2100	31.669	150.720	124.093	55.917	- 184.333	- 138.536	14.417
2200	31.680	152.193	125.337	59.084	- 184.438	- 136.352	13.545
2300	31.690	153.602	126.535	62.253	- 184.553	- 134.160	12.748
2400	31.699	154.951	127.691	65.422	- 184.682	- 131.966	12.017
2500	31.706	156.245	128.808	68.593	- 184.827	- 129.770	11.344
2600	31.713	157.488	129.887	71.764	- 184.982	- 127.559	10.722
2700	31.719	158.685	130.932	74.935	- 185.151	- 125.349	10.146
2800	31.724	159.839	131.944	78.107	- 327.395	- 120.914	9.437
2900	31.729	160.952	132.925	81.280	- 327.088	- 113.544	8.556
3000	31.734	162.028	133.877	84.453	- 326.791	- 106.189	7.735
3100	31.738	163.069	134.802	87.627	- 326.501	- 98.847	6.968
3200	31.741	164.076	135.701	90.801	- 326.219	- 91.499	6.249
3300	31.744	165.053	136.576	93.975	- 325.949	- 84.168	5.574
3400	31.747	166.001	137.428	97.150	- 325.688	- 76.846	4.939
3500	31.750	166.921	138.257	100.324	- 325.440	- 69.537	4.342
3600	31.753	167.816	139.066	103.500	- 325.202	- 62.222	3.777
3700	31.755	168.686	139.855	106.675	- 324.979	- 54.923	3.244
3800	31.757	169.533	140.625	109.851	- 324.769	- 47.632	2.739
3900	31.759	170.358	141.376	113.026	- 324.574	- 40.334	2.260
4000	31.761	171.162	142.111	116.202	- 324.396	- 33.052	1.806
4100	31.763	171.946	142.829	119.379	- 324.231	- 25.776	1.374
4200	31.764	172.711	143.532	122.555	- 324.085	- 18.497	.962
4300	31.766	173.459	144.219	125.731	- 323.955	- 11.220	.570
4400	31.767	174.189	144.892	128.908	- 323.844	- 3.942	.196
4500	31.768	174.903	145.551	132.085	- 323.753	3.320	- .161
4600	31.769	175.601	146.197	135.262	- 323.680	10.588	- .503
4700	31.771	176.285	146.829	138.439	- 323.627	17.851	- .830
4800	31.772	176.953	147.450	141.616	- 323.596	25.119	- 1.144
4900	31.773	177.609	148.059	144.793	- 323.585	32.385	- 1.444
5000	31.774	178.250	148.656	147.970	- 323.594	39.656	- 1.733
5100	31.774	178.880	149.243	151.148	- 323.624	46.921	- 2.011
5200	31.775	179.497	149.819	154.325	- 323.677	54.181	- 2.277
5300	31.776	180.102	150.384	157.503	- 323.755	61.449	- 2.534
5400	31.777	180.696	150.940	160.680	- 323.854	68.716	- 2.781
5500	31.777	181.279	151.487	163.858	- 323.976	75.990	- 3.019
5600	31.778	181.852	152.024	167.036	- 324.120	83.258	- 3.249
5700	31.779	182.414	152.552	170.214	- 324.288	90.535	- 3.471
5800	31.779	182.967	153.072	173.392	- 324.478	97.826	- 3.686
5900	31.780	183.510	153.583	176.570	- 324.694	105.097	- 3.893
6000	31.780	184.044	154.086	179.748	- 324.932	112.384	- 4.093

Dec. 31, 1960; June 30, 1965

BERYLLIUM DICHLORIDE, DIMERIC (Be_2Cl_4) (IDEAL GAS) MOL. WT. = 159.8364

Point Group $[D_{2h}]$

$S^\circ_{298.15}$ = [91.15] cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-180] kcal. mole⁻¹

$\Delta H^\circ_{f\ 298.15}$ = [-179] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹	ω, cm.⁻¹	ω, cm.⁻¹
[220](1)	[185](1)	[250](1)
[110](1)	[100](1)	[200](1)
[180](1)	860 (1)	[400](1)
[105](1)	[300](1)	640 (1)

Bond Distance: Be-Cl = [1.7]Å

Be-Cl' (in ring) = [1.8]Å

Bond Angle: Cl'-Be-Cl' (in ring) = [88°]

Cl'-Be-Cl = [136°]

σ = 4

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.62616 x 10^{-112} g.³ cm.⁶

Heat of Formation.

The heat of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was ~5% at 500°K. as reported by D. L. Hildenbrand, L. P. Theard, E. Murad and F. Ju, Aeronutronic Div. of Philco Corp., Report U-3068, April 1965 under contract AF 04(611)-8523, giving an effective K_p = 5.5 x 10^{-4} for $2BeCl_2(g) \rightarrow Be_2Cl_4$ at 500°K.

Heat Capacity and Entropy.

The structure was assumed planar with a D_{2h} symmetry, the bond lengths were estimated from the values for $BeCl_2$ (g), a lengthening being assumed in the ring. The frequencies were estimated using K_2Cl_2 as a basis for the ring vibrations. Two polymeric frequencies had been observed by A. Snelson, IIT Research Institute, Report No. IITRI-C6013-4, May 1964, under Contract No. DA-31-124-ARO(D)-111. These were observed in matrix isolated $BeCl_2$ gas and were ascribed to polymeric species on account of their warm up behavior. They are here assigned to the B_{3u} asymmetric stretching mode and the B_{1u} symmetric out of plane wag of the non ring chlorines. The order of the frequencies listed above is arbitrary and not related to their specie types. The individual moments of inertia are: I_A = 18.396 x 10^{-39} g. cm.², I_B = 110.638 x 10^{-39} g. cm.² and I_C = 129.034 g. cm.²

Diberyllium Oxide Difluoride (Be_2OF_2)

(Ideal Gas) GFW = 72.0206

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.964	- 287.780	- 287.780	INFINITE
100	11.386	55.324	85.736	- 3.041	- 287.929	- 287.290	627.872
200	15.661	64.654	73.005	- 1.670	- 287.874	- 286.669	313.257
298	18.200	71.415	71.415	.000	- 287.900	- 286.083	209.704
300	18.239	71.528	71.415	.034	- 287.901	- 286.072	208.403
400	20.032	77.034	72.154	1.952	- 287.986	- 285.450	155.962
500	21.344	81.653	73.604	4.024	- 288.094	- 284.804	124.488
600	22.307	85.634	75.285	6.209	- 288.203	- 284.135	103.496
700	23.019	89.129	77.018	8.477	- 288.319	- 283.448	88.497
800	23.550	92.239	78.730	10.807	- 288.444	- 282.746	77.243
900	23.952	95.037	80.389	13.183	- 288.585	- 282.024	68.485
1000	24.261	97.577	81.983	15.594	- 288.752	- 281.286	61.475
1100	24.503	99.901	83.508	18.033	- 288.953	- 280.530	55.736
1200	24.695	102.042	84.964	20.493	- 289.192	- 279.754	50.950
1300	24.849	104.025	86.355	22.971	- 289.470	- 278.956	46.897
1400	24.974	105.871	87.684	25.462	- 289.789	- 278.137	43.419
1500	25.078	107.598	88.954	27.965	- 290.153	- 277.292	40.401
1600	25.164	109.219	90.171	30.477	- 296.072	- 276.264	37.736
1700	25.237	110.747	91.337	32.997	- 296.297	- 275.019	35.356
1800	25.298	112.191	92.456	35.524	- 296.533	- 273.762	33.239
1900	25.351	113.560	93.531	38.057	- 296.778	- 272.489	31.343
2000	25.396	114.862	94.565	40.594	- 297.034	- 271.206	29.636
2100	25.435	116.102	95.561	43.136	- 297.300	- 269.908	28.090
2200	25.469	117.286	96.522	45.681	- 297.580	- 268.597	26.683
2300	25.500	118.419	97.450	48.229	- 297.871	- 267.270	25.396
2400	25.526	119.505	98.346	50.781	- 298.174	- 265.933	24.216
2500	25.550	120.547	99.213	53.334	- 298.494	- 264.586	23.130
2600	25.570	121.550	100.053	55.890	- 298.823	- 263.221	22.126
2700	25.589	122.515	100.867	58.448	- 299.163	- 261.843	21.195
2800	25.606	123.446	101.657	61.008	- 441.575	- 258.241	20.157
2900	25.621	124.345	102.424	63.570	- 441.438	- 251.691	18.968
3000	25.635	125.214	103.169	66.132	- 441.309	- 245.155	17.860
3100	25.647	126.054	103.894	68.696	- 441.183	- 238.621	16.823
3200	25.658	126.869	104.599	71.262	- 441.064	- 232.085	15.851
3300	25.669	127.658	105.286	73.828	- 440.953	- 225.554	14.938
3400	25.678	128.425	105.956	76.395	- 440.853	- 219.031	14.079
3500	25.687	129.169	106.608	78.964	- 440.759	- 212.509	13.270
3600	25.695	129.893	107.245	81.533	- 440.676	- 205.983	12.505
3700	25.702	130.597	107.867	84.103	- 440.605	- 199.469	11.782
3800	25.709	131.283	108.474	86.673	- 440.547	- 192.953	11.097
3900	25.715	131.951	109.067	89.244	- 440.501	- 186.438	10.448
4000	25.721	132.602	109.648	91.816	- 440.469	- 179.925	9.831
4100	25.726	133.237	110.215	94.388	- 440.454	- 173.416	9.244
4200	25.731	133.857	110.771	96.961	- 440.452	- 166.902	8.685
4300	25.736	134.462	111.315	99.535	- 440.467	- 160.378	8.151
4400	25.740	135.054	111.848	102.108	- 440.503	- 153.869	7.643
4500	25.744	135.633	112.370	104.683	- 440.556	- 147.358	7.157
4600	25.748	136.199	112.882	107.257	- 440.630	- 140.843	6.692
4700	25.751	136.752	113.384	109.832	- 440.724	- 134.324	6.246
4800	25.755	137.294	113.876	112.408	- 440.839	- 127.797	5.819
4900	25.758	137.826	114.360	114.983	- 440.976	- 121.280	5.409
5000	25.761	138.346	114.834	117.559	- 441.135	- 114.748	5.016
5100	25.764	138.856	115.300	120.135	- 441.320	- 108.221	4.638
5200	25.766	139.356	115.758	122.712	- 441.526	- 101.691	4.274
5300	25.769	139.847	116.208	125.289	- 441.759	- 95.147	3.923
5400	25.771	140.329	116.650	127.866	- 442.015	- 88.615	3.586
5500	25.773	140.802	117.085	130.443	- 442.297	- 82.066	3.261
5600	25.776	141.266	117.513	133.020	- 442.604	- 75.510	2.947
5700	25.777	141.723	117.933	135.598	- 442.936	- 68.953	2.644
5800	25.779	142.171	118.347	138.176	- 443.292	- 62.380	2.351
5900	25.781	142.612	118.755	140.754	- 443.676	- 55.822	2.068
6000	25.783	143.045	119.156	143.332	- 444.085	- 49.246	1.794

June 30, 1966

DIBERYLLIUM OXIDE DIFLUORIDE (Be_2OF_2) (IDEAL GAS) GFW = 72.0206

Point Group $[C_{2v}]$

$S^\circ_{298.15}$ = [71.4] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -287.8 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -287.9 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[1200](1)	[1500](1)
[600](1)	[900](1)
[400](1)	[300](1)
[100](1)	[300](1)
[300](1)	

Bond Distance: Be-O = [1.33] Å Be-F = [1.43] Å

Bond Angle: O-Be-F = [180]° Be-O-Be = [150]° σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.5543474] X 10^{-114} g^3 cm^6

Heat of Formation.

J. Efimenko, NBS Report 8186, Jan. 1964, has studied mass spectrometrically the reaction $BeO(c) + BeF_2(g) \rightarrow Be_2OF_2(g)$ and also reported two sets of equilibrium constants. Using JANAF thermodynamic functions, the heat of reaction has been calculated from those reported equilibrium constants by the second law and the third law methods.

	Number of Measurements	Temperature Range (°K)	ΔHr°_{298} kcal/mol 2nd law value	ΔHr°_{298} kcal/mol 3rd law value	3rd law Drift (eu)
1st Set	13	1570-1891	41.448 ± 3.04	41.981	0.408 ± 1.726
2nd Set	21*	1872-2195	42.553 ± 0.70	42.714	0.015 ± 0.359

*Four points are rejected due to failure of statistical test.

A weighted average value, ΔHr°_{298} = 42.70 kcal/mol, was chosen for the heat of reaction. The heat of formation, ΔHf°_{298} (Be_2OF_2, g) = -287.9 ± 5 kcal/mol, was calculated from the selected heat of reaction, using ΔHf°_{298} (BeO, c) = 143.1 kcal/mol and ΔHf°_{298} (BeF_2, g) = -187.5 kcal/mol.

Heat Capacity and Entropy.

The adopted "V" shape molecular structure with nine fundamental vibrational frequencies was obtained from an estimation by D. E. Mann, NBS Report 8186, Jan. 1, 1964. The bond distances Be-O and Be-F were estimated to be the same as those in BeO(g) and $BeF_2(g)$, respectively. The three principal moments of inertia are I_A = 1.0103 X 10^{-39}, I_B = 49.7805 X 10^{-39} and I_C = 50.7908 X 10^{-39} g cm^2.

Diberyllium Oxide (Be$_2$O)

(Ideal Gas) Mol. Wt. = 34.026

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.372	-15.399	-15.399	INFINITE
100	7.110	43.794	60.544	-1.675	-15.078	-17.355	37.928
200	8.493	49.111	53.610	-.900	-14.919	-19.714	21.541
298	9.788	52.754	52.754	.000	-15.000	-22.064	16.172
300	9.809	52.815	52.754	.018	-15.002	-22.107	16.104
400	10.840	55.783	53.152	1.053	-15.201	-24.448	13.357
500	11.656	58.294	53.936	2.179	-15.448	-26.731	11.683
600	12.292	60.477	54.848	3.378	-15.711	-28.963	10.549
700	12.783	62.411	55.793	4.633	-15.989	-31.150	9.725
800	13.161	64.143	56.730	5.931	-16.280	-33.297	9.096
900	13.454	65.711	57.642	7.262	-16.590	-35.405	8.597
1000	13.683	67.141	58.522	8.619	-16.926	-37.477	8.190
1100	13.865	68.454	59.366	9.997	-17.296	-39.514	7.850
1200	14.011	69.667	60.174	11.391	-17.704	-41.517	7.561
1300	14.129	70.793	60.948	12.798	-18.149	-43.483	7.310
1400	14.226	71.844	61.690	14.216	-18.635	-45.415	7.089
1500	14.306	72.828	62.400	15.643	-19.164	-47.311	6.893
1600	14.374	73.754	63.081	17.077	-25.246	-49.011	6.694
1700	14.430	74.627	63.734	18.517	-25.633	-50.485	6.490
1800	14.479	75.453	64.363	19.963	-26.028	-51.935	6.305
1900	14.520	76.237	64.967	21.413	-26.432	-53.364	6.138
2000	14.556	76.983	65.550	22.867	-26.844	-54.772	5.985
2100	14.587	77.694	66.111	24.324	-27.265	-56.157	5.844
2200	14.614	78.373	66.653	25.784	-27.697	-57.523	5.714
2300	14.638	79.023	67.177	27.247	-28.138	-58.866	5.593
2400	14.659	79.647	67.684	28.711	-28.591	-60.191	5.481
2500	14.677	80.245	68.174	30.178	-29.056	-61.502	5.376
2600	14.694	80.821	68.650	31.647	-29.529	-62.787	5.277
2700	14.709	81.376	69.111	33.117	-30.012	-64.057	5.185
2800	14.722	81.911	69.558	34.589	-172.566	-63.094	4.924
2900	14.734	82.428	69.993	36.061	-172.567	-59.181	4.460
3000	14.745	82.928	70.416	37.535	-172.574	-55.272	4.026
3100	14.755	83.412	70.828	39.010	-172.583	-51.367	3.621
3200	14.764	83.880	71.228	40.486	-172.596	-47.451	3.241
3300	14.772	84.335	71.619	41.963	-172.616	-43.541	2.883
3400	14.780	84.776	71.999	43.441	-172.644	-39.631	2.547
3500	14.787	85.204	72.370	44.919	-172.677	-35.721	2.230
3600	14.793	85.621	72.733	46.398	-172.719	-31.802	1.931
3700	14.799	86.026	73.086	47.878	-172.770	-27.891	1.647
3800	14.804	86.421	73.432	49.358	-172.833	-23.974	1.379
3900	14.809	86.806	73.770	50.839	-172.904	-20.052	1.124
4000	14.814	87.181	74.101	52.320	-172.989	-16.136	.882
4100	14.818	87.547	74.424	53.801	-173.087	-12.217	.651
4200	14.822	87.904	74.741	55.283	-173.197	-8.291	.431
4300	14.826	88.253	75.051	56.766	-173.323	-4.357	.221
4400	14.830	88.593	75.355	58.249	-173.465	-.429	.021
4500	14.833	88.927	75.653	59.732	-173.625	3.505	-.170
4600	14.836	89.253	75.945	61.215	-173.803	7.443	-.354
4700	14.839	89.572	76.232	62.699	-173.998	11.382	-.529
4800	14.841	89.884	76.513	64.183	-174.214	15.332	-.698
4900	14.844	90.190	76.789	65.667	-174.448	19.282	-.860
5000	14.846	90.490	77.060	67.152	-174.703	23.243	-1.016
5100	14.849	90.784	77.326	68.637	-174.980	27.205	-1.166
5200	14.851	91.073	77.588	70.122	-175.279	31.163	-1.310
5300	14.853	91.356	77.845	71.607	-175.601	35.143	-1.449
5400	14.855	91.633	78.098	73.092	-175.944	39.118	-1.583
5500	14.856	91.906	78.346	74.578	-176.311	43.104	-1.713
5600	14.858	92.174	78.591	76.063	-176.701	47.097	-1.838
5700	14.860	92.437	78.831	77.549	-177.113	51.100	-1.959
5800	14.861	92.695	79.068	79.035	-177.550	55.115	-2.077
5900	14.863	92.949	79.301	80.521	-178.011	59.122	-2.190
6000	14.864	93.199	79.531	82.008	-178.494	63.142	-2.300

Sept. 30, 1963.

DIBERYLLIUM OXIDE (Be$_2$O) (IDEAL GAS) MOL. WT. = 34.026

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [52.7] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [3]

$\Delta H^\circ_{f\ 0}$ = -15.4 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -15 ± 10 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	g_i
[1100]	(1)
[500]	(2)
[1600]	(1)

Bond distance: Be-O = [1.4] Å

Bond Angle: Be-O-Be = [180°]

σ = 2

Moment of Inertia: I_A = 5.8656 X 10^{-39} g. cm.^{2}

Heat of Formation.

D. L. Hildenbrand, L. P. Theard, and F. Ju, Ford Motor Co., Aeronutronic Division, Third Quarterly Technical Report U-2231, April-June 1963, have reported the heat of formation. Equilibrium constants were determined in a mass spectrometer for the reactions $2BeO(c) \rightarrow Be_2O(g) + O(g)$ - (1) $2BeO(g) \rightarrow Be_2O(g) + O(g)$ - (2) and $Be_2O_2(g) \rightarrow Be_2O(g) + O(g)$ - (3). Using our own free energy functions we obtain $\Delta H^\circ_{f\ 298}$ $Be_2O(g)$ = -13.1, -14.5, and -16.7 kcal. mole^{-1}, all ± 10; the 2nd law treatment of reaction 1 gives -18.3 ± 10 kcal. mole^{-1}. We adopt a median value -15 ± 10 kcal. mole^{-1}.

Heat Capacity and Entropy.

A. Buchler, J. L. Stauffer, W. Klemperer and C. Wharton, A. D. Little, Inc., Interim Technical Report No. 5, 1963, have shown Li_2O to be linear. Also A. D. Walsh, J. Chem. Soc. London 2269 (1953) preducted that AB_2 molecules with less than 16 bonding electrons would be linear. Thus Be_2O was taken to be linear and symmetrical, with a Be-O bond length of 1.4 Å, which is a little longer than in BeO(g). The vibrational frequencies were estimated by taking ω_3 to be larger than the stretch in BeO(g) and then calculating ω_1 from the valence force field assumption. The bending force constant was estimated as 1/20th of the stretching force constant. The two outermost electrons were considered unpaired and so gave a $^3\Sigma$ ground state.

Beryllium Oxide, Dimeric (Be_2O_2)

(Ideal Gas) Mol. Wt. = 50.026

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.726	-97.716	-97.716	INFINITE
100	8.089	48.886	68.186	-1.930	-97.652	-98.362	214.961
200	9.670	54.897	60.166	-1.054	-97.732	-99.061	108.243
298	11.792	59.156	59.156	.000	-98.000	-99.667	73.054
300	11.831	59.229	59.156	.022	-98.005	-99.677	72.611
400	13.689	62.897	59.643	1.302	-98.314	-100.188	54.738
500	15.105	66.112	60.622	2.745	-98.610	-100.621	43.979
600	16.146	68.963	61.779	4.310	-98.884	-100.998	36.787
700	16.911	71.512	62.991	5.965	-99.151	-101.329	31.635
800	17.477	73.809	64.202	7.686	-99.418	-101.623	27.761
900	17.904	75.893	65.387	9.456	-99.696	-101.881	24.739
1000	18.231	77.797	66.534	11.263	-99.996	-102.107	22.314
1100	18.486	79.547	67.639	13.099	-100.327	-102.303	20.325
1200	18.687	81.165	68.699	14.958	-100.694	-102.467	18.661
1300	18.849	82.667	69.717	16.836	-101.097	-102.598	17.247
1400	18.980	84.069	70.692	18.727	-101.542	-102.698	16.031
1500	19.088	85.382	71.628	20.631	-102.029	-102.765	14.972
1600	19.178	86.617	72.527	22.544	-108.071	-102.639	14.019
1700	19.254	87.782	73.390	24.466	-108.417	-102.289	13.149
1800	19.318	88.885	74.221	26.395	-108.773	-101.918	12.374
1900	19.372	89.930	75.020	28.329	-109.140	-101.527	11.678
2000	19.419	90.925	75.791	30.269	-109.516	-101.119	11.049
2100	19.460	91.874	76.534	32.213	-109.903	-100.688	10.478
2200	19.496	92.780	77.252	34.161	-110.303	-100.240	9.957
2300	19.527	93.647	77.947	36.112	-110.714	-99.771	9.480
2400	19.555	94.479	78.618	38.066	-111.138	-99.284	9.041
2500	19.579	95.278	79.269	40.023	-111.577	-98.787	8.636
2600	19.601	96.046	79.899	41.982	-112.026	-98.262	8.259
2700	19.620	96.786	80.511	43.943	-112.487	-97.724	7.910
2800	19.637	97.500	81.105	45.906	-255.021	-94.954	7.411
2900	19.653	98.189	81.682	47.870	-255.005	-89.233	6.724
3000	19.667	98.856	82.244	49.836	-254.996	-83.519	6.084
3100	19.680	99.501	82.790	51.804	-254.991	-77.808	5.485
3200	19.692	100.126	83.322	53.772	-254.993	-72.087	4.923
3300	19.702	100.732	83.841	55.742	-255.003	-66.372	4.395
3400	19.712	101.320	84.346	57.713	-255.023	-60.657	3.899
3500	19.721	101.892	84.839	59.684	-255.050	-54.944	3.431
3600	19.729	102.448	85.321	61.657	-255.087	-49.220	2.988
3700	19.737	102.988	85.791	63.630	-255.136	-43.504	2.570
3800	19.744	103.515	86.251	65.604	-255.197	-37.783	2.173
3900	19.750	104.028	86.700	67.579	-255.268	-32.058	1.796
4000	19.756	104.528	87.139	69.554	-255.355	-26.338	1.439
4100	19.762	105.016	87.569	71.530	-255.456	-20.615	1.099
4200	19.767	105.492	87.990	73.507	-255.570	-14.885	.775
4300	19.772	105.957	88.403	75.483	-255.702	-9.145	.465
4400	19.776	106.412	88.807	77.461	-255.851	-3.413	.170
4500	19.781	106.856	89.203	79.439	-256.018	2.326	-.113
4600	19.784	107.291	89.592	81.417	-256.205	8.069	-.383
4700	19.788	107.717	89.973	83.396	-256.410	13.813	-.642
4800	19.792	108.133	90.347	85.375	-256.636	19.569	-.891
4900	19.795	108.541	90.714	87.354	-256.882	25.322	-1.129
5000	19.798	108.941	91.075	89.334	-257.149	31.089	-1.359
5100	19.801	109.333	91.429	91.314	-257.440	36.858	-1.579
5200	19.804	109.718	91.777	93.294	-257.752	42.621	-1.791
5300	19.806	110.095	92.119	95.274	-258.089	48.410	-1.996
5400	19.809	110.465	92.455	97.255	-258.447	54.189	-2.193
5500	19.811	110.829	92.786	99.236	-258.829	59.985	-2.383
5600	19.813	111.186	93.111	101.217	-259.236	65.783	-2.567
5700	19.815	111.537	93.432	103.199	-259.664	71.594	-2.745
5800	19.817	111.881	93.747	105.180	-260.118	77.418	-2.917
5900	19.819	112.220	94.057	107.162	-260.596	83.233	-3.083
6000	19.821	112.553	94.362	109.144	-261.097	89.062	-3.244

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE DIMERIC (Be_2O_2) (IDEAL GAS) MOL. WT. = 50.026

Point Group $[V_h]$

$S^\circ_{298.15}$ = [59.156] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0} = -97.7 \pm 12$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -98 \pm 12$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[1120] (1)	[460] (1)
[630] (1)	[920] (1)
[760] (1)	[1480] (1)

Bond Distance: Be-O = [1.63] Å

σ = 4

Bond Angle: Be-O-Be = [90°] O-Be-O = [90°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.0957] X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) studied the temperature dependence of the $(BeO)_2^+$ ion in a mass spectrometer and obtained a second law heat of vaporization of 172 ± 8 kcal. mole^{-1} at 2150°K. No correction was made for fragmentation of higher polymers and this is reflected in the uncertainty. We adopted a heat of sublimation of 178 kcal. mole^{-1} in order to match more closely the equilibrium constant found by Chupka, et al. However, it was not possible to alter either the heat or entropy sufficiently to obtain exact agreement, the predicted pressure being too high by a factor of 20.

Heat Capacity and Entropy.

A planar ring configuration was assumed which has six vibrational frequencies of the type $2A_{1g}$, B_{1g}, B_{1u}, B_{2u}, and B_{3u}. These were estimated by comparison with $(LiO)_2$ for which values have been calculated by D. White, K. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, prepublication communication, July, 1963. It seems unlikely that any other structure than that of a ring is possible, as, in order to approach the observed equilibrium constant an even lower entropy is needed. A non-linear chain would have a higher entropy due to the change in symmetry number and the two odd electrons. A linear chain would have approximately the same entropy due to cancellation of opposite effects. The vibrational frequencies were also made as high as possible by normalizing them using B_{3u} equal to the BeO stretch in BeO(g). The bond length was taken as the sum of the covalent radii of O and Be, which is in general agreement with other polymeric structures which generally increase in bond length by 10-20% in going from monomer to polymer. The bond angle was chosen arbitrarily, however, changes in the angle would change the entropy less than 1 eu.

The individual moments of inertia were $I_A = 7.057$, $I_B = 3.976$, and $I_C = 11.033 \times 10^{-39}$ g. cm.^{2}

Beryllium Orthosilicate (Be_2SiO_4)

(Crystal) Mol. Wt. = 110.108

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.922	- 503.096	- 503.096	INFINITE
100	4.492	1.785	29.700	- 2.791	- 504.475	- 496.232	1084.462
200	14.444	7.946	17.172	- 1.845	- 505.446	- 487.581	532.778
298	22.840	15.342	15.342	.000	- 506.029	- 478.682	350.866
300	22.968	15.483	15.342	.042	- 506.036	- 478.512	348.579
400	28.860	22.946	16.320	2.651	- 506.235	- 469.299	256.401
500	32.730	29.819	18.343	5.738	- 506.168	- 460.066	201.085
600	35.650	36.054	20.784	9.162	- 505.911	- 450.868	164.221
700	37.970	41.732	23.377	12.848	- 505.515	- 441.725	137.906
800	39.680	46.920	26.000	16.735	- 505.016	- 432.647	118.188
900	40.810	51.662	28.592	20.763	- 504.464	- 423.631	102.867
1000	41.600	56.005	31.119	24.885	- 503.901	- 414.679	90.624
1100	42.150	59.996	33.566	29.074	- 503.350	- 405.784	80.618
1200	42.590	63.683	35.924	33.312	- 502.824	- 396.938	72.289
1300	42.934	67.106	38.192	37.588	- 502.328	- 388.133	65.248
1400	43.240	70.300	40.373	41.897	- 501.865	- 379.369	59.219
1500	43.472	73.291	42.469	46.233	- 501.440	- 370.636	53.999
1600	43.702	76.104	44.484	50.592	- 506.564	- 361.769	49.413
1700	43.930	78.760	46.423	54.973	- 518.089	- 352.628	45.331
1800	44.156	81.277	48.290	59.378	- 517.471	- 342.913	41.633
1900	44.380	83.671	50.090	63.804	- 516.854	- 333.234	38.329
2000	44.600	85.953	51.826	68.253	- 516.234	- 323.588	35.358
2100	44.812	88.134	53.504	72.724	- 515.612	- 313.968	32.673
2200	45.024	90.224	55.125	77.216	- 514.993	- 304.383	30.236
2300	45.236	92.230	56.695	81.729	- 514.371	- 294.822	28.013
2400	45.448	94.159	58.216	86.263	- 513.750	- 285.284	25.977
2500	45.660	96.019	59.692	90.818	- 513.132	- 275.784	24.108
2600	45.872	97.814	61.123	95.395	- 512.508	- 266.298	22.383
2700	46.084	99.549	62.515	99.993	- 511.883	- 256.841	20.789
2800	46.296	101.229	63.868	104.612	- 653.317	- 245.192	19.137
2900	46.508	102.857	65.184	109.252	- 652.186	- 230.630	17.380
3000	46.720	104.437	66.466	113.913	- 651.048	- 216.114	15.743

Sept. 30, 1961; June 30, 1965

BERYLLIUM ORTHOSILICATE (Be_2SiO_4) (CRYSTAL) MOL. WT. = 110.108

$\Delta H_f^\circ{}_0 = -503.1 \pm 7$ kcal. mole^{-1}

$S^\circ_{298.15} = 15.342 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = [-506.0 \pm 7]$ kcal. mole^{-1}

$T_m = 1833$°K.

Heat of Formation.

The $\Delta H_f^\circ{}_{298.15}$ was estimated from the $\Delta H_r^\circ{}_{298.15}$ of Mg, Ca and Ba oxides with SiO_2 given by K. K. Kelley in the report of investigations 5901, U. S. Department of the Interior, Bureau of Mines 1962, and from the $\Delta H_f^\circ{}_{298.15}$ of BeO(c) (Sept. 30, 1963) and SiO_2(c) (Dec. 31, 1962) in JANAF tables. The $\Delta H_r^\circ{}_{298.15} = 0 \pm 7$ kcal. mole^{-1} was estimated for the reaction $2BeO(c) + SiO_2(c) \rightarrow Be_2SiO_4(c)$.

Heat Capacity and Entropy.

At low temperatures C_p was used from K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). Above 298.15°K. C_p values were estimated by summation of the component oxides using JANAF tables, BeO (Sept. 30, 1963) and SiO_2 (Dec. 31, 1962). The entropy was calculated at 54.7°K. using the Debye and Planck-Einstein functions $D(\frac{422}{T}) + 2E(\frac{527}{T})$ given by K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). The value of $S^\circ_{54.7} = 13.59$ cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The incongruent melting point was taken from Kubaschewski and Evans, "Metallurgical Thermochemistry" 3rd edition, Pergamon Press., New York 1958.

Beryllium Nitride, Alpha (α -Be_3N_2)

(Crystal) GFW = 55.050

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.691	-138.815	-138.815	INFINITE
100	1.460	.441	17.011	-1.657	-139.504	-135.692	296.555
200	8.482	3.421	9.351	-1.186	-140.143	-131.623	143.831
298	15.382	8.157	8.157	.000	-140.600	-127.346	93.347
300	15.456	8.252	8.157	.029	-140.605	-127.264	92.711
400	20.180	13.393	8.826	1.827	-140.821	-122.778	67.083
500	23.306	18.254	10.232	4.011	-140.852	-118.260	51.691
600	25.458	22.704	11.946	6.455	-140.746	-113.749	41.433
700	26.989	26.750	13.776	9.082	-140.563	-109.265	34.114
800	28.105	30.431	15.632	11.839	-140.334	-104.810	28.633
900	28.930	33.791	17.465	14.693	-140.090	-100.382	24.376
1000	29.544	36.872	19.254	17.618	-139.859	-95.983	20.977
1100	30.000	39.710	20.986	20.596	-139.661	-91.604	18.200
1200	30.335	42.336	22.658	23.614	-139.511	-87.244	15.889
1300	30.575	44.774	24.266	26.660	-139.412	-82.892	13.935
1400	30.740	47.046	25.813	29.726	-139.375	-78.548	12.262
1500	30.843	49.171	27.300	32.806	-139.404	-74.204	10.811
1600	30.896	51.163	28.730	35.893	-147.770	-69.616	9.509
1700	30.908	53.037	30.105	38.983	-147.602	-64.739	8.323
1800	30.919	54.803	31.429	42.075	-147.453	-59.867	7.269
1900	30.930	56.475	32.703	45.167	-147.323	-55.004	6.327
2000	30.940	58.062	33.932	48.260	-147.212	-50.150	5.480
2100	30.949	59.572	35.117	51.355	-147.118	-45.300	4.714
2200	30.957	61.012	36.262	54.450	-147.043	-40.453	4.019
2300	30.965	62.388	37.368	57.546	-146.985	-35.605	3.383
2400	30.972	63.706	38.438	60.643	-146.943	-30.761	2.801
2500	30.979	64.971	39.474	63.741	-146.922	-25.927	2.267
2600	30.984	66.186	40.479	66.839	-146.915	-21.083	1.772
2700	30.989	67.355	41.452	69.938	-146.921	-16.241	1.315
2800	30.994	68.482	42.398	73.037	-360.034	-8.080	.631
2900	30.997	69.570	43.316	76.136	-359.317	4.483	-.338
3000	31.000	70.621	44.209	79.236	-358.608	17.013	-1.239

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1964; Mar. 31, 1967

BERYLLIUM NITRIDE, ALPHA (α-Be_3N_2) (CRYSTAL) GFW = 55.050

$\Delta Hf°_0$ = -138.8 ± 0.3 kcal/mol

$S°_{298.15}$ = 8.157 gibbs/mol

$\Delta Hf°_{298.15}$ = -140.6 ± 0.3 kcal/mol

Tm = 2473°K

ΔHm° = [30.9] kcal/mol

Heat of Formation.

P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, Trans. Faraday Soc. 62, 2719 (1966), have measured the heat of chlorination of α-Be_3N_2 to α-$BeCl_2$, and the heat of reaction of Be with ammonia. The chlorination reaction (A) $\alpha\text{-}Be_3N_2(c) + 3Cl_2(g) \rightarrow 3\ \alpha\text{-}BeCl_2(c) + N_2(g)$ had a $\Delta Hr°_{298}$ = -210.3 ± 1.1 kcal/mol, which, combined with the value of -117.1 ± 0.4 kcal/mol for α-$BeCl_2$ reported in the same paper, yields $\Delta Hf°_{298}(\alpha\text{-}Be_3N_2,c)$ = -141.0 ± 1.6 kcal/mol. Reaction (B) $3\ Be(c) + 2\ NH_3(g) = \alpha\text{-}Be_3N_2(c) + 3\ H_2(g)$ had a $\Delta Hr°_{298}$ = -214.6 ± 0.3 kcal/mol, which, combined with the JANAF value for $NH_3(g)$, yields $\Delta Hf°_{298}(\alpha\text{-}Be_3N_2,c)$ = -140.3 ± 0.3 kcal/mol. A weighted mean value of the above two determinations is adopted.

The decomposition $Be_3N_2(c) = 3\ Be(g) + N_2(g)$ has been studied by R. E. Yates, M. A. Greenbaum and M. Farber, J. Phys. Chem. 68, 2682 (1964), using the torsion effusion technique. The same decomposition has also been investigated by C. L. Hoenig, UCRL-7521, April 1964, using the Knudsen technique. An analysis of these data sets by 2nd and 3rd law methods is given below.

	Range		$\Delta Hr°_{298}$ kcal/mol		Drift	$^{**}\Delta Hf°_{298.15}$ Be_3N_2
Reference	°K	Points	2nd law	3rd law	eu	kcal/mol
Yates - 1	1478-1592	9*	364.5±5.9	374.00	6.0±3.8	-139.23
Yates - 2	1541-1652	15*	369.6±8.3	376.51	4.0±5.3	-141.74
Yates - 3	1438-1661	14	347.7±3.7	374.54	16.9±2.4	-139.77
Yates - 4	1450-1646	17*	366.7±8.9	375.28	4.8±5.7	-140.51
Yates	1473-1661	52*	358.9±5.1	375.41	10.3±3.3	-140.64
Hoenig - 1	1767-1946	14	355.8±3.3	377.77	11.9±1.8	-143.00
Hoenig - 2	1660-1891	10	395.0±5.6	378.69	-9.1±3.1	-143.92
Hoenig - 3	1648-1893	10	416.9±8.4	383.15	-19.5±4.6	-148.38

*Points rejected due to failure of statistical test.

**Calculated from 3rd law $\Delta Hr°_{298}$.

The data of Yates et al. are seen to be in good agreement with the adopted $\Delta Hf°_{298}$.

Heat Capacity and Entropy.

The low temperature heat capacity of α-Be_3N_2 has been measured, from 25° - 310°K, by B. H. Justice, The Dow Chemical Co., 1st Quarterly Report under Contract AF04611-67-C-0009, April 1967. These measurements are joined smoothly with the high temperature enthalpies reported by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 7587, July 1962. Above 1200°K the values were smoothly extrapolated to a limiting value of 6.2 gibbs/g-atom. The entropy at 298° was calculated by integration of the low temperature data based on S_{25} = 0.002 eu.

Melting Data.

See $Be_3N_2(l)$ for details.

Beryllium Nitride (Be_3N_2)

(Liquid) GFW = 55.050

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	32.000	9.425	9.425	.000	-116.400	-103.524	75.885
300	32.000	9.623	9.426	.059	-116.375	-103.444	75.359
400	32.000	18.829	10.681	3.259	-115.189	-99.320	54.266
500	32.000	25.969	13.051	6.459	-114.204	-95.469	41.730
600	32.000	31.804	15.705	9.659	-113.342	-91.805	33.440
700	32.000	36.736	18.366	12.859	-112.586	-88.278	27.561
800	32.000	41.009	20.935	16.059	-111.914	-84.852	23.181
900	32.000	44.779	23.379	19.259	-111.324	-81.505	19.792
1000	32.000	48.150	25.691	22.459	-110.818	-78.220	17.095
1100	32.000	51.200	27.873	25.659	-110.398	-74.980	14.897
1200	32.000	53.984	29.935	28.859	-110.066	-71.776	13.072
1300	32.000	56.546	31.885	32.059	-109.813	-68.596	11.532
1400	32.000	58.917	33.732	35.259	-109.642	-65.434	10.215
1500	32.000	61.125	35.485	38.459	-109.551	-62.281	9.074
1600	32.000	63.190	37.153	41.659	-117.804	-58.893	8.044
1700	32.000	65.130	38.742	44.859	-117.526	-55.221	7.099
1800	32.000	66.959	40.260	48.059	-117.269	-51.563	6.261
1900	32.000	68.689	41.711	51.259	-117.031	-47.918	5.512
2000	32.000	70.331	43.101	54.459	-116.813	-44.289	4.840
2100	32.000	71.892	44.435	57.659	-116.614	-40.667	4.232
2200	32.000	73.381	45.717	60.859	-116.434	-37.056	3.681
2300	32.000	74.803	46.951	64.059	-116.272	-33.447	3.178
2400	32.000	76.165	48.140	67.259	-116.127	-29.847	2.718
2500	32.000	77.471	49.288	70.459	-116.004	-26.259	2.296
2600	32.000	78.726	50.396	73.659	-115.895	-22.667	1.905
2700	32.000	79.934	51.468	76.859	-115.800	-19.083	1.545
2800	32.000	81.098	52.505	80.059	-328.812	-12.182	.951
2900	32.000	82.221	53.511	83.259	-327.994	-.883	.067
3000	32.000	83.306	54.486	86.459	-327.185	10.381	-.756
3100	32.000	84.355	55.433	89.659	-326.380	21.611	-1.524
3200	32.000	85.371	56.352	92.859	-325.580	32.833	-2.242
3300	32.000	86.356	57.247	96.059	-324.791	44.020	-2.915
3400	32.000	87.311	58.117	99.259	-324.011	55.184	-3.547
3500	32.000	88.238	58.964	102.459	-323.239	66.322	-4.141
3600	32.000	89.140	59.790	105.659	-322.481	77.447	-4.702
3700	32.000	90.017	60.595	108.859	-321.735	88.540	-5.230
3800	32.000	90.870	61.381	112.059	-321.006	99.620	-5.729
3900	32.000	91.701	62.148	115.259	-320.289	110.688	-6.203
4000	32.000	92.511	62.897	118.459	-319.592	121.724	-6.651

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1964; Mar. 31, 1967

BERYLLIUM NITRIDE (Be_3N_2) (LIQUID) GFW = 55.050

$S^\circ_{298.15}$ = [9.425] gibbs/mol

Tm = 2473°K

$\Delta Hf^\circ_{298.15}$ = [-116.4] kcal/mol

ΔHm° = [30.9] kcal/mol

Heat of Formation.

The heat of formation of $Be_3N_2(l)$ is calculated from ΔHf°_{298} $Be_2N_2(c)$ by adding ΔHm° and the difference between $H_{2473} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is estimated to be constant and slightly greater than the maximum for $Be_3N_2(c)$. The entropy at 298°K is estimated in a manner analogous to that of the heat of formation.

Melting Data.

The melting point was reported by F. Fichter and E. Brunner, Z. Anorg. Allgem. Chem. 93, 84 (1915). The heat of melting was calculated on the assumption that each g-atom contributed 2.5 gibbs to ΔSm°.

Beryllium Oxide, Trimeric (Be_3O_3)

(Ideal Gas) Mol. Wt. = 75.039

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.184	-250.668	-250.668	INFINITE
100	8.863	52.853	76.561	-2.371	-250.954	-249.972	546.287
200	11.980	59.926	66.588	-1.333	-251.350	-248.859	271.927
298	15.167	65.304	65.304	.000	-252.000	-247.515	181.425
300	15.226	65.398	65.305	.028	-252.012	-247.487	180.286
400	18.307	70.208	65.939	1.707	-252.717	-245.872	134.332
500	20.961	74.588	67.238	3.675	-253.357	-244.084	106.684
600	23.091	78.606	68.802	5.882	-253.909	-242.176	88.208
700	24.745	82.295	70.470	8.277	-254.397	-240.182	74.985
800	26.018	85.686	72.163	10.818	-254.838	-238.123	65.049
900	27.002	88.809	73.841	13.471	-255.257	-236.006	57.307
1000	27.770	91.696	75.484	16.212	-255.677	-233.844	51.104
1100	28.376	94.372	77.081	19.020	-256.119	-231.639	46.020
1200	28.861	96.863	78.627	21.883	-256.595	-229.394	41.776
1300	29.253	99.189	80.120	24.789	-257.110	-227.106	38.178
1400	29.573	101.369	81.561	27.731	-257.673	-224.779	35.088
1500	29.838	103.418	82.951	30.702	-258.288	-222.409	32.403
1600	30.060	105.351	84.291	33.697	-267.225	-219.759	30.016
1700	30.246	107.180	85.584	36.713	-267.612	-216.780	27.868
1800	30.405	108.913	86.832	39.745	-268.007	-213.779	25.955
1900	30.541	110.561	88.038	42.793	-268.411	-210.755	24.241
2000	30.658	112.130	89.204	45.853	-268.825	-207.713	22.697
2100	30.759	113.629	90.331	48.924	-269.250	-204.645	21.297
2200	30.848	115.062	91.423	52.004	-269.692	-201.559	20.022
2300	30.926	116.435	92.481	55.093	-270.146	-198.448	18.856
2400	30.995	117.752	93.507	58.189	-270.617	-195.317	17.785
2500	31.056	119.019	94.502	61.292	-271.108	-192.178	16.799
2600	31.111	120.238	95.469	64.400	-271.612	-189.004	15.886
2700	31.159	121.413	96.408	67.514	-272.131	-185.817	15.040
2800	31.203	122.547	97.321	70.632	-485.758	-179.289	13.993
2900	31.242	123.643	98.210	73.754	-485.558	-168.341	12.686
3000	31.278	124.702	99.076	76.880	-485.368	-157.407	11.467
3100	31.310	125.729	99.919	80.010	-485.183	-146.486	10.327
3200	31.340	126.723	100.741	83.142	-485.005	-135.556	9.258
3300	31.366	127.688	101.543	86.278	-484.840	-124.639	8.254
3400	31.391	128.625	102.326	89.415	-484.689	-113.728	7.310
3500	31.413	129.535	103.090	92.556	-484.545	-102.826	6.420
3600	31.434	130.420	103.837	95.698	-484.418	-91.912	5.580
3700	31.453	131.282	104.567	98.842	-484.307	-81.016	4.785
3800	31.471	132.121	105.282	101.989	-484.213	-70.116	4.032
3900	31.487	132.938	105.980	105.137	-484.134	-59.217	3.318
4000	31.502	133.736	106.664	108.286	-484.077	-48.328	2.640
4100	31.516	134.514	107.334	111.437	-484.042	-37.440	1.996
4200	31.529	135.273	107.990	114.589	-484.026	-26.547	1.381
4300	31.541	136.015	108.633	117.743	-484.035	-15.642	.795
4400	31.553	136.741	109.264	120.897	-484.071	-4.755	.236
4500	31.563	137.450	109.882	124.053	-484.132	6.139	-.298
4600	31.573	138.144	110.489	127.210	-484.223	17.036	-.809
4700	31.583	138.823	111.085	130.368	-484.341	27.929	-1.299
4800	31.591	139.488	111.670	133.527	-484.490	38.836	-1.768
4900	31.599	140.139	112.244	136.686	-484.668	49.734	-2.218
5000	31.607	140.778	112.808	139.846	-484.878	60.651	-2.651
5100	31.614	141.404	113.363	143.008	-485.123	71.566	-3.067
5200	31.621	142.018	113.908	146.169	-485.400	82.468	-3.466
5300	31.628	142.620	114.444	149.332	-485.713	93.404	-3.851
5400	31.634	143.211	114.972	152.495	-486.058	104.325	-4.222
5500	31.640	143.792	115.490	155.659	-486.439	115.265	-4.580
5600	31.645	144.362	116.001	158.823	-486.857	126.206	-4.925
5700	31.651	144.922	116.503	161.988	-487.307	137.161	-5.259
5800	31.655	145.473	116.998	165.153	-487.794	148.134	-5.582
5900	31.660	146.014	117.485	168.319	-488.318	159.090	-5.893
6000	31.665	146.546	117.965	171.485	-488.877	170.064	-6.194

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE TRIMERIC (Be_3O_3) (IDEAL GAS) MOL. WT. = 75.039

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [65.3] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -250.7 ± 9 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -252 ± 9 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[730] (1)	[1380] (2)
[990] (1)	[1450] (2)
[1480] (1)	[610] (2)
[1100] (1)	[320] (2)

Bond Distance: Be-O = [1.63] Å

σ = [6]

Bond Angle: Be-O-Be = [120°] O-Be-O = [120°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.0658] X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) measured the change in the intensity of the $(BeO)_3^+$ ion with temperature and obtained a second law heat of vaporization of 161 ± 6 kcal. mole^{-1} at 2150°K. The uncertainty is large because of an approximate correction of 8 kcal. mole^{-1} and the neglect of fragmentation effects. We adopted a heat of sublimation at 2150°K. of 163 kcal. mole^{-1} in order to bring the equilibrium vapor pressure into agreement with that measured by Chupka, et al.

Heat Capacity and Entropy.

The assumed D_{3h} symmetry implies eight vibrational frequencies of the types $2A_1'$, A_2', A_2'', 3E', and E_2''. The frequencies were estimated by comparison with the values for the $B_3O_3(O^-)_3$ skeleton as given by J. L. Parsons, J. Chem. Phys. 33, 1860 (1960) and the partial assignment of Boroxine by S. K. Gupta and R. F. Porter, J. Phys. Chem. 67, 1286 (1963). The bond length was taken as that in $Be_2O_2(g)$, while the bond angle was arbitrarily taken as 120°. The individual moments of inertia were $I_A = I_B$ = 16.550, I_C = 33.010 X 10^{-39} g. cm.^{2}

Beryllium Oxide, Tetrameric (Be_4O_4)

(Ideal Gas) Mol. Wt. = 100.052

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.950	-377.929	-377.929	INFINITE
100	10.385	56.378	87.199	-3.082	-378.526	-375.807	821.287
200	15.434	65.025	74.054	-1.806	-379.162	-372.866	407.429
298	21.364	72.292	72.292	.000	-380.000	-369.614	270.921
300	21.473	72.425	72.293	.040	-380.014	-369.549	269.203
400	26.784	79.358	73.202	2.463	-380.769	-365.942	199.932
500	30.818	85.792	75.085	5.353	-381.357	-362.163	158.294
600	33.745	91.684	77.368	8.589	-381.799	-358.281	130.497
700	35.860	97.053	79.803	12.075	-382.157	-354.333	110.622
800	37.407	101.948	82.270	15.742	-382.466	-350.339	95.704
900	38.559	106.423	84.708	19.543	-382.761	-346.303	84.090
1000	39.434	110.533	87.088	23.445	-383.073	-342.234	74.792
1100	40.110	114.325	89.394	27.424	-383.428	-338.133	67.178
1200	40.642	117.838	91.620	31.462	-383.842	-333.999	60.827
1300	41.067	121.109	93.764	35.549	-384.317	-329.825	55.446
1400	41.412	124.165	95.828	39.673	-384.865	-325.616	50.829
1500	41.694	127.033	97.813	43.829	-385.491	-321.364	46.820
1600	41.929	129.731	99.725	48.010	-397.220	-316.751	43.264
1700	42.125	132.279	101.565	52.213	-397.553	-311.711	40.071
1800	42.291	134.692	103.339	56.434	-397.902	-306.652	37.231
1900	42.433	136.982	105.050	60.671	-398.267	-301.573	34.687
2000	42.555	139.162	106.702	64.920	-398.650	-296.478	32.396
2100	42.660	141.241	108.297	69.181	-399.051	-291.356	30.320
2200	42.752	143.227	109.840	73.452	-399.476	-286.219	28.432
2300	42.832	145.130	111.334	77.731	-399.921	-281.056	26.705
2400	42.903	146.954	112.780	82.018	-400.390	-275.874	25.121
2500	42.966	148.707	114.182	86.311	-400.889	-270.686	23.662
2600	43.022	150.393	115.543	90.611	-401.405	-265.459	22.313
2700	43.072	152.018	116.864	94.916	-401.944	-260.220	21.062
2800	43.117	153.585	118.147	99.225	-686.629	-250.531	19.554
2900	43.157	155.099	119.396	103.539	-686.211	-234.956	17.706
3000	43.193	156.562	120.610	107.856	-685.808	-219.405	15.983
3100	43.226	157.979	121.793	112.177	-685.413	-203.875	14.372
3200	43.256	159.352	122.945	116.502	-685.028	-188.338	12.862
3300	43.284	160.684	124.069	120.829	-684.661	-172.823	11.445
3400	43.309	161.976	125.165	125.158	-684.314	-157.321	10.112
3500	43.332	163.232	126.235	129.490	-683.978	-141.834	8.856
3600	43.353	164.453	127.279	133.825	-683.663	-126.336	7.669
3700	43.372	165.641	128.300	138.161	-683.371	-110.866	6.548
3800	43.390	166.798	129.298	142.499	-683.103	-95.395	5.486
3900	43.407	167.925	130.274	146.839	-682.855	-79.928	4.479
4000	43.422	169.024	131.229	151.180	-682.638	-64.479	3.523
4100	43.436	170.097	132.164	155.523	-682.449	-49.034	2.614
4200	43.449	171.144	133.080	159.867	-682.287	-33.586	1.748
4300	43.462	172.166	133.977	164.213	-682.157	-18.126	.921
4400	43.473	173.165	134.856	168.560	-682.064	-2.693	.134
4500	43.484	174.142	135.719	172.908	-682.006	12.746	-.619
4600	43.494	175.098	136.564	177.257	-681.987	28.187	-1.339
4700	43.504	176.034	137.394	181.607	-682.005	43.619	-2.028
4800	43.512	176.950	138.209	185.957	-682.065	59.066	-2.689
4900	43.521	177.847	139.009	190.309	-682.163	74.499	-3.323
5000	43.529	178.726	139.794	194.661	-682.305	89.953	-3.932
5100	43.536	179.588	140.566	199.015	-682.493	105.403	-4.517
5200	43.543	180.434	141.325	203.369	-682.723	120.833	-5.078
5300	43.550	181.263	142.070	207.723	-683.003	136.306	-5.620
5400	43.556	182.078	142.804	212.079	-683.325	151.755	-6.142
5500	43.562	182.877	143.525	216.434	-683.696	167.227	-6.645
5600	43.567	183.662	144.235	220.791	-684.115	182.699	-7.130
5700	43.573	184.433	144.933	225.148	-684.578	198.187	-7.599
5800	43.578	185.191	145.621	229.505	-685.091	213.696	-8.052
5900	43.582	185.936	146.298	233.863	-685.653	229.179	-8.489
6000	43.587	186.668	146.965	238.222	-686.260	244.686	-8.912

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE TETRAMERIC (Be_4O_4) (IDEAL GAS) MOL. WT. = 100.052

Point Group $[D_{4h}]$

$S^\circ_{298.15}$ = [72.3] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -378 ± 12 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -380 ± 12 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[700] (1)	[200] (2)
[850] (1)	[900] (1)
[1400] (1)	[400] (1)
[1000] (1)	[500] (1)
[800] (1)	[1150] (2)
[1000] (1)	[1200] (2)
[800] (1)	[600] (2)

Bond Distance: Be-O = [1.63] Å

σ = [8]

Bond Angle: Be-O-Be = [115°] O-Be-O = [155°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.11656] X 10^{-112} g.^{3} cm.^{6}

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) measured the variation of intensity of the $(BeO)_4^+$ ion with temperature in a mass spectrometer. They reported a second law heat of vaporization of 177 ± 8 kcal. mole^{-1} at 2150°K., which included an approximate correction of 9 kcal. mole^{-1}, and this value was adopted here.

Heat Capacity and Entropy.

The assumed D_{4h} structure has 14 vibrational frequencies of the type $2A_{1g}$, A_{2g}, $2B_{1g}$, $2B_{2g}$, E_g, A_{2u}, B_{2u}, B_{1u}, and $3E_u$. The frequencies were estimated by comparison with $(BeO)_3$ and cyclobutane from G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Am. Chem. Soc. 75, 5634 (1953). The estimated structure and frequencies gave an entropy which was in excellent agreement with the experimental heat and equilibrium constant determined by Chupka, et al.

The bond lengths were taken equal to those in $Be_2O_2(g)$ and the angles were chosen so that O-Be-O was almost linear. The individual moments of inertia were calculated to be $I_A = I_B$ = 38.219, I_C = 76.438 X 10^{-39} g. cm.^{2}

Beryllium Oxide, Pentameric (Be$_5$O$_5$)

(Ideal Gas) Mol. Wt. = 125.065

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.562	-502.035	-502.035	INFINITE
100	10.823	58.498	95.370	-3.687	-502.992	-498.397	1089.193
200	18.621	68.262	79.430	-2.234	-503.929	-493.455	539.196
298	26.773	77.240	77.240	.000	-505.000	-488.104	357.773
300	26.917	77.406	77.241	.050	-505.018	-487.998	355.490
400	33.868	86.143	78.385	3.103	-505.937	-482.181	263.439
500	39.085	94.292	80.762	6.765	-506.623	-476.156	208.118
600	42.853	101.770	83.650	10.872	-507.113	-470.015	171.195
700	45.571	108.591	86.733	15.301	-507.489	-463.801	144.798
800	47.557	114.813	89.860	19.962	-507.798	-457.542	124.989
900	49.035	120.503	92.953	24.795	-508.085	-451.239	109.571
1000	50.156	125.730	95.973	29.757	-508.390	-444.906	97.229
1100	51.023	130.553	98.901	34.818	-508.747	-438.540	87.126
1200	51.705	135.023	101.727	39.956	-509.174	-432.141	78.700
1300	52.249	139.184	104.450	45.154	-509.678	-425.700	71.563
1400	52.690	143.073	107.071	50.402	-510.271	-419.222	65.440
1500	53.051	146.721	109.594	55.690	-510.960	-412.696	60.127
1600	53.351	150.154	112.023	61.010	-525.527	-405.726	55.417
1700	53.603	153.396	114.362	66.358	-525.849	-398.220	51.193
1800	53.815	156.467	116.617	71.729	-526.191	-390.712	47.437
1900	53.997	159.381	118.792	77.120	-526.552	-383.176	44.073
2000	54.153	162.155	120.891	82.528	-526.935	-375.624	41.044
2100	54.288	164.800	122.919	87.950	-527.340	-368.045	38.301
2200	54.405	167.329	124.881	93.385	-527.775	-360.451	35.806
2300	54.508	169.749	126.780	98.831	-528.234	-352.829	33.525
2400	54.599	172.071	128.619	104.286	-528.724	-345.187	31.432
2500	54.679	174.302	130.402	109.750	-529.250	-337.542	29.506
2600	54.751	176.448	132.132	115.222	-529.798	-329.852	27.725
2700	54.815	178.515	133.811	120.700	-530.375	-322.151	26.075
2800	54.872	180.510	135.444	126.184	-886.133	-308.891	24.109
2900	54.924	182.436	137.031	131.674	-885.513	-288.276	21.724
3000	54.970	184.299	138.576	137.169	-884.911	-267.695	19.501
3100	55.012	186.102	140.080	142.668	-884.319	-247.144	17.423
3200	55.051	187.849	141.546	148.171	-883.741	-226.587	15.474
3300	55.086	189.544	142.975	153.678	-883.184	-206.062	13.646
3400	55.118	191.189	144.369	159.188	-882.652	-185.554	11.927
3500	55.147	192.787	145.729	164.702	-882.133	-165.069	10.307
3600	55.174	194.341	147.058	170.218	-881.642	-144.572	8.776
3700	55.199	195.853	148.357	175.736	-881.179	-124.114	7.331
3800	55.222	197.325	149.626	181.257	-880.745	-103.656	5.961
3900	55.243	198.760	150.868	186.781	-880.337	-83.206	4.663
4000	55.262	200.159	152.082	192.306	-879.967	-62.782	3.430
4100	55.281	201.524	153.272	197.833	-879.632	-42.365	2.258
4200	55.298	202.856	154.436	203.362	-879.331	-21.947	1.142
4300	55.313	204.157	155.578	208.893	-879.070	-1.515	.077
4400	55.328	205.429	156.696	214.425	-878.855	18.880	-.938
4500	55.342	206.673	157.793	219.958	-878.684	39.281	-1.908
4600	55.355	207.889	158.869	225.493	-878.562	59.681	-2.835
4700	55.367	209.080	159.925	231.029	-878.486	80.068	-3.723
4800	55.378	210.246	160.961	236.566	-878.461	100.472	-4.574
4900	55.389	211.388	161.978	242.105	-878.485	120.857	-5.390
5000	55.399	212.507	162.978	247.644	-878.563	141.266	-6.174
5100	55.408	213.604	163.960	253.184	-878.701	161.667	-6.928
5200	55.417	214.680	164.925	258.726	-878.889	182.042	-7.651
5300	55.426	215.735	165.874	264.268	-879.140	202.469	-8.349
5400	55.434	216.772	166.807	269.811	-879.444	222.863	-9.019
5500	55.441	217.789	167.724	275.355	-879.808	243.285	-9.667
5600	55.448	218.788	168.627	280.899	-880.233	263.705	-10.291
5700	55.455	219.769	169.516	286.444	-880.713	284.143	-10.894
5800	55.461	220.734	170.391	291.990	-881.255	304.605	-11.477
5900	55.468	221.682	171.252	297.536	-881.859	325.034	-12.039
6000	55.473	222.614	172.100	303.084	-882.519	345.491	-12.584

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE PENTAMERIC (Be$_5$O$_5$) (IDEAL GAS) MOL. WT. = 125.065

Point Group [D_{5h}]

$S^\circ_{298.15}$ = [77.24] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -502 ± 18 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -505 ± 18 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[700] (1)	[1200] (2)
[850] (1)	[600] (2)
[1400] (1)	[500] (2)
[1100] (2)	[900] (1)
[900] (2)	[200] (2)
[1000] (2)	[400] (2)
[1200] (2)	[500] (2)

Bond Distance: Be-O = [1.63] Å

σ = [10]

Bond Angle: Be-O-Be = [110°] O-Be-O = [178°]

Product of the Moment of Inertia: $I_AI_BI_C$ = [6.9653] X 10^{-112} g.^{3} cm.^{6}

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) measured the variation in intensity of the $(BeO)_5^+$ ion with temperature in a mass spectrometer. They calculated a second law heat of vaporization of 193 ± 12 kcal. mole^{-1} at 2150°K., the uncertainty reflects the inclusion of an approximate correction of 10 kcal. mole^{-1}. This value was adopted here.

Heat Capacity and Entropy.

The assumed D_{5h} structure has 14 vibrations of the type $2A_1'$, A_2', $3E_1'$, $4E_2'$, A_2'', E_1'', and $2E_2''$. These were estimated by comparison with similar motions in other ring structures including $(BeO)_3$ and $(BeO)_4$. The estimated structure and frequencies gave an entropy in good agreement with the experimental heat and equilibrium constant determined by Chupka, et al.

The bond length was assumed to be the same as in Be_2O_2(g) and the angles were chosen so as to make O-Be-O almost linear. The individual moments of inertia are calculated to be $I_A = I_B$ = 70.356, I_C = 140.713 X 10^{-39} g. cm.^{2}

Beryllium Oxide, Hexameric (Be_6O_6)

(Ideal Gas) Mol. Wt. = 150.078

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 5.133	- 632.101	- 632.101	INFINITE
100	12.043	60.631	102.856	- 4.223	- 633.389	- 626.917	1370.060
200	21.158	71.620	84.546	- 2.585	- 634.619	- 619.991	677.463
298	31.459	82.000	82.000	.000	- 636.000	- 612.538	448.981
300	31.644	82.195	82.000	.058	- 636.023	- 612.392	446.106
400	40.551	92.573	83.355	3.687	- 637.161	- 604.334	330.177
500	47.149	102.371	86.190	8.091	- 637.974	- 596.025	260.510
600	51.861	111.408	89.651	13.054	- 638.528	- 587.581	214.016
700	55.231	119.670	93.358	18.418	- 638.930	- 579.057	180.781
800	57.682	127.214	97.126	24.070	- 639.242	- 570.486	155.842
900	59.499	134.117	100.858	29.933	- 639.523	- 561.870	136.434
1000	60.874	140.461	104.506	35.955	- 639.822	- 553.225	120.901
1100	61.935	146.315	108.044	42.098	- 640.180	- 544.548	108.186
1200	62.769	151.741	111.462	48.335	- 640.621	- 535.837	97.585
1300	63.434	156.792	114.757	54.646	- 641.153	- 527.082	88.606
1400	63.972	161.513	117.930	61.017	- 641.790	- 518.288	80.905
1500	64.413	165.943	120.984	67.437	- 642.543	- 509.443	74.222
1600	64.778	170.112	123.926	73.897	- 659.948	- 500.069	68.303
1700	65.085	174.048	126.760	80.391	- 660.258	- 490.067	62.999
1800	65.344	177.776	129.491	86.913	- 660.591	- 480.046	58.283
1900	65.565	181.315	132.126	93.458	- 660.949	- 470.006	54.060
2000	65.754	184.683	134.671	100.024	- 661.331	- 459.952	50.259
2100	65.919	187.895	137.129	106.608	- 661.740	- 449.869	46.816
2200	66.062	190.965	139.507	113.207	- 662.185	- 439.771	43.685
2300	66.187	193.904	141.809	119.820	- 662.658	- 429.644	40.824
2400	66.297	196.724	144.039	126.444	- 663.168	- 419.495	38.198
2500	66.395	199.432	146.201	133.079	- 663.721	- 409.346	35.783
2600	66.482	202.038	148.298	139.723	- 664.301	- 399.148	33.550
2700	66.560	204.548	150.335	146.375	- 664.915	- 388.938	31.481
2800	66.629	206.970	152.315	153.035	-1091.746	- 372.061	29.039
2900	66.692	209.310	154.240	159.701	-1090.924	- 346.360	26.101
3000	66.740	211.572	156.114	166.373	-1090.123	- 320.703	23.362
3100	66.800	213.761	157.938	173.050	-1089.335	- 295.084	20.802
3200	66.847	215.883	159.716	179.733	-1088.562	- 269.460	18.402
3300	66.889	217.940	161.449	186.420	-1087.815	- 243.878	16.151
3400	66.928	219.938	163.140	193.111	-1087.098	- 218.318	14.033
3500	66.964	221.878	164.791	199.805	-1086.397	- 192.788	12.038
3600	66.997	223.765	166.403	206.503	-1085.729	- 167.247	10.153
3700	67.027	225.601	167.978	213.204	-1085.094	- 141.754	8.373
3800	67.055	227.389	169.518	219.908	-1084.495	- 116.263	6.686
3900	67.080	229.131	171.025	226.615	-1083.926	- 90.784	5.087
4000	67.104	230.830	172.499	233.324	-1083.403	- 65.338	3.570
4100	67.126	232.487	173.942	240.036	-1082.922	- 39.903	2.127
4200	67.147	234.105	175.355	246.750	-1082.481	- 14.467	.753
4300	67.166	235.685	176.740	253.465	-1082.090	10.983	- .558
4400	67.184	237.229	178.097	260.183	-1081.753	36.386	- 1.807
4500	67.201	238.739	179.428	266.902	-1081.469	61.794	- 3.001
4600	67.216	240.217	180.733	273.623	-1081.243	87.200	- 4.143
4700	67.231	241.662	182.014	280.345	-1081.073	112.589	- 5.235
4800	67.245	243.078	183.272	287.069	-1080.964	137.996	- 6.283
4900	67.258	244.465	184.507	293.794	-1080.914	163.379	- 7.287
5000	67.270	245.824	185.719	300.521	-1080.928	188.789	- 8.252
5100	67.281	247.156	186.911	307.248	-1081.014	214.188	- 9.178
5200	67.292	248.462	188.082	313.977	-1081.161	239.554	- 10.068
5300	67.302	249.744	189.234	320.707	-1081.382	264.981	- 10.926
5400	67.312	251.002	190.366	327.437	-1081.569	290.367	- 11.751
5500	67.321	252.238	191.480	334.169	-1082.026	315.785	- 12.548
5600	67.330	253.451	192.575	340.902	-1082.457	341.199	- 13.315
5700	67.338	254.642	193.654	347.635	-1082.954	366.633	- 14.057
5800	67.346	255.814	194.716	354.369	-1083.525	392.096	- 14.774
5900	67.353	256.965	195.761	361.104	-1084.170	417.516	- 15.465
6000	67.360	258.097	196.790	367.840	-1084.883	442.969	- 16.134

Dec. 31, 1960; Sept. 30, 1963

BERYLLIUM OXIDE HEXAMERIC (Be_6O_6) (IDEAL GAS) MOL. WT. = 150.078

Point Group [D_{6h}]

$S^\circ_{298.15}$ = [82] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -632 ± 22 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -636 ± 22 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[700] (1)	[600] (2)	[900] (1)	[1100] (2)
[850] (1)	[750] (2)	[1100] (1)	[1200] (2)
[1400] (1)	[850] (2)	[1000] (1)	[500] (2)
[500] (1)	[850] (2)	[800] (1)	[200] (2)
[400] (1)	[950] (2)	[1400] (1)	[250] (2)

Bond Distance: Be-O = [1.63] Å

σ = [12]

Bond Angle: Be-O-Be = [110°] O-Be-O = [190°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.1266] X 10^{-111} g.^{3} cm.^{6}

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) measured the temperature dependence of the $(BeO)_6^+$ ion in a mass spectrometer. They calculated a second law heat of vaporization of 203 ± 15 kcal. mole^{-1} which was adopted here. The uncertainty reflects in part an approximate correction of 10 kcal. mole^{-1} and the small observed intensities.

Heat Capacity and Entropy.

The assumed symmetry D_{6h} has 20 vibrational frequencies of the type $2A_{1g}$, A_{2g}, B_{1g}, B_{2g}, E_{1g}, $4E_{2g}$, A_{2u}, $2B_{1u}$, $2B_{2u}$, $3E_{1u}$, and $2E_{2u}$. The frequencies were estimated by comparison with similar motions in other ring molecules including benzene, $(BeO)_3$ and $(BeO)_4$. The assumed structure and vibrational frequencies gave an entropy in good agreement with the heat and equilibrium constant determined by Chupka, et al. The bond length was taken equal to that in Be_2O_2(s) the angles were chosen so that the O-Be-O angle was almost linear but with the Be-O-Be angle less than 120°. The individual moments of inertia were calculated to be $I_A = I_B$ = 116.059, I_C = 232.118 X 10^{-39} g. cm.^{2}

Bromine, Monatomic (Br)

(Ideal Gas) Mol. Wt. = 79.916

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-1,481	28,188	28,188	INFINITE
100	4,968	36,378	46,222	-,984	28,351	25,357	-55,415
200	4,968	39,821	42,260	-,488	28,262	22,388	-24,463
298	4,968	41,805	41,805	,000	26,740	19,700	-14,440
300	4,968	41,836	41,805	,009	26,733	19,656	-14,319
400	4,968	43,265	42,000	,506	23,110	18,044	-9,858
500	4,971	44,374	42,368	1,003	23,165	16,771	-7,330
600	4,979	45,281	42,780	1,500	23,218	15,487	-5,641
700	4,997	46,050	43,194	1,999	23,271	14,194	-4,431
800	5,026	46,719	43,593	2,500	23,324	12,894	-3,522
900	5,063	47,313	43,974	3,005	23,379	11,587	-2,814
1000	5,107	47,848	44,335	3,513	23,438	10,274	-2,245
1100	5,153	48,337	44,677	4,026	23,500	8,954	-1,779
1200	5,199	48,788	45,001	4,544	23,566	7,629	-1,389
1300	5,243	49,206	45,309	5,066	23,635	6,299	-1,059
1400	5,284	49,596	45,601	5,592	23,709	4,962	-,775
1500	5,320	49,961	45,880	6,122	23,785	3,620	-,527
1600	5,351	50,306	46,146	6,656	23,864	2,274	-,311
1700	5,377	50,631	46,400	7,192	23,945	,922	-,119
1800	5,398	50,939	46,644	7,731	24,029	-,435	,053
1900	5,415	51,231	46,878	8,272	24,113	-1,796	,207
2000	5,428	51,509	47,102	8,814	24,199	-3,162	,346
2100	5,437	51,775	47,319	9,357	24,285	-4,532	,472
2200	5,443	52,028	47,527	9,901	24,371	-5,907	,587
2300	5,446	52,270	47,728	10,446	24,457	-7,284	,692
2400	5,447	52,501	47,922	10,991	24,543	-8,666	,789
2500	5,445	52,724	48,110	11,535	24,628	-10,052	,879
2600	5,442	52,937	48,291	12,080	24,712	-11,440	,962
2700	5,438	53,143	48,467	12,624	24,796	-12,833	1,039
2800	5,432	53,340	48,638	13,167	24,878	-14,228	1,110
2900	5,425	53,531	48,803	13,710	24,959	-15,626	1,178
3000	5,418	53,715	48,964	14,252	25,039	-17,027	1,240
3100	5,410	53,892	49,120	14,794	25,118	-18,430	1,299
3200	5,402	54,064	49,272	15,334	25,195	-19,836	1,355
3300	5,393	54,230	49,420	15,874	25,271	-21,245	1,407
3400	5,384	54,391	49,563	16,413	25,346	-22,656	1,456
3500	5,375	54,547	49,704	16,951	25,419	-24,068	1,503
3600	5,366	54,698	49,840	17,488	25,490	-25,484	1,547
3700	5,357	54,845	49,973	18,024	25,561	-26,901	1,589
3800	5,348	54,988	50,104	18,559	25,630	-28,319	1,629
3900	5,339	55,126	50,231	19,093	25,697	-29,739	1,666
4000	5,330	55,261	50,355	19,627	25,763	-31,163	1,703
4100	5,321	55,393	50,476	20,159	25,827	-32,587	1,737
4200	5,312	55,521	50,595	20,691	25,890	-34,012	1,770
4300	5,304	55,646	50,711	21,222	25,952	-35,438	1,801
4400	5,295	55,768	50,824	21,752	26,013	-36,866	1,831
4500	5,287	55,887	50,935	22,281	26,072	-38,297	1,860
4600	5,279	56,003	51,044	22,809	26,130	-39,727	1,887
4700	5,271	56,116	51,151	23,337	26,186	-41,159	1,914
4800	5,264	56,227	51,256	23,863	26,241	-42,594	1,939
4900	5,256	56,336	51,358	24,389	26,295	-44,027	1,964
5000	5,249	56,442	51,459	24,915	26,348	-45,463	1,987
5100	5,242	56,546	51,557	25,439	26,399	-46,901	2,010
5200	5,236	56,647	51,654	25,963	26,449	-48,338	2,032
5300	5,229	56,747	51,749	26,486	26,498	-49,776	2,052
5400	5,223	56,845	51,843	27,009	26,546	-51,217	2,073
5500	5,217	56,940	51,935	27,531	26,593	-52,656	2,092
5600	5,211	57,034	52,025	28,052	26,638	-54,099	2,111
5700	5,205	57,126	52,114	28,573	26,683	-55,540	2,129
5800	5,199	57,217	52,201	29,093	26,726	-56,982	2,147
5900	5,194	57,306	52,287	29,613	26,769	-58,426	2,164
6000	5,189	57,393	52,371	30,132	26,810	-59,873	2,181

September 30, 1961

BROMINE, MONATOMIC (Br) (IDEAL GAS) MOL. WT. = 79.916

ΔH°_{f0} = 28.188 ± .070 kcal. mole^{-1}

Ground State = $^2P_{3/2}$

$\Delta H^\circ_{f\ 298}$ = 26.740 kcal. mole^{-1}

S°_{298} = 41.805 cal. mole^{-1} deg.$^{-1}$

Electronic Levels and Multiplicities

ω_i, cm.$^{-1}$	g_i	ω_i, cm.$^{-1}$	g_i	ω_i, cm.$^{-1}$	g_i
0.00	4	74666	6	86430	2
3685.00	2	75531	22	87500	10
63429.82	6	76736	4	88561	38
64900.50	4	77317	10	89700	56
66877.16	2	78540	14	90371	44
67176.87	4	79517	10	91737	70
68963.52	2	85724	30	92733	12

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities listed by C. E. Moore [Natl. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in good agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 147 (1955)], who used essentially the same data.

Heat of Formation.

The heat of formation is calculated from the dissociation energy of bromine selected by Evans, Munson, and Wagman (loc. cit.) and the heat of sublimation derived for diatomic bromine. Evans, Munson, and Wagman list experimental vapor density measurements from the literature which agree with the spectroscopic value within their estimated uncertainty.

Bromine Monochloride (BrCl)

(Ideal Gas) Mol. Wt. = 115.362

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.247	5.279	5.279	INFINITE
100	7.101	48.926	64.421	-1.550	5.292	3.303	-7.218
200	7.884	54.089	58.089	-.800	5.096	1.384	-1.512
298	8.363	57.337	57.337	.000	3.500	-.227	.166
300	8.369	57.389	57.337	.015	3.491	-.250	.182
400	8.611	59.833	57.669	.866	-.193	-.741	.405
500	8.744	61.771	58.302	1.734	-.193	-.878	.384
600	8.826	63.373	59.018	2.613	-.192	-1.015	.370
700	8.881	64.738	59.740	3.499	-.192	-1.153	.360
800	8.921	65.926	60.440	4.389	-.193	-1.290	.352
900	8.952	66.979	61.109	5.282	-.194	-1.427	.347
1000	8.977	67.923	61.744	6.179	-.194	-1.564	.342
1100	8.998	68.780	62.346	7.078	-.195	-1.701	.338
1200	9.016	69.563	62.915	7.978	-.196	-1.837	.335
1300	9.033	70.286	63.454	8.881	-.197	-1.974	.332
1400	9.048	70.956	63.967	9.785	-.198	-2.111	.330
1500	9.063	71.581	64.454	10.690	-.199	-2.249	.328
1600	9.076	72.166	64.918	11.597	-.201	-2.385	.326
1700	9.089	72.717	65.360	12.506	-.202	-2.521	.324
1800	9.102	73.236	65.784	13.415	-.203	-2.657	.323
1900	9.114	73.729	66.189	14.326	-.204	-2.792	.321
2000	9.126	74.197	66.578	15.238	-.207	-2.930	.320
2100	9.137	74.642	66.951	16.151	-.208	-3.065	.319
2200	9.148	75.068	67.311	17.065	-.211	-3.203	.318
2300	9.160	75.474	67.657	17.981	-.214	-3.336	.317
2400	9.171	75.865	67.991	18.897	-.217	-3.473	.316
2500	9.182	76.239	68.313	19.815	-.221	-3.608	.315
2600	9.192	76.599	68.625	20.734	-.224	-3.742	.315
2700	9.203	76.947	68.927	21.653	-.229	-3.881	.314
2800	9.214	77.281	69.219	22.574	-.235	-4.012	.313
2900	9.224	77.605	69.503	23.496	-.241	-4.149	.313
3000	9.235	77.918	69.778	24.419	-.248	-4.285	.312
3100	9.245	78.221	70.046	25.343	-.257	-4.419	.311
3200	9.256	78.514	70.306	26.268	-.266	-4.551	.311
3300	9.266	78.799	70.559	27.194	-.276	-4.685	.310
3400	9.276	79.076	70.805	28.121	-.287	-4.819	.310
3500	9.287	79.345	71.045	29.050	-.299	-4.952	.309
3600	9.297	79.607	71.280	29.979	-.312	-5.085	.309
3700	9.307	79.862	71.508	30.909	-.325	-5.218	.308
3800	9.317	80.110	71.731	31.840	-.339	-5.350	.308
3900	9.328	80.352	71.949	32.772	-.355	-5.479	.307
4000	9.338	80.589	72.162	33.706	-.371	-5.615	.307
4100	9.348	80.819	72.371	34.640	-.387	-5.744	.306
4200	9.358	81.045	72.574	35.575	-.404	-5.877	.306
4300	9.368	81.265	72.774	36.512	-.421	-6.005	.305
4400	9.378	81.481	72.969	37.449	-.439	-6.135	.305
4500	9.389	81.691	73.161	38.387	-.457	-6.262	.304
4600	9.399	81.898	73.349	39.327	-.475	-6.393	.304
4700	9.409	82.100	73.533	40.267	-.493	-6.518	.303
4800	9.419	82.298	73.713	41.208	-.512	-6.648	.303
4900	9.429	82.493	73.890	42.151	-.530	-6.777	.302
5000	9.439	82.683	74.064	43.094	-.547	-6.902	.302
5100	9.449	82.870	74.235	44.039	-.565	-7.029	.301
5200	9.459	83.054	74.403	44.984	-.582	-7.157	.301
5300	9.469	83.234	74.568	45.931	-.599	-7.282	.300
5400	9.479	83.411	74.730	46.878	-.616	-7.409	.300
5500	9.490	83.585	74.890	47.826	-.632	-7.532	.299
5600	9.500	83.756	75.046	48.776	-.648	-7.659	.299
5700	9.510	83.925	75.201	49.726	-.664	-7.789	.299
5800	9.520	84.090	75.353	50.678	-.679	-7.908	.298
5900	9.530	84.253	75.502	51.630	-.694	-8.036	.298
6000	9.540	84.413	75.649	52.584	-.708	-8.160	.297

Sept. 30, 1962; Sept. 30, 1965

BROMINE MONOCHLORIDE (BrCl) (IDEAL GAS) MOL. WT. = 115.362

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 57.337 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 5.28 ± 0.30 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 3.50 ± 0.3 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	g_i
0	1

ω_e = 443.1 cm.$^{-1}$

B_e = 0.150797 cm.$^{-1}$

$\omega_e x_e$ = 1.8 cm.$^{-1}$

α_e = 0.0007597 cm.$^{-1}$

σ = 1

r_e = 2.136 Å

Heat of Formation.

The average $\Delta H^\circ_{r\ 298.15}$ = -0.406 kcal. mole^{-1} for the reaction $Br_2(g) + Cl_2(g) = 2BrCl(g)$ and the $\Delta H^\circ_{f\ 298.15}$ = 3.694 kcal. mole^{-1} for 1/2 $Br_2(g)$ from JANAF tables were used to calculate the $\Delta H^\circ_{f\ 298.15}$ = 3.5 ± 0.3 kcal. mole^{-1}. Other equilibrium measurements not included below have been summarized by Beeson and Yost, loc. cit.

Source	T°K	Method	Third Law $\Delta H^\circ_{r\ 298.15}$ kcal. mole^{-1}
1	301	Light absorption	- .51
2	298	Light absorption	- 0.34
3	372-492	Total pressure Run III	- 0.39
3	372-492	Total pressure Run II	- 0.47
4	313±5	Mass spectrometric	- 0.32
		Average	- 0.406

Source

1 H. G. Vesper and G. K. Rollefson, J. Am. Chem. Soc. 56, 620 (1934).

2 G. Braune and E. Victor, Z Elektrochem. 41, 508 (1935).

3 C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939).

4 H. C. Mattraw, C. F. Pachucki and N. J. Hawkins, General Electric Co., Report No. KAPL-1016 (1953) Knolls Atomic Power Laboratory, Schenectady, New York.

Heat Capacity and Entropy.

All spectroscopic and molecular constants were obtained from W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. of Standards, 55, 147 (1955) except r_e which was calculated from B_e. The value of r_e was reported to be 2.13 Å and 2.11 Å by C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939) and L. G. Cole and G. W. Elverum Jr., J. Chem. Phys., 20, 1543 (1952), respectively. Ground state configuration was taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

Bromine Monofluoride (BrF)

(Ideal Gas)   Mol. Wt. = 98.9074

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.156	- 12.144	- 12.144	INFINITE
100	6.970	46.743	61.346	- 1.460	- 12.130	- 14.126	30.872
200	7.352	51.663	55.404	- .748	- 12.354	- 16.042	17.529
298	7.877	54.700	54.700	.000	- 13.973	- 17.636	12.927
300	7.885	54.749	54.700	.015	- 13.982	- 17.658	12.863
400	8.255	57.072	55.014	.823	- 17.679	- 18.125	9.903
500	8.488	58.941	55.619	1.661	- 17.686	- 18.237	7.971
600	8.640	60.503	56.306	2.518	- 17.689	- 18.347	6.682
700	8.744	61.843	57.004	3.387	- 17.691	- 18.456	5.762
800	8.820	63.015	57.683	4.266	- 17.694	- 18.565	5.071
900	8.877	64.058	58.335	5.151	- 17.696	- 18.674	4.534
1000	8.922	64.995	58.955	6.041	- 17.698	- 18.782	4.105
1100	8.960	65.848	59.543	6.935	- 17.701	- 18.891	3.753
1200	8.992	66.629	60.102	7.833	- 17.703	- 18.999	3.460
1300	9.019	67.349	60.632	8.733	- 17.707	- 19.105	3.212
1400	9.044	68.019	61.136	9.636	- 17.710	- 19.214	2.999
1500	9.067	68.644	61.616	10.542	- 17.714	- 19.321	2.815
1600	9.087	69.229	62.073	11.450	- 17.718	- 19.427	2.654
1700	9.107	69.781	62.511	12.359	- 17.723	- 19.534	2.511
1800	9.125	70.302	62.929	13.271	- 17.728	- 19.642	2.385
1900	9.143	70.796	63.330	14.184	- 17.732	- 19.747	2.271
2000	9.160	71.265	63.715	15.099	- 17.738	- 19.853	2.169
2100	9.176	71.713	64.086	16.016	- 17.743	- 19.960	2.077
2200	9.192	72.140	64.442	16.935	- 17.749	- 20.065	1.993
2300	9.207	72.549	64.786	17.855	- 17.755	- 20.170	1.916
2400	9.222	72.941	65.117	18.776	- 17.761	- 20.274	1.846
2500	9.237	73.318	65.438	19.699	- 17.768	- 20.380	1.782
2600	9.252	73.680	65.748	20.623	- 17.776	- 20.482	1.722
2700	9.266	74.030	66.048	21.549	- 17.783	- 20.588	1.666
2800	9.280	74.367	66.339	22.477	- 17.790	- 20.691	1.615
2900	9.295	74.693	66.622	23.405	- 17.798	- 20.794	1.567
3000	9.309	75.008	66.896	24.336	- 17.806	- 20.898	1.522
3100	9.322	75.314	67.163	25.267	- 17.815	- 21.002	1.481
3200	9.336	75.610	67.422	26.200	- 17.823	- 21.103	1.441
3300	9.350	75.897	67.675	27.134	- 17.833	- 21.205	1.404
3400	9.363	76.177	67.921	28.070	- 17.841	- 21.309	1.370
3500	9.377	76.448	68.160	29.007	- 17.851	- 21.407	1.337
3600	9.390	76.713	68.394	29.945	- 17.861	- 21.511	1.306
3700	9.404	76.970	68.623	30.885	- 17.871	- 21.612	1.276
3800	9.417	77.221	68.846	31.826	- 17.881	- 21.712	1.249
3900	9.430	77.466	69.064	32.769	- 17.892	- 21.814	1.222
4000	9.444	77.705	69.277	33.712	- 17.903	- 21.915	1.197
4100	9.457	77.938	69.485	34.657	- 17.915	- 22.015	1.173
4200	9.470	78.166	69.689	35.604	- 17.926	- 22.114	1.151
4300	9.483	78.389	69.889	36.551	- 17.938	- 22.212	1.129
4400	9.496	78.607	70.084	37.500	- 17.950	- 22.311	1.108
4500	9.509	78.821	70.276	38.451	- 17.962	- 22.413	1.088
4600	9.523	79.030	70.464	39.402	- 17.975	- 22.510	1.069
4700	9.536	79.235	70.649	40.355	- 17.988	- 22.608	1.051
4800	9.549	79.436	70.830	41.309	- 18.001	- 22.708	1.034
4900	9.562	79.633	71.007	42.265	- 18.015	- 22.804	1.017
5000	9.575	79.826	71.182	43.222	- 18.028	- 22.901	1.001
5100	9.588	80.016	71.353	44.180	- 18.043	- 23.002	.986
5200	9.601	80.202	71.522	45.139	- 18.057	- 23.096	.971
5300	9.614	80.385	71.687	46.100	- 18.071	- 23.191	.956
5400	9.627	80.565	71.850	47.062	- 18.087	- 23.292	.943
5500	9.640	80.742	72.010	48.025	- 18.101	- 23.387	.929
5600	9.653	80.916	72.167	48.990	- 18.117	- 23.485	.916
5700	9.666	81.086	72.322	49.956	- 18.133	- 23.574	.904
5800	9.678	81.255	72.475	50.923	- 18.148	- 23.673	.892
5900	9.691	81.420	72.625	51.892	- 18.165	- 23.767	.880
6000	9.704	81.583	72.773	52.861	- 18.182	- 23.864	.869

June 30, 1962; Sept. 30, 1965

BROMINE MONOFLUORIDE (BrF)   (IDEAL GAS)   MOL. WT. = 98.9074

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 54.700 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -12.1 ± 0.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -14.0 ± 0.4 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	g_1
0	1

ω_e = 673 cm.$^{-1}$ $\omega_e x_e$ = 4 cm.$^{-1}$ σ = 1

B_e = 0.356319 cm.$^{-1}$ α_e = 0.005206 cm.$^{-1}$ r_e = 1.7555 Å

Heat of Formation.

The equilibrium constant for the reaction $Br_2(g) + BrF_3(g) = 3BrF(g)$ has been measured over the temperature range 328-380°K. by R. K. Steunenberg, R. C. Vogel and J. Fischer, J. Am. Chem. Soc. 79, 1320 (1957). Third law analysis of the data yields a $\Delta H^\circ_{r\ 298}$ = 11.785 ± 0.2 kcal. mole^{-1}, with a drift of -0.6 ± 1.2 cal. mole^{-1} deg.$^{-1}$. Second law analysis yields $\Delta H^\circ_{r\ 298}$ = 11.98 ± 0.45 kcal. mole^{-1}, thus it is obvious that the data is thermodynamically self consistent. There is an uncertainty in the entropy of $BrF_3(g)$ of ± 1 cal. mole^{-1} deg.$^{-1}$ but this corresponds only to ± 0.35 kcal. mole^{-1} in $\Delta H^\circ_{r\ 298}$, thus a best value of $\Delta H^\circ_{r\ 298}$ = 11.78 ± 0.5 kcal. mole^{-1} is adopted. This yields $\Delta H^\circ_{f\ 298}$ BrF = -13.973 ± 0.4 kcal. mole^{-1}, the uncertainty in the heat of formation being a maximum value comprising the sum of the uncertainties in Br_2, BrF_3 and ΔH°_r.

Attempts have been made to analyse the spectra of BrF to obtain a D°_o value. P. H. Brodersen and J. E. Sicre, Z. Physik 141, 515 (1955) obtained two dissociation limits for BrF of 65.52 kcal. mole^{-1} and 54.98 kcal. mole^{-1}. The difference corresponds to the $Br(^2P_{1/2}) - Br(^2P_{3/2})$ excitation energy, indicating that the upper state goes to $F(^2P_{3/2})$ and $Br(^2P_{1/2})$. This yields a heat of formation of BrF of -10.23 kcal. mole^{-1}. Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error. W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Std. 55, 147 (1955) have also analysed the spectra and conclude that a heat of formation of -14.4 kcal. mole^{-1} is possible. However W. H. Evans, private communication Nov. 1965, now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards 55, 147 (1955) except r_e and ground state configuration which were taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

Bromine Trifluoride (BrF_3)

(Ideal Gas) Mol. Wt. = 136.9042

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.412	-58.404	-58.404	INFINITE
100	9.347	56.276	82.142	-2.587	-58.956	-57.835	126.393
200	13.336	64.017	71.250	-1.446	-59.451	-56.501	61.739
298	15.893	69.867	69.867	.000	-61.087	-54.827	40.187
300	15.929	69.966	69.868	.029	-61.095	-54.789	39.912
400	17.345	74.763	70.512	1.700	-64.699	-51.940	28.377
500	18.145	78.727	71.770	3.478	-64.573	-48.765	21.314
600	18.627	82.081	73.217	5.319	-64.425	-45.616	16.615
700	18.936	84.978	74.695	7.198	-64.268	-42.494	13.267
800	19.145	87.521	76.142	9.103	-64.111	-39.396	10.762
900	19.291	89.785	77.535	11.025	-63.952	-36.315	8.818
1000	19.398	91.823	78.863	12.960	-63.794	-33.253	7.267
1100	19.478	93.676	80.127	14.904	-63.639	-30.207	6.001
1200	19.540	95.373	81.328	16.855	-63.485	-27.173	4.949
1300	19.588	96.939	82.469	18.811	-63.336	-24.152	4.060
1400	19.627	98.392	83.555	20.772	-63.188	-21.144	3.301
1500	19.658	99.748	84.590	22.736	-63.045	-18.146	2.644
1600	19.684	101.017	85.577	24.704	-62.904	-15.157	2.070
1700	19.705	102.211	86.521	26.673	-62.767	-12.176	1.565
1800	19.723	103.338	87.424	28.644	-62.634	-9.207	1.118
1900	19.738	104.405	88.290	30.617	-62.503	-6.241	.718
2000	19.751	105.417	89.121	32.592	-62.376	-3.281	.359
2100	19.762	106.381	89.921	34.568	-62.252	-.332	.035
2200	19.772	107.301	90.690	36.544	-62.133	2.613	-.260
2300	19.781	108.180	91.431	38.522	-62.017	5.555	-.528
2400	19.788	109.022	92.147	40.500	-61.904	8.490	-.773
2500	19.795	109.830	92.838	42.480	-61.796	11.420	-.998
2600	19.800	110.606	93.507	44.459	-61.691	14.349	-1.206
2700	19.806	111.354	94.154	46.440	-61.588	17.271	-1.398
2800	19.810	112.074	94.781	48.420	-61.490	20.189	-1.576
2900	19.815	112.769	95.390	50.402	-61.395	23.108	-1.741
3000	19.818	113.441	95.980	52.383	-61.305	26.015	-1.895
3100	19.822	114.091	96.554	54.365	-61.217	28.925	-2.039
3200	19.825	114.721	97.112	56.348	-61.133	31.830	-2.174
3300	19.828	115.331	97.655	58.330	-61.053	34.733	-2.300
3400	19.830	115.923	98.183	60.313	-60.975	37.635	-2.419
3500	19.833	116.497	98.698	62.296	-60.903	40.541	-2.531
3600	19.835	117.056	99.201	64.280	-60.833	43.438	-2.637
3700	19.837	117.600	99.691	66.263	-60.767	46.330	-2.736
3800	19.839	118.129	100.169	68.247	-60.704	49.226	-2.831
3900	19.840	118.644	100.636	70.231	-60.647	52.116	-2.920
4000	19.842	119.146	101.093	72.215	-60.591	55.009	-3.005
4100	19.843	119.636	101.539	74.199	-60.541	57.896	-3.086
4200	19.845	120.115	101.975	76.184	-60.493	60.782	-3.163
4300	19.846	120.581	102.403	78.168	-60.448	63.676	-3.236
4400	19.847	121.038	102.821	80.153	-60.408	66.558	-3.306
4500	19.848	121.484	103.231	82.138	-60.371	69.440	-3.372
4600	19.849	121.920	103.632	84.123	-60.337	72.327	-3.436
4700	19.850	122.347	104.026	86.108	-60.308	75.212	-3.497
4800	19.851	122.765	104.412	88.093	-60.282	78.095	-3.556
4900	19.852	123.174	104.791	90.078	-60.259	80.981	-3.612
5000	19.853	123.575	105.163	92.063	-60.241	83.862	-3.665
5100	19.854	123.968	105.528	94.049	-60.226	86.738	-3.717
5200	19.854	124.354	105.886	96.034	-60.214	89.624	-3.767
5300	19.855	124.732	106.238	98.020	-60.205	92.509	-3.814
5400	19.856	125.103	106.584	100.005	-60.202	95.382	-3.860
5500	19.856	125.468	106.924	101.991	-60.201	98.265	-3.905
5600	19.857	125.825	107.258	103.976	-60.205	101.151	-3.947
5700	19.858	126.177	107.587	105.962	-60.212	104.031	-3.989
5800	19.858	126.522	107.911	107.948	-60.221	106.915	-4.028
5900	19.859	126.862	108.229	109.934	-60.235	109.788	-4.067
6000	19.859	127.195	108.542	111.920	-60.252	112.674	-4.104

June 30, 1962; Sept. 30, 1965

BROMINE TRIFLUORIDE (BrF_3) (IDEAL GAS) MOL. WT. = 136.9042

Point Group C_{2v}

$\Delta H^\circ_{f\ 0} = -58.4 \pm 0.7$ kcal. mole^{-1}

$S^\circ_{298.15} = 69.867$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -61.1 \pm 0.7$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
674 (1)	613 (1)
[528] (1)	[384] (1)
[300] (1)	[289] (1)

Bond Distance: $Br\text{-}F_1 = Br\text{-}F_3 = 1.8061$ Å $Br\text{-}F_2 = 1.721$ Å

Bond Angle: $F_1\text{-}Br\text{-}F_2 = 86°\ 12.6'$ $F_2\text{-}Br\text{-}F_3 = 86°\ 12.6'$ $F_3\text{-}Br\text{-}F_1 = 187°\ 34.8'$ $\sigma = 2$

Product of the Moment of Inertia: $I_AI_BI_C = 4.519225 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15} = -61.087 \pm 0.7$ kcal. mole^{-1} is from L. Stein, J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta H^\circ_{f\ 298.15} = -64.78$ kcal. mole^{-1} was based upon gaseous Br_2, which has been adjusted to the liquid Br_2 reference state at 298.15°K.

Heat Capacity and Entropy.

D. W. Magnuson, Report No. K-1179, Carbide and Carbon Chemicals Co., K-25 plant, Oak Ridge, Tennessee (December, 1954) determined the moments of inertia and quadrupole coupling coefficients of both $Br^{79}F_3$ and $Br^{81}F_3$ from a number of microwave transitions. From the moment of inertia the bromine trifluoride molecule was found to have a distorted -"T" structure with one short, 1.721 Å, and two long, 1.810 Å Br-F bonds. The FBrF angle was found to be 86° 12.6'.

H. H. Claassen, B. Weinstock, and J. G. Malm, J. Chem. Phys. 28, 285 (1958), observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of $BrF_3(g)$, from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is 71.9 e.u. at 316.27°K. compared with a value of 70.82 e.u. from this table, the difference is probably within the uncertainty of the data. The three principal moments of inertia are: $I_A = 7.7514 \times 10^{-39}$, $I_B = 2.05791 \times 10^{-38}$ and $I_C = 2.83306 \times 10^{-38}$ g. cm.^{2}

Bromine Pentafluoride (BrF_5)

(Ideal Gas) Mol. Wt. = 174.901

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.584	- 98.846	- 98.846	INFINITE
100	11.313	58.201	95.297	- 3.710	- 100.043	- 95.045	207.712
200	19.311	68.612	79.417	- 2.161	- 100.829	- 89.690	98.004
298	24.236	77.337	77.337	.000	- 102.466	- 83.989	61.563
300	24.304	77.487	77.338	.045	- 102.473	- 83.875	61.100
400	27.005	84.888	78.328	2.624	- 105.939	- 76.946	42.039
500	28.524	91.092	80.278	5.407	- 105.614	- 69.736	30.480
600	29.439	96.380	82.532	8.309	- 105.237	- 62.594	22.799
700	30.024	100.965	84.845	11.284	- 104.835	- 55.518	17.333
800	30.419	105.002	87.118	14.307	- 104.425	- 48.503	13.250
900	30.697	108.602	89.308	17.364	- 104.007	- 41.538	10.086
1000	30.899	111.847	91.403	20.444	- 103.590	- 34.619	7.566
1100	31.050	114.799	93.398	23.542	- 103.173	- 27.743	5.512
1200	31.167	117.506	95.295	26.653	- 102.756	- 20.902	3.807
1300	31.258	120.005	97.101	29.775	- 102.344	- 14.097	2.370
1400	31.331	122.324	98.821	32.904	- 101.935	- 7.325	1.143
1500	31.390	124.488	100.461	36.040	- 101.531	- .580	.084
1600	31.439	126.515	102.027	39.182	- 101.131	6.136	- .838
1700	31.479	128.422	103.524	42.328	- 100.735	12.831	- 1.649
1800	31.513	130.223	104.957	45.478	- 100.346	19.494	- 2.367
1900	31.542	131.927	106.332	48.630	- 99.959	26.145	- 3.007
2000	31.566	133.546	107.653	51.786	- 99.578	32.773	- 3.581
2100	31.588	135.087	108.923	54.943	- 99.203	39.376	- 4.098
2200	31.606	136.556	110.146	58.103	- 98.833	45.968	- 4.566
2300	31.622	137.962	111.325	61.265	- 98.468	52.543	- 4.992
2400	31.636	139.308	112.463	64.427	- 98.109	59.101	- 5.382
2500	31.649	140.600	113.563	67.592	- 97.757	65.642	- 5.738
2600	31.660	141.841	114.627	70.757	- 97.409	72.174	- 6.066
2700	31.670	143.036	115.657	73.924	- 97.065	78.691	- 6.369
2800	31.678	144.188	116.655	77.091	- 96.727	85.192	- 6.649
2900	31.686	145.300	117.624	80.259	- 96.395	91.687	- 6.909
3000	31.694	146.374	118.565	83.428	- 96.071	98.160	- 7.151
3100	31.700	147.413	119.479	86.598	- 95.749	104.632	- 7.376
3200	31.706	148.420	120.367	89.768	- 95.434	111.091	- 7.587
3300	31.711	149.396	121.232	92.939	- 95.125	117.537	- 7.784
3400	31.716	150.342	122.075	96.111	- 94.820	123.980	- 7.969
3500	31.721	151.262	122.896	99.282	- 94.523	130.415	- 8.143
3600	31.725	152.156	123.696	102.455	- 94.229	136.837	- 8.307
3700	31.729	153.025	124.477	105.627	- 93.942	143.251	- 8.461
3800	31.732	153.871	125.239	108.800	- 93.660	149.661	- 8.607
3900	31.735	154.695	125.984	111.974	- 93.386	156.056	- 8.745
4000	31.738	155.499	126.712	115.147	- 93.115	162.449	- 8.875
4100	31.741	156.283	127.424	118.321	- 92.852	168.831	- 8.999
4200	31.744	157.047	128.120	121.496	- 92.593	175.215	- 9.117
4300	31.746	157.794	128.801	124.670	- 92.338	181.594	- 9.229
4400	31.748	158.524	129.469	127.845	- 92.093	187.959	- 9.336
4500	31.750	159.238	130.122	131.020	- 91.850	194.314	- 9.437
4600	31.752	159.936	130.763	134.195	- 91.613	200.671	- 9.534
4700	31.754	160.619	131.391	137.370	- 91.384	207.024	- 9.626
4800	31.756	161.287	132.007	140.546	- 91.158	213.376	- 9.715
4900	31.758	161.942	132.611	143.721	- 90.939	219.719	- 9.799
5000	31.759	162.584	133.204	146.897	- 90.726	226.052	- 9.880
5100	31.761	163.212	133.786	150.073	- 90.518	232.381	- 9.958
5200	31.762	163.829	134.358	153.249	- 90.316	238.720	- 10.033
5300	31.763	164.434	134.920	156.426	- 90.118	245.048	- 10.104
5400	31.764	165.028	135.472	159.602	- 89.929	251.356	- 10.172
5500	31.766	165.611	136.015	162.779	- 89.743	257.681	- 10.239
5600	31.767	166.183	136.548	165.955	- 89.565	264.000	- 10.303
5700	31.768	166.745	137.073	169.132	- 89.392	270.315	- 10.364
5800	31.769	167.298	137.590	172.309	- 89.222	276.622	- 10.423
5900	31.770	167.841	138.098	175.486	- 89.060	282.920	- 10.480
6000	31.770	168.375	138.598	178.663	- 88.903	289.223	- 10.534

Sept. 30, 1962; Sept. 30, 1965

BROMINE PENTAFLUORIDE (BrF_5) (IDEAL GAS) MOL. WT. = 174.901

Point Group C_{4v}

$\Delta H_{f\,0}^\circ$ = -98.8 ± 0.5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 77.34 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\,298.15}$ = -102.5 ± 0.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ν, cm.$^{-1}$	ν, cm.$^{-1}$	ν, cm.$^{-1}$
683 (1)	535 (1)	644 (2)
587 (1)	[281](1)	415 (2)
369 (1)	312 (1)	245 (2)

Bond Distance: $Br\text{-}F_{(equatorial)} = 1.79$ Å $Br\text{-}F_{(axial)} = 1.68$ Å

Bond Angle: $F_{(equatorial)}\text{-}Br\text{-}F_{(equatorial)} = [90°]$ and $F_{(axial)}\text{-}Br\text{-}F_{(equatorial)} = [90°]$ $\sigma = 4$

Product of the Moment of Inertia: $I_AI_BI_C$ = 3.2035 X 10^{-113} g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\,298.15}$ = -102.466 ± 0.5 kcal. mole^{-1} is from L. Stein J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta H^\circ_{f\,298.15}$ = -106.16 kcal. mole^{-1} was based upon gaseous Br_2 which has been adjusted to the liquid Br_2 reference state at 298.15°K.

Heat Capacity and Entropy.

G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965) report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF_5, IF_5, ClF_5 and $XeOF_4$. The fundamental frequencies are taken from Begun, et al., except for ν_9 which was beyond the range of their infrared measurements. The value ν_9 = 245 cm.$^{-1}$ for the gas has been observed by R. S. McDowell and L. B. Asprey, J. Chem. Phys. 37, 165 (1962) and is confirmed by 237 cm.$^{-1}$ found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals ν_4 and ν_6. One Raman active frequency, persumably ν_5, is not observed in any of the four molecules. The value ν_5 = 281 cm.$^{-1}$ was obtained from the normal coordinate calculation. Previous Raman studies were reported by C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 1830 (1952).

A tetragonal pyramidal structure (C_{4v} symmetry) with the above parameters was used by Begun, et al., in the analysis of the spectra. This symmetry is consistent with the NMR spectra of H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951), with the dipole moment determined by M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, J. Am. Chem. Soc. 78, 44 (1956), and with the X-ray crystal structure obtained by R. D. Burbank and F. N. Bensey, Jr., J. Chem. Phys. 27, 982 (1957). Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (80.5-86.5°). Begun, et al., indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle. The three principal moments of inertia are: $I_A = 2.81497 \times 10^{-38}$, $I_B = 2.81497 \times 10^{-38}$ and $I_C = 4.04277 \times 10^{-38}$ g. cm.^{2}

Hydrogen Bromide (HBr)

(Ideal Gas) Mol. Wt. = 80.91697

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.067	-6.836	-6.836	INFINITE
100	6.959	39.861	53.655	-1.379	-6.861	-8.985	19.635
200	6.961	44.685	48.102	-.683	-7.052	-11.048	12.072
298	6.965	47.465	47.465	.000	-8.710	-12.785	9.372
300	6.965	47.508	47.465	.013	-8.720	-12.810	9.332
400	6.984	49.514	47.739	.710	-12.490	-13.405	7.324
500	7.040	51.078	48.256	1.411	-12.580	-13.625	5.955
600	7.139	52.369	48.837	2.120	-12.665	-13.825	5.036
700	7.272	53.479	49.422	2.840	-12.743	-14.012	4.374
800	7.423	54.460	49.992	3.575	-12.809	-14.189	3.876
900	7.576	55.343	50.538	4.325	-12.864	-14.358	3.486
1000	7.725	56.149	51.060	5.090	-12.908	-14.521	3.173
1100	7.863	56.892	51.557	5.869	-12.942	-14.681	2.917
1200	7.989	57.582	52.030	6.662	-12.968	-14.838	2.702
1300	8.103	58.226	52.482	7.466	-12.988	-14.993	2.520
1400	8.205	58.830	52.914	8.282	-13.003	-15.146	2.364
1500	8.296	59.399	53.328	9.107	-13.014	-15.298	2.229
1600	8.378	59.937	53.724	9.941	-13.024	-15.451	2.110
1700	8.451	60.448	54.105	10.782	-13.031	-15.602	2.006
1800	8.517	60.933	54.471	11.631	-13.037	-15.755	1.913
1900	8.577	61.395	54.823	12.486	-13.041	-15.904	1.829
2000	8.630	61.836	55.163	13.346	-13.045	-16.055	1.754
2100	8.679	62.258	55.491	14.212	-13.048	-16.205	1.686
2200	8.724	62.663	55.808	15.082	-13.052	-16.356	1.625
2300	8.765	63.052	56.114	15.956	-13.056	-16.506	1.568
2400	8.803	63.426	56.411	16.835	-13.060	-16.655	1.517
2500	8.838	63.786	56.699	17.717	-13.065	-16.806	1.469
2600	8.870	64.133	56.978	18.602	-13.070	-16.954	1.425
2700	8.900	64.468	57.250	19.491	-13.075	-17.103	1.384
2800	8.929	64.792	57.513	20.382	-13.082	-17.252	1.347
2900	8.955	65.106	57.770	21.276	-13.088	-17.400	1.311
3000	8.980	65.410	58.019	22.173	-13.095	-17.550	1.278
3100	9.004	65.705	58.262	23.072	-13.103	-17.699	1.248
3200	9.027	65.991	58.500	23.974	-13.111	-17.846	1.219
3300	9.048	66.269	58.731	24.877	-13.121	-17.993	1.192
3400	9.069	66.540	58.957	25.783	-13.131	-18.144	1.166
3500	9.088	66.803	59.177	26.691	-13.142	-18.289	1.142
3600	9.107	67.059	59.392	27.601	-13.155	-18.436	1.119
3700	9.125	67.309	59.603	28.513	-13.168	-18.583	1.098
3800	9.143	67.553	59.809	29.426	-13.182	-18.730	1.077
3900	9.160	67.790	60.011	30.341	-13.198	-18.872	1.058
4000	9.176	68.023	60.208	31.258	-13.215	-19.023	1.039
4100	9.192	68.249	60.401	32.176	-13.232	-19.165	1.022
4200	9.208	68.471	60.591	33.096	-13.251	-19.310	1.005
4300	9.223	68.688	60.777	34.018	-13.271	-19.454	.989
4400	9.238	68.900	60.959	34.941	-13.292	-19.597	.973
4500	9.252	69.108	61.138	35.866	-13.314	-19.743	.959
4600	9.266	69.311	61.313	36.791	-13.338	-19.881	.945
4700	9.280	69.511	61.485	37.719	-13.362	-20.024	.931
4800	9.294	69.706	61.655	38.647	-13.388	-20.166	.918
4900	9.307	69.898	61.821	39.578	-13.414	-20.306	.906
5000	9.320	70.086	61.984	40.509	-13.442	-20.447	.894
5100	9.333	70.271	62.145	41.442	-13.471	-20.589	.882
5200	9.346	70.452	62.303	42.375	-13.501	-20.726	.871
5300	9.358	70.630	62.459	43.311	-13.532	-20.862	.860
5400	9.371	70.805	62.612	44.247	-13.564	-21.003	.850
5500	9.383	70.977	62.762	45.185	-13.597	-21.138	.840
5600	9.395	71.147	62.910	46.124	-13.632	-21.281	.831
5700	9.407	71.313	63.056	47.064	-13.667	-21.413	.821
5800	9.419	71.477	63.200	48.005	-13.703	-21.551	.812
5900	9.430	71.638	63.342	48.948	-13.741	-21.685	.803
6000	9.442	71.796	63.481	49.891	-13.779	-21.819	.795

Sept. 30, 1961; Sept. 30, 1965

HYDROGEN BROMIDE (HBr) (IDEAL GAS) MOL. WT. = 80.91697

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0} = -6.84 \pm 0.13$ kcal. mole^{-1}

$S^\circ_{298.15} = 47.465$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -8.71 \pm 0.10$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	1

$\omega_e = 2649.218 \pm 0.016$ cm.$^{-1}$

$\omega_e x_e = 45.246 \pm 0.008$ cm.$^{-1}$

$\sigma = 1$

$B_e = 8.46571 \pm 1.8 \times 10^{-4}$ cm.$^{-1}$

$\alpha_e = 0.23248 \pm 7 \times 10^{-5}$ cm.$^{-1}$

$r_e = 1.414$ Å

Heat of Formation.

The enthalpy change, $\Delta H^\circ_{r\ 376.2} = -12.47 \pm 0.13$ kcal. mole^{-1}, for the reaction (1) 1/2 $H_2(g)$ + 1/2 $Br_2(g)$ = HBr(g) was reported by J. R. Lacher, L. Casali and J. D. Park, J. Phys. Chem. 60, 608 (1956). Using $\Delta H^\circ_{f\ 298.15}$ (Br_2, g) = 7.39 kcal. mole^{-1}, the $\Delta H^\circ_{f\ 298.15}$ (HBr, g) was derived as -8.71 ± 0.13 kcal. mole^{-1}.

The heat of oxidation of aqueous sulfur dioxide with gaseous chlorine and liquid bromine were determined by calorimetric methods by W. H. Johnson and J. R. Ambrose, J. Res. Natl. Bur. Std. 67A, 427 (1963) and W. H. Johnson and S. Sunner, Acta Chem. Scand., 17, 1917 (1963), respectively. The results were given as $\Delta H^\circ_{r\ 298.15} = -77.28 \pm$ 0.14 kcal. mole^{-1} ($X_2 = Cl_2(g)$) and -55.47 ± 0.11 kcal. mole^{-1} ($X_2 = Br_2(l)$) for the reaction $X_2 + SO_2\cdot2500\ H_2O$ + 2 $H_2O(l) = H_2SO_4\cdot2500\ H_2O$ + 2 (HX·1250 H_2O). The enthalpy change for the reaction $Cl_2(g)$ + 2 (HBr·1250 H_2O = $Br_2(l)$ + 2 (HCl·1250 H_2O) was calculated to be -21.82 ± 0.18 kcal. mole^{-1}. Using $\Delta H^\circ_{f\ 298.15}$ (HCl·1250 H_2O) = -39.93 ± 0.05 kcal. mole^{-1}, the heat of formation for HBr·1250 H_2O was derived to be -28.932 ± 0.10 kcal. mole^{-1}. Employing ΔH° (HBr·1250 H_2O → HBr·∞H_2O) = -0.084 kcal. mole^{-1}, leads to $\Delta H^\circ_{f\ 298.15}$ (HBr·∞H_2O) = -29.016 ± 0.10 kcal. mole^{-1}. Based on the value, $\Delta H^\circ_{r\ 298.15} = -20.350 \pm 0.012$ kcal. mole^{-1} for the reaction HBr(g) = HBr (∞ H_2O) reported by C. E. Vanderzee and J. D. Nutter, J. Phys. Chem. 67, 2521 (1963), the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for HBr(g) was evaluated as -8.67 ± 0.10 kcal. mole^{-1}.

The heats of oxidation of As_2O_3 to As_2O_5 in aqueous solution with $Br_2(l)$ and $Cl_2(g)$ were measured by L. Bjellerup, S. Sunner and I. Wadsö, Acta Chem. Scand. 11, 1761 (1957) and S. Sunner and S. Thoren, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July, 1963. Using the values $\Delta H^\circ_r = -56.61 \pm 0.11$ kcal. mole^{-1} ($X_2 = Br_2(l)$) and -100.09 ± 0.08 kcal. mole^{-1} ($X_2 = Cl_2$ (g)) for the reaction As_2O_3(aq.) + 2X_2 + 2 H_2O(aq.) → As_2O_5(aq.) + 4 HX(aq.) obtained from H. A. Skinner, Pure Appl. Chem. 8, 95 (1964), the ethalpy change for the reaction 2Br_2(l) + 4HCl(aq.) = 2Cl_2 + 4HBr(aq.) was calculated to be +43.48 ± 0.14 kcal. mole^{-1}. Based on $\Delta H^\circ_{f\ 298.15}$ (HCl, ∞ H_2O) = -39.93 ± 0.05 kcal. mole^{-1}, the value of $\Delta H^\circ_{f\ 298.15}$ (HBr, ∞ H_2O) was derived to be -29.06 ± 0.06 kcal. mole^{-1}, yielding $\Delta H^\circ_{f\ 298.15}$ (HBr, g) = -8.71 ± 0.06 kcal. mole^{-1}.

The value of $\Delta H^\circ_{f\ 298.15}$ (HBr, g) adopted is -8.71 ± 0.10 kcal. mole^{-1}.

Heat Capacity and Entropy.

The values of ω_e, $\omega_e x_e$, B_e and α_e were taken from T. C. James and R. J. Thibault, J. Chem. Phys. 42, 1450 (1965), and corrected to the average isotopic species. Submillimeter-wave spectra of HBr were measured by G. Jones and W. Gordy, Phys. Rev. 136, A 1229 (1964). The molecular constants derived were close to the values adopted. The ground state configuration was obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950, in which molecular constants for HBr(g) were also given. A precise measurement of the infrared fundamental bands of HBr has been made by E. K. Plyler, J. Res. Natl. Bur. Std., 64, 377 (1960). The corresponding rotational and vibrational constants have been calculated from the observed data. The moment of inertia is 3.30614 X 10^{-40} g. cm.^{2}

Ammonium Bromide (NH_4Br)

(Crystal) Mol. Wt. = 97.94758

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 4.052	- 60.939	- 60.939	INFINITE
100	10.584	8.530	43.950	- 3.542	- 62.623	- 56.049	122.490
200	18.805	18.610	28.875	- 2.053	- 63.277	- 49.203	53.764
298	21.194	26.970	26.970	.000	- 64.900	- 42.085	30.847
300	21.246	27.101	26.970	.039	- 64.910	- 41.943	30.554
400	22.160	33.381	27.820	2.224	- 68.581	- 33.532	18.320
500	20.840	39.597	29.714	4.942	- 68.055	- 24.908	10.887
600	24.480	43.728	31.707	7.213	- 67.984	- 16.279	5.929
700	27.500	47.731	33.712	9.814	- 67.597	- 7.687	2.400
800	30.300	51.591	35.707	12.707	- 66.935	.827	- .226
900	32.700	55.300	37.679	15.859	- 66.036	9.247	- 2.245
1000	34.900	58.861	39.621	19.241	- 64.927	17.554	- 3.836
1100	36.831	62.279	41.526	22.829	- 63.636	25.741	- 5.114
1200	38.600	65.561	43.393	26.602	- 62.183	33.805	- 6.156
1300	40.183	68.714	45.221	30.542	- 60.589	41.739	- 7.017
1400	41.650	71.746	47.008	34.634	- 58.868	49.547	- 7.734
1500	43.000	74.667	48.755	38.868	- 57.035	57.228	- 8.338

Mar. 31. 1962; Sept. 30, 1965

AMMONIUM BROMIDE (NH_4Br) (CRYSTAL) MOL. WT. = 97.94758

BrH$_4$N

$S^\circ_{298.15}$ = 26.97 cal. deg.$^{-1}$ mole^{-1}

T_t = 411°K.

T_m = 815.2°K.

T_d = 670°K.

$\Delta H^\circ_{f\ 0}$ = -60.9 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -64.9 ± 0.3 kcal. mole^{-1}

ΔH°_t = 0.77 kcal. mole^{-1}

ΔH°_m = Unknown

Heat of Formation.

The equilibrium pressures for the reaction $NH_4Br(c) \rightarrow NH_3(g) + HBr(g)$ have been measured by several investigators. Using the densi-tensimeter, A. Smits and R. Purcell, J. Chem. Soc 2944 (1928), determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method", from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes (ΔH°_r) of the decomposition reaction by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	Equipment Used
Smith and Calvert (1)	576.40-676.02	45.12 ± 0.13	44.93	Isoteniscope
Smits and Purcell (2)	604.95-668.15	45.50 ∓ 0.17	45.08	Densi-tensimeter
Johnson (3)	573.15-667.75	45.41 ∓ 0.44	44.85	Spiral Manometer

(1) A. Smith and R. P. Calvert, J. Am. Chem. Soc. 36, 1363 (1914).
(2) A. Smits and R. Purcell, J. Chem. Soc. 2944 (1928).
(3) F. M. G. Johnson, Z. physik. Chem. 65, 38 (1909).

The value of $\Delta H^\circ_{r\ 298.15}$ adopted is 45.2 ± 0.2 kcal. mole^{-1}. Using $\Delta H^\circ_{f\ 298.15}$ = -10.97 and -8.71 kcal. mole^{-1} for $NH_3(g)$ and HBr(g), respectively, the value of $\Delta H^\circ_{f\ 298.15}$ for $NH_4Br(c)$ is evaluated as -64.9 ± 0.3 kcal. mole^{-1}. The corresponding $\Delta H^\circ_{r\ 298.15}$ value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS2, National Bureau of Standards, April 1, 1965, is 45.5 ± 0.2 kcal. mole^{-1}.

The vapor densities (573-661°K.) of dissociation products of $NH_4Br(c)$ were also measured by A. Smith and R. H. Lombard, J. Am. Chem. Soc. 37, 38 (1915). Using the equilibrium pressures reported by A. Smith and R. P. Calvert, loc. cit, they derived the corresponding degrees of dissociation of $NH_4Br(c)$ at different temperatures. The calculated results indicated that only 48% of $NH_4Br(c)$ decomposed at 573°K. and as reaction temperatures increased to 661°K. the degree of dissociation decreased to 10%. This conclusion was stated to be erroneous by Smits and Purcell, loc. cit., probably because of incorrect density determinations.

Heat Capacity and Entropy.

The low temperature (13-305°K.) heat capacities and $S^\circ_{298.15}$ were obtained from M. Sorai, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 38, 1125 (1965). The C_p values above 305°K. were estimated by comparison with those for NaCl(c), NaBr(c) and $NH_4Cl(c)$. The low temperature heat capacities were also measured by R. Ewald, Ann. Physik, 44, 1213 (1914), 139-301°K., and F. Simon, C. V. Simson and M. Ruhemann, Z. phys. Chem. 129, 339 (1927), 201.2-277.1°K.

Transition Data.

The temperature (T_t) and heat of transition (ΔH°_t) were given by P. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 91 (1916-17). T_t = 419.5 ± 0.6°K. was reported by M. M. Markowitz and D. A. Boryta, J. Phys. Chem. 66, 1477 (1962), which was determined by differential thermal analysis. According to Sorai, Suga and Seki, loc. cit., there are 3 solid phase transitions, namely Phase IV (CsCl) → Phase III (tetragonal) at 108°K., Phase III (tetragonal) → Phase II (CsCl) at 235°K. and Phase II (CsCl) → Phase I (NaCl) at 411°K.

Melting Temperature.

The value of T_m was taken from H. Rassow, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Temperature of Decomposition.

The temperature of decomposition (T_d) was calculated as the temperature at which the total pressure of the decomposition products for the reaction $NH_4Br(c) \rightarrow NH_3(g) + HBr(g)$ equals 1 atm. T_d = 674 and 668.4°K. were reported by N. W. Luft, Ind. Chemist, 31, 502 (1955) and M. M. Markowitz and D. A Boryta, loc. cit., respectively.

BrH$_4$N

Mercurous Bromide (HgBr)

(Ideal Gas) Mol. Wt. = 280.526

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.450	27.612	27.612	INFINITE
100	8.107	55.494	72.643	-1.715	27.606	23.589	-51.552
200	8.722	61.355	65.684	-.866	27.252	19.701	-21.527
298	8.894	64.875	64.875	.000	24.900	16.399	-12.020
300	8.896	64.930	64.875	.016	24.868	16.347	-11.908
400	8.978	67.502	65.225	.910	21.001	14.287	-7.806
500	9.031	69.511	65.889	1.811	20.808	12.631	-5.521
600	9.072	71.161	66.634	2.716	20.620	11.012	-4.011
700	9.108	72.562	67.383	3.625	6.408	10.996	-3.433
800	9.140	73.781	68.108	4.538	6.375	11.654	-3.184
900	9.171	74.859	68.800	5.453	6.346	12.317	-2.991
1000	9.201	75.827	69.455	6.372	6.317	12.982	-2.837
1100	9.230	76.705	70.075	7.294	6.291	13.649	-2.712
1200	9.259	77.510	70.661	8.218	6.267	14.319	-2.608
1300	9.287	78.252	71.217	9.145	6.245	14.991	-2.520
1400	9.315	78.941	71.744	10.075	6.226	15.665	-2.445
1500	9.343	79.585	72.246	11.008	6.208	16.340	-2.381
1600	9.371	80.189	72.724	11.944	6.192	17.015	-2.324
1700	9.398	80.758	73.180	12.883	6.179	17.693	-2.275
1800	9.426	81.296	73.616	13.824	6.167	18.369	-2.230
1900	9.453	81.806	74.033	14.768	6.159	19.049	-2.191
2000	9.481	82.291	74.434	15.714	6.152	19.727	-2.156
2100	9.508	82.755	74.820	16.664	6.147	20.405	-2.123
2200	9.535	83.198	75.190	17.616	6.145	21.083	-2.094
2300	9.563	83.622	75.548	18.571	6.144	21.763	-2.068
2400	9.590	84.030	75.893	19.529	6.147	22.445	-2.044
2500	9.617	84.422	76.226	20.489	6.150	23.121	-2.021
2600	9.644	84.799	76.549	21.452	6.156	23.800	-2.001
2700	9.671	85.164	76.861	22.418	6.165	24.479	-1.981
2800	9.699	85.546	77.164	23.386	6.175	25.156	-1.963
2900	9.726	85.857	77.458	24.357	6.188	25.836	-1.947
3000	9.753	86.187	77.743	25.331	6.203	26.512	-1.931
3100	9.780	86.507	78.021	26.308	6.220	27.189	-1.917
3200	9.807	86.818	78.291	27.287	6.239	27.866	-1.903
3300	9.834	87.120	78.554	28.270	6.261	28.541	-1.890
3400	9.861	87.414	78.810	29.254	6.285	29.215	-1.878
3500	9.889	87.701	79.060	30.242	6.311	29.890	-1.866
3600	9.916	87.980	79.304	31.232	6.339	30.562	-1.855
3700	9.943	88.252	79.542	32.225	6.369	31.234	-1.845
3800	9.970	88.517	79.775	33.221	6.401	31.908	-1.835
3900	9.997	88.777	80.002	34.219	6.435	32.579	-1.826
4000	10.024	89.030	80.225	35.220	6.472	33.248	-1.816
4100	10.051	89.278	80.443	36.224	6.511	33.914	-1.808
4200	10.078	89.520	80.656	37.230	6.552	34.583	-1.799
4300	10.105	89.758	80.865	38.239	6.595	35.251	-1.792
4400	10.132	89.990	81.070	39.251	6.640	35.916	-1.784
4500	10.160	90.218	81.271	40.266	6.688	36.581	-1.777
4600	10.187	90.442	81.467	41.283	6.737	37.244	-1.769
4700	10.214	90.661	81.661	42.303	6.788	37.911	-1.763
4800	10.241	90.877	81.851	43.326	6.840	38.567	-1.756
4900	10.268	91.088	82.037	44.351	6.896	39.230	-1.750
5000	10.295	91.296	82.220	45.380	6.954	39.891	-1.744
5100	10.322	91.500	82.400	46.410	7.012	40.549	-1.738
5200	10.349	91.701	82.577	47.444	7.072	41.206	-1.732
5300	10.376	91.898	82.751	48.480	7.134	41.862	-1.726
5400	10.403	92.092	82.922	49.519	7.198	42.512	-1.720
5500	10.430	92.283	83.091	50.561	7.264	43.168	-1.715
5600	10.457	92.472	83.256	51.605	7.330	43.822	-1.710
5700	10.484	92.657	83.420	52.652	7.399	44.475	-1.705
5800	10.511	92.840	83.581	53.702	7.468	45.121	-1.700
5900	10.539	93.019	83.739	54.755	7.538	45.767	-1.695
6000	10.566	93.197	83.895	55.810	7.610	46.413	-1.691

December 31, 1961

Mercurous Bromide (HgBr) (IDEAL GAS) MOL. WT. = 280.526

Ground State Configuration $^2\Sigma$

$S^\circ_{298.15}$ = 64.875 cal deg^{-1} mole^{-1} $\Delta H^\circ_{f\ 298.15}$ = 24.9 ± 9.0 kcal mole^{-1}

Electronic Levels and Multiplicities

ε, cm^{-1}	g_i
0	2

ω_e = 187.29 cm^{-1} $\omega_e x_e$ = 0.9665 cm^{-1} σ = 1

B_e = [0.0545] cm^{-1} α_e = [0.0003] cm^{-1} r_e = [2.33] Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 0.7 ± 0.4 e.v. for the dissociation energy into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from K. Wieland, Zeits. f. Electrochemie 64, 761 (1960) were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York, 1950. The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides.

Iodine Monobromide (IBr)
(Ideal Gas) GFW = 206.8134

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.370	11.906	11.906	INFINITE
100	7.625	52.834	69.408	-1.657	11.921	8.010	-17.505
200	8.457	58.428	62.656	-.846	11.558	4.232	-4.624
298	8.731	61.864	61.864	.000	9.770	.887	-.650
300	8.734	61.918	61.864	.016	9.758	.833	-.606
400	8.853	64.449	62.208	.896	3.932	-1.287	.703
500	8.919	66.432	62.862	1.785	-1.382	-2.086	.912
600	8.961	68.062	63.597	2.679	-1.381	-2.227	.811
700	8.993	69.446	64.336	3.577	-1.379	-2.369	.740
800	9.019	70.649	65.052	4.478	-1.377	-2.511	.686
900	9.041	71.712	65.734	5.381	-1.375	-2.652	.644
1000	9.061	72.666	66.380	6.286	-1.372	-2.794	.611
1100	9.080	73.530	66.991	7.193	-1.370	-2.936	.583
1200	9.098	74.321	67.570	8.102	-1.367	-3.079	.561
1300	9.116	75.050	68.117	9.012	-1.363	-3.221	.541
1400	9.136	75.726	68.637	9.925	-1.360	-3.364	.525
1500	9.159	76.357	69.131	10.840	-1.355	-3.508	.511
1600	9.186	76.949	69.601	11.757	-1.350	-3.650	.499
1700	9.220	77.507	70.050	12.677	-1.342	-3.795	.488
1800	9.261	78.035	70.479	13.601	-1.332	-3.940	.478
1900	9.312	78.537	70.890	14.530	-1.319	-4.084	.470
2000	9.374	79.017	71.285	15.464	-1.302	-4.233	.463
2100	9.450	79.476	71.664	16.405	-1.279	-4.379	.456
2200	9.539	79.917	72.029	17.354	-1.249	-4.527	.450
2300	9.643	80.344	72.381	18.313	-1.210	-4.678	.444
2400	9.762	80.756	72.722	19.283	-1.162	-4.826	.440
2500	9.897	81.158	73.051	20.266	-1.102	-4.983	.436
2600	10.046	81.549	73.371	21.263	-1.029	-5.139	.432
2700	10.210	81.931	73.681	22.276	-.942	-5.299	.429
2800	10.386	82.305	73.982	23.306	-.839	-5.460	.426
2900	10.575	82.673	74.275	24.353	-.719	-5.628	.424
3000	10.773	83.035	74.561	25.421	-.580	-5.802	.423
3100	10.980	83.391	74.840	26.508	-.423	-5.975	.421
3200	11.193	83.743	75.113	27.617	-.245	-6.157	.421
3300	11.411	84.091	75.380	28.747	-.048	-6.346	.420
3400	11.631	84.435	75.641	29.899	.170	-6.541	.420
3500	11.851	84.775	75.897	31.073	.409	-6.739	.421
3600	12.069	85.112	76.149	32.269	.669	-6.949	.422
3700	12.283	85.446	76.395	33.487	.950	-7.166	.423
3800	12.491	85.776	76.638	34.726	1.250	-7.388	.425
3900	12.692	86.103	76.876	35.985	1.569	-7.617	.427
4000	12.884	86.427	77.111	37.264	1.907	-7.861	.430
4100	13.066	86.748	77.342	38.562	2.263	-8.110	.432
4200	13.237	87.064	77.570	39.877	2.634	-8.363	.435
4300	13.396	87.378	77.794	41.209	3.022	-8.633	.439
4400	13.542	87.688	78.016	42.556	3.423	-8.910	.443
4500	13.675	87.993	78.234	43.917	3.837	-9.191	.446
4600	13.794	88.295	78.450	45.290	4.262	-9.485	.451
4700	13.901	88.593	78.662	46.675	4.698	-9.790	.455
4800	13.993	88.887	78.872	48.070	5.142	-10.105	.460
4900	14.073	89.176	79.079	49.473	5.594	-10.424	.465
5000	14.139	89.461	79.284	50.884	6.052	-10.756	.470
5100	14.194	89.742	79.487	52.301	6.514	-11.101	.476
5200	14.236	90.018	79.686	53.722	6.980	-11.451	.481
5300	14.267	90.289	79.884	55.148	7.450	-11.805	.487
5400	14.288	90.556	80.079	56.575	7.919	-12.174	.493
5500	14.299	90.818	80.272	58.005	8.390	-12.548	.499
5600	14.301	91.076	80.463	59.435	8.860	-12.938	.505
5700	14.294	91.329	80.651	60.865	9.328	-13.329	.511
5800	14.280	91.578	80.837	62.294	9.795	-13.733	.517
5900	14.259	91.822	81.021	63.721	10.259	-14.144	.524
6000	14.232	92.061	81.203	65.145	10.718	-14.560	.530

Sept. 30, 1962; Dec. 31, 1966

IODINE MONOBROMIDE (IBr) (IDEAL GAS) GFW = 206.8134

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 61.86 gibbs/mol

ΔHf°_0 = 11.91 ± 0.02 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 9.77 ± 0.02 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	16880	1
12230	6	[51677]	2
[16155]	5	[56349]	2

ω_e = 267.38 cm^{-1} $\omega_e X_e$ = 0.774 cm^{-1} σ = 1

B_e = 0.05568 cm^{-1} α_e = 0.00034 cm^{-1} r_e = 2.485 Å

Heat of Formation.

The equilibrium constants for the reaction (A) $I_2(g) + Br_2(g) = 2\ IBr(g)$ were determined to be 0.01124 and 0.01303 at 547.7 and 578°K, respectively, by W. Müller, Z. Physik. Chem. 123, 1 (1926), who studied the rate of reaction between $H_2(g)$ and $Br_2(g)$ in the presence of $I_2(g)$. M. Bodenstein and A. Schmidt, Z. Physik. Chem. 123, 28 (1926), derived two values of the equilibrium constants at 1495°K for the same reaction by vapor density studies on the system I_2, I, Br_2, Br and BrI. The equilibrium between $CuBr_2(c)$, $I_2(g)$, CuBr(c) and IBr(g) was investigated by J. McMorris and D. M. Yost, J. Am. Chem. Soc. 53, 2625 (1931), and the equilibrium constants at 115.0, 151.2 and 176.0°C for reaction (A) were evaluated. Based on these reported equilibrium constants, the corresponding enthalpy changes for reaction (A) are calculated by both the second and third law methods.

R. M. Badger and D. M. Yost, Phys. Rev. 37, 1548 (1931), observed the infrared bands of IBr and classified them as the $A^3\pi_2 \leftarrow X'\Sigma$ transition. They have shown that the dissociation products of the upper state are normal atoms.
W. G. Brown, Phys. Rev. 42 355 (1932), assigned a faint set of bands in the red as the $B^3\pi_{0^+} \leftarrow X'\Sigma$ system. By means of a vibrational analysis he found that the absorption spectrum of IBr is analogous to that of ICl. The heat of dissociation for IBr was evaluated to be 14,660 ± 5 cm^{-1} or 1.817 eV. Hence the enthalpy change for the reaction (B) $IBr(g) = I(g) + Br(g)$ is calculated as 41.92 kcal/mol.

The heats of formation for BrI(g) derived from the enthalpy changes for reaction (A) and (B) are presented in the following table. The value of $\Delta Hf^\circ_{298.15}$(IBr,g) adopted is 9.77 ± 0.02 kcal/mol.

Investigator	Reaction	Temperature °K	No. of Points	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$* kcal/mol
Müller (1926)	(A)	547.7, 578	2	-3.07	-3.38	-0.55	9.47
Bodenstein and Schmidt (1926)	"	1495	1	-	-2.92	-	9.70
McMorris and Yost (1931)	"	388.2-449.2	14	-2.46	-2.85	-0.9 ± 0.4	9.73
Brown (1932)	(B)	298	-	-	41.92**		9.77**

*Calculation based on third law $\Delta Hr^\circ_{298.15}$ value.

**The value is derived from D°_0(I-Br).

Heat Capacity and Entropy.

The ground state configuration, electronic levels, quantum weights, ω_e and $\omega_e X_e$ are obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., New York, 1950. The values of B_e, α_e (corrected to the average isotopic species) and r_e were reported by T. S. Jaseja, J. Mol. Spectry. 5, 445 (1960), who analyzed the microwave spectrum of IBr, corresponding to the transitions J = 4 → 5 and J = 5 → 6, for the two isotopic species, $I^{127}Br^{79}$ and $I^{127}Br^{81}$. The moment of inertia is 5.007 x 10^{-38} g cm^2.

The infrared absorption spectrum of IBr at 8000 - 6800 Å, associated with a $^3\pi_1 \leftarrow X^1\Sigma^+$ transition, was observed by L. E. Selin, Arkiv Fysik 21, 479 (1962). The derived rotational constants are different from those reported by Jaseja, loc. cit.

Potassium Bromide (KBr)

(Crystal) GFW = 119.011

T, °K	gibbs/mol Cp°	S°	−(G°−H°$_{298}$)/T	kcal/mol H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.919	-92.417	-92.417	INFINITE
100	10.312	10.265	33.595	-2.333	-92.579	-92.111	201.307
200	11.920	18.047	24.052	-1.201	-92.652	-91.615	100.112
298	12.500	22.930	22.930	.000	-94.120	-90.924	66.649
300	12.510	23.007	22.930	.023	-94.126	-90.904	66.223
400	12.860	26.655	23.425	1.292	-98.292	-88.980	48.616
500	13.205	29.558	24.371	2.593	-98.175	-86.666	37.882
600	13.470	31.988	25.444	3.927	-98.011	-84.378	30.735
700	13.883	34.094	26.532	5.293	-97.807	-82.121	25.639
800	14.440	35.981	27.597	6.708	-97.553	-79.897	21.827
900	15.222	37.725	28.626	8.188	-97.233	-77.709	18.870
1000	16.255	39.380	29.620	9.760	-96.833	-75.561	16.514
1100	17.460	40.987	30.580	11.448	-115.233	-72.432	14.391
1200	18.370	42.547	31.513	13.241	-114.388	-68.577	12.490
1300	19.030	44.045	32.420	15.113	-113.466	-64.798	10.894
1400	19.550	45.474	33.302	17.042	-112.486	-61.089	9.536
1500	20.000	46.839	34.159	19.020	-111.459	-57.454	8.371

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE (KBr) (CRYSTAL) GFW = 119.011

$S^\circ_{298.15}$ = 22.93 ± 0.01 gibbs/mol

Tm = 1007°K

ΔHf°_0 = -92.42 ± 0.1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -94.12 ± 0.1 kcal/mol

ΔHm° = 6.1 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to monomer) = 51.08 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to dimer) = 59.04 kcal/mol

Heat of Formation.

The heat of solution (ΔHsoln) of KBr(c) in $H_2O(l)$ has been measured by many investigators. The results were reviewed in detail by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. Eight pertinent ΔH°_∞ values are reproduced in the table below. Adopting the best value, ΔHr°_{298} = 4.75 ± 0.02 kcal/mol, for the reaction KBr(c) = $K^+(\infty H_2O) + Br^-(\infty H_2O)$, we derive ΔHf°_{298} = -94.12 kcal/mol for KBr(c). The auxiliary values ΔHf°_{298} = -60.32 and -29.05 kcal/mol for $K^+(\infty H_2O)$ and $Br^-(\infty H_2O)$, respectively, are obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.

ΔH°_∞ * kcal/mol	Temperature °C	m**	Investigator
4.727	16.6	0.28	P. T. Walden, Z. Physik. Chem. 58, 479 (1907).
4.777	25	0.37	J. Wüst and E. Lange, Z. Physik. Chem. 116, 161 (1925).
4.753	25	0.09	H. R. Chipman, F. M. G. Johnson, and O. Maass, Proc. Trans. Nova Scotian Inst. Sci. 17, 149 (1929).
4.684	20	0.19	M. M. Popov, A. Bundel, and V. Choller, Z. Physik. Chem. A147, 302 (1930).
4.889	23.5	0.14	A. S. Fedorov and G. F. Sil'chenko, Ukrain. Khim. Zhur. 12, 53 (1937).
4.783	25	0.13	E. Lange and W. Martin, Z. Physik. Chem. A180, 233 (1937).
4.542	20.5	0.12	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, Zhur. Obshchei Khim. 10, 2023 (1940).
4.739	25	0.28	J. Hietala, Ann. Acad. Sci. Fennicae Ser. A VI No. 63, 1 (1960).

*Values are adjusted to 298.15°K and to infinite dilution.

**Lowest experimental molality.

Heat Capacity and Entropy.

The low temperature heat capacities, 2.9 - 272.2°K, were measured by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A 242, 467 (1957), using an adiabatic calorimeter. The high temperature heat capacities, 325.25 - 711.75°K, are taken from A. Mustajoki, Ann. Acad. Sci. Fennicae, Ser. A I, 98, 7 (1951). These two sets of Cp data are joined smoothly at 298°K. The Cp values at temperatures, 720 - 1007°K, are extrapolated graphically, so that the derived enthalpy change ($H^\circ_{1007} - H^\circ_{298}$) = 9.9 kcal/mol agrees with that determined by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964. The derived enthalpies at 700, 800 and 900°K are also in good agreement with those measured by S. M. Skuratov and S. A. Lapushkin, J. Gen. Chem. USSR (Eng. Transl.) 21, 2485 (1951). The Cp values above 1007°K are obtained by graphical extrapolation.

The S°_{298} is calculated from the adopted low temperature Cp, based on $S^\circ_{2.9}$ = 0.0015 eu.

The heat capacities of KBr(c) were also measured by W. Nernst and F. A. Lindemann, Z. Elektrochem. 17, 817 (1911), 78.7 - 89.2°K; F. Koref, Ann. Physik 4, 49 (1911), 137 - 234°K; and K. Clusius, J. Goldmann, and A. Perlick, Z. Naturforsch. 4A, 424 (1949). The enthalpies of KBr(c) were determined by A. Magnus, Phys. Z. 14, 5 (1913), and C. B. Cooper, J. Chem. Phys. 21, 777 (1953). The results are in reasonable agreement with the adopted functions except for those reported by Cooper.

Melting Data.

See KBr(l) table for details.

Heat of Sublimation.

The heats of sublimation to monomer and dimer are calculated as the enthalpy changes for the following two reactions: KBr(c) = KBr(g) and 2 KBr(c) = $K_2Br_2(g)$.

Potassium Bromide (KBr)

(Liquid) GFW = 119.011

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	16.700	25.225	25.225	.000	- 89.984	- 87.472	64.119
300	16.700	25.328	25.225	.031	- 89.983	- 87.456	63.712
400	16.700	30.133	25.880	1.701	- 93.747	- 85.826	46.893
500	16.700	33.859	27.117	3.371	- 93.261	- 83.903	36.674
600	16.700	36.904	28.502	5.041	- 92.761	- 82.077	29.897
700	16.700	39.478	29.891	6.711	- 92.254	- 80.336	25.082
800	16.700	41.708	31.232	8.381	- 91.744	- 78.670	21.492
900	16.700	43.675	32.507	10.051	- 91.235	- 77.065	18.714
1000	16.700	45.435	33.714	11.721	- 90.736	- 75.519	16.505
1100	16.700	47.026	34.853	13.391	- 109.154	- 72.996	14.503
1200	16.700	48.479	35.929	15.061	- 108.432	- 69.740	12.701
1300	16.700	49.816	36.946	16.731	- 107.712	- 66.546	11.187
1400	16.700	51.054	37.910	18.401	- 106.992	- 63.406	9.898
1500	16.700	52.206	38.825	20.071	- 106.273	- 60.318	8.788
1600	16.700	53.284	39.696	21.741	- 105.554	- 57.277	7.824
1700	16.700	54.296	40.525	23.411	- 104.837	- 54.283	6.978
1800	16.700	55.251	41.317	25.081	- 104.121	- 51.330	6.232
1900	16.700	56.154	42.074	26.751	- 103.407	- 48.417	5.569
2000	16.700	57.010	42.800	28.421	- 102.694	- 45.540	4.976
2100	16.700	57.825	43.496	30.091	- 101.983	- 42.700	4.444
2200	16.700	58.602	44.165	31.761	- 101.276	- 39.893	3.963
2300	16.700	59.344	44.809	33.431	- 100.571	- 37.119	3.527
2400	16.700	60.055	45.430	35.101	- 99.870	- 34.375	3.130
2500	16.700	60.737	46.028	36.771	- 99.175	- 31.662	2.768

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE (KBr) (LIQUID) GFW = 119.011

$S^\circ_{298.15}$ = 25.225 gibbs/mol

Tm = 1007°K

Tb = 1671°K

$\Delta Hf^\circ_{298.15}$ = -89.984 kcal/mol

ΔHm° = 6.1 kcal/mol

ΔHv° = 35.65 kcal/mol

Heat of Formation.

The heat of formation (ΔHf°_{298}) for KBr(l) is obtained from ΔHf°_{298}(KBr, c) by adding ΔHm° and the difference between $H^\circ_{1007} - H^\circ_{298}$ for crystal and liquid.

J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. 17, 1502 (1963), studied the chemical equilibrium for the reaction KBr(l) + HCl(g) = KCl(l) + HBr(g). They obtained ΔGr°_{1073} = 3.50 ± 0.08 and 3.54 kcal/mol from partial pressure data and emf data, respectively. The corresponding value calculated from these tables is 3.78 kcal/mol. Combination of the experimental results with JANAF auxiliary data leads to -89.70 and -89.74 kcal/mol for ΔHf°_{298}.

Heat Capacity and Entropy.

The heat capacity of 16.7 gibbs/mol was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964, from enthalpy data in the range 1010 - 1100°K. This Cp value is adopted here for the temperature range 298 - 2500°K.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The adopted Tm and ΔHm° were determined by J. W. Johnson and M. A. Bredig, J. Phys. Chem. 62, 604 (1958), and A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960), respectively.

Heats of melting of 6.2 kcal/mol from phase diagram studies and 6.7 kcal/mol from calorimetric measurements were obtained by E. Aukrust, B. Bjørge, H. Flood, and T. Forland, Annals of the New York Academy of Sciences 79, Art. 11, 830 (1960).

Vaporization Data.

The boiling point, Tb = 1671°K, is calculated as the temperature at which the sum of the partial pressures of KBr(g) and K_2Br_2(g) over KBr(l) equals one atmosphere. The value of ΔHv° is calculated as the heat required to produce one mole of vapor mixture, which contains 19.5% dimer (K_2Br_2) and 80.5% monomer (KBr).

Tb was reported to be 1648 and 1668°K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921), respectively.

Potassium Bromide (KBr)

(Ideal Gas) GFW = 119.011

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.416	-40.834	-40.834	INFINITE
100	7.901	50.613	67.529	-1.692	-40.857	-44.424	97.089
200	8.618	56.366	60.654	-.858	-41.229	-47.555	52.293
298	8.824	59.852	59.852	.000	-43.040	-50.852	37.276
300	8.827	59.906	59.852	.016	-43.053	-50.900	37.081
400	8.919	62.460	60.199	.904	-47.599	-52.610	28.745
500	8.972	64.456	60.858	1.799	-47.889	-53.929	23.529
600	9.011	66.095	61.599	2.698	-48.160	-54.991	20.030
700	9.041	67.487	62.343	3.601	-48.420	-56.109	17.518
800	9.068	68.696	63.063	4.506	-48.674	-57.191	15.624
900	9.092	69.765	63.749	5.414	-48.927	-58.239	14.142
1000	9.114	70.724	64.400	6.324	-49.188	-59.260	12.951
1100	9.136	71.594	65.015	7.237	-68.363	-59.231	11.768
1200	9.157	72.390	65.597	8.152	-68.397	-58.398	10.636
1300	9.178	73.124	66.148	9.068	-68.430	-57.565	9.677
1400	9.198	73.805	66.671	9.987	-68.461	-56.727	8.856
1500	9.218	74.440	67.168	10.908	-68.491	-55.888	8.143
1600	9.238	75.035	67.641	11.831	-68.520	-55.045	7.519
1700	9.257	75.596	68.093	12.756	-68.548	-54.204	6.968
1800	9.277	76.126	68.524	13.682	-68.575	-53.360	6.479
1900	9.296	76.628	68.938	14.611	-68.603	-52.513	6.040
2000	9.315	77.105	69.334	15.541	-68.629	-51.665	5.646
2100	9.334	77.560	69.715	16.474	-68.656	-50.816	5.289
2200	9.354	77.995	70.082	17.408	-68.684	-49.967	4.964
2300	9.373	78.411	70.435	18.345	-68.713	-49.115	4.667
2400	9.392	78.810	70.776	19.283	-68.744	-48.261	4.395
2500	9.411	79.194	71.105	20.223	-68.779	-47.409	4.144
2600	9.430	79.563	71.423	21.165	-68.815	-46.549	3.913
2700	9.449	79.920	71.731	22.109	-68.855	-45.697	3.699
2800	9.468	80.264	72.030	23.055	-68.902	-44.838	3.500
2900	9.487	80.596	72.319	24.003	-68.952	-43.975	3.314
3000	9.506	80.918	72.601	24.952	-69.009	-43.114	3.141
3100	9.525	81.230	72.874	25.904	-69.074	-42.248	2.979
3200	9.544	81.533	73.140	26.857	-69.147	-41.382	2.826
3300	9.563	81.827	73.399	27.813	-69.229	-40.516	2.683
3400	9.582	82.113	73.651	28.770	-69.323	-39.646	2.548
3500	9.601	82.391	73.897	29.729	-69.429	-38.771	2.421
3600	9.620	82.661	74.136	30.690	-69.550	-37.889	2.300
3700	9.639	82.925	74.370	31.653	-69.685	-37.010	2.186
3800	9.658	83.182	74.599	32.618	-69.840	-36.124	2.078
3900	9.676	83.434	74.822	33.584	-70.014	-35.238	1.975
4000	9.695	83.679	75.041	34.553	-70.211	-34.343	1.876
4100	9.714	83.918	75.254	35.523	-70.434	-33.441	1.783
4200	9.733	84.153	75.463	36.496	-70.685	-32.538	1.693
4300	9.752	84.382	75.668	37.470	-70.965	-31.625	1.607
4400	9.771	84.606	75.869	38.446	-71.282	-30.705	1.525
4500	9.790	84.826	76.065	39.424	-71.635	-29.778	1.446
4600	9.809	85.042	76.258	40.404	-72.028	-28.848	1.371
4700	9.828	85.253	76.447	41.386	-72.466	-27.902	1.297
4800	9.846	85.460	76.633	42.370	-72.950	-26.949	1.227
4900	9.865	85.663	76.815	43.355	-73.484	-25.984	1.159
5000	9.884	85.863	76.994	44.343	-74.070	-25.013	1.093
5100	9.903	86.058	77.170	45.332	-74.712	-24.018	1.029
5200	9.922	86.251	77.343	46.323	-75.412	-23.022	.968
5300	9.941	86.440	77.512	47.316	-76.170	-22.006	.907
5400	9.960	86.626	77.680	48.312	-76.988	-20.980	.849
5500	9.979	86.809	77.844	49.308	-77.869	-19.934	.792
5600	9.997	86.989	78.006	50.307	-78.810	-18.873	.737
5700	10.016	87.166	78.165	51.308	-79.812	-17.793	.682
5800	10.035	87.340	78.321	52.311	-80.873	-16.694	.629
5900	10.054	87.512	78.476	53.315	-81.994	-15.577	.577
6000	10.073	87.681	78.628	54.321	-83.170	-14.440	.526

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE (KBr) (IDEAL GAS) GFW = 119.011

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 59.852 gibbs/mol

ΔHf°_0 = -40.83 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -43.04 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 218.47 cm^{-1} $\omega_e x_e$ = 0.7533 cm^{-1} σ = 1

B_e = 0.0807 cm^{-1} α_e = 0.000401 cm^{-1} r_e = 2.821 Å

Heat of Formation.

The heat of formation is derived from the sublimation and vaporization data analyzed below. Numerous investigators have obtained total pressures by static methods or "apparent" pressures by effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_2Br_2(g)$ table] which are consistent with the dimer-monomer equilibrium data of Hagemark et al.(6). Second and third law analyses of the monomer pressures show remarkable consistency over temperatures from 637 to 1668°K. The selected value of ΔHf°_{298} = -43.0 ± 0.5 kcal/mol may be compared with -43.8 kcal/mol derived from D°_0 = 3.95 eV which is reported by Gaydon(14) based on atomic fluorescence data.

Investigator	Reaction	Temperature, °K	No. of Points	ΔHr°_{298}, kcal/mol Second Law	ΔHr°_{298}, kcal/mol Third Law	Drift eu	ΔHf°_{298}* kcal/mol
1. Wartenberg-Albrecht	(A)	1368.15-1654.15	14	48.28±0.31	46.70	-1.1±0.2	-43.28
2. Ruff-Mugdan	"	1361.15-1668.15	10	49.06±0.56	47.16	-1.4±0.4	-42.82
3. Fiock-Rodebush	"	1179.15-1335.75	10	47.80±0.05	46.95	-0.7±0.1	-43.03
4. Hintz-Jellinek	"	1523.15	1	-	47.34	-	-42.64
5. Murgulescu-Marta	"	1373.15-1473.15	5	46.20±1.15	47.69	1.1±0.8	-42.29
6. Hagemark et al.	"	1138.95-1416.02	26	47.15±0.49	46.94	-0.2±0.4	-43.04
7. Niwa	(B)	823.15-923.15	6	48.04±0.51	51.67	4.1±0.6	-42.45
8. Mayer-Wintner	"	884.90-929.40	6	56.15±3.17	51.49	-5.2±3.5	-42.63
9. Zimm-Mayer	"	636.94-900.09	15	50.71±0.21	50.58	-0.1±0.2	-43.54

*Based on the third law ΔHr°_{298} value. (A) KBr(l) = KBr (g), (B) KBr(c) = KBr(g).

Heat Capacity and Entropy.

Rusk and Gordy(10) have investigated the pure rotational spectra of KBr in the 1.5 to 5.0 mm range of the microwave region by millimeter wave molecular beam spectroscopy. The reported values of ω_e, $\omega_e x_e$, B_e and r_e are adopted here and corrected to the average isotopic species. The value of α_e is obtained from Fabricand et al.(11). Molecular constants for KBr(g) have also been reported by Herzberg(12) and Rice and Klemperer(13). They are in good agreement with the values adopted. Herzberg(12) also lists an A state at 31770 cm^{-1} based on observed electronic spectra. The moment of inertia is 3.4604 x 10^{-38} g cm^2.

References:

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Lithium Bromide (LiBr)

(Crystal) GFW = 86.848

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	11.692	17.700	17.700	.000	-83.870	-81.650	59.851
300	11.710	17.772	17.700	.022	-83.876	-81.636	59.472
400	12.245	21.216	18.166	1.220	-87.419	-80.155	43.795
500	12.770	24.003	19.063	2.470	-88.028	-78.279	34.216
600	13.405	26.385	20.089	3.777	-87.878	-76.342	27.807
700	14.285	28.513	21.143	5.159	-87.642	-74.437	23.240
800	15.405	30.493	22.189	6.643	-87.299	-72.573	19.826
900	16.365	32.365	23.217	8.233	-86.849	-70.759	17.183
1000	17.060	34.127	24.221	9.906	-86.315	-68.998	15.080
1100	17.580	35.778	25.197	11.639	-85.721	-67.295	13.370
1200	17.980	37.326	26.144	13.418	-85.082	-65.648	11.956
1300	18.270	38.777	27.061	15.232	-84.407	-64.055	10.769
1400	18.470	40.139	27.947	17.069	-83.707	-62.516	9.759
1500	18.600	41.418	28.803	18.923	-82.990	-61.028	8.892
1600	18.690	42.622	29.629	20.788	-82.261	-59.587	8.139
1700	18.740	43.756	30.427	22.660	-116.571	-56.864	7.310
1800	18.780	44.829	31.198	24.536	-115.648	-53.379	6.481
1900	18.810	45.845	31.942	26.415	-114.721	-49.942	5.745
2000	18.820	46.810	32.661	28.297	-113.794	-46.558	5.088

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE (LiBr) (CRYSTAL) GFW = 86.848

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [17.7] gibbs/mol

$\Delta Hf^\circ_{298.15} = -83.87 \pm 0.1$ kcal/mol

Tm = 823°K

$\Delta Hm^\circ = 4.22$ kcal/mol

Heat of Formation.

The heat of formation, ΔHf°_{298} (LiBr,c) = -83.87 kcal/mol, was calculated from the heat of solution of lithium bromide (c) at infinite dilution and the ionic heats of formation of $Li^+(\infty H_2O)$ and $Br^-(\infty H_2O)$.

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, April 1, 1965, reviewed the heat of solution data in the literature and gave the "best" value, $\Delta H^\circ_\infty = -11,670 \pm 50$ cal/mol for $LiBr(c) \rightarrow LiBr(\infty H_2O)$ at 298.15°K. The ionic heat of formation, ΔHf°_{298} $(Li^+ \cdot \infty H_2O)$ = -66.49 kcal/mol, was calculated from ΔHf°_{298} $(LiOH \cdot \infty H_2O)$ = -121.46 kcal/mol (see JANAF LiOH(c) table, Mar. 31, 1966) with ΔHf°_{298} $(OH^- \cdot \infty H_2O)$ = -54.97 kcal/mol from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1965. The value ΔHf°_{298} $(Br^- \cdot \infty H_2O)$ = -29.05 kcal/mol was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of $Li^+(\infty H_2O)$ and $Br^-(\infty H_2O)$ gives the heat of formation of $LiBr(\infty H_2O)$, ΔHf°_{298} = -95.54 kcal/mol.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method (723-883°K), yielding $H_{823}-H_{298}$ = 7.0 kcal/mol for the crystal at the melting point. Heat capacities derived from his data were $Cp_{773°}$ = 15.1 and $Cp_{853°}$ = 15.6 gibbs/mol for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(c), NaCl(c) and NaBr(c).

The entropy, $S^\circ_{298.15}$ = 17.7 eu, was estimated by adding the entropy difference between NaBr(c) and NaCl(c) to the entropy of lithium chloride (c) at 298.15°K. Comparisons with other alkali halides give results within ± 0.5 eu of this value. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) and 592 (1961), has estimated the heat capacities ($Cp = 11.50 + 3.02 \times 10^{-3}T$ gibbs/mol) and the entropy ($S^\circ_{298} = 16.0 \pm 0.5$ eu)

Melting Data.

The selected heat of fusion (ΔH°_{823} = 4.22 kcal/mol) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

K. K. Kelley, U. S. Bur. Mines Bull. 393 (1936), reviewed some phase diagram studies of the lithium bromide system in the literature, and gave the heat of fusion ΔH°_{825} = 2.90 kcal/mol. M. Blanc, Compt. rend. 246, 570 (1958), reported the heat of fusion ΔH°_{819} = 3.095 kcal/mol by a cryoscopic method. Both values are too low.

Lithium Bromide (LiBr)

(Liquid) GFW = 86.848

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.600	20.220	20.220	.000	-80.839	-79.370	58.180
300	15.600	20.316	20.220	.029	-80.838	-79.361	57.814
400	15.600	24.804	20.832	1.589	-84.019	-78.190	42.721
500	15.600	28.285	21.988	3.149	-84.318	-76.710	33.530
600	15.600	31.130	23.281	4.709	-83.915	-75.226	27.401
700	15.600	33.534	24.579	6.269	-83.502	-73.811	23.045
800	15.600	35.617	25.831	7.829	-83.082	-72.456	19.794
900	15.600	37.455	27.023	9.389	-82.662	-71.153	17.278
1000	15.600	39.098	28.150	10.949	-82.242	-69.896	15.276
1100	15.600	40.585	29.214	12.509	-81.821	-68.682	13.646
1200	15.600	41.943	30.219	14.069	-81.400	-67.507	12.295
1300	15.600	43.191	31.169	15.629	-80.979	-66.365	11.157
1400	15.600	44.347	32.070	17.189	-80.557	-65.257	10.187
1500	15.600	45.424	32.924	18.749	-80.134	-64.180	9.351
1600	15.600	46.431	33.737	20.309	-79.709	-63.130	8.623
1700	15.600	47.376	34.512	21.869	-114.331	-60.778	7.814
1800	15.600	48.268	35.252	23.429	-113.724	-57.645	6.999
1900	15.600	49.111	35.959	24.989	-113.117	-54.543	6.274
2000	15.600	49.912	36.637	26.549	-112.512	-51.480	5.625
2100	15.600	50.673	37.288	28.109	-111.908	-48.444	5.042
2200	15.600	51.398	37.913	29.669	-111.306	-45.433	4.513
2300	15.600	52.092	38.514	31.229	-110.704	-42.454	4.034
2400	15.600	52.756	39.094	32.789	-110.106	-39.499	3.597
2500	15.600	53.393	39.653	34.349	-109.510	-36.570	3.197
2600	15.600	54.004	40.193	35.909	-108.916	-33.663	2.830
2700	15.600	54.593	40.716	37.469	-108.325	-30.781	2.492
2800	15.600	55.161	41.222	39.029	-107.738	-27.921	2.179
2900	15.600	55.708	41.712	40.589	-107.155	-25.079	1.890
3000	15.600	56.237	42.187	42.149	-106.575	-22.259	1.622

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE (LiBr) (LIQUID) GFW = 86.848

$S^\circ_{298.15}$ = [20.220] gibbs/mol

Tm = 823°K

Tb(to equilibrium mixture) = 1562°K

Tb(to monomer only) = [1611]°K

$\Delta Hf^\circ_{298.15}$ = -80.839 kcal/mol

ΔHm°=4.22 kcal/mol

ΔHv°(to equilibrium mixture) = 25.6 kcal/mol

ΔHv°(to monomer only) = [35.2] kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between $H^\circ_{823}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity (Cp = 15.6 gibbs/mol) from enthalpy measurements (823° - 883°K) by the drop method. The liquid heat capacity was assumed to be a constant, 15.6 gibbs/mol. The entropy (S°_{298} = 20.220 eu) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiBr(c) table for detail.

Vaporization Data.

Tb (to monomer only) is taken as the temperature at which the calculated Gibbs energy change is zero for LiBr(l) → LiBr(g), while ΔHv°(to monomer only) is the corresponding heat of reaction.

Tb (to equilibrium mixture) is taken as the temperature at which the sum of the calculated partial vapor pressures of LiBr(g) and $Li_2Br_2(g)$ reaches one atmosphere (trimer and higher polymers have been neglected in calculation). This value (1562°K) is in good agreement with the boiling point of 1583°K obtained from total vapor pressure measurements by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), and also the boiling point of 1538°K by O. Ruff and S. Mugdan, Z. anorg. Chem. 117, 147 (1921). ΔHv°(to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 29.23 mole percent of dimer. For detailed information see LiBr(g) and $Li_2Br_2(g)$ table.

Lithium Bromide (LiBr)

(Ideal Gas) GFW = 86.848

T, °K	gibbs/mol Cp°	S°	-(G°-H°298)/T	kcal/mol H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.193	-34.959	-34.959	INFINITE
100	7.002	45.454	60.429	-1.498	-34.716	-38.442	84.015
200	7.575	50.460	54.319	-.772	-35.016	-42.070	45.972
298	8.115	53.593	53.593	.000	-36.800	-45.281	33.192
300	8.122	53.643	53.593	.015	-36.812	-45.334	33.026
400	8.446	56.028	53.916	.845	-40.724	-47.385	25.890
500	8.637	57.935	54.535	1.700	-41.728	-48.945	21.394
600	8.758	59.521	55.238	2.570	-42.015	-50.361	18.344
700	8.842	60.878	55.949	3.450	-42.281	-51.732	16.151
800	8.903	62.063	56.641	4.338	-42.534	-53.065	14.497
900	8.951	63.114	57.303	5.230	-42.781	-54.365	13.202
1000	8.990	64.059	57.932	6.127	-43.024	-55.639	12.160
1100	9.023	64.918	58.529	7.028	-43.262	-56.890	11.303
1200	9.052	65.704	59.094	7.932	-43.498	-58.118	10.585
1300	9.078	66.430	59.631	8.838	-43.730	-59.327	9.974
1400	9.101	67.103	60.141	9.747	-43.959	-60.518	9.447
1500	9.124	67.732	60.626	10.659	-44.185	-61.694	8.989
1600	9.145	68.322	61.089	11.572	-44.407	-62.853	8.585
1700	9.165	68.877	61.531	12.488	-79.673	-62.672	8.057
1800	9.184	69.401	61.954	13.405	-79.709	-61.669	7.488
1900	9.202	69.898	62.359	14.324	-79.742	-60.664	6.978
2000	9.220	70.370	62.748	15.245	-79.776	-59.660	6.519
2100	9.238	70.821	63.122	16.168	-79.809	-58.656	6.104
2200	9.256	71.251	63.481	17.093	-79.842	-57.647	5.727
2300	9.273	71.663	63.828	18.019	-79.875	-56.638	5.382
2400	9.290	72.058	64.163	18.948	-79.908	-55.626	5.065
2500	9.306	72.437	64.486	19.877	-79.942	-54.612	4.774
2600	9.323	72.803	64.799	20.809	-79.977	-53.601	4.506
2700	9.339	73.155	65.102	21.742	-80.013	-52.586	4.257
2800	9.356	73.495	65.396	22.677	-80.051	-51.569	4.025
2900	9.372	73.823	65.681	23.613	-80.092	-50.550	3.810
3000	9.388	74.141	65.958	24.551	-80.134	-49.529	3.608
3100	9.404	74.449	66.227	25.491	-80.181	-48.507	3.420
3200	9.420	74.748	66.488	26.432	-80.230	-47.486	3.243
3300	9.436	75.038	66.743	27.375	-80.284	-46.463	3.077
3400	9.452	75.320	66.991	28.319	-80.342	-45.436	2.921
3500	9.467	75.594	67.233	29.265	-80.404	-44.408	2.773
3600	9.483	75.861	67.469	30.213	-80.472	-43.379	2.633
3700	9.499	76.121	67.699	31.162	-80.544	-42.349	2.501
3800	9.515	76.375	67.924	32.112	-80.623	-41.314	2.376
3900	9.530	76.622	68.144	33.065	-80.708	-40.277	2.257
4000	9.546	76.864	68.359	34.018	-80.800	-39.244	2.144
4100	9.561	77.100	68.569	34.974	-80.898	-38.203	2.036
4200	9.577	77.330	68.775	35.931	-81.005	-37.159	1.934
4300	9.592	77.556	68.977	36.889	-81.118	-36.115	1.836
4400	9.608	77.777	69.174	37.849	-81.240	-35.066	1.742
4500	9.624	77.993	69.368	38.811	-81.371	-34.016	1.652
4600	9.639	78.204	69.558	39.774	-81.512	-32.959	1.566
4700	9.654	78.412	69.744	40.739	-81.662	-31.905	1.484
4800	9.670	78.615	69.927	41.705	-81.824	-30.845	1.404
4900	9.685	78.815	70.106	42.673	-81.997	-29.783	1.328
5000	9.701	79.011	70.282	43.642	-82.181	-28.714	1.255
5100	9.716	79.203	70.455	44.613	-82.380	-27.642	1.185
5200	9.732	79.392	70.625	45.585	-82.592	-26.567	1.117
5300	9.747	79.577	70.792	46.559	-82.819	-25.486	1.051
5400	9.762	79.759	70.957	47.534	-83.062	-24.401	.988
5500	9.778	79.939	71.118	48.512	-83.321	-23.314	.926
5600	9.793	80.115	71.278	49.490	-83.599	-22.223	.867
5700	9.809	80.289	71.434	50.470	-83.895	-21.124	.810
5800	9.824	80.459	71.588	51.452	-84.212	-20.015	.754
5900	9.839	80.627	71.740	52.435	-84.550	-18.906	.700
6000	9.855	80.793	71.890	53.420	-84.910	-17.794	.648

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE (LiBr) (IDEAL GAS) GFW = 86.848

Ground State Configuration $^1\Sigma$

$S^\circ_{298.15}$ = 53.593 gibbs/mol

ΔHf°_0 = -35.0 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -36.8 ± 3 kcal/mol

Electronic Levels and Quantum Weights

ϵ, cm.$^{-1}$	g_i
0	1

ω_e = 563.16 cm^{-1}

$\omega_e x_e$ = 3.53 cm^{-1}

σ = 1

B_e = 0.56112 cm^{-1}

α_e = 0.00573 cm^{-1}

r_e = 2.1704 Å

Heat of Formation.

The heat of formation (ΔHf°_{298} (LiBr, g) = -36.8 ± 3 kcal/mol) was calculated from the selected heat of vaporization and the heat of formation for lithium bromide (1). Lithium bromide vaporizes to a mixture of monomeric and dimeric gases. (Higher polymers have been neglected in the calculation.) The heats of vaporization to monomer and to dimer were chosen to satisfy (1) the total vapor pressure data measured by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), and O. Ruff and S. Mugdan, Z. anorg Chem. 117, 147 (1921); (2) the partial vapor pressures of monomer and dimer derived from R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956), 28, 981 (1958), in an analysis of the velocity distribution of molecules in alkali halide vapor. The selected heats of vaporization are ΔHv°_{298}(to monomer) = 44.0 ± 3 kcal/mol and ΔHv°_{298}(to dimer) = 42.0 ± 5 kcal/mol which combine with the heat of formation of lithium bromide (1) (ΔHf°_{298} = -80.84 kcal/mol) to give the standard heats of formation of LiBr(g) and Li_2Br_2(g) -36.8 and -119.7 kcal/mol, respectively. The derived heat of dissociation is ΔH°_{298} = 46.0 kcal/mol for $Li_2Br_2(g) \rightarrow 2LiBr(g)$.

J. Berkowitz, H. A. Tasman and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962), have measured mass-spectrometrically the heat of dissociation ΔH°_{850} = 45.9 kcal/mol (ΔH°_{298} = 46.9 kcal/mol) for $Li_2Br_2(g) \rightarrow 2LiBr(g)$ in a double oven apparatus by the second law method. D. L. Hildenbrand, L. P. Theard, W. F. Hall and N. D. Potter, Philco Report U-2289, under Contract NOw61-0905-C, Sept. 15, 1963, have determined mass-spectrometrically the heats of sublimation of lithium bromide by the second law method as ΔHs°_{740} (to monomer) = 46.9 and ΔHs°_{740} (to dimer) = 45.0 kcal/mol (equivalent to ΔHv°_{298} (to monomer) = 45.82 kcal/mol and ΔHv°_{298} (to dimer) = 41.93 kcal/mol). These values are in reasonable agreement with those selected in the tabulation.

Heat Capacity and Entropy.

The bond distance (r_e) was obtained from the microwave studies by A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 96, 629 (1954). The vibrational constants (ω_e and $\omega_e x_e$) were determined from the infrared spectrum by W. Klemperer, W. G. Norris, A. Büchler, and A. G. Emslie, J. Chem. Phys. 33, 1534 (1960). The rotational constants which have been corrected to the average isotopic species were obtained by A. J. Herbert, F. W. Breivogel, Jr., and K. Street, Jr., J. Chem. Phys. 41, 2368 (1964), using microwave spectra. Their data are in good agreement with those reported by Honig et al., loc. cit., and J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

Magnesium Monobromide (MgBr)

(Ideal Gas) GFW = 104.221

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.289	-11.164	-11.164	INFINITE
100	7.234	49.853	65.740	-1.589	-10.951	-15.066	32.926
200	8.104	55.157	59.249	-.918	-11.328	-19.163	20.941
298	8.517	58.481	58.481	.000	-13.000	-22.682	16.627
300	8.522	58.534	58.481	.016	-13.012	-22.742	16.568
400	8.715	61.015	58.818	.879	-16.883	-25.203	13.770
500	8.820	62.972	59.460	1.756	-17.089	-27.259	11.915
600	8.884	64.586	60.184	2.641	-17.317	-29.273	10.663
700	8.929	65.959	60.913	3.532	-17.565	-31.245	9.755
800	8.962	67.153	61.620	4.427	-17.844	-33.181	9.065
900	8.989	68.211	62.295	5.324	-18.156	-35.080	8.519
1000	9.011	69.159	62.935	6.224	-20.625	-36.760	8.034
1100	9.031	70.019	63.540	7.126	-20.976	-38.359	7.621
1200	9.049	70.805	64.113	8.030	-21.351	-39.922	7.271
1300	9.065	71.530	64.656	8.936	-21.750	-41.453	6.969
1400	9.081	72.203	65.172	9.843	-52.540	-42.475	6.631
1500	9.095	72.830	65.661	10.752	-52.582	-41.755	6.084
1600	9.109	73.417	66.126	11.662	-52.624	-41.032	5.605
1700	9.123	73.970	66.573	12.574	-52.664	-40.305	5.182
1800	9.137	74.492	66.999	13.487	-52.703	-39.578	4.805
1900	9.150	74.986	67.406	14.401	-52.741	-38.846	4.468
2000	9.163	75.456	67.797	15.317	-52.779	-38.115	4.165
2100	9.175	75.903	68.172	16.234	-52.817	-37.382	3.890
2200	9.188	76.330	68.534	17.152	-52.853	-36.644	3.640
2300	9.200	76.739	68.882	18.071	-52.890	-35.906	3.412
2400	9.213	77.131	69.217	18.992	-52.925	-35.168	3.203
2500	9.225	77.507	69.541	19.914	-52.960	-34.428	3.010
2600	9.238	77.869	69.855	20.837	-52.995	-33.684	2.831
2700	9.250	78.218	70.158	21.762	-53.030	-32.942	2.667
2800	9.263	78.554	70.452	22.687	-53.065	-32.197	2.513
2900	9.275	78.880	70.737	23.614	-53.100	-31.451	2.370
3000	9.288	79.194	71.014	24.542	-53.136	-30.703	2.237
3100	9.301	79.499	71.282	25.472	-53.172	-29.955	2.112
3200	9.314	79.795	71.544	26.402	-53.210	-29.208	1.995
3300	9.328	80.081	71.798	27.335	-53.248	-28.456	1.885
3400	9.342	80.360	72.046	28.268	-53.289	-27.702	1.781
3500	9.356	80.631	72.287	29.203	-53.332	-26.951	1.683
3600	9.371	80.895	72.523	30.139	-53.378	-26.197	1.590
3700	9.386	81.152	72.753	31.077	-53.427	-25.440	1.503
3800	9.402	81.402	72.977	32.016	-53.479	-24.681	1.419
3900	9.419	81.647	73.196	32.958	-53.535	-23.926	1.341
4000	9.436	81.885	73.410	33.900	-53.596	-23.164	1.266
4100	9.454	82.119	73.620	34.845	-53.662	-22.406	1.194
4200	9.47	82.347	73.825	35.791	-53.733	-21.643	1.126
4300	9.493	82.570	74.026	36.739	-53.811	-20.877	1.061
4400	9.514	82.788	74.223	37.690	-53.894	-20.107	.999
4500	9.535	83.002	74.415	38.642	-53.985	-19.337	.939
4600	9.558	83.212	74.604	39.597	-54.083	-18.566	.882
4700	9.581	83.418	74.790	40.554	-54.188	-17.793	.827
4800	9.606	83.620	74.971	41.513	-54.302	-17.018	.775
4900	9.631	83.818	75.150	42.475	-54.424	-16.239	.724
5000	9.658	84.013	75.325	43.440	-54.555	-15.458	.676
5100	9.685	84.205	75.496	44.407	-54.697	-14.682	.629
5200	9.714	84.393	75.667	45.377	-54.847	-13.892	.584
5300	9.743	84.578	75.833	46.349	-55.008	-13.098	.540
5400	9.774	84.761	75.997	47.325	-55.179	-12.314	.498
5500	9.805	84.940	76.158	48.304	-55.361	-11.712	.457
5600	9.838	85.117	76.316	49.286	-55.555	-10.715	.418
5700	9.871	85.292	76.472	50.272	-55.760	-9.912	.380
5800	9.905	85.464	76.626	51.261	-55.976	-9.110	.343
5900	9.941	85.633	76.777	52.253	-56.207	-8.293	.307
6000	9.977	85.801	76.926	53.249	-56.449	-7.489	.273

June 30, 1966

MAGNESIUM MONOBROMIDE (MgBr) (IDEAL GAS) GFW = 104.221

Ground State Configuration $^2\Sigma$

ΔHf°_0 = -11 kcal/mol

$S^\circ_{298.15}$ = 58.481 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -13 ± 7 kcal/mol

Electronic Levels and Quantum Weights

ϵ, cm^{-1}	g_i
0	2
25800	4
39200	4

ω_e = 373.8 cm^{-1}

$\omega_e x_e$ = 1.34 cm^{-1}

σ = 1

B_e = [0.165162] cm^{-1}

α_e = [0.000809] cm^{-1}

r_e = [2.34] Å

Heat of Formation.

The heat of formation was calculated from that of $MgBr_2(g)$ using the relation $D(MgBr)/\Delta Hatom\ (MgBr_2) = 0.46 \pm 0.04$ which has been shown to apply to several dihalides. This results in $\Delta Hf^\circ_{298} = -13 \pm 7$ and $D_0 = 74.4 \pm 7$ kcal/mol. The selected value is in good agreement with $D_0 \leqslant 77$ kcal/mol obtained from predissociation by G. Herzberg, "Spectra of Diatomic Molecules," second edition, D. van Nostrand Co., Inc., New York, 1950, and with the linear Birge-Sponer extrapolation of D_0 = 74 kcal/mol given by A. G. Gaydon, "Dissociation Energies," second edition, Chapman and Hall Ltd, London, 1953. Gaydon's selected value of $D_0 = 58 \pm 23$ kcal/mol was discounted since it would require the unlikely ratio $D(MgBr)/\Delta Hatom(MgBr_2) = 0.28$.

Heat Capacity and Entropy.

The molecular constants ω_e, $\omega_e x_e$ and ground state configuration ($^2\Sigma$) were taken from G. Herzberg, loc. cit., while α_e was calculated from the above constants. The bond distance was estimated to be the same as in $MgBr_2(g)$.

Nitrogen Monobromide (NBr)

(Ideal Gas) Mol. Wt. = 93.924

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.148	73.700	73.700	INFINITE
100	6.967	48.333	62.863	- 1.453	73.719	71.435	- 156.113
200	7.310	53.240	56.956	- .743	73.492	69.232	- 75.650
298	7.819	56.256	56.256	.000	71.883	67.357	- 49.372
300	7.828	56.305	56.256	.014	71.874	67.329	- 49.047
400	8.196	58.611	56.568	.817	68.209	66.563	- 36.370
500	8.430	60.467	57.168	1.649	68.248	66.154	- 28.914
600	8.581	62.018	57.851	2.500	68.299	65.731	- 23.941
700	8.683	63.349	58.544	3.364	68.352	65.298	- 20.386
800	8.755	64.514	59.219	4.236	68.404	64.858	- 17.718
900	8.808	65.548	59.866	5.114	68.454	64.412	- 15.641
1000	8.849	66.478	60.481	5.997	68.500	63.960	- 13.978
1100	8.881	67.323	61.065	6.884	68.542	63.504	- 12.616
1200	8.907	68.097	61.619	7.773	68.579	63.045	- 11.481
1300	8.929	68.811	62.146	8.665	68.613	62.582	- 10.521
1400	8.948	69.473	62.646	9.559	68.643	62.117	- 9.696
1500	8.964	70.091	63.122	10.454	68.670	61.649	- 8.982
1600	8.979	70.670	63.575	11.352	68.695	61.181	- 8.357
1700	8.992	71.215	64.009	12.250	68.717	60.711	- 7.805
1800	9.004	71.729	64.424	13.150	68.737	60.239	- 7.314
1900	9.015	72.216	64.821	14.051	68.755	59.768	- 6.875
2000	9.026	72.679	65.203	14.953	68.771	59.293	- 6.479
2100	9.036	73.120	65.569	15.856	68.787	58.819	- 6.121
2200	9.045	73.540	65.922	16.760	68.800	58.344	- 5.796
2300	9.054	73.943	66.262	17.665	68.812	57.868	- 5.498
2400	9.063	74.328	66.590	18.571	68.823	57.393	- 5.226
2500	9.071	74.698	66.907	19.478	68.833	56.916	- 4.975
2600	9.079	75.054	67.214	20.385	68.842	56.439	- 4.744
2700	9.087	75.397	67.510	21.293	68.850	55.962	- 4.530
2800	9.095	75.728	67.798	22.203	68.857	55.484	- 4.331
2900	9.102	76.047	68.077	23.112	68.864	55.007	- 4.145
3000	9.110	76.356	68.348	24.023	68.871	54.529	- 3.972
3100	9.117	76.654	68.611	24.934	68.876	54.051	- 3.810
3200	9.124	76.944	68.867	25.846	68.881	53.572	- 3.659
3300	9.132	77.225	69.116	26.759	68.885	53.093	- 3.516
3400	9.139	77.498	69.358	27.673	68.889	52.615	- 3.382
3500	9.146	77.763	69.595	28.587	68.892	52.136	- 3.255
3600	9.152	78.020	69.825	29.502	68.895	51.657	- 3.136
3700	9.159	78.271	70.050	30.417	68.898	51.178	- 3.023
3800	9.166	78.515	70.270	31.334	68.900	50.700	- 2.916
3900	9.173	78.754	70.484	32.251	68.902	50.222	- 2.814
4000	9.180	78.986	70.694	33.168	68.903	49.741	- 2.718
4100	9.186	79.213	70.899	34.087	68.904	49.262	- 2.626
4200	9.193	79.434	71.099	35.006	68.904	48.783	- 2.538
4300	9.199	79.651	71.296	35.925	68.905	48.305	- 2.455
4400	9.206	79.862	71.488	36.845	68.904	47.826	- 2.375
4500	9.213	80.069	71.677	37.766	68.904	47.346	- 2.299
4600	9.219	80.272	71.861	38.688	68.903	46.869	- 2.227
4700	9.226	80.470	72.042	39.610	68.903	46.390	- 2.157
4800	9.232	80.664	72.220	40.533	68.901	45.910	- 2.090
4900	9.239	80.855	72.394	41.457	68.899	45.430	- 2.026
5000	9.245	81.041	72.565	42.381	68.897	44.953	- 1.965
5100	9.251	81.225	72.733	43.306	68.895	44.471	- 1.906
5200	9.258	81.404	72.898	44.231	68.893	43.994	- 1.849
5300	9.264	81.581	73.060	45.157	68.890	43.515	- 1.794
5400	9.271	81.754	73.220	46.084	68.886	43.035	- 1.742
5500	9.277	81.924	73.377	47.011	68.883	42.560	- 1.691
5600	9.283	82.091	73.531	47.939	68.879	42.079	- 1.642
5700	9.290	82.256	73.682	48.868	68.874	41.602	- 1.595
5800	9.296	82.417	73.832	49.797	68.870	41.125	- 1.550
5900	9.302	82.576	73.978	50.727	68.865	40.644	- 1.505
6000	9.309	82.733	74.123	51.658	68.860	40.164	- 1.463

December 31, 1962

NITROGEN MONOBROMIDE (NBr) (IDEAL GAS) MOL. WT. = 93.924

$\Delta H_{f\ 0}^\circ = 73.7 \pm 5$ kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 71.9 \pm 5$ kcal. mole^{-1}

Ground State Configuration $^3\Sigma^-$

$S^\circ_{298.15} = 56.25 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_1
0	3

$\omega_e = 699.1$ cm.$^{-1}$

$\omega_e x_e = 4.7$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.443$ cm.$^{-1}$

$\alpha_e = 0.00399$ cm.$^{-1}$

$r_e = 1.79$ Å

Heat of Formation.

E. R. V. Miller and H. B. Dunford, J. Chem. Phys. 35, 1202 (1961) have extrapolated the ground state vibrational levels and obtain $D_0^\circ = 67 \pm 5$ kcal. mole^{-1} or $\Delta H_{f\ 0}^\circ = 73.7 \pm 5$ kcal. mole^{-1}.

Heat Capacity and Entropy.

Miller and Dunford loc. cit. give all the vibrational and rotational constants, which have been adjusted to the normally occurring isotopic mixture for bromine.

Nitrosyl Bromide (NOBr)
(Ideal Gas) GFW = 109.9151

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.785	21.848	21.848	INFINITE
100	8.665	54.694	74.420	-1.973	21.633	20.785	-45.426
200	10.068	61.162	66.319	-1.031	21.293	20.071	-21.933
298	10.868	65.347	65.347	.000	19.630	19.699	-14.440
300	10.879	65.414	65.347	.020	19.621	19.700	-14.351
400	11.382	68.617	65.781	1.135	15.911	20.487	-11.193
500	11.774	71.200	66.614	2.293	15.911	21.631	-9.455
600	12.107	73.377	67.565	3.488	15.928	22.774	-8.295
700	12.388	75.265	68.533	4.713	15.954	23.913	-7.466
800	12.621	76.935	69.481	5.963	15.986	25.047	-6.842
900	12.813	78.433	70.394	7.235	16.022	26.178	-6.357
1000	12.970	79.791	71.267	8.525	16.061	27.305	-5.967
1100	13.098	81.034	72.099	9.828	16.100	28.426	-5.648
1200	13.204	82.178	72.892	11.144	16.140	29.546	-5.381
1300	13.292	83.239	73.647	12.469	16.178	30.661	-5.155
1400	13.365	84.226	74.368	13.802	16.216	31.774	-4.960
1500	13.427	85.151	75.056	15.141	16.251	32.883	-4.791
1600	13.479	86.019	75.715	16.487	16.286	33.991	-4.643
1700	13.524	86.838	76.345	17.837	16.318	35.097	-4.512
1800	13.562	87.612	76.950	19.191	16.348	36.200	-4.395
1900	13.594	88.346	77.530	20.549	16.376	37.304	-4.291
2000	13.623	89.044	78.089	21.910	16.401	38.403	-4.196
2100	13.648	89.709	78.626	23.274	16.424	39.503	-4.111
2200	13.670	90.345	79.145	24.639	16.443	40.600	-4.033
2300	13.689	90.953	79.645	26.007	16.460	41.698	-3.962
2400	13.706	91.536	80.128	27.377	16.474	42.796	-3.897
2500	13.722	92.095	80.596	28.749	16.485	43.893	-3.837
2600	13.735	92.634	81.049	30.122	16.493	44.989	-3.782
2700	13.747	93.152	81.487	31.496	16.498	46.086	-3.730
2800	13.758	93.653	81.913	32.871	16.500	47.180	-3.683
2900	13.768	94.136	82.326	34.247	16.500	48.277	-3.638
3000	13.777	94.603	82.728	35.625	16.496	49.372	-3.597
3100	13.785	95.054	83.118	37.003	16.490	50.470	-3.558
3200	13.793	95.492	83.498	38.382	16.481	51.565	-3.522
3300	13.800	95.917	83.868	39.761	16.468	52.659	-3.487
3400	13.806	96.329	84.228	41.142	16.454	53.757	-3.455
3500	13.812	96.729	84.580	42.522	16.437	54.855	-3.425
3600	13.817	97.118	84.923	43.904	16.417	55.954	-3.397
3700	13.822	97.497	85.257	45.286	16.395	57.051	-3.370
3800	13.826	97.866	85.584	46.668	16.371	58.150	-3.344
3900	13.830	98.225	85.904	48.051	16.345	59.250	-3.320
4000	13.834	98.575	86.216	49.434	16.315	60.349	-3.297
4100	13.838	98.917	86.522	50.818	16.284	61.450	-3.276
4200	13.841	99.250	86.821	52.202	16.251	62.554	-3.255
4300	13.844	99.576	87.114	53.586	16.216	63.658	-3.235
4400	13.847	99.894	87.401	54.971	16.179	64.761	-3.217
4500	13.850	100.205	87.682	56.356	16.140	65.867	-3.199
4600	13.853	100.510	87.957	57.741	16.099	66.973	-3.182
4700	13.855	100.808	88.228	59.126	16.057	68.079	-3.166
4800	13.857	101.099	88.493	60.512	16.012	69.189	-3.150
4900	13.859	101.385	88.753	61.898	15.966	70.292	-3.135
5000	13.861	101.665	89.008	63.284	15.919	71.404	-3.121
5100	13.863	101.940	89.259	64.670	15.869	72.509	-3.107
5200	13.865	102.209	89.506	66.056	15.819	73.622	-3.094
5300	13.867	102.473	89.748	67.443	15.767	74.737	-3.082
5400	13.868	102.732	89.986	68.830	15.713	75.847	-3.070
5500	13.870	102.987	90.220	70.216	15.658	76.964	-3.058
5600	13.871	103.237	90.450	71.603	15.601	78.075	-3.047
5700	13.872	103.482	90.677	72.991	15.544	79.196	-3.037
5800	13.874	103.723	90.900	74.378	15.485	80.317	-3.026
5900	13.875	103.961	91.119	75.765	15.424	81.428	-3.016
6000	13.876	104.194	91.335	77.153	15.362	82.547	-3.007

Mar. 31, 1962; Dec. 31, 1966

NITROSYL BROMIDE (NOBr) (IDEAL GAS) GFW = 109.9151

Point Group C_s

$S^\circ_{298.15}$ = 65.35 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = 21.85 ± 0.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 19.63 ± 0.2 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1801 (1)
542 (1)
[265] (1)

Bond Distance: O-N = 1.15 ± 0.04 Å N-Br = 2.14 ± 0.02 Å

Bond Angle: O-N-Br = 117 ± 3° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 5.1631 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation.

The chemical equilibrium of the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ has been studied by Trautz and Dalal[1], Blair, Brass and Yost[2], and Krauss[3], respectively. Using the reported equilibrium constants, the enthalpy changes ($\Delta Hr^\circ_{298.15}$) of this reaction are evaluated by both the second and third law methods. Based on the third law $\Delta Hr^\circ_{298.15}$ values, the heats of formation for NOBr(g) are derived. The results obtained are presented in the table below. The value of $\Delta Hf^\circ_{298.15}$ (NOBr,g) adopted is 19.63 ± 0.2 kcal/mol.

			$\Delta Hr^\circ_{298.15}$, kcal/mol			
Investigator	No. of Points	Temperature, °K	Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$ kcal/mol
1. Trautz and Dalal	*	258.2 - 603.2	-11.11	-11.30	-0.4	19.62
2. Blair et al.	30	296.9 - 502.9	-11.74 + 0.07	-11.26	1.3 ± 0.2	19.64
3. Krauss	23	264.0 - 290.1	-13.46 + 0.30	- 9.62	-13.7 ± 1.1	20.46

*The data points employed for evaluation are calculated from a given equation.

1. M. Trautz and V. P. Dalal, Z. Anorg. Chem. 110, 1 (1920).
2. C. M. Blair, Jr., P.D. Brass and D. M. Yost, J. Am. Chem. Soc. 56, 1916 (1934).
3. W. Krauss, Z. Physik. Chem. A175, 295 (1936).

Heat Capacity and Entropy.

The molecular structure of NOBr(g) has been determined by electron diffraction by J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. 59, 2629 (1937). The results were confirmed later by T. L. Weatherly and Q. Williams, J Chem. Phys. 25, 717 (1956), who studied the microwave spectrum of NOBr(g) in the region 20,000 - 40,000 Mc/sec and analyzed the J = 2→3 transition. The values of bond length and angle adopted are obtained from Ketelaar and Palmer, loc. cit. The infrared absorption spectrum of NOBr(g) has been examined from 400 to 5303 cm^{-1} by W. G. Burns and H. J. Bernstein, J. Chem. Phys. 18, 1669 (1950). The authors observed the first two fundamental vibrational frequencies and obtained the third from combination and overtones. These assignments are adopted. The three principal moments of inertia are: $I_A = 9.404 \times 10^{-40}$, $I_B = 2.2965 \times 10^{-38}$ and $I_C = 2.3906 \times 10^{-38}\ g\ cm^2$.

Sodium Bromide (NaBr)

(Crystal) Mol. Wt. = 102.907

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.770	-84.680	-84.680	INFINITE
100	9.600	8.510	31.150	-2.264	-84.828	-84.466	184.591
200	11.650	15.970	21.850	-1.176	-84.912	-84.071	91.864
298	12.285	20.750	20.750	.000	-86.380	-83.476	61.187
300	12.295	20.826	20.750	.023	-86.386	-83.457	60.796
400	12.775	24.433	21.239	1.278	-90.595	-81.693	44.633
500	13.110	27.321	22.176	2.573	-90.482	-79.479	34.739
600	13.400	29.737	23.240	3.898	-90.322	-77.293	28.153
700	13.700	31.825	24.321	5.253	-90.119	-75.138	23.458
800	14.000	33.674	25.376	6.638	-89.877	-73.014	19.945
900	14.300	35.340	26.392	8.053	-89.601	-70.921	17.221
1000	14.600	36.862	27.364	9.498	-89.296	-68.861	15.049
1100	14.900	38.268	28.292	10.973	-88.968	-66.836	13.278
1200	15.200	39.577	29.179	12.478	-111.855	-64.381	11.725
1300	15.500	40.805	30.026	14.013	-111.269	-60.447	10.162
1400	15.800	41.965	30.837	15.578	-110.654	-56.562	8.829
1500	16.096	43.065	31.617	17.173	-110.011	-52.720	7.681
1600	16.400	44.113	32.365	18.798	-109.337	-48.921	6.682
1700	16.713	45.117	33.085	20.453	-108.633	-45.167	5.806
1800	17.033	46.081	33.781	22.140	-107.898	-41.455	5.033
1900	17.362	47.011	34.453	23.860	-107.131	-37.783	4.346
2000	17.700	47.910	35.104	25.613	-106.333	-34.155	3.732

Sept. 30, 1964

SODIUM BROMIDE (NaBr) (CRYSTAL) MOL. WT. = 102.907

$S^\circ_{298.15}$ = 20.75 ± 0.06 cal. deg.$^{-1}$ mole^{-1}

T_m = 1020°K.

$\Delta H^\circ_{f\ 0}$ = -84.68 ± 0.10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -86.38 ± 0.10 kcal. mole^{-1}

ΔH°_m = 6.24 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 51.98 kcal. mole^{-1} to monomer gas

Heat of Formation.

The heat of solution of NaBr(c) in water has been measured by F. A. Askew, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty and J. H. Wolfenden, J. Chem. Soc. 1368 (1934) and W. E. Wallace, J. Am. Chem. Soc. 71, 2485 (1949) to be +0.01 and -0.144 kcal. mole^{-1}, respectively. Using $\Delta H^\circ_{f\ 298.15}$ (Na^+, aq.) = -57.39 and $\Delta H^\circ_{f\ 298.15}$ (Br^-, aq.) = -29.05 kcal. mole^{-1}, obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964, the respective value of $\Delta H^\circ_{f\ 298.15}$ for NaBr(c) was found to be -86.3 and -86.45 kcal. mole^{-1}. The adopted value is the average of these two.

Heat Capacity and Entropy.

The low temperature heat capacities (7.21 - 301.63°K.) were measured by T. E. Gardner and A. R. Taylor, Jr., U. S. Bur. Mines RI 6435 (1964). The high temperature enthalpy changes (290 - 645, 290 - 816°K.) were determined by A. Magnus, Phys. Z. 14, 5 (1913). Based upon the latter data the high temperature heat capacities were derived. The two sets of C_p data were joined smoothly at 298°K. by graphical method. $S^\circ_{298.15}$ was obtained from T. E. Gardner and A. R. Taylor, Jr., loc. cit., using S°_{10} = 0.034 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m and ΔH°_m were reported by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960). The values, T_m = 1014°K. and ΔH°_m = 5.52 kcal. mole^{-1}, reported by M. Blanc, Compt. Rend., 246, 570 (1958), were not used.

Heat of Sublimation.

The value of $\Delta H^\circ_{s\ 298.15}$ was derived from six sets of vapor pressure data by both the second and third law methods. See NaBr(g) table for detail.

Sodium Bromide (NaBr)

(Liquid) Mol. Wt. = 102.907

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	14.900	24.940	24.940	.000	- 81.105	- 79.450	58.236
300	14.900	25.032	24.940	.028	- 81.106	- 79.439	57.869
400	14.900	29.318	25.525	1.518	- 85.080	- 78.132	42.687
500	14.900	32.643	26.628	3.008	- 84.772	- 76.430	33.406
600	14.900	35.360	27.864	4.498	- 84.447	- 74.793	27.242
700	14.900	37.657	29.103	5.988	- 84.110	- 73.211	22.856
800	14.900	39.647	30.300	7.478	- 83.763	- 71.678	19.581
900	14.900	41.402	31.438	8.968	- 83.412	- 70.188	17.043
1000	14.900	42.972	32.514	10.458	- 83.062	- 68.737	15.022
1100	14.900	44.392	33.531	11.948	- 82.719	- 67.323	13.375
1200	14.900	45.688	34.490	13.438	- 105.620	- 65.480	11.925
1300	14.900	46.881	35.398	14.928	- 105.080	- 62.157	10.449
1400	14.900	47.985	36.258	16.418	- 104.540	- 58.875	9.190
1500	14.900	49.013	37.075	17.908	- 104.001	- 55.633	8.105
1600	14.900	49.975	37.851	19.398	- 103.462	- 52.426	7.161
1700	14.900	50.878	38.592	20.888	- 102.923	- 49.251	6.331
1800	14.900	51.730	39.298	22.378	- 102.386	- 46.111	5.598
1900	14.900	52.536	39.974	23.868	- 101.849	- 42.998	4.946
2000	14.900	53.300	40.621	25.358	- 101.314	- 39.916	4.362
2100	14.900	54.027	41.242	26.848	- 100.778	- 36.860	3.836
2200	14.900	54.720	41.839	28.338	- 100.244	- 33.828	3.360
2300	14.900	55.382	42.414	29.828	- 99.710	- 30.821	2.929
2400	14.900	56.016	42.967	31.318	- 99.178	- 27.835	2.535
2500	14.900	56.624	43.501	32.808	- 98.647	- 24.874	2.174

Sept. 30, 1964

SODIUM BROMIDE (NaBr) (LIQUID) MOL. WT. = 102.907

$S^\circ_{298.15}$ = [24.940] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-81.105] kcal. mole^{-1}

T_m = 1020°K.

ΔH°_m = 6.24 kcal. mole^{-1}

T_b = [1720]°K. to monomer gas

ΔH°_v = 38.42 kcal. mole^{-1} to monomer gas

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$(l) was obtained from $\Delta H^\circ_{f\ 298.15}$(c) by adding ΔH°_m and the difference between $H^\circ - H^\circ_{298.15}$ for crystal and liquid. The equilibrium constant of the reaction NaBr(l) + HCl(g) = NaCl(l) + HBr(g) has been determined by J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. 17, 1502 (1963). From the reported data, $\ln K_{800°C} = -1.19 \pm 0.01$, the heat of reaction ($\Delta H^\circ_{r\ 298.15}$) was derived to be 2.11 kcal. mole^{-1}. Using $\Delta H^\circ_{f\ 298.15}$ (HCl,g) = -22.062, $\Delta H^\circ_{f\ 298.15}$ (NaCl, l) = -92.24 and $\Delta H^\circ_{f\ 298.15}$ (HBr, g) = -8.70 kcal. mole^{-1}, the value of $\Delta H^\circ_{f\ 298.15}$ for NaBr(l) was evaluated to be -81.0 ± 0.5 kcal. mole^{-1} which is in reasonable agreement with the value adopted. The values of $\Delta H^\circ_{f\ 298.15}$ for HCl(g) and HBr(g) were obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964.

Heat Capacity and Entropy.

Heat capacity for NaBr(l) was estimated by comparison with those for NaCl(c), AgCl(c) and AgCl(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH°_m were reported by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960). The values, T_m = 1014°K. and ΔH°_m = 5.52 kcal. mole^{-1}, reported by M. Blanc, Compt. Rend., 246, 570 (1958), were not used.

Vaporization Data.

The boiling point, T_b, was calculated as the temperature at which the value of ΔF°_r becomes zero for the reaction NaBr(l) → NaBr(g). The difference between ΔH°_f for NaBr(l) and NaBr(g) at T_b is the heat of vaporization, ΔH°_v.

Sodium Bromide (NaBr)

(Ideal Gas) Mol. Wt. = 102.907

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.344	-32.274	-32.274	INFINITE
100	7.475	48.724	65.090	-1.637	-32.220	-35.880	78.412
200	8.355	54.221	58.413	-.838	-32.594	-39.404	43.056
298	8.681	57.628	57.628	.000	-34.400	-42.491	31.145
300	8.685	57.681	57.628	.016	-34.412	-42.540	30.989
400	8.833	60.203	57.971	.893	-39.000	-44.406	24.261
500	8.915	62.183	58.622	1.781	-39.294	-45.722	19.984
600	8.970	63.814	59.356	2.675	-39.565	-46.983	17.113
700	9.010	65.200	60.094	3.574	-39.818	-48.200	15.048
800	9.043	66.405	60.809	4.477	-40.059	-49.380	13.489
900	9.072	67.472	61.491	5.383	-40.292	-50.531	12.270
1000	9.098	68.429	62.138	6.291	-40.523	-51.655	11.289
1100	9.121	69.297	62.750	7.202	-40.760	-52.759	10.482
1200	9.144	70.092	63.329	8.115	-64.238	-53.382	9.722
1300	9.166	70.825	63.878	9.031	-64.272	-52.476	8.822
1400	9.187	71.505	64.399	9.948	-64.304	-51.568	8.050
1500	9.208	72.139	64.894	10.868	-64.335	-50.656	7.380
1600	9.228	72.734	65.365	11.790	-64.365	-49.743	6.794
1700	9.248	73.294	65.816	12.714	-64.392	-48.827	6.277
1800	9.268	73.823	66.246	13.639	-64.419	-47.911	5.817
1900	9.287	74.325	66.658	14.567	-64.444	-46.993	5.405
2000	9.307	74.802	67.053	15.497	-64.470	-46.076	5.035
2100	9.326	75.256	67.433	16.428	-64.492	-45.155	4.699
2200	9.345	75.691	67.799	17.362	-64.514	-44.235	4.394
2300	9.364	76.106	68.151	18.297	-64.536	-43.311	4.115
2400	9.383	76.505	68.491	19.235	-64.556	-42.386	3.860
2500	9.402	76.889	68.819	20.174	-64.575	-41.465	3.625
2600	9.421	77.258	69.137	21.115	-64.595	-40.539	3.407
2700	9.440	77.614	69.444	22.058	-64.615	-39.615	3.206
2800	9.459	77.957	69.742	23.003	-64.635	-38.688	3.020
2900	9.478	78.290	70.031	23.950	-64.655	-37.760	2.846
3000	9.497	78.611	70.312	24.899	-64.676	-36.832	2.683
3100	9.515	78.923	70.585	25.849	-64.699	-35.904	2.531
3200	9.534	79.225	70.850	26.802	-64.722	-34.973	2.388
3300	9.553	79.519	71.108	27.756	-64.749	-34.045	2.255
3400	9.572	79.805	71.360	28.713	-64.776	-33.117	2.129
3500	9.590	80.082	71.605	29.671	-64.808	-32.180	2.009
3600	9.609	80.353	71.844	30.631	-64.844	-31.250	1.897
3700	9.628	80.616	72.078	31.592	-64.883	-30.317	1.791
3800	9.647	80.873	72.306	32.556	-64.926	-29.379	1.690
3900	9.665	81.124	72.529	33.522	-64.977	-28.445	1.594
4000	9.684	81.369	72.747	34.489	-65.033	-27.509	1.503
4100	9.703	81.608	72.960	35.459	-65.096	-26.567	1.416
4200	9.721	81.842	73.169	36.430	-65.169	-25.628	1.333
4300	9.740	82.071	73.373	37.403	-65.250	-24.683	1.254
4400	9.759	82.296	73.573	38.378	-65.342	-23.745	1.179
4500	9.777	82.515	73.770	39.355	-65.446	-22.793	1.107
4600	9.796	82.730	73.962	40.333	-65.564	-21.846	1.038
4700	9.815	82.941	74.151	41.314	-65.697	-20.894	.972
4800	9.833	83.148	74.336	42.296	-65.847	-19.943	.908
4900	9.852	83.351	74.518	43.280	-66.016	-18.981	.847
5000	9.871	83.550	74.697	44.267	-66.205	-18.018	.788
5100	9.889	83.746	74.872	45.255	-66.418	-17.055	.731
5200	9.908	83.938	75.045	46.244	-66.655	-16.085	.676
5300	9.926	84.127	75.214	47.236	-66.919	-15.109	.623
5400	9.945	84.312	75.381	48.230	-67.213	-14.126	.572
5500	9.964	84.495	75.545	49.225	-67.540	-13.142	.522
5600	9.982	84.675	75.707	50.222	-67.901	-12.153	.474
5700	10.001	84.852	75.865	51.222	-68.298	-11.153	.428
5800	10.019	85.026	76.022	52.223	-68.734	-10.146	.382
5900	10.038	85.197	76.176	53.225	-69.213	-9.127	.338
6000	10.057	85.366	76.328	54.230	-69.734	-8.108	.295

Sept. 30, 1964

SODIUM BROMIDE (NaBr) (IDEAL GAS) MOL. WT. = 102.907

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0} = -32.27 \pm 0.50$ kcal. mole^{-1}

$S^\circ_{298.15} = 57.628$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -34.40 \pm 0.50$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	1

$\omega_e = 302.1 \pm 4$ cm.$^{-1}$

$\omega_e x_e = 1.50$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.1495$ cm.$^{-1}$

$\alpha_e = 0.000939$ cm.$^{-1}$

$r_e = 2.5020 \pm 0.0001$ Å

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) was calculated from $\Delta H^\circ_{f\ 298.15}$ and $\Delta H^\circ_{s\ 298.15}$ for NaBr(c). The latter was derived from six sets of corrected vapor pressure data, due to the presence of dimeric species in the vapor, by both the second and third law methods. The results are listed as follows.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H^\circ_{f\ 298.15}$* kcal. mole^{-1}
Niwa[1]	NaBr(c) → NaBr(g)	51.97	50.31	-35.24
Cogin and Kimball[2]	NaBr(c) → NaBr(g)	52.26	52.14	-34.18
Mayer and Wintner[3]	NaBr(c) → NaBr(g)	52.59	65.30	-33.79**
Ruff and Mugdan[4]	NaBr(l) → NaBr(g)	46.43	47.48	-34.15
Wartenberg and Albrecht[5]	NaBr(l) → NaBr(g)	46.38	47.54	-34.15
Bloom et al.[6]	NaBr(l) → NaBr(g)	46.23	51.53	-34.88**

*Based on the average of the second and third law values.

**Only the third law value being used.

[1] K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).

[2] G. E. Cogin and G. E. Kimball, J. Chem. Phys. 16, 1035 (1948).

[3] J. E. Mayer and I. H. Wintner, J. Chem. Phys., 6, 301 (1938).

[4] O. Ruff and S. Mugdan, Z. anorg. allgem. Chem., 117, 147 (1921).

[5] H. von Wartenberg and P. Albrecht, Z. Electrochem., 27, 162 (1921).

[6] H. Bloom, J. O'M. Bockris, N. E. Richards and R. G. Taylor, J. Am. Chem. Soc. 80, 2044 (1958).

The value of $\Delta H^\circ_{f\ 298.15}$ for NaBr(g) adopted is the average value of the six $\Delta H^\circ_{f\ 298.15}$ values listed in the above table. The dissociation energy (D°_0) was calculated to be 86.28 kcal. mole^{-1} or 3.74 e.v. which is in good agreement with the values, $D^\circ_0 = 3.84 \pm 1$ and 3.85 e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953 and G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950, respectively. According to L. Brewer, private communication, October 23, 1964, Gaydon's original reported value, $D^\circ_0 = 3.8$, is an average of the value of 3.84 e.v. from atomic fluorescence and the value of 3.75 e.v. calculated for Gaydon by Brewer from pressure data available at that time.

Heat Capacity and Entropy.

The values of ω_e, $\omega_e x_e$, B_e and α_e were taken from S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957). The adopted bond distance (r_e) was reported by A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 96, 629 (1954), which was derived from microwave spectrum. By electron-diffraction method, the Na-Br bond distance was determined as 2.64 ± 0.01 Å by L. R. Maxwell, S. B. Hendricks and V. M. Mosley, Phys. Rev. 52, 968 (1937). The discrepancy may be due to the presence of a large proportion of dimer at the higher pressures used in the electron-diffraction determination. The ground state configuration was reported by G. Herzberg, loc. cit.

Phosphorus Monobromide (PBr)

(Ideal Gas) Mol. Wt. = 110.891

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.272	44.519	44.519	INFINITE
100	7.175	50.995	66.728	- 1.573	44.793	40.487	- 88.479
200	8.019	56.241	60.299	- .811	44.652	36.217	- 39.574
298	8.460	59.537	59.537	.000	43.000	32.298	- 23.674
300	8.465	59.589	59.537	.016	42.990	32.232	- 23.480
400	8.677	62.057	59.872	.874	39.195	29.418	- 16.072
500	8.792	64.007	60.511	1.748	39.057	26.988	- 11.796
600	8.863	65.616	61.231	2.631	38.895	24.589	- 8.956
700	8.912	66.986	61.958	3.520	38.704	22.219	- 6.937
800	8.947	68.179	62.663	4.413	18.066	14.568	- 3.980
900	8.975	69.234	63.335	5.309	18.078	14.130	- 3.431
1000	8.999	70.181	63.973	6.208	18.087	13.691	- 2.992
1100	9.019	71.040	64.577	7.109	18.096	13.250	- 2.632
1200	9.037	71.825	65.149	8.012	18.105	12.809	- 2.333
1300	9.054	72.549	65.691	8.916	18.113	12.369	- 2.079
1400	9.069	73.221	66.205	9.822	18.121	11.927	- 1.862
1500	9.083	73.847	66.694	10.730	18.128	11.484	- 1.673
1600	9.097	74.434	67.159	11.639	18.136	11.040	- 1.508
1700	9.111	74.986	67.604	12.549	18.143	10.597	- 1.362
1800	9.124	75.507	68.029	13.461	18.152	10.153	- 1.233
1900	9.137	76.001	68.435	14.374	18.160	9.709	- 1.117
2000	9.149	76.469	68.825	15.288	18.167	9.262	- 1.012
2100	9.161	76.916	69.200	16.204	18.175	8.817	- .918
2200	9.173	77.343	69.561	17.121	18.183	8.372	- .832
2300	9.185	77.751	69.908	18.039	18.192	7.925	- .753
2400	9.197	78.142	70.243	18.958	18.200	7.478	- .681
2500	9.209	78.518	70.566	19.878	18.209	7.033	- .615
2600	9.221	78.879	70.879	20.799	18.218	6.584	- .553
2700	9.232	79.227	71.182	21.722	18.227	6.136	- .497
2800	9.244	79.563	71.475	22.646	18.236	5.689	- .444
2900	9.255	79.888	71.760	23.571	18.247	5.241	- .395
3000	9.267	80.202	72.036	24.497	18.257	4.793	- .349
3100	9.278	80.506	72.304	25.424	18.267	4.345	- .306
3200	9.289	80.800	72.565	26.353	18.278	3.894	- .266
3300	9.301	81.086	72.819	27.282	18.289	3.444	- .228
3400	9.312	81.364	73.066	28.213	18.300	2.994	- .192
3500	9.323	81.634	73.307	29.144	18.311	2.544	- .159
3600	9.334	81.897	73.542	30.077	18.323	2.092	- .127
3700	9.346	82.153	73.772	31.011	18.335	1.641	- .097
3800	9.357	82.402	73.995	31.946	18.348	1.191	- .069
3900	9.368	82.646	74.214	32.883	18.360	.741	- .042
4000	9.379	82.883	74.428	33.820	18.373	.285	- .016
4100	9.390	83.115	74.637	34.759	18.387	- .167	.009
4200	9.402	83.341	74.842	35.698	18.400	- .616	.032
4300	9.413	83.562	75.042	36.639	18.413	- 1.072	.054
4400	9.424	83.779	75.238	37.581	18.428	- 1.522	.076
4500	9.435	83.991	75.430	38.524	18.442	- 1.977	.096
4600	9.446	84.198	75.618	39.468	18.457	- 2.433	.116
4700	9.457	84.402	75.803	40.413	18.472	- 2.885	.134
4800	9.468	84.601	75.984	41.359	18.487	- 3.341	.152
4900	9.479	84.796	76.162	42.307	18.503	- 3.793	.169
5000	9.491	84.988	76.337	43.255	18.519	- 4.248	.186
5100	9.502	85.176	76.508	44.205	18.534	- 4.706	.202
5200	9.513	85.360	76.677	45.155	18.551	- 5.163	.217
5300	9.524	85.542	76.842	46.107	18.568	- 5.617	.232
5400	9.535	85.720	77.005	47.060	18.585	- 6.076	.246
5500	9.546	85.895	77.165	48.014	18.603	- 6.529	.259
5600	9.557	86.067	77.323	48.969	18.620	- 6.989	.273
5700	9.568	86.236	77.477	49.926	18.638	- 7.444	.285
5800	9.579	86.403	77.630	50.883	18.657	- 7.903	.298
5900	9.590	86.567	77.780	51.841	18.676	- 8.362	.310
6000	9.601	86.728	77.928	52.801	18.694	- 8.821	.321

June 30, 1963; Dec. 31, 1963

PHOSPHORUS MONOBROMIDE (PBr) (IDEAL GAS) MOL. WT. = 110.891

Ground State Configuration $[{}^3\Sigma]$

$S^\circ_{298.15}$ = [59.5] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [45] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [43] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	[3]

ω_e = [400] cm.$^{-1}$

$\omega_e x_e$ = [1.5] cm.$^{-1}$

σ = 1

B_e = [0.1519] cm.$^{-1}$

α_e = [0.0008] cm.$^{-1}$

r_e = [2.23] Å

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as 40.8 kcal. mole^{-1} by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, August 25, 1961. This $\Delta H^\circ_{f\ 298.15}$ was changed from the white (α) to red (V) phosphorus reference state.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

Lead Monobromide (PbBr)

(Ideal Gas) Mol. Wt. = 287.13

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.424	15.449	15.449	INFINITE
100	7.963	55,664	72.630	-1.697	15.420	11.377	-24.864
200	8.639	61,446	65.739	-.859	15.069	7.464	-8.156
298	8.825	64,936	64.936	.000	13.300	3.980	-2.917
300	8.827	64,991	64.936	.016	13.288	3.922	-2.857
400	8.906	67,542	65.284	.903	9.403	1.586	-.867
500	8.951	69,535	65.942	1.796	9.181	-.344	.150
600	8.982	71,170	66.681	2.693	8.944	-2.226	.811
700	9.006	72,556	67.424	3.593	7.527	-3.878	1.211
800	9.027	73,760	68.142	4.494	7.260	-5.489	1.499
900	9.046	74,825	68.827	5.398	7.001	-7.067	1.716
1000	9.064	75,779	69.475	6.304	6.750	-8.616	1.883
1100	9.084	76,643	70.088	7.211	6.507	-10.141	2.015
1200	9.105	77,435	70.668	8.120	6.274	-11.643	2.120
1300	9.130	78,164	71.217	9.032	6.048	-13.127	2.207
1400	9.158	78,842	71.737	9.946	5.824	-14.594	2.278
1500	9.191	79,475	72.232	10.864	5.603	-16.044	2.337
1600	9.228	80,069	72.704	11.785	5.383	-17.480	2.388
1700	9.269	80,630	73.154	12.709	5.163	-18.902	2.430
1800	9.314	81,161	73.584	13.639	4.943	-20.313	2.466
1900	9.362	81,666	73.996	14.572	4.723	-21.710	2.497
2000	9.413	82,147	74.392	15.511	4.502	-23.095	2.524
2100	9.466	82,608	74.772	16.455	-38.170	-22.917	2.385
2200	9.521	83,049	75.138	17.404	-38.298	-22.188	2.204
2300	9.576	83,474	75.492	18.359	-38.443	-21.452	2.038
2400	9.632	83,883	75.833	19.320	-38.603	-20.709	1.886
2500	9.687	84,277	76.163	20.286	-38.782	-19.962	1.745
2600	9.742	84,658	76.482	21.257	-38.976	-19.205	1.614
2700	9.796	85,027	76.792	22.234	-39.186	-18.441	1.493
2800	9.847	85,384	77.092	23.216	-39.413	-17.668	1.379
2900	9.898	85,730	77.384	24.203	-39.654	-16.886	1.273
3000	9.946	86,067	77.668	25.196	-39.907	-16.097	1.173
3100	9.992	86,394	77.944	26.193	-40.173	-15.299	1.079
3200	10.036	86,711	78.213	27.194	-40.451	-14.492	.990
3300	10.078	87,021	78.476	28.200	-40.737	-13.677	.906
3400	10.117	87,322	78.731	29.209	-41.032	-12.852	.826
3500	10.154	87,616	78.981	30.223	-41.333	-12.019	.750
3600	10.189	87,903	79.225	31.240	-41.639	-11.177	.678
3700	10.221	88,182	79.463	32.261	-41.949	-10.327	.610
3800	10.251	88,455	79.696	33.284	-42.261	-9.466	.544
3900	10.279	88,722	79.924	34.311	-42.576	-8.599	.482
4000	10.306	88,982	80.147	35.340	-42.890	-7.728	.422
4100	10.330	89,237	80.366	36.372	-43.204	-6.844	.365
4200	10.353	89,486	80.580	37.406	-43.517	-5.952	.310
4300	10.373	89,730	80.790	38.442	-43.827	-5.056	.257
4400	10.393	89,969	80.996	39.481	-44.134	-4.147	.206
4500	10.410	90,203	81.198	40.521	-44.438	-3.237	.157
4600	10.427	90,432	81.396	41.563	-44.739	-2.317	.110
4700	10.442	90,656	81.591	42.606	-45.034	-1.393	.065
4800	10.456	90,876	81.782	43.651	-45.327	-.459	.021
4900	10.469	91,092	81.970	44.697	-45.613	.477	-.021
5000	10.480	91,303	82.155	45.745	-45.895	1.420	-.062
5100	10.491	91,511	82.336	46.793	-46.173	2.368	-.101
5200	10.501	91,715	82.514	47.843	-46.445	3.324	-.140
5300	10.511	91,915	82.690	48.893	-46.713	4.286	-.177
5400	10.519	92,112	82.863	49.945	-46.976	5.249	-.212
5500	10.527	92,305	83.032	50.997	-47.235	6.219	-.247
5600	10.535	92,494	83.200	52.050	-47.489	7.193	-.281
5700	10.542	92,681	83.364	53.104	-47.739	8.169	-.313
5800	10.548	92,864	83.527	54.159	-47.985	9.157	-.345
5900	10.554	93,045	83.686	55.214	-48.229	10.142	-.376
6000	10.560	93,222	83.844	56.269	-48.468	11.129	-.405

June 30, 1962

Lead Monobromide (PbBr) (Ideal Gas)

Mol. Wt. = 287.13

$\Delta H_f^\circ{}_{298.15} = 13.3 \pm 9.2$ kcal. mole^{-1}

$S^\circ_{298.15} = 64.936$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi_{1/2}$

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_i
0	2
[8000]	2

$\omega_e = 207.5$ cm.$^{-1}$ $\omega_e x_e = 0.50$ cm.$^{-1}$

$B_e = [0.04874]$ cm.$^{-1}$ $\alpha_e = [0.00016]$ cm.$^{-1}$

$\sigma = 1$

Heat of Formation. $\Delta H_f^\circ{}_{298.15}$ was calculated from the dissociation energy of PbBr(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). B_e and α_e were estimated by J. S. Gordon, Astrosystems, Inc., private communication, May, 1962. Electronic levels and multiplicities were estimated from those for PbF(g).

Titanium Monobromide (TiBr)

(Ideal Gas) GFW = 127.809

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.375	52.506	52.506	INFINITE
100	7.511	53.139	69.804	-1.667	52.747	48.273	-105.502
200	8.466	58.674	62.987	-.862	52.508	43.876	-47.946
298	9.087	62.175	62.175	.000	50.800	39.871	-29.226
300	9.098	62.231	62.175	.017	50.789	39.803	-28.997
400	9.601	64.920	62.538	.953	46.987	36.916	-20.170
500	9.961	67.104	63.240	1.932	46.879	34.409	-15.040
600	10.194	68.943	64.041	2.941	46.778	31.924	-11.628
700	10.333	70.525	64.857	3.968	46.672	29.457	-9.197
800	10.411	71.911	65.654	5.005	46.552	27.005	-7.378
900	10.453	73.140	66.419	6.049	46.410	24.571	-5.967
1000	10.475	74.242	67.147	7.095	46.243	22.153	-4.841
1100	10.489	75.241	67.838	8.144	46.051	19.754	-3.925
1200	10.500	76.154	68.493	9.193	44.897	17.410	-3.171
1300	10.511	76.995	69.116	10.244	44.781	15.124	-2.543
1400	10.524	77.775	69.707	11.295	44.651	12.847	-2.005
1500	10.539	78.501	70.269	12.349	44.505	10.580	-1.541
1600	10.557	79.182	70.805	13.403	44.342	8.325	-1.137
1700	10.576	79.823	71.317	14.460	44.161	6.078	-.781
1800	10.596	80.428	71.806	15.518	43.959	3.843	-.467
1900	10.618	81.001	72.275	16.579	43.737	1.621	-.186
2000	10.640	81.546	72.725	17.642	39.045	-.436	.048
2100	10.662	82.066	73.158	18.707	38.803	-2.403	.250
2200	10.684	82.563	73.574	19.775	38.562	-4.361	.433
2300	10.706	83.038	73.975	20.844	38.323	-6.306	.599
2400	10.727	83.494	74.362	21.916	38.086	-8.240	.750
2500	10.747	83.932	74.737	22.989	37.850	-10.166	.889
2600	10.766	84.354	75.098	24.065	37.616	-12.083	1.016
2700	10.784	84.761	75.449	25.142	37.382	-13.990	1.132
2800	10.801	85.153	75.788	26.222	37.150	-15.888	1.240
2900	10.816	85.533	76.118	27.303	36.920	-17.776	1.340
3000	10.831	85.900	76.438	28.385	36.690	-19.659	1.432
3100	10.845	86.255	76.749	29.469	36.461	-21.532	1.518
3200	10.858	86.599	77.051	30.554	36.233	-23.402	1.598
3300	10.870	86.934	77.346	31.640	36.005	-25.261	1.673
3400	10.881	87.258	77.633	32.728	35.779	-27.114	1.743
3500	10.892	87.574	77.912	33.817	35.553	-28.961	1.808
3600	10.902	87.881	78.185	34.906	-66.299	-30.538	1.854
3700	10.911	88.180	78.451	35.997	-66.496	-29.543	1.745
3800	10.920	88.471	78.711	37.088	-66.706	-28.544	1.642
3900	10.929	88.755	78.965	38.181	-66.929	-27.533	1.543
4000	10.937	89.031	79.213	39.274	-67.164	-26.521	1.449
4100	10.945	89.302	79.456	40.368	-67.412	-25.502	1.359
4200	10.952	89.565	79.693	41.463	-67.671	-24.478	1.274
4300	10.960	89.823	79.926	42.559	-67.943	-23.447	1.192
4400	10.967	90.075	80.154	43.655	-68.225	-22.409	1.113
4500	10.975	90.322	80.377	44.752	-68.518	-21.364	1.038
4600	10.982	90.563	80.596	45.850	-68.821	-20.309	.965
4700	10.989	90.799	80.810	46.949	-69.133	-19.251	.895
4800	10.997	91.031	81.021	48.048	-69.456	-18.188	.828
4900	11.004	91.258	81.227	49.148	-69.787	-17.119	.764
5000	11.012	91.480	81.430	50.249	-70.125	-16.038	.701
5100	11.020	91.698	81.629	51.350	-70.472	-14.954	.641
5200	11.027	91.912	81.825	52.453	-70.826	-13.861	.583
5300	11.036	92.122	82.017	53.556	-71.187	-12.764	.526
5400	11.044	92.329	82.206	54.660	-71.555	-11.657	.472
5500	11.052	92.531	82.392	55.765	-71.927	-10.541	.419
5600	11.061	92.731	82.575	56.870	-72.307	-9.428	.368
5700	11.070	92.927	82.755	57.977	-72.690	-8.297	.318
5800	11.079	93.119	82.932	59.084	-73.078	-7.164	.270
5900	11.089	93.309	83.106	60.193	-73.470	-6.024	.223
6000	11.098	93.495	83.278	61.302	-73.866	-4.883	.178

Dec. 31, 1961; June 30, 1964; Sept. 30, 1964; June 30, 1968

TITANIUM MONOBROMIDE (TiBr) (IDEAL GAS) GFW = 127.809

Ground State Configuration [$^4\Sigma$]

ΔHf°_0 = [52.5 ± 10.0] kcal/mol

$S^\circ_{298.15}$ = 62.18 ± 2.0 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [50.8 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

ω_e = [295] cm^{-1}

B_e = [0.0904] cm^{-1}

$\omega_e x_e$ = [2.21] cm^{-1}

α_e = [0.00067] cm^{-1}

σ = 1

r_e = [2.5] Å

Heat of Formation

The heat of formation, ΔHf°_{298}, of TiBr (g) is calculated from the dissociation energy, D°_0, which is estimated as 104 kcal/mol. This estimate is obtained from the relation $D(TiBr_4) < D^\circ_0(TiBr) < D(TiBr_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e, and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+ (3). α_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. 58, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Tungsten Monobromide (WBr)

(Ideal Gas)   GFW = 263.759

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.324	141.894	141.894	INFINITE
100	7.389	56.323	72.519	- 1.620	142.109	137.350	- 300.178
200	8.268	61.754	65.909	- .831	141.832	132.683	- 144.990
298	8.512	65.130	65.130	.000	140.100	128.433	- 94.144
300	8.516	65.183	65.130	.016	140.088	128.361	- 93.511
400	8.767	67.685	65.470	.886	136.249	125.230	- 68.423
500	8.846	69.651	66.117	1.767	136.088	122.493	- 53.542
600	8.895	71.268	66.845	2.654	135.920	119.790	- 43.634
700	8.931	72.642	67.577	3.546	135.744	117.116	- 36.565
800	8.961	73.837	68.287	4.440	135.558	114.466	- 31.271
900	8.992	74.894	68.963	5.339	135.364	111.842	- 27.159
1000	9.025	75.843	69.604	6.239	135.161	109.240	- 23.874
1100	9.062	76.705	70.211	7.143	134.950	106.657	- 21.191
1200	9.102	77.495	70.786	8.051	134.732	104.095	- 18.958
1300	9.144	78.225	71.330	8.963	134.506	101.552	- 17.072
1400	9.189	78.905	71.847	9.880	134.272	99.024	- 15.458
1500	9.234	79.540	72.339	10.801	134.032	96.516	- 14.062
1600	9.279	80.137	72.808	11.727	133.784	94.024	- 12.843
1700	9.324	80.701	73.256	12.657	133.528	91.546	- 11.769
1800	9.369	81.236	73.685	13.592	133.265	89.082	- 10.816
1900	9.413	81.743	74.096	14.531	132.995	86.637	- 9.966
2000	9.458	82.227	74.490	15.474	132.717	84.205	- 9.201
2100	9.503	82.690	74.870	16.422	132.431	81.785	- 8.511
2200	9.549	83.133	75.235	17.375	132.136	79.378	- 7.885
2300	9.596	83.558	75.588	18.332	131.835	76.989	- 7.316
2400	9.646	83.968	75.929	19.294	131.526	74.611	- 6.794
2500	9.698	84.363	76.258	20.261	131.210	72.245	- 6.316
2600	9.753	84.744	76.577	21.234	130.886	69.894	- 5.875
2700	9.811	85.113	76.887	22.212	130.551	67.555	- 5.468
2800	9.872	85.471	77.187	23.196	130.195	65.229	- 5.091
2900	9.937	85.819	77.478	24.187	129.809	62.911	- 4.741
3000	10.005	86.157	77.762	25.184	129.388	60.614	- 4.416
3100	10.077	86.486	78.038	26.188	128.920	58.328	- 4.112
3200	10.151	86.807	78.307	27.199	128.400	56.059	- 3.829
3300	10.228	87.121	78.570	28.218	127.821	53.805	- 3.563
3400	10.307	87.427	78.826	29.245	127.175	51.574	- 3.315
3500	10.388	87.727	79.076	30.280	126.448	49.362	- 3.082
3600	10.471	88.021	79.320	31.322	125.614	47.169	- 2.863
3700	10.554	88.309	79.559	32.374	116.344	45.048	- 2.661
3800	10.638	88.591	79.793	33.433	116.087	43.129	- 2.480
3900	10.722	88.869	80.022	34.501	115.838	41.211	- 2.309
4000	10.805	89.141	80.247	35.578	115.597	39.301	- 2.147
4100	10.888	89.409	80.467	36.662	115.363	37.396	- 1.993
4200	10.969	89.673	80.683	37.755	115.138	35.495	- 1.847
4300	11.049	89.932	80.895	38.856	114.920	33.602	- 1.708
4400	11.127	90.186	81.104	39.965	114.709	31.716	- 1.575
4500	11.202	90.437	81.308	41.081	114.505	29.831	- 1.449
4600	11.275	90.684	81.509	42.205	114.309	27.953	- 1.328
4700	11.345	90.928	81.707	43.336	114.119	26.076	- 1.213
4800	11.411	91.167	81.902	44.474	113.935	24.206	- 1.102
4900	11.475	91.403	82.093	45.619	113.757	22.335	- .996
5000	11.535	91.636	82.282	46.769	113.585	20.472	- .895
5100	11.592	91.865	82.467	47.925	113.418	18.609	- .797
5200	11.645	92.090	82.650	49.087	113.256	16.755	- .704
5300	11.695	92.312	82.831	50.254	113.099	14.903	- .615
5400	11.741	92.531	83.008	51.426	112.946	13.051	- .528
5500	11.783	92.747	83.183	52.602	112.797	11.204	- .445
5600	11.822	92.960	83.356	53.783	112.652	9.354	- .365
5700	11.857	93.170	83.526	54.966	112.509	7.506	- .288
5800	11.889	93.376	83.694	56.154	112.370	5.670	- .214
5900	11.917	93.580	83.860	57.344	112.233	3.832	- .142
6000	11.943	93.780	84.024	58.537	- 81.806	4.078	- .149

June 30, 1967

TUNGSTEN MONOBROMIDE (WBr)   (IDEAL GAS)   GFW = 263.759

Ground State Configuration [$^2\Delta$] ΔHf°_0 = [141.9 ± 20] kcal/mol

$S^\circ_{298.15}$ = [65.1] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [140.1 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[5000]	[2]
[15000]	[20]

ω_e = [321.4] cm^{-1} $\omega_e x_e$ = [0.80] cm^{-1} σ = 1

B_e = [0.05254] cm^{-1} α_e = [0.00015] cm^{-1} r_e = [2.40] Å

Heat of Formation

The heat of formation, ΔHf°_{298}(WBr, g) = 140.1 kcal/mol, is calculated from the bond dissociation energy, D°_{298}(W-Br) = 90 ± 20 kcal/mol. This value of D°_{298} is estimated to be slightly higher than the average bond dissociation energy of WBr_6(g), by analogy with the WCl_x system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WBr_6(g). This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D^\circ_0 + 0.5\ \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is 53.27×10^{-39} g cm^2.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g). See WF(g) table (March 31, 1967) for details.

Zirconium Monobromide (ZrBr)

(Ideal Gas) GFW = 171.129

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.328	73.923	73.923	INFINITE
100	7.404	54.620	70.843	-1.622	74.082	69.599	-152.108
200	8.282	60.063	64.222	-.832	73.761	65.227	-71.277
298	8.620	63.443	63.442	.000	72.000	61.286	-44.923
300	8.624	63.496	63.443	.016	71.988	61.220	-44.598
400	8.776	66.000	63.783	.887	68.116	58.414	-31.916
500	8.875	67.969	64.430	1.769	67.906	56.011	-24.482
600	8.973	69.596	65.160	2.662	67.677	53.654	-19.543
700	9.086	70.987	65.895	3.565	67.427	51.335	-16.028
800	9.215	72.209	66.609	4.480	67.161	49.055	-13.401
900	9.353	73.302	67.293	5.408	66.879	46.808	-11.367
1000	9.492	74.295	67.945	6.350	66.582	44.595	-9.746
1100	9.626	75.206	68.564	7.306	66.270	42.411	-8.426
1200	9.751	76.049	69.153	8.275	65.091	40.307	-7.341
1300	9.865	76.834	69.714	9.256	64.925	38.249	-6.430
1400	9.968	77.569	70.249	10.248	64.759	36.204	-5.652
1500	10.058	78.260	70.760	11.249	64.591	34.170	-4.979
1600	10.136	78.911	71.249	12.259	64.418	32.147	-4.391
1700	10.203	79.528	71.718	13.276	64.242	30.136	-3.874
1800	10.260	80.113	72.169	14.299	64.060	28.134	-3.416
1900	10.308	80.669	72.602	15.328	63.871	26.144	-3.007
2000	10.348	81.199	73.018	16.360	63.675	24.163	-2.640
2100	10.380	81.704	73.420	17.397	63.471	22.192	-2.310
2200	10.407	82.188	73.808	18.436	58.256	20.408	-2.027
2300	10.428	82.651	74.182	19.478	58.039	18.693	-1.776
2400	10.446	83.095	74.544	20.522	57.824	16.987	-1.547
2500	10.459	83.522	74.895	21.567	57.610	15.290	-1.337
2600	10.470	83.932	75.235	22.614	57.396	13.602	-1.143
2700	10.479	84.327	75.564	23.661	57.183	11.921	-.965
2800	10.485	84.709	75.884	24.709	56.970	10.249	-.800
2900	10.491	85.077	76.195	25.758	56.757	8.584	-.647
3000	10.495	85.432	76.497	26.807	56.544	6.926	-.505
3100	10.498	85.777	76.790	27.857	56.331	5.276	-.372
3200	10.501	86.110	77.077	28.907	56.118	3.633	-.248
3300	10.504	86.433	77.355	29.957	55.904	1.995	-.132
3400	10.506	86.747	77.627	31.008	55.691	.364	-.023
3500	10.508	87.051	77.892	32.058	55.476	-1.259	.079
3600	10.511	87.347	78.150	33.109	55.262	-2.877	.175
3700	10.513	87.635	78.403	34.161	55.048	-4.490	.265
3800	10.516	87.916	78.649	35.212	54.833	-6.095	.351
3900	10.519	88.189	78.891	36.264	54.617	-7.695	.431
4000	10.522	88.455	79.126	37.316	54.402	-9.292	.508
4100	10.525	88.715	79.357	38.368	54.186	-10.882	.580
4200	10.529	88.969	79.583	39.421	53.970	-12.466	.649
4300	10.533	89.217	79.804	40.474	53.754	-14.044	.714
4400	10.537	89.459	80.021	41.527	53.538	-15.618	.776
4500	10.542	89.696	80.233	42.581	53.322	-17.188	.835
4600	10.546	89.927	80.441	43.636	53.106	-18.752	.891
4700	10.552	90.154	80.646	44.691	52.890	-20.311	.944
4800	10.557	90.377	80.846	45.746	-88.483	-21.185	.965
4900	10.563	90.594	81.043	46.802	-88.803	-19.778	.882
5000	10.568	90.808	81.236	47.859	-89.129	-18.366	.803
5100	10.574	91.017	81.426	48.916	-89.461	-16.950	.726
5200	10.581	91.222	81.612	49.973	-89.796	-15.524	.652
5300	10.587	91.424	81.795	51.032	-90.134	-14.092	.581
5400	10.593	91.622	81.976	52.091	-90.477	-12.655	.512
5500	10.600	91.816	82.153	53.151	-90.823	-11.209	.445
5600	10.607	92.008	82.327	54.211	-91.172	-9.759	.381
5700	10.614	92.195	82.496	55.272	-91.525	-8.302	.318
5800	10.620	92.380	82.667	56.334	-91.878	-6.838	.258
5900	10.627	92.562	82.833	57.396	-92.234	-5.369	.199
6000	10.634	92.740	82.997	58.459	-92.593	-3.897	.142

Sept. 30, 1964; June 30, 1970

ZIRCONIUM MONOBROMIDE (ZrBr) (IDEAL GAS) GFW = 171.129

Ground State Configuration $[{}^4\Sigma]$

$\Delta Hf^\circ_0 = [73.9 \pm 10]$ kcal/mol

$S^\circ_{298.15} = [63.4 \pm 2]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = [72 \pm 10]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

$\omega_e = [317]$ cm^{-1} $\omega_e x_e = [0.69]$ cm^{-1} $\sigma = 1$

$B_e = [0.065]$ cm^{-1} $\alpha_e = [0.00018]$ cm^{-1} $r = [2.47]$ Å

Heat of Formation

The heat of formation, ΔHf°_{298}(ZrBr, g) = 72 kcal/mol, is derived from the estimated bond dissociation energy, D°_{298}(Zr-Br) = 103.5 ± 10 kcal/mol. The value of D°_{298}(Zr-Br) is calculated from the relation D°_{298}(Zr-Br)/D°_{298}(Ti-Br) = D°_{298}(Zr-Br_4)/D°_{298}(Ti-Br_4) where the average bond dissociation energies, D°_{298}(Zr-Br_4) = 102.2 kcal/mol, D°_{298}(Ti-Br_4) = 87.9 kcal/mol and D°_{298}(Ti-Cl) = 89.0 kcal/mol, all calculated from JANAF ΔHf°_{298} for $ZrBr_4$(g), $TiBr_4$(g), TiCl(g), Zr(g), Ti(g) and Br(g).

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $ZrBr_4$(g), which was estimated as 2.47 Å by Godnev, Aleksandrovskaia and Rigina, Optics and Spectroscopy, 7, 172 (1959). The estimated bond distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 416 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4\ (D^\circ_0 + 0.5\ \omega_e) = 0.0021$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is 42.1488×10^{-39} g cm^2.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952. The electronic levels and quantum weights are estimated to be the same as those of ZrF(g).

Bromine (Br_2)

(Reference State) Mol. Wt. = 159.832

T, °K.	cal. mole⁻¹deg.⁻¹ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole⁻¹ $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-5.859	.000	.000	.000
100	10.419	12.870	64.780	-5.191	.000	.000	.000
200	12.851	20.898	40.998	-4.020	.000	.000	.000
298	18.090	36.384	36.384	.000	.000	.000	.000
300	18.077	36.496	36.384	.033	.000	.000	.000
400	8.775	61.203	40.520	8.273	.000	.000	.000
500	8.857	63.172	44.860	9.156	.000	.000	.000
600	8.908	64.791	48.051	10.044	.000	.000	.000
700	8.944	66.167	50.543	10.937	.000	.000	.000
800	8.970	67.363	52.573	11.833	.000	.000	.000
900	8.992	68.421	54.276	12.731	.000	.000	.000
1000	9.011	69.370	55.739	13.631	.000	.000	.000
1100	9.027	70.229	57.018	14.533	.000	.000	.000
1200	9.042	71.015	58.152	15.436	.000	.000	.000
1300	9.056	71.740	59.169	16.341	.000	.000	.000
1400	9.069	72.411	60.092	17.247	.000	.000	.000
1500	9.082	73.037	60.934	18.155	.000	.000	.000
1600	9.094	73.624	61.709	19.064	.000	.000	.000
1700	9.106	74.176	62.426	19.974	.000	.000	.000
1800	9.118	74.696	63.094	20.885	.000	.000	.000
1900	9.128	75.190	63.717	21.797	.000	.000	.000
2000	9.141	75.658	64.303	22.711	.000	.000	.000
2100	9.152	76.104	64.854	23.625	.000	.000	.000
2200	9.163	76.530	65.375	24.541	.000	.000	.000
2300	9.174	76.938	65.869	25.458	.000	.000	.000
2400	9.185	77.329	66.339	26.376	.000	.000	.000
2500	9.196	77.704	66.786	27.295	.000	.000	.000
2600	9.206	78.065	67.213	28.215	.000	.000	.000
2700	9.217	78.412	67.621	29.136	.000	.000	.000
2800	9.228	78.748	68.013	30.059	.000	.000	.000
2900	9.238	79.072	68.388	30.982	.000	.000	.000
3000	9.249	79.385	68.750	31.906	.000	.000	.000
3100	9.260	79.689	69.098	32.832	.000	.000	.000
3200	9.270	79.983	69.433	33.758	.000	.000	.000
3300	9.281	80.268	69.757	34.686	.000	.000	.000
3400	9.291	80.545	70.071	35.614	.000	.000	.000
3500	9.302	80.815	70.374	36.544	.000	.000	.000
3600	9.312	81.077	70.667	37.475	.000	.000	.000
3700	9.323	81.332	70.952	38.406	.000	.000	.000
3800	9.333	81.581	71.229	39.339	.000	.000	.000
3900	9.344	81.824	71.497	40.273	.000	.000	.000
4000	9.354	82.060	71.758	41.208	.000	.000	.000
4100	9.365	82.291	72.012	42.144	.000	.000	.000
4200	9.375	82.517	72.260	43.081	.000	.000	.000
4300	9.386	82.738	72.501	44.019	.000	.000	.000
4400	9.396	82.954	72.736	44.958	.000	.000	.000
4500	9.406	83.165	72.965	45.898	.000	.000	.000
4600	9.417	83.372	73.189	46.839	.000	.000	.000
4700	9.427	83.575	73.408	47.781	.000	.000	.000
4800	9.438	83.773	73.622	48.725	.000	.000	.000
4900	9.448	83.968	73.831	49.669	.000	.000	.000
5000	9.458	84.159	74.036	50.614	.000	.000	.000
5100	9.469	84.346	74.236	51.561	.000	.000	.000
5200	9.479	84.530	74.432	52.508	.000	.000	.000
5300	9.490	84.711	74.625	53.456	.000	.000	.000
5400	9.500	84.888	74.813	54.406	.000	.000	.000
5500	9.510	85.063	74.998	55.356	.000	.000	.000
5600	9.521	85.234	75.179	56.308	.000	.000	.000
5700	9.531	85.403	75.357	57.261	.000	.000	.000
5800	9.542	85.569	75.532	58.214	.000	.000	.000
5900	9.552	85.732	75.703	59.169	.000	.000	.000
6000	9.562	85.892	75.872	60.125	.000	.000	.000

September 30, 1961

BROMINE (Br_2) **(REFERENCE STATE)** **MOL. WT. = 159.832**

0°K to 265.90°K	Crystal
265.90°K to 332.62°K	Liquid
332.62°K to 6000°K	Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal and Liquid.

Low temperature thermal data have been adopted from the work of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. 80, 4129 (1958)]. References to older work are given by Hildenbrand, et al., and are not given any weight here.

Heat of Melting and Melting Point.

Hildenbrand, et al., (loc. cit.) report T_m = 265.90°K and ΔH_m = 2.527 kcal. mole^{-1}.

Heat of Sublimation, Ideal Gas Functions.

See ideal gas tables for details.

Bromine (Br_2)
(Liquid) Mol. Wt. = 159.832

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
0							
100							
200							
298	18,090	36,384	36,384	,000	,000	,000	,000
300	18,077	36,496	36,384	,033	,000	,000	,000
400	18,000	41,676	37,091	1,834	-6,439	1,372	-,749
500	18,000	45,692	38,425	3,634	-5,522	3,218	-1,406
600	18,000	48,974	39,918	5,434	-4,610	4,880	-1,777
700	18,000	51,749	41,415	7,234	-3,703	6,390	-1,995
800	18,000	54,153	42,860	9,034	-2,799	7,769	-2,122
900	18,000	56,273	44,235	10,834	-1,897	9,036	-2,194
1000	18,000	58,169	45,535	12,634	-,997	10,204	-2,230

September 30, 1961

BROMINE (Br_2) (LIQUID) MOL. WT. = 159.832

$\Delta H_{f\ 298}^\circ = 0$

$T_m = 265.90°K.$

$\Delta H_m = 2.527$ kcal. mole^{-1}

$T_b = 332.62°K.$

$\Delta H_v = 7.064$ kcal. mole^{-1}

__Heat of Formation.__

The heat of formation at 298.15°K is zero by definition.

__Heat Capacity.__

The liquid heat capacity data of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. __80__, 4129 (1958)] were extrapolated to a constant value of 18.0 cal. mole^{-1} deg.$^{-1}$

__Entropy.__

The entropy is that given by Hildenbrand, et al., (loc. cit.) for liquid bromine at 298.15°K.

__Vaporization.__

See ideal gas tables for details.

Bromine, Diatomic (Br_2)
(Ideal Gas) Mol. Wt. = 159.832

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	,000	,000	INFINITE	-2,324	10,922	10,922	INFINITE
100	7,385	49,841	66,037	-1,620	10,958	7,261	-15,869
200	8,268	55,270	59,426	-,831	10,576	3,701	-4,045
298	8,616	58,647	58,647	,000	7,387	,749	-,549
300	8,620	58,700	58,647	,016	7,370	,709	-,516
400	8,775	61,204	58,987	,887	.000	,000	-,000
500	8,857	63,171	59,634	1,769	.000	,000	,000
600	8,908	64,791	60,363	2,657	.000	.000	,000
700	8,944	66,167	61,096	3,550	.000	.000	,000
800	8,970	67,363	61,806	4,445	.000	.000	,000
900	8,992	68,421	62,484	5,344	.000	.000	,000
1000	9,011	69,369	63,126	6,244	.000	.000	,000
1100	9,027	70,229	63,733	7,146	.000	.000	,000
1200	9,042	71,015	64,307	8,049	.000	.000	,000
1300	9,056	71,739	64,852	8,954	.000	.000	,000
1400	9,069	72,411	65,368	9,860	.000	.000	,000
1500	9,082	73,037	65,859	10,768	.000	.000	,000
1600	9,094	73,624	66,326	11,677	,000	.000	,000
1700	9,106	74,175	66,771	12,587	,000	.000	,000
1800	9,118	74,696	67,197	13,498	,000	.000	,000
1900	9,129	75,190	67,605	14,410	,000	.000	,000
2000	9,141	75,658	67,996	15,324	,000	.000	,000
2100	9,152	76,104	68,372	16,238	,000	.000	,000
2200	9,163	76,530	68,733	17,154	,000	.000	,000
2300	9,174	76,938	69,081	18,071	,000	.000	,000
2400	9,185	77,329	69,416	18,989	,000	.000	,000
2500	9,196	77,704	69,740	19,908	,000	.000	,000
2600	9,206	78,065	70,054	20,828	,000	.000	,000
2700	9,217	78,412	70,357	21,749	,000	.000	,000
2800	9,228	78,748	70,651	22,672	,000	.000	,000
2900	9,238	79,072	70,935	23,595	,000	.000	,000
3000	9,249	79,385	71,212	24,519	,000	.000	,000
3100	9,260	79,688	71,480	25,445	,000	.000	,000
3200	9,270	79,983	71,742	26,371	,000	.000	,000
3300	9,281	80,268	71,996	27,299	,000	.000	,000
3400	9,291	80,545	72,243	28,227	,000	.000	,000
3500	9,302	80,815	72,484	29,157	,000	.000	,000
3600	9,312	81,077	72,719	30,088	,000	.000	,000
3700	9,323	81,332	72,949	31,019	,000	.000	,000
3800	9,333	81,581	73,172	31,952	,000	.000	,000
3900	9,344	81,823	73,391	32,886	,000	.000	,000
4000	9,354	82,060	73,605	33,821	,000	.000	,000
4100	9,365	82,291	73,814	34,757	,000	.000	,000
4200	9,375	82,517	74,019	35,694	,000	.000	,000
4300	9,386	82,738	74,219	36,632	,000	.000	,000
4400	9,396	82,954	74,415	37,571	,000	.000	,000
4500	9,406	83,165	74,607	38,511	,000	.000	,000
4600	9,417	83,372	74,795	39,452	,000	.000	,000
4700	9,427	83,574	74,980	40,394	,000	.000	,000
4800	9,438	83,773	75,161	41,338	,000	.000	,000
4900	9,448	83,968	75,339	42,282	,000	.000	,000
5000	9,458	84,159	75,513	43,227	,000	.000	,000
5100	9,469	84,346	75,685	44,174	.000	.000	,000
5200	9,479	84,530	75,853	45,121	.000	.000	,000
5300	9,490	84,711	76,018	46,070	.000	.000	,000
5400	9,500	84,888	76,181	47,019	.000	.000	,000
5500	9,510	85,063	76,341	47,970	.000	.000	,000
5600	9,521	85,234	76,498	48,921	.000	.000	,000
5700	9,531	85,403	76,653	49,874	.000	.000	,000
5800	9,542	85,569	76,805	50,827	.000	.000	,000
5900	9,552	85,732	76,955	51,782	.000	.000	,000
6000	9,562	85,892	77,103	52,738	.000	.000	,000

December 31, 1961

BROMINE, DIATOMIC (Br_2) (IDEAL GAS) MOL. WT. = 159.832

$\Delta H^\circ_{f0} = 10.922 \pm .030$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298} = 7.387$ kcal. mole^{-1}

Ground State = $^1\Sigma$

$S^\circ_{298} = 58.647$ cal. deg.$^{-1}$ mole^{-1}

$\omega_e = 323.22$ cm.$^{-1}$

$\omega_e x_e = 1.070$ cm.$^{-1}$

$B_e = 0.08092$ cm.$^{-1}$

$\alpha_e = 0.000275$ cm.$^{-1}$

$\sigma = 2$

Thermodynamic Functions.

Spectroscopic data listed by G. Herzberg [Spectra of Diatomic Molecules, D. Van Nostrand Company, New York, 1950] have been adjusted to the isotopic mixture (50.52% Br^{79}, 49.48% Br^{81}). The calculated functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 147 (1955)] who used the same spectroscopic data.

Heat of Formation.

The heat of vaporization at 298.15°K was reported by D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. 80, 4129 (1958)] as 7.387 ± .027 kcal. mole^{-1}, which calculates to 10.922 kcal. mole^{-1} at 0°K. Vapor pressure data from the literature and the above adopted thermodynamic functions for liquid and gas were used to calculate ΔH°_0 as follows:

	ΔH°_0, kcal. mole^{-1}
Liquid range	
Fischer and Bingle[1] (298° to 389°K)	10.905 ± .019
Ramsay and Young[2] (265° to 329°K)	10.924 ± .008
Scheffer and Voogd[3] (270° to 362°K)	10.906 ± .018
Solid range	
Frey and Gregory[4] (177° to 195°K)	10.941 ± .029
Henglein, Rosenberg, and Muchlinski[5] (177° to 241°K)	10.912 ± .034
Ramsay and Young[2] (256° to 262°K)	10.986 ± .014
Scheffer and Voogd[3] (253° to 264°K)	10.961 ± .014

For the liquid range, the data of Fischer and Bingle as well as that of Scheffer and Voogd show a decided decrease with increasing temperature, starting at about 10.94 and decreasing to 10.87 kcal. mole^{-1}. The data of Ramsay and Young show only a small trend with temperature and are in good agreement with the calorimetric value. For the solid range, the data are too scattered to be conclusive. The calorimetric value, as supported by Ramsay and Young, is adopted as the heat of formation of the ideal gas.

References to Vapor Pressure Data

(1) J. Fischer and J. Bingle, J. Am. Chem. Soc. 77, 6511 (1955).
(2) J. Ramsay and J. Young, J. Chem. Soc. 49, 453 (1886).
(3) F. E. C. Scheffer and M. Voogd, Rec. trav. chim. 45, 214 (1926).
(4) M. B. Frey and N. W. Gregory, J. Am. Chem. Soc. 82, 1068 (1960).
(5) F. A. Henglein, G. von Rosenberg, and A. Muchlinski, Z. Physik. 11, 1 (1922).

Iron Dibromide ($FeBr_2$)
(Crystal) GFW = 215.665

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	19.176	33.620	33.620	.000	-59.500	-56.729	41.584
300	19.186	33.739	33.620	.035	-59.509	-56.712	41.314
400	19.718	39.331	34.379	1.981	-66.429	-54.335	29.687
500	20.250	43.788	35.830	3.979	-65.989	-51.363	22.451
600	20.782	47.527	37.476	6.031	-65.555	-48.479	17.658
700	21.314	50.924	39.159	8.235	-65.033	-45.674	14.260
800	21.846	53.805	40.813	10.393	-64.639	-42.937	11.730
900	22.378	56.409	42.404	12.605	-64.301	-40.244	9.773
1000	22.910	58.794	43.925	14.869	-64.094	-37.584	8.214
1100	23.442	61.003	45.379	17.187	-64.053	-34.931	6.940
1200	23.974	63.065	46.767	19.557	-63.749	-32.301	5.883
1300	24.506	65.005	48.096	21.981	-63.053	-29.708	4.994
1400	25.038	66.841	49.370	24.459	-62.320	-27.171	4.242
1500	25.570	68.586	50.594	26.989	-61.551	-24.687	3.597

Sept. 30, 1966

IRON DIBROMIDE ($FeBr_2$) (CRYSTAL) GFW = 215.665

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = 33.62 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -59.5 ± 0.5 kcal/mol

Tt = 650°K

ΔHt° = 0.1 kcal/mol

Tm = 964°K

ΔHm° = [12 ± 3] kcal/mol

$\Delta Hs^\circ_{298.15}$ (to monomer) = [49.6] kcal/mol

$\Delta Hs^\circ_{298.15}$ (to dimer) = [58.5] kcal/mol

Heat of Formation.

The heats of solution of Fe(c), Br_2(l) and $FeBr_2$(c) in Br_2-KBr aqueous solution were measured by use of ice calorimeter by (1) W. Hieber and A. Woerner, Z. Elektrochem. 40, 287 (1934). From the results obtained the heat of formation for $FeBr_2$(c) was reported to be -59.87 kcal/mol.

The heats of solution of $FeBr_2$(c) in water were determined by (2) J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952) and (3) P. Paoletti, Trans. Faraday Soc. 61, 219 (1965), to be -20.1 ± 0.4 and -20.06 ± 0.06 kcal/mol, respectively. Using $\Delta Hf^\circ_{298.15}$ = -29.05 and -21.3 kcal/mol for Br^-(aq) and Fe^{++}(aq), the corresponding heats of formation for $FeBr_2$(c) were calculated as -59.3 and -59.34 kcal/mol. The value of $\Delta Hf^\circ_{298.15}$ (Br^-, aq) was taken from "Selected Values of Chemical Thermodynamic Properties," Part I, Technical Note 270-1, by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, National Bureau of Standards, 1965. The value of $\Delta Hf^\circ_{298.15}$ (Fe^{++}, aq) was derived from heats of solution and formation for $FeCl_2$(c) using $\Delta Hf^\circ_{298.15}$(Cl^-,aq) = -39.952 kcal/mol from the same source as $\Delta Hf^\circ_{298.15}$ (Br^-, aq)

The value of $\Delta Hf^\circ_{298.15}$ ($FeBr_2$,c) adopted is -59.5 ± 0.5 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 323-633°K, were measured by N. W. Gregory and H. E. O'Neal, J. Am. Chem. Soc. 81, 2649 (1959). Those for temperatures below 323°K and above 633°K were estimated by linear extrapolation. Low temperature heat capacities, 12-110°K, were reported by G. Miljutin and N. Nachimowitsch, Phys. Trans. Ukrain. Acad. Sci. 9, 71 (1940). However, these data are inadequate for obtaining an accurate entropy at 298°K. The adopted $S^\circ_{298.15}$ value was reported by N. W. Gregory and R. O. MacLaren, J. Phys. Chem. 59, 110 (1955). It was obtained from E. F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, by private communication. A magnetic transition at 11°K was reported by H. Bizette, C. Terrier, and B. Tsai, Compt. rend. 245, 507 (1957).

Transition Data.

Tt and ΔHt° were taken from N. W. Gregory and H. E. O'Neal, loc. cit.

Melting Data.

Tm adopted was reported by R. O. MacLaren and N. W. Gregory, J. Phys. Chem. 59, 184 (1955). The value was calculated from the vapor pressure equations and is slightly above the previously reported value, 684°C (957°K), by A. Ferrari, A. Celeri and F. Giorgi, Atti accad. Nazl. Lincei 9, 782,1134 (1929). However, it agrees well with 962 ± 2 °K obtained by the differential thermocouple cooling curve analysis by the same authors. The ΔHm° value was estimated from the vapor pressure data in order to obtain good agreement between the second and third law heats of vaporization. See the $FeBr_2$(g) table for details.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ (to monomer) is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for $FeBr_2$(g) and $FeBr_2$(c). $\Delta Hs^\circ_{298.15}$(to dimer) is calculated as the difference between those for Fe_2Br_4(g) and 2 $FeBr_2$(c).

Iron Dibromide ($FeBr_2$)

(Liquid) GFW = 215.665

T, °K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0							
100							
200							
298	25.500	40.483	40.483	.000	-50.431	-49.706	36.436
300	25.500	40.641	40.483	.047	-50.428	-49.702	36.208
400	25.500	47.977	41.484	2.597	-56.744	-48.108	26.285
500	25.500	53.667	43.372	5.147	-55.752	-46.065	20.135
600	25.500	58.316	45.487	7.697	-54.820	-44.217	16.106
700	25.500	62.247	47.608	10.247	-53.952	-42.519	13.275
800	25.500	65.652	49.655	12.797	-53.166	-40.942	11.185
900	25.500	68.655	51.603	15.347	-52.490	-39.454	9.581
1000	25.500	71.342	53.445	17.897	-51.997	-38.035	8.313
1100	25.500	73.772	55.184	20.447	-51.724	-36.647	7.281
1200	25.500	75.991	56.827	22.997	-51.240	-35.304	6.430
1300	25.500	78.032	58.381	25.547	-50.418	-34.008	5.717
1400	25.500	79.922	59.853	28.097	-49.613	-32.776	5.117
1500	25.500	81.681	61.250	30.647	-48.824	-31.602	4.604
1600	25.500	83.327	62.579	33.197	-48.052	-30.479	4.163
1700	25.500	84.873	63.845	35.747	-47.587	-29.399	3.779
1800	25.500	86.331	65.054	38.297	-46.939	-28.348	3.442
1900	25.500	87.709	66.211	40.847	-49.978	-27.146	3.122
2000	25.500	89.017	67.319	43.397	-49.398	-25.962	2.837

Sept. 30, 1966

IRON DIBROMIDE ($FeBr_2$) (LIQUID) GFW = 215.665

$S°_{298.15}$ = [40.483] gibbs/mol $\Delta Hf°_{298.15}$ =[-50.431] kcal/mol

Tm = 964°K $\Delta H\dot{m}$ = [12 + 3] kcal/mol

Tb = [1207] °K $\Delta H\dot{v}$ =[29.4] kcal/mol

Heat of Formation.

The value of $\Delta Hf°_{298.15}$ (l) was obtained from $\Delta Hf°_{298.15}$ (c) by adding ΔHm° and the difference between $H°_{Tm}-H°_{298.15}$ for $FeBr_2$(c) and $FeBr_2$(l).

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K and was estimated on the basis of 8.5 gibbs/g-atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $FeBr_2$(c) table for details.

Vaporization Data.

Tb is calculated as the temperature at which the total pressure of $FeBr_2$(g) and Fe_2Br_4(g) over $FeBr_2$(l) equals one atmosphere. Based on the vapor composition and the values of $\Delta H\dot{v}$ for both the monomer and dimer at Tb, the heat of vaporization is derived.

Iron Dibromide ($FeBr_2$)
(Ideal Gas) GFW = 215.665

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.829	-6.795	-6.795	INFINITE
100	12.721	65.559	93.157	-2.760	-6.497	-11.619	25.394
200	14.081	74.890	81.919	-1.406	-6.736	-16.674	18.220
298	14.496	80.604	80.604	.000	-9.900	-21.138	15.494
300	14.501	80.693	80.604	.027	-9.917	-21.206	15.449
400	14.669	84.891	81.175	1.486	-17.324	-23.454	12.814
500	14.752	88.174	82.259	2.958	-17.410	-24.977	10.917
600	14.802	90.869	83.476	4.436	-17.550	-26.479	9.645
700	14.842	93.153	84.699	5.918	-17.750	-27.952	8.727
800	14.886	95.138	85.883	7.404	-18.028	-29.393	8.030
900	14.939	96.894	87.010	8.895	-18.411	-30.790	7.477
1000	15.004	98.472	88.079	10.393	-18.970	-32.138	7.024
1100	15.080	99.905	89.090	11.897	-19.743	-33.413	6.639
1200	15.164	101.221	90.047	13.409	-20.297	-34.637	6.308
1300	15.253	102.438	90.954	14.930	-20.504	-35.822	6.022
1400	15.344	103.572	91.815	16.459	-20.720	-36.993	5.775
1500	15.435	104.633	92.635	17.998	-20.942	-38.148	5.558
1600	15.523	105.632	93.416	19.546	-21.172	-39.287	5.366
1700	15.606	106.576	94.163	21.103	-21.700	-40.407	5.195
1800	15.682	107.470	94.877	22.667	-22.038	-41.498	5.038
1900	15.751	108.320	95.563	24.239	-26.055	-42.384	4.875
2000	15.812	109.129	96.221	25.817	-26.447	-43.235	4.724
2100	15.865	109.902	96.854	27.401	-26.837	-44.063	4.586
2200	15.910	110.641	97.464	28.990	-27.228	-44.874	4.458
2300	15.948	111.349	98.053	30.583	-27.620	-45.668	4.339
2400	15.979	112.029	98.621	32.179	-28.014	-46.446	4.229
2500	16.002	112.682	99.170	33.778	-28.410	-47.205	4.127
2600	16.020	113.310	99.702	35.380	-28.808	-47.950	4.031
2700	16.032	113.914	100.217	36.982	-29.211	-48.678	3.940
2800	16.039	114.498	100.717	38.586	-29.618	-49.392	3.855
2900	16.042	115.061	101.202	40.190	-30.029	-50.091	3.775
3000	16.041	115.604	101.673	41.794	-30.445	-50.773	3.699
3100	16.036	116.130	102.131	43.398	-30.867	-51.442	3.627
3200	16.029	116.639	102.576	45.001	-114.719	-50.655	3.460
3300	16.019	117.132	103.010	46.604	-114.689	-48.656	3.222
3400	16.006	117.610	103.433	48.205	-114.669	-46.655	2.999
3500	15.992	118.074	103.844	49.805	-114.659	-44.656	2.788
3600	15.977	118.525	104.246	51.403	-114.661	-42.657	2.590
3700	15.960	118.962	104.638	53.000	-114.671	-40.656	2.401
3800	15.942	119.387	105.020	54.595	-114.694	-38.656	2.223
3900	15.924	119.801	105.394	56.189	-114.727	-36.649	2.054
4000	15.905	120.204	105.759	57.780	-114.773	-34.653	1.893
4100	15.885	120.597	106.116	59.370	-114.829	-32.649	1.740
4200	15.866	120.979	106.466	60.957	-114.899	-30.643	1.595
4300	15.846	121.352	106.808	62.543	-114.980	-28.632	1.455
4400	15.826	121.716	107.142	64.126	-115.074	-26.625	1.322
4500	15.806	122.072	107.470	65.708	-115.180	-24.618	1.196
4600	15.786	122.419	107.791	67.287	-115.299	-22.599	1.074
4700	15.766	122.758	108.106	68.865	-115.431	-20.580	.957
4800	15.747	123.090	108.415	70.441	-115.576	-18.564	.845
4900	15.727	123.415	108.718	72.014	-115.735	-16.544	.738
5000	15.709	123.732	109.015	73.586	-115.906	-14.516	.634
5100	15.690	124.043	109.306	75.156	-116.091	-12.490	.535
5200	15.672	124.347	109.593	76.724	-116.289	-10.453	.439
5300	15.654	124.646	109.874	78.290	-116.500	-8.417	.347
5400	15.636	124.938	110.150	79.855	-116.725	-6.376	.258
5500	15.619	125.225	110.422	81.418	-116.962	-4.328	.172
5600	15.603	125.506	110.689	82.979	-117.214	-2.280	.089
5700	15.586	125.782	110.951	84.538	-117.479	-.224	.009
5800	15.571	126.053	111.209	86.096	-117.756	1.840	-.069
5900	15.555	126.319	111.463	87.652	-118.047	3.900	-.144
6000	15.540	126.581	111.713	89.207	-118.350	5.964	-.217

Sept. 30, 1966

IRON DIBROMIDE ($FeBr_2$) (IDEAL GAS) GFW = 215.665

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [80.6] gibbs/mol

ΔHf°_0 = [-6.8 ± 0.5] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-9.9 ± 0.5] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[10]
[4450]	[10]
[6900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[150] (1)
[35] (2)
[300] (1)

Bond Distance: Fe-Br = [2.24] Å

Bond Angle: Br-Fe-Br = [180]°

σ = [2]

Rotational Constant: B_o = [0.02102] cm^{-1}

Heat of Formation.

The vapor pressures of $FeBr_2(c)$ and $FeBr_2(l)$ have been measured in the temperature range from 623.15 to 962.15°K by several investigators. Using the reported data the corresponding enthalpy changes (ΔHr°) for the reactions (A) $FeBr_2(c) = FeBr_2(g)$ and (B) $FeBr_2(l) = FeBr_2(g)$ were evaluated by both the second and third law methods. The results obtained are presented in the following table. The values of $\Delta Hf^\circ_{298.15}$ for $FeBr_2(g)$ are calculated based on the third law values for $\Delta Hr^\circ_{298.15}$. The value of $\Delta Hf^\circ_{298.15}$ for $FeBr_2(g)$ adopted is -9.9 ± 0.5 kcal/mol.

Reference	Reaction	Temperature, °K	Method	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	$\Delta Hr^\circ_{298.15}$, kcal/mol Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$ kcal/mol
1	(A)	673.15- 962.15	Transpiration	50.04	49.56	- 0.75	- 9.94
1	(A)	623.15- 718.15	Effusion	49.21	50.14	+ 1.37	- 9.36
1	(A)	873.15- 962.15	Diaphragm	59.20	49.95	-10.09	- 9.55
2	(A)	670.0 - 740.0	Torsion - Effusion	49.11	49.59	+ 0.71	- 9.91
1	(B)	962.15-1182.15	Diaphragm	39.77	40.84	+ 0.93	- 9.59

1. R. O. MacLaren and N. W. Gregory, J. Phys. Chem. 59, 184 (1955).
2. R. J. Sime and N. W. Gregory, J. Phys. Chem. 64, 86 (1960).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The electronic levels and quantum weights were estimated by comparison with those for $FeCl_2(g)$ reported by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The bond distance was estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The vibrational frequencies were estimated in order to obtain good agreement between the second and third law heats of sublimation and vaporization. The moment of inertia is 1.33148 x 10^{-37} g cm^2.

Mercury Dibromide ($HgBr_2$)

(Crystal) Mol. Wt. = 360.442

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	18.000	40.706	40.706	.000	-40.500	-36.371	26.659
300	18.013	40.817	40.706	.033	-40.512	-36.345	26.476
400	18.714	46.095	41.421	1.870	-47.576	-33.487	18.296
500	19.414	50.347	42.794	3.776	-47.205	-30.007	13.116
600	20.114	53.948	44.361	5.752	-46.766	-26.609	9.692
700	20.814	57.101	45.960	7.799	-60.287	-21.717	6.780
800	21.514	59.926	47.532	9.915	-59.564	-16.256	4.441
900	22.214	62.501	49.054	12.102	-58.771	-10.888	2.644
1000	22.914	64.877	50.519	14.358	-57.912	-5.613	1.227
1100	23.614	67.094	51.926	16.684	-56.985	-.428	.085
1200	24.314	69.179	53.278	19.081	-55.988	4.670	-.850
1300	25.014	71.153	54.578	21.547	-54.924	9.683	-1.628
1400	25.714	73.032	55.829	24.084	-53.789	14.611	-2.281
1500	26.414	74.830	57.036	26.690	-52.588	19.454	-2.834

March 31, 1962

Br_2Hg

MERCURY DIBROMIDE ($HgBr_2$) (Crystal)

Mol. Wt. = 360.442

$\Delta H_f^\circ{}_{298.15} = -40.500 \pm 0.5$ kcal. mole^{-1}

$S^\circ_{298.15} = [40.706] \pm 1.5$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 514$°K

$\Delta H_m = 4.280 \pm 0.08$ kcal. mole^{-1}

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952).

Heat Capacity and Entropy. C_p was assumed to be a linear function of temperature and was fitted to the data of M. Guinchant, Comp. Rend. 145, 320 (1907) and G. J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959). The entropy was estimated by adjusting its value until the melting, sublimation and vaporization data were in agreement.

Melting. T_m was taken from National Bureau of Standards (U.S.) Circular 500 (loc. cit.). ΔH_m was given by G. J. Janz and J. Goodkin (loc. cit.).

Br_2Hg

Mercury Dibromide ($HgBr_2$)
(Liquid) Mol. Wt. = 360.442

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	18,000	46,797	46,797	,000	-37,158	-34,845	25,541
300	18,013	46,908	46,797	,033	-37,170	-34,830	25,372
400	24,400	53,091	47,579	2,205	-43,899	-32,608	17,816
500	24,400	58,536	49,246	4,645	-42,994	-29,891	13,065
600	24,400	62,984	51,176	7,085	-42,091	-27,356	9,964
700	24,400	66,745	53,139	9,525	-55,219	-23,400	7,306
800	24,400	70,004	55,048	11,965	-54,172	-18,926	5,170
900	24,400	72,878	56,872	14,405	-53,126	-14,582	3,541
1000	24,400	75,448	58,604	16,845	-52,083	-10,356	2,263
1100	24,400	77,774	60,242	19,285	-51,042	-6,234	1,238
1200	24,400	79,897	61,793	21,725	-50,002	-2,206	,402
1300	24,400	81,850	63,262	24,165	-48,964	1,736	-,292
1400	24,400	83,658	64,655	26,605	-47,926	5,597	-,874
1500	24,400	85,342	65,978	29,045	-46,891	9,383	-1,367

March 31, 1962

MERCURY DIBROMIDE ($HgBr_2$) (Liquid)

Mol. Wt. = 360.442

ΔH_f° 298.15 = -37.158 ± 0.58 kcal. mole^{-1}

$S^\circ_{298.15}$ = [46.797] ± 1.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 514°K

ΔH_m = 4.280 ± 0.08 kcal. mole^{-1}

T_b = 592°K

ΔH_v = 14.148 ± 0.25 kcal. mole^{-1}

Heat of Formation. Calculated from $\Delta H_f^\circ(c)$.

Heat Capacity and Entropy. C_p obtained from the data of G. J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959) in the range 507-544°K, it was assumed constant above and below this value. A glass type transition was assumed at 343°K below which the heat capacity was equal to that of the crystal. The entropy was obtained from S°(c), the entropy of fusion and the estimated heat capacity.

Melting and Vaporization. T_m and T_b were taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952). ΔH_m was given by G. J. Janz and J. Goodkin (loc. cit.) and ΔH_v was obtained from the data of E. B. R. Prideaux, J. Chem. Soc. (London) 97, 2032 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Mercury Dibromide ($HgBr_2$)

(Ideal Gas) Mol. Wt. = 360.442

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F°-H°_{298})/T$	$H°-H°_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.742	-16.074	-16.074	INFINITE
100	12.240	61.744	88.909	-2.716	-16.124	-20.122	43.975
200	13.896	70.850	77.816	-1.393	-16.589	-23.950	26.170
298	14.407	76.511	76.511	.000	-20.424	-26.970	19.769
300	14.412	76.600	76.511	.027	-20.442	-27.010	19.676
400	14.618	80.779	77.080	1.480	-27.890	-27.675	15.120
500	14.718	84.052	78.159	2.947	-27.958	-27.613	12.069
600	14.774	86.741	79.372	4.422	-28.020	-27.539	10.031
700	14.808	89.021	80.591	5.901	-42.109	-25.883	8.081
800	14.830	91.000	81.772	7.383	-42.020	-23.571	6.439
900	14.846	92.748	82.896	8.867	-41.930	-21.270	5.165
1000	14.857	94.313	83.961	10.352	-41.842	-18.979	4.148
1100	14.865	95.729	84.967	11.838	-41.755	-16.697	3.317
1200	14.871	97.023	85.919	13.325	-41.668	-14.423	2.627
1300	14.876	98.213	86.819	14.812	-41.583	-12.155	2.043
1400	14.880	99.316	87.673	16.300	-41.497	-9.895	1.545
1500	14.883	100.343	88.484	17.788	-41.414	-7.641	1.113
1600	14.886	101.303	89.255	19.277	-41.331	-5.393	.737
1700	14.888	102.206	89.991	20.765	-41.250	-3.147	.405
1800	14.890	103.057	90.693	22.254	-41.169	-.912	.111
1900	14.891	103.862	91.366	23.743	-41.088	1.326	-.153
2000	14.893	104.626	92.010	25.233	-41.009	3.555	-.388
2100	14.894	105.353	92.628	26.722	-40.931	5.780	-.602
2200	14.895	106.045	93.222	28.211	-40.855	8.002	-.795
2300	14.895	106.708	93.794	29.701	-40.779	10.222	-.971
2400	14.896	107.341	94.345	31.190	-40.704	12.441	-1.133
2500	14.897	107.950	94.878	32.680	-40.630	14.651	-1.281
2600	14.897	108.534	95.392	34.170	-40.557	16.862	-1.417
2700	14.898	109.096	95.889	35.660	-40.485	19.068	-1.543
2800	14.898	109.638	96.370	37.149	-40.416	21.272	-1.660
2900	14.899	110.161	96.837	38.639	-40.345	23.476	-1.769
3000	14.899	110.666	97.289	40.129	-40.276	25.674	-1.870
3100	14.900	111.154	97.729	41.619	-40.209	27.872	-1.965
3200	14.900	111.627	98.156	43.109	-40.142	30.068	-2.053
3300	14.900	112.086	98.571	44.599	-40.077	32.259	-2.136
3400	14.900	112.531	98.975	46.089	-40.011	34.450	-2.214
3500	14.901	112.963	99.369	47.579	-39.948	36.640	-2.288
3600	14.901	113.382	99.752	49.069	-39.886	38.827	-2.357
3700	14.901	113.791	100.126	50.559	-39.824	41.011	-2.422
3800	14.901	114.188	100.491	52.049	-39.764	43.198	-2.484
3900	14.901	114.575	100.847	53.539	-39.705	45.381	-2.543
4000	14.902	114.952	101.195	55.030	-39.646	47.560	-2.598
4100	14.902	115.320	101.535	56.520	-39.589	49.736	-2.651
4200	14.902	115.679	101.868	58.010	-39.533	51.916	-2.701
4300	14.902	116.030	102.193	59.500	-39.478	54.094	-2.749
4400	14.902	116.373	102.511	60.990	-39.424	56.269	-2.795
4500	14.902	116.708	102.823	62.481	-39.370	58.443	-2.838
4600	14.902	117.035	103.128	63.971	-39.319	60.615	-2.880
4700	14.902	117.356	103.426	65.461	-39.269	62.793	-2.920
4800	14.902	117.669	103.721	66.951	-39.221	64.957	-2.957
4900	14.903	117.977	104.009	68.442	-39.172	67.130	-2.994
5000	14.903	118.278	104.291	69.932	-39.125	69.301	-3.029
5100	14.903	118.573	104.568	71.422	-39.081	71.468	-3.062
5200	14.903	118.862	104.841	72.912	-39.038	73.635	-3.095
5300	14.903	119.146	105.108	74.403	-38.995	75.802	-3.126
5400	14.903	119.425	105.370	75.893	-38.955	77.962	-3.155
5500	14.903	119.698	105.628	77.384	-38.915	80.131	-3.184
5600	14.903	119.967	105.882	78.873	-38.880	82.295	-3.212
5700	14.903	120.230	106.131	80.364	-38.844	84.462	-3.238
5800	14.903	120.490	106.377	81.854	-38.811	86.622	-3.264
5900	14.903	120.744	106.618	83.345	-38.780	88.781	-3.288
6000	14.903	120.995	106.856	84.835	-38.751	90.940	-3.312

March 31, 1962

MERCURY DIBROMIDE ($HgBr_2$) (Ideal Gas)

Mol. Wt. = 360.442

ΔH_f° 298.15 = -20.424 ± 2.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = 76.511 cal. deg.$^{-1}$ mole^{-1}

Point Group = $D_{\infty h}$

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
225 (1)
41 (2)
293 (1)

Hg-Br distance = 2.41 Å

Moment of Inertia = 154.12 X 10^{-39} g. cm.^{2} σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952, was combined with the 3rd law heat of sublimation at 298°K from the data of K. Niwa and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser III 2, 183 (1938) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is an average of the values given by H. Braune and S. Knoke, Zeits. phys. Chemie B23, 163 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Farad. Soc. 33, 852, (1937) and P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).

Mercury Monobromide, Dimeric (Hg_2Br_2)

(Crystal) Mol. Wt. = 561.052 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	25.000	52.283	52.283	.000	-48.800	-42.705	31.302
300	25.025	52.438	52.283	.046	-48.811	-42.666	31.081
400	26.200	59.805	53.280	2.610	-55.809	-39.158	21.394
500	27.020	65.744	55.198	5.273	-55.333	-35.049	15.319
600	27.630	70.726	57.382	8.007	-54.785	-31.044	11.307
700	28.090	75.022	59.602	10.794	-82.241	-23.992	7.490
800	28.470	78.799	61.770	13.623	-81.302	-15.734	4.298
900	28.780	82.171	63.853	16.486	-80.329	-7.594	1.844
1000	29.050	85.217	65.840	19.377	-79.332	.433	-.095
1100	29.293	87.997	67.729	22.295	-78.310	8.361	-1.661
1200	29.510	90.556	69.526	25.235	-77.267	16.193	-2.949
1300	29.687	92.924	71.236	28.195	-76.206	23.940	-4.024
1400	29.910	95.132	72.865	31.174	-75.125	31.604	-4.933
1500	30.180	97.205	74.419	34.178	-74.023	39.188	-5.709

March 31, 1962

MERCURY MONOBROMIDE, DIMERIC (Hg_2Br_2) (Crystal)

Mol. Wt. = 561.052

$\Delta H_f^\circ{}_{298.15} = -48.800 \pm 0.2$ kcal. mole^{-1}

$S^\circ_{298.15} = 52.283 \pm 0.75$ cal. deg.$^{-1}$ mole^{-1}

$T_{sub} = 666°K$ (decomp.)

Heat of Formation. The average of the values obtained from the cell measurements of T. W. Dakin and D. T. Ewing, J. Am. Chem. Soc. 62, 2280 (1940) and those of F. Ishikawa and Y. Ueda, J. Chem. Soc. Japan 51, 59 (1930) was adopted.

Heat Capacity and Entropy. The heat capacity was estimated by analogy with mercurous chloride. The entropy of formation was obtained from the free energy and heat of formation data listed under heat of formation.

Sublimation. The vapor pressure over mercurous bromide reaches one atmosphere at 666°K according to G. Jung and W. Ziegler Zeits. f. physik. Chem. A150, 139 (1930). At this point the vapor is dissociated into Hg(g) and $HgBr_2$(g).

Potassium Bromide, Dimeric (K_2Br_2)

(Ideal Gas) GFW = 238.022

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 5.022	- 124.977	- 124.977	INFINITE
100	17.368	69.388	106.954	- 3.757	- 125.208	- 129.158	282.274
200	19.165	82.165	91.681	- 1.903	- 125.765	- 132.905	145.231
298	19.546	89.902	89.902	.000	- 129.200	- 135.939	99.646
300	19.550	90.023	89.903	.036	- 129.223	- 135.980	99.062
400	19.689	95.669	90.672	1.999	- 138.128	- 136.449	74.552
500	19.754	100.071	92.127	3.972	- 138.524	- 135.984	59.438
600	19.790	103.676	93.761	5.949	- 138.887	- 135.440	49.334
700	19.812	106.728	95.401	7.929	- 139.232	- 134.838	42.098
800	19.826	109.375	96.986	9.911	- 139.570	- 134.189	36.659
900	19.835	111.710	98.495	11.894	- 139.909	- 133.494	32.417
1000	19.842	113.801	99.922	13.878	- 140.267	- 132.764	29.016
1100	19.847	115.692	101.271	15.863	- 178.458	- 129.947	25.818
1200	19.851	117.419	102.546	17.848	- 178.370	- 125.539	22.864
1300	19.854	119.008	103.752	19.833	- 178.284	- 121.141	20.366
1400	19.857	120.480	104.895	21.818	- 178.199	- 116.748	18.225
1500	19.859	121.850	105.980	23.804	- 178.115	- 112.362	16.371
1600	19.860	123.131	107.013	25.790	- 178.032	- 107.979	14.749
1700	19.861	124.335	107.996	27.776	- 177.952	- 103.606	13.319
1800	19.863	125.471	108.936	29.762	- 177.873	- 99.238	12.049
1900	19.863	126.545	109.835	31.749	- 177.798	- 94.869	10.912
2000	19.864	127.563	110.696	33.735	- 177.726	- 90.504	9.890
2100	19.865	128.533	111.522	35.721	- 177.658	- 86.146	8.965
2200	19.866	129.457	112.317	37.708	- 177.597	- 81.789	8.125
2300	19.866	130.340	113.081	39.695	- 177.541	- 77.436	7.358
2400	19.867	131.185	113.818	41.681	- 177.493	- 73.083	6.655
2500	19.867	131.996	114.529	43.668	- 177.455	- 68.735	6.009
2600	19.867	132.776	115.216	45.655	- 177.424	- 64.384	5.412
2700	19.868	133.525	115.880	47.641	- 177.407	- 60.040	4.860
2800	19.868	134.248	116.524	49.628	- 177.405	- 55.694	4.347
2900	19.868	134.945	117.147	51.615	- 177.415	- 51.343	3.869
3000	19.868	135.619	117.751	53.602	- 177.440	- 47.000	3.424
3100	19.869	136.270	118.338	55.589	- 177.487	- 42.647	3.007
3200	19.869	136.901	118.909	57.575	- 177.553	- 38.295	2.615
3300	19.869	137.512	119.463	59.562	- 177.642	- 33.946	2.248
3400	19.869	138.106	120.003	61.549	- 177.757	- 29.595	1.902
3500	19.869	138.681	120.528	63.536	- 177.900	- 25.230	1.575
3600	19.869	139.241	121.040	65.523	- 178.076	- 20.864	1.267
3700	19.869	139.786	121.540	67.510	- 178.286	- 16.500	.975
3800	19.870	140.316	122.027	69.497	- 178.538	- 12.125	.697
3900	19.870	140.832	122.502	71.484	- 178.833	- 7.740	.434
4000	19.870	141.335	122.967	73.471	- 179.177	- 3.349	.183
4100	19.870	141.825	123.421	75.458	- 179.576	1.054	- .056
4200	19.870	142.304	123.865	77.445	- 180.036	5.465	- .284
4300	19.870	142.772	124.299	79.432	- 180.559	9.888	- .503
4400	19.870	143.229	124.724	81.419	- 181.157	14.322	- .711
4500	19.870	143.675	125.140	83.406	- 181.832	18.778	- .912
4600	19.870	144.112	125.548	85.393	- 182.592	23.240	- 1.104
4700	19.870	144.539	125.948	87.380	- 183.443	27.728	- 1.289
4800	19.870	144.957	126.339	89.367	- 184.392	32.232	- 1.468
4900	19.870	145.367	126.723	91.354	- 185.445	36.755	- 1.639
5000	19.870	145.769	127.100	93.341	- 186.605	41.295	- 1.805
5100	19.871	146.162	127.470	95.328	- 187.881	45.873	- 1.966
5200	19.871	146.548	127.833	97.315	- 189.275	50.466	- 2.121
5300	19.871	146.926	128.190	99.302	- 190.790	55.093	- 2.272
5400	19.871	147.298	128.541	101.289	- 192.431	59.739	- 2.418
5500	19.871	147.662	128.885	103.276	- 194.198	64.429	- 2.560
5600	19.871	148.020	129.223	105.263	- 196.091	69.148	- 2.699
5700	19.871	148.372	129.556	107.251	- 198.108	73.901	- 2.834
5800	19.871	148.718	129.884	109.238	- 200.250	78.689	- 2.965
5900	19.871	149.057	130.206	111.225	- 202.512	83.526	- 3.094
6000	19.871	149.391	130.523	113.212	- 204.891	88.395	- 3.220

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE, DIMERIC (K_2Br_2) (IDEAL GAS) GFW = 238.022

Point Group [D_{2h}]

$S^\circ_{298.15}$ = [89.9] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -125.0 ± 4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -129.2 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[135] (1)	[80] (1)
[80] (1)	[125] (1)
[130] (1)	[150] (1)

Bond Distances: K-Br = [3.07]Å K-K = [1.94]Å Br-Br = [2.39]Å

Bond Angles: Br-K-Br = [102]° K-Br-K = [78]° σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.473 x 10^{-111}] g^3 cm^6

Heat of Formation.

Vapor densities and vapor pressures of KBr were measured, using a liquid gold isoteniscope, by K. I. Hagemark, M. Blander, and E. B. Luchsinger, J. Phys. Chem. 70, 276 (1966), and K. I. Hagemark, private communication, 3M Company, St. Paul, Minn., Feb. 6, 1967. Based on the equilibrium constants for the reaction 2KBr(g) = K_2Br_2(g) in the temperature range 1267 - 1434°K, the enthalpy change (ΔHr°_{298}) of this reaction is evaluated by the second and third law methods to be -42.80 ± 4.26 and -43.12 kcal/mol, respectively. The heat of formation for K_2Br_2(g) is calculated to be -129.2 ± 4 kcal/mol, using the third law ΔHr°_{298} value and ΔHf°_{298}(KBr,g) = -43.04 kcal/mol. The drift in the third law ΔHr°_{298} values is 0.01 ± 3.2 eu.

Heat Capacity and Entropy.

The molecular structure and bond distances were estimated by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), and are tentatively adopted. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), has calculated vibrational frequencies on the basis of the potential function for an ionic model. These values are adjusted so that the third law ΔHr°_{298} value for the reaction 2KBr(g) = K_2Br_2(g) agrees with the second law value. The three principal moments of inertia are: I_A = 4.867 x 10^{-38}, I_B = 1.513 x 10^{-37} and I_C = 2.000 x 10^{-37} g cm^2.

Lithium Bromide, Dimeric (Li_2Br_2)

(Ideal Gas) GFW = 173.696

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	- 3.990	- 115.621	- 115.621	INFINITE
100	11.439	58.709	89.697	- 3.099	- 115.636	- 119.868	261.971
200	16.141	68.315	76.743	- 1.686	- 116.274	- 123.860	135.348
298	17.937	75.148	75.148	.000	- 119.700	- 127.111	93.175
300	17.958	75.259	75.148	.033	- 119.722	- 127.157	92.634
400	18.735	80.545	75.864	1.873	- 127.364	- 128.082	69.981
500	19.125	84.772	77.237	3.768	- 129.188	- 128.073	55.981
600	19.346	88.281	78.794	5.692	- 129.578	- 127.813	46.556
700	19.482	91.274	80.368	7.634	- 129.929	- 127.492	39.805
800	19.571	93.881	81.898	9.587	- 130.256	- 127.122	34.728
900	19.634	96.190	83.360	11.547	- 130.576	- 126.710	30.769
1000	19.678	98.261	84.748	13.513	- 130.890	- 126.263	27.595
1100	19.711	100.139	86.063	15.483	- 131.198	- 125.786	24.991
1200	19.737	101.855	87.309	17.455	- 131.505	- 125.282	22.817
1300	19.757	103.435	88.489	19.430	- 131.807	- 124.749	20.972
1400	19.772	104.900	89.610	21.406	- 132.107	- 124.195	19.388
1500	19.785	106.265	90.675	23.384	- 132.403	- 123.622	18.012
1600	19.796	107.542	91.690	25.363	- 132.695	- 123.024	16.804
1700	19.804	108.742	92.658	27.343	- 203.079	- 119.755	15.396
1800	19.811	109.875	93.583	29.324	- 203.003	- 114.855	13.945
1900	19.818	110.946	94.469	31.306	- 202.927	- 109.957	12.648
2000	19.823	111.962	95.319	33.288	- 202.855	- 105.067	11.481
2100	19.827	112.930	96.134	35.270	- 202.785	- 100.183	10.426
2200	19.831	113.852	96.919	37.253	- 202.718	- 95.296	9.467
2300	19.835	114.734	97.675	39.236	- 202.652	- 90.416	8.592
2400	19.838	115.578	98.403	41.220	- 202.592	- 85.537	7.789
2500	19.840	116.388	99.106	43.204	- 202.535	- 80.660	7.051
2600	19.843	117.166	99.786	45.188	- 202.483	- 75.788	6.371
2700	19.845	117.915	100.444	47.172	- 202.438	- 70.918	5.740
2800	19.847	118.637	101.081	49.157	- 202.398	- 66.046	5.155
2900	19.848	119.333	101.698	51.142	- 202.368	- 61.176	4.610
3000	19.850	120.006	102.297	53.127	- 202.343	- 56.306	4.102
3100	19.851	120.657	102.879	55.112	- 202.332	- 51.437	3.626
3200	19.853	121.287	103.445	57.097	- 202.327	- 46.570	3.181
3300	19.854	121.898	103.995	59.082	- 202.336	- 41.705	2.762
3400	19.855	122.491	104.530	61.068	- 202.354	- 36.836	2.368
3500	19.856	123.067	105.051	63.053	- 202.385	- 31.970	1.996
3600	19.857	123.626	105.560	65.039	- 202.430	- 27.099	1.645
3700	19.857	124.170	106.055	67.024	- 202.488	- 22.231	1.313
3800	19.858	124.700	106.539	69.010	- 202.561	- 17.353	.998
3900	19.859	125.215	107.011	70.996	- 202.649	- 12.473	.699
4000	19.859	125.718	107.473	72.982	- 202.754	- 7.602	.415
4100	19.860	126.209	107.924	74.968	- 202.876	- 2.722	.145
4200	19.861	126.687	108.365	76.954	- 203.017	2.161	- .112
4300	19.861	127.154	108.796	78.940	- 203.175	7.052	- .358
4400	19.862	127.611	109.219	80.926	- 203.352	11.945	- .593
4500	19.862	128.057	109.632	82.912	- 203.552	16.840	- .818
4600	19.862	128.494	110.038	84.899	- 203.772	21.738	- 1.033
4700	19.863	128.921	110.435	86.885	- 204.016	26.641	- 1.239
4800	19.863	129.339	110.824	88.871	- 204.286	31.548	- 1.436
4900	19.864	129.749	111.207	90.857	- 204.582	36.464	- 1.626
5000	19.864	130.150	111.581	92.844	- 204.902	41.393	- 1.809
5100	19.864	130.544	111.949	94.830	- 205.255	46.318	- 1.985
5200	19.864	130.929	112.311	96.817	- 205.637	51.258	- 2.154
5300	19.865	131.308	112.666	98.803	- 206.053	56.196	- 2.317
5400	19.865	131.679	113.014	100.790	- 206.502	61.149	- 2.475
5500	19.865	132.043	113.357	102.776	- 206.990	66.118	- 2.627
5600	19.865	132.401	113.694	104.763	- 207.515	71.079	- 2.774
5700	19.866	132.753	114.025	106.749	- 208.082	76.063	- 2.916
5800	19.866	133.099	114.351	108.736	- 208.692	81.053	- 3.054
5900	19.866	133.438	114.672	110.722	- 209.347	86.055	- 3.188
6000	19.866	133.772	114.987	112.709	- 210.050	91.066	- 3.317

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE, DIMERIC (Li_2Br_2) (IDEAL GAS) GFW = 173.696

Point Group D_{2h} $\Delta Hf^\circ_0 = -115.6 \pm 5$ kcal/mol

$S^\circ_{298.15} = [75.15]$ gibbs/mol $\Delta Hf^\circ_{298.15} = -119.7 \pm 5$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm $^{-1}$	ω, cm $^{-1}$
[202](1)	[327](1)
[203](1)	413 (1)
[353](1)	295 (1)

Bond Distance: Li-Br = 2.35 Å Li-Li = 2.70 Å

Bond Angle: Br-Li-Br = 110° $\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 4.220745 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation.

This was obtained from the heat of formation of the liquid and the selected heat of vaporization to the dimer, which derivation has been given in the LiBr(g) table.

Heat Capacity and Entropy.

J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure for dimeric lithium bromide, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Akischin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances ($r_{Br-Br} = 4.20$ Å and $r_{Li-Li} = 2.60$ Å) calculated by Berkowitz are in reasonable agreement with those selected. The three principal moments of inertia are $I_A = 4.1866 \times 10^{-39}$, $I_B = 98.3352 \times 10^{-39}$ and $I_C = 102.5218 \times 10^{-39}\ g\ cm^2$

S. H. Bauer, T. Ino and R. F. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (576, 576, 202, 230, 329 and 365 cm $^{-1}$) for $Li_2Br_2(g)$ in the electron diffraction studies of $Li_2Cl_2(g)$. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), have observed two fundamental vibrational frequencies (413 and 295 cm $^{-1}$) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; and these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.

Magnesium Dibromide ($MgBr_2$)

(Crystal) GFW = 184.130

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.515	28.500	28.500	.000	- 124.000	- 119.320	87.464
300	17.520	28.608	28.500	.032	- 124.012	- 119.290	86.903
400	18.260	33.754	29.197	1.823	- 131.075	- 116.250	63.516
500	18.830	37.891	30.535	3.678	- 130.745	- 112.581	49.209
600	19.330	41.369	32.059	5.586	- 130.394	- 108.982	39.697
700	19.790	44.385	33.609	7.543	- 130.023	- 105.442	32.921
800	20.150	47.051	35.126	9.540	- 129.647	- 101.957	27.853
900	20.510	49.445	36.586	11.573	- 129.273	- 98.518	23.923
1000	20.880	51.625	37.982	13.643	- 131.022	- 94.938	20.749
1100	21.240	53.632	39.315	15.749	- 130.620	- 91.352	18.150
1200	21.600	55.495	40.587	17.890	- 130.209	- 87.799	15.990
1300	21.970	57.239	41.801	20.069	- 129.788	- 84.281	14.169
1400	22.330	58.880	42.963	22.284	- 159.723	- 80.318	12.538
1500	22.700	60.433	44.076	24.535	- 158.877	- 74.676	10.880
1600	23.070	61.910	45.145	26.824	- 157.994	- 69.091	9.437
1700	23.419	63.319	46.173	29.149	- 157.076	- 63.561	8.171
1800	23.770	64.668	47.163	31.508	- 156.125	- 58.090	7.053
1900	24.124	65.963	48.119	33.903	- 155.138	- 52.669	6.058
2000	24.480	67.209	49.043	36.333	- 154.119	- 47.303	5.169

June 30, 1966

MAGNESIUM DIBROMIDE ($MgBr_2$) (CRYSTAL) GFW = 184.130

ΔHf_0° = Unknown

$S_{298.15}^\circ$ = [28.5 ± 2] gibbs/mol

$\Delta Hf_{298.15}^\circ$ = -124.0 ± 1 kcal/mol

Tm = 984°K

ΔHm° = 8.3 ± 2 kcal/mol

Heat of Formation

The heat of formation was calculated from ΔHf° values for Mg^{++}(H_2O) and Br^-(H_2O) and ΔHsol°(H_2O) for $MgBr_2$(c). The value for Br^- was obtained from D. D. Wagman et al., NBS Tech. Note 270-1, Natl. Bur. of Std., Washington, D.C., 1965. Values for Mg^{++} and ΔHsol° were taken from F. D. Rossini et al., NBS Circ. 500, Natl. Bur. of Std., Washington, D.C., 1952, since a survey of the literature revealed no new data which would significantly change these values. ΔHsol° is based on measurements of Beketoff, Bull. acad. sci. Russ. 34, 291 (1892), while Mg^{++} is presumably based on data for $MgCl_2$.

The selected heat of formation is confirmed by ΔGr_{1073}° = -0.267 kcal/mol for $MgBr_2(l) + HCl(g) = MgCl_2(l) + HBr(g)$ observed by J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. 7, 1502 (1963). Based on JANAF functions, this leads to ΔHf_{298}° = -124.9 kcal/mol for $MgBr_2$(c).

Heat Capacity and Entropy

The entropy and heat capacity were estimated by comparison with the corresponding values for $MgCl_2$, NaCl and NaBr. W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, has estimated S_{298}° = 29.4 eu which is also a reasonable value. Use of 29.4 eu would give almost exact agreement between the selected ΔHf° and the equilibrium data of Toguri et al., but this may be fortuitous because of uncertainties in the enthalpy and heat of melting for $MgBr_2$.

Melting Data

Tm and ΔHm° are the values obtained by K. K. Kelley, USBM Bulletin 393, 1936, from phase diagrams for the systems $MgBr_2$ - NaBr and $MgBr_2$ - KBr studied by G. Kellner, Z. Anorg. Chem. 99, 137 (1912), and for $MgBr_2$ - LiBr studied by A. Ferrari and C. Colla, Atti accad. Lencei, ser. 6, 13, 78 (1931).

Magnesium Dibromide ($MgBr_2$)
(Liquid) GFW = 184.130

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	23.750	31.968	31.968	- .000	- 118.337	- 114.691	84.070
300	23.250	32.113	31.968	.043	- 118.338	- 114.667	83.535
400	23.250	38.802	32.881	2.368	- 124.867	- 112.061	61.227
500	23.250	43.990	34.603	4.693	- 124.067	- 108.952	47.623
600	23.250	48.229	36.532	7.018	- 123.299	- 106.003	38.612
700	23.250	51.813	38.465	9.343	- 122.560	- 103.179	32.214
800	23.250	54.918	40.332	11.668	- 121.856	- 100.460	27.444
900	23.250	57.656	42.108	13.993	- 121.190	- 97.825	23.755
1000	23.250	60.106	43.787	16.318	- 122.684	- 95.081	20.780
1100	23.250	62.322	45.373	18.643	- 122.063	- 92.353	18.349
1200	23.250	64.345	46.871	20.968	- 121.468	- 89.678	16.333
1300	23.250	66.206	48.288	23.293	- 120.901	- 87.051	14.635
1400	23.250	67.929	49.630	25.618	- 150.726	- 83.989	13.111
1500	23.250	69.533	50.904	27.943	- 149.806	- 79.255	11.547
1600	23.250	71.033	52.116	30.268	- 148.887	- 74.581	10.187
1700	23.250	72.443	53.270	32.593	- 147.969	- 69.964	8.994
1800	23.250	73.772	54.373	34.918	- 147.052	- 65.404	7.941
1900	23.250	75.029	55.427	37.243	- 146.135	- 60.891	7.004
2000	23.250	76.221	56.437	39.568	- 145.221	- 56.429	6.166

June 30, 1966

MAGNESIUM DIBROMIDE ($MgBr_2$) (LIQUID) GFW = 184.130

$S^\circ_{298.15}$ = [31.968] gibbs/mol

Tm = 984°K

Tb = [1557]°K

$\Delta Hf^\circ_{298.15}$ = [-118.337] kcal/mol

ΔHm° = 8.3 kcal/mol

ΔHv° = [32.9] kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298.15}$ was obtained from $\Delta Hf^\circ_{298.15}(c)$ by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed constant and estimated as 23.25 gibbs/mol using 7.75 gibbs/g-atom as suggested by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $MgBr_2(c)$ table.

Vaporization Data.

Tb was calculated as the temperature at which ΔGr° = 0 for $MgBr_2(c) \rightarrow MgBr_2(g)$. ΔHv° is the corresponding enthalpy change.

Magnesium Dibromide ($MgBr_2$)

(Ideal Gas) GFW = 184.130

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.257	-70.802	-70.802	INFINITE
100	10.047	54.314	78.938	-2.462	-70.829	-74.746	163.358
200	12.697	62.244	68.760	-1.303	-71.403	-78.566	85.853
298	13.714	67.532	67.532	.000	-74.600	-81.557	59.783
300	13.727	67.617	67.532	.025	-74.619	-81.600	59.445
400	14.190	71.637	68.077	1.424	-82.074	-82.402	45.023
500	14.430	74.832	69.120	2.856	-82.167	-82.473	36.049
600	14.568	77.476	70.298	4.307	-82.273	-82.526	30.060
700	14.654	79.729	71.489	5.768	-82.398	-82.558	25.776
800	14.711	81.690	72.644	7.237	-82.550	-82.572	22.558
900	14.751	83.425	73.747	8.710	-82.736	-82.563	20.049
1000	14.779	84.980	74.794	10.186	-85.079	-82.350	17.998
1100	14.800	86.390	75.785	11.665	-85.304	-82.069	16.306
1200	14.817	87.679	76.723	13.146	-85.553	-81.764	14.891
1300	14.829	88.865	77.612	14.629	-85.828	-81.436	13.691
1400	14.840	89.964	78.456	16.112	-116.495	-80.607	12.583
1500	14.848	90.989	79.258	17.596	-116.416	-78.049	11.372
1600	14.855	91.947	80.021	19.082	-116.336	-75.493	10.312
1700	14.860	92.848	80.749	20.567	-116.258	-72.942	9.377
1800	14.865	93.697	81.445	22.054	-116.179	-70.396	8.547
1900	14.869	94.501	82.111	23.540	-116.101	-67.854	7.805
2000	14.872	95.264	82.750	25.027	-116.025	-65.319	7.138
2100	14.875	95.989	83.363	26.515	-115.948	-62.785	6.534
2200	14.878	96.682	83.953	28.002	-115.874	-60.255	5.986
2300	14.880	97.343	84.521	29.490	-115.800	-57.727	5.485
2400	14.882	97.976	85.069	30.978	-115.727	-55.204	5.027
2500	14.884	98.584	85.597	32.467	-115.655	-52.685	4.606
2600	14.885	99.168	86.108	33.955	-115.585	-50.166	4.217
2700	14.886	99.729	86.602	35.444	-115.516	-47.652	3.857
2800	14.888	100.271	87.081	36.932	-115.450	-45.142	3.523
2900	14.889	100.793	87.545	38.421	-115.384	-42.629	3.213
3000	14.890	101.298	87.995	39.910	-115.321	-40.123	2.923
3100	14.891	101.786	88.432	41.399	-115.261	-37.615	2.656
3200	14.891	102.259	88.856	42.888	-115.203	-35.113	2.398
3300	14.892	102.717	89.270	44.377	-115.149	-32.612	2.160
3400	14.893	103.162	89.672	45.867	-115.097	-30.111	1.936
3500	14.893	103.594	90.063	47.356	-115.051	-27.614	1.724
3600	14.894	104.013	90.445	48.845	-115.010	-25.114	1.525
3700	14.894	104.421	90.817	50.335	-114.972	-22.617	1.336
3800	14.895	104.818	91.180	51.824	-114.941	-20.120	1.157
3900	14.895	105.205	91.535	53.314	-114.915	-17.626	.988
4000	14.896	105.582	91.882	54.803	-114.897	-15.133	.827
4100	14.896	105.950	92.220	56.293	-114.886	-12.640	.674
4200	14.897	106.309	92.551	57.782	-114.883	-10.147	.528
4300	14.897	106.660	92.876	59.272	-114.888	-7.655	.389
4400	14.897	107.002	93.193	60.762	-114.901	-5.156	.256
4500	14.897	107.337	93.503	62.252	-114.924	-2.663	.129
4600	14.898	107.664	93.808	63.741	-114.958	-.165	.008
4700	14.898	107.985	94.106	65.231	-115.001	2.330	-.108
4800	14.898	108.298	94.398	66.721	-115.057	4.828	-.220
4900	14.898	108.606	94.685	68.211	-115.123	7.323	-.327
5000	14.899	108.907	94.967	69.701	-115.201	9.824	-.429
5100	14.899	109.202	95.243	71.190	-115.294	12.319	-.528
5200	14.899	109.491	95.514	72.680	-115.398	14.826	-.623
5300	14.899	109.775	95.780	74.170	-115.515	17.335	-.715
5400	14.899	110.053	96.042	75.660	-115.647	19.839	-.803
5500	14.900	110.327	96.299	77.150	-115.793	22.351	-.888
5600	14.900	110.595	96.552	78.640	-115.955	24.863	-.970
5700	14.900	110.859	96.801	80.130	-116.132	27.383	-1.050
5800	14.900	111.118	97.046	81.620	-116.324	29.900	-1.127
5900	14.900	111.373	97.286	83.110	-116.534	32.423	-1.201
6000	14.900	111.623	97.523	84.600	-116.760	34.944	-1.273

June 30, 1966

MAGNESIUM DIBROMIDE ($MgBr_2$) (IDEAL GAS) GFW = 184.130

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = [67.5 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -70.8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -74.6 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[179](1)
[220](2)
491 (1)

Bond Distance: Mg-Br = 2.34 Å

Bond Angle: Br-Mg-Br = 180°

Rotational Constant: B = 0.019264 cm^{-1}

$\sigma = 2$

Heat of Formation.

The $\Delta Hf^\circ_{298.15}$ was calculated from the $\Delta Hr^\circ_{298.15}$ = 49.4 kcal/mol for the reaction $MgBr_2(c) = MgBr_2(g)$, based on third law analysis of pressures at 798 and 842°K determined from Knudsen effusion - mass spectrometric studies by J. Berkowitz and J. R. Marquert, J. Chem. Phys. 37, 1853 (1962). Second law analysis of ion intensities (635 - 850°K) gave ΔHr° = 50.3 kcal/mol at 727°K, corresponding to ΔHr° = 52.2 kcal/mol at 298.15°K. The absolute pressure at 842°K was calibrated by integrating the ion current during complete volatilization of the sample. Data for $(MgBr_2)_2$ indicate that the dimer mole fraction (about 0.04 at 842°K) over the crystal increases with increasing temperature; this behavior is similar to that of the alkali halides.

Heat Capacity and Entropy.

Bond distance and bond angle were taken from the electron diffraction studies of P. A. Akishin, V. P. Spiridonov, G. A. Sobolev and V. A. Naumov, Zhur. Fiz. Khim. 31, 461 (1957). Electric deflection experiments of A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964), also suggest a linear structure for $MgBr_2$ within the sensitivity of the measurements. The antisymmetric stretching vibration ν_3 is that observed in the infrared spectra of the vapor by S. P. Randall, F. T. Greene and J. L. Margrave, J. Phys. Chem. 63, 758 (1959). The other frequencies were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963), from a valence force model using k = 1.5 and $k\delta/l^2$ = 0.15 md/Å.

Sodium Bromide, Dimeric (Na_2Br_2)
(Ideal Gas) Mol. Wt. = 205.814

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.633	-111.932	-111.932	INFINITE
100	15.116	64.123	99.740	-3.562	-112.169	-116.156	253.847
200	18.347	75.880	85.116	-1.847	-112.799	-119.906	131.021
298	19.150	83.384	83.384	.000	-116.240	-122.920	90.098
300	19.159	83.503	83.384	.035	-116.262	-122.960	89.572
400	19.463	89.062	84.140	1.969	-125.256	-123.531	67.491
500	19.608	93.422	85.576	3.923	-125.667	-123.051	53.783
600	19.688	97.005	87.191	5.888	-126.032	-122.493	44.616
700	19.737	100.044	88.816	7.860	-126.365	-121.879	38.051
800	19.768	102.682	90.388	9.835	-126.676	-121.216	33.113
900	19.790	105.011	91.886	11.813	-126.976	-120.514	29.263
1000	19.806	107.097	93.304	13.793	-127.276	-119.779	26.176
1100	19.817	108.986	94.646	15.774	-127.589	-119.019	23.646
1200	19.826	110.710	95.913	17.756	-174.390	-117.309	21.364
1300	19.833	112.298	97.114	19.739	-174.306	-112.556	18.921
1400	19.838	113.767	98.251	21.723	-174.222	-107.809	16.829
1500	19.843	115.136	99.332	23.707	-174.140	-103.069	15.016
1600	19.846	116.417	100.360	25.691	-174.059	-98.332	13.431
1700	19.849	117.620	101.340	27.676	-173.976	-93.600	12.033
1800	19.852	118.755	102.277	29.661	-173.896	-88.876	10.791
1900	19.854	119.828	103.172	31.646	-173.817	-84.152	9.679
2000	19.856	120.847	104.031	33.632	-173.741	-79.439	8.680
2100	19.857	121.816	104.855	35.618	-173.653	-74.728	7.777
2200	19.859	122.739	105.647	37.603	-173.590	-70.016	6.955
2300	19.860	123.622	106.409	39.589	-173.517	-65.311	6.206
2400	19.861	124.467	107.144	41.575	-173.447	-60.603	5.518
2500	19.862	125.278	107.854	43.562	-173.377	-55.907	4.887
2600	19.863	126.057	108.539	45.548	-173.313	-51.207	4.304
2700	19.863	126.807	109.202	47.534	-173.252	-46.517	3.765
2800	19.864	127.529	109.843	49.520	-173.197	-41.823	3.264
2900	19.865	128.226	110.465	51.507	-173.143	-37.127	2.798
3000	19.865	128.900	111.069	53.493	-173.097	-32.442	2.363
3100	19.866	129.551	111.654	55.480	-173.056	-27.753	1.956
3200	19.866	130.182	112.224	57.467	-173.021	-23.066	1.575
3300	19.866	130.793	112.777	59.453	-172.997	-18.382	1.217
3400	19.867	131.386	113.316	61.440	-172.978	-13.698	.880
3500	19.867	131.962	113.840	63.426	-172.972	-9.007	.562
3600	19.867	132.522	114.352	65.413	-172.976	-4.327	.263
3700	19.868	133.066	114.850	67.400	-172.990	.355	-.021
3800	19.868	133.596	115.336	69.387	-173.018	5.046	-.290
3900	19.868	134.112	115.811	71.374	-173.063	9.730	-.545
4000	19.868	134.615	116.275	73.360	-173.124	14.416	-.788
4100	19.869	135.106	116.728	75.347	-173.203	19.108	-1.018
4200	19.869	135.585	117.172	77.334	-173.303	23.795	-1.238
4300	19.869	136.052	117.605	79.321	-173.424	28.495	-1.448
4400	19.869	136.509	118.030	81.308	-173.572	33.188	-1.648
4500	19.869	136.955	118.445	83.295	-173.747	37.897	-1.840
4600	19.869	137.392	118.853	85.282	-173.953	42.596	-2.024
4700	19.870	137.819	119.252	87.269	-174.192	47.309	-2.200
4800	19.870	138.238	119.643	89.256	-174.471	52.017	-2.368
4900	19.870	138.647	120.026	91.243	-174.790	56.749	-2.531
5000	19.870	139.049	120.403	93.230	-175.154	61.476	-2.687
5100	19.870	139.442	120.772	95.217	-175.568	66.212	-2.837
5200	19.870	139.828	121.135	97.204	-176.034	70.955	-2.982
5300	19.870	140.207	121.491	99.191	-176.559	75.710	-3.122
5400	19.870	140.578	121.841	101.178	-177.148	80.475	-3.257
5500	19.870	140.943	122.185	103.165	-177.805	85.249	-3.387
5600	19.870	141.301	122.524	105.152	-178.534	90.036	-3.514
5700	19.871	141.652	122.856	107.139	-179.340	94.847	-3.636
5800	19.871	141.998	123.183	109.126	-180.228	99.662	-3.755
5900	19.871	142.338	123.505	111.113	-181.204	104.498	-3.871
6000	19.871	142.672	123.822	113.100	-182.269	109.343	-3.983

Sept. 30, 1964

SODIUM BROMIDE, DIMERIC (Na_2Br_2) (IDEAL GAS) MOL. WT. = 205.814

Point Group $[D_{2h}]$

$S^\circ_{298.15}$ = [83.384] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -111.93 ± 0.90 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -116.24 ± 0.90 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[182] (1)	[134] (1)
[120] (1)	[188] (1)
[207] (1)	[228] (1)

Bond Distance: Na-Br = [2.75] Å

Bond Angle: Na-Br-Na = [71]° Br-Na-Br = [109]° $\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.97701 X 10^{-112}] g.^{3} cm.^{6}

Heat of Formation.

The temperature dependence of the equilibrium constants (1293-1434°K.) for the reaction $(NaBr)_2(g) \rightleftarrows 2NaBr(g)$ has been studied by S. Datz, W. T. Smith, Jr. and E. H. Taylor, J. Chem. Phys. 34, 558 (1961). The dissociation energy ($\Delta E_{1300°K.}$) was evaluated to be 42.9 ± 1.3 kcal. mole^{-1}. The vapor mixture contains 37 to 17% of dimers in the temperature range of 1293 to 1434°K. Hence the vapor pressure data on NaBr(g) reported by the previous investigators were reexamined. In other words, the reported vapor pressure of NaBr(g) is the sum of the partial pressures of both the monomer (NaBr) and the dimer (Na_2Br_2). The partial pressures of $Na_2Br_2(g)$ thus obtained were used to evaluate the heats of vaporization by both the second and third law methods. The values of $\Delta H^\circ_{f\ 298.15}$ for $Na_2Br_2(g)$ were then calculated. The results are presented as follows.

Investigator	Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value	$\Delta H^\circ_{f\ 298.15}$* kcal. mole^{-1}
Niwa[1]	$2NaBr(c) \rightarrow Na_2Br_2(g)$	56.51	54.84	-117.08
Cogin and Kimball[2]	$2NaBr(c) \rightarrow Na_2Br_2(g)$	56.80	56.69	-116.01
Mayer and Wintner[3]	$2NaBr(c) \rightarrow Na_2Br_2(g)$	57.13	68.78	-115.63**
Ruff and Mugdan[4]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	45.70	46.71	-116.00
Wartenberg and Albrecht[5]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	45.64	46.77	-116.00
Bloom et al.[6]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	45.49	51.17	-116.72**

*Based on the average of the second and third law values.

**Only the third law value being used.

[1] K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser. III, 2 201 (1938).

[2] G. E. Cogin and G. E. Kimball, J. Chem. Phys. 16, 1035 (1948).

[3] J. E. Mayer and I. H. Wintner, J. Chem. Phys., 6, 301 (1938).

[4] O. Ruff and S. Mugdan, Z. anorg. allgem. Chem., 117, 147 (1921).

[5] H. von Wartenberg and P. Albrecht, Z. Electrochem., 27, 162 (1921).

[6] H. Bloom, J. O'M. Bockris, N. E. Richards and R. G. Taylor, J. Am. Chem. Soc. 80, 2044 (1958).

The value of $\Delta H^\circ_{f\ 298.15}$ for $Na_2Br_2(g)$ adopted is the average of the six $\Delta H^\circ_{f\ 298.15}$ values listed in the above table.

Heat Capacity and Entropy.

Bond distance and angles were calculated based on the related data reported by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958). The vibrational frequencies were calculated by J. Berkowitz, J. Chem. Phys., 32, 1519 (1960), from an assumed model. The ground state quantum weight was estimated. The three principal moments of inertia are I_A = 1.94452 X 10^{-38}, I_B = 1.33619 X 10^{-37} and I_C = 1.53065 X 10^{-37} g. cm.^{2}

Lead Dibromide (PbBr$_2$)

(Crystal) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.629	-63.199	-63.199	INFINITE
100	16.290	19.003	55.163	-3.616	-63.277	-63.010	137.702
200	18.495	31.116	40.396	-1.856	-63.291	-62.740	68.556
298	19.246	38.658	38.658	.000	-66.073	-62.134	45.544
300	19.250	38.777	38.658	.036	-66.082	-62.110	45.245
400	19.470	44.345	39.416	1.972	-73.038	-59.336	32.418
500	19.690	48.713	40.854	3.930	-72.636	-55.958	24.458
600	19.910	52.323	42.473	5.910	-72.234	-52.659	19.180
700	20.130	55.408	44.106	7.912	-72.995	-49.238	15.372
800	20.350	58.111	45.691	9.936	-72.588	-45.872	12.531
900	20.570	60.520	47.207	11.982	-72.154	-42.558	10.334
1000	20.790	62.699	48.649	14.050	-71.692	-39.293	8.587
1100	21.010	64.691	50.018	16.140	-71.203	-36.078	7.168
1200	21.230	66.528	51.319	18.252	-70.685	-32.906	5.993
1300	21.450	68.236	52.555	20.386	-70.142	-29.779	5.006
1400	21.670	69.834	53.733	22.542	-69.577	-26.697	4.167
1500	21.890	71.337	54.857	24.720	-68.991	-23.653	3.446
1600	22.110	72.756	55.932	26.920	-68.387	-20.650	2.821
1700	22.330	74.103	56.961	29.142	-67.764	-17.685	2.273
1800	22.550	75.386	57.949	31.386	-67.125	-14.760	1.792
1900	22.770	76.611	58.900	33.652	-66.469	-11.867	1.365
2000	22.990	77.784	59.815	35.940	-65.798	-9.011	.985
2100	23.210	78.911	60.697	38.250	-107.560	-4.636	.482
2200	23.430	79.996	61.550	40.582	-106.764	.245	-.024
2300	23.650	81.043	62.375	42.936	-105.968	5.093	-.484
2400	23.870	82.054	63.174	45.312	-105.172	9.906	-.902
2500	24.090	83.033	63.949	47.710	-104.378	14.682	-1.283

March 31, 1962

Lead Dibromide (PbBr$_2$) (Crystal)

Mol. Wt. = 367.04

ΔH_f° 298.15 = -66.07 ± 0.20 kcal. mole^{-1}

$S^\circ_{298.15}$ = 38.66 ± 0.5 cal. deg.$^{-1}$ mole^{-1}

ΔH_s° 298.15 = 41.90 ± 0.17 kcal. mole^{-1}

T_m = 640°K.

ΔH_m = 4.96 kcal. mole^{-1}

Heat of Formation. Recalculated from the data reported by H. Braune and F. Koref, Z. anorg. Chem., 87, 175 (1914) and C. Krahmer, Z. Elektrochem., 26, 97 (1920).

Heat Capacity, Entropy, and Melting Data. C_p (18.4° to 297.0°K.) reported by W. M. Latimer and H. D. Hoenshel, J. Am. Chem. Soc., 48, 19 (1926). Above 298.15°K., C_p given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. T_m and ΔH_m° obtained from M. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of H. Bloom, J. O'M. Bockris, N. E. Richards and R. G. Taylor, J. Am. Chem. Soc., 80, 2044 (1958), H. von Wartenberg and O. Bosse, Z. Elektrochem., 28, 384 (1922), F. Volmer, Phys. Z., 30, 590 (1929), and B. Greiner and K. Jellinek, Z. physik. Chem., A165, 97 (1933) which are in good agreement.

Lead Dibromide $(PbBr_2)$

(Liquid) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	19,246	42,699	42,699	,000	- 63,001	- 60,267	44,175
300	19,250	42,818	42,699	,036	- 63,010	- 60,250	43,890
400	27,600	48,386	43,457	1,972	- 69,966	- 57,880	31,623
500	27,600	54,545	45,082	4,732	- 68,762	- 55,000	24,039
600	27,600	59,577	47,091	7,492	- 67,580	- 52,358	19,070
700	27,600	63,831	49,186	10,252	- 67,583	- 49,722	15,523
800	27,600	67,517	51,252	13,012	- 66,440	- 47,249	12,907
900	27,600	70,768	53,244	15,772	- 65,292	- 44,919	10,907
1000	27,600	73,676	55,144	18,532	- 64,138	- 42,716	9,335
1100	27,600	76,306	56,950	21,292	- 62,979	- 40,631	8,072
1200	27,600	78,708	58,665	24,052	- 61,813	- 38,649	7,039
1300	27,600	80,917	60,293	26,812	- 60,644	- 36,766	6,181
1400	27,600	82,962	61,840	29,572	- 59,475	- 34,974	5,459
1500	27,600	84,866	63,312	32,332	- 58,307	- 33,264	4,846
1600	27,600	86,648	64,715	35,092	- 57,143	- 31,632	4,321
1700	27,600	88,321	66,055	37,852	- 55,982	- 30,072	3,866
1800	27,600	89,898	67,336	40,612	- 54,827	- 28,584	3,470
1900	27,600	91,391	68,564	43,372	- 53,677	- 27,157	3,124
2000	27,600	92,806	69,741	46,132	- 52,534	- 25,791	2,818
2100	27,600	94,153	70,871	48,892	- 93,846	- 22,929	2,386
2200	27,600	95,437	71,959	51,652	- 92,622	- 19,582	1,945
2300	27,600	96,664	73,007	54,412	- 91,420	- 16,288	1,548
2400	27,600	97,838	74,017	57,172	- 90,240	- 13,045	1,188
2500	27,600	98,965	74,992	59,932	- 89,084	- 9,855	,861
2600	27,600	100,048	75,935	62,692	- 87,950	- 6,707	,564
2700	27,600	101,089	76,848	65,452	- 86,837	- 3,605	,292
2800	27,600	102,093	77,732	68,212	- 85,748	- ,541	,042
2900	27,600	103,061	78,588	70,972	- 84,677	2,484	- ,187
3000	27,600	103,997	79,420	73,732	- 83,625	5,471	- ,399

March 31, 1962

Lead Dibromide $(PbBr_2)$ (Liquid)

Mol. Wt. = 367.04

$\Delta H_f^\circ{}_{298.15}$ = [-63.00 ± 0.20] kcal. mole^{-1}

$S^\circ_{298.15}$ = [42.699] cal. deg.$^{-1}$ mole^{-1}

T_m = 640°K.

ΔH_m° = 4.96 kcal. mole^{-1}

T_b = 1187°K.

ΔH_v° = 27.44 ± 0.17 kcal. mole^{-1}

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). T_m and ΔH_m° reported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959). A glass transition temperature of 400°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v° calculated from $\Delta H_s^\circ{}_{298.15}$ and free energy functions for condensed and gaseous states.

Lead Dibromide ($PbBr_2$)

(Ideal Gas) Mol. Wt. = 367.04 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	,000	,000	INFINITE	-3,667	-20,340	-20,340	INFINITE
100	12,340	68,022	94,374	-2,635	-20,399	-25,034	54,709
200	13,424	77,009	83,672	-1,333	-20,871	-29,498	32,233
298	13,682	82,426	82,426	,000	-24,176	-33,287	24,399
300	13,685	82,511	82,427	,025	-24,196	-33,343	24,289
400	13,781	86,463	82,965	1,399	-31,714	-34,858	19,045
500	13,827	89,544	83,984	2,780	-31,889	-35,626	15,571
600	13,853	92,067	85,127	4,164	-32,083	-36,354	13,241
700	13,868	94,204	86,275	5,550	-33,460	-36,860	11,508
800	13,878	96,056	87,384	6,938	-33,689	-37,330	10,198
900	13,885	97,691	88,441	8,326	-33,913	-37,771	9,172
1000	13,890	99,155	89,440	9,714	-34,131	-38,187	8,345
1100	13,893	100,479	90,384	11,104	-34,342	-38,583	7,665
1200	13,896	101,688	91,277	12,493	-34,547	-38,959	7,095
1300	13,898	102,800	92,121	13,883	-34,748	-39,318	6,610
1400	13,900	103,830	92,921	15,273	-34,949	-39,663	6,191
1500	13,901	104,789	93,680	16,663	-35,151	-39,992	5,827
1600	13,903	105,686	94,403	18,053	-35,357	-40,308	5,506
1700	13,904	106,529	95,092	19,443	-35,566	-40,610	5,220
1800	13,904	107,324	95,750	20,834	-35,780	-40,903	4,966
1900	13,905	108,076	96,379	22,224	-36,000	-41,180	4,737
2000	13,906	108,789	96,982	23,615	-36,226	-41,448	4,529
2100	13,906	109,467	97,560	25,005	-78,908	-40,151	4,178
2200	13,906	110,114	98,116	26,396	-79,053	-38,303	3,805
2300	13,907	110,732	98,651	27,787	-79,220	-36,446	3,463
2400	13,907	111,324	99,167	29,177	-79,410	-34,581	3,149
2500	13,907	111,892	99,665	30,568	-79,623	-32,711	2,859
2600	13,908	112,437	100,146	31,959	-79,858	-30,829	2,591
2700	13,908	112,962	100,611	33,350	-80,114	-28,940	2,342
2800	13,908	113,468	101,061	34,740	-80,395	-27,038	2,110
2900	13,908	113,956	101,497	36,131	-80,693	-25,127	1,893
3000	13,909	114,428	101,920	37,522	-81,010	-23,205	1,690
3100	13,909	114,884	102,331	38,913	-81,345	-21,273	1,500
3200	13,909	115,325	102,730	40,304	-81,696	-19,330	1,320
3300	13,909	115,753	103,119	41,695	-82,061	-17,376	1,151
3400	13,909	116,169	103,496	43,086	-82,438	-15,410	,990
3500	13,909	116,572	103,864	44,477	-82,828	-13,432	,839
3600	13,909	116,964	104,223	45,867	-83,226	-11,444	,695
3700	13,909	117,345	104,572	47,258	-83,631	-9,445	,558
3800	13,909	117,716	104,913	48,649	-84,042	-7,433	,427
3900	13,909	118,077	105,246	50,040	-84,459	-5,410	,303
4000	13,909	118,429	105,571	51,431	-84,879	-3,383	,185
4100	13,910	118,773	105,889	52,822	-85,302	-1,340	,071
4200	13,910	119,108	106,200	54,213	-85,726	,715	-,037
4300	13,910	119,435	106,504	55,604	-86,151	2,777	-,141
4400	13,910	119,755	106,801	56,995	-86,575	4,853	-,241
4500	13,910	120,067	107,093	58,386	-86,998	6,933	-,337
4600	13,910	120,373	107,378	59,777	-87,420	9,027	-,429
4700	13,910	120,672	107,658	61,168	-87,839	11,127	-,517
4800	13,910	120,965	107,932	62,559	-88,257	13,238	-,603
4900	13,910	121,252	108,201	63,950	-88,671	15,356	-,685
5000	13,910	121,533	108,465	65,341	-89,082	17,483	-,764
5100	13,910	121,809	108,724	66,732	-89,491	19,616	-,841
5200	13,910	122,079	108,978	68,123	-89,895	21,762	-,915
5300	13,910	122,344	109,228	69,514	-90,296	23,916	-,986
5400	13,910	122,604	109,473	70,905	-90,695	26,072	-1,055
5500	13,910	122,859	109,714	72,296	-91,090	28,239	-1,122
5600	13,910	123,109	109,951	73,687	-91,482	30,411	-1,187
5700	13,910	123,356	110,184	75,078	-91,872	32,590	-1,249
5800	13,910	123,598	110,413	76,469	-92,258	34,782	-1,311
5900	13,910	123,835	110,639	77,860	-92,643	36,972	-1,369
6000	13,910	124,069	110,861	79,251	-93,025	39,166	-1,427

March 31, 1962

Lead Dibromide ($PbBr_2$) (Ideal Gas)

Mol. Wt. = 367.04

ΔH_f° 298.15 = -24.18 ± 0.26 kcal. mole^{-1}

$S^\circ_{298.15}$ = 82.426 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
[140] (1)
[45] (1)
[200] (1)

Pb-Br distance = 2.60 ± 0.03 Å BrPbBr angle = 95° $\sigma = 2$

$I_A = 46.245 \times 10^{-39}$ g. cm.^{2} $I_B = 97.514 \times 10^{-39}$ g. cm.^{2}

$I_C = I_A + I_B = 143.759 \times 10^{-39}$ g. cm.^{2}

Heat of Formation. Calculated from ΔH_s° 298.15 and ΔH_f° 298.15 for $PbBr_2(c)$.

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for $HgBr_2(g)$.

Titanium Dibromide ($TiBr_2$)

(Crystal) GFW = 207.718

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.807	25.900	25.900	.000	- 96.900	- 91.590	67.137
300	18.812	26.016	25.900	.035	- 96.909	- 91.557	66.699
400	19.086	31.466	26.642	1.930	- 103.872	- 88.322	48.257
500	19.360	35.754	28.050	3.852	- 103.479	- 84.481	36.927
600	19.634	39.308	29.639	5.802	- 103.083	- 80.719	29.402
700	19.908	42.355	31.243	7.779	- 102.685	- 77.023	24.048
800	20.182	45.032	32.802	9.783	- 102.287	- 73.385	20.048
900	20.456	47.424	34.296	11.815	- 101.889	- 69.795	16.949
1000	20.730	49.594	35.719	13.874	- 101.494	- 66.250	14.479
1100	21.004	51.583	37.072	15.961	- 101.098	- 62.745	12.466
1200	21.278	53.422	38.359	18.075	- 101.639	- 59.238	10.789
1300	21.552	55.136	39.584	20.217	- 101.116	- 55.725	9.368
1400	21.826	56.743	40.753	22.386	- 100.582	- 52.254	8.157
1500	22.100	58.258	41.870	24.582	- 100.039	- 48.822	7.113

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM DIBROMIDE ($TiBr_2$) (CRYSTAL) GFW = 207.718

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = [25.9 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -96.9 ± 5.0 kcal/mol

Ts = [1208.8]°K

ΔHs° = [49.29] kcal/mol

Heat of Formation

The heat of formation of $TiBr_2$ crystal is derived from the data of Hall and Blocher (1) for the reaction $2TiBr_3(c) = TiBr_4(g) + TiBr_2(c)$. Second and third law analyses of these data are not useful because of the formation of solid solutions in the above process. Hall and Blocher obtained a value of ΔHr°_{800} of 31.3 kcal/mol for the reaction by integrating the incremental free energy changes over varying compositions of the solid solutions. The coresponding ΔHr°_{298} and ΔHf°_{298} are calculated as 34.6 kcal/mol and -96.9 kcal/mol, respectively, using auxiliary JANAF heats of formation and enthalpy data.

Heat Capacity and Entropy

The heat capacity of $TiBr_2(c)$ was estimated by Kelley (2). The value of $S^\circ_{298.15}$ is estimated from that of $TiCl_2(c)$ and the difference between ionic entropy contributions of Cl^- and Br^-.

Heat of Sublimation

The heat of sublimation of $TiBr_2(c)$ is taken as the difference in the heats of formation of $TiBr_2(c)$ and $TiBr_2(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta Gr^\circ = 0$ for the reaction $TiBr_2(c) = TiBr_2(g)$. The heat of formation of $TiBr_2(g)$, upon which these quantities depend, is an estimated quantity.

References

1. E. H. Hall and J. M. Blocher, Jr., J. Phys. Chem. 63, 1525 (1959).
2. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1960.

Titanium Dibromide ($TiBr_2$)

(Ideal Gas) GFW = 207.718

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.615	- 39.404	- 39.404	INFINITE
100	11.939	59.147	86.056	- 2.691	- 39.282	- 43.713	95.534
200	13.785	68.125	75.050	- 1.385	- 39.605	- 48.037	52.492
298	14.346	73.752	73.752	.000	- 42.800	- 51.757	37.939
300	14.353	73.841	73.752	.027	- 42.817	- 51.812	37.745
400	14.581	78.005	74.319	1.475	- 50.227	- 53.293	29.118
500	14.694	81.273	75.394	2.939	- 50.292	- 54.053	23.627
600	14.756	83.958	76.604	4.412	- 50.373	- 54.798	19.960
700	14.795	86.235	77.822	5.890	- 50.474	- 55.529	17.337
800	14.822	88.213	79.000	7.370	- 50.600	- 56.243	15.365
900	14.844	89.960	80.122	8.854	- 50.750	- 56.939	13.827
1000	14.867	91.525	81.186	10.339	- 50.929	- 57.617	12.592
1100	14.894	92.943	82.191	11.827	- 51.132	- 58.275	11.578
1200	14.930	94.241	83.142	13.318	- 52.296	- 58.877	10.723
1300	14.975	95.437	84.042	14.814	- 52.419	- 59.420	9.989
1400	15.030	96.549	84.896	16.314	- 52.554	- 59.955	9.359
1500	15.096	97.588	85.708	17.820	- 52.701	- 60.479	8.812
1600	15.171	98.565	86.482	19.333	- 52.860	- 60.991	8.331
1700	15.254	99.487	87.220	20.855	- 53.031	- 61.494	7.906
1800	15.343	100.362	87.926	22.384	- 53.218	- 61.988	7.526
1900	15.437	101.194	88.602	23.923	- 53.418	- 62.469	7.186
2000	15.532	101.988	89.252	25.472	- 58.081	- 62.787	6.861
2100	15.628	102.748	89.877	27.030	- 58.287	- 63.016	6.558
2200	15.722	103.477	90.478	28.597	- 58.486	- 63.238	6.282
2300	15.815	104.178	91.059	30.174	- 58.676	- 63.449	6.029
2400	15.905	104.853	91.620	31.760	- 58.858	- 63.651	5.796
2500	15.990	105.504	92.162	33.355	- 59.032	- 63.847	5.582
2600	16.072	106.133	92.687	34.958	- 59.199	- 64.037	5.383
2700	16.149	106.741	93.197	36.569	- 59.359	- 64.221	5.198
2800	16.222	107.330	93.691	38.188	- 59.513	- 64.398	5.026
2900	16.290	107.900	94.171	39.813	- 59.661	- 64.567	4.866
3000	16.354	108.453	94.638	41.446	- 59.802	- 64.735	4.716
3100	16.414	108.991	95.092	43.084	- 59.940	- 64.895	4.575
3200	16.470	109.513	95.535	44.728	- 60.072	- 65.056	4.443
3300	16.523	110.020	95.966	46.378	- 60.200	- 65.210	4.319
3400	16.573	110.514	96.387	48.033	- 60.323	- 65.359	4.201
3500	16.620	110.995	96.797	49.692	- 60.444	- 65.505	4.090
3600	16.665	111.464	97.198	51.356	- 162.187	- 65.386	3.969
3700	16.707	111.921	97.590	53.025	- 162.271	- 62.697	3.703
3800	16.748	112.367	97.973	54.698	- 162.366	- 60.007	3.451
3900	16.787	112.803	98.348	56.375	- 162.471	- 57.307	3.211
4000	16.825	113.228	98.715	58.055	- 162.587	- 54.612	2.984
4100	16.861	113.644	99.074	59.739	- 162.713	- 51.911	2.767
4200	16.896	114.051	99.425	61.427	- 162.848	- 49.208	2.561
4300	16.930	114.449	99.770	63.119	- 162.992	- 46.501	2.363
4400	16.963	114.839	100.108	64.813	- 163.146	- 43.789	2.175
4500	16.995	115.220	100.440	66.511	- 163.308	- 41.075	1.995
4600	17.026	115.594	100.765	68.212	- 163.478	- 38.353	1.822
4700	17.056	115.960	101.085	69.916	- 163.656	- 35.630	1.657
4800	17.085	116.320	101.398	71.623	- 163.843	- 32.907	1.498
4900	17.113	116.672	101.706	73.333	- 164.036	- 30.179	1.346
5000	17.140	117.018	102.009	75.046	- 164.235	- 27.442	1.199
5100	17.166	117.358	102.307	76.761	- 164.442	- 24.707	1.059
5200	17.191	117.692	102.599	78.479	- 164.654	- 21.964	.923
5300	17.214	118.019	102.887	80.199	- 164.872	- 19.219	.792
5400	17.237	118.341	103.171	81.922	- 165.096	- 16.468	.666
5500	17.258	118.658	103.449	83.647	- 165.323	- 13.709	.545
5600	17.279	118.969	103.724	85.373	- 165.558	- 10.958	.428
5700	17.297	119.275	103.994	87.102	- 165.795	- 8.189	.314
5800	17.315	119.576	104.260	88.833	- 166.036	- 5.422	.204
5900	17.331	119.872	104.522	90.565	- 166.282	- 2.651	.098
6000	17.346	120.163	104.780	92.299	- 166.531	.117	- .004

June 30, 1964; June 30, 1968

TITANIUM DIBROMIDE ($TiBr_2$) (IDEAL GAS) GFW = 207.718

Point Group [$D_{\infty h}$]

ΔHf°_0 = -39.4 ± 5.0 kcal/mol

$S^\circ_{298.15}$ = [73.8 ± 3.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -42.8 ± 5.0 kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[160] (1)
[105] (2)
[333] (1)

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [180°] σ = 2

Rotational Constant: B_0 = [0.0183] cm^{-1}

Heat of Formation

The heat of formation of $TiBr_2(g)$ is calculated from the estimated Ti-Br bond energy. The bond energy is estimated as being the same as the average Ti-Cl bond energy of $TiCl_2(g)$. This estimate is used because the measured average bond energies of $TiBr_3(g)$ and $TiCl_3(g)$ and those of $TiBr_4(g)$ and $TiCl_4(g)$ are very nearly equal.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(g)$, $TiCl_4(g)$ and $TiBr_4(g)$. The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.2 millidynes Å^{-1}, and the constant k_δ/ℓ^2 is assumed to be 0.06 millidynes Å^{-1}. These values are derived by a correlation with other dihalides.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2(g)$ are estimated by assuming that they correspond to the inverted states of $NiCl_2(g)$ (1). The linear configuration is adopted since experimental evidence indicates that other transition metal dihalides are linear (2, 3, 4, 5).

References

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3. J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961).
4. G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
5. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

Zirconium Dibromide ($ZrBr_2$)

(Crystal) GFW = 251.038

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	20.727	27.700	27.700	.000	-96.700	-91.334	66.950
300	20.732	27.828	27.700	.038	-96.706	-91.300	66.512
400	21.006	33.830	28.517	2.125	-103.482	-88.076	48.122
500	21.280	38.547	30.068	4.240	-102.901	-84.292	36.844
600	21.554	42.451	31.815	6.381	-102.326	-80.625	29.368
700	21.828	45.794	33.579	8.550	-101.756	-77.054	24.057
800	22.102	48.727	35.293	10.747	-101.188	-73.563	20.097
900	22.376	51.346	36.934	12.971	-100.624	-70.144	17.033
1000	22.650	53.717	38.495	15.222	-100.062	-66.787	14.596
1100	22.924	55.889	39.979	17.501	-99.502	-63.487	12.614
1200	23.198	57.895	41.390	19.807	-99.795	-60.186	10.961
1300	23.472	59.763	42.732	22.140	-99.061	-56.914	9.568
1400	23.746	61.513	44.012	24.501	-98.311	-53.700	8.383
1500	24.020	63.160	45.234	26.890	-97.546	-50.540	7.364

Mar. 31, 1962; June 30, 1970

ZIRCONIUM DIBROMIDE ($ZrBr_2$) (CRYSTAL) GFW = 251.038

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [27.7 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-96.7 ± 10] kcal/mol

Tm = [900]°K

ΔHm° = [15.0 ± 10] kcal/mol

$\Delta Hs^\circ_{298.15}$ = [55.0 ± 5] kcal/mol

Heat of Formation

The value of $\Delta Hf^\circ_{298}(ZrBr_2, c) = -96.7$ kcal/mol is calculated from the estimated $\Delta Hs^\circ_{298} = 55 \pm 5$ kcal/mol for $ZrBr_2(c) \rightarrow ZrBr_2(g)$, using $\Delta Hf^\circ_{298}(ZrBr_2, g) = -41.7$ kcal/mol (1). The estimated ΔHs°_{298} is obtained as an average of the heats of sublimation at 298°K for $CrBr_2$, $MnBr_2$, $CoBr_2$, $NiBr_2$ given by Brewer, Somayajulu and Brackett (2) and $TiBr_2$ and $FeBr_2$ listed in JANAF tables (3).

Heat Capacity and Entropy

The heat capacities of $ZrBr_2(c)$ are estimated from $TiBr_2(c)$ (3), based on the assumption $Cp(ZrBr_2) = Cp(TiBr_2) + 3/2\ R\ln[(\text{at. wt. of Zr})/(\text{at. wt. of Ti})]$. The entropy, $S^\circ_{298} = 27.7$ eu, is estimated in a similar manner based on $TiCl_2(c)$ (4) and $TiBr_2(c)$ (3).

Melting Data

The heat of fusion is roughly estimated, so that the entropy of vaporization is about 20 eu. The melting point was estimated by Brewer (5).

References

1. JANAF $ZrBr_2(g)$ table dated June 30, 1970.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. JANAF $TiBr_2(c)$ table dated June 30, 1968 and $FeBr_2(c)$ table dated Sept. 30, 1966.
4. JANAF $TiCl_2(c)$ table dated Dec. 31, 1968.
5. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill Ed., McGraw-Hill Book Company, New York, 1949.

Zirconium Dibromide ($ZrBr_2$)

(Liquid) GFW = 251.038

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	21.750	43.983	43.983	.000	-81.820	-81.308	59.600
300	21.750	44.117	43.983	.040	-81.823	-81.304	59.230
400	21.750	50.375	44.836	2.215	-88.511	-79.723	43.559
500	21.750	55.228	46.447	4.390	-87.870	-77.602	33.920
600	21.750	59.193	48.251	6.565	-87.261	-75.606	27.539
700	21.750	62.546	50.060	8.740	-86.685	-73.710	23.013
800	21.750	65.451	51.806	10.915	-86.139	-71.893	19.640
900	21.750	68.012	53.468	13.090	-85.624	-70.144	17.033
1000	21.750	70.304	55.039	15.265	-85.138	-68.450	14.960
1100	21.750	72.377	56.522	17.440	-84.682	-66.804	13.273
1200	21.750	74.269	57.923	19.615	-85.106	-65.146	11.865
1300	21.750	76.010	59.249	21.790	-84.530	-63.505	10.676
1400	21.750	77.622	60.504	23.965	-83.966	-61.909	9.664
1500	21.750	79.123	61.696	26.140	-83.415	-60.353	8.793
1600	21.750	80.526	62.829	28.315	-82.877	-58.833	8.036
1700	21.750	81.845	63.910	30.490	-82.350	-57.345	7.372
1800	21.750	83.088	64.941	32.665	-81.836	-55.891	6.786
1900	21.750	84.264	65.927	34.840	-81.334	-54.462	6.265
2000	21.750	85.380	66.872	37.015	-80.845	-53.062	5.798

Mar. 31, 1962; June 30, 1970

ZIRCONIUM DIBROMIDE ($ZrBr_2$) (LIQUID) GFW = 251.038

$S°_{298.15}$ = [43.983] gibbs/mol

$\Delta Hf°_{298.15}$ = [-81.820] kcal/mol

Tm = [900]°K

ΔHm° = [15.0 ± 10] kcal/mol

Tb = [1555.1]°K

ΔHv° = [31.5] kcal/mol

Heat of Formation

The $\Delta Hf°_{298}(ZrBr_2, \ell)$ is calculated from $\Delta Hf°_{298}(ZrBr_2, c)$ by adding ΔHm° and the difference between $H_{900}-H_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

See $ZrBr_2(c)$ table for details.

Vaporization Data

Tb is the temperature at which the Gibbs energy change approaches zero for the process $ZrBr_2(\ell) \rightarrow ZrBr_2(g)$. The difference between ΔHf° for $ZrBr_2(\ell)$ and $ZrBr_2(g)$ at Tb is ΔHv°.

Zirconium Dibromide ($ZrBr_2$)

(Ideal Gas) GFW = 251.038

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.720	-38.240	-38.240	INFINITE
100	12.447	60.706	88.224	-2.752	-38.152	-42.600	93.103
200	14.073	69.970	77.000	-1.406	-38.503	-46.928	51.281
298	14.504	75.684	75.684	.000	-41.700	-50.640	37.120
300	14.509	75.774	75.685	.027	-41.717	-50.695	36.931
400	14.676	79.974	76.256	1.487	-49.120	-52.171	28.505
500	14.756	83.258	77.340	2.959	-49.182	-52.929	23.135
600	14.801	85.953	78.558	4.437	-49.270	-53.670	19.549
700	14.828	88.237	79.781	5.919	-49.387	-54.395	16.983
800	14.847	90.218	80.965	7.403	-49.532	-55.101	15.053
900	14.864	91.968	82.092	8.888	-49.707	-55.787	13.547
1000	14.883	93.535	83.159	10.376	-49.908	-56.451	12.337
1100	14.908	94.955	84.168	11.865	-50.138	-57.095	11.344
1200	14.941	96.253	85.122	13.357	-51.245	-57.664	10.502
1300	14.984	97.451	86.025	14.854	-51.347	-58.194	9.783
1400	15.039	98.563	86.881	16.355	-51.457	-58.717	9.166
1500	15.103	99.603	87.695	17.862	-51.574	-59.232	8.630
1600	15.178	100.580	88.470	19.376	-51.697	-59.739	8.160
1700	15.260	101.502	89.210	20.898	-51.823	-60.236	7.744
1800	15.349	102.377	89.917	22.428	-51.954	-60.729	7.374
1900	15.441	103.210	90.595	23.967	-52.088	-61.211	7.041
2000	15.536	104.004	91.246	25.516	-52.225	-61.690	6.741
2100	15.631	104.764	91.872	27.075	-52.363	-62.160	6.469
2200	15.726	105.494	92.474	28.642	-57.509	-62.446	6.203
2300	15.818	106.195	93.056	30.220	-57.648	-62.666	5.955
2400	15.907	106.870	93.617	31.806	-57.780	-62.881	5.726
2500	15.993	107.521	94.160	33.401	-57.904	-63.091	5.515
2600	16.074	108.150	94.687	35.004	-58.021	-63.296	5.321
2700	16.151	108.758	95.196	36.616	-58.130	-63.499	5.140
2800	16.224	109.347	95.691	38.235	-58.234	-63.695	4.972
2900	16.292	109.917	96.172	39.860	-58.332	-63.887	4.815
3000	16.355	110.471	96.640	41.493	-58.423	-64.078	4.668
3100	16.415	111.008	97.094	43.131	-58.511	-64.264	4.531
3200	16.471	111.530	97.537	44.776	-58.592	-64.448	4.402
3300	16.524	112.038	97.969	46.425	-58.671	-64.632	4.280
3400	16.574	112.532	98.390	48.080	-58.744	-64.812	4.166
3500	16.621	113.013	98.801	49.740	-58.814	-64.988	4.058
3600	16.666	113.482	99.202	51.405	-58.880	-65.164	3.956
3700	16.708	113.939	99.595	53.073	-58.943	-65.338	3.859
3800	16.749	114.385	99.978	54.746	-59.003	-65.509	3.768
3900	16.786	114.821	100.353	56.423	-59.060	-65.678	3.681
4000	16.826	115.246	100.720	58.104	-59.114	-65.850	3.598
4100	16.862	115.662	101.079	59.788	-59.166	-66.019	3.519
4200	16.897	116.069	101.431	61.476	-59.215	-66.184	3.444
4300	16.931	116.467	101.777	63.168	-59.261	-66.348	3.372
4400	16.964	116.856	102.115	64.862	-59.306	-66.512	3.304
4500	16.996	117.238	102.447	66.560	-59.348	-66.677	3.238
4600	17.027	117.612	102.772	68.261	-59.388	-66.838	3.176
4700	17.057	117.978	103.092	69.966	-59.425	-66.998	3.115
4800	17.086	118.338	103.406	71.673	-200.619	-66.479	3.027
4900	17.113	118.690	103.714	73.383	-200.757	-63.681	2.840
5000	17.140	119.036	104.017	75.095	-200.900	-60.882	2.661
5100	17.166	119.376	104.315	76.811	-201.046	-58.083	2.489
5200	17.191	119.710	104.608	78.529	-201.194	-55.276	2.323
5300	17.215	120.037	104.896	80.249	-201.345	-52.468	2.164
5400	17.237	120.359	105.179	81.972	-201.499	-49.660	2.010
5500	17.259	120.676	105.456	83.696	-201.656	-46.844	1.861
5600	17.279	120.987	105.733	85.423	-201.814	-44.030	1.718
5700	17.298	121.293	106.003	87.152	-201.975	-41.210	1.580
5800	17.316	121.594	106.269	88.883	-202.136	-38.386	1.446
5900	17.332	121.890	106.531	90.615	-202.300	-35.563	1.317
6000	17.347	122.181	106.790	92.349	-202.466	-32.740	1.193

Mar. 31, 1962; June 30, 1970

ZIRCONIUM DIBROMIDE ($ZrBr_2$) (IDEAL GAS) GFW = 251.038

Point Group $[D_{\infty h}]$

$\Delta Hf^\circ_0 = [-38.2 \pm 10]$ kcal/mol

$S^\circ_{298.15} = [75.7 \pm 3]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = [-41.7 \pm 10]$ kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[160] (1)
[84] (2)
[265] (1)

Bond Distance: Zr-Br = [2.47] Å

Bond Angle: Br-Zr-Br = [180°]

$\sigma = [2]$

Rotational Constant: $B_0 = [0.01729]$ cm^{-1}

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298}(ZrBr_2, g) = -41.7$ kcal/mol, is derived from the estimated $\Delta Hr^\circ_{298} = 243.5 \pm 10$ kcal/mol for $ZrBr_2(g) \rightarrow Zr(g) + 2Br(g)$. The value of ΔHr°_{298} is twice the average bond dissociation energy, $D^\circ_{298}(Zr\text{-}Br_2) = 121.75$ kcal/mol, which is calculated from the relation $D^\circ_{298}(Zr\text{-}Br_2)/D^\circ_{298}(Ti\text{-}Br_2) = D^\circ_{298}(Zr\text{-}Br_4)/D^\circ_{298}(Ti\text{-}Br_4)$. The average bond dissociation energies, $D^\circ_{298}(Zr\text{-}Br_4) = 102.2$ kcal/mol, $D^\circ_{298}(Ti\text{-}Br_4) = 87.9$ kcal/mol and $D^\circ_{298}(Ti\text{-}Br_2) = 104.6$ kcal/mol, are all calculated from JANAF ΔHf°_{298} for $ZrBr_4(g)$, $TiBr_4(g)$, $TiBr_2(g)$, Zr(g), Ti(g) and Br(g).

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the transition metal dihalides are generally linear (1, 2, 3, 4, 5) even though a few fluorides are bent (6). The bond distance is assumed to be the same as that in $ZrBr_4(g)$ which was estimated as 2.47 Å by Godnev et al. (7). The moment of inertia is 161.8979 × 10^{-39} g cm^2.

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 1.2 millidyne/Å and the bending force constant 0.06 millidyne/Å. These values are derived from force constants of transition metal dihalides listed by Brewer, Somayajulu and Brackett (8). The electronic levels and quantum weights are estimated to be the same as those of gaseous $TiCl_2$ (9).

References

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3. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).
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8. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
9. JANAF $TiCl_2(g)$ table dated Dec. 31, 1968.

Phosphoryl Bromide ($POBr_3$)

(Ideal Gas) Mol. Wt. = 286.723

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 4.744	- 87.056	- 87.056	INFINITE
100	14.159	66.247	103.348	- 3.710	- 87.472	- 89.940	196.555
200	19.200	77.835	87.881	- 2.009	- 88.185	- 92.136	100.676
298	21.478	85.978	85.978	.000	- 93.000	- 93.432	68.485
300	21.508	86.111	85.979	.040	- 93.025	- 93.434	68.063
400	22.770	92.487	86.839	2.259	- 104.055	- 91.305	49.884
500	23.567	97.660	88.502	4.579	- 103.996	- 88.125	38.517
600	24.105	102.007	90.401	6.964	- 103.921	- 84.958	30.944
700	24.480	105.753	92.332	9.394	- 103.852	- 81.803	25.539
800	24.751	109.040	94.220	11.856	- 124.216	- 83.969	22.938
900	24.951	111.968	96.032	14.342	- 123.920	- 78.955	19.172
1000	25.102	114.605	97.760	16.845	- 123.620	- 73.973	16.166
1100	25.218	117.009	99.402	19.361	- 123.317	- 69.025	13.713
1200	25.309	119.201	100.961	21.888	- 123.012	- 64.103	11.674
1300	25.382	121.230	102.443	24.422	- 122.708	- 59.204	9.953
1400	25.441	123.113	103.853	26.964	- 122.402	- 54.331	8.481
1500	25.489	124.870	105.196	29.510	- 122.099	- 49.480	7.209
1600	25.529	126.516	106.478	32.061	- 121.797	- 44.649	6.098
1700	25.563	128.065	107.703	34.616	- 121.497	- 39.835	5.121
1800	25.591	129.527	108.875	37.174	- 121.198	- 35.042	4.254
1900	25.615	130.911	109.999	39.734	- 120.902	- 30.260	3.481
2000	25.636	132.226	111.077	42.296	- 120.611	- 25.502	2.787
2100	25.654	133.477	112.114	44.861	- 120.319	- 20.752	2.160
2200	25.670	134.671	113.113	47.427	- 120.034	- 16.018	1.591
2300	25.683	135.812	114.075	49.995	- 119.751	- 11.296	1.073
2400	25.695	136.905	115.004	52.564	- 119.472	- 6.585	.600
2500	25.706	137.955	115.901	55.134	- 119.196	- 1.887	.165
2600	25.716	138.963	116.769	57.705	- 118.924	2.800	- .235
2700	25.724	139.934	117.609	60.277	- 118.655	7.474	- .605
2800	25.732	140.869	118.423	62.850	- 118.391	12.143	- .948
2900	25.739	141.772	119.213	65.423	- 118.129	16.801	- 1.266
3000	25.745	142.645	119.979	67.997	- 117.872	21.448	- 1.562
3100	25.750	143.489	120.724	70.572	- 117.618	26.091	- 1.839
3200	25.756	144.307	121.448	73.148	- 117.368	30.720	- 2.098
3300	25.760	145.100	122.153	75.723	- 117.121	35.342	- 2.340
3400	25.764	145.869	122.839	78.300	- 116.878	39.958	- 2.568
3500	25.768	146.615	123.508	80.876	- 116.639	44.569	- 2.783
3600	25.772	147.341	124.160	83.453	- 116.403	49.170	- 2.985
3700	25.775	148.048	124.796	86.031	- 116.169	53.766	- 3.176
3800	25.778	148.735	125.417	88.608	- 115.940	58.358	- 3.356
3900	25.781	149.405	126.024	91.186	- 115.714	62.944	- 3.527
4000	25.784	150.057	126.616	93.764	- 115.491	67.515	- 3.689
4100	25.786	150.694	127.196	96.343	- 115.271	72.088	- 3.842
4200	25.788	151.316	127.763	98.922	- 115.054	76.659	- 3.989
4300	25.790	151.922	128.318	101.501	- 114.840	81.221	- 4.128
4400	25.792	152.515	128.861	104.080	- 114.629	85.781	- 4.261
4500	25.794	153.095	129.393	106.659	- 114.421	90.331	- 4.387
4600	25.796	153.662	129.914	109.239	- 114.215	94.878	- 4.508
4700	25.798	154.217	130.426	111.818	- 114.012	99.426	- 4.623
4800	25.799	154.760	130.927	114.398	- 113.814	103.960	- 4.733
4900	25.801	155.292	131.419	116.978	- 113.615	108.498	- 4.839
5000	25.802	155.813	131.901	119.558	- 113.420	113.029	- 4.940
5100	25.803	156.324	132.375	122.138	- 113.230	117.552	- 5.037
5200	25.804	156.825	132.841	124.719	- 113.039	122.073	- 5.130
5300	25.805	157.317	133.298	127.299	- 112.851	126.600	- 5.220
5400	25.806	157.799	133.747	129.880	- 112.667	131.108	- 5.306
5500	25.807	158.273	134.189	132.461	- 112.483	135.630	- 5.389
5600	25.808	158.738	134.623	135.041	- 112.304	140.132	- 5.469
5700	25.809	159.194	135.050	137.622	- 112.127	144.642	- 5.546
5800	25.810	159.643	135.470	140.203	- 111.950	149.148	- 5.620
5900	25.811	160.084	135.884	142.784	- 111.776	153.645	- 5.691
6000	25.812	160.518	136.291	145.365	- 111.606	158.138	- 5.760

Mar. 31, 1963; Dec. 31, 1963

PHOSPHORYL BROMIDE ($POBr_3$) (IDEAL GAS) MOL. WT. = 286.723

Point Group C_{3v}

$\Delta H_{f\ 0}^\circ$ = [-87] kcal. mole^{-1}

$S^\circ_{298.15}$ = 85.978 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-93] kcal. mole^{-1}

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
118 (2)	340 (1)
173 (1)	488 (2)
267 (2)	1261 (1)

Bond Distance: P-O = 1.41 ± 0.07 Å P-Br = 2.06 ± 0.03 Å

Bond Angle: Br-P-Br = 108° ± 3° $\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = 2.2602 \times 10^{-112}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ of $POBr_3(g)$ was calculated from the heat of formation of the crystal and the heat of sublimation. The heat of sublimation was obtained by combining the ΔH_v and an estimated ΔH_m. The heat of formation of the crystal was derived from the heats observed for the reaction: $POBr_3(c) + (n+3)H_2O(l) \rightarrow [H_3PO_4+3HBr]$ in $nH_2O(l)$. The data used in these calculations may be summarized as follows:

Data	Source
$\Delta H^\circ_{f\ 298.15}$(water solutions)$H_3PO_4$	Obtained graphically from W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).
$\Delta H^\circ_{f\ 298.15}$(water solutions)HBr	Obtained graphically from, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds., Circular 500.
$\Delta H^\circ_{f\ 298.15}$(liquid)$H_2O$ = -68.3174 kcal. mole^{-1}	"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.
$\Delta H^\circ_{f\ 298.15}$(crystal)$POBr_3$ = -109.1 kcal. mole^{-1}	Recalculated from Heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).
$\Delta H_{m\ 298.15}$ = [3.7] kcal. mole^{-1}	Estimated from comparison with $POCl_3$.
$\Delta H_{v\ 298.15}$ = [12.1] kcal. mole^{-1}	Estimated from the ΔH_v at T_b (10.6 kcal. mole^{-1} at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Heat Capacity and Entropy.

The molecular constants used were calculated from electron diffraction measurements by J. H. Secrist and L. O. Brockway, J. Am. Chem. Soc. 66, 1941 (1944). The calculated moments are $I_A = I_B = 8.68174 \times 10^{-38}$ g. cm.^{2} and $I_C = 1.474471 \times 10^{-37}$ g. cm.^{2}

From the Raman spectra of $POBr_3$ the vibrational frequencies were measured and assigned by H. Gerding and M. van Driel, Rec. trav. Chim. 61, 419 (1942). The Raman spectra was studied and the vibrational frequencies were listed by M. L. Delwaulle and F. Francois, Compt. Rend. 220, 817 (1945). The frequencies may also be found in Compt. Rend. 222, 550 (1946) and J. Chim. Phys. 46, 87 (1949) by Delwaulle and Francois.

Phosphorus Tribromide (PBr_3)

(Ideal Gas) Mol. Wt. = 270.723

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.243	-25.293	-25.293	INFINITE
100	13.090	65.896	98.214	-3.232	-25.374	-29.884	65.308
200	16.674	76.227	84.829	-1.721	-25.038	-34.190	37.359
298	18.173	83.206	83.206	.000	-30.700	-37.611	27.568
300	18.191	83.318	83.206	.034	-30.725	-37.653	27.429
400	18.863	88.655	83.929	1.890	-41.761	-37.697	20.596
500	19.206	92.905	85.314	3.796	-41.751	-36.684	16.034
600	19.402	96.426	86.881	5.727	-41.753	-35.671	12.992
700	19.523	99.427	88.464	7.674	-41.779	-34.656	10.820
800	19.603	102.039	90.001	9.630	-62.249	-38.946	10.639
900	19.659	104.352	91.470	11.593	-62.069	-36.043	8.752
1000	19.699	106.425	92.863	13.561	-61.890	-33.160	7.247
1100	19.729	108.304	94.183	15.533	-61.713	-30.297	6.019
1200	19.751	110.022	95.432	17.507	-61.536	-27.449	4.999
1300	19.769	111.603	96.616	19.483	-61.361	-24.613	4.138
1400	19.783	113.069	97.740	21.461	-61.188	-21.794	3.402
1500	19.795	114.434	98.808	23.440	-61.017	-18.986	2.766
1600	19.804	115.712	99.825	25.420	-60.847	-16.190	2.211
1700	19.812	116.913	100.795	27.400	-60.680	-13.402	1.723
1800	19.818	118.045	101.722	29.382	-60.513	-10.628	1.290
1900	19.824	119.117	102.610	31.364	-60.347	-7.858	.904
2000	19.829	120.134	103.461	33.347	-60.186	-5.104	.558
2100	19.833	121.102	104.278	35.330	-60.024	-2.353	.245
2200	19.836	122.024	105.064	37.313	-59.865	.390	-.039
2300	19.839	122.906	105.821	39.297	-59.708	3.125	-.297
2400	19.842	123.751	106.550	41.281	-59.553	5.854	-.533
2500	19.844	124.561	107.254	43.265	-59.398	8.578	-.750
2600	19.847	125.339	107.935	45.250	-59.247	11.293	-.949
2700	19.848	126.088	108.594	47.235	-59.096	14.001	-1.133
2800	19.850	126.810	109.231	49.220	-58.949	16.707	-1.304
2900	19.852	127.506	109.850	51.205	-58.801	19.407	-1.463
3000	19.853	128.180	110.450	53.190	-58.656	22.101	-1.610
3100	19.854	128.831	111.032	55.175	-58.514	24.793	-1.748
3200	19.855	129.461	111.598	57.161	-58.372	27.476	-1.876
3300	19.856	130.072	112.149	59.146	-58.233	30.155	-1.997
3400	19.857	130.665	112.685	61.132	-58.095	32.831	-2.110
3500	19.858	131.240	113.207	63.118	-57.959	35.506	-2.217
3600	19.859	131.800	113.715	65.104	-57.826	38.171	-2.317
3700	19.860	132.344	114.212	67.090	-57.692	40.836	-2.412
3800	19.860	132.873	114.696	69.076	-57.562	43.499	-2.502
3900	19.861	133.389	115.168	71.062	-57.434	46.161	-2.587
4000	19.862	133.892	115.630	73.048	-57.307	48.808	-2.667
4100	19.862	134.383	116.082	75.034	-57.182	51.459	-2.743
4200	19.863	134.861	116.523	77.020	-57.059	54.111	-2.816
4300	19.863	135.329	116.955	79.007	-56.938	56.755	-2.884
4400	19.863	135.785	117.378	80.993	-56.818	59.402	-2.950
4500	19.864	136.232	117.792	82.979	-56.701	62.040	-3.013
4600	19.864	136.668	118.198	84.966	-56.584	64.675	-3.073
4700	19.865	137.096	118.595	86.952	-56.469	67.315	-3.130
4800	19.865	137.514	118.985	88.939	-56.359	69.942	-3.184
4900	19.865	137.923	119.367	90.925	-56.247	72.577	-3.237
5000	19.866	138.325	119.742	92.912	-56.138	75.206	-3.287
5100	19.866	138.718	120.111	94.898	-56.033	77.826	-3.335
5200	19.866	139.104	120.472	96.885	-55.927	80.449	-3.381
5300	19.866	139.482	120.827	98.871	-55.824	83.075	-3.425
5400	19.867	139.854	121.176	100.858	-55.723	85.689	-3.468
5500	19.867	140.218	121.519	102.845	-55.622	88.315	-3.509
5600	19.867	140.576	121.856	104.831	-55.526	90.925	-3.548
5700	19.867	140.928	122.188	106.818	-55.430	93.544	-3.586
5800	19.867	141.273	122.514	108.805	-55.335	96.157	-3.623
5900	19.868	141.613	122.835	110.792	-55.243	98.766	-3.658
6000	19.868	141.947	123.150	112.778	-55.153	101.370	-3.692

Dec. 31, 1963

PHOSPHORUS TRIBROMIDE (PBr_3) (IDEAL GAS) MOL. WT. = 270.723

Point Group C_{3v}

$S^\circ_{298.15}$ = 83.206 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -25.3 ± 1.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -30.7 ± 1.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
392 (1)	392.2 (2)
161.3 (1)	115.7 (2)

Bond Distance: P-Br = 2.20 ± 0.03 Å

Bond Angle: Br-P-Br = 106° ± 3°

$\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C$ = 1.1897 X 10^{-111} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation of PBr_3 gas from white (α) phosphorus, -34.9 kcal. mole^{-1}, was obtained by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953). This was changed from white (α) to the red (V) phosphorus reference state to give the value used in this table (-30.7 kcal. mole^{-1}). To obtain their value (-34.9 kcal. mole^{-1}), Charnley and Skinner measured the heat of formation of the liquid, and combined it and their estimate of the liquid enthalpy with the heat of vaporization (9.5 kcal. mole^{-1}) calculated by M. Van Driel and H. Gerding, Rec. Trav. Chem. 60, 943 (1941). For the liquid heat of formation Charnley and Skinner observed the ΔH°_r = -67.2 ± 0.6 kcal. mole^{-1} for $PBr_3(l) + (n+3)H_2O(l) \rightarrow [H_3PO_3 + 3HBr]$ in $nH_2O(l)$. Van Driel and Gerding measured the vapor pressure over $PBr_3(l)$ and calculated the heat of vaporization with the aid of a modified Clapeyron equation. The uncertainties on the heats of formation are estimates.

Heat Capacity and Entropy.

Q. Williams and W. Gordy, Phys. Rev. 79, 225 (1950) have reported moments of inertia from the microwave spectrum of PBr_3. From this data D. H. Whiffen in "Tables of Interatomic Distances and Configuration in Molecules and Ions", Scientific Editor, L. E. Sutton, Special Publication No. 11, The Chemical Society (London) 1958, has calculated the selected molecular constants. From these constants the principal moments of inertia were calculated as $I_A = I_B$ = 8.5214 X 10^{-38} g. cm.^{2} and I_C = 1.6383 X 10^{-37} g. cm.^{2}

M. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941) have reported P-Br = 2.23 ± 0.04 Å and the angle P-Br-P = 100° ± 2°. S. M. Swingle has measured P-Br = 2.18 ± 0.03 Å and the angle P-Br-P = 101.5° ± 1.5°. The work of Swingle was reported in a private communication from L. Pauling and V. Schomaker, California Institute of Technology to P. W. Allen and L. E. Sutton, Acta. Cryst. 3, 46 (1950). Swingle's data as well as that of Lister and Sutton was obtained by electron diffraction. The 106° angle was selected since 101.5° and 100° give imaginary force constants with the ranges allowed for the type A, 392 cm.$^{-1}$ frequency and the form of the potential function assumed by P. W. Davis and R. A. Oetjen, J. Molecular Spec. 2, 253 (1958).

The vibrational frequencies were measured and assigned in the infrared by Davis and Oetjen. Raman measurements and assignments by J. Cabannes and A. Rausset, Ann. Phys. (Paris) 19, 229 (1933) were also listed by M. L. Delwaulle, Compt. Rend. 222, 1391 (1946) and Compt. Rend. 224, 389 (1947). The Raman assignments were as follows: type A, 380 cm.$^{-1}$ and 162 cm.$^{-1}$ and type E, 400 cm.$^{-1}$ and 116 cm.$^{-1}$.

Thiophosphoryl Bromide ($PSBr_3$)

(Ideal Gas) Mol. Wt. = 302.789

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-5.064	-57.361	-57.361	INFINITE
100	15.556	67.925	107.578	-3.965	-57.519	-61.935	135.352
200	20.462	80.447	91.099	-2.131	-58.152	-66.123	72.253
298	22.690	89.084	89.084	.000	-63.000	-69.389	50.861
300	22.719	89.225	89.085	.042	-63.026	-69.427	50.575
400	23.861	95.934	89.992	2.377	-74.683	-69.261	37.841
500	24.491	101.333	91.738	4.797	-75.097	-67.858	29.659
600	24.868	105.834	93.723	7.267	-75.417	-66.380	24.178
700	25.109	109.687	95.735	9.767	-75.690	-64.828	20.239
800	25.270	113.051	97.693	12.286	-109.422	-69.838	19.078
900	25.384	116.034	99.569	14.819	-109.110	-64.908	15.761
1000	25.467	118.713	101.351	17.362	-108.798	-60.012	13.115
1100	25.529	121.144	103.042	19.912	-108.485	-55.151	10.957
1200	25.577	123.367	104.644	22.467	-108.171	-50.316	9.163
1300	25.614	125.416	106.164	25.027	-107.858	-45.504	7.650
1400	25.644	127.315	107.608	27.590	-107.546	-40.720	6.356
1500	25.668	129.085	108.982	30.155	-107.236	-35.960	5.239
1600	25.688	130.743	110.290	32.723	-106.927	-31.217	4.264
1700	25.705	132.300	111.540	35.293	-106.619	-26.494	3.406
1800	25.718	133.770	112.734	37.864	-106.312	-21.792	2.646
1900	25.730	135.161	113.878	40.437	-106.007	-17.100	1.967
2000	25.740	136.481	114.976	43.010	-105.705	-12.433	1.359
2100	25.749	137.737	116.030	45.585	-105.404	-7.777	.809
2200	25.757	138.935	117.044	48.160	-105.106	-3.133	.311
2300	25.763	140.080	118.021	50.736	-104.809	1.494	-.142
2400	25.769	141.177	118.963	53.313	-104.514	6.111	-.556
2500	25.774	142.229	119.873	55.890	-104.220	10.716	-.937
2600	25.779	143.240	120.752	58.467	-103.929	15.306	-1.287
2700	25.783	144.213	121.603	61.045	-103.640	19.884	-1.609
2800	25.786	145.150	122.428	63.624	-103.354	24.454	-1.909
2900	25.789	146.055	123.227	66.203	-103.067	29.015	-2.187
3000	25.792	146.930	124.002	68.782	-102.784	33.565	-2.445
3100	25.795	147.775	124.756	71.361	-102.503	38.107	-2.686
3200	25.797	148.594	125.488	73.941	-102.224	42.637	-2.912
3300	25.800	149.388	126.200	76.521	-101.946	47.156	-3.123
3400	25.802	150.159	126.894	79.101	-101.671	51.672	-3.321
3500	25.803	150.906	127.569	81.681	-101.399	56.178	-3.508
3600	25.805	151.633	128.228	84.261	-101.128	60.674	-3.683
3700	25.807	152.340	128.870	86.842	-100.859	65.166	-3.849
3800	25.808	153.029	129.496	89.423	-100.592	69.651	-4.006
3900	25.809	153.699	130.108	92.004	-100.328	74.130	-4.154
4000	25.811	154.353	130.706	94.585	-100.065	78.596	-4.294
4100	25.812	154.990	131.291	97.166	-99.804	83.058	-4.427
4200	25.813	155.612	131.863	99.747	-99.547	87.520	-4.554
4300	25.814	156.219	132.422	102.328	-99.290	91.968	-4.674
4400	25.815	156.813	132.970	104.910	-99.036	96.417	-4.789
4500	25.816	157.393	133.506	107.491	-98.785	100.856	-4.898
4600	25.816	157.960	134.031	110.073	-98.534	105.286	-5.002
4700	25.817	158.516	134.547	112.654	-98.285	109.718	-5.102
4800	25.818	159.059	135.052	115.236	-98.041	114.135	-5.196
4900	25.819	159.591	135.547	117.818	-97.796	118.561	-5.288
5000	25.819	160.113	136.033	120.400	-97.555	122.972	-5.375
5100	25.820	160.624	136.510	122.982	-97.318	127.376	-5.458
5200	25.820	161.126	136.979	125.564	-97.079	131.779	-5.538
5300	25.821	161.618	137.439	128.146	-96.843	136.182	-5.615
5400	25.821	162.100	137.891	130.728	-96.611	140.572	-5.689
5500	25.822	162.574	138.336	133.310	-96.379	144.969	-5.760
5600	25.822	163.039	138.773	135.892	-96.152	149.351	-5.828
5700	25.823	163.496	139.203	138.475	-95.926	153.735	-5.894
5800	25.823	163.945	139.625	141.057	-95.700	158.114	-5.958
5900	25.823	164.387	140.041	143.639	-95.477	162.483	-6.018
6000	25.824	164.821	140.451	146.222	-95.258	166.853	-6.077

March 31, 1963

THIOPHOSPHORYL BROMIDE ($PSBr_3$) (IDEAL GAS) MOL. WT. = 302.789

Point Group C_{3v}

$S^\circ_{298.15}$ = 89.084 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\,0}$ = [-57] kcal. mole^{-1}

$\Delta H^\circ_{f\,298.15}$ = [-63] kcal. mole^{-1}

<u>Vibrational Frequencies and Degeneracies</u>

ω, cm.$^{-1}$
299 (1)
438 (2)
718 (1)
115 (2)
165 (1)
179 (2)

Bond Distance: P-Br = 2.13 ± 0.03 Å P-S = 1.89 ± 0.06 Å

Bond Angle: Br-P-Br = 106° ± 3° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 1.8780 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\,298.15}$ of $PSBr_3(g)$ was calculated from the $\Delta H^\circ_{f\,298.15}$ of $POBr_3(g)$ and estimated strengths for P-S and P-O bonds.

The difference in the P-S and P-O bond strengths was assumed to be the same for $POF_3 - PSF_3$ and $POBr_3 - PSBr_3$. For the P-S bond strength in PSF_3, C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia, estimated 91 kcal., from a consideration of unpublished data. The P-O bond was estimated to be 115 kcal. by E. Neale and L. T. D. Williams, J. Chem. Soc. 2485 (1955) and E. Neale, L. T. D. Williams, and V. T. Moores, J. Chem. Soc., 422 (1956).

The $\Delta H^\circ_{f\,298.15}$ of $POBr_3(g)$, [-93] kcal. mole^{-1}, was taken from the March 31, 1963, JANAF Table. The $\Delta H^\circ_{f\,298.15}$ of O(g) and S(g) were taken from June 30, 1962, and March 31, 1961, JANAF Tables.

Heat Capacity and Entropy.

The molecular constants were determined from electron diffraction data by J. H. Secrist and L. O. Brockway, J. Am. Chem. Soc. 66, 1941 (1944). The principal moments of inertia calculated from these constants were $I_A = I_B = 1.105941 \times 10^{-37}$ g. cm.^{2}, and $I_C = 1.535429 \times 10^{-37}$ g. cm.^{2}

The vibrational frequencies obtained from the Raman spectra of $PSBr_3$ were reported by M. L. Delwaulle and F. Francois, Compt. Rend. 224, 1422 (1947).

Titanium Tribromide ($TiBr_3$)

(Crystal) GFW = 287.627

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.490	- 127.050	- 127.050	INFINITE
100	16.887	17.719	63.209	- 4.549	- 127.245	- 126.889	277.316
200	23.379	32.802	44.337	- 2.307	- 127.217	- 126.494	138.226
298	24.308	42.171	42.171	.000	- 131.500	- 125.618	92.080
300	24.325	42.321	42.171	.045	- 131.516	- 125.580	91.485
400	25.291	49.424	43.134	2.516	- 142.022	- 121.415	66.338
500	27.416	55.287	44.992	5.148	- 141.361	- 116.337	50.851
600	29.597	60.511	47.150	8.017	- 140.490	- 111.410	40.581
700	32.794	65.350	49.408	11.159	- 139.373	- 106.649	33.297
800	35.200	69.900	51.688	14.570	- 138.017	- 102.064	27.883
900	36.300	74.110	53.949	18.145	- 136.525	- 97.658	23.715
1000	37.446	77.995	56.162	21.833	- 134.951	- 93.423	20.418
1100	38.500	81.614	58.313	25.631	- 133.294	- 89.350	17.752
1200	39.463	85.006	60.397	29.530	- 132.502	- 85.392	15.552
1300	40.333	88.199	62.414	33.520	- 130.583	- 81.543	13.709
1400	41.113	91.217	64.365	37.594	- 128.598	- 77.846	12.152
1500	41.800	94.078	66.251	41.740	- 126.559	- 74.293	10.824

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TRIBROMIDE ($TiBr_3$) (CRYSTAL) GFW = 287.627

ΔHf°_0 = -127.0 ± 2.0 kcal/mol

$S^\circ_{298.15}$ = 42.2 ± 0.8 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -131.5 ± 2.0 kcal/mol

Tt = 179.9°K

ΔHt° = 0 kcal/mol

Ts = 1067.2°K

ΔHs° = 33.165 kcal/mol

Heat of Formation

The heat of formation of $TiBr_3(c)$ is based on the vapor pressure data reported by Hall and Blocher (1) for the process $1/2Hg_2Br_2(c) + TiBr_3(c) = TiBr_4(g) + Hg(\ell)$ over the temperature range 430 to 546°K. Second and third law analyses of these data give values for the heat of reaction of 24.2 ± 0.3 and 24.4 kcal/mol, respectively, for seventy three points, with ten points rejected due to failure of a statistical test. The third law drift in the data is calculated as 0.6 ± 0.6eu. The third law value of 24.4 kcal/mol is combined with the JANAF heats of formation of $TiBr_4(g)$ and $Hg_2Br_2(c)$ to obtain the adopted heat of formation.

Heat Capacity and Entropy

The heat capacity and entropy of $TiBr_3(c)$ have been measured over the temperature range 51° to 800°K by King et al. (2). Heat capacities above 800°K are estimated from graphical extrapolation. The value of S°_{298} is derived from these data, based on S°_{51} = 8.60 eu. The value of S°_{51} is estimated from a Debye-Einstein extrapolation of the measured heat capacities, the equation being $C_p = D(70.0/T) + E(120/T) + 2E(306/T)$. It is assumed that all electronic entropy is contained within the measured and extrapolated heat capacities.

Transition Data

A second order transition at 179.9°K was observed by King et al. (2). The heat capacity at this temperature is in excess of 56.1 gibbs/mol. King et al. measured the value of $H^\circ_{188} - H^\circ_{160}$ as 0.773 kcal/mol.

Heat of Sublimation

The heat of sublimation is claculated from the heats of formation of $TiBr_3(c)$ and $TiBr_3(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which ΔGr = 0 for the process $TiBr_3(c) = TiBr_3(g)$.

References

1. E. H. Hall and J. M. Blocher, Jr., J. Electrochem. Soc. 105, 40 (1958).
2. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI5799, 1961.

Titanium Tribromide ($TiBr_3$)

(Ideal Gas) GFW = 287.627

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.331	-83.991	-83.991	INFINITE
100	13.160	68.156	101.187	-3.303	-84.099	-88.787	194.043
200	17.023	78.568	87.460	-1.778	-84.788	-93.219	101.865
298	18.961	85.777	85.777	.000	-89.600	-96.719	70.897
300	18.985	85.895	85.776	.035	-89.625	-96.762	70.491
400	19.862	91.493	86.535	1.983	-100.655	-96.875	52.930
500	20.271	95.974	87.990	3.992	-100.617	-95.936	41.934
600	20.462	99.689	89.639	6.030	-100.577	-95.004	34.605
700	20.547	102.851	91.306	8.081	-100.551	-94.078	29.372
800	20.579	105.597	92.925	10.138	-100.549	-93.154	25.448
900	20.587	108.021	94.470	12.196	-100.573	-92.227	22.396
1000	20.585	110.191	95.936	14.255	-100.629	-91.297	19.953
1100	20.579	112.152	97.322	16.313	-100.712	-90.360	17.953
1200	20.571	113.942	98.634	18.371	-101.761	-89.376	16.278
1300	20.562	115.589	99.875	20.427	-101.776	-88.343	14.852
1400	20.553	117.112	101.053	22.483	-101.809	-87.309	13.630
1500	20.544	118.530	102.171	24.538	-101.861	-86.273	12.570
1600	20.535	119.855	103.235	26.592	-101.933	-85.230	11.642
1700	20.526	121.100	104.250	28.645	-102.028	-84.183	10.822
1800	20.518	122.273	105.219	30.697	-102.147	-83.132	10.094
1900	20.509	123.382	106.146	32.748	-102.291	-82.070	9.440
2000	20.501	124.434	107.034	34.799	-106.910	-80.849	8.835
2100	20.494	125.434	107.887	36.849	-107.081	-79.541	8.278
2200	20.487	126.387	108.706	38.898	-107.256	-78.227	7.771
2300	20.480	127.298	109.495	40.946	-107.433	-76.902	7.307
2400	20.474	128.169	110.255	42.994	-107.612	-75.569	6.882
2500	20.468	129.005	110.989	45.041	-107.794	-74.231	6.489
2600	20.463	129.808	111.697	47.088	-107.977	-72.885	6.127
2700	20.458	130.580	112.382	49.134	-108.162	-71.534	5.790
2800	20.453	131.324	113.045	51.179	-108.351	-70.173	5.477
2900	20.449	132.041	113.688	53.224	-108.541	-68.803	5.185
3000	20.445	132.735	114.312	55.269	-108.732	-67.431	4.912
3100	20.441	133.405	114.917	57.313	-108.927	-66.049	4.656
3200	20.437	134.054	115.505	59.357	-109.122	-64.665	4.416
3300	20.433	134.683	116.076	61.401	-109.320	-63.274	4.190
3400	20.429	135.293	116.633	63.444	-109.519	-61.875	3.977
3500	20.425	135.885	117.174	65.486	-109.722	-60.470	3.776
3600	20.421	136.460	117.702	67.529	-211.552	-58.798	3.570
3700	20.417	137.020	118.217	69.571	-211.728	-54.554	3.222
3800	20.413	137.564	118.719	71.612	-211.921	-50.305	2.893
3900	20.409	138.094	119.209	73.653	-212.129	-46.044	2.580
4000	20.405	138.611	119.687	75.694	-212.352	-41.787	2.283
4100	20.401	139.115	120.155	77.734	-212.590	-37.520	2.000
4200	20.397	139.606	120.612	79.774	-212.841	-33.248	1.730
4300	20.392	140.086	121.060	81.814	-213.107	-28.968	1.472
4400	20.388	140.555	121.497	83.853	-213.385	-24.682	1.226
4500	20.383	141.013	121.926	85.891	-213.677	-20.390	.990
4600	20.379	141.461	122.346	87.929	-213.980	-16.088	.764
4700	20.374	141.899	122.757	89.967	-214.296	-11.780	.548
4800	20.370	142.328	123.160	92.004	-214.624	-7.473	.340
4900	20.365	142.748	123.556	94.041	-214.963	-3.155	.141
5000	20.360	143.159	123.944	96.077	-215.311	1.175	-.051
5100	20.355	143.562	124.325	98.113	-215.671	5.504	-.236
5200	20.350	143.958	124.698	100.148	-216.039	9.846	-.414
5300	20.346	144.345	125.065	102.183	-216.416	14.194	-.585
5400	20.341	144.726	125.426	104.217	-216.804	18.547	-.751
5500	20.336	145.099	125.780	106.251	-217.197	22.915	-.911
5600	20.331	145.465	126.129	108.284	-217.601	27.276	-1.064
5700	20.326	145.825	126.471	110.317	-218.010	31.659	-1.214
5800	20.321	146.178	126.808	112.349	-218.427	36.044	-1.358
5900	20.316	146.526	127.139	114.381	-218.850	40.433	-1.498
6000	20.311	146.867	127.465	116.413	-219.280	44.822	-1.633

June 30, 1964; June 30, 1968

TITANIUM TRIBROMIDE ($TiBr_3$) (IDEAL GAS) GFW = 287.627

Point Group C_{3v}

$\Delta Hf^\circ_0 = -84.0 \pm 2.5$ kcal/mol

$S^\circ_{298.15} = [85.8 \pm 1.2]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -89.6 \pm 2.5$ kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[380] (1)	[427] (2)
[162] (1)	[103] (2)

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [100°] σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = [1.70 \times 10^{-111}]\ g^3\ cm^6$

Heat of Formation

The heat of formation of $TiBr_3$(g) is calculated from the heat of sublimation of $TiBr_3$(c). A tentative equation for the vapor pressure of $TiBr_3$(c) was reported by Hall and Blocher (1). Second and third law analyses of the equation over the temperature range 700° to 900°K give values of ΔHs°_{298} of 45.2 and 41.9 kcal/mol, respectively, with a third law drift of -4.2 eu. The chosen value of ΔHf°_{298} is based on the third law ΔHs°_{298}.

Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiCl_4$, $TiCl_3$ and $TiBr_4$. The pyramidal bond angle is estimated by asssuming that $TiBr_3$(g) is similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 9.76 \times 10^{-38}$ g cm^2 and $I_C = 1.78$ g cm^2. The vibraional frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3} (2).

References

1. E. H. Hall and J. M. Blocher, J. Phys. Chem. 63, 1525 (1959).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Tribromide ($ZrBr_3$)

(Crystal) Mol. Wt. = 330.968

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 5.347	- 147.242	- 147.242	INFINITE
100	17.787	17.852	61.092	- 4.324	- 147.433	- 146.950	321.144
200	22.283	31.907	43.257	- 2.270	- 147.658	- 146.380	159.949
298	23.777	41.122	41.122	.000	- 152.000	- 145.213	106.439
300	23.796	41.269	41.122	.044	- 152.016	- 145.170	105.751
400	24.500	48.226	42.066	2.464	- 162.591	- 140.692	76.867
500	24.800	53.733	43.868	4.932	- 162.119	- 135.273	59.125
600	25.000	58.274	45.902	7.423	- 161.664	- 129.946	47.331
700	25.100	62.136	47.952	9.929	- 161.222	- 124.696	38.930
800	25.200	65.495	49.939	12.444	- 160.789	- 119.508	32.646
900	25.300	68.469	51.836	14.969	- 160.356	- 114.373	27.772
1000	25.350	71.137	53.635	17.502	- 159.927	- 109.285	23.883
1100	25.370	73.554	55.338	20.038	- 159.514	- 104.242	20.710
1200	25.390	75.763	56.949	22.576	- 160.069	- 99.187	18.064
1300	25.410	77.796	58.476	25.116	- 159.660	- 94.130	15.824
1400	25.420	79.679	59.924	27.658	- 159.260	- 89.105	13.909
1500	25.430	81.434	61.300	30.200	- 158.867	- 84.109	12.254
1600	25.440	83.075	62.610	32.744	- 158.482	- 79.135	10.809
1700	25.450	84.618	63.860	35.288	- 158.106	- 74.188	9.537
1800	25.460	86.073	65.054	37.834	- 157.736	- 69.263	8.409
1900	25.470	87.449	66.197	40.380	- 157.373	- 64.356	7.402
2000	25.480	88.756	67.292	42.928	- 157.021	- 59.473	6.499

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TRIBROMIDE ($ZrBr_3$) (CRYSTAL) MOL. WT. = 330.968

$\Delta H_f^\circ{}_0$ = [-147] kcal. mole^{-1}

$S^\circ{}_{298.15}$ = [41.12] cal. mole^{-1} deg.$^{-1}$

$\Delta H_f^\circ{}_{298.15}$ = [-152] kcal. mole^{-1}

T_s = [1100]°K.

$\Delta H_s^\circ{}_{298.15}$ = [49] kcal. mole^{-1}

Heat of Formation.

E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956), studied the reaction $Zr(c) + 3ZrBr_4(g) = 4ZrBr_3(c)$ in the temperature range 473 to 973°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, for a series of temperatures, as a function of the reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature, the equilibrium constant was assumed to be 1, and $\Delta H_{r\ 298}$ accordingly calculated. These values and the heat of formation of $ZrBr_4(g)$ [see $ZrBr_4$ table] were used to compute a series of values for the standard heat of formation of $ZrBr_3(c)$. The following table gives representative values at four temperatures.

T(°K.)	K_p	$\Delta H_r^\circ{}_{298}$	$\Delta H_f^\circ{}_{298.15}$ [$ZrBr_3(c)$]
500	1	-70.26 kcal. mole^{-1}	-132.8 kcal. mole^{-1}
700	1	-96.48 kcal. mole^{-1}	-139.3 kcal. mole^{-1}
900	1	-121.75 kcal. mole^{-1}	-145.6 kcal. mole^{-1}
1100	1	-146.28 kcal. mole^{-1}	-151.8 kcal. mole^{-1}

If one assumes an initial pressure of from 5 to 10 atm. for $ZrBr_4$ and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of $ZrBr_4$ to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate about 82% reaction at 973°K. It was assumed that around 1100°K. the equilibrium constant attains a value of 1 giving -152 kcal. mole^{-1} for the heat of formation of $ZrBr_3(c)$ at 298.15°K. The limits of error were taken to be ±16 kcal. mole^{-1} which corresponds to a ±500° temperature spread in the above table.

A second law calculation of their data was carried out but the results are of doubtful value in view of the uncertainty in the attainment of equilibrium at the lower temperatures.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $ZrBr_4(c)$ [see $ZrBr_4(c)$ table]. The values for Θ_D and Θ_E were taken to be the same as those estimated for $ZrBr_4(c)$. The internal contribution was obtained from the estimated $ZrBr_3$ vibrational frequencies and the anharmonicity factor "a" was taken to be 2.5×10^{-3}. The specific heat above 300°K. was obtained by graphical extrapolation.

It was assumed, in the above estimation, that the crystalline lattice is made up of $ZrBr_3$ molecules. However, E. Holze [see R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] concluded that crystalline ZrI_3 was composed of a chain lattice of $(Zr_2I_6)_n$ units. A chain lattice of $(Zr_2Br_6)_n$ units is probably a better representation of the solid state structure of $ZrBr_3$. Until more quantitative data becomes available, however, it is felt that the above analysis gives a fair approximation to the heat capacity of $ZrBr_3$.

Temperature of Disproportionation.

As detailed in the "Heat of Formation" section, this was assumed to be 1100 ± 500°K.

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.

Zirconium Tribromide ($ZrBr_3$)
(Ideal Gas) Mol. Wt. = 330.968

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.613	- 97.508	- 97.508	INFINITE
100	14.892	69.838	104.918	- 3.508	- 97.616	- 102.333	223.637
200	18.063	81.371	90.501	- 1.826	- 98.214	- 106.829	116.732
298	18.988	88.787	88.787	.000	- 103.000	- 110.424	80.939
300	18.998	88.905	88.787	.035	- 103.025	- 110.469	80.473
400	19.365	94.427	89.538	1.956	- 114.100	- 110.681	60.470
500	19.543	98.770	90.966	3.902	- 114.149	- 109.821	48.001
600	19.642	102.342	92.573	5.862	- 114.225	- 108.949	39.683
700	19.702	105.375	94.191	7.829	- 114.322	- 108.063	33.737
800	19.742	108.009	95.757	9.802	- 114.432	- 107.162	29.274
900	19.769	110.336	97.250	11.777	- 114.548	- 106.245	25.799
1000	19.789	112.420	98.665	13.755	- 114.674	- 105.314	23.015
1100	19.803	114.306	100.002	15.735	- 114.818	- 104.373	20.736
1200	19.814	116.030	101.267	17.716	- 115.929	- 103.368	18.825
1300	19.823	117.616	102.464	19.698	- 116.079	- 102.315	17.200
1400	19.830	119.086	103.600	21.680	- 116.237	- 101.252	15.805
1500	19.835	120.454	104.678	23.663	- 116.404	- 100.176	14.595
1600	19.840	121.734	105.705	25.647	- 116.579	- 99.086	13.534
1700	19.843	122.937	106.683	27.631	- 116.763	- 97.988	12.597
1800	19.847	124.071	107.618	29.616	- 116.954	- 96.879	11.762
1900	19.849	125.145	108.513	31.601	- 117.153	- 95.756	11.014
2000	19.852	126.163	109.370	33.586	- 117.363	- 94.628	10.340
2100	19.853	127.131	110.193	35.571	- 117.579	- 93.486	9.729
2200	19.855	128.055	110.984	37.556	- 122.707	- 92.169	9.156
2300	19.857	128.938	111.745	39.542	- 122.947	- 90.774	8.625
2400	19.858	129.783	112.480	41.528	- 123.188	- 89.368	8.138
2500	19.859	130.593	113.188	43.514	- 123.431	- 87.954	7.689
2600	19.860	131.372	113.872	45.499	- 123.675	- 86.531	7.273
2700	19.861	132.122	114.535	47.486	- 123.920	- 85.099	6.888
2800	19.862	132.844	115.176	49.472	- 124.169	- 83.656	6.529
2900	19.863	133.541	115.797	51.458	- 124.417	- 82.202	6.195
3000	19.863	134.215	116.400	53.444	- 124.667	- 80.744	5.882
3100	19.864	134.866	116.985	55.431	- 124.919	- 79.276	5.589
3200	19.864	135.497	117.554	57.417	- 125.172	- 77.799	5.313
3300	19.865	136.108	118.107	59.403	- 125.428	- 76.316	5.054
3400	19.865	136.701	118.645	61.390	- 125.683	- 74.823	4.809
3500	19.866	137.277	119.169	63.376	- 125.942	- 73.323	4.578
3600	19.866	137.836	119.680	65.363	- 126.201	- 71.819	4.360
3700	19.866	138.381	120.178	67.350	- 126.461	- 70.305	4.153
3800	19.867	138.910	120.664	69.336	- 126.724	- 68.781	3.956
3900	19.867	139.426	121.139	71.323	- 126.988	- 67.250	3.768
4000	19.867	139.929	121.602	73.310	- 127.254	- 65.720	3.591
4100	19.868	140.420	122.055	75.297	- 127.521	- 64.179	3.421
4200	19.868	140.899	122.498	77.283	- 127.790	- 62.628	3.259
4300	19.868	141.366	122.931	79.270	- 128.060	- 61.072	3.104
4400	19.868	141.823	123.356	81.257	- 128.332	- 59.512	2.956
4500	19.868	142.270	123.771	83.244	- 128.605	- 57.947	2.814
4600	19.869	142.706	124.178	85.231	- 128.880	- 56.371	2.678
4700	19.869	143.134	124.577	87.217	- 129.156	- 54.788	2.548
4800	19.869	143.552	124.968	89.204	- 265.868	- 51.684	2.353
4900	19.869	143.962	125.351	91.191	- 266.202	- 47.219	2.106
5000	19.869	144.363	125.727	93.178	- 266.543	- 42.745	1.868
5100	19.869	144.756	126.097	95.165	- 266.890	- 38.270	1.640
5200	19.869	145.142	126.459	97.152	- 267.243	- 33.780	1.420
5300	19.870	145.521	126.815	99.139	- 267.602	- 29.289	1.208
5400	19.870	145.892	127.165	101.126	- 267.967	- 24.790	1.003
5500	19.870	146.257	127.509	103.113	- 268.335	- 20.281	.806
5600	19.870	146.615	127.847	105.100	- 268.710	- 15.768	.615
5700	19.870	146.966	128.179	107.087	- 269.089	- 11.249	.431
5800	19.870	147.312	128.506	109.074	- 269.471	- 6.717	.253
5900	19.870	147.652	128.828	111.061	- 269.858	- 2.184	.081
6000	19.870	147.986	129.144	113.048	- 270.248	2.347	- .085

June 30, 1964

ZIRCONIUM TRIBROMIDE ($ZrBr_3$) (IDEAL GAS) MOL. WT. = 330.968

Point Group = [C_{3v}]

$\Delta H_{f\ 0}^\circ$ = [-98] kcal. mole^{-1}

$S^\circ_{298.15}$ = [88.79] cal. mole^{-1} deg.$^{-1}$

$\Delta H_{f\ 298.15}^\circ$ = [-103] kcal. mole^{-1}

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[255] (1)
[120] (1)
[273] (2)
[95] (2)

Bond Distance: Zr-Br = [2.39] Å

Bond Angle: Br-Zr-Br = [98°]

σ = [3]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.7757×10^{-111}] gm.^{3} cm.^{6}

Heat of Formation.

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole^{-1} greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium tribromide, the heat of formation from the gaseous atoms was -329 kcal. mole^{-1} and from the elements in their standard state, -103 kcal. mole^{-1}.

Heat Capacity and Entropy.

The measured internuclear distances for the tribromides of P, As, and Sb were plotted as a function of the atomic weight of these atoms and a smooth curve was drawn through the points. The internuclear distance for $ZrBr_3$ was taken from this plot. The bond angle was assumed to be intermediate between the bond angles of $AsBr_3$ and $SbBr_3$; it was taken to be 98°. The individual moments of inertia are: $I_A = I_B = 101.408 \times 10^{-39}$ gm. cm.^{2}, I_C = 172.669 gm. cm.^{2}.

The measured vibrational frequencies for the tribromides of phosphorus, arsenic, and antimony were plotted as a function of internuclear distance. Smooth curves through these points were obtained for ω_1, ω_2, and ω_4; these curves and the estimated $ZrBr_3$ bond distance were used to obtain correlation values of ω_1, ω_2, and ω_4 for $ZrBr_3$. Force constants, assuming a valence force field and a Br-Zr-Br angle of 98°, were derived from the above values for ω_1 and ω_2. These force constants were then used to derive values for ω_3 and ω_4. By a process of successive approximation, a set of force constants was obtained which gave frequencies in good agreement with the three correlation values. The three correlation frequencies and the derived frequency were used in this table.

Iron Dibromide, Dimeric (Fe_2Br_4)

(Ideal Gas) GFW = 431.330

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-7.937	-54.569	-54.569	INFINITE
100	27.639	90.587	150.521	-5.993	-54.167	-60.359	131.915
200	30.586	110.946	126.145	-3.040	-54.400	-66.509	72.678
298	31.234	123.304	123.304	.000	-60.500	-71.674	52.538
300	31.240	123.497	123.304	.058	-60.530	-71.742	52.264
400	31.479	132.522	124.533	3.195	-75.125	-72.481	39.602
500	31.593	139.560	126.860	6.350	-75.086	-71.826	31.395
600	31.659	145.326	129.472	9.512	-75.160	-71.170	25.923
700	31.709	150.210	132.094	12.681	-75.355	-70.492	22.008
800	31.759	154.447	134.630	15.854	-75.710	-69.776	19.062
900	31.817	158.191	137.043	19.033	-76.279	-69.001	16.756
1000	31.888	161.547	139.329	22.218	-77.208	-68.147	14.894
1100	31.970	164.590	141.489	25.411	-78.569	-67.167	13.345
1200	32.063	167.376	143.532	28.612	-79.500	-66.100	12.039
1300	32.164	169.946	145.466	31.824	-79.744	-64.971	10.923
1400	32.270	172.333	147.301	35.045	-80.013	-63.824	9.963
1500	32.377	174.563	149.045	38.278	-80.302	-62.661	9.130
1600	32.482	176.656	150.706	41.521	-80.615	-61.473	8.397
1700	32.584	178.629	152.291	44.774	-81.532	-60.256	7.746
1800	32.681	180.494	153.807	48.037	-82.073	-58.989	7.162
1900	32.770	182.263	155.258	51.310	-89.978	-57.319	6.593
2000	32.850	183.946	156.651	54.591	-90.637	-55.589	6.074
2100	32.922	185.551	157.989	57.880	-91.296	-53.818	5.601
2200	32.985	187.084	159.277	61.175	-91.961	-52.018	5.167
2300	33.039	188.551	160.518	64.476	-92.630	-50.188	4.769
2400	33.084	189.958	161.716	67.783	-93.303	-48.327	4.401
2500	33.121	191.310	162.873	71.093	-93.983	-46.438	4.060
2600	33.149	192.609	163.991	74.407	-94.669	-44.523	3.743
2700	33.171	193.861	165.075	77.723	-95.363	-42.586	3.447
2800	33.185	195.068	166.124	81.041	-96.067	-40.616	3.170
2900	33.194	196.232	167.143	84.360	-96.778	-38.622	2.911
3000	33.197	197.358	168.131	87.679	-97.499	-36.605	2.667
3100	33.196	198.446	169.092	90.999	-98.231	-34.557	2.436
3200	33.190	199.500	170.026	94.318	-265.822	-29.604	2.022
3300	33.180	200.521	170.934	97.637	-265.649	-22.231	1.472
3400	33.167	201.511	171.819	100.954	-265.494	-14.856	.955
3500	33.152	202.473	172.681	104.270	-265.358	-7.488	.468
3600	33.134	203.406	173.522	107.584	-265.244	-.118	.007
3700	33.115	204.314	174.342	110.897	-265.145	7.241	-.428
3800	33.094	205.197	175.142	114.207	-265.071	14.598	-.840
3900	33.072	206.056	175.924	117.516	-265.016	21.969	-1.231
4000	33.048	206.893	176.688	120.822	-264.984	29.316	-1.602
4100	33.024	207.709	177.434	124.125	-264.973	36.677	-1.955
4200	33.000	208.504	178.165	127.426	-264.986	44.034	-2.291
4300	32.975	209.281	178.879	130.725	-265.021	51.395	-2.612
4400	32.950	210.038	179.579	134.021	-265.079	58.753	-2.918
4500	32.924	210.779	180.264	137.315	-265.161	66.107	-3.211
4600	32.899	211.502	180.935	140.606	-265.266	73.478	-3.491
4700	32.874	212.209	181.593	143.895	-265.397	80.847	-3.759
4800	32.849	212.901	182.238	147.181	-265.553	88.212	-4.016
4900	32.825	213.578	182.871	150.465	-265.733	95.583	-4.263
5000	32.801	214.241	183.492	153.746	-265.938	102.957	-4.500
5100	32.777	214.890	184.101	157.025	-266.169	110.333	-4.728
5200	32.753	215.527	184.699	160.301	-266.425	117.715	-4.947
5300	32.730	216.150	185.287	163.576	-266.704	125.114	-5.159
5400	32.708	216.762	185.864	166.848	-267.012	132.501	-5.363
5500	32.686	217.362	186.431	170.117	-267.343	139.910	-5.560
5600	32.665	217.951	186.989	173.385	-267.701	147.309	-5.749
5700	32.644	218.529	187.537	176.650	-268.084	154.725	-5.932
5800	32.623	219.096	188.077	179.914	-268.490	162.160	-6.110
5900	32.603	219.654	188.607	183.175	-268.923	169.577	-6.282
6000	32.584	220.201	189.129	186.434	-269.380	177.014	-6.448

Sept. 30, 1966

IRON DIBROMIDE, DIMERIC (Fe_2Br_4) (IDEAL GAS) GFW = 431.330

Point Group [D_{2h}]

ΔHf°_0 = [-54.6 ± 2] kcal/mol

$S^\circ_{298.15}$ = [123.3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-60.5 ± 2] kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1
0	[5]
[4450]	[5]
[6900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[110] (1)	[75] (1)	[95] (2)
[70] (1)	[100] (1)	[24] (2)
[110] (1)	[115] (1)	[190] (2)

Bond Distance: Fe-Br = [2.24] Å

Bond Angles: $Fe\text{-}Br_{bridge}\text{-}Fe$ = [90]° $Br_{bridge}\text{-}Fe\text{-}Br_{bridge}$ = [90]°

$Br\text{-}Fe\text{-}Br_{bridge}$ = [135]° σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C = [1.4498 \times 10^{-110}]\ g^3\ cm^6$

Heat of Formation.

The chemical equilibria, 622-665°K, for the reaction $Fe_2Br_4(g) = 2\ FeBr_2(g)$ were studied by R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 63, 626 (1959), using a mass spectrometer. Based on the reported partial pressures for the two species, the enthalpy change ($\Delta Hr^\circ_{298.15}$) for the reaction was evaluated by both the second and third law methods to be 40.36 ± 2.0 and 40.75 ± 0.2 kcal/mol, respectively. Using the third law ΔHr° value and $\Delta Hf^\circ_{298.15}$ ($FeBr_2$,g) = -9.9 ± 0.5 kcal/mol, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $Fe_2Br_4(g)$ was calculated as -60.5 ± 2.0 kcal/mol and was adopted.

Heat Capacity and Entropy.

The molecular structure is assumed to be planar. The two Fe atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two Br atoms. The two remaining Br atoms are situated outside the square on a straight line joining the two Fe atoms. The Fe-Br bond distance was estimated to be the same as that in the $FeBr_2(g)$ molecule. The first six vibrational frequencies were estimated by comparison with those for $K_2Br_2(g)$ calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The last three degenerate frequencies were assigned arbitrarily in order to give good second and third law agreement for the heats of dissociation of dimer to monomer. The order of the frequencies listed above is arbitrary and not related to their species types.

The electronic levels and quantum weights were estimated by comparison with those for $FeBr_2(g)$. The three principal moments of inertia are: $I_A = 6.6576 \times 10^{-38}$, $I_B = 4.3456 \times 10^{-37}$ and $I_C = 5.0113 \times 10^{-37}\ g\ cm^2$.

Lead Tetrabromide ($PbBr_4$)

(Ideal Gas) Mol. Wt. = 526.87

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 6.189	- 36.827	- 36.827	INFINITE
100	20.684	76.248	123.241	- 4.699	- 37.096	- 41.267	90.184
200	24.109	91.924	104.016	- 2.418	- 37.760	- 45.192	49.381
298	25.008	101.750	101.750	.000	- 44.000	- 48.024	35.201
300	25.018	101.905	101.751	.046	- 44.032	- 48.048	35.002
400	25.365	109.156	102.737	2.568	- 58.642	- 46.383	25.341
500	25.530	114.836	104.609	5.113	- 58.536	- 43.333	18.940
600	25.622	119.500	106.714	7.671	- 58.444	- 40.300	14.679
700	25.678	123.454	108.830	10.237	- 59.534	- 37.092	11.580
800	25.714	126.885	110.877	12.806	- 59.478	- 33.891	9.258
900	25.739	129.915	112.827	15.379	- 59.415	- 30.695	7.453
1000	25.757	132.628	114.674	17.954	- 59.346	- 27.506	6.011
1100	25.771	135.084	116.420	20.530	- 59.273	- 24.328	4.833
1200	25.781	137.327	118.070	23.108	- 59.192	- 21.153	3.852
1300	25.789	139.391	119.632	25.687	- 59.109	- 17.985	3.023
1400	25.795	141.302	121.112	28.266	- 59.027	- 14.826	2.314
1500	25.800	143.082	122.518	30.845	- 58.948	- 11.672	1.700
1600	25.804	144.747	123.856	33.426	- 58.872	- 8.522	1.164
1700	25.808	146.312	125.131	36.006	- 58.801	- 5.376	.691
1800	25.811	147.787	126.349	38.587	- 58.736	- 2.239	.272
1900	25.813	149.182	127.515	41.168	- 58.677	.901	- .104
2000	25.815	150.506	128.631	43.750	- 58.626	4.033	- .441
2100	25.817	151.766	129.703	46.331	- 101.031	8.718	- .907
2200	25.818	152.967	130.734	48.913	- 100.901	13.939	- 1.385
2300	25.820	154.115	131.725	51.495	- 100.794	19.159	- 1.820
2400	25.821	155.214	132.681	54.077	- 100.710	24.374	- 2.219
2500	25.822	156.268	133.604	56.659	- 100.651	29.583	- 2.586
2600	25.823	157.280	134.495	59.242	- 100.614	34.792	- 2.924
2700	25.824	158.255	135.357	61.824	- 100.600	39.997	- 3.237
2800	25.825	159.194	136.192	64.406	- 100.612	45.206	- 3.528
2900	25.825	160.100	137.001	66.989	- 100.641	50.416	- 3.799
3000	25.826	160.976	137.785	69.571	- 100.691	55.625	- 4.052
3100	25.826	161.823	138.547	72.154	- 100.760	60.837	- 4.289
3200	25.827	162.643	139.288	74.737	- 100.845	66.051	- 4.511
3300	25.827	163.437	140.007	77.319	- 100.947	71.266	- 4.720
3400	25.828	164.209	140.708	79.902	- 101.060	76.486	- 4.916
3500	25.828	164.957	141.390	82.485	- 101.187	81.712	- 5.102
3600	25.829	165.685	142.055	85.068	- 101.324	86.938	- 5.278
3700	25.829	166.392	142.703	87.651	- 101.468	92.169	- 5.444
3800	25.829	167.081	143.336	90.234	- 101.620	97.407	- 5.602
3900	25.829	167.752	143.953	92.816	- 101.780	102.650	- 5.752
4000	25.830	168.406	144.556	95.400	- 101.942	107.885	- 5.894
4100	25.830	169.044	145.146	97.982	- 102.110	113.132	- 6.030
4200	25.830	169.666	145.722	100.565	- 102.279	118.388	- 6.160
4300	25.830	170.274	146.286	103.148	- 102.450	123.643	- 6.284
4400	25.831	170.868	146.838	105.732	- 102.620	128.907	- 6.403
4500	25.831	171.449	147.379	108.315	- 102.791	134.167	- 6.516
4600	25.831	172.016	147.908	110.898	- 102.962	139.438	- 6.624
4700	25.831	172.572	148.427	113.481	- 103.131	144.710	- 6.729
4800	25.831	173.116	148.936	116.064	- 103.301	149.982	- 6.829
4900	25.831	173.648	149.435	118.647	- 103.467	155.261	- 6.925
5000	25.831	174.170	149.924	121.230	- 103.631	160.543	- 7.017
5100	25.832	174.682	150.405	123.813	- 103.795	165.824	- 7.106
5200	25.832	175.183	150.876	126.397	- 103.954	171.115	- 7.191
5300	25.832	175.675	151.339	128.979	- 104.111	176.412	- 7.274
5400	25.832	176.158	151.795	131.563	- 104.267	181.700	- 7.353
5500	25.832	176.632	152.242	134.146	- 104.420	187.002	- 7.430
5600	25.832	177.098	152.682	136.729	- 104.572	192.298	- 7.504
5700	25.832	177.555	153.114	139.312	- 104.723	197.601	- 7.576
5800	25.832	178.004	153.539	141.896	- 104.869	202.913	- 7.646
5900	25.832	178.446	153.958	144.479	- 105.017	208.216	- 7.712
6000	25.832	178.880	154.370	147.062	- 105.163	213.516	- 7.777

June 30, 1962

Lead Tetrabromide ($PbBr_4$) (Ideal Gas)

Mol. Wt. = 526.87

ΔH_f° 298.15 = [-44] kcal. mole^{-1}

$S^\circ_{298.15}$ = 101.8 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
207 (1)
59 (2)
231 (3)
73 (3)

Pb-Br distance = 2.54 Å Br-Pb-Br angle = 109° 28'

$I_AI_BI_C = 1.1920 \times 10^{-110}$ g.^{3} cm.^{6} $\sigma = 12$

Heat of Formation. ΔH_f° 298.15 was estimated by comparison with the value of ΔH_f° 298.15 for $PbBr_2(g)$.

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Titanium Tetrabromide ($TiBr_4$)

(Crystal) GFW = 367.536

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 6.825	- 141.655	- 141.655	INFINITE
100	22.490	28.901	83.641	- 5.474	- 141.774	- 141.893	310.107
200	28.029	46.402	60.992	- 2.918	- 142.018	- 141.925	155.089
298	31.430	58.227	58.227	.000	- 147.700	- 141.181	103.488
300	31.505	58.422	58.228	.058	- 147.719	- 141.139	102.820
400	31.974	67.612	59.479	3.253	- 161.622	- 136.049	74.333
500	31.974	74.746	61.845	6.450	- 160.837	- 129.749	56.713
600	31.974	80.576	64.496	9.648	- 160.081	- 123.603	45.022
700	31.974	85.505	67.154	12.845	- 159.356	- 117.582	36.711
800	31.974	89.774	69.721	16.043	- 158.660	- 111.662	30.505
900	31.974	93.540	72.162	19.240	- 157.995	- 105.827	25.698
1000	31.974	96.909	74.472	22.437	- 157.362	- 100.064	21.869
1100	31.974	99.956	76.652	25.635	- 156.757	- 94.363	18.748
1200	31.974	102.739	78.712	28.832	- 157.118	- 88.679	16.151
1300	31.974	105.298	80.660	32.030	- 156.444	- 83.002	13.954
1400	31.974	107.667	82.505	35.227	- 155.788	- 77.379	12.079
1500	31.974	109.873	84.257	38.424	- 155.152	- 71.801	10.461

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TETRABROMIDE ($TiBr_4$) (CRYSTAL) GFW = 367.536

ΔHf°_0 = -141.7 ± 1.1 kcal/mol

$S^\circ_{298.15}$ = 58.2 ± 1.6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -147.7 ± 1.0 kcal/mol

Tm = 311.4°K

ΔHm° = 3.08 kcal/mol

Heat of Formation

The heat of formation, ΔHf°_{298}, of $TiBr_4(c)$ has been determined calorimetrically by several investigators as follows.

Investigators	Reaction	$\Delta Hf^\circ_{298.15}$, kcal/mol
Nelson, Johnson and Prosen (1)	$Ti(c) + 2Br_2(g) = TiBr_4(c)$	-147.3 ± 1.1
Johnson, Gilliland and Prosen (2)	$TiCl_4(\ell) + 2Br_2(\ell) = TiBr_4(c) + 2Cl_2(g)$	-147.6 ± 1.3
Schlafer and Schmidtke (3)	$Ti(c) + 2Br_2(\ell) = TiBr_4(c)$	-147.7 ± 0.3
Gross, Hayman and Levi (4)	$Ti(c) + 2Br_2(\ell) = TiBr_4(c)$	-148.1 ± 0.3

The chosen value of ΔHf°_{298} is the average of these determinations. The value from the work of Nelson et al. (1) is obtained from their heat of reaction and the JANAF value for the heat of vaporization of bromine. The value obtained from Johnson et al. (2) is a combination of their heat of reaction and the JANAF value for the heat of formation of $TiCl_4(\ell)$.

Heat Capacity and Entropy

The heat capacity of $TiBr_4(c)$ has been measured over the temperature range 51° to 298°K by King et al. (5). They reported a value of 42.74 eu for $S^\circ_{298} - S^\circ_{51}$ based on their measurements. The value of S°_{51} is estimated as 15.46 eu. King et al. (5) reported an estimate of 14.75 ± 1.60 for the same quantity. The former estimate is used so that the values of ΔHs°_{298} obtained by both second and third law methods are in agreement. See $TiBr_4(g)$ table for details. The value of $H^\circ_{51} - H^\circ_0$ is estimated as 0.372 kcal/mol. This estimate is based on a Debye-Einstein extrapolation of the measured heat capacity with vibrational contributions removed.

Melting Data

The melting temperature and heat of melting were reported by King et al. (5).

References

1. R. A. Nelson, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. 62, 67 (1959).
2. W. H. Johnson, A. A. Gilliland and E. J. Prosen, J. Res. Natl. Bur. Std. 63, 161 (1959).
3. H. L. Schlafer and H. H. Schmidtke, Z. Physik. Chem. 11, 297 (1959).
4. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. 53, 1601 (1957).
5. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Titanium Tetrabromide ($TiBr_4$)

(Liquid) GFW = 367.536

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	36.300	67.918	67.918	.000	-144.681	-141.051	103.393
300	36.300	68.142	67.918	.067	-144.691	-141.027	102.738
400	36.300	78.585	69.342	3.697	-158.159	-136.975	74.840
500	36.300	86.685	72.031	7.327	-156.941	-131.822	57.620
600	36.300	93.304	75.042	10.957	-155.753	-126.911	46.227
700	36.300	98.899	78.060	14.587	-154.595	-122.197	38.152
800	36.300	103.746	80.975	18.217	-153.467	-117.646	32.139
900	36.300	108.022	83.747	21.847	-152.369	-113.234	27.497
1000	36.300	111.847	86.369	25.477	-151.303	-108.942	23.809
1100	36.300	115.306	88.845	29.107	-150.266	-104.757	20.813
1200	36.300	118.465	91.184	32.737	-150.194	-100.626	18.327
1300	36.300	121.370	93.396	36.367	-149.088	-96.540	16.230
1400	36.300	124.060	95.491	39.997	-147.999	-92.540	14.446
1500	36.300	126.565	97.480	43.627	-146.930	-88.617	12.911

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TETRABROMIDE ($TiBr_4$) (LIQUID) GFW = 367.536

$S°_{298.15}$ = 67.918 ± 1.6 gibbs/mol

$\Delta Hf°_{298.15}$ = -144.681 ± 1.0 kcal/mol

Tm = 311.4°K

ΔHm° = 3.08 kcal/mol

Tb = 504.1°K

ΔHv° = 10.80 kcal/mol

Heat of Formation

The heat of formation of $TiBr_4(\ell)$ is calculated from the heat of melting, $\Delta Hm°_{311.4}$, the heat of formation of $TiBr_4(c)$, and the values of $H°_{311.4} - H°_{298.15}$ for both crystal and liquid.

Heat Capacity and Entropy

King et al, (1) reported the heat capacity of $TiBr_4(\ell)$ between the melting point and normal boiling point, The entropy, $S°_{298}$, of $TiBr_4(\ell)$ is calculated from $\Delta Sm°_{311.4}$, the values of $S°_{311.4} - S°_{298.15}$ of both crystal and liquid and the value of $S°_{298.15}$ of $TiBr_4(c)$.

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, Tb, is taken as the point at which Kp = 1 for the reaction $TiBr_4(\ell) = TiBr_4(g)$. The heat of vaporization is calculated as the difference between ΔHf° of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $TiBr_4(g)$.

Reference

1. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Titanium Tetrabromide ($TiBr_4$)

(Ideal Gas) GFW = 367.536

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.713	-124.343	-124.343	INFINITE
100	18.359	71.735	115.405	-4.367	-124.467	-128.870	281.644
200	22.469	85.929	97.406	-2.295	-125.195	-133.008	145.345
298	24.070	95.246	95.246	.000	-131.500	-136.018	99.704
300	24.089	95.395	95.246	.045	-131.532	-136.045	99.108
400	24.793	102.434	96.201	2.493	-146.182	-134.538	73.508
500	25.148	108.008	98.025	4.992	-146.095	-131.638	57.539
600	25.350	112.613	100.083	7.518	-146.011	-128.755	46.899
700	25.475	116.531	102.160	10.059	-145.942	-125.886	39.303
800	25.557	119.938	104.174	12.611	-145.892	-123.025	33.609
900	25.614	122.952	106.096	15.170	-145.865	-120.167	29.181
1000	25.655	125.653	107.919	17.733	-145.866	-117.311	25.638
1100	25.686	128.099	109.644	20.301	-145.891	-114.455	22.740
1200	25.709	130.335	111.277	22.870	-146.880	-111.557	20.317
1300	25.727	132.394	112.823	25.442	-146.832	-108.614	18.260
1400	25.742	134.301	114.290	28.016	-146.799	-105.677	16.497
1500	25.753	136.078	115.684	30.590	-146.786	-102.742	14.969
1600	25.763	137.740	117.011	33.166	-146.791	-99.803	13.632
1700	25.771	139.302	118.277	35.743	-146.817	-96.866	12.453
1800	25.778	140.775	119.486	38.321	-146.866	-93.929	11.405
1900	25.783	142.169	120.644	40.899	-146.939	-90.983	10.465
2000	25.788	143.492	121.753	43.477	-151.487	-87.884	9.604
2100	25.792	144.750	122.819	46.056	-151.586	-84.701	8.815
2200	25.796	145.950	123.843	48.636	-151.688	-81.515	8.098
2300	25.799	147.097	124.829	51.215	-151.793	-78.321	7.442
2400	25.802	148.195	125.780	53.795	-151.899	-75.122	6.841
2500	25.804	149.248	126.698	56.376	-152.006	-71.922	6.287
2600	25.807	150.260	127.585	58.956	-152.116	-68.716	5.776
2700	25.808	151.234	128.443	61.537	-152.227	-65.509	5.303
2800	25.810	152.173	129.274	64.118	-152.342	-62.294	4.862
2900	25.812	153.079	130.079	66.699	-152.457	-59.073	4.452
3000	25.813	153.954	130.860	69.280	-152.574	-55.853	4.069
3100	25.814	154.800	131.619	71.862	-152.694	-52.624	3.710
3200	25.816	155.620	132.356	74.443	-152.815	-49.396	3.374
3300	25.817	156.414	133.073	77.025	-152.939	-46.165	3.057
3400	25.818	157.185	133.771	79.607	-153.063	-42.927	2.759
3500	25.818	157.933	134.451	82.188	-153.192	-39.684	2.478
3600	25.819	158.661	135.113	84.770	-254.948	-36.178	2.196
3700	25.820	159.368	135.759	87.352	-255.050	-30.101	1.778
3800	25.821	160.057	136.390	89.934	-255.169	-24.021	1.382
3900	25.821	160.727	137.005	92.516	-255.303	-17.931	1.005
4000	25.822	161.381	137.606	95.098	-255.452	-11.848	.647
4100	25.822	162.019	138.194	97.681	-255.615	-5.756	.307
4200	25.823	162.641	138.769	100.263	-255.793	.340	-.018
4300	25.823	163.249	139.331	102.845	-255.985	6.442	-.327
4400	25.824	163.842	139.881	105.428	-256.189	12.548	-.623
4500	25.824	164.423	140.420	108.010	-256.407	18.657	-.906
4600	25.825	164.990	140.948	110.592	-256.637	24.777	-1.177
4700	25.825	165.546	141.466	113.175	-256.878	30.900	-1.437
4800	25.825	166.089	141.973	115.757	-257.134	37.019	-1.686
4900	25.826	166.622	142.471	118.340	-257.398	43.149	-1.925
5000	25.826	167.144	142.959	120.923	-257.672	49.290	-2.154
5100	25.826	167.655	143.438	123.505	-257.959	55.426	-2.375
5200	25.826	168.157	143.909	126.088	-258.253	61.576	-2.588
5300	25.827	168.648	144.371	128.671	-258.556	67.730	-2.793
5400	25.827	169.131	144.825	131.253	-258.871	73.887	-2.990
5500	25.827	169.605	145.271	133.836	-259.190	80.060	-3.181
5600	25.827	170.071	145.710	136.419	-259.520	86.221	-3.365
5700	25.828	170.528	146.141	139.001	-259.857	92.406	-3.543
5800	25.828	170.977	146.566	141.584	-260.199	98.590	-3.715
5900	25.828	171.418	146.983	144.167	-260.549	104.777	-3.881
6000	25.828	171.852	147.394	146.750	-260.905	110.960	-4.042

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TETRABROMIDE ($TiBr_4$) (IDEAL GAS) GFW = 367.536

Point Group T_d

$\Delta Hf°_0 = -124.3 \pm 1.2$ kcal/mol

$S°_{298.15} = 95.25 \pm 1.0$ gibbs/mol

$\Delta Hf°_{298.15} = -131.5 \pm 1.2$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
229.5 (1)	382 (3)
74 (2)	90.5 (3)

Bond Distance: Ti-Br = 2.31 Å

σ = 12

Bond Angle: Br-Ti-Br = 109° 28'

Product of the Moments of Inertia: $I_AI_BI_C = 6.76 \times 10^{-111}$ g^3 cm^6

Heat of Formation

The heat of formation of $TiBr_4(g)$ is calculated from those of $TiBr_4(c)$ and $TiBr_4(\ell)$ and the heats of reaction for the processes (A) $TiBr_4(c) = TiBr_4(g)$ and (B) $TiBr_4(\ell) = TiBr_4(g)$. Second and third law analyses of the vapor pressure data for these processes yield the following results. The first four investigations employed the spoon gauge method, the last investigation being a manometric determination.

Source	Reaction	No. Pts.	Range T°K	$\Delta Hr°_{299}$, kcal/mol Second law	Third	Drift, eu	$\Delta Hf°_{298.15}$** kcal/mol
Boni, 1966 (1)	A	13	275 - 311	16.4 ± 0.2	16.19	-0.6 ± 0.5	-131.5
Funaki et al., 1961 (2)	B	14	385 - 493	12.2 ± 0.3	12.92	1.6 ± 0.3	-131.8
Seki, 1941 (3)	A	12	286 - 306	15.4 ± 0.5	15.90	1.6 ± 1.6	-131.8
Hall et al., 1958 (4)	B	89*	341 - 499	13.2 ± 0.1	13.14	-0.1 ± 0.1	-131.5
Keavney & Smith, 1960 (5)	A	14	287 - 310	16.1 ± 0.3	16.14	0.2 ± 0.8	-131.6

* Four points rejected due to failure of a statistical test.

** Calculation beased on third law $\Delta Hr°_{298}$.

The adopted value of 131.5 kcal/mol is that obtained from the data of Hall et al. (4),whose third law drift was adjusted to zero by changing the entropy of the crystal within its uncertainty.

Heat Capacity and Entropy

The interatomic distance was reported by Lister and Sutton (6). The tetrahedral configuration is confirmed by spectroscopic studies (7,8). The individual moments of inertia are $I_A = I_B = I_C = 1.89 \times 10^{-37}$ g cm^2.

The vibrational frequencies have been reported by Delwaulle and Francois (7) and by Miller and Carlson (8). These values are based primarily on the Raman and infrared spectra of $TiBr_4(\ell)$, the value of ν_3 being the only frequency measured for $TiBr_4(g)$.

The electronic spectra of $TiBr_4$ in solution have been measured by Dijkgraaf (9). Di Sipio et al. (10) have reported the near ultraviolet spectra of $TiBr_4(g)$. Both of these studies indicate that $TiBr_4$ has no low lying electronic levels which would contribute significantly to the entropy.

References

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3. S. Seki, J. Chem. Soc. Japan 62, 789 (1941).
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Zirconium Tetrabromide ($ZrBr_4$)

(Crystal) Mol. Wt. = 410.884

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-6.731	-175.296	-175.296	INFINITE
100	22.377	24.695	78.605	-5.391	-175.504	-175.063	382.580
200	27.743	42.188	56.373	-2.837	-175.815	-174.504	190.680
298	29.829	53.702	53.702	.000	-181.600	-173.140	126.909
300	29.856	53.887	53.703	.055	-181.622	-173.086	126.087
400	30.900	62.638	54.889	3.100	-195.692	-167.317	91.413
500	31.600	69.615	57.159	6.228	-195.001	-160.303	70.065
600	31.900	75.409	59.732	9.406	-194.303	-153.429	55.884
700	32.150	80.346	62.333	12.609	-193.611	-146.672	45.791
800	32.400	84.655	64.859	15.836	-192.914	-140.015	38.249
900	32.550	88.481	67.275	19.085	-192.206	-133.444	32.403
1000	32.600	91.914	69.571	22.343	-191.502	-126.951	27.744
1100	32.620	95.022	71.745	25.604	-190.815	-120.531	23.946
1200	32.640	97.861	73.805	28.867	-191.096	-114.123	20.784
1300	32.650	100.474	75.757	32.132	-190.415	-107.735	18.111
1400	32.660	102.894	77.610	35.397	-189.744	-101.402	15.829
1500	32.670	105.148	79.372	38.664	-189.081	-95.116	13.858

Mar. 31, 1962; Mar. 31, 1964

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) (CRYSTAL) MOL. WT. = 410.884

$S^\circ_{298.15}$ = [53.70] cal. deg.$^{-1}$ mole^{-1}

T_m = 723°K.

T_s = 630°K.

$\Delta H_f^\circ{}_0$ = [-175.3] ± 0.8 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -181.6 ± 0.6 kcal. mole^{-1}

$\Delta H_s^\circ{}_{298.15}$ = 28.0 ± 1.0 kcal. mole^{-1}

Heat of Formation.

A. G. Turnbull, J. Phys. Chem. 65, 1652 (1961), measured the heat effect accompanying the following reactions:

(1) $ZrBr_4(s) + 4NaOH(aq.) = ZrO_2(hyd.) + 4NaBr(aq.) + 2H_2O$

(2) $ZrBr_4(s) + 2H_2O = ZrOOH^+_{(aq.)} + 4Br^-_{(aq.)} + 3H^+_{(aq.)}$

Turnbull also measured the chlorine analogue of the above reactions. He used the measured heat of formation of zirconium tetrachloride, reported by Gross, Hyman and Levi [see $ZrCl_4$ table], to calculate the heats of formation of ZrO_2(hyd.) and $ZrOOH^+$(aq.). The heat of formation of solid zirconium tetrabromide from reaction (1) was -182.2 ± 0.7 kcal. mole^{-1} and from reaction (2) was -181.0 ± 0.6 kcal. mole^{-1}. An average of the two was taken to represent the heat of formation of the tetrabromide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated by means of the relationship $C_p = C_{VT}(\Theta_D^{3^\circ} = 85°K.) + C_{VR}(\Theta_E^{3^\circ} = 155°K.) + C_{Vi} + a^2C_V{}^2T$, where C_{VT} represents the hindered translational, C_{VR} the librational, and C_{Vi} the internal vibrational contributions to the heat capacity of the solid. $C_V = C_{VT} + C_{VR} + C_{Vi}$ represents the constant volume heat capacity to which $a^2C_V{}^2T$, the anharmonic contribution, is added to convert to a heat capacity at constant pressure. The internal contribution, C_{Vi}, was obtained from the estimated vibrational frequencies [see gas table]. The values for Θ_D and Θ_E were obtained from an elaborate correlation with the corresponding values for $ZrCl_4$ [see $ZrCl_4$ crystal table]. C_p was computed using a number of values for the constant term "a". The value, a = 2.5 X 10^{-3}, was chosen from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. was obtained by a graphical extrapolation.

Melting Point.

This was reported by O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.) and by H. L. Schlafer and H. Skoludek, Z. Elektrochem. 66, 367 (1962). The heat of sublimation results, for two values of "a", are given in the following table.

Reference	"a"	$\Delta H_{s(298)}$ [3rd Law]	$\Delta H_{s(298)}$ [2nd Law]	
			A	B
Schlafer	3.0 X 10^{-3}	27.43	28.82	28.82
Schlafer	2.5 X 10^{-3}	27.73	28.68	28.68
Rahlfs	3.0 X 10^{-3}	27.52	28.35	28.15
Rahlfs	2.5 X 10^{-3}	27.85	28.19	27.99

All heat values are in kcal. mole^{-1}. Two sets of second law heat values are given; set "A" was obtained from the slope reported by the authors and set "B" from a least squares fit performed at The Dow Thermal Laboratory. Various high temperature extrapolations were carried out for a particular value of "a" but only insignificant changes in the heat of sublimation resulted. The data of Schlafer and Skoludek showed a considerable temperature dependent third law heat of sublimation at 298°K. when "a" was taken as 3.0 X 10^{-3}, and a moderate temperature dependence when "a" was taken as 2.5 X 10^{-3}. The data of Rahlfs and Fischer showed a very slight temperature dependence for a = 3.0 X 10^{-3} and no temperature dependence for a = 2.5 X 10^{-3}.

In both sets of data there are large differences between 2nd and 3rd law values for a = 3.0 X 10^{-3}, good 2nd and 3rd law agreement for the data of Rahlfs and Fischer and a = 2.5 X 10^{-3}, and only fair agreement for the data of Schlafer and Skoludek and a = 2.5 X 10^{-3}. Extrapolation of the data of Schlafer and Skoludek for a = 2.0 X 10^{-3} indicated a continuing temperature dependent third law heat of sublimation and disagreement between 2nd and 3rd law values. The heat of sublimation was taken as the average of the third law and two second law values calculated from the data of Rahlfs and Fischer using "a" = 2.5 X 10^{-3}. The results of this analysis should not be considered conclusive since all of the data is estimated.

The sublimation point reported by Rahlfs and Fischer (loc. cit.) was 630°K., that calculated from the data of Schlafer and Skoludek was 624°K. and that obtained from the free energy crossover between solid and gas was 630°K. The sublimation point was taken as 630°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Zirconium Tetrabromide ($ZrBr_4$)

(Ideal Gas) Mol. Wt. = 410.884

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 5.962	- 146.527	- 146.527	INFINITE
100	19.371	74.781	119.935	- 4.515	- 146.628	- 151.195	330.422
200	23.211	89.622	101.382	- 2.352	- 147.330	- 155.505	169.920
298	24.511	99.173	99.173	.000	- 153.600	- 158.697	116.322
300	24.525	99.325	99.174	.045	- 153.632	- 158.727	115.627
400	25.066	106.464	100.143	2.528	- 168.264	- 157.419	86.006
500	25.332	112.089	101.990	5.050	- 168.179	- 154.718	67.624
600	25.482	116.722	104.071	7.591	- 168.118	- 152.032	55.375
700	25.573	120.658	106.166	10.144	- 168.076	- 149.356	46.629
800	25.634	124.077	108.196	12.705	- 168.045	- 146.684	40.070
900	25.675	127.099	110.132	15.270	- 168.021	- 144.015	34.970
1000	25.705	129.805	111.966	17.839	- 168.006	- 141.346	30.890
1100	25.728	132.256	113.701	20.411	- 168.008	- 138.682	27.552
1200	25.744	134.496	115.342	22.985	- 168.978	- 135.967	24.762
1300	25.758	136.557	116.896	25.560	- 168.987	- 133.215	22.394
1400	25.768	138.466	118.369	28.136	- 169.005	- 130.465	20.365
1500	25.777	140.244	119.769	30.713	- 169.032	- 127.712	18.607
1600	25.784	141.908	121.101	33.291	- 169.067	- 124.953	17.067
1700	25.789	143.472	122.371	35.870	- 169.111	- 122.195	15.708
1800	25.794	144.946	123.585	38.449	- 169.163	- 119.435	14.501
1900	25.798	146.340	124.746	41.029	- 169.223	- 116.668	13.419
2000	25.802	147.664	125.859	43.609	- 169.295	- 113.905	12.446
2100	25.805	148.923	126.928	46.189	- 169.373	- 111.133	11.565
2200	25.808	150.123	127.955	48.770	- 174.364	- 108.193	10.747
2300	25.810	151.271	128.944	51.351	- 174.467	- 105.181	9.994
2400	25.812	152.369	129.897	53.932	- 174.572	- 102.164	9.303
2500	25.814	153.423	130.818	56.513	- 174.679	- 99.146	8.667
2600	25.815	154.435	131.707	59.095	- 174.787	- 96.122	8.079
2700	25.817	155.410	132.566	61.676	- 174.898	- 93.097	7.535
2800	25.818	156.348	133.399	64.258	- 175.012	- 90.064	7.029
2900	25.819	157.254	134.206	66.840	- 175.126	- 87.026	6.558
3000	25.820	158.130	134.989	69.422	- 175.242	- 83.988	6.118
3100	25.821	158.976	135.749	72.004	- 175.362	- 80.944	5.706
3200	25.822	159.796	136.488	74.586	- 175.482	- 77.896	5.320
3300	25.822	160.591	137.207	77.168	- 175.606	- 74.846	4.957
3400	25.823	161.362	137.906	79.750	- 175.730	- 71.791	4.614
3500	25.824	162.110	138.587	82.333	- 175.857	- 68.730	4.291
3600	25.824	162.838	139.250	84.915	- 175.987	- 65.671	3.987
3700	25.825	163.545	139.897	87.498	- 176.116	- 62.605	3.698
3800	25.825	164.234	140.529	90.080	- 176.250	- 59.533	3.424
3900	25.826	164.905	141.145	92.663	- 176.385	- 56.456	3.164
4000	25.826	165.559	141.747	95.245	- 176.523	- 53.385	2.917
4100	25.827	166.196	142.336	97.828	- 176.662	- 50.306	2.681
4200	25.827	166.819	142.911	100.411	- 176.803	- 47.220	2.457
4300	25.827	167.426	143.475	102.993	- 176.047	- 44.130	2.243
4400	25.828	168.020	144.026	105.576	- 177.092	- 41.041	2.038
4500	25.828	168.601	144.565	108.159	- 177.239	- 37.949	1.843
4600	25.828	169.168	145.094	110.742	- 177.388	- 34.850	1.656
4700	25.828	169.724	145.612	113.324	- 177.540	- 31.745	1.476
4800	25.829	170.268	146.120	115.907	- 314.128	- 27.124	1.235
4900	25.829	170.800	146.618	118.490	- 314.338	- 21.142	.943
5000	25.829	171.322	147.107	121.073	- 314.555	- 15.155	.662
5100	25.829	171.833	147.587	123.656	- 314.780	- 9.170	.393
5200	25.830	172.335	148.058	126.239	- 315.010	- 3.171	.133
5300	25.830	172.827	148.521	128.822	- 315.247	2.827	- .117
5400	25.830	173.310	148.976	131.405	- 315.491	8.828	- .357
5500	25.830	173.784	149.422	133.988	- 315.738	14.841	- .590
5600	25.830	174.249	149.862	136.571	- 315.993	20.851	- .814
5700	25.830	174.706	150.293	139.154	- 316.252	26.869	- 1.030
5800	25.831	175.156	150.718	141.737	- 316.515	32.896	- 1.240
5900	25.831	175.597	151.136	144.320	- 316.783	38.921	- 1.442
6000	25.831	176.031	151.547	146.903	- 317.055	44.941	- 1.637

Mar. 31, 1962; Mar. 31, 1964

ZIRCONIUM TETRABROMIDE ($ZrBr_4$) (IDEAL GAS) MOL. WT. = 410.884

Point Group = [T_d]

$S^\circ_{298.15}$ = [99.17] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-146.5 ± 1.6] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -153.6 ± 1.6 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[217] (1)
[60] (2)
[322] (3)
[70] (3)

Bond Distance: Zr-Br = [2.45] Å

Bond Angle: Br-Zr-Br = [109° 28'] σ = [12]

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.5782 X 10^{-111}] gm.^{3} cm.^{6}

Heat of Formation.

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy.

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Godnev, A. M. Aleksandrovskaya, and I. V. Regina, Optics and Spectroscopy 7, 172 (1959), estimated the interatomic distance and report 2.47 Å as the Zr-Br distance. The bond angle was taken to be the tetrahedral angle. The three principal moments of inertia are: $I_A = I_B = I_C$ = 2.1237 X 10^{-37} gm. cm.^{2}.

The fundamental vibrational frequencies are all estimated. The product of ω_1 and internuclear distance for the tetrabromides of Si, Ti, Ge, Sn, and Pb was found to be nearly constant. Utilizing the estimated Zr-Br distance, a value of 218 cm.$^{-1}$ was obtained for ω_1. A plot of ω_1 and ω_2 versus internuclear distance for these molecules gave nearly linear smooth curves. Values of ω_1 and ω_2 obtained from these plots were 216 cm.$^{-1}$ and 58 cm.$^{-1}$ respectively. These values for ω_1 and ω_2 were used in a valence force field calculation to derive values for ω_3 and ω_4. Central and valence force field calculations, using estimated force constants were carried out but the results proved to be inconsistent. Therefore, ω_1 was taken as the average of the two empirically derived values, ω_2 as its empirically derived value, and ω_3 and ω_4 as those derived from the empirical values and the valence force field calculation. Godnev, Aleksandrovskaya, and Regina (loc. cit.) estimated the vibrational frequencies; they obtained ω_1 = 224 cm.$^{-1}$, ω_2 = 65 cm.$^{-1}$, ω_3 = 309 cm.$^{-1}$, and ω_4 = 78 cm.$^{-1}$.

Tungsten Pentabromide (WBr_5)
(Crystal)   GFW = 583.395

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	37.156	65.000	65.000	.000	-74.500	-64.433	47.230
300	37.200	65.230	65.001	.069	-74.525	-64.369	46.893
400	39.600	76.260	66.488	3.909	-91.874	-57.361	31.340
500	42.000	85.351	69.377	7.987	-90.604	-48.877	21.364
600	44.400	93.231	72.710	12.313	-89.109	-40.668	14.813
700	46.800	100.255	76.152	16.873	-87.403	-32.726	10.218
800	49.200	106.661	79.570	21.673	-85.476	-25.046	6.842
900	51.600	112.595	82.914	26.713	-83.323	-17.618	4.278
1000	54.000	118.155	86.163	31.993	-80.947	-10.440	2.282

Dec. 31, 1962; June 30, 1967

TUNGSTEN PENTABROMIDE (WBr_5)   (CRYSTAL)   GFW = 583.395

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = [65 ± 5] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -74.5 ± 3 kcal/mol

Tm = 559° ±10°K ΔHm° = 4.10 kcal/mol

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction ΔHr°_{298} = -187.475 ± 0.9 kcal/mol for $WBr_5(c) + 1/2Br_2(\ell) + 8NaOH(77.4H_2O) \rightarrow Na_2WO_4(c) + 6NaBr(c) + 4H_2O(\ell)$. This leads to $\Delta Hf^\circ_{298}(WBr_5, c)$ = -74.5 ± 3 kcal/mol, using $\Delta Hf^\circ_{298}(NaOH \cdot 77.4H_2O)$ = -112.348 kcal/mol (2), $\Delta Hf^\circ_{298}(NaWO_4, c)$ = -369.2 kcal/mol (3), $\Delta Hf^\circ_{298}(NaBr, c)$ = -86.38 kcal/mol (4) and $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol (5).

Heat Capacity and Entropy

Cp_{300} = 6.2 gibbs/g-atom and Cp_{559} = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. Ll. Evans (6). Between 300°K and 559°K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S°_{298} = 65 eu, is estimated from that of $WCl_5(c)$ (7) and the entropy difference between bromides and chlorides. The latter is estimated to be 13 eu based on an extrapolation to pentavalent compounds of the entropy values of bromides and chlorides given by W. M. Latimer (9). Both WBr_5 and WCl_5 are paramagnetic with an effective moment of about 1.1 Bohr magnetons as indicated by B. N. Figgis and J. L. Lewis, "Progress in Inorg. Chem.," Vol. 6, page 121, Interscience Publishers, New York, 1964.

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (8) have found the melting point, 559°K, by the thermographic method and 568°K by the tensimetric method. The value of 559°K is adopted in the tabulation.

The heat of melting is calculated from the difference between the heats of sublimation and vaporization at the melting point. The heats are both calculated from a second law analysis of the vapor pressure data reported by Shchukarev et al. (8), who gave the uncorrected heat of fusion, 5 kcal/mol. This value, when corrected for ΔCp of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. 9, 1309 (1964).
2. The value $\Delta Hf^\circ_{298}(NaOH \cdot 77.4H_2O)$ = -112.348 kcal/mol is calculated from $\Delta Hf^\circ_{298}(NaOH \cdot \infty H_2O)$ = -112.448 kcal/mol and ϕ_L = 100 cal/mol for $NaOH(\infty H_2O) \rightarrow NaOH(77.4H_2O)$. The former is obtained from JANAF NaOH(c) table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
3. JANAF Na_2WO_4(c) table (June 30, 1967).
4. JANAF NaBr(c) table (Sept. 30, 1964).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. JANAF WCl_5(c) table (Dec. 31, 1966).
8. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).
9. W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951).

Tungsten Pentabromide (WBr_5)

(Liquid) GFW = 583.395

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	43.500	70.113	70.113	.000	-71.236	-62.693	45.955
300	43.500	70.382	70.114	.080	-71.249	-62.639	45.632
400	43.500	82.896	71.820	4.430	-88.088	-56.229	30.722
500	43.500	92.603	75.042	8.780	-86.547	-48.446	21.176
600	43.500	100.534	78.650	13.130	-85.028	-40.968	14.923
700	43.500	107.240	82.267	17.480	-83.531	-33.744	10.535
800	43.500	113.048	85.760	21.830	-82.054	-26.734	7.303
900	43.500	118.172	89.082	26.180	-80.591	-19.905	4.834
1000	43.500	122.755	92.224	30.530	-79.145	-13.238	2.893

Dec. 31, 1962; June 30, 1967

TUNGSTEN PENTABROMIDE (WBr_5) (LIQUID) GFW = 583.395

$S°_{298.15}$ = [70.113] gibbs/mol $\Delta Hf°_{298.15}$ =[-71.236] kcal/mol

Tm = 559° ± 10°K   ΔHm° = 4.10 kcal/mol

Tb = 633.5°K   ΔHv° = 19.48 kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf°_{298}(WBr_5, \ell)$ = -71.236 kcal/mol, is calculated from that of WBr_5(c) by adding the heat of melting and the difference between $H°_{559} - H°_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be a constant, 7.25 gibbs/g-atom.

The entropy, $S°_{298}$ = 70.113 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data

See WBr_5(c) table (June 30, 1967) for details.

Vaporization Data

Tb is calculated as the temperature at which the Gibbs energy of reaction $WBr_5(\ell) \rightarrow WBr_5(g)$ approaches zero. The difference between the heats of formation for liquid and gas at the boiling point is ΔHv°.

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959), derived the boiling point 665°K and the heat of vaporization 14.5 ± 0.5 kcal/mol from vapor pressure data. Our second law values, corrected for ΔCp, are Tb = 666°K and ΔHv° = 13.8 kcal/mol.' The adopted values are significantly different because the second law value of ΔSv is not adopted in the table.

Tungsten Pentabromide (WBr_5)
(Ideal Gas) GFW = 583.395

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-7.175	-38.939	-38.939	INFINITE
100	23.608	79.955	136.076	-5.612	-39.202	-43.750	95.615
200	28.928	98.376	112.997	-2.924	-39.921	-48.035	52.490
298	30.404	110.252	110.252	.000	-47.600	-51.025	37.402
300	30.420	110.441	110.253	.056	-47.637	-51.045	37.186
400	31.000	119.282	111.455	3.131	-65.751	-48.447	26.470
500	31.279	126.233	113.740	6.247	-65.444	-44.158	19.302
600	31.434	131.951	116.313	9.383	-65.139	-39.930	14.544
700	31.529	136.804	118.902	12.531	-64.844	-35.752	11.162
800	31.591	141.019	121.409	15.688	-64.561	-31.617	8.637
900	31.536	144.742	123.799	18.849	-64.286	-27.514	6.681
1000	31.572	148.077	126.063	22.015	-64.025	-23.440	5.123
1100	31.704	151.097	128.204	25.183	-63.775	-19.396	3.854
1200	31.735	153.857	130.228	28.355	-63.536	-15.371	2.799
1300	31.768	156.399	132.145	31.530	-63.309	-11.365	1.911
1400	31.805	158.754	133.962	34.709	-63.092	-7.379	1.152
1500	31.845	160.950	135.689	37.892	-62.888	-3.408	.497
1600	31.889	163.007	137.333	41.078	-62.693	.552	-.075
1700	31.937	164.941	138.901	44.269	-62.508	4.501	-.579
1800	31.987	166.768	140.398	47.466	-62.331	8.434	-1.024
1900	32.039	168.499	141.832	50.667	-62.163	12.365	-1.422
2000	32.093	170.144	143.207	53.874	-62.006	16.280	-1.779
2100	32.149	171.711	144.527	57.086	-61.856	20.191	-2.101
2200	32.204	173.208	145.797	60.303	-61.717	24.092	-2.393
2300	32.259	174.641	147.020	63.526	-61.587	27.991	-2.660
2400	32.314	176.015	148.200	66.755	-61.465	31.887	-2.904
2500	32.367	177.335	149.339	69.989	-61.352	35.773	-3.127
2600	32.419	178.605	150.441	73.228	-61.249	39.658	-3.334
2700	32.469	179.830	151.507	76.473	-61.160	43.532	-3.524
2800	32.518	181.012	152.539	79.722	-61.097	47.411	-3.701
2900	32.565	182.153	153.541	82.976	-61.066	51.286	-3.865
3000	32.609	183.258	154.513	86.235	-61.073	55.161	-4.018
3100	32.651	184.328	155.458	89.498	-61.134	59.036	-4.162
3200	32.691	185.365	156.376	92.765	-61.250	62.915	-4.297
3300	32.729	186.372	157.270	96.036	-61.433	66.792	-4.423
3400	32.764	187.350	158.140	99.311	-61.687	70.680	-4.543
3500	32.797	188.300	158.989	102.589	-62.031	74.583	-4.657
3600	32.828	189.224	159.816	105.870	-62.488	78.489	-4.765
3700	32.856	190.124	160.623	109.154	-71.388	82.458	-4.871
3800	32.883	191.001	161.411	112.441	-71.283	86.616	-4.982
3900	32.907	191.855	162.180	115.731	-71.179	90.777	-5.087
4000	32.929	192.688	162.933	119.023	-71.074	94.922	-5.186
4100	32.949	193.502	163.668	122.317	-70.970	99.067	-5.281
4200	32.967	194.296	164.388	125.612	-70.867	103.217	-5.371
4300	32.983	195.072	165.093	128.910	-70.765	107.363	-5.457
4400	32.997	195.830	165.783	132.209	-70.663	111.506	-5.539
4500	33.010	196.572	166.459	135.509	-70.563	115.640	-5.616
4600	33.020	197.298	167.121	138.811	-70.464	119.778	-5.691
4700	33.030	198.008	167.771	142.113	-70.366	123.920	-5.762
4800	33.037	198.703	168.408	145.417	-70.273	128.046	-5.830
4900	33.044	199.385	169.033	148.721	-70.179	132.176	-5.895
5000	33.049	200.052	169.647	152.025	-70.087	136.311	-5.958
5100	33.052	200.707	170.250	155.330	-69.999	140.427	-6.018
5200	33.055	201.349	170.842	158.636	-69.911	144.552	-6.075
5300	33.056	201.978	171.423	161.941	-69.826	148.685	-6.131
5400	33.056	202.596	171.995	165.247	-69.745	152.800	-6.184
5500	33.055	203.203	172.557	168.552	-69.665	156.927	-6.236
5600	33.054	203.798	173.109	171.858	-69.589	161.041	-6.285
5700	33.051	204.383	173.653	175.163	-69.516	165.161	-6.333
5800	33.048	204.958	174.188	178.468	-69.444	169.281	-6.379
5900	33.044	205.523	174.714	181.773	-69.377	173.396	-6.423
6000	33.039	206.078	175.232	185.077	-263.217	179.583	-6.541

Dec. 31, 1962; June 30, 1967

TUNGSTEN PENTABROMIDE (WBr_5) (IDEAL GAS) GFW = 583.395

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [110.3] gibbs/mol

Ground State Quantum Weight = [2]

ΔHf°_0 = -38.9 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -47.6 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[300] (1)	[240] (2)
[250] (1)	[100] (2)
[235] (1)	[70] (2)
[90] (1)	[110] (2)

Bond Distance: W-Br = [2.40] Å

Bond Angles: Br*-W-Br* = [120°], Br*-W-Br** = [90°]
Br**-W-Br** = [180°]

σ = [6]

*Equatorial **Axial

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.640] x 10^{-110} g^3 cm^6

Heat of Formation

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959), measured the vapor pressure of WBr_5(c, ℓ) using a null manometer. Their results are given as below. The adopted heat of formation is -47.6 kcal/mol.

Reactions	No. of Points	ΔHr°_{298}(kcal/mol) 2nd law	ΔHr°_{298}(kcal/mol) 3rd law	Temp. Range (°K)	Drift (eu)	ΔHf°_{298} kcal/mol
$WBr_5(\ell) \rightarrow WBr_5(g)$	13	18.37	24.11	573.3-657.5	9.4±0.1	-47.13
$WBr_5(c) \rightarrow WBr_5(g)$	6	21.61	26.46	443.5-496.5	9.4±0.4	-48.04

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $MoCl_5$ determined by electron diffraction (1). The bond distance is estimated to be the same as that in $WBr_6(g)$. The three principal moments of inertia are $I_A = I_B = 267.5 \times 10^{-39}$ and $I_C = 229.3 \times 10^{-39}$ g cm^2.

All vibrational frequencies are estimated from those of $WCl_5(g)$ (2), using the average value of $\nu(WBr_5)/\nu(WCl_5) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of $ReX_6^=$, $SnX_6^=$ and $PtX_6^=$ summarized by H. Siebert (3) and K. Nakamoto (4).

The electronic levels and quantum weights are estimated to be the same as those in $WCl_5(g)$ (2).

References

1. R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938).
2. JANAF $WCl_5(g)$ table (Dec. 31, 1966).
3. H. Siebert, "Anwendugen der Schwingunsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.
4. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

Tungsten Hexabromide (WBr_6)

(Crystal) GFW = 663.304

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	43.352	75.000	75.000	.000	-82.000	-69.490	50.938
300	43.400	75.268	75.001	.080	-82.030	-69.411	50.566
400	46.000	88.110	76.734	4.550	-102.869	-60.855	33.250
500	48.600	98.654	90.093	9.280	-101.389	-50.520	22.082
600	51.200	107.744	83.961	14.270	-99.674	-40.503	14.753
700	53.800	115.832	87.946	19.520	-97.724	-30.793	9.614
800	56.400	123.186	91.898	25.030	-95.535	-21.380	5.841
900	59.000	129.979	95.756	30.800	-93.101	-12.252	2.975
1000	61.600	136.330	99.499	35.830	-90.425	-3.408	.745

Dec. 31, 1962; June 30, 1967

TUNGSTEN HEXABROMIDE (WBr_6) (CRYSTAL) GFW = 663.304

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = [75 ± 5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -82.0 ± 3 kcal/mol

Tm = 582°K

ΔHm° = Unknown

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction ΔHr°_{298} = -180.0 ± 0.8 kcal/mol for $WBr_6(c) + 8NaOH(77.4H_2O) \rightarrow Na_2WO_4(c) + 6NaBr(c) + 4H_2O(\ell)$. This leads to $\Delta Hf^\circ_{298}(WBr_6, c)$ = -82.0 ± 3 kcal/mol, using $\Delta Hf^\circ_{298}(NaOH{\cdot}77.4H_2O)$ = -112.348 kcal/mol (2), $\Delta Hf^\circ_{298}(Na_2WO_4, c)$ = -369.2 kcal/mol (3), $\Delta Hf^\circ_{298}(NaBr, c)$ = -86.38 kcal/mol (4) and $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol (5).

Heat Capacity and Entropy

Cp_{300} = 6.2 gibbs/g-atom and Cp_{582} = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. Ll. Evans (6). Between 300° and 582°K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S^\circ_{298}(WBr_6, c)$ = 75 eu, is estimated by assuming $S^\circ_{298}(WBr_6) = S^\circ_{298}(WCl_6) + 6[S^\circ_{298}(Br^-) - S^\circ_{298}(Cl^-)]$. The value, $S^\circ_{298}(WCl_6, c)$ = 57 eu, is obtained from the JANAF $WCl_6(\alpha)$ table (Dec. 31, 1966); and the value, $S^\circ_{298}(Br^-) - S^\circ_{298}(Cl^-)$ = 3 gibbs/mol, is obtained from the average entropy values for Br^- and Cl^- ions given by W. M. Latimer (7) and K. K. Kelley (8).

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (9) have found the melting point, 582°K, under 50 atm pressure of $Br_2(g)$ by the thermographic method. The heat of fusion is unknown.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. 9, 1309 (1964).
2. This value, $\Delta Hf^\circ_{298}(NaOH{\cdot}77.4H_2O)$ = -112.348 kcal/mol is calculated from $\Delta Hf^\circ_{298}(NaOH{\cdot}\infty H_2O)$ = 112.448 kcal/mol and ϕ_L = 100 cal/mol for $NaOH(\infty H_2O) \rightarrow NaOH(77.4H_2O)$. The former is obtained from JANAF NaOH(c) table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
3. JANAF Na_2WO_4(c) table (June 30, 1967).
4. JANAF NaBr(c) table (June 30, 1964).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951).
8. K. K. Kelley, private communication, June, 1960.
9. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).

Tungsten Hexabromide (WBr_6)

(Ideal Gas) GFW = 663.304

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-8.414	-47.748	-47.748	INFINITE
100	27.538	79.306	146.082	-6.679	-48.172	-52.012	113.671
200	34.458	101.200	118.607	-3.481	-48.968	-55.557	60.710
298	36.178	115.340	115.340	.000	-58.100	-57.618	42.235
300	36.196	115.564	115.341	.067	-58.143	-57.613	41.971
400	36.858	126.081	116.770	3.724	-79.795	-52.970	28.941
500	37.175	134.343	119.488	7.428	-79.341	-46.317	20.245
600	37.351	141.138	122.547	11.155	-78.889	-39.755	14.481
700	37.457	146.904	125.625	14.895	-78.449	-33.265	10.387
800	37.527	151.911	128.605	18.645	-78.020	-26.845	7.334
900	37.575	156.334	131.445	22.400	-77.601	-20.472	4.971
1000	37.609	160.295	134.135	26.159	-77.196	-14.144	3.091
1100	37.634	163.880	136.679	29.922	-76.803	-7.860	1.562
1200	37.654	167.156	139.084	33.686	-76.423	-1.608	.293
1300	37.669	170.170	141.361	37.452	-76.058	4.615	-.776
1400	37.681	172.962	143.520	41.220	-75.705	10.805	-1.687
1500	37.691	175.562	145.570	44.988	-75.369	16.971	-2.473
1600	37.698	177.995	147.522	48.758	-75.045	23.115	-3.158
1700	37.705	180.281	149.382	52.528	-74.736	29.244	-3.760
1800	37.711	182.436	151.159	56.299	-74.440	35.349	-4.292
1900	37.715	184.475	152.859	60.070	-74.158	41.446	-4.767
2000	37.719	186.410	154.489	63.842	-73.893	47.519	-5.193
2100	37.723	188.250	156.053	67.614	-73.640	53.584	-5.577
2200	37.726	190.005	157.557	71.386	-73.405	59.634	-5.924
2300	37.728	191.682	159.004	75.159	-73.183	65.679	-6.241
2400	37.730	193.288	160.400	78.932	-72.976	71.715	-6.531
2500	37.732	194.828	161.746	82.705	-72.784	77.735	-6.796
2600	37.734	196.308	163.047	86.478	-72.607	83.757	-7.040
2700	37.736	197.732	164.306	90.252	-72.449	89.764	-7.266
2800	37.737	199.105	165.524	94.025	-72.324	95.772	-7.475
2900	37.739	200.429	166.705	97.799	-72.234	101.772	-7.670
3000	37.740	201.708	167.851	101.573	-72.188	107.773	-7.851
3100	37.741	202.946	168.963	105.347	-72.201	113.771	-8.021
3200	37.742	204.144	170.044	109.121	-72.273	119.772	-8.180
3300	37.743	205.305	171.095	112.895	-72.417	125.772	-8.330
3400	37.743	206.432	172.118	116.670	-72.635	131.780	-8.471
3500	37.744	207.526	173.114	120.444	-72.945	137.801	-8.605
3600	37.745	208.590	174.084	124.219	-73.377	143.821	-8.731
3700	37.745	209.624	175.031	127.993	-82.252	149.908	-8.855
3800	37.746	210.630	175.955	131.768	-82.126	156.187	-8.983
3900	37.746	211.611	176.856	135.542	-82.004	162.460	-9.104
4000	37.747	212.567	177.737	139.317	-81.884	168.715	-9.218
4100	37.747	213.499	178.598	143.092	-81.767	174.979	-9.327
4200	37.748	214.408	179.440	146.866	-81.654	181.245	-9.431
4300	37.748	215.296	180.264	150.641	-81.543	187.508	-9.530
4400	37.749	216.164	181.070	154.416	-81.435	193.763	-9.624
4500	37.749	217.013	181.859	158.191	-81.330	200.010	-9.714
4600	37.749	217.842	182.632	161.966	-81.228	206.267	-9.800
4700	37.749	218.654	183.390	165.741	-81.129	212.522	-9.882
4800	37.750	219.449	184.133	169.516	-81.036	218.757	-9.960
4900	37.750	220.227	184.862	173.291	-80.943	225.008	-10.036
5000	37.750	220.990	185.577	177.066	-80.853	231.252	-10.108
5100	37.750	221.737	186.278	180.841	-80.769	237.486	-10.177
5200	37.751	222.471	186.967	184.616	-80.685	243.722	-10.243
5300	37.751	223.190	187.644	188.391	-80.604	249.967	-10.308
5400	37.751	223.895	188.309	192.166	-80.529	256.199	-10.369
5500	37.751	224.588	188.962	195.941	-80.454	262.444	-10.429
5600	37.751	225.268	189.605	199.716	-80.385	268.669	-10.485
5700	37.752	225.936	190.236	203.491	-80.319	274.905	-10.540
5800	37.752	226.593	190.857	207.267	-80.252	281.140	-10.594
5900	37.752	227.238	191.468	211.042	-80.192	287.372	-10.645
6000	37.752	227.873	192.070	214.817	-274.039	295.667	-10.770

Dec. 31, 1962; June 30, 1967

TUNGSTEN HEXABROMIDE (WBr_6) (IDEAL GAS) GFW = 663.304

Point Group [O_h]

$\Delta Hf°_0$ = [-47.7 ± 10] kcal/mol

$S°_{298.15}$ = [115.3 ± 10] gibbs/mol

$\Delta Hf°_{298.15}$ = [-58.1 ± 10] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[250] (1)	[110] (3)
[200] (2)	[130] (3)
[250] (3)	[70] (3)

Bond Distance: W-Br = [2.40] Å

Bond Angle: Br-W-Br = [90°] σ = [24]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.857] x 10^{-110} g^3 cm^6

Heat of Formation

The heat of formation, $\Delta Hf°_{298}(WBr_6, g)$ = -58.1 kcal/mol, is calculated from that of the crystal plus the estimated heat of sublimation $\Delta Hs°_{298}$ = 23.9 kcal/mol for $WBr_6(c) \rightarrow WBr_6(g)$. The value of $\Delta Hs°_{298}$ is assumed to be the same as that for $WCl_6(c) \rightarrow WCl_6(g)$. See WCl_6 table (Dec. 31, 1966) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be an octahedron similar to those of $WF_6(g)$, and $WCl_6(g)$ determined by electron diffraction. The bond distance is estimated to be 2.40 Å by assuming $r_{W-Br} = r_{W-Cl} + (r_{Na-Br} - r_{Na-Cl})$. The bond distances,W-Cl, Na-Br and Na-Cl,are given in JANAF WCl(g) and NaBr(g) and NaCl(g) tables, as 2.26 Å, 2.50 Å and 2.36 Å, respectively. The three principal moments of inertia are: $I_A = I_B = I_C = 305.7 \times 10^{-39}$ g cm^2.

All vibrational frequencies are estimated from those of $WCl_6(g)$ (1), using the average value of $\nu(WBr_6)/\nu(WCl_6)$ = 0.62 for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of $ReX_6^=$, $SnX_6^=$ and $PtX_6^=$ summarized by H. Siebert (2), and K. Nakamoto (3).

References

1. J. C. Evans and G. Y-S Lo, The Dow Chemical Company, private communication, June 6, 1967, have obtained the six fundamental vibrational frequencies of 408, 312, 367, 165, 206 and 97 cm^{-1} for $WCl_6(g)$ by infrared spectrometry.
2. H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie." Springer-Verlag, Berlin.
3. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

Carbon (C)

(Reference State - Graphite) Mol. Wt. = 12.011

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	- ,252	,000	,000	,000
100	,395	,210	?,591	- ,238	,000	,000	,000
200	1,202	,720	1,520	- ,160	,000	,000	,000
298	2,038	1,359	1,359	,000	,000	,000	,000
300	2,054	1,372	1,359	,004	,000	,000	,000
400	2,851	2,075	1,450	,250	,000	,000	,000
500	3,496	2,784	1,646	,569	,000	,000	,000
600	4,038	3,471	1,893	,947	,000	,000	,000
700	4,440	4,126	2,166	1,372	,000	,000	,000
800	4,740	4,739	2,449	1,831	,000	,000	,000
900	4,970	5,311	2,736	2,318	,000	,000	,000
1000	5,149	5,844	3,020	2,824	,000	,000	,000
1100	5,304	6,342	3,300	3,347	,000	,000	,000
1200	5,430	6,809	3,573	3,883	,000	,000	,000
1300	5,527	7,248	3,839	4,432	,000	,000	,000
1400	5,605	7,661	4,098	4,988	,000	,000	,000
1500	5,669	8,050	4,348	5,552	,000	,000	,000
1600	5,721	8,417	4,591	6,122	,000	,000	,000
1700	5,765	8,765	4,827	6,696	,000	,000	,000
1800	5,803	9,096	5,055	7,275	,000	,000	,000
1900	5,836	9,411	5,276	7,857	,000	,000	,000
2000	5,865	9,711	5,490	8,442	,000	,000	,000
2100	5,891	9,998	5,698	9,029	,000	,000	,000
2200	5,914	10,272	5,900	9,620	,000	,000	,000
2300	5,936	10,536	6,095	10,212	,000	,000	,000
2400	5,956	10,789	6,286	10,807	,000	,000	,000
2500	5,974	11,032	6,471	11,403	,000	,000	,000
2600	5,992	11,267	6,651	12,002	,000	,000	,000
2700	6,009	11,493	6,826	12,602	,000	,000	,000
2800	6,026	11,712	6,997	13,203	,000	,000	,000
2900	6,042	11,924	7,163	13,807	,000	,000	,000
3000	6,057	12,129	7,325	14,412	,000	,000	,000
3100	6,073	12,328	7,483	15,018	,000	,000	,000
3200	6,088	12,521	7,638	15,626	,000	,000	,000
3300	6,103	12,708	7,788	16,236	,000	,000	,000
3400	6,119	12,891	7,936	16,847	,000	,000	,000
3500	6,134	13,068	8,080	17,460	,000	,000	,000
3600	6,150	13,241	8,221	18,074	,000	,000	,000
3700	6,165	13,410	8,359	18,690	,000	,000	,000
3800	6,181	13,575	8,494	19,307	,000	,000	,000
3900	6,197	13,736	8,626	19,926	,000	,000	,000
4000	6,213	13,893	8,756	20,546	,000	,000	,000
4100	6,230	14,046	8,883	21,168	,000	,000	,000
4200	6,247	14,197	9,008	21,792	,000	,000	,000
4300	6,264	14,344	9,130	22,418	,000	,000	,000
4400	6,281	14,488	9,250	23,045	,000	,000	,000
4500	6,299	14,629	9,368	23,674	,000	,000	,000
4600	6,317	14,768	9,484	24,305	,000	,000	,000
4700	6,335	14,904	9,598	24,937	,000	,000	,000
4800	6,354	15,038	9,710	25,572	,000	,000	,000
4900	6,373	15,169	9,820	26,208	,000	,000	,000
5000	6,392	15,298	9,928	26,846	,000	,000	,000
5100	6,412	15,424	10,035	27,487	,000	,000	,000
5200	6,432	15,549	10,140	28,129	,000	,000	,000
5300	6,452	15,672	10,243	28,773	,000	,000	,000
5400	6,473	15,793	10,345	29,419	,000	,000	,000
5500	6,494	15,912	10,445	30,068	,000	,000	,000
5600	6,516	16,029	10,543	30,718	,000	,000	,000
5700	6,538	16,144	10,641	31,371	,000	,000	,000
5800	6,560	16,258	10,737	32,026	,000	,000	,000
5900	6,583	16,371	10,831	32,683	,000	,000	,000
6000	6,606	16,481	10,924	33,342	,000	,000	,000

March 31, 1961

CARBON (C) (REFERENCE STATE - GRAPHITE) MOL. WT. = 12.011

$\Delta H^\circ_{f0} = 0$

$\Delta H^\circ_{f\ 298.15} = 0$

$\Delta H^\circ_{S\ 298.15} = 170.89 \pm 0.5$ kcal. mole^{-1}

$\Delta S^\circ_{298.15} = 1.359$ cal. deg.$^{-1}$ mole^{-1}

Heat of Formation

Zero by definition.

Heat Capacity and Extrapolation

The low temperature C_p measurements of P. H. Keesom and N. Pearlman (1° to 4°K. and 10° to 20°K.), Phys. Rev. 99, 1119 (1955), and of W. DeSorbo and G. E. Nichols (1° to 20°K.), The Phys. and Chem. of Solids 6, 352 (1958), were joined smoothly with the C_p measurements of W. DeSorbo and W. W. Tyler (13° to 300°K.), J. Chem. Phys. 21, 1660 (1953). C_p values above 300°K were taken from National Bureau of Standards Report 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960. Heat capacity values above 1000°K were adjusted to give smooth results. Above 4000°K. the C_p values are estimated.

S°_{15} and H°_{15} were calculated to be 0.00265 cal. deg.$^{-1}$ mole^{-1} and 0.03982 cal. mole^{-1} respectively from smooth C_p values using Weddle's rule.

Carbon, Monatomic (C)

(Ideal Gas) At. Wt. = 12.011

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	,000	,000	INFINITE	- 1,562	169,576	169,576	INFINITE
100	5,085	32,283	42,203	- ,992	170,132	166,925	- 364,796
200	4,997	35,770	38,217	- ,489	170,557	163,547	- 178,707
298	4,981	37,761	37,761	,000	170,886	160,033	- 117,302
300	4,981	37,792	37,761	,009	170,891	159,965	- 116,529
400	4,975	39,224	37,956	,507	171,143	156,283	- 85,385
500	4,973	40,334	38,325	1,004	171,321	152,546	- 66,675
600	4,971	41,240	38,738	1,502	171,441	148,779	- 54,190
700	4,970	42,006	39,151	1,999	171,513	144,996	- 45,268
800	4,970	42,670	39,551	2,496	171,551	141,206	- 38,574
900	4,970	43,255	39,930	2,993	171,561	137,411	- 33,366
1000	4,969	43,779	40,290	3,490	171,552	133,616	- 29,200
1100	4,969	44,253	40,629	3,986	171,525	129,824	- 25,792
1200	4,970	44,685	40,949	4,483	171,486	126,035	- 22,953
1300	4,971	45,083	41,252	4,980	171,434	122,249	- 20,551
1400	4,972	45,451	41,539	5,478	171,376	118,469	- 18,493
1500	4,975	45,794	41,811	5,975	171,309	114,692	- 16,710
1600	4,978	46,116	42,070	6,473	171,237	110,919	- 15,150
1700	4,984	46,418	42,317	6,971	171,161	107,151	- 13,775
1800	4,990	46,703	42,553	7,469	171,080	103,388	- 12,552
1900	4,998	46,973	42,779	7,969	170,998	99,631	- 11,460
2000	5,008	47,229	42,995	8,469	170,913	95,876	- 10,476
2100	5,019	47,474	43,202	8,970	170,827	92,128	- 9,587
2200	5,032	47,708	43,402	9,473	170,739	88,380	- 8,779
2300	5,046	47,932	43,594	9,977	170,651	84,641	- 8,042
2400	5,061	48,147	43,779	10,482	170,561	80,903	- 7,367
2500	5,077	48,354	43,958	10,989	170,472	77,168	- 6,746
2600	5,094	48,553	44,131	11,497	170,381	73,438	- 6,173
2700	5,112	48,746	44,298	12,008	170,292	69,710	- 5,642
2800	5,130	48,932	44,460	12,520	170,203	65,987	- 5,150
2900	5,149	49,112	44,618	13,034	170,113	62,267	- 4,692
3000	5,168	49,287	44,771	13,550	170,024	58,549	- 4,265
3100	5,187	49,457	44,919	14,067	169,935	54,836	- 3,866
3200	5,206	49,622	45,063	14,587	169,847	51,124	- 3,491
3300	5,224	49,782	45,204	15,108	169,758	47,413	- 3,140
3400	5,243	49,938	45,341	15,632	169,671	43,709	- 2,809
3500	5,261	50,091	45,474	16,157	169,583	40,003	- 2,498
3600	5,279	50,239	45,605	16,684	169,496	36,303	- 2,204
3700	5,296	50,384	45,732	17,213	169,409	32,605	- 1,926
3800	5,313	50,526	45,856	17,743	169,322	28,910	- 1,663
3900	5,329	50,664	45,978	18,275	169,235	25,217	- 1,413
4000	5,345	50,799	46,097	18,809	169,149	21,526	- 1,176
4100	5,360	50,931	46,213	19,344	169,062	17,834	- ,951
4200	5,375	51,060	46,327	19,881	168,975	14,149	- ,736
4300	5,388	51,187	46,438	20,419	168,887	10,462	- ,532
4400	5,402	51,311	46,548	20,959	168,800	6,778	- ,337
4500	5,414	51,433	46,655	21,499	168,711	3,096	- ,150
4600	5,426	51,552	46,760	22,041	168,622	- ,582	,028
4700	5,437	51,668	46,863	22,585	168,534	- 4,259	,198
4800	5,448	51,783	46,965	23,129	168,443	- 7,933	,361
4900	5,459	51,896	47,064	23,674	168,352	- 11,608	,518
5000	5,468	52,006	47,162	24,221	168,261	- 15,279	,668
5100	5,477	52,114	47,258	24,768	168,167	- 18,954	,812
5200	5,486	52,221	47,352	25,316	168,073	- 22,620	,951
5300	5,494	52,325	47,445	25,865	167,978	- 26,284	1,084
5400	5,502	52,428	47,536	26,415	167,882	- 29,947	1,212
5500	5,509	52,529	47,626	26,966	167,784	- 33,611	1,335
5600	5,516	52,628	47,715	27,517	167,685	- 37,272	1,455
5700	5,523	52,726	47,802	28,069	167,584	- 40,934	1,569
5800	5,529	52,822	47,888	28,621	167,481	- 44,591	1,680
5900	5,535	52,917	47,972	29,175	167,378	- 48,243	1,787
6000	5,541	53,010	48,055	29,728	167,272	- 51,901	1,890

March 31, 1961

CARBON, MONATOMIC (C) (IDEAL GAS) AT. WT. = 12.011

ΔH°_{f0} = 169.58 ± 0.45 kcal. mole^{-1}

Ground State Configuration $^3P_0$

$\Delta H^\circ_{f\ 298.15}$ = 170.89 ± 0.45 kcal. mole^{-1}

$S^\circ_{298.15}$ = 37.76 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i
0	1	60,360	9
16.4	3	61,982	3
43.5	5	64,090	15
10,194	5	70,000	34
21,648	1	75,000	99
33,735	5	85,000	401

Heat of Formation

The ΔH°_{f0} is given by the following cycle at 0°K.

(I)	$C(c) + 1/2\ O_2(g) = CO(g)$	-27.1995 kcal. mole^{-1}
(II)	$CO(g) = C(g) + O(g)$	255.764
(III)	$O(g) = 1/2\ O_2(g)$	-58.989

For details concerning (I), (II), and (III) see the CO(g) and O_2(g) sheets. A definitive review of the heat of sublimation of carbon is given by L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956).

Heat Capacities and Entropies

The electronic energy levels are those listed by C. E. Moore, Nat. Bur. Standards (U. S.) Circ. 467, (1949). Levels above 60,000 cm.$^{-1}$ have been averaged.

Carbon Uninegative Ion (C^-)

(Ideal Gas) At. Wt. = 12.0117

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	36.156	36.156	.000	140.500	131.612	-96.470
300	4.968	36.187	36.156	.009	140.496	131.557	-95.835
400	4.968	37.616	36.351	.506	140.250	128.613	-70.267
500	4.968	38.724	36.719	1.003	139.931	125.739	-54.958
600	4.968	39.630	37.131	1.500	139.553	122.935	-44.777
700	4.968	40.396	37.544	1.996	139.128	120.200	-37.526
800	4.968	41.059	37.943	2.493	138.669	117.527	-32.105
900	4.968	41.645	38.322	2.990	138.182	114.911	-27.903
1000	4.968	42.168	38.681	3.487	137.676	112.353	-24.554
1100	4.968	42.642	39.020	3.984	137.153	109.844	-21.823
1200	4.968	43.074	39.340	4.481	136.617	107.386	-19.557
1300	4.968	43.472	39.643	4.977	136.068	104.972	-17.647
1400	4.968	43.840	39.930	5.474	135.512	102.602	-16.016
1500	4.968	44.182	40.202	5.971	134.948	100.272	-14.609
1600	4.968	44.503	40.461	6.468	134.378	97.978	-13.383
1700	4.968	44.804	40.707	6.965	133.804	95.720	-12.305
1800	4.968	45.088	40.943	7.461	133.225	93.498	-11.352
1900	4.969	45.357	41.168	7.958	132.643	91.305	-10.502
2000	4.969	45.612	41.384	8.455	132.058	89.144	-9.741
2100	4.970	45.854	41.591	8.952	131.471	87.016	-9.055
2200	4.971	46.085	41.790	9.449	130.880	84.911	-8.435
2300	4.972	46.306	41.982	9.946	130.289	82.838	-7.871
2400	4.975	46.518	42.167	10.444	129.695	80.785	-7.356
2500	4.978	46.721	42.345	10.941	129.099	78.759	-6.885
2600	4.982	46.917	42.517	11.439	128.501	76.756	-6.452
2700	4.987	47.105	42.683	11.938	127.903	74.775	-6.052
2800	4.993	47.286	42.844	12.437	127.304	72.821	-5.684
2900	5.001	47.462	43.001	12.936	126.703	70.884	-5.342
3000	5.010	47.631	43.152	13.437	126.102	68.973	-5.024
3100	5.022	47.796	43.299	13.938	125.500	67.078	-4.729
3200	5.035	47.955	43.442	14.441	124.898	65.202	-4.453
3300	5.050	48.110	43.582	14.945	124.295	63.344	-4.195
3400	5.066	48.261	43.717	15.451	123.694	61.508	-3.954
3500	5.085	48.409	43.849	15.959	123.092	59.682	-3.727
3600	5.107	48.552	43.978	16.468	122.490	57.881	-3.514
3700	5.130	48.692	44.103	16.980	121.889	56.100	-3.314
3800	5.155	48.829	44.226	17.494	121.289	54.330	-3.125
3900	5.183	48.964	44.345	18.011	120.690	52.573	-2.946
4000	5.213	49.095	44.463	18.531	120.094	50.838	-2.778
4100	5.244	49.224	44.577	19.054	119.498	49.113	-2.618
4200	5.278	49.351	44.689	19.580	118.903	47.402	-2.466
4300	5.314	49.476	44.799	20.110	118.310	45.704	-2.323
4400	5.351	49.598	44.907	20.643	117.719	44.023	-2.187
4500	5.390	49.719	45.012	21.180	117.131	42.354	-2.057
4600	5.431	49.838	45.116	21.721	116.544	40.699	-1.934
4700	5.473	49.955	45.218	22.266	115.960	39.059	-1.816
4800	5.517	50.071	45.318	22.816	115.378	37.430	-1.704
4900	5.561	50.185	45.416	23.369	114.798	35.810	-1.597
5000	5.607	50.298	45.512	23.928	114.223	34.203	-1.495
5100	5.654	50.409	45.607	24.491	113.648	32.609	-1.397
5200	5.702	50.520	45.701	25.059	113.077	31.021	-1.304
5300	5.751	50.629	45.793	25.631	112.508	29.452	-1.214
5400	5.800	50.737	45.883	26.209	111.943	27.892	-1.129
5500	5.849	50.844	45.972	26.791	111.379	26.338	-1.047
5600	5.899	50.949	46.060	27.379	110.821	24.805	-.968
5700	5.949	51.054	46.147	27.971	110.263	23.264	-.892
5800	6.000	51.158	46.233	28.569	109.709	21.746	-.819
5900	6.050	51.261	46.317	29.171	109.157	20.238	-.750
6000	6.100	51.363	46.400	29.779	108.609	18.729	-.682

Sept. 30, 1965

CARBON UNINEGATIVE ION (C^-) (IDEAL GAS) AT. WT. = 12.0117

Ground State Configuration $^4S^\circ_{3/2}$

$\Delta H_f^\circ{}_0 = 140.8 \pm 0.8$ kcal. mole^{-1}

$S^\circ_{298.15} = 36.156$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 140.5 \pm 0.8$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

$\mathcal{E}_i$, cm.$^{-1}$	g_i	$\mathcal{E}_i$, cm.$^{-1}$	g_i
0	4	86223.2	4
19223.9	6	96751.7	4
19233.1	4	96788.2	4
28840.0	6	96864.2	6
83285.5	2	97770.1	2
83319.3	4	97805.8	4
83366.0	6	99663.0	10
86131.4	2		

Heat of Formation.

The heat of formation was calculated from the equation: $C(g) + e^- \rightarrow C^-(g)$ with the JANAF auxiliary value for C(g); using an electron affinity = 1.25 e.v. (28.83 kcal/mole) obtained from M. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962). Other values for the electron affinity are: 1.17 e.v. reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 1.12 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964); and 1.24 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case nitrogen. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.481 kcal/mole.

Aluminum Carbide (AlC)

(Ideal Gas) Mol. Wt. = 38.991

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.134	164.012	164.012	INFINITE
100	6.963	45.523	59.912	- 1.439	164.587	160.221	- 350.146
200	7.228	50.404	54.070	- .733	164.773	155.750	- 170.188
298	7.710	53.380	53.380	.000	164.800	151.308	- 110.906
300	7.718	53.428	53.381	.014	164.799	151.224	- 110.161
400	8.106	55.705	53.688	.807	164.749	146.705	- 80.152
500	8.366	57.544	54.281	1.631	164.627	142.207	- 62.156
600	8.540	59.085	54.957	2.477	164.439	137.739	- 50.169
700	8.660	60.411	55.644	3.337	164.187	133.308	- 41.619
800	8.747	61.574	56.314	4.208	163.883	128.918	- 35.217
900	8.813	62.608	56.957	5.086	163.527	124.567	- 30.248
1000	8.864	63.539	57.569	5.970	160.633	120.444	- 26.322
1100	8.906	64.386	58.151	6.859	160.299	116.440	- 23.133
1200	8.940	65.163	58.703	7.751	159.955	112.469	- 20.482
1300	8.970	65.879	59.228	8.646	159.601	108.525	- 18.244
1400	8.996	66.545	59.727	9.545	159.244	104.612	- 16.330
1500	9.019	67.166	60.203	10.445	158.881	100.722	- 14.674
1600	9.040	67.749	60.656	11.348	158.513	96.856	- 13.229
1700	9.059	68.298	61.090	12.253	158.144	93.013	- 11.957
1800	9.077	68.816	61.505	13.160	157.772	89.192	- 10.829
1900	9.093	69.307	61.903	14.069	157.399	85.394	- 9.822
2000	9.109	69.774	62.285	14.979	157.024	81.614	- 8.918
2100	9.125	70.219	62.652	15.890	156.648	77.852	- 8.102
2200	9.139	70.644	63.006	16.804	156.271	74.108	- 7.362
2300	9.153	71.050	63.347	17.718	155.893	70.383	- 6.688
2400	9.167	71.440	63.676	18.634	155.514	66.673	- 6.071
2500	9.180	71.815	63.994	19.552	155.136	62.979	- 5.505
2600	9.194	72.175	64.302	20.470	154.755	59.299	- 4.984
2700	9.206	72.522	64.600	21.390	154.375	55.633	- 4.503
2800	9.219	72.857	64.889	22.312	83.442	53.638	- 4.186
2900	9.232	73.181	65.169	23.234	83.263	52.576	- 3.962
3000	9.244	73.494	65.441	24.158	83.085	51.522	- 3.753
3100	9.256	73.797	65.706	25.083	82.907	50.473	- 3.558
3200	9.268	74.091	65.964	26.009	82.727	49.430	- 3.376
3300	9.280	74.377	66.214	26.937	82.548	48.390	- 3.205
3400	9.292	74.654	66.458	27.865	82.368	47.358	- 3.044
3500	9.303	74.924	66.696	28.795	82.187	46.327	- 2.893
3600	9.315	75.186	66.929	29.726	82.006	45.308	- 2.750
3700	9.327	75.441	67.155	30.658	81.824	44.290	- 2.616
3800	9.338	75.690	67.377	31.591	81.642	43.281	- 2.489
3900	9.350	75.933	67.593	32.526	81.459	42.276	- 2.369
4000	9.361	76.170	67.804	33.461	81.275	41.272	- 2.255
4100	9.372	76.401	68.011	34.398	81.090	40.270	- 2.147
4200	9.384	76.627	68.214	35.336	80.903	39.281	- 2.044
4300	9.395	76.848	68.412	36.274	80.714	38.291	- 1.946
4400	9.406	77.064	68.606	37.215	80.525	37.303	- 1.853
4500	9.417	77.275	68.796	38.156	80.334	36.326	- 1.764
4600	9.429	77.483	68.983	39.098	80.140	35.352	- 1.680
4700	9.440	77.685	69.166	40.041	79.945	34.377	- 1.598
4800	9.451	77.884	69.346	40.986	79.747	33.411	- 1.521
4900	9.462	78.079	69.522	41.932	79.547	32.451	- 1.447
5000	9.473	78.271	69.695	42.878	79.343	31.490	- 1.376
5100	9.484	78.458	69.865	43.826	79.136	30.532	- 1.308
5200	9.495	78.643	70.032	44.775	78.926	29.580	- 1.243
5300	9.506	78.824	70.196	45.725	78.713	28.636	- 1.181
5400	9.517	79.001	70.358	46.676	78.495	27.696	- 1.121
5500	9.528	79.176	70.516	47.629	78.273	26.754	- 1.063
5600	9.539	79.348	70.672	48.582	78.046	25.821	- 1.008
5700	9.550	79.517	70.826	49.537	77.814	24.885	- .954
5800	9.561	79.683	70.977	50.492	77.576	23.961	- .903
5900	9.572	79.847	71.126	51.449	77.333	23.044	- .854
6000	9.583	80.007	71.273	52.407	77.083	22.120	- .806

Dec. 31, 1960; June 30, 1963

ALUMINUM CARBIDE (AlC) (IDEAL GAS) MOL. WT. = 38.991

Ground State Configuration $^2\Pi$

$S^\circ_{298.15}$ = [53.4] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [164] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [164.8] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	4

ω_e = [760] cm.$^{-1}$

$\omega_e x_e$ = [5.0] cm.$^{-1}$

σ = 1

B_e = [0.650] cm.$^{-1}$

α_e = [0.006] cm.$^{-1}$

r_e = [1.77] Å

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was calculated from D_0, 83.0 kcal. mole^{-1}, estimated by J. S. Gordon, Astrosystems International, Livingston, N. J., private communication, June 6, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated. P. Zeeman, Can. J. Phys. 32, 9 (1954) reported a D_0 = 1.6 ± 0.2 e.v., 36.9 kcal. mole^{-1}, for a molecule that was apparently AlC(g). However, H. Wooley, Nat'l Bur. Std. Report No. 6928, July 1, 1960, surmised that this D_0 and the reported molecular constants were for the $Al_2(g)$ molecule. His judgment was accepted.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

Boron Carbide (BC)

(Ideal Gas) Mol. Wt. = 22.831

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.080	196.464	196.464	INFINITE
100	6.957	42.195	56.049	- 1.385	197.139	192.948	- 421.667
200	6.972	47.020	50.466	- .689	197.682	188.532	- 206.008
298	7.099	49.822	49.822	.000	198.000	183.966	- 134.844
300	7.102	49.866	49.822	.013	198.004	183.879	- 133.949
400	7.359	51.942	50.103	.736	198.144	179.145	- 97.876
500	7.642	53.615	50.644	1.486	198.155	174.392	- 76.223
600	7.895	55.031	51.260	2.263	198.080	169.645	- 61.790
700	8.102	56.265	51.889	3.063	197.939	164.917	- 51.487
800	8.267	57.358	52.505	3.882	197.750	160.212	- 43.766
900	8.398	58.339	53.100	4.715	197.519	155.532	- 37.767
1000	8.504	59.230	53.669	5.561	197.257	150.881	- 32.973
1100	8.589	60.044	54.212	6.416	196.966	146.257	- 29.057
1200	8.659	60.795	54.730	7.278	196.650	141.661	- 25.799
1300	8.717	61.490	55.223	8.147	196.312	137.093	- 23.046
1400	8.766	62.138	55.694	9.021	195.958	132.552	- 20.691
1500	8.809	62.744	56.144	9.900	195.589	128.036	- 18.654
1600	8.845	63.314	56.575	10.783	195.207	123.543	- 16.874
1700	8.877	63.851	56.987	11.669	194.815	119.076	- 15.308
1800	8.906	64.360	57.383	12.558	194.413	114.632	- 13.918
1900	8.932	64.842	57.763	13.450	194.003	110.211	- 12.677
2000	8.955	65.300	58.128	14.344	193.587	105.812	- 11.562
2100	8.976	65.738	58.480	15.241	193.165	101.435	- 10.556
2200	8.996	66.156	58.820	16.139	192.736	97.076	- 9.643
2300	9.014	66.556	59.148	17.040	187.704	92.739	- 8.812
2400	9.031	66.940	59.464	17.942	187.261	88.618	- 8.069
2500	9.047	67.309	59.771	18.846	186.819	84.516	- 7.388
2600	9.062	67.664	60.068	19.751	186.375	80.432	- 6.761
2700	9.076	68.007	60.355	20.658	185.932	76.365	- 6.181
2800	9.090	68.337	60.635	21.567	185.490	72.317	- 5.644
2900	9.103	68.656	60.906	22.476	185.045	68.282	- 5.146
3000	9.116	68.965	61.169	23.387	184.601	64.265	- 4.682
3100	9.128	69.264	61.426	24.299	184.157	60.263	- 4.248
3200	9.140	69.554	61.675	25.213	183.713	56.273	- 3.843
3300	9.151	69.835	61.918	26.127	183.267	52.292	- 3.463
3400	9.163	70.109	62.155	27.043	182.822	48.332	- 3.107
3500	9.174	70.375	62.386	27.960	182.376	44.383	- 2.771
3600	9.184	70.633	62.612	28.878	181.930	40.446	- 2.455
3700	9.195	70.885	62.832	29.797	181.483	36.524	- 2.157
3800	9.205	71.130	63.047	30.717	181.036	32.614	- 1.876
3900	9.215	71.369	63.257	31.638	180.588	28.712	- 1.609
4000	9.225	71.603	63.463	32.560	58.999	26.363	- 1.440
4100	9.235	71.831	63.664	33.483	58.801	25.546	- 1.362
4200	9.245	72.053	63.861	34.407	58.603	24.740	- 1.287
4300	9.254	72.271	64.054	35.332	58.403	23.938	- 1.217
4400	9.264	72.484	64.244	36.258	58.202	23.138	- 1.149
4500	9.273	72.692	64.429	37.184	57.999	22.340	- 1.085
4600	9.283	72.896	64.611	38.112	57.796	21.552	- 1.024
4700	9.292	73.096	64.789	39.041	57.592	20.768	- .966
4800	9.301	73.292	64.964	39.971	57.385	19.985	- .910
4900	9.310	73.484	65.136	40.901	57.176	19.208	- .857
5000	9.319	73.672	65.305	41.833	56.967	18.438	- .806
5100	9.328	73.856	65.471	42.765	56.753	17.665	- .757
5200	9.337	74.038	65.634	43.698	56.539	16.902	- .710
5300	9.346	74.216	65.794	44.632	56.323	16.141	- .666
5400	9.355	74.390	65.952	45.568	56.105	15.387	- .623
5500	9.364	74.562	66.107	46.503	55.883	14.633	- .581
5600	9.372	74.731	66.259	47.440	55.660	13.885	- .542
5700	9.381	74.897	66.409	48.378	55.433	13.140	- .504
5800	9.390	75.060	66.557	49.316	55.203	12.399	- .467
5900	9.398	75.221	66.703	50.256	54.972	11.668	- .432
6000	9.407	75.379	66.846	51.196	54.737	10.933	- .398

Dec. 31, 1962; June 30, 1963

BORON CARBIDE (BC) (IDEAL GAS) MOL. WT. = 22.831

Ground State Configuration [$^2\Pi$]

$\Delta H^\circ_{f\ 0} = 196 \pm 10$ kcal. mole^{-1}

$S^\circ_{298.15} = [49.822]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 198 \pm 10$ kcal. mole^{-1}

$\omega_e = [1350]$ cm.$^{-1}$

$\omega_e x_e = [12.0]$ cm.$^{-1}$

$B_e = [1.555]$ cm.$^{-1}$

$\alpha_e = [0.018]$ cm.$^{-1}$

$\sigma = 1$

Heat of Formation.

The heat of formation at 298.15°K. was calculated from $\Delta H^\circ_0 = 105 \pm 10$ kcal. mole^{-1} for the reaction BC(g) = B(g) + C(g) reported by G. Verhaegen, F. E. Stafford, M. Ackerman, and J. Drowart, Nature, 193, 1280 (1962).

Heat Capacity and Entropy.

All spectroscopic constants were obtained from J. S. Gordon, Astrosystems, International, West Caldwell, New Jersey, private communication, November 2, 1962.

Tetraboron Monocarbide (B_4C)

(Crystal) Mol. Wt. = 55.25515

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.343	-9.219	-9.219	INFINITE
100	1.212	.391	13.526	-1.314	-9.228	-9.213	20.135
200	6.555	2.703	7.449	-.949	-9.261	-9.187	10.039
298	12.690	6.483	6.483	.000	-9.296	-9.151	6.707
300	12.820	6.562	6.483	.024	-9.296	-9.151	6.666
400	18.250	11.047	7.058	1.596	-9.258	-9.105	4.974
500	21.460	15.486	8.304	3.591	-9.234	-9.071	3.965
600	23.510	19.591	9.848	5.846	-9.257	-9.036	3.291
700	24.780	23.315	11.511	8.263	-9.329	-8.994	2.808
800	25.730	26.687	13.200	10.790	-9.441	-8.939	2.442
900	26.527	29.764	14.872	13.403	-9.579	-8.871	2.154
1000	27.318	32.601	16.505	16.095	-9.733	-8.782	1.919
1100	28.044	35.239	18.090	18.864	-9.903	-8.681	1.725
1200	28.726	37.708	19.623	21.703	-10.076	-8.558	1.559
1300	29.376	40.033	21.104	24.608	-10.256	-8.427	1.417
1400	30.003	42.233	22.536	27.577	-10.431	-8.275	1.292
1500	30.614	44.324	23.919	30.608	-10.608	-8.121	1.183
1600	31.211	46.319	25.257	33.699	-10.779	-7.947	1.085
1700	31.799	48.229	26.553	36.850	-10.942	-7.767	.998
1800	32.379	50.063	27.808	40.059	-11.092	-7.577	.920
1900	32.953	51.829	29.026	43.325	-11.220	-7.378	.849
2000	33.522	53.534	30.209	46.649	-11.317	-7.171	.784
2100	34.087	55.183	31.359	50.030	-11.383	-6.959	.724
2200	34.649	56.782	32.479	53.467	-11.417	-6.749	.670
2300	35.207	58.334	33.569	56.959	-11.417	-6.536	.621
2400	35.764	59.844	34.633	60.508	-11.383	-6.321	.576
2500	36.318	61.316	35.671	64.112	-32.859	-5.679	.496
2600	36.871	62.751	36.685	67.771	-32.719	-4.597	.386
2700	37.423	64.153	37.676	71.486	-32.524	-3.515	.285
2800	37.973	65.524	38.647	75.256	-32.275	-2.449	.191
2900	38.523	66.866	39.597	79.081	-31.974	-1.379	.104
3000	39.071	68.181	40.528	82.961	-31.619	-.335	.024
3100	39.618	69.471	41.440	86.895	-31.211	.697	-.049
3200	40.165	70.738	42.336	90.884	-30.750	1.721	-.118
3300	40.711	71.982	43.216	94.928	-30.236	2.731	-.181
3400	41.257	73.205	44.080	99.026	-29.669	3.726	-.240
3500	41.802	74.409	44.929	103.179	-29.049	4.688	-.293

Dec. 31, 1960; June 30, 1963; Sept. 30, 1965; Dec. 31, 1965

TETRABORON MONOCARBIDE (B_4C) (CRYSTAL) MOL. WT. = 55.25515

$S^\circ_{298.15}$ = 6.483 ± 0.03 cal. deg.$^{-1}$ mole^{-1}

T_m = 2743 ± 20 °K.

$\Delta H^\circ_{f\ 0}$ = -9.2 ± 2.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -9.3 ± 2.4 kcal. mole^{-1}

ΔH°_m = [25] kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was calculated from $\Delta H^\circ_{r\ 298.15}$ = -683.3 ± 2.2 kcal. mole^{-1} for the reaction $B_4C(c) + 4O_2(g) \rightarrow 2B_2O_3(amorph) + CO_2(g)$ measured by D. Smith, A. S. Dworkin and E. R. Van Artsdalen, J. Am. Chem. Soc. 77, 2654-6 (1955) and the heat of formation for B_2O_3(amorph) (Dec. 31, 1964) and for CO_2(g) (March 31, 1961) in JANAF Tables.

Heat Capacity and Entropy.

The low temperature heat capacities, 54-294°K., were taken from K. K. Kelley, J. Am. Chem. Soc. 63, 1137 (1941). Above 298°K., C_p was calculated using the equation $C_p = 22.99 + 5.40 \times 10^{-3}T - 10.72 \times 10^5 T^{-2}$ obtained from the enthalpy data in the range 298 to 1726°K. reported by E. G. King, Ind. Eng. Chem. 41, 1298 (1949). The values from the two sources join smoothly at 298°K. The $S^\circ_{298.15}$ was calculated based on the low temperature heat capacities measured by K. K. Kelley, loc. cit., using $S^\circ_{53.1}$ = 0.047 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m was determined by Dolloff, WADD Tech. Rept. 60-143, 1960 and ΔH°_m was estimated.

Tetraboron Monocarbide (B_4C)

(Liquid) Mol. Wt. = 55.25515

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	12.545	16.592	16.592	- .000	18.095	15.226	- 11.161
300	12.700	16.670	16.592	.023	18.094	15.208	- 11.078
400	18.450	21.215	17.173	1.617	18.154	14.240	- 7.780
500	21.400	25.669	18.432	3.618	18.184	13.256	- 5.794
600	23.250	29.742	19.983	5.855	18.143	12.273	- 4.470
700	24.580	33.430	21.645	8.249	18.048	11.303	- 3.529
800	25.640	36.783	23.331	10.761	17.921	10.347	- 2.827
900	26.530	39.855	24.999	13.371	17.780	9.406	- 2.284
1000	27.320	42.692	26.628	16.064	17.627	8.487	- 1.855
1100	28.040	45.330	28.210	18.832	17.456	7.578	- 1.506
1200	28.730	47.799	29.740	21.671	17.283	6.692	- 1.219
1300	29.380	50.125	31.220	24.577	17.104	5.813	- .977
1400	30.000	52.325	32.649	27.546	16.929	4.956	- .774
1500	30.610	54.416	34.031	30.576	16.751	4.100	- .597
1600	31.210	56.410	35.368	33.667	16.580	3.267	- .446
1700	31.800	58.320	36.663	36.818	16.417	2.438	- .313
1800	32.500	60.162	37.917	40.040	16.280	1.618	- .196
1900	32.500	61.919	39.135	43.290	16.136	.807	- .093
2000	32.500	63.586	40.316	46.540	15.965	.007	- .001
2100	32.500	65.172	41.462	49.790	15.768	- .784	.082
2200	32.500	66.684	42.574	53.040	15.547	- 1.569	.156
2300	32.500	68.128	43.654	56.290	15.305	- 2.340	.222
2400	32.500	69.511	44.703	59.540	15.040	- 3.099	.282
2500	32.500	70.838	45.722	62.790	- 6.790	- 3.415	.298
2600	32.500	72.113	46.713	66.040	- 7.059	- 3.278	.276
2700	32.500	73.339	47.676	69.290	- 7.329	- 3.122	.253
2800	32.500	74.521	48.614	72.540	- 7.600	- 2.966	.231
2900	32.500	75.662	49.527	75.790	- 7.874	- 2.787	.210
3000	32.500	76.764	50.417	79.040	- 8.149	- 2.614	.190
3100	32.500	77.829	51.284	82.290	- 8.425	- 2.426	.171
3200	32.500	78.861	52.130	85.540	- 8.703	- 2.226	.152
3300	32.500	79.861	52.955	88.790	- 8.983	- 2.016	.134
3400	32.500	80.831	53.761	92.040	- 9.264	- 1.797	.116
3500	32.500	81.773	54.548	95.290	- 9.547	- 1.584	.099

Dec. 31, 1960; June 30, 1963; Dec. 31, 1965

TETRABORON MONOCARBIDE (B_4C) (LIQUID) MOL. WT. = 55.25515

$S^\circ_{298.15}$ = 16.592 cal. deg.$^{-1}$ mole^{-1}

T_m = 2743 ± 20°K.

$\Delta H^\circ_{f\ 298.15}$ = 18.1 ± 2.5 kcal. mole^{-1}

ΔH°_m = [25] kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was obtained from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1750°K. The heat capacity below 1750°K. was obtained from the heat capacity of the crystal. Above 1750°K. the heat capacity was assumed constant and estimated as 32.50 cal. deg.$^{-1}$ mole^{-1} or 6.5 cal. deg.$^{-1}$ per g-atom.

The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $B_4C(c)$ table.

Diberyllium Monocarbide Be_2C
(Crystal) Mol. Wt. = 30.037

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	10.337	3.900	3.900	.000	-21.700	-21.098	15.465
300	10.356	3.964	3.900	.019	-21.699	-21.094	15.366
400	11.380	7.084	4.319	1.106	-21.736	-20.891	11.414
500	11.891	9.678	5.139	2.270	-21.899	-20.662	9.031
600	12.402	11.891	6.084	3.484	-22.147	-20.394	7.428
700	14.444	13.969	7.062	4.835	-22.365	-20.082	6.270
800	15.465	15.976	8.052	6.339	-22.510	-19.746	5.394
900	16.486	17.856	9.038	7.937	-22.633	-19.393	4.709
1000	17.507	19.646	10.010	9.636	-22.720	-19.028	4.158
1100	18.529	21.363	10.965	11.438	-22.769	-18.656	3.706
1200	19.550	23.019	11.901	13.342	-22.779	-18.281	3.329
1300	20.318	24.616	12.818	15.337	-22.757	-17.907	3.010
1400	20.860	26.142	13.715	17.398	-22.724	-17.535	2.737
1500	21.243	27.595	14.593	19.504	-22.702	-17.166	2.501
1600	21.517	28.976	15.449	21.643	-28.211	-16.641	2.273
1700	21.712	30.286	16.283	23.805	-28.009	-15.924	2.047
1800	21.833	31.531	17.096	25.983	-27.806	-15.219	1.848
1900	21.898	32.714	17.887	28.170	-27.607	-14.525	1.671
2000	21.922	33.838	18.657	30.361	-27.417	-13.842	1.513
2100	21.940	34.908	19.406	32.554	-27.237	-13.166	1.370
2200	21.961	35.929	20.134	34.749	-27.069	-12.502	1.242
2300	21.980	36.905	20.842	36.946	-26.910	-11.838	1.125
2400	22.000	37.841	21.531	39.145	-26.762	-11.186	1.019
2500	22.025	38.740	22.201	41.346	-26.625	-10.544	.922
2600	22.049	39.604	22.854	43.550	-26.496	-9.900	.832
2700	22.072	40.437	23.490	45.756	-26.374	-9.265	.750
2800	22.094	41.240	24.109	47.965	-168.320	-6.418	.501
2900	22.116	42.015	24.714	50.175	-167.714	-.643	.048
3000	22.137	42.765	25.303	52.388	-167.110	5.106	-.372
3100	22.157	43.492	25.878	54.602	-166.508	10.832	-.764
3200	22.177	44.195	26.439	56.819	-165.907	16.549	-1.130
3300	22.195	44.878	26.988	59.038	-165.312	22.240	-1.473
3400	22.213	45.541	27.524	61.258	-164.723	27.914	-1.794
3500	22.230	46.185	28.048	63.480	-164.138	33.566	-2.096

Dec. 31, 1960; Mar. 31, 1962; June 30, 1963

DIBERYLLIUM MONOCARBIDE (Be_2C) (CRYSTAL) MOL. WT. = 30.037

$\Delta H_{f\ 0}^\circ$ = Unknown

$S^\circ_{298.15}$ = [3.9 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = 21.7 ± 2.5 kcal. mole^{-1}

T_m = [2400]°K.

ΔH_m° = [18] kcal. mole^{-1}

Heat of Formation.

The selected $\Delta H_{f\ 298.15}^\circ$ was calculated by the 3rd law method using vapor pressures reported by B. D. Pollock, J. Phys. Chem. 63, 587 (1959). Pressures for the reaction $Be_2C(c) \rightarrow 2Be(g) + C_{(graphite)}$ were measured by Pollock in the temperature range 1430-1669°K. by Knudsen technique. Vapor pressure data for this decomposition reaction have also been reported by J. Baboin, French Patents 1.193.790 (1959), J. Quirk, Reactor Handbook 3, 98 (1955) and F. Muratov and A. Novoselova, Dokl. Akad. Nauk SSSR 129, 334 (1959). The calculated $\Delta H_{f\ 298.15}^\circ$ values are summarized as follows:

Calc. Method	Number of Pressures	T, °K.	$\Delta H_{r\ 298.15}^\circ$ kcal. mole^{-1}	$\Delta H_{f\ 298.15}^\circ$ kcal. mole^{-1}	References
3rd law	14	1430-1669	89.117	-21.7	B. D. Pollock
2nd law	14	1430-1669	90.8	-25.1	Least squares fit of Pollock's v.p. to the equation: log P (atm.) = 6.946-19,593/T
3rd law	6	1673-1953	71.411	+13.7	F. Muratov and A. Novoselova
3rd law	8	1900-2600	81.278	- 6.1	J. Quirk
3rd law	8	1600-2300	96.266	-36.0	J. Baboin

H. L. Schick, D. F. Anthrop, P. L. Hanst, R. E. Dreikorn, and M. B. Panish, "Thermodynamics of Certain Refractory Compounds, Part II", 1 March 1963 to 31 May 1963 have listed the measured vapor pressures. The vapor pressures reported by J. Baboin (loc. cit.) used in the 3rd law calculation were those listed by H. L. Schick, et al.

Heat Capacity and Entropy.

The heat capacity values, from 298.15 to 1200°K., were derived from the mean C_p data measured by J. J. Neely, E. Teeter, Jr., and J. B. Trice, J. Am. Ceramic Soc. 33, 363 (1950). Neely, et al., estimated an overall error of 15% in their mean heat capacity data. The powdered Be_2C material which was used analyzed 80 to 74% Be_2C. The impurities were mainly oxide and nitride of Be. No corrections were made for the effect of these impurities.

From 1200-2400°K. the C_p was extrapolated so as to approach the value, 22 cal. deg.$^{-1}$ mole^{-1} calculated from O. H. Krikorian, "Estimation of High-Temperature Heat Capacities of Carbides," University of California, UCRL 6785, February 6, 1962. The $S^\circ_{298.15}$, 3.9 cal. deg.$^{-1}$ mole^{-1}, was estimated by Krikorian (loc. cit.).

Melting Data.

H. L. Schick, et al., (loc. cit.) have summarized the available melting data i.e.: Y. Oishi and Y. Hamona, Osaka Kogyo Gijutsu Shikenjo Kiho 8, 89 (1957) have reported decomposition upon heating as low as 1873°K. L. Brewer, L. Bromley, P. Gilles, and N. Lofgren, "The Chemistry and Metallurgy of Miscellaneous Materials," in "Thermodynamics", McGraw-Hill, New York (1950) and I. S. Gaev, AEC TR 3036 Transl. from Zh. Neorg. Khim. 1, 196 (1956) reported melting or dissociation between 2373° and 2423°K.

The melting point is assumed to be 2400°K. as estimated by T. B. Douglas and A. C. Victor, National Bureau of Standards Preliminary Report 6645, 1 January 1960 and H. L. Schick, et al. (loc. cit.). From the estimated melting point, 2400°K., and an estimated 2.5 cal. g. atom^{-1} deg.$^{-1}$ for the entropy of melting, the heat of melting was calculated.

Diberyllium Monocarbide (Be_2C)

(Liquid) Mol. Wt. = 30.037

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	10.337	11.345	11.345	.000	-3.798	-5.416	3.970
300	10.356	11.409	11.345	.019	-3.797	-5.426	3.952
400	11.380	14.529	11.764	1.106	-3.834	-5.967	3.260
500	11.891	17.123	12.584	2.270	-3.997	-6.483	2.834
600	12.402	19.336	13.529	3.484	-4.245	-6.959	2.535
700	14.444	21.414	14.507	4.835	-4.463	-7.392	2.308
800	15.465	23.421	15.497	6.339	-4.608	-7.800	2.131
900	16.486	25.301	16.483	7.937	-4.731	-8.192	1.989
1000	17.507	27.091	17.455	9.636	-4.818	-8.571	1.873
1100	18.529	28.808	18.410	11.438	-4.867	-8.943	1.777
1200	19.550	30.464	19.346	13.342	-4.877	-9.313	1.696
1300	20.318	32.060	20.263	15.337	-4.855	-9.684	1.628
1400	20.860	33.587	21.160	17.398	-4.822	-10.056	1.570
1500	21.243	35.040	22.038	19.504	-4.800	-10.431	1.520
1600	22.000	36.421	22.894	21.643	-10.309	-10.651	1.455
1700	22.000	37.754	23.729	23.843	-10.069	-10.680	1.373
1800	22.000	39.012	24.544	26.043	-9.844	-10.722	1.302
1900	22.000	40.201	25.337	28.243	-9.632	-10.777	1.240
2000	22.000	41.330	26.108	30.443	-9.433	-10.843	1.185
2100	22.000	42.403	26.859	32.643	-9.246	-10.916	1.136
2200	22.000	43.427	27.589	34.843	-9.073	-11.002	1.093
2300	22.000	44.405	28.299	37.043	-8.911	-11.088	1.054
2400	22.000	45.341	28.990	39.243	-8.762	-11.186	1.019
2500	22.000	46.239	29.662	41.443	-8.626	-11.293	.987
2600	22.000	47.102	30.316	43.643	-8.501	-11.400	.958
2700	22.000	47.932	30.953	45.843	-8.385	-11.515	.932
2800	22.000	48.732	31.574	48.043	-150.340	-9.416	.735
2900	22.000	49.504	32.179	50.243	-149.744	-4.391	.331
3000	22.000	50.250	32.769	52.443	-149.153	.610	-.044
3100	22.000	50.971	33.345	54.643	-148.565	5.588	-.394
3200	22.000	51.670	33.906	56.843	-147.981	10.557	-.721
3300	22.000	52.347	34.455	59.043	-147.405	15.500	-1.026
3400	22.000	53.004	34.991	61.243	-146.836	20.428	-1.313
3500	22.000	53.641	35.515	63.443	-146.273	25.334	-1.582

Dec. 31, 1960; Mar. 31, 1962; June 30, 1963

DIBERYLLIUM MONOCARBIDE (Be_2C) (LIQUID) MOL. WT. = 30.037

$S^\circ_{298.15}$ = [11.345] cal. deg.$^{-1}$ mole^{-1}

T_m = [2400]°K.

$\Delta H^\circ_{f\ 298.15}$ = [3.798 ± 10] kcal. mole^{-1}

ΔH°_m = [18] kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was calculated from the heat of formation of the crystal and the estimated heat of melting.

Heat Capacity and Entropy.

The heat capacity was assumed constant and equal to the heat capacity of the solid Be_2C at the estimated melting point.

Melting Data.

The National Bureau of Standards Report 6645, January, 1960, states that Be_2C seems to decompose easily only at temperatures above its reported melting point. For this reason they extended their Be_2C table into the liquid region. For detailed melting data see the Be_2C (c) table.

Carbon Monobromide (CBr)

(Ideal Gas)   GFW = 91.92015

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°₂₉₈)/T	H°-H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.266	122.915	122.915	INFINITE
100	7.074	47.282	62.975	-1.569	123.264	119.201	-260.512
200	7.986	52.448	56.541	-.819	123.351	115.096	-125.770
298	8.514	55.770	55.770	.000	122.000	111.201	-81.513
300	8.621	55.823	55.770	.016	121.995	111.135	-80.961
400	8.876	58.344	56.112	.893	118.506	108.239	-59.139
500	8.973	60.337	56.764	1.786	118.639	105.656	-46.182
600	9.012	61.977	57.501	2.686	118.717	103.050	-37.536
700	9.031	63.367	58.242	3.588	118.747	100.437	-31.358
800	9.041	64.574	58.960	4.492	118.744	97.821	-26.724
900	9.049	65.639	59.644	5.396	118.713	95.207	-23.119
1000	9.056	66.593	60.292	6.301	118.662	92.598	-20.237
1100	9.062	67.456	60.905	7.207	118.594	89.994	-17.880
1200	9.069	68.245	61.484	8.114	118.513	87.398	-15.917
1300	9.076	68.971	62.032	9.021	118.418	84.809	-14.258
1400	9.083	69.644	62.552	9.929	118.317	82.229	-12.836
1500	9.090	70.271	63.046	10.837	118.208	79.654	-11.606
1600	9.098	70.858	63.516	11.747	118.093	77.086	-10.530
1700	9.105	71.410	63.965	12.657	117.974	74.527	-9.581
1800	9.113	71.930	64.393	13.568	117.850	71.976	-8.739
1900	9.121	72.423	64.803	14.480	117.724	69.432	-7.986
2000	9.129	72.891	65.195	15.392	117.595	66.893	-7.310
2100	9.138	73.337	65.573	16.305	117.464	64.361	-6.698
2200	9.146	73.762	65.935	17.220	117.329	61.834	-6.143
2300	9.154	74.169	66.284	18.135	117.194	59.316	-5.636
2400	9.163	74.559	66.621	19.050	117.055	56.802	-5.173
2500	9.171	74.933	66.946	19.967	116.917	54.294	-4.746
2600	9.180	75.293	67.260	20.885	116.775	51.792	-4.354
2700	9.188	75.640	67.564	21.803	116.633	49.292	-3.990
2800	9.197	75.974	67.859	22.722	116.490	46.803	-3.653
2900	9.206	76.297	68.144	23.642	116.344	44.317	-3.340
3000	9.214	76.609	68.421	24.563	116.198	41.836	-3.048
3100	9.223	76.911	68.690	25.485	116.051	39.362	-2.775
3200	9.232	77.204	68.952	26.408	115.903	36.890	-2.519
3300	9.241	77.488	69.206	27.332	115.753	34.421	-2.280
3400	9.249	77.764	69.454	28.256	115.602	31.960	-2.054
3500	9.258	78.033	69.695	29.182	115.450	29.498	-1.842
3600	9.267	78.294	69.930	30.108	115.296	27.044	-1.642
3700	9.276	78.548	70.160	31.035	115.142	24.596	-1.453
3800	9.285	78.795	70.384	31.963	114.987	22.155	-1.274
3900	9.295	79.036	70.603	32.892	114.830	19.716	-1.105
4000	9.304	79.272	70.816	33.822	114.672	17.276	-.944
4100	9.313	79.502	71.025	34.753	114.513	14.840	-.791
4200	9.323	79.726	71.230	35.685	114.352	12.416	-.646
4300	9.333	79.946	71.430	36.618	114.190	9.988	-.508
4400	9.342	80.160	71.626	37.551	114.027	7.569	-.376
4500	9.352	80.370	71.818	38.486	113.863	5.150	-.250
4600	9.363	80.576	72.006	39.422	113.697	2.736	-.130
4700	9.373	80.778	72.191	40.359	113.531	.324	-.015
4800	9.384	80.975	72.372	41.296	113.362	-2.081	.095
4900	9.394	81.169	72.549	42.235	113.193	-4.486	.200
5000	9.405	81.359	72.724	43.175	113.022	-6.885	.301
5100	9.417	81.545	72.895	44.116	112.849	-9.286	.398
5200	9.428	81.728	73.063	45.059	112.676	-11.677	.491
5300	9.440	81.908	73.228	46.002	112.501	-14.066	.580
5400	9.452	82.084	73.390	46.947	112.325	-16.449	.666
5500	9.465	82.258	73.550	47.892	112.146	-18.833	.748
5600	9.477	82.428	73.707	48.840	111.968	-21.212	.828
5700	9.490	82.596	73.861	49.788	111.786	-23.591	.905
5800	9.504	82.761	74.014	50.738	111.605	-25.963	.978
5900	9.518	82.924	74.163	51.689	111.421	-28.332	1.049
6000	9.532	83.084	74.311	52.641	111.237	-30.705	1.118

June 30, 1967

CARBON MONOBROMIDE (CBr)   (IDEAL GAS)   GFW = 91.92015

Ground State Configuration $^2\Pi$

$S^\circ_{298.15}$ = [55.8] gibbs/mol

ΔHf°_0 = 123 ± 15 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 122 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
465	2
33163	2
33218	2
[40000]	[2]

ω_e = [736] cm^{-1} $\omega_e x_e$ = [4.0] cm^{-1} σ = 1

B_e = 0.4890 cm^{-1} α_e = [0.0036] cm^{-1} r_e = 1.8170 Å

Heat of Formation

Dixon and Kroto (1) have observed predissociation of CBr(g) which indicates that the dissociation energy (D°_0) is less than 94.7 kcal/mol. They evaluated the kinetic data of Simons and Yarwood (2), obtaining a value of D°_0 = 97 ± 5 kcal/mol, based on the heat of formation of bromoform and the dissociation energy of HBr, and concluded that the true value of D°_0 is very close to the upper limit of 94.7 kcal/mol. Comparisons of C-X bond energies of CX_4 and CX compounds, however, indicate that this value is too high to be consistent with other carbon halides. Therefore the value of D°_0 adopted is 75 ± 15 kcal/mol. The corresponding ΔHf°_{298} for CBr(g) is 122 ± 15 kcal/mol.

Heat Capacity and Entropy

The rotational structure of the near UV spectra of CBr(g) has been investigated by Dixon and Kroto (1) in the 3000 Å region. They assigned the above doublet electronic levels to the ground ($^2\Pi$) and first excited ($^2\Delta$) states and reported a value of B_0 = 0.4872 ± 0.0003 cm^{-1} for the ground state. An additional electronic level ($^2\Sigma$) is expected to be close to the first excited state by analogy with CF(g) and CCl(g).

The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for single bonded molecules (3). The anharmonic vibrational term $\omega_e x_e$ is estimated by assuming $\omega_e x_e = \omega_e^2/(4D_0 + 2\omega_e)$. The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + \alpha_e/2$. The bond distance is calculated from B_e.

References

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Bromotrifluoromethane ($CBrF_3$)

(Ideal Gas) GFW = 148.91535

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.458	-152.211	-152.211	INFINITE
100	9.398	57.362	83.681	-2.632	-152.776	-151.743	331.635
200	13.485	65.167	72.578	-1.482	-153.340	-150.476	164.432
298	16.570	71.155	71.155	.000	-155.100	-148.819	109.087
300	16.620	71.258	71.156	.031	-155.111	-148.780	108.386
400	18.946	76.375	71.837	1.815	-158.847	-145.903	79.717
500	20.627	80.794	73.197	3.798	-158.835	-142.668	62.360
600	21.824	84.667	74.793	5.924	-158.779	-139.439	50.791
700	22.682	88.099	76.453	8.152	-158.700	-136.221	42.530
800	23.306	91.170	78.104	10.453	-158.605	-133.018	36.339
900	23.770	93.944	79.713	12.808	-158.500	-129.826	31.526
1000	24.121	96.467	81.264	15.203	-158.388	-126.646	27.679
1100	24.392	98.779	82.752	17.629	-158.274	-123.479	24.533
1200	24.605	100.911	84.178	20.080	-158.156	-120.319	21.913
1300	24.775	102.887	85.542	22.549	-158.043	-117.170	19.698
1400	24.913	104.729	86.848	25.034	-157.928	-114.029	17.801
1500	25.026	106.452	88.098	27.531	-157.815	-110.897	16.158
1600	25.119	108.070	89.296	30.038	-157.705	-107.775	14.721
1700	25.198	109.595	90.445	32.554	-157.595	-104.656	13.454
1800	25.264	111.037	91.550	35.077	-157.489	-101.548	12.330
1900	25.320	112.405	92.612	37.606	-157.384	-98.441	11.323
2000	25.369	113.705	93.634	40.141	-157.282	-95.340	10.418
2100	25.411	114.943	94.620	42.680	-157.182	-92.247	9.600
2200	25.448	116.126	95.570	45.223	-157.087	-89.159	8.857
2300	25.480	117.258	96.489	47.769	-156.994	-86.070	8.178
2400	25.508	118.343	97.377	50.319	-156.906	-82.989	7.557
2500	25.533	119.385	98.237	52.871	-156.821	-79.912	6.986
2600	25.555	120.387	99.070	55.425	-156.740	-76.837	6.459
2700	25.575	121.352	99.877	57.982	-156.661	-73.765	5.971
2800	25.593	122.282	100.661	60.540	-156.586	-70.697	5.518
2900	25.609	123.181	101.422	63.100	-156.516	-67.627	5.097
3000	25.624	124.049	102.162	65.662	-156.451	-64.569	4.704
3100	25.637	124.890	102.881	68.225	-156.388	-61.505	4.336
3200	25.649	125.704	103.582	70.789	-156.330	-58.444	3.992
3300	25.660	126.493	104.264	73.355	-156.277	-55.390	3.668
3400	25.670	127.259	104.929	75.921	-156.227	-52.331	3.364
3500	25.679	128.004	105.578	78.489	-156.184	-49.274	3.077
3600	25.687	128.727	106.211	81.057	-156.142	-46.220	2.806
3700	25.695	129.431	106.829	83.626	-156.107	-43.168	2.550
3800	25.702	130.116	107.433	86.196	-156.076	-40.112	2.307
3900	25.709	130.784	108.023	88.767	-156.050	-37.063	2.077
4000	25.715	131.435	108.600	91.338	-156.028	-34.011	1.858
4100	25.720	132.070	109.165	93.909	-156.012	-30.965	1.651
4200	25.726	132.690	109.718	96.482	-156.000	-27.912	1.452
4300	25.730	133.295	110.259	99.055	-155.992	-24.861	1.264
4400	25.735	133.887	110.790	101.628	-155.992	-21.813	1.083
4500	25.739	134.465	111.309	104.202	-155.994	-18.768	.911
4600	25.743	135.031	111.819	106.776	-156.002	-15.716	.747
4700	25.747	135.585	112.319	109.350	-156.016	-12.664	.589
4800	25.751	136.127	112.809	111.925	-156.034	-9.611	.438
4900	25.754	136.658	113.290	114.500	-156.058	-6.560	.293
5000	25.757	137.178	113.763	117.076	-156.087	-3.510	.153
5100	25.760	137.688	114.227	119.652	-156.123	-.469	.020
5200	25.763	138.188	114.683	122.228	-156.162	2.592	-.109
5300	25.765	138.679	115.131	124.804	-156.207	5.649	-.233
5400	25.768	139.161	115.572	127.381	-156.259	8.697	-.352
5500	25.770	139.634	116.005	129.958	-156.315	11.757	-.467
5600	25.772	140.098	116.431	132.535	-156.377	14.812	-.578
5700	25.775	140.554	116.850	135.112	-156.446	17.868	-.685
5800	25.777	141.002	117.263	137.690	-156.518	20.928	-.789
5900	25.778	141.443	117.669	140.268	-156.597	23.987	-.889
6000	25.780	141.876	118.069	142.846	-156.681	27.042	-.985

June 30, 1969

BROMOTRIFLUOROMETHANE ($CBrF_3$) (IDEAL GAS) GFW = 148.91535

Point Group C_{3v}

$\Delta Hf^\circ_0 = -152.2 \pm 0.7$ kcal/mol

$S^\circ_{298.15} = 71.155 \pm 0.12$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -155.1 \pm 0.7$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1086 (1)	1206 (2)
761 (1)	549 (2)
348 (1)	300 (2)

Bond Distance: C-F = 1.328 Å C-Br = 1.909 Å

Bond Angle: F-C-F = 108.6 ± 1° F-C-Br = 110.33° $\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = 2.3403 \times 10^{-113}$ g^3 cm^6

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2, 3, 4) have determined equilibrium data for $CClF_3(g) + BrCl(g) = CBrF_3(g) + Cl_2(g)$ and for $CF_3X(g) + Br_2(g) = CF_3Br(g) + BrX(g)$ where X = H, Cl, and CF_3. Equilibrium data for $CF_3I(g) + BrI(g) = CBrF_3(g) + I_2(g)$ were obtained by Lord et al. (5). These data link $CBrF_3$ with C_2F_6, CHF_3, $CClF_3$ and CF_3I.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Sharbaugh et al. (6), Bowen (7), and Anderson (8) and from microwave data by Sheridan and Gordy (9). The adopted parameters are an average of those reported by (8, 9). Infrared spectra of the gas were observed by several investigators (10, 11, 12) and Raman spectra of the liquid were obtained by Edgell and May (12). The vibrational assignments of (11, 12) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. The value for ν_6 is taken as 300 cm^{-1} which is between the values of 305 and 297 ± 3 cm^{-1} derived from Raman spectra and IR (combination and overtone) spectra, respectively.

The thermodynamic functions of this table are essentially the same as those calculated by (11). Uncertainty in the entropy is estimated to vary from 0.12 to 0.5 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for $CClF_3(g)$ and $CF_4(g)$. The principal moments of inertia are $I_A = 14.68 \times 10^{-39}$ and $I_B = I_C = 39.93 \times 10^{-39}$ g cm^2.

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Cyanogen Bromide (BrCN)

(Ideal Gas) GFW = 105.92685

T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.647	46.071	46.071	INFINITE
100	7.699	48.996	68.366	-1.937	46.086	43.759	-95.636
200	9.970	55.071	60.306	-1.047	45.965	41.483	-45.331
298	11.263	59.334	59.334	.000	44.500	39.462	-28.926
300	11.280	59.404	59.334	.021	44.494	39.431	-28.725
400	11.983	62.751	59.786	1.186	40.944	38.478	-21.024
500	12.451	65.477	60.660	2.408	41.055	37.848	-16.543
600	12.826	67.781	61.659	3.673	41.141	37.198	-13.549
700	13.150	69.783	62.680	4.972	41.205	36.536	-11.407
800	13.433	71.557	63.681	6.301	41.256	35.865	-9.798
900	13.680	73.154	64.646	7.657	41.296	35.188	-8.545
1000	13.895	74.607	65.571	9.036	41.332	34.508	-7.542
1100	14.081	75.940	66.454	10.435	41.363	33.823	-6.720
1200	14.244	77.173	67.296	11.852	41.397	33.137	-6.035
1300	14.386	78.318	68.100	13.283	41.416	32.448	-5.455
1400	14.511	79.389	68.869	14.728	41.442	31.758	-4.958
1500	14.621	80.394	69.604	16.185	41.466	31.066	-4.526
1600	14.720	81.341	70.308	17.652	41.491	30.371	-4.148
1700	14.809	82.236	70.984	19.129	41.517	29.675	-3.815
1800	14.890	83.085	71.633	20.614	41.543	28.977	-3.518
1900	14.965	83.892	72.257	22.106	41.571	28.281	-3.253
2000	15.033	84.661	72.858	23.606	41.600	27.579	-3.014
2100	15.096	85.396	73.438	25.113	41.631	26.878	-2.797
2200	15.155	86.100	73.997	26.625	41.662	26.173	-2.600
2300	15.211	86.775	74.538	28.144	41.695	25.470	-2.420
2400	15.263	87.423	75.062	29.667	41.729	24.764	-2.255
2500	15.313	88.047	75.569	31.196	41.765	24.056	-2.103
2600	15.361	88.649	76.060	32.730	41.801	23.347	-1.962
2700	15.406	89.230	76.538	34.268	41.840	22.635	-1.832
2800	15.450	89.791	77.001	35.811	41.880	21.924	-1.711
2900	15.492	90.334	77.451	37.358	41.920	21.211	-1.599
3000	15.533	90.859	77.890	38.910	41.962	20.496	-1.493
3100	15.573	91.369	78.316	40.465	42.005	19.780	-1.395
3200	15.612	91.864	78.732	42.024	42.050	19.063	-1.302
3300	15.650	92.345	79.137	43.587	42.094	18.341	-1.215
3400	15.687	92.813	79.533	45.154	42.141	17.623	-1.133
3500	15.723	93.268	79.918	46.725	42.187	16.898	-1.055
3600	15.758	93.712	80.296	48.299	42.235	16.175	-.982
3700	15.793	94.144	80.664	49.876	42.284	15.451	-.913
3800	15.828	94.566	81.024	51.457	42.333	14.728	-.847
3900	15.861	94.977	81.377	53.042	42.384	14.002	-.785
4000	15.895	95.379	81.722	54.629	42.435	13.272	-.725
4100	15.928	95.772	82.060	56.221	42.487	12.540	-.668
4200	15.961	96.156	82.391	57.815	42.539	11.812	-.615
4300	15.993	96.532	82.715	59.413	42.591	11.080	-.563
4400	16.025	96.900	83.034	61.014	42.645	10.345	-.514
4500	16.057	97.261	83.346	62.618	42.698	9.608	-.467
4600	16.088	97.614	83.652	64.225	42.753	8.876	-.422
4700	16.119	97.960	83.953	65.835	42.808	8.139	-.378
4800	16.150	98.300	84.248	67.449	42.861	7.401	-.337
4900	16.181	98.633	84.538	69.065	42.917	6.660	-.297
5000	16.212	98.961	84.824	70.685	42.973	5.922	-.259
5100	16.242	99.282	85.104	72.308	43.027	5.172	-.222
5200	16.273	99.598	85.380	73.934	43.083	4.433	-.186
5300	16.303	99.908	85.651	75.562	43.139	3.691	-.152
5400	16.333	100.213	85.918	77.194	43.195	2.946	-.119
5500	16.363	100.513	86.180	78.829	43.249	2.204	-.088
5600	16.392	100.808	86.439	80.467	43.305	1.454	-.057
5700	16.422	101.098	86.694	82.107	43.360	.705	-.027
5800	16.452	101.384	86.944	83.751	43.415	-.043	.002
5900	16.481	101.666	87.192	85.398	43.470	-.790	.029
6000	16.510	101.943	87.435	87.047	43.524	-1.548	.056

Sept. 30, 1962; June 30, 1963; June 30, 1969

CYANOGEN BROMIDE (BrCN) (IDEAL GAS) GFW = 105.92685

Point Group $C_{\infty v}$

$\Delta Hf_0^\circ = 46.1 \pm 1.5$ kcal/mol

$S^\circ_{298.15} = 59.33 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 44.5 \pm 1.5$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
575	(1)
342.5	(2)
2200	(1)

Bond Distance: C-Br = 1.789 Å C-N = 1.158 Å

Bond Angle: Br-C-N = 180° $\sigma = 1$

Rotational Constants: $B_0 = 0.13705$ $D_0 = 2.929 \times 10^{-8}$ cm^{-1}

Spectroscopic constants used in calculating corrections to rigid-rotator-harmonic oscillator approximation (cm^{-1}).

$\alpha_1 = 5.17 \times 10^{-4}$ $x_{11} = [-3.0]$ $x_{12} = [-4.0]$

$\alpha_2 = -3.84 \times 10^{-4}$ $x_{22} = -0.86$ $x_{23} = -6.19$

$\alpha_3 = 6.77 \times 10^{-4}$ $x_{33} = [-5.0]$ $x_{13} = [-3.0]$

$g_{22} = 1.14$

Heat of Formation

The heat of formation is calculated from ΔHf°_{298}(BrCN, c) = 33.58 kcal/mol (1) and ΔHs°_{298} = 10.92 ± 0.1 kcal/mol. This latter is obtained from an analysis of the vapor pressure data of Lord and Woolf (2) and Baxter et al. (3).

The heat of formation of the crystal is calculated from ΔHr°_{298} = -56.0 kcal/mol obtained by Lord and Woolf (2) for the reaction

$$BrCN(c) + 2NaOH(56\ H_2O) = NaCNO(2800\ H_2O) + NaBr(2800\ H_2O) + H_2O(\ell).$$

The auxiliary data used were $\Delta Hf^\circ_{298}(NaOH\cdot 56\ H_2O)$ = -112.26 kcal/mol (1, 4), $\Delta Hf(NaCNO\cdot 2800\ H_2O)$ = -92.25 kcal/mol (1, 4) and $\Delta Hf^\circ_{298}(NaBr\cdot 2800\ H_2O)$ = -70.54 kcal/mol (1, 4). The uncertainty in the final value reflects the uncertainty in $\Delta Hf(NaCNO\cdot 2800\ H_2O)$ which was determined by Lord and Woolf (2) to be -93.6 kcal/mol in excess $NaOH\cdot 56\ H_2O$.

Heat Capacity and Entropy

J. S. Gordon (5) used the constants given above to calculate the adopted table, using the method of Pennington and Kobe (6) for anharmonicity, vibration rotation interaction, and centrifugal stretching corrections.

The bond lengths and angle were reported by Tyler and Sheridan (7).

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Carbon Tetrabromide (CBr_4)

(Ideal Gas) Mol. Wt. = 331.675

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.872	19.097	19.097	INFINITE
100	15.186	65.290	103.227	-3.794	18.826	14.892	-32.545
200	19.456	77.319	87.489	-2.034	18.166	11.205	-12.244
298	21.793	85.563	85.563	.000	12.000	8.590	-6.297
300	21.826	85.698	85.563	.040	11.970	8.570	-6.243
400	23.204	92.183	86.438	2.298	-2.498	10.421	-5.694
500	24.012	97.456	88.131	4.662	-2.219	13.618	-5.952
600	24.510	101.881	90.064	7.090	-1.945	16.759	-6.104
700	24.834	105.685	92.030	9.559	-1.687	19.855	-6.199
800	25.054	109.017	93.949	12.054	-1.443	22.915	-6.260
900	25.210	111.977	95.791	14.567	-1.213	25.946	-6.300
1000	25.324	114.639	97.545	17.094	-.992	28.953	-6.327
1100	25.409	117.057	99.211	19.631	-.782	31.935	-6.345
1200	25.475	119.271	100.791	22.176	-.579	34.902	-6.356
1300	25.527	121.312	102.292	24.726	-.388	37.852	-6.363
1400	25.569	123.206	103.719	27.281	-.201	40.787	-6.367
1500	25.602	124.971	105.078	29.839	-.023	43.707	-6.368
1600	25.630	126.624	106.374	32.401	-.151	46.616	-6.367
1700	25.653	128.179	107.611	34.965	-.321	49.516	-6.365
1800	25.672	129.646	108.795	37.531	-.486	52.403	-6.362
1900	25.689	131.034	109.929	40.099	-.648	55.287	-6.359
2000	25.703	132.352	111.017	42.669	-.805	58.155	-6.355
2100	25.715	133.606	112.064	45.240	-.961	61.020	-6.350
2200	25.725	134.803	113.070	47.812	-1.110	63.874	-6.345
2300	25.735	135.947	114.040	50.385	-1.257	66.727	-6.340
2400	25.743	137.042	114.976	52.959	-1.400	69.572	-6.335
2500	25.750	138.093	115.880	55.534	-1.541	72.408	-6.330
2600	25.756	139.103	116.754	58.109	-1.677	75.241	-6.324
2700	25.762	140.075	117.599	60.685	-1.811	78.063	-6.318
2800	25.767	141.012	118.419	63.261	-1.940	80.888	-6.313
2900	25.771	141.917	119.214	65.838	-2.067	83.706	-6.308
3000	25.776	142.790	119.985	68.415	-2.191	86.518	-6.302
3100	25.779	143.636	120.735	70.993	-2.311	89.330	-6.297
3200	25.783	144.454	121.463	73.571	-2.429	92.135	-6.292
3300	25.786	145.247	122.172	76.150	-2.542	94.930	-6.287
3400	25.789	146.017	122.862	78.728	-2.653	97.730	-6.282
3500	25.791	146.765	123.534	81.307	-2.759	100.525	-6.277
3600	25.793	147.491	124.190	83.887	-2.863	103.315	-6.272
3700	25.796	148.198	124.829	86.466	-2.964	106.105	-6.267
3800	25.798	148.886	125.453	89.046	-3.061	108.894	-6.263
3900	25.800	149.556	126.063	91.626	-3.154	111.682	-6.258
4000	25.801	150.210	126.658	94.206	-3.244	114.458	-6.253
4100	25.803	150.847	127.240	96.786	-3.330	117.234	-6.249
4200	25.804	151.468	127.810	99.366	-3.412	120.015	-6.245
4300	25.806	152.076	128.367	101.947	-3.491	122.792	-6.241
4400	25.807	152.669	128.913	104.527	-3.566	125.566	-6.237
4500	25.808	153.249	129.447	107.108	-3.638	128.334	-6.232
4600	25.809	153.816	129.971	109.689	-3.706	131.107	-6.229
4700	25.810	154.371	130.484	112.270	-3.771	133.880	-6.225
4800	25.811	154.915	130.987	114.851	-3.829	136.642	-6.221
4900	25.812	155.447	131.481	117.432	-3.886	139.411	-6.218
5000	25.813	155.968	131.966	120.014	-3.940	142.178	-6.214
5100	25.814	156.479	132.441	122.595	-3.986	144.932	-6.210
5200	25.815	156.981	132.908	125.176	-4.031	147.698	-6.207
5300	25.815	157.472	133.367	127.758	-4.073	150.467	-6.204
5400	25.816	157.955	133.818	130.339	-4.108	153.224	-6.201
5500	25.817	158.429	134.261	132.921	-4.141	155.992	-6.198
5600	25.817	158.894	134.697	135.503	-4.169	158.746	-6.195
5700	25.818	159.351	135.126	138.085	-4.192	161.507	-6.192
5800	25.819	159.800	135.547	140.666	-4.212	164.270	-6.190
5900	25.819	160.241	135.962	143.248	-4.227	167.030	-6.187
6000	25.820	160.675	136.370	145.830	-4.238	169.777	-6.184

Dec. 31, 1963

CARBON TETRABROMIDE (CBr_4) (IDEAL GAS) MOL. WT. = 331.675

Point Group T_d

ΔH_f° = [19] kcal. mole^{-1}

$S^\circ_{298.15}$ = 85.563 cal. deg.$^{-1}$ mole^{-1}

ΔH_f° 298.15 = [12] kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
267.2 (1)	670.7 (3)
122.5 (2)	182.5 (3)

Bond Distance: C-Br = 1.942 Å

Bond Angle: Br-C-Br = 109° 28'

σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = 2.3756 X 10^{-111} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation, ΔH_f° 298.15, was calculated and reported by F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Circular 500, 1952.

Heat Capacity and Entropy.

The molecular constants, bond distance, and bond angle were determined by electron diffraction by C. Finbak, O. Hassel, and B. Ottar, Arch. Math. Naturv B44, No. 13 (1941) and C. Finbak, O. Hassel, and O. Olaussen, Tidsskr. Kjemi Bergv. 3, 13 (1943). The constants reported by C. Finbak, et al., in 1943 were selected. These constants are listed in, "Tables of Interatomic Distances and Configuration In Molecules and Ions," Special Publication No. 11, The Chemical Society (London), 1958. The principal moments of inertia calculated from these constants were $I_A = I_B = I_C$ = 1.3343 X 10^{-37} g. cm.^{2}

The vibrational frequencies used were assigned by A. G. Meister, S. E. Rosser, and F. F. Cleveland, J. Chem. Phys. 18, 346 (1950). They measured the infrared and Raman spectrum, considered the previous literature, calculated force constants and made most probable value assignments for the frequencies. A more recent paper by B. Moszynska and J. P. Mathieu, Compt. Rend 256, 2820 (1963) made assignments from Raman and Infrared spectra which agreed with all of Meister, et al.'s assignments except ν_2 which they found was 126 cm.$^{-1}$ rather than 122 cm.$^{-1}$.

Carbon Monochloride (CCl)

(Ideal Gas) GFW = 47.46415

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.245	119.104	119.104	INFINITE
100	7.780	45.342	60.362	-1.502	119.485	117.229	-256.204
200	7.488	50.612	54.330	-.744	119.802	114.840	-125.491
298	7.709	53.634	53.634	.000	120.000	112.358	-82.361
300	7.715	53.681	53.634	.014	120.003	112.311	-81.818
400	8.029	55.945	53.940	.802	120.129	109.726	-59.952
500	8.278	57.764	54.529	1.618	120.200	107.117	-46.821
600	8.459	59.291	55.199	2.455	120.225	104.497	-38.063
700	8.588	60.605	55.879	3.308	120.213	101.876	-31.807
800	8.684	61.758	56.543	4.172	120.175	99.259	-27.116
900	8.757	62.785	57.181	5.044	120.115	96.647	-23.469
1000	8.814	63.711	57.788	5.923	120.041	94.043	-20.553
1100	8.859	64.553	58.366	6.806	119.953	91.446	-18.169
1200	8.897	65.326	58.914	7.694	119.855	88.860	-16.184
1300	8.929	66.039	59.435	8.585	119.746	86.281	-14.505
1400	8.957	66.702	59.931	9.480	119.633	83.712	-13.068
1500	8.981	67.321	60.403	10.377	119.513	81.151	-11.824
1600	9.003	67.901	60.854	11.276	119.388	78.596	-10.736
1700	9.023	68.448	61.284	12.177	119.261	76.051	-9.777
1800	9.041	68.964	61.697	13.080	119.129	73.512	-8.926
1900	9.058	69.453	62.092	13.985	118.996	70.983	-8.165
2000	9.074	69.918	62.472	14.892	118.860	68.459	-7.481
2100	9.089	70.361	62.837	15.800	118.724	65.943	-6.863
2200	9.103	70.784	63.189	16.710	118.584	63.431	-6.301
2300	9.118	71.189	63.528	17.621	118.443	60.930	-5.790
2400	9.131	71.578	63.855	18.533	118.300	58.432	-5.321
2500	9.145	71.951	64.172	19.447	118.156	55.939	-4.890
2600	9.159	72.310	64.478	20.362	118.010	53.454	-4.493
2700	9.172	72.656	64.774	21.279	117.862	50.973	-4.126
2800	9.186	72.989	65.062	22.197	117.714	48.500	-3.786
2900	9.200	73.312	65.341	23.116	117.563	46.030	-3.469
3000	9.215	73.624	65.612	24.037	117.410	43.565	-3.174
3100	9.229	73.926	65.875	24.959	117.257	41.107	-2.898
3200	9.245	74.220	66.131	25.883	117.102	38.653	-2.640
3300	9.260	74.504	66.381	26.808	116.944	36.202	-2.398
3400	9.277	74.781	66.624	27.735	116.787	33.760	-2.170
3500	9.294	75.050	66.861	28.663	116.627	31.317	-1.956
3600	9.311	75.312	67.092	29.594	116.467	28.883	-1.753
3700	9.329	75.568	67.318	30.526	116.305	26.453	-1.563
3800	9.348	75.817	67.538	31.459	116.142	24.028	-1.382
3900	9.368	76.060	67.753	32.395	115.979	21.607	-1.211
4000	9.388	76.297	67.964	33.333	115.815	19.190	-1.048
4100	9.409	76.529	68.170	34.273	115.650	16.773	-.894
4200	9.431	76.756	68.372	35.215	115.484	14.366	-.748
4300	9.453	76.979	68.569	36.159	115.318	11.959	-.608
4400	9.476	77.196	68.763	37.106	115.152	9.558	-.475
4500	9.500	77.409	68.953	38.054	114.985	7.157	-.348
4600	9.524	77.618	69.139	39.006	114.819	4.764	-.226
4700	9.549	77.823	69.321	39.959	114.653	2.375	-.110
4800	9.574	78.025	69.501	40.915	114.486	-.012	.001
4900	9.600	78.222	69.677	41.874	114.320	-2.395	.107
5000	9.626	78.417	69.850	42.835	114.155	-4.776	.209
5100	9.653	78.608	70.019	43.799	113.989	-7.156	.307
5200	9.680	78.795	70.186	44.766	113.825	-9.528	.400
5300	9.708	78.980	70.351	45.735	113.661	-11.898	.491
5400	9.736	79.162	70.512	46.708	113.498	-14.264	.577
5500	9.764	79.341	70.671	47.683	113.334	-16.628	.661
5600	9.793	79.517	70.827	48.661	113.173	-18.991	.741
5700	9.822	79.690	70.981	49.641	113.010	-21.355	.819
5800	9.851	79.861	71.133	50.625	112.849	-23.708	.893
5900	9.880	80.030	71.282	51.611	112.689	-26.058	.965
6000	9.909	80.196	71.429	52.601	112.529	-28.412	1.035

Mar. 31, 1961; Dec. 31, 1969

CARBON MONOCHLORIDE (CCl) (IDEAL GAS) GFW = 47.46415

ΔHf°_0 = 119.1 ± 5 kcal/mol

$S^\circ_{298.15}$ = 53.63 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 120 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Pi$	0	2
	134.92	2
$^4\Sigma$	[20000]	4
$A^2\Delta$	36004	4

ω_e = 876.4 cm^{-1} $\omega_e x_e$ = 6.15 cm^{-1} σ = 1

B_e = 0.69666 cm^{-1} α_e = [0.0066] cm^{-1} r_e = 1.642 Å

Heat of Formation

The data of Miller and Palmer (1) provide a value of D_{C-Cl} = 80 ± 5 kcal/mol, which appears to be reasonably substantiated. They studied the chemiluminescence from flames of $CHCl_3$ and CCl_4 burning in potassium vapor. These flames exhibit C_2 Swan band radiation with major departures from vibrational and rotational equilibrium. The spectra are interpreted as due to the reaction $C + CCl \rightarrow C_2^* + Cl$ where the carbon atom is either ^3D ground state or ^1D first excited state. The separation between the ground and first excited state of the carbon atom is matched closely by the difference in preferential population of the excited C_2 levels. The assumption is made that all the exothermicity of the reaction is retained as vibrational excitation of the C_2, thus the populated levels are measures of the heat of reaction. In this manner we obtain a heat of reaction of 67 ± 2.5 kcal for the reaction $C + CCl \rightarrow C_2 + Cl$ which, using JANAF auxiliary data, gives $\Delta Hf^\circ(CCl, g)$ = 124 ± 2.5 kcal/mol; however, this represents the initial state of the CCl which in the flame is presumed to have about 4 kcal of vibrational energy at roughly 2000°K. Thus, we obtain $\Delta Hf^\circ_{298}(CCl, g)$ = 120 ± 5 kcal/mol, which is adopted.

The heat of formation can also be estimated from the dissociation energy calculated from the linear Birge-Sponer extrapolation of the ground state vibrational constants. This yields D_0 = 89 kcal or ΔHf°_{298} = 111 kcal/mol. There are several indications that this dissociation energy is probably a maximum value, for example, Hildenbrand (5) has applied an ionic-covalent correction to the linear extrapolation which gives D°_0 = 72 kcal. We would expect this heat of formation to be a minimum value. A real minimum for the dissociation energy can be obtained from the knowledge that the first vibrational level of the $^2\Delta$ state is occupied and so the dissociation energy of this state must be greater than 850 cm^{-1}. This yields a minimum dissociation energy of the ground state of 76 kcal, assuming the dissociation products are $C(^1\Delta)$ and $Cl(^2P)$, and $\Delta Hf^\circ_{298}(CCl, g)$ = 124 kcal/mol which is the maximum value of the heat of formation.

Heat Capacity and Entropy

The rotational and electronic constants are those of Verma and Mulliken (2). The vibrational constants are those derived by Ovcharenko et al. (3) from the data of Gordon and King (4). The anharmonicities listed by Verma and Mulliken are not used, since these are based only on the 0,0 and 0,1 transitions. The $^4\Sigma$ level is estimated by analogy with CF(g). The value for α_e was obtained from the other constants assuming a Morse potential function.

References

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2. R. D. Verma and R. S. Mulliken, J. Mol. Spectry. 6, 419 (1961).
3. I. E. Ovcharenko, Yu. Ya. Kuzyakov, and V. M. Tatievskii, Opt. Spectry. (Eng. Transl.) 19, 294 (1965).
4. R. D. Gordon and G. W. King, Can. J. Phys. 39, 252 (1961).
5. D. L. Hildenbrand, Douglas Advanced Research Laboratories, Huntington Beach, Calif., private communication, Dec. 30, 1969.

Carbonyl Chloride Fluoride (COClF)

(Ideal Gas) Mol. Wt. = 82.47

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2,845	- 101,404	- 101,404	INFINITE
100	8,223	55,343	75,802	- 2,046	- 101,670	- 100,815	220,321
200	10,349	61,629	67,263	- 1,127	- 101,882	- 99,871	109,128
298	12,523	66,184	66,184	.000	- 102,000	- 98,856	72,460
300	12,559	66,261	66,184	,023	- 102,002	- 98,837	71,999
400	14,199	70,111	66,698	1,366	- 102,060	- 97,771	53,417
500	15,390	73,415	67,719	2,848	- 102,093	- 96,695	42,263
600	16,273	76,303	68,914	4,433	- 102,114	- 95,613	34,825
700	16,941	78,864	70,156	6,096	- 102,130	- 94,528	29,511
800	17,453	81,161	71,390	7,816	- 102,143	- 93,441	25,526
900	17,850	83,240	72,593	9,582	- 102,155	- 92,354	22,425
1000	18,163	85,138	73,754	11,384	- 102,162	- 91,264	19,945
1100	18,413	86,881	74,869	13,213	- 102,171	- 90,175	17,915
1200	18,613	88,492	75,938	15,065	- 102,177	- 89,082	16,223
1300	18,777	89,989	76,962	16,934	- 102,188	- 87,990	14,792
1400	18,912	91,385	77,943	18,819	- 102,198	- 86,898	13,565
1500	19,024	92,694	78,883	20,716	- 102,210	- 85,804	12,501
1600	19,118	93,925	79,785	22,623	- 102,223	- 84,711	11,570
1700	19,198	95,086	80,651	24,539	- 102,236	- 83,615	10,749
1800	19,266	96,185	81,484	26,462	- 102,254	- 82,521	10,019
1900	19,324	97,229	82,286	28,392	- 102,273	- 81,422	9,365
2000	19,374	98,221	83,058	30,327	- 102,294	- 80,325	8,777
2100	19,418	99,168	83,803	32,267	- 102,317	- 79,225	8,245
2200	19,457	100,072	84,522	34,210	- 102,346	- 78,127	7,761
2300	19,491	100,937	85,217	36,158	- 102,376	- 77,023	7,319
2400	19,521	101,768	85,889	38,108	- 102,411	- 75,920	6,913
2500	19,547	102,565	86,540	40,062	- 102,450	- 74,817	6,540
2600	19,571	103,332	87,172	42,018	- 102,492	- 73,711	6,196
2700	19,592	104,071	87,784	43,976	- 102,539	- 72,603	5,877
2800	19,611	104,784	88,378	45,936	- 102,588	- 71,493	5,580
2900	19,628	105,473	88,956	47,898	- 102,643	- 70,381	5,304
3000	19,644	106,138	89,518	49,862	- 102,702	- 69,269	5,046
3100	19,658	106,783	90,064	51,827	- 102,764	- 68,151	4,804
3200	19,671	107,407	90,597	53,793	- 102,831	- 67,034	4,578
3300	19,683	108,012	91,115	55,761	- 102,903	- 65,918	4,365
3400	19,694	108,600	91,621	57,730	- 102,978	- 64,793	4,165
3500	19,704	109,171	92,114	59,700	- 103,058	- 63,671	3,976
3600	19,713	109,726	92,596	61,671	- 103,141	- 62,544	3,797
3700	19,721	110,267	93,066	63,642	- 103,230	- 61,415	3,627
3800	19,729	110,793	93,526	65,615	- 103,322	- 60,280	3,467
3900	19,736	111,305	93,975	67,588	- 103,419	- 59,149	3,314
4000	19,743	111,805	94,415	69,562	- 103,519	- 58,011	3,169
4100	19,749	112,293	94,845	71,536	- 103,624	- 56,874	3,032
4200	19,755	112,769	95,266	73,512	- 103,733	- 55,730	2,900
4300	19,760	113,233	95,678	75,487	- 103,847	- 54,586	2,774
4400	19,765	113,688	96,082	77,464	- 103,965	- 53,441	2,654
4500	19,770	114,132	96,479	79,440	- 104,087	- 52,294	2,540
4600	19,774	114,567	96,867	81,417	- 104,213	- 51,138	2,429
4700	19,778	114,992	97,248	83,395	- 104,342	- 49,981	2,324
4800	19,782	115,408	97,622	85,373	- 104,477	- 48,822	2,223
4900	19,786	115,816	97,989	87,351	- 104,615	- 47,663	2,126
5000	19,789	116,216	98,350	89,330	- 104,757	- 46,499	2,032
5100	19,792	116,608	98,704	91,309	- 104,905	- 45,339	1,943
5200	19,795	116,992	99,052	93,289	- 105,055	- 44,167	1,856
5300	19,798	117,369	99,394	95,268	- 105,209	- 42,989	1,773
5400	19,801	117,739	99,730	97,248	- 105,368	- 41,818	1,692
5500	19,803	118,103	100,061	99,228	- 105,531	- 40,635	1,615
5600	19,806	118,460	100,387	101,209	- 105,699	- 39,457	1,540
5700	19,808	118,810	100,707	103,190	- 105,870	- 38,275	1,467
5800	19,810	119,155	101,022	105,171	- 106,046	- 37,085	1,397
5900	19,812	119,493	101,332	107,152	- 106,225	- 35,893	1,329
6000	19,814	119,826	101,638	109,133	- 106,408	- 34,704	1,264

June 30, 1961

CARBONYL CHLORIDE FLUORIDE (COClF) (IDEAL GAS) MOL. WT. = 82.47

ΔH°_{f0} = -101 ± 8 kcal. mole^{-1}

Point Group C_s

$\Delta H^\circ_{f\ 298.15}$ = -102 ± 8 kcal. mole^{-1}

$S^\circ_{298.15}$ = [66.184] cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	ω, cm.$^{-1}$
776 (1)	1095 (1)
1868 (1)	415 (1)
501 (1)	667 (1)

Moments of inertia: $I_A = [7.480 \times 10^{-39}]$g cm.^{2} $I_B = [16.008 \times 10^{-39}]$g. cm.^{2} $I_C = [23.31 \times 10^{-39}]$g cm.^{2}

$\sigma = 1$

Heat of Formation

The heats of formation of $COCl_2$ and COF_2 have been averaged to obtain that of COClF.

Heat Capacity and Entropy

The molecular constants are from R. J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. 22, 1953 (1954).

Chlorotrifluoromethane ($CClF_3$)

(Ideal Gas) GFW = 104.45935

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.294	-167.980	-167.980	INFINITE
100	8.799	55.209	80.045	-2.484	-168.574	-165.712	362.164
200	12.679	62.465	69.536	-1.414	-168.996	-162.666	177.753
298	15.986	68.174	68.174	.000	-169.200	-159.510	116.924
300	16.040	68.273	68.174	.030	-169.203	-159.450	116.159
400	18.531	73.247	68.835	1.765	-169.284	-156.184	85.335
500	20.320	77.586	70.161	3.712	-169.292	-152.907	66.836
600	21.590	81.409	71.724	5.811	-169.254	-149.633	54.504
700	22.498	84.810	73.355	8.018	-169.187	-146.367	45.698
800	23.159	87.859	74.980	10.303	-169.104	-143.114	39.097
900	23.650	90.617	76.567	12.645	-169.008	-139.871	33.965
1000	24.022	93.129	78.100	15.029	-168.904	-136.641	29.863
1100	24.309	95.432	79.572	17.446	-168.796	-133.420	26.508
1200	24.534	97.557	80.983	19.889	-168.685	-130.207	23.714
1300	24.714	99.528	82.335	22.351	-168.577	-127.005	21.351
1400	24.859	101.365	83.629	24.830	-168.467	-123.810	19.328
1500	24.979	103.085	84.870	27.322	-168.358	-120.623	17.575
1600	25.078	104.700	86.059	29.825	-168.252	-117.447	16.042
1700	25.161	106.223	87.201	32.337	-168.145	-114.273	14.691
1800	25.231	107.663	88.298	34.857	-168.043	-111.110	13.491
1900	25.291	109.029	89.354	37.383	-167.941	-107.947	12.417
2000	25.342	110.328	90.370	39.915	-167.842	-104.791	11.451
2100	25.387	111.565	91.350	42.452	-167.745	-101.642	10.578
2200	25.425	112.747	92.296	44.992	-167.654	-98.499	9.785
2300	25.459	113.878	93.210	47.536	-167.564	-95.354	9.061
2400	25.489	114.962	94.094	50.084	-167.479	-92.217	8.398
2500	25.516	116.003	94.950	52.634	-167.398	-89.085	7.788
2600	25.539	117.004	95.779	55.187	-167.321	-85.953	7.225
2700	25.560	117.969	96.583	57.742	-167.248	-82.825	6.704
2800	25.579	118.899	97.363	60.299	-167.178	-79.699	6.221
2900	25.596	119.797	98.121	62.858	-167.114	-76.573	5.771
3000	25.611	120.665	98.859	65.418	-167.056	-73.458	5.351
3100	25.625	121.505	99.576	67.980	-167.001	-70.337	4.959
3200	25.638	122.318	100.274	70.543	-166.952	-67.219	4.591
3300	25.650	123.108	100.954	73.108	-166.909	-64.106	4.246
3400	25.660	123.873	101.617	75.673	-166.869	-60.988	3.920
3500	25.670	124.617	102.263	78.240	-166.837	-57.875	3.614
3600	25.679	125.341	102.894	80.807	-166.808	-54.760	3.324
3700	25.687	126.044	103.510	83.375	-166.786	-51.648	3.051
3800	25.694	126.729	104.112	85.944	-166.768	-48.534	2.791
3900	25.701	127.397	104.701	88.514	-166.757	-45.425	2.546
4000	25.708	128.048	105.277	91.085	-166.749	-42.312	2.312
4100	25.714	128.683	105.840	93.656	-166.748	-39.206	2.090
4200	25.719	129.302	106.391	96.227	-166.753	-36.092	1.878
4300	25.725	129.908	106.931	98.799	-166.762	-32.980	1.676
4400	25.729	130.499	107.460	101.372	-166.777	-29.869	1.484
4500	25.734	131.077	107.978	103.945	-166.797	-26.763	1.300
4600	25.738	131.643	108.487	106.519	-166.822	-23.648	1.124
4700	25.742	132.196	108.985	109.093	-166.852	-20.534	.955
4800	25.746	132.738	109.474	111.667	-166.887	-17.417	.793
4900	25.749	133.269	109.955	114.242	-166.928	-14.302	.638
5000	25.753	133.790	110.426	116.817	-166.973	-11.189	.489
5100	25.756	134.300	110.889	119.393	-167.024	-8.081	.346
5200	25.759	134.800	111.344	121.968	-167.080	-4.955	.208
5300	25.762	135.290	111.791	124.544	-167.140	-1.835	.076
5400	25.764	135.772	112.231	127.121	-167.207	1.279	-.052
5500	25.767	136.245	112.663	129.697	-167.278	4.403	-.175
5600	25.769	136.709	113.089	132.274	-167.354	7.525	-.294
5700	25.771	137.165	113.507	134.851	-167.436	10.645	-.408
5800	25.773	137.613	113.919	137.428	-167.522	13.772	-.519
5900	25.775	138.054	114.324	140.006	-167.614	16.897	-.626
6000	25.777	138.487	114.723	142.583	-167.711	20.022	-.729

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1969

CHLOROTRIFLUOROMETHANE ($CClF_3$) (IDEAL GAS) GFW = 104.45935

Point Group C_{3v}

ΔHf°_0 = -168.0 ± 0.8 kcal/mol

$S^\circ_{298.15}$ = 68.174 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -169.2 ± 0.8 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1106 (1)	1217 (2)
782 (1)	560 (2)
474 (1)	350 (2)

Bond Distance: C-F = 1.328 Å C-Cl = 1.751 Å

Bond Angle: F-C-F = 108.6 ± 0.5° F-C-Cl = 110.33° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 9.4425 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2) have determined equilibrium data for $CClF_3(g) + BrX(g) = CBrF_3(g) + ClX(g)$ where X = Cl and Br. Lord et al. (3) studied the analogous equilibria $CF_3I(g) + ClI(g) = CClF_3(g) + I_2(g)$. These data link $CClF_3$ with $CBrF_3$ and CF_3I.

Other data which were omitted from the adjustment include those of Baibuz (4, 5), Mears (6), Kolesov (7), Kirkbride (8), and von Wartenberg (9). Baibuz (4, 5) derived ΔHf° = -166.2 ± 2.2 kcal/mol by applying the method of explosion in a spherical bomb to mixtures of H_2, O_2 and $CClF_3$. By comparison with similar data for CF_4 and CCl_4, we estimate the bias in Baibuz' value to be about +2 kcal/mol. Mears (6) gave a preliminary report of values of ΔHr at 300°C for reactions involving HF, HCl and CCl_nF_{4-n} (n = 1, 2, 3, 4). We derive ΔHf° = -172 and -173 kcal/mol from two different combinations of reactions; however, no detailed account of the data has been published. The other authors (7, 8, 9) measured ΔHr for reaction of $CClF_3$ with an alkali metal (Na or K) to form amorphous carbon and mixtures of the fluoride and chloride. Discrepancies of many kcal/mol exist in these studies, presumably due to inadequate characterization of the thermochemical reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (10) and Bartell (11). Results from Bartell are adopted. These parameters are consistent with the microwave data of Coles (12). Principal moments of inertia are $I_A = 14.68 \times 10^{-39}$ and $I_B = I_C = 25.37 \times 10^{-39}\ g\ cm^2$. Vibrational assignments are based on the work of Claassen (13) and the gas-phase Raman spectra observed by Holzer and Moser (14).

The largest uncertainty in Cp° and S° probably results from the neglect of anharmonicity. Barho (15) and Albright (16) have given estimates for the anharmonic contributions. These vary from 0.1 to 0.3 gibbs/mol in both Cp° and S° over the range from 300 to 1000°K, respectively. Somewhat larger contributions are possible based on the anharmonic functions calculated by McBride (17) for $CF_4(g)$. We estimate the overall uncertainty in the entropy of this JANAF table to be 0.1 eu at 300°K and 0.4 eu at 1000°K. Cp° is consistent with Cv° measured at 300°K by the wire-ribbon method (18).

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Cyanogen Chloride (ClCN)

(Ideal Gas) GFW = 61.47085

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.554	32.801	32.801	INFINITE
100	7.468	46.584	65.084	-1.850	32.797	32.325	-70.646
200	9.475	52.389	57.389	-1.000	32.858	31.838	-34.794
298	10.820	56.459	56.459	.000	32.970	31.309	-22.950
300	10.838	56.526	56.459	.020	32.972	31.299	-22.801
400	11.644	59.760	56.895	1.146	33.089	30.723	-16.786
500	12.195	62.420	57.742	2.339	33.185	30.120	-13.166
600	12.627	64.683	58.715	3.581	33.258	29.500	-10.745
700	12.991	66.657	59.711	4.862	33.311	28.869	-9.013
800	13.302	68.413	60.691	6.177	33.353	28.232	-7.712
900	13.571	69.995	61.638	7.521	33.385	27.589	-6.700
1000	13.802	71.437	62.547	8.890	33.414	26.943	-5.888
1100	13.983	72.761	63.416	10.279	33.438	26.294	-5.224
1200	14.150	73.985	64.247	11.686	33.458	25.645	-4.671
1300	14.304	75.124	65.040	13.109	33.475	24.992	-4.202
1400	14.444	76.189	65.799	14.546	33.494	24.341	-3.800
1500	14.570	77.190	66.525	15.997	33.514	23.686	-3.451
1600	14.667	78.134	67.222	17.459	33.534	23.028	-3.145
1700	14.757	79.026	67.890	18.930	33.555	22.371	-2.876
1800	14.843	79.872	68.532	20.410	33.576	21.712	-2.636
1900	14.923	80.676	69.151	21.899	33.600	21.056	-2.422
2000	14.997	81.444	69.746	23.395	33.624	20.393	-2.228
2100	15.060	82.177	70.321	24.898	33.652	19.732	-2.054
2200	15.120	82.879	70.876	26.407	33.678	19.066	-1.894
2300	15.178	83.552	71.412	27.922	33.707	18.405	-1.749
2400	15.233	84.199	71.932	29.442	33.736	17.739	-1.615
2500	15.285	84.822	72.435	30.968	33.766	17.070	-1.492
2600	15.332	85.423	72.923	32.499	33.797	16.401	-1.379
2700	15.378	86.002	73.397	34.034	33.829	15.731	-1.273
2800	15.423	86.562	73.857	35.574	33.862	15.062	-1.176
2900	15.466	87.104	74.305	37.119	33.895	14.390	-1.084
3000	15.508	87.629	74.740	38.668	33.929	13.716	-.999
3100	15.547	88.138	75.164	40.220	33.963	13.043	-.919
3200	15.586	88.633	75.577	41.777	33.997	12.365	-.844
3300	15.624	89.113	75.980	43.338	34.030	11.687	-.774
3400	15.661	89.580	76.373	44.902	34.064	11.012	-.708
3500	15.698	90.034	76.757	46.470	34.098	10.331	-.645
3600	15.733	90.477	77.132	48.041	34.132	9.652	-.586
3700	15.768	90.909	77.499	49.616	34.166	8.971	-.530
3800	15.802	91.329	77.857	51.195	34.201	8.294	-.477
3900	15.836	91.740	78.208	52.777	34.235	7.614	-.427
4000	15.870	92.142	78.551	54.362	34.269	6.927	-.378
4100	15.902	92.534	78.887	55.951	34.304	6.241	-.333
4200	15.935	92.918	79.217	57.543	34.338	5.557	-.289
4300	15.967	93.293	79.540	59.138	34.372	4.872	-.248
4400	15.998	93.660	79.857	60.736	34.407	4.188	-.208
4500	16.030	94.020	80.167	62.337	34.441	3.497	-.170
4600	16.061	94.373	80.472	63.942	34.477	2.811	-.134
4700	16.093	94.719	80.772	65.550	34.513	2.121	-.099
4800	16.124	95.058	81.066	67.161	34.548	1.433	-.065
4900	16.154	95.391	81.355	68.774	34.584	.740	-.033
5000	16.185	95.717	81.639	70.391	34.621	.054	-.002
5100	16.215	96.038	81.918	72.011	34.658	-.644	.028
5200	16.246	96.353	82.193	73.635	34.696	-1.332	.056
5300	16.276	96.663	82.463	75.261	34.734	-2.027	.084
5400	16.305	96.967	82.729	76.890	34.772	-2.717	.110
5500	16.335	97.267	82.990	78.522	34.810	-3.413	.136
5600	16.364	97.562	83.248	80.157	34.849	-4.113	.161
5700	16.394	97.851	83.501	81.795	34.888	-4.807	.184
5800	16.423	98.137	83.751	83.435	34.927	-5.505	.207
5900	16.451	98.418	83.998	85.079	34.966	-6.201	.230
6000	16.480	98.694	84.240	86.726	35.006	-6.898	.251

Dec. 31, 1960; June 30, 1961; June 30, 1966

CYANOGEN CHLORIDE (ClCN) (IDEAL GAS) GFW = 61.47085

Point Group $C_{\infty v}$

ΔHf°_0 = 32.8 kcal/mol

$S^\circ_{298.15}$ = 56.459 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 32.97 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm $^{-1}$
714.52 (1)
378.3 (2)
2215.5 (1)

Bond Distance: Cl-C = 1.631 Å C-N = 1.162 Å

Bond Angle: Cl-C-N = 180°

σ = 1

Rotational constants: B_o = 0.19817 cm.$^{-1}$ D_o = 5.503 X 10^{-8} cm $^{-1}$

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm $^{-1}$):

α_1 = 8.25 X 10^{-4} x_{11} = [-4] x_{12} = [-6.8] g_{22} = 0.95

α_2 = -5.46 X 10^{-4} x_{22} = -0.65 x_{23} = -7.236

α_3 = 1.06 X 10^{-3} x_{33} = [-7] x_{13} = -2.8

Heat of Formation.

The heat of formation was taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties" NBS Technical Note 270-1, Washington, 1965.

Heat Capacity and Entropy.

J. S. Gordon, Astrosystems International Inc., Fairfield, N. J., (private communication, Feb., 1966), has used the constants listed above to calculate C from 298.15 to 6000°K using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants B_o and D_o were taken from C. A. Burrus and W. Gordy, Phys. Rev. 101, 599 (1956); ω_1, α_1, α_3, x_{22}, x_{23}, x_{13} and g_{22} were obtained from W. J. Lafferty, D. R. Lide and R. A. Toth, J. Chem. Phys. 43, 2063 (1965); α_2 has been taken from C. H. Townes, A. N. Holden and F. R. Merritt, Phys. Rev. 74, 1113 (1948); and x_{11}, x_{33} and x_{12} were estimated by Gordon, loc. cit. The bond distances and bond angle were taken from Lafferty et al., loc. cit.

Carbonyl Monochloride (COCl)

(Ideal Gas) Mol. Wt. = 63. 46355

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.761	-15.374	-15.374	INFINITE
100	8.576	53.008	72.519	-1.951	-15.286	-16.230	35.468
200	9.951	59.401	64.505	-1.021	-15.134	-17.231	18.828
298	10.773	63.542	63.542	.000	-15.000	-18.291	13.407
300	10.784	63.609	63.543	.020	-14.998	-18.311	13.339
400	11.297	66.786	63.972	1.126	-14.909	-19.430	10.616
500	11.690	69.351	64.800	2.275	-14.870	-20.566	8.989
600	12.022	71.512	65.743	3.462	-14.874	-21.706	7.906
700	12.306	73.387	66.704	4.678	-14.910	-22.841	7.131
800	12.544	75.046	67.645	5.921	-14.968	-23.971	6.548
900	12.742	76.536	68.551	7.186	-15.043	-25.093	6.093
1000	12.906	77.887	69.419	8.469	-15.126	-26.205	5.727
1100	13.041	79.124	70.245	9.766	-15.220	-27.309	5.426
1200	13.152	80.263	71.033	11.076	-15.320	-28.403	5.173
1300	13.245	81.320	71.784	12.396	-15.429	-29.489	4.957
1400	13.323	82.304	72.501	13.724	-15.540	-30.565	4.771
1500	13.389	83.226	73.186	15.060	-15.657	-31.635	4.609
1600	13.445	84.092	73.841	16.402	-15.778	-32.698	4.466
1700	13.492	84.908	74.468	17.749	-15.900	-33.749	4.339
1800	13.533	85.681	75.069	19.100	-16.028	-34.797	4.225
1900	13.569	86.413	75.647	20.455	-16.158	-35.834	4.122
2000	13.599	87.110	76.203	21.814	-16.292	-36.867	4.028
2100	13.626	87.774	76.739	23.175	-16.428	-37.891	3.943
2200	13.650	88.409	77.255	24.539	-16.570	-38.913	3.865
2300	13.671	89.016	77.753	25.905	-16.714	-39.923	3.793
2400	13.689	89.598	78.234	27.273	-16.862	-40.928	3.727
2500	13.706	90.157	78.700	28.643	-17.014	-41.929	3.665
2600	13.720	90.695	79.151	30.014	-17.171	-42.922	3.608
2700	13.734	91.213	79.589	31.387	-17.331	-43.911	3.554
2800	13.746	91.713	80.013	32.761	-17.495	-44.891	3.504
2900	13.756	92.195	80.425	34.136	-17.664	-45.865	3.456
3000	13.766	92.662	80.825	35.512	-17.838	-46.837	3.412
3100	13.775	93.114	81.214	36.889	-18.014	-47.801	3.370
3200	13.783	93.551	81.593	38.267	-18.197	-48.758	3.330
3300	13.791	93.975	81.961	39.646	-18.383	-49.712	3.292
3400	13.797	94.387	82.321	41.025	-18.574	-50.656	3.256
3500	13.804	94.787	82.671	42.405	-18.769	-51.601	3.222
3600	13.809	95.176	83.013	43.786	-18.968	-52.535	3.189
3700	13.815	95.554	83.347	45.167	-19.172	-53.462	3.158
3800	13.819	95.923	83.673	46.549	-19.379	-54.386	3.128
3900	13.824	96.282	83.992	47.931	-19.590	-55.305	3.099
4000	13.828	96.632	84.304	49.313	-19.806	-56.218	3.071
4100	13.832	96.974	84.609	50.696	-20.025	-57.130	3.045
4200	13.836	97.307	84.907	52.080	-20.248	-58.029	3.019
4300	13.839	97.632	85.199	53.463	-20.475	-58.923	2.995
4400	13.842	97.951	85.485	54.848	-20.704	-59.818	2.971
4500	13.845	98.262	85.766	56.232	-20.938	-60.707	2.948
4600	13.848	98.566	86.041	57.617	-21.174	-61.583	2.926
4700	13.851	98.864	86.310	59.002	-21.414	-62.459	2.904
4800	13.853	99.156	86.575	60.387	-21.657	-63.331	2.883
4900	13.855	99.441	86.835	61.772	-21.903	-64.195	2.863
5000	13.858	99.721	87.090	63.158	-22.151	-65.056	2.843
5100	13.860	99.996	87.340	64.544	-22.403	-65.917	2.825
5200	13.861	100.265	87.586	65.930	-22.657	-66.766	2.806
5300	13.863	100.529	87.828	67.316	-22.914	-67.609	2.788
5400	13.865	100.788	88.065	68.702	-23.174	-68.450	2.770
5500	13.867	101.042	88.299	70.089	-23.436	-69.281	2.753
5600	13.868	101.292	88.529	71.476	-23.701	-70.116	2.736
5700	13.870	101.538	88.755	72.863	-23.969	-70.951	2.720
5800	13.871	101.779	88.977	74.250	-24.239	-71.767	2.704
5900	13.872	102.016	89.196	75.637	-24.512	-72.582	2.688
6000	13.874	102.249	89.412	77.024	-24.787	-73.396	2.673

Dec. 31, 1965

CARBONYL MONOCHLORIDE (COCl) (IDEAL GAS) MOL. WT. = 63.46355

Point Group C_s

$S^\circ_{298.15}$ = [64] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 2

$\Delta H^\circ_{f\ 0}$ = [-15 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-15 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
570 (1)
281 (1)
1880 (1)

Bond Distance: C-Cl = [1.75] Å C-O = [1.17]Å

Bond Angle: Cl-C-O = [120] ° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.27603 x 10^{-115}] g.^{3} cm.^{6}

Heat of Formation.

The enthalpy change (ΔH_r°) for the reaction $COCl_2(g) = CO(g) + 2Cl(g)$ is calculated to be 82 kcal. mole^{-1}, which is the sum of two bond energies, i.e. D(Cl-COCl) + D(Cl-CO). By comparison with the values, D(H_3C-COCH_3)/D(H_3C-CO) = 72/18 = 4.0 for $CH_3COCH_3(g)$ and D(H_3C-COCl)/D(Cl-CO) = 4.3 for $CH_3COCl(g)$, the ratio of D(Cl-COCl)/D(Cl-CO) is estimated to be 4.0 for $COCl_2(g)$. Hence the enthalpy change for the reaction $COCl_2(g) = COCl(g) + Cl(g)$ is calculated as 82 x (4/5) = 65.6 kcal. mole^{-1}. Using the ΔH_r° value obtained, the heat of formation for COCl(g) is derived to be -15 ± 10 kcal. mole-1.

Heat Capacity and Entropy.

The vibrational frequencies were reported by M. E. Jacox and D. E. Milligan, J. Chem. Phys. 43, 866 (1965). The bond distances and angle were estimated by Jacox and Milligan, loc. cit. Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 1.29987 x 10^{-38}, I_B = 7.1580 x 10^{-40}, and I_C = 1.37145 x 10^{-38} g. cm.^{2}

Carbon Dichloride (CCl_2)

(Ideal Gas) GFW = 82.91715

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.722	56.724	56.724	INFINITE
100	8.292	53.086	72.287	- 1.920	56.816	56.043	- 122.482
200	9.720	59.250	64.363	- 1.023	56.909	55.235	- 60.358
298	11.054	63.392	63.392	.000	57.000	54.393	- 39.871
300	11.075	63.461	63.392	.020	57.001	54.377	- 39.613
400	11.984	66.781	63.839	1.177	57.082	53.489	- 29.225
500	12.559	69.522	64.709	2.406	57.139	52.584	- 22.985
600	12.949	71.848	65.710	3.683	57.169	51.670	- 18.821
700	13.259	73.868	66.734	4.993	57.176	50.753	- 15.846
800	13.546	75.657	67.740	6.334	57.172	49.835	- 13.614
900	13.835	77.269	68.711	7.703	57.164	48.918	- 11.879
1000	14.132	78.742	69.641	9.101	57.162	48.001	- 10.491
1100	14.428	80.103	70.531	10.529	57.170	47.084	- 9.355
1200	14.713	81.371	71.382	11.986	57.191	46.167	- 8.408
1300	14.975	82.559	72.197	13.471	57.225	45.247	- 7.607
1400	15.206	83.677	72.977	14.980	57.274	44.325	- 6.919
1500	15.401	84.733	73.726	16.511	57.335	43.398	- 6.323
1600	15.557	85.732	74.445	18.059	57.405	42.465	- 5.800
1700	15.677	86.679	75.138	19.621	57.484	41.531	- 5.339
1800	15.762	87.578	75.804	21.193	57.566	40.589	- 4.928
1900	15.816	88.432	76.446	22.772	57.651	39.646	- 4.560
2000	15.843	89.244	77.066	24.355	57.734	38.695	- 4.228
2100	15.847	90.017	77.664	25.940	57.817	37.741	- 3.928
2200	15.834	90.754	78.243	27.524	57.892	36.781	- 3.654
2300	15.806	91.457	78.802	29.106	57.963	35.823	- 3.404
2400	15.767	92.129	79.344	30.685	58.026	34.859	- 3.174
2500	15.721	92.772	79.868	32.260	58.081	33.891	- 2.963
2600	15.668	93.387	80.376	33.829	58.126	32.923	- 2.767
2700	15.612	93.978	80.869	35.393	58.162	31.952	- 2.586
2800	15.554	94.544	81.347	36.951	58.188	30.983	- 2.418
2900	15.495	95.089	81.812	38.504	58.204	30.010	- 2.262
3000	15.436	95.613	82.263	40.050	58.209	29.036	- 2.115
3100	15.378	96.119	82.702	41.591	58.205	28.065	- 1.979
3200	15.322	96.606	83.129	43.126	58.190	27.093	- 1.850
3300	15.267	97.077	83.545	44.655	58.164	26.120	- 1.730
3400	15.215	97.532	83.949	46.179	58.130	25.152	- 1.617
3500	15.165	97.972	84.344	47.698	58.085	24.178	- 1.510
3600	15.118	98.398	84.728	49.213	58.033	23.212	- 1.409
3700	15.073	98.812	85.103	50.722	57.970	22.247	- 1.314
3800	15.030	99.213	85.469	52.227	57.900	21.282	- 1.224
3900	14.990	99.603	85.827	53.728	57.821	20.322	- 1.139
4000	14.952	99.982	86.176	55.225	57.734	19.361	- 1.058
4100	14.917	100.351	86.517	56.719	57.641	18.399	- .981
4200	14.883	100.710	86.851	58.209	57.539	17.445	- .908
4300	14.852	101.060	87.177	59.695	57.430	16.490	- .838
4400	14.822	101.401	87.497	61.179	57.316	15.542	- .772
4500	14.795	101.734	87.809	62.660	57.195	14.590	- .709
4600	14.769	102.059	88.116	64.138	57.069	13.647	- .648
4700	14.745	102.376	88.416	65.614	56.938	12.706	- .591
4800	14.722	102.686	88.710	67.087	56.800	11.765	- .536
4900	14.701	102.990	88.998	68.558	56.658	10.831	- .483
5000	14.681	103.286	89.281	70.027	56.512	9.895	- .433
5100	14.662	103.577	89.558	71.495	56.362	8.963	- .384
5200	14.645	103.862	89.831	72.960	56.207	8.037	- .338
5300	14.628	104.140	90.098	74.424	56.048	7.111	- .293
5400	14.613	104.414	90.361	75.886	55.885	6.191	- .251
5500	14.598	104.682	90.619	77.346	55.717	5.274	- .210
5600	14.584	104.945	90.872	78.805	55.547	4.355	- .170
5700	14.571	105.203	91.121	80.263	55.372	3.437	- .132
5800	14.559	105.456	91.366	81.720	55.195	2.532	- .095
5900	14.548	105.705	91.607	83.175	55.013	1.626	- .060
6000	14.537	105.949	91.844	84.629	54.828	.720	- .026

Mar. 31, 1965; Dec. 31, 1968

CARBON DICHLORIDE (CCl_2) (IDEAL GAS) GFW = 82.91715

Point Group C_{2v}

ΔHf°_0 = 56.7 ± 5 kcal/mol

$S^\circ_{298.15}$ = 63.4 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 57.0 ± 5 kcal/mol

Ground State Quantum Weight = 1

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[4000]	[3]
[17500]	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
721 (1)
[350] (1)
748 (1)

Bond Distance: C-Cl = [1.76] Å

Bond Angle: Cl-C-Cl = [100 ± 10°]

σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [1.1017] x 10^{-114} g^3cm^6

Heat of Formation

Shapiro and Lossing (1) have measured mass-spectrometrically the appearance potentials 12.2 and 14.7 eV for the processes $CHCl_3(g) + e^- \rightarrow CCl_2^+(g) + HCl(g) + 2e^-$ and $C_2Cl_4(g) + e^- \rightarrow CCl_2^+(g) + CCl_2(g) + 2e^-$, respectively. The difference in these two processes gives ΔHr° = 2.5 eV (57.65 kcal/mol) for the reaction $C_2Cl_4(g) + HCl(g) \rightarrow CCl_2(g) + CHCl_3(g)$ which leads to ΔHf°_{298} (CCl_2, g) = 57.32 kcal/mol, using JANAF ΔHf°_{298} = -2.97, -22.063 and -24.7 kcal/mol for $C_2Cl_4(g)$, HCl(g) and $CHCl_3(g)$, respectively. Since the authors claimed that the experimental error was probably 5 kcal/mol, the value, 57 ± 5 kcal/mol, is adopted for the heat of formation.

Heat Capacity and Entropy

Milligan and Jacox (2) have found two stretching fundamentals (721 and 748 cm^{-1}) for the CCl_2 radical in the infrared and ultraviolet spectra by matrix-isolation, and proposed a bent molecular structure (the valence angle = 100 ± 10°) with a ground singlet state which was based on the analogy with the electronic absorption spectrum of CF_2. L. Andrews (3) has confirmed all these observations in his infrared spectrometric studies of dichlorocarbene in solid argon, and made vibrational assignment to the fundamentals and also eliminated the possibility of a linear molecular structure for CCl_2. The bending frequency (350 cm^{-1}) is estimated by the valence force method (4), using the same ratio of bending over stretching force constants from $CF_2(g)$ (5). The bond distance is estimated to be the same as that of $CCl_4(g)$ measured by Bartell et al (6). The three principal moments of inertia are $I_A = 2.1828 \times 10^{-39}$, $I_B = 21.4013 \times 10^{-39}$, and $I_C = 23.5840 \times 10^{-39}$ g cm^2.

The triplet low lying electronic level of 4000 cm^{-1} is estimated by analogy with that of $CF_2(g)$. The other level of 17,500 cm^{-1} is also estimated based on a weak band appearing between 4400 and 5600 Å in the spectra of CCl_2 observed by Milligan and Jacox (2).

References

(1) J. S. Shapiro and F. P. Lossing, J. Phys. Chem. 72, 1552 (1968).
(2) D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 703 (1967).
(3) L. Andrews, J. Chem. Phys. 48, 979 (1968).
(4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co. Inc., New York, 1945.
(5) JANAF $CF_2(g)$ table dated Sept. 30, 1966.
(6) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, J. Chem. Phys. 23, 1854 (1955).

Dichlorodifluoromethane (CCl_2F_2)

(Ideal Gas) GFW = 120.9140

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-3.553	-116.497	-116.497	INFINITE
100	9.473	57.674	84.928	-2.725	-117.074	-114.236	249.663
200	14.005	65.665	73.396	-1.546	-117.399	-111.248	121.566
298	17.307	71.911	71.911	.000	-117.500	-108.202	79.315
300	17.358	72.018	71.911	.032	-117.501	-108.145	78.784
400	19.683	77.351	72.623	1.891	-117.488	-105.026	57.383
500	21.276	81.926	74.037	3.944	-117.414	-101.918	44.548
600	22.371	85.907	75.691	6.130	-117.307	-98.828	35.998
700	23.136	89.417	77.406	8.408	-117.183	-95.758	29.897
800	23.684	92.544	79.106	10.750	-117.052	-92.707	25.326
900	24.087	95.358	80.758	13.140	-116.915	-89.672	21.775
1000	24.389	97.912	82.348	15.564	-116.776	-86.654	18.938
1100	24.621	100.248	83.871	18.015	-116.637	-83.649	16.620
1200	24.802	102.398	85.326	20.487	-116.498	-80.655	14.689
1300	24.946	104.390	86.717	22.974	-116.365	-77.673	13.058
1400	25.063	106.243	88.046	25.475	-116.231	-74.701	11.661
1500	25.158	107.975	89.318	27.986	-116.101	-71.739	10.452
1600	25.237	109.601	90.535	30.506	-115.974	-68.787	9.396
1700	25.303	111.133	91.702	33.033	-115.848	-65.840	8.464
1800	25.358	112.581	92.822	35.566	-115.727	-62.904	7.638
1900	25.406	113.954	93.899	38.105	-115.606	-59.970	6.898
2000	25.446	115.258	94.934	40.647	-115.491	-57.044	6.234
2100	25.482	116.500	95.932	43.194	-115.376	-54.126	5.633
2200	25.512	117.686	96.894	45.743	-115.269	-51.214	5.088
2300	25.539	118.821	97.823	48.296	-115.162	-48.301	4.590
2400	25.563	119.909	98.721	50.851	-115.061	-45.397	4.134
2500	25.583	120.952	99.589	53.408	-114.965	-42.498	3.715
2600	25.602	121.956	100.430	55.968	-114.872	-39.600	3.329
2700	25.619	122.923	101.245	58.529	-114.784	-36.708	2.971
2800	25.633	123.855	102.036	61.091	-114.701	-33.816	2.639
2900	25.647	124.754	102.804	63.655	-114.624	-30.928	2.331
3000	25.659	125.624	103.551	66.221	-114.552	-28.048	2.043
3100	25.670	126.466	104.276	68.787	-114.485	-25.164	1.774
3200	25.680	127.281	104.982	71.355	-114.424	-22.283	1.522
3300	25.689	128.071	105.670	73.923	-114.370	-19.406	1.285
3400	25.697	128.838	106.340	76.492	-114.320	-16.526	1.062
3500	25.705	129.583	106.994	79.062	-114.278	-13.653	.853
3600	25.712	130.307	107.631	81.633	-114.239	-10.776	.654
3700	25.718	131.012	108.254	84.205	-114.207	-7.902	.467
3800	25.724	131.698	108.862	86.777	-114.180	-5.029	.289
3900	25.730	132.366	109.456	89.350	-114.160	-2.157	.121
4000	25.735	133.018	110.037	91.923	-114.145	.716	-.039
4100	25.739	133.653	110.605	94.497	-114.135	3.583	-.191
4200	25.744	134.274	111.161	97.071	-114.132	6.456	-.336
4300	25.748	134.879	111.706	99.645	-114.133	9.328	-.474
4400	25.752	135.471	112.239	102.220	-114.140	12.201	-.606
4500	25.755	136.050	112.762	104.796	-114.151	15.066	-.732
4600	25.759	136.616	113.275	107.371	-114.167	17.940	-.852
4700	25.762	137.170	113.777	109.947	-114.188	20.814	-.968
4800	25.765	137.713	114.270	112.524	-114.213	23.688	-1.079
4900	25.767	138.244	114.754	115.100	-114.244	26.564	-1.185
5000	25.770	138.764	115.229	117.677	-114.278	29.435	-1.287
5100	25.772	139.275	115.695	120.254	-114.317	32.304	-1.384
5200	25.775	139.775	116.154	122.832	-114.359	35.186	-1.479
5300	25.777	140.266	116.604	125.409	-114.407	38.062	-1.570
5400	25.779	140.748	117.047	127.987	-114.459	40.936	-1.657
5500	25.781	141.221	117.482	130.565	-114.515	43.818	-1.741
5600	25.783	141.686	117.910	133.143	-114.575	46.696	-1.822
5700	25.785	142.142	118.331	135.722	-114.640	49.571	-1.901
5800	25.786	142.591	118.746	138.300	-114.708	52.457	-1.977
5900	25.788	143.031	119.154	140.879	-114.781	55.338	-2.050
6000	25.789	143.465	119.555	143.458	-114.858	58.219	-2.121

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

DICHLORODIFLUOROMETHANE (CCl_2F_2) (IDEAL GAS) GFW = 120.9140

Point Group C_{2v}

ΔHf°_0 = -116.5 ± 2 kcal/mol

$S^\circ_{298.15}$ = 71.91 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -117.5 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1099 (1)	457.5 (1)	436 (1)
261.5 (1)	322 (1)	1162 (1)
667.2 (1)	922 (1)	446 (1)

Bond Distance: C-Cl = 1.77 ± 0.02 Å C-F = 1.33 ± 0.02 Å

Bond Angle: F-C-F = 109.5 ± 3° Cl-C-Cl = 108.5 ± 2° $\sigma = 2$

F-C-F plane perpendicular to Cl-C-Cl plane

Product of the Moments of Inertia: $I_AI_BI_C = 2.5841 \times 10^{-113}\ g^3cm^{-6}$

Heat of Formation

Mears and Stahl (1) investigated several heats of reaction involving CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, HF and HCl. Using JANAF values for all compounds except CF_2Cl_2 and $CFCl_3$ we obtain the following observations:

1. $\Delta Hf_{298}(CCl_3F, g) = -70.12 \pm 1.1$ kcal/mol
2. $\Delta Hf_{298}(CCl_2F_2, g) = -116.53 \pm 1.5$ kcal/mol
3. $\Delta Hf_{298}(CCl_2F_2, g) - \Delta Hf_{298}(CCl_3F, g) = -49.39 \pm 1.0$ kcal/mol
4. $\Delta Hf_{298}(CCl_2F_2, g) - 2\Delta Hf_{298}(CCl_3F, g) = 20.34 \pm 1.0$ kcal/mol
5. $\Delta Hf_{298}(CCl_3F, g) - 2\Delta Hf_{298}(CCl_2F_2, g) = 165.47 \pm 1.0$ kcal/mol

The sum of the squares of the deviations is smallest when $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -117.5$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -69$ kcal/mol, and all the values are within their uncertainty ranges.

Petersen and Pitzer (8) obtained an approximate equilibrium constant for the reaction $2CClF_3(g) + CCl_4(g) = 3CCl_2F_2(g)$ of log $K_{400} = -3.0$. This on 3rd law reduction gives $\Delta Hr^\circ_{298} = 7.64$ kcal and with $\Delta Hf^\circ_{298}(CClF_3, g) = -169.2$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_4, g) = -22.94$ kcal/mol this yields $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -117.9$ kcal/mol.

Kirkbride and Davidson (2) investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -115.1 \pm 2$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -72.9 \pm 4$ kcal/mol after correction with JANAF auxiliary data. Wartenberg and Schiefer (3) investigated the same reaction and we obtain, after correction with JANAF auxiliary data, $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -112.7$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -63.1$ kcal/mol. Kolesov et al. (4) have reported analogous data for the reaction with sodium which, after correction with JANAF auxiliary data, yields $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -114.4 \pm 3.5$ kcal/mol.

We adopt the values calculated above from Mears and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF_4 to CCl_4. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Claassen (5) chose the frequencies given above from his own gas-phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6). Masi (9) has measured the gas phase heat capacities at 243, 273, 318 and 363°K, within this range our adopted heat capacities are from .3 to .7% high. The entropies agree to within 0.05% and further adjustment to obtain better fits was not considered necessary. The molecular structure was determined from the microwave measurements of Long et al. (7). The individual moments of inertia were: $I_A = 31.929 \times 10^{-39}\ g\ cm^2$, $I_B = 21.216 \times 10^{-39}\ g\ cm^2$, and $I_C = 38.148 \times 10^{-39}\ g\ cm^2$.

References

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Carbonyl Dichloride ($COCl_2$)

(Ideal Gas) Mol. Wt. = 98.925

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	,000	,000	INFINITE	- 3,075	- 52.192	- 52.192	INFINITE
100	8,733	55,853	78,489	- 2,264	- 52,447	- 51,420	112,373
200	11,559	62,754	69,012	- 1,252	- 52,579	- 50,331	54,996
298	13,790	67,816	67,816	,000	- 52,600	- 49,221	36,078
300	13,823	67,901	67,816	,026	- 52,600	- 49,200	35,840
400	15,282	72,092	68,377	1,486	- 52,570	- 48,070	26,263
500	16,269	75,615	69,482	3,066	- 52,528	- 46,949	20,520
600	16,981	78,647	70,763	4,731	- 52,488	- 45,837	16,695
700	17,515	81,307	72,083	6,457	- 52,455	- 44,732	13,965
800	17,924	83,674	73,387	8,230	- 52,425	- 43,630	11,919
900	18,242	85,804	74,650	10,039	- 52,401	- 42,534	10,328
1000	18,493	87,739	75,864	11,876	- 52,378	- 41,437	9,056
1100	18,693	89,512	77,025	13,736	- 52,358	- 40,346	8,016
1200	18,855	91,145	78,134	15,613	- 52,341	- 39,252	7,148
1300	18.986	92,660	79,194	17,505	- 52,329	- 38,162	6,415
1400	19,095	94,071	80,207	19,410	- 52,319	- 37,074	5,787
1500	19,186	95,392	81,176	21,324	- 52,311	- 35,985	5,243
1600	19,262	96,632	82,103	23,246	- 52,306	- 34,897	4,767
1700	19,326	97,802	82,993	25,176	- 52,302	- 33,808	4,346
1800	19,381	98,908	83,847	27,111	- 52,303	- 32,722	3,973
1900	19,428	99,957	84,667	29,052	- 52,306	- 31,632	3,638
2000	19,469	100,955	85,457	30,997	- 52,311	- 30,545	3,338
2100	19,504	101,906	86,218	32,945	- 52,320	- 29,455	3,065
2200	19,536	102,814	86,951	34,897	- 52,333	- 28,368	2,818
2300	19,563	103,683	87,660	36,852	- 52,348	- 27,276	2,592
2400	19,587	104,516	88,345	38,810	- 52,367	- 26,186	2,384
2500	19.609	105,316	89,008	40,770	- 52,390	- 25,096	2,194
2600	19,628	106,086	89,650	42,731	- 52,418	- 24,003	2,018
2700	19,645	106,827	90,273	44,695	- 52,449	- 22,910	1,854
2800	19,661	107,541	90,877	46,660	- 52,483	- 21,814	1,703
2900	19,675	108,231	91,463	48,627	- 52,522	- 20,719	1,561
3000	19,687	108,899	92,034	50,595	- 52,565	- 19.622	1,429
3100	19,699	109,544	92,588	52,565	- 52,611	- 18,520	1,306
3200	19,709	110,170	93,128	54,535	- 52,661	- 17,420	1,190
3300	19,719	110,777	93,653	56,506	- 52,717	- 16,322	1,081
3400	19,727	111,365	94,166	58,479	- 52,775	- 15,215	,978
3500	19,735	111,937	94,665	60,452	- 52,838	- 14,114	,881
3600	19,743	112,493	95,153	62,426	- 52,905	- 13,006	,790
3700	19,750	113,035	95,629	64,400	- 52,976	- 11,896	,703
3800	19,756	113,561	96,094	66,376	- 53,050	- 10,782	,620
3900	19,762	114,075	96,548	68,352	- 53,128	- 9,670	,542
4000	19,767	114,575	96,993	70,328	- 53,211	- 8,554	,467
4100	19,772	115,063	97,428	72,305	- 53,296	- 7,438	,396
4200	19,777	115,540	97,853	74,282	- 53,386	- 6,315	,329
4300	19,781	116,005	98,270	76,260	- 53,481	- 5,196	,264
4400	19,785	116,460	98,678	78,239	- 53,578	- 4,073	,202
4500	19,789	116,904	99,078	80,217	- 53,680	- 2,949	,143
4600	19,793	117,339	99,471	82,196	- 53,786	- 1,817	,086
4700	19,796	117,765	99,855	84,176	- 53,894	- ,684	,032
4800	19,799	118,182	100,233	86,156	- 54,008	,448	- ,020
4900	19,802	118,590	100,603	88,136	- 54,123	1,584	- ,071
5000	19,805	118,990	100,967	90,116	- 54,244	2,722	- ,119
5100	19,807	119,383	101,324	92,097	- 54,369	3,857	- ,165
5200	19,810	119,767	101,675	94,077	- 54,497	5,001	- ,210
5300	19,812	120,145	102,020	96,059	- 54,628	6,152	- ,254
5400	19,814	120,515	102,359	98,040	- 54,763	7,297	- ,295
5500	19,816	120,878	102,693	100,021	- 54,902	8,453	- ,336
5600	19,818	121,236	103,021	102,003	- 55,045	9,601	- ,375
5700	19,820	121,586	103,343	103,985	- 55,192	10,755	- ,412
5800	19,822	121,931	103,661	105,967	- 55,343	11,917	- ,449
5900	19,824	122,270	103,973	107,949	- 55,497	13,080	- ,484
6000	19,825	122,603	104,281	109,932	- 55,654	14,237	- ,519

June 30, 1961

CARBONYL DICHLORIDE ($COCl_2$) (IDEAL GAS) MOL. WT. = 98.925

ΔH°_{f0} = - 52.2 ± 0.8 kcal. mole⁻¹

Point Group C_{2v}

$\Delta H^\circ_{f\ 298.15}$ = -52.6 ± 0.8 kcal. mole⁻¹

$S^\circ_{298.15}$ = 67.816 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm.⁻¹	
[570]	(1)
1827	(1)
285	(1)
849	(1)
440	(1)
[585]	(1)

Interatomic distances:		
	C-O	1.166 ± 0.002 Å
	Cl-O	2.589 ± 0.001
	Cl-Cl	2.884 ± 0.001
	C-Cl	1.746 ± 0.004
	Cl-C-Cl angle	111.3 ± 0.1°

Moments of inertia: $I_A = 1.0690 \times 10^{-38}$ g. cm.² $I_B = 2.4489 \times 10^{-38}$ $I_C = 3.5291 \times 10^{-38}$ $\sigma = 2$

Heat of Formation

J. Thomsen, Thermochemische Untersuchungen, Barth, Leipzig, 1882, Vol. 2, p. 361, reports the heat of alkaline hydrolysis of $COCl_2$, from which $\Delta H^\circ_{f\ 298.15}$ is calculated to be -54.4 ± 0.3 kcal. mole⁻¹. From the heat of combustion of $COCl_2$ in O_2 and H_2, reported by Thomsen, op. cit., p. 363, $\Delta H^\circ_{f\ 298.15}$ is calculated to be -51.73 ± 0.43 kcal. mole⁻¹. M. Bodenstein and H. Plaut, Z. Phys. Chem. 110, 399 (1924), J. A. Christiansen, ibid. 103, 99 (1923), and M. Bodenstein and G. Dunant, ibid. 61, 437 (1908), report 10 values of K_p from 647° to 876°K for the reaction $CO + Cl_2 \rightleftarrows COCl_2$. These yield -25.91 ± 0.04 kcal. for $\Delta H^\circ_{r\ 298.15}$, whence $\Delta H^\circ_{f\ 298.15}$ for $COCl_2$ is -52.33 ± 0.62 kcal. mole⁻¹. The average of the 3 foregoing values of $\Delta H^\circ_{f\ 298.15}$, weighted for the uncertainties, is adopted here. Values calculated from the degree of dissociation of $COCl_2$ from 374° to 778°K, reported by R. H. Atkinson, C. T. Heycock, and W. J. Pope, J. Chem. Soc. 117, 1410 (1920), range from -47.06 to -53.11 kcal. mole⁻¹ and are ignored.

Heat Capacity and Entropy

The vibrational frequencies were assigned by E. Catalano and K. S. Pitzer, J. Am. Chem. Soc. 80, 1054 (1958), on the basis of their own infra-red spectra and other data. The molecular dimensions listed above were deduced from microwave spectra by G. W. Robinson, J. Chem. Phys. 21, 1741 (1953), and are confirmed by electron-diffraction values compiled by P. W. Allen and L. E. Sutton, Acta Cryst. 3, 46 (1950). The moments of inertia are weighted for the isotopes and were calculated from Robinson's dimensions by W. F. Giauque and J. B. Ott, J. Am. Chem. Soc., 82, 2689 (1960). Giauque and Ott, loc. cit., determined $S^\circ_{298.15}$ experimentally to be 67.81 cal. deg.⁻¹ mole⁻¹, with which the value calculated here agrees.

Trichloromethyl (CCl_3)

(Ideal Gas) GFW = 118.37015

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.392	19.151	19.151	INFINITE
100	9.795	57.405	82.894	-2.549	18.936	19.989	-43.686
200	13.070	65.271	72.246	-1.395	18.923	21.060	-23.013
298	15.212	70.918	70.918	.000	19.000	22.093	-16.195
300	15.245	71.012	70.918	.028	19.002	22.112	-16.109
400	16.658	75.606	71.535	1.628	19.111	23.133	-12.639
500	17.564	79.428	72.742	3.343	19.227	24.126	-10.545
600	18.156	82.686	74.135	5.131	19.333	25.095	-9.141
700	18.555	85.517	75.563	6.968	19.428	26.048	-8.133
800	18.834	88.014	76.966	8.838	19.510	26.987	-7.373
900	19.035	90.244	78.320	10.732	19.582	27.917	-6.779
1000	19.184	92.258	79.615	12.643	19.647	28.838	-6.303
1100	19.297	94.092	80.849	14.567	19.702	29.755	-5.912
1200	19.385	95.775	82.023	16.502	19.751	30.667	-5.585
1300	19.454	97.329	83.142	18.444	19.791	31.574	-5.308
1400	19.509	98.773	84.207	20.392	19.827	32.481	-5.071
1500	19.555	100.121	85.224	22.345	19.857	33.384	-4.864
1600	19.592	101.384	86.195	24.303	19.883	34.283	-4.683
1700	19.623	102.573	87.123	26.264	19.906	35.185	-4.523
1800	19.650	103.695	88.013	28.227	19.924	36.081	-4.381
1900	19.672	104.758	88.867	30.193	19.940	36.982	-4.254
2000	19.691	105.768	89.687	32.162	19.951	37.877	-4.139
2100	19.708	106.729	90.476	34.131	19.961	38.773	-4.035
2200	19.722	107.646	91.235	36.103	19.965	39.667	-3.941
2300	19.735	108.523	91.968	38.076	19.967	40.566	-3.855
2400	19.746	109.363	92.675	40.050	19.965	41.461	-3.776
2500	19.755	110.169	93.359	42.025	19.958	42.355	-3.703
2600	19.764	110.944	94.021	44.001	19.947	43.252	-3.636
2700	19.772	111.690	94.661	45.978	19.932	44.147	-3.573
2800	19.779	112.409	95.282	47.955	19.912	45.047	-3.516
2900	19.785	113.104	95.885	49.933	19.887	45.943	-3.462
3000	19.791	113.774	96.470	51.912	19.857	46.841	-3.412
3100	19.796	114.423	97.039	53.892	19.822	47.742	-3.366
3200	19.800	115.052	97.592	55.871	19.780	48.643	-3.322
3300	19.805	115.661	98.131	57.852	19.733	49.544	-3.281
3400	19.808	116.253	98.655	59.832	19.682	50.452	-3.243
3500	19.812	116.827	99.166	61.813	19.624	51.352	-3.207
3600	19.815	117.385	99.664	63.795	19.562	52.262	-3.173
3700	19.818	117.928	100.151	65.776	19.493	53.173	-3.141
3800	19.821	118.457	100.625	67.758	19.421	54.083	-3.110
3900	19.824	118.971	101.089	69.741	19.343	54.999	-3.082
4000	19.826	119.473	101.543	71.723	19.260	55.914	-3.055
4100	19.828	119.963	101.986	73.706	19.173	56.827	-3.029
4200	19.830	120.441	102.420	75.689	19.080	57.748	-3.005
4300	19.832	120.907	102.844	77.672	18.983	58.668	-2.982
4400	19.834	121.363	103.260	79.655	18.883	59.597	-2.960
4500	19.836	121.809	103.667	81.639	18.778	60.517	-2.939
4600	19.837	122.245	104.066	83.622	18.671	61.449	-2.919
4700	19.839	122.672	104.458	85.606	18.560	62.382	-2.901
4800	19.840	123.089	104.841	87.590	18.445	63.314	-2.883
4900	19.841	123.499	105.218	89.574	18.328	64.253	-2.866
5000	19.842	123.899	105.588	91.558	18.209	65.189	-2.849
5100	19.843	124.292	105.951	93.542	18.086	66.130	-2.834
5200	19.845	124.678	106.307	95.527	17.962	67.075	-2.819
5300	19.846	125.056	106.657	97.511	17.834	68.019	-2.805
5400	19.847	125.427	107.001	99.496	17.704	68.968	-2.791
5500	19.847	125.791	107.340	101.481	17.571	69.921	-2.778
5600	19.848	126.148	107.672	103.465	17.437	70.870	-2.766
5700	19.849	126.500	108.000	105.450	17.299	71.819	-2.754
5800	19.850	126.845	108.322	107.435	17.161	72.783	-2.743
5900	19.851	127.184	108.638	109.420	17.019	73.743	-2.732
6000	19.851	127.518	108.950	111.405	16.875	74.703	-2.721

Mar. 31, 1965; Dec. 31, 1967; Dec. 31, 1969; June 30, 1970

TRICHLOROMETHYL (CCl_3) (IDEAL GAS) GFW = 118.37015

Point Group D_{3h}

ΔHf°_0 = 19.15 ± 2 kcal/mol

$S^\circ_{298.15}$ = 70.92 ± 1.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 19 ± 2 kcal/mol

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[450] (1)
[460] (1)
898 (2)
[240] (2)

Bond Distance: C-Cl = [1.74] Å

Bond Angle: Cl-C-Cl = [120°]

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.8215 x 10^{-113}] g^3 cm^6.

Heat of Formation

Benson (1) has reanalysed the kinetic data of Sullivan and Davidson (2) for the reaction $Br_2(g) + CHCl_3(g) = HBr(g) + CBrCl_3(g)$ and has obtained from it the heat of the initial step, $Br(g) + CHCl_3(g) \rightarrow CCl_3(g) + HBr(g)$, as 8.2 ± 1 kcal/mol. Substituting this value and $\Delta Hf^\circ_{298}(Br)$ = 26.74 kcal/mol, $\Delta Hf^\circ_{298}(CHCl_3)$ = -24.66 kcal/mol and $\Delta Hf^\circ_{298}(HBr)$ = -8.71 kcal/mol, we obtain $\Delta Hf^\circ_{298}(CCl_3, g)$ = 19 ± 2 kcal/mol, which is adopted here.

Heat Capacity and Entropy

Walsh (3) has predicted that CCl_3 is non-planar on the basis of his orbital correlation diagram. Andrews (4) indicates that his matrix infrared observations of the symmetric and antisymmetric stretches are consistent with a non-planar C_{3v} structure and a near tetrahedral angle. The antisymmetric stretch has been confirmed by Current and Burdett (5). They rationalize the absence of the symmetric stretch and claim support of the C_{3v} structure. Rogers et al. (6) have made a thorough search for the symmetric stretch and did not find it in the region where it was reported by Andrews (4). Thus, they conclude that since only the antisymmetric stretch has been confirmed, the possibility of a planar D_{3h} molecule cannot be excluded. Magat et al. (7) have observed the NMR spectrum of trapped CCl_3 and find it consistent with a planar molecule. The absence of the symmetric stretch strongly implies a planar configuration, and we adopt such a configuration until more definitive proof of the non-planarity can be obtained. The remaining vibrational frequencies are estimated by comparison with those of BCl_3. The bond length was estimated as 1.74 Å by Andrews (4) from a correlation with related molecules. The individual moments of inertia are $I_A = I_B = 2.6734 \times 10^{-38}$ g cm^2 and I_C = 5.3468 x 10^{-38} g cm^2.

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Trichlorofluoromethane (CCl_3F)

(Ideal Gas) GFW = 137.3686

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.838	-68.240	-68.240	INFINITE
100	10.354	58.377	88.222	-2.985	-68.792	-65.801	143.809
200	15.394	67.203	75.612	-1.682	-69.006	-62.702	68.517
298	18.646	74.002	74.001	.000	-69.000	-59.604	43.691
300	18.695	74.117	74.002	.035	-68.999	-59.546	43.379
400	20.829	79.810	74.764	2.019	-68.891	-56.409	30.820
500	22.211	84.617	76.266	4.175	-68.736	-53.305	23.300
600	23.123	88.753	78.011	6.445	-68.564	-50.236	18.298
700	23.745	92.367	79.809	8.790	-68.386	-47.194	14.735
800	24.182	95.568	81.583	11.188	-68.210	-44.180	12.070
900	24.498	98.435	83.299	13.623	-68.035	-41.187	10.002
1000	24.734	101.029	84.944	16.085	-67.862	-38.215	8.352
1100	24.913	103.395	86.515	18.568	-67.694	-35.259	7.005
1200	25.053	105.569	88.014	21.066	-67.530	-32.316	5.886
1300	25.163	107.579	89.443	23.577	-67.372	-29.389	4.941
1400	25.252	109.447	90.806	26.098	-67.217	-26.471	4.132
1500	25.324	111.192	92.107	28.627	-67.066	-23.566	3.434
1600	25.384	112.828	93.352	31.163	-66.920	-20.673	2.824
1700	25.434	114.369	94.543	33.704	-66.776	-17.784	2.286
1800	25.476	115.824	95.685	36.249	-66.637	-14.909	1.810
1900	25.512	117.202	96.782	38.799	-66.499	-12.035	1.384
2000	25.543	118.512	97.836	41.351	-66.368	-9.172	1.002
2100	25.569	119.758	98.850	43.907	-66.236	-6.317	.657
2200	25.592	120.948	99.828	46.465	-66.113	-3.469	.345
2300	25.613	122.087	100.771	49.025	-65.991	-.620	.059
2400	25.630	123.177	101.682	51.588	-65.874	2.219	-.202
2500	25.646	124.224	102.563	54.151	-65.763	5.052	-.442
2600	25.660	125.230	103.416	56.717	-65.655	7.884	-.663
2700	25.672	126.198	104.241	59.283	-65.553	10.709	-.867
2800	25.684	127.132	105.042	61.851	-65.456	13.534	-1.056
2900	25.694	128.034	105.820	64.420	-65.366	16.353	-1.232
3000	25.703	128.905	106.575	66.990	-65.282	19.166	-1.396
3100	25.711	129.748	107.309	69.561	-65.202	21.981	-1.550
3200	25.718	130.564	108.023	72.132	-65.130	24.792	-1.693
3300	25.725	131.356	108.718	74.704	-65.065	27.600	-1.828
3400	25.731	132.124	109.395	77.277	-65.004	30.411	-1.955
3500	25.737	132.870	110.055	79.851	-64.952	33.211	-2.074
3600	25.742	133.595	110.699	82.424	-64.905	36.019	-2.187
3700	25.747	134.300	111.327	84.999	-64.864	38.822	-2.293
3800	25.752	134.987	111.941	87.574	-64.828	41.624	-2.394
3900	25.756	135.656	112.541	90.149	-64.800	44.426	-2.490
4000	25.760	136.308	113.127	92.725	-64.777	47.227	-2.580
4100	25.763	136.944	113.700	95.301	-64.759	50.022	-2.666
4200	25.766	137.565	114.261	97.878	-64.748	52.823	-2.749
4300	25.769	138.171	114.810	100.454	-64.741	55.622	-2.827
4400	25.772	138.764	115.347	103.032	-64.739	58.425	-2.902
4500	25.775	139.343	115.874	105.609	-64.743	61.217	-2.973
4600	25.777	139.910	116.391	108.186	-64.749	64.019	-3.042
4700	25.780	140.464	116.897	110.764	-64.761	66.821	-3.107
4800	25.782	141.007	117.394	113.342	-64.777	69.620	-3.170
4900	25.784	141.538	117.881	115.921	-64.797	72.423	-3.230
5000	25.786	142.059	118.359	118.499	-64.820	75.221	-3.288
5100	25.788	142.570	118.829	121.078	-64.847	78.020	-3.343
5200	25.789	143.071	119.290	123.657	-64.877	80.826	-3.397
5300	25.791	143.562	119.744	126.236	-64.912	83.627	-3.448
5400	25.793	144.044	120.189	128.815	-64.950	86.429	-3.498
5500	25.794	144.517	120.627	131.394	-64.991	89.236	-3.546
5600	25.795	144.982	121.058	133.974	-65.034	92.037	-3.592
5700	25.797	145.439	121.482	136.553	-65.083	94.835	-3.636
5800	25.798	145.887	121.899	139.133	-65.133	97.648	-3.679
5900	25.799	146.328	122.309	141.713	-65.187	100.453	-3.721
6000	25.800	146.762	122.713	144.293	-65.245	103.259	-3.761

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

TRICHLOROFLUOROMETHANE (CCl_3F) (IDEAL GAS) GFW = 137.3686

Point Group C_{3v}

$\Delta Hf^\circ_0 = -68.24 \pm 1.5$ kcal/mol

$S^\circ_{298.15} = 74.00 \pm 0.05$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -69.0 \pm 1.5$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
349.5 (1)	241 (2)
535.3 (1)	398 (2)
1085 (1)	847 (2)

Bond Distance: C-Cl = 1.76 Å C-F = 1.33 Å

Bond Angle: Cl-C-Cl = 109°40' F-C-Cl = 109°28' σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 5.73499 \times 10^{-113}\ g^3cm^{-6}$

Heat of Formation

Mears and Stahl (1) investigated several heats of reaction involving CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, HF and HCl. Using JANAF values for all compounds except CF_2Cl_2 and $CFCl_3$, we obtain the following observations:

1. $\Delta Hf_{298}(CCl_3F, g) = -70.12 \pm 1.1$ kcal/mol
2. $\Delta Hf_{298}(CCl_2F_2, g) = -116.53 \pm 1.5$ kcal/mol
3. $\Delta Hf_{298}(CCl_2F_2, g) - \Delta Hf_{298}(CCl_3F, g) = -49.39 \pm 1.0$ kcal/mol
4. $\Delta Hf_{298}(CCl_2F_2, g) - 2\Delta Hf_{298}(CCl_3F, g) = 20.34 \pm 1.0$ kcal/mol
5. $\Delta Hf_{298}(CCl_3F, g) - 2\Delta Hf_{298}(CCl_2F_2, g) = 165.47 \pm 1.0$ kcal/mol

The sum of the squares of the deviations is smallest when $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -117.5$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -69$ kcal/mol, and all the values are within their uncertainty ranges.

Petersen and Pitzer (9) obtained an approximate equilibrium constant for the reaction $CClF_3(g) + 2CCl_4(g) = 3CCl_3F(g)$ of $\log K_{400} = -4.5$. This on 3rd law reduction gives $\Delta Hr^\circ_{298} = 10.56$ kcal and with $\Delta Hf^\circ_{298}(CClF_3, g) = -169.2$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_4, g) = -22.94$ kcal/mol this yields $\Delta Hf^\circ_{298}(CCl_3F, g) = -68.2$ kcal/mol.

Kirkbride and Davidson (2) investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -115.1 \pm 2$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -72.9 \pm 4$ kcal/mol after correction with JANAF auxiliary data. Wartenberg and Schiefer (3) investigated the same reaction and we obtain, after correction with JANAF auxiliary data, $\Delta Hf^\circ_{298}(CCl_2F_2, g) = -112.7$ kcal/mol and $\Delta Hf^\circ_{298}(CCl_3F, g) = -63.1$ kcal/mol. Baibuz (4) has reported $\Delta Hf^\circ_{298}(CCl_3F, g) = -66.4 \pm 2.1$ from heat of explosion measurements. A correlation of his other results would indicate that this value is not negative enough, possibly by as much as 3 kcal.

We adopt the values calculated above from Mears and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF_4 to CCl_4. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Claassen (5) chose the frequencies given above from his own gas phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6), and the matrix studies of King (7). The molecular structure was determined from the microwave measurements of Long et al. (8). The individual moments of inertia were: $I_A = I_C = 34.301 \times 10^{-39}\ g\ cm^2$ and $I_B = 48.744 \times 10^{-39}\ g\ cm^2$.

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Carbon Tetrachloride (CCl_4)

(Ideal Gas) GFW = 153.82315

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.120	-22.420	-22.420	INFINITE
100	11.291	57.033	89.401	-3.237	-22.943	-19.595	42.825
200	16.729	66.689	75.750	-1.812	-23.048	-16.180	17.680
298	19.933	74.019	74.019	.000	-22.940	-12.827	9.403
300	19.979	74.142	74.019	.037	-22.937	-12.765	9.299
400	21.918	80.180	74.829	2.140	-22.740	-9.402	5.137
500	23.088	85.207	76.416	4.395	-22.510	-6.093	2.663
600	23.823	89.486	78.247	6.743	-22.278	-2.832	1.032
700	24.306	93.197	80.124	9.151	-22.051	.391	-.122
800	24.638	96.466	81.966	11.600	-21.833	3.581	-.978
900	24.874	99.382	83.742	14.076	-21.624	6.745	-1.638
1000	25.047	102.012	85.440	16.572	-21.422	9.884	-2.160
1100	25.178	104.406	87.057	19.084	-21.227	13.005	-2.584
1200	25.279	106.601	88.595	21.607	-21.040	16.110	-2.934
1300	25.359	108.628	90.059	24.139	-20.861	19.198	-3.227
1400	25.423	110.510	91.454	26.678	-20.686	22.274	-3.477
1500	25.474	112.265	92.783	29.223	-20.517	25.336	-3.691
1600	25.517	113.911	94.053	31.773	-20.353	28.386	-3.877
1700	25.552	115.459	95.267	34.326	-20.192	31.431	-4.041
1800	25.582	116.920	96.430	36.883	-20.036	34.460	-4.184
1900	25.608	118.304	97.545	39.443	-19.882	37.488	-4.312
2000	25.629	119.618	98.616	42.005	-19.735	40.502	-4.426
2100	25.648	120.869	99.646	44.569	-19.588	43.510	-4.528
2200	25.664	122.063	100.638	47.134	-19.450	46.509	-4.620
2300	25.679	123.204	101.595	49.701	-19.313	49.508	-4.704
2400	25.691	124.297	102.518	52.270	-19.181	52.497	-4.781
2500	25.702	125.346	103.410	54.840	-19.055	55.480	-4.850
2600	25.712	126.354	104.273	57.410	-18.934	58.460	-4.914
2700	25.721	127.325	105.109	59.982	-18.818	61.432	-4.973
2800	25.729	128.260	105.919	62.554	-18.709	64.406	-5.027
2900	25.736	129.163	106.706	65.128	-18.605	67.370	-5.077
3000	25.742	130.036	107.469	67.701	-18.509	70.331	-5.124
3100	25.748	130.880	108.210	70.276	-18.418	73.292	-5.167
3200	25.753	131.698	108.932	72.851	-18.335	76.249	-5.208
3300	25.758	132.490	109.634	75.427	-18.259	79.202	-5.245
3400	25.762	133.259	110.317	78.003	-18.188	82.159	-5.281
3500	25.766	134.006	110.983	80.579	-18.127	85.102	-5.314
3600	25.770	134.732	111.633	83.156	-18.070	88.055	-5.346
3700	25.773	135.438	112.267	85.733	-18.021	91.003	-5.375
3800	25.776	136.125	112.886	88.310	-17.977	93.947	-5.403
3900	25.779	136.795	113.490	90.888	-17.940	96.896	-5.430
4000	25.782	137.448	114.081	93.466	-17.910	99.840	-5.455
4100	25.784	138.084	114.659	96.044	-17.884	102.778	-5.479
4200	25.787	138.706	115.224	98.623	-17.865	105.721	-5.501
4300	25.789	139.312	115.777	101.202	-17.850	108.662	-5.523
4400	25.791	139.905	116.319	103.781	-17.840	111.611	-5.544
4500	25.793	140.485	116.849	106.360	-17.836	114.545	-5.563
4600	25.794	141.052	117.369	108.939	-17.834	117.490	-5.582
4700	25.796	141.607	117.879	111.519	-17.836	120.435	-5.600
4800	25.797	142.150	118.379	114.098	-17.844	123.374	-5.617
4900	25.799	142.682	118.870	116.678	-17.854	126.321	-5.634
5000	25.800	143.203	119.351	119.258	-17.866	129.260	-5.650
5100	25.801	143.714	119.824	121.838	-17.881	132.203	-5.665
5200	25.803	144.215	120.288	124.418	-17.899	135.149	-5.680
5300	25.804	144.706	120.744	126.999	-17.920	138.089	-5.694
5400	25.805	145.189	121.193	129.579	-17.944	141.034	-5.708
5500	25.806	145.662	121.633	132.160	-17.970	143.982	-5.721
5600	25.807	146.127	122.066	134.740	-17.998	146.921	-5.734
5700	25.808	146.584	122.493	137.321	-18.030	149.858	-5.746
5800	25.809	147.033	122.912	139.902	-18.062	152.813	-5.758
5900	25.809	147.474	123.324	142.483	-18.098	155.757	-5.770
6000	25.810	147.908	123.730	145.064	-18.136	158.703	-5.781

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1968

CARBON TETRACHLORIDE (CCl_4) (IDEAL GAS) GFW = 153.82315

Point Group T_d $\Delta Hf_0^\circ = -22.42 \pm 0.5$ kcal/mol

$S_{298.15}^\circ = 74.02 \pm 0.01$ gibbs/mol $\Delta Hf_{298.15}^\circ = -22.94 \pm 0.5$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
458 (1)
218 (2)
776 (3)
314 (3)

Bond Distance: C-Cl = 1.760 Å

Bond Angle: Cl-C-Cl = 109.47° $\sigma = 12$

Product of the Moments of Inertia: $I_AI_BI_C = 1.14972 \times 10^{-112}\ g^3cm^6$

Heat of Formation

Hu and Sinke (1) have measured the heat of combustion of $CCl_4(\ell)$ in the rotating platinum bomb calorimeter, using As_2O_3 solution as the reducing agent. They reported $\Delta Hc_{298}^\circ = -86.02$ kcal/mol for $CCl_4(\ell) + 2H_2O(\ell) \rightarrow CO_2(g) + 4HCl(600H_2O, aq)$ which leads to $\Delta Hf_{298}^\circ (CCl_4, \ell) = -30.69$ kcal/mol, using $\Delta Hf_{298}^\circ = -94.051$, -39.823 and -68.315 kcal/mol for $CO_2(g)$, $HCl(600H_2O, aq)$ and $H_2O(\ell)$, respectively (2). The standard deviation of five combustion runs was ±0.074 kcal/mol. Employing the heat of vaporization of $CCl_4(\ell)$ at 298°K as 7.75 kcal/mol (3), we obtain $\Delta Hf_{298}^\circ (CCl_4, g) = -22.94$ kcal/mol which is adopted in the tabulation.

L. Smith et al. (5), based on the combustion data of E. Eftring (4), re-evaluated the heat of combustion of carbon tetrachloride at 18.7°C as $\Delta E_c^\circ/M = -567.5$ cal/g for $CCl_4(\ell) + 2H_2O(\ell) \rightarrow CO_2(g) + 4HCl(600H_2O)$. This value needs to be further corrected for a change in the heat of oxidation of As_2O_3 (6) and calculated to 25°C to give $\Delta E_{c298}^\circ = -88.105$ kcal/mol, $\Delta Hc_{298}^\circ = -87.513$ kcal/mol, $\Delta Hf_{298}^\circ(CCl_4, \ell) = -29.20$ kcal/mol and $\Delta Hf_{298}^\circ(CCl_4, g) = -21.45$ kcal/mol.

C. A. Neugebauer (7) has measured the heat of reaction of CCl_4 with Mg in presence of hydrogen in the stationary bomb calorimeter and then derived the heat of formation, $\Delta Hf_{298}^\circ (CCl_4, \ell) = -32.3 \pm 2$ kcal/mol which yields $\Delta Hf_{298}^\circ (CCl_4, g) = -24.55 \pm 2$ kcal/mol. V. F. Baibuz (8), using an explosion technique, obtained $\Delta Hf_{298}^\circ (CCl_4, g) = -24.6 \pm 1.9$ kcal/mol. Bodenstein and Gunther (9) have measured calorimetrically $\Delta H_{r293}^\circ = -62.57 \pm 0.35$ kcal/mole for $CCl_4(g) + 2H_2(g) \rightarrow C(c) + 4HCl(g)$. They calibrated their calorimeter by means of the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ for which they took $\Delta H_{293}^\circ = -44$ kcal/mol. Their data have been re-evaluated to give $\Delta Hf_{298}^\circ (CCl_4, g) = -25.68$ kcal/mol, but no correction is applied for the heat of formation of carbon which was not the reference state "graphite" formed in the reaction. Domalski and Armstrong (10) reviewed several cases of active carbon formed in similar reactions and quoted a heat of formation of carbon from +1.9 to +3.95 kcal/mol. If this correction is applied to the data of Bodenstein, their heat of formation of $CCl_4(g)$ should be 2 to 4 kcal/mol less negative than -25.68 kcal/mol.

Heat Capacity and Entropy

Bartell, Brockway and Schwendeman (11) have measured the bond distance as 1.760 ± 0.004 Å by the electron diffraction measurement. The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (12) in which they are essentially the same as those frequencies determined from Raman and infrared spectra by Classen (13). The three principal moments of inertia are $I_A = I_B = I_C = 48.627 \times 10^{-39}\ g\ cm^2$.

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Carbon Monofluoride (CF)

(Ideal Gas) GFW = 31.0096

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	,000	.000	INFINITE	-2.171	60.136	60.136	INFINITE
100	7.413	43.028	57.245	-1.422	60.524	58.277	-127.364
200	7.117	48.043	51.542	-.700	60.818	55.907	-61.093
298	7.184	50.889	50,889	,000	61.000	53.455	-39.183
300	7.188	50.934	50.889	.013	61.002	53.408	-38.907
400	7.432	53,033	51,174	,744	61.102	50,860	-27,789
500	7,709	54.721	51.720	1.501	61.136	48,294	-21,109
600	7,954	56.149	52.342	2.284	61.126	45,726	-16,656
700	8,154	57.391	52,976	3.090	61,081	43.163	-13.476
800	8,312	58.490	53.598	3.914	61.013	40,607	-11,093
900	8.438	59.477	54,197	4.751	60,925	38.061	-9.242
1000	8.538	60.371	54.771	5,600	60.826	35.525	-7.764
1100	8,619	61.189	55,318	6,458	60.715	33,000	-6.556
1200	8,686	61.942	55,839	7.324	60,596	30,487	-5,552
1300	8,742	62,639	56,335	8.195	60.467	27,983	-4,704
1400	8,789	63,289	56,809	9,072	60,334	25,490	-3,979
1500	8,829	63.897	57.261	9,953	60.195	23.006	-3.352
1600	8,864	64.468	57,694	10,837	60,052	20,530	-2,804
1700	8,895	65.006	58,109	11.725	59,907	18.065	-2.322
1800	8,923	65.515	58,506	12,616	59,758	15,607	-1,895
1900	8,947	65.998	58.888	13.510	59.608	13.159	-1.514
2000	8.970	66,458	59,255	14.406	59.455	10.719	-1.171
2100	8,991	66.896	59,608	15,304	59,301	8,286	-,862
2200	9,010	67.315	59,949	16,204	59,144	5,858	-,582
2300	9,027	67,716	60,278	17,106	58,986	3.442	-,327
2400	9,044	68,100	60,596	18,009	58,826	1,030	-,094
2500	9,060	68,470	60,904	18,914	58,664	-1.376	,120
2600	9,075	68.825	61,202	19,821	58,501	-3,774	,317
2700	9,089	69,168	61,490	20,729	58,336	-6,167	,499
2800	9,103	69,499	61,771	21,639	58,172	-8,552	,668
2900	9,117	69,819	62,043	22,550	58,004	-10,931	,824
3000	9,130	70,128	62,307	23,462	57,834	-13,307	,969
3100	9,143	70,427	62,564	24,376	57,665	-15,674	1,105
3200	9,156	70,718	62,814	25,291	57,493	-18,037	1,232
3300	9,168	71,000	63,058	26,207	57,320	-20,397	1,351
3400	9,181	71,274	63,296	27,125	57,146	-22,748	1,462
3500	9,193	71,540	63,528	28,043	56,970	-25,096	1,567
3600	9,206	71,799	63,754	28,963	56,793	-27,438	1,666
3700	9,219	72,052	63,975	29,884	56,614	-29,775	1,759
3800	9,232	72,298	64,190	30,807	56,435	-32,105	1,846
3900	9,245	72,538	64,401	31,731	56,253	-34,433	1,930
4000	9,259	72,772	64,608	32,656	56,072	-36,755	2,008
4100	9,272	73,001	64,810	33,583	55,888	-39,077	2,083
4200	9,286	73,224	65,007	34,511	55,702	-41,388	2,154
4300	9,301	73,443	65,201	35,440	55,515	-43,698	2,221
4400	9,316	73,657	65,391	36,371	55,327	-46,004	2,285
4500	9,331	73,866	65,577	37,303	55,138	-48,307	2,346
4600	9,346	74,072	65,759	38,237	54,947	-50,602	2,404
4700	9,362	74,273	65,938	39,172	54,756	-52,894	2,460
4800	9,379	74,470	66,114	40,109	54,562	-55,180	2,512
4900	9,395	74,664	66,286	41,048	54,368	-57,465	2,563
5000	9,413	74,854	66,456	41,988	54,172	-59,745	2,611
5100	9,430	75,040	66,622	42,931	53,975	-62,028	2,658
5200	9,448	75,223	66,786	43,874	53,776	-64,297	2,702
5300	9,467	75,404	66,947	44,820	53,577	-66,564	2,745
5400	9,486	75,581	67,105	45,768	53,376	-68,829	2,786
5500	9,505	75,755	67,261	46,717	53,174	-71,090	2,825
5600	9,525	75,926	67,414	47,669	52,971	-73,348	2,863
5700	9,545	76,095	67,565	48,622	52,766	-75,605	2,899
5800	9,565	76,261	67,713	49,578	52,560	-77,854	2,934
5900	9,586	76,425	67,860	50,535	52,353	-80,099	2,967
6000	9,607	76,586	68,004	51,495	52,145	-82,346	2,999

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1966; Dec. 31, 1967; June 30, 1970

CARBON MONOFLUORIDE (CF) (IDEAL GAS) GFW = 31.0096

Ground State Configuration $^2\Pi_r$

ΔHf°_0 = 60.1 ± 2 kcal/mol

$S^\circ_{298.15}$ = 50.889 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 61 ± 2 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	2
77.11	2
[25000]	4
42705	2
49452	2

ω_e = 1308.1 cm^{-1} $\omega_e x_e$ = 11.10 cm^{-1} σ = 1

B_e = 1.4172 cm^{-1} α_e = 0.0184 cm^{-1} r_e = 1.2667 Å

Heat of Formation

M. Farber et al. (1) have studied the weight change of graphite in CF_4 at high temperatures. Our reanalysis of their data uses the equilibrium constants for CF_4, CF_3 and CF_2 from the JANAF Tables (2); the only other C-F species considered is assumed to be CF. This treatment yields negative values for the CF pressure except at the highest temperature, where 3rd law analysis of the equilibrium constant yields ΔHf°_{298}(CF, g) = 59.4 kcal/mol. Farber et al. also investigated mass-spectrometrically the vapor species present at equilibrium and followed the intensities of CF^+ and F^+. From a second law treatment of the intensities they report ΔHf°_{2300}(CF, g) = 62.0 kcal/mol, or ΔHf°_{298}(CF, g) = 64 kcal/mol.

Porter et al. (3) have investigated the A-X band system under high dispersion. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of 126.9 ± 2.9 kcal/mol, which yields ΔHf°_{298}(CF, g) = 61.9 ± 2.9 kcal/mol.

The predissociation limit of CF(g) has been reported by Thrush and Zwolenik (4) as $\leq$132 kcal/mol; Kuzyakov and Tatievsky (5) determined the same quantity as $\leq$133 kcal/mol. These results yield ΔHf°_{298}(CF, g) $\geq$ 56 kcal/mol. Thrush and Zwolenik (4) also report a predissociation limit for the reaction $CF_2 \rightarrow CF + F$ which is $\leq$120 kcal/mol. This value has now been shown to be erroneous (see the CF_2(g) table for details).

Modica (6) has studied the equilibrium $CF_2 \rightarrow CF + F$ in a shock tube in the range 2680° to 3400°K. Since functions for CF_2, CF and F are well established, the data were analyzed using 2nd and 3rd law treatments. The 2nd law analysis gives ΔHr°_{298} = 107.2 ± 7.6 kcal/mol, in agreement with the value reported by Modica. The 3rd law analysis yields ΔHr°_{298} = 134.9 ± 7.2 kcal/mol and a drift of 9.7 ± 2.5 eu. The excessive drift indicates that the reported equilibrium constants do not represent the stated reaction.

Andrews and Barrow (7) report a dissociation energy of 114 kcal from an extrapolation of four B state levels. This extrapolation is considered unreliable by Porter et al. (3) since this state is formed from an avoided crossing and is likely to be perturbed.

The adopted value of ΔHf°_{298}(CF, g) is 61 ± 2 kcal/mol, which is within the uncertainties and ranges of the acceptable investigations.

Heat Capacity and Entropy

The vibrational and rotational constants are from Porter et al. (3); the higher electronic levels are those reported by Andrews and Barrow (7), except that the B state is now considered to be $^2\Sigma$. The estimated level at 25000 cm^{-1} is proposed in order to explain the low bond dissociation energy of C_2F_2, by analogy with the reasoning used by Simons (8) for C_2F_4. This level would be a $^4\Sigma$ level and could correlate with the ground state atoms.

References

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2. JANAF Thermochemical Tables; CF_4 dated 6-30-69; CF_3 dated 6-30-69; CF_2 dated 6-30-70.
3. T. L. Porter, D. E. Mann and N. Acquista, J. Mol. Spectry. 16, 228 (1965).
4. B. A. Thrush and J. J. Zwolenik, Trans. Faraday Soc. 59, 582 (1963).
5. Yu. Ya. Kuzyakov and V. M. Tatievsky, Opt. i. Spektroskopiya 5, 699 (1958).
6. A. P. Modica, J. Chem. Phys. 44, 1585 (1966).
7. E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London), 64A, 481 (1951).
8. J. P. Simons, Nature 205, 1308 (1965).

Cyanogen Fluoride (FCN)

(Ideal Gas) GFW = 45 .01625

T, °K	Cp° gibbs/mol	S° gibbs/mol	-(G°-H°298)/T gibbs/mol	H°-H°298 kcal/mol	ΔHf° kcal/mol	ΔGf° kcal/mol	Log Kp
0	,000	,000	INFINITE	-2,455	8,488	8,488	INFINITE
100	7,301	44,462	62,003	-1,754	8,481	7,999	-17,482
200	8,960	50,037	54,737	-,940	8,519	7,509	-8,206
298	10,113	53,846	53,846	,000	8,600	6,997	-5,129
300	10,130	53,908	53,846	,019	8,601	6,986	-5,089
400	10,934	56,939	54,254	1,074	8,677	6,437	-3,517
500	11,542	59,447	55,049	2,199	8,728	5,869	-2,566
600	12,031	61,596	55,965	3,379	8,758	5,295	-1,929
700	12,438	63,482	56,907	4,603	8,767	4,717	-1,473
800	12,779	65,166	57,836	5,864	8,765	4,138	-1,131
900	13,066	66,688	58,736	7,157	8,753	3,560	-,864
1000	13,306	68,077	59,602	8,476	8,737	2,983	-,652
1100	13,508	69,355	60,431	9,817	8,715	2,409	-,479
1200	13,677	70,538	61,225	11,176	8,689	1,838	-,335
1300	13,820	71,639	61,984	12,551	8,658	1,267	-,213
1400	13,942	72,668	62,711	13,940	8,627	,701	-,109
1500	14,045	73,633	63,407	15,339	8,592	,136	-,020
1600	14,133	74,542	64,075	16,748	8,556	-,427	,058
1700	14,210	75,402	64,716	18,165	8,518	-,987	,127
1800	14,275	76,216	65,333	19,590	8,478	-1,546	,188
1900	14,333	76,989	65,926	21,020	8,438	-2,100	,242
2000	14,383	77,726	66,498	22,456	8,396	-2,654	,290
2100	14,427	78,428	67,049	23,896	8,354	-3,205	,334
2200	14,465	79,100	67,582	25,341	8,308	-3,756	,373
2300	14,500	79,744	68,097	26,789	8,262	-4,302	,409
2400	14,530	80,362	68,595	28,241	8,214	-4,847	,441
2500	14,558	80,956	69,078	29,695	8,165	-5,392	,471
2600	14,582	81,527	69,545	31,152	8,113	-5,933	,499
2700	14,604	82,078	69,999	32,612	8,060	-6,472	,524
2800	14,624	82,609	70,440	34,073	8,007	-7,009	,547
2900	14,642	83,123	70,869	35,536	7,950	-7,543	,568
3000	14,658	83,620	71,286	37,002	7,891	-8,078	,588
3100	14,673	84,100	71,691	38,468	7,832	-8,609	,607
3200	14,687	84,567	72,086	39,936	7,769	-9,138	,624
3300	14,699	85,019	72,472	41,405	7,704	-9,668	,640
3400	14,711	85,458	72,847	42,876	7,638	-10,190	,655
3500	14,721	85,884	73,213	44,348	7,569	-10,716	,669
3600	14,731	86,299	73,571	45,820	7,498	-11,237	,682
3700	14,740	86,703	73,921	47,294	7,424	-11,756	,694
3800	14,748	87,096	74,262	48,768	7,349	-12,271	,706
3900	14,756	87,479	74,596	50,243	7,270	-12,786	,717
4000	14,763	87,853	74,923	51,719	7,190	-13,299	,727
4100	14,769	88,217	75,243	53,196	7,107	-13,813	,736
4200	14,776	88,573	75,556	54,673	7,021	-14,319	,745
4300	14,781	88,921	75,863	56,151	6,933	-14,826	,754
4400	14,787	89,261	76,163	57,629	6,841	-15,333	,762
4500	14,792	89,593	76,458	59,108	6,747	-15,838	,769
4600	14,797	89,919	76,747	60,588	6,650	-16,336	,776
4700	14,801	90,237	77,031	62,068	6,551	-16,835	,783
4800	14,805	90,549	77,309	63,548	6,448	-17,329	,789
4900	14,809	90,854	77,583	65,029	6,343	-17,826	,795
5000	14,813	91,153	77,851	66,510	6,234	-18,316	,801
5100	14,816	91,446	78,115	67,991	6,122	-18,814	,806
5200	14,819	91,734	78,374	69,473	6,007	-19,296	,811
5300	14,823	92,016	78,629	70,955	5,890	-19,781	,816
5400	14,825	92,294	78,879	72,438	5,769	-20,265	,820
5500	14,828	92,566	79,126	73,920	5,643	-20,744	,824
5600	14,831	92,833	79,368	75,403	5,516	-21,223	,828
5700	14,833	93,095	79,606	76,886	5,384	-21,702	,832
5800	14,836	93,353	79,841	78,370	5,249	-22,175	,836
5900	14,838	93,607	80,072	79,854	5,111	-22,645	,839
6000	14,840	93,856	80,300	81,337	4,969	-23,119	,842

Dec. 31, 1960; June 30, 1961: June 30, 1969

CYANOGEN FLUORIDE (FCN) (IDEAL GAS) GFW = 45.01625

CFN

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = 53.85 ± 0.2 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = 8.5 ± 4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 8.6 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1077 (1)
[420] (2)
2290 (1)

Bond Distances: C-F = 1.262 Å C-N = 1.159 Å

Bond Angle: F-C-N = 180°

Rotational Constants: $B_0 = 0.3531\ cm^{-1}$

σ = 1

Heat of Formation

Davis and Okabe (1) have determined the dissociation energy of FCN to F(g) and CN(g) by measuring the threshold energies of incident photon radiation to produce $B^2\Sigma^+$ CN which is monitored by its fluorescence. The dissociation energy determined by this technique is ≤ 111 kcal/mol with an uncertainty of about 1 kcal in the determination of the limit.

Dibeler and Liston (2) have reported a dissociation energy of ≤ 115.6 kcal/mol from the threshold of the CN^+ ion as determined by photoionization.

We adopt a median value of 113.1 ± 2.5 kcal/mol which leads to ΔHf°_{298}(FCN, g) = 8.6 ± 4 kcal/mol with auxiliary JANAF values for F(g) and CN(g).

Heat Capacity and Entropy

The molecular structure and bond lengths and angle were determined using microwave spectroscopy by Tyler and Sheridan (3). The vibrational frequencies were reported by Aynsley et. al. (4) from the infra-red spectrum, except for the bending frequency which is estimated from the values for ClCN, BrCN and ICN, by comparison of bending force constants. The reasonable limits for this value as calculated from generous limits on the bending force constant are 405-450 cm^{-1}.

References:

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2. V. H. Dibeler and S. K. Liston, J. Chem. Phys. 47, 4548 (1967).
3. J. K. Tyler and J. Sheridan, Trans. Faraday. Soc. 59, 2661 (1963).
4. E. E. Aynsley, R. E. Dodd, and R. Little, Proc. Chem. Soc. (London), 1959, 265 (1959).

Carbonyl Monofluoride (COF)

(Ideal Gas) Mol. Wt. = 47.00895

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.484	- 41.139	- 41.139	INFINITE
100	7.969	50.185	67.074	- 1.689	- 41.062	- 41.949	91.675
200	8.476	55.826	60.187	- .872	- 41.014	- 42.857	46.830
298	9.305	59.363	59.363	.000	- 41.000	- 43.766	32.080
300	9.320	59.420	59.363	.017	- 41.000	- 43.784	31.895
400	10.106	62.212	59.738	.990	- 41.014	- 44.710	24.427
500	10.768	64.541	60.472	2.034	- 41.058	- 45.629	19.944
600	11.310	66.554	61.322	3.139	- 41.124	- 46.538	16.951
700	11.748	68.331	62.199	4.293	- 41.210	- 47.433	14.809
800	12.099	69.923	63.066	5.486	- 41.308	- 48.315	13.199
900	12.381	71.365	63.910	6.710	- 41.416	- 49.186	11.943
1000	12.607	72.682	64.722	7.960	- 41.528	- 50.043	10.936
1100	12.791	73.892	65.501	9.230	- 41.646	- 50.890	10.110
1200	12.940	75.012	66.248	10.517	- 41.768	- 51.724	9.420
1300	13.063	76.053	66.963	11.817	- 41.897	- 52.549	8.834
1400	13.165	77.025	67.647	13.129	- 42.027	- 53.362	8.330
1500	13.251	77.936	68.303	14.450	- 42.161	- 54.167	7.892
1600	13.323	78.794	68.932	15.779	- 42.298	- 54.965	7.508
1700	13.384	79.603	69.536	17.114	- 42.436	- 55.751	7.167
1800	13.436	80.370	70.117	18.455	- 42.580	- 56.532	6.864
1900	13.482	81.097	70.676	19.801	- 42.725	- 57.300	6.591
2000	13.521	81.790	71.214	21.151	- 42.874	- 58.065	6.345
2100	13.555	82.451	71.734	22.505	- 43.024	- 58.821	6.121
2200	13.585	83.082	72.235	23.862	- 43.181	- 59.571	5.918
2300	13.611	83.686	72.720	25.222	- 43.339	- 60.309	5.730
2400	13.634	84.266	73.189	26.584	- 43.501	- 61.044	5.559
2500	13.655	84.823	73.644	27.949	- 43.667	- 61.774	5.400
2600	13.674	85.359	74.084	29.315	- 43.837	- 62.494	5.253
2700	13.690	85.875	74.511	30.683	- 44.011	- 63.208	5.116
2800	13.705	86.373	74.926	32.053	- 44.187	- 63.914	4.988
2900	13.719	86.855	75.329	33.424	- 44.369	- 64.616	4.869
3000	13.731	87.320	75.721	34.797	- 44.554	- 65.313	4.758
3100	13.742	87.770	76.102	36.171	- 44.742	- 6 .999	4.653
3200	13.752	88.207	76.474	37.545	- 44.935	- 66.684	4.554
3300	13.761	88.630	76.836	38.921	- 45.132	- 67.362	4.461
3400	13.770	89.041	77.189	40.297	- 45.332	- 68.030	4.373
3500	13.778	89.440	77.533	41.675	- 45.537	- 68.696	4.289
3600	13.785	89.829	77.869	43.053	- 45.744	- 69.356	4.210
3700	13.791	90.206	78.198	44.432	- 45.956	- 70.006	4.135
3800	13.797	90.574	78.519	45.811	- 46.171	- 70.651	4.063
3900	13.803	90.933	78.832	47.191	- 46.391	- 71.296	3.995
4000	13.808	91.282	79.139	48.572	- 46.613	- 71.929	3.930
4100	13.813	91.623	79.440	49.953	- 46.840	- 72.561	3.868
4200	13.818	91.956	79.734	51.334	- 47.071	- 73.184	3.808
4300	13.822	92.281	80.022	52.716	- 47.305	- 73.801	3.751
4400	13.826	92.599	80.304	54.099	- 47.543	- 74.418	3.696
4500	13.829	92.910	80.581	55.482	- 47.784	- 75.029	3.644
4600	13.833	93.214	80.852	56.865	- 48.029	- 75.629	3.593
4700	13.836	93.511	81.118	58.248	- 48.277	- 76.224	3.544
4800	13.839	93.803	81.379	59.632	- 48.530	- 76.816	3.497
4900	13.842	94.088	81.636	61.016	- 48.785	- 77.403	3.452
5000	13.845	94.368	81.888	62.400	- 49.044	- 77.987	3.409
5100	13.847	94.642	82.135	63.785	- 49.308	- 78.567	3.367
5200	13.850	94.911	82.378	65.170	- 49.574	- 79.136	3.326
5300	13.852	95.175	82.617	66.555	- 49.844	- 79.699	3.286
5400	13.854	95.434	82.852	67.940	- 50.117	- 80.263	3.248
5500	13.856	95.688	83.083	69.326	- 50.394	- 80.815	3.211
5600	13.858	95.938	83.311	70.711	- 50.675	- 81.369	3.175
5700	13.860	96.183	83.534	72.097	- 50.960	- 81.916	3.141
5800	13.862	96.424	83.754	73.483	- 51.247	- 82.454	3.107
5900	13.863	96.661	83.971	74.870	- 51.538	- 82.988	3.074
6000	13.865	96.894	84.185	76.256	- 51.833	- 83.522	3.042

Dec. 31, 1965

CARBONYL MONOFLUORIDE (COF) (IDEAL GAS) MOL. WT. = 47.00895

Point Group C_s

$S^\circ_{298.15}$ = [59] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 2

$\Delta H^\circ_{f\ 0}$ = [-41 ± 15] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-41 ± 15] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1018 (1)
626 (1)
1855 (1)

Bond Distance: C-F = [1.34] Å C-O = [1.18] Å

Bond Angle: F-C-O = [135] °

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.1986 x 10^{-116}] g.^{3} cm.^{6}

Heat of Formation.

The enthalpy change (ΔH°_r) for the reaction $COF_2(g) = CO(g) + 2F(g)$ was calculated as 160.5 kcal. mole^{-1}. By analogy with D(Cl-COCl)/D(Cl-CO), the value of D(F-COF)/D(F-CO) was taken to be 4. Based on ΔH°_r = 160.5 x (4/5) = 128.4 kcal. mole^{-1} for the reaction $COF_2(g) = COF(g) + F(g)$, the heat of formation for COF(g) was derived as -41 ± 15 kcal. mole^{-1}.

Heat Capacity and Entropy.

The vibrational frequencies were reported by D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford and D. E. Mann, J. Chem. Phys. 42, 3187 (1965). The bond distances and angle were estimated by comparison with those for HFCO (g). Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 7.8757 x 10^{-39}, I_B = 3.3980 x 10^{-40}, and I_C = 8.2155 x 10^{-39} g. cm.^{2}

Carbon Difluoride (CF_2)

(Ideal Gas) GFW = 50.00795

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.475	-43.613	-43.613	INFINITE
100	7.961	48.404	65.199	-1.680	-43.527	-44.276	96.766
200	8.402	54.018	58.354	-.867	-43.492	-45.043	49.221
298	9.309	57.533	57.533	.000	-43.500	-45.804	33.575
300	9.327	57.591	57.534	.017	-43.501	-45.819	33.379
400	10.300	60.410	57.911	1.000	-43.534	-46.586	25.453
500	11.105	62.799	58.656	2.071	-43.589	-47.343	20.694
600	11.716	64.880	59.524	3.214	-43.656	-48.088	17.516
700	12.168	66.722	60.423	4.409	-43.737	-48.820	15.242
800	12.504	68.370	61.315	5.644	-43.827	-49.541	13.534
900	12.757	69.858	62.183	6.908	-43.926	-50.250	12.202
1000	12.950	71.213	63.019	8.193	-44.032	-50.947	11.135
1100	13.100	72.454	63.821	9.496	-44.144	-51.634	10.259
1200	13.219	73.599	64.589	10.812	-44.261	-52.308	9.527
1300	13.314	74.661	65.323	12.139	-44.386	-52.974	8.906
1400	13.391	75.651	66.026	13.474	-44.514	-53.629	8.372
1500	13.454	76.577	66.699	14.817	-44.646	-54.275	7.908
1600	13.507	77.447	67.344	16.165	-44.783	-54.914	7.501
1700	13.552	78.267	67.963	17.518	-44.922	-55.542	7.140
1800	13.591	79.043	68.557	18.875	-45.066	-56.165	6.819
1900	13.625	79.779	69.128	20.236	-45.211	-56.776	6.531
2000	13.655	80.478	69.678	21.600	-45.359	-57.380	6.270
2100	13.683	81.145	70.209	22.967	-45.509	-57.977	6.034
2200	13.710	81.782	70.720	24.337	-45.663	-58.569	5.818
2300	13.737	82.392	71.215	25.709	-45.818	-59.150	5.621
2400	13.763	82.978	71.693	27.084	-45.976	-59.727	5.439
2500	13.791	83.540	72.155	28.462	-46.135	-60.298	5.271
2600	13.819	84.081	72.604	29.842	-46.297	-60.861	5.116
2700	13.850	84.604	73.039	31.225	-46.459	-61.418	4.971
2800	13.882	85.108	73.461	32.612	-46.620	-61.969	4.837
2900	13.917	85.596	73.871	34.002	-46.784	-62.512	4.711
3000	13.954	86.068	74.269	35.395	-46.949	-63.055	4.594
3100	13.994	86.526	74.657	36.793	-47.111	-63.588	4.483
3200	14.036	86.971	75.035	38.194	-47.275	-64.117	4.379
3300	14.081	87.404	75.404	39.600	-47.438	-64.643	4.281
3400	14.129	87.825	75.763	41.011	-47.599	-65.159	4.188
3500	14.178	88.235	76.113	42.426	-47.761	-65.674	4.101
3600	14.231	88.635	76.456	43.846	-47.920	-66.183	4.018
3700	14.285	89.026	76.790	45.272	-48.078	-66.688	3.939
3800	14.341	89.408	77.117	46.703	-48.234	-67.186	3.864
3900	14.398	89.781	77.437	48.140	-48.389	-67.685	3.793
4000	14.457	90.146	77.750	49.583	-48.540	-68.176	3.725
4100	14.517	90.504	78.057	51.032	-48.690	-68.668	3.660
4200	14.578	90.854	78.357	52.486	-48.839	-69.151	3.598
4300	14.639	91.198	78.652	53.947	-48.984	-69.632	3.539
4400	14.701	91.535	78.941	55.414	-49.128	-70.112	3.483
4500	14.762	91.866	79.225	56.887	-49.269	-70.591	3.428
4600	14.824	92.191	79.503	58.367	-49.407	-71.061	3.376
4700	14.885	92.511	79.776	59.852	-49.544	-71.530	3.326
4800	14.946	92.825	80.045	61.344	-49.678	-71.993	3.278
4900	15.005	93.134	80.309	62.841	-49.811	-72.457	3.232
5000	15.064	93.437	80.568	64.345	-49.941	-72.918	3.187
5100	15.122	93.736	80.824	65.854	-50.071	-73.385	3.145
5200	15.178	94.031	81.075	67.369	-50.198	-73.834	3.103
5300	15.233	94.320	81.322	68.889	-50.324	-74.285	3.063
5400	15.286	94.605	81.565	70.415	-50.449	-74.740	3.025
5500	15.338	94.886	81.805	71.947	-50.572	-75.186	2.988
5600	15.388	95.163	82.041	73.483	-50.695	-75.632	2.952
5700	15.436	95.436	82.274	75.024	-50.818	-76.080	2.917
5800	15.482	95.705	82.503	76.570	-50.939	-76.521	2.883
5900	15.526	95.970	82.729	78.120	-51.061	-76.960	2.851
6000	15.568	96.231	82.952	79.675	-51.182	-77.402	2.819

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1966; June 30, 1970

Point Group C_{2v}

$S°_{298.15}$ = 57.53 ± 0.01 gibbs/mol

$\Delta Hf°_0$ = -43.6 ± 1.5 kcal/mol

$\Delta Hf°_{298.15}$ = -43.5 ± 1.5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X^1A_1	0	1	a^3B_1	[16000]	3	A^1B_1	37226	1

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
1222 (1)	665 (1)	1110 (1)

Bond Distance: C-F = 1.300 Å Bond Angle: F-C-F = 104.9° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 4.87896 \times 10^{-116}\ g^3\ cm^6$

Heat of Formation

Thrush and Zwolenik (1) reported a predissociation limit for $CF_2 \rightarrow CF + F$; however, Marsigny et al. (2) have since observed in emission the assumed predissociated level, and others above it, which invalidates the reported limit.

Walter et al. (3) have obtained the photoionization threshold at 0°K for onset of the reaction $C_2F_4 + e^- \rightarrow CF_2^+ + CF_2 + 2e^-$, as 14.63 ± 0.04 eV (337.37 kcal). The ionization potential of CF_2 has been reported as 11.7 eV (4), 11.8 ± 0.3 eV (5) and 11.86 ± 0.1 eV (6). Since these values were obtained by electron impact methods, there may be excess energy involved. Thus, adopting the lowest value as 11.7 ± 0.2 eV, we obtain $\Delta Hf°_{298}(CF_2, g)$ = -44.4 ± 2.5 kcal/mol (7). All previous electron impact methods are considered superseded by this photoionization result.

Modica and LaGraff (8) determined equilibrium constants for the reaction (A) $C_2F_4 \rightarrow 2CF_2$ by use of a shock tube to achieve high temperatures and ultra violet absorption to detect the CF_2 concentration. Carlson (9) has studied the same reaction using a similar technique, and also Zmbov et al. (5) have investigated this equilibrium in a mass spectrometer. A 2nd and 3rd law analysis of all three sets of data is given below, along with our recalculated equilibrium data of Farber et al. (10) for the reaction (B) $C + 2F \rightarrow CF_2$ from weight loss experiments in the system $C + CF_4$.

Kinetic methods were used by Edwards and Small (11) to study the equilibrium (C) $CHF_2Cl(g) \rightleftarrows CF_2(g) + HCl(g)$. They analysed their data by assuming that the only other equilibrium occurring was $2CF_2(g) \rightleftarrows C_2F_4(g)$, and fit their kinetic data by trial and error. In this manner they obtained activation energies of the forward and back reaction (C) of 55.79 ± 0.49 and 6.21 ± 3.0 kcal, thus ΔE_a = 49.6 ± 3.0 and ΔH_{900} = 51.4 ± 3 kcal, which yields $\Delta Hf_{298}(CF_2)$ = -42 ± 4 kcal/mol (7). They also obtained the activation energy of reaction (A) as 70.36 ± 1.3 kcal. Dalby (12) has reported the activation energy of the reverse of (A) as 1.2 ± 0.2 kcal, thus, ΔE_a = 69.2 ± 1.3 and ΔH_{900} = 71.0 ± 1.3 kcal, which yields $\Delta Hf_{298}(CF_2)$ = -42.6 ± 1.0 kcal/mol (7). Gozzo and Patrick (13) also investigated the kinetics of reaction C and obtained activation energies of 51.4 ± 2.5 and 14.4 ± 5 kcal, the latter value being corrected for the activation energy of CF_2 recombination (12). Thus, we obtain ΔE_a = 37 ± 7 and ΔH_{1000} = 39 ± 7 kcal, which yields $\Delta Hf_{298}(CF_2)$ = -54 ± 9 kcal/mol (7).

Modica and LaGraff (14) investigated the kinetics of CHF_3 decomposition by a mass spectrometer coupled to a shock tube. They investigated the pressure dependence of the rate and concluded that at the high pressure limit E_o = 58.4 ± 2.2 kcal. Taking this value as $\Delta H°_0$ for the reaction (D) $CHF_3(g) \rightarrow CF_2(g) + HF(g)$, we obtain $\Delta Hf_{298}(CF_2)$ = -41.3 ± 2.5 kcal/mol (7). However, any activation energy of the reverse reaction (D) will make this value more negative. Since values of the reverse activation energy of analogous reaction (C) range from 6.2 to 14.4 kcal, it appears likely that reverse reaction (D) will have a significant activation energy; thus, $\Delta Hf_{298}(CF_2)$ < -41.3 ± 2.5 kcal. Tschiukow-Roux (15) has investigated the same reaction in a shock tube, but was unable to obtain sufficient variation of rate with pressure to calculate the high pressure limit.

Reference and Reaction	Points	Range °K	ΔHr_{298}, kcal/mol 2nd law	3rd law	Drift eu	**$\Delta Hf_{298}(CF_2, g)$ kcal/mol
8. A	20*	1165-1620	70.89±2.7	66.68±2.28	-2.4±2.1	-45.4±2.0
9. A	35*	1240-1742	67.92±0.7	68.40±0.72	0.3±0.5	-44.5±0.7
5. A	11	1127-1244	77.3 ±2.1	75.13±0.5	-1.8±1.8	-41.15±1.5
10. B	8	2023-2474	-73.8 ±1.4	-80.04±1.0	-2.8±0.6	-42.3±1.0

*Points omitted due to failure of a statistical test **Calculated from the 3rd law heat of reaction.

A median value of $\Delta Hf_{298}(CF_2, g)$ covering the area of maximum probability is adopted as -43.5 ± 1.5 kcal/mol.

Heat Capacity and Entropy

The structure of CF_2 has been reported by Powell and Lide (16) from microwave measurements and has been confirmed by Mathews (17) from the fine structure of the 2500Å absorption band. Mathews also reported ω_2, and Herr and Pimentel (18) reported ω_3, both from gas phase studies. Milligan et al. (19) have observed all three vibrations in matrix-isolated CF_2 as 1222, 668 and 1102 cm^{-1}. The electronic levels are from Mathews (17) with the triplet level estimated by Simons (20) to explain the low C=C bond energy of 70 kcal in C_2F_4. The individual moments of inertia are $I_A = 0.9512 \times 10^{-39}\ g\ cm^2$, $I_B = 6.7020 \times 10^{-39}\ g\ cm^2$, and $I_C = 7.6532 \times 10^{-39}\ g\ cm^2$.

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Carbonyl Fluoride (COF_2)

(Ideal Gas) GFW = 66.0074

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.657	-151.958	-151.958	INFINITE
100	8.004	51.917	70.536	-1.862	-152.218	-151.250	330.556
200	9.296	57.767	62.820	-1.011	-152.493	-150.172	164.100
298	11.294	61.851	61.851	.000	-152.700	-148.986	109.210
300	11.330	61.921	61.851	.021	-152.704	-148.963	108.520
400	13.092	65.432	62.318	1.245	-152.851	-147.692	80.695
500	14.460	68.507	63.255	2.626	-152.961	-146.390	63.987
600	15.505	71.240	64.362	4.127	-153.048	-145.067	52.841
700	16.306	73.693	65.523	5.719	-153.121	-143.730	44.874
800	16.924	75.912	66.685	7.382	-153.182	-142.385	38.898
900	17.406	77.935	67.824	9.099	-153.235	-141.033	34.247
1000	17.786	79.789	68.929	10.860	-153.279	-139.675	30.526
1100	18.089	81.499	69.995	12.654	-153.319	-138.313	27.480
1200	18.334	83.084	71.021	14.475	-153.355	-136.946	24.941
1300	18.533	84.559	72.006	16.319	-153.391	-135.577	22.793
1400	18.697	85.939	72.952	18.181	-153.425	-134.204	20.950
1500	18.834	87.234	73.862	20.058	-153.458	-132.830	19.353
1600	18.949	88.453	74.736	21.947	-153.492	-131.456	17.956
1700	19.046	89.605	75.577	23.847	-153.526	-130.076	16.722
1800	19.129	90.696	76.387	25.756	-153.562	-128.697	15.626
1900	19.201	91.732	77.168	27.672	-153.599	-127.314	14.644
2000	19.262	92.719	77.921	29.596	-153.638	-125.929	13.761
2100	19.316	93.660	78.648	31.525	-153.678	-124.542	12.961
2200	19.363	94.559	79.351	33.459	-153.724	-123.156	12.234
2300	19.404	95.421	80.031	35.397	-153.771	-121.763	11.570
2400	19.441	96.248	80.690	37.339	-153.823	-120.370	10.961
2500	19.474	97.042	81.328	39.285	-153.878	-118.978	10.401
2600	19.503	97.806	81.947	41.234	-153.937	-117.579	9.883
2700	19.529	98.543	82.548	43.186	-153.999	-116.180	9.404
2800	19.552	99.253	83.132	45.140	-154.065	-114.778	8.959
2900	19.573	99.940	83.700	47.096	-154.137	-113.371	8.544
3000	19.592	100.604	84.252	49.054	-154.213	-111.968	8.157
3100	19.609	101.247	84.790	51.014	-154.291	-110.556	7.794
3200	19.625	101.869	85.314	52.976	-154.376	-109.144	7.454
3300	19.639	102.473	85.825	54.939	-154.464	-107.733	7.135
3400	19.653	103.060	86.323	56.904	-154.557	-106.313	6.834
3500	19.665	103.630	86.810	58.870	-154.655	-104.893	6.550
3600	19.676	104.184	87.285	60.837	-154.756	-103.469	6.281
3700	19.686	104.723	87.749	62.805	-154.863	-102.042	6.027
3800	19.696	105.248	88.202	64.774	-154.974	-100.610	5.786
3900	19.704	105.760	88.646	66.744	-155.090	-99.181	5.558
4000	19.713	106.259	89.080	68.715	-155.209	-97.745	5.341
4100	19.720	106.746	89.505	70.686	-155.334	-96.309	5.134
4200	19.727	107.221	89.921	72.659	-155.463	-94.866	4.936
4300	19.734	107.685	90.329	74.632	-155.596	-93.419	4.748
4400	19.740	108.139	90.729	76.605	-155.735	-91.975	4.568
4500	19.746	108.583	91.121	78.580	-155.877	-90.527	4.397
4600	19.751	109.017	91.505	80.555	-156.023	-89.070	4.232
4700	19.756	109.442	91.882	82.530	-156.175	-87.612	4.074
4800	19.761	109.858	92.252	84.506	-156.331	-86.148	3.922
4900	19.765	110.265	92.616	86.482	-156.491	-84.687	3.777
5000	19.769	110.665	92.973	88.459	-156.656	-83.221	3.638
5100	19.773	111.056	93.323	90.436	-156.826	-81.757	3.504
5200	19.777	111.440	93.668	92.413	-157.000	-80.279	3.374
5300	19.780	111.817	94.007	94.391	-157.177	-78.797	3.249
5400	19.784	112.187	94.340	96.369	-157.361	-77.322	3.129
5500	19.787	112.550	94.668	98.348	-157.548	-75.834	3.013
5600	19.790	112.906	94.991	100.327	-157.740	-74.348	2.902
5700	19.793	113.256	95.308	102.306	-157.937	-72.861	2.794
5800	19.795	113.601	95.620	104.285	-158.137	-71.364	2.689
5900	19.798	113.939	95.928	106.265	-158.342	-69.866	2.588
6000	19.800	114.272	96.231	108.245	-158.552	-68.368	2.490

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

CARBONYL FLUORIDE (COF_2) (IDEAL GAS) GFW = 66.0074

Point Group C_{2v}

$S^\circ_{298.15}$ = 61.85 ± 0.02 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -152.0 ± 0.4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -152.7 ± 0.4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
965 (1)	1249 (1)
1928 (1)	584 (1)
626 (1)	774 (1)

Bond Distances: C-F = 1.312 Å C-O = 1.174 Å

Bond Angles: F-C-F = 108° F-C-O = 126° 1'

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 7.243 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

Ruff and Li (1) measured equilibrium constants for the reaction

$$2COF_2(g) \rightleftarrows CO_2(g) + CF_4(g)$$

in the temperature range 573-1273°K. These equilibrium data were recently analyzed by Stull, Westrum, and Sinke (2). Their third law analysis of the data clearly indicates that the three low temperature points are in error and should not be used in calculating ΔHr_{298}. They reported, ΔHr_{298} = -12 ± 3 kcal/mol, based upon an average of the five high temperature points. Combining this result with the heat of formation of carbon dioxide and carbon tetrafluoride (3), we derive,

$$\Delta Hf^\circ_{298}(CF_2O, g) = -152.5 \pm 3.3 \text{ kcal/mol.}$$

Wartenberg and Riteris (4) measured the heat of hydrolysis of CF_2O. They reported, ΔHr = -26.7 ± 0.2 kcal/mol, for the reaction

$$COF_2(g) + H_2O(\ell) \rightarrow CO_2(g) + 2HF\cdot 300\ H_2O.$$

Combining this result with heat of formation data for carbon dioxide and HF($\Delta Hf^\circ_{298}(HF\cdot 300\ H_2O)$ = -76.84 kcal/mol (5)), we derive,

$$\Delta Hf^\circ_{298}(CF_2O, g) = -152.7 \pm 0.4 \text{ kcal/mol.}$$

Armstrong, Coyle, and Krieger (6) measured the heats of combustion of CH_4 in O_2-F_2 mixtures and found $\Delta Hf^\circ_{298}(CF_2O, g)$ = -154.8 kcal/mol. The value calculated from Wartenberg's data is adopted here.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Hopper et al. (7) and are in good agreement with the results of Lovell et al. (8) and Nielsen et al. (9). The molecular constants are from the microwave studies of Laurie et al. (10) and are in reasonable agreement with the electron-diffraction work of Brown and Livingston (11). Individual moments of inertia calculated from the rotational constants of Laurie et al. (10) are $I_A = 7.105 \times 10^{-39}$ g cm^2, $I_B = 7.144 \times 10^{-39}$ g cm^2, and $I_C = 14.27 \times 10^{-39}$ g cm^2.

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Trifluoromethyl (CF_3)

(Ideal Gas) GFW = 69.00635

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.754	-111.737	-111.737	INFINITE
100	8.112	52.920	72.493	-1.957	-111.997	-111.164	242.948
200	9.855	59.007	64.352	-1.069	-112.237	-110.231	120.455
298	11.903	63.329	63.329	.000	-112.400	-109.210	80.053
300	11.940	63.403	63.329	.022	-112.403	-109.190	79.545
400	13.735	67.092	63.820	1.309	-112.517	-108.100	59.063
500	15.133	70.315	64.803	2.756	-112.600	-106.986	46.764
600	16.172	73.170	65.964	4.323	-112.658	-105.858	38.559
700	16.936	75.724	67.180	5.981	-112.702	-104.720	32.695
800	17.503	78.024	68.394	7.704	-112.737	-103.578	28.296
900	17.928	80.111	69.582	9.477	-112.765	-102.432	24.874
1000	18.253	82.018	70.731	11.286	-112.789	-101.283	22.135
1100	18.506	83.770	71.838	13.125	-112.812	-100.132	19.894
1200	18.706	85.389	72.901	14.986	-112.832	-98.977	18.026
1300	18.865	86.893	73.920	16.865	-112.857	-97.821	16.445
1400	18.995	88.296	74.897	18.758	-112.880	-96.663	15.090
1500	19.102	89.610	75.835	20.663	-112.905	-95.502	13.915
1600	19.190	90.846	76.735	22.578	-112.933	-94.344	12.887
1700	19.265	92.011	77.599	24.501	-112.961	-93.180	11.979
1800	19.328	93.114	78.431	26.430	-112.994	-92.018	11.172
1900	19.382	94.161	79.231	28.366	-113.026	-90.850	10.450
2000	19.428	95.156	80.003	30.306	-113.061	-89.680	9.800
2100	19.468	96.105	80.747	32.251	-113.098	-88.511	9.212
2200	19.503	97.012	81.466	34.200	-113.140	-87.342	8.677
2300	19.533	97.879	82.161	36.152	-113.183	-86.165	8.188
2400	19.560	98.711	82.833	38.106	-113.230	-84.991	7.739
2500	19.584	99.510	83.485	40.064	-113.280	-83.814	7.327
2600	19.606	100.279	84.116	42.023	-113.334	-82.634	6.946
2700	19.625	101.019	84.728	43.985	-113.390	-81.452	6.593
2800	19.642	101.733	85.323	45.948	-113.448	-80.268	6.265
2900	19.657	102.422	85.901	47.913	-113.513	-79.079	5.960
3000	19.671	103.089	86.463	49.879	-113.581	-77.896	5.675
3100	19.683	103.734	87.009	51.847	-113.650	-76.703	5.408
3200	19.695	104.359	87.542	53.816	-113.725	-75.510	5.157
3300	19.705	104.966	88.061	55.786	-113.803	-74.317	4.922
3400	19.715	105.554	88.567	57.757	-113.884	-73.117	4.700
3500	19.724	106.126	89.060	59.729	-113.972	-71.916	4.491
3600	19.732	106.681	89.542	61.702	-114.060	-70.712	4.293
3700	19.739	107.222	90.012	63.675	-114.155	-69.507	4.106
3800	19.746	107.749	90.472	65.649	-114.253	-68.295	3.928
3900	19.752	108.262	90.922	67.624	-114.356	-67.088	3.760
4000	19.758	108.762	91.362	69.600	-114.462	-65.872	3.599
4100	19.763	109.250	91.792	71.576	-114.573	-64.660	3.447
4200	19.768	109.726	92.213	73.553	-114.689	-63.438	3.301
4300	19.773	110.191	92.626	75.530	-114.808	-62.215	3.162
4400	19.778	110.646	93.030	77.507	-114.933	-60.993	3.030
4500	19.782	111.090	93.427	79.485	-115.062	-59.769	2.903
4600	19.786	111.525	93.816	81.464	-115.195	-58.537	2.781
4700	19.789	111.951	94.197	83.442	-115.333	-57.303	2.665
4800	19.793	112.367	94.571	85.421	-115.476	-56.063	2.553
4900	19.796	112.775	94.939	87.401	-115.623	-54.824	2.445
5000	19.799	113.175	95.299	89.380	-115.776	-53.583	2.342
5100	19.802	113.568	95.654	91.360	-115.934	-52.347	2.243
5200	19.804	113.952	96.002	93.341	-116.095	-51.090	2.147
5300	19.807	114.329	96.344	95.321	-116.262	-49.836	2.055
5400	19.809	114.700	96.681	97.302	-116.434	-48.586	1.966
5500	19.811	115.063	97.012	99.283	-116.611	-47.325	1.881
5600	19.813	115.420	97.337	101.264	-116.794	-46.063	1.798
5700	19.815	115.771	97.657	103.246	-116.982	-44.801	1.718
5800	19.817	116.115	97.973	105.227	-117.173	-43.533	1.640
5900	19.819	116.454	98.283	107.209	-117.371	-42.262	1.565
6000	19.821	116.787	98.589	109.191	-117.573	-40.991	1.493

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

Point Group C_{3v}

$S°_{298.15}$ = 63.329 ± 1.0 gibbs/mol

Ground State Quantum Weight = 2

$\Delta Hf°_0$ = -111.7 ± 1.0 kcal/mol

$\Delta Hf°_{298.15}$ = -112.4 ± 1.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1090 (1)	1259 (2)
701 (1)	[500] (2)

Bond Distance: C-F = [1.33] Å

Bond Angle: F-C-F = [112°]

σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.608×10^{-115}] g^3 cm^6

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Kinetic data provide the most consistent paths to ΔHf° of $CF_3(g)$. Forward and reverse activation energies for the reactions $CHF_3(g) + X(g) \rightarrow CF_3(g) + HX(g)$ have been reported for X = Cl by Coomber (2), for X = Br by Amphlett (3), and for X = I by Goy (4). Increases of about 0.3 kcal/mol in the reverse activation energies for X = Cl and Br were proposed by Arthur (5) on the basis of additional data. Combining these values and reducing to 298.15°K, we get ΔHr° = 2.93 ± 0.7 (X = Cl), 18.89 ± 0.7 (X = Br), and 35.5 ± 3 kcal/mol (X = I). Coomber (2) reviewed data for the analogous reactions with X = CH_3 and CD_3; these yield ΔHr° = 0.6 ± 2 kcal/mol at 298.15°K for X = CH_3. Activation energies have also been reported (6) for $CF_3I(g) + I(g) \rightarrow CF_3(g) + I_2(g)$ from which we derive the average value ΔHr° = 17.1 ± 2 kcal/mol. The data of Tschuikow-Roux (7) for $C_2F_6(g) \rightarrow 2CF_3(g)$, recalculated as suggested by Coomber (8) but with JANAF functions, yield ΔHr° = 97.6 ± 6 kcal/mol. Differences between the calculated and observed values of ΔHr° are all less than half of the uncertainties assigned to the observed values.

The thorough discussion of photoionization data by Noutary (9) emphasized that CF_3^+ is formed with large amounts of excess energy both during ionization of CF_3 and during fragmentation of other fluorides. The amount of excess energy varies with the parent molecule. This may also be involved in electron-impact studies and could account for some of the discrepancies in bond-dissociation energies derived from appearance potentials and ionization potentials. Such data have been summarized by Coomber (10). Ionization data were omitted from the simultaneous adjustment due to uncertainty in the amounts of excess energy.

Also omitted was the mass-spectrometric study of $3C_2F_4(g) \rightarrow 4CF_3(g) + 2C(graphite)$ by Ehlert (11) which gave ΔHf° = -102 ± 3 kcal/mol. The discrepancy of 10 kcal/mol suggests that the data may not represent equilibrium for the above reaction. This reaction was one of many which resulted from heating MnF_3 in an effusion cell made of graphite.

Heat Capacity and Entropy

The bond length is assumed to be 1.33 Å by comparison with the molecules CF_3X, and the bond angle is estimated from molecular-orbital calculations of Morokuma (12) and Pople and coworkers (13). The nonplanar structure is consistent with electron-spin-resonance spectra (14) of CF_3 in krypton and xenon matrices, with infrared spectra of CF_3 in various matrices (15) and in the gaseous phase (16), and with photoionization spectra (17). The observed vibrational fundamentals of Carlson (16) are confirmed by the matrix spectra of Milligan (15). The latter estimated ν_4 to be in the range of 500 to 600 cm^{-1}. We choose the lower value by comparison with CF_3H, SiF_3H and SiF_3 (18).

The uncertainty in ν_4 corresponds to an uncertainty in the entropy of 0.4 eu at 300°K and 0.7 eu at 1000°K. Coomber (2) and Amphlett (19) used kinetic data to derive entropies of 63.2 eu at 350°K and 71.5 eu at 600°K. The calculated entropies from this table are higher by 2.0 and 1.7 eu, respectively. These differences are only slightly larger than our estimate of the uncertainty in the kinetic results. We estimate the overall uncertainty in the calculated entropies as 1.0 eu at 298°K and 1.6 eu at 1000°K.

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Trifluoroiodomethane (CF_3I)

(Ideal Gas) GFW = 195.91075

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.587	-139.393	-139.393	INFINITE
100	10.018	59.074	86.480	-2.741	-139.968	-139.021	303.829
200	14.036	67.323	74.960	-1.527	-140.471	-137.859	150.645
298	16.955	73.498	73.498	.000	-140.800	-136.503	100.060
300	17.002	73.603	73.498	.031	-140.806	-136.477	99.423
400	19.230	78.815	74.194	1.849	-142.975	-134.927	73.721
500	20.846	83.290	75.576	3.857	-148.258	-132.413	57.878
600	21.996	87.198	77.194	6.002	-148.187	-129.250	47.079
700	22.819	90.654	78.875	8.245	-148.095	-126.100	39.370
800	23.418	93.743	80.544	10.559	-147.990	-122.966	33.593
900	23.862	96.528	82.168	12.924	-147.878	-119.846	29.102
1000	24.198	99.060	83.732	15.328	-147.760	-116.737	25.513
1100	24.457	101.379	85.233	17.761	-147.642	-113.642	22.579
1200	24.661	103.516	86.669	20.217	-147.521	-110.554	20.135
1300	24.824	105.497	88.042	22.692	-147.405	-107.478	18.069
1400	24.955	107.342	89.355	25.181	-147.288	-104.410	16.299
1500	25.063	109.067	90.612	27.682	-147.174	-101.351	14.767
1600	25.152	110.687	91.817	30.193	-147.063	-98.302	13.427
1700	25.227	112.215	92.972	32.712	-146.953	-95.257	12.246
1800	25.290	113.658	94.082	35.238	-146.847	-92.221	11.197
1900	25.344	115.027	95.148	37.770	-146.743	-89.187	10.259
2000	25.391	116.328	96.175	40.307	-146.641	-86.160	9.415
2100	25.431	117.568	97.165	42.848	-146.543	-83.139	8.652
2200	25.466	118.752	98.119	45.392	-146.450	-80.125	7.960
2300	25.496	119.885	99.041	47.941	-146.358	-77.108	7.327
2400	25.523	120.971	99.932	50.492	-146.272	-74.100	6.748
2500	25.547	122.013	100.795	53.045	-146.189	-71.096	6.215
2600	25.568	123.015	101.630	55.601	-146.111	-68.093	5.724
2700	25.587	123.981	102.440	58.159	-146.036	-65.094	5.269
2800	25.604	124.911	103.226	60.718	-145.963	-62.097	4.847
2900	25.620	125.810	103.990	63.280	-145.897	-59.101	4.454
3000	25.633	126.679	104.732	65.842	-145.836	-56.115	4.088
3100	25.646	127.520	105.453	68.406	-145.776	-53.123	3.745
3200	25.657	128.334	106.156	70.971	-145.723	-50.134	3.424
3300	25.668	129.124	106.840	73.538	-145.674	-47.150	3.123
3400	25.677	129.890	107.506	76.105	-145.629	-44.163	2.839
3500	25.686	130.635	108.157	78.673	-145.589	-41.178	2.571
3600	25.694	131.358	108.791	81.242	-145.553	-38.195	2.319
3700	25.701	132.062	109.411	83.812	-145.523	-35.214	2.080
3800	25.708	132.748	110.016	86.382	-145.496	-32.229	1.854
3900	25.714	133.416	110.607	88.953	-145.477	-29.252	1.639
4000	25.720	134.067	111.186	91.525	-145.459	-26.271	1.435
4100	25.726	134.702	111.751	94.097	-145.449	-23.293	1.242
4200	25.731	135.322	112.305	96.670	-145.443	-20.311	1.057
4300	25.735	135.928	112.848	99.244	-145.441	-17.332	.881
4400	25.740	136.519	113.379	101.817	-145.447	-14.355	.713
4500	25.744	137.098	113.900	104.391	-145.457	-11.378	.553
4600	25.748	137.664	114.410	106.966	-145.471	-8.396	.399
4700	25.751	138.217	114.911	109.541	-145.491	-5.416	.252
4800	25.755	138.760	115.402	112.116	-145.516	-2.431	.111
4900	25.758	139.291	115.884	114.692	-145.547	.551	-.025
5000	25.761	139.811	116.357	117.268	-145.584	3.531	-.154
5100	25.763	140.321	116.822	119.844	-145.626	6.503	-.279
5200	25.766	140.822	117.279	122.420	-145.674	9.495	-.399
5300	25.769	141.312	117.728	124.997	-145.726	12.483	-.515
5400	25.771	141.794	118.169	127.574	-145.785	15.464	-.626
5500	25.773	142.267	118.603	130.151	-145.850	18.452	-.733
5600	25.775	142.731	119.030	132.729	-145.920	21.440	-.837
5700	25.777	143.188	119.450	135.306	-145.997	24.427	-.937
5800	25.779	143.636	119.863	137.884	-146.078	27.418	-1.033
5900	25.781	144.077	120.269	140.462	-146.165	30.410	-1.126
6000	25.783	144.510	120.670	143.041	-146.258	33.400	-1.217

June 30, 1969

Point Group C_{3v}

ΔHf°_0 = -139.4 ± 0.8 kcal/mol

$S^\circ_{298.15}$ = 73.498 ± 0.15 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -140.8 ± 0.8 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1074 (1)	1185 (2)
742 (1)	539 (2)
284 (1)	260 (2)

Bond Distance: C-F = 1.332 Å C-I = 2.130 Å

Bond Angle: F-C-F = 108.3 ± 1° F-C-I = 110.62° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 4.4095 \times 10^{-113}$ g^3 cm^6

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Lord, Goy and Pritchard (2, 3) report equilibrium data for the reactions $CF_3X(g) + I_2(g) = CF_3I(g) + XI(g)$ where X = H, Cl, and Br. In addition to these prime links, there is a weak link to CF_3 through kinetic studies of $CF_3I(g) + I(g) \rightarrow CF_3(g) + I_2(g)$. Data for this reaction (3, 12) yield the average value ΔHr° = 17.1 ± 2 kcal/mol at 298.15°K.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (4), Anderson (5), and Wong and Schomaker (6). Differences among the data are small. The results of Anderson are adopted since they are intermediate between the others. Microwave data (7) are consistent with the adopted parameters. Infrared spectra of the gas were observed by several investigators (8, 9, 10) and Raman spectra of the liquid were obtained by Edgell and May (10). The vibrational assignments of (9, 10) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. In particular, ν_6 is taken as 260 cm^{-1} (from overtone and combination bands of the gas) rather than 265 cm^{-1} (from the Raman spectra of the liquid). The approximate values of ν_2, ν_3 and ν_6 have been confirmed by analysis (11) of absorption spectra in the UV.

The thermodynamic functions of this table are essentially the same as those calculated by (9). Uncertainty in the entropy is estimated to vary from 0.15 to 0.6 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for $CClF_3(g)$ and $CF_4(g)$. The principal moments of inertia are $I_A = 14.71 \times 10^{-39}$ and $I_B = I_C = 54.75 \times 10^{-39}$ g cm^2.

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Carbon Tetrafluoride (CF_4)

(Ideal Gas) GFW = 88.00475

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.043	- 221.611	- 221.611	INFINITE
100	8.304	50.729	73.154	- 2.242	- 222.214	- 219.127	478.902
200	11.322	57.306	63.686	- 1.276	- 222.726	- 215.826	235.843
298	14.592	62.454	62.454	.000	- 223.040	- 212.366	155.669
300	14.648	62.544	62.454	.027	- 223.045	- 212.301	154.661
400	17.304	67.139	63.062	1.631	- 223.227	- 208.687	114.021
500	19.290	71.225	64.294	3.465	- 223.326	- 205.041	89.623
600	20.741	74.877	65.759	5.471	- 223.362	- 201.379	73.352
700	21.799	78.158	67.300	7.600	- 223.360	- 197.714	61.729
800	22.580	81.122	68.846	9.821	- 223.330	- 194.054	53.013
900	23.166	83.817	70.362	12.110	- 223.280	- 190.398	46.235
1000	23.613	86.282	71.832	14.450	- 223.216	- 186.748	40.814
1100	23.960	88.550	73.250	16.829	- 223.144	- 183.106	36.380
1200	24.234	90.647	74.614	19.239	- 223.064	- 179.467	32.685
1300	24.453	92.595	75.923	21.674	- 222.984	- 175.837	29.561
1400	24.631	94.414	77.179	24.129	- 222.899	- 172.213	26.884
1500	24.777	96.119	78.386	26.599	- 222.815	- 168.594	24.564
1600	24.899	97.722	79.545	29.083	- 222.731	- 164.985	22.536
1700	25.001	99.234	80.659	31.578	- 222.646	- 161.377	20.746
1800	25.087	100.666	81.731	34.083	- 222.564	- 157.778	19.157
1900	25.161	102.024	82.764	36.595	- 222.482	- 154.179	17.735
2000	25.224	103.317	83.759	39.115	- 222.401	- 150.584	16.455
2100	25.279	104.549	84.720	41.640	- 222.323	- 146.997	15.298
2200	25.327	105.726	85.648	44.170	- 222.250	- 143.414	14.247
2300	25.369	106.853	86.546	46.705	- 222.177	- 139.829	13.287
2400	25.406	107.933	87.415	49.244	- 222.109	- 136.251	12.407
2500	25.439	108.971	88.256	51.786	- 222.045	- 132.677	11.599
2600	25.468	109.969	89.072	54.332	- 221.984	- 129.102	10.852
2700	25.494	110.931	89.864	56.880	- 221.926	- 125.530	10.161
2800	25.518	111.858	90.633	59.430	- 221.871	- 121.962	9.520
2900	25.539	112.754	91.381	61.983	- 221.822	- 118.391	8.922
3000	25.558	113.620	92.108	64.538	- 221.778	- 114.832	8.365
3100	25.575	114.459	92.815	67.095	- 221.735	- 111.266	7.844
3200	25.591	115.271	93.504	69.653	- 221.699	- 107.702	7.356
3300	25.605	116.059	94.176	72.213	- 221.667	- 104.143	6.897
3400	25.618	116.823	94.831	74.774	- 221.639	- 100.579	6.465
3500	25.630	117.566	95.470	77.336	- 221.618	- 97.017	6.058
3600	25.641	118.288	96.094	79.900	- 221.598	- 93.456	5.674
3700	25.651	118.991	96.703	82.465	- 221.585	- 89.898	5.310
3800	25.661	119.675	97.299	85.030	- 221.577	- 86.335	4.965
3900	25.669	120.342	97.881	87.597	- 221.575	- 82.781	4.639
4000	25.677	120.992	98.451	90.164	- 221.576	- 79.219	4.328
4100	25.685	121.626	99.008	92.732	- 221.584	- 75.664	4.033
4200	25.692	122.245	99.554	95.301	- 221.597	- 72.101	3.752
4300	25.698	122.849	100.089	97.870	- 221.614	- 68.540	3.484
4400	25.704	123.440	100.613	100.440	- 221.639	- 64.982	3.228
4500	25.710	124.018	101.127	103.011	- 221.667	- 61.426	2.983
4600	25.715	124.583	101.630	105.582	- 221.701	- 57.863	2.749
4700	25.720	125.136	102.125	108.154	- 221.741	- 54.299	2.525
4800	25.725	125.678	102.610	110.726	- 221.786	- 50.731	2.310
4900	25.729	126.208	103.086	113.299	- 221.837	- 47.168	2.104
5000	25.733	126.728	103.554	115.872	- 221.894	- 43.604	1.906
5100	25.737	127.238	104.013	118.446	- 221.957	- 40.049	1.716
5200	25.741	127.737	104.464	121.020	- 222.025	- 36.471	1.533
5300	25.744	128.228	104.908	123.594	- 222.099	- 32.899	1.357
5400	25.747	128.709	105.345	126.168	- 222.181	- 29.336	1.187
5500	25.750	129.182	105.774	128.743	- 222.267	- 25.760	1.024
5600	25.753	129.646	106.196	131.318	- 222.360	- 22.185	.866
5700	25.756	130.101	106.611	133.894	- 222.459	- 18.612	.714
5800	25.759	130.549	107.020	136.470	- 222.562	- 15.034	.567
5900	25.761	130.990	107.423	139.046	- 222.673	- 11.457	.424
6000	25.764	131.423	107.819	141.622	- 222.790	- 7.880	.287

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

CARBON TETRAFLUORIDE (CF_4) (IDEAL GAS) GFW = 88.00475

Point Group T_d

$S^\circ_{298.15}$ = 62.454 ± 0.06 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -221.61 ± 0.3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -223.04 ± 0.3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
908.5 (1)	1283.0 (3)
435.0 (2)	631.5 (3)

Bond Distance: C-F = 1.320 Å

Bond Angle: F-C-F = 109.47° σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 3.1489 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of HF(g), HF(50 H_2O) and five closely related fluorides. Adjustment of 23 selected observations relating the 7 variables gives the following heats of formation in kcal/mol at 298.15°K: HF(g), -65.14 ± 0.2; HF(50 H_2O), -76.78 ± 0.1; NaF(c), -137.52 ± 0.2; BF_3(g), -271.42 ± 0.4; CF_4(g), -223.04 ± 0.3; NF_3(g), -31.43 ± 0.3; and C_2F_4(polymer), -198.2 ± 0.7. The ± values are estimates of the overall uncertainty including systematic error. Further details of the simultaneous adjustment are given in (1).

The selected value is essentially the same as that obtained by Greenberg and Hubbard (2) in their thorough calorimetric study of the combustion in fluorine of natural and synthetic graphite. Their result is confirmed by the data of Domalski and Armstrong (3) for combustion of graphite-Teflon mixtures. Reliable data (1) also link CF_4(g) with HF(n H_2O), NF_3(g) and C_2F_4(polymer). Armstrong (4, 3) critically reviewed the more uncertain data which were omitted from the adjustment.

Heat Capacity and Entropy

The fundamental vibrations are those observed in the gas-phase Raman spectra by Monostori and Weber (5) and the gas-phase infrared spectra by Maki et al. (6) and Chalmers and McKean (7). The frequencies are essentially the same as those selected by Shimanouchi (8) who also lists earlier spectral studies. Electron-diffraction studies of the gas were reported by Thornton (9) and Hoffman and Livingston (10). The adopted bond length is the average of these two results which differ by only 0.006 Å. The principal moments of inertia are $I_A = I_B = I_C = 14.657 \times 10^{-39}\ g\ cm^2$.

The most significant uncertainty in the calculated thermodynamic functions is due to neglect of anharmonic contributions. Estimates for these contributions were given by Barho (11) and Albright et al. (12), and functions calculated with anharmonic terms were given by McBride et al. (13). Differences between McBride and this JANAF table vary from 0.1 to 0.75 gibbs/mol in Cp° and 0.05 to 0.49 gibbs/mol in S° over the range from 300 to 1000°K. Measurements (14) of C_v(303-473°K) suggest that anharmonic contributions are significant, but the data are not sufficiently accurate to test the calculations of McBride (13). Heat capacity data (15) for the condensed phases were reviewed by Kelley and King (16) who derived $S^\circ_{298.15}$ = 62.8 ± 0.5 gibbs/mol for CF_4(g).

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Trifluoromethyl Hypofluorite (CF_3OF)

(Ideal Gas) GFW = 104.004

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100	11.991	60.647	91.647	-3.100	-182.142	-177.976	388.967
200	15.734	70.138	78.666	-1.706	-182.573	-173.617	189.720
298	18.966	77.061	77.061	.000	-182.800	-169.176	124.010
300	19.029	77.179	77.061	.035	-182.803	-169.092	123.184
400	21.755	83.042	77.842	2.080	-182.900	-164.503	89.880
500	23.871	88.134	79.402	4.366	-182.911	-159.902	69.893
600	25.445	92.632	81.240	6.835	-182.863	-155.304	56.569
700	26.543	96.641	83.159	9.437	-182.777	-150.716	47.056
800	27.374	100.242	85.073	12.135	-182.669	-146.145	39.925
900	27.985	103.502	86.943	14.904	-182.546	-141.587	34.382
1000	28.451	106.476	88.749	17.726	-182.413	-137.043	29.951
1100	28.830	109.206	90.487	20.591	-182.275	-132.514	26.328
1200	29.106	111.727	92.153	23.488	-182.132	-127.994	23.311
1300	29.345	114.066	93.750	26.411	-181.992	-123.488	20.760
1400	29.539	116.248	95.280	29.356	-181.850	-118.992	18.575
1500	29.698	118.292	96.746	32.318	-181.709	-114.506	16.683
1600	29.829	120.213	98.154	35.295	-181.571	-110.033	15.030
1700	29.925	122.024	99.505	38.282	-181.434	-105.564	13.571
1800	30.019	123.737	100.804	41.280	-181.304	-101.109	12.276
1900	30.099	125.363	102.054	44.286	-181.176	-96.654	11.118
2000	30.167	126.908	103.259	47.299	-181.052	-92.208	10.076
2100	30.227	128.381	104.420	50.319	-180.931	-87.770	9.134
2200	30.279	129.789	105.542	53.344	-180.819	-83.339	8.279
2300	30.324	131.136	106.625	56.374	-180.709	-78.907	7.498
2400	30.364	132.427	107.674	59.409	-180.606	-74.484	6.783
2500	30.399	133.668	108.689	62.447	-180.510	-70.066	6.125
2600	30.416	134.868	109.673	65.488	-180.420	-65.649	5.518
2700	30.435	136.008	110.627	68.530	-180.337	-61.235	4.957
2800	30.460	137.116	111.553	71.575	-180.259	-56.827	4.436
2900	30.483	138.185	112.453	74.622	-180.189	-52.415	3.950
3000	30.504	139.219	113.328	77.672	-180.127	-48.017	3.498
3100	30.522	140.219	114.180	80.723	-180.069	-43.612	3.075
3200	30.539	141.189	115.009	83.776	-180.019	-39.211	2.678
3300	30.555	142.129	115.816	86.831	-179.975	-34.815	2.306
3400	30.569	143.041	116.604	89.887	-179.937	-30.413	1.955
3500	30.582	143.927	117.372	92.944	-179.908	-26.015	1.624
3600	30.594	144.789	118.121	96.003	-179.882	-21.617	1.312
3700	30.605	145.627	118.853	99.063	-179.865	-17.221	1.017
3800	30.615	146.444	119.569	102.124	-179.853	-12.821	.737
3900	30.624	147.239	120.268	105.186	-179.850	-8.432	.472
4000	30.633	148.014	120.952	108.249	-179.852	-4.033	.220
4100	30.641	148.771	121.622	111.313	-179.861	.358	-.019
4200	30.648	149.509	122.277	114.377	-179.877	4.757	-.248
4300	30.655	150.231	122.918	117.442	-179.898	9.157	-.465
4400	30.662	150.936	123.547	120.508	-179.929	13.550	-.673
4500	30.668	151.625	124.164	123.575	-179.964	17.943	-.871
4600	30.674	152.299	124.768	126.642	-180.005	22.345	-1.062
4700	30.680	152.959	125.361	129.709	-180.055	26.746	-1.244
4800	30.685	153.604	125.942	132.778	-180.109	31.151	-1.418
4900	30.689	154.237	126.513	135.846	-180.171	35.551	-1.586
5000	30.693	154.857	127.074	138.915	-180.239	39.952	-1.746
5100	30.697	155.465	127.625	141.985	-180.315	44.347	-1.900
5200	30.701	156.061	128.166	145.055	-180.396	48.762	-2.049
5300	30.705	156.646	128.698	148.125	-180.483	53.175	-2.193
5400	30.709	157.220	129.221	151.196	-180.579	57.574	-2.330
5500	30.712	157.784	129.735	154.267	-180.680	61.991	-2.463
5600	30.715	158.337	130.241	157.338	-180.788	66.405	-2.592
5700	30.717	158.881	130.738	160.410	-180.904	70.817	-2.715
5800	30.720	159.415	131.228	163.482	-181.023	75.236	-2.835
5900	30.723	159.940	131.711	166.554	-181.151	79.653	-2.951
6000	30.726	160.456	132.185	169.626	-181.285	84.072	-3.062

Mar. 31, 1965; Dec. 31, 1969

TRIFLUOROMETHYL HYPOFLUORITE (CF_4O) (IDEAL GAS) GFW = 104.004

Point Group C_s

$\Delta Hf^\circ_0 = -181.9 \pm 3$ kcal/mol

$S^\circ_{298.15} = 77.06 \pm 0.7$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -182.8 \pm 3$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1294.4 (1)	679.0 (1)	1223.2 (1)
1262.5 (1)	584.1 (1)	607.5 (1)
947.3 (1)	433.7 (1)	250.0 (1)
882.1 (1)	227.5 (1)	internal rotation

Bond Distances: C-F = [1.33] Å F-O = [1.42] Å C-O = [1.43] Å

Bond Angles: C-O-F = [103.2°] F-C-F = [109.5°]

σ = 1

Product of Moments of Inertia: $I_AI_BI_C = 1.138 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

Porter and Cady (1) measured equilibrium constants for the reaction

$$CF_3OF(g) \rightleftarrows COF_2(g) + F_2(g)$$

in the temperature range 630-750°K. Equilibrium constants were also determined with excess fluorine added to the system. Second and third law analyses of these data yield the following heats of reaction:

	ΔH°_{298} 2nd law	ΔH°_{298} 3rd law	Drift
	kcal/mol		gibbs/mol
Set 1	27.65 ± 0.2	30.10	3.6 ± 0.3
Set added fluorine	25.11 ± 0.3	30.09	7.2 ± 0.5

The third law analyses indicate significant trends within each set of equilibrium data. If the entire error is assigned to the free energy functions, then the drifts in the third law analysis imply that the free energy functions for CF_3OF should be increased by 3.6 or 7.2 gibbs/mol. However, the real error in these free energy functions is probably no larger than 1 gibbs/mol in the temperature range of the experimental data. Apparently, the equilibrium reaction investigated by Porter and Cady (1) was affected by side reactions possibly involving perfluorodimethyl peroxide. However, since the only other approach to the heat of formation of CF_3OF involves bond energies, we adopt the third law value, $\Delta Hr^\circ = 30.1$ kcal/mol, and derive $\Delta Hf^\circ_{298}(CF_3OF, g) = -182.8 \pm 3$ kcal/mol with $\Delta Hf^\circ_{298}(COF_2, g) = -152.7 \pm 0.4$ kcal/mol (2).

Czarnowski et al. (3) recently determined the O-F bond energy in CF_3OF from kinetic studies on the thermal decomposition of CF_3OF in the presence of SO_3. They reported the value D(O-F) = 43.5 ± 0.5 kcal/mol. Combining this result with the following data,

$\Delta Hf^\circ_{298}(C, g) = 170.89 \pm 0.45$ kcal/mol (4)
$\Delta Hf^\circ_{298}(F, g) = 18.86 \pm 0.40$ kcal/mol (5)
$\Delta Hf^\circ_{298}(O, g) = 59.559 \pm 0.03$ kcal/mol (6)
Do(C-F) = 117.4 kcal/mol (from $\Delta Hf^\circ_{298}(CF_4, g) = -223.04 \pm 0.3$ kcal/mol (7))
Do(C-O) = 84 kcal/mol (8)

we derive $\Delta Hf^\circ_{298}(CF_3OF, g) = -173.8$ kcal/mol.

The value determined from Porter and Cady's equilibrium data is adopted here. $H^\circ_0-H^\circ_{298}$ is determined to be -4.086 kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared and Raman studies of Wilt and Jones (9) and are in reasonable agreement with nine of the twelve expected fundamentals observed by Lagemann et al. (10). Bond lengths and angles are estimated quantities chosen by Wilt and Jones (9). Individual moments of inertia calculated from these estimated molecular constants are $I_A = 14.723 \times 10^{-39}\ g\ cm^2$, $I_B = 27.796 \times 10^{-39}\ g\ cm^2$, and $I_C = 27.801 \times 10^{-39}\ g\ cm^2$. The contributions of hindered internal rotation to the thermodynamic properties of CF_3OF are from the tables of Pitzer and Gwinn (11). The reduced moment of inertia, I_r, and the potential barrier, V_o, are from the work of Wilt and Jones (9) and are:

$I_r = 2.939 \times 10^{-39}\ g\ cm^2$
$V_o = 1130$ cal/mol ($\nu_{12} = 56\ cm^{-1}$)

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Methylidyne (CH)

(Ideal Gas) GFW = 13.01912

	gibbs/mol			kcal/mol			
T, °K	$C_p°$	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.084	141.178	141.178	INFINITE
100	6.993	36.099	49.920	-1.382	141.488	139.119	-304.044
200	6.972	40.937	44.358	-.684	141.807	136.615	-149.286
298	6.972	43.721	43.721	.000	142.000	134.022	-98.241
300	6.972	43.764	43.721	.013	142.002	133.973	-97.599
400	6.984	45.771	43.994	.711	142.107	131.278	-71.727
500	7.027	47.333	44.512	1.411	142.139	128.566	-56.196
600	7.112	48.621	45.092	2.117	142.117	125.852	-45.842
700	7.240	49.727	45.677	2.835	142.059	123.146	-38.448
800	7.401	50.704	46.245	3.566	141.978	120.450	-32.905
900	7.586	51.586	46.791	4.316	141.885	117.763	-28.597
1000	7.783	52.395	47.311	5.084	141.788	115.088	-25.152
1100	7.985	53.146	47.808	5.872	141.690	112.422	-22.336
1200	8.186	53.850	48.282	6.681	141.596	109.767	-19.991
1300	8.380	54.513	48.736	7.509	141.503	107.117	-18.008
1400	8.564	55.141	49.171	8.357	141.418	104.477	-16.310
1500	8.735	55.737	49.589	9.222	141.336	101.842	-14.838
1600	8.893	56.306	49.992	10.103	141.258	99.209	-13.551
1700	9.036	56.850	50.379	11.000	141.187	96.584	-12.417
1800	9.165	57.370	50.753	11.910	141.120	93.962	-11.409
1900	9.280	57.869	51.115	12.832	141.057	91.345	-10.507
2000	9.382	58.347	51.464	13.766	140.998	88.730	-9.696
2100	9.472	58.807	51.803	14.708	140.942	86.119	-8.963
2200	9.551	59.250	52.132	15.660	140.886	83.508	-8.296
2300	9.619	59.676	52.450	16.618	140.833	80.903	-7.687
2400	9.678	60.087	52.760	17.583	140.780	78.298	-7.130
2500	9.730	60.483	53.061	18.554	140.727	75.694	-6.617
2600	9.774	60.865	53.354	19.529	140.673	73.095	-6.144
2700	9.811	61.235	53.639	20.508	140.619	70.495	-5.706
2800	9.844	61.592	53.917	21.491	140.564	67.899	-5.300
2900	9.871	61.938	54.187	22.477	140.507	65.307	-4.922
3000	9.895	62.273	54.451	23.465	140.448	62.713	-4.569
3100	9.916	62.598	54.709	24.456	140.389	60.124	-4.239
3200	9.933	62.913	54.960	25.448	140.326	57.536	-3.930
3300	9.949	63.219	55.206	26.442	140.261	54.949	-3.639
3400	9.962	63.516	55.446	27.438	140.194	52.365	-3.366
3500	9.975	63.805	55.681	28.435	140.123	49.781	-3.108
3600	9.985	64.086	55.910	29.433	140.051	47.201	-2.865
3700	9.995	64.360	56.135	30.432	139.974	44.624	-2.636
3800	10.005	64.627	56.355	31.432	139.896	42.050	-2.418
3900	10.014	64.887	56.571	32.433	139.814	39.476	-2.212
4000	10.023	65.140	56.782	33.435	139.730	36.905	-2.016
4100	10.032	65.388	56.989	34.437	139.643	34.333	-1.830
4200	10.040	65.630	57.191	35.441	139.552	31.768	-1.653
4300	10.050	65.866	57.390	36.445	139.458	29.201	-1.484
4400	10.059	66.097	57.586	37.451	139.362	26.637	-1.323
4500	10.069	66.323	57.777	38.457	139.262	24.074	-1.169
4600	10.079	66.545	57.966	39.465	139.160	21.518	-1.022
4700	10.089	66.762	58.150	40.473	139.055	18.963	-.882
4800	10.100	66.974	58.332	41.482	138.947	16.410	-.747
4900	10.112	67.183	58.511	42.493	138.838	13.858	-.618
5000	10.124	67.387	58.686	43.505	138.725	11.307	-.494
5100	10.137	67.588	58.859	44.518	138.608	8.757	-.375
5200	10.150	67.785	59.028	45.532	138.491	6.213	-.261
5300	10.164	67.978	59.195	46.548	138.370	3.673	-.151
5400	10.178	68.168	59.360	47.565	138.247	1.133	-.046
5500	10.193	68.355	59.522	48.583	138.121	-1.405	.056
5600	10.208	68.539	59.681	49.603	137.994	-3.943	.154
5700	10.224	68.720	59.838	50.625	137.864	-6.478	.248
5800	10.240	68.898	59.993	51.648	137.731	-9.010	.339
5900	10.257	69.073	60.145	52.673	137.596	-11.534	.427
6000	10.274	69.245	60.295	53.700	137.460	-14.066	.512

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1967

METHYLIDYNE (CH) (IDEAL GAS) GFW = 13.01912

Ground State Configuration $^2\Pi$

$\Delta Hf°_0 = 141.2 \pm 0.1$ kcal/mol

$S°_{298.15} = 43.72 \pm 0.01$ gibbs/mol

$\Delta Hf°_{298.15} = 142.0 \pm 0.1$ kcal/mol

Electronic Levels and Multiplicities

ε_i, cm^{-1}	g_i
0	2
17.9	2
[4500]	4
23150	4
25949	2
31821	2

$\omega_e = 2861.39$ cm^{-1}

$\omega_e x_e = 64.29$ cm^{-1}

$\sigma = 1$

$B_e = 14.455$ cm^{-1}

$\alpha_e = 0.5339$ cm^{-1}

$r_e = 1.1198$ Å

Heat of Formation

G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, reanalyzed the rotational predissociation reported by T. Shidei, Japan J. Phys. 11, 23 (1936), and concluded that $D°_0$ = 80.0 kcal/mol (3.47 eV). This yields $\Delta Hf°_{298.15}$(CH, g) = 142.0 kcal/mol and is the adopted value.

R. G. Brewer and F. L. Kester, J. Chem. Phys. 40, 812 (1964), have confirmed the value as 142 ± 5 kcal/mol, from an equilibrium study of the temperature variation of the intensity of the $^2\Delta \rightarrow {}^2\Pi$ emission band.

M. Linevsky, J. Chem. Phys. 47, 3485 (1967), determined the concentration of CH radicals in equilibrium with 1 atm. of hydrogen gas, by application of a high resolution spectro-photographic technique to three electronic transitions in absorbtion. A third law analysis, using the present functions, of 27 determinations in the temperature range 3065 - 3155°K yielded $\Delta Hf°_{298}$(CH, g) = 142.01 ± 1.28 kcal/mol with a negligible drift. This value is in excellent agreement with the spectroscopic predissociation value.

Heat Capacity and Entropy

The vibrational and rotational constants and electronic levels are from Herzberg, loc. cit., with the exception of the estimated $^4\Sigma$ level. All the constants have been adjusted to the normal isotopic abundances for both carbon and hydrogen. The $^4\Sigma$ level is estimated from the ab initio calculations of A. C. Hurley, Proc. Roy. Soc. (London), 249A, 402 (1959), which include electron correlation effects. Earlier LCAO calculations had predicted the $^4\Sigma$ level to be the ground state, but J. Higuchi, J. Chem. Phys. 22, 1339 (1954), used LCAO-SCF calculations and obtained the $^4\Sigma$ level at 800 cm^{-1}. M. Krauss and J. F. Wehner, J. Chem. Phys. 29, 1287 (1958), using essentially the same technique as Hurley, obtained $^4\Sigma$ at 3000 cm^{-1}.

Monochloromethylene (CHCl)

(Ideal Gas) GFW = 48.47212

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.427	79.934	79.934	INFINITE
100	7.951	47.199	63.519	-1.632	79.987	78.765	-172.142
200	8.170	52.750	56.900	-.830	80.047	77.509	-84.697
298	8.780	56.118	56.118	.000	80.000	76.270	-55.907
300	8.793	56.173	56.118	.016	79.998	76.247	-55.546
400	9.494	58.799	56.472	.931	79.905	75.009	-40.983
500	10.148	60.989	57.162	1.913	79.792	73.799	-32.257
600	10.786	62.895	57.962	2.960	79.677	72.610	-26.448
700	11.434	64.606	58.791	4.071	79.572	71.442	-22.305
800	12.080	66.176	59.617	5.247	79.493	70.286	-19.201
900	12.694	67.634	60.428	6.486	79.444	69.137	-16.789
1000	13.247	69.001	61.217	7.784	79.430	67.993	-14.860
1100	13.720	70.286	61.984	9.133	79.445	66.848	-13.281
1200	14.104	71.497	62.727	10.525	79.484	65.702	-11.966
1300	14.403	72.639	63.446	11.951	79.538	64.551	-10.852
1400	14.624	73.715	64.141	13.402	79.604	63.397	-9.897
1500	14.779	74.729	64.814	14.873	79.675	62.238	-9.068
1600	14.881	75.686	65.464	16.357	79.746	61.071	-8.342
1700	14.941	76.591	66.092	17.848	79.815	59.903	-7.701
1800	14.970	77.446	66.699	19.344	79.878	58.729	-7.131
1900	14.975	78.255	67.286	20.841	79.934	57.554	-6.620
2000	14.964	79.023	67.854	22.338	79.981	56.374	-6.160
2100	14.942	79.753	68.403	23.834	80.020	55.194	-5.744
2200	14.912	80.447	68.935	25.326	80.047	54.009	-5.365
2300	14.879	81.109	69.450	26.816	80.065	52.827	-5.020
2400	14.843	81.742	69.949	28.302	80.072	51.643	-4.703
2500	14.807	82.347	70.433	29.784	80.069	50.456	-4.411
2600	14.771	82.927	70.903	31.263	80.057	49.273	-4.142
2700	14.737	83.484	71.358	32.739	80.035	48.088	-3.892
2800	14.704	84.019	71.801	34.211	80.004	46.906	-3.661
2900	14.673	84.534	72.231	35.680	79.963	45.726	-3.446
3000	14.645	85.031	72.650	37.145	79.914	44.544	-3.245
3100	14.618	85.511	73.057	38.609	79.858	43.367	-3.057
3200	14.593	85.975	73.453	40.069	79.792	42.191	-2.882
3300	14.571	86.424	73.840	41.527	79.718	41.016	-2.716
3400	14.550	86.858	74.216	42.983	79.638	39.846	-2.561
3500	14.531	87.280	74.583	44.437	79.549	38.674	-2.415
3600	14.513	87.689	74.942	45.890	79.455	37.508	-2.277
3700	14.497	88.086	75.292	47.340	79.352	36.345	-2.147
3800	14.482	88.473	75.633	48.789	79.244	35.186	-2.024
3900	14.469	88.849	75.968	50.237	79.128	34.029	-1.907
4000	14.456	89.215	76.294	51.683	79.006	32.874	-1.796
4100	14.445	89.572	76.614	53.128	78.878	31.719	-1.691
4200	14.434	89.920	76.926	54.572	78.744	30.573	-1.591
4300	14.424	90.259	77.232	56.015	78.604	29.426	-1.496
4400	14.415	90.591	77.532	57.457	78.459	28.285	-1.405
4500	14.406	90.915	77.826	58.898	78.307	27.142	-1.318
4600	14.398	91.231	78.114	60.338	78.151	26.010	-1.236
4700	14.390	91.541	78.396	61.777	77.990	24.880	-1.157
4800	14.383	91.844	78.673	63.216	77.823	23.752	-1.081
4900	14.377	92.140	78.945	64.654	77.652	22.628	-1.009
5000	14.370	92.430	79.212	66.091	77.477	21.505	-.940
5100	14.364	92.715	79.474	67.528	77.296	20.385	-.874
5200	14.358	92.994	79.731	68.964	77.111	19.272	-.810
5300	14.353	93.267	79.984	70.400	76.921	18.164	-.749
5400	14.347	93.535	80.233	71.835	76.726	17.057	-.690
5500	14.342	93.799	80.477	73.269	76.527	15.954	-.634
5600	14.337	94.057	80.717	74.703	76.324	14.852	-.580
5700	14.332	94.311	80.953	76.136	76.115	13.753	-.527
5800	14.327	94.560	81.186	77.569	75.902	12.663	-.477
5900	14.323	94.805	81.415	79.002	75.685	11.577	-.429
6000	14.318	95.046	81.640	80.434	75.464	10.488	-.382

Dec. 31, 1969

MONOCHLOROMETHYLENE (CHCl) (IDEAL GAS) GFW = 48.47212

Point Group C_s

ΔHf°_0 = [79.9 ± 10] kcal/mol

$S^\circ_{298.15}$ = 56.12 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [80 ± 10] kcal/mol

Ground State Quantum Weight = 1

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[3000]	3
12288	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2800] (1)
1201 (1)
815 (1)

Bond Distance: C-H = 1.12 Å C-Cl = 1.689 Å

Bond Angle: H-C-Cl = 103.4° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 3.9877 \times 10^{-117}\ g^3\ cm^6$

Heat of Formation

The heat of formation can be estimated as the average of those of the CH_2 and CCl_2 radicals, which gives ΔHf°_{298}(CHCl, g) = 74.5 ± 15 kcal/mol. A better value for the heat of formation can be obtained by considering the reactions CHCl → CH + Cl and CHCl → CCl + H. When ΔHf°_{298}(CCl, g) = 74.5 kcal/mol is substituted into the above equations it gives D_{C-Cl} = 96 kcal and D_{C-H} = 98 kcal. Although these values are not unreasonable the D_{C-H} value appears to be too high compared to that in CFH. Thus, we adopt ΔHf°_{298}(CHCl, g) = 80 kcal/mol which gives D_{C-Cl} = 91 kcal and D_{C-H} = 92 kcal.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CCl_2 and CH_2 as given in these tables. The vibrational levels are from Jacox and Milligan (2) who investigated the infrared spectrum of matrix-isolated CHCl, and also estimated the missing frequency.

The individual moments of inertia are $I_A = 4.6455 \times 10^{-39}$ g cm^2, $I_B = 1.780 \times 10^{-40}$ g cm^2, and $I_C = 4.8235 \times 10^{-39}$ g cm^2.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys. 44, 525 (1966).
2. M. E. Jacox and D. E. Milligan, J. Chem. Phys. 47, 1626 (1967).

Chlorodifluoromethane ($CHClF_2$)

(Ideal Gas) GFW = 86.4689

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	,000	,000	INFINITE	- 2,967	- 113,596	- 113,596	INFINITE
100	8,368	55,720	77,369	- 2,165	- 114,230	- 112,235	245,289
200	10,930	62,245	68,288	- 1,209	- 114,717	- 110,045	120,252
298	13,653	67,126	67,126	,000	- 115,100	- 107,668	78,922
300	13,701	67,211	67,126	,025	- 115,107	- 107,622	78,402
400	16,039	71,485	67,693	1,517	- 115,393	- 105,080	57,413
500	17,849	75,268	68,837	3,215	- 115,597	- 102,478	44,793
600	19,221	78,649	70,196	5,072	- 115,735	- 99,840	36,367
700	20,271	81,694	71,624	7,049	- 115,824	- 97,182	30,342
800	21,093	84,457	73,058	9,118	- 115,875	- 94,516	25,821
900	21,750	86,980	74,467	11,262	- 115,896	- 91,845	22,303
1000	22,286	89,301	75,836	13,464	- 115,890	- 89,174	19,489
1100	22,728	91,446	77,159	15,716	- 115,865	- 86,504	17,187
1200	23,096	93,440	78,434	18,008	- 115,823	- 83,835	15,268
1300	23,407	95,301	79,660	20,333	- 115,773	- 81,172	13,646
1400	23,670	97,046	80,840	22,687	- 115,711	- 78,511	12,256
1500	23,895	98,687	81,976	25,066	- 115,643	- 75,855	11,052
1600	24,089	100,235	83,069	27,465	- 115,572	- 73,208	10,000
1700	24,256	101,701	84,123	29,883	- 115,494	- 70,560	9,071
1800	24,401	103,091	85,138	32,316	- 115,416	- 67,922	8,247
1900	24,528	104,414	86,118	34,762	- 115,335	- 65,283	7,509
2000	24,640	105,675	87,065	37,221	- 115,253	- 62,650	6,846
2100	24,738	106,880	87,980	39,690	- 115,171	- 60,023	6,247
2200	24,825	108,033	88,865	42,168	- 115,091	- 57,401	5,702
2300	24,902	109,138	89,723	44,655	- 115,011	- 54,777	5,205
2400	24,971	110,199	90,554	47,148	- 114,934	- 52,160	4,750
2500	25,033	111,220	91,360	49,649	- 114,860	- 49,548	4,332
2600	25,089	112,203	92,143	52,155	- 114,789	- 46,936	3,945
2700	25,139	113,150	92,904	54,666	- 114,720	- 44,328	3,588
2800	25,184	114,066	93,643	57,182	- 114,654	- 41,722	3,257
2900	25,225	114,950	94,363	59,703	- 114,593	- 39,116	2,948
3000	25,263	115,806	95,063	62,227	- 114,536	- 36,519	2,660
3100	25,297	116,635	95,746	64,755	- 114,482	- 33,918	2,391
3200	25,328	117,438	96,411	67,286	- 114,434	- 31,319	2,139
3300	25,357	118,218	97,060	69,821	- 114,390	- 28,725	1,902
3400	25,383	118,976	97,694	72,358	- 114,350	- 26,127	1,679
3500	25,407	119,712	98,312	74,897	- 114,318	- 23,534	1,470
3600	25,429	120,428	98,917	77,439	- 114,288	- 20,939	1,271
3700	25,450	121,125	99,508	79,983	- 114,265	- 18,346	1,084
3800	25,469	121,804	100,086	82,529	- 114,247	- 15,751	,906
3900	25,487	122,466	100,651	85,077	- 114,235	- 13,161	,738
4000	25,503	123,111	101,204	87,626	- 114,228	- 10,568	,577
4100	25,519	123,741	101,746	90,177	- 114,226	- 7,981	,425
4200	25,533	124,356	102,277	92,730	- 114,231	- 5,386	,280
4300	25,546	124,957	102,798	95,284	- 114,240	- 2,795	,142
4400	25,559	125,545	103,308	97,839	- 114,256	- ,203	,010
4500	25,571	126,119	103,809	100,396	- 114,277	2,384	- ,116
4600	25,582	126,681	104,300	102,953	- 114,302	4,980	- ,237
4700	25,592	127,231	104,782	105,512	- 114,334	7,575	- ,352
4800	25,602	127,770	105,255	108,072	- 114,371	10,171	- ,463
4900	25,611	128,298	105,720	110,632	- 114,413	12,767	- ,569
5000	25,619	128,816	106,177	113,194	- 114,461	15,360	- ,671
5100	25,627	129,323	106,626	115,756	- 114,514	17,952	- ,769
5200	25,635	129,821	107,067	118,319	- 114,572	20,556	- ,864
5300	25,642	130,309	107,501	120,883	- 114,636	23,157	- ,955
5400	25,649	130,789	107,928	123,448	- 114,706	25,753	- 1,042
5500	25,656	131,259	108,348	126,013	- 114,780	28,358	- 1,127
5600	25,662	131,722	108,761	128,579	- 114,861	30,960	- 1,208
5700	25,668	132,176	109,168	131,145	- 114,947	33,561	- 1,287
5800	25,673	132,622	109,569	133,712	- 115,038	36,169	- 1,363
5900	25,679	133,061	109,963	136,280	- 115,134	38,777	- 1,436
6000	25,684	133,493	110,352	138,848	- 115,236	41,382	- 1,507

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1964; June 30, 1970

CHLORODIFLUOROMETHANE ($CHClF_2$) (IDEAL GAS) GFW = 86.4689

Point Group C_s

ΔHf_0° = -113.6 ± 3 kcal/mol

$S_{298.15}^\circ$ = 67.126 ± 0.2 gibbs/mol

$\Delta Hf_{298.15}^\circ$ = -115.1 ± 3 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
3024 (1)	812 (1)	1350 (1)
1312 (1)	598 (1)	1108 (1)
836 (1)	417 (1)	400 (1)

Bond Distance: C-H = 1.09 Å C-Cl = 1.74 Å C-F = 1.35 Å

Bond Angle: H-C-Cl = 107° Cl-C-F = 110.5° F-C-F = 107°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 3.43433 \times 10^{-114}\ g^3\ cm^6$.

Heat of Formation

Edwards and Small (1) determined a single equilibrium constant at 600°C for the reaction $2CHClF_2(g) \rightarrow C_2F_4(g) + 2HCl(g)$. The value was not obtained directly but was obtained by extrapolation to eliminate the effects of side reactions. The equilibrium constant was used with JANAF free energy functions (2) to obtain ΔHr_{298}° = 28.75 kcal, which yields ΔHf_{298}° ($CHClF_2$, g) = -115.1 kcal/mol. An uncertainty of ±3 kcal/mol corresponds to an uncertainty of about ±500% in the equilibrium constant.

Heat Capacity and Entropy

The gas phase vibrational frequencies have been observed in the Raman by Holzer and Moser (3); they do not see anything in the 1350 cm^{-1} region as reported in the liquid by Glockler and Edgell (4). Plyler and Benedict (5) in their assignment replaced an 831 cm^{-1} frequency by 1178 cm^{-1}. We essentially adopt Glockler and Edgell's assignment with updated gas phase values for the observed frequencies. The microwave spectrum has been analysed by McLay and Mann (6) and Beeson et al. (7), who derive bond lengths and angles in excellent agreement with each other. The values given by Beeson et al. are adopted here.

Neilson and White (8) have measured the low temperature heat capacity and heat of vaporization and have reported an entropy in the gas phase at 232.5°K of 63.919 ± 0.28 gibbs/mol. This compares with 63.959 gibbs/mol calculated from our adopted functions.

The individual moments of inertia are $I_A = 8.203 \times 10^{-39}\ g\ cm^2$, $I_B = 17.402 \times 10^{-39}\ g\ cm^2$ and $I_C = 24.060 \times 10^{-39}\ g\ cm^2$.

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Dichlorofluoromethane ($CHCl_2F$)

(Ideal Gas) GFW = 102.9235

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.177	-66.364	-66.364	INFINITE
100	9.004	57.617	81.204	-2.359	-66.983	-64.954	141.957
200	11.993	64.786	71.322	-1.307	-67.387	-62.762	68.583
298	14.578	70.069	70.069	.000	-67.700	-60.423	44.291
300	14.623	70.159	70.069	.027	-67.705	-60.378	43.986
400	16.785	74.674	70.670	1.602	-67.939	-57.898	31.634
500	18.447	78.607	71.873	3.367	-68.098	-55.368	24.201
600	19.701	82.087	73.291	5.277	-68.201	-52.812	19.237
700	20.661	85.199	74.774	7.298	-68.260	-50.241	15.686
800	21.413	88.009	76.255	9.403	-68.286	-47.666	13.022
900	22.017	90.567	77.705	11.575	-68.285	-45.088	10.949
1000	22.510	92.913	79.110	13.802	-68.259	-42.513	9.291
1100	22.918	95.078	80.465	16.074	-68.216	-39.941	7.936
1200	23.260	97.087	81.767	18.384	-68.158	-37.372	6.806
1300	23.549	98.961	83.019	28.725	-68.092	-34.810	5.852
1400	23.795	100.715	84.221	23.092	-68.015	-32.251	5.035
1500	24.005	102.364	85.376	25.482	-67.933	-29.698	4.327
1600	24.186	103.919	86.487	27.892	-67.848	-27.155	3.709
1700	24.343	105.390	87.556	30.319	-67.757	-24.611	3.164
1800	24.479	106.786	88.586	32.760	-67.665	-22.079	2.681
1900	24.599	108.113	89.579	35.214	-67.570	-19.546	2.248
2000	24.703	109.377	90.537	37.679	-67.476	-17.021	1.860
2100	24.796	110.585	91.463	40.154	-67.380	-14.501	1.509
2200	24.878	111.740	92.359	42.638	-67.287	-11.987	1.191
2300	24.951	112.848	93.226	45.130	-67.194	-9.472	.900
2400	25.016	113.911	94.066	47.628	-67.104	-6.964	.634
2500	25.075	114.933	94.880	50.133	-67.017	-4.463	.390
2600	25.127	115.918	95.670	52.643	-66.933	-1.961	.165
2700	25.175	116.867	96.438	55.158	-66.852	.535	-.043
2800	25.217	117.783	97.184	57.678	-66.774	3.031	-.237
2900	25.256	118.669	97.910	60.201	-66.701	5.524	-.416
3000	25.292	119.526	98.616	62.729	-66.633	8.009	-.583
3100	25.324	120.356	99.304	65.260	-66.568	10.497	-.740
3200	25.354	121.160	99.975	67.793	-66.510	12.983	-.887
3300	25.381	121.941	100.628	70.330	-66.457	15.465	-1.024
3400	25.406	122.699	101.266	72.870	-66.408	17.949	-1.154
3500	25.429	123.436	101.889	75.411	-66.367	20.426	-1.275
3600	25.450	124.152	102.498	77.955	-66.329	22.908	-1.391
3700	25.469	124.850	103.093	80.501	-66.298	25.387	-1.500
3800	25.487	125.529	103.674	83.049	-66.271	27.865	-1.603
3900	25.504	126.191	104.243	85.599	-66.252	30.343	-1.700
4000	25.520	126.837	104.800	88.150	-66.238	32.820	-1.793
4100	25.534	127.468	105.345	90.703	-66.229	35.293	-1.881
4200	25.548	128.083	105.879	93.257	-66.227	37.771	-1.965
4300	25.561	128.685	106.403	95.812	-66.229	40.246	-2.046
4400	25.573	129.272	106.916	98.369	-66.237	42.724	-2.122
4500	25.584	129.847	107.419	100.927	-66.250	45.194	-2.195
4600	25.594	130.410	107.913	103.486	-66.267	47.675	-2.265
4700	25.604	130.960	108.397	106.045	-66.291	50.154	-2.332
4800	25.613	131.499	108.873	108.606	-66.319	52.632	-2.396
4900	25.622	132.027	109.340	111.168	-66.351	55.113	-2.458
5000	25.630	132.545	109.799	113.731	-66.388	57.589	-2.517
5100	25.638	133.053	110.250	116.294	-66.430	60.066	-2.574
5200	25.645	133.551	110.693	118.858	-66.476	62.551	-2.629
5300	25.652	134.039	111.129	121.423	-66.527	65.034	-2.682
5400	25.658	134.519	111.558	123.989	-66.583	67.514	-2.732
5500	25.665	134.990	111.980	126.555	-66.644	70.001	-2.782
5600	25.670	135.452	112.395	129.121	-66.708	72.482	-2.829
5700	25.676	135.907	112.803	131.689	-66.778	74.964	-2.874
5800	25.681	136.353	113.205	134.257	-66.851	77.455	-2.919
5900	25.686	136.792	113.601	136.825	-66.930	79.944	-2.961
6000	25.691	137.224	113.992	139.394	-67.013	82.430	-3.003

Dec. 31, 1960; Sept. 30, 1964; June 30, 1970

Point Group C_s

ΔHf°_0 = [-66.36 ± 3] kcal/mol

$S^\circ_{298.15}$ = 70.07 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-67.7 ± 3] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
3023 (1)	741 (1)	1242 (1)
1313 (1)	455 (1)	806 (1)
1079 (1)	270 (1)	368 (1)

Bond Distance: C-H = 1.09 Å C-Cl = 1.75 Å C-F = 1.367 Å

Bond Angle: Cl-C-Cl = 112°12' F-C-Cl = 109° H-C-Cl = 109°45' σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = 1.11593 x 10^{-113} g^3 cm^6.

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl in the CF_4 to CCl_4 series follows a regular pattern (see CCl_2F_2 table). A similar pattern is to be expected in the CHF_3 to $CHCl_3$ series. The first replacement of the series is, in fact, 4 kcal higher than the mean versus 3.8 kcal higher in the CF_4-CCl_4 series. Thus, we have selected the atomization energy of the second and third replacements to continue this pattern. In this manner we have selected the atomization energy of $CHCl_2F$ as 367.4 kcal which corresponds to $\Delta Hf^\circ_{298}(CHCl_2F, g)$ = -67.7 kcal/mol. With this adopted value, the successive replacement of F by Cl changes the heat of atomization by 41.4, 37.3 and 33.0 kcal.

Heat Capacity and Entropy

Holzer (1) has reported the gas phase Raman spectrum which is in excellent agreement with the assignments of Plyler and Benedict (2). The only discrepancy is in ν_7, which Plyler and Benedict assign at 1242 cm^{-1}, and Holzer (1) does not report a band in this region. Holzer does, however, report a band at 728 cm^{-1} which has not been reported in the earlier liquid studies. There is strong evidence from correlations with $CHCl_3$ and CHF_3 that two frequencies should occur between 1220 and 1376 cm^{-1}. On this basis we adopt the assignment of Plyler and Benedict for ν_7, while accepting the gas phase values of Holzer for the other frequencies. The extra band at 728 cm^{-1} is not used. It is probable that the bands at 741 and 728 cm^{-1} are due to Fermi resonance of ν_4 with $2\nu_9$; the unperturbed level would lie at 735 cm^{-1}. The symmetry classes of ν_4 and $2\nu_9$ are identical and thus Fermi resonance is allowed.

McLay (3) has reported the molecular structure from his microwave investigations. The individual principal moments of inertia are I_A = 12.053 x 10^{-39} g cm^2, I_B = 25.684 x 10^{-39} g cm^2 and I_C = 36.047 x 10^{-39} g cm^2.

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Chloroform ($CHCl_3$)

(Ideal Gas) GFW = 119.3781

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.383	-23.488	-23.488	INFINITE
100	9.637	57.180	82.642	-2.546	-24.089	-21.794	47.630
200	12.978	64.933	71.975	-1.408	-24.419	-19.363	21.159
298	15.627	70.628	70.628	.000	-24.660	-16.828	12.335
300	15.671	70.724	70.628	.029	-24.664	-16.780	12.224
400	17.747	75.532	71.269	1.705	-24.826	-14.125	7.717
500	19.266	79.664	72.545	3.560	-24.919	-11.437	4.999
600	20.378	83.280	74.039	5.545	-24.966	-8.736	3.182
700	21.217	86.487	75.592	7.626	-24.977	-6.029	1.882
800	21.872	89.365	77.137	9.782	-24.963	-3.324	.908
900	22.398	91.972	78.643	11.996	-24.926	-.621	.151
1000	22.831	94.355	80.097	14.258	-24.870	2.075	-.454
1100	23.191	96.549	81.494	16.560	-24.800	4.766	-.947
1200	23.494	98.580	82.834	18.895	-24.718	7.452	-1.357
1300	23.751	100.471	84.119	21.257	-24.630	10.128	-1.703
1400	23.971	102.239	85.351	23.644	-24.532	12.800	-1.998
1500	24.160	103.900	86.533	26.050	-24.432	15.463	-2.253
1600	24.323	105.464	87.667	28.475	-24.328	18.117	-2.475
1700	24.465	106.943	88.758	30.914	-24.220	20.770	-2.670
1800	24.589	108.345	89.808	33.367	-24.111	23.411	-2.842
1900	24.697	109.677	90.819	35.832	-23.999	26.051	-2.997
2000	24.793	110.947	91.794	38.306	-23.890	28.682	-3.134
2100	24.877	112.159	92.735	40.790	-23.778	31.307	-3.258
2200	24.952	113.318	93.644	43.281	-23.670	33.926	-3.370
2300	25.019	114.428	94.524	45.780	-23.561	36.545	-3.473
2400	25.079	115.494	95.376	48.285	-23.456	39.156	-3.566
2500	25.133	116.519	96.201	50.796	-23.355	41.760	-3.651
2600	25.181	117.506	97.002	53.311	-23.256	44.365	-3.729
2700	25.224	118.457	97.779	55.832	-23.161	46.962	-3.801
2800	25.264	119.375	98.534	58.356	-23.071	49.559	-3.868
2900	25.300	120.262	99.268	60.884	-22.985	52.152	-3.930
3000	25.332	121.121	99.982	63.416	-22.905	54.738	-3.988
3100	25.362	121.952	100.677	65.951	-22.828	57.326	-4.041
3200	25.389	122.757	101.355	68.488	-22.759	59.911	-4.092
3300	25.414	123.539	102.015	71.028	-22.696	62.492	-4.139
3400	25.437	124.298	102.659	73.571	-22.636	65.075	-4.183
3500	25.458	125.036	103.288	76.116	-22.585	67.649	-4.224
3600	25.478	125.753	103.902	78.663	-22.538	70.229	-4.26
3700	25.496	126.452	104.502	81.211	-22.499	72.807	-4.301
3800	25.513	127.132	105.089	83.762	-22.464	75.382	-4.335
3900	25.528	127.795	105.663	86.314	-22.436	77.959	-4.369
4000	25.543	128.441	106.224	88.867	-22.415	80.533	-4.400
4100	25.556	129.072	106.774	91.422	-22.397	83.102	-4.430
4200	25.569	129.688	107.312	93.979	-22.387	85.677	-4.458
4300	25.581	130.290	107.839	96.536	-22.382	88.248	-4.485
4400	25.592	130.878	108.356	99.095	-22.381	90.824	-4.511
4500	25.602	131.453	108.863	101.654	-22.387	93.390	-4.536
4600	25.611	132.016	109.361	104.215	-22.395	95.967	-4.559
4700	25.621	132.567	109.848	106.777	-22.409	98.543	-4.582
4800	25.629	133.106	110.327	109.339	-22.428	101.115	-4.604
4900	25.637	133.635	110.798	111.902	-22.451	103.693	-4.625
5000	25.645	134.153	111.260	114.467	-22.477	106.264	-4.645
5100	25.652	134.661	111.713	117.031	-22.507	108.839	-4.664
5200	25.659	135.159	112.160	119.597	-22.541	111.417	-4.683
5300	25.665	135.648	112.598	122.163	-22.579	113.993	-4.701
5400	25.671	136.128	113.029	124.730	-22.621	116.569	-4.718
5500	25.677	136.599	113.454	127.297	-22.666	119.150	-4.735
5600	25.682	137.061	113.871	129.865	-22.714	121.724	-4.751
5700	25.687	137.516	114.282	132.434	-22.768	124.298	-4.766
5800	25.692	137.963	114.686	135.003	-22.823	126.885	-4.781
5900	25.697	138.402	115.085	137.572	-22.883	129.466	-4.796
6000	25.701	138.834	115.477	140.142	-22.947	132.046	-4.810

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1968

CHLOROFORM ($CHCl_3$) (IDEAL GAS) GFW = 119.3781

$CHCl_3$

Point Group C_{3v}

ΔHf°_0 = -23.49 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 70.628 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -24.66 ± 0.3 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
3034 (1)	1220 (2)
680 (1)	774 (2)
363 (1)	261 (2)

Bond Distances: C-H = 1.100Å C-Cl = 1.758Å

Bond Angles: Cl-C-Cl = 111°18' H-C-Cl = 107°34' σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 3.2811 \times 10^{-113}\ g^3cm^6$

Heat of Formation

Hu and Sinke (1) have measured the heat of combustion of $CHCl_3(\ell)$ in the rotating bomb calorimeter, using As_2O_3 solution as the reducing agent. The reported ΔHc°_{298} = -113.10 kcal/mol for $CHCl_3(\ell) + 0.5O_2 + H_2O(\ell) \rightarrow CO_2(g) + 3HCl(600H_2O, aq)$ which leads to $\Delta Hf^\circ_{298}(CHCl_3, \ell)$ = -32.10 kcal/mol, using ΔHf°_{298} = -94.051, -39.823, -68.315 kcal/mol for $CO_2(g)$, $HCl(600H_2O, aq)$ and $H_2O(\ell)$, respectively (2). The standard deviation of six combustion runs was 0.09 kcal/mol. Employing the heat of vaporization of chloroform at 298°K as 7.44 kcal/mol (3), we obtain ΔHf°_{298} ($CHCl_3$, g) = -24.66 kcal/mol which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Eftring (5), re-evaluated the heat of combustion of chloroform at 18.7°C as $\Delta E^\circ_c/M$ = -947.7 cal/g for $CHCl_3(\ell) + 0.5O_2(g) + H_2O(\ell) \rightarrow CO_2(g) + 3HCl(600H_2O, aq)$. This value needs to be further corrected for a change in the heat of oxidation of As_2O_3 (6) and calculated to 25°C to give ΔHc°_{298} = -113.44 kcal/mol, $\Delta Hf^\circ_{298}(CHCl_3, \ell)$ = -31.76 kcal/mol and $\Delta Hf^\circ_{298}(CHCl_3, g)$ = -24.32 kcal/mol.

Heat Capacity and Entropy

The assigned fundamental vibrational freqencies are obtained from Shimanouchi's selection (7), based on infrared and Raman spectra measured by Nielsen and Ward (8), Madigan and Cleveland (9), Gibian and McKinney (10) and Stanevich and Yaroslavskii (11).

The bond distances and angles were obtained from the microwave spectra by Jen and Lide (12). The three principal moments of inertia are $I_A = I_B = 25.719 \times 10^{-39}$ and $I_C = 49.603 \times 10^{-39}\ g\ cm^2$.

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Monofluoromethylene (CHF)

(Ideal Gas) GFW = 32.01752

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.386	29.933	29.933	INFINITE
100	7.949	44.609	60.518	-1.591	29.987	28.801	-62.945
200	7.986	50.123	54.100	-.795	30.053	27.579	-30.137
298	8.271	53.355	53.355	.000	30.000	26.372	-19.331
300	8.279	53.406	53.355	.015	29.998	26.349	-19.195
400	8.810	55.857	53.685	.869	29.873	25.151	-13.742
500	9.387	57.885	54.328	1.779	29.711	23.988	-10.485
600	9.919	59.645	55.071	2.744	29.533	22.860	-8.327
700	10.387	61.210	55.838	3.760	29.347	21.763	-6.795
800	10.795	62.624	56.599	4.820	29.162	20.692	-5.653
900	11.149	63.916	57.341	5.918	28.979	19.644	-4.770
1000	11.458	65.107	58.059	7.048	28.802	18.616	-4.068
1100	11.727	66.212	58.751	8.208	28.629	17.605	-3.498
1200	11.962	67.243	59.416	9.392	28.462	16.612	-3.025
1300	12.171	68.209	60.056	10.599	28.297	15.630	-2.628
1400	12.357	69.118	60.671	11.826	28.137	14.664	-2.289
1500	12.526	69.976	61.263	13.070	27.979	13.707	-1.997
1600	12.682	70.790	61.833	14.331	27.823	12.758	-1.743
1700	12.830	71.563	62.383	15.606	27.672	11.823	-1.520
1800	12.971	72.300	62.913	16.896	27.523	10.893	-1.323
1900	13.110	73.005	63.426	18.200	27.380	9.975	-1.147
2000	13.246	73.681	63.922	19.518	27.242	9.063	-.990
2100	13.382	74.331	64.402	20.849	27.109	8.157	-.849
2200	13.517	74.956	64.868	22.194	26.981	7.256	-.721
2300	13.653	75.560	65.320	23.553	26.860	6.365	-.605
2400	13.789	76.144	65.759	24.925	26.745	5.476	-.499
2500	13.925	76.710	66.186	26.311	26.637	4.590	-.401
2600	14.061	77.259	66.601	27.710	26.536	3.711	-.312
2700	14.195	77.792	67.006	29.123	26.443	2.834	-.229
2800	14.328	78.311	67.400	30.549	26.358	1.961	-.153
2900	14.458	78.816	67.785	31.989	26.279	1.094	-.082
3000	14.586	79.308	68.161	33.441	26.208	.223	-.016
3100	14.709	79.788	68.528	34.906	26.146	-.641	.045
3200	14.829	80.257	68.888	36.382	26.089	-1.503	.103
3300	14.943	80.715	69.239	37.871	26.039	-2.367	.157
3400	15.053	81.163	69.583	39.371	25.995	-3.226	.207
3500	15.157	81.601	69.920	40.881	25.956	-4.085	.255
3600	15.255	82.029	70.251	42.402	25.924	-4.943	.300
3700	15.347	82.448	70.575	43.932	25.895	-5.799	.343
3800	15.434	82.859	70.893	45.471	25.871	-6.653	.383
3900	15.513	83.261	71.205	47.019	25.849	-7.509	.421
4000	15.587	83.655	71.511	48.574	25.831	-8.363	.457
4100	15.655	84.040	71.812	50.136	25.815	-9.221	.492
4200	15.716	84.418	72.108	51.705	25.799	-10.072	.524
4300	15.771	84.789	72.398	53.279	25.785	-10.927	.555
4400	15.821	85.152	72.684	54.859	25.771	-11.782	.585
4500	15.865	85.508	72.965	56.443	25.757	-12.639	.614
4600	15.904	85.857	73.241	58.032	25.743	-13.489	.641
4700	15.937	86.199	73.514	59.624	25.727	-14.341	.667
4800	15.965	86.535	73.781	61.219	25.709	-15.191	.692
4900	15.989	86.865	74.045	62.816	25.689	-16.043	.716
5000	16.008	87.188	74.305	64.416	25.666	-16.896	.739
5100	16.023	87.505	74.560	66.018	25.639	-17.752	.761
5200	16.034	87.816	74.812	67.621	25.610	-18.599	.782
5300	16.042	88.122	75.061	69.225	25.577	-19.445	.802
5400	16.046	88.422	75.305	70.829	25.539	-20.297	.821
5500	16.047	88.716	75.546	72.434	25.496	-21.145	.840
5600	16.045	89.005	75.784	74.038	25.449	-21.993	.858
5700	16.041	89.289	76.019	75.643	25.396	-22.842	.876
5800	16.034	89.568	76.250	77.246	25.337	-23.688	.893
5900	16.024	89.842	76.478	78.849	25.273	-24.530	.909
6000	16.013	90.111	76.703	80.451	25.204	-25.379	.924

Dec. 31, 1969

MONOFLUOROMETHYLENE (CHF) (IDEAL GAS) GFW = 32.01752

Point Group C_s

ΔHf°_0 = [29.9 ± 7] kcal/mol

$S^\circ_{298.15}$ = 53.35 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [30 ± 7] kcal/mol

Ground State Quantum Weight = 1

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[10000]	3
17287	1

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[3000] (1)
1403 (1)
1182 (1)

Bond Distance: C-H = 1.121 Å C-F = 1.314 Å

Bond Angle: H-C-F = 101.6°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 1.0217 \times 10^{-117}$ g^3 cm^6

Heat of Formation

The heat of formation can be estimated as the average of those of the CH_2 and CF_2 radicals, which gives $\Delta Hf^\circ_{298}(CHF, g)$ = 25 ± 20 kcal/mol. A better value for the heat of formation can be obtained by considering the bond energies $CHF \rightarrow CH + F$ and $CHF \rightarrow CF + H$. When $\Delta Hf^\circ_{298}(CHF, g)$ = 25 kcal/mol is substituted into the above equations it gives D_{C-F} = 136 kcal and D_{C-H} = 86 kcal. These are not unreasonable values but are probably close to the upper and lower limits respectively. A value of $\Delta Hf^\circ_{298}(CHF, g)$ = 30 kcal/mol gives D_{C-F} = 131 kcal and D_{C-H} = 81 kcal which are more probable since both fall within the bounds of normal bond strengths. The strongest established C-F bond is 135 kcal in CF_3 and the weakest established C-H bond is 80 kcal in CH. We adopt $\Delta Hf^\circ_{298}(CHF, g)$ = 30 ± 7 kcal/mol.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CF_2 and CH_2 as given in these tables. The vibrational levels are from Merer and Travis (1) and Jacox and Milligan (2), the latter investigated the infrared spectrum of matrix-isolated HCF and also estimated the missing frequency.

The individual moments of inertia are $I_A = 2.2979 \times 10^{-39}$ g cm^2, $I_B = 1.795 \times 10^{-40}$ g cm^2, and $I_C = 2.4774 \times 10^{-39}$ g cm^2.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys. 44, 1541 (1966).
2. M. E. Jacox and D. E. Milligan, J. Chem. Phys. 50, 3252 (1969).

Formyl Fluoride (CHFO)

(Ideal Gas) Mol. Wt. = 48.019

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.496	-89.139	-89.139	INFINITE
100	7.962	49.744	66.753	-1.701	-89.442	-89.065	194.642
200	8.474	55.371	59.803	-.886	-89.697	-88.597	96.810
298	9.659	58.961	58.961	.000	-90.000	-87.994	64.498
300	9.685	59.020	58.961	.018	-90.006	-87.982	64.092
400	11.078	61.998	59.357	1.056	-90.301	-87.261	47.675
500	12.352	64.610	60.152	2.229	-90.566	-86.471	37.794
600	13.432	66.961	61.094	3.520	-90.796	-85.630	31.189
700	14.330	69.101	62.087	4.910	-90.997	-84.751	26.459
800	15.077	71.065	63.088	6.381	-91.170	-83.848	22.905
900	15.701	72.878	64.077	7.921	-91.318	-82.924	20.136
1000	16.223	74.560	65.042	9.518	-91.442	-81.984	17.917
1100	16.662	76.127	65.979	11.163	-91.549	-81.034	16.099
1200	17.034	77.593	66.887	12.848	-91.639	-80.072	14.582
1300	17.351	78.970	67.764	14.568	-91.720	-79.106	13.298
1400	17.621	80.266	68.611	16.317	-91.790	-78.131	12.196
1500	17.853	81.489	69.429	18.091	-91.854	-77.153	11.241
1600	18.053	82.648	70.219	19.886	-91.913	-76.173	10.404
1700	18.226	83.748	70.983	21.700	-91.967	-75.187	9.665
1800	18.377	84.794	71.721	23.531	-92.019	-74.199	9.009
1900	18.509	85.791	72.436	25.375	-92.069	-73.207	8.420
2000	18.625	86.744	73.128	27.232	-92.118	-72.213	7.891
2100	18.728	87.655	73.798	29.100	-92.167	-71.215	7.411
2200	18.819	88.528	74.448	30.977	-92.219	-70.219	6.975
2300	18.899	89.367	75.078	32.863	-92.270	-69.215	6.577
2400	18.971	90.173	75.691	34.757	-92.325	-68.211	6.211
2500	19.036	90.948	76.285	36.657	-92.383	-67.209	5.875
2600	19.094	91.696	76.864	38.564	-92.443	-66.199	5.564
2700	19.146	92.418	77.427	40.476	-92.506	-65.189	5.276
2800	19.194	93.115	77.975	42.393	-92.571	-64.176	5.009
2900	19.237	93.789	78.508	44.314	-92.642	-63.158	4.759
3000	19.276	94.442	79.029	46.240	-92.716	-62.143	4.527
3100	19.312	95.075	79.536	48.170	-92.792	-61.121	4.309
3200	19.344	95.688	80.031	50.102	-92.874	-60.099	4.104
3300	19.374	96.284	80.515	52.038	-92.960	-59.075	3.912
3400	19.402	96.863	80.987	53.977	-93.049	-58.046	3.731
3500	19.427	97.426	81.449	55.919	-93.144	-57.016	3.560
3600	19.450	97.973	81.900	57.862	-93.243	-55.981	3.398
3700	19.472	98.506	82.342	59.809	-93.347	-54.944	3.245
3800	19.492	99.026	82.774	61.757	-93.454	-53.902	3.100
3900	19.510	99.532	83.197	63.707	-93.568	-52.861	2.962
4000	19.528	100.027	83.612	65.659	-93.685	-51.815	2.831
4100	19.544	100.509	84.018	67.612	-93.807	-50.770	2.706
4200	19.559	100.980	84.417	69.567	-93.935	-49.716	2.587
4300	19.573	101.441	84.807	71.524	-94.066	-48.661	2.473
4400	19.586	101.891	85.190	73.482	-94.203	-47.606	2.365
4500	19.598	102.331	85.566	75.441	-94.345	-46.549	2.261
4600	19.609	102.762	85.935	77.402	-94.491	-45.480	2.161
4700	19.620	103.184	86.298	79.363	-94.643	-44.413	2.065
4800	19.630	103.597	86.654	81.326	-94.799	-43.340	1.973
4900	19.640	104.002	87.004	83.289	-94.959	-42.268	1.885
5000	19.649	104.399	87.348	85.254	-95.125	-41.193	1.800
5100	19.657	104.788	87.686	87.219	-95.297	-40.116	1.719
5200	19.665	105.170	88.019	89.185	-95.471	-39.031	1.640
5300	19.673	105.544	88.346	91.152	-95.651	-37.938	1.564
5400	19.680	105.912	88.668	93.120	-95.836	-36.852	1.491
5500	19.687	106.273	88.985	95.088	-96.026	-35.756	1.421
5600	19.693	106.628	89.296	97.057	-96.221	-34.660	1.353
5700	19.700	106.977	89.604	99.027	-96.421	-33.562	1.287
5800	19.705	107.319	89.906	100.997	-96.625	-32.456	1.223
5900	19.711	107.656	90.204	102.968	-96.834	-31.345	1.161
6000	19.716	107.988	90.498	104.939	-97.048	-30.238	1.101

June 30, 1961

FORMYL FLUORIDE (CHFO) (IDEAL GAS) MOL. WT. = 48.019

ΔH°_{f0} = [-92] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-90] kcal. mole^{-1}

Point Group C_1

$S_{298.15}$ = 58.96 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω cm.$^{-1}$	ω cm.$^{-1}$
2981 (1)	1064.8 (1)
1836.9 (1)	662.5 (1)
1342.5 (1)	[1030] (1)

Bond Lengths and Angles

C-F = 1.31 ± 0.02 Å C-O = 1.183 ± 0.003 A C-H = 1.10 ± 0.02 A

∡ FCO = 122.7 ± 0.05° ∡ HCF = 108 ± 3° ∡ HCO = 129 ± 3°

Moments of Inertia

$I_A = 0.92052 \times 10^{-39}$ g. cm.^{2} $I_B = 7.13510 \times 10^{-39}$ g. cm.^{2} $\sigma = 1$

$I_C = 8.07064 \times 10^{-39}$ g. cm.^{2}

Heat of Formation

ΔH_r for III was estimated to be the average of the ΔH_r's of I and II.

(I) $CH_2O(g) = CO(g) + 2H(g)$ 106 kcal.

(II) $CF_2O(g) = CO(g) + 2F(g)$ 162 kcal.

(III) $CHFO(g) = CO(g) + F(g) + H(g)$ [134] kcal.

The auxiliary $\Delta H_{f\ 298.15}$ of CH_2O = -28, H = 52, F = 19, CO = -26, CF_2O = -150 kcal. mole^{-1} was used. See the respective sheets for details. The estimated heat of formation is consistent with the instability of CHFO(g) at room temperature.

Heat Capacities and Entropies

The molecular structural parameters were obtained by O. H. LeBlanc, V. W. Laurie and W. D. Gwinn, J. Chem. Phys. 33, 598 (1960), from combining the results of microwave measurements with those of electron diffraction determined by M. E. Jones, K. Hedberg, and V. Schomaker, J. Am. Chem. Soc. 77, 5278 (1955). Agreement within the assigned uncertainties was obtained by R. F. Stratton and A. H. Nielsen, J. Mol. Spect. 4, 373 (1960), on the basis of infrared measurements.

Five of the fundamentals were observed by Stratton and Nielsen, loc. cit. in agreement with those obtained by H. W. Morgan, P. A. Staats and J. H. Goldstein, J. Chem. Phys. 25, 337 (1956). The estimated frequency was based upon the observed value of 857.4 cm.$^{-1}$ for the fundamental in the infrared spectrum of the deuterated compound and the application of the Teller-Redlich isotope rule.

Trifluoromethane (CHF_3)

(Ideal Gas) GFW = 70.01432

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-2.764	-164.935	-164.935	INFINITE
100	8.100	51.595	71.264	-1.967	-165.574	-163.389	357.086
200	9.853	57.667	63.071	-1.081	-166.117	-160.991	175.923
298	12.199	62.032	62.032	.000	-166.600	-158.371	116.089
300	12.244	62.108	62.033	.023	-166.609	-158.320	115.336
400	14.579	65.956	62.542	1.366	-167.014	-155.493	84.957
500	16.557	69.430	63.577	2.926	-167.332	-152.575	66.690
600	18.128	72.593	64.820	4.664	-167.571	-149.600	54.492
700	19.359	75.484	66.140	6.541	-167.746	-146.589	45.767
800	20.331	78.135	67.476	8.527	-167.871	-143.558	39.218
900	21.109	80.576	68.798	10.600	-167.955	-140.514	34.122
1000	21.742	82.834	70.090	12.744	-168.004	-137.463	30.043
1100	22.262	84.931	71.345	14.945	-168.027	-134.408	26.704
1200	22.694	86.888	72.560	17.193	-168.027	-131.350	23.922
1300	23.057	88.719	73.733	19.481	-168.014	-128.294	21.568
1400	23.363	90.439	74.866	21.803	-167.986	-125.239	19.551
1500	23.624	92.060	75.958	24.152	-167.950	-122.185	17.802
1600	23.847	93.592	77.013	26.526	-167.908	-119.139	16.274
1700	24.040	95.044	78.031	28.921	-167.858	-116.090	14.924
1800	24.207	96.422	79.015	31.333	-167.806	-113.050	13.726
1900	24.352	97.735	79.966	33.761	-167.749	-110.007	12.654
2000	24.480	98.988	80.886	36.203	-167.690	-106.968	11.689
2100	24.592	100.185	81.777	38.657	-167.630	-103.935	10.817
2200	24.691	101.331	82.640	41.121	-167.572	-100.905	10.024
2300	24.780	102.431	83.476	43.595	-167.513	-97.873	9.300
2400	24.858	103.487	84.288	46.077	-167.456	-94.847	8.637
2500	24.929	104.503	85.077	48.566	-167.402	-91.825	8.027
2600	24.992	105.482	85.843	51.062	-167.349	-88.801	7.464
2700	25.049	106.427	86.588	53.564	-167.298	-85.781	6.943
2800	25.100	107.338	87.313	56.072	-167.249	-82.764	6.460
2900	25.147	108.220	88.019	58.584	-167.204	-79.743	6.010
3000	25.189	109.073	88.706	61.101	-167.164	-76.734	5.590
3100	25.228	109.900	89.377	63.622	-167.124	-73.719	5.197
3200	25.263	110.701	90.031	66.146	-167.090	-70.706	4.829
3300	25.296	111.479	90.669	68.674	-167.060	-67.696	4.483
3400	25.325	112.235	91.292	71.205	-167.033	-64.684	4.158
3500	25.353	112.969	91.901	73.739	-167.013	-61.673	3.851
3600	25.378	113.684	92.496	76.276	-166.994	-58.663	3.561
3700	25.401	114.380	93.078	78.815	-166.983	-55.654	3.287
3800	25.423	115.057	93.648	81.356	-166.974	-52.641	3.028
3900	25.443	115.718	94.205	83.899	-166.974	-49.636	2.782
4000	25.462	116.362	94.751	86.445	-166.975	-46.625	2.547
4100	25.479	116.991	95.286	88.992	-166.984	-43.620	2.325
4200	25.495	117.605	95.810	91.540	-166.998	-40.607	2.113
4300	25.510	118.206	96.324	94.091	-167.016	-37.597	1.911
4400	25.524	118.792	96.828	96.642	-167.042	-34.589	1.718
4500	25.537	119.366	97.322	99.195	-167.073	-31.584	1.534
4600	25.550	119.927	97.808	101.750	-167.108	-28.569	1.357
4700	25.561	120.477	98.284	104.305	-167.151	-25.556	1.188
4800	25.572	121.015	98.752	106.862	-167.198	-22.539	1.026
4900	25.583	121.543	99.212	109.420	-167.252	-19.524	.871
5000	25.592	122.060	99.664	111.979	-167.311	-16.511	.722
5100	25.602	122.566	100.108	114.538	-167.378	-13.503	.579
5200	25.610	123.064	100.545	117.099	-167.450	-10.478	.440
5300	25.618	123.552	100.974	119.660	-167.527	-7.454	.307
5400	25.626	124.030	101.397	122.223	-167.612	-4.440	.180
5500	25.633	124.501	101.812	124.785	-167.703	-1.414	.056
5600	25.640	124.963	102.222	127.349	-167.800	1.610	-.063
5700	25.647	125.417	102.625	129.914	-167.904	4.634	-.178
5800	25.653	125.863	103.022	132.479	-168.013	7.662	-.289
5900	25.659	126.301	103.412	135.044	-168.130	10.692	-.396
6000	25.665	126.733	103.797	137.610	-168.252	13.719	-.500

Dec. 31, 1960; Dec. 31, 1963; June 30, 1969

Point Group C_{3v}

ΔHf°_0 = -164.9 ± 0.8 kcal/mol

$S^\circ_{298.15}$ = 62.032 ± 0.08 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -166.6 ± 0.8 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
3035 (1)	1376 (2)
1137 (1)	1152 (2)
700 (1)	508 (2)

Bond Distance: C-F = 1.333 Å C-H = 1.098 Å

Bond Angle: F-C-F = 108.6 ± 0.5° F-C-H = 110.33° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = 9.7204 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Trifluoromethane is linked to HF(21.5 H_2O) by calorimetric data, to $CBrF_3(g)$ and $CF_3I(g)$ by equilibrium data, and to $CF_3(g)$ by kinetic data. Neugebauer (2) reported calorimetric data for $CHF_3(g) + 0.5\ O_2(g) + H_2O(\ell) \to CO_2(g) + 3\ HF(21.5\ H_2O)$, where $CF_4(g)$ was also formed in a competing reaction. Recalculation of the original data with $\Delta Hf^\circ_{298.15}(CF_4, g) = -223.0$ kcal/mol yields the mean value of $\Delta Hr^\circ_{298.15} = -90.35 \pm 0.7$ kcal/mol, but the individual values of ΔHr° show a disturbing trend with the amount of competing reaction. Possible causes for the trend include corrosion and error in the analysis of the reaction products. Calibration was done in the presence of HF in an attempt to eliminate the heat due to corrosion. Because of this unexplained trend, we increase the uncertainty to ± 1.0 kcal/mol. Goy (3) and Coomber (4) determined equilibrium data for $CHF_3(g) + X_2(g) = CF_3X(g) + HX(g)$ where X = I and Br. Kinetic data pertinent to CHF_3 are noted on the table for $CF_3(g)$.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Thornton (5) and from microwave data by Ghosh (6). The results are in close agreement and average values are adopted. Vibrational frequencies are from the assignment of Long (7) who reviewed the spectral data and gave force-constant calculations. Preference has been given to the gas-phase spectra, particularly the Raman data of Claassen (8). Shimanouchi (9) assigned ν_2 = 1117 rather than 1137 cm^{-1}, but he apparently did not consider the gas-phase data of (8, 10). Principal moments of inertia are $I_A = 14.786 \times 10^{-39}$ and $I_B = I_C = 8.108 \times 10^{-39}\ g\ cm^2$.

Valentine (11) used low-temperature calorimetric data to derive the ideal gas entropy at the normal boiling point of 190.97°K. The experimental value of 57.18 gibbs/mol is in good agreement with 57.216 gibbs/mol obtained from this table. Schwing (12) measured C_v for CHF_3 vapor (25-100°C) and confirmed that the vibrational assignment is adequate. Uncertainty in Cp° and S° increases at higher temperatures due to neglect of anharmonicity in the calculations. Discussions of anharmonic contributions are given on the tables for $CF_4(g)$ and $CClF_3(g)$. The error probably does not exceed 0.3 gibbs/mol in S° at 1000°K. Cp° is consistent with Cv° measured at 300°K by the wire-ribbon method (13).

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Hydrogen Cyanide (HCN)

(Ideal Gas) GFW = 27.02582

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.207	32.393	32.393	INFINITE
100	6.971	40.033	55.163	-1.513	32.347	31.493	-68.827
200	7.581	44.997	48.962	-.793	32.340	30.635	-33.477
298	8.570	48.212	48.212	.000	32.300	29.806	-21.849
300	8.587	48.265	48.212	.016	32.299	29.791	-21.702
400	9.376	50.849	48.559	.916	32.258	28.961	-15.823
500	9.974	53.008	49.239	1.885	32.206	28.142	-12.301
600	10.470	54.871	50.026	2.907	32.145	27.335	-9.957
700	10.909	56.519	50.838	3.976	32.074	26.539	-8.286
800	11.309	58.002	51.642	5.088	32.002	25.754	-7.036
900	11.674	59.355	52.425	6.237	31.929	24.976	-6.065
1000	12.005	60.603	53.181	7.421	31.861	24.207	-5.290
1100	12.305	61.761	53.909	8.637	31.797	23.444	-4.658
1200	12.574	62.843	54.609	9.881	31.737	22.689	-4.132
1300	12.815	63.860	55.282	11.151	31.680	21.936	-3.688
1400	13.031	64.817	55.929	12.443	31.629	21.190	-3.308
1500	13.224	65.723	56.552	13.756	31.581	20.446	-2.979
1600	13.396	66.582	57.152	15.087	31.535	19.704	-2.691
1700	13.551	67.399	57.731	16.435	31.493	18.966	-2.438
1800	13.689	68.177	58.290	17.797	31.454	18.230	-2.213
1900	13.813	68.921	58.830	19.172	31.417	17.498	-2.013
2000	13.925	69.632	59.353	20.559	31.383	16.766	-1.832
2100	14.027	70.314	59.859	21.957	31.350	16.037	-1.669
2200	14.118	70.969	60.349	23.364	31.318	15.306	-1.521
2300	14.202	71.598	60.824	24.780	31.288	14.581	-1.385
2400	14.278	72.204	61.286	26.204	31.258	13.856	-1.262
2500	14.347	72.789	61.734	27.636	31.228	13.129	-1.148
2600	14.411	73.353	62.171	29.074	31.199	12.407	-1.043
2700	14.470	73.898	62.595	30.518	31.170	11.683	-.946
2800	14.523	74.425	63.008	31.967	31.141	10.962	-.856
2900	14.573	74.935	63.411	33.422	31.112	10.244	-.772
3000	14.620	75.430	63.803	34.882	31.082	9.524	-.694
3100	14.662	75.910	64.186	36.346	31.054	8.805	-.621
3200	14.702	76.377	64.560	37.814	31.023	8.088	-.552
3300	14.739	76.830	64.925	39.286	30.990	7.371	-.488
3400	14.774	77.270	65.281	40.762	30.959	6.657	-.428
3500	14.806	77.699	65.630	42.241	30.924	5.940	-.371
3600	14.836	78.116	65.971	43.723	30.889	5.227	-.317
3700	14.864	78.523	66.305	45.208	30.851	4.516	-.267
3800	14.890	78.920	66.631	46.696	30.813	3.807	-.219
3900	14.914	79.307	66.952	48.186	30.772	3.098	-.174
4000	14.937	79.685	67.265	49.679	30.730	2.388	-.130
4100	14.959	80.054	67.573	51.173	30.685	1.678	-.089
4200	14.979	80.415	67.874	52.670	30.637	.974	-.051
4300	14.998	80.767	68.170	54.169	30.588	.267	-.014
4400	15.015	81.112	68.460	55.670	30.536	-.439	.022
4500	15.031	81.450	68.745	57.172	30.481	-1.145	.056
4600	15.046	81.781	69.025	58.676	30.424	-1.843	.088
4700	15.060	82.104	69.300	60.181	30.364	-2.544	.118
4800	15.073	82.421	69.570	61.688	30.300	-3.242	.148
4900	15.085	82.732	69.835	63.196	30.234	-3.942	.176
5000	15.096	83.037	70.096	64.705	30.165	-4.638	.203
5100	15.107	83.336	70.353	66.215	30.092	-5.339	.229
5200	15.116	83.630	70.605	67.726	30.017	-6.030	.253
5300	15.124	83.918	70.854	69.238	29.938	-6.720	.277
5400	15.131	84.200	71.098	70.751	29.856	-7.412	.300
5500	15.137	84.478	71.339	72.264	29.769	-8.099	.322
5600	15.143	84.751	71.576	73.778	29.679	-8.790	.343
5700	15.148	85.019	71.810	75.293	29.585	-9.477	.363
5800	15.152	85.283	72.040	76.808	29.487	-10.161	.383
5900	15.155	85.542	72.266	78.323	29.386	-10.841	.402
6000	15.157	85.796	72.490	79.839	29.280	-11.527	.420

Dec. 31, 1960; Mar. 31, 1961; June 30, 1969; Dec. 31, 1969

HYDROGEN CYANIDE (HCN) (IDEAL GAS) GFW = 27.02582

Point Group $C_{\infty v}$

$\Delta Hf°_0$ = 32.39 ± 2.0 kcal/mol

$S°_{298.15}$ = 48.21 ± 0.01 gibbs/mol

$\Delta Hf°_{298.15}$ = 32.3 ± 2.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
2096.3 (1)
713.5 (2)
3311.5 (1)

Bond Distances: C-H = 1.066 Å C-N = 1.153 Å
Bond Angle: H-C-N = 180°
Rotational Constant: B_0 = 1.4782 cm^{-1}

σ = 1

Spectroscopic constants used in calculating corrections to the rigid-rotator harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 10.10 \times 10^{-3}$ $-x_{11} = 7.07$ $-x_{12} = 2.53$

$\alpha_2 = -3.61 \times 10^{-3}$ $-x_{22} = 2.65$ $-x_{23} = 19.01$

$\alpha_3 = 10.42 \times 10^{-3}$ $-x_{33} = 52.49$ $-x_{13} = 10.44$

$g_{22} = 5.16$

Heat of Formation

The value adopted is from reference 1. The data of Thomsen (2) who measured both C_2N_2 and HCN and Berthelot (3) were used in conjunction with the well established value for C_2N_2 to derive the adopted value (4).

Badger (5) studied the equilibrium $NH_3(g) + C(c) = HCN(g) + H_2(g)$ from both sides; we obtain a 3rd law $\Delta Hr°_{298}$ = 46 ± 0.9 kcal and a 2nd law $\Delta Hr°_{298}$ = 34.5 ± 19 kcal, the 3rd law drift is 14 ± 24 eu. The 3rd law value leads to $\Delta Hf°_{298}$(HCN, g) = 35 ± 1 kcal/mol.

Horiuchi et al. (6) studied the equilibrium $2\ CO(g) + NH_3(g) = HCN(g) + CO_2(g) + H_2(g)$. We obtain $\Delta Hr°_{298}$ = 1.1 ± 0.5 kcal from a 3rd law analysis with a drift of -2 ± 3 eu, and a 2nd law value of 2.9 ± 2.6 kcal. The 3rd law value leads to $\Delta Hf°_{298}$(HCN, g) = 31.35 ± 0.6 kcal/mol. The two sets of equilibrium data are self-consistent but disagree with each other and the direct combustions. We adopt an uncertainty of 2.0 kcal/mol to draw attention to this unsatisfactory situation.

Heat Capacity and Entropy

McBride et al. (7) used the constants listed above to calculate the adopted table which includes first and second corrections for anharmonicity, vibration-rotation interaction and centrifugal stretching. The bond lengths and molecular constants are those listed by Rank et al. (8). A more extensive set of anharmonic constants has recently been determined by Nakagawa and Morino (9), they are in generally good agreement with the values used.

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Isocyanic Acid (HNCO)

(Ideal Gas) Mol. Wt. = 43.027 **INTERIM TABLE**

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H_{298}^\circ$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.615	-27.179	-27.179	INFINITE
100	8.000	47.153	65.350	-1.820	-27.470	-26.966	58.932
200	9.121	52.963	57.839	-.975	-27.701	-26.375	28.820
298	10.724	56.909	56.909	.000	-27.900	-25.681	18.823
300	10.752	56.975	56.909	.020	-27.904	-25.667	18.698
400	12.085	60.259	57.348	1.165	-28.055	-24.897	13.602
500	13.114	63.071	58.218	2.427	-28.179	-24.093	10.531
600	13.934	65.537	59.236	3.781	-28.287	-23.266	8.474
700	14.613	67.738	60.296	5.209	-28.387	-22.421	7.000
800	15.191	69.728	61.353	6.700	-28.479	-21.561	5.890
900	15.690	71.546	62.386	8.244	-28.563	-20.691	5.024
1000	16.125	73.222	63.387	9.836	-28.639	-19.814	4.330
1100	16.507	74.778	64.352	11.468	-28.705	-18.927	3.760
1200	16.842	76.229	65.282	13.136	-28.764	-18.036	3.285
1300	17.136	77.589	66.177	14.835	-28.818	-17.140	2.881
1400	17.394	78.868	67.038	16.561	-28.867	-16.239	2.535
1500	17.622	80.076	67.868	18.313	-28.915	-15.336	2.234
1600	17.823	81.220	68.667	20.085	-28.964	-14.430	1.971
1700	18.001	82.306	69.437	21.876	-29.003	-13.520	1.738
1800	18.159	83.339	70.181	23.685	-29.039	-12.608	1.531
1900	18.299	84.325	70.900	25.508	-29.075	-11.694	1.345
2000	18.424	85.267	71.595	27.344	-29.109	-10.778	1.178
2100	18.535	86.168	72.268	29.192	-29.144	-9.861	1.026
2200	18.635	87.033	72.919	31.050	-29.180	-8.942	.888
2300	18.725	87.863	73.551	32.918	-29.218	-8.021	.762
2400	18.805	88.662	74.164	34.795	-29.258	-7.098	.646
2500	18.878	89.431	74.760	36.679	-29.301	-6.174	.540
2600	18.944	90.173	75.338	38.570	-29.346	-5.249	.441
2700	19.004	90.889	75.901	40.468	-29.393	-4.321	.350
2800	19.059	91.581	76.449	42.371	-29.442	-3.390	.265
2900	19.108	92.251	76.982	44.279	-29.494	-2.458	.185
3000	19.154	92.899	77.502	46.193	-29.549	-1.526	.111
3100	19.195	93.528	78.009	48.110	-29.607	-.592	.042
3200	19.234	94.138	78.503	50.032	-29.668	.344	-.023
3300	19.269	94.731	78.986	51.957	-29.732	1.284	-.085
3400	19.301	95.306	79.458	53.885	-29.800	2.224	-.143
3500	19.331	95.866	79.919	55.817	-29.872	3.169	-.198
3600	19.359	96.411	80.369	57.751	-29.949	4.112	-.250
3700	19.384	96.942	80.810	59.688	-30.029	5.059	-.299
3800	19.408	97.459	81.241	61.628	-30.112	6.009	-.346
3900	19.430	97.964	81.664	63.570	-30.201	6.963	-.390
4000	19.451	98.456	82.077	65.514	-30.294	7.914	-.432
4100	19.470	98.936	82.483	67.460	-30.391	8.871	-.473
4200	19.488	99.406	82.880	69.408	-30.492	9.833	-.512
4300	19.505	99.865	83.270	71.358	-30.597	10.792	-.548
4400	19.521	100.313	83.652	73.309	-30.706	11.757	-.584
4500	19.536	100.752	84.027	75.262	-30.820	12.722	-.618
4600	19.550	101.182	84.395	77.216	-30.937	13.690	-.650
4700	19.563	101.602	84.757	79.172	-31.058	14.663	-.682
4800	19.575	102.014	85.112	81.129	-31.184	15.640	-.712
4900	19.586	102.418	85.461	83.087	-31.313	16.617	-.741
5000	19.597	102.814	85.804	85.046	-31.446	17.590	-.769
5100	19.608	103.202	86.142	87.006	-31.584	18.575	-.796
5200	19.617	103.583	86.474	88.968	-31.725	19.559	-.822
5300	19.627	103.956	86.800	90.930	-31.870	20.550	-.847
5400	19.635	104.323	87.121	92.893	-32.019	21.538	-.872
5500	19.644	104.684	87.437	94.857	-32.172	22.532	-.895
5600	19.652	105.038	87.748	96.822	-32.328	23.524	-.918
5700	19.659	105.386	88.055	98.787	-32.488	24.525	-.940
5800	19.666	105.728	88.356	100.753	-32.653	25.529	-.962
5900	19.673	106.064	88.654	102.720	-32.821	26.530	-.983
6000	19.679	106.395	88.947	104.688	-32.993	27.535	-1.003

December 31, 1960.

ISOCYANIC ACID (HNCO) (Ideal Gas)

Mol. Wt. = 43.027

$\Delta H_{f\ 298.15}^\circ = -27.9$ kcal. mole^{-1}

$S_{298.15}^\circ = 56.909$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities
ω cm.$^{-1}$
572 (1)
670 (1)
797 (1)
1327 (1)
2274 (1)
3531 (1)

Moments of Inertia: $I_A = 7.7276 \times 10^{-39}$ g. cm.^{2}, $I_B = 7.636 \times 10^{-39}$ g. cm.^{2}, $I_C = 0.09157 \times 10^{-39}$ g. cm.^{2} $\sigma = 1.$

Data from J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Formyl (HCO)

(Ideal Gas) Mol. Wt. = 29.019

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.387	-2.986	-2.986	INFINITE
100	7.949	44.930	60.855	-1.593	-2.941	-4.118	8.998
200	7.999	50.447	54.429	-.796	-2.864	-5.334	5.829
298	8.264	53.683	53.683	.000	-2.900	-6.543	4.796
300	8.271	53.734	53.683	.015	-2.902	-6.566	4.783
400	8.703	56.171	54.012	.863	-3.002	-7.773	4.247
500	9.184	58.164	54.649	1.758	-3.142	-8.950	3.912
600	9.660	59.881	55.381	2.700	-3.305	-10.097	3.678
700	10.108	61.404	56.135	3.689	-3.481	-11.214	3.501
800	10.518	62.781	56.881	4.720	-3.661	-12.307	3.362
900	10.888	64.042	57.607	5.791	-3.840	-13.378	3.248
1000	11.216	65.206	58.310	6.896	-4.013	-14.428	3.153
1100	11.505	66.289	58.986	8.033	-4.182	-15.462	3.072
1200	11.758	67.301	59.638	9.196	-4.346	-16.479	3.001
1300	11.979	68.251	60.264	10.383	-4.508	-17.484	2.939
1400	12.172	69.146	60.867	11.591	-4.665	-18.475	2.884
1500	12.341	69.992	61.447	12.817	-4.822	-19.456	2.835
1600	12.489	70.793	62.007	14.059	-4.978	-20.429	2.790
1700	12.618	71.554	62.546	15.314	-5.131	-21.388	2.750
1800	12.732	72.279	63.067	16.582	-5.285	-22.341	2.712
1900	12.832	72.970	63.570	17.860	-5.440	-23.283	2.678
2000	12.921	73.630	64.057	19.148	-5.594	-24.219	2.646
2100	13.000	74.263	64.528	20.444	-5.750	-25.145	2.617
2200	13.071	74.869	64.984	21.747	-5.909	-26.067	2.589
2300	13.133	75.452	65.427	23.058	-6.068	-26.978	2.563
2400	13.190	76.012	65.856	24.374	-6.232	-27.883	2.539
2500	13.240	76.551	66.273	25.695	-6.398	-28.784	2.516
2600	13.286	77.071	66.678	27.022	-6.566	-29.675	2.494
2700	13.327	77.574	67.073	28.353	-6.738	-30.562	2.474
2800	13.365	78.059	67.456	29.687	-6.912	-31.440	2.454
2900	13.399	78.529	67.830	31.025	-7.091	-32.311	2.435
3000	13.430	78.983	68.194	32.367	-7.273	-33.179	2.417
3100	13.458	79.424	68.550	33.711	-7.457	-34.039	2.400
3200	13.484	79.852	68.896	35.058	-7.646	-34.894	2.383
3300	13.508	80.267	69.234	36.408	-7.839	-35.744	2.367
3400	13.530	80.671	69.565	37.760	-8.035	-36.586	2.352
3500	13.550	81.063	69.888	39.114	-8.235	-37.425	2.337
3600	13.569	81.445	70.204	40.470	-8.439	-38.255	2.322
3700	13.586	81.817	70.513	41.828	-8.648	-39.080	2.308
3800	13.602	82.180	70.815	43.187	-8.859	-39.897	2.294
3900	13.617	82.533	71.111	44.548	-9.075	-40.711	2.281
4000	13.631	82.878	71.401	45.911	-9.294	-41.520	2.268
4100	13.644	83.215	71.685	47.275	-9.518	-42.325	2.256
4200	13.656	83.544	71.963	48.640	-9.746	-43.119	2.244
4300	13.667	83.866	72.236	50.006	-9.978	-43.912	2.232
4400	13.678	84.180	72.504	51.373	-10.214	-44.700	2.220
4500	13.688	84.487	72.767	52.741	-10.454	-45.484	2.209
4600	13.697	84.788	73.025	54.111	-10.698	-46.255	2.198
4700	13.706	85.083	73.279	55.481	-10.946	-47.025	2.187
4800	13.714	85.372	73.527	56.852	-11.198	-47.789	2.176
4900	13.722	85.654	73.772	58.224	-11.453	-48.551	2.165
5000	13.729	85.932	74.013	59.596	-11.712	-49.306	2.155
5100	13.736	86.204	74.249	60.969	-11.977	-50.057	2.145
5200	13.742	86.470	74.481	62.343	-12.244	-50.802	2.135
5300	13.749	86.732	74.710	63.718	-12.515	-51.535	2.125
5400	13.754	86.989	74.935	65.093	-12.791	-52.272	2.115
5500	13.760	87.242	75.157	66.469	-13.070	-52.999	2.106
5600	13.765	87.490	75.375	67.845	-13.353	-53.725	2.097
5700	13.770	87.733	75.589	69.222	-13.640	-54.446	2.087
5800	13.775	87.973	75.801	70.599	-13.932	-55.158	2.078
5900	13.779	88.208	76.009	71.977	-14.226	-55.862	2.069
6000	13.784	88.440	76.214	73.355	-14.525	-56.570	2.060

March 31, 1961

FORMYL (HCO) (IDEAL GAS) MOL. WT. = 29.019

ΔH°_{f0} = -3.0 ± 3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -2.9 ± 3 kcal. mole^{-1}

Point Group C_s

$S^\circ_{298.15}$ = [53.683] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [2]

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
[3000] (1)
1860 (1)
1083 (1)

HC bond length = [1.08] Å CO bond length = 1.198 ± 0.005 Å HCO angle = 119°30' ± 1°

Product of Moments of Inertia = $I_AI_BI_C$ = 4.73 X 10^{-118} g.^{3} cm.^{6} σ = 1

Heat of Formation

Calculated from ΔH_0 = 75.1 ± 2.3 kcal. for the reaction $H_2CO(g) \rightarrow HCO(g) + H(g)$, reported by J. C. D. Brand and R. T. Reed, J. Chem. Soc. 2386 (1957).

Heat Capacity and Entropy

The vibrational levels and multiplicities are from G. E. Ewing, W. E. Thompson, and G. C. Pimentel, J. Chem. Phys. 32, 927 (1960), while the ground state multiplicity and structural data are from G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. A233, 34 (1955).

Formyl Unipositive Ion (HCO^+)

(Ideal Gas) GFW = 29.01797

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.617	48.344	48.344	.000	204.400	200.862	- 147.236
300	8.634	48.397	48.344	.016	204.408	200.839	- 146.311
400	9.393	50.992	48.693	.920	204.860	199.582	- 109.046
500	9.942	53.150	49.374	1.888	205.291	198.212	- 86.638
600	10.385	55.002	50.162	2.905	205.700	196.757	- 71.669
700	10.777	56.633	50.972	3.963	206.089	195.235	- 60.955
800	11.138	58.096	51.772	5.059	206.471	193.659	- 52.905
900	11.472	59.428	52.550	6.190	206.849	192.034	- 46.632
1000	11.781	60.653	53.300	7.353	207.230	190.367	- 41.605
1100	12.064	61.789	54.021	8.545	207.614	188.663	- 37.484
1200	12.320	62.850	54.713	9.764	208.003	186.924	- 34.044
1300	12.552	63.845	55.377	11.008	208.394	185.150	- 31.127
1400	12.760	64.783	56.016	12.274	208.792	183.349	- 28.622
1500	12.946	65.670	56.630	13.560	209.192	181.518	- 26.447
1600	13.113	66.511	57.222	14.863	209.594	179.657	- 24.540
1700	13.262	67.310	57.792	16. 82	210.002	177.776	- 22.855
1800	13.395	68.072	58.342	17.515	210.409	175.867	- 21.353
1900	13.515	68.800	58.873	18.860	210.819	173.939	- 20.008
2000	13.622	69.496	59.387	20.217	211.230	171.986	- 18.794
2100	13.718	70.163	59.885	21.584	211.643	170.014	- 17.694
2200	13.804	70.803	60.366	22.960	212.053	168.021	- 16.691
2300	13.882	71.418	60.834	24.345	212.464	166.012	- 15.775
2400	13.953	72.011	61.287	25.737	212.873	163.984	- 14.933
2500	14.017	72.582	61.728	27.135	213.281	161.935	- 14.156
2600	14.075	73.133	62.156	28.540	213.688	159.874	- 13.439
2700	14.127	73.665	62.572	29.950	214.092	157.797	- 12.773
2800	14.175	74.179	62.978	31.365	214.496	155.707	- 12.153
2900	14.219	74.678	63.372	32.785	214.894	153.600	- 11.576
3000	14.260	75.160	63.757	34.209	215.292	151.479	- 11.035
3100	14.296	75.629	64.133	35.637	215.688	149.343	- 10.529
3200	14.330	76.083	64.499	37.068	216.080	147.200	- 10.053
3300	14.362	76.524	64.857	38.503	216.470	145.041	- 9.606
3400	14.390	76.954	65.206	39.940	216.855	142.870	- 9.184
3500	14.417	77.371	65.548	41.381	217.238	140.688	- 8.785
3600	14.442	77.778	65.882	42.824	217.619	138.494	- 8.408
3700	14.465	78.174	66.209	44.269	217.994	136.289	- 8.050
3800	14.486	78.560	66.529	45.716	218.368	134.081	- 7.711
3900	14.506	78.936	66.842	47.166	218.738	131.860	- 7.389
4000	14.524	79.304	67.149	48.618	219.104	129.624	- 7.082
4100	14.541	79.663	67.450	50.071	219.466	127.378	- 6.790
4200	14.558	80.013	67.745	51.526	219.825	125.136	- 6.512
4300	14.573	80.356	68.034	52.982	220.180	122.876	- 6.245
4400	14.587	80.691	68.318	54.440	220.532	120.608	- 5.991
4500	14.600	81.019	68.597	55.900	220.879	118.329	- 5.747
4600	14.613	81.340	68.870	57.360	221.224	116.052	- 5.514
4700	14.624	81.654	69.139	58.822	221.565	113.763	- 5.290
4800	14.635	81.962	69.403	60.285	221.902	111.466	- 5.075
4900	14.646	82.264	69.662	61.749	222.236	109.161	- 4.869
5000	14.655	82.560	69.917	63.214	222.565	106.850	- 4.670
5100	14.665	82.851	70.168	64.680	222.890	104.524	- 4.479
5200	14.674	83.135	70.415	66.147	223.213	102.206	- 4.296
5300	14.682	83.415	70.657	67.615	223.532	99.878	- 4.119
5400	14.690	83.690	70.896	69.084	223.847	97.536	- 3.947
5500	14.697	83.959	71.131	70.553	224.158	95.200	- 3.783
5600	14.704	84.224	71.363	72.023	224.465	92.845	- 3.623
5700	14.711	84.484	71.591	73.494	224.769	90.497	- 3.470
5800	14.717	84.740	71.815	74.965	225.069	88.136	- 3.321
5900	14.723	84.992	72.036	76.437	225.365	85.774	- 3.177
6000	14.729	85.239	72.254	77.910	225.658	83.407	- 3.038

June 30, 1966

FORMYL UNIPOSITIVE ION (HCO^+) (IDEAL GAS) GFW = 29.01797

Point Group [$C_{\infty v}$]

ΔHf°_0 = 203.0 ± 10 kcal/mol

$S^\circ_{298.15}$ = [48.3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 204.4 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[2310](1)
[700](2)
[3540](1)

Bond Distance: C-H = [1.029] Å C-O = [1.090] Å

Bond Angle: H-C-O = [180°] σ = [1]

Rotational Constant: B_o = [1.56015] cm^{-1}

Heat of Formation.

The selected heat of formation, ΔHf°_0 (HCO^+, g) = 203 kcal/mol was obtained from electron impact studies on cis-and trans-HCOOH by F. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957. A higher value, ΔHf°_0 = 220 kcal/mol has also been reported from appearance potential measurements on CH_3CHO by J. R. Majer, C. R. Patrick and J. C. Robb, Trans. Faraday Soc. 57, 14 (1961). Generally, errors in the heat of formation derived from electron impact studies are such as to cause the quantities to be high because of unaccounted excitations or residual kinetic energy in the fragments; therefore, the value of 203 kcal/mol is preferable, assuming the same reliability of the experiments.

Heat Capacity and Entropy.

Since the molecule HCO^+(g) has the same number of valence electrons as HCN(g), a linear molecular configuration is assumed for HCO^+(g) in the tabulation. The bond distances H-C and C-O were estimated by comparison with those in similar molecules by D. G. Clifton, J. Chem. Phys. 41, 3656 (1964). The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton. The principal moment of inertia is 1.7941 X 10^{-39} g cm^2.

Methinophosphide (HCP)

(Ideal Gas) GFW = 43.99292

		gibbs/mol		kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.235	39.891	39.891	INFINITE
100	6.978	43.067	58.470	-1.540	40.101	37.184	-81.266
200	7.714	48.070	52.142	-.814	40.130	34.235	-37.411
298	8.883	51.375	51.375	.000	40.000	31.365	-22.991
300	8.904	51.430	51.375	.016	39.997	31.311	-22.810
400	9.902	54.134	51.737	.959	39.813	28.443	-15.541
500	10.658	56.428	52.452	1.988	39.603	25.624	-11.200
600	11.236	58.424	53.284	3.084	39.370	22.849	-8.323
700	11.696	60.192	54.147	4.231	39.108	20.116	-6.281
800	12.082	61.779	55.004	5.420	18.402	12.112	-3.309
900	12.415	63.222	55.838	6.646	18.349	11.329	-2.751
1000	12.707	64.545	56.643	7.902	18.301	10.551	-2.306
1100	12.967	65.769	57.418	9.186	18.258	9.777	-1.943
1200	13.199	66.907	58.162	10.494	18.220	9.008	-1.641
1300	13.407	67.972	58.876	11.825	18.186	8.242	-1.386
1400	13.592	68.973	59.562	13.175	18.158	7.480	-1.168
1500	13.759	69.916	60.221	14.543	18.133	6.719	-.979
1600	13.909	70.809	60.855	15.926	18.110	5.956	-.814
1700	14.045	71.656	61.466	17.324	18.093	5.198	-.668
1800	14.168	72.463	62.054	18.735	18.078	4.440	-.539
1900	14.279	73.232	62.623	20.157	18.066	3.684	-.424
2000	14.381	73.967	63.172	21.590	18.057	2.925	-.320
2100	14.475	74.671	63.703	23.033	18.051	2.171	-.226
2200	14.561	75.346	64.217	24.485	18.045	1.413	-.140
2300	14.640	75.995	64.715	25.945	18.042	.658	-.063
2400	14.715	76.620	65.198	27.413	18.039	-.098	.009
2500	14.783	77.222	65.667	28.888	18.040	-.854	.075
2600	14.849	77.803	66.122	30.370	18.040	-1.610	.135
2700	14.910	78.365	66.565	31.857	18.041	-2.367	.192
2800	14.968	78.908	66.997	33.351	18.044	-3.122	.244
2900	15.023	79.434	67.416	34.851	18.048	-3.876	.292
3000	15.076	79.944	67.826	36.356	18.052	-4.633	.338
3100	15.129	80.440	68.225	37.866	18.058	-5.389	.380
3200	15.179	80.921	68.614	39.382	18.064	-6.146	.420
3300	15.229	81.389	68.994	40.902	18.071	-6.904	.457
3400	15.278	81.844	69.365	42.427	18.077	-7.660	.492
3500	15.328	82.287	69.728	43.958	18.085	-8.418	.526
3600	15.377	82.720	70.083	45.493	18.094	-9.178	.557
3700	15.428	83.142	70.430	47.033	18.103	-9.934	.587
3800	15.481	83.554	70.770	48.579	18.114	-10.688	.615
3900	15.533	83.957	71.103	50.129	18.125	-11.444	.641
4000	15.588	84.351	71.429	51.685	18.138	-12.205	.667
4100	15.648	84.736	71.749	53.247	18.153	-12.966	.691
4200	15.706	85.114	72.063	54.815	18.168	-13.719	.714
4300	15.769	85.485	72.371	56.388	18.185	-14.484	.736
4400	15.836	85.848	72.673	57.969	18.206	-15.242	.757
4500	15.905	86.204	72.970	59.556	18.228	-16.006	.777
4600	15.978	86.555	73.261	61.150	18.254	-16.767	.797
4700	16.056	86.899	73.548	62.752	18.284	-17.526	.815
4800	16.136	87.238	73.830	64.361	18.316	-18.287	.833
4900	16.222	87.572	74.107	65.979	18.354	-19.048	.850
5000	16.312	87.900	74.379	67.606	18.397	-19.813	.866
5100	16.407	88.224	74.648	69.241	18.442	-20.582	.882
5200	16.507	88.544	74.912	70.887	18.496	-21.348	.897
5300	16.610	88.859	75.172	72.543	18.554	-22.111	.912
5400	16.718	89.171	75.428	74.209	18.620	-22.880	.926
5500	16.832	89.479	75.681	75.887	18.692	-23.647	.940
5600	16.950	89.783	75.930	77.576	18.771	-24.421	.953
5700	17.073	90.084	76.176	79.277	18.858	-25.194	.966
5800	17.200	90.382	76.418	80.991	18.954	-25.970	.979
5900	17.333	90.677	76.657	82.717	19.059	-26.740	.991
6000	17.469	90.970	76.893	84.457	19.173	-27.522	1.002

Dec. 31, 1969

METHINOPHOSPHIDE (HCP) (IDEAL GAS) GFW = 43.99292

CHP

Point Group $C_{\infty v}$

ΔHf°_0 = [39.9 ± 15] kcal/mol

$S^\circ_{298.15}$ = 51.37 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [40 ± 15] kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a^3\Sigma^+$	24440	3
$b^3\Pi$	30430	6
$c^3\Sigma^-$	31024	3
A^1A''	34746	1
$B^1\Pi$	35927	2
$d^3\Pi$	35976	6
C^1A'	40248	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
3216.9 (1)
674.7 (2)
1278.4 (1)

Spectroscopic constants used in calculating corrections to the rigid-rotator harmonic oscillator model (cm^{-1}):

$\alpha_1 = 3.4 \times 10^{-3}$ $-x_{11} = [3.7]$ $-x_{12} = [1.9]$

$\alpha_2 = -3.4 \times 10^{-4}$ $-x_{22} = [2.4]$ $-x_{23} = [18.0]$

$\alpha_3 = 3.1 \times 10^{-3}$ $-x_{23} = [51.0]$ $-x_{13} = [8.0]$

Bond Distances: C-H = 1.0667 Å C-P = 1.5421 Å

Bond Angle: H-C-P = 180° $\sigma = 1$

Rotational Constant: B_0 = 0.66633 cm^{-1}

Heat of Formation

The bonding in HCP and HCN is very similar, as evidenced by the bond lengths and vibrational frequencies. We assume that the C-H bond strength is thus the same in these two molecules. For the reaction HCN → H + CN we derive ΔHr = 123.8 kcal from ΔHf°_{298}(HCN) = 32.3, ΔHf°_{298}(H) = 52.1 and ΔHf°_{298}(CN) = 104 kcal/mol. Applying this to the reaction HCP → H + CP, we obtain ΔHf°_{298}(HCP, g) = 40 ± 15 kcal/mol, from ΔHf°_{298}(CP) = 111.7 kcal/mol.

Heat Capacity and Entropy

The molecular configuration was first reported by Gier (1), and later the bond lengths were determined by Tyler (2) using microwave spectroscopy. The vibrational frequencies and electronic levels were obtained from an analysis of the ultraviolet spectrum by Johns et al. (3). Since the first excited state is above 24000 cm^{-1} and the first nonlinear state at 34,000 cm^{-1}, there is negligible error introduced by assuming ground state molecular constants for all excited states. The anharmonic constants were estimated from those of HCN by Gordon (4) and the adopted table includes these corrections and the electronic contributions.

References
1. T. E. Gier, J. Amer. Chem. Soc. 83, 1769 (1961).
2. J. K. Tyler, J. Chem. Phys. 40, 1170 (1964).
3. J. W. C. Johns, H. F. Shurvell and J. K. Tyler, Can. J. Phys. 47, 893 (1969).
4. J. S. Gordon, Atlantic Research Corp., Alexandria, Va., private communication, Jan. 12, 1970.

Methylene (CH_2)

(Ideal Gas) GFW = 14.02709

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.096	92.250	92.250	INFINITE
100	6.956	35.550	49.628	-1.408	92.165	91.070	-199.033
200	7.040	40.383	43.933	-.710	92.182	89.953	-98.296
298	7.492	43.266	43.266	.000	92.070	88.880	-65.151
300	7.504	43.312	43.266	.014	92.067	88.860	-64.735
400	8.172	45.561	43.568	.797	91.910	87.815	-47.980
500	8.820	47.455	44.161	1.647	91.742	86.810	-37.944
600	9.407	49.116	44.851	2.559	91.576	85.838	-31.267
700	9.947	50.607	45.568	3.527	91.417	84.896	-26.506
800	10.451	51.969	46.285	4.547	91.272	83.974	-22.941
900	10.919	53.227	46.987	5.616	91.142	83.069	-20.172
1000	11.349	54.400	47.670	6.730	91.032	82.178	-17.960
1100	11.738	55.500	48.332	7.885	90.938	81.297	-16.152
1200	12.087	56.537	48.973	9.076	90.859	80.425	-14.647
1300	12.397	57.517	49.593	10.301	90.791	79.558	-13.375
1400	12.671	58.446	50.193	11.554	90.734	78.697	-12.285
1500	12.912	59.328	50.773	12.834	90.684	77.840	-11.341
1600	13.125	60.169	51.334	14.136	90.638	76.982	-10.515
1700	13.312	60.970	51.877	15.458	90.599	76.132	-9.787
1800	13.478	61.736	52.404	16.798	90.563	75.281	-9.140
1900	13.625	62.469	52.914	18.153	90.530	74.434	-8.562
2000	13.755	63.171	53.410	19.522	90.499	73.587	-8.041
2100	13.872	63.845	53.891	20.903	90.469	72.744	-7.571
2200	13.976	64.493	54.358	22.296	90.439	71.898	-7.142
2300	14.070	65.116	54.812	23.698	90.410	71.058	-6.752
2400	14.154	65.716	55.254	25.109	90.379	70.218	-6.394
2500	14.231	66.296	55.684	26.529	90.348	69.376	-6.065
2600	14.301	66.855	56.103	27.955	90.315	68.540	-5.761
2700	14.364	67.396	56.512	29.389	90.282	67.701	-5.480
2800	14.422	67.920	56.910	30.828	90.247	66.865	-5.219
2900	14.475	68.427	57.298	32.273	90.210	66.033	-4.976
3000	14.524	68.918	57.677	33.723	90.171	65.198	-4.750
3100	14.569	69.395	58.048	35.178	90.132	64.367	-4.538
3200	14.610	69.859	58.410	36.637	90.089	63.537	-4.339
3300	14.648	70.309	58.763	38.100	90.043	62.706	-4.153
3400	14.683	70.747	59.109	39.566	89.995	61.879	-3.978
3500	14.716	71.173	59.448	41.036	89.943	61.052	-3.812
3600	14.746	71.588	59.779	42.509	89.889	60.227	-3.656
3700	14.774	71.992	60.104	43.985	89.830	59.405	-3.509
3800	14.800	72.386	60.422	45.464	89.770	58.586	-3.369
3900	14.824	72.771	60.734	46.945	89.704	57.767	-3.237
4000	14.846	73.147	61.040	48.429	89.636	56.949	-3.112
4100	14.867	73.514	61.339	49.914	89.563	56.130	-2.992
4200	14.886	73.872	61.633	51.402	89.486	55.319	-2.879
4300	14.904	74.223	61.922	52.892	89.405	54.503	-2.770
4400	14.921	74.565	62.206	54.383	89.320	53.691	-2.667
4500	14.936	74.901	62.484	55.876	89.230	52.879	-2.568
4600	14.951	75.229	62.758	57.370	89.136	52.077	-2.474
4700	14.964	75.551	63.026	58.866	89.038	51.273	-2.384
4800	14.977	75.866	63.291	60.363	88.935	50.472	-2.298
4900	14.989	76.175	63.550	61.861	88.828	49.672	-2.215
5000	15.000	76.478	63.806	63.361	88.717	48.871	-2.136
5100	15.010	76.775	64.057	64.861	88.599	48.074	-2.060
5200	15.020	77.067	64.305	66.363	88.479	47.280	-1.987
5300	15.029	77.353	64.548	67.865	88.353	46.494	-1.917
5400	15.037	77.634	64.788	69.368	88.222	45.703	-1.850
5500	15.045	77.910	65.024	70.873	88.087	44.917	-1.785
5600	15.053	78.181	65.257	72.377	87.946	44.132	-1.722
5700	15.060	78.448	65.486	73.883	87.801	43.349	-1.662
5800	15.067	78.710	65.711	75.389	87.650	42.570	-1.604
5900	15.073	78.967	65.934	76.896	87.495	41.799	-1.548
6000	15.079	79.221	66.153	78.404	87.336	41.019	-1.494

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1962; June 30, 1969

Point Group $D_{\infty h}$

ΔHf°_0 = 92.25 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 43.27 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 92.07 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

	ϵ_i, cm^{-1}	g_i
$X^3\Sigma_g^-$	0	3
a^1A_1	[2600]	1
b^1B_1	[9700]	1
c^1A_1	[30300]	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[2960] (1)
[1114] (2)
[3200] (1)

Bond Distance: C-H = 1.029 Å

Bond Angle: H-C-H = 180°

σ = 2

Rotational Constant: B_0 = 7.8974 cm^{-1}

Heat of Formation

Chupka and Livshitz (1) have recently obtained the photoionization threshold for the production of CH_2^+ from CH_3 as 15.09 ± 0.03 eV. In conjunction with the spectroscopic ionization potential determined by Herzberg (2), they report $D_0(CH_2\text{-}H)$ = 4.694 ± 0.033 eV (108.25 ± 0.77 kcal). Use of $\Delta Hf^\circ_0(CH_3, g)$ = 35.62 kcal/mol from these tables yields $\Delta Hf^\circ_0(CH_2, g)$ = 92.25 ± 1.0 kcal/mol, which is adopted.

Chupka (3) and Dibeler et al. (4) have determined the photoionization threshold for the production of CH_2^+ from CH_4. If the latter value is corrected for rotational energy effects as suggested by Chupka the two values are identical and yield $\Delta Hf^\circ_0(CH_2, g)$ = 94.6 kcal/mol. However, Chupka indicates that this is a maximum value since the process of H_2 elimination is likely to occur with excess energy in the products at the threshold. Chupka et al. (14) have obtained the appearance threshold of CH_2^+ from $C_2H_4(g)$ by photoionization and obtain a maximum value of $\Delta Hf^\circ_0(CH_2, g)$ = 95.5 kcal/mol.

Dibeler and Liston (5) have also reported the photoionization threshold for the process $CH_3CN \rightarrow CH_2^+ + HCN$ as 14.94 eV (344.55 kcal). Using auxiliary data from (2) and (13) we obtain $\Delta Hf^\circ_0(CH_2, g)$ = 95 kcal/mol, however the above process is also likely to occur with excess energy and so this is a maximum value.

The older electron impact data of Langer et al. (6) contained several inconsistencies with presently accepted values and was reanalysed by Prophet (7) to give $\Delta Hf^\circ_{298}(CH_2, g)$ = 95 ± 5 kcal/mol. Chupka et al. (8) have also reported a heat of formation, from chemical equilibria measured in a mass spectrometer, as 86.8 ± 6 kcal/mol.

Heat Capacity and Entropy

The ground state configuration, bond length and angle are from Herzberg (9). The excited electronic states are from the calculations of Goldberg and Riter (10) who have tried to allow for correlation energy effects in the different states. The separation between the a^1A_1 and b^1B_1 states is established as 7100 cm^{-1}. The degenerate bending frequency was listed as a possible fundamental of CH_2 by Milligan and Pimentel (11). There is considerable uncertainty that it is in fact the ground state bending frequency, excited state bending frequencies of 1353 and 557 cm^{-1} have been reported. The symmetric stretch was estimated to be that listed by Herzberg (12) for a bent molecule. The asymmetric stretch was estimated using the valence force field approximation.

The uncertainty in the entropy reflects the possible errors in the vibrational frequencies and the uncertain position of the low lying electronic levels and their varying geometries.

References:

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Chlorofluoromethane (CH_2ClF)

(Ideal Gas) GFW = 68.4785

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.689	-60.861	-60.861	INFINITE
100	8.195	53.043	71.942	-1.890	-61.530	-60.083	131.311
200	9.458	59.077	64.138	-1.012	-62.047	-58.444	63.865
298	11.242	63.171	63.171	.000	-62.600	-56.558	41.458
300	11.279	63.240	63.171	.021	-62.611	-56.521	41.176
400	13.281	66.761	63.637	1.249	-63.122	-54.411	29.729
500	15.072	69.923	64.583	2.670	-63.550	-52.183	22.809
600	16.561	72.807	65.717	4.254	-63.894	-49.876	18.167
700	17.786	75.455	66.922	5.973	-64.166	-47.516	14.835
800	18.804	77.898	68.143	7.804	-64.376	-45.124	12.327
900	19.660	80.164	69.354	9.728	-64.534	-42.707	10.371
1000	20.386	82.274	70.542	11.732	-64.644	-40.277	8.803
1100	21.005	84.246	71.699	13.802	-64.717	-37.837	7.517
1200	21.536	86.098	72.823	15.930	-64.758	-35.389	6.445
1300	21.993	87.840	73.911	18.107	-64.777	-32.942	5.538
1400	22.387	89.484	74.966	20.326	-64.773	-30.491	4.760
1500	22.729	91.041	75.986	22.582	-64.755	-28.042	4.086
1600	23.026	92.517	76.973	24.870	-64.727	-25.599	3.497
1700	23.285	93.921	77.929	27.186	-64.685	-23.152	2.976
1800	23.512	95.259	78.855	29.526	-64.638	-20.713	2.515
1900	23.712	96.536	79.752	31.888	-64.582	-18.272	2.102
2000	23.888	97.756	80.622	34.268	-64.523	-15.836	1.730
2100	24.045	98.926	81.466	36.665	-64.460	-13.403	1.395
2200	24.184	100.048	82.286	39.076	-64.397	-10.975	1.090
2300	24.308	101.125	83.081	41.501	-64.330	-8.545	.812
2400	24.419	102.162	83.855	43.937	-64.265	-6.121	.557
2500	24.519	103.161	84.607	46.384	-64.202	-3.703	.324
2600	24.609	104.125	85.340	48.841	-64.138	-1.282	.108
2700	24.690	105.055	86.053	51.306	-64.077	1.133	-.092
2800	24.764	105.954	86.747	53.778	-64.017	3.547	-.277
2900	24.830	106.824	87.425	56.258	-63.961	5.962	-.449
3000	24.891	107.667	88.086	58.744	-63.908	8.368	-.610
3100	24.947	108.484	88.731	61.236	-63.857	10.777	-.760
3200	24.998	109.277	89.360	63.734	-63.811	13.184	-.900
3300	25.045	110.047	89.976	66.236	-63.770	15.589	-1.032
3400	25.088	110.795	90.577	68.743	-63.731	17.994	-1.157
3500	25.128	111.523	91.165	71.253	-63.700	20.396	-1.274
3600	25.165	112.232	91.740	73.768	-63.671	22.799	-1.384
3700	25.198	112.922	92.304	76.286	-63.650	25.202	-1.489
3800	25.230	113.594	92.855	78.808	-63.631	27.605	-1.588
3900	25.259	114.250	93.395	81.332	-63.621	30.006	-1.681
4000	25.286	114.890	93.925	83.859	-63.615	32.407	-1.771
4100	25.312	115.514	94.444	86.389	-63.614	34.804	-1.855
4200	25.335	116.124	94.953	88.922	-63.620	37.208	-1.936
4300	25.357	116.721	95.452	91.456	-63.631	39.607	-2.013
4400	25.378	117.304	95.942	93.993	-63.647	42.007	-2.087
4500	25.397	117.875	96.423	96.532	-63.671	44.403	-2.157
4600	25.415	118.433	96.896	99.072	-63.698	46.810	-2.224
4700	25.432	118.980	97.360	101.615	-63.732	49.215	-2.288
4800	25.448	119.515	97.816	104.159	-63.772	51.619	-2.350
4900	25.464	120.040	98.264	106.705	-63.816	54.025	-2.410
5000	25.478	120.555	98.704	109.252	-63.867	56.427	-2.466
5100	25.491	121.060	99.138	111.800	-63.924	58.831	-2.521
5200	25.504	121.555	99.564	114.350	-63.985	61.241	-2.574
5300	25.516	122.041	99.984	116.901	-64.053	63.653	-2.625
5400	25.527	122.518	100.397	119.453	-64.126	66.059	-2.674
5500	25.538	122.986	100.803	122.006	-64.206	68.473	-2.721
5600	25.548	123.446	101.203	124.561	-64.290	70.883	-2.766
5700	25.558	123.899	101.598	127.116	-64.382	73.296	-2.810
5800	25.567	124.343	101.986	129.672	-64.478	75.713	-2.853
5900	25.576	124.780	102.369	132.229	-64.580	78.133	-2.894
6000	25.584	125.210	102.746	134.787	-64.688	80.547	-2.934

Dec. 31, 1960; Sept. 30, 1964; June 30, 1970

CHLOROFLUOROMETHANE (CH_2ClF) (IDEAL GAS) GFW = 68.4785

Point Group C_s

ΔHf°_0 = [-60.9 ± 3] kcal/mol

$S^\circ_{298.15}$ = 63.17 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-62.6 ± 3] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2993 (1)	1068 (1)	3048 (1)
1470 (1)	760 (1)	1236 (1)
1351 (1)	385 (1)	1004 (1)

Bond Distance: C-H = 1.078 Å C-Cl = 1.759 Å C-F = 1.378 Å

Bond Angle: H-C-H = 111°54' F-C-Cl = 110° H-C-Cl = 109°06' σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = 4.8154 x 10^{-115} g^3 cm^6

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl, in the CF_4 to CCl_4 series and CHF_3 to $CHCl_3$ series, follows a regular pattern (see CCl_2F_2 and $CHCl_2F$ tables). We make the assumption that this same regular variation occurs also in the CH_2F_2 to CH_2Cl_2 series. Thus, the difference between the atomization energies of CH_2F_2 and CH_2Cl_2 is divided into two unequal parts which fall into the pattern established in the CF_4 and CHF_3 sequences. We adopt a heat of atomization of 385.5 kcal which corresponds to a $\Delta Hf^\circ_{298}(CH_2ClF, g)$ = -62.6 kcal/mol. The changes, in kcal, in the heat of atomization by successive replacement of F by Cl are tabulated, below for all three series.

CF_4		
43.8		
CF_3Cl	CHF_3	
41.6	41.4	
CF_2Cl_2	CHF_2Cl	CH_2F_2
38.5	37.3	35.0
$CFCl_3$	$CHFCl_2$	CH_2FCl
36.0	33.0	29.7
CCl_4	$CHCl_3$	CH_2Cl_2

Heat Capacity and Entropy

Plyler and Benedict (1) assigned the vibrational frequencies from the infrared and Raman data for the liquid. The molecular structure was obtained from the microwave measurements of Muller (2). The individual moments of inertia are I_A = 2.008 x 10^{-39} g cm^2, I_B = 16.241 x 10^{-39} g cm^2, and I_C = 14.766 x 10^{-39} g cm^2.

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Dichloromethane (CH_2Cl_2)

(Ideal Gas) GFW = 84.9331

		gibbs/mol			kcal/mol		
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.830	-21.190	-21.190	INFINITE
100	8.547	53.781	73.991	-2.021	-21.850	-20.253	44.264
200	10.126	60.160	65.619	-1.092	-22.328	-18.481	20.195
298	12.164	64.574	64.574	.000	-22.830	-16.485	12.084
300	12.204	64.650	64.575	.023	-22.839	-16.446	11.981
400	14.237	68.446	65.078	1.347	-23.285	-14.245	7.783
500	15.933	71.811	66.095	2.858	-23.645	-11.941	5.220
600	17.296	74.841	67.304	4.522	-23.928	-9.573	3.487
700	18.403	77.593	68.580	6.309	-24.146	-7.162	2.236
800	19.321	80.113	69.867	8.197	-24.309	-4.725	1.291
900	20.095	82.434	71.136	10.168	-24.427	-2.270	.551
1000	20.755	84.586	72.375	12.212	-24.501	.195	-.043
1100	21.322	86.592	73.577	14.316	-24.543	2.667	-.530
1200	21.809	88.469	74.741	16.474	-24.555	5.143	-.937
1300	22.231	90.231	75.865	18.676	-24.548	7.616	-1.280
1400	22.596	91.892	76.951	20.918	-24.520	10.092	-1.575
1500	22.913	93.462	78.000	23.194	-24.480	12.563	-1.830
1600	23.190	94.950	79.013	25.499	-24.431	15.028	-2.053
1700	23.431	96.363	79.993	27.830	-24.370	17.496	-2.249
1800	23.644	97.709	80.940	30.184	-24.303	19.954	-2.423
1900	23.831	98.992	81.856	32.558	-24.229	22.414	-2.578
2000	23.996	100.219	82.744	34.950	-24.152	24.866	-2.717
2100	24.143	101.393	83.604	37.357	-24.071	27.315	-2.843
2200	24.274	102.520	84.439	39.778	-23.991	29.758	-2.956
2300	24.391	103.601	85.249	42.211	-23.908	32.202	-3.060
2400	24.495	104.642	86.035	44.656	-23.826	34.641	-3.154
2500	24.589	105.644	86.799	47.110	-23.747	37.072	-3.241
2600	24.674	106.610	87.543	49.573	-23.668	39.506	-3.321
2700	24.751	107.542	88.266	52.045	-23.591	41.931	-3.394
2800	24.820	108.444	88.971	54.523	-23.518	44.358	-3.462
2900	24.883	109.316	89.658	57.008	-23.448	46.782	-3.526
3000	24.941	110.160	90.327	59.500	-23.381	49.200	-3.584
3100	24.994	110.979	90.980	61.996	-23.318	51.619	-3.639
3200	25.042	111.773	91.618	64.498	-23.260	54.035	-3.690
3300	25.086	112.545	92.240	67.005	-23.207	56.450	-3.738
3400	25.127	113.294	92.848	69.515	-23.158	58.864	-3.784
3500	25.165	114.023	93.443	72.030	-23.116	61.272	-3.826
3600	25.199	114.732	94.025	74.548	-23.078	63.684	-3.866
3700	25.231	115.423	94.594	77.070	-23.047	66.096	-3.904
3800	25.261	116.097	95.151	79.594	-23.020	68.505	-3.940
3900	25.289	116.753	95.696	82.122	-23.000	70.915	-3.974
4000	25.315	117.394	96.231	84.652	-22.986	73.323	-4.006
4100	25.338	118.019	96.754	87.185	-22.976	75.727	-4.037
4200	25.361	118.630	97.268	89.720	-22.974	78.137	-4.066
4300	25.382	119.227	97.772	92.257	-22.977	80.541	-4.094
4400	25.401	119.811	98.266	94.796	-22.985	82.951	-4.120
4500	25.420	120.382	98.751	97.337	-23.000	85.352	-4.145
4600	25.437	120.941	99.228	99.880	-23.018	87.766	-4.170
4700	25.453	121.488	99.695	102.424	-23.043	90.177	-4.193
4800	25.468	122.024	100.155	104.971	-23.072	92.584	-4.215
4900	25.482	122.549	100.607	107.518	-23.107	94.997	-4.237
5000	25.496	123.064	101.051	110.067	-23.146	97.404	-4.258
5100	25.509	123.569	101.487	112.617	-23.191	99.816	-4.277
5200	25.521	124.065	101.917	115.169	-23.239	102.229	-4.297
5300	25.532	124.551	102.339	117.721	-23.294	104.644	-4.315
5400	25.543	125.028	102.755	120.275	-23.353	107.056	-4.333
5500	25.553	125.497	103.164	122.830	-23.417	109.474	-4.350
5600	25.563	125.957	103.567	125.386	-23.485	111.887	-4.367
5700	25.572	126.410	103.964	127.942	-23.560	114.301	-4.38
5800	25.581	126.855	104.355	130.500	-23.638	116.723	-4.398
5900	25.589	127.292	104.740	133.059	-23.721	119.146	-4.413
6000	25.597	127.722	105.119	135.618	-23.809	121.563	-4.428

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1968

DICHLOROMETHANE (CH_2Cl_2) (IDEAL GAS) GFW = 84.9331

Point Group C_{2v}

$\Delta Hf^\circ_0 = -21.19 \pm 0.3$ kcal/mol

$S^\circ_{298.15} = 64.574 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -22.83 \pm 0.3$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2999 (1)	282 (1)	898 (1)
1467 (1)	1153 (1)	1268 (1)
717 (1)	3040 (1)	758 (1)

Bond Distances: C-H = 1.068Å C-Cl = 1.7724Å

Bond Angles: H-C-H = 112° Cl-C-Cl = 111.8° $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 1.8686 \times 10^{-114}\ g^3cm^6$.

Heat of Formation

Hu and Sinke (1) have measured the heat of combustion of $CH_2Cl_2(\ell)$ in the rotating bomb calorimeter, using As_2O_3 solution as the reducing agent. They reported $\Delta Hc^\circ_{298} = -144.00$ kcal/mole for $CH_2Cl_2(\ell) + O_2(g) \rightarrow CO_2(g) + 2HCl(600H_2O, aq)$ which leads to $\Delta Hf^\circ_{298}(CH_2Cl_2, \ell) = -29.70$ kcal/mol, using $\Delta Hf^\circ_{298} = -94.051$ and -39.823 kcal/mol for $CO_2(g)$ and $HCl(600H_2O, aq)$, respectively (2). The standard deviation of five combustion runs was 0.12 kcal/mol. Employing the heat of vaporization of $CH_2Cl_2(\ell)$ at 298°K as 6.87 kcal/mol (3), we obtain $\Delta Hf^\circ_{298}(CH_2Cl_2, g) = -22.83$ kcal/mol which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Eftring (5), re-evaluated the heat of combustion of dichloromethane at 18.7°C as $\Delta E^\circ_c/M = -1701.4$ cal/g for $CH_2Cl_2(\ell) + O_2(g) \rightarrow CO_2(g) + 2HCl(600H_2O, aq)$. This value needs to be further corrected for a change in the heat of oxidation of As_2O_3 (6) and calculated to 25°C to give $\Delta E^\circ_{c298} = \Delta Hc^\circ_{298} = -144.89$ kcal/mol, $\Delta Hf^\circ_{298}(CH_2Cl_2, \ell) = -28.80$ kcal/mol and $\Delta Hf^\circ_{298}(CH_2Cl_2, g) = -21.93$ kcal/mol.

J. Lacher et al. (7) have measured the heat of hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C as -40.07 kcal/mol. Correction to 298°K gives $\Delta Hf^\circ_{298}(CH_2Cl_2, g) = -23.05$ kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy

The bond distances and angles have been determined from the microwave spectra by R. J. Myers and W. D. Gwinn (8). The three principal moments of inertia are $I_A = 2.630 \times 10^{-39}$, $I_B = 2.5623 \times 10^{-38}$ and $I_C = 2.7727 \times 10^{-38}$ g cm^2.

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (9), based on infrared and Raman spectra by Shimanouchi and Syzuki (10), **Palma** et al. (11), and **Welsh** et al. (12).

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Difluoromethane (CH_2F_2)

(Ideal Gas) GFW = 52.0239

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.555	- 105.879	- 105.879	INFINITE
100	8.005	49.445	67.038	- 1.759	- 106.551	- 104.967	229.404
200	8.766	55.182	59.818	- .927	- 107.100	- 103.180	112.750
298	10.243	58.935	58.935	.000	- 107.710	- 101.127	74.128
300	10.277	58.998	58.935	.019	- 107.722	- 101.087	73.642
400	12.216	62.217	59.361	1.142	- 108.309	- 98.784	53.973
500	14.095	65.149	60.229	2.460	- 108.816	- 96.343	42.111
600	15.719	67.866	61.278	3.953	- 109.233	- 93.808	34.169
700	17.079	70.394	62.402	5.595	- 109.569	- 91.208	28.476
800	18.215	72.751	63.550	7.361	- 109.834	- 88.567	24.195
900	19.169	74.953	64.696	9.232	- 110.038	- 85.896	20.858
1000	19.975	77.016	65.826	11.190	- 110.189	- 83.206	18.185
1100	20.659	78.953	66.932	13.223	- 110.297	- 80.503	15.994
1200	21.241	80.776	68.011	15.318	- 110.369	- 77.789	14.167
1300	21.740	82.496	69.059	17.468	- 110.415	- 75.072	12.621
1400	22.169	84.124	70.078	19.664	- 110.436	- 72.351	11.295
1500	22.538	85.666	71.066	21.900	- 110.441	- 69.629	10.145
1600	22.858	87.131	72.025	24.170	- 110.434	- 66.912	9.140
1700	23.137	88.525	72.955	26.470	- 110.413	- 64.190	8.252
1800	23.381	89.855	73.857	28.796	- 110.385	- 61.475	7.464
1900	23.594	91.125	74.733	31.145	- 110.348	- 58.757	6.759
2000	23.782	92.340	75.583	33.514	- 110.306	- 56.042	6.124
2100	23.949	93.504	76.409	35.901	- 110.260	- 53.330	5.550
2200	24.097	94.622	77.211	38.303	- 110.214	- 50.622	5.029
2300	24.228	95.696	77.992	40.720	- 110.163	- 47.912	4.553
2400	24.346	96.730	78.751	43.149	- 110.114	- 45.206	4.117
2500	24.452	97.726	79.490	45.589	- 110.066	- 42.506	3.716
2600	24.547	98.687	80.210	48.039	- 110.018	- 39.802	3.346
2700	24.633	99.615	80.912	50.498	- 109.971	- 37.103	3.003
2800	24.711	100.512	81.596	52.965	- 109.925	- 34.406	2.686
2900	24.781	101.380	82.263	55.439	- 109.883	- 31.705	2.389
3000	24.846	102.222	82.915	57.921	- 109.843	- 29.016	2.114
3100	24.904	103.037	83.551	60.408	- 109.804	- 26.321	1.856
3200	24.958	103.829	84.172	62.902	- 109.769	- 23.628	1.614
3300	25.007	104.598	84.779	65.400	- 109.739	- 20.938	1.387
3400	25.053	105.345	85.373	67.903	- 109.711	- 18.247	1.173
3500	25.094	106.072	85.954	70.410	- 109.690	- 15.556	.971
3600	25.133	106.779	86.523	72.922	- 109.670	- 12.867	.781
3700	25.169	107.468	87.080	75.437	- 109.658	- 10.177	.601
3800	25.202	108.140	87.625	77.955	- 109.649	- 7.485	.430
3900	25.232	108.795	88.160	80.477	- 109.647	- 4.799	.269
4000	25.261	109.434	88.684	83.002	- 109.648	- 2.108	.115
4100	25.287	110.058	89.197	85.529	- 109.656	.576	- .031
4200	25.312	110.668	89.701	88.059	- 109.670	3.269	- .170
4300	25.335	111.264	90.196	90.592	- 109.688	5.957	- .303
4400	25.357	111.846	90.681	93.126	- 109.714	8.644	- .429
4500	25.377	112.417	91.158	95.663	- 109.745	11.330	- .550
4600	25.396	112.974	91.626	98.202	- 109.781	14.026	- .666
4700	25.414	113.521	92.086	100.742	- 109.825	16.719	- .777
4800	25.431	114.056	92.538	103.284	- 109.874	19.414	- .884
4900	25.447	114.581	92.983	105.828	- 109.929	22.109	- .986
5000	25.462	115.095	93.420	108.374	- 109.990	24.801	- 1.084
5100	25.476	115.599	93.850	110.921	- 110.059	27.492	- 1.178
5200	25.489	116.094	94.273	113.469	- 110.133	30.194	- 1.269
5300	25.502	116.580	94.689	116.018	- 110.214	32.899	- 1.357
5400	25.513	117.056	95.099	118.569	- 110.302	35.593	- 1.441
5500	25.525	117.525	95.503	121.121	- 110.396	38.298	- 1.522
5600	25.535	117.985	95.900	123.674	- 110.497	41.002	- 1.600
5700	25.546	118.437	96.291	126.228	- 110.605	43.707	- 1.676
5800	25.555	118.881	96.677	128.783	- 110.719	46.414	- 1.749
5900	25.564	119.318	97.057	131.339	- 110.840	49.127	- 1.820
6000	25.573	119.748	97.432	133.896	- 110.967	51.832	- 1.888

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1969

DIFLUOROMETHANE (CH_2F_2) (IDEAL GAS) GFW = 52.0239

Point Group C_{2v}

ΔHf°_0 = -105.9 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 58.93 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -107.7 ± 0.4 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2949 (1)	529 (1)	1176 (1)
1508 (1)	1262 (1)	1435 (1)
1116 (1)	3013 (1)	1090 (1)

Bond Distances: C-F = 1.358 ± 0.001 Å C-H = 1.092 ± 0.003 Å

Bond Angles: F-C-F = 108° 17' ± 6' H-C-H = 111° 52' ± 25' $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 1.2272 \times 10^{-115}$ g^3 cm^6

Heat of Formation

Neugebauer and Margrave (1) measured the enthalpy of combustion of CH_2F_2. Their result for the combustion reaction

$$CH_2F_2(g) + O_2(g) \rightarrow CO_2(g) + 2HF\cdot 21.5\ H_2O$$

was ΔH_{298} = -139.84 ± 0.22 kcal/mole. Using $\Delta Hf^\circ_{298}(HF\cdot 21.5\ H_2O)$ = -76.75 ± 0.1 kcal/mol (2), obtained with dilution data compiled by Parker (3), we derive,

$$\Delta Hf^\circ_{298}(CH_2F_2,\ g) = -107.7 \pm 0.4\ \text{kcal/mol},$$

from Margrave's data.

Heat Capacity and Entropy

The vibrational frequencies are average values from the infrared studies of Stewart and Nielsen (4) and Plyler and Benedict (5). Individual moments of inertia are calculated from the rotational constants reported by Lide (6) with the result $I_A = 1.7082 \times 10^{-39}$ g cm^2, $I_B = 7.9160 \times 10^{-39}$ g cm^2, and $I_C = 9.0754 \times 10^{-39}$ g cm^2. The molecular structure data are from the microwave studies of Lide (6) and are in excellent agreement with electron-diffraction studies of Brockway, Thornton, and Bartell whose results are reported in the Annual Review of Physical Chemistry (7).

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Formaldehyde (CH_2O)

(Ideal Gas) Mol. Wt. = 30.027

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	,000	,000	INFINITE	- 2,395	- 26,782	- 26,782	INFINITE
100	7,949	43,479	59,481	- 1,600	- 27,116	- 26,928	58,849
200	8,007	48,996	53,016	- ,804	- 27,341	- 26,669	29,141
298	8,461	52,261	52,261	,000	- 27,700	- 26,266	19,253
300	8,475	52,313	52,261	,016	- 27,708	- 26,258	19,128
400	9,385	54,869	52,603	,906	- 28,113	- 25,713	14,048
500	10,460	57,077	53,281	1,898	- 28,505	- 25,068	10,957
600	11,524	59,079	54,083	2,998	- 28,860	- 24,347	8,868
700	12,505	60,931	54,931	4,200	- 29,174	- 23,568	7,358
800	13,380	62,659	55,790	5,495	- 29,443	- 22,749	6,214
900	14,149	64,280	56,644	6,872	- 29,672	- 21,898	5,317
1000	14,817	65,806	57,485	8,322	- 29,860	- 21,024	4,595
1100	15,395	67,246	58,307	9,833	- 30,017	- 20,134	4,000
1200	15,893	68,608	59,110	11,398	- 30,146	- 19,228	3,502
1300	16,322	69,897	59,890	13,009	- 30,256	- 18,314	3,079
1400	16,693	71,121	60,649	14,660	- 30,347	- 17,391	2,715
1500	17,013	72,284	61,386	16,346	- 30,427	- 16,461	2,398
1600	17,291	73,391	62,102	18,062	- 30,498	- 15,531	2,121
1700	17,534	74,446	62,798	19,803	- 30,558	- 14,592	1,876
1800	17,746	75,455	63,473	21,567	- 30,615	- 13,652	1,658
1900	17,932	76,419	64,129	23,351	- 30,666	- 12,707	1,462
2000	18,095	77,343	64,767	25,153	- 30,715	- 11,761	1,235
2100	18,240	78,230	65,387	26,970	- 30,761	- 10,811	1,125
2200	18,369	79,081	65,990	28,800	- 30,810	- 9,862	,980
2300	18,483	79,900	66,577	30,643	- 30,856	- 8,907	,846
2400	18,585	80,689	67,149	32,497	- 30,905	- 7,950	,724
2500	18,677	81,450	67,706	34,360	- 30,957	- 6,997	,612
2600	18,760	82,184	68,249	36,232	- 31,010	- 6,035	,507
2700	18,834	82,893	68,778	38,112	- 31,066	- 5,075	,411
2800	18,902	83,580	69,295	39,998	- 31,125	- 4,111	,321
2900	18,963	84,244	69,799	41,892	- 31,188	- 3,142	,237
3000	19,019	84,888	70,291	43,791	- 31,254	- 2,176	,159
3100	19,070	85,512	70,772	45,695	- 31,322	- 1,205	,085
3200	19,116	86,119	71,242	47,605	- 31,396	- ,233	,016
3300	19,159	86,707	71,702	49,518	- 31,474	,741	- ,049
3400	19,198	87,280	72,152	51,436	- 31,556	1,718	- ,110
3500	19,235	87,837	72,592	53,358	- 31,643	2,697	- ,168
3600	19,268	88,379	73,023	55,283	- 31,734	3,680	- ,223
3700	19,299	88,908	73,445	57,212	- 31,831	4,666	- ,276
3800	19,327	89,423	73,859	59,143	- 31,932	5,657	- ,325
3900	19,354	89,925	74,264	61,077	- 32,039	6,647	- ,372
4000	19,379	90,415	74,662	63,014	- 32,150	7,640	- ,417
4100	19,401	90,894	75,052	64,953	- 32,266	8,634	- ,460
4200	19,423	91,362	75,435	66,894	- 32,389	9,636	- ,501
4300	19,443	91,819	75,811	68,837	- 32,516	10,637	- ,541
4400	19,462	92,267	76,180	70,782	- 32,649	11,639	- ,578
4500	19,479	92,704	76,542	72,729	- 32,787	12,645	- ,614
4600	19,496	93,132	76,898	74,678	- 32,930	13,662	- ,649
4700	19,511	93,552	77,248	76,628	- 33,079	14,677	- ,682
4800	19,526	93,963	77,592	78,580	- 33,232	15,695	- ,715
4900	19,539	94,366	77,930	80,534	- 33,390	16,714	- ,745
5000	19,552	94,760	78,263	82,488	- 33,554	17,736	- ,775
5100	19,564	95,148	78,590	84,444	- 33,725	18,763	- ,804
5200	19,576	95,528	78,912	86,401	- 33,899	19,793	- ,832
5300	19,587	95,901	79,229	88,359	- 34,078	20,834	- ,859
5400	19,597	96,267	79,541	90,318	- 34,264	21,867	- ,885
5500	19,607	96,627	79,849	92,278	- 34,454	22,911	- ,910
5600	19,616	96,980	80,151	94,240	- 34,650	23,952	- ,935
5700	19,625	97,327	80,450	96,202	- 34,851	24,998	- ,958
5800	19,633	97,669	80,744	98,164	- 35,058	26,051	- ,982
5900	19,641	98,004	81,033	100,128	- 35,269	27,110	- 1,004
6000	19,648	98,334	81,319	102,093	- 35,485	28,164	- 1,026

March 31, 1961

FORMALDEHYDE (CH_2O) (IDEAL GAS) MOL. WT. = 30.027

$\Delta H^\circ_{f0} = -26.8 \pm 1.5$ kcal. mole^{-1}

$\Delta H_{f\ 298.15} = -27.7 \pm 1.5$ kcal. mole^{-1}

Point Group C_{2v}

$S_{298.15} = 52.26 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.⁻¹	ω, cm.⁻¹
2766.4 (1)	2843.4 (1)
1746.07 (1)	1247.4 (1)
1500.6 (1)	1163.5 (1)

Bond Lengths and Angles C-H = 1.12 ± 0.01 Å C-O = 1.21 ± 0.01 Å ∡ H-C-H = 118 ± 2°

Moments of Inertia $I_A = 2.975 \times 10^{-40}$ g. cm.^{2} $I_B = 2.161 \times 10^{-39}$ g. cm.^{2} $I_C = 2.468 \times 10^{-39}$ g. cm.^{2}

$\sigma = 2$

Heats of Formation

M. Delepine and M. Badoche, Compt. rend. 214, 777 (1942), measured the heat of combustion of a formaldehyde polymer. Their value is revised to $\Delta H_{f\ 298.15} = -25.0$ kcal. mole^{-1} based on the following thermochemical cycle:

I	$C_{(c)} + 1/2O_{2(g)} + H_{2(g)} = \frac{1}{n}(CH_2O)_{n(c)}$	-42.3 kcal.
II	$\frac{1}{n}(CH_2O)_{n(c)} + H_2O = CH_2O(aq)$	2.4
III	$CH_2O(g) = CH_2O(aq)$	14.9

Equation I and II are based upon data listed by Delepine and Badoche. For reaction III Delepine and Badoche obtained 15 kcal. mole^{-1}. Whereas, F. Walker, J. Am. Chem. Soc. 55, 2821 (1933) obtained 14.8 kcal. mole^{-1}. A value of -27.7 kcal. mole^{-1} is obtained from the combustion experiments of H. von Wartenberg and B. Lerner-Steinberg, Z. angew. Chem. 38, 591 (1925). Corrections of -0.6 and 0.1 kcal. mole^{-1} were applied to obtain a heat of reaction at constant pressure and at 298.15°K.

Equilibrium constant determinations of reaction (IV) by R. H. Newton and B. F. Dodge, J. Am. Chem. Soc. 55, 4747 (1933), lead to a $\Delta H^\circ_{f\ 298.15} = -29.0$ kcal. mole^{-1}.

IV $H_{2(g)} + CO_{(g)} = H_2CO_{(g)}$

The value obtained from the measurements of Wartenberg and Lerner-Steinberg is believed to be the most reliable.

Heat Capacities and Entropies

Frequencies were measured by H. H. Blau and H. H. Nielsen, J. Molec. Spect. 1, 124 (1957) in the I. R. Microwave determinations of R. B. Lawrence and M. P. W. Strandberg, Phys. Rev. 83, 363 (1951), and those of G. Erlandson, J. Chem. Phys. 25, 579 (1956) are in essential agreement.

Methyl (CH_3)

(Ideal Gas) GFW = 15.03506

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.487	35.621	35.621	INFINITE
100	7.982	37.178	54.100	- 1.692	35.263	35.225	- 76.983
200	8.518	42.846	47.203	- .871	35.102	35.232	- 38.500
298	9.248	46.381	46.381	.000	34.820	35.354	- 25.915
300	9.262	46.438	46.381	.017	34.814	35.357	- 25.757
400	10.048	49.210	46.754	.983	34.492	35.586	- 19.443
500	10.815	51.536	47.483	2.026	34.168	35.897	- 15.690
600	11.541	53.572	48.332	3.144	33.858	36.271	- 13.212
700	12.231	55.404	49.213	4.333	33.569	36.698	- 11.458
800	12.888	57.080	50.093	5.589	33.307	37.163	- 10.152
900	13.510	58.634	50.957	6.910	33.073	37.659	- 9.145
1000	14.090	60.088	51.798	8.290	32.870	38.179	- 8.344
1100	14.624	61.456	52.615	9.726	32.694	38.718	- 7.693
1200	15.109	62.750	53.406	11.213	32.544	39.274	- 7.153
1300	15.547	63.977	54.172	12.746	32.412	39.839	- 6.698
1400	15.939	65.144	54.915	14.321	32.300	40.417	- 6.309
1500	16.289	66.256	55.634	15.933	32.199	41.001	- 5.974
1600	16.602	67.317	56.331	17.578	32.107	41.587	- 5.681
1700	16.880	68.332	57.007	19.252	32.026	42.185	- 5.423
1800	17.129	69.304	57.664	20.953	31.953	42.783	- 5.195
1900	17.350	70.236	58.301	22.677	31.886	43.388	- 4.991
2000	17.548	71.131	58.920	24.422	31.823	43.995	- 4.808
2100	17.726	71.992	59.522	26.186	31.764	44.606	- 4.642
2200	17.885	72.820	60.108	27.966	31.706	45.217	- 4.492
2300	18.028	73.618	60.678	29.762	31.651	45.834	- 4.355
2400	18.157	74.389	61.234	31.571	31.595	46.453	- 4.230
2500	18.274	75.132	61.775	33.393	31.538	47.069	- 4.115
2600	18.380	75.851	62.302	35.226	31.482	47.694	- 4.009
2700	18.476	76.546	62.817	37.069	31.424	48.317	- 3.911
2800	18.563	77.220	63.320	38.921	31.366	48.943	- 3.820
2900	18.643	77.873	63.810	40.781	31.305	49.576	- 3.736
3000	18.716	78.506	64.290	42.649	31.242	50.204	- 3.657
3100	18.783	79.121	64.758	44.524	31.179	50.837	- 3.584
3200	18.844	79.718	65.216	46.405	31.111	51.473	- 3.515
3300	18.901	80.299	65.665	48.293	31.040	52.110	- 3.451
3400	18.953	80.864	66.103	50.185	30.967	52.748	- 3.391
3500	19.001	81.414	66.533	52.083	30.889	53.390	- 3.334
3600	19.045	81.950	66.954	53.986	30.808	54.033	- 3.280
3700	19.087	82.472	67.366	55.892	30.720	54.682	- 3.230
3800	19.125	82.982	67.771	57.803	30.630	55.333	- 3.182
3900	19.161	83.479	68.167	59.717	30.534	55.985	- 3.137
4000	19.194	83.965	68.556	61.635	30.433	56.639	- 3.095
4100	19.225	84.439	68.937	63.556	30.328	57.292	- 3.054
4200	19.254	84.903	69.312	65.480	30.217	57.956	- 3.016
4300	19.281	85.356	69.680	67.406	30.100	58.614	- 2.979
4400	19.306	85.800	70.041	69.336	29.979	59.276	- 2.944
4500	19.330	86.234	70.396	71.268	29.851	59.940	- 2.911
4600	19.352	86.659	70.745	73.202	29.718	60.616	- 2.880
4700	19.374	87.075	71.088	75.138	29.580	61.290	- 2.850
4800	19.393	87.483	71.426	77.076	29.435	61.967	- 2.821
4900	19.412	87.883	71.757	79.017	29.286	62.647	- 2.794
5000	19.430	88.276	72.084	80.959	29.131	63.325	- 2.768
5100	19.447	88.661	72.405	82.903	28.968	64.010	- 2.743
5200	19.462	89.038	72.721	84.848	28.802	64.698	- 2.719
5300	19.477	89.409	73.033	86.795	28.629	65.396	- 2.697
5400	19.492	89.773	73.339	88.744	28.449	66.088	- 2.675
5500	19.505	90.131	73.641	90.693	28.263	66.787	- 2.654
5600	19.518	90.483	73.939	92.645	28.072	67.486	- 2.634
5700	19.531	90.828	74.232	94.597	27.875	68.192	- 2.615
5800	19.543	91.168	74.521	96.551	27.670	68.899	- 2.596
5900	19.554	91.502	74.806	98.506	27.461	69.617	- 2.579
6000	19.565	91.831	75.087	100.462	27.246	70.325	- 2.562

Dec. 31, 1960; June 30, 1961; Dec. 31, 1962; June 30, 1969

METHYL (CH_3) (IDEAL GAS) GFW = 15.03506

CH_3

Point Group D_{3h}

ΔHf°_0 = 35.62 ± 0.2 kcal/mol

$S^\circ_{298.15}$ = 46.38 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 34.82 ± 0.2 kcal/mol

Electronic Levels and Multiplicities

ϵ_i, cm^{-1}	g_i
0	2
46205	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[3002] (1)
580 (1)
[3184] (2)
1383 (2)

Bond Distance: C-H = 1.079 Å

Bond Angle: H-C-H = 120°

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 4.99 \times 10^{-119}\ g^3\ cm^6$

Heat of Formation

W. A. Chupka (1) has measured the photoionization spectrum of methane and from the onset of CH_3^+ production has reported $D_0(CH_3\text{-}H) = 103.244 \pm 0.12$ kcal. This value was corrected for the thermal rotation energy of the fragment ions and is the value adopted here.

V. H. Dibeler et al. (2) had earlier reported $D_0(CH_3\text{-}H) = 101.7 \pm 0.5$ kcal but they did not apply the rotational energy correction, which would bring them closer to Chupka.

The photoionization values are in good agreement with earlier electron impact determinations as summarized by Stevenson (3) who gives $D_0(CH_3\text{-}H) = 101.9 \pm 1$ kcal. Kinetic determinations have been recently reviewed by Kerr (4) and yield $D_0(CH_3\text{-}H) = 102.5 \pm 1$ kcal again in excellent agreement.

Heat Capacity and Entropy

The structure, bond length, angles and electronic levels are those reported by Herzberg (5). A set of vibrational frequencies have been reported by Andrews and Pimentel (6) in an argon matrix, of which only two were observed. Milligan and Jacox (7) observed $\nu_2 = 611\ cm^{-1}$ in an argon matrix and disagreed with Andrews and Pimentel who reported 730 cm^{-1}. Later Tan and Pimentel (8) agreed that the earlier values were for a methyl radical interacting with an alkali halide molecule. This would affect the ν_2 mode strongest, thus, we adopt the remaining in plane frequencies which appear to be of the correct magnitudes. The ν_2 mode is taken from the analysis of Herzberg (5) since this represents the gas phase molecule and is in reasonable agreement with the matrix value of Milligan and Jacox. The uncertainty in the entropy reflects the uncertainties in the vibrational frequencies.

The individual moments of inertia are $I_A = I_B = 2.923 \times 10^{-40}\ g\ cm^2$, $I_C = 5.846 \times 10^{-40}\ g\ cm^2$.

References:
1. W. A. Chupka, J. Chem. Phys. 48, 2337 (1968).
2. V. H. Dibeler, M. Krauss, R. M. Reese and F. N. Harllee, J. Chem. Phys. 42, 3791 (1965).
3. D. P. Stevenson, Discuss. Faraday Soc. 10, 35 (1951).
4. J. A. Kerr, Chem. Revs. 66, 465 (1966).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
6. L. Andrews and G. C. Pimentel, J. Chem. Phys. 47, 3637 (1967).
7. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 5146 (1967).
8. L. Y. Tan and G. C. Pimentel, J. Chem. Phys. 48, 5202 (1968).

Methyl Chloride (CH_3Cl)

(Ideal Gas) Mol. Wt. = 50.492

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.489	-18.764	-18.764	INFINITE
100	7.955	46.811	63.749	-1.694	-19.472	-18.214	39.806
200	8.399	52.409	56.828	-.884	-20.005	-16.771	18.326
298	9.726	55.987	55.987	.000	-20.660	-15.046	11.029
300	9.756	56.047	55.987	.018	-20.673	-15.012	10.935
400	11.496	59.090	56.390	1.080	-21.313	-13.026	7.117
500	13.167	61.838	57.209	2.315	-21.872	-10.888	4.759
600	14.639	64.372	58.194	3.707	-22.343	-8.646	3.149
700	15.917	66.727	59.247	5.236	-22.731	-6.330	1.976
800	17.031	68.927	60.321	6.885	-23.043	-3.966	1.083
900	18.005	70.990	61.393	8.637	-23.290	-1.566	.380
1000	18.857	72.932	62.451	10.481	-23.476	.857	-.187
1100	19.603	74.765	63.488	12.405	-23.613	3.298	-.655
1200	20.253	76.500	64.501	14.399	-23.706	5.749	-1.047
1300	20.822	78.144	65.487	16.453	-23.768	8.205	-1.379
1400	21.318	79.705	66.448	18.561	-23.799	10.669	-1.665
1500	21.752	81.191	67.381	20.715	-23.811	13.132	-1.913
1600	22.133	82.607	68.289	22.909	-23.808	15.592	-2.130
1700	22.467	83.959	69.171	25.140	-23.786	18.057	-2.321
1800	22.761	85.252	70.029	27.401	-23.755	20.515	-2.491
1900	23.021	86.490	70.863	29.691	-23.712	22.975	-2.643
2000	23.251	87.677	71.674	32.005	-23.663	25.430	-2.779
2100	23.456	88.816	72.464	34.340	-23.608	27.885	-2.902
2200	23.638	89.912	73.232	36.695	-23.551	30.332	-3.013
2300	23.802	90.966	73.980	39.067	-23.489	32.784	-3.115
2400	23.948	91.982	74.709	41.455	-23.428	35.231	-3.208
2500	24.080	92.962	75.420	43.856	-23.367	37.670	-3.293
2600	24.199	93.909	76.113	46.270	-23.304	40.112	-3.372
2700	24.307	94.825	76.789	48.696	-23.243	42.546	-3.444
2800	24.404	95.710	77.449	51.131	-23.184	44.984	-3.511
2900	24.493	96.568	78.094	53.576	-23.126	47.421	-3.574
3000	24.574	97.400	78.723	56.030	-23.072	49.848	-3.631
3100	24.648	98.207	79.339	58.491	-23.018	52.278	-3.685
3200	24.716	98.991	79.941	60.959	-22.970	54.705	-3.736
3300	24.779	99.752	80.530	63.434	-22.926	57.134	-3.784
3400	24.836	100.493	81.106	65.915	-22.884	59.557	-3.828
3500	24.889	101.214	81.670	68.401	-22.850	61.980	-3.870
3600	24.938	101.915	82.223	70.892	-22.819	64.406	-3.910
3700	24.983	102.599	82.765	73.389	-22.795	66.830	-3.947
3800	25.025	103.266	83.295	75.889	-22.773	69.253	-3.983
3900	25.064	103.917	83.816	78.394	-22.760	71.674	-4.016
4000	25.101	104.552	84.326	80.902	-22.752	74.096	-4.048
4100	25.134	105.172	84.827	83.414	-22.749	76.514	-4.078
4200	25.166	105.778	85.319	85.929	-22.753	78.939	-4.107
4300	25.196	106.371	85.802	88.447	-22.763	81.355	-4.135
4400	25.223	106.950	86.276	90.968	-22.778	83.779	-4.161
4500	25.249	107.517	86.741	93.491	-22.801	86.196	-4.186
4600	25.273	108.072	87.199	96.017	-22.828	88.625	-4.210
4700	25.296	108.616	87.649	98.546	-22.862	91.049	-4.234
4800	25.318	109.149	88.091	101.077	-22.902	93.472	-4.256
4900	25.338	109.671	88.526	103.609	-22.947	95.900	-4.277
5000	25.357	110.183	88.954	106.144	-22.998	98.322	-4.297
5100	25.375	110.686	89.376	108.681	-23.057	100.746	-4.317
5200	25.392	111.179	89.790	111.219	-23.119	103.173	-4.336
5300	25.408	111.662	90.198	113.759	-23.189	105.612	-4.355
5400	25.423	112.137	90.600	116.301	-23.265	108.039	-4.372
5500	25.438	112.604	90.996	118.844	-23.347	110.471	-4.390
5600	25.452	113.063	91.386	121.388	-23.434	112.898	-4.406
5700	25.465	113.513	91.770	123.934	-23.528	115.335	-4.422
5800	25.477	113.956	92.149	126.481	-23.629	117.772	-4.438
5900	25.489	114.392	92.522	129.030	-23.735	120.213	-4.453
6000	25.500	114.820	92.890	131.579	-23.847	122.649	-4.467

Dec. 31, 1960; Sept. 30, 1964

METHYL CHLORIDE (CH_3Cl) (IDEAL GAS) MOL. WT. = 50.492

Point Group C_{3v}

$S^\circ_{298.15}$ = 55.99 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -18.76 ± 0.17 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -20.66 ± 0.17 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
2928 (1)	3047 (2)
1355 (1)	1460 (2)
732 (1)	1020 (2)

Bond Distance: C-H = 1.0959Å C-Cl = 1.7812Å

Bond Angle: H-C-H = 108° H-C-Cl = 110°54'

$\sigma = 3$

Product of the Moments of Inertia: $I_A I_B I_C = 21.460 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was measured using hydrogenation to give methane and hydrogen chloride, by J. R. Lacher, E. Emery, E. Bohmfalk and J. D. Park, J. Phys. Chem. 60, 492 (1956). The value adopted was recalculated using JANAF auxiliary data for methane and HCl.

Heat Capacity and Entropy.

The vibrational frequencies were tabulated by E. K. Plyler and W. S. Benedict, J. Research Natl. Bur. Standards 47, 202 (1951). C. C. Costain, J. Chem. Phys. 29, 864 (1958) has calculated the bond distances and angles based on an isotopic substitution method. From these the individual moments of inertia were calculated to be $I_A = 0.5262 \times 10^{-39}$ g. cm.^{2} and $I_B = I_C = 6.3863 \times 10^{-39}$ g. cm.^{2}

Trichloromethylsilane $(Si(CH_3)Cl_3)$

(Ideal Gas) Mol. Wt. - 149.496 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	24,470	83,900	83,900	,000	- 126,400	- 111,898	82,020
300	24,530	84,052	83,900	,045	- 126,410	- 111,808	81,448
400	27,420	91,521	84,899	2,649	- 126,846	- 106,873	58,390
500	29,610	97,883	86,875	5,504	- 127,188	- 101,838	44,511
600	31,340	103,442	89,183	8,555	- 127,441	- 96,744	35,237
700	32,750	108,382	91,579	11,762	- 127,621	- 91,613	28,601
800	33,930	112,834	93,962	15,098	- 127,733	- 86,459	23,618
900	34,950	116,891	96,288	18,543	- 127,792	- 81,295	19,740
1000	35,820	120,620	98,537	22,083	- 127,802	- 76,128	16,637
1100	36,580	124,070	100,703	25,704	- 127,771	- 70,963	14,098
1200	37,230	127,282	102,786	29,395	- 127,705	- 65,799	11,983
1300	37,800	130,285	104,787	33,147	- 127,612	- 60,644	10,195
1400	38,290	133,104	106,710	36,952	- 127,499	- 55,499	8,663
1500	38,720	135,761	108,559	40,803	- 127,374	- 50,360	7,337

December 31, 1960.

Trichloromethylsilane $(Si(CH_3)Cl_3)$ (Ideal Gas)

Mol. Wt. = 149.496

ΔH_f° 298.15 = [-126.4] kcal. mole^{-1}

$S^\circ_{298.15}$ = 83.9 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Heat of Formation. ΔH_f° 298.15 was estimated.

Heat Capacity and Entropy. C_p and $S^\circ_{298.15}$ were taken from G. J. Janz, Y. Mikawa, and F. Behnke, private communication, March 16, 1960.

Fluoromethane (CH_3F)

(Ideal Gas) Mol. Wt. 34.035

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.422	-54.079	-54.079	INFINITE
100	7.949	44.362	60.636	-1.627	-54.784	-53.507	116.934
200	8.085	49.890	54.036	-.829	-55.319	-52.042	56.867
298	8.963	53.252	53.252	.000	-56.000	-50.293	36.864
300	8.988	53.308	53.252	.017	-56.014	-50.258	36.611
400	10.556	56.099	53.622	.991	-56.712	-48.232	26.351
500	12.256	58.638	54.375	2.132	-57.342	-46.038	20.122
600	13.832	61.015	55.285	3.438	-57.880	-43.726	15.926
700	15.226	63.254	56.265	4.892	-58.329	-41.328	12.903
800	16.447	65.369	57.272	6.477	-58.695	-38.875	10.620
900	17.512	67.369	58.284	8.176	-58.989	-36.379	8.834
1000	18.440	69.263	59.288	9.975	-59.216	-33.855	7.399
1100	19.246	71.059	60.277	11.860	-59.388	-31.311	6.221
1200	19.948	72.765	61.247	13.821	-59.513	-28.750	5.236
1300	20.557	74.386	62.196	15.847	-59.604	-26.184	4.402
1400	21.087	75.929	63.122	17.929	-59.662	-23.609	3.685
1500	21.550	77.400	64.076	20.062	-59.698	-21.031	3.064
1600	21.953	78.804	64.906	22.237	-59.717	-18.457	2.521
1700	22.307	80.146	65.763	24.451	-59.717	-15.875	2.041
1800	22.618	81.430	66.598	26.697	-59.706	-13.299	1.615
1900	22.893	82.660	67.411	28.973	-59.683	-10.720	1.233
2000	23.135	83.841	68.203	31.275	-59.652	-8.143	.890
2100	23.351	84.975	68.975	33.599	-59.616	-5.568	.579
2200	23.542	86.066	69.728	35.944	-59.576	-2.997	.298
2300	23.714	87.116	70.461	38.307	-59.531	-.424	.040
2400	23.867	88.129	71.176	40.686	-59.487	2.146	-.195
2500	24.006	89.106	71.874	43.080	-59.442	4.709	-.412
2600	24.130	90.050	72.555	45.487	-59.395	7.277	-.612
2700	24.243	90.963	73.220	47.906	-59.350	9.839	-.796
2800	24.345	91.846	73.869	50.335	-59.304	12.399	-.968
2900	24.438	92.702	74.504	52.774	-59.261	14.964	-1.128
3000	24.523	93.532	75.125	55.223	-59.220	17.518	-1.276
3100	24.600	94.337	75.731	57.679	-59.179	20.076	-1.415
3200	24.671	95.120	76.325	60.142	-59.143	22.633	-1.546
3300	24.736	95.880	76.906	62.613	-59.111	25.187	-1.668
3400	24.796	96.619	77.475	65.089	-59.080	27.740	-1.783
3500	24.851	97.339	78.032	67.572	-59.056	30.295	-1.892
3600	24.902	98.040	78.579	70.059	-59.035	32.846	-1.994
3700	24.949	98.722	79.114	72.552	-59.020	35.400	-2.091
3800	24.993	99.388	79.639	75.049	-59.008	37.955	-2.183
3900	25.034	100.038	80.153	77.551	-59.004	40.506	-2.270
4000	25.072	100.672	80.658	80.056	-59.004	43.058	-2.352
4100	25.107	101.292	81.154	82.565	-59.010	45.606	-2.431
4200	25.140	101.897	81.641	85.077	-59.022	48.162	-2.506
4300	25.170	102.489	82.119	87.593	-59.040	50.712	-2.577
4400	25.199	103.068	82.588	90.111	-59.064	53.262	-2.645
4500	25.226	103.635	83.050	92.633	-59.095	55.810	-2.710
4600	25.251	104.190	83.503	95.156	-59.132	58.370	-2.773
4700	25.275	104.733	83.949	97.683	-59.175	60.927	-2.833
4800	25.298	105.265	84.388	100.211	-59.225	63.484	-2.890
4900	25.319	105.787	84.819	102.742	-59.280	66.042	-2.945
5000	25.338	106.299	85.244	105.275	-59.343	68.596	-2.998
5100	25.357	106.801	85.662	107.810	-59.414	71.153	-3.049
5200	25.375	107.293	86.073	110.347	-59.489	73.715	-3.098
5300	25.392	107.777	86.478	112.885	-59.572	76.284	-3.145
5400	25.408	108.252	86.877	115.425	-59.662	78.842	-3.191
5500	25.423	108.718	87.270	117.966	-59.759	81.410	-3.235
5600	25.437	109.176	87.657	120.509	-59.863	83.975	-3.277
5700	25.450	109.627	88.038	123.054	-59.974	86.544	-3.318
5800	25.463	110.069	88.414	125.599	-60.093	89.114	-3.358
5900	25.475	110.505	88.785	128.146	-60.218	91.692	-3.396
6000	25.487	110.933	89.150	130.694	-60.349	94.260	-3.433

Dec. 31, 1960; Dec. 31, 1963

FLUOROMETHANE (CH_3F) (IDEAL GAS) MOL. WT. = 34.035

Point Group = C_{3v}

$S^\circ_{298.15}$ = 53.25 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -54 ± 8 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -56 ± 7 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
2965 (1)	3006 (2)
1464 (1)	1467 (2)
1049 (1)	1182 (2)

Bond Distances: C-F = 1.391 ± 0.005 Å C-H = 1.095 ± 0.010 Å

Bond Angles: H-C-H = 109.5° ± 2° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = 5.96 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

Appearance potentials for CH_3^+ from CH_4^* and CH_3F reported by F. P. Lossing, K. V. Ingold, and I. H. S. Henderson, J. Chem. Phys. 22, 1489 (1954), the heats of dissociation of hydrogen (104.20 kcal.) and fluorine (37.72 kcal.), and the heat of formation of Methane (-17.90 kcal.) were used to calculate the heat of formation of gaseous CH_3F. These authors measured an appearance potential for CH_3^+ from CH_3F of 14.6 ± 0.6 e.v., which would give an uncertainty of about ±15 kcal. mole^{-1} in the heat of formation of methyl fluoride. However, a correlation of the heats of formation from the atoms of the methyl fluorides and methyl chlorides indicates that the uncertainty can be reduced to ± 7 kcal. mole^{-1}.

Heat Capacity and Entropy.

Fundamental vibrational frequencies were taken from the summary reported by W. L. Smith and I. M. Mills, J. Mol. Spect. 11, 11 (1963). Moments of inertia from the microwave results of O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. 75, 1014 (1949) are: I_A = 5.52 X 10^{-40} g. cm.^{2}, $I_B = I_C$ = 32.854 X 10^{-40} g. cm.^{2}. Bond parameters are the values of L. O. Brockway, C. G. Thornton, and L. S. Bartell, whose electron diffraction results are given in the Annual Review of Physical Chemistry 5, 397 (1954). These values are in close agreement with the microwave parameters reported by Gilliam, Edwards, and Gordy (loc. cit.).

Trifluoromethylsilane (Si(CH$_3$)F$_3$)

(Ideal Gas) Mol. Wt. = 100.125

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	21,720	75,070	75,070	,000	- 294,625	- 279,656	204,984
300	21,790	75,205	75,070	,040	- 294,638	- 279,564	203,652
400	25,160	81,954	75,968	2,395	- 295,235	- 274,445	149,942
500	27,840	87,867	77,768	5,049	- 295,707	- 269,191	117,658
600	29,950	93,138	79,899	7,944	- 296,062	- 263,853	96,104
700	31,640	97,885	82,135	11,025	- 296,325	- 258,462	80,692
800	33,040	102,205	84,378	14,262	- 296,507	- 253,041	69,124
900	34,210	106,166	86,581	17,626	- 296,625	- 247,598	60,122
1000	35,200	109,823	88,725	21,098	- 296,690	- 242,149	52,919
1100	36,060	113,219	90,799	24,662	- 296,706	- 236,694	47,024
1200	36,780	116,389	92,801	28,305	- 296,684	- 231,237	42,112
1300	37,410	119,358	94,731	32,015	- 296,633	- 225,785	37,956
1400	37,960	122,151	96,591	35,785	- 296,557	- 220,338	34,395
1500	38,460	124,787	98,383	39,606	- 296,465	- 214,895	31,309

December 31, 1960.

Trifluoromethylsilane (Si(CH$_3$)F$_3$) (Ideal Gas)

Mol. Wt. = 100.125

ΔH_f° 298.15 = [-294.625] kcal. mole^{-1}

$S^\circ_{298.15}$ = 75.07 cal. deg.$^{-1}$ mole^{-1}

Heat of Formation. ΔH_f° 298.15 was estimated.

Heat Capacity and Entropy. C_p and $S^\circ_{298.15}$ were taken from G. Janz, Y. Mikawa, and F. Behnke, private communication, March 16, 1960.

Methane (CH_4)

(Ideal Gas) Mol. Wt. = 16.043

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.396	-15.991	-15.991	INFINITE
100	7.949	35.706	51.716	-1.601	-16.728	-15.400	33.656
200	8.001	41.222	45.247	-.805	-17.216	-13.909	15.198
298	8.518	44.490	44.490	.000	-17.895	-12.145	8.902
300	8.535	44.543	44.490	.016	-17.909	-12.110	8.822
400	9.680	47.144	44.837	.923	-18.636	-10.066	5.500
500	11.076	49.453	45.533	1.960	-19.316	-7.845	3.429
600	12.483	51.597	46.367	3.138	-19.916	-5.493	2.001
700	13.813	53.622	47.260	4.454	-20.429	-3.046	.951
800	15.041	55.548	48.176	5.897	-20.857	-.533	.146
900	16.157	57.385	49.098	7.458	-21.207	2.029	-.493
1000	17.160	59.141	50.016	9.125	-21.482	4.625	-1.011
1100	18.052	60.819	50.922	10.887	-21.696	7.247	-1.440
1200	18.842	62.424	51.814	12.732	-21.854	9.887	-1.801
1300	19.538	63.960	52.690	14.652	-21.971	12.535	-2.107
1400	20.150	65.431	53.548	16.637	-22.050	15.195	-2.372
1500	20.688	66.840	54.387	18.679	-22.104	17.859	-2.602
1600	21.161	68.191	55.208	20.772	-22.137	20.520	-2.803
1700	21.579	69.486	56.010	22.910	-22.148	23.189	-2.981
1800	21.947	70.730	56.794	25.086	-22.144	25.854	-3.139
1900	22.273	71.926	57.559	27.298	-22.127	28.522	-3.281
2000	22.562	73.076	58.306	29.540	-22.099	31.187	-3.408
2100	22.820	74.183	59.036	31.809	-22.065	33.851	-3.523
2200	23.050	75.250	59.749	34.103	-22.026	36.511	-3.627
2300	23.256	76.279	60.445	36.418	-21.981	39.173	-3.722
2400	23.441	77.273	61.126	38.753	-21.935	41.833	-3.809
2500	23.608	78.233	61.791	41.106	-21.888	44.483	-3.889
2600	23.758	79.162	62.441	43.474	-21.839	47.141	-3.962
2700	23.894	80.062	63.077	45.857	-21.790	49.791	-4.030
2800	24.018	80.933	63.700	48.253	-21.741	52.440	-4.093
2900	24.131	81.778	64.309	50.660	-21.694	55.093	-4.152
3000	24.233	82.597	64.905	53.079	-21.649	57.736	-4.206
3100	24.327	83.394	65.488	55.507	-21.602	60.381	-4.257
3200	24.413	84.167	66.060	57.944	-21.561	63.026	-4.304
3300	24.493	84.920	66.620	60.389	-21.524	65.669	-4.349
3400	24.565	85.652	67.169	62.842	-21.488	68.309	-4.391
3500	24.633	86.365	67.707	65.302	-21.459	70.951	-4.430
3600	24.695	87.060	68.235	67.768	-21.433	73.589	-4.467
3700	24.752	87.737	68.753	70.241	-21.414	76.231	-4.503
3800	24.806	88.398	69.262	72.719	-21.397	78.872	-4.536
3900	24.855	89.043	69.761	75.202	-21.389	81.511	-4.568
4000	24.901	89.673	70.251	77.690	-21.386	84.150	-4.598
4100	24.944	90.288	70.732	80.182	-21.387	86.785	-4.626
4200	24.984	90.890	71.205	82.678	-21.397	89.429	-4.653
4300	25.022	91.478	71.669	85.179	-21.412	92.063	-4.679
4400	25.057	92.054	72.126	87.683	-21.434	94.700	-4.704
4500	25.090	92.617	72.575	90.190	-21.463	97.335	-4.727
4600	25.121	93.169	73.017	92.701	-21.498	99.983	-4.750
4700	25.150	93.710	73.452	95.214	-21.540	102.625	-4.772
4800	25.177	94.240	73.879	97.730	-21.589	105.268	-4.793
4900	25.203	94.759	74.300	100.249	-21.644	107.912	-4.813
5000	25.227	95.268	74.714	102.771	-21.706	110.552	-4.832
5100	25.250	95.768	75.122	105.295	-21.777	113.198	-4.851
5200	25.272	96.259	75.524	107.821	-21.853	115.844	-4.869
5300	25.292	96.740	75.920	110.349	-21.937	118.501	-4.886
5400	25.311	97.213	76.310	112.879	-22.029	121.145	-4.903
5500	25.330	97.678	76.694	115.411	-22.128	123.799	-4.919
5600	25.347	98.134	77.073	117.945	-22.234	126.449	-4.935
5700	25.364	98.583	77.446	120.481	-22.348	129.106	-4.950
5800	25.379	99.024	77.814	123.018	-22.469	131.762	-4.965
5900	25.394	99.458	78.178	125.557	-22.598	134.428	-4.979
6000	25.409	99.885	78.536	128.097	-22.732	137.081	-4.993

March 31, 1961

METHANE (CH_4) (IDEAL GAS) MOL. WT. = 16.043

$\Delta H^\circ_{f0} = -15.99 \pm 0.08$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -17.895 \pm 0.08$ kcal. mole^{-1}

Point Group T_d

$S_{298.15} = 44.48 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
2916.5 (1)
1534.0 (2)
3018.7 (3)
1306 (3)

Bond Lengths and Angles $\angle$ H-C-H = 109° 28' C-H = 1.091 ± 0.002 Å

Moments of Inertia $I_A = I_B = I_C = 5.313 \times 10^{-40}$ g. cm.^{2}

Heat of Formation

F. D. Rossini, J. Research Nat. Bur. Standards 6, 37 (1931) measured the heat of combustion of methane gas. His value at 298.15°K was corrected to the presently accepted molecular weight of water. The heat of formation was calculated using -68.3174 and -94.0540 kcal. mole^{-1} for the heat of formation of $H_2O(l)$ and $CO_2(g)$ respectively.

Heat Capacities and Entropies

D. P. Stevenson and J. A. Ibers, J. Chem. Phys. 33, 762 (1960), calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by L. H. Jones and R. S. McDowell, J. Mol. Spect. 3, 632 (1959), are consistent with their results of a force constant calculation.

Cyanogen Iodide (ICN)

(Ideal Gas) GFW = 152.92225

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.741	54.124	54.124	INFINITE
100	8.023	50.687	70.913	-2.023	54.117	51.707	-113.006
200	10.443	57.069	62.507	-1.088	54.037	49.336	-53.912
298	11.573	61.479	61.479	.000	54.000	47.037	-34.479
300	11.587	61.550	61.479	.021	53.999	46.993	-34.235
400	12.152	64.969	61.941	1.211	52.008	44.735	-24.442
500	12.523	67.722	62.831	2.446	46.811	43.407	-18.973
600	12.825	70.033	63.844	3.713	46.896	42.718	-15.560
700	13.090	72.030	64.874	5.009	46.953	42.017	-13.118
800	13.323	73.794	65.881	6.330	46.993	41.309	-11.285
900	13.524	75.375	66.849	7.673	47.017	40.596	-9.858
1000	13.698	76.809	67.775	9.034	47.033	39.881	-8.716
1100	13.845	78.122	68.656	10.412	47.040	39.165	-7.781
1200	13.971	79.332	69.496	11.803	47.040	38.450	-7.003
1300	14.078	80.454	70.296	13.205	47.034	37.734	-6.344
1400	14.169	81.501	71.060	14.618	47.024	37.021	-5.779
1500	14.247	82.481	71.789	16.039	47.010	36.306	-5.290
1600	14.314	83.403	72.486	17.467	46.993	35.593	-4.862
1700	14.372	84.273	73.154	18.901	46.974	34.881	-4.484
1800	14.422	85.096	73.795	20.341	46.951	34.170	-4.149
1900	14.466	85.877	74.411	21.785	46.928	33.462	-3.849
2000	14.504	86.619	75.003	23.234	46.902	32.752	-3.579
2100	14.537	87.328	75.573	24.686	46.876	32.047	-3.335
2200	14.567	88.005	76.123	26.141	46.846	31.339	-3.113
2300	14.593	88.653	76.653	27.599	46.815	30.637	-2.911
2400	14.617	89.275	77.166	29.060	46.783	29.934	-2.726
2500	14.638	89.872	77.663	30.522	46.748	29.232	-2.555
2600	14.656	90.446	78.143	31.987	46.712	28.532	-2.398
2700	14.673	91.000	78.609	33.454	46.674	27.833	-2.253
2800	14.689	91.534	79.062	34.922	46.635	27.137	-2.118
2900	14.702	92.049	79.501	36.391	46.593	26.442	-1.993
3000	14.715	92.548	79.927	37.862	46.550	25.746	-1.876
3100	14.726	93.031	80.342	39.334	46.505	25.055	-1.766
3200	14.737	93.498	80.746	40.807	46.458	24.363	-1.664
3300	14.746	93.952	81.139	42.282	46.409	23.672	-1.568
3400	14.755	94.392	81.523	43.757	46.358	22.986	-1.478
3500	14.763	94.820	81.897	45.233	46.305	22.296	-1.392
3600	14.771	95.236	82.261	46.709	46.250	21.611	-1.312
3700	14.778	95.641	82.617	48.187	46.193	20.928	-1.236
3800	14.784	96.035	82.965	49.665	46.134	20.248	-1.165
3900	14.790	96.419	83.305	51.144	46.073	19.569	-1.097
4000	14.795	96.794	83.638	52.623	46.009	18.888	-1.032
4100	14.800	97.159	83.963	54.103	45.944	18.211	-.971
4200	14.805	97.516	84.282	55.583	45.875	17.538	-.913
4300	14.810	97.864	84.594	57.064	45.804	16.862	-.857
4400	14.814	98.205	84.899	58.545	45.731	16.188	-.804
4500	14.818	98.538	85.199	60.026	45.655	15.517	-.754
4600	14.821	98.863	85.492	61.508	45.577	14.851	-.706
4700	14.825	99.182	85.780	62.991	45.497	14.182	-.659
4800	14.828	99.494	86.062	64.473	45.413	13.520	-.616
4900	14.831	99.800	86.340	65.956	45.327	12.854	-.573
5000	14.834	100.100	86.612	67.439	45.238	12.194	-.533
5100	14.836	100.394	86.879	68.923	45.146	11.527	-.494
5200	14.839	100.682	87.142	70.407	45.052	10.872	-.457
5300	14.841	100.964	87.400	71.891	44.955	10.217	-.421
5400	14.843	101.242	87.654	73.375	44.855	9.565	-.387
5500	14.846	101.514	87.903	74.859	44.751	8.912	-.354
5600	14.848	101.782	88.149	76.344	44.645	8.259	-.322
5700	14.850	102.045	88.390	77.829	44.536	7.608	-.292
5800	14.851	102.303	88.628	79.314	44.423	6.963	-.262
5900	14.853	102.557	88.862	80.799	44.308	6.320	-.234
6000	14.855	102.806	89.092	82.284	44.189	5.674	-.207

Sept. 30, 1962; Dec. 31, 1966; June 30, 1969

Point Group $C_{\infty v}$

$\Delta Hf°_0$ = 54.1 ± 1.5 kcal/mol

$S°_{298.15}$ = 61.48 ± 0.01 gibbs/mol

$\Delta Hf°_{298.15}$ = 54.0 ± 1.5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
485.8 (1)
304.5 (2)
2188 (1)

Bond Distance: C-I = 1.994 Å C-N = 1.159 Å

Bond Angle: I-C-N = 180°

σ = 1

Rotational Constant: B_0 = 0.1076 cm^{-1}

Heat of Formation

The heat of formation is calculated from ΔHf_{298}(ICN, c) = 39.71 kcal/mol (1) and $\Delta Hs°_{298}$ = 14.29 ± 0.15 kcal/mol. This latter value is obtained from a 2nd and 3rd law analysis of the vapor pressure data of Yost and Stone (2) and Ketelaar and Kruyer (3), which are in good agreement after dropping the lowest point in the first set and the lowest 3 points in the second set.

The heat of formation of the crystal is calculated from ΔHr_{298} = -46.3 ± 0.08 kcal obtained by Lord and Woolf (4) for the reaction ICN(c) + 2 NaOH(56 H_2O) = NaCNO(2800 H_2O) + NaI(2800 H_2O) + $H_2O(\ell)$. The auxiliary data used were ΔHf_{298}(NaOH·56 H_2O) = -112.26 kcal/mol (1, 5); ΔHf_{298}(NaCNO·2800 H_2O) = -92.25 kcal/mol (1, 5) and ΔHf_{298}(NaI·2800 H_2O) = -70.54 kcal/mol (1, 5). The uncertainty in the final value reflects the uncertainty in ΔHf_{298}(NaCNO·2800 H_2O) which was determined by Lord and Woolf to be -93.6 kcal/mol in excess NaOH·56 H_2O.

Heat Capacity and Entropy

The molecular structure, bond distances and angle were determined using microwave spectroscopy by Tyler and Sheridan (6). The infrared spectrum of the gas has been reported by Hemple and Nixon (7) using a 10m folded path cell. The fundamentals have been confirmed by the Raman data of West and Farnsworth (8) on a solution in methanol; and by the infrared data of Freitag and Nixon (9) on solid ICN.

References:

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6. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963).
7. S. Hemple and E. R. Nixon, J. Chem. Phys. 47, 4273 and 48, 5288 (1968).
8. W. West and M. Farnsworth, J. Chem. Phys. 1, 402 (1933).
9. W. O. Freitag and E. R. Nixon, J. Chem. Phys. 24, 109 (1956).

Potassium Cyanide (KCN)

(Crystal) Mol. Wt. = 65.11985

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.145	-28.284	-28.284	INFINITE
100	13.261	11.762	45.884	-3.412	-28.322	-26.720	58.397
200	15.972	24.186	31.994	-1.562	-27.521	-25.358	27.710
298	15.868	30.540	30.540	.000	-27.120	-24.389	17.877
300	15.866	30.638	30.540	.029	-27.114	-24.372	17.755
400	15.850	35.198	31.162	1.614	-27.438	-23.390	12.780
500	15.859	38.736	32.336	3.200	-27.266	-22.400	9.791
600	15.868	41.628	33.651	4.786	-27.139	-21.439	7.809
700	15.878	44.075	34.970	6.373	-27.057	-20.496	6.399
800	15.887	46.196	36.244	7.962	-27.011	-19.562	5.344
900	15.897	48.068	37.455	9.551	-27.001	-18.633	4.525
1000	15.906	49.743	38.602	11.141	-27.024	-17.703	3.869
1100	15.915	51.259	39.685	12.732	-45.987	-15.744	3.128
1200	15.925	52.645	40.708	14.324	-45.829	-13.001	2.368
1300	15.934	53.920	41.676	15.917	-45.687	-10.273	1.727
1400	15.944	55.101	42.593	17.511	-45.557	-7.551	1.179
1500	15.953	56.201	43.464	19.106	-45.438	-4.840	.705
1600	15.962	57.231	44.293	20.702	-45.327	-2.138	.292
1700	15.972	58.199	45.082	22.298	-45.224	.556	-.072
1800	15.981	59.112	45.837	23.896	-45.128	3.247	-.394
1900	15.991	59.977	46.558	25.494	-45.038	5.932	-.682
2000	16.000	60.797	47.250	27.094	-44.952	8.614	-.941

June 30, 1962; Mar. 31, 1966

POTASSIUM CYANIDE (KCN) (CRYSTAL) MOL. WT. = 65.11985

$S^\circ_{298.15}$ = 30.54 ± 0.25 cal. deg.$^{-1}$ mole^{-1}

T_t = 168.3 ± 0.1°K.

T_m = 895 ± 2°K.

$\Delta H^\circ_{f\ 0}$ = -28.28 ± 0.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -27.12 ± 0.2 kcal. mole^{-1}

ΔH°_t = 0.279 kcal. mole^{-1}

ΔH°_m = 3.5 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to dimer) = 52 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to monomer) = 46 ± 5 kcal. mole^{-1}

Heat of Formation.

The enthalpy change, $\Delta H^\circ_{r\ 298.15}$ = 2.80 ± 0.10 kcal. mole^{-1}, for the reaction KCN(c) → KCN(∞H_2O) was reported by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heat of formation for K^+(∞ H_2O) and CN^-(∞ H_2O), reported by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of $\Delta H^\circ_{f\ 298.15}$ for KCN(c) was evaluated to be -27.12 ± 0.2 kcal. mole^{-1}.

Heat Capacity and Entropy.

The heat capacity for KCN(c) has been measured with a heat conduction method by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941), 101.6-345.8°K., and adiabatically by H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc. Japan, 38, 1115 (1965), 14.23-308.5°K. The data of Suga, Matsuo and Seki were adopted after correction for curvature. The anomalous region between 50-105°K. has been treated as second order by inclusion of the enthalpy in the heat capacity. The C_p values above 310°K. were estimated by graphical extrapolation. The value of $S^\circ_{298.15}$ was evaluated based on S°_{15} = 0.193 cal. deg.$^{-1}$ mole^{-1}. This extrapolated value appears more reasonable than the value, S°_{15} = 0.307 cal. deg^{-1}mole^{-1} reported by Suga, Matsuo and Seki.

Transition Data.

T_t was taken from Suga, Matsuo and Seki, loc. cit. ΔH°_t was calculated as the difference between the total enthalpy change, $H^\circ_{173.80}-H^\circ_{159.02}$ = 0.533 kcal. mole^{-1} obtained from C_p values measured by Messer and Ziegler, loc. cit., and the enthalpy change, 0.254 kcal. mole^{-1}, calculated from the arbitrarily smoothed C_p curve. Suga, et al. reported ΔH_t = 0.339 kcal. mole^{-1}; however, their C_p data do not adequately define the total enthalpy change through the transition region. The values of T_t and ΔH°_t reported by Messer and Ziegler, loc. cit., were 168.3 ± 0.4°K. and 0.30 kcal. mole^{-1}, respectively. The lower transition, T = 82.9 ± 0.2°K. and ΔH° = 0.095 ± 0.001 kcal. mole^{-1} reported by Suga, et al., was treated as second order by inclusion of the enthalpy in the heat capacity.

Melting Data.

See KCN(l) table.

Heat of Sublimation.

The difference between $\Delta H^\circ_{f\ 298.15}$ for $(KCN)_2$(g) and 2KCN(c) is $\Delta H^\circ_{s\ 298.15}$ (to dimer) and for KCN(g) and KCN(c) is $\Delta H^\circ_{s\ 298.15}$ (to monomer).

Potassium Cyanide (KCN)

(Liquid) Mol. Wt. = 65.11985

CKN

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	18.000	32.104	32.104	.000	-24.891	-22.626	16.58
300	18.000	32.215	32.104	.033	-24.881	-22.612	16.473
400	18.000	37.394	32.810	1.833	-24.990	-21.821	11.922
500	18.000	41.410	34.144	3.633	-24.603	-21.075	9.212
600	18.000	44.692	35.636	5.433	-24.263	-20.401	7.431
700	18.000	47.467	37.133	7.233	-23.968	-19.781	6.176
800	18.000	49.870	38.579	9.033	-23.711	-19.201	5.245
900	18.000	51.990	39.953	10.833	-23.489	-18.652	4.529
1000	18.000	53.887	41.254	12.633	-23.303	-18.126	3.961
1100	18.000	55.602	42.481	14.433	-42.057	-16.591	3.296
1200	18.000	57.169	43.641	16.233	-41.691	-14.292	2.603
1300	18.000	58.609	44.738	18.033	-41.342	-12.023	2.021
1400	18.000	59.943	45.777	19.833	-41.006	-9.779	1.527
1500	18.000	61.185	46.763	21.633	-40.681	-7.560	1.101
1600	18.000	62.347	47.701	23.433	-40.366	-5.363	.733
1700	18.000	63.438	48.595	25.233	-40.060	-3.186	.410
1800	18.000	64.467	49.449	27.033	-39.761	-1.025	.124
1900	18.000	65.440	50.265	28.833	-39.470	1.120	-.129
2000	18.000	66.364	51.047	30.633	-39.184	3.248	-.355
2100	18.000	67.242	51.797	32.433	-38.904	5.364	-.558
2200	18.000	68.079	52.518	34.233	-38.633	7.465	-.742
2300	18.000	68.879	53.213	36.033	-38.366	9.555	-.908
2400	18.000	69.645	53.881	37.833	-38.107	11.633	-1.059
2500	18.000	70.380	54.527	39.633	-37.855	13.699	-1.198
2600	18.000	71.086	55.150	41.433	-37.611	15.758	-1.325
2700	18.000	71.765	55.753	43.233	-37.374	17.804	-1.441
2800	18.000	72.420	56.337	45.033	-37.147	19.843	-1.549
2900	18.000	73.052	56.902	46.833	-36.929	21.876	-1.649
3000	18.000	73.662	57.451	48.633	-36.720	23.899	-1.741

June 30, 1962; Mar. 31, 1966

POTASSIUM CYANIDE (KCN) (LIQUID) MOL. WT. = 65.11985

$S^\circ_{298.15}$ = 32.104 cal. deg.$^{-1}$ mole^{-1}

T_m = 895 ± 2° K.

T_b = [1898]°K.

ΔH_f° 298.15 = -24.891 kcal. mole^{-1}

ΔH_m° = 3.5 kcal. mole^{-1}

ΔH_v° = [37.55] kcal. mole^{-1}

Heat of Formation.

ΔH_f° 298.15(l) was obtained from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{895}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity was estimated and assumed constant in the temperature range 298.15-3000°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by W. Truthe, Z. anorg. Chem. 76, 129 (1912). The value of ΔH_m° was taken from K. K. Kelley, U. S. Bur. Mines Bull, 393, 1936, based on phase diagrams of the systems KCN-AgCN, KCN-$Cu_2(CN)_2$, KCN-KCl, KCN-NaCN, and KCN-$Zn(CN)_2$ reported by W. Truthe, loc. cit.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction KCN(l) = KCN(g) becomes zero. The difference between ΔH_f° for KCN(g) and KCN(l) at T_b is ΔH_v°.

CKN

Potassium Cyanide (KCN)

(Ideal Gas) Mol. Wt. = 65.11985

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	- 2.977	19.004	19.004	INFINITE
100	9.223	48.562	70.691	- 2.213	18.998	16.919	- 36.976
200	11.406	55.760	61.569	- 1.162	18.999	14.847	- 16.224
298	12.155	60.477	60.477	.000	19.000	12.806	- 9.387
300	12.164	60.552	60.477	.022	18.999	12.767	- 9.301
400	12.520	64.104	60.959	1.258	18.326	10.811	- 5.907
500	12.778	66.926	61.880	2.523	18.178	8.948	- 3.911
600	13.015	69.277	62.922	3.813	18.008	7.119	- 2.593
700	13.238	71.301	63.978	5.126	17.816	5.318	- 1.660
800	13.443	73.082	65.007	6.460	17.607	3.547	- .969
900	13.625	74.676	65.994	7.814	17.382	1.802	- .438
1000	13.782	76.120	66.935	9.184	17.139	.083	- .018
1100	13.918	77.440	67.831	10.570	- 2.030	- .586	.116
1200	14.034	78.656	68.683	11.967	- 2.066	- .451	.082
1300	14.133	79.783	69.494	13.376	- 2.109	- .316	.053
1400	14.218	80.834	70.267	14.793	- 2.155	- .175	.027
1500	14.290	81.817	71.005	16.219	- 2.205	- .031	.005
1600	14.352	82.742	71.710	17.651	- 2.257	.114	- .016
1700	14.406	83.613	72.385	19.089	- 2.313	.263	- .034
1800	14.453	84.438	73.032	20.532	- 2.371	.417	- .051
1900	14.494	85.221	73.653	21.979	- 2.433	.573	- .066
2000	14.529	85.965	74.250	23.431	- 2.495	.735	- .080
2100	14.561	86.675	74.825	24.885	- 2.561	.898	- .093
2200	14.589	87.353	75.379	26.343	- 2.632	1.063	- .106
2300	14.613	88.002	75.914	27.803	- 2.706	1.233	- .117
2400	14.635	88.624	76.430	29.265	- 2.784	1.407	- .128
2500	14.655	89.222	76.930	30.730	- 2.868	1.581	- .138
2600	14.672	89.797	77.414	32.196	- 2.957	1.763	- .148
2700	14.688	90.351	77.883	33.664	- 3.052	1.944	- .157
2800	14.702	90.886	78.338	35.134	- 3.155	2.130	- .166
2900	14.715	91.402	78.780	36.605	- 3.266	2.323	- .175
3000	14.727	91.901	79.209	38.077	- 3.386	2.517	- .183
3100	14.738	92.384	79.626	39.550	- 3.516	2.717	- .192
3200	14.747	92.852	80.032	41.024	- 3.656	2.921	- .200
3300	14.756	93.306	80.427	42.499	- 3.810	3.125	- .207
3400	14.765	93.747	80.813	43.975	- 3.977	3.338	- .215
3500	14.772	94.175	81.188	45.452	- 4.159	3.553	- .222
3600	14.779	94.591	81.555	46.930	- 4.359	3.779	- .229
3700	14.786	94.996	81.913	48.408	- 4.576	4.008	- .237
3800	14.791	95.390	82.262	49.887	- 4.816	4.246	- .244
3900	14.797	95.775	82.604	51.366	- 5.077	4.486	- .251
4000	14.802	96.149	82.938	52.846	- 5.364	4.738	- .259
4100	14.807	96.515	83.264	54.327	- 5.680	4.990	- .266
4200	14.811	96.872	83.584	55.808	- 6.028	5.257	- .274
4300	14.815	97.220	83.897	57.289	- 6.409	5.532	- .281
4400	14.819	97.561	84.204	58.771	- 6.828	5.811	- .289
4500	14.823	97.894	84.505	60.253	- 7.288	6.104	- .296
4600	14.826	98.220	84.799	61.735	- 7.791	6.407	- .304
4700	14.830	98.539	85.088	63.218	- 8.340	6.721	- .313
4800	14.833	98.851	85.372	64.701	- 8.941	7.053	- .321
4900	14.835	99.157	85.650	66.185	- 9.594	7.389	- .330
5000	14.838	99.457	85.923	67.668	- 10.303	7.742	- .338
5100	14.841	99.751	86.191	69.152	- 11.072	8.106	- .347
5200	14.843	100.039	86.455	70.637	- 11.901	8.493	- .357
5300	14.845	100.321	86.714	72.121	- 12.793	8.898	- .367
5400	14.847	100.599	86.968	73.606	- 13.748	9.313	- .377
5500	14.849	100.871	87.219	75.090	- 14.770	9.752	- .387
5600	14.851	101.139	87.465	76.575	- 15.855	10.204	- .398
5700	14.853	101.402	87.707	78.061	- 17.005	10.677	- .409
5800	14.855	101.660	87.945	79.546	- 18.220	11.174	- .421
5900	14.856	101.914	88.180	81.032	- 19.496	11.697	- .433
6000	14.858	102.164	88.411	82.517	- 20.832	12.234	- .446

June 30, 1962; Mar. 31, 1966

POTASSIUM CYANIDE (KCN) (IDEAL GAS) MOL. WT. = 65.11985

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [60.48] cal. deg.$^{-1}$. mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [19 ± 5] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [19 ± 5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[370] (1)
207 (2)
2158 (1)

Bond Distance: C-N = 1.16 ± 0.01 Å K-C = [2.294] Å

Bond Angle: K-C-N = 180°

Rotational Constant: B = 0.11891 cm.$^{-1}$

σ = 1

Heat of Formation.

The vapor pressure of KCN(g) at 870°C. was estimated to be 1-10 mm. Hg by D. S. Villars, J. Am. Chem. Soc. 53, 405 (1931). Assuming the vapor pressure at this temperature to be 1 mm. Hg, the heat of vaporization ($\Delta H^\circ_{v\ 298.15}$) for KCN(l) was evaluated as 44 kcal. mole^{-1}. Based on $\Delta H^\circ_{f\ 298.15}$ = -24.89 kcal. mole^{-1} for KCN(l), the value of $\Delta H^\circ_{f\ 298.15}$ for KCN(g) was calculated to be 19 ± 5 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure of KCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was determined by N. Elliott and J. Hastings, Acta Cryst. 14, 1018 (1961) by use of neutron diffraction measurements. The K-C bond distance was taken from G. E. Leroi, Ph. D. Thesis, Harvard University, 1961, which was estimated. The vibrational frequencies, ν_2 and ν_3, were obtained from G. E. Leroi and W. Klemperer, J. Chem. Phys. 35, 774 (1961). The value of ν_1 was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is 2.3540 X 10^{-38} g. cm.^{2}

Potassium Carbonate (K_2CO_3)

(Crystal) Mol. Wt. = 138. 21335

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 5.419	- 273.569	- 273.569	INFINITE
100	17.300	12.690	58.810	- 4.612	- 274.673	- 267.991	585.693
200	23.695	27.012	39.557	- 2.509	- 274.908	- 261.183	285.407
298	27.351	37.170	37.170	.000	- 274.900	- 254.444	186.513
300	27.414	37.339	37.171	.051	- 274.899	- 254.317	185.270
400	30.625	45.675	38.285	2.956	- 275.934	- 247.254	135.093
500	33.473	52.821	40.494	6.164	- 275.628	- 240.115	104.954
600	36.010	59.152	43.086	9.640	- 275.114	- 233.056	84.891
700	38.356	64.881	45.796	13.359	- 274.419	- 226.099	70.591
800	40.641	70.152	48.515	17.309	- 273.549	- 219.255	59.898
900	42.905	75.070	51.196	21.487	- 272.503	- 212.530	51.609
1000	45.160	79.707	53.817	25.890	- 271.288	- 205.929	45.006
1100	47.400	84.117	56.373	30.518	- 307.716	- 197.413	39.222
1200	49.640	88.337	58.862	35.370	- 305.666	- 187.471	34.143
1300	51.880	92.399	61.286	40.446	- 303.418	- 177.714	29.876
1400	54.120	96.325	63.649	45.746	- 300.964	- 168.132	26.247
1500	56.360	100.136	65.955	51.270	- 298.305	- 158.736	23.128
1600	58.600	103.845	68.208	57.018	- 295.436	- 149.524	20.424
1700	60.840	107.464	70.411	62.990	- 292.357	- 140.499	18.062
1800	63.080	111.005	72.568	69.186	- 289.070	- 131.659	15.986
1900	65.320	114.476	74.683	75.606	- 285.574	- 123.009	14.149
2000	67.560	117.883	76.758	82.250	- 281.865	- 114.547	12.517

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CARBONATE (K_2CO_3) (CRYSTAL) MOL. WT. = 138.21335

$\Delta H^\circ_{f\ 0}$ = -273.57 ± 0.5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 37.17 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{298.15}$ = -274.9 ± 0.5 kcal. mole^{-1}

T_m = 1174 ± 1°K.

ΔH°_m = 6.6 ± 0.1 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from the heat of solution ΔH°_{∞} = -7.6 ± 0.5 kcal. mole^{-1} and the heats of formation for K^+(aq) and CO_3^{--} (aq), -60.32 and -161.84 kcal. mole^{-1}, respectively. The standard heat of solution, ΔH°_{∞} = -7.6 ± 0.5 kcal. mole^{-1}, was calculated by extrapolation to infinite dilution of the calorimetric data of L. Benjamin, J. Chem. Eng. Data 7, 239-40 (1962), using the methods suggested by J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, J. Phys. Chem. 69, 3059-62 (1965). The equilibrium constant for the hydrolysis CO_3^{--} (∞H_2O) + H_2O(1) → HCO_3^-(∞H_2O) + OH^-(∞H_2O) was taken as K = 2.1 X 10^{-4} based on the selected values of D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965. The resulting extrapolations were not so consistent as those of Rupert et al. (loc. cit.) for Na_2CO_3. The ionic heats of formation were taken from Wagman et al. (loc. cit.). This procecure was adopted even though it may involve an inconsistency between the extrapolations for ΔH°_{∞} and CO_3^{--}(∞H_2O). The alternative evaluation of $\Delta H^\circ_{f\ 298.15}$ for K_2CO_3(~1900 H_2O) from the heats of mixing given by J. A. Muller, Ann. chim. phys. (6), 15, 517 (1888) and M. Berthelot, Ann. chim. phys. (4) 29, 433 (1873) may be subject to significant error if dissolved CO_2 was not excluded from the solutions. Presumably, this path was used by D. D. Wagman, NBS Report 8628, January 1965, in the selection of $\Delta H^\circ_{f\ 298.15}$ = -274.3 kcal. mole^{-1}. This value is 0.6 kcal. mole^{-1} less negative than the value adopted here.

Heat Capacity and Entropy.

The low temperature heat capacity, 14.0-315°K. was measured by F. L. Oetting, unpublished data, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan, 1963. G. I. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963) measured the heat content by drop calorimetry in the temperature range 630-1250°K., and gave enthalpy and heat capacity equations based on their measurements. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity above 298°K. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was **graphically extrapolated above the melting point.** The entropy at 14.0°K. was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S^\circ_{14.0}$ = 0.109 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m was obtained from A. Reisman, J. Am. Chem. Soc. 80, 3558 (1958) and ΔH°_m was taken from Janz et al. (loc. cit.).

CK_2O_3

Potassium Carbonate (K_2Co_3)

(Liquid) Mol. St. = 138. 21335

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	27.351	40.719	40.719	.000	- 270.220	- 250.822	183.858
300	27.414	40.888	40.720	.051	- 270.219	- 250.702	182.636
400	30.625	49.224	41.834	2.956	- 271.254	- 243.994	133.312
500	33.473	56.370	44.043	6.164	- 270.948	- 237.209	103.684
600	36.010	62.701	46.635	9.640	- 270.434	- 230.506	83.962
700	38.356	68.430	49.345	13.359	- 269.739	- 223.903	69.906
800	50.000	73.699	52.062	17.309	- 268.869	- 217.413	59.394
900	50.000	79.588	54.800	22.309	- 267.001	- 211.094	51.260
1000	50.000	84.856	57.546	27.309	- 265.189	- 204.979	44.798
1100	50.000	89.621	60.249	32.309	- 301.245	- 196.996	39.139
1200	50.000	93.972	62.881	37.309	- 299.047	- 187.614	34.169
1300	50.000	97.974	65.428	42.309	- 296.875	- 178.419	29.995
1400	50.000	101.679	67.887	47.309	- 294.721	- 169.384	26.442
1500	50.000	105.129	70.256	52.309	- 292.586	- 160.506	23.386
1600	50.000	108.356	72.538	57.309	- 290.465	- 151.771	20.731
1700	50.000	111.387	74.735	62.309	- 288.358	- 143.169	18.406
1800	50.000	114.245	76.851	67.309	- 286.267	- 134.688	16.353
1900	50.000	116.948	78.891	72.309	- 284.191	- 126.323	14.530
2000	50.000	119.513	80.858	77.309	- 282.126	- 118.068	12.902
2100	50.000	121.953	82.758	82.309	- 280.075	- 109.914	11.439
2200	50.000	124.279	84.593	87.309	- 278.044	- 101.861	10.119
2300	50.000	126.501	86.367	92.309	- 276.024	- 93.897	8.922
2400	50.000	128.629	88.084	97.309	- 274.022	- 86.020	7.833
2500	50.000	130.670	89.747	102.309	- 272.040	- 78.232	6.839

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CARBONATE (K_2CO_3) (LIQUID) MOL. WT. = 138.21335

$S^\circ_{298.15}$ = 40.719 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

T_m = 1174 ± 1°K.

ΔH_f° 298.15 = -270.22 ± 0.5 kcal. mole^{-1}

ΔH_m° = 6.60 ± 0.1 kcal. mole^{-1}

Heat of Formation.

The ΔH_f° 298.15 was obtained from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{T_m} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 800°K. The heat capacity below 800°K. was obtained from the heat capacity of the crystal. Above 800°K. the heat capacity was adopted as 50.0 cal. deg.$^{-1}$ mole^{-1}, based on the enthalpy measurements in the range 1169-1250°K. reported by G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See K_2CO_3(c) table.

CK_2O_3

Lithium Carbonate (Li_2CO_3)

(Crystal) Mol. Wt. = 73.88735

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.627	-288.692	-288.692	INFINITE
100	8.320	4.792	37.848	-3.306	-289.693	-283.571	619.744
200	17.310	13.507	23.487	-1.996	-290.361	-277.152	302.857
298	23.000	21.551	21.551	.000	-290.640	-270.598	198.353
300	23.080	21.694	21.552	.043	-290.643	-270.474	197.040
400	26.810	28.860	22.504	2.543	-290.697	-263.738	144.099
500	30.820	35.259	24.424	5.418	-292.074	-256.855	112.271
600	35.700	41.295	26.736	8.736	-291.692	-249.839	91.004
700	33.670	48.033	29.279	13.127	-290.293	-242.954	75.854
800	38.000	52.811	31.923	16.711	-289.749	-236.225	64.534
900	42.310	57.535	34.507	20.726	-288.824	-229.586	55.751
1000	46.540	62.225	37.044	25.181	-287.495	-223.070	48.752
1100	49.220	66.795	39.542	29.978	-285.856	-216.706	43.056
1200	50.830	71.152	41.997	34.986	-284.032	-210.500	38.337
1300	51.760	75.259	44.399	40.118	-282.107	-204.451	34.371
1400	52.420	79.120	46.743	45.329	-280.118	-198.549	30.995
1500	52.840	82.752	49.023	50.592	-278.091	-192.795	28.090
1600	53.200	86.174	51.239	55.896	-276.035	-187.174	25.567
1700	53.400	89.405	53.390	61.226	-344.056	-179.027	23.016
1800	53.600	92.463	55.477	66.576	-341.612	-169.387	20.566
1900	53.800	95.367	57.501	71.946	-339.161	-159.885	18.391
2000	54.000	98.131	59.464	77.336	-336.702	-150.516	16.448

Mar. 31, 1966

LITHIUM CARBONATE (Li_2CO_3) (CRYSTAL) MOL. WT. = 73.88735

$S^\circ_{298.15}$ = 21.551 ± 0.05 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 623°K.

T_{t_2} = 683 ± 3°K.

T_m = 993 ± 1°K.

$\Delta H^\circ_{f\ 0}$ = -288.69 ± 0.04 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -290.84 ± 0.04 kcal. mole^{-1}

$\Delta H^\circ_{t_1}$ = [0.134] kcal. mole^{-1}

$\Delta H^\circ_{t_2}$ = [0.535] kcal. mole^{-1}

ΔH°_m = 10.70 ± 0.1 kcal. mole^{-1}

Heat of Formation.

The heat of formation was derived from the enthalpy change of the following reactions:

	Reaction	$\Delta H^\circ_{r\ 298.15}$ kcal. mole^{-1}	References
a	$2Li^+(\infty H_2O) + CO_3^{--}(\infty H_2O) = Li_2CO_3(c)$	4.20	(1)
b	$2Li(c) + 2H_2O(l) = 2Li^+(\infty H_2O) + 2\ OH^-(\infty H_2O) + H_2(g)$	-106.310	(2)(3)(4)(5)

Summation of these two reactions gives

$2Li(c) + 2H_2O(l) + CO_3^{--}(\infty H_2O) = Li_2CO_3(c) + 2\ OH^-(\infty H_2O) + H_2(g)$ -102.110

Using ΔH_f° of $H_2O(l)$, $CO_3^{--}(\infty H_2O)$ and $OH^-(\infty H_2O)$ from Ref. 6 yields ΔH_f° Li_2CO_3 = -290.64 kcal. mole^{-1}.

References

(1) O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228(1936).

(2) JANAF table for LiOH(c), March 31, 1966.

(3) S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," UCRL-7992, Oct. 1964.

(4) C. B. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955).

(5) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes" NSRDS-NBS 2 Natl. Bur. Std., April 1, 1965.

(6) D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965.

Heat Capacity and Entropy.

The low temperature heat capacity, 16.68-300.20°K., was measured by O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228 (1936). G. I. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963) measured the heat content by drop calorimetry in the temperature range 560-1150°K., and gave enthalpy and heat capacity equations based on their measurement. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 16.68°K. was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S^\circ_{16.68}$ = 0.053 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_t were taken from A. Reisman, J. Am. Chem. Soc. 80, 3558 (1958). The enthalpies of transition were estimated from the relative areas of the transitions and the heat of fusion of the differential analysis curve reported by Reisman loc. cit.

Melting Data.

T_m was obtained from Reisman loc cit. and ΔH°_m was taken from Janz et. al. (loc. cit.).

Lithium Carbonate (Li_2Co_3)

(Liquid) Mol. Wt. = 73.88735

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	23.000	30.423	30.423	.000	- 281.629	- 264.232	193.687
300	23.080	30.566	30.423	.043	- 281.632	- 264.125	192.415
400	26.810	37.732	31.376	2.543	- 281.686	- 258.275	141.115
500	30.820	44.131	33.296	5.418	- 283.063	- 252.280	110.271
600	35.700	50.167	35.608	8.736	- 282.681	- 246.151	89.661
700	44.320	56.387	38.136	12.776	- 281.633	- 240.142	74.976
800	44.320	62.305	40.795	17.208	- 280.241	- 234.312	64.011
900	44.320	67.525	43.481	21.640	- 278.899	- 228.652	55.524
1000	44.320	72.195	46.123	26.072	- 277.593	- 223.138	48.767
1100	44.320	76.419	48.688	30.504	- 276.319	- 217.755	43.264
1200	44.320	80.275	51.162	34.936	- 275.071	- 212.487	38.699
1300	44.320	83.823	53.540	39.368	- 273.845	- 207.322	34.854
1400	44.320	87.107	55.822	43.800	- 272.635	- 202.248	31.572
1500	44.320	90.165	58.010	48.232	- 271.440	- 197.263	28.741
1600	44.320	93.026	60.110	52.664	- 270.255	- 192.358	26.275
1700	44.320	95.712	62.126	57.096	- 339.174	- 184.868	23.766
1800	44.320	98.246	64.063	61.528	- 337.649	- 175.833	21.349
1900	44.320	100.642	65.926	65.960	- 336.135	- 166.882	19.196
2000	44.320	102.915	67.719	70.392	- 334.634	- 158.016	17.267

Mar. 31, 1966

LITHIUM CARBONATE (Li_2CO_3) (LIQUID) MOL. WT. = 73.88735

$S^\circ_{298.15} = 30.423 \pm 0.05$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 993.15 \pm 1$°K.

$\Delta H^\circ_{f\ 298.15} = -281.63 \pm 0.04$ kcal. mole^{-1}

$\Delta H^\circ_m = 10.7 \pm 0.1$ kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was obtained from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 683.15°K. The heat capacity below 683.15°K. was obtained from the heat capacity of the crystal. Above 683.15°K. the heat capacity was adopted as 44.32 cal. deg.$^{-1}$ mole^{-1}, based on the enthalpy measurements in the range 996-1150°K. reported by G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $Li_2CO_3(c)$ table.

Magnesium Carbonate ($MgCO_3$)

(Crystal) GFW = 84.32135

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.794	- 263.933	- 263.933	INFINITE
100	5.899	2.576	28.648	- 2.607	- 264.956	- 258.756	565.510
200	13.760	9.356	17.274	- 1.584	- 265.616	- 252.371	275.778
298	18.215	15.740	15.740	.000	- 265.700	- 245.742	180.134
300	18.284	15.852	15.740	.034	- 265.701	- 245.618	178.933
400	21.476	21.571	16.498	2.029	- 265.632	- 238.930	130.545
500	23.915	26.631	18.028	4.301	- 265.417	- 232.276	101.528
600	26.060	31.187	19.848	6.803	- 265.095	- 225.678	82.203
700	27.780	35.337	21.769	9.498	- 264.685	- 219.138	68.418
800	29.220	39.142	23.706	12.349	- 264.215	- 212.664	58.097
900	30.500	42.660	25.619	15.337	- 263.696	- 206.251	50.085
1000	31.500	45.928	27.488	18.440	- 265.259	- 199.716	43.648

Dec. 31, 1960; Dec. 31, 1966

MAGNESIUM CARBONATE ($MgCO_3$) (CRYSTAL) GFW = 84.32135

$S°_{298.15}$ = 15.74 gibbs/mol

Td = 675°K

$\Delta Hf°_0$ = -263.9 ± 2 kcal/mol

$\Delta Hf°_{298.15}$ = -265.7 ± 2 kcal/mol

Heat of Formation.

The adopted $\Delta Hf°_{298.15}$ = -265.7 ± 2 kcal/mol is the average value derived from the dissociation pressures of $MgCO_3(c)$ in the temperature range 671-782°K measured by Marc and from the $\Delta Hr°_{923}$ = 25.9 ± 0.6 kcal/mol determined by Thomasson using a high temperature differential calorimeter. The decomposition of $MgCO_3$ has been studied in a bomb calorimeter by Roth; this yields $\Delta Hr°_{293}$ = 23.8 kcal/mol when corrected to constant pressure. The value is derived from the small difference between two large heats of combustion,so the uncertainty is probably large. Roth also reported $\Delta Hr°_{363}$ = 26.15 kcal/mol from calorimetric data on the heat of solution in HCl. Berthelot measured the heat of solution of $MgSO_4(aq)$ with $K_2CO_3(aq)$. Analyzing his data we find $\Delta Hf°_{298.15}$ = -268.6 kcal/mol.

Discrepancies are apparent in the wide range of the calorimetric results and in the third law drift of the equilibrium data. Possible sources for the drift include lack of true equilibrium (e.g., excess surface energy for MgO) and uncertainty in the high temperature entropy of $MgCO_3$(see entropy write-up). Non-standard state behavior of the crystal phases may also be a problem in the calorimetric studies. The data of Thomasson and Cunningham, based on a high temperature differential thermal analysis technique, are probably the most reliable of the calorimetric values; however, there are uncertainties in the absolute energy calibration. The first result of Roth may be dismissed as too discrepant and the remaining two calorimetric values are within ± 3 kcal of the selected heat of formation.

Source	Method	Reaction	T, °K	$\Delta Hr°_T$ (kcal/mol)	$\Delta Hr°_{298.15}$ (kcal/mol)	Drift eu	$\Delta Hf°_{298.15}$ kcal/mol
1. Marc	Kp	$MgCO_3(c) = MgO(c) + CO_2(g)$	671-782	—	28.3	4.8 ± 0.9	-266.04
2. Thomasson	Calorimetric	$MgCO_3(c) = MgO(c) + CO_2(g)$	923	25.9	27.7		-265.45
3. Roth	Calorimetric	$MgCO_3(c) = MgO(c) + CO_2(g)$	293	23.8	23.8		-260.35
Roth	Calorimetric	$MgCO_3(c) = MgO(c) + CO_2(g)$	363	26.15	26.10		-263.95
4. Berthelot	Calorimetric	$K_2CO_3\ (\sim .5m) + MgSO_4(\sim .5m) = MgCO_3(c) + K_2SO_4(\sim .5m)$	288	1.05	1.35		-268.6

Source:

1. R. Marc and A. Simek, Z. Anorg. Chem. 82, 17 (1913).
2. C. V. Thomasson and D. A. Cunningham, J. Sci. Instr. 41, 308-10 (1964).
3. W. A. Roth, J. Prakt. Chem. 158, 117 (1941).
4. Berthelot, Ann. Chim. Phys. 4, 160-179 (1875).

Heat Capacity and Entropy.

Low temperature heat capacities (56.3 - 291.6°K) were measured by C. T. Anderson, J. Am. Chem. Soc. 56, 849 (1934). The high temperature heat capacities are derived by a Shomate analysis of smoothed enthalpies reported by K. K. Kelley, Bulletin 584, p. 114, U.S. Bureau of Mines, Washington, D.C. 1960. Kelley obtained the smoothed values from unpublished high temperature (400-743°K) enthalpy measurements by C. H. Shomate, Berkeley Thermodynamics Laboratory, Region II, Bureau of Mines, Berkeley, California. The data were joined smoothly at 298°K and extrapolated graphically above 743°K. The entropy was obtained from the heat capacities using $S°_{56.2}$ = 0.57 eu.

Because of the drift in the decomposition pressure data, it is pertinent to assess the uncertainty in the functions. The greatest potential source for error is in the values above room temperature where the increment of entropy is about 20 eu between 298 and 700°K. Unfortunately, no evaluation of the unpublished enthalpies is possible, but an increase of 10% in the entropy increment would reduce the drift to a tolerable level.

Decomposition Data.

Td is calculated as the temperature at which ΔGr° equals zero for $MgCO_3(c) = MgO(c) + CO_2(g)$.

Cyano (CN)

(Ideal Gas) GFW = 26.01785

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.073	103.215	103.215	INFINITE
100	6.956	40.804	54.593	- 1.379	103.549	101.398	- 221.604
200	6.957	45.626	49.043	- .683	103.818	99.136	- 108.331
298	6.968	48.406	48.406	.000	104.000	96.796	- 70.954
300	6.969	48.449	48.406	.013	104.002	96.751	- 70.483
400	7.029	50.460	48.680	.712	104.107	94.317	- 51.532
500	7.155	52.041	49.199	1.421	104.145	91.863	- 40.153
600	7.326	53.360	49.786	2.145	104.135	89.407	- 32.567
700	7.510	54.503	50.380	2.886	104.088	86.956	- 27.149
800	7.689	55.518	50.960	3.647	104.018	84.514	- 23.088
900	7.852	56.433	51.518	4.424	103.928	82.080	- 19.932
1000	7.996	57.268	52.052	5.216	103.828	79.657	- 17.409
1100	8.123	58.036	52.561	6.022	103.717	77.245	- 15.347
1200	8.235	58.748	53.048	6.840	103.598	74.845	- 13.631
1300	8.337	59.411	53.512	7.669	103.473	72.453	- 12.180
1400	8.431	60.033	53.956	8.508	103.345	70.073	- 10.939
1500	8.522	60.617	54.380	9.355	103.214	67.701	- 9.864
1600	8.612	61.170	54.788	10.212	103.082	65.337	- 8.925
1700	8.702	61.695	55.179	11.078	102.953	62.981	- 8.097
1800	8.794	62.195	55.555	11.952	102.824	60.634	- 7.362
1900	8.890	62.673	55.917	12.837	102.700	58.295	- 6.705
2000	8.989	63.131	56.266	13.730	102.579	55.961	- 6.115
2100	9.090	63.572	56.604	14.634	102.465	53.633	- 5.582
2200	9.195	63.998	56.930	15.549	102.356	51.309	- 5.097
2300	9.302	64.409	57.246	16.474	102.254	48.992	- 4.655
2400	9.411	64.807	57.553	17.409	102.159	46.678	- 4.251
2500	9.519	65.193	57.851	18.356	102.072	44.367	- 3.879
2600	9.628	65.569	58.141	19.313	101.992	42.061	- 3.536
2700	9.735	65.934	58.423	20.281	101.921	39.757	- 3.218
2800	9.840	66.290	58.697	21.260	101.858	37.456	- 2.924
2900	9.942	66.637	58.965	22.249	101.802	35.158	- 2.650
3000	10.040	66.976	59.227	23.248	101.754	32.860	- 2.394
3100	10.135	67.307	59.482	24.257	101.713	30.565	- 2.155
3200	10.225	67.630	59.732	25.275	101.679	28.270	- 1.931
3300	10.310	67.946	59.976	26.302	101.651	25.974	- 1.720
3400	10.390	68.255	60.215	27.337	101.630	23.684	- 1.522
3500	10.464	68.557	60.449	28.379	101.614	21.388	- 1.336
3600	10.534	68.853	60.678	29.429	101.603	19.097	- 1.159
3700	10.598	69.142	60.903	30.486	101.596	16.806	- .993
3800	10.656	69.426	61.123	31.549	101.594	14.516	- .835
3900	10.710	69.703	61.340	32.617	101.595	12.226	- .685
4000	10.758	69.975	61.552	33.690	101.600	9.934	- .543
4100	10.802	70.241	61.761	34.768	101.606	7.640	- .407
4200	10.841	70.502	61.966	35.851	101.615	5.351	- .278
4300	10.876	70.758	62.168	36.937	101.625	3.058	- .155
4400	10.906	71.008	62.366	38.026	101.636	.764	- .038
4500	10.933	71.253	62.560	39.118	101.647	- 1.530	.074
4600	10.956	71.494	62.752	40.212	101.659	- 3.820	.182
4700	10.975	71.730	62.941	41.309	101.672	- 6.114	.284
4800	10.991	71.961	63.126	42.407	101.682	- 8.406	.383
4900	11.005	72.188	63.309	43.507	101.693	- 10.702	.477
5000	11.016	72.410	63.489	44.608	101.702	- 12.993	.568
5100	11.024	72.628	63.666	45.710	101.709	- 15.294	.655
5200	11.031	72.843	63.840	46.813	101.716	- 17.585	.739
5300	11.035	73.053	64.012	47.916	101.720	- 19.878	.820
5400	11.038	73.259	64.181	49.020	101.723	- 22.172	.897
5500	11.039	73.462	64.348	50.123	101.722	- 24.465	.972
5600	11.039	73.660	64.513	51.227	101.720	- 26.760	1.044
5700	11.036	73.856	64.675	52.331	101.714	- 29.057	1.114
5800	11.034	74.048	64.835	53.435	101.706	- 31.350	1.181
5900	11.029	74.236	64.993	54.538	101.694	- 33.641	1.246
6000	11.025	74.422	65.148	55.640	101.680	- 35.940	1.309

Dec. 31, 1960; June 30, 1961; Dec. 31, 1962; Dec. 31, 1966; June 30, 1969

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 48.41 ± 0.01 gibbs/mol

ΔHf°_0 = 103.2 ± 2.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 104.0 ± 2.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	58960	2
9118	4	59683	4
25798	2	60939	4
53955	4	64782	4

$\omega_e = 2068.61\ cm^{-1}$ $\omega_e x_e = 13.114\ cm^{-1}$ $\sigma = 1$

$B_e = 1.8989\ cm^{-1}$ $\alpha_e = 0.0172\ cm^{-1}$ $r_e = 1.175\ \text{Å}$

Heat of Formation

The heat of formation of CN has been the subject of considerable uncertainty for many years. J. Berkowitz (1) has reviewed the earlier work and he concludes that ΔHf°_0(CN, g) = 109 kcal/mol. Since this review a considerable body of work has emerged which supports a value near 100 kcal/mol.

Tsang et al. (2) obtained ΔHf°_{298}(CN, g) = 100 ± 4 kcal/mol from shock tube studies of the decomposition of cyanogen.

Dibeler and Liston (3, 4) have studied a series of cyanogen compounds and obtained their heats of dissociation from photoionization threshold measurements. The values below are obtained from the halogen ion threshold measurements using JANAF auxilliary data, except for HCN which is from the CN^+ threshold measurements. The value below is calculated using the ionization potential from CNCl measurements (3).

Davis and Okabe (5) employed a direct photodissociation technique to obtain dissociation energies for many of the same molecules. The method determines the disappearance threshold for fluorescence due to decay of excited molecules CN $B^2\Sigma^+$ - $X^2\Sigma^+$. This corresponds to the energy needed to just break the bond and form excited cyanogen in the $B^2\Sigma^+$ state, whose energy above ground is well known.

Setser and Stedman (6) used metastable excited argon atoms with a maximum electronic energy of 270 kcal/mol to break the bonds in HCN and $(CN)_2$. From the emission spectra of the excited $B^2\Sigma^+$ CN they were able to calculate the highest populated vibrational level and thus a maximum limit to the dissociation energy.

Berkowitz et al. (7) have recently examined the photoionization spectrum of HCN using the H^+ ion threshold. They also determined the threshold for the CN^+ ion which agrees exactly with that of Dibeler and Liston (4) when the latter is corrected for rotational energy contributions (0.7 kcal). Berkowitz et al. (7) suggest that the HCN limit of Setser and Steadman (6) should be ≤105 due to neglect of the significant vibrational population of the first harmonic of the bending mode. However, if the same allowance is made for the C_2N_2 data the limit is only ≤104 and this presumes significant occupation of the third harmonic of the bending mode of C_2N_2.

It is apparent from the data that considerable scatter still exists and several sources of error are probable. HCN and the cyanogen halides all have significant uncertainties in their heats of formation, and the effects of rotational and vibrational contributions at 300°K are uncertain, but could be eliminated by using refrigerated gases. We choose to adopt a median value within the range of almost all determinations of ΔHf°_0(CN, g) = 103.2 ± 2.5 kcal/mol.

X	$\Delta Hr^\circ_0(CNX \rightarrow CN + X)$ kcal					ΔHf°_0(CN, g) kcal/mole				
Reference	2	3, 4	5	6	7	2	3, 4	5	6	7
Cl		99.23±0.5	99.86±1.2				103.5±2.0	104.1±2.5		
Br		84.72±0.5	86.94±1.2				102.6±2.0	104.8±2.5		
I		72.95±0.5	71.72±1.0				101.4±2.0	100.2±2.5		
H		119.99±0.5	119.92±1.2	≤124	124.57±0.3		100.7±2.5	100.7±3.0	≤103	105.3±2.5
CN	125±8		129.61±1.2	≤133		100±4		101.5±0.8	≤103	

Heat Capacity and Entropy

The thermodynamic functions are taken from Johnston et al. (8) calculated based on the direct summation of the energy levels. All the electronic levels and molecular constants listed above are from Carroll (9). Johnston et al. used only the first two excited electronic states but the contribution of the higher levels is negligible.

References

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Cyano Unipositive Ion (CN^+)

(Ideal Gas) GFW = 26.01730

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.034	50.986	50.986	.000	429.400	419.940	-307.824
300	7.037	51.029	50.986	.013	429.412	419.881	-305.883
400	7.240	53.079	51.264	.726	430.027	416.610	-227.625
500	7.514	54.723	51.796	1.463	430.591	413.189	-180.605
600	7.788	56.118	52.403	2.229	431.119	409.659	-149.218
700	8.027	57.337	53.023	3.020	431.617	406.042	-126.772
800	8.225	58.422	53.631	3.833	432.097	402.356	-109.918
900	8.385	59.400	54.219	4.664	432.558	398.610	-96.796
1000	8.516	60.291	54.782	5.509	433.007	394.813	-86.286
1100	8.624	61.108	55.320	6.366	433.444	390.973	-77.679
1200	8.716	61.862	55.835	7.233	433.872	387.094	-70.499
1300	8.797	62.563	56.325	8.109	434.289	383.177	-64.418
1400	8.870	63.218	56.795	8.992	434.703	379.231	-59.201
1500	8.937	63.832	57.244	9.883	435.112	375.255	-54.675
1600	9.001	64.411	57.674	10.779	435.518	371.250	-50.710
1700	9.061	64.958	58.086	11.683	435.923	367.221	-47.209
1800	9.119	65.478	58.482	12.592	436.324	363.167	-44.094
1900	9.175	65.972	58.864	13.506	436.727	359.095	-41.305
2000	9.229	66.444	59.231	14.427	437.131	354.998	-38.792
2100	9.281	66.896	59.585	15.352	437.535	350.881	-36.517
2200	9.331	67.329	59.928	16.283	437.939	346.744	-34.446
2300	9.379	67.745	60.258	17.218	438.344	342.590	-32.553
2400	9.425	68.145	60.579	18.158	438.750	338.419	-30.817
2500	9.469	68.530	60.889	19.103	439.159	334.229	-29.218
2600	9.510	68.903	61.190	20.052	439.567	330.024	-27.741
2700	9.550	69.262	61.483	21.005	439.978	325.803	-26.372
2800	9.587	69.610	61.767	21.962	440.390	321.567	-25.099
2900	9.622	69.947	62.043	22.923	440.802	317.317	-23.914
3000	9.656	70.274	62.312	23.886	441.215	313.050	-22.806
3100	9.687	70.591	62.574	24.854	441.630	308.771	-21.768
3200	9.716	70.899	62.829	25.824	442.045	304.481	-20.795
3300	9.743	71.199	63.078	26.797	442.460	300.174	-19.880
3400	9.769	71.490	63.322	27.772	442.876	295.858	-19.018
3500	9.793	71.773	63.559	28.750	443.292	291.525	-18.204
3600	9.815	72.050	63.791	29.731	443.708	287.184	-17.434
3700	9.835	72.319	64.018	30.713	444.125	282.828	-16.706
3800	9.854	72.581	64.240	31.698	444.541	278.467	-16.015
3900	9.872	72.838	64.457	32.684	444.958	274.093	-15.360
4000	9.888	73.088	64.670	33.672	445.373	269.704	-14.736
4100	9.903	73.332	64.878	34.662	445.788	265.303	-14.142
4200	9.917	73.571	65.082	35.653	446.202	260.903	-13.576
4300	9.930	73.804	65.282	36.645	446.615	256.485	-13.036
4400	9.942	74.033	65.479	37.639	447.028	252.058	-12.520
4500	9.953	74.256	65.671	38.633	447.438	247.618	-12.026
4600	9.963	74.475	65.860	39.629	447.848	243.177	-11.554
4700	9.972	74.690	66.046	40.626	448.258	238.722	-11.101
4800	9.980	74.900	66.228	41.624	448.665	234.260	-10.666
4900	9.988	75.106	66.407	42.622	449.071	229.789	-10.249
5000	9.995	75.307	66.583	43.621	449.475	225.313	-9.848
5100	10.001	75.505	66.756	44.621	449.877	220.816	-9.463
5200	10.007	75.700	66.926	45.622	450.278	216.327	-9.092
5300	10.012	75.890	67.094	46.622	450.677	211.823	-8.735
5400	10.017	76.078	67.258	47.624	451.074	207.313	-8.390
5500	10.022	76.261	67.420	48.626	451.468	202.798	-8.058
5600	10.025	76.442	67.580	49.628	451.861	198.268	-7.738
5700	10.029	76.619	67.737	50.631	452.251	193.740	-7.428
5800	10.032	76.794	67.891	51.634	452.639	189.198	-7.129
5900	10.035	76.965	68.044	52.637	453.025	184.655	-6.840
6000	10.037	77.134	68.194	53.641	453.409	180.102	-6.560

June 30, 1969

Ground State Configuration $[^3\Pi]$

$\Delta Hf^\circ_0 = 428.6 \pm 3.0$ kcal/mol

$S^\circ_{298.15} = 50.98 \pm 1.5$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 429.4 \pm 3.0$ kcal/mol

Electronic Levels and Degeneracies

ε_i, cm^{-1}	g_i
0	[6]
[1500]	[1]
[6000]	[2]
[8000]	[3]
[15000]	[2]

$\omega_e = [1580]\ cm^{-1}$ $\omega_e x_e = [12.5]\ cm^{-1}$ $\sigma = 1$

$B_e = [1.566]\ cm^{-1}$ $\alpha_e = [0.017]\ cm^{-1}$ $r_e = 1.29$ Å

Heat of Formation

Dibeler and Liston (1) have measured the photoionization thresholds for the processes:

$ClCN + h\nu \rightarrow Cl^+ + CN + e^-$ $\Delta Hr^\circ_0 = 399.44 \pm 0.5$ kcal

$ClCN + h\nu \rightarrow Cl + CN^+ + e^-$ $\Delta Hr^\circ_0 = 426.65 \pm 0.5$ kcal

By subtraction we obtain

$Cl + CN^+ \rightarrow Cl^+ + CN$ $\Delta Hr^\circ_0 = -27.21 \pm 0.7$ kcal

Using JANAF values for Cl, Cl^+ and CN we obtain $\Delta Hf^\circ_0(CN^+) = 430.6 \pm 3.0$ kcal/mol and the ionization potential of CN, g = 327.42 ± 0.7 kcal/mol.

Berkowitz et al. (2) have measured the photoionization thresholds for the processes:

$HCN + h\nu \rightarrow H^+ + CN + e^-$ $\Delta Hr^\circ_0 = 438.18 \pm 0.3$ kcal

$HCN + h\nu \rightarrow H + CN^+$ $\Delta Hr^\circ_0 = 448.09 \pm 0.3$ kcal

By subtraction we obtain

$H + CN^+ \rightarrow H^+ + CN$ $\Delta Hr^\circ_0 = -9.91 \pm 0.4$ kcal

Using JANAF values for H, H^+ and CN we obtain $\Delta Hf^\circ_0(CN^+) = 426.7 \pm 3.0$ kcal/mol, and the ionization potential of CN, g = 323.51 ± 0.4 kcal/mol.

We adopt a median value for $\Delta Hf^\circ_0(CN^+) = 428.6 \pm 3.0$ kcal/mol and 325.4 ± 2 kcal/mol for the ionization potential of CN.

Heat Capacity and Entropy

The molecule has eight valence electrons and thus we expect that its molecular constants should fall between those for C_2 and BN. The ground electronic state is either $^1\Sigma$ or $^3\Pi$ and the two levels are likely to be very close. As a consequence the thermodynamic functions are dominated by the $^3\Pi$ contribution and so we choose this to be the ground state. The other levels are estimated based on the values of Fougere and Nesbet (3) for C_2 and of Verhaegen et al. (4) for BN. The vibrational constants and bond length are estimated between those for the $^3\Pi$ states of BN and C_2. The rotational constants B_e is obtained from the estimated bond length and α_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.076 kcal/mol.

References:

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Cyano Uninegative Ion (CN^-)

(Ideal Gas) GFW = 26.01840

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.963	46.813	46.813	.000	16.000	10.758	- 7.886
300	6.963	46.856	46.813	.013	15.993	10.726	- 7.814
400	7.002	48.863	47.086	.711	15.600	9.027	- 4.932
500	7.097	50.435	47.604	1.415	15.137	7.436	- 3.250
600	7.240	51.741	48.188	2.132	14.622	5.944	- 2.165
700	7.406	52.869	48.778	2.864	14.069	4.542	- 1.418
800	7.575	53.869	49.353	3.613	13.491	3.220	- .880
900	7.735	54.770	49.905	4.379	12.893	1.970	- .478
1000	7.880	55.593	50.434	5.159	12.284	.789	- .173
1100	8.008	56.350	50.937	5.954	11.664	- .331	.066
1200	8.120	57.052	51.418	6.760	11.037	- 1.394	.254
1300	8.218	57.706	51.877	7.578	10.404	- 2.403	.404
1400	8.303	58.318	52.315	8.404	9.767	- 3.364	.525
1500	8.377	58.893	52.735	9.238	9.125	- 4.279	.623
1600	8.442	59.436	53.137	10.079	8.481	- 5.153	.704
1700	8.498	59.950	53.523	10.926	7.836	- 5.985	.769
1800	8.548	60.437	53.893	11.778	7.189	- 6.779	.823
1900	8.592	60.900	54.250	12.635	6.540	- 7.537	.867
2000	8.631	61.342	54.594	13.496	5.890	- 8.261	.903
2100	8.666	61.764	54.925	14.361	5.240	- 8.951	.932
2200	8.698	62.168	55.245	15.230	4.588	- 9.614	.955
2300	8.726	62.555	55.555	16.101	3.936	- 10.242	.973
2400	8.752	62.927	55.854	16.975	3.283	- 10.846	.988
2500	8.775	63.285	56.144	17.851	2.629	- 11.422	.999
2600	8.796	63.629	56.426	18.730	1.973	- 11.971	1.006
2700	8.816	63.962	56.699	19.610	1.317	- 12.497	1.012
2800	8.834	64.283	56.964	20.493	.661	- 12.995	1.014
2900	8.850	64.593	57.222	21.377	.004	- 13.471	1.015
3000	8.866	64.893	57.472	22.263	- .655	- 13.923	1.014
3100	8.880	65.184	57.716	23.150	- 1.313	- 14.354	1.012
3200	8.894	65.466	57.954	24.039	- 1.974	- 14.767	1.009
3300	8.906	65.740	58.186	24.929	- 2.636	- 15.158	1.004
3400	8.918	66.006	58.412	25.820	- 3.297	- 15.525	.998
3500	8.929	66.265	58.633	26.712	- 3.960	- 15.879	.992
3600	8.940	66.517	58.848	27.606	- 4.625	- 16.210	.984
3700	8.950	66.762	59.059	28.500	- 5.290	- 16.518	.976
3800	8.960	67.001	59.265	29.396	- 5.957	- 16.813	.967
3900	8.969	67.233	59.466	30.292	- 6.624	- 17.089	.958
4000	8.978	67.461	59.663	31.190	- 7.292	- 17.348	.948
4100	8.986	67.682	59.856	32.088	- 7.962	- 17.592	.938
4200	8.994	67.899	60.045	32.987	- 8.634	- 17.819	.927
4300	9.002	68.111	60.230	33.887	- 9.307	- 18.031	.916
4400	9.009	68.318	60.412	34.787	- 9.982	- 18.228	.905
4500	9.017	68.520	60.589	35.688	- 10.657	- 18.407	.894
4600	9.024	68.719	60.764	36.590	- 11.335	- 18.570	.882
4700	9.030	68.913	60.935	37.493	- 12.013	- 18.720	.870
4800	9.037	69.103	61.104	38.397	- 12.694	- 18.852	.858
4900	9.043	69.289	61.269	39.301	- 13.376	- 18.978	.846
5000	9.050	69.472	61.431	40.205	- 14.059	- 19.084	.834
5100	9.056	69.651	61.590	41.110	- 14.746	- 19.182	.822
5200	9.062	69.827	61.747	42.016	- 15.433	- 19.261	.810
5300	9.067	70.000	61.901	42.923	- 16.123	- 19.326	.797
5400	9.073	70.169	62.053	43.830	- 16.814	- 19.378	.784
5500	9.079	70.336	62.202	44.737	- 17.508	- 19.419	.772
5600	9.084	70.500	62.349	45.646	- 18.202	- 19.445	.759
5700	9.090	70.660	62.493	46.554	- 18.900	- 19.469	.746
5800	9.095	70.819	62.635	47.463	- 19.600	- 19.469	.734
5900	9.100	70.974	62.775	48.373	- 20.301	- 19.458	.721
6000	9.105	71.127	62.913	49.283	- 21.005	- 19.445	.708

June 30, 1969

CYANO UNINEGATIVE ION (CN^-) (IDEAL GAS) GFW = 26.01840

Ground State Configuration $[^1\Sigma^+]$

ΔHf°_0 = 15.2 ± 3 kcal/mol

$S^\circ_{298.15}$ = 46.81 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 16 ± 3 kcal/mol

Electronic Levels and Degeneracies

ϵ_i, cm^{-1}	g_i
0	[1]
[67000]	[2]

ω_e = [2250] cm^{-1} $\omega_e x_e$ = [13.8] cm^{-1} σ = 1

B_e = [2.116] cm^{-1} α_e = [0.0177] cm^{-1} r_e = [1.11] Å

Heat of Formation

Berkowitz et al. (1) have recently obtained 88 ± 0.5 kcal for the electron affinity of CN from the photoionization thresholds of the reactions $HCN \rightarrow H^+ + CN^-$ and $HCN \rightarrow H^+ + CN + e^-$.

Other values have been reported by Page (2), who reinterpreted his earlier data (3), to yield 73 ± 1 kcal/mol; Bakulina and Ionov (4) in conjunction with the data of Branscomb and Smith (5) reported 78 ± 5 kcal/mol and Inoue (6) who obtained 83 ± 7 kcal/mol.

We adopt the value given by Berkowitz et al. (1) as being the most well defined in terms of both the precision of measurements and the reactions being studied. This leads to $\Delta Hf^\circ_0(CN^-, g)$ = 15.2 ± 3 kcal/mol or $\Delta Hf^\circ_{298}(CN^-, g)$ = 16 ± 3 kcal/mol.

Heat Capacity and Entropy

The electronic structure and molecular constants are estimated by analogy with the isoelectronic species CO and N_2. The uncertainties in the constants are generally small since N_2 and CO are quite similar, thus the entropy has an uncertainty of only 0.5 eu. The enthalpy at 0°K is -2.072 kcal/mol.

References:

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2. F. M. Page, J. Chem. Phys. 49, 2466 (1968).
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Sodium Cyanide (NaCN)

(Crystal) Mol. Wt. = 49. 00765

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 4.642	- 23.493	- 23.493	INFINITE
100	11.320	8.400	47.821	- 3.942	- 23.470	- 21.814	47.674
200	16.223	19.138	30.913	- 2.355	- 22.899	- 20.339	22.225
298	16.415	28.315	28.315	- .000	- 21.680	- 19.227	14.094
300	16.390	28.416	28.315	.030	- 21.672	- 19.211	13.995
400	16.410	33.141	28.960	1.672	- 21.969	- 18.397	10.052
500	16.432	36.805	30.176	3.315	- 21.738	- 17.531	7.663
600	16.455	39.803	31.538	4.959	- 21.549	- 16.709	6.086
700	16.478	42.341	32.905	6.606	- 21.397	- 15.915	4.969
800	16.502	44.543	34.225	8.255	- 21.273	- 15.140	4.136
900	16.526	46.488	35.482	9.906	- 21.179	- 14.380	3.492
1000	16.550	48.231	36.671	11.560	- 21.108	- 13.629	2.979
1100	16.576	49.809	37.795	13.216	- 21.064	- 12.885	2.560
1200	16.602	51.253	38.857	14.875	- 44.282	- 11.685	2.128
1300	16.628	52.582	39.862	16.536	- 44.072	- 8.976	1.509
1400	16.653	53.816	40.815	18.200	- 43.872	- 6.284	.981
1500	16.678	54.965	41.721	19.867	- 43.681	- 3.605	.525
1600	16.703	56.043	42.583	21.536	- 43.496	- .941	.129
1700	16.728	57.056	43.404	23.208	- 43.316	1.714	- .220
1800	16.752	58.013	44.190	24.882	- 43.143	4.357	- .529
1900	16.776	58.919	44.941	26.558	- 42.972	6.994	- .805
2000	16.800	59.780	45.662	28.237	- 42.805	9.619	- 1.051

Dec. 31, 1960; Mar. 31, 1966

SODIUM CYANIDE (NaCN) (CRYSTAL) MOL. WT. = 49.00765

$S^\circ_{298.15}$ = [28.32 ± 0.5] cal. deg.$^{-1}$ mole^{-1}

T_m = 835° K.

$\Delta H^\circ_{f\ 0}$ = -23.49 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -21.68 ± 0.3 kcal. mole^{-1}

ΔH°_m = [2.1] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to dimer) = [41.3] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to monomer) = 44.21 kcal. mole^{-1}

Heat of Formation.

The enthalpy change for the reaction NaCN(c) → NaCN(∞ H_2O) was reported to be 0.29 ± 0.20 kcal. mole^{-1} by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heats of formation for Na^+(∞ H_2O), -57.39, and CN^-(∞ H_2O), 36.0 kcal. mole^{-1}, reported by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properites," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of $\Delta H^\circ_{f\ 298.15}$ for NaCN(c) was derived and adopted.

G. Lord and A. A. Woolf, J. Chem. Soc. 2546 (1954), determined the value, $\Delta H^\circ_{f\ 298.15}$(NaCN, c) = -21.4 kcal. mole^{-1}, by solution calorimetry. This value is in agreement with the adopted one.

Heat Capacity and Entropy.

The low temperature heat capacities, 101.6-345.8°K., were reported by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941). The C_p values above 345.8°K. were estimated by graphical extrapolation. $S^\circ_{298.15}$ was derived from low temperature heat capacities, based on S°_{100} = 8.4 cal. deg.$^{-1}$ mole^{-1} which was estimated by comparison with the $S^\circ_{298.15}$ values for NaCl, KCl, and KCN crystals.

Transition Data.

The transition temperatures, T_{t_2} and T_{t_1}, were determined by C. E. Messer and W. T. Ziegler, loc. cit. The corresponding enthalpies of transition were reported to be 0.15 and 0.70 kcal. mole^{-1}, respectively. However, these quantities were incorporated with C_p values used to evaluate $H^\circ-H^\circ_{298.15}$. Therefore ΔH_t°'s are not listed.

Melting Data.

ee NaCN(l) table for details.

Heat Sublimation.

The difference between $\Delta H^\circ_{f\ 298.15}$ for $(NaCN)_2$(g) and 2NaCN(c) is $\Delta H^\circ_{s\ 298.15}$ (to dimer) and for NaCN(g) and NaCN(c) is $\Delta H^\circ_{s\ 298.15}$(to monomer).

Sodium Cyanide (NaCN)

(Liquid) Mol. Wt. = 49.00765

CNNa

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	16.415	29.996	29.996	.000	-20.160	-18.208	13.347
300	16.390	30.097	29.996	.030	-20.152	-18.196	13.256
400	16.410	34.822	30.641	1.672	-20.449	-17.549	9.588
500	16.432	38.486	31.857	3.315	-20.218	-16.852	7.366
600	19.000	41.484	33.219	4.959	-20.029	-16.197	5.900
700	19.000	44.413	34.614	6.859	-19.624	-15.592	4.868
800	19.000	46.950	36.001	8.759	-19.249	-15.041	4.109
900	19.000	49.188	37.345	10.659	-18.906	-14.537	3.530
1000	19.000	51.190	38.631	12.559	-18.589	-14.069	3.075
1100	19.000	53.001	39.856	14.459	-18.302	-13.633	2.709
1200	19.000	54.654	41.021	16.359	-41.278	-12.762	2.324
1300	19.000	56.175	42.129	18.259	-40.830	-10.404	1.749
1400	19.000	57.583	43.184	20.159	-40.393	-8.080	1.261
1500	19.000	58.894	44.188	22.059	-39.969	-5.787	.843
1600	19.000	60.120	45.146	23.959	-39.554	-3.522	.481
1700	19.000	61.272	46.061	25.859	-39.145	-1.282	.165
1800	19.000	62.358	46.936	27.759	-38.746	.934	-.113
1900	19.000	63.385	47.775	29.659	-38.351	3.130	-.360
2000	19.000	64.360	48.580	31.559	-37.963	5.301	-.579
2100	19.000	65.287	49.354	33.459	-37.578	7.454	-.776
2200	19.000	66.170	50.098	35.359	-37.200	9.591	-.953
2300	19.000	67.015	50.816	37.259	-36.825	11.709	-1.113
2400	19.000	67.824	51.507	39.159	-36.454	13.812	-1.258
2500	19.000	68.599	52.176	41.059	-36.087	15.897	-1.390
2600	19.000	69.345	52.822	42.959	-35.725	17.969	-1.510
2700	19.000	70.062	53.447	44.859	-35.367	20.025	-1.621
2800	19.000	70.753	54.053	46.759	-35.012	22.070	-1.723
2900	19.000	71.419	54.640	48.659	-34.662	24.108	-1.817
3000	19.000	72.063	55.210	50.559	-34.318	26.128	-1.903

Dec. 31, 1960; Mar. 31, 1966

SODIUM CYANIDE (NaCN) (LIQUID) MOL. WT. = 49.00765

$S^\circ_{298.15}$ = [29.996] cal. deg.$^{-1}$ mole^{-1}

T_m = 835° K.

T_b = [1803]°K.

$\Delta H^\circ_{f\ 298.15}$ = [-20.160] kcal. mole^{-1}

ΔH°_m = [2.1] kcal. mole^{-1}

ΔH°_v = [35.39] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}(l)$ was obtained from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{835}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with those for NaCN(c), KCN(c) and KCN(l). A glass transition temperature is assumed at 600°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by W. Truthe, Z. anorg. Chem. 76, 129 (1912). ΔH°_m was estimated such that the derived third law value for ΔH°_v (NaCN, l) agrees with the second law value. See NaCN(g) table for details.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction NaCN(l) = NaCN(g) becomes zero. The difference between ΔH°_f for NaCN(g) and NACN(l) at T_b is ΔH°_v.

CNNa

Sodium Cyanide (NaCN)

(Ideal Gas) Mol. Wt. = 49.00765

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.898	22.461	22.461	INFINITE
100	8.775	46.583	68.119	- 2.154	22.529	20.366	- 44.510
200	11.119	53.511	59.214	- 1.141	22.525	18.211	- 19.900
298	11.993	58.139	58.139	.000	22.530	16.091	- 11.795
300	12.003	58.213	58.139	.022	22.530	16.051	- 11.693
400	12.419	61.729	58.616	1.245	21.814	13.951	- 7.622
500	12.707	64.532	59.528	2.502	21.660	12.003	- 5.246
600	12.960	66.872	60.562	3.786	21.488	10.087	- 3.674
700	13.194	68.887	61.611	5.093	21.301	8.200	- 2.560
800	13.405	70.663	62.634	6.424	21.106	6.343	- 1.733
900	13.592	72.253	63.616	7.774	20.899	4.509	- 1.095
1000	13.754	73.694	64.552	9.141	20.684	2.699	- .590
1100	13.893	75.011	65.444	10.524	20.453	.911	- .181
1200	14.012	76.225	66.293	11.919	- 3.028	- .397	.072
1300	14.113	77.351	67.101	13.326	- 3.073	- .177	.030
1400	14.200	78.400	67.871	14.741	- 3.121	.049	- .008
1500	14.274	79.382	68.606	16.165	- 3.172	.278	- .040
1600	14.338	80.306	69.308	17.596	- 3.227	.508	- .069
1700	14.393	81.177	69.981	19.032	- 3.282	.743	- .096
1800	14.441	82.001	70.626	20.474	- 3.340	.982	- .119
1900	14.483	82.783	71.246	21.921	- 3.399	1.225	- .141
2000	14.520	83.527	71.841	23.371	- 3.461	1.469	- .160
2100	14.552	84.236	72.415	24.824	- 3.523	1.717	- .179
2200	14.580	84.914	72.968	26.281	- 3.588	1.966	- .195
2300	14.606	85.562	73.501	27.740	- 3.653	2.222	- .211
2400	14.628	86.184	74.017	29.202	- 3.721	2.481	- .226
2500	14.648	86.782	74.515	30.666	- 3.790	2.737	- .239
2600	14.666	87.357	74.998	32.132	- 3.862	3.000	- .252
2700	14.682	87.911	75.466	33.599	- 3.936	3.263	- .264
2800	14.697	88.445	75.920	35.068	- 4.013	3.532	- .276
2900	14.710	88.961	76.361	36.538	- 4.093	3.806	- .287
3000	14.722	89.460	76.790	38.010	- 4.176	4.078	- .297
3100	14.733	89.943	77.206	39.483	- 4.263	4.354	- .307
3200	14.743	90.411	77.612	40.957	- 4.354	4.633	- .316
3300	14.753	90.864	78.006	42.432	- 4.451	4.916	- .326
3400	14.761	91.305	78.391	43.907	- 4.551	5.202	- .334
3500	14.769	91.733	78.766	45.384	- 4.659	5.489	- .343
3600	14.776	92.149	79.132	46.861	- 4.773	5.781	- .351
3700	14.782	92.554	79.489	48.339	- 4.893	6.074	- .359
3800	14.789	92.948	79.838	49.817	- 5.020	6.378	- .367
3900	14.794	93.332	80.180	51.297	- 5.157	6.680	- .374
4000	14.799	93.707	80.513	52.776	- 5.302	6.984	- .382
4100	14.804	94.073	80.839	54.256	- 5.459	7.290	- .389
4200	14.809	94.429	81.159	55.737	- 5.627	7.607	- .396
4300	14.813	94.778	81.471	57.218	- 5.807	7.923	- .403
4400	14.817	95.118	81.778	58.700	- 6.001	8.244	- .409
4500	14.821	95.452	82.078	60.182	- 6.211	8.567	- .416
4600	14.824	95.777	82.372	61.664	- 6.437	8.902	- .423
4700	14.828	96.096	82.661	63.146	- 6.681	9.236	- .429
4800	14.831	96.408	82.944	64.629	- 6.947	9.580	- .436
4900	14.834	96.714	83.222	66.113	- 7.233	9.926	- .443
5000	14.836	97.014	83.495	67.596	- 7.544	10.281	- .449
5100	14.839	97.308	83.763	69.080	- 7.883	10.633	- .456
5200	14.841	97.596	84.026	70.564	- 8.248	11.003	- .462
5300	14.844	97.879	84.285	72.048	- 8.644	11.376	- .469
5400	14.846	98.156	84.539	73.533	- 9.074	11.762	- .476
5500	14.848	98.429	84.789	75.017	- 9.541	12.148	- .483
5600	14.850	98.696	85.035	76.502	- 10.044	12.549	- .490
5700	14.852	98.959	85.277	77.987	- 10.589	12.955	- .497
5800	14.853	99.217	85.515	79.472	- 11.177	13.375	- .504
5900	14.855	99.471	85.749	80.958	- 11.810	13.808	- .511
6000	14.857	99.721	85.980	82.443	- 12.489	14.241	- .519

Dec. 31, 1960; Mar. 31, 1966

SODIUM CYANIDE (NaCN) (IDEAL GAS) MOL. WT. = 49.00765

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = [58.14] cal. deg.$^{-1}$ mole^{-1}

Group State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = 22.46 ± 0.50 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 22.53 ± 0.50 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[400](1)
239 (2)
2176 (1)

Bond Distance: Na-C = [1.992] Å C-N = [1.16] Å

Bond Angle: Na-C-N = [180]°

Rotational Constant: B = [0.18272] cm.$^{-1}$

σ = 1

Heat of Formation.

The vapor pressures of NaCN(l) at temperatures 805-1353°K. were measured by C. K. Ingold, J. Chem. Soc. 123, 885 (1923). According to the investigation reported by R. F. Porter, J. Chem. Phys. 35, 318 (1961), the vapor consists of NaCN and $(NaCN)_2$. Based on his data the dimer/monomer ratios at temperatures 805-1353°C. (1078.2-1626.2°K.) were calculated to be 0.29-0.09. Hence the respective partial pressures for NaCN(g) and $(NaCN)_2(g)$ were derived. By the second and third law methods, the values of $\Delta H_v^\circ{}_{298.15}$ (l → monomer) were evaluated to be 43.43 and 42.69 kcal. mole^{-1}, respectively. The heat of formation ($\Delta H_f^\circ{}_{298.15}$) for NaCN(g) was calculated from $\Delta H_f^\circ{}_{298.15}$ (NaCN, c) and the third law value for ΔH_v°.

Heat Capacity and Entropy.

The molecular structure of NaCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was assumed to be the same as that in KCN(g) and the Na-C bond distance was taken from G. E. Leroi, Ph. D. Dissertation, Harvard University, 1961, which was calculated. The vibrational frequencies, ν_2 and ν_3, were measured by G. E. Leroi and W. Klemperer, J. Chem. Phys. 35, 774 (1961) from infrared absorption spectra. The value of ν_1 was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is 1.53187 X 10^{-38} g. cm.^{2}

CNN Radical (CN_2)

(Ideal Gas)   GFW = 40.02455

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.479	139.545	139.545	INFINITE
100	7.403	45.837	63.598	-1.776	139.541	138.795	-303.337
200	9.100	51.517	56.250	-.947	139.596	138.035	-150.838
298	10.105	55.354	55.354	.000	139.700	137.248	-100.605
300	10.120	55.417	55.355	.019	139.702	137.232	-99.973
400	10.803	58.427	55.760	1.067	139.807	136.393	-74.522
500	11.323	60.896	56.548	2.174	139.892	135.529	-59.240
600	11.745	62.999	57.452	3.328	139.956	134.650	-49.046
700	12.104	64.837	58.378	4.521	139.996	133.762	-41.762
800	12.416	66.474	59.290	5.747	140.020	132.871	-36.299
900	12.691	67.953	60.172	7.003	140.030	131.975	-32.048
1000	12.933	69.302	61.018	8.284	140.031	131.080	-28.648
1100	13.144	70.545	61.828	9.588	140.024	130.185	-25.865
1200	13.330	71.697	62.603	10.912	140.011	129.292	-23.547
1300	13.491	72.771	63.345	12.254	139.993	128.398	-21.586
1400	13.633	73.776	64.054	13.610	139.972	127.508	-19.905
1500	13.756	74.720	64.734	14.979	139.948	126.619	-18.448
1600	13.864	75.612	65.386	16.361	139.924	125.730	-17.174
1700	13.959	76.455	66.013	17.752	139.898	124.844	-16.050
1800	14.042	77.255	66.615	19.152	139.870	123.960	-15.051
1900	14.115	78.017	67.196	20.560	139.843	123.077	-14.157
2000	14.180	78.742	67.755	21.975	139.815	122.197	-13.353
2100	14.238	79.436	68.295	23.396	139.787	121.315	-12.625
2200	14.290	80.099	68.816	24.822	139.756	120.436	-11.964
2300	14.336	80.735	69.321	26.253	139.726	119.560	-11.361
2400	14.377	81.346	69.809	27.689	139.696	118.684	-10.808
2500	14.414	81.934	70.283	29.129	139.665	117.807	-10.299
2600	14.447	82.500	70.742	30.572	139.632	116.934	-9.829
2700	14.477	83.046	71.187	32.018	139.599	116.060	-9.394
2800	14.505	83.573	71.620	33.467	139.566	115.189	-8.991
2900	14.530	84.082	72.041	34.919	139.532	114.322	-8.616
3000	14.552	84.575	72.451	36.373	139.496	113.453	-8.265
3100	14.573	85.053	72.850	37.829	139.460	112.583	-7.937
3200	14.592	85.516	73.238	39.288	139.423	111.717	-7.630
3300	14.610	85.965	73.617	40.748	139.383	110.851	-7.341
3400	14.626	86.402	73.987	42.209	139.343	109.988	-7.070
3500	14.640	86.826	74.348	43.673	139.302	109.121	-6.814
3600	14.654	87.238	74.700	45.137	139.258	108.262	-6.572
3700	14.667	87.640	75.044	46.604	139.215	107.402	-6.344
3800	14.679	88.031	75.381	48.071	139.169	106.546	-6.128
3900	14.689	88.413	75.710	49.539	139.122	105.688	-5.923
4000	14.700	88.785	76.033	51.009	139.074	104.830	-5.728
4100	14.709	89.148	76.348	52.479	139.023	103.972	-5.542
4200	14.718	89.502	76.657	53.950	138.970	103.123	-5.366
4300	14.726	89.849	76.960	55.423	138.917	102.268	-5.198
4400	14.734	90.187	77.257	56.896	138.861	101.417	-5.037
4500	14.741	90.519	77.548	58.369	138.802	100.561	-4.884
4600	14.748	90.843	77.833	59.844	138.743	99.716	-4.738
4700	14.754	91.160	78.113	61.319	138.682	98.868	-4.597
4800	14.760	91.471	78.388	62.795	138.617	98.023	-4.463
4900	14.766	91.775	78.659	64.271	138.551	97.175	-4.334
5000	14.771	92.073	78.924	65.748	138.483	96.338	-4.211
5100	14.776	92.366	79.185	67.225	138.411	95.484	-4.092
5200	14.781	92.653	79.441	68.703	138.339	94.649	-3.978
5300	14.785	92.935	79.693	70.181	138.263	93.807	-3.868
5400	14.789	93.211	79.941	71.660	138.186	92.972	-3.763
5500	14.794	93.482	80.184	73.139	138.104	92.141	-3.661
5600	14.797	93.749	80.424	74.619	138.022	91.301	-3.563
5700	14.801	94.011	80.660	76.099	137.936	90.466	-3.469
5800	14.804	94.268	80.893	77.579	137.847	89.637	-3.378
5900	14.808	94.521	81.121	79.059	137.755	88.809	-3.290
6000	14.811	94.770	81.347	80.540	137.661	87.975	-3.204

June 30, 1966

CNN RADICAL (CN_2)   (IDEAL GAS)   GFW = 40.02455

Point Group $C_{\infty v}$ ΔHf°_0 = [139.5 ± 30] kcal/mol

$S^\circ_{298.15}$ = 55.35 gibbs/mol $\Delta Hf^\circ_{298.15}$ = [139.7 ± 30] kcal/mol

Ground State Quantum Weight = 3

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1241 (1)
393 (2)
2847 (1)

Bond Distance: C-N = [1.15] Å   N-N = [1.25] Å

Bond Angle: C-N-N = 180° σ = 1

Rotational Constant: B_o = [0.450388] cm^{-1}

Heat of Formation.

The heat of formation is calculated from the estimated heat of reaction ΔHr°_0 = 255 ± 30 kcal/mol for CNN(g) → C(g) + 2N(g). Since CNN radical can dissociate to give C + N_2 or CN + N, the molecule must have more energy than either CN or N_2. It is assumed that the extra bond will be quite weak, for this we estimate 30 ± 30 kcal/mol which gives ΔHr°_0 = 255 ± 30 kcal/mol for the first path and ΔHr° = 204 ± 30 kcal/mol for the second. We adopt the former value.

Heat Capacity and Entropy.

D. E. Milligan and M. E. Jacox, J. Chem. Phys. 44, 2850 (1966), have measured three fundamental vibrational frequencies for CNN radical (g) in the infrared and ultraviolet spectra by matrix-isolation, and proposed a linear molecular configuration with a $^3\Sigma$ ground state which has been confirmed by E. Wasserman, L. Barash and W. A. Yager, J. Am. Chem. Soc. 87, 2075 (1965), in the electron paramagnetic resonance observations. Also Milligan and Jacox suggested a "C≡N=N" bond structure, based on the agreement between the C-N and N-N stretching force constants (calculated from observed vibrational frequencies in the CNN radical) and the typical C≡N and N=N stretching force constants. In addition, they estimated the bond distances r_{C-N} = 1.15Å and r_{N-N} = 1.25 Å from the proposed structure. The principal moment of inertia is 6.2148 X 10^{-39} g cm^2.

NCN Radical (CN_2)

(Ideal Gas) GFW = 40.02455

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.485	102.639	102.639	INFINITE
100	7.294	44.683	62.531	- 1.785	102.640	102.004	- 222.930
200	9.098	50.280	55.114	- .967	102.677	101.363	- 110.764
298	10.515	54.194	54.194	.000	102.800	100.694	- 73.810
300	10.537	54.259	54.194	.019	102.802	100.680	- 73.345
400	11.551	57.437	54.621	1.127	102.967	99.949	- 54.610
500	12.292	60.099	55.457	2.321	103.139	99.174	- 43.349
600	12.840	62.391	56.426	3.579	103.307	98.366	- 35.830
700	13.248	64.402	57.425	4.884	103.459	97.530	- 30.450
800	13.555	66.192	58.411	6.225	103.598	96.674	- 26.410
900	13.789	67.803	59.367	7.593	103.720	95.800	- 23.263
1000	13.970	69.265	60.284	8.981	103.828	94.914	- 20.743
1100	14.112	70.604	61.163	10.385	103.921	94.017	- 18.679
1200	14.225	71.837	62.001	11.802	104.001	93.114	- 16.958
1300	14.316	72.979	62.802	13.230	104.069	92.204	- 15.501
1400	14.391	74.043	63.568	14.665	104.127	91.289	- 14.251
1500	14.452	75.038	64.300	16.107	104.176	90.370	- 13.167
1600	14.504	75.972	65.000	17.555	104.218	89.449	- 12.218
1700	14.547	76.853	65.672	19.008	104.254	88.524	- 11.380
1800	14.583	77.685	66.316	20.464	104.282	87.598	- 10.636
1900	14.615	78.475	66.936	21.924	104.307	86.672	- 9.969
2000	14.642	79.225	67.532	23.387	104.327	85.743	- 9.370
2100	14.665	79.940	68.106	24.853	104.344	84.814	- 8.827
2200	14.686	80.623	68.659	26.320	104.354	83.881	- 8.333
2300	14.704	81.276	69.194	27.790	104.363	82.952	- 7.882
2400	14.720	81.902	69.710	29.261	104.368	82.021	- 7.469
2500	14.734	82.503	70.210	30.733	104.369	81.089	- 7.089
2600	14.746	83.081	70.694	32.207	104.367	80.159	- 6.738
2700	14.757	83.638	71.163	33.683	104.364	79.227	- 6.413
2800	14.767	84.175	71.618	35.159	104.358	78.295	- 6.111
2900	14.776	84.693	72.060	36.636	104.349	77.367	- 5.831
3000	14.785	85.194	72.490	38.114	104.337	76.437	- 5.568
3100	14.792	85.679	72.907	39.593	104.324	75.506	- 5.323
3200	14.799	86.149	73.314	41.073	104.308	74.576	- 5.093
3300	14.805	86.605	73.710	42.553	104.288	73.644	- 4.877
3400	14.811	87.047	74.096	44.034	104.268	72.719	- 4.674
3500	14.816	87.476	74.472	45.515	104.244	71.788	- 4.483
3600	14.821	87.893	74.839	46.997	104.218	70.864	- 4.302
3700	14.825	88.300	75.197	48.479	104.190	69.935	- 4.131
3800	14.829	88.695	75.547	49.962	104.160	69.013	- 3.969
3900	14.833	89.080	75.889	51.445	104.128	68.092	- 3.816
4000	14.836	89.456	76.224	52.928	104.093	67.165	- 3.670
4100	14.839	89.822	76.551	54.417	104.056	66.242	- 3.531
4200	14.842	90.180	76.871	55.896	104.016	65.321	- 3.399
4300	14.845	90.529	77.185	57.380	103.974	64.402	- 3.273
4400	14.848	90.870	77.492	58.865	103.930	63.481	- 3.153
4500	14.850	91.204	77.793	60.350	103.883	62.559	- 3.038
4600	14.853	91.531	78.088	61.835	103.834	61.643	- 2.929
4700	14.855	91.850	78.378	63.320	103.783	60.727	- 2.824
4800	14.857	92.163	78.662	64.806	103.728	59.813	- 2.723
4900	14.859	92.469	78.940	66.292	103.672	58.896	- 2.627
5000	14.860	92.769	79.214	67.778	103.613	57.988	- 2.535
5100	14.862	93.064	79.482	69.264	103.550	57.063	- 2.445
5200	14.864	93.352	79.746	70.750	103.486	56.161	- 2.360
5300	14.865	93.635	80.006	72.237	103.419	55.252	- 2.278
5400	14.866	93.913	80.261	73.723	103.349	54.344	- 2.199
5500	14.868	94.186	80.512	75.210	103.275	53.439	- 2.123
5600	14.869	94.454	80.758	76.697	103.200	52.531	- 2.050
5700	14.870	94.717	81.001	78.184	103.121	51.627	- 1.979
5800	14.871	94.976	81.239	79.671	103.039	50.723	- 1.911
5900	14.873	95.230	81.474	81.158	102.954	49.824	- 1.846
6000	14.874	95.480	81.706	82.645	102.866	48.920	- 1.782

June 30, 1966

NCN RADICAL (CN_2) (IDEAL GAS) GFW = 40.02455

Point Group $D_{\infty h}$

ΔHf°_0 = [102.6 ± 25] kcal/mol

$S^\circ_{298.15}$ = 54.194 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [102.8 ± 25] kcal/mol

Ground State Quantum Weight = 3

<u>Vibrational Frequencies and Degeneracies</u>

ω, cm^{-1}
[808](1)
423 (2)
1475 (1)

Bond Distance: C-N = 1.232 Å

Bond Angle: N-C-N = 180°

σ = 2

Rotational Constant: B_o = 0.3968 cm^{-1}

Heat of Formation.

The heat of formation of NCN radical (g), ΔHf°_{298} = 102.8 ± 25 kcal/mol, was calculated from the heat of reaction ΔHr°_{298} = 294 ± 25 kcal/mol for N=C=N → 2N(g) + C(g) which was estimated as twice the C=N bond dissociation energy (147 kcal/mol). The value of C=N bond dissociation energy was derived from the heat of combustion for n-butyl-isobutylidine amine, determined by G. E. Coates and L. E. Sutton, J. Chem. Soc. 1187 (1948).

Heat Capacity and Entropy.

G. Herzberg and D. N. Travis, Can. J. Phys. 42, 1658 (1964), have found NCN radical (g) is a linear symmetric molecule with a $^3\Sigma^-_g$ ground state in the rotational spectra by a flash photolysis technique, and determined the bond distance r_{C-N} = 1.232 Å and rotational constant B_o = 0.3968 cm^{-1} which have been adopted in the tabulation. Also the structure "N=C=N" has been suggested by Herzberg and Travis, based on the bond distance of 1.232 Å, which is in good agreement with the C=N bond length observed in the HNCO, HNCS and CH_3NCS. The principal moment of inertia is 7.0601 X 10^{-39} g cm^2.

D. E. Milligan, M. E. Jacox and A. M. Bass, J. Chem. Phys. 43, 3149 (1965), have found two infrared-active vibrational fundamentals of NCN(g) at 423 and 1475 cm^{-1} in the infrared and ultraviolet spectra by a matrix-isolation method. They also estimated the symmetric stretching frequency (ν_1 = 808 cm^{-1}) by valence force calculation.

E. Wasserman, L. Barash and W. A. Yager, J. Am. Chem. Soc. 87, 2075 (1965), have confirmed the NCN radical(g) is a linear molecule with a triplet ground state by electron paramagnetic resonance.

Sodium Carbonate (Na_4CO_3)

(Crystal)   Mol. Wt. = 105.98895

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 4.974	- 268.788	- 268.738	INFINITE
100	14.637	10.334	53.814	- 4.348	- 269.885	- 263.531	575.947
200	22.500	23.367	35.485	- 2.424	- 270.233	- 257.002	280.839
298	26.530	33.173	33.173	.000	- 270.260	- 250.496	183.619
300	26.590	33.338	33.174	.049	- 270.258	- 250.373	182.397
400	29.900	41.421	34.254	2.867	- 271.441	- 24[illegible] 556	133.127
500	33.990	48.520	36.408	6.056	- 271.150	- 236.735	103.477
600	39.030	55.153	38.983	9.702	- 270.456	- 229.910	83.745
700	44.830	61.597	41.755	13.890	- 269.272	- 223.240	69.699
800	36.650	66.889	44.594	17.837	- 268.371	- 216.743	59.211
900	39.730	71.383	47.322	21.655	- 267.641	- 210.331	51.075
1000	42.830	75.729	49.947	25.782	- 266.640	- 204.013	44.587
1100	45.900	79.956	52.484	30.220	- 265.376	- 197.813	39.302
1200	47.980	84.065	54.946	34.944	- 310.340	- 190.821	34.753
1300	49.280	87.960	57.337	39.811	- 308.302	- 180.943	30.419
1400	50.130	91.645	59.657	44.783	- 306.176	- 171.226	26.730
1500	50.800	95.127	61.907	49.830	- 303.993	- 161.662	23.554
1600	51.330	98.422	64.087	54.937	- 301.766	- 152.246	20.796
1700	51.840	101.550	66.199	60.096	- 299.495	- 142.969	18.380
1800	52.260	104.525	68.246	65.302	- 297.196	- 133.827	16.249
1900	52.630	107.361	70.231	70.546	- 294.870	- 124.814	14.357
2000	53.000	110.070	72.156	75.828	- 292.520	- 115.928	12.668

Dec. 31, 1960; Mar. 31, 1966

SODIUM CARBONATE (Na_2CO_3)   (CRYSTAL)   MOL. WT. = 105.98895

$S^\circ_{298.15}$ = 33.17 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

T_t = 723.15°K.

T_m = 1123.15°K.

$\Delta H^\circ_{f\ 0}$ = -268.79 ± 0.05 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -270.26 ± 0.05 kcal. mole^{-1}

ΔH°_t = 0.165 kcal. mole^{-1}

ΔH°_m = 7.090 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from the heat of solution ΔH°_∞ = -6.36 kcal. mole^{-1} and the heats of formation for $Na^+(aq)$ and $CO_2^{--}(aq)$, -57.39 and -161.84 kcal. mole^{-1}, respectively. The heat of solution was taken from J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, J. Phys. Chem. 69, 3059-62 (1965). The ionic heats of formation were taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm "Selected Values of Chemical Thermodynamic Properties" NBS Technical Note 270-1, October 1, 1965.

A value of $\Delta H^\circ_{f\ 298.15}$ = -270.9 kcal. mole^{-1} has been selected by D. D. Wagman, Natl. Bur. Std. Rept. No. 8628, 87, Jan. 1965.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.6-292.1°K., were measured by C. T. Anderson, J. Am. Chem. Soc. 55, 3621 (1933). In the temperature range 473.15-873.15°K. Popov and Galchenko (Source 1) measured the heat capacities (by heat conduction calorimetry) and observed two transformations, one at about 623°K. and the other at about 750°K. Popov and Ginzburg (Source 2) measured enthalpies in the temperature range 480-1350°K. and tabulated their data only in the range 476-872°K. Ginzburg (Source 3) has given heat capacity equations based on the data from Source 1 and 2 and has tabulated thermodynamic functions in the range 500-1500°K. There appear to be inconsistencies among the data, equations and functions. Rolin and Recapet (Source 4) also measured the enthalpy in the temperature range 645-1322°K. Janz, Neuenschwander and Kelly (Source 5) have given an enthalpy equation based on their heat content measured data in the range 707-1127°K. May (Source 6) has tabulated smoothed measured enthalpy values in the range 400-1500°K. All the above information was used in a Shomate analysis in order to smooth the enthalpies and calculate heat capacities. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point.

The entropy was calculated at 54.60° using the Debye and Einstein function $D(\frac{138}{T}) + 2E(\frac{266}{T}) + 2D(\frac{737}{T})$ given by Anderson, loc. cit. The value of $S^\circ_{54.6}$ = 3.943 cal. deg.$^{-1}$ mole^{-1}.

Source

1 M. M. Popov and G. L. Galchenko, Zh. Obshch. Khim. 21, 2220 (1951).
2 M. M. Popov and D. M. Ginzburg, Zh. Obshch. Khim. 26, 971-80 (1956).
3 D. M. Ginzburg, Zh. Obshch. Khim. 26, 968-70 (1956).
4 M. Rolin and J. M. Recapet, Bull. Soc. chim., 2504 (1964).
5 G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963).
6 M. N. May, Tappi, 35, 511 (1952).

Transition Data.

T_t was taken from Ginzburg loc. cit. and ΔH°_t was obtained from the above reported enthalpy measurements by means of Shomate function analysis. The heat of transition at 593.15°K. has been incorporated in the heat capacity.

Melting Data.

T_m was taken from Ginzburg loc. cit. and ΔH°_m was obtained from the above reported enthalpy measurements by means of Shomate function analysis.

Sodium Carbonate (Na_2CO_3)

(Liquid) Mol. Wt. = 105.98895

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	26.530	37.143	37.143	.000	- 265.205	- 246.625	180.781
300	26.590	37.307	37.144	.049	- 265.203	- 246.509	179.581
400	29.900	45.391	38.224	2.867	- 266.386	- 240.189	131.233
500	33.990	52.485	40.378	6.054	- 266.097	- 233.665	102.135
600	39.030	59.116	42.952	9.698	- 265.405	- 227.236	82.771
700	44.830	65.564	45.723	13.889	- 264.218	- 220.963	68.988
800	45.300	71.620	48.590	18.424	- 262.729	- 214.886	58.704
900	45.300	76.956	51.451	22.954	- 261.287	- 208.993	50.750
1000	45.300	81.729	54.245	27.484	- 259.884	- 203.257	44.422
1100	45.300	86.046	56.943	32.014	- 258.527	- 197.664	39.272
1200	45.300	89.988	59.535	36.544	- 303.685	- 191.273	34.836
1300	45.300	93.614	62.018	41.074	- 301.984	- 181.975	30.593
1400	45.300	96.971	64.397	45.604	- 300.300	- 172.807	26.976
1500	45.300	100.096	66.674	50.134	- 298.634	- 163.757	23.859
1600	45.300	103.020	68.855	54.664	- 296.984	- 154.821	21.147
1700	45.300	105.766	70.946	59.194	- 295.343	- 145.983	18.767
1800	45.300	108.355	72.953	63.724	- 293.719	- 137.244	16.664
1900	45.300	110.805	74.881	68.254	- 292.108	- 128.595	14.792
2000	45.300	113.128	76.736	72.784	- 290.509	- 120.033	13.117
2100	45.300	115.338	78.522	77.314	- 288.917	- 111.547	11.609
2200	45.300	117.446	80.244	81.844	- 287.342	- 103.141	10.246
2300	45.300	119.459	81.905	86.374	- 285.774	- 94.802	9.008
2400	45.300	121.387	83.511	90.904	- 284.220	- 86.527	7.879
2500	45.300	123.236	85.063	95.434	- 282.676	- 78.329	6.847

Dec. 31, 1960; Mar. 31, 1966

SODIUM CARBONATE (Na_2CO_3) (LIQUID) MOL. WT. = 105.98895

$S^\circ_{298.15}$ = 37.14 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

T_m = 1123.15°K.

$\Delta H^\circ_{f\ 298.15}$ = -265.21 ± 0.05 kcal. mole^{-1}

ΔH°_m = 7.090 kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was obtained from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 723.15°K. The heat capacity below 723.15°K. was obtained from the heat capacity of the crystal. Above 723.15°K. the heat capacity was adopted as 45.30 cal. deg.$^{-1}$ mole^{-1}, based on the enthalpy measurements in the range 1127-1210°K. reported by G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $Na_2CO_3(c)$ table.

Carbon Monoxide (CO)

(Ideal Gas) Mol. Wt. = 28.01055

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.072	- 27.200	- 27.200	INFINITE
100	6.956	39.613	53.401	- 1.379	- 26.876	- 28.741	62.809
200	6.957	44.435	47.851	- .683	- 26.599	- 30.718	33.566
298	6.965	47.214	47.214	.000	- 26.417	- 32.783	24.029
300	6.965	47.257	47.214	.013	- 26.414	- 32.823	23.910
400	7.013	49.265	47.488	.711	- 26.318	- 34.975	19.109
500	7.121	50.841	48.006	1.417	- 26.296	- 37.144	16.235
600	7.276	52.152	48.591	2.137	- 26.332	- 39.311	14.318
700	7.450	53.287	49.182	2.873	- 26.409	- 41.468	12.946
800	7.624	54.293	49.759	3.627	- 26.514	- 43.612	11.914
900	7.786	55.200	50.314	4.397	- 26.637	- 45.744	11.108
1000	7.931	56.028	50.845	5.183	- 26.771	- 47.859	10.459
1100	8.057	56.790	51.351	5.983	- 26.914	- 49.962	9.926
1200	8.168	57.496	51.834	6.794	- 27.062	- 52.049	9.479
1300	8.263	58.154	52.295	7.616	- 27.218	- 54.126	9.099
1400	8.346	58.769	52.736	8.446	- 27.376	- 56.189	8.771
1500	8.417	59.348	53.158	9.285	- 27.537	- 58.241	8.485
1600	8.480	59.893	53.562	10.130	- 27.700	- 60.284	8.234
1700	8.535	60.409	53.950	10.980	- 27.865	- 62.315	8.011
1800	8.583	60.898	54.322	11.836	- 28.032	- 64.337	7.811
1900	8.626	61.363	54.681	12.697	- 28.201	- 66.349	7.631
2000	8.664	61.807	55.026	13.561	- 28.372	- 68.353	7.469
2100	8.698	62.230	55.359	14.430	- 28.543	- 70.346	7.321
2200	8.728	62.635	55.680	15.301	- 28.719	- 72.335	7.185
2300	8.756	63.024	55.991	16.175	- 28.894	- 74.311	7.061
2400	8.781	63.397	56.292	17.052	- 29.074	- 76.282	6.946
2500	8.804	63.756	56.584	17.931	- 29.254	- 78.247	6.840
2600	8.825	64.102	56.866	18.813	- 29.438	- 80.202	6.741
2700	8.844	64.435	57.140	19.696	- 29.623	- 82.153	6.649
2800	8.863	64.757	57.407	20.582	- 29.810	- 84.093	6.563
2900	8.879	65.069	57.666	21.469	- 30.001	- 86.028	6.483
3000	8.895	65.370	57.917	22.357	- 30.194	- 87.957	6.407
3100	8.910	65.662	58.163	23.248	- 30.388	- 89.878	6.336
3200	8.924	65.945	58.401	24.139	- 30.586	- 91.795	6.269
3300	8.937	66.220	58.634	25.032	- 30.786	- 93.707	6.206
3400	8.949	66.487	58.861	25.927	- 30.988	- 95.609	6.145
3500	8.961	66.746	59.083	26.822	- 31.192	- 97.509	6.088
3600	8.973	66.999	59.299	27.719	- 31.399	- 99.400	6.034
3700	8.984	67.245	59.511	28.617	- 31.608	- 101.286	5.982
3800	8.994	67.485	59.717	29.516	- 31.818	- 103.164	5.933
3900	9.004	67.718	59.919	30.416	- 32.031	- 105.039	5.886
4000	9.014	67.946	60.117	31.316	- 32.247	- 106.908	5.841
4100	9.024	68.169	60.311	32.218	- 32.464	- 108.774	5.798
4200	9.033	68.387	60.501	33.121	- 32.684	- 110.630	5.756
4300	9.042	68.599	60.687	34.025	- 32.906	- 112.483	5.717
4400	9.051	68.807	60.869	34.930	- 33.130	- 114.333	5.679
4500	9.059	69.011	61.047	35.835	- 33.356	- 116.177	5.642
4600	9.068	69.210	61.223	36.741	- 33.584	- 118.012	5.607
4700	9.076	69.405	61.395	37.649	- 33.814	- 119.845	5.573
4800	9.084	69.596	61.564	38.557	- 34.046	- 121.672	5.540
4900	9.092	69.784	61.729	39.465	- 34.280	- 123.497	5.508
5000	9.100	69.967	61.892	40.375	- 34.516	- 125.315	5.477
5100	9.107	70.148	62.052	41.285	- 34.755	- 127.132	5.448
5200	9.115	70.325	62.210	42.196	- 34.995	- 128.941	5.419
5300	9.123	70.498	62.365	43.108	- 35.237	- 130.741	5.391
5400	9.130	70.669	62.517	44.021	- 35.480	- 132.542	5.364
5500	9.138	70.836	62.667	44.934	- 35.727	- 134.336	5.338
5600	9.145	71.001	62.814	45.849	- 35.974	- 136.129	5.312
5700	9.153	71.163	62.959	46.763	- 36.225	- 137.919	5.288
5800	9.160	71.322	63.102	47.679	- 36.476	- 139.698	5.264
5900	9.167	71.479	63.242	48.595	- 36.730	- 141.473	5.240
6000	9.175	71.633	63.381	49.513	- 36.985	- 143.249	5.218

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON MONOXIDE (CO) (IDEAL GAS) MOL. WT. = 28.01055

Ground State Configuration $^1\Sigma^+$

$\Delta H_{f\ 0}^\circ$ = -27.20 ± 0.04 kcal. mole^{-1}

$S^\circ_{298.15}$ = 47.21 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = -26.42 ± 0.04 kcal. mole^{-1}

ω_e = 2169.52 cm.$^{-1}$

$\omega_e x_e$ = 13.453 cm.$^{-1}$

σ = 1

B_e = 1.9302 cm.$^{-1}$

α_e = 0.01746 cm.$^{-1}$

r_e = 1.1281 Å

Heat of Formation.

The enthalpy change ($\Delta H_{r\ 298.15}^\circ$) for the reaction: CO(g) + 1/2 O_2(g) = CO_2(g) was reported to be -67.636 ± 0.029 kcal. mole^{-1}, based on molecular weight of CO_2 = 44.010, by F. D. Rossini, J. Research Nat. Bur. Standards 22, 407 (1939). It was recalculated to be -67.638 ± 0.03 kcal. mole^{-1}, using molecular weight of CO_2 = 44.011, for internal consistency. From the value of $\Delta H_{r\ 298.15}^\circ$, the heat of formation ($\Delta H_{f\ 298.15}^\circ$) for CO(g) was derived to be -26.417 ± 0.04 kcal. mole^{-1}, which yields D_0(CO) = 11.09 e.v.

The D_0(CO) value has been proposed to be 6.92 to 11.11 e.v. in the past few decades in order to explain data collected from spectroscopic, flame, shock-wave, detonation, and electron-impact studies. Recent evaluations by L. Brewer and A. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956); M. A. Fineman and A. W. Petrocelli, J. Chem. Phys. 36, 25 (1962); and C. F. Giese and W. B. Maier II, J. Chem. Phys. 39, 197 (1963) favored the value 11.11 e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 1953.

The heat of combustion of CO(g) was also determined by J. H. Awbery and E. Griffiths, Proc. Roy. Soc. (London) [A] 141, 1 (1933), R. W. Fenning and F. T. Cotton, ibid., [A] 141, 17 (1933), and W. A. Roth and H. Banse, Arch. Eisenhutten 6, 43 (1932-33).

Heat Capacity and Entropy.

The functions adopted here were obtained from J. Belzer, L. G. Savedoff and H. L. Johnston, Ohio State University, TR 316-6, May 1, 1953, assuming the thermodynamic functions for the naturally occurring isotopic mixture to be the same as those for $C^{12}O^{16}$(g). The spectroscopic constants employed for calculation were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950. The tabulated functions include the second order corrections to the rigid-rotator and harmonic-oscillator molecular model for vibrational anharmonicity, rotational stretching and rotational-vibrational interaction.

The spectroscopic constants listed above are for the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

Thermodynamic properties for CO from 70 to 300°K., with pressures to 300 atmospheres were reported by J. G. Hust and R. B. Stewart, NBS-TN-202, National Bureau of Standards, 1963. Calculations of the vapor pressure and heats of vaporization and sublimation of CO and CO_2 below one atmosphere were reported by J. C. Mullins, B. S. Kirk and W. T. Ziegler, U. S. Atomic Energy Commission NP-13862 (1963).

Carbon Oxide Sulfide (COS)

(Ideal Gas) Mol. Wt. = 60.077

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	,000	,000	INFINITE	- 2,373	- 33,111	- 33,111	INFINITE
100	7,077	46,387	63,147	- 1,676	- 32,948	- 35,193	76,911
200	8,478	51,665	56,195	- ,906	- 32,989	- 37,430	40,900
298	9,918	55,323	55,323	,000	- 33,080	- 39,589	29,018
300	9,940	55,384	55,323	,018	- 33,082	- 39,629	28,869
400	10,959	58,390	55,726	1,066	- 33,735	- 41,774	22,823
500	11,688	60,920	56,519	2,201	- 34,223	- 43,726	19,112
600	12,249	63,102	57,438	3,398	- 34,638	- 45,587	16,604
700	12,700	65,025	58,387	4,647	- 35,003	- 47,358	14,785
800	13,068	66,746	59,326	5,936	- 48,397	- 50,368	13,759
900	13,370	68,303	60,239	7,258	- 48,407	- 50,615	12,290
1000	13,621	69,725	61,117	8,608	- 48,418	- 50,859	11,115
1100	13,829	71,034	61,960	9,981	- 48,430	- 51,104	10,153
1200	14,005	72,245	62,767	11,373	- 48,442	- 51,345	9,351
1300	14,153	73,372	63,540	12,781	- 48,457	- 51,586	8,672
1400	14,280	74,425	64,280	14,203	- 48,470	- 51,825	8,090
1500	14,390	75,414	64,990	15,636	- 48,484	- 52,066	7,586
1600	14,485	76,346	65,671	17,080	- 48,496	- 52,304	7,144
1700	14,569	77,227	66,325	18,533	- 48,508	- 52,542	6,754
1800	14,643	78,062	66,954	19,994	- 48,520	- 52,779	6,408
1900	14,710	78,855	67,560	21,461	- 48,532	- 53,014	6,098
2000	14,770	79,611	68,144	22,935	- 48,544	- 53,251	5,819
2100	14,824	80,333	68,707	24,415	- 48,556	- 53,485	5,566
2200	14,874	81,024	69,251	25,900	- 48,570	- 53,720	5,336
2300	14,920	81,686	69,778	27,390	- 48,583	- 53,953	5,126
2400	14,962	82,322	70,287	28,884	- 48,598	- 54,185	4,934
2500	15,002	82,934	70,781	30,382	- 48,613	- 54,420	4,757
2600	15,038	83,523	71,260	31,884	- 48,630	- 54,651	4,594
2700	15,073	84,091	71,724	33,390	- 48,647	- 54,884	4,442
2800	15,106	84,640	72,176	34,899	- 48,666	- 55,115	4,302
2900	15,137	85,170	72,615	36,411	- 48,687	- 55,343	4,171
3000	15,167	85,684	73,042	37,926	- 48,709	- 55,572	4,048
3100	15,196	86,182	73,458	39,444	- 48,730	- 55,799	3,934
3200	15,223	86,665	73,863	40,965	- 48,755	- 56,028	3,826
3300	15,250	87,134	74,258	42,489	- 48,781	- 56,259	3,726
3400	15,275	87,589	74,644	44,015	- 48,808	- 56,481	3,630
3500	15,300	88,032	75,020	45,544	- 48,837	- 56,712	3,541
3600	15,324	88,464	75,387	47,075	- 48,866	- 56,934	3,456
3700	15,347	88,884	75,746	48,609	- 48,898	- 57,156	3,376
3800	15,370	89,293	76,098	50,144	- 48,930	- 57,377	3,300
3900	15,392	89,693	76,441	51,682	- 48,964	- 57,600	3,228
4000	15,414	90,083	76,777	53,223	- 48,999	- 57,818	3,159
4100	15,436	90,464	77,106	54,765	- 49,035	- 58,042	3,094
4200	15,457	90,836	77,429	56,310	- 49,073	- 58,258	3,031
4300	15,477	91,200	77,745	57,857	- 49,112	- 58,477	2,972
4400	15,498	91,556	78,055	59,405	- 49,153	- 58,696	2,915
4500	15,518	91,905	78,359	60,956	- 49,194	- 58,912	2,861
4600	15,537	92,246	78,657	62,509	- 49,237	- 59,126	2,809
4700	15,557	92,580	78,950	64,064	- 49,280	- 59,341	2,759
4800	15,576	92,908	79,237	65,620	- 49,326	- 59,554	2,711
4900	15,595	93,229	79,519	67,179	- 49,372	- 59,766	2,666
5000	15,614	93,545	79,797	68,739	- 49,420	- 59,980	2,622
5100	15,633	93,854	80,069	70,302	- 49,470	- 60,193	2,579
5200	15,651	94,158	80,337	71,866	- 49,520	- 60,402	2,538
5300	15,670	94,456	80,601	73,432	- 49,571	- 60,607	2,499
5400	15,688	94,749	80,860	75,000	- 49,623	- 60,815	2,461
5500	15,706	95,037	81,115	76,569	- 49,677	- 61,021	2,425
5600	15,724	95,320	81,366	78,141	- 49,733	- 61,228	2,389
5700	15,742	95,599	81,614	79,714	- 49,789	- 61,438	2,356
5800	15,760	95,873	81,857	81,289	- 49,847	- 61,639	2,322
5900	15,777	96,142	82,097	82,866	- 49,905	- 61,841	2,291
6000	15,795	96,407	82,333	84,445	- 49,965	- 62,042	2,260

March 31, 1961

CARBON OXIDE SULFIDE (COS) (IDEAL GAS) MOL. WT. = 60.077

ΔH°_{f0} = -33.11 ± 0.25 kcal. mole^{-1}

Point Group $C_{\infty v}$

$\Delta H^\circ_{f\ 298.15}$ = -33.08 ± 0.25 kcal. mole^{-1}

$S^\circ_{298.15}$ = 55.323 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
859 (1)
524 (2)
2064 (1)

Rotational Constant, B_{000} = 0.20287 cm.$^{-1}$ $\sigma = 1$

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 0.0006044$
$\alpha_2 = 0.0003539$
$\alpha_3 = 0.001838$
$g_{22} = 3.2$
$X_{11} = -4.0$
$X_{22} = -0.4$
$X_{33} = -7.0$
$X_{12} = -6.8$
$X_{23} = -11.5$
$X_{13} = -4.5$
$A_{000} = 0$
$C_{000} = 0$
$D_{000} = 4.37 \times 10^{-8}$

Heat of Formation

E. Terres and H. Wesemann, Angew. Chem. 45, 795 (1932), report equilibrium constants from 623° to 873°K for the reaction $CO_2(g) + H_2S(g) \rightleftarrows COS(g) + H_2O(g)$. These yield $\Delta H_{r\ 700}$ = 8.19 ± 0.23 kcal, whence $\Delta H_{f\ 298.15}$ for COS is -33.08 ± 0.25 kcal. mole^{-1}. The same authors report equilibrium constants for the reaction $COS(g) + H_2S(g) \rightleftarrows CS_2(g) + H_2O(g)$, but regard these as less reliable than the others. The resulting value of -26.39 kcal. mole^{-1} for $\Delta H_{f\ 298.15}$ of COS has been disregarded.

Heat Capacity and Entropy

J. S. Gordon (private communication, February 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants have been taken from C. A. Burrus and W. Gordy, Phys. Rev. 93, 897 (1954), H. J. Callomon, D. C. McKean, and H. W. Thompson, Proc. Roy. Soc. (London) A208, 341 (1951), A222, 431 (1954), M. W. P. Strandberg, T. Wentink, and R. L. Kyhl, Phys. Rev. 75, 270 (1949), C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. 74, 1113 (1948), and T. Wentink, J. Chem. Phys. 30, 105 (1959). The thermodynamic functions below 298.15°K have been calculated for the rigidly rotating harmonic oscillator.

Carbon Dioxide (CO_2)

(Ideal Gas) Mol. Wt. = 44.00995

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.238	-93.965	-93.965	INFINITE
100	6.981	42.758	58.188	-1.543	-93.997	-94.100	205.645
200	7.734	47.769	51.849	-.816	-94.028	-94.191	102.922
298	8.874	51.072	51.072	.000	-94.054	-94.265	69.095
300	8.896	51.127	51.072	.016	-94.055	-94.267	68.670
400	9.877	53.830	51.434	.958	-94.070	-94.335	51.540
500	10.666	56.122	52.148	1.987	-94.091	-94.399	41.260
600	11.310	58.126	52.981	3.087	-94.124	-94.458	34.405
700	11.846	59.910	53.845	4.245	-94.169	-94.510	29.506
800	12.293	61.522	54.706	5.453	-94.218	-94.556	25.830
900	12.667	62.992	55.546	6.702	-94.270	-94.596	22.970
1000	12.980	64.344	56.359	7.984	-94.321	-94.628	20.680
1100	13.243	65.594	57.143	9.296	-94.371	-94.658	18.806
1200	13.466	66.756	57.896	10.632	-94.419	-94.681	17.243
1300	13.656	67.841	58.620	11.988	-94.469	-94.701	15.920
1400	13.815	68.859	59.315	13.362	-94.515	-94.716	14.785
1500	13.953	69.817	59.984	14.750	-94.562	-94.728	13.801
1600	14.074	70.722	60.627	16.152	-94.607	-94.739	12.940
1700	14.177	71.578	61.246	17.565	-94.650	-94.746	12.180
1800	14.269	72.391	61.843	18.987	-94.696	-94.750	11.504
1900	14.352	73.165	62.418	20.418	-94.742	-94.751	10.898
2000	14.424	73.903	62.974	21.857	-94.788	-94.752	10.353
2100	14.489	74.608	63.512	23.303	-94.834	-94.746	9.860
2200	14.547	75.284	64.031	24.755	-94.885	-94.744	9.411
2300	14.600	75.931	64.535	26.212	-94.936	-94.735	9.001
2400	14.648	76.554	65.023	27.674	-94.991	-94.724	8.625
2500	14.692	77.153	65.496	29.141	-95.048	-94.714	8.280
2600	14.734	77.730	65.956	30.613	-95.107	-94.698	7.960
2700	14.771	78.286	66.402	32.088	-95.170	-94.683	7.664
2800	14.807	78.824	66.836	33.567	-95.235	-94.662	7.388
2900	14.841	79.344	67.259	35.049	-95.305	-94.639	7.132
3000	14.873	79.848	67.670	36.535	-95.377	-94.615	6.892
3100	14.902	80.336	68.071	38.024	-95.451	-94.587	6.668
3200	14.930	80.810	68.461	39.515	-95.530	-94.560	6.458
3300	14.956	81.270	68.843	41.010	-95.611	-94.531	6.260
3400	14.982	81.717	69.215	42.507	-95.696	-94.495	6.074
3500	15.006	82.151	69.578	44.006	-95.784	-94.462	5.898
3600	15.030	82.574	69.933	45.508	-95.874	-94.421	5.732
3700	15.053	82.986	70.280	47.012	-95.968	-94.379	5.574
3800	15.075	83.388	70.620	48.518	-96.064	-94.331	5.425
3900	15.097	83.780	70.953	50.027	-96.162	-94.286	5.283
4000	15.119	84.162	71.278	51.538	-96.263	-94.237	5.149
4100	15.139	84.536	71.597	53.051	-96.367	-94.186	5.020
4200	15.159	84.901	71.909	54.566	-96.473	-94.130	4.898
4300	15.179	85.258	72.216	56.082	-96.583	-94.072	4.781
4400	15.197	85.607	72.516	57.601	-96.694	-94.015	4.670
4500	15.216	85.949	72.811	59.122	-96.807	-93.954	4.563
4600	15.234	86.284	73.100	60.644	-96.923	-93.885	4.460
4700	15.254	86.611	73.384	62.169	-97.040	-93.818	4.362
4800	15.272	86.933	73.663	63.695	-97.160	-93.746	4.268
4900	15.290	87.248	73.937	65.223	-97.281	-93.678	4.178
5000	15.306	87.557	74.206	66.753	-97.404	-93.603	4.091
5100	15.327	87.860	74.471	68.285	-97.530	-93.528	4.008
5200	15.349	88.158	74.731	69.819	-97.656	-93.450	3.927
5300	15.371	88.451	74.988	71.355	-97.783	-93.361	3.850
5400	15.393	88.738	75.239	72.893	-97.912	-93.280	3.775
5500	15.415	89.021	75.488	74.433	-98.042	-93.190	3.703
5600	15.437	89.299	75.732	75.976	-98.173	-93.104	3.633
5700	15.459	89.572	75.972	77.521	-98.305	-93.017	3.566
5800	15.481	89.841	76.209	79.068	-98.438	-92.918	3.501
5900	15.503	90.106	76.442	80.617	-98.572	-92.820	3.438
6000	15.525	90.367	76.672	82.168	-98.707	-92.724	3.377

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON DIOXIDE (CO_2) (IDEAL GAS) MOL. WT. = 44.00995

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = 51.07 ± 0.03 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0$ = -93.965 ± 0.011 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -94.054 ± 0.011 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å

Bond Angle: O-C-O = 180°

Rotational Constant: B_o = 0.39038 cm.$^{-1}$

$\sigma = 2$

Heat of Formation.

The enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of the reaction C(c, graphite) + O_2(g) = CO_2(g) has been measured by F. H. Dewey and D. R. Harper, J. Res. Natl. Bur. Std. 21, 457 (1938), R. S. Jessup, ibid. 21, 491 (1938), and E. J. Prosen and F. D. Rossini, ibid., 33, 439 (1944). Based on these data, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for CO_2(g) was reported to be -94.0518 ± 0.0108 kcal. mole^{-1}, using molecular weight of CO_2 = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rossini, J. Research Natl. Bur. Standards 33, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole^{-1}, based on molecular weight of CO_2 = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, J. Research Nat. Bur. Standards 52, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., J. Chem. Phys. 30, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtoy, Mem. soc. roy. Liege 18, 496 (1957) and V. R. Stull, P. J. Wyatt and G. N. Plass, J. Chem. Phys. 37, 1442 (1962). The high-resolution infrared spectrum of O^{18} - enriched CO_2 was examined in the region 5400-1620 cm.$^{-1}$, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.$^{-1}$ by C. V. Berney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B_o, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B_e which was derived from B_o, using B_e-B_o = 0.0011 cm.$^{-1}$ given in G. Herzberg, loc. cit. The principal moment of inertia is I = 7.1495 X 10^{-39} g. cm.^{2}

Heat capacities of CO_2(g) at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, Teploenergetika, 12 (7), 58 (1965); K. Krueger, Ver. Deut. Ingr. Z., 106 (32) 1620 (1964), and M. P. Vukalovich and A. N. Gureev, Teploenergetika, 11 (8), 80 (1964).

Carbon Dioxide Uninegative Ion (CO_2^-)

(Ideal Gas) GFW = 44.0105

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0							
100							
200							
298	8.746	57.489	57.489	.000	-105.500	-106.137	77.801
300	8.759	57.543	57.489	.016	-105.510	-106.141	77.324
400	9.497	60.163	57.842	.929	-106.051	-106.271	58.064
500	10.226	62.362	58.531	1.915	-106.612	-106.261	46.447
600	10.864	64.284	59.333	2.971	-107.186	-106.138	38.661
700	11.389	66.000	60.165	4.084	-107.772	-105.915	33.068
800	11.811	67.549	60.993	5.245	-108.365	-105.611	28.851
900	12.148	68.960	61.801	6.444	-108.964	-105.231	25.554
1000	12.417	70.255	62.582	7.672	-109.566	-104.784	22.900
1100	12.632	71.449	63.335	8.925	-110.172	-104.278	20.718
1200	12.807	72.555	64.058	10.197	-110.781	-103.714	18.889
1300	12.950	73.586	64.751	11.485	-111.395	-103.099	17.333
1400	13.068	74.551	65.417	12.787	-112.010	-102.439	15.991
1500	13.166	75.456	66.057	14.098	-112.631	-101.733	14.822
1600	13.249	76.308	66.671	15.419	-113.254	-100.987	13.794
1700	13.318	77.113	67.262	16.748	-113.878	-100.200	12.882
1800	13.378	77.876	67.830	18.083	-114.507	-99.377	12.066
1900	13.429	78.601	68.378	19.423	-115.141	-98.520	11.332
2000	13.473	79.291	68.907	20.768	-115.778	-97.630	10.668
2100	13.512	79.949	69.417	22.118	-116.417	-96.703	10.064
2200	13.546	80.579	69.910	23.470	-117.065	-95.753	9.512
2300	13.575	81.182	70.387	24.827	-117.712	-94.768	9.005
2400	13.602	81.760	70.849	26.185	-118.368	-93.756	8.538
2500	13.625	82.316	71.297	27.547	-119.027	-92.720	8.106
2600	13.646	82.850	71.731	28.910	-119.692	-91.651	7.704
2700	13.664	83.366	72.153	30.276	-120.361	-90.564	7.331
2800	13.681	83.863	72.562	31.643	-121.035	-89.445	6.982
2900	13.696	84.343	72.960	33.012	-121.714	-88.303	6.655
3000	13.710	84.808	73.347	34.382	-122.399	-87.140	6.348
3100	13.722	85.258	73.724	35.754	-123.087	-85.952	6.060
3200	13.734	85.694	74.091	37.127	-123.781	-84.748	5.788
3300	13.744	86.116	74.449	38.501	-124.480	-83.517	5.531
3400	13.753	86.527	74.799	39.876	-125.183	-82.265	5.288
3500	13.762	86.926	75.139	41.251	-125.892	-80.997	5.058
3600	13.770	87.313	75.472	42.628	-126.604	-79.700	4.838
3700	13.777	87.691	75.797	44.005	-127.322	-78.385	4.630
3800	13.784	88.058	76.115	45.383	-128.043	-77.050	4.431
3900	13.790	88.416	76.426	46.762	-128.768	-75.701	4.242
4000	13.796	88.766	76.730	48.141	-129.497	-74.333	4.061
4100	13.802	89.106	77.028	49.521	-130.231	-72.941	3.888
4200	13.807	89.439	77.320	50.902	-130.968	-71.538	3.723
4300	13.811	89.764	77.605	52.283	-131.710	-70.113	3.564
4400	13.816	90.082	77.885	53.664	-132.456	-68.678	3.411
4500	13.820	90.392	78.160	55.046	-133.204	-67.216	3.264
4600	13.824	90.696	78.429	56.428	-133.957	-65.739	3.123
4700	13.827	90.993	78.693	57.811	-134.713	-64.246	2.987
4800	13.831	91.284	78.952	59.194	-135.473	-62.734	2.856
4900	13.834	91.570	79.207	60.577	-136.236	-61.222	2.731
5000	13.837	91.849	79.457	61.960	-137.002	-59.682	2.609
5100	13.840	92.123	79.703	63.344	-137.773	-58.126	2.491
5200	13.842	92.392	79.944	64.728	-138.546	-56.563	2.377
5300	13.845	92.656	80.181	66.113	-139.321	-54.972	2.267
5400	13.847	92.914	80.415	67.497	-140.101	-53.371	2.160
5500	13.850	93.168	80.644	68.882	-140.883	-51.755	2.057
5600	13.852	93.418	80.870	70.267	-141.668	-50.130	1.956
5700	13.854	93.663	81.093	71.652	-142.457	-48.498	1.860
5800	13.856	93.904	81.311	73.038	-143.248	-46.835	1.765
5900	13.857	94.141	81.527	74.423	-144.043	-45.164	1.673
6000	13.859	94.374	81.739	75.809	-144.840	-43.488	1.584

June 30, 1966; Dec. 31, 1966

CARBON DIOXIDE UNINEGATIVE ION (CO_2^-) (IDEAL GAS) GFW = 44.0105

Point group [C_{2v}]

$S^\circ_{298.15}$ = [57.5] gibbs/mol

Ground State Quantum Weight = [2]

ΔHf°_0 = [-104.1 ± 27] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-105.5 ± 27] kcal/mol

Vibrational Frequencies and Degeneracies

ω cm^{-1}
[1400] (1)
[800] (1)
1671 (1)

Bond Distance: C-O = [1.25] Å

Bond Angle: O-C-O = 127° ± 8°

σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.1296] x 10^{-116} g^3 cm^6

Heat of Formation.

The heat of formation, ΔHf°_{298} (CO_2^-,g) = -105.5 ± 27 kcal/mol, is estimated from ΔHr°_{298} = 88.6 ± 10 kcal/mol for $HCO_2^-(g) \rightarrow H(g) + CO_2^-(g)$, using the ΔHf°_{298} (HCO_2^-,g) = -142 ± 17 kcal/mol and ΔHf°_{298} (H,g) = 52.1 kcal/mol. The value of ΔHr°_{298} is assumed to be the same as that for $HCOOH(g) \rightarrow H(g) + COOH(g)$. The values of ΔHf°_{298} (HCOOH,g) and ΔHf°_{298} (H,g), -90.5 and 52.1 kcal/mol, respectively, are from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. Tech. Note 270-1, Washington, D. C., Oct. 1965, and the value of ΔHf°_{298} (COOH,g), -54 ± 3 kcal/mol, is from S. W. Benson, J. Chem. Ed. 42, 502 (1965). The value of ΔHf°_{298} (HCO_2^-,g) is estimated from an approximate lattice energy calculation for sodium formate. The derived electron affinity of CO_2(g) is 11.5 kcal/mol (0.5 eV) with an estimated uncertainty range of 0-40 kcal/mol.

Heat Capacity and Entropy.

The correlations of A. D. Walsh, J. Chem. Soc. 1953, 2266, predict a bent molecular structure for CO_2^- based on its 17 valence electrons. K. O. Hartman and I. C. Hisatsune, J. Chem. Phys. 44, 1913 (1966), measured the asymmetric C-O stretching frequency and derived the bond angle of 127° ± 8° from the infrared spectrum of matrix-isolated CO_2^-. They also estimated the bond distance C-O and the symmetric stretching and the bending vibrational frequencies by the valence force method. These molecular constants are adopted in the tabulation. The three principal moments of inertia are $I_A = 0.4511 \times 10^{-39}$, $I_B = 6.6491 \times 10^{-39}$ and $I_C = 7.1002 \times 10^{-39}$ g cm^2.

D. W. Ovenall and D. H. Whiffen, Mol. Phys. 4, 135 (1961), have derived a bond angle of 134° which is in good agreement with the value selected. This result was obtained from electron spin resonance for the CO_2^- radical trapped in sodium formate.

Carbon Phosphide (CP)

(Ideal Gas) Mol. Wt. = 42.986

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.083	110.731	110.731	INFINITE
100	6.957	44.023	57.905	-1.388	111.321	107.089	-234.031
200	6.981	48.848	52.308	-.692	111.621	102.719	-112.241
298	7.149	51.661	51.661	.000	111.700	98.327	-72.072
300	7.154	51.705	51.661	.013	111.700	98.244	-71.568
400	7.446	53.802	51.945	.743	111.651	93.764	-51.228
500	7.741	55.496	52.491	1.502	111.520	89.306	-39.034
600	7.989	56.930	53.115	2.289	111.328	84.879	-30.916
700	8.184	58.177	53.751	3.098	111.079	80.490	-25.129
800	8.335	59.280	54.374	3.925	90.364	70.830	-19.349
900	8.452	60.269	54.975	4.764	90.280	68.392	-16.607
1000	8.545	61.164	55.550	5.614	90.185	65.965	-14.416
1100	8.619	61.982	56.098	6.473	90.080	63.547	-12.625
1200	8.679	62.735	56.620	7.338	89.966	61.141	-11.135
1300	8.728	63.432	57.118	8.208	89.843	58.744	-9.875
1400	8.770	64.080	57.592	9.083	89.717	56.358	-8.797
1500	8.805	64.686	58.045	9.962	89.586	53.980	-7.864
1600	8.835	65.256	58.478	10.844	89.451	51.608	-7.049
1700	8.861	65.792	58.893	11.729	89.314	49.248	-6.331
1800	8.884	66.299	59.290	12.616	89.174	46.895	-5.694
1900	8.905	66.780	59.672	13.505	89.032	44.552	-5.124
2000	8.923	67.237	60.039	14.397	88.889	42.212	-4.613
2100	8.940	67.673	60.392	15.290	88.745	39.884	-4.151
2200	8.955	68.089	60.733	16.185	88.598	37.559	-3.731
2300	8.969	68.488	61.061	17.081	88.451	35.244	-3.349
2400	8.982	68.870	61.379	17.979	88.302	32.932	-2.999
2500	8.994	69.237	61.686	18.877	88.153	30.630	-2.678
2600	9.005	69.590	61.983	19.777	88.001	28.330	-2.381
2700	9.016	69.930	62.271	20.678	87.849	26.037	-2.107
2800	9.026	70.258	62.550	21.581	87.698	23.752	-1.854
2900	9.036	70.575	62.822	22.484	87.544	21.471	-1.618
3000	9.045	70.881	63.085	23.388	87.389	19.196	-1.398
3100	9.054	71.178	63.341	24.293	87.234	16.926	-1.193
3200	9.063	71.465	63.591	25.199	87.077	14.659	-1.001
3300	9.071	71.744	63.834	26.105	86.919	12.397	-.821
3400	9.079	72.015	64.070	27.013	86.760	10.143	-.652
3500	9.087	72.279	64.301	27.921	86.600	7.890	-.493
3600	9.095	72.535	64.526	28.830	86.439	5.642	-.342
3700	9.102	72.784	64.746	29.740	86.277	3.401	-.201
3800	9.110	73.027	64.961	30.651	86.115	1.166	-.067
3900	9.117	73.264	65.171	31.562	85.950	-1.065	.060
4000	9.124	73.495	65.376	32.474	85.785	-3.297	.180
4100	9.131	73.720	65.577	33.387	85.619	-5.524	.294
4200	9.137	73.940	65.773	34.300	85.450	-7.739	.403
4300	9.144	74.155	65.966	35.214	85.280	-9.961	.506
4400	9.151	74.365	66.154	36.129	85.110	-12.171	.605
4500	9.157	74.571	66.339	37.044	84.937	-14.383	.698
4600	9.164	74.772	66.520	37.960	84.764	-16.589	.788
4700	9.170	74.970	66.698	38.877	84.590	-18.789	.874
4800	9.176	75.163	66.872	39.794	84.412	-20.984	.955
4900	9.182	75.352	67.043	40.712	84.235	-23.177	1.034
5000	9.189	75.538	67.211	41.631	84.056	-25.367	1.109
5100	9.195	75.720	67.376	42.550	83.873	-27.560	1.181
5200	9.201	75.898	67.539	43.470	83.691	-29.743	1.250
5300	9.207	76.073	67.698	44.390	83.506	-31.920	1.316
5400	9.213	76.246	67.855	45.311	83.320	-34.095	1.380
5500	9.219	76.415	68.009	46.233	83.132	-36.266	1.441
5600	9.225	76.581	68.160	47.155	82.942	-38.437	1.500
5700	9.231	76.744	68.310	48.078	82.750	-40.605	1.557
5800	9.237	76.905	68.456	49.001	82.556	-42.769	1.612
5900	9.243	77.063	68.601	49.925	82.361	-44.924	1.664
6000	9.248	77.218	68.743	50.850	82.164	-47.083	1.715

June 30, 1962

CARBON PHOSPHIDE (CP) (IDEAL GAS) MOL. WT. = 42.986

$\Delta H^\circ_{f\ 0} = 110.7 \pm 23.1$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 111.7 \pm 23.1$ kcal. mole^{-1}

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15} = 51.66$ cal. deg.$^{-1}$ mole^{-1}

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_i
0	2

$\omega_e = 1239.67$ cm.$^{-1}$

$\omega_e x_e = 6.86$ cm.$^{-1}$

$r_e = 1.562$ Å

$B_e = 0.7986$ cm.$^{-1}$

$\alpha_e = 0.00597$ cm.$^{-1}$

$\sigma = 1$

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was calculated from the dissociation energy (D°_0) given by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall (1953). H. Barwald, G. Herzberg, and L. Herzberg, Ann. Physik 20, 569 (1934) reported a $D^\circ_0 = 6.9$ e.v. A. G. Gaydon (loc. cit.) reports that a linear Birge-Sponer extrapolation for $X^2\Sigma(\nu, 0\text{-}9)$ gives a $D^\circ_0 = 6.9$ e.v. and that a linear Birge-Sponer extrapolation of the excited states $A^2\Pi$ and $B^2\Sigma$ favored a similar value. Using the spectral data of H. Barwald et al. (loc. cit.), Gaydon concludes that D°_0 is 6 ± 1 e.v. The uncertainty reported by Gaydon (loc. cit.) ± 1 e.v. corresponds to an uncertainty of ± 23.1 kcal. mole^{-1} for the $\Delta H^\circ_{f\ 298.15}$. The 6.9 e.v. of H. Barwald et al. (loc. cit.) would give a $\Delta H^\circ_{f\ 298.15} = 90.6$ kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular constants were taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York (1950).

Carbon Monosulphide (CS)

(Ideal Gas) Mol. Wt. = 44.077

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.081	54.224	54.224	INFINITE
100	6.957	42.667	56.533	- 1.387	54.740	50.791	- 110.999
200	6.975	47.492	50.944	- .690	54.966	46.736	- 51.068
298	7.122	50.299	50.299	.000	55.000	42.684	- 31.287
300	7.126	50.343	50.299	.013	54.999	42.607	- 31.038
400	7.401	52.429	50.582	.739	54.380	38.508	- 21.039
500	7.690	54.112	51.125	1.494	53.878	34.598	- 15.122
600	7.939	55.537	51.744	2.276	53.425	30.785	- 11.213
700	8.137	56.776	52.376	3.080	53.004	27.069	- 8.451
800	8.293	57.873	52.996	3.902	39.542	22.125	- 6.044
900	8.415	58.858	53.594	4.737	39.452	19.952	- 4.845
1000	8.512	59.749	54.165	5.584	39.352	17.791	- 3.888
1100	8.589	60.564	54.711	6.439	39.241	15.638	- 3.107
1200	8.651	61.314	55.230	7.301	39.123	13.499	- 2.458
1300	8.703	62.009	55.725	8.169	38.997	11.369	- 1.911
1400	8.746	62.656	56.197	9.041	38.866	9.250	- 1.444
1500	8.783	63.260	56.648	9.918	38.731	7.137	- 1.040
1600	8.814	63.828	57.080	10.798	38.593	5.036	- .688
1700	8.841	64.363	57.492	11.681	38.453	2.942	- .378
1800	8.865	64.869	57.888	12.566	38.309	.857	- .104
1900	8.886	65.349	58.268	13.453	38.164	- 1.217	.140
2000	8.904	65.805	58.634	14.343	38.018	- 3.287	.359
2100	8.921	66.240	58.986	15.234	37.870	- 5.348	.557
2200	8.937	66.656	59.325	16.127	37.720	- 7.403	.735
2300	8.951	67.053	59.653	17.022	37.570	- 9.450	.898
2400	8.964	67.435	59.969	17.917	37.417	- 11.491	1.046
2500	8.976	67.801	60.275	18.814	37.265	- 13.526	1.182
2600	8.987	68.153	60.571	19.713	37.111	- 15.555	1.307
2700	8.998	68.492	60.858	20.612	36.956	- 17.580	1.423
2800	9.008	68.820	61.137	21.512	36.800	- 19.597	1.530
2900	9.018	69.136	61.407	22.413	36.642	- 21.607	1.628
3000	9.027	69.442	61.670	23.316	36.484	- 23.612	1.720
3100	9.036	69.738	61.926	24.219	36.326	- 25.612	1.806
3200	9.044	70.025	62.174	25.123	36.165	- 27.608	1.885
3300	9.052	70.303	62.416	26.028	36.004	- 29.602	1.960
3400	9.060	70.574	62.652	26.933	35.841	- 31.584	2.030
3500	9.067	70.837	62.882	27.839	35.676	- 33.569	2.096
3600	9.075	71.092	63.107	28.747	35.513	- 35.544	2.158
3700	9.082	71.341	63.326	29.654	35.345	- 37.514	2.216
3800	9.089	71.583	63.540	30.563	35.179	- 39.480	2.271
3900	9.095	71.819	63.749	31.472	35.010	- 41.443	2.322
4000	9.102	72.050	63.954	32.382	34.841	- 43.397	2.371
4100	9.109	72.274	64.154	33.292	34.670	- 45.355	2.418
4200	9.115	72.494	64.350	34.204	34.498	- 47.302	2.461
4300	9.121	72.709	64.542	35.115	34.323	- 49.249	2.503
4400	9.128	72.918	64.730	36.028	34.148	- 51.192	2.543
4500	9.134	73.124	64.914	36.941	33.971	- 53.129	2.580
4600	9.140	73.324	65.095	37.855	33.793	- 55.063	2.616
4700	9.146	73.521	65.272	38.769	33.614	- 56.993	2.650
4800	9.152	73.714	65.446	39.684	33.432	- 58.918	2.682
4900	9.157	73.902	65.617	40.599	33.249	- 60.837	2.713
5000	9.163	74.087	65.784	41.515	33.064	- 62.758	2.743
5100	9.169	74.269	65.949	42.432	32.877	- 64.675	2.771
5200	9.175	74.447	66.111	43.349	32.689	- 66.584	2.798
5300	9.180	74.622	66.270	44.267	32.500	- 68.491	2.824
5400	9.186	74.793	66.426	45.185	32.308	- 70.392	2.849
5500	9.191	74.962	66.580	46.104	32.114	- 72.293	2.873
5600	9.197	75.128	66.731	47.023	31.918	- 74.189	2.895
5700	9.202	75.291	66.879	47.943	31.720	- 76.087	2.917
5800	9.208	75.451	67.026	48.864	31.521	- 77.975	2.938
5900	9.213	75.608	67.170	49.785	31.320	- 79.860	2.958
6000	9.219	75.763	67.312	50.706	31.116	- 81.744	2.977

Dec. 31, 1960; Dec. 31, 1962

CARBON MONOSULPHIDE (CS) (IDEAL GAS) MOL. WT. = 44.077

$\Delta H_{f\ 0}^\circ = 54.2 \pm 5$ kcal. mole^{-1}

$\Delta H^\circ_{298.15} = 55.0 \pm 5$ kcal. mole^{-1}

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15} = 50.3 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_i
0	1

$\omega_e = 1285.08$ cm.$^{-1}$

$\omega_e x_e = 6.46$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.82005$ cm.$^{-1}$

$\alpha_e = 0.00592$ cm.$^{-1}$

$r_e = 1.535$ Å

Heat of Formation.

A. Lagerqvist, H. Westerlund, C. V. Wright and R. F. Barrow, Arkiv for Fysik 14, 387 (1958) examined the UV band system of CS and made a new extrapolation of the ground state vibrational levels to find $D_0^\circ = 7.85$ e.v., which leads to $\Delta H_{f\ 298}^\circ$ CS = 55 ± 5.0 kcal. mole^{-1}. H. Schaffer and H. Wiedemeier, Paper presented at the XVIIIth IUPAC Congress Montreal (1961). have measured $\Delta H_{f\ 298.15}^\circ$ CS(g) by an equilibrium method and found 58 ± 3 kcal. mole^{-1}. E. Gallegos and R. W. Kiser, J. Phys. Chem. 65, 1177 (1961) obtained a value of $\Delta H_{f\ 298.15}^\circ$ CS(g) = 55.0 kcal. mole^{-1} from the heat of formation of CS^+ and the ionization potential of CS. C. J. Fincham and R. A. Bergman, J. Metals, 9, 690 (1957) measured the equilibrium between CS_2 and sulphur containing ores. Combining these with similar experiments for H_2S the heat of formation of CS at 298 is calculated to be 69.0 kcal. mole^{-1}. The gases assumed are CS_2, CS, S, S_2, H_2, H_2S, and HS — because of the complex equilibria and the use of outside data for the H_2S equilibrium, the assumption of $P_{H_2} = 1$ atm. and the uncertainty in HS values, this value was given no weight.

Heat Capacity and Entropy.

A. Lagerqvist, et al., loc. cit., give the vibrational constants. The rotational constants are from the microwave measurements of R. C. Mockler and R. Bird, Phys. Rev. 98, 1837 (1955).

Carbon Disulfide (CS_2)

(Ideal Gas) Mol. Wt. = 76.143

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.551	27.787	27.787	INFINITE
100	7.404	47.013	65.493	-1.848	28.148	24.061	-52.582
200	9.461	52.776	57.796	-1.004	28.128	19.966	-21.816
298	10.875	56.832	56.832	.000	27.980	15.991	-11.721
300	10.895	56.899	56.832	.020	27.976	15.917	-11.595
400	11.820	60.166	57.271	1.158	26.670	11.973	-6.541
500	12.480	62.880	58.129	2.375	25.692	8.413	-3.677
600	12.974	65.200	59.119	3.649	24.874	5.036	-1.834
700	13.348	67.230	60.136	4.966	24.166	1.835	-.573
800	13.636	69.032	61.137	6.316	-2.593	-3.847	1.051
900	13.858	70.651	62.106	7.691	-2.581	-4.005	.973
1000	14.033	72.121	63.035	9.086	-2.574	-4.163	.910
1100	14.172	73.465	63.923	10.497	-2.572	-4.325	.859
1200	14.283	74.703	64.770	11.919	-2.574	-4.482	.816
1300	14.375	75.850	65.579	13.352	-2.580	-4.639	.780
1400	14.450	76.918	66.351	14.794	-2.588	-4.796	.749
1500	14.513	77.917	67.089	16.242	-2.600	-4.957	.722
1600	14.567	78.856	67.796	17.696	-2.612	-5.113	.698
1700	14.612	79.740	68.473	19.155	-2.625	-5.269	.677
1800	14.652	80.577	69.122	20.618	-2.641	-5.425	.659
1900	14.686	81.370	69.746	22.085	-2.656	-5.576	.641
2000	14.716	82.124	70.346	23.556	-2.672	-5.730	.626
2100	14.742	82.843	70.924	25.028	-2.691	-5.884	.612
2200	14.766	83.529	71.482	26.504	-2.710	-6.034	.599
2300	14.787	84.186	72.020	27.982	-2.730	-6.185	.588
2400	14.806	84.816	72.540	29.461	-2.752	-6.334	.577
2500	14.824	85.420	73.043	30.943	-2.772	-6.483	.567
2600	14.839	86.002	73.531	32.426	-2.796	-6.631	.557
2700	14.854	86.562	74.003	33.911	-2.819	-6.781	.549
2800	14.867	87.103	74.461	35.397	-2.844	-6.929	.541
2900	14.880	87.625	74.906	36.884	-2.871	-7.072	.533
3000	14.892	88.129	75.339	38.373	-2.899	-7.215	.526
3100	14.902	88.618	75.759	39.862	-2.926	-7.358	.519
3200	14.913	89.091	76.168	41.353	-2.957	-7.501	.512
3300	14.922	89.550	76.567	42.845	-2.987	-7.647	.506
3400	14.931	89.996	76.955	44.337	-3.020	-7.782	.500
3500	14.940	90.429	77.334	45.831	-3.055	-7.930	.495
3600	14.948	90.850	77.704	47.325	-3.089	-8.066	.490
3700	14.956	91.259	78.065	48.821	-3.127	-8.201	.484
3800	14.963	91.658	78.417	50.317	-3.164	-8.337	.479
3900	14.971	92.047	78.762	51.813	-3.205	-8.474	.475
4000	14.977	92.426	79.099	53.311	-3.245	-8.602	.470
4100	14.984	92.796	79.428	54.809	-3.287	-8.741	.466
4200	14.991	93.157	79.751	56.307	-3.333	-8.869	.461
4300	14.997	93.510	80.067	57.807	-3.379	-9.004	.458
4400	15.003	93.855	80.376	59.307	-3.428	-9.135	.454
4500	15.009	94.192	80.679	60.807	-3.479	-9.262	.450
4600	15.015	94.522	80.977	62.309	-3.530	-9.391	.446
4700	15.021	94.845	81.268	63.810	-3.583	-9.519	.443
4800	15.026	95.161	81.555	65.313	-3.639	-9.646	.439
4900	15.031	95.471	81.835	66.816	-3.696	-9.764	.435
5000	15.037	95.775	82.111	68.319	-3.757	-9.892	.432
5100	15.042	96.073	82.382	69.823	-3.820	-10.015	.429
5200	15.047	96.365	82.648	71.327	-3.884	-10.134	.426
5300	15.052	96.652	82.910	72.832	-3.949	-10.253	.423
5400	15.057	96.933	83.167	74.338	-4.017	-10.367	.420
5500	15.062	97.209	83.420	75.844	-4.088	-10.486	.417
5600	15.066	97.481	83.668	77.350	-4.162	-10.600	.414
5700	15.071	97.747	83.913	78.857	-4.238	-10.721	.411
5800	15.076	98.010	84.154	80.364	-4.316	-10.833	.408
5900	15.080	98.267	84.391	81.872	-4.395	-10.946	.405
6000	15.085	98.521	84.624	83.380	-4.478	-11.053	.403

June 30, 1961

CARBON DISULFIDE (CS_2) (IDEAL GAS) MOL. WT. = 76.143

ΔH_{f0}° = 27.79 ± 0.19 kcal. mole^{-1}

Point Group $D_{\infty h}$

$\Delta H_{f\ 298.15}^\circ$ = 27.98 ± 0.19 kcal. mole^{-1}

$S_{298.15}^\circ$ = 56.833 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
658 (1)
396.8 (2)
1532.5 (1)

Bond Length and Angle C-S dist. = 1.553 Å S-C-S angle = 180° σ = 2

Moment of Inertia I = 25.6805 X 10^{-39} g. cm.^{3}

Heat of Formation

W. Good and J. P. McCullough, private communication, September 21, 1960, report $\Delta H_{f\ 298.15}^\circ$ from an analysis of combustion calorimetry data of CS_2.

Heat Capacity and Entropy

Functions at 100° and 200°K were calculated by the RRHO approximation using the fundamental vibrational levels of T. Wentink, Jr., J. Chem. Phys. 29, 188 (1958) calculated from zero order levels reported by B. P. Stoicheff, Can. J. Phys. 36, 218 (1958). $S_{298.15}^\circ$ and C_p from 298.15° to 6000°K taken from J. S. Gordon, private communication, February 7, 1961. In addition to the fundamental levels listed above, Gordon, in his calculation of the functions, used the anharmonic constants derived from high resolution Raman spectra by Stoicheff, and the vibration-rotation interaction constants reported by A. H. Guenther, T. A. Wiggins and D. H. Rank, J. Chem. Phys. 28, 682 (1958).

J. P. McCullough, private communication, February 17, 1961, has correlated and summarized the experimental thermodynamic data for CS_2 by a set of empirical equations. The result for C_p is:

$$C_p\ (\pm 0.2\%) = 6.478 + 1.8931 \times 10^{-2}T - 1.3873 \times 10^{-5}T^2 \text{ cal. deg.}^{-1}\text{ mole}^{-1}\ (325\text{-}502°\text{K.})$$

The experimental values of C_p were then fit within 0.08% by a given set of molecular parameters different from that used by Gordon. However, in the temperature range given above, Gordon's calculation is within the uncertainty indicated by McCullough.

Since no method of calculating anharmonic corrections for polyatomic molecules has been programed, Gordon's values were employed.

Silicon Carbide, Alpha(α-SiC)

(Crystal) GFW = 40.09715

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-.777	-16.856	-16.856	INFINITE
100	1.003	.338	7.855	-.752	-16.909	-16.830	36.782
200	3.883	1.901	4.449	-.510	-17.026	-16.704	18.253
298	6.396	3.940	3.940	.000	-17.100	-16.528	12.116
300	6.437	3.980	3.940	.012	-17.101	-16.525	12.039
400	8.150	6.086	4.216	.748	-17.118	-16.329	8.922
500	9.228	8.029	4.787	1.621	-17.108	-16.132	7.051
600	9.972	9.781	5.476	2.583	-17.092	-15.940	5.806
700	10.518	11.361	6.206	3.608	-17.077	-15.748	4.917
800	10.939	12.794	6.941	4.682	-17.062	-15.559	4.251
900	11.274	14.102	7.665	5.793	-17.050	-15.372	3.733
1000	11.549	15.305	8.370	6.935	-17.038	-15.187	3.319
1100	11.779	16.417	9.051	8.102	-17.029	-15.003	2.981
1200	11.976	17.450	9.709	9.290	-17.022	-14.818	2.699
1300	12.147	18.416	10.342	10.496	-17.020	-14.636	2.461
1400	12.297	19.321	10.951	11.718	-17.019	-14.450	2.256
1500	12.431	20.174	11.538	12.955	-17.021	-14.266	2.079
1600	12.552	20.981	12.103	14.204	-17.027	-14.085	1.924
1700	12.661	21.745	12.648	15.465	-29.028	-13.795	1.773
1800	12.762	22.472	13.174	16.736	-28.986	-12.899	1.566
1900	12.854	23.164	13.681	18.017	-28.937	-12.006	1.381
2000	12.940	23.826	14.172	19.307	-28.882	-11.116	1.215
2100	13.020	24.459	14.647	20.605	-28.821	-10.228	1.064
2200	13.094	25.066	15.107	21.910	-28.757	-9.346	.928
2300	13.165	25.650	15.553	23.223	-28.686	-8.464	.804
2400	13.232	26.212	15.985	24.543	-28.611	-7.587	.691
2500	13.296	26.753	16.405	25.870	-28.530	-6.713	.587
2600	13.356	27.276	16.813	27.202	-28.447	-5.842	.491
2700	13.414	27.781	17.210	28.541	-28.358	-4.976	.403
2800	13.470	28.270	17.597	29.885	-28.265	-4.109	.321
2900	13.523	28.743	17.973	31.235	-28.169	-3.247	.245
3000	13.575	29.203	18.340	32.590	-28.069	-2.392	.174
3100	13.625	29.649	18.697	33.950	-27.965	-1.538	.108
3200	13.673	30.082	19.046	35.314	-27.859	-.684	.047
3300	13.720	30.503	19.387	36.684	-27.749	.163	-.011
3400	13.765	30.914	19.720	38.058	-27.636	1.006	-.065
3500	13.810	31.313	20.046	39.437	-27.520	1.845	-.115
3600	13.853	31.703	20.364	40.820	-119.362	4.939	-.300
3700	13.895	32.083	20.676	42.208	-119.141	8.390	-.496
3800	13.937	32.454	20.981	43.599	-118.918	11.837	-.681
3900	13.977	32.817	21.280	44.995	-118.693	15.272	-.856
4000	14.017	33.171	21.572	46.395	-118.465	18.707	-1.022

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

SILICON CARBIDE, ALPHA (SiC) (CRYSTAL) GFW = 40.09715

$S^\circ_{298.15}$ = 3.94 ± 0.03 gibbs/mol

Td = [3245] °K

ΔHf°_0 = -16.9 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -17.1 ± 1.5 kcal/mol

Heat of Formation.

The heat of formation is calculated from ΔHr°_{298} = -591.9 kcal/mol for $SiC(\alpha) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$ based on the tentative value of ΔHf°_{298} = -223± 1 kcal/mol for $CF_4(g)$. Greenberg[1] determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey[2] obtained by oxygen bomb calorimetry yield a ΔHf° which is over 2 kcal more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained mass spectrometrically by Drowart[3] are in close agreement with the selected ΔHf°, but Knudsen weight loss data of Grieveson[4] and solubility-activity data of Kirkwood[5] yield values less negative by 2 and 3 kcal, respectively. The results are summarized below.

The data of Drowart show a significant drift while those of Grieveson do not, but the latter should be corrected for $C_2Si(g)$ and $CSi_2(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin[6] and Ghoshtagore[7] yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol) 2nd Law	ΔHr°_{298} (kcal/mol) 3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Greenberg (1966)	F_2Calorimetry	A	298	-	-591.9		-	-17.1
Humphrey (1952)	O_2Calorimetry	B	303	-	-292.0		-	-19.6
Drowart (1958)	Mass Spec.	C	2149-2316	7	136.9±0.7	124.61	-5.6±0.3	-16.9(-17.6)*
Grieveson (1960)	Knudsen Wt. Loss	C	1785-2004	10	122.9±0.7	122.66	-0.2±0.4	-15.0
Kirkwood (1961)	Soly. in Pb	D	1693	1	-	25.66	-	-14.1

A) $SiC(\alpha) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$

B) $SiC(\alpha) + 2O_2(g) \rightarrow SiO_2(\text{low-quartz}) + CO_2(g)$

C) $SiC(\alpha) \rightarrow C(\text{graph}) + Si(g)$

D) $SiC(\alpha) \rightarrow C(\text{graph}) + Si(l)$

*Value in parentheses is based on authors' data for $Si(l) \rightarrow Si(g)$ rather than JANAF value.

Heat Capacity and Entropy.

Low temperature heat capacities are from data (54-296°K) of Humphrey[2] and are in good agreement with earlier data (54-295°K) of Kelley[8]. The entropy is obtained from Cp° using S°_{50} = 0.038 eu. Cp° above room temperature is based on enthalpy data of Humphrey[2] [389-1789°K], Walker[9] [373-1073°K] and Magnus[10] [372-1172°K]. Maximum deviations of the data from the selected values are 1.4, 2 and -1.7%, respectively; these occur in the range 370-621°K. Kirillin[11] obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by -1±1.5% from the selected values. Enthalpies (793-1790°K) of Fieldhouse[12] are high by 1-8% while those of Maksimenko[13] were not available for analysis.

Transition Data.

SiC(α), also called hexagonal II or 6H, is one of the more common of many hexagonal forms which arise from various possible stacking sequences of the hexagonal SiC layers[14]. The properties of these phases are so similar that they have not been adequately differentiated thermodynamically. It has frequently been assumed that cubic SiC(β) transforms to alpha at about 2300°K, but this seems unlikely since both phases have been prepared over temperature ranges of 1700-3000°K[14]. Heat of formation and equilibrium data indicate that alpha is less stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data.

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor consisting of C_2Si(44.3 mol %), Si(32.0%), CSi_2(21.2%), Si_2(1.9%), CSi(0.27%), and Si_3(0.25%). The tables predict decomposition to graphite and pure liquid silicon at about 3280°K; however, Scace[15] observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103±40°K. In contrast, Dolloff[16] reported the peritectic at 2813±40°K and 27 percent carbon. Badami[17] has shown that decomposition in vacuum at lower temperatures (2400°K) leads to graphite.

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Silicon Carbide, Beta (β -SiC)

(Crystal) GFW = 40.09715

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-.782	-17.261	-17.261	INFINITE
100	1.019	.349	7.902	-.755	-17.312	-17.235	37.666
200	3.896	1.920	4.479	-.512	-17.428	-17.110	18.697
298	6.415	3.970	3.970	.000	-17.500	-16.937	12.415
300	6.455	4.010	3.970	.012	-17.501	-16.934	12.336
400	8.150	6.118	4.246	.749	-17.517	-16.741	9.147
500	9.235	8.061	4.818	1.622	-17.507	-16.547	7.233
600	9.988	9.815	5.507	2.585	-17.490	-16.358	5.958
700	10.542	11.398	6.238	3.613	-17.472	-16.170	5.048
800	10.965	12.835	6.974	4.689	-17.455	-15.986	4.367
900	11.301	14.146	7.699	5.803	-17.440	-15.802	3.837
1000	11.573	15.351	8.405	6.947	-17.426	-15.621	3.414
1100	11.798	16.465	9.088	8.116	-17.415	-15.442	3.068
1200	11.988	17.500	9.746	9.305	-17.407	-15.263	2.780
1300	12.151	18.466	10.380	10.512	-17.404	-15.085	2.536
1400	12.292	19.372	10.990	11.735	-17.402	-14.905	2.327
1500	12.415	20.224	11.578	12.970	-17.406	-14.726	2.146
1600	12.524	21.029	12.144	14.217	-17.414	-14.548	1.987
1700	12.621	21.791	12.689	15.474	-29.419	-14.263	1.834
1800	12.708	22.515	13.215	16.741	-29.381	-13.372	1.624
1900	12.786	23.205	13.723	18.016	-29.338	-12.485	1.436
2000	12.858	23.862	14.213	19.298	-29.291	-11.597	1.267
2100	12.923	24.491	14.688	20.587	-29.239	-10.713	1.115
2200	12.983	25.094	15.147	21.882	-29.185	-9.836	.977
2300	13.039	25.672	15.592	23.183	-29.126	-8.955	.851
2400	13.090	26.228	16.024	24.490	-29.064	-8.078	.736
2500	13.137	26.764	16.443	25.801	-28.999	-7.209	.630
2600	13.182	27.280	16.850	27.117	-28.932	-6.338	.533
2700	13.224	27.778	17.245	28.438	-28.861	-5.471	.443
2800	13.263	28.260	17.630	29.762	-28.788	-4.604	.359
2900	13.299	28.726	18.005	31.090	-28.714	-3.742	.282
3000	13.334	29.177	18.370	32.422	-28.637	-2.882	.210
3100	13.367	29.615	18.726	33.757	-28.558	-2.025	.143
3200	13.398	30.040	19.072	35.095	-28.478	-1.169	.080
3300	13.428	30.452	19.411	36.436	-28.397	-.317	.021
3400	13.456	30.854	19.742	37.781	-28.313	.532	-.034
3500	13.483	31.244	20.065	39.128	-28.229	1.377	-.086
3600	13.509	31.624	20.381	40.477	-120.105	4.480	-.272
3700	13.534	31.995	20.690	41.829	-119.920	7.938	-.469
3800	13.557	32.356	20.992	43.184	-119.733	11.394	-.655
3900	13.580	32.709	21.288	44.541	-119.547	14.839	-.832
4000	13.602	33.053	21.578	45.900	-119.360	18.284	-.999

Mar. 31, 1967

SILICON CARBIDE, BETA (SiC) (CRYSTAL) GFW = 40.09715

ΔHf°_0 = -17.3 ± 1.5 kcal/mol

$S^\circ_{298.15}$ = 3.97 ± 0.03 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -17.5 ± 1.5 kcal/mol

Td = [3259] °K

Heat of Formation.

The heat of formation is calculated from ΔHr°_{298} = -591.5 kcal/mol for $SiC(\beta)+4F_2(g) \rightarrow SiF_4(g)+CF_4(g)$, based on the tentative value of ΔHf°_{298} = -223 ± 1 kcal/mol for $CF_4(g)$. Greenberg[1] determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey[2] obtained by oxygen bomb calorimetry yield a ΔHf° which is over 3 kcal more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained with the Knudsen weight loss method by Davis[3] are in good agreement with the selected ΔHf°, but similar data of Grieveson[4] and solubility-activity data of Rein[5] and d'Entremont[6] yield values less negative by 1.6 to 2.5 kcal. The results are summarized below. Other equilibrium data[5] relating SiC and SiO_2 are not included, pending the revision of tables for SiO_2.

The data of Davis show a serious drift, while those of Grieveson do not; but the latter should be corrected for $C_2Si(g)$ and $CSi_2(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin[7] and Ghoshtagore[8] yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol) 2nd law	ΔHr°_{298} (kcal/mol) 3rd law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Greenberg (1966)	F_2 Calorimetry	A	298	-	-591.5		-	-17.5
Humphrey (1952)	O_2 Calorimetry	B	303	-	-290.9		-	-20.6
Davis (1961)	Knudsen Wt. Loss	C	2117-2171	8	167±28	126.10	-19±13	-18.4(-17.6)*
Grieveson (1960)	" " "	C	1808-1973	6	123.3±0.3	122.65	-0.4±0.2	-15.0
Rein (1963)	Soly. in C-Fe	D	1823-1873	2	32.0	27.43	-2.5	-15.9
d'Entremont (1963)	Soly. in Ag	D	1693	1	-	27.31	-	-15.7

A) $SiC(\beta) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$

B) $SiC(\beta) + 2O_2(g) \rightarrow SiO_2(\text{low quartz}) + CO_2(g)$

C) $SiC(\beta) \rightarrow C(\text{graph}) + Si(g)$

D) $SiC(\beta) \rightarrow C(\text{graph}) + Si(l)$

*Value in parentheses is based on author's data for $Si(l) \rightarrow Si(g)$ rather than JANAF value.

Heat Capacity and Entropy.

Low temperature heat capacities are from data (54-296°K) of Humphrey[2]. The entropy is obtained from Cp° using S°_{50} = 0.041 eu. Cp° above room temperature is based on Humphrey's enthalpy data (389-1693°K), which show a maximum deviation of ± 1.2% from the selected functions. Humphrey's sample contained about 1% of α-SiC and about 0.6% of other impurities. Kirillin[9] obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by -1±2% from the selected values.

Transition Data.

SiC(β), also called cubic or 3C, has a structure of the diamond or zinc blende type[10]. The cubic phase differs from the many hexagonal forms only in the order of the stacking sequence of the hexagonal SiC layers. It has frequently been assumed that β transforms into α at about 2300°K, but this seems unlikely, since both phases have been prepared over temperature ranges of 1700-3000°K[10]. Heat of formation and equilibrium data indicate that β is more stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data.

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor consisting of C_2Si(45.4 mol %), Si(32.1%), CSi_2(20.1%), Si_2(1.8%), CSi(0.28%) and Si_3(0.23%). The tables predict decomposition to graphite and pure liquid silicon at about 3337°K; however, Scace[11] observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103±40°K. In contrast, Dolloff[12] reported the peritectic at 2813±40°K and 27 percent carbon.

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Silicon Carbide (SiC)

(Ideal Gas) GFW = 40.09715

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.215	170.806	170.806	INFINITE
100	6.958	42.719	57.917	-1.520	171.423	167.264	-365.555
200	7.441	47.617	51.671	-.811	171.773	162.951	-178.065
298	9.182	50.892	50.892	.000	172.000	158.573	-116.237
300	9.216	50.949	50.892	.017	172.004	158.489	-115.459
400	10.574	53.813	51.273	1.016	172.250	153.948	-84.113
500	10.857	56.219	52.030	2.095	172.466	149.347	-65.279
600	10.610	58.180	52.897	3.170	172.595	144.708	-52.710
700	10.264	59.790	53.770	4.214	172.629	140.057	-43.728
800	9.972	61.140	54.609	5.225	172.581	135.406	-36.991
900	9.761	62.302	55.401	6.211	172.468	130.765	-31.754
1000	9.620	63.323	56.143	7.179	172.306	126.139	-27.568
1100	9.532	64.235	56.838	8.137	172.106	121.532	-24.146
1200	9.483	65.062	57.489	9.087	171.875	116.945	-21.299
1300	9.460	65.820	58.101	10.034	171.618	112.377	-18.892
1400	9.455	66.521	58.678	10.980	171.343	107.832	-16.833
1500	9.462	67.173	59.223	11.925	171.049	103.306	-15.052
1600	9.477	67.784	59.739	12.872	170.741	98.799	-13.495
1700	9.497	68.360	60.229	13.821	158.428	94.416	-12.138
1800	9.520	68.903	60.696	14.772	158.150	90.661	-11.008
1900	9.544	69.418	61.142	15.725	157.871	86.919	-9.998
2000	9.567	69.909	61.568	16.681	157.592	83.192	-9.091
2100	9.591	70.376	61.977	17.639	157.313	79.480	-8.272
2200	9.614	70.823	62.369	18.599	157.032	75.777	-7.528
2300	9.635	71.250	62.746	19.561	156.752	72.094	-6.850
2400	9.655	71.661	63.108	20.526	156.472	68.418	-6.230
2500	9.674	72.055	63.459	21.492	156.192	64.755	-5.661
2600	9.692	72.435	63.797	22.461	155.912	61.103	-5.136
2700	9.708	72.801	64.123	23.431	155.632	57.460	-4.651
2800	9.723	73.155	64.440	24.402	155.352	53.830	-4.202
2900	9.736	73.496	64.746	25.375	155.071	50.210	-3.784
3000	9.749	73.826	65.043	26.349	154.790	46.598	-3.395
3100	9.761	74.146	65.332	27.325	154.510	42.997	-3.031
3200	9.771	74.456	65.612	28.301	154.228	39.406	-2.691
3300	9.781	74.757	65.885	29.279	153.946	35.919	-2.372
3400	9.790	75.049	66.150	30.258	153.664	32.246	-2.073
3500	9.799	75.333	66.408	31.237	153.380	28.675	-1.791
3600	9.806	75.609	66.660	32.217	61.135	27.375	-1.662
3700	9.813	75.878	66.906	33.198	60.949	26.439	-1.562
3800	9.820	76.140	67.145	34.180	60.763	25.510	-1.467
3900	9.826	76.395	67.379	35.162	60.574	24.585	-1.378
4000	9.831	76.644	67.608	36.145	60.385	23.665	-1.293
4100	9.837	76.887	67.831	37.129	60.194	22.744	-1.212
4200	9.841	77.124	68.049	38.113	60.002	21.836	-1.136
4300	9.846	77.355	68.263	39.097	59.808	20.932	-1.064
4400	9.850	77.582	68.472	40.082	59.613	20.026	-.995
4500	9.853	77.803	68.677	41.067	59.417	19.133	-.929
4600	9.857	78.020	68.878	42.052	59.219	18.238	-.866
4700	9.860	78.232	69.075	43.038	59.020	17.350	-.807
4800	9.863	78.439	69.268	44.024	58.819	16.469	-.750
4900	9.865	78.643	69.457	45.011	58.618	15.586	-.695
5000	9.868	78.842	69.643	45.997	58.414	14.709	-.643
5100	9.870	79.038	69.825	46.984	58.208	13.833	-.593
5200	9.872	79.229	70.004	47.971	58.001	12.969	-.545
5300	9.874	79.417	70.180	48.958	57.793	12.107	-.499
5400	9.875	79.602	70.353	49.946	57.583	11.246	-.455
5500	9.877	79.783	70.522	50.934	57.370	10.389	-.413
5600	9.878	79.961	70.689	51.921	57.155	9.539	-.372
5700	9.880	80.136	70.854	52.909	56.938	8.688	-.333
5800	9.881	80.308	71.015	53.897	56.718	7.842	-.295
5900	9.882	80.477	71.174	54.885	56.496	7.001	-.259
6000	9.883	80.643	71.330	55.874	56.273	6.161	-.224

Mar. 31, 1967

SILICON CARBIDE (SiC) (IDEAL GAS) GFW = 40.09715

Ground State Configuration [$^1\Sigma$]

$S^\circ_{298.15}$ = [50.9] gibbs/mol

ΔHf°_0 = 170.8 ± 8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 172 ± 8 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[8000]	[2]
[1000]	[6]	[14000]	[2]
[5000]	[3]	[18000]	[1]

ω_e = [1226] cm^{-1} $\omega_e x_e$ = [5] cm^{-1} σ = 1

B_e = [0.6933] cm^{-1} α_e = [0.006] cm^{-1} r_e = [1.7] Å

Heat of Formation.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibrium over the systems SiC-graphite[1] and boron-silicon-graphite[2]. Third law analysis of the partial pressures of Si and SiC yields the results summarized below. The adopted value, ΔHf°_{298} = 172 ± 8, is the mean of the two results and the uncertainty reflects the possible effect of an error of up to 4 eu in the functions. The corresponding dissociation energy is D°_0 = 106.5 ± 8 kcal/mol.

Source	Method	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol)* 2nd Law	ΔHr°_{298} (kcal/mol)* 3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Drowart (1958)	Mass Spec.	2181-2316	3	27.1±4	65.94	17±2	173.6
Verhaegen (1964)	" "	2249-2344	3	48.7±4	62.67	6±2	170.4

*For the reaction C(graphite) + Si(g) = SiC(g)

Heat Capacity and Entropy.

The ground state is assumed to be $^1\Sigma$, as suggested by Weltner and McLeod[3]. By analogy with C_2, there should be a low-lying $^3\Pi$ excited state; this would dominate the thermodynamic functions at temperatures above 2000°K if the level lies below 5000 cm^{-1}. The $^3\Pi$ level is assumed to lie at 1000 cm^{-1}, intermediate between the value[4] observed for C_2 and that estimated for Si_2 (see JANAF table). Additional excited states, $^3\Sigma$, $^1\Pi$, $^1\Delta$ and $^1\Sigma$, are estimated by comparison with those observed or predicted[5] for C_2. The estimates for the electronic levels are relatively uncertain and probably yield an upper limit for the entropy at temperatures where SiC(g) is significant. A probable lower limit for the electronic contribution may be obtained by increasing the $^3\Pi$ level to 7000 cm^{-1} and omitting the other excited states. This would reduce the entropy by 3.5 and 2.0 eu at 2000 and 4000°K.

The vibrational frequency is that estimated by Weltner[3] from a valence bond calculation using $k = 7.44 \times 10^5$ dyn/cm obtained from C_2Si. The constants $\omega_e x_e$, α_e and r_e are estimated by interpolation between those[6,4] for the $^3\Pi_u$ states of Si_2 and C_2. Use of constants based on the $^3\Pi$ state is consistent with the assumption that this state dominates the electronic partition function at high temperatures. B_e is calculated from r_e.

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Disilicon Carbide (Si_2C)

(Ideal Gas) GFW = 68.18315

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°₂₉₈)/T (gibbs/mol)	H°−H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.722	127.068	127.068	INFINITE
100	8.204	47.187	67.144	-1.996	127.652	123.138	-269.117
200	10.233	53.571	58.886	-1.063	127.945	118.490	-129.480
298	11.334	57.881	57.881	.000	128.000	113.830	-83.440
300	11.351	57.951	57.881	.021	127.999	113.742	-82.861
400	12.082	61.322	58.336	1.195	127.913	109.000	-59.555
500	12.630	64.080	59.217	2.431	127.742	104.291	-45.586
600	13.057	66.422	60.227	3.717	127.514	99.620	-36.287
700	13.391	68.461	61.261	5.040	127.242	94.993	-29.658
800	13.652	70.267	62.276	6.392	126.935	90.406	-24.698
900	13.857	71.887	63.255	7.768	126.600	85.861	-20.850
1000	14.019	73.356	64.193	9.162	126.240	81.352	-17.780
1100	14.149	74.698	65.088	10.571	125.856	76.882	-15.275
1200	14.254	75.934	65.941	11.991	125.450	72.448	-13.194
1300	14.341	77.078	66.754	13.421	125.021	68.047	-11.440
1400	14.416	78.144	67.530	14.859	124.573	63.683	-9.941
1500	14.482	79.141	68.271	16.304	124.104	59.351	-8.647
1600	14.543	80.077	68.980	17.755	123.615	55.049	-7.519
1700	14.604	80.961	69.659	19.213	99.123	50.989	-6.555
1800	14.666	81.797	70.311	20.676	98.707	48.172	-5.849
1900	14.733	82.592	70.936	22.146	98.295	45.374	-5.219
2000	14.806	83.349	71.538	23.623	97.887	42.603	-4.655
2100	14.887	84.074	72.118	25.107	97.484	39.848	-4.147
2200	14.978	84.768	72.677	26.601	97.087	37.110	-3.687
2300	15.078	85.436	73.218	28.103	96.697	34.395	-3.268
2400	15.188	86.080	73.740	29.614	96.315	31.695	-2.886
2500	15.307	86.703	74.246	31.141	95.944	29.007	-2.536
2600	15.436	87.306	74.737	32.678	95.582	26.336	-2.214
2700	15.574	87.891	75.213	34.229	95.233	23.677	-1.917
2800	15.719	88.460	75.676	35.793	94.896	21.038	-1.642
2900	15.869	89.014	76.127	37.373	94.572	18.406	-1.387
3000	16.025	89.555	76.565	38.967	94.261	15.781	-1.150
3100	16.184	90.083	76.993	40.578	93.966	13.170	-.929
3200	16.345	90.599	77.410	42.204	93.684	10.574	-.722
3300	16.507	91.104	77.817	43.847	93.417	7.980	-.528
3400	16.667	91.600	78.216	45.506	93.165	5.394	-.347
3500	16.825	92.085	78.605	47.180	92.926	2.812	-.176
3600	16.980	92.561	78.986	48.870	-91.220	4.756	-.289
3700	17.130	93.028	79.359	50.576	-91.232	7.425	-.439
3800	17.274	93.487	79.725	52.296	-91.231	10.092	-.580
3900	17.411	93.938	80.084	54.031	-91.219	12.755	-.715
4000	17.541	94.380	80.436	55.778	-91.196	15.424	-.843
4100	17.663	94.815	80.781	57.538	-91.164	18.081	-.964
4200	17.776	95.242	81.120	59.311	-91.119	20.748	-1.080
4300	17.880	95.661	81.454	61.093	-91.067	23.412	-1.190
4400	17.975	96.073	81.781	62.886	-91.007	26.073	-1.295
4500	18.061	96.478	82.103	64.688	-90.938	28.740	-1.396
4600	18.137	96.876	82.420	66.498	-90.863	31.396	-1.492
4700	18.204	97.267	82.732	68.315	-90.784	34.053	-1.583
4800	18.263	97.651	83.039	70.139	-90.699	36.707	-1.671
4900	18.312	98.028	83.341	71.967	-90.611	39.362	-1.756
5000	18.352	98.398	83.638	73.801	-90.519	42.011	-1.836
5100	18.385	98.762	83.931	75.638	-90.427	44.661	-1.914
5200	18.409	99.119	84.220	77.477	-90.334	47.310	-1.988
5300	18.426	99.470	84.504	79.319	-90.238	49.958	-2.060
5400	18.436	99.815	84.785	81.162	-90.145	52.599	-2.129
5500	18.440	100.153	85.061	83.006	-90.054	55.240	-2.195
5600	18.437	100.485	85.333	84.850	-89.964	57.887	-2.259
5700	18.429	100.812	85.602	86.694	-89.877	60.523	-2.321
5800	18.415	101.132	85.867	88.536	-89.796	63.161	-2.380
5900	18.397	101.447	86.129	90.377	-89.718	65.794	-2.437
6000	18.374	101.756	86.386	92.215	-89.645	68.425	-2.492

Mar. 31, 1967

DISILICON CARBIDE (CSi_2) (IDEAL GAS) GFW = 68.1815

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [57.9] gibbs/mol

ΔHf°_0 = 127.1 ± 6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 128 ± 6 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[1]
[12000]	[6]
[19000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[670] (1)
[275] (2)
[1600] (1)

Bond Distance: C-Si = [1.75] Å

Bond Angle: C-Si-Si = [180°] σ = [2]

Rotational Constant: B_0 = [0.0980] cm^{-1}

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the SiC-graphite[1], SiC-silicon[2] and boron-carbon-silicon[3] systems. Third law analysis of the partial pressures of CSi_2 and Si yields the concordant values 127.4, 127.9 and 128.6 kcal/mol. Two of the drifts are rather large, but they are opposite in sign so that no consistent entropy difference is apparent between the data and the tabulated functions. The drifts may be related to the low condensation coefficient for CSi_2 suggested by Drowart[2]. Rates of free evaporation reported by Voronin[4] yield apparent pressures which are lower by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of ΔHf°_{298} = 128 ± 6 kcal/mol includes allowance for an error in the entropy of up to 3 eu.

Source	Method	Reaction	Range, T°K	No. of Points	ΔHf°_{298} (kcal/mol) 2nd Law	3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Drowart (1958)	Mass Spec.	A	2149-2316	7	-104±7	-88.0	7.4±3.0	127.4
Drowart (1960)	" "	B	1825-2160	7	141±3	134.4	-3.4±1.7	127.9
Verhaegen (1964)	" "	A	2083-2344	6	- 68±25	-86.8	-9±12	128.6

A) $C(graph) + 2\,Si(g) = CSi_2(g)$ B) $SiC(\alpha) + Si(l) = CSi_2(g)$

Heat Capacity and Entropy.

Weltner and McLeod[5] observed a band system in absorption at 5300 Å in matrix isolation and assigned this tentatively to the transition $^1\Pi_u \leftarrow X^1\Sigma_g^+$ of CSi_2. This assignment is adopted, although the evidence is not at all conclusive. A $^3\Pi_u$ excited state is assumed to lie at 12000 cm^{-1}, presumably arising from the same molecular orbital configuration as the $^1\Pi_u$ state. A linear, symmetric structure is assumed, as suggested by Weltner. The bond distance is estimated by comparison with Si_2, C_2 and C_3. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 7.46 \times 10^5$ and $k\delta/l^2 = 0.11 \times 10^5$ dyn/cm. The stretching force constant is taken from C_2Si[5], while the bending force constant is from C_2Si and the $^1\Pi_u$ excited state of C_3[5]. The moment of inertia is 28.56×10^{-39} g cm^2.

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Titanium Carbide (TiC)

(Crystal) GFW = 59.91115

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.101	-43.697	-43.697	INFINITE
100	1.753	.622	11.162	-1.054	-43.798	-43.642	95.380
200	3.567	3.054	6.459	-.681	-43.961	-43.414	47.441
298	8.080	5.791	5.791	.000	-44.000	-43.137	31.621
300	8.111	5.841	5.791	.015	-44.000	-43.132	31.422
400	9.724	8.408	6.130	.911	-43.968	-42.845	23.410
500	10.795	10.702	6.820	1.941	-43.903	-42.573	18.609
600	11.388	12.727	7.639	3.053	-43.835	-42.314	15.413
700	11.719	14.509	8.496	4.209	-43.790	-42.064	13.133
800	11.927	16.087	9.348	5.392	-43.776	-41.818	11.424
900	12.087	17.502	10.177	6.592	-43.799	-41.573	10.095
1000	12.232	18.783	10.974	7.808	-43.853	-41.324	9.031
1100	12.379	19.955	11.738	9.039	-43.934	-41.067	8.159
1200	12.535	21.039	12.469	10.284	-44.977	-40.763	7.424
1300	12.702	22.049	13.167	11.546	-44.978	-40.413	6.794
1400	12.881	22.997	13.836	12.825	-44.984	-40.061	6.254
1500	13.071	23.892	14.477	14.123	-44.995	-39.709	5.786
1600	13.272	24.742	15.092	15.440	-45.011	-39.356	5.376
1700	13.481	25.553	15.683	16.777	-45.031	-39.003	5.014
1800	13.699	26.329	16.253	18.136	-45.056	-38.648	4.693
1900	13.923	27.076	16.804	19.517	-45.084	-38.291	4.404
2000	14.154	27.796	17.335	20.921	-49.563	-37.779	4.128
2100	14.390	28.492	17.850	22.348	-49.573	-37.187	3.870
2200	14.631	29.167	18.349	23.799	-49.563	-36.600	3.636
2300	14.876	29.823	18.834	25.275	-49.529	-36.010	3.422
2400	15.125	30.461	19.305	26.775	-49.474	-35.423	3.226
2500	15.377	31.084	19.764	28.300	-49.395	-34.840	3.046
2600	15.631	31.692	20.211	29.850	-49.294	-34.260	2.880
2700	15.889	32.287	20.647	31.426	-49.168	-33.685	2.727
2800	16.148	32.869	21.073	33.028	-49.017	-33.113	2.585
2900	16.410	33.440	21.490	34.656	-48.843	-32.546	2.453
3000	16.673	34.001	21.898	36.310	-48.644	-31.988	2.330
3100	16.938	34.552	22.297	37.991	-48.419	-31.435	2.216
3200	17.204	35.094	22.689	39.698	-48.170	-30.894	2.110
3300	17.472	35.628	23.073	41.431	-47.897	-30.359	2.011
3400	17.740	36.153	23.450	43.192	-47.597	-29.829	1.917
3500	18.010	36.671	23.820	44.979	-47.273	-29.315	1.830
3600	18.280	37.182	24.184	46.794	-148.548	-28.543	1.733
3700	18.552	37.687	24.542	48.636	-148.144	-25.215	1.489
3800	18.824	38.185	24.895	50.504	-147.728	-21.899	1.259
3900	19.097	38.678	25.242	52.400	-147.299	-18.590	1.042
4000	19.371	39.165	25.584	54.324	-146.856	-15.295	.836

Dec. 31, 1960; Dec. 31, 1964; June 30, 1968

TITANIUM CARBIDE (TiC) (CRYSTAL) GFW = 59.91115

$\Delta Hf^\circ_0 = -43.7 \pm 1$ kcal/mol

$S^\circ_{298.15} = 5.79 \pm 0.05$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -44.0 \pm 1$ kcal/mol

$Tm = 3290 \pm 15°K$

$\Delta Hm^\circ = [17]$ kcal/mol

Heat of Formation

The adopted $\Delta Hf^\circ_{298} = -44.0$ kcal/mol is derived from $\Delta Hr^\circ_{298} = -275.72$ kcal/mol for reaction (a) determined by Humphrey (1) who burned TiC(c) in an oxygen bomb calorimeter. The author reported that the combustion product TiO_x was >95 per cent rutile and <5 per cent anatase, the heat of formation is calculated assuming the above distribution. The uncertainty adopted is due mainly to the uncertainty in TiO_2(rutile).

Using atomic absorbtion spectroscopy Vidale (2) determined that the pressure ($\log P_{Ti} = -7.269$) of Ti(g) at 1666°K was equal to the pressure of TiC(c) at 2220°K. Using this data for reaction (b) we obtain a $\Delta Hf^\circ_{298} = -43.02$ kcal/mol. Lowell and Williams (3) measured the $\Delta Hf^\circ_{2028} = -43.3 \pm 4$ kcal/mol of TiC(c) directly using a high temperature calorimeter, which reduces to $\Delta Hf^\circ_{298} = -37.7 \pm 4$ kcal/mol.

Fujishiro and Gokcen (4) determined the equilibrium pressure of Ti(g) in reaction (d) in the temperature range 2383-2593°K. Third law analysis of the data yields a $\Delta Hf^\circ_{298} = -31.6$ kcal/mol. Brantley and Beckman (5) measured equilibrium pressures of CO for reaction (e) in the temperature range 1278 - 1428°K. Third law analysis of the data yields a $\Delta Hf^\circ_{298} = -61.9$ kcal/mol.

Heat Capacity and Entropy

Low temperature heat capacities (55 - 295°K) have been taken from Kelley (6). Naylor (7) measured heat contents from 360 to 1738°K and Levinson (8) from 1274 to 2799°K. High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 2799°K the heat capacity is graphically extrapolated. The entropy is based on $S^\circ_{50} - S^\circ_0 = 0.065$ eu.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	ΔHr°_{298} kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} kcal/mol
1	Calorimetry	(a) $TiC(c) + 2O_2(g) \rightarrow CO_2(g) + TiO_2(rutile)$	298	-275.72			-44.00
2	Equilibrium	(b) $TiC(c) \rightarrow Ti(g) + C(c)$			156.02		-43.02
3	Calorimetry	(c) $Ti(c) + C(c) \rightarrow TiC(c)$		-37.7±4			-37.7
4	Equilibrium	(d) $TiC(c) \rightarrow C(graph) + Ti(g)$	2383-2593	169.5±10.3	144.6	-10.0±4.1	-31.60
5	Equilibrium	(e) $TiO_2(rutile) + 3C(graph) \rightarrow TiC(c) + 2CO(g)$	1278-1428	48.07±1.83	111.07	48.7±1.36	-61.90

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Titanium Carbide (TiC)

(Liquid) GFW = 59.91115

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	8.080	11.329	11.329	.000	-25.892	-26.681	19.557
300	8.111	11.379	11.329	.015	-25.892	-26.686	19.440
400	9.724	13.946	11.668	.911	-25.860	-26.953	14.726
500	10.795	16.240	12.358	1.941	-25.795	-27.234	11.904
600	11.388	18.265	13.177	3.053	-25.727	-27.529	10.027
700	11.719	20.047	14.034	4.209	-25.682	-27.833	8.690
800	11.927	21.626	14.886	5.392	-25.668	-28.141	7.688
900	12.087	23.040	15.715	6.592	-25.691	-28.450	6.909
1000	12.232	24.321	16.512	7.808	-25.745	-28.754	6.284
1100	12.379	25.493	17.276	9.039	-25.826	-29.051	5.772
1200	12.535	26.577	18.007	10.284	-26.869	-29.301	5.336
1300	12.702	27.587	18.705	11.546	-26.870	-29.505	4.960
1400	12.881	28.535	19.374	12.825	-26.876	-29.706	4.637
1500	13.071	29.430	20.015	14.123	-26.887	-29.908	4.358
1600	13.272	30.280	20.630	15.440	-26.903	-30.109	4.113
1700	13.481	31.091	21.222	16.777	-26.923	-30.310	3.897
1800	13.699	31.867	21.792	18.136	-26.948	-30.509	3.704
1900	13.923	32.614	22.342	19.517	-26.976	-30.705	3.532
2000	14.154	33.334	22.873	20.921	-31.455	-30.747	3.360
2100	14.390	34.030	23.388	22.348	-31.465	-30.709	3.196
2200	15.000	34.705	23.887	23.799	-31.455	-30.676	3.047
2300	15.000	35.372	24.372	25.299	-31.397	-30.640	2.911
2400	15.000	36.010	24.844	26.799	-31.342	-30.608	2.787
2500	15.000	36.623	25.303	28.299	-31.288	-30.579	2.673
2600	15.000	37.211	25.750	29.799	-31.237	-30.553	2.568
2700	15.000	37.777	26.185	31.299	-31.187	-30.528	2.471
2800	15.000	38.323	26.609	32.799	-31.138	-30.504	2.381
2900	15.000	38.849	27.022	34.299	-31.092	-30.480	2.297
3000	15.000	39.358	27.424	35.799	-31.047	-30.460	2.219
3100	15.000	39.849	27.817	37.299	-31.003	-30.440	2.146
3200	15.000	40.326	28.201	38.799	-30.961	-30.425	2.078
3300	15.000	40.787	28.575	40.299	-30.921	-30.410	2.014
3400	15.000	41.235	28.941	41.799	-30.882	-30.392	1.954
3500	15.000	41.670	29.299	43.299	-30.845	-30.382	1.897
3600	15.000	42.092	29.648	44.799	-132.435	-30.106	1.828
3700	15.000	42.503	29.990	46.299	-132.373	-27.264	1.610
3800	15.000	42.903	30.325	47.799	-132.325	-24.425	1.405
3900	15.000	43.293	30.652	49.299	-132.292	-21.582	1.209
4000	15.000	43.673	30.973	50.799	-132.273	-18.744	1.024
4100	15.000	44.043	31.287	52.299	-132.269	-15.907	.848
4200	15.000	44.405	31.595	53.799	-132.279	-13.068	.680
4300	15.000	44.758	31.897	55.299	-132.303	-10.232	.520
4400	15.000	45.102	32.193	56.799	-132.339	-7.394	.367
4500	15.000	45.440	32.484	58.299	-132.388	-4.554	.221

Dec. 31, 1960; Dec. 31, 1964; June 30, 1968

TITANIUM CARBIDE (TiC) (LIQUID) GFW = 59.91115

$S^\circ_{298.15}$ = [11.329] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-25.892 ± 1] kcal/mol

Tm = 3290 ± 15°K

ΔHm° = [17] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K the heat capacity is obtained from that of the crystal, above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The adopted Tm is taken from the phase diagram of the system Ti-C, at the composition 50% Ti and 50% C, reported by E. Rudy and D. P. Harmon, Aerojet-General Corporation, BSPN No. 64-6899-735001, Contract AF-33(6115), April 1, 1965. Earlier reports by E. Friederich and L. Sittig, Z. Anorg. Chem. 144, 171(1925) and C. Agte and K. Moers, Z. Anorg. Chem. 198, 233 (1931), gave a Tm of 3430 ± 100°K and 3410 ± 90°K, respectively. ΔHm° is derived from an estimated ΔSm = 2.5 gibbs/g-atom, as suggested by O. Kubaschewski, E. Ll. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

Zirconium Carbide (ZrC)

(Crystal) Mol. Wt. = 103.231

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 1.401	- 46.832	- 46.832	INFINITE
100	3.055	1.394	14.394	- 1.300	- 46.957	- 46.738	102.142
200	6.861	4.773	8.728	- .791	- 47.049	- 46.470	50.777
298	9.058	7.964	7.964	.000	- 47.000	- 46.194	33.859
300	9.089	8.020	7.964	.017	- 46.998	- 46.188	33.646
400	10.419	10.833	8.339	.998	- 46.898	- 45.933	25.096
500	11.265	13.257	9.086	2.086	- 46.800	- 45.703	19.976
600	11.802	15.362	9.960	3.241	- 46.727	- 45.492	16.570
700	12.181	17.215	10.867	4.443	- 46.675	- 45.290	14.140
800	12.445	18.859	11.765	5.675	- 46.640	- 45.094	12.319
900	12.628	20.336	12.637	6.929	- 46.618	- 44.903	10.903
1000	12.760	21.673	13.475	8.198	- 46.609	- 44.713	9.772
1100	12.961	22.899	14.277	9.485	- 46.615	- 44.524	8.846
1200	13.045	24.031	15.043	10.785	- 47.589	- 44.285	8.065
1300	13.129	25.078	15.775	12.094	- 47.603	- 44.010	7.398
1400	13.213	26.054	16.475	13.411	- 47.624	- 43.732	6.827
1500	13.297	26.969	17.144	14.737	- 47.650	- 43.453	6.331
1600	13.381	27.829	17.785	16.071	- 47.681	- 43.171	5.897
1700	13.465	28.643	18.400	17.413	- 47.716	- 42.890	5.514
1800	13.549	29.415	18.991	18.764	- 47.753	- 42.604	5.173
1900	13.633	30.150	19.559	20.123	- 47.792	- 42.317	4.867
2000	13.717	30.851	20.106	21.490	- 47.834	- 42.028	4.592
2100	13.801	31.523	20.634	22.866	- 47.875	- 41.737	4.343
2200	13.885	32.167	21.144	24.250	- 52.822	- 41.280	4.101
2300	13.969	32.786	21.637	25.643	- 52.871	- 40.752	3.872
2400	14.053	33.382	22.114	27.044	- 52.915	- 40.224	3.663
2500	14.137	33.957	22.576	28.454	- 52.951	- 39.694	3.470
2600	14.221	34.514	23.024	29.872	- 52.982	- 39.166	3.292
2700	14.305	35.052	23.460	31.298	- 53.006	- 38.634	3.127
2800	14.389	35.574	23.883	32.733	- 53.022	- 38.101	2.974
2900	14.473	36.080	24.295	34.176	- 53.033	- 37.565	2.831
3000	14.557	36.572	24.696	35.627	- 53.037	- 37.032	2.698
3100	14.641	37.051	25.087	37.087	- 53.033	- 36.501	2.573
3200	14.725	37.517	25.468	38.555	- 53.023	- 35.967	2.456
3300	14.809	37.971	25.840	40.032	- 53.006	- 35.433	2.347
3400	14.893	38.415	26.204	41.517	- 52.982	- 34.901	2.243
3500	14.977	38.848	26.559	43.011	- 52.951	- 34.373	2.146
3600	15.061	39.271	26.906	44.513	- 52.913	- 33.844	2.055
3700	15.145	39.684	27.246	46.023	- 52.869	- 33.311	1.967
3800	15.229	40.089	27.579	47.542	- 52.817	- 32.780	1.885
3900	15.313	40.486	27.904	49.069	- 52.759	- 32.253	1.807
4000	15.397	40.875	28.224	50.604	- 52.694	- 31.730	1.734
4100	15.481	41.256	28.537	52.148	- 52.622	- 31.208	1.663
4200	15.565	41.630	28.844	53.700	- 52.544	- 30.683	1.597
4300	15.649	41.997	29.146	55.261	- 52.459	- 30.163	1.533
4400	15.733	42.358	29.442	56.830	- 52.367	- 29.650	1.473
4500	15.817	42.713	29.733	58.408	- 52.268	- 29.138	1.415
4600	15.901	43.061	30.019	59.994	- 52.163	- 28.621	1.360
4700	15.985	43.404	30.300	61.588	- 52.051	- 28.109	1.307
4800	16.069	43.741	30.577	63.191	- 188.366	- 26.074	1.187
4900	16.153	44.074	30.849	64.802	- 188.296	- 22.701	1.012
5000	16.237	44.401	31.117	66.421	- 188.225	- 19.320	.844

Mar. 31, 1962; June 30, 1964; Dec. 31, 1964

ZIRCONIUM CARBIDE (ZrC) (CRYSTAL) MOL. WT. = 103.231

$\Delta H^\circ_{f\ 0}$ = -46.8 kcal. mole^{-1}

$S^\circ_{298.15}$ = 7.964 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -47.0 ± 3 kcal. mole^{-1}

T_m = 3805 ± 125°K

ΔH°_m = [19] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ = -47.16 ± 1.5 kcal mole^{-1} was calculated from the standard free energy of formation of -38.9 ± 1.5 kcal. mole^{-1} at 2675°K. reported by B. D. Pollock, J. Phys, Chem. 65, 731 (1961). Using spectrophotometric data reported by G. L. Vidale, Missle and Space Vehicle Department, General Electric R61SD147, August, 1961, we calculated $\Delta H_{f\ 298.15}$ = -46.9 ± 1 kcal. mole^{-1}. These values were averaged with $\Delta H_{f\ 298.15}$ = 47.0 ± 0.6 kcal. mole^{-1} reported by A. D. Mah, U. S. Bureau of Mines RI6518 (1964). The equilibria data reported by C. H. Prescott Jr., J. Am. Chem. Soc. 48, 2534 (1926) and V. S. Kutsev, B. F. Ormont, and V. A. Epel'baum, Doklady Akad, Nauk SSSR 104, 567 (1955) were considered but not used.

Heat Capacity and Entropy.

Heat content data over the range 470.8° to 1,174.4°K. were taken from a preliminary report by R. Mezaki, T. F. Jambois, A. K. Gangopadhyay, and J. L. Margrave, Univ. of Wisconsin, Madison, Wisconsin, "Thermodynamic Properties of Inorganic Substances VIII. The High Temperature Heat Contents of Zirconium Carbide and Tantalum Carbide". These data were smoothed by means of the Shomate plot into low temperature data reported by E. F. Westrum Jr. and G. Feick, J. Chem. Eng. Data, 8, 176 (1963). High temperature data reported by D. S. Neel, C. D. Pears, S. Oglesby Jr., Southern Reasearch Institute, Birmingham, Alabama, Technical Documentary Report No. WADD 60-924, p. 134, February 1962, and R. A. McDonald, F. L. Oetting, and H. Prophet, CPIA Publication No. 44(u), P. 213, February 1964 were then used to obtain the heat capacity above 1174°K.

Melting Data.

Melting points were measured by C. Agte and H. Alterthum, Z. tech. Physik 11, 182 (1930) and E. Friederich and L. Sittig, Z. Anorg. Chem., 144, 169 (1925). The value of 3805 ± 125°K. by Agte and Alterthum was chosen. Friederich and Sittig obtained a measurement of 3300°K. but estimated 3500°K. because of the clouding formation of ZrO_2. Wayne L. Worrell, J. Phys. Chem., 68, 954(1964) quoted a value of 3480°C taken from E. K. Storms, Los Alamos Scientific Lab Report LAMS-2674, (1962). The heat of melting is derived from an estimated ΔS_m = 2.5 cal. deg.$^{-1}$ gm. atom^{-1}.

Zirconium Carbide (ZrC)

(Liquid) Mol. Wt. = 103.231

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	9.058	12.815	12.815	.000	- 28.386	- 29.026	21.275
300	9.089	12.871	12.815	.017	- 28.384	- 29.030	21.147
400	10.419	15.684	13.190	.998	- 28.284	- 29.260	15.986
500	11.265	18.108	13.937	2.086	- 28.186	- 29.515	12.900
600	11.802	20.213	14.811	3.241	- 28.113	- 29.788	10.850
700	12.181	22.066	15.718	4.443	- 28.061	- 30.072	9.388
800	12.445	23.710	16.616	5.675	- 28.026	- 30.361	8.294
900	12.628	25.187	17.488	6.929	- 28.004	- 30.655	7.444
1000	12.760	26.524	18.326	8.198	- 27.995	- 30.950	6.764
1100	12.961	27.750	19.128	9.485	- 28.001	- 31.246	6.208
1200	13.045	28.882	19.894	10.785	- 28.975	- 31.492	5.735
1300	13.129	29.929	20.626	12.094	- 28.989	- 31.702	5.329
1400	13.213	30.905	21.326	13.411	- 29.010	- 31.909	4.981
1500	13.297	31.820	21.995	14.737	- 29.036	- 32.116	4.679
1600	13.381	32.680	22.636	16.071	- 29.067	- 32.319	4.414
1700	13.465	33.494	23.251	17.413	- 29.102	- 32.523	4.181
1800	13.549	34.266	23.842	18.764	- 29.139	- 32.721	3.973
1900	13.633	35.001	24.410	20.123	- 29.178	- 32.919	3.786
2000	13.717	35.702	24.957	21.490	- 29.220	- 33.116	3.619
2100	13.801	36.374	25.485	22.866	- 29.261	- 33.310	3.466
2200	13.885	37.018	25.995	24.250	- 34.208	- 33.339	3.312
2300	13.969	37.637	26.488	25.643	- 34.257	- 33.296	3.164
2400	14.053	38.233	26.965	27.044	- 34.301	- 33.252	3.028
2500	15.000	38.808	27.427	28.454	- 34.337	- 33.207	2.903
2600	15.000	39.397	27.876	29.954	- 34.286	- 33.166	2.788
2700	15.000	39.963	28.313	31.454	- 34.236	- 33.124	2.681
2800	15.000	40.508	28.739	32.954	- 34.187	- 33.081	2.582
2900	15.000	41.035	29.154	34.454	- 34.141	- 33.042	2.490
3000	15.000	41.543	29.559	35.954	- 34.096	- 33.004	2.404
3100	15.000	42.035	29.953	37.454	- 34.052	- 32.970	2.324
3200	15.000	42.511	30.338	38.954	- 34.010	- 32.935	2.249
3300	15.000	42.973	30.714	40.454	- 33.970	- 32.904	2.179
3400	15.000	43.421	31.081	41.954	- 33.931	- 32.870	2.113
3500	15.000	43.856	31.440	43.454	- 33.894	- 32.844	2.051
3600	15.000	44.278	31.791	44.954	- 33.858	- 32.814	1.992
3700	15.000	44.689	32.134	46.454	- 33.824	- 32.785	1.936
3800	15.000	45.089	32.470	47.954	- 33.791	- 32.754	1.884
3900	15.000	45.479	32.798	49.454	- 33.760	- 32.727	1.834
4000	15.000	45.859	33.120	50.954	- 33.730	- 32.702	1.787
4100	15.000	46.229	33.435	52.454	- 33.702	- 32.677	1.742
4200	15.000	46.590	33.744	53.954	- 33.676	- 32.647	1.699
4300	15.000	46.943	34.047	55.454	- 33.652	- 32.625	1.658
4400	15.000	47.288	34.344	56.954	- 33.629	- 32.604	1.619
4500	15.000	47.625	34.636	58.454	- 33.608	- 32.582	1.582
4600	15.000	47.955	34.922	59.954	- 33.589	- 32.559	1.547
4700	15.000	48.278	35.202	61.454	- 33.571	- 32.537	1.513
4800	15.000	48.593	35.478	62.954	- 169.989	- 30.986	1.411
4900	15.000	48.903	35.749	64.454	- 170.030	- 28.097	1.253
5000	15.000	49.206	36.015	65.954	- 170.078	- 25.198	1.101
5100	15.000	49.503	36.276	67.454	- 170.133	- 22.305	.956
5200	15.000	49.794	36.534	68.954	- 170.194	- 19.399	.815
5300	15.000	50.080	36.787	70.454	- 170.262	- 16.504	.681
5400	15.000	50.360	37.035	71.954	- 170.335	- 13.595	.550
5500	15.000	50.635	37.280	73.454	- 170.414	- 10.694	.425
5600	15.000	50.906	37.521	74.954	- 170.498	- 7.790	.304
5700	15.000	51.171	37.758	76.454	- 170.587	- 4.888	.187
5800	15.000	51.432	37.992	77.954	- 170.682	- 1.978	.075
5900	15.000	51.688	38.222	79.454	- 170.780	.939	- .035
6000	15.000	51.941	38.448	80.954	- 170.882	3.838	- .140

Mar. 31, 1962; June 30, 1964; Dec. 31, 1964

CZr

ZIRCONIUM CARBIDE (ZrC) (LIQUID) MOL. WT. = 103.231

$S^\circ_{298.15}$ = [12.815] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-28.39] kcal. mole^{-1}

T_m = 3805 ± 125°K.

ΔH°_m = [19] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ (l) was obtained from $\Delta H^\circ_{f\ 298.15}$(c) by adding ΔH°_m and the difference between $\Delta H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p(l) at and below 2500°K. were assumed to be equal to those of ZrC(c). Above 2500°K. the heat capacity was estimated to be constant. $S^\circ_{298.15}$(l) is calculated based on $S^\circ_{298.15}$(c) and an estimated ΔS°_m = 2.5 cal. deg.$^{-1}$ g. atom^{-1}.

Melting Data.

See ZrC(c) table for details.

CZr

Carbon, Diatomic (C_2)

(Ideal Gas) GFW = 24.0223

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	,000	.000	INFINITE	- 2,528	198,200	198,200	INFINITE
100	7,114	37.918	56,242	- 1,832	198,868	195,118	- 426,429
200	9,669	43,548	48,571	- 1,005	199,539	191,118	- 208,844
298	10,312	47,627	47,627	,000	200,224	186,835	- 136,953
300	10,301	47,690	47,627	,019	200,235	186,751	- 136,048
400	9,476	50,544	48,022	1,009	200,733	182,175	- 99,536
500	8,877	52,587	48,740	1,924	201,010	177,500	- 77,585
600	8,604	54,178	49,519	2,795	201,125	172,784	- 62,936
700	8,514	55,496	50,281	3,650	201,130	168,060	- 52,471
800	8,509	56,632	51,005	4,501	201,063	163,340	- 44,622
900	8,543	57,636	51,687	5,353	200,941	158,629	- 38,520
1000	8,595	58,538	52,328	6,210	200,786	153,936	- 33,643
1100	8,655	59,360	52,931	7,073	200,603	149,259	- 29,655
1200	8,719	60,116	53,498	7,941	200,399	144,602	- 26,336
1300	8,785	60,817	54,035	8,817	200,177	139,960	- 23,529
1400	8,852	61,470	54,543	9,698	199,946	135,339	- 21,127
1500	8,920	62,083	55,025	10,587	199,707	130,732	- 19,048
1600	8,989	62,661	55,485	11,482	199,462	126,139	- 17,230
1700	9,057	63,208	55,923	12,385	199,217	121,564	- 15,628
1800	9,125	63,728	56,342	13,294	198,968	117,004	- 14,206
1900	9,191	64,223	56,744	14,210	198,720	112,458	- 12,936
2000	9,256	64,696	57,130	15,132	198,472	107,924	- 11,793
2100	9,320	65,149	57,501	16,061	198,227	103,405	- 10,762
2200	9,381	65,584	57,859	16,996	197,980	98,892	- 9,824
2300	9,441	66,002	58,204	17,937	197,737	94,397	- 8,970
2400	9,498	66,405	58,537	18,884	197,494	89,908	- 8,187
2500	9,554	66,794	58,860	19,837	197,255	85,429	- 7,468
2600	9,607	67,170	59,172	20,795	197,015	80,961	- 6,805
2700	9,659	67,534	59,475	21,758	196,778	76,500	- 6,192
2800	9,709	67,886	59,769	22,726	196,544	72,052	- 5,624
2900	9,758	68,227	60,055	23,700	196,310	67,610	- 5,095
3000	9,805	68,559	60,333	24,678	196,078	63,175	- 4,602
3100	9,852	68,881	60,604	25,661	195,849	58,751	- 4,142
3200	9,897	69,195	60,867	26,648	195,620	54,332	- 3,711
3300	9,941	69,500	61,124	27,640	195,392	49,915	- 3,306
3400	9,985	69,797	61,375	28,636	195,166	45,514	- 2,926
3500	10,029	70,087	61,620	29,637	194,941	41,111	- 2,567
3600	10,071	70,371	61,859	30,642	194,718	36,719	- 2,229
3700	10,114	70,647	62,093	31,651	194,495	32,335	- 1,910
3800	10,157	70,917	62,321	32,665	194,275	27,959	- 1,608
3900	10,199	71,182	62,545	33,683	194,055	23,587	- 1,322
4000	10,242	71,441	62,764	34,705	193,837	19,219	- 1,050
4100	10,284	71,694	62,979	35,731	193,619	14,851	- ,792
4200	10,327	71,942	63,189	36,762	193,402	10,499	- ,546
4300	10,370	72,186	63,396	37,797	193,185	6,144	- ,312
4400	10,413	72,425	63,598	38,836	192,970	1,796	- ,089
4500	10,456	72,659	63,797	39,879	192,755	- 2,550	,124
4600	10,500	72,889	63,992	40,927	192,541	- 6,885	,327
4700	10,544	73,116	64,184	41,979	192,329	- 11,217	,522
4800	10,588	73,338	64,372	43,036	192,116	- 15,543	,708
4900	10,632	73,557	64,558	44,097	191,905	- 19,868	,886
5000	10,676	73,772	64,740	45,162	191,694	- 24,187	1,057
5100	10,721	73,984	64,919	46,232	191,482	- 28,512	1,222
5200	10,766	74,193	65,095	47,306	191,272	- 32,820	1,379
5300	10,812	74,398	65,269	48,385	191,063	- 37,124	1,531
5400	10,857	74,601	65,440	49,469	190,855	- 41,424	1,677
5500	10,903	74,800	65,608	50,557	190,645	- 45,725	1,817
5600	10,949	74,997	65,774	51,649	190,437	- 50,022	1,952
5700	10,995	75,191	65,938	52,746	190,228	- 54,321	2,083
5800	11,041	75,383	66,099	53,848	190,020	- 58,608	2,208
5900	11,088	75,572	66,258	54,955	189,813	- 62,885	2,329
6000	11,134	75,759	66,415	56,066	189,606	- 67,175	2,447

Sept. 30, 1961; Dec. 31, 1969

Symmetry number = 2

$S^\circ_{298.15}$ = 47.627 ± 0.01 gibbs/mol

ΔHf°_0 = 198.2 ± 0.9 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 200.2 ± 0.9 kcal/mol

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$x^1\Sigma_g^+$	0	1	1.2425	1.81984	0.01765	1854.71	13.34
$X'^3\Pi_u$	610	6	1.3119	1.63246	0.01661	1641.35	11.67
$A'^3\Sigma_g^-$	6243.5	3	1.3693	1.49852	0.01634	1470.45	11.19
$b^1\Pi_u$	8268.33	2	1.3184	1.61634	0.01686	1608.35	12.078
$A''^3\Sigma_u^+$	13365	3	1.23	1.87	[0.018]	1961.6	13.65
$^1\Delta_g$	[15000]	2	[1.39]	[1.454]	[0.015]	[1510]	[11.1]
$^1\Sigma_g^+$	[18570]	1	[1.38]	[1.475]	[0.013]	[1510]	[10.0]
$A^3\Pi_g$	19916	6	1.266	1.7527	0.01608	1788.2	16.44
$^5\Pi_g$	[22260]	10	[1.46]	[1.324]	[0.012]	[1400]	[9.9]
$^5\Sigma_g^+$	[30320]	5	[1.35]	[1.557]	[0.015]	[1550]	[11.7]
$c^1\Pi_g$	34262	2	1.2552	1.7334	0.018	1809.1	15.81
$^3\Delta_u$	[34530]	6	[1.51]	[1.23]	[0.013]	[1160]	[9.2]
$^1\Sigma_u^-$	[34760]	1	[1.90]	[0.778]	[0.005]	[1025]	[5.8]
$^3\Phi_g$	[38020]	6	[1.53]	[1.20]	[0.011]	[1290]	[9.0]
$B^3\Pi_g$	40690	6	1.535	1.1922	0.0242	1106.56	39.26
$^3\Delta_u$	[40780]	6	[1.51]	[1.23]	[0.011]	[1380]	[9.2]
$^3\Pi_g$	[42370]	6	[1.49]	[1.265]	[0.012]	[1340]	[9.5]
$^1\Phi_g$	[42860]	2	[1.51]	[1.232]	[0.011]	[1360]	[9.2]
$d^1\Sigma_u^+$	43240	1	1.2378	1.8334	0.0204	1829.57	13.97
$^3\Sigma_u^+$	[43360]	3	[1.44]	[1.355]	[0.011]	[1660]	[10.2]

Heat of Formation

Messerle and Krauss (1) have reported the dissociation energy as 49300 ± 300 cm^{-1} from the variation of the rotational structure cut-off with vibrational level in the $c^1\Pi_g$ state. This state dissociates into $C(^3P) + C^3(P)$, due to an avoided crossing (2), these dissociation products are those of the ground state. The uncertainty in the determination is generous and thus we adopt D°_0 = 140.95 ± 0.9 kcal or $\Delta Hf^\circ_0(C_2, g)$ = 198.2 ± 0.9 kcal/mol, using $\Delta Hf^\circ_0(C, g)$ = 169.576 kcal/mol (3).

Brewer et al. (4) have reviewed several other earlier determinations which confirm ΔHf°_0 = 195 ± 5 kcal/mol. The extensive mass spectrometric data of Drowart et al. (5) yield a 3rd law ΔHf°_0 = 199.2 ± 1.4 kcal/mol in excellent agreement with the adopted value.

Heat Capacity and Entropy

The observed molecular constants and electronic levels were taken from Ballik and Ramsay (2). The estimated parameters are from the correlation calculations of Fougere and Nesbet (6) and Clementi (7), the electronic levels are T_o values. Not all predicted states were included since the contribution of levels above 40000 cm^{-1} is negligible. The functions were calculated from the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2\epsilon_i/T)$, the values for Q^i_r and Q^i_v were calculated with first order anharmonic corrections. The functions are similar to those reported by Altman (8) and Clementi (7) but include several additional states.

References

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4. L. Brewer, W. T. Hicks, and O. H. Krikorian, J. Chem. Phys. 36, 182 (1962).
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6. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. 44, 285 (1966).
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Dimeric Carbon Uninegative Ion (C_2^-)

(Ideal Gas) GFW = 24.02285

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.989	46.961	46.961	.000	106.000	94.296	-69.121
300	6.990	47.004	46.961	.013	105.996	94.224	-68.642
400	7.105	49.029	47.236	.717	105.711	90.339	-49.359
500	7.292	50.633	47.761	1.436	105.295	86.541	-37.827
600	7.506	51.982	48.355	2.176	104.782	82.836	-30.173
700	7.713	53.154	48.958	2.937	104.197	79.226	-24.735
800	7.897	54.197	49.549	3.718	103.563	75.702	-20.681
900	8.055	55.136	50.119	4.516	102.890	72.256	-17.546
1000	8.189	55.992	50.664	5.328	102.193	68.890	-15.056
1100	8.303	56.778	51.184	6.153	101.475	65.593	-13.032
1200	8.402	57.505	51.681	6.988	100.741	62.364	-11.358
1300	8.490	58.181	52.155	7.833	99.992	59.197	-9.952
1400	8.571	58.813	52.609	8.686	99.236	56.090	-8.756
1500	8.648	59.407	53.042	9.547	98.472	53.034	-7.727
1600	8.724	59.968	53.458	10.416	97.704	50.028	-6.833
1700	8.801	60.499	53.856	11.292	96.935	47.071	-6.051
1800	8.879	61.004	54.240	12.176	96.165	44.161	-5.362
1900	8.960	61.486	54.608	13.068	95.396	41.293	-4.750
2000	9.044	61.948	54.964	13.968	94.629	38.465	-4.203
2100	9.130	62.391	55.307	14.877	93.867	35.680	-3.713
2200	9.218	62.818	55.639	15.794	93.105	32.922	-3.270
2300	9.308	63.230	55.960	16.720	92.351	30.208	-2.870
2400	9.398	63.628	56.271	17.656	91.600	27.520	-2.506
2500	9.489	64.013	56.573	18.600	90.855	24.864	-2.174
2600	9.580	64.387	56.867	19.553	90.113	22.240	-1.869
2700	9.670	64.750	57.152	20.516	89.379	19.640	-1.590
2800	9.758	65.104	57.430	21.487	88.651	17.073	-1.333
2900	9.844	65.448	57.700	22.468	87.928	14.530	-1.095
3000	9.928	65.783	57.964	23.456	87.209	12.012	-.875
3100	10.009	66.110	58.222	24.453	86.497	9.519	-.671
3200	10.086	66.429	58.473	25.458	85.789	7.044	-.481
3300	10.160	66.740	58.719	26.470	85.084	4.590	-.304
3400	10.230	67.045	58.959	27.490	84.386	2.165	-.139
3500	10.296	67.342	59.195	28.516	83.689	-.248	.015
3600	10.359	67.633	59.425	29.549	82.997	-2.636	.160
3700	10.417	67.918	59.651	30.588	82.307	-5.001	.295
3800	10.472	68.196	59.872	31.632	81.620	-7.350	.423
3900	10.523	68.469	60.089	32.682	80.935	-9.681	.542
4000	10.569	68.736	60.302	33.737	80.254	-11.994	.655
4100	10.612	68.997	60.511	34.796	79.572	-14.295	.762
4200	10.652	69.254	60.716	35.859	78.890	-16.574	.862
4300	10.688	69.505	60.917	36.926	78.208	-18.841	.958
4400	10.720	69.751	61.115	37.996	77.527	-21.093	1.048
4500	10.749	69.992	61.310	39.070	76.847	-23.327	1.133
4600	10.775	70.228	61.501	40.146	76.164	-25.544	1.214
4700	10.799	70.460	61.689	41.225	75.482	-27.746	1.290
4800	10.819	70.688	61.874	42.306	74.796	-29.931	1.363
4900	10.837	70.911	62.056	43.388	74.109	-32.109	1.432
5000	10.852	71.130	62.236	44.473	73.422	-34.270	1.498
5100	10.865	71.345	62.412	45.559	72.729	-36.423	1.561
5200	10.876	71.557	62.586	46.646	72.035	-38.556	1.620
5300	10.885	71.764	62.757	47.734	71.338	-40.671	1.677
5400	10.892	71.967	62.926	48.823	70.638	-42.774	1.731
5500	10.898	72.167	63.092	49.912	69.932	-44.870	1.783
5600	10.901	72.364	63.256	51.002	69.226	-46.949	1.832
5700	10.903	72.557	63.418	52.093	68.514	-49.029	1.880
5800	10.904	72.746	63.577	53.183	67.797	-51.081	1.925
5900	10.904	72.933	63.734	54.273	67.076	-53.116	1.968
6000	10.902	73.116	63.889	55.364	66.352	-55.159	2.009

June 30, 1966; Dec. 31, 1969

DIMERIC CARBON UNINEGATIVE ION (C_2^-) (IDEAL GAS) GFW = 24.02285

Ground State Configuration $[^2\Sigma]$

$\Delta Hf^\circ_0 = 106 \pm 20$ kcal/mol

$S^\circ_{298.15} = 46.96 \pm 0.05$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 106 \pm 20$ kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	2
[9000]	[4]
18484	[2]

$\omega_e = 1781.04\ cm^{-1}$ $\omega_e x_e = 11.585\ cm^{-1}$ $\sigma = 2$

$B_e = 1.74685\ cm^{-1}$ $\alpha_e = 0.0167\ cm^{-1}$ $r_e = 1.2682$ Å

Heat of Formation

The electron affinity of C_2 has been obtained by Honig (1) as 4 ± 0.8 ev from the difference in heats of sublimation of neutral C_2 and C_2^- and the work function of graphite. Thus, we have the reaction

$$C_2(g) + e^- \rightarrow C_2^-(g) \qquad \Delta H_o = -92.2 \pm 20 \text{ kcal.}$$

Using $\Delta Hf^\circ_0(C_2, g) = 198.2$ kcal/mol (2), we obtain $\Delta Hf^\circ_0(C_2^-, g) = 106 \pm 20$ kcal/mol, which is adopted.

A value for the heat of formation may be obtained from a linear Birge-Sponer extrapolation of the ground state vibrational levels, which gives 195.8 kcal for the reaction

$$C_2^-(g) \rightarrow C(g) + C^-(g).$$

With auxiliary data (2) this yields $\Delta Hf^\circ_0(C_2^-, g) = 114.5$ kcal/mol, in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants and electronic levels are from Herzberg and Lagerqvist (3). The values are not definitely ascribed to C_2^- by Herzberg and Lagerqvist, but there is a good deal of evidence to support this assignment. Recently Milligan and Jacox (4) have shown that matrix isolated bands previously attributed to $C_2(g)$ are enhanced in the presence of a photoelectron source. The matrix spectra correspond to the gas system reported by Herzberg and Lagerqvist (3) and leave little doubt that the species is C_2^-.

The estimated electronic level is assumed to be a $^2\Pi$ state and is obtained from the isoelectronic CN(g) (2).

References

1. R. E. Honig, J. Chem. Phys. 22, 126 (1954).
2. JANAF Thermochemical Tables, Dec. 31, 1969.
3. G. Herzberg and A. Lagerqvist, Can. J. Phys. 42, 2363 (1968).
4. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 51, 1952 (1969).

Beryllium Carbide (BeC_2)

(Ideal Gas) Mol. Wt. = 33.035

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.436	133.535	133.535	INFINITE
100	7.292	42.924	60.288	-1.736	134.198	129.960	-284.014
200	8.894	48.481	53.107	-.925	134.715	125.509	-137.143
298	9.867	52.232	52.232	.000	135.000	120.917	-88.630
300	9.881	52.293	52.232	.018	135.003	120.830	-88.020
400	10.553	55.231	52.628	1.041	135.095	116.087	-63.424
500	11.150	57.651	53.398	2.127	135.039	111.339	-48.664
600	11.696	59.733	54.284	3.269	134.883	106.611	-38.831
700	12.174	61.573	55.106	4.463	134.655	101.917	-31.819
800	12.580	63.226	56.098	5.702	134.381	97.260	-26.569
900	12.918	64.727	56.975	6.977	134.065	92.636	-22.494
1000	13.197	66.103	57.820	8.283	133.719	88.051	-19.243
1100	13.427	67.372	58.631	9.615	133.341	83.502	-16.589
1200	13.618	68.549	59.409	10.968	132.933	78.990	-14.385
1300	13.776	69.646	60.155	12.338	132.493	74.512	-12.526
1400	13.909	70.672	60.870	13.722	132.029	70.071	-10.938
1500	14.021	71.635	61.556	15.119	131.538	65.662	-9.567
1600	14.115	72.543	62.215	16.526	128.266	61.363	-8.381
1700	14.196	73.401	62.848	17.941	127.840	57.195	-7.353
1800	14.266	74.215	63.457	19.364	127.407	53.052	-6.441
1900	14.326	74.988	64.043	20.794	126.970	48.934	-5.628
2000	14.378	75.724	64.609	22.229	126.527	44.838	-4.899
2100	14.423	76.426	65.155	23.669	126.080	40.767	-4.242
2200	14.463	77.098	65.683	25.114	125.625	36.711	-3.647
2300	14.499	77.742	66.193	26.562	125.166	32.685	-3.106
2400	14.530	78.360	66.688	28.013	124.699	28.673	-2.611
2500	14.558	78.954	67.166	29.468	124.228	24.679	-2.157
2600	14.583	79.525	67.631	30.925	123.749	20.708	-1.741
2700	14.605	80.076	68.082	32.384	123.266	16.752	-1.356
2800	14.625	80.607	68.520	33.846	51.749	13.926	-1.087
2900	14.644	81.121	68.945	35.309	51.504	12.581	-.948
3000	14.660	81.618	69.359	36.774	51.257	11.242	-.819
3100	14.675	82.099	69.763	38.241	51.009	9.911	-.699
3200	14.689	82.565	70.155	39.709	50.757	8.592	-.587
3300	14.701	83.017	70.538	41.179	50.500	7.274	-.482
3400	14.713	83.456	70.912	42.650	50.239	5.971	-.384
3500	14.723	83.883	71.276	44.121	49.972	4.667	-.291
3600	14.733	84.297	71.632	45.594	49.701	3.379	-.205
3700	14.742	84.701	71.980	47.068	49.423	2.095	-.124
3800	14.750	85.094	72.320	48.543	49.139	.824	-.047
3900	14.758	85.478	72.653	50.018	48.847	-.440	.025
4000	14.765	85.851	72.978	51.494	48.548	-1.702	.093
4100	14.771	86.216	73.296	52.971	48.240	-2.961	.158
4200	14.778	86.572	73.608	54.448	47.922	-4.200	.219
4300	14.783	86.920	73.914	55.927	47.595	-5.437	.276
4400	14.789	87.260	74.213	57.405	47.257	-6.669	.331
4500	14.794	87.592	74.507	58.884	46.908	-7.894	.383
4600	14.798	87.917	74.795	60.364	46.547	-9.106	.433
4700	14.803	88.236	75.077	61.844	46.176	-10.312	.479
4800	14.807	88.547	75.355	63.324	45.789	-11.506	.524
4900	14.811	88.853	75.627	64.805	45.392	-12.696	.566
5000	14.814	89.152	75.895	66.287	44.982	-13.874	.606
5100	14.818	89.445	76.158	67.768	44.554	-15.057	.645
5200	14.821	89.733	76.416	69.250	44.115	-16.222	.682
5300	14.824	90.016	76.670	70.732	43.660	-17.372	.716
5400	14.827	90.293	76.920	72.215	43.192	-18.518	.749
5500	14.830	90.565	77.165	73.698	42.706	-19.658	.781
5600	14.833	90.832	77.407	75.181	42.207	-20.788	.811
5700	14.835	91.095	77.645	76.664	41.691	-21.913	.840
5800	14.837	91.353	77.879	78.148	41.160	-23.021	.867
5900	14.840	91.606	78.109	79.632	40.613	-24.118	.893
6000	14.842	91.856	78.336	81.116	40.051	-25.221	.919

Dec. 31, 1960; Sept. 30, 1962; June 30, 1963; Dec. 31, 1963

BERYLLIUM CARBIDE (BeC_2) (IDEAL GAS) MOL. WT. = 33.035

Point Group $[C_{\infty v}]$

$S^\circ_{298.15}$ = [52.2] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = [134] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [135] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[1580] (1)

[423] (1)

[1947] (1)

Bond Distances: Be-C = [1.407] Å C≡C = [1.2] Å

Bond Angle: Be-C≡C = [180°] σ = 1

Rotational Constant: B_0 = [0.4809] cm.$^{-1}$

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was estimated as a lower positive limit by National Bureau of Standards Report No. 6645, "Preliminary Report on the Thermodynamic Properties of Light-Element Compounds," January, 1960.

Heat Capacity and Entropy.

The vibrational frequencies, bond angle, configuration and moment of inertia, 5.82×10^{-39} g. cm.^{2}, were estimated by Chupka, Berkowitz, Giese, and Inghram, J. Phys. Chem. 62, 611 (1958). Bond distances were calculated assuming the C-C bond distance was the same as in acetylene.

Dichloroacetylene (C_2Cl_2)

(Ideal Gas) GFW = 94.9283

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.481	49.317	49.317	INFINITE
100	10.188	50.780	77.543	-2.676	49.398	48.877	-106.820
200	13.823	59.088	66.371	-1.457	49.735	48.237	-52.711
298	15.672	64.989	64.989	.000	50.100	47.422	-34.761
300	15.698	65.086	64.989	.029	50.106	47.405	-34.535
400	16.782	69.762	65.619	1.657	50.412	46.457	-25.383
500	17.507	73.590	66.842	3.374	50.638	45.441	-19.862
600	18.048	76.831	68.244	5.153	50.792	44.385	-16.167
700	18.478	79.647	69.676	6.980	50.891	43.310	-13.522
800	18.827	82.138	71.081	8.846	50.953	42.222	-11.535
900	19.115	84.373	72.436	10.743	50.986	41.127	-9.987
1000	19.352	86.399	73.732	12.667	51.004	40.030	-8.748
1100	19.549	88.253	74.969	14.612	51.006	38.931	-7.735
1200	19.713	89.962	76.149	16.576	50.998	37.835	-6.891
1300	19.850	91.545	77.273	18.554	50.976	36.738	-6.176
1400	19.966	93.020	78.345	20.545	50.951	35.647	-5.565
1500	20.064	94.401	79.370	22.546	50.918	34.555	-5.035
1600	20.148	95.699	80.351	24.557	50.881	33.462	-4.571
1700	20.220	96.923	81.290	26.576	50.843	32.376	-4.162
1800	20.282	98.080	82.191	28.601	50.799	31.290	-3.799
1900	20.335	99.178	83.056	30.632	50.754	30.211	-3.475
2000	20.382	100.223	83.889	32.668	50.705	29.130	-3.183
2100	20.423	101.218	84.690	34.708	50.656	28.054	-2.920
2200	20.460	102.169	85.463	36.752	50.600	26.975	-2.680
2300	20.492	103.079	86.210	38.800	50.545	25.907	-2.462
2400	20.520	103.952	86.931	40.850	50.484	24.836	-2.262
2500	20.546	104.790	87.629	42.904	50.422	23.767	-2.078
2600	20.568	105.596	88.304	44.959	50.354	22.703	-1.908
2700	20.589	106.373	88.959	47.017	50.284	21.638	-1.751
2800	20.607	107.122	89.594	49.077	50.211	20.581	-1.606
2900	20.624	107.845	90.211	51.139	50.132	19.524	-1.471
3000	20.639	108.545	90.811	53.202	50.049	18.468	-1.345
3100	20.653	109.222	91.394	55.266	49.962	17.419	-1.228
3200	20.665	109.878	91.961	57.332	49.870	16.370	-1.118
3300	20.677	110.514	92.514	59.399	49.772	15.321	-1.015
3400	20.687	111.131	93.053	61.468	49.672	14.284	-.918
3500	20.697	111.731	93.578	63.537	49.564	13.237	-.827
3600	20.706	112.314	94.090	65.607	49.453	12.203	-.741
3700	20.714	112.882	94.590	67.678	49.336	11.172	-.660
3800	20.722	113.434	95.079	69.750	49.216	10.143	-.583
3900	20.729	113.973	95.557	71.822	49.089	9.120	-.511
4000	20.736	114.497	96.024	73.896	48.959	8.097	-.442
4100	20.742	115.010	96.480	75.969	48.823	7.071	-.377
4200	20.747	115.509	96.928	78.044	48.682	6.059	-.315
4300	20.753	115.998	97.365	80.119	48.536	5.043	-.256
4400	20.758	116.475	97.794	82.194	48.386	4.035	-.200
4500	20.762	116.941	98.215	84.270	48.231	3.023	-.147
4600	20.767	117.398	98.627	86.347	48.073	2.023	-.096
4700	20.771	117.844	99.031	88.424	47.911	1.026	-.048
4800	20.774	118.282	99.427	90.501	47.742	.031	-.001
4900	20.778	118.710	99.817	92.579	47.571	-.960	.043
5000	20.781	119.130	100.199	94.657	47.396	-1.949	.085
5100	20.785	119.542	100.574	96.735	47.215	-2.941	.126
5200	20.788	119.945	100.943	98.814	47.032	-3.919	.165
5300	20.791	120.341	101.305	100.892	46.843	-4.896	.202
5400	20.793	120.730	101.661	102.972	46.652	-5.868	.237
5500	20.796	121.111	102.011	105.051	46.454	-6.837	.272
5600	20.798	121.486	102.356	107.131	46.255	-7.809	.305
5700	20.801	121.854	102.694	109.211	46.049	-8.781	.337
5800	20.803	122.216	103.028	111.291	45.840	-9.736	.367
5900	20.805	122.572	103.356	113.371	45.626	-10.687	.396
6000	20.807	122.921	103.679	115.452	45.409	-11.647	.424

Dec. 31, 1968

DICHLOROACETYLENE (C_2Cl_2) (IDEAL GAS) GFW = 94.9283

Point Group $D_{\infty h}$

ΔHf°_0 = [49.3 ± 10] kcal/mol

$S^\circ_{298.15}$ = [65 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [50.1 ± 10] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[410] (1)
[2200] (1)
[925] (1)
[380] (2)
[165] (2)

Bond Distances: C-C = 1.195Å C-Cl = 1.64Å

Bond Angle: Cl-C-C = 180°

σ = 2

Rotational Constant: $B_0 = 0.046368\ cm^{-1}$

Heat of Formation

The heat of formation of dichloroacetylene is calculated from the estimated $\Delta Hr^\circ_{298} = -53 \pm 10$ kcal/mol for ClC≡CCl(g) + Cl_2(g) → $Cl_2C{=}CCl_2$(g), using $\Delta Hf^\circ_{298}(C_2Cl_4, g) = -2.9$ kcal/mol (1). The value of ΔHr°_{298} is assumed to be the same as that for the reaction HC≡CH(g) + Cl_2(g) → CHCl=CHCl(g), using ΔHf°_{298}(CHCl=CHCl, g) = 1.2 kcal/mol (2).

Heat Capacity and Entropy

The linear molecular structure and bond distances were determined from electron diffraction studies by Hassel and Viervoll (3). The principal moment of inertia is 6.03668×10^{-38} g cm^2.

All five fundamental vibrational frequencies are calculated by the modified valence force method (4) from estimated force constants which are interpolated from those of C_2I_2 (5), CH≡CF (6), CH≡CCl (6), CH≡CBr (6), and C_2D_2 (4).

References

(1) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.

(2) This is an average value of 0.9 and 1.47 kcal/mol for cis- and trans- CHCl = CHCl(g), respectively, which are obtained from reference (1).

(3) O. Hassel and H. Viervoll, Acta Chem. Scand. 1, 149 (1947).

(4) G. Herzberg, "Infrared and Raman Spectra," pages 188-189, D. Van Nostrand Co., Inc., New York, 1950.

(5) The vibrational frequencies were observed by A. G. Meister and F. F. Cleveland, J. Chem. Phys. 17, 212 (1949).

(6) The vibrational frequencies were observed by G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961).

Tetrachloroethylene (C_2Cl_4)

(Ideal Gas) GFW = 165.8343

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.759	-2.837	-2.837	INFINITE
100	13.588	62.201	99.858	-3.766	-3.264	-.412	.900
200	19.423	73.612	84.041	-2.086	-3.192	2.436	-2.662
298	22.836	82.052	82.052	.000	-2.970	5.153	-3.777
300	22.887	82.194	82.053	.042	-2.966	5.203	-3.790
400	25.194	89.115	82.981	2.454	-2.706	7.887	-4.309
500	26.784	94.918	84.803	5.057	-2.447	10.506	-4.592
600	27.905	99.906	86.915	7.795	-2.203	13.073	-4.762
700	28.712	104.272	89.089	10.628	-1.976	15.601	-4.871
800	29.304	108.146	91.234	13.530	-1.764	18.097	-4.944
900	29.749	111.625	93.309	16.484	-1.564	20.566	-4.994
1000	30.089	114.777	95.301	19.476	-1.372	23.013	-5.030
1100	30.353	117.658	97.204	22.499	-1.189	25.442	-5.055
1200	30.562	120.308	99.021	25.545	-1.015	27.857	-5.073
1300	30.730	122.761	100.754	28.610	-.852	30.256	-5.086
1400	30.866	125.044	102.408	31.690	-.692	32.645	-5.096
1500	30.979	127.177	103.989	34.783	-.539	35.021	-5.103
1600	31.072	129.180	105.502	37.885	-.393	37.383	-5.106
1700	31.151	131.066	106.950	40.996	-.248	39.743	-5.109
1800	31.217	132.848	108.340	44.115	-.109	42.090	-5.110
1900	31.274	134.538	109.675	47.240	.028	44.434	-5.111
2000	31.323	136.143	110.959	50.369	.157	46.767	-5.111
2100	31.365	137.673	112.195	53.504	.288	49.094	-5.109
2200	31.402	139.133	113.386	56.642	.408	51.411	-5.107
2300	31.435	140.529	114.536	59.784	.528	53.734	-5.106
2400	31.463	141.868	115.647	62.929	.641	56.043	-5.103
2500	31.489	143.153	116.722	66.077	.749	58.346	-5.101
2600	31.511	144.388	117.762	69.227	.851	60.651	-5.098
2700	31.532	145.578	118.771	72.379	.947	62.944	-5.095
2800	31.550	146.725	119.749	75.533	1.037	65.244	-5.093
2900	31.566	147.832	120.698	78.689	1.119	67.535	-5.090
3000	31.581	148.903	121.620	81.846	1.194	69.819	-5.086
3100	31.594	149.938	122.517	85.005	1.263	72.110	-5.084
3200	31.606	150.942	123.390	88.165	1.323	74.392	-5.081
3300	31.617	151.914	124.240	91.326	1.374	76.674	-5.078
3400	31.628	152.858	125.068	94.488	1.420	78.961	-5.076
3500	31.637	153.775	125.875	97.652	1.456	81.231	-5.072
3600	31.645	154.667	126.662	100.816	1.486	83.512	-5.070
3700	31.653	155.534	127.431	103.981	1.507	85.793	-5.068
3800	31.661	156.378	128.182	107.146	1.522	88.071	-5.065
3900	31.668	157.201	128.915	110.313	1.529	90.351	-5.063
4000	31.674	158.002	129.632	113.480	1.528	92.632	-5.061
4100	31.680	158.785	130.334	116.648	1.522	94.899	-5.059
4200	31.685	159.548	131.020	119.816	1.506	97.182	-5.057
4300	31.691	160.294	131.693	122.985	1.485	99.456	-5.055
4400	31.696	161.022	132.351	126.154	1.458	101.743	-5.054
4500	31.700	161.735	132.996	129.324	1.424	104.010	-5.051
4600	31.705	162.431	133.628	132.494	1.386	106.298	-5.050
4700	31.709	163.113	134.248	135.665	1.343	108.583	-5.049
4800	31.714	163.781	134.857	138.836	1.292	110.862	-5.048
4900	31.718	164.435	135.454	142.008	1.238	113.149	-5.047
5000	31.722	165.076	136.040	145.180	1.180	115.430	-5.045
5100	31.726	165.704	136.615	148.352	1.116	117.712	-5.044
5200	31.729	166.320	137.181	151.525	1.049	120.004	-5.044
5300	31.733	166.924	137.736	154.698	.976	122.293	-5.043
5400	31.737	167.518	138.282	157.871	.899	124.581	-5.042
5500	31.741	168.100	138.819	161.045	.817	126.877	-5.042
5600	31.745	168.672	139.347	164.220	.734	129.164	-5.041
5700	31.749	169.234	139.866	167.394	.642	131.446	-5.040
5800	31.753	169.786	140.378	170.569	.549	133.752	-5.040
5900	31.757	170.329	140.881	173.745	.451	136.051	-5.040
6000	31.762	170.863	141.376	176.921	.349	138.343	-5.039

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TETRACHLOROETHYLENE (C_2Cl_4) (IDEAL GAS) GFW = 165.8343

Point Group D_{2h}

$\Delta Hf^\circ_0 = -2.84 \pm 0.7$ kcal/mol

$S^\circ_{298.15} = 82.052$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -2.97 \pm 0.7$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	63557	[1]
[37700]	[1]	70097	[1]
[50350]	[1]	72410	[1]
[59000]	[1]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1571 (1)	1000 (1)	918 (1)
447 (1)	347 (1)	176 (1)
235 (1)	324 (1)	777 (1)
110 (1)	512 (1)	288 (1)

Bond Distances: Cl - C = 1.724 Å C - C = 1.327 Å

Bond Angle: Cl - C - Cl = 113.3° $\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 3.43114 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The heat of combustion (ΔE_{293}) of $C_2Cl_4(\ell)$ has been determined by the "Quartz Wool" method by L. Smith, L. Bjellerup, S. Krook and H. Westermark, Acta Chem. Scand. 7, 65 (1953). The free chlorine produced from combustion was reduced to hydrogen chloride by a quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Based on the reported results, the enthalpy change at 298°K for the reaction $C_2Cl_4(\ell)+O_2(g)+2H_2O(\ell) = 2CO_2(g)+4HCl(600H_2O)$ is evaluated as -198.40 kcal/mol, using recent auxiliary data from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965 and V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965, and Cp for $C_2Cl_4(\ell)$ from V. Y. Kurbatov, J. Gen. Chem. USSR(Eng. Transl.) 18, 372 (1948). Employing $\Delta Hf^\circ_{298} = -94.054, -39.823$ and -68.315 kcal/mol for $CO_2(g)$, $HCl(600H_2O)$ and $H_2O(\ell)$, respectively, we calculate the heat of formation for $C_2Cl_4(\ell)$ as -12.367 kcal/mol. Incorporating this value with the value $\Delta Hv^\circ_{298} = 9.4$ kcal/mol obtained from E. Eftring, Ph.D. Thesis, University of Lund, 1938, we derive $\Delta Hf^\circ_{298} = -2.97 \pm 0.7$ kcal/mol for $C_2Cl_4(g)$.

Heat Capacity and Entropy

The molecular structure of $C_2Cl_4(g)$ was investigated by the sector-visual method of electron diffraction by C. H. Ramachandra and R. L. Livingston, Current Sci. 27, 330 (1958). The reported bond distances and angle are in agreement with those measured by I. L. Karle and J. Karle, J. Chem. Phys. 20, 63 (1952), using the sector-microphotometer method, and W. N. Lipscomb, Ph.D. Thesis, California Institute of Technology, 1946. The molecular structure has also been determined by L. O. Brockway, J. Y. Beach and L. Pauling, J. Am. Chem. Soc. 57, 2693 (1935), H. de Laszlo, Nature 135, 474 (1935), and R. W. Dornte, J. Chem. Phys. 1, 566 (1933), by use of electron diffraction. The values reported by Ramachandra and Livingston, loc. cit., are adopted.

The vibrational spectra of tetrachloroethylene have been studied by numerous investigators. The vibrational frequencies assigned by D. E. Mann, N. Acquista and E. K. Plyler, J. Res. Natl. Bur. Std. 52, 67 (1954), are adopted here. These authors also reviewed the results of earlier investigations in detail.

The electronic levels and quantum weights are obtained from G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.

The three principal moments of inertia are: $I_A = 4.88344 \times 10^{-38}$, $I_B = 6.28884 \times 10^{-38}$ and $I_C = 1.11723 \times 10^{-37}$ g cm^2.

Hexachloroethane (C_2Cl_6)

(Ideal Gas) GFW = 236.7403

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100	18.253	67.031	120.572	-5.354	-32.464	-25.580	55.905
200	27.716	82.894	97.948	-3.011	-32.455	-18.652	20.382
298	33.206	95.069	95.069	.000	-32.080	-11.950	8.760
300	33.286	95.275	95.070	.062	-32.071	-11.826	8.615
400	36.677	105.355	96.421	3.573	-31.542	-5.155	2.817
500	38.781	113.782	99.074	7.354	-30.958	1.377	-.602
600	40.142	120.981	102.140	11.305	-30.370	7.788	-2.837
700	41.061	127.242	105.289	15.367	-29.792	14.101	-4.403
800	41.714	132.769	108.385	19.507	-29.228	20.332	-5.554
900	42.193	137.711	111.374	23.703	-28.676	26.494	-6.434
1000	42.551	142.176	114.234	27.941	-28.132	32.591	-7.123
1100	42.813	146.244	116.962	32.210	-27.600	38.638	-7.677
1200	43.024	149.979	119.560	36.502	-27.080	44.637	-8.130
1300	43.177	153.429	122.034	40.813	-26.573	50.592	-8.505
1400	43.296	156.633	124.393	45.136	-26.074	56.512	-8.822
1500	43.374	159.623	126.643	49.470	-25.586	62.394	-9.091
1600	43.435	162.424	128.792	53.811	-25.109	68.241	-9.321
1700	43.459	165.058	130.849	58.155	-24.640	74.066	-9.522
1800	43.478	167.543	132.819	62.502	-24.184	79.854	-9.696
1900	43.491	169.894	134.709	66.851	-23.735	85.629	-9.850
2000	43.500	172.125	136.525	71.200	-23.301	91.371	-9.985
2100	43.481	174.247	138.271	75.549	-22.871	97.094	-10.105
2200	43.461	176.269	139.952	79.896	-22.460	102.793	-10.212
2300	43.442	178.201	141.574	84.242	-22.055	108.483	-10.308
2400	43.423	180.049	143.139	88.585	-21.665	114.151	-10.395
2500	43.404	181.821	144.651	92.926	-21.288	119.800	-10.473
2600	43.385	183.523	146.113	97.266	-20.921	125.438	-10.544
2700	43.366	185.160	147.529	101.603	-20.568	131.056	-10.608
2800	43.348	186.737	148.902	105.939	-20.227	136.671	-10.668
2900	43.329	188.258	150.233	110.273	-19.900	142.265	-10.721
3000	43.311	189.726	151.525	114.605	-19.586	147.850	-10.771
3100	43.291	191.146	152.780	118.935	-19.285	153.428	-10.817
3200	43.271	192.520	154.001	123.263	-18.999	158.995	-10.859
3300	43.252	193.852	155.188	127.589	-18.728	164.547	-10.898
3400	43.233	195.143	156.344	131.913	-18.467	170.104	-10.934
3500	43.215	196.395	157.471	136.236	-18.223	175.638	-10.967
3600	43.198	197.613	158.569	140.556	-17.990	181.177	-10.999
3700	43.181	198.796	159.640	144.875	-17.771	186.710	-11.028
3800	43.165	199.947	160.686	149.193	-17.561	192.233	-11.056
3900	43.150	201.068	161.707	153.508	-17.367	197.757	-11.082
4000	43.135	202.161	162.705	157.823	-17.184	203.268	-11.106
4100	43.122	203.226	163.680	162.135	-17.011	208.768	-11.128
4200	43.109	204.265	164.634	166.447	-16.851	214.275	-11.150
4300	43.097	205.279	165.568	170.757	-16.700	219.775	-11.170
4400	43.085	206.269	166.482	175.067	-16.557	225.284	-11.190
4500	43.074	207.238	167.377	179.374	-16.427	230.763	-11.207
4600	43.063	208.184	168.253	183.681	-16.301	236.262	-11.225
4700	43.052	209.110	169.113	187.987	-16.184	241.757	-11.242
4800	43.041	210.016	169.956	192.292	-16.077	247.241	-11.257
4900	43.031	210.904	170.782	196.595	-15.977	252.729	-11.272
5000	43.021	211.773	171.594	200.898	-15.881	258.209	-11.286
5100	43.011	212.625	172.390	205.199	-15.793	263.687	-11.300
5200	43.002	213.460	173.172	209.500	-15.710	269.172	-11.313
5300	42.993	214.279	173.939	213.800	-15.635	274.646	-11.325
5400	42.985	215.083	174.694	218.099	-15.565	280.123	-11.337
5500	42.977	215.871	175.435	222.397	-15.502	285.606	-11.349
5600	42.969	216.646	176.164	226.694	-15.442	291.069	-11.359
5700	42.961	217.406	176.881	230.991	-15.391	296.530	-11.370
5800	42.954	218.153	177.587	235.286	-15.343	302.016	-11.380
5900	42.947	218.887	178.280	239.582	-15.301	307.488	-11.390
6000	42.941	219.609	178.963	243.876	-15.265	312.953	-11.399

Sept. 30, 1967

HEXACHLOROETHANE (C_2Cl_6) (IDEAL GAS) GFW = 236.7403

Point Group D_{3d}

$S^\circ_{298.15}$ = 95.07 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -31.54 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -32.08 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
976 (1)	678 (1)	223 (2)
431 (1)	377 (1)	778 (2)
164 (1)	858 (2)	267 (2)
Internal rotation	340 (2)	139 (2)

Bond Distances: Cl-C = 1.74 Å C-C = 1.55 Å

Bond Angles: Cl-C-Cl = 110° Cl-C-C = 109° $\sigma = 6$

Product of the Moments of Inertia: $I_AI_BI_C = 1.2358 \times 10^{-111}$ g^3 cm^6

Heat of Formation

Smith et al. (1) determined the heat of combustion of $C_2Cl_6(c)$ to be ΔE_{293} = -718.7 ± 2 cal/g (uncorrected) by use of the "Quartz Wool" method. The free chlorine produced was reduced to HCl by employing the quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Adopting the reported results and recent auxiliary data (2, 3, 4), we evaluate the values ΔHc°_{298} = -173.525 and ΔHf°_{298} = -48.58 kcal/mol for $C_2Cl_6(c)$. Kirkbride (5) measured the enthalpy changes as -32.0 and 4.7 kcal/mol for the following two reactions by solution calorimetry: $C_2Cl_4(\ell)+Cl_2(g) = C_2Cl_6(aq)$ and $C_2Cl_6(c) = C_2Cl_6(aq)$. Hence we obtain ΔHf°_{298} = -49.07 kcal/mol for $C_2Cl_6(c)$, using ΔHf°_{298} (C_2Cl_4, ℓ) = -12.37 kcal/mol. This value is in reasonable agreement with the adopted value -48.58 kcal/mol.

Hexachloroethane (c) has three modifications, namely triclinic, monoclinic and cubic, with transition temperatures of 318 and 345°K (4). The sublimation pressures over the different phases have been measured by Ivin (8), Lee (7), and Nitta (26). Based on these data, values for ΔHs°_{298} (triclinic) are derived by a modified second law method to be 16.5, 17.1 and 14.8 kcal/mol, respectively. The analysis depends on the Cp and ΔHt° data determined by (4). The order of magnitude of the two ΔHt° values is confirmed by R. A. McDonald, private communication, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan. Pressures reported by Nelson (6) are systematically lower than the above data by about 10 per cent; therefore, his data are not used. Third law analysis is not applicable to the pressure data due to lack of S°_{298} (triclinic). Adopting ΔHs°_{298} = 16.5 and ΔHf°_{298} = -48.58 kcal/mol for C_2Cl_6 (triclinic), we obtain ΔHf°_{298} = -32.08 kcal/mol for $C_2Cl_6(g)$.

The equilibrium constant at 776°K for the reaction $C_2Cl_6(g) = C_2Cl_4(g) + Cl_2(g)$ was reported as 0.8 ± 0.1 (atm) by Puyo et al. (9). The corresponding enthalpy change at 298°K is evaluated to be 30.8 kcal/mol by the third law method, yielding $\Delta Hf^\circ_{298}(C_2Cl_6, g)$ = -33.77 kcal/mol which is in fair agreement with the adopted one.

Heat Capacity and Entropy

The molecular structure of C_2Cl_6 has been studied previously by means of infrared and Raman spectroscopy (10), X-ray (11), and electron diffraction (12-18). The molecule was found to be in the staggered position in the vapor and solid states. The bond distances and angles adopted here are those reported by Swick et al. (16).

Incomplete assignments of vibrational frequencies for $C_2Cl_6(g)$ were reported by many investigators (21-24). The adopted frequencies, except the torsional mode ν_4, are obtained from Carney et al. (19). The torsional mode is treated as a hindered internal rotation, and thermodynamic properties are calculated (25) from the barrier height of V_0 = 12.8 kcal/mol which was evaluated by Karle (20) from electron diffraction data. The value of S°_{298} is calculated based on S°_{400} = 105.355 eu which is derived from the free rotor value S°_{400} = 108.121 eu by subtraction of the entropy difference between a free rotor and hindered rotor at 400°K. Internal rotation contributions to Cp at temperatures below 350°K could not be calculated since they are beyond the range of the values tabulated by Pitzer (25). These Cp contributions are estimated by graphical interpolation between internal rotation values above 350°K and the corresponding harmonic oscillator values (ν_4 = 67 cm^{-1}) below 150°K. This calculation presumes that the internal rotation approaches harmonic oscillation as $V/RT \gg 1$.

The three principal moments of inertia are: $I_A = I_C = 1.1367 \times 10^{-37}$ and $I_B = 9.5648 \times 10^{-38}$ g cm^2.

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Difluoroacetylene (C_2F_2)

(Ideal Gas) GFW = 62.0191

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.964	4.650	4.650	INFINITE
100	8.228	46.483	68.902	-2.242	4.649	4.112	-8.988
200	11.556	53.280	59.489	-1.242	4.793	3.534	-3.862
298	13.508	58.305	58.305	.000	5.000	2.871	-2.105
300	13.539	58.389	58.305	.025	5.003	2.858	-2.082
400	15.117	62.525	58.859	1.467	5.183	2.115	-1.156
500	16.242	66.025	59.951	3.037	5.308	1.332	-.582
600	17.111	69.066	61.222	4.706	5.389	.528	-.192
700	17.785	71.757	62.539	6.453	5.435	-.285	.089
800	18.310	74.167	63.844	8.258	5.456	-1.104	.302
900	18.722	76.349	65.114	10.111	5.459	-1.926	.468
1000	19.049	78.339	66.339	12.000	5.451	-2.747	.600
1100	19.311	80.167	67.514	13.919	5.432	-3.566	.709
1200	19.523	81.857	68.639	15.861	5.405	-4.381	.798
1300	19.696	83.426	69.717	17.822	5.365	-5.196	.873
1400	19.839	84.892	70.749	19.799	5.323	-6.004	.937
1500	19.958	86.264	71.738	21.789	5.274	-6.811	.992
1600	20.058	87.556	72.687	23.790	5.220	-7.618	1.041
1700	20.143	88.774	73.598	25.800	5.164	-8.418	1.082
1800	20.215	89.928	74.473	27.818	5.102	-9.217	1.119
1900	20.278	91.023	75.316	29.843	5.039	-10.008	1.151
2000	20.332	92.064	76.127	31.873	4.972	-10.798	1.180
2100	20.379	93.057	76.910	33.909	4.904	-11.584	1.206
2200	20.420	94.006	77.656	35.949	4.829	-12.371	1.229
2300	20.456	94.915	78.396	37.993	4.754	-13.147	1.249
2400	20.488	95.786	79.103	40.040	4.673	-13.925	1.268
2500	20.516	96.623	79.787	42.090	4.590	-14.700	1.285
2600	20.542	97.428	80.450	44.143	4.502	-15.469	1.300
2700	20.564	98.204	81.093	46.199	4.412	-16.237	1.314
2800	20.585	98.952	81.718	48.256	4.321	-16.998	1.327
2900	20.603	99.675	82.325	50.315	4.222	-17.756	1.338
3000	20.620	100.373	82.915	52.376	4.120	-18.516	1.349
3100	20.635	101.050	83.489	54.439	4.017	-19.266	1.358
3200	20.649	101.705	84.048	56.503	3.909	-20.015	1.367
3300	20.662	102.341	84.593	58.569	3.795	-20.766	1.375
3400	20.673	102.958	85.124	60.636	3.679	-21.504	1.382
3500	20.684	103.557	85.642	62.704	3.557	-22.245	1.389
3600	20.694	104.140	86.148	64.772	3.432	-22.981	1.395
3700	20.703	104.707	86.642	66.842	3.302	-23.712	1.401
3800	20.711	105.259	87.124	68.913	3.169	-24.436	1.405
3900	20.719	105.797	87.596	70.984	3.029	-25.161	1.410
4000	20.726	106.322	88.058	73.057	2.888	-25.881	1.414
4100	20.732	106.834	88.510	75.129	2.739	-26.604	1.418
4200	20.738	107.334	88.952	77.203	2.586	-27.312	1.421
4300	20.744	107.822	89.385	79.277	2.428	-28.023	1.424
4400	20.750	108.299	89.810	81.352	2.265	-28.731	1.427
4500	20.755	108.765	90.226	83.427	2.097	-29.439	1.430
4600	20.759	109.221	90.634	85.503	1.924	-30.134	1.432
4700	20.764	109.668	91.034	87.579	1.746	-30.828	1.434
4800	20.768	110.105	91.427	89.655	1.561	-31.515	1.435
4900	20.772	110.533	91.812	91.732	1.372	-32.203	1.436
5000	20.775	110.953	92.191	93.810	1.178	-32.886	1.437
5100	20.779	111.364	92.563	95.887	.975	-33.578	1.439
5200	20.782	111.768	92.928	97.966	.770	-34.246	1.439
5300	20.785	112.164	93.287	100.044	.558	-34.913	1.440
5400	20.788	112.552	93.641	102.123	.340	-35.582	1.440
5500	20.791	112.934	93.988	104.202	.115	-36.244	1.440
5600	20.793	113.308	94.330	105.281	-.115	-36.903	1.440
5700	20.796	113.676	94.666	108.360	-.353	-37.564	1.440
5800	20.798	114.038	94.997	110.440	-.595	-38.214	1.440
5900	20.801	114.394	95.322	112.520	-.844	-38.855	1.439
6000	20.803	114.743	95.643	114.600	-1.099	-39.506	1.439

Dec. 31, 1960; Dec. 31, 1966; Dec. 31, 1967

DIFLUOROACETYLENE (C_2F_2) (IDEAL GAS) GFW = 62.0191

Point Group [$D_{\infty h}$]

ΔHf_0° = [4.65 ± 5] kcal/mol

$S^\circ_{298.15}$ = [58.3 ± 1.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [5 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[1050] (1)	[450] (2)
[1900] (1)	[300] (2)
1149 (1)	

Bond Distance: C-F = [1.28] Å C-C = [1.20] Å

Bond Angle: F-C-C = [180°] σ = 2

Rotational Constant: B_0 = [0.1179] cm^{-1}

Heat of Formation

M. Farber, M. A. Greenbaum, M. A. Frisch, H. C. Ko, G. Grenier and E. Graper, Rocket Power Inc., 3rd Quarterly Report, AFRPL-TR-67-147, Contract F04611-67-C-0010, May 1967, have obtained equilibrium-weight-change data over the C-CF_4 system. Our reanalysis of these data assumes that the equilibrium constants for CF_4, CF_3 and CF_2 are those in the JANAF Tables, and that C_2F_2 was the only other C-F species present at equilibrium. This gives maximum possible concentrations of C_2F_2 and places a lower limit on the heat of formation. The $\Delta Hf^\circ_{298}(C_2F_2, g)$ values so obtained range from +10 kcal/mol from data at 2023°K to -10 kcal/mol from data at 2373°K; we adopt a weighted mean of +5±5 kcal/mol. This value still predicts complete dimerization of CF at 1 atmosphere pressure below about 2200°K, but only CF would exist under experimental conditions such as the study by Farber.

Farber et al. also investigated the mass spectrum of the vapor over the C-CF_4 system and did not detect any ion ascribable to C_2F_2. This is additional support for the value adopted.

The C-C bond dissociation energy in C_2F_2 is 113 kcal/mol, using the JANAF CF(g) table (Dec. 31st, 1967). This value is 115 kcal weaker than the bond dissociation energy of acetylene. In order to explain such a large decrease, a crossing of the repulsive approach of two $^2\Pi$ CF molecules with an attractive approach of two $^4\Sigma$ CF molecules may be postulated. This follows the reasoning used by J. P. Simons, Nature 205, 1308 (1965), to explain the bond dissociation energy of C_2F_4.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for $C_2H_2(g)$. The C-F and C-C bond distances are estimated from those in HC ≡ CF reported by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59. 2661, 1936. The assymmetric stretching frequency, ν_3 = 1149 cm^{-1}, was observed by J. Heicklen and V. Knight, J. Phys. Chem. 69, 2484 (1965). The other vibrational frequencies were estimated by comparison with those for $C_2H_2(g)$ and $C_2HF(g)$ reported by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. 1961, 13 (1961). The moment of inertia is 2.3735 x 10^{-38} g cm^2.

Trifluoroacetonitrile (CF_3CN)

(Ideal Gas) GFW = 95.0242

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.799	-117.494	-117.494	INFINITE
100	10.459	56.021	85.281	-2.926	-118.038	-115.585	252.611
200	14.924	64.627	72.920	-1.659	-118.325	-113.000	123.480
298	18.703	71.324	71.324	.000	-118.400	-110.365	80.900
300	18.765	71.440	71.324	.035	-118.401	-110.316	80.365
400	21.622	77.250	72.097	2.061	-118.370	-107.622	58.802
500	23.724	82.313	73.645	4.334	-118.297	-104.944	45.871
600	25.285	86.783	75.469	6.788	-118.203	-102.282	37.256
700	26.465	90.774	77.376	9.378	-118.103	-99.635	31.108
800	27.371	94.369	79.279	12.072	-117.998	-97.005	26.500
900	28.078	97.636	81.140	14.846	-117.892	-94.389	22.921
1000	28.638	100.624	82.941	17.683	-117.781	-91.784	20.059
1100	29.087	103.375	84.675	20.570	-117.672	-89.191	17.721
1200	29.450	105.922	86.341	23.497	-117.563	-86.604	15.773
1300	29.748	108.292	87.940	26.458	-117.460	-84.028	14.126
1400	29.995	110.506	89.473	29.445	-117.356	-81.458	12.716
1500	30.201	112.582	90.945	32.455	-117.255	-78.897	11.495
1600	30.375	114.537	92.359	35.484	-117.156	-76.347	10.428
1700	30.522	116.383	93.719	38.529	-117.058	-73.798	9.487
1800	30.648	118.131	95.027	41.588	-116.964	-71.258	8.652
1900	30.757	119.791	96.287	44.658	-116.871	-68.718	7.904
2000	30.851	121.371	97.502	47.739	-116.779	-66.185	7.232
2100	30.934	122.879	98.675	50.828	-116.690	-63.658	6.625
2200	31.006	124.319	99.808	53.925	-116.608	-61.139	6.074
2300	31.069	125.699	100.904	57.029	-116.525	-58.614	5.570
2400	31.126	127.023	101.965	60.139	-116.447	-56.100	5.109
2500	31.176	128.294	102.993	63.254	-116.373	-53.589	4.685
2600	31.221	129.518	103.989	66.374	-116.304	-51.078	4.293
2700	31.261	130.697	104.957	69.498	-116.237	-48.571	3.932
2800	31.297	131.835	105.897	72.626	-116.172	-46.066	3.596
2900	31.329	132.933	106.810	75.757	-116.115	-43.559	3.283
3000	31.359	133.996	107.699	78.892	-116.063	-41.064	2.992
3100	31.386	135.025	108.564	82.029	-116.011	-38.563	2.719
3200	31.410	136.022	109.406	85.169	-115.967	-36.065	2.463
3300	31.433	136.988	110.227	88.311	-115.928	-33.573	2.223
3400	31.453	137.927	111.028	91.455	-115.893	-31.073	1.997
3500	31.472	138.839	111.810	94.602	-115.864	-28.582	1.785
3600	31.489	139.726	112.573	97.750	-115.839	-26.087	1.584
3700	31.505	140.589	113.319	100.899	-115.820	-23.593	1.394
3800	31.520	141.429	114.048	104.051	-115.806	-21.096	1.213
3900	31.533	142.248	114.760	107.203	-115.799	-18.606	1.043
4000	31.546	143.047	115.457	110.357	-115.795	-16.112	.880
4100	31.558	143.826	116.140	113.513	-115.798	-13.626	.726
4200	31.569	144.586	116.808	116.669	-115.809	-11.127	.579
4300	31.579	145.329	117.463	119.826	-115.823	-8.634	.439
4400	31.589	146.056	118.104	122.985	-115.846	-6.145	.305
4500	31.598	146.766	118.733	126.144	-115.874	-3.657	.178
4600	31.606	147.460	119.350	129.304	-115.907	-1.158	.055
4700	31.614	148.140	119.956	132.465	-115.947	1.337	-.062
4800	31.621	148.806	120.550	135.627	-115.995	3.839	-.175
4900	31.628	149.458	121.133	138.789	-116.049	6.333	-.282
5000	31.635	150.097	121.706	141.952	-116.109	8.833	-.386
5100	31.641	150.723	122.269	145.116	-116.178	11.316	-.485
5200	31.646	151.338	122.822	148.281	-116.252	13.828	-.581
5300	31.652	151.940	123.366	151.445	-116.333	16.334	-.674
5400	31.657	152.532	123.900	154.611	-116.422	18.834	-.762
5500	31.662	153.113	124.426	157.777	-116.519	21.344	-.848
5600	31.667	153.684	124.944	160.943	-116.622	23.851	-.931
5700	31.671	154.244	125.453	164.110	-116.734	26.355	-1.011
5800	31.675	154.795	125.954	167.278	-116.852	28.867	-1.088
5900	31.679	155.337	126.447	170.445	-116.978	31.383	-1.163
6000	31.683	155.869	126.933	173.613	-117.112	33.891	-1.234

Dec. 31, 1969

TRIFLUOROACETONITRILE (CF_3CN) (IDEAL GAS) GFW = 95.0242

C_2F_3N

Point Group C_{3v}

ΔHf°_0 = -117.5 ± 0.7 kcal/mol

$S^\circ_{298.15}$ = 71.32 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -118.4 ± 0.7 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
2271 (1)	1215 (2)
1228 (1)	625 (2)
801 (1)	464 (2)
521 (1)	192 (2)

Bond Distance: C-F = 1.335 Å C-C = 1.461 Å CN = 1.153 Å

Bond Angle: F-C-F = 107.5° F-C-C = 111.38° $\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = 1.18645 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, C_2F_4, and CF_3X (X = H, Cl, Br, I, CN). Details of the input data and adjustment are given in (1). Input included a calorimetric link to $NF_3(g)$ and $CF_4(g)$ plus an equilibrium link to $C_2F_6(g)$ and $C_2N_2(g)$. The calorimetric study (2) gave ΔHr° = -824.4 ± 0.6 kcal/mol at 298.15 K for the reaction $3CF_3CN(g) + 5NF_3(g) \rightarrow 6CF_4(g) + 4N_2(g)$. Equilibrium data (3) in the range 865-925 K give ΔHr° (3rd law) = 10.59 and ΔHr° (2nd law) = 10.59 ± 0.20 kcal/mol at 298.15 K for the reaction $C_2F_6(g) + C_2N_2(g) \rightarrow 2CF_3CN(g)$. The entropy difference, ΔSr° (2nd law) - ΔSr° (3rd law), is 0.0 ± 1.5 gibbs/mol. Deviations between the selected ΔHf° and the two observations are 1.37 and 0.15 kcal/mol, respectively, both considerably less than the overall uncertainties including those in auxiliary values of ΔHf°. Subsequent to the adjustment, Curnutt and Sinke (4) reported ΔHr° = -197.6 ± 0.9 kcal/mol from a calorimetric study of $CF_3CN(g) + 1.25\ O_2(g) + 1.5\ H_2O(\ell) \rightarrow 2\ CO_2(g) + 0.5\ N_2(g) + 3\ HF(120\ H_2O)$. Their result of ΔHf° = -118.4 ± 1.2 kcal/mol is confirmation of the selected value.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Danford and Livingston (5) and from microwave data by Sheridan and Gordy (6) and Thomas et al. (7). These studies are in substantial agreement except for a difference of about 0.04 Å in the C-C bond distance. We adopt the results of Thomas et al. (7) since they are based on data for several isotopic species. Principal moments of inertia are $I_A = 14.626 \times 10^{-39}$ and $I_B = I_C = 28.482 \times 10^{-39}\ g\ cm^2$. Vibrational frequencies are taken from the assignments of Edgell and Potter (8). All values except ν_8 are from infrared spectra of the vapor phase. Raman spectra of the liquid provide ν_8 and confirm the infrared data. Similar assignments have been given by Janz and Wait (9) based on spectra of Wait and Janz (10).

Pace and Bobka (11) used low temperature calorimetric data to derive the entropy of the ideal gas at the normal boiling point of 205.47 K. The experimental value of 65.01 ± 0.2 gibbs/mol is in good agreement with 65.03 gibbs/mol obtained from this table. The largest uncertainty in Cp° and S° probably arises from neglect of anharmonicity and rotational distortion. Uncertainty in the entropy is estimated to vary from 0.1 to 0.5 gibbs/mol over the range 300 to 1000°K. Discussions of the neglect of anharmonicity are given on the tables for $CClF_3(g)$ and $CF_4(g)$.

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C_2F_3N

Tetrafluoroethylene (C_2F_4)

(Ideal Gas) GFW = 100.0159

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.903	-156.579	-156.579	INFINITE
100	10.562	55.830	86.157	-3.033	-157.127	-154.529	337.722
200	15.583	64.734	73.329	-1.719	-157.369	-151.810	165.890
298	19.230	71.678	71.678	.000	-157.400	-149.072	109.272
300	19.287	71.797	71.679	.036	-157.400	-149.021	108.561
400	21.965	77.731	72.469	2.105	-157.363	-146.230	79.896
500	23.989	82.860	74.046	4.407	-157.313	-143.454	62.704
600	25.531	87.377	75.899	6.887	-157.253	-140.688	51.246
700	26.708	91.405	77.832	9.501	-157.191	-137.930	43.064
800	27.611	95.033	79.759	12.219	-157.123	-135.184	36.931
900	28.310	98.327	81.642	15.016	-157.052	-132.448	32.163
1000	28.858	101.339	83.463	17.876	-156.974	-129.719	28.350
1100	29.292	104.111	85.216	20.784	-156.896	-126.998	25.232
1200	29.641	106.675	86.899	23.732	-156.814	-124.281	22.635
1300	29.924	109.059	88.513	26.710	-156.740	-121.573	20.438
1400	30.157	111.286	90.061	29.715	-156.661	-118.869	18.556
1500	30.350	113.373	91.546	32.740	-156.586	-116.171	16.926
1600	30.512	115.337	92.972	35.784	-156.512	-113.483	15.501
1700	30.648	117.191	94.343	38.842	-156.438	-110.795	14.244
1800	30.764	118.946	95.661	41.913	-156.369	-108.115	13.127
1900	30.864	120.612	96.931	44.994	-156.300	-105.433	12.128
2000	30.950	122.198	98.155	48.085	-156.233	-102.756	11.229
2100	31.025	123.709	99.336	51.184	-156.168	-100.084	10.416
2200	31.091	125.154	100.477	54.290	-156.110	-97.419	9.678
2300	31.148	126.538	101.580	57.402	-156.052	-94.747	9.003
2400	31.199	127.864	102.648	60.519	-156.001	-92.085	8.385
2500	31.244	129.139	103.682	63.641	-155.953	-89.425	7.818
2600	31.285	130.365	104.685	66.768	-155.910	-86.763	7.293
2700	31.321	131.547	105.658	69.898	-155.870	-84.105	6.808
2800	31.353	132.686	106.603	73.032	-155.832	-81.448	6.357
2900	31.382	133.787	107.522	76.169	-155.803	-78.788	5.938
3000	31.409	134.851	108.415	79.308	-155.780	-76.140	5.547
3100	31.433	135.882	109.285	82.450	-155.758	-73.482	5.180
3200	31.454	136.880	110.131	85.595	-155.743	-70.828	4.837
3300	31.474	137.848	110.957	88.741	-155.735	-68.179	4.515
3400	31.493	138.788	111.762	91.889	-155.731	-65.521	4.212
3500	31.509	139.701	112.547	95.040	-155.734	-62.869	3.926
3600	31.525	140.589	113.314	98.191	-155.741	-60.214	3.656
3700	31.539	141.453	114.062	101.344	-155.756	-57.561	3.400
3800	31.552	142.294	114.794	104.499	-155.775	-54.901	3.158
3900	31.564	143.114	115.510	107.655	-155.803	-52.250	2.928
4000	31.575	143.913	116.210	110.812	-155.834	-49.591	2.710
4100	31.586	144.693	116.895	113.970	-155.874	-46.941	2.502
4200	31.595	145.454	117.566	117.129	-155.921	-44.277	2.304
4300	31.604	146.198	118.224	120.289	-155.973	-41.618	2.115
4400	31.613	146.924	118.868	123.450	-156.034	-38.961	1.935
4500	31.621	147.635	119.499	126.611	-156.101	-36.306	1.763
4600	31.628	148.330	120.118	129.774	-156.174	-33.639	1.598
4700	31.635	149.010	120.726	132.937	-156.255	-30.973	1.440
4800	31.642	149.676	121.322	136.101	-156.343	-28.300	1.289
4900	31.648	150.329	121.907	139.265	-156.439	-25.632	1.143
5000	31.654	150.968	122.482	142.430	-156.542	-22.963	1.004
5100	31.659	151.595	123.047	145.596	-156.654	-20.306	.870
5200	31.664	152.210	123.602	148.762	-156.772	-17.620	.741
5300	31.669	152.813	124.147	151.929	-156.897	-14.937	.616
5400	31.674	153.405	124.684	155.096	-157.032	-12.264	.496
5500	31.678	153.986	125.211	158.264	-157.174	-9.579	.381
5600	31.682	154.557	125.730	161.432	-157.324	-6.893	.269
5700	31.686	155.118	126.241	164.600	-157.484	-4.211	.161
5800	31.690	155.669	126.743	167.769	-157.649	-1.520	.057
5900	31.693	156.211	127.238	170.938	-157.824	1.176	-.044
6000	31.696	156.744	127.726	174.107	-158.007	3.864	-.141

June 30, 1962; June 30, 1963; Mar. 31, 1964; Sept. 30, 1964; June 30, 1969

TETRAFLUOROETHYLENE (C_2F_4) (IDEAL GAS) GFW = 100.0159

Point Group D_{2h}

ΔHf°_0 = -156.6 ± 0.7 kcal/mol

$S^\circ_{298.15}$ = 71.678 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -157.4 ± 0.7 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1872 (1)	1340 (1)	1337 (1)
778 (1)	551 (1)	218 (1)
394 (1)	406 (1)	1186 (1)
190 (1)	508 (1)	558 (1)

Bond Distance: C-F = 1.313 Å C-C = 1.313 Å

Bond Angle: F-C-F = 114°

σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 1.5877 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). In this case, the selected ΔHf° corresponds to the weighted average of three calorimetric studies (2, 3) which may be reduced to the following:

Reference	Reaction	$\Delta Hr^\circ_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
(2)	$C_2F_4(g) + CF_4(g) + C(graphite)$	-65.4 ± 0.5	-157.6 ± 0.6
(2)	$C_2F_4(g) + 2H_2(g) \rightarrow 4HF(50\ H_2O) + 2C(graphite)$	-150.9 ± 1.2	-156.2 ± 1.3
(3)	$C_2F_4(g) + 4Na(c) \rightarrow 4NaF(c) + 2C(graphite)$	-392.9 ± 1.3	-157.2 ± 1.4

Amorphous carbon was formed in all three calorimetric reactions and separate combustions were made to refer the observed product to the standard state of graphite. Other calorimetric studies (4, 5, 6) are omitted because of apparent uncertainties in the reductions to the standard-state reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Karle (7), Broun (8) and Young (9). The resulting structures differ in minor respects, particularly in the exact location of the two carbons. Values from Karle (7) are adopted since they are intermediate between the others. Values from Young (9) and Broun (8) correspond to changes of ± 2.2% in the product of the moments of inertia. Principal moments of inertia for the adopted structure are $I_A = 15.30 \times 10^{-39}$, $I_B = 25.46 \times 10^{-39}$ and $I_C = 40.76 \times 10^{-39}$ g cm^2. Vibrational fundamentals are those selected by Shimanouchi (10) from the data of Mann (11), Monfils (12) and Nielsen (13).

Furukawa (14) reported low-temperature calorimetric data from which the ideal gas entropy may be derived as 64.54 ± 0.09 gibbs/mol at 197.53°K. The calculated entropy from this table is also 64.54 eu. The range in values of $I_AI_BI_C$ corresponds to an entropy change of ±0.022 eu.

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Hexafluoroethane (C_2F_6)
(Ideal Gas) GFW = 138.0127

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°₂₉₈)/T	H°-H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.841	-319.207	-319.207	INFINITE
100	12.700	59.332	97.852	-3.852	-320.331	-314.014	686.276
200	19.703	70.413	81.548	-2.227	-320.962	-307.430	335.944
298	25.432	79.368	79.368	.000	-321.200	-300.720	220.433
300	25.528	79.526	79.368	.047	-321.203	-300.594	218.982
400	30.006	87.513	80.427	2.834	-321.218	-293.714	160.478
500	33.255	94.578	82.565	6.007	-321.104	-286.852	125.383
600	35.542	100.855	85.100	9.453	-320.910	-280.018	101.997
700	37.157	106.463	87.759	13.093	-320.673	-273.220	85.303
800	38.315	111.504	90.417	16.869	-320.413	-266.460	72.793
900	39.150	116.067	93.018	20.744	-320.140	-259.734	63.072
1000	39.791	120.226	95.534	24.692	-319.859	-253.038	55.301
1100	40.263	124.041	97.954	28.695	-319.578	-246.371	48.949
1200	40.652	127.562	100.277	32.742	-319.294	-239.724	43.660
1300	40.941	130.827	102.503	36.822	-319.021	-233.105	39.188
1400	41.185	133.870	104.636	40.928	-318.748	-226.504	35.359
1500	41.375	136.719	106.681	45.057	-318.480	-219.922	32.043
1600	41.541	139.394	108.643	49.203	-318.219	-213.365	29.144
1700	41.661	141.916	110.526	53.363	-317.961	-206.817	26.588
1800	41.771	144.301	112.337	57.535	-317.713	-200.292	24.319
1900	41.869	146.562	114.079	61.717	-317.467	-193.772	22.289
2000	41.957	148.712	115.758	65.908	-317.227	-187.265	20.463
2100	42.021	150.761	117.376	70.107	-316.992	-180.774	18.813
2200	42.080	152.717	118.938	74.312	-316.768	-174.297	17.315
2300	42.135	154.589	120.448	78.523	-316.546	-167.820	15.947
2400	42.185	156.383	121.908	82.739	-316.334	-161.361	14.694
2500	42.230	158.106	123.322	86.960	-316.128	-154.910	13.542
2600	42.266	159.763	124.692	91.185	-315.930	-148.464	12.480
2700	42.299	161.359	126.020	95.413	-315.737	-142.026	11.496
2800	42.330	162.897	127.310	99.644	-315.549	-135.597	10.584
2900	42.358	164.383	128.563	103.879	-315.372	-129.167	9.734
3000	42.384	165.820	129.781	108.116	-315.204	-122.759	8.943
3100	42.406	167.210	130.966	112.355	-315.039	-116.344	8.202
3200	42.426	168.557	132.120	116.597	-314.884	-109.935	7.508
3300	42.445	169.862	133.244	120.840	-314.738	-103.539	6.857
3400	42.462	171.130	134.340	125.086	-314.597	-97.136	6.244
3500	42.478	172.361	135.409	129.333	-314.468	-90.741	5.666
3600	42.491	173.558	136.452	133.581	-314.343	-84.348	5.121
3700	42.503	174.722	137.470	137.831	-314.229	-77.962	4.605
3800	42.515	175.856	138.466	142.082	-314.122	-71.571	4.116
3900	42.525	176.960	139.439	146.334	-314.027	-65.196	3.653
4000	42.534	178.037	140.390	150.587	-313.936	-58.812	3.213
4100	42.541	179.087	141.321	154.841	-313.857	-52.442	2.795
4200	42.548	180.113	142.233	159.095	-313.788	-46.061	2.397
4300	42.555	181.114	143.125	163.350	-313.725	-39.685	2.017
4400	42.560	182.092	144.000	167.606	-313.675	-33.316	1.655
4500	42.565	183.049	144.857	171.862	-313.632	-26.953	1.309
4600	42.569	183.984	145.697	176.119	-313.598	-20.579	.978
4700	42.572	184.900	146.522	180.376	-313.575	-14.207	.661
4800	42.575	185.796	147.331	184.633	-313.561	-7.830	.356
4900	42.578	186.674	148.125	188.891	-313.557	-1.461	.065
5000	42.580	187.534	148.904	193.149	-313.563	4.906	-.214
5100	42.581	188.377	149.670	197.407	-313.581	11.257	-.482
5200	42.582	189.204	150.422	201.665	-313.607	17.642	-.741
5300	42.583	190.015	151.162	205.923	-313.643	24.019	-.990
5400	42.584	190.811	151.889	210.182	-313.691	30.379	-1.229
5500	42.585	191.593	152.604	214.440	-313.749	36.757	-1.461
5600	42.586	192.360	153.307	218.699	-313.817	43.132	-1.683
5700	42.587	193.114	153.998	222.957	-313.898	49.501	-1.898
5800	42.588	193.855	154.679	227.216	-313.985	55.878	-2.106
5900	42.589	194.583	155.349	231.475	-314.085	62.255	-2.306
6000	42.590	195.298	156.009	235.734	-314.195	68.627	-2.500

Sept. 30, 1965; June 30, 1969

Point Group D_{3d}

ΔHf°_0 = -319.2 ± 1.2 kcal/mol

$S^\circ_{298.15}$ = 79.368 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -321.2 ± 1.2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1228 (1)	1117 (1)	376 (2)
807 (1)	714 (1)	1251 (2)
348 (1)	1243 (2)	523 (2)
Torsion	619 (2)	220 (2)

Bond Distance: C-F = 1.32 Å C-C = 1.56 Å

Bond Angle: C-C-F = 109.5 ± 1.5° σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 6.007 \times 10^{-113}$ g^3 cm^6

Reduced Moment of Inertia: $I_{red} = 7.32 \times 10^{-39}$ g cm^2

Barrier to Internal Rotation: V = 3.96 kcal/mol

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in (1). Data pertinent to C_2F_6 are summarized below. Calorimetric data (7) for the reaction of C_2F_6 with potassium were omitted from the adjustment due to insufficient characterization of the products.

Source	Method	Reaction	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
(2)	Calorimetric	$3C_2F_6(g) + 2NF_3(g) \rightarrow 6CF_4(g) + N_2(g)$	-311.6 ± 3.0	-321.3 ± 1.2
(3)	Calorimetric	$3CF_3CN(g) + 5NF_3(g) \rightarrow 6CF_4(g) + 4N_2(g)$	-824.4 ± 0.6	----
(4)	Equilibrium	$2CF_3CN(g) \rightarrow C_2F_6(g) + C_2N_2(g)$	-10.59 ± 0.5	-322.2 ± 1.8
(5)	Equilibrium	$C_2F_6(g) + Br_2(g) \rightarrow 2CBrF_3(g)$	3.30 ± 0.7	-320.9 ± 1.6
(6, 5)	Kinetic	$C_2F_6(g) \rightarrow 2CF_3(g)$	97.6 ± 6	-322.4 ± 6

Heat Capacity and Entropy

The adopted molecular structure was derived from electron-diffraction data by Swick and Karle (8). The vibrational frequencies are from the assignment of Carney et al. (9), who reviewed the extensive spectral data. Shimanouchi (10) has selected the same frequencies. Low-temperature calorimetric data were used by Pace and Aston (11) to derive a value for the entropy of the ideal gas of 69.88 ± 0.20 gibbs/mol at 194.87°K. This value is used to fix the barrier to internal rotation at 3960 cal/mol. Thermodynamic functions are calculated from these parameters, using hindered internal rotation in place of a torsional vibration.

An uncertainty of ±0.2 gibbs/mol in the third-law entropy corresponds to a variation in the barrier to internal rotation of about ±700 cal/mol. This range easily includes the barrier of 4300 cal/mol derived by Karle (12) from analysis of the electron-diffraction data (8). Uncertainty in the entropy of this table should not exceed 0.5 gibbs at 1000°K.

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CCH Radical (C_2H)
(Ideal Gas) GFW = 25.0303

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.248	113.268	113.268	INFINITE
100	6.989	41.186	56.717	-1.553	113.555	110.698	-241.931
200	7.816	46.228	50.332	-.821	113.830	107.725	-117.716
298	8.868	49.553	49.553	.000	114.000	104.688	-76.739
300	8.885	49.608	49.554	.016	114.002	104.630	-76.223
400	9.555	52.276	49.912	.946	114.092	101.491	-55.452
500	10.234	54.495	50.613	1.941	114.100	98.335	-42.984
600	10.716	56.404	51.423	2.989	114.042	95.190	-34.673
700	11.141	58.089	52.257	4.082	113.934	92.056	-28.741
800	11.523	59.602	53.082	5.216	113.797	88.941	-24.297
900	11.867	60.979	53.884	6.386	113.637	85.841	-20.845
1000	12.176	62.246	54.658	7.588	113.468	82.761	-18.087
1100	12.453	63.420	55.402	8.820	113.291	79.698	-15.834
1200	12.701	64.514	56.116	10.078	113.110	76.654	-13.961
1300	12.925	65.540	56.802	11.359	112.921	73.622	-12.377
1400	13.129	66.505	57.461	12.662	112.735	70.610	-11.023
1500	13.317	67.417	58.094	13.985	112.547	67.608	-9.850
1600	13.492	68.282	58.704	15.325	112.358	64.615	-8.826
1700	13.656	69.105	59.292	16.683	112.174	61.637	-7.924
1800	13.813	69.890	59.859	18.054	111.991	58.670	-7.123
1900	13.964	70.641	60.407	19.445	111.813	55.714	-6.409
2000	14.109	71.361	60.937	20.849	111.639	52.765	-5.766
2100	14.250	72.053	61.450	22.267	111.471	49.828	-5.186
2200	14.386	72.719	61.947	23.698	111.305	46.892	-4.658
2300	14.519	73.362	62.430	25.144	111.147	43.971	-4.178
2400	14.648	73.982	62.898	26.602	110.992	41.054	-3.739
2500	14.773	74.583	63.353	28.073	110.843	38.140	-3.334
2600	14.893	75.165	63.797	29.557	110.699	35.235	-2.962
2700	15.008	75.729	64.228	31.052	110.560	32.333	-2.617
2800	15.119	76.277	64.649	32.558	110.428	29.439	-2.298
2900	15.224	76.809	65.059	34.075	110.298	26.552	-2.001
3000	15.324	77.327	65.459	35.603	110.174	23.664	-1.724
3100	15.418	77.831	65.850	37.140	110.055	20.784	-1.465
3200	15.506	78.322	66.232	38.686	109.938	17.906	-1.223
3300	15.589	78.800	66.606	40.241	109.823	15.029	-.995
3400	15.665	79.267	66.971	41.804	109.713	12.160	-.782
3500	15.736	79.722	67.329	43.374	109.602	9.289	-.580
3600	15.801	80.166	67.680	44.951	109.495	6.425	-.390
3700	15.861	80.600	68.023	46.534	109.386	3.564	-.211
3800	15.915	81.023	68.360	48.123	109.280	.712	-.041
3900	15.963	81.438	68.690	49.716	109.172	-2.146	.120
4000	16.007	81.842	69.013	51.315	109.065	-4.995	.273
4100	16.046	82.238	69.331	52.918	108.955	-7.852	.419
4200	16.080	82.625	69.643	54.524	108.843	-10.693	.556
4300	16.110	83.004	69.949	56.134	108.728	-13.542	.688
4400	16.136	83.374	70.250	57.744	108.612	-16.383	.814
4500	16.158	83.737	70.546	59.361	108.492	-19.227	.934
4600	16.177	84.093	70.837	60.978	108.368	-22.063	1.048
4700	16.192	84.441	71.122	62.596	108.242	-24.895	1.158
4800	16.203	84.782	71.404	64.216	108.109	-27.724	1.262
4900	16.212	85.116	71.680	65.837	107.973	-30.552	1.363
5000	16.219	85.444	71.952	67.459	107.832	-33.380	1.459
5100	16.223	85.765	72.220	69.080	107.684	-36.210	1.552
5200	16.224	86.080	72.483	70.703	107.532	-39.027	1.640
5300	16.224	86.389	72.743	72.325	107.375	-41.839	1.725
5400	16.221	86.692	72.998	73.947	107.211	-44.651	1.807
5500	16.217	86.990	73.250	75.569	107.039	-47.464	1.886
5600	16.212	87.282	73.498	77.191	106.863	-50.273	1.962
5700	16.205	87.569	73.742	78.811	106.679	-53.083	2.035
5800	16.196	87.851	73.983	80.432	106.488	-55.886	2.106
5900	16.187	88.127	74.220	82.051	106.291	-58.670	2.173
6000	16.177	88.399	74.454	83.669	106.087	-61.475	2.239

Dec. 31, 1966; Mar. 31, 1967

CCH RADICAL (C_2H) (IDEAL GAS) GFW = 25.0303

Point Group [$C_{\infty v}$] ΔHf_0° = [113.3 ± 7] kcal/mol

$S^\circ_{298.15}$ = [49.55 ± 1.3] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [114 ± 7] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[9000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1920] (1)
[640] (2)
[3220] (1)

Bond Distance: C-C = [1.207]Å C-H = [1.061]Å

Bond Angle: C-C-H = [180°] σ = 1

Rotational Constant: B_0 = [1.475]cm^{-1}.

Heat of Formation.

The heat of formation of $C_2H(g)$ is not well established; however, we can place reliable upper and lower limits on the value.

T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, New York, 1958, gives an upper limit for the C-H bond dissociation energy in acetylene, D(HCC-H) $<$121 kcal. This was obtained from the fact that ultra-violet light of 121 kcal/mol energy causes acetylene to form diacetylene and hydrogen; assuming that this process occurs through the CCH radical, the light energy is equated with D(HCC-H). This value of D(HCC-H) gives an upper limit for ΔHf°_{298}(CCH,g) $<$123 kcal/mol.

A lower limit for D(HCC-H) is obtained from a consideration of the C-H bond dissociation energies in ethylene and ethane, D(C_2H_3-H) = 103 kcal and D(C_2H_5-H) = 98 kcal. The heats of formation of the C_2H_3 and C_2H_5 radicals and their parent compounds are taken from S. W. Benson, J. Chem. Educ. 42, 502 (1965). The vibrational frequency of the C-H stretch increases steadily from ethane to ethylene and acetylene. Similarly we expect the bond strength to increase, and so D(HCC-H) $>$103 kcal; this yields ΔHf°_{298}(CCH,g) $>$105 kcal/mol.

F. H. Coats and R. C. Anderson, J. Am. Chem. Soc. 79, 1340 (1957), obtained several values for ΔHf°_{298}(CCH,g) from mass-spectroscopic measurements; their values range from 110 kcal/mol to 153 kcal/mol, but they chose to adopt 112 ± 3 kcal/mol.

Our adopted value of ΔHf°_{298}(CCH,g), 114 ± 7 kcal/mol, is 2 kcal smaller than that estimated by W. Tsang, S. H. Bauer and M. Cowperthwaite, J. Chem. Phys. 36, 1768 (1962).

Heat Capacity and Entropy.

The molecule is assumed to be linear; the bond lengths are assumed to be the same as in acetylene and were taken from L. E. Sutton, "Interatomic Distances Supplement," Special Publication No. 18, The Chemical Society, London, 1965.

The vibrational frequencies are those estimated by M. N. Plooster and T. B. Reed, J. Chem. Phys. 31, 66 (1959). It should be noted that the values of the free energy function given by Plooster and Reed are incorrect due to the neglect of the electronic contributions.

The electronic levels, $X^2\Sigma$ and $A^2\Pi$, were estimated by analogy with those of CN(g) which is isoelectronic; this assumption holds very well in the parent molecules HCCH and HCN (G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966). The molecule $C_2H_2^+$, which is also isoelectronic with CCH, is predicted to have a $^2\Pi$ ground state by Herzberg, loc. cit.

Chloroacetylene (C_2HCl)

(Ideal Gas) GFW = 60.48327

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.817	50.896	50.896	INFINITE
100	7.828	46.738	67.777	-2.104	50.854	49.699	-108.616
200	10.774	53.065	58.935	-1.174	50.963	48.506	-53.004
298	12.982	57.811	57.811	.000	51.100	47.270	-34.650
300	13.015	57.892	57.812	.024	51.102	47.246	-34.419
400	14.394	61.840	58.341	1.400	51.224	45.942	-25.102
500	15.300	65.156	59.381	2.887	51.297	44.612	-19.500
600	15.971	68.007	60.587	4.452	51.322	43.271	-15.761
700	16.516	70.511	61.829	6.077	51.307	41.931	-13.091
800	16.981	72.748	63.057	7.753	51.268	40.594	-11.090
900	17.388	74.772	64.248	9.472	51.212	39.261	-9.534
1000	17.746	76.623	65.394	11.229	51.151	37.936	-8.291
1100	18.061	78.329	66.493	13.019	51.084	36.617	-7.275
1200	18.340	79.913	67.546	14.840	51.016	35.307	-6.430
1300	18.585	81.391	68.555	16.686	50.941	33.999	-5.716
1400	18.802	82.776	69.522	18.556	50.870	32.702	-5.105
1500	18.992	84.080	70.449	20.446	50.796	31.407	-4.576
1600	19.161	85.311	71.340	22.354	50.721	30.113	-4.113
1700	19.310	86.477	72.197	24.277	50.648	28.829	-3.706
1800	19.442	87.585	73.021	26.215	50.574	27.547	-3.345
1900	19.559	88.639	73.816	28.165	50.501	26.272	-3.022
2000	19.663	89.645	74.582	30.126	50.427	24.998	-2.732
2100	19.756	90.607	75.322	32.097	50.355	23.730	-2.470
2200	19.839	91.528	76.038	34.077	50.278	22.460	-2.231
2300	19.914	92.412	76.731	36.065	50.202	21.202	-2.015
2400	19.981	93.260	77.402	38.060	50.123	19.942	-1.816
2500	20.042	94.077	78.053	40.061	50.043	18.683	-1.633
2600	20.097	94.865	78.685	42.068	49.960	17.432	-1.465
2700	20.147	95.624	79.298	44.080	49.874	16.180	-1.310
2800	20.192	96.358	79.894	46.097	49.787	14.936	-1.166
2900	20.233	97.067	80.474	48.119	49.695	13.694	-1.032
3000	20.271	97.753	81.039	50.144	49.600	12.452	-.907
3100	20.306	98.419	81.589	52.173	49.504	11.217	-.791
3200	20.337	99.064	82.125	54.205	49.402	9.983	-.682
3300	20.367	99.690	82.648	56.240	49.295	8.749	-.579
3400	20.393	100.299	83.158	58.278	49.186	7.526	-.484
3500	20.418	100.890	83.656	60.319	49.071	6.297	-.393
3600	20.441	101.466	84.143	62.362	48.953	5.078	-.308
3700	20.462	102.026	84.619	64.407	48.828	3.863	-.228
3800	20.482	102.572	85.084	66.454	48.702	2.652	-.153
3900	20.500	103.104	85.539	68.503	48.568	1.444	-.081
4000	20.517	103.623	85.985	70.554	48.431	.238	-.013
4100	20.533	104.130	86.421	72.607	48.289	-.971	.052
4200	20.548	104.625	86.849	74.661	48.141	-2.165	.113
4300	20.562	105.109	87.268	76.716	47.987	-3.365	.171
4400	20.575	105.582	87.679	78.773	47.830	-4.557	.226
4500	20.587	106.044	88.082	80.831	47.667	-5.751	.279
4600	20.599	106.497	88.477	82.891	47.499	-6.932	.329
4700	20.610	106.940	88.865	84.951	47.327	-8.112	.377
4800	20.620	107.374	89.246	87.013	47.148	-9.288	.423
4900	20.629	107.799	89.621	89.075	46.966	-10.461	.467
5000	20.638	108.216	89.988	91.138	46.778	-11.633	.508
5100	20.647	108.625	90.350	93.203	46.583	-12.806	.549
5200	20.655	109.026	90.705	95.268	46.385	-13.965	.587
5300	20.663	109.419	91.055	97.334	46.182	-15.120	.623
5400	20.670	109.806	91.398	99.400	45.973	-16.274	.659
5500	20.677	110.185	91.736	101.468	45.757	-17.424	.692
5600	20.683	110.558	92.069	103.536	45.538	-18.574	.725
5700	20.689	110.924	92.397	105.604	45.312	-19.724	.756
5800	20.695	111.284	92.719	107.673	45.080	-20.861	.786
5900	20.701	111.638	93.037	109.743	44.844	-21.988	.815
6000	20.706	111.986	93.350	111.814	44.602	-23.129	.842

Dec. 31, 1968

Point Group $C_{\infty v}$ ΔHf°_0 = [50.9 ± 10] kcal/mol

$S^\circ_{298.15}$ = 57.811 gibbs/mol $\Delta Hf^\circ_{298.15}$ = [51.1 ± 10] kcal/mol

Ground State Quantum Weight = 1

Vibrational Freqencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
3340 (1)	604 (2)
2110 (1)	326 (2)
756 (1)	

Bond Distances: C-C = 1.204Å C-H = 1.055Å C-Cl = 1.637Å

Bond Angles: Cl-C-C = 180° C-C-H = 180° $\sigma = 1$

Rotational Constant: $B_0 = 0.188641\ cm^{-1}$

Heat of Formation

The value of ΔHf°_{298} = 51.1 kcal/mol is calculated from the estimated ΔHr°_{298} = -53 ± 10 kcal/mol for HC≡CCl(g) + Cl_2(g) → CHCl=CCl_2(g), using ΔHf°_{298}(CHCl=CCl_2, g) = -1.86 kcal/mol (1). The value of ΔHr°_{298} is assumed to be the same as that for the reaction HC≡CH(g) + Cl_2(g) → CHCl=CHCl(g), using ΔHf°_{298}(C_2H_2, g) = 54.19 kcal/mol (1) and ΔHf°_{298}(CHCl=CHCl, g) = 1.2 kcal/mol (2).

Heat Capacity and Entropy

The linear molecular structure and bond distances were determined from the microwave spectrometrical studies by Tyler and Sheridan (3). Their results are in good agreement with those of Westenberg, Goldstein and Wilson (4). The principal moment of inertia is 1.48381×10^{-38} g cm^2.

The vibrational frequencies were observed in the infrared spectra by Hunt and Wilson (5), and Richardson and Goldstein (6).

References

(1) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.

(2) This is an average value of 0.9 and 1.47 kcal/mol for cis- and trans- CHCl = CHCl(g), respectively which are obtained from reference (1).

(3) J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963).

(4) A. A. Westenberg, J. H. Goldstein and E. B. Wilson, Jr., J. Chem. Phys. 17, 1319 (1949).

(5) G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961).

(6) W. S. Richardson and J. H. Goldstein, J. Chem. Phys. 18, 1314 (1950).

Monofluoroacetylene (C_2HF)

(Ideal Gas) GFW = 44.02867

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.737	29.834	29.834	INFINITE
100	7.591	44.639	64.942	-2.030	29.786	28.618	-62.544
200	10.404	50.753	56.412	-1.132	29.877	27.420	-29.964
298	12.505	55.329	55.329	.000	30.000	26.188	-19.197
300	12.536	55.407	55.330	.023	30.002	26.164	-19.061
400	13.907	59.215	55.840	1.350	30.105	24.869	-13.588
500	14.852	62.425	56.844	2.791	30.154	23.553	-10.295
600	15.570	65.199	58.011	4.313	30.155	22.232	-8.098
700	16.159	67.645	59.216	5.900	30.115	20.915	-6.530
800	16.564	69.836	60.409	7.542	30.053	19.605	-5.356
900	17.105	71.825	61.568	9.231	29.974	18.301	-4.444
1000	17.494	73.648	62.686	10.962	29.891	17.009	-3.717
1100	17.837	75.332	63.760	12.728	29.803	15.724	-3.124
1200	18.139	76.897	64.791	14.528	29.715	14.450	-2.632
1300	18.405	78.360	65.779	16.355	29.620	13.181	-2.216
1400	18.639	79.732	66.727	18.207	29.530	11.922	-1.861
1500	18.845	81.025	67.637	20.082	29.438	10.668	-1.554
1600	19.028	82.248	68.513	21.976	29.346	9.416	-1.286
1700	19.188	83.406	69.355	23.887	29.256	8.174	-1.051
1800	19.331	84.507	70.166	25.813	29.165	6.936	-.842
1900	19.457	85.556	70.949	27.752	29.075	5.705	-.656
2000	19.570	86.557	71.705	29.704	28.986	4.479	-.489
2100	19.670	87.514	72.435	31.666	28.897	3.256	-.339
2200	19.760	88.431	73.141	33.637	28.804	2.033	-.202
2300	19.841	89.311	73.825	35.618	28.713	.823	-.078
2400	19.913	90.157	74.488	37.605	28.618	-.388	.035
2500	19.979	90.971	75.131	39.600	28.523	-1.598	.140
2600	20.038	91.756	75.756	41.601	28.424	-2.799	.235
2700	20.092	92.513	76.362	43.607	28.325	-4.001	.324
2800	20.141	93.245	76.952	45.619	28.225	-5.195	.405
2900	20.185	93.953	77.527	47.635	28.119	-6.384	.481
3000	20.226	94.638	78.086	49.656	28.011	-7.575	.552
3100	20.263	95.301	78.630	51.680	27.902	-8.758	.617
3200	20.297	95.945	79.161	53.708	27.789	-9.938	.679
3300	20.328	96.570	79.679	55.740	27.671	-11.119	.736
3400	20.357	97.178	80.185	57.774	27.552	-12.290	.790
3500	20.384	97.768	80.679	59.811	27.426	-13.463	.841
3600	20.409	98.343	81.162	61.851	27.299	-14.629	.888
3700	20.432	98.902	81.634	63.893	27.165	-15.790	.933
3800	20.453	99.447	82.095	65.937	27.030	-16.945	.975
3900	20.473	99.979	82.547	67.983	26.887	-18.100	1.014
4000	20.491	100.497	82.990	70.032	26.743	-19.251	1.052
4100	20.508	101.004	83.423	72.082	26.592	-20.405	1.088
4200	20.524	101.498	83.847	74.133	26.436	-21.543	1.121
4300	20.539	101.981	84.263	76.186	26.274	-22.686	1.153
4400	20.553	102.454	84.671	78.241	26.108	-23.825	1.183
4500	20.566	102.916	85.072	80.297	25.937	-24.963	1.212
4600	20.579	103.368	85.465	82.354	25.760	-26.087	1.239
4700	20.590	103.810	85.850	84.413	25.579	-27.211	1.265
4800	20.601	104.244	86.229	86.472	25.390	-28.329	1.290
4900	20.611	104.669	86.601	88.533	25.197	-29.447	1.313
5000	20.621	105.085	86.965	90.594	24.998	-30.561	1.336
5100	20.630	105.494	87.326	92.657	24.792	-31.680	1.358
5200	20.639	105.895	87.679	94.721	24.581	-32.780	1.378
5300	20.647	106.288	88.026	96.785	24.364	-33.876	1.397
5400	20.655	106.674	88.368	98.850	24.141	-34.974	1.415
5500	20.662	107.053	88.704	100.916	23.910	-36.066	1.433
5600	20.669	107.425	89.035	102.982	23.675	-37.156	1.450
5700	20.676	107.791	89.361	105.050	23.432	-38.245	1.466
5800	20.682	108.151	89.682	107.118	23.183	-39.325	1.482
5900	20.688	108.504	89.998	109.186	22.927	-40.393	1.496
6000	20.694	108.852	90.310	111.255	22.666	-41.475	1.511

Dec. 31, 1967

MONOFLUOROACETYLENE (C_2HF) (IDEAL GAS) GFW = 44.02867

Point Group $C_{\infty v}$

ΔHf°_0 = [30 ± 15] kcal/mol

$S^\circ_{298.15}$ = 55.33 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [30 ± 15] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
3360 (1)
2250 (1)
1060 (1)
580 (2)
367 (2)

Bond Distances: C-F = 1.279 Å C-C = 1.198 Å C-H = 1.053 Å

Bond Angles: F-C-C = 180° C-C-H = 180° σ = 1

Rotational Constant: B_0 = 0.323571 cm^{-1}

Heat of Formation

The heat of formation is estimated by assuming that the C-C bond strength is the average of those in C_2F_2(113 kcal) and C_2H_2(229 kcal). Combining the average value (171 kcal) with the heats of formation of CF and CH from the JANAF Tables, yields $\Delta Hf^\circ_{298}(C_2HF, g)$ = 30 ± 15 kcal/mol.

Heat Capacity and Entropy

G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. (London) 1961, 13 (1961), have reported the infrared spectrum and have assigned the fundamental frequencies. The frequencies used in the present table are median values of the two sets and are generally within 5 cm^{-1} of each set.

The molecule has been shown to be linear by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963), who reported the rotational constant B_0.

The electronic ground state is assumed to be $^1\Sigma$ by analogy with C_2H_2.

Acetylene (C_2H_2)

(Ideal Gas) Mol. Wt. = 26.038

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.393	54.325	54.325	INFINITE
100	7.014	39.002	55.982	- 1.698	54.233	52.814	- 115.418
200	8.505	44.213	48.903	- .938	54.234	51.383	- 56.146
298	10.539	48.004	48.004	.000	54.190	49.993	- 36.644
300	10.571	48.069	48.004	.020	54.189	49.966	- 36.399
400	12.065	51.326	48.438	1.155	54.138	48.567	- 26.534
500	13.114	54.139	49.303	2.418	54.064	47.181	- 20.622
600	13.931	56.604	50.319	3.771	53.961	45.813	- 16.687
700	14.615	58.805	51.377	5.199	53.837	44.466	- 13.882
800	15.239	60.798	52.432	6.693	53.707	43.137	- 11.784
900	15.801	62.625	53.464	8.245	53.573	41.821	- 10.155
1000	16.318	64.317	54.466	9.852	53.450	40.522	- 8.856
1100	16.769	65.895	55.434	11.507	53.333	39.234	- 7.795
1200	17.221	67.375	56.368	13.208	53.228	37.960	- 6.913
1300	17.613	68.769	57.269	14.950	53.128	36.690	- 6.168
1400	17.968	70.087	58.138	16.729	53.041	35.432	- 5.531
1500	18.291	71.338	58.977	18.543	52.961	34.177	- 4.979
1600	18.582	72.528	59.787	20.387	52.887	32.923	- 4.497
1700	18.845	73.663	60.570	22.258	52.823	31.679	- 4.072
1800	19.085	74.747	61.327	24.155	52.765	30.436	- 3.695
1900	19.302	75.785	62.061	26.074	52.714	29.199	- 3.358
2000	19.504	76.780	62.772	28.015	52.670	27.962	- 3.055
2100	19.684	77.736	63.462	29.974	52.631	26.730	- 2.782
2200	19.853	78.656	64.132	31.951	52.594	25.493	- 2.532
2300	20.004	79.541	64.783	33.944	52.564	24.266	- 2.306
2400	20.151	80.396	65.416	35.952	52.535	23.037	- 2.098
2500	20.282	81.221	66.032	37.974	52.510	21.804	- 1.906
2600	20.404	82.019	66.631	40.008	52.486	20.579	- 1.730
2700	20.519	82.791	67.216	42.055	52.466	19.349	- 1.566
2800	20.625	83.540	67.785	44.112	52.448	18.124	- 1.415
2900	20.726	84.265	68.341	46.179	52.429	16.901	- 1.274
3000	20.820	84.969	68.884	48.257	52.413	15.674	- 1.142
3100	20.910	85.654	69.414	50.343	52.399	14.451	- 1.019
3200	20.996	86.319	69.932	52.439	52.385	13.227	- .903
3300	21.078	86.966	70.438	54.542	52.369	12.000	- .795
3400	21.154	87.596	70.934	56.654	52.356	10.779	- .693
3500	21.225	88.211	71.418	58.773	52.340	9.554	- .597
3600	21.297	88.810	71.893	60.899	52.325	8.331	- .506
3700	21.367	89.394	72.358	63.032	52.307	7.111	- .420
3800	21.431	89.965	72.814	65.172	52.291	5.894	- .339
3900	21.494	90.522	73.261	67.319	52.272	4.675	- .262
4000	21.557	91.067	73.699	69.471	52.252	3.455	- .189
4100	21.615	91.600	74.130	71.630	52.231	2.230	- .119
4200	21.670	92.122	74.552	73.794	52.206	1.017	- .053
4300	21.728	92.632	74.966	75.964	52.179	- .205	.010
4400	21.782	93.133	75.374	78.139	52.151	- 1.425	.071
4500	21.835	93.623	75.774	80.320	52.120	- 2.648	.129
4600	21.883	94.103	76.167	82.506	52.087	- 3.858	.183
4700	21.935	94.574	76.554	84.697	52.052	- 5.073	.236
4800	21.985	95.037	76.934	86.893	52.013	- 6.286	.286
4900	22.036	95.490	77.308	89.094	51.973	- 7.500	.335
5000	22.077	95.936	77.676	91.300	51.930	- 8.715	.381
5100	22.129	96.374	78.038	93.510	51.881	- 9.935	.426
5200	22.174	96.804	78.395	95.725	51.832	- 11.144	.468
5300	22.219	97.227	78.746	97.945	51.780	- 12.348	.509
5400	22.263	97.642	79.093	100.169	51.724	- 13.559	.549
5500	22.309	98.051	79.434	102.397	51.663	- 14.767	.587
5600	22.349	98.454	79.770	104.630	51.601	- 15.977	.624
5700	22.393	98.850	80.101	106.867	51.534	- 17.188	.659
5800	22.433	99.239	80.428	109.108	51.463	- 18.394	.693
5900	22.474	99.623	80.750	111.354	51.390	- 19.588	.726
6000	22.521	100.001	81.067	113.603	51.313	- 20.802	.758

March 31, 1961

ACETYLENE (C_2H_2) (IDEAL GAS) MOL. WT. = 26.038

$\Delta H^\circ_{f0} = 54.33 \pm 0.19$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 54.19 \pm 0.19$ kcal. mole^{-1}

Point Group $D_{\infty h}$

$S^\circ_{298.15} = 48.004$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
3373.7 (1)
1973.8 (1)
3281.9 (1)
611.6 (2)
729.3 (2)

Rotational Constant $B_0 = 1.17684 \pm 0.00016$ cm.$^{-1}$ $\sigma = 2$

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.$^{-1}$):

$X_{11} = -24.08$ $X_{22} = -7.92$ $X_{34} = -9.06$ $D_0 = 2.19 \times 10^{-6}$

$X_{12} = -16.94$ $X_{23} = -1.38$ $X_{35} = -5.73$ $g_{44} = 1.1$

$X_{13} = -99.01$ $X_{24} = -6.15$ $X_{44} = 5.38$ $g_{55} = 2.49$

$X_{14} = -16.46$ $X_{25} = -0.85$ $X_{45} = -12.65$

$X_{15} = -11.75$ $X_{33} = -25.69$ $X_{55} = -2.27$

Values of α_1 not available.

Heat of Formation

Taken from D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, J. Research Natl. Bureau Standards 35, 467 (1945).

Heat Capacity and Entropy

J. S. Gordon (private communication, February, 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). The constants are from E. E. Bell and H. H. Nielsen, J. Chem. Phys. 18, 1382 (1950) and H. C. Allen, E. D. Tidwell, and E. K. Plyler, J. Research Natl. Bureau Standards 57, 213 (1956). Heat capacities below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Ethylene (C_2H_4)

(Ideal Gas) Mol. Wt. = 28.05418

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.514	14.578	14.578	INFINITE
100	7.952	43.125	60.316	-1.719	13.827	14.434	-31.544
200	8.451	48.721	53.267	-.909	13.275	15.227	-16.638
298	10.250	52.396	52.396	.000	12.540	16.338	-11.975
300	10.292	52.459	52.396	.019	12.525	16.361	-11.918
400	12.679	55.745	52.828	1.167	11.793	17.752	-9.699
500	14.933	58.821	53.722	2.550	11.140	19.319	-8.444
600	16.889	61.721	54.816	4.143	10.577	21.008	-7.652
700	18.574	64.454	55.999	5.918	10.098	22.788	-7.114
800	20.039	67.033	57.219	7.851	9.701	24.628	-6.728
900	21.320	69.468	58.446	9.920	9.372	26.514	-6.438
1000	22.443	71.774	59.665	12.109	9.113	28.431	-6.213
1100	23.427	73.960	60.866	14.404	8.910	30.373	-6.034
1200	24.290	76.036	62.044	16.791	8.757	32.334	-5.889
1300	25.044	78.011	63.197	19.258	8.638	34.302	-5.766
1400	25.706	79.892	64.323	21.797	8.557	36.282	-5.664
1500	26.285	81.686	65.421	24.397	8.497	38.266	-5.575
1600	26.794	83.399	66.492	27.051	8.455	40.246	-5.497
1700	27.242	85.037	67.535	29.753	8.435	42.237	-5.430
1800	27.636	86.605	68.551	32.498	8.428	44.224	-5.369
1900	27.986	88.109	69.541	35.279	8.433	46.215	-5.316
2000	28.296	89.552	70.506	38.094	8.448	48.204	-5.267
2100	28.571	90.940	71.446	40.937	8.469	50.192	-5.223
2200	28.818	92.275	72.362	43.807	8.493	52.174	-5.183
2300	29.038	93.561	73.256	46.700	8.524	54.163	-5.146
2400	29.236	94.801	74.128	49.614	8.554	56.148	-5.113
2500	29.414	95.998	74.979	52.546	8.584	58.124	-5.081
2600	29.575	97.155	75.810	55.496	8.616	60.109	-5.052
2700	29.721	98.274	76.621	58.461	8.647	62.085	-5.025
2800	29.853	99.357	77.414	61.440	8.678	64.064	-5.000
2900	29.973	100.407	78.189	64.431	8.705	66.047	-4.977
3000	30.083	101.425	78.947	67.434	8.730	68.019	-4.955
3100	30.184	102.413	79.688	70.447	8.755	69.996	-4.934
3200	30.276	103.373	80.413	73.470	8.774	71.971	-4.915
3300	30.360	104.305	81.123	76.502	8.788	73.947	-4.897
3400	30.438	105.213	81.818	79.542	8.800	75.920	-4.880
3500	30.510	106.096	82.499	82.590	8.804	77.894	-4.864
3600	30.577	106.957	83.167	85.644	8.804	79.864	-4.848
3700	30.638	107.795	83.821	88.705	8.795	81.844	-4.834
3800	30.695	108.613	84.463	91.772	8.784	83.822	-4.821
3900	30.748	109.411	85.092	94.844	8.762	85.798	-4.808
4000	30.797	110.190	85.710	97.921	8.735	87.775	-4.796
4100	30.843	110.951	86.317	101.003	8.701	89.746	-4.784
4200	30.886	111.695	86.912	104.090	8.658	91.729	-4.773
4300	30.926	112.422	87.497	107.180	8.606	93.703	-4.762
4400	30.964	113.134	88.071	110.275	8.549	95.678	-4.752
4500	30.999	113.830	88.636	113.373	8.481	97.653	-4.742
4600	31.032	114.512	89.191	116.475	8.407	99.643	-4.734
4700	31.063	115.180	89.737	119.579	8.323	101.628	-4.725
4800	31.093	115.834	90.274	122.687	8.231	103.617	-4.718
4900	31.120	116.475	90.802	125.798	8.132	105.608	-4.710
5000	31.146	117.104	91.322	128.911	8.023	107.593	-4.703
5100	31.171	117.721	91.834	132.027	7.903	109.582	-4.696
5200	31.194	118.327	92.337	135.145	7.777	111.574	-4.689
5300	31.216	118.921	92.833	138.266	7.642	113.583	-4.683
5400	31.236	119.505	93.322	141.388	7.496	115.577	-4.677
5500	31.256	120.078	93.803	144.513	7.341	117.583	-4.672
5600	31.275	120.641	94.277	147.639	7.177	119.586	-4.667
5700	31.292	121.195	94.745	150.768	7.004	121.591	-4.662
5800	31.309	121.740	95.205	153.898	6.820	123.597	-4.657
5900	31.325	122.275	95.660	157.030	6.628	125.625	-4.653
6000	31.340	122.802	96.108	160.163	6.427	127.627	-4.649

Dec. 31, 1960; Sept. 30, 1965

ETHYLENE (C_2H_4) (IDEAL GAS) MOL. WT. = 28.05418

Point Group D_{2h}

$S^\circ_{298.15}$ = 52.396 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = 14.58 ± 0.07 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 12.54 ± 0.07 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
3026.4 (1)	3102.5 (1)	3105.5 (1)
1622.9 (1)	1222.0 (1)	826.0 (1)
1342.2 (1)	949.3 (1)	2988.7 (1)
1023.0 (1)	943.0 (1)	1443.5 (1)

Bond Distance: H-C = 1.086 Å C-C = 1.337 Å

Bond Angle: H-C-H = 117° 22' H-C-C = 121° 19'

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 5.4466 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of combustion of ethylene was measured by F. D. Rossini and J. W. Knowlton, J. Res. Natl. Bur. Std. 19, 249 (1937). From the value, $\Delta H^\circ_{r\ 298.15} = -337.28 \pm 0.07$ kcal. mole^{-1} for the reaction $C_2H_4(g) + 3\ O_2(g) = 2\ CO_2(g) + 2\ H_2O(l)$, the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for $C_2H_4(g)$ was derived to be 12.54 ± 0.07 kcal. mole^{-1}. The values of $\Delta H^\circ_{f\ 298.15}$ for $CO_2(g)$ and $H_2O(l)$ used for calculation were obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and Irving Jaffe, "Selected Values of Chemical Thermodynamic Properties", Circular of the National Bureau of Standards 500, 1952.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Am. Chem. Soc. 80, 2673 (1958). The vibrational frequencies were taken from W. L. Smith and I. M. Mills, J. Chem. Phys. 40, 2095 (1964). Eight of the twelve frequencies were reported by R. L. Arnett and B. L. Crawford, J. Chem. Phys. 18, 118 (1950); B. L. Crawford, J. E. Lancaster and R. Inskeep, J. Chem. Phys. 21, 678 (1953); B. P. Stoicheff, J. Chem. Phys. 21, 755 (1953); T. Feldman, J. Romanko and H. L. Welsh, Can. J. Phys. 34, 737 (1956); and H. C. Allen and E. K. Plyler, loc. cit. G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, 1945, also reported the vibrational frequencies for ethylene as 3019.3 (1), 1623.3 (1), 1342.4 (1), 825.0 (1), 3272.3 (1), 1050 (1), 949.2 (1), 943 (1), 3105.5 (1), 995 (1), 2989.5 (1) and 1443.5 (1) which are very close to the values adopted. The infrared and Raman spectra of ethylene before 1945 have been summarized by G. Herzberg, loc. cit. The molecular structure of ethylene was also determined by L. S. Bartell and R. A. Bonham, J. Chem. Phys. 27, 1414 (1957). Their results, $r_{C-H} = 1.085$ Å, $r_{C-C} = 1.334$ Å and ∡ H-C-H = 116° are in excellent agreement with the values adopted. The three principal moments of inertia are $I_A = 0.5762 \times 10^{-39}$, $I_B = 2.7999 \times 10^{-39}$ and $I_C = 3.3761 \times 10^{-39}$ g. cm.^{2}

Ethylene Oxide (C_2H_4O)

(Ideal Gas) Mol. Wt. = 44.05358

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.596	-9.587	-9.587	INFINITE
100	7.956	48.444	66.457	-1.801	-10.694	-8.543	18.670
200	8.772	54.102	59.006	-.981	-11.576	-6.077	6.640
298	11.449	58.056	58.056	.000	-12.580	-3.164	2.319
300	11.510	58.127	58.056	.021	-12.599	-3.107	2.263
400	14.913	61.904	58.548	1.342	-13.514	.201	-.110
500	18.023	65.575	59.589	2.993	-14.264	3.719	-1.625
600	20.629	69.099	60.882	4.930	-14.861	7.373	-2.685
700	22.793	72.446	62.297	7.104	-15.330	11.119	-3.471
800	24.611	75.612	63.766	9.477	-15.686	14.922	-4.076
900	26.155	78.602	65.250	12.017	-15.951	18.764	-4.556
1000	27.477	81.428	66.727	14.701	-16.129	22.631	-4.946
1100	28.615	84.102	68.187	17.507	-16.240	26.512	-5.267
1200	29.597	86.635	69.619	20.418	-16.293	30.404	-5.537
1300	30.447	89.038	71.021	23.422	-16.304	34.294	-5.765
1400	31.184	91.322	72.391	26.504	-16.273	38.189	-5.961
1500	31.826	93.496	73.726	29.655	-16.218	42.078	-6.131
1600	32.386	95.568	75.027	32.867	-16.141	45.957	-6.277
1700	32.876	97.547	76.294	36.130	-16.040	49.837	-6.407
1800	33.306	99.438	77.527	39.440	-15.927	53.708	-6.521
1900	33.686	101.249	78.728	42.790	-15.801	57.576	-6.622
2000	34.022	102.986	79.898	46.175	-15.665	61.433	-6.713
2100	34.319	104.653	81.038	49.593	-15.522	65.288	-6.794
2200	34.585	106.256	82.148	53.038	-15.379	69.128	-6.867
2300	34.822	107.799	83.230	56.509	-15.228	72.969	-6.933
2400	35.034	109.285	84.284	60.002	-15.080	76.804	-6.994
2500	35.226	110.719	85.313	63.515	-14.933	80.622	-7.048
2600	35.398	112.104	86.317	67.046	-14.786	84.446	-7.098
2700	35.554	113.443	87.297	70.594	-14.641	88.256	-7.143
2800	35.695	114.739	88.254	74.157	-14.498	92.063	-7.186
2900	35.824	115.994	89.189	77.733	-14.360	95.872	-7.225
3000	35.941	117.210	90.103	81.321	-14.226	99.667	-7.260
3100	36.048	118.390	90.997	84.921	-14.093	103.464	-7.294
3200	36.146	119.537	91.871	88.530	-13.968	107.251	-7.325
3300	36.237	120.650	92.726	92.150	-13.850	111.037	-7.353
3400	36.319	121.733	93.563	95.777	-13.736	114.820	-7.380
3500	36.396	122.787	94.383	99.413	-13.631	118.597	-7.405
3600	36.466	123.813	95.187	103.056	-13.531	122.375	-7.429
3700	36.532	124.814	95.974	106.706	-13.442	126.148	-7.451
3800	36.592	125.789	96.746	110.363	-13.356	129.925	-7.472
3900	36.649	126.740	97.503	114.025	-13.282	133.696	-7.492
4000	36.701	127.668	98.245	117.692	-13.214	137.466	-7.510
4100	36.750	128.575	98.974	121.365	-13.155	141.226	-7.528
4200	36.795	129.461	99.689	125.042	-13.106	144.998	-7.545
4300	36.838	130.328	100.392	128.724	-13.067	148.755	-7.560
4400	36.878	131.175	101.082	132.410	-13.034	152.516	-7.575
4500	36.915	132.004	101.760	136.099	-13.013	156.272	-7.589
4600	36.950	132.816	102.426	139.793	-12.999	160.043	-7.603
4700	36.983	133.611	103.081	143.489	-12.996	163.806	-7.617
4800	37.014	134.390	103.725	147.189	-13.001	167.570	-7.629
4900	37.043	135.153	104.359	150.892	-13.015	171.333	-7.641
5000	37.071	135.902	104.982	154.598	-13.039	175.089	-7.653
5100	37.097	136.636	105.596	158.306	-13.075	178.851	-7.664
5200	37.121	137.357	106.200	162.017	-13.117	182.611	-7.675
5300	37.144	138.064	106.794	165.730	-13.169	186.389	-7.686
5400	37.166	138.759	107.380	169.446	-13.232	190.145	-7.695
5500	37.187	139.441	107.957	173.164	-13.305	193.916	-7.705
5600	37.207	140.111	108.525	176.883	-13.387	197.680	-7.714
5700	37.226	140.770	109.085	180.605	-13.480	201.445	-7.723
5800	37.243	141.417	109.637	184.328	-13.583	205.219	-7.733
5900	37.260	142.054	110.181	188.054	-13.694	209.001	-7.742
6000	37.277	142.681	110.717	191.780	-13.815	212.760	-7.749

Dec. 31, 1960; Sept. 30, 1965

ETHYLENE OXIDE (C_2H_4O) (IDEAL GAS) MOL. WT. = 44.05358

Point Group C_{2v}

$S^\circ_{298.15}$ = 58.06 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -9.59 ± 0.15 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -12.58 ± 0.15 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
3005 (1)	3063 (1)	1153 (1)
1490 (1)	[1345](1)	892 (1)
1266 (1)	807 (1)	3079 (1)
1120 (1)	3019 (1)	1143 (1)
877 (1)	1470 (1)	832 (1)

Bond Distance: C-H = 1.0802 Å C-O = 1.4363 Å C-C = 1.4728 Å

Bond Angle: H-C-H = 116° 51' H_2-C-C = 158° 5'

H_2-C-O = 142° 45.6'

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 7.42336 \times 10^{-116}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of combustion of ethylene oxide (g) was determined by A. S. Pell and G. Pilcher, Trans. Faraday Soc. 61, 71 (1965) and R. S. Crog and H. Hunt, J. Phys. Chem. 46, 1162 (1942), as -312.15 ± 0.14 and -312.55 ± 0.20 kcal. mole^{-1}, respectively. The corresponding value of $\Delta H^\circ_{f\ 298.15}$ (C_2H_4O, g) was evaluated to be -12.58 ± 0.15 and -12.19 ± 0.22 kcal. mole^{-1}. The former value is adopted.

Heat Capacity and Entropy.

The vibrational frequencies were taken from R. C. Lord and B. Nolin, J. Chem. Phys. 24, 656 (1956). The infrared and Raman sepctra of ethylene oxide have also been examined by J. W. Linnett, J. Chem Phys. 6, 692 (1938) and H. W. Thompson and W. T. Cave, Trans. Faraday Soc., 47, 946 (1951). The vibrational frequencies assigned were slightly different from the ones reported by R. C. Lord and B. Nolin, loc. cit. As a result of analogies between ethylene oxide and ethylene imine, small changes of R. C. Lord and B. Nolin's assignment have been made by W. J. Potts, Spectrochim. Acta, 21, 511 (1965). The bond distances and angles were obtained from G. L. Cunningham, A. W. Boyd and W. D. Gwinn, J. Chem. Phys. 17, 211 (1949). The investigation of the structure of ethylene oxide by electron diffraction was reported by P. C. Ackermann and J. E. Mayer, J. Chem. Phys. 4, 377 (1936) and M. Igarashi, Bull. Chem. Soc. Japan, 26, 330 (1953). The three principal moments of inertia are: $I_A = 3.8052 \times 10^{-39}$, $I_B = 3.2788 \times 10^{-39}$ and $I_C = 5.9499 \times 10^{-39}$ g. cm.^{2}

The calculated heat capacities (307.2 - 371.2°K.) are in good agreement with the experimentally measured ones reported by G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. 8, 618 (1940).

Potassium Cyanide, Dimeric $((KCN)_2)$

(Ideal Gas) Mol. Wt. = 130.2397

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 5.924	- 1.962	- 1.962	INFINITE
100	18.534	63.656	111.235	- 4.758	- 2.337	- 3.147	6.879
200	24.722	78.921	91.523	- 2.520	- 2.198	- 3.983	4.353
298	26.353	89.153	89.153	.000	- 2.000	- 4.907	3.597
300	26.371	89.316	89.153	.049	- 1.998	- 4.925	3.588
400	27.081	97.009	90.197	2.725	- 3.139	- 5.690	3.109
500	27.586	103.108	92.190	5.459	- 3.232	- 6.319	2.762
600	28.050	108.179	94.444	8.241	- 3.370	- 6.924	2.522
700	28.489	112.536	96.725	11.068	- 3.553	- 7.501	2.342
800	28.893	116.367	98.945	13.937	- 3.769	- 8.051	2.199
900	29.252	119.791	101.075	16.845	- 4.018	- 8.573	2.082
1000	29.565	122.890	103.104	19.786	- 4.305	- 9.066	1.981
1100	29.834	125.721	105.033	22.756	- 42.443	- 7.479	1.486
1200	30.064	128.327	106.867	25.752	- 42.314	- 4.303	.784
1300	30.261	130.741	108.612	28.768	- 42.201	- 1.143	.192
1400	30.429	132.990	110.274	31.803	- 42.093	2.015	- .315
1500	30.573	135.094	111.859	34.853	- 41.994	5.163	- .752
1600	30.697	137.072	113.374	37.917	- 41.900	8.302	- 1.134
1700	30.804	138.936	114.823	40.992	- 41.812	11.434	- 1.470
1800	30.897	140.699	116.212	44.077	- 41.730	14.565	- 1.768
1900	30.979	142.372	117.545	47.171	- 41.653	17.692	- 2.035
2000	31.050	143.963	118.827	50.273	- 41.579	20.815	- 2.275
2100	31.112	145.479	120.060	53.381	- 41.511	23.935	- 2.491
2200	31.167	146.928	121.249	56.495	- 41.455	27.046	- 2.687
2300	31.216	148.315	122.395	59.614	- 41.403	30.159	- 2.866
2400	31.260	149.644	123.503	62.738	- 41.360	33.270	- 3.030
2500	31.299	150.921	124.575	65.866	- 41.329	36.376	- 3.180
2600	31.334	152.149	125.612	68.998	- 41.308	39.489	- 3.319
2700	31.365	153.332	126.617	72.133	- 41.300	42.591	- 3.448
2800	31.394	154.474	127.591	75.271	- 41.307	45.697	- 3.567
2900	31.419	155.576	128.537	78.411	- 41.331	48.810	- 3.678
3000	31.443	156.641	129.456	81.554	- 41.371	51.917	- 3.782
3100	31.464	157.673	130.350	84.700	- 41.431	55.028	- 3.879
3200	31.483	158.672	131.220	87.847	- 41.514	58.144	- 3.971
3300	31.501	159.641	132.066	90.996	- 41.623	61.252	- 4.057
3400	31.518	160.582	132.891	94.147	- 41.758	64.373	- 4.138
3500	31.533	161.495	133.695	97.300	- 41.923	67.494	- 4.215
3600	31.547	162.384	134.480	100.454	- 42.123	70.625	- 4.288
3700	31.559	163.248	135.246	103.609	- 42.360	73.761	- 4.357
3800	31.571	164.090	135.994	106.766	- 42.639	76.905	- 4.423
3900	31.582	164.910	136.725	109.923	- 42.964	80.058	- 4.486
4000	31.592	165.710	137.440	113.082	- 43.339	83.217	- 4.547
4100	31.602	166.490	138.139	116.242	- 43.772	86.382	- 4.605
4200	31.611	167.252	138.823	119.402	- 44.270	89.568	- 4.661
4300	31.619	167.996	139.493	122.564	- 44.832	92.759	- 4.715
4400	31.627	168.723	140.149	125.726	- 45.472	95.962	- 4.766
4500	31.634	169.434	140.792	128.889	- 46.192	99.185	- 4.817
4600	31.641	170.129	141.422	132.053	- 46.999	102.427	- 4.866
4700	31.647	170.810	142.040	135.217	- 47.899	105.683	- 4.914
4800	31.653	171.476	142.646	138.382	- 48.902	108.970	- 4.962
4900	31.659	172.129	143.241	141.548	- 50.010	112.263	- 5.007
5000	31.664	172.768	143.826	144.714	- 51.229	115.591	- 5.052
5100	31.669	173.395	144.399	147.881	- 52.568	118.934	- 5.097
5200	31.674	174.010	144.963	151.048	- 54.027	122.315	- 5.141
5300	31.678	174.614	145.517	154.215	- 55.612	125.717	- 5.184
5400	31.682	175.206	146.061	157.383	- 57.324	129.154	- 5.227
5500	31.686	175.787	146.596	160.552	- 59.169	132.627	- 5.270
5600	31.690	176.358	147.122	163.720	- 61.141	136.131	- 5.313
5700	31.694	176.919	147.640	166.890	- 63.242	139.666	- 5.355
5800	31.697	177.470	148.150	170.059	- 65.473	143.246	- 5.398
5900	31.700	178.012	148.651	173.229	- 67.826	146.875	- 5.441
6000	31.703	178.545	149.145	176.399	- 70.300	150.530	- 5.483

June 30, 1962; Mar. 31, 1966

POTASSIUM CYANIDE, DIMERIC $((KCN)_2)$ (IDEAL GAS) MOL. WT. = 130.2397

Point Group $[D_{2h}]$

$S^\circ_{298.15}$ = [89.15] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-2 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-2 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[240] (1)	[220] (1)	[2158] (1)
[130] (1)	[225] (1)	[2158] (1)
[205] (1)	[207] (1)	[2158] (1)
[130] (1)	[207] (1)	[2158] (1)

Bond Distance: K-C = [2.75] Å C-N = [1.16] Å

Bond Angle: N-C-K = [140]° C-K-C = [100]° K-C-K = [80]° σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = [2.94818 \times 10^{-112}]$ g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ $((KCN)_2$, g) was calculated based on an estimated heat of dissociation, 40 kcal. mole^{-1} for the reaction $(KCN)_2(g) \rightarrow 2KCN(g)$, which was obtained by comparison with that for $(NaCN)_2(g)$.

Heat Capacity and Entropy.

The molecular structure and bond angles were assumed to be the same as those for KCN(c) reported by J. M. Bijvoet and J. A. Lely, Rec. trav. chim. 59, 908 (1940). The C-N bond distance was assumed to be the same as that for KCN(g), and the K-C bond distance was assumed to be 10% longer than that in KCN(g). The vibrational frequencies were estimated by comparison with those for $K_2F_2(g)$. The last six frequencies were adopted from the bending and asymmetric stretching frequencies for KCN(g). The three principal moments of inertia are: $I_A = 4.05745 \times 10^{-38}$, $I_B = 6.73351 \times 10^{-38}$ and $I_C = 1.079096 \times 10^{-37}$ g. cm.^{2}

Dilithium Dicarbide (Li_2C_2)
(Solid) Mol. Wt. = 37.902

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	17,100	14,000	14,000*	,000	-14,200	-13,415	9,833
300	17,200	14,106	14,000	,032	-14,198	-13,410	9,769
400	20,890	19,630	14,728	1,961	-14,003	-13,173	7,197
500	22,720	24,508	16,208	4,150	-15,288	-12,839	5,612
600	23,830	28,756	17,953	6,482	-15,138	-12,363	4,503
700	24,600	32,491	19,769	8,906	-14,964	-11,916	3,720
800	25,180	35,815	21,571	11,396	-14,776	-11,491	3,139
900	25,660	38,810	23,322	13,938	-14,588	-11,092	2,693
1000	26,070	41,535	25,009	16,525	-14,395	-10,715	2,342
1100	26,430	44,037	26,627	19,151	-14,189	-10,356	2,057
1200	26,770	46,352	28,175	21,811	-13,977	-10,019	1,825
1300	27,090	48,507	29,657	24,504	-13,750	-9,697	1,630
1400	27,390	50,525	31,077	27,228	-13,508	-9,394	1,466
1500	27,680	52,425	32,437	29,982	-13,248	-9,110	1,327
1600	27,960	54,221	33,743	32,764	-12,970	-8,843	1,208
1700	28,240	55,924	34,998	35,574	-82,764	-5,938	,763
1800	28,510	57,546	36,206	38,411	-82,077	-1,433	,174
1900	28,780	59,094	37,370	41,276	-81,370	3,027	-,348
2000	29,040	60,577	38,494	44,167	-80,643	7,446	-,814

December 31, 1960.

DILITHIUM DICARBIDE (Li_2C_2) (Solid)

Mol. Wt. = 37.902

$\Delta H_f^\circ{}_{298.15} = -14.2 \pm 2$ kcal mole^{-1}

$S^\circ_{298.15} = 14 \pm 1$ cal. deg.$^{-1}$ mole^{-1}

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Monomagnesium Dicarbide (MgC_2)

(Solid) Mol. Wt. = 48.33

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	13,440	13,000	13,000	,000	21,000	20,270	-14,857
300	13,490	13,083	13,000	,025	21,006	20,265	-14,762
400	15,390	17,259	13,557	1,481	21,360	19,966	-10,908
500	16,350	20,807	14,662	3,073	21,677	19,578	-8,557
600	16,940	23,844	15,945	4,739	21,926	19,133	-6,969
700	17,360	26,489	17,266	6,455	22,101	18,653	-5,823
800	17,690	28,829	18,568	8,208	22,212	18,154	-4,959
900	17,960	30,928	19,827	9,991	22,262	17,643	-4,284
1000	18,200	32,833	21,034	11,799	20,136	17,305	-3,782
1100	18,410	34,578	22,187	13,630	20,122	17,024	-3,382
1200	18,610	36,189	23,287	15,482	20,075	16,744	-3,049
1300	18,810	37,686	24,338	17,353	19,999	16,469	-2,769
1400	18,990	39,087	25,342	19,243	-10,531	16,665	-2,601
1500	19,170	40,403	26,303	21,151	-10,248	18,598	-2,710
1600	19,340	41,646	27,223	23,076	-9,962	20,509	-2,801
1700	19,510	42,823	28,106	25,018	-9,666	22,406	-2,880
1800	19,680	43,943	28,955	26,978	-9,359	24,286	-2,949
1900	19,840	45,011	29,773	28,954	-9,044	26,145	-3,007
2000	20,010	46,033	30,560	30,946	-8,717	27,987	-3,058
2100	20,170	47,013	31,320	32,955	-8,379	29,815	-3,103
2200	20,330	47,955	32,055	34,980	-8,033	31,626	-3,142
2300	20,490	48,863	32,766	37,021	-7,677	33,420	-3,176
2400	20,650	49,738	33,455	39,078	-7,311	35,200	-3,205
2500	20,810	50,584	34,124	41,151	-6,934	36,966	-3,231

December 31, 1960.

MONOMAGNESIUM DICARBIDE (MgC_2) (Solid)

Mol. Wt. = 48.33

ΔH_f° $_{298.15}$ = 21 ± 5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 13 ± 2 cal. deg.$^{-1}$ mole^{-1}

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

CNC Radical (C_2N)

(Ideal Gas) GFW = 38.029

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.648	131.892	131.892	INFINITE
100	7.878	44.960	64.000	-1.904	132.261	129.716	-283.494
200	9.723	51.039	56.120	-1.016	132.645	127.025	-138.806
298	10.935	55.157	55.157	.000	133.000	124.188	-91.033
300	10.955	55.225	55.157	.020	133.006	124.133	-90.431
400	11.914	58.514	55.599	1.166	133.311	121.129	-66.182
500	12.630	61.253	56.464	2.395	133.550	118.054	-51.602
600	13.147	63.604	57.463	3.685	133.729	114.937	-41.866
700	13.521	65.661	58.490	5.020	133.849	111.795	-34.904
800	13.794	67.485	59.502	6.386	133.926	108.640	-29.679
900	13.997	69.122	60.482	7.776	133.962	105.474	-25.613
1000	14.151	70.605	61.421	9.184	133.971	102.308	-22.359
1100	14.270	71.959	62.319	10.605	133.952	99.142	-19.698
1200	14.363	73.205	63.175	12.037	133.912	95.980	-17.480
1300	14.438	74.358	63.991	13.477	133.849	92.821	-15.605
1400	14.499	75.430	64.770	14.924	133.773	89.670	-13.998
1500	14.548	76.432	65.515	16.376	133.683	86.523	-12.606
1600	14.589	77.373	66.227	17.833	133.582	83.379	-11.389
1700	14.624	78.258	66.909	19.294	133.473	80.245	-10.316
1800	14.653	79.095	67.563	20.758	133.354	77.117	-9.363
1900	14.678	79.888	68.191	22.225	133.231	73.998	-8.512
2000	14.699	80.641	68.795	23.693	133.100	70.884	-7.746
2100	14.718	81.359	69.376	25.164	132.966	67.779	-7.054
2200	14.734	82.044	69.936	26.637	132.824	64.673	-6.425
2300	14.748	82.699	70.477	28.111	132.680	61.583	-5.852
2400	14.761	83.327	70.999	29.587	132.530	58.494	-5.327
2500	14.772	83.930	71.505	31.063	132.377	55.410	-4.844
2600	14.781	84.509	71.994	32.541	132.218	52.337	-4.399
2700	14.790	85.068	72.468	34.019	132.057	49.263	-3.988
2800	14.798	85.606	72.927	35.499	131.894	46.201	-3.606
2900	14.805	86.125	73.374	36.979	131.725	43.145	-3.252
3000	14.812	86.627	73.807	38.460	131.553	40.094	-2.921
3100	14.818	87.113	74.228	39.941	131.380	37.048	-2.612
3200	14.823	87.583	74.638	41.423	131.202	34.010	-2.323
3300	14.828	88.039	75.038	42.906	131.019	30.972	-2.051
3400	14.833	88.482	75.427	44.389	130.835	27.946	-1.796
3500	14.837	88.912	75.806	45.872	130.647	24.917	-1.556
3600	14.841	89.330	76.176	47.356	130.456	21.900	-1.329
3700	14.845	89.737	76.537	48.841	130.261	18.887	-1.116
3800	14.849	90.133	76.889	50.325	130.064	15.883	-.914
3900	14.853	90.519	77.234	51.810	129.863	12.882	-.722
4000	14.856	90.895	77.571	53.296	129.659	9.885	-.540
4100	14.860	91.262	77.900	54.782	129.452	6.888	-.367
4200	14.864	91.620	78.223	56.268	129.240	3.908	-.203
4300	14.868	91.970	78.538	57.755	129.025	.923	-.047
4400	14.872	92.311	78.847	59.241	128.806	-2.052	.102
4500	14.876	92.646	79.150	60.729	128.584	-5.030	.244
4600	14.880	92.973	79.447	62.217	128.359	-7.992	.380
4700	14.884	93.293	79.739	63.705	128.131	-10.954	.509
4800	14.889	93.606	80.024	65.194	127.897	-13.905	.633
4900	14.894	93.913	80.304	66.683	127.661	-16.860	.752
5000	14.899	94.214	80.580	68.172	127.421	-19.804	.866
5100	14.905	94.509	80.850	69.663	127.175	-22.757	.975
5200	14.911	94.799	81.115	71.153	126.928	-25.692	1.080
5300	14.917	95.083	81.376	72.645	126.676	-28.622	1.180
5400	14.923	95.362	81.633	74.137	126.421	-31.548	1.277
5500	14.930	95.636	81.885	75.629	126.160	-34.470	1.370
5600	14.937	95.905	82.133	77.123	125.897	-37.390	1.459
5700	14.945	96.169	82.377	78.617	125.629	-40.307	1.545
5800	14.953	96.429	82.617	80.112	125.357	-43.215	1.628
5900	14.961	96.685	82.853	81.607	125.081	-46.114	1.708
6000	14.970	96.936	83.096	83.104	124.801	-49.019	1.786

Mar. 31, 1967

CNC RADICAL (C_2N) (IDEAL GAS) GFW = 38.029

Point Group $D_{\infty h}$

ΔHf°_0 = [131.9] kcal/mol

$S^\circ_{298.15}$ = [55 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [133 ± 30] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
26.41	2
30338.53	4
34802.33	2

Vibrational Frequencies and Degeneracies

w, cm^{-1}	
[1200]	(1)
321	(2)
[900]	(1)

Bond Distance: C-N = 1.245 Å

Bond Angle: C-N-C = 180°

$\sigma = 2$

Rotational Constant: B_0 = 0.4535 cm^{-1}

Heat of Formation.

A. J. Merer and D. N. Travis, Can. J. Phys. 44, 353 (1966), state that the observed bond length in CNC(g) indicates double-bonded CN links. The value of the C = N dissociation energy is derived as 147 kcal from the heat of combustion of n-butyl-isobutylidine amine determined by G. E. Coates and L. E. Sutton, J. Chem. Soc. 1187, (1948). However, due to possible extra binding energy from the unpaired electron, we assume here a slightly higher value of 160 kcal. This yields a ΔHf°_{298}(CNC,g) = 133 kcal/mol. It is also possible to calculate another value by assuming that the ratio of the heat of atomization (ΔHa) of Si_2N to that of C_2N(g) is equal to the ratio of the dissociation energies of SiN(g) and CN(g); by this method ΔHf°_{298}(CNC,g) = 144 kcal/mol.

Heat Capacity and Entropy.

Merer and Travis, loc. cit., have observed the ultraviolet absorption spectrum of the CNC radical. They have assigned the configuration, bond distance, and the electronic levels. In addition, they have derived w_2; the remaining frequencies are estimated by comparison with the $^1\Pi$ state of C_3(g), which has been assigned by W. Weltner and D. J. McLeod, J. Chem. Phys. 40, 1305 (1964), and J. Chem. Phys. 45, 3096 (1966).

Cyanogen (C_2N_2)

(Ideal Gas) Mol. Wt. = 52.038

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-3,018	73,428	73,428	INFINITE
100	8,700	45,654	68,408	-2,275	73,450	72,742	-158,970
200	11,690	52,663	58,898	-1,247	73,626	71,978	-78,650
298	13,563	57,711	57,711	,000	73,870	71,117	-52,128
300	13,590	57,795	57,711	,025	73,874	71,100	-51,794
400	14,771	61,878	58,260	1,447	74,107	70,140	-38,321
500	15,615	65,269	59,332	2,968	74,287	69,125	-30,213
600	16,305	68,178	60,569	4,565	74,415	68,079	-24,797
700	16,899	70,737	61,843	6,226	74,499	67,017	-20,923
800	17,415	73,028	63,100	7,942	74,554	65,945	-18,015
900	17,858	75,106	64,321	9,707	74,586	64,865	-15,751
1000	18,237	77,007	65,496	11,512	74,604	63,784	-13,939
1100	18,559	78,761	66,623	13,352	74,610	62,700	-12,457
1200	18,833	80,388	67,703	15,222	74,608	61,619	-11,222
1300	19,066	81,905	68,738	17,117	74,594	60,536	-10,177
1400	19,264	83,325	69,729	19,034	74,578	59,458	-9,281
1500	19,434	84,660	70,681	20,969	74,556	58,378	-8,505
1600	19,579	85,919	71,594	22,920	74,531	57,299	-7,826
1700	19,705	87,110	72,472	24,885	74,505	56,222	-7,228
1800	19,815	88,240	73,317	26,861	74,475	55,147	-6,695
1900	19,910	89,314	74,131	28,847	74,444	54,077	-6,220
2000	19,993	90,337	74,916	30,842	74,412	53,006	-5,792
2100	20,066	91,314	75,674	32,845	74,379	51,938	-5,405
2200	20,131	92,249	76,406	34,855	74,342	50,865	-5,053
2300	20,188	93,145	77,115	36,871	74,306	49,803	-4,732
2400	20,239	94,006	77,801	38,893	74,267	48,738	-4,438
2500	20,285	94,833	78,465	40,919	74,227	47,672	-4,167
2600	20,326	95,629	79,110	42,949	74,183	46,612	-3,918
2700	20,363	96,397	79,736	44,984	74,140	45,549	-3,687
2800	20,396	97,138	80,345	47,022	74,096	44,496	-3,473
2900	20,426	97,855	80,936	49,063	74,047	43,439	-3,273
3000	20,454	98,548	81,512	51,107	73,997	42,385	-3,088
3100	20,479	99,219	82,072	53,154	73,947	41,333	-2,914
3200	20,502	99,869	82,618	55,203	73,893	40,279	-2,751
3300	20,522	100,500	83,151	57,254	73,836	39,228	-2,598
3400	20,542	101,113	83,670	59,307	73,778	38,183	-2,454
3500	20,559	101,709	84,177	61,362	73,716	37,131	-2,318
3600	20,575	102,288	84,672	63,419	73,653	36,089	-2,191
3700	20,590	102,852	85,156	65,477	73,587	35,047	-2,070
3800	20,604	103,402	85,629	67,537	73,519	34,012	-1,956
3900	20,617	103,937	86,091	69,598	73,447	32,973	-1,848
4000	20,629	104,459	86,544	71,660	73,373	31,937	-1,745
4100	20,640	104,969	86,987	73,724	73,296	30,895	-1,647
4200	20,651	105,466	87,421	75,788	73,215	29,871	-1,554
4300	20,660	105,952	87,847	77,854	73,130	28,835	-1,465
4400	20,669	106,427	88,264	79,920	73,043	27,806	-1,381
4500	20,678	106,892	88,672	81,988	72,953	26,774	-1,300
4600	20,686	107,346	89,073	84,056	72,859	25,753	-1,223
4700	20,693	107,791	89,467	86,125	72,763	24,732	-1,150
4800	20,700	108,227	89,853	88,195	72,661	23,714	-1,080
4900	20,707	108,654	90,233	90,265	72,556	22,693	-1,012
5000	20,713	109,072	90,605	92,336	72,448	21,676	-,947
5100	20,719	109,483	90,971	94,407	72,333	20,652	-,885
5200	20,724	109,885	91,331	96,480	72,217	19,645	-,826
5300	20,730	110,280	91,685	98,552	72,096	18,636	-,768
5400	20,734	110,667	92,033	100,626	71,972	17,635	-,714
5500	20,739	111,048	92,375	102,699	71,841	16,628	-,661
5600	20,744	111,422	92,712	104,773	71,708	15,621	-,610
5700	20,748	111,789	93,044	106,848	71,570	14,617	-,560
5800	20,752	112,150	93,370	108,923	71,427	13,620	-,513
5900	20,756	112,504	93,691	110,998	71,279	12,631	-,468
6000	20,759	112,853	94,008	113,074	71,128	11,630	-,424

March 31, 1961

CYANOGEN (C_2N_2) (IDEAL GAS) MOL. WT. = 52.038

ΔH°_{f0} = 73.428 kcal. mole^{-1}

Point Group $D_{\infty h}$

$\Delta H^\circ_{f\ 298.15}$ = 73.87 ± 0.43 kcal. mole^{-1}

$S^\circ_{298.15}$ = 57.711 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
2328.5 (1)
850.6 (1)
2149 (1)
507.2 (2)
240 (2)

Rotational constant B_0 = 0.15752 ± 0.00015 cm.$^{-1}$ CN distance = 1.157 Å CC distance = 1.380 Å σ = 2

Moment of inertia = 1.776(9) X 10^{-38} g. cm.^{2}

Heat of Formation

J. W. Knowlton and E. J. Prosen, J. Research Natl. Bur. Standards 46, 489 (1951), report $\Delta H^\circ_{298.15}$ = -261.94 ± 0.43 kcal. for the reaction $C_2N_2(g) + 2\ O_2(g) \rightarrow 2\ CO_2(g) + N_2(g)$. When corrected for a change in the atomic weight of carbon, this becomes $\Delta H^\circ_{298.15}$ = -261.95 ± 0.43 kcal., whence $\Delta H^\circ_{f\ 298.15}$ for $C_2N_2(g)$ is found to be 73.87 ± 0.43 kcal. mole^{-1}.

Heat Capacity and Entropy

A Langseth and C. K. Møller, Acta Chem. Scand. 4, 725 (1950), determined the vibrational frequencies by Raman spectroscopy. C. K. Møller and B. P. Stoicheff, Can. J. Phys. 32, 625 (1954), determined B_0 by Raman spectroscopy and calculated the bond lengths listed above. These agree with lengths found from electron-diffraction measurements by Langseth and Møller, loc. cit., (CN distance = 1.15 Å, CC distance = 1.38 Å) and L. Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939) (CN distance = 1.16 ± 0.02 Å, CC distance = 1.37 ± 0.02 Å). From measurements reported by R. A. Ruehrwein and W. F. Giauque, J. Am. Chem. Soc. 61, 2940 (1939), $S^\circ_{298.15}$ is calculated by the third law to be 57.63 cal. deg.$^{-1}$ mole^{-1}, in satisfactory agreement with the value calculated here.

Sodium Cyanide, Dimeric $((NaCN)_2)$

(Ideal Gas) Mol. Wt. = 98.0153

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-5.540	-1.982	-1.982	INFINITE
100	16.175	59.048	104.034	-4.499	-2.294	-3.207	7.009
200	23.539	73.050	85.231	-2.436	-2.264	-4.099	4.479
298	25.737	82.932	82.932	.000	-2.100	-5.036	3.692
300	25.762	83.091	82.932	.048	-2.097	-5.054	3.682
400	26.716	90.647	83.956	2.676	-3.346	-5.948	3.250
500	27.339	96.678	85.918	5.380	-3.465	-6.586	2.879
600	27.867	101.710	88.142	8.141	-3.614	-7.196	2.621
700	28.346	106.043	90.397	10.952	-3.793	-7.782	2.430
800	28.776	109.856	92.595	13.809	-3.987	-8.336	2.277
900	29.155	113.268	94.706	16.706	-4.203	-8.869	2.154
1000	29.482	116.357	96.719	19.638	-4.437	-9.375	2.049
1100	29.763	119.181	98.635	22.601	-4.700	-9.861	1.959
1200	30.002	121.781	100.457	25.589	-51.465	-9.400	1.712
1300	30.206	124.191	102.191	28.600	-51.357	-5.900	.992
1400	30.381	126.436	103.843	31.629	-51.255	-2.406	.376
1500	30.530	128.537	105.420	34.675	-51.160	1.081	-.157
1600	30.659	130.512	106.927	37.735	-51.070	4.559	-.623
1700	30.770	132.374	108.370	40.806	-50.982	8.034	-1.033
1800	30.866	134.135	109.753	43.888	-50.901	11.503	-1.397
1900	30.950	135.806	111.081	46.979	-50.821	14.972	-1.722
2000	31.024	137.396	112.357	50.078	-50.746	18.430	-2.014
2100	31.088	138.911	113.586	53.184	-50.670	21.887	-2.278
2200	31.145	140.359	114.770	56.295	-50.603	25.337	-2.517
2300	31.196	141.744	115.913	59.412	-50.535	28.790	-2.736
2400	31.241	143.073	117.017	62.534	-50.472	32.240	-2.936
2500	31.282	144.349	118.085	65.661	-50.410	35.680	-3.119
2600	31.318	145.577	119.119	68.791	-50.357	39.124	-3.289
2700	31.350	146.759	120.121	71.924	-50.307	42.562	-3.445
2800	31.380	147.900	121.093	75.060	-50.262	46.000	-3.590
2900	31.406	149.002	122.036	78.200	-50.222	49.442	-3.726
3000	31.431	150.067	122.953	81.342	-50.191	52.877	-3.852
3100	31.453	151.098	123.844	84.486	-50.165	56.311	-3.970
3200	31.473	152.097	124.712	87.632	-50.149	59.746	-4.080
3300	31.491	153.065	125.556	90.780	-50.145	63.177	-4.184
3400	31.508	154.006	126.379	93.930	-50.147	66.613	-4.282
3500	31.524	154.919	127.182	97.082	-50.163	70.048	-4.374
3600	31.538	155.807	127.964	100.235	-50.192	73.482	-4.461
3700	31.551	156.672	128.729	103.389	-50.234	76.913	-4.543
3800	31.563	157.513	129.475	106.545	-50.290	80.362	-4.622
3900	31.575	158.333	130.205	109.702	-50.365	83.799	-4.696
4000	31.585	159.133	130.918	112.860	-50.457	87.239	-4.767
4100	31.595	159.913	131.616	116.019	-50.571	90.682	-4.834
4200	31.604	160.674	132.298	119.179	-50.709	94.132	-4.898
4300	31.613	161.418	132.967	122.340	-50.870	97.583	-4.960
4400	31.621	162.145	133.622	125.502	-51.060	101.030	-5.018
4500	31.628	162.856	134.264	128.664	-51.281	104.491	-5.075
4600	31.635	163.551	134.893	131.827	-51.535	107.956	-5.129
4700	31.642	164.231	135.510	134.991	-51.823	111.427	-5.181
4800	31.648	164.898	136.115	138.156	-52.156	114.903	-5.232
4900	31.654	165.550	136.709	141.321	-52.531	118.390	-5.280
5000	31.659	166.190	137.293	144.486	-52.955	121.885	-5.328
5100	31.664	166.817	137.865	147.653	-53.432	125.374	-5.373
5200	31.669	167.432	138.428	150.819	-53.964	128.889	-5.417
5300	31.674	168.035	138.981	153.986	-54.559	132.415	-5.460
5400	31.678	168.627	139.524	157.154	-55.219	135.952	-5.502
5500	31.682	169.208	140.059	160.322	-55.955	139.499	-5.543
5600	31.686	169.779	140.585	163.490	-56.763	143.057	-5.583
5700	31.690	170.340	141.102	166.659	-57.653	146.630	-5.622
5800	31.694	170.891	141.611	169.828	-58.630	150.223	-5.661
5900	31.697	171.433	142.111	172.998	-59.697	153.842	-5.699
6000	31.700	171.966	142.605	176.168	-60.857	157.459	-5.735

Mar. 31, 1966

SODIUM CYANIDE, DIMERIC $((NaCN)_2)$ (IDEAL GAS) MOL. WT. = 98.0153

Point Group $[D_{2h}]$

$\Delta H_f^\circ{}_0 = [-2.0 \pm 3]$ kcal. mole^{-1}

$S^\circ_{298.15} = [82.93]$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = [-2.1 \pm 3]$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[295](1)	[250](1)	[2176](1)
[175](1)	[290](1)	[2176](1)
[250](1)	[239](1)	[2176](1)
[170](1)	[239](1)	[2176](1)

Bond Distance: N-C = [1.16] Å C-Na = [2.19] Å

Bond Angle: C-Na-C = [105]° Na-C-Na = [75]° N-C-Na = [142.5]° $\sigma = [4]$

Product of the Moments of Inertia: $I_AI_BI_C = [4.48269 \times 10^{-113}]$ g.^{3} cm.^{6}

Heat of Formation.

The mass spectra of vapors from samples of NaCN have been observed by R. F. Porter, J. Chem. Phys. 35, 318 (1961), at temperatures around 1000°K. The results indicate that the compound evaporates as NaCN(g) and $Na_2(CN)_2(g)$. A comparison of relative ion currents produced by electron bombardment of NaCN vapors effusing from single - and double-oven-type Knudsen cells, yielded information on the partial pressures of monomer and dimer. Based on the partial pressures for NaCN(g) and $(NaCN)_2(g)$ reported at temperatures, 903-1049°K., the vapor pressures of $(NaCN)_2(g)$ over NaCN(l), 1078.2-1626.2°K., were calculated from the total vapor pressure measurements reported by C. K. Ingold, J. Chem. Soc. 123, 885 (1923). By the second and third law methods, the values of $\Delta H_v^\circ{}_{298.15}(l \rightarrow \text{dimer})$ were evaluated to be 38.89 and 38.21 kcal. mole^{-1}, respectively. Using the third law value, the heat of formation for $(NaCN)_2(g)$ was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distances and C-Na-C bond angle were estimated by R. F. Porter, loc. cit. The vibrational frequencies were estimated by comparison with those for NaCl(g). The last six frequencies were the bending and asymmetric stretching frequencies for NaCN(g). The three principal moments of inertia are: $I_A = 1.3570 \times 10^{-38}$, $I_B = 5.1090 \times 10^{-38}$ and $I_C = 6.4660 \times 10^{-38}$ g. cm.^{2}

CCO Radical (C_2O)
(Ideal Gas) GFW = 40.0217

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.503	67.538	67.538	INFINITE
100	7.456	46.046	64.034	- 1.799	67.868	65.375	- 142.877
200	9.209	51.783	56.587	- .961	68.202	62.755	- 68.575
298	10.292	55.677	55.677	.000	68.500	60.016	- 43.993
300	10.309	55.741	55.677	.019	68.505	59.963	- 43.683
400	11.094	58.819	56.092	1.091	68.729	57.079	- 31.187
500	11.722	61.364	56.899	2.233	68.867	54.150	- 23.669
600	12.243	63.549	57.829	3.432	68.933	51.198	- 18.649
700	12.682	65.470	58.786	4.679	68.941	48.242	- 15.062
800	13.056	67.189	59.731	5.966	68.911	45.287	- 12.372
900	13.377	68.745	60.647	7.288	68.852	42.335	- 10.280
1000	13.657	70.170	61.529	8.640	68.779	39.393	- 8.609
1100	13.903	71.483	62.375	10.018	68.691	36.457	- 7.243
1200	14.122	72.702	63.186	11.420	68.597	33.533	- 6.107
1300	14.315	73.840	63.962	12.842	68.492	30.615	- 5.147
1400	14.488	74.908	64.706	14.282	68.389	27.707	- 4.325
1500	14.641	75.913	65.420	15.739	68.282	24.804	- 3.614
1600	14.776	76.862	66.106	17.210	68.174	21.907	- 2.992
1700	14.896	77.761	66.765	18.693	68.069	19.020	- 2.445
1800	15.001	78.616	67.400	20.188	67.961	16.137	- 1.959
1900	15.093	79.429	68.012	21.693	67.855	13.263	- 1.526
2000	15.172	80.206	68.602	23.206	67.748	10.390	- 1.135
2100	15.241	80.948	69.173	24.727	67.642	7.528	- .783
2200	15.300	81.658	69.724	26.254	67.531	4.664	- .463
2300	15.350	82.339	70.258	27.787	67.422	1.813	- .172
2400	15.392	82.993	70.775	29.324	67.308	- 1.037	.094
2500	15.428	83.623	71.276	30.865	67.193	- 3.887	.340
2600	15.457	84.228	71.763	32.409	67.073	- 6.725	.565
2700	15.480	84.812	72.236	33.956	66.951	- 9.564	.774
2800	15.499	85.375	72.695	35.505	66.827	- 12.392	.967
2900	15.513	85.919	73.142	37.056	66.695	- 15.218	1.147
3000	15.524	86.446	73.576	38.608	66.561	- 18.044	1.314
3100	15.531	86.955	74.000	40.161	66.423	- 20.859	1.471
3200	15.536	87.448	74.412	41.714	66.279	- 23.673	1.617
3300	15.538	87.926	74.815	43.268	66.130	- 26.486	1.754
3400	15.538	88.390	75.207	44.821	65.976	- 29.286	1.883
3500	15.536	88.840	75.590	46.375	65.817	- 32.090	2.004
3600	15.533	89.278	75.964	47.929	65.654	- 34.885	2.118
3700	15.528	89.703	76.330	49.482	65.484	- 37.672	2.225
3800	15.523	90.117	76.687	51.034	65.310	- 40.454	2.327
3900	15.516	90.521	77.037	52.586	65.130	- 43.238	2.423
4000	15.509	90.913	77.379	54.137	64.945	- 46.011	2.514
4100	15.501	91.296	77.714	55.688	64.754	- 48.787	2.601
4200	15.492	91.670	78.042	57.238	64.557	- 51.552	2.683
4300	15.483	92.034	78.363	58.786	64.354	- 54.313	2.760
4400	15.474	92.390	78.678	60.334	64.146	- 57.074	2.835
4500	15.465	92.738	78.986	61.881	63.933	- 59.831	2.906
4600	15.455	93.077	79.289	63.427	63.713	- 62.571	2.973
4700	15.445	93.410	79.586	64.972	63.489	- 65.317	3.037
4800	15.435	93.735	79.877	66.516	63.258	- 68.051	3.098
4900	15.426	94.053	80.163	68.059	63.022	- 70.787	3.157
5000	15.416	94.364	80.444	69.601	62.781	- 73.512	3.213
5100	15.406	94.670	80.720	71.143	62.532	- 76.247	3.267
5200	15.396	94.969	80.991	72.683	62.279	- 78.964	3.319
5300	15.387	95.262	81.258	74.222	62.020	- 81.671	3.368
5400	15.377	95.549	81.520	75.760	61.756	- 84.376	3.415
5500	15.368	95.831	81.777	77.297	61.485	- 87.079	3.460
5600	15.358	96.108	82.031	78.833	61.209	- 89.781	3.504
5700	15.349	96.380	82.280	80.369	60.926	- 92.483	3.546
5800	15.340	96.647	82.526	81.903	60.638	- 95.170	3.586
5900	15.331	96.909	82.767	83.437	60.345	- 97.846	3.624
6000	15.323	97.167	83.005	84.970	60.046	- 100.535	3.662

June 30, 1966; Sept. 30, 1966

CCO RADICAL (C_2O) (IDEAL GAS) GFW = 40.0217

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = 55.7 gibbs/mol

ΔHf°_0 = 67.5 ± 15 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 68.5 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1
0	3
[4050]	[2]
[6450]	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1074 (1)
381 (2)
1978 (1)

Bond Distance: C-C = [1.160] Å C-O = [1.279] Å

Bond Angle: C-C-O = [180]°

Rotational Constant: Bo = [0.408475] cm^{-1}

$\sigma = 1$

Heat of Formation.

The adopted heat of formation, $\Delta Hf^\circ_{298.15}$ (C_2O,g) = 68.5 kcal/mol, was calculated from the heat of reaction ΔHr°_{298} = 65.5 kcal/mol for $C_3O_2(g) = C_2O(g) + CO(g)$ using all JANAF functions (dated Sept. 30, 1965). The value of ΔHr° was obtained from the third law calculation of the equilibrium constant (Kp = 3.3 x 10^{-6} atm at 1060°K) which was determined in the studies of decomposition rate of $C_3O_2(g)$ by H. B. Palmer and W. D. Cross, Carbon 3, 475 (1966).

M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. 43, 3745 (1965), have observed the photo-dissociation of C_2O near 5000Å, which corresponds to a minimum of 57 kcal/mol for $C_2O(g) \rightarrow C(g) + CO(g)$. This yields $\Delta Hf^\circ_{298}(C_2O,g) \leq 87$ kcal/mol, which was not adopted because the irradiation was not monochromatic and thus possibly contained all wavelengths below 5000Å.

Heat Capacity and Entropy.

Jacox et al., loc. cit., have observed three vibrational fundamentals in the infrared spectrum by matrix isolation, and suggested a linear structure with $^3\Sigma$ ground state for the CCO radical (g). They also estimated the bond distances C-C = 1.160 Å and C-O = 1.279 Å based on the structural analogy between the carbon suboxide and the CCO radical. The principal moment of inertia is 6.8525 x 10^{-39} g cm^2. K. D. Bayes, J. Am. Chem. Soc. 85, 1730 (1963), has predicted that the $^1\Delta$ and $^1\Sigma$ states lie respectively 0.5 and 0.8 eV above the ground state. These two electronic states have been included in the tabulation.

Silicon Dicarbide (SiC_2)

(Ideal Gas) GFW = 52.1083

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.642	145.631	145.631	INFINITE
100	7.972	46.234	65.472	- 1.924	146.257	141.767	- 309.832
200	9.553	52.409	57.519	- 1.022	146.722	137.086	- 149.800
298	10.901	56.553	56.553	.000	147.000	132.290	- 96.971
300	10.917	56.620	56.553	.020	147.003	132.199	- 96.307
400	11.671	59.869	56.991	1.151	147.135	127.241	- 69.521
500	12.259	62.539	57.841	2.349	147.151	122.264	- 53.442
600	12.729	64.817	58.819	3.599	147.077	117.291	- 42.723
700	13.105	66.809	59.821	4.892	146.935	112.339	- 35.073
800	13.403	68.579	60.807	6.218	146.743	107.408	- 29.343
900	13.641	70.172	61.761	7.570	146.509	102.504	- 24.891
1000	13.831	71.619	62.675	8.944	146.247	97.628	- 21.337
1100	13.984	72.945	63.549	10.335	145.957	92.779	- 18.433
1200	14.109	74.167	64.384	11.740	145.645	87.960	- 16.020
1300	14.212	75.301	65.181	13.156	145.308	83.164	- 13.981
1400	14.298	76.357	65.942	14.582	144.957	78.401	- 12.239
1500	14.372	77.346	66.669	16.015	144.587	73.660	- 10.732
1600	14.438	78.276	67.366	17.456	144.203	68.940	- 9.417
1700	14.498	79.153	68.034	18.903	131.814	64.354	- 8.273
1800	14.557	79.983	68.675	20.356	131.459	60.398	- 7.333
1900	14.616	80.772	69.291	21.814	131.103	56.460	- 6.494
2000	14.677	81.523	69.884	23.279	130.748	52.542	- 5.741
2100	14.743	82.241	70.455	24.750	130.395	48.642	- 5.062
2200	14.815	82.928	71.007	26.228	130.041	44.753	- 4.446
2300	14.893	83.589	71.540	27.713	129.692	40.887	- 3.885
2400	14.980	84.224	72.055	29.206	129.345	37.034	- 3.372
2500	15.074	84.838	72.554	30.709	129.006	33.191	- 2.902
2600	15.178	85.431	73.038	32.222	128.671	29.366	- 2.468
2700	15.289	86.006	73.508	33.745	128.344	25.549	- 2.068
2800	15.409	86.564	73.964	35.280	128.027	21.753	- 1.698
2900	15.535	87.107	74.408	36.827	127.716	17.962	- 1.354
3000	15.669	87.636	74.840	38.387	127.416	14.181	- 1.033
3100	15.808	88.152	75.261	39.961	127.128	10.413	- .734
3200	15.951	88.656	75.672	41.549	126.850	6.654	- .454
3300	16.098	89.149	76.073	43.151	126.582	2.898	- .192
3400	16.247	89.632	76.465	44.769	126.327	- .843	.054
3500	16.398	90.105	76.848	46.401	126.084	- 4.585	.286
3600	16.548	90.569	77.222	48.048	33.892	- 6.057	.368
3700	16.698	91.024	77.589	49.710	33.771	- 7.162	.423
3800	16.845	91.472	77.949	51.387	33.663	- 8.266	.475
3900	16.989	91.911	78.301	53.079	33.565	- 9.366	.525
4000	17.129	92.343	78.647	54.785	33.479	- 10.465	.572
4100	17.264	92.768	78.986	56.505	33.402	- 11.571	.617
4200	17.393	93.185	79.319	58.238	33.335	- 12.660	.659
4300	17.516	93.596	79.646	59.983	33.276	- 13.757	.699
4400	17.633	94.000	79.968	61.741	33.227	- 14.852	.738
4500	17.742	94.398	80.284	63.509	33.185	- 15.946	.774
4600	17.843	94.789	80.595	65.289	33.151	- 17.035	.809
4700	17.936	95.173	80.901	67.078	33.123	- 18.121	.843
4800	18.022	95.552	81.203	68.876	33.099	- 19.212	.875
4900	18.099	95.924	81.499	70.682	33.081	- 20.300	.905
5000	18.168	96.291	81.792	72.495	33.066	- 21.394	.935
5100	18.230	96.651	82.079	74.315	33.052	- 22.487	.964
5200	18.283	97.006	82.363	76.141	33.042	- 23.576	.991
5300	18.329	97.354	82.643	77.972	33.034	- 24.657	1.017
5400	18.367	97.697	82.918	79.807	33.025	- 25.744	1.042
5500	18.398	98.035	83.190	81.645	33.013	- 26.838	1.066
5600	18.423	98.366	83.458	83.486	33.002	- 27.920	1.090
5700	18.440	98.693	83.722	85.329	32.987	- 29.017	1.113
5800	18.452	99.013	83.983	87.174	32.969	- 30.100	1.134
5900	18.458	99.329	84.241	89.019	32.947	- 31.186	1.155
6000	18.458	99.639	84.495	90.865	32.922	- 32.280	1.176

Mar. 31, 1967

SILICON DICARBIDE (C_2Si) (IDEAL GAS) GFW = 52.1083

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = 56.55 gibbs/mol

ΔHf°_0 = 145.6 ± 7 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 147 ± 7 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[13000]	[6]
20085	2

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
853 (1)
300 (2)
1742 (1)

Bond Distance: C-C = [1.28] Å C-Si = [1.75] Å

Bond Angle: C-C-Si = 180° σ = 1

Rotational Constant: B_0 = [0.2012] cm^{-1}

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite[1], SiC-silicon[2] and boron-carbon-silicon[3]. Third law analysis of the partial pressures of C_2Si and Si lead to the concordant values 146.7, 149.0 and 146.0 kcal/mol. Although the drifts all suggest that the entropy of C_2Si may be about 3.5 eu less than tabulated, this is of doubtful significance because the uncertainty bands are so large. The low condensation coefficient suggested by Drowart[2] may also be involved. Rates of free evaporation reported by Voronin[4] lead to apparent pressures which are smaller by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of ΔHf°_{298} = 147 ± 7 kcal/mol includes allowance for the unlikely possibility that the entropy may be in error by up to 3.5 eu.

Source	Method	Reaction	Range, T°K	No. of Points	ΔHr°_{298}(kcal/mol) 2nd Law	3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Drowart (1958)	Mass Spec.	A	2149-2316	7	31±9	38.98	3.5±4.1	146.7
Drowart (1960)	" "	B	1935-2160	4	188±10	194.8	3.3±4.9	149.0
Verhaegen (1964)	" "	A	2166-2344	5	30±16	38.31	3.9±7.2	146.0

A) 2 C(graph) + Si(g) = $C_2Si(g)$

B) 2SiC(α) = Si(l) + $C_2Si(g)$

Heat Capacity and Entropy.

The known molecular constants are from the assignments of Weltner and McLeod[5]. These authors observed the infrared spectrum, emission spectrum and visible absorption spectrum of C_2Si in matrix isolation. The matrix data allowed more certain assignment of the A-X band system of the gas as observed by Kleman[6] and McKellar[7]. Weltner concluded that this system probably involves transitions between a $^1\Sigma^+$ ground state and a $^1\Pi$ excited state. The two stretching frequencies were observed in the matrix infrared spectrum,whereas the bending mode, 300 cm^{-1}, was derived solely from the analysis of the A-X band system. The analysis presumed a linear unsymmetrical structure for the molecule.

A $^3\Pi$ excited state is assumed to lie 7000 cm^{-1} below the $^1\Pi$ state,which presumably arises from the same molecular orbital configuration. The effect of the estimated level is to increase the entropy by about 0.2 and 1.8 eu at 3000 and 6000°K. Bond distances are estimated by comparison with those in Si_2, C_2 and C_3. The moment of inertia is 13.91 x 10^{-39} g cm^2.

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Carbon, Triatomic (C_3)

(Ideal Gas) GFW = 36.03345

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.811	193.945	193.945	INFINITE
100	10.148	46.107	65.054	-1.895	194.819	190.272	-415.838
200	9.527	52.984	57.515	-.906	195.574	185.409	-202.605
298	9.020	56.677	56.677	.000	196.000	180.317	-132.176
300	9.015	56.733	56.677	.017	196.005	180.220	-131.290
400	8.962	59.318	57.029	.912	196.162	174.928	-95.576
500	9.173	61.338	57.694	1.818	196.111	169.622	-74.142
600	9.490	63.029	58.445	2.750	195.909	164.340	-59.861
700	9.829	64.518	59.208	3.716	195.600	159.103	-49.674
800	10.153	65.852	59.957	4.716	195.223	153.915	-42.048
900	10.448	67.065	60.680	5.746	194.792	148.774	-36.127
1000	10.711	68.179	61.375	6.804	194.332	143.685	-31.402
1100	10.943	69.211	62.041	7.887	193.846	138.642	-27.546
1200	11.149	70.173	62.679	8.992	193.343	133.648	-24.341
1300	11.332	71.072	63.291	10.116	192.820	128.693	-21.635
1400	11.495	71.918	63.877	11.258	192.294	123.784	-19.324
1500	11.642	72.716	64.440	12.415	191.759	118.909	-17.325
1600	11.775	73.472	64.981	13.586	191.220	114.066	-15.581
1700	11.896	74.190	65.502	14.769	190.681	109.261	-14.046
1800	12.006	74.873	66.004	15.964	190.139	104.487	-12.686
1900	12.108	75.525	66.488	17.170	189.599	99.745	-11.473
2000	12.202	76.148	66.955	18.386	189.060	95.030	-10.384
2100	12.290	76.746	67.407	19.610	188.523	90.345	-9.402
2200	12.371	77.319	67.845	20.844	187.984	85.677	-8.511
2300	12.448	77.871	68.269	22.085	187.449	81.044	-7.701
2400	12.520	78.402	68.680	23.333	186.912	76.428	-6.960
2500	12.588	78.915	69.079	24.588	186.379	71.833	-6.280
2600	12.652	79.410	69.467	25.850	185.844	67.262	-5.654
2700	12.712	79.888	69.844	27.119	185.313	62.708	-5.076
2800	12.770	80.352	70.211	28.393	184.784	58.180	-4.541
2900	12.825	80.801	70.569	29.672	184.251	53.669	-4.045
3000	12.877	81.236	70.917	30.958	183.722	49.174	-3.582
3100	12.927	81.659	71.257	32.248	183.194	44.700	-3.151
3200	12.974	82.070	71.588	33.543	182.665	40.241	-2.748
3300	13.020	82.470	71.912	34.842	182.134	35.791	-2.370
3400	13.064	82.860	72.228	36.147	181.606	31.371	-2.016
3500	13.106	83.239	72.538	37.455	181.075	26.953	-1.683
3600	13.146	83.609	72.840	38.768	180.546	22.557	-1.369
3700	13.185	83.970	73.136	40.084	180.014	18.178	-1.074
3800	13.222	84.322	73.426	41.405	179.484	13.817	-.795
3900	13.258	84.666	73.709	42.729	178.951	9.466	-.530
4000	13.293	85.002	73.988	44.056	178.418	5.128	-.280
4100	13.326	85.330	74.260	45.387	177.883	.795	-.042
4200	13.359	85.652	74.528	46.722	177.346	-3.510	.183
4300	13.390	85.967	74.790	48.059	176.805	-7.813	.397
4400	13.420	86.275	75.048	49.400	176.265	-12.103	.601
4500	13.450	86.577	75.300	50.743	175.721	-16.382	.796
4600	13.478	86.873	75.549	52.089	175.174	-20.641	.981
4700	13.506	87.163	75.793	53.439	174.628	-24.891	1.157
4800	13.532	87.447	76.033	54.791	174.075	-29.125	1.326
4900	13.558	87.727	76.268	56.145	173.521	-33.355	1.488
5000	13.583	88.001	76.500	57.502	172.964	-37.570	1.642
5100	13.608	88.270	76.729	58.862	172.401	-41.789	1.791
5200	13.631	88.535	76.953	60.224	171.837	-45.978	1.932
5300	13.654	88.794	77.174	61.588	171.269	-50.156	2.068
5400	13.677	89.050	77.392	62.954	170.697	-54.325	2.199
5500	13.698	89.301	77.606	64.323	170.119	-58.488	2.324
5600	13.719	89.548	77.817	65.694	169.540	-62.641	2.445
5700	13.740	89.791	78.025	67.067	168.954	-66.792	2.561
5800	13.760	90.030	78.230	68.442	168.364	-70.921	2.672
5900	13.780	90.266	78.432	69.819	167.770	-75.030	2.779
6000	13.799	90.497	78.631	71.198	167.172	-79.154	2.883

Dec. 31, 1960; Dec. 31, 1969

Point Group $D_{\infty h}$

ΔHf°_0 = 194 ± 4 kcal/mol

$S^\circ_{298.15}$ = 56.7 ± 3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 196 ± 4 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
1225 (1)
63.5 (2)
2040 (1)

The contribution of the doubly degenerate bending frequency was approximated by direct summation of the following levels (cm^{-1}): 0, 63.5, 132.7, 207.4, 286.5, 370.5, 458.2, and 650 x n where n = 1 to 76. The contribution to each function due to these levels was doubled to account for the degeneracy.

Bond Distance: C-C = 1.277 Å

Bond Angle: C-C-C = 180°

σ = 2

Rotational Constant: B_0 = 0.4305 cm^{-1}

Heat of Formation

Drowart et al. (1) have measured mass spectrometrically the ion intensity ratio C_3^+/C^+ as a function of temperature from 1800 to 2700°K. We derive from a 2nd law analysis of their data ΔHf_{2200} = 185.2 ± 3.3 kcal, and S_{2200} = 74.9 ± 2.8 eu by calculation of the absolute pressure from the vapor pressure of monatomic carbon and a relative ionization cross-section ratio of 2.3. The entropy uncertainty includes 1.3 eu for uncertainty in the absolute pressure. Several earlier mass-spectrometric determinations (2, 3, 4) are in reasonable agreement. The absolute magnitude of the pressure is also confirmed by the work of Thorn and Winslow (5) who measured the total pressure of all species over graphite as 1.2 to 4.8 x 10^{-7} atm. at 2400°K. Subtracting the JANAF values for C and C_2 we obtain C_3 = 5.4 x 10^{-8} to 2.2 x 10^{-7} atm., which compares with Drowart's value of 3.3 x 10^{-8} to 1.3 x 10^{-7} atm. The 2nd law heat of formation is reported (5) to be ΔH_{2400} = 184.4 but the range is only 80°K. It does, however, confirm the magnitude of the mass-spectrometric values for both heat and entropy. We have adopted a heat of formation within the uncertainty limits of Drowart's measurements which with the adopted functions yields pressures in the 2000-3000°K range consistent with the measurements. We were not able to generate functions which agree exactly with the 2nd law entropies, since even direct summation over only the observed levels of the bending frequency gives an entropy which is already too large.

Heat Capacity and Entropy

The stretching frequencies are from Merer (6), Weltner et al. (7) and Weltner and McLeod (8). The bending frequency and its harmonics are from Gausset et al. (9) and Merer (6). The rotational constant and bond distance are from Gausset et al. (9).

As indicated briefly above, the calculated entropy of C_3 gas is higher than the experimental value even when a summation is performed only over the observed first six levels of the bending frequency. Treatment of the vibration as a harmonic oscillator or as a anharmonic oscillator gives values considerably higher. Strauss and Thiele (10) have also calculated functions based on a quartic potential function which still yields values several units higher than the experiments. In order to reduce the entropy to the approximate range of the measurements we have made the assumption that the potential function is of an unusual form above the sixth vibrational level. We assume that the large amplitude of the bending vibration causes a drastic change in the function, possibly due to the increasing repulsion between end carbons, as the amplitude increases. Thus, we assume a very steeply rising potential above the sixth vibrational level. We have chosen to represent this part of the potential by a harmonic oscillator of 650 cm^{-1}. The choice of 650 cm^{-1} is arbitrary, but is not unreasonable for a bending vibration, and yields functions which approximate the experimental data.

In order to explain the observed spectrum of C_3O_2, a molecule with a bending frequency of 63 cm^{-1}, Smith and Barrett (11) have proposed that potential maxima occur in the bending potential away from linearity. Thus, the adoption of an unusual potential function for C_3 bending may be justifiable. We do not claim that our functions are necessarily correct but only that they include all known facts and satisfy the experimental equilibrium observations. Further investigation of the carbon vapor pressure and of the higher vibrational levels of C_3 is desirable.

References

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Tetraluminum Tricarbide (Al_4C_3)

(Crystal) Mol. Wt. = 143.95945

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.936	-50.354	-50.354	INFINITE
100	7.099	2.808	40.088	-3.728	-50.612	-50.170	109.641
200	19.622	11.759	23.579	-2.364	-51.250	-49.512	54.102
298	27.912	21.264	21.264	.000	-51.550	-48.602	35.624
300	28.035	21.437	21.265	.052	-51.554	-48.585	35.392
400	33.104	30.269	22.434	3.134	-51.598	-47.581	25.996
500	36.064	37.997	24.792	6.603	-51.594	-46.579	20.359
600	38.050	44.757	27.568	10.313	-51.642	-45.575	16.600
700	39.479	50.734	30.459	14.192	-51.786	-44.553	13.909
800	40.561	56.079	33.333	18.196	-52.023	-43.503	11.884
900	41.411	60.907	36.133	22.296	-52.372	-42.419	10.300
1000	42.099	65.307	38.834	26.473	-62.801	-40.552	8.862
1100	42.669	69.346	41.426	30.712	-62.931	-38.322	7.613
1200	43.150	73.080	43.911	35.004	-63.047	-36.077	6.570
1300	43.563	76.551	46.290	39.340	-63.158	-33.829	5.687
1400	43.922	79.793	48.568	43.714	-63.252	-31.564	4.927
1500	44.239	82.834	50.752	48.123	-63.335	-29.297	4.268
1600	44.521	85.698	52.848	52.561	-63.407	-27.028	3.692
1700	44.774	88.405	54.860	57.026	-63.464	-24.755	3.182
1800	45.004	90.971	56.796	61.515	-63.512	-22.478	2.729
1900	45.213	93.410	58.659	66.026	-63.547	-20.191	2.322
2000	45.406	95.734	60.455	70.557	-63.571	-17.909	1.957
2100	45.562	97.953	62.188	75.105	-63.584	-15.626	1.626
2200	45.710	100.076	63.863	79.669	-63.593	-13.345	1.326
2300	45.850	102.111	65.482	84.247	-63.591	-11.057	1.051
2400	45.982	104.065	67.049	88.839	-63.584	-8.773	.799
2500	46.106	105.945	68.567	93.443	-63.568	-6.490	.567
2600	46.222	107.755	70.040	98.060	-63.548	-4.211	.354
2700	46.330	109.502	71.469	102.687	-63.521	-1.936	.157
2800	46.430	111.189	72.858	107.325	-345.702	6.961	-.543
2900	46.522	112.819	74.208	111.973	-344.854	19.540	-1.472
3000	46.606	114.398	75.522	116.630	-344.000	32.095	-2.338

Dec. 31, 1960; June 30, 1963; Sept. 30, 1965

TETRALUMINUM TRICARBIDE (Al_4C_3) (CRYSTAL) MOL. WT. = 143.95945

$\Delta H_f^\circ{}_0 = -50.35 \pm 1.6$ kcal. mole^{-1}

$S_{298.15} = 21.26 \pm 0.3$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -51.55 \pm 1.6$ kcal. mole^{-1}

$T_m = [2500]$°K.

ΔH_m° = Unknown

Heat of Formation.

The $\Delta H_f^\circ{}_{298.15} = -51.55 \pm 1.6$ kcal. mole^{-1} is the average value of $\Delta H_f^\circ{}_{298.15} = -49.7 \pm 1.2$ kcal. mole^{-1} by R. C. King and G. T. Armstrong, National Bureau of Standards Report No. 8504 (1964) and that of $\Delta H_f^\circ{}_{298.15} = -53.4 \pm 2.0$ kcal. mole^{-1} by A. D. Mah, United States Bureau of Mines, Report No. 6415 (1964). Both measured the heat of reaction $Al_4C_3(c) + 6O_2(g) \rightarrow 2Al_2O_3(c,\alpha) + 3CO_2(g)$ and used their $\Delta H_r^\circ{}_{298.15}$ and the $\Delta H_f^\circ{}_{298.15}$ of $Al_2O_3(c)$ and $CO_2(g)$ to calculate the $\Delta H_f^\circ{}_{298.15}$ of $Al_4C_3(c)$. The $\Delta H_r^\circ{}_{298.15}$ measured by King and Armstrong was -1033.3 ± 1.1 kcal. mole^{-1}, the $\Delta H_r^\circ{}_{298.15}$ measured by Mah was -1029.6 ± 1.9 kcal. mole.

Heat Capacity and Entropy.

The low temperature heat capacities, 18-390°K., were measured by W. G. Saba and G. T. Furukawa, National Bureau of Standards Report 7587, July 1, 1962. The high temperature heat capacities, 273-1173°K., were measured by A. C. Victor, W. R. Thurber, and T. B. Douglas, National Bureau of Standards Report 7437, January 1, 1962. These two sets of heat capacity data were joined smoothly and extrapolated to 2000°K. by W. G. Saba and G. T. Furukawa, loc. cit. The values of C_p above 2000°K were estimated by extrapolation graphically. $S^\circ_{298.15}$ was reported by W. G. Saba and G. T. Furukawa, loc. cit., using S°_{20}(extrap.) = 0.013 cal. deg.$^{-1}$ mole^{-1}.

Melting Temperature.

T_m was estimated by O. Ruff and E. Jellinek, Z. anorg. u. allgem. Chem. 97, 312 (1916).

Dimagnesium Tricarbide (Mg_2C_3)

(Solid) Mol. Wt. = 84.67

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	22.410	24.000	24.000	.000	19.000	17.729	-12.995
300	22.500	24.139	24.000	.042	19.008	17.721	-12.909
400	25.660	31.105	24.929	2.470	19.478	17.223	-9.410
500	27.260	37.019	26.772	5.124	19.901	16.606	-7.258
600	28.250	42.084	28.912	7.903	20.224	15.916	-5.797
700	28.950	46.493	31.115	10.764	20.428	15.180	-4.739
800	29.490	50.395	33.286	13.687	20.526	14.425	-3.941
900	29.940	53.895	35.385	16.659	20.518	13.662	-3.317
1000	30.340	57.071	37.397	19.673	16.171	13.257	-2.897
1100	30.700	59.979	39.320	22.726	16.056	12.972	-2.577
1200	31.030	62.665	41.155	25.812	15.880	12.699	-2.313
1300	31.350	65.161	42.906	28.931	15.652	12.442	-2.092
1400	31.650	67.495	44.580	32.081	-45.482	13.134	-2.050
1500	31.950	69.689	46.182	35.261	-44.988	17.304	-2.521
1600	32.240	71.760	47.716	38.471	-44.485	21.436	-2.928
1700	32.520	73.723	49.189	41.709	-43.964	25.543	-3.284
1800	32.800	75.590	50.604	44.975	-43.426	29.619	-3.596
1900	33.070	77.371	51.966	48.269	-42.872	33.660	-3.872
2000	33.350	79.074	53.279	51.590	-42.297	37.670	-4.116
2100	33.620	80.708	54.547	54.938	-41.704	41.656	-4.335
2200	33.880	82.278	55.772	58.313	-41.096	45.611	-4.531
2300	34.150	83.790	56.957	61.715	-40.470	49.538	-4.707
2400	34.420	85.249	58.106	65.143	-39.827	53.439	-4.866
2500	34.680	86.659	59.220	68.598	-39.165	57.314	-5.010

December 31, 1960.

C_3Mg_2

DIMAGNESIUM TRICARBIDE (Mg_2C_3) (Solid)

Mol. Wt. = 84.67

$\Delta H_{f\ 298.15}^\circ = 19 \pm 8$ kcal. mole^{-1}

$S_{298.15}^\circ = 24 \pm 3$ cal. deg.$^{-1}$ mole^{-1}

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

C_3Mg_2

Carbon Suboxide (C_3O_2)

(Ideal Gas) GFW = 68.03225

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.589	-23.138	-23.138	INFINITE
100	10.829	51.896	78.373	-2.648	-22.933	-23.920	52.277
200	13.397	60.096	67.345	-1.450	-22.665	-25.008	27.328
298	16.010	65.959	65.959	.000	-22.380	-26.220	19.219
300	16.052	66.058	65.959	.030	-22.375	-26.244	19.119
400	17.919	70.947	66.613	1.734	-22.120	-27.573	15.065
500	19.313	75.102	67.906	3.598	-21.944	-28.958	12.657
600	20.436	78.725	69.413	5.587	-21.844	-30.372	11.063
700	21.368	81.948	70.978	7.679	-21.805	-31.796	9.927
800	22.147	84.853	72.534	9.856	-21.803	-33.224	9.076
900	22.796	87.501	74.052	12.104	-21.830	-34.653	8.415
1000	23.337	89.931	75.520	14.411	-21.868	-36.075	7.884
1100	23.787	92.177	76.933	16.768	-21.919	-37.495	7.450
1200	24.164	94.264	78.292	19.166	-21.977	-38.906	7.086
1300	24.480	96.211	79.596	21.599	-22.048	-40.315	6.778
1400	24.747	98.035	80.849	24.061	-22.118	-41.714	6.512
1500	24.973	99.750	82.052	26.547	-22.195	-43.111	6.281
1600	25.167	101.368	83.209	29.054	-22.275	-44.507	6.079
1700	25.332	102.899	84.323	31.579	-22.354	-45.893	5.900
1800	25.476	104.351	85.396	34.120	-22.439	-47.276	5.740
1900	25.600	105.732	86.430	36.674	-22.526	-48.651	5.596
2000	25.708	107.048	87.428	39.239	-22.616	-50.025	5.466
2100	25.804	108.305	88.392	41.815	-22.706	-51.389	5.348
2200	25.887	109.507	89.325	44.400	-22.806	-52.759	5.241
2300	25.962	110.659	90.228	46.992	-22.906	-54.113	5.142
2400	26.027	111.766	91.102	49.592	-23.013	-55.467	5.051
2500	26.086	112.829	91.950	52.198	-23.123	-56.822	4.967
2600	26.139	113.853	92.773	54.809	-23.241	-58.165	4.889
2700	26.186	114.841	93.572	57.425	-23.363	-59.510	4.817
2800	26.229	115.794	94.349	60.046	-23.488	-60.843	4.749
2900	26.268	116.715	95.104	62.671	-23.623	-62.173	4.685
3000	26.303	117.606	95.840	65.299	-23.763	-63.501	4.626
3100	26.335	118.469	96.556	67.931	-23.906	-64.820	4.570
3200	26.364	119.306	97.254	70.566	-24.057	-66.139	4.517
3300	26.390	120.117	97.934	73.204	-24.215	-67.460	4.468
3400	26.415	120.906	98.598	75.844	-24.379	-68.761	4.420
3500	26.437	121.672	99.247	78.487	-24.549	-70.072	4.376
3600	26.458	122.417	99.880	81.132	-24.724	-71.368	4.333
3700	26.477	123.142	100.499	83.778	-24.908	-72.659	4.292
3800	26.495	123.848	101.104	86.427	-25.095	-73.941	4.253
3900	26.511	124.537	101.696	89.077	-25.290	-75.224	4.215
4000	26.526	125.208	102.276	91.729	-25.490	-76.502	4.180
4100	26.540	125.863	102.843	94.382	-25.698	-77.781	4.146
4200	26.554	126.503	103.399	97.037	-25.912	-79.041	4.113
4300	26.566	127.128	103.943	99.693	-26.134	-80.305	4.082
4400	26.577	127.739	104.477	102.350	-26.361	-81.566	4.051
4500	26.588	128.336	105.001	105.009	-26.594	-82.822	4.022
4600	26.598	128.921	105.515	107.668	-26.835	-84.062	3.994
4700	26.608	129.493	106.019	110.328	-27.081	-85.303	3.967
4800	26.616	130.053	106.514	112.989	-27.336	-86.534	3.940
4900	26.625	130.602	107.000	115.652	-27.594	-87.771	3.915
5000	26.633	131.140	107.477	118.314	-27.861	-88.995	3.890
5100	26.640	131.667	107.946	120.978	-28.137	-90.226	3.866
5200	26.647	132.185	108.407	123.642	-28.417	-91.439	3.843
5300	26.654	132.692	108.861	126.307	-28.703	-92.638	3.820
5400	26.660	133.191	109.307	128.973	-28.996	-93.843	3.798
5500	26.666	133.680	109.745	131.639	-29.298	-95.038	3.776
5600	26.672	134.160	110.177	134.306	-29.605	-96.236	3.756
5700	26.677	134.633	110.602	136.974	-29.920	-97.434	3.736
5800	26.682	135.097	111.020	139.642	-30.242	-98.610	3.716
5900	26.687	135.553	111.432	142.310	-30.571	-99.776	3.696
6000	26.691	136.001	111.836	144.979	-30.906	-100.958	3.677

Dec. 31, 1960; Sept. 30, 1965; June 30, 1968

CARBON SUBOXIDE (C_3O_2) (IDEAL GAS) GFW = 68.03225

Point Group $D_{\infty h}$

$\Delta Hf^\circ_0 = -23.14 \pm 0.44$ kcal/mol

$S^\circ_{298.15} = 65.959 \pm 0.2$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -22.38 \pm 0.44$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
2200 (1)	2258 (1)	550 (2)
830 (1)	1573 (1)	63 (2)
	577 (2)	

Bond Distances: C-C = 1.28 Å C-O = 1.16 Å

Bond Angles: C-C-C = 180° O-C-C = 180° σ = 2

Rotational Constant: $B_0 = 0.073206\ cm^{-1}$

Heat of Formation

Kybett et al. (1) have determined the heat of combustion of the liquid form under its own pressure using the sample from the heat capacity determinations (2).

The average of four determinations gave $\Delta Hf^\circ_{298}(\ell) = -28.03 \pm 0.24$ kcal/mol; the authors report -29.03 due to an arithmetic error. The sample was 99.98 mole percent pure. McDougall et al. (2) measured $\Delta Hv^\circ_{230} = 6.421 \pm 0.012$ kcal/mol from which we calculate $\Delta Hv^\circ_{298} = 5.65 \pm 0.2$ kcal/mol. Thus the heat of formation of the gas is found to be -22.38 ± 0.44 kcal/mol.

Heat Capacity and Entropy

There has been considerable controversy as to the configuration of this molecule and the assignment of its vibrational frequencies. However, the evidence seems fairly conclusive for the linearity of the molecule from the work of Lafferty et al. (3) and Miller et al. (4). The rotational constant adopted here is that found by Lafferty et al. (3) and the vibrational frequencies are those reported by Miller et al. (4), except for ν_7 which is taken from Miller et al. (5) and Borgers (7). The low frequency Π_u mode is confirmed by the work of McDougall et al. (2), who measured the low temperature entropy of $C_3O_2(c)$ and (ℓ) and also the heat of vaporization. From a comparison of the entropy calculated statistically and that measured, they conclude $\nu_7 = 63.2\ cm^{-1}$. The values adopted are confirmed by third law analysis of the vapor pressure data of McDougall et al. (5) which indicate a heat of vaporization in fair agreement with their calorimetric value. The drift in the third law analysis indicates that the entropy of the solid is too low or that of the gas is too high by 1 eu. Alternatively as systematic error in the pressure measurements could have caused this deviation.

The bond distances are taken from the electron diffraction experiments of Livingston et al. (6) and are in good accord with the adopted rotational constant.

References

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Carbon, Tetratomic (C_4)

(Ideal Gas) GFW = 48.0446

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.579	230.429	230.429	INFINITE
100	7.138	44.675	63.489	-1.881	231.071	226.687	-495.424
200	9.531	50.253	55.567	-1.063	231.577	222.103	-242.702
298	11.992	54.543	54.543	.000	232.000	217.359	-159.328
300	12.031	54.618	54.544	.022	232.006	217.267	-158.279
400	13.780	58.333	55.038	1.318	232.318	212.305	-115.998
500	15.057	61.552	56.026	2.763	232.487	207.279	-90.601
600	16.045	64.388	57.188	4.320	232.532	202.229	-73.662
700	16.831	66.923	58.401	5.965	232.477	197.184	-61.564
800	17.463	69.213	59.612	7.681	232.357	192.151	-52.493
900	17.973	71.300	60.796	9.454	232.182	187.131	-45.442
1000	18.387	73.216	61.944	11.272	231.976	182.136	-39.806
1100	18.725	74.985	63.050	13.129	231.741	177.162	-35.199
1200	19.003	76.627	64.114	15.015	231.483	172.215	-31.365
1300	19.234	78.157	65.136	16.928	231.200	167.285	-28.123
1400	19.426	79.590	66.117	18.861	230.909	162.385	-25.349
1500	19.588	80.935	67.061	20.812	230.604	157.501	-22.948
1600	19.724	82.204	67.968	22.778	230.290	152.632	-20.849
1700	19.841	83.404	68.841	24.756	229.972	147.788	-18.999
1800	19.942	84.541	69.682	26.745	229.645	142.964	-17.358
1900	20.028	85.621	70.493	28.744	229.316	138.159	-15.892
2000	20.104	86.650	71.275	30.751	228.983	133.370	-14.574
2100	20.169	87.633	72.031	32.764	228.648	128.603	-13.384
2200	20.227	88.573	72.761	34.784	228.304	123.838	-12.302
2300	20.278	89.473	73.469	36.810	227.962	119.105	-11.318
2400	20.324	90.337	74.154	38.840	227.612	114.378	-10.416
2500	20.364	91.167	74.818	40.874	227.262	109.664	-9.587
2600	20.400	91.967	75.462	42.912	226.904	104.968	-8.823
2700	20.432	92.737	76.088	44.954	226.546	100.280	-8.117
2800	20.461	93.481	76.696	46.999	226.187	95.615	-7.463
2900	20.488	94.199	77.287	49.046	225.818	90.959	-6.855
3000	20.512	94.894	77.862	51.096	225.448	86.313	-6.288
3100	20.533	95.567	78.423	53.148	225.076	81.685	-5.759
3200	20.553	96.219	78.969	55.203	224.699	77.065	-5.263
3300	20.571	96.852	79.501	57.259	224.315	72.449	-4.798
3400	20.588	97.467	80.020	59.317	223.929	67.860	-4.362
3500	20.603	98.064	80.527	61.377	223.537	63.266	-3.951
3600	20.617	98.644	81.023	63.438	223.142	58.693	-3.563
3700	20.630	99.209	81.507	65.500	222.740	54.134	-3.198
3800	20.642	99.760	81.980	67.563	222.335	49.589	-2.852
3900	20.653	100.296	82.442	69.628	221.924	45.052	-2.525
4000	20.663	100.819	82.895	71.694	221.510	40.523	-2.214
4100	20.673	101.329	83.339	73.761	221.089	35.994	-1.919
4200	20.682	101.828	83.773	75.829	220.661	31.495	-1.639
4300	20.690	102.314	84.199	77.897	220.225	26.991	-1.372
4400	20.698	102.790	84.616	79.967	219.787	22.500	-1.118
4500	20.705	103.255	85.025	82.037	219.341	18.014	-.875
4600	20.712	103.710	85.426	84.108	218.888	13.551	-.644
4700	20.718	104.156	85.820	86.179	218.431	9.094	-.423
4800	20.724	104.592	86.206	88.251	217.963	4.651	-.212
4900	20.730	105.019	86.586	90.324	217.492	.209	-.009
5000	20.735	105.438	86.959	92.397	217.013	-4.218	.184
5100	20.740	105.849	87.325	94.471	216.523	-8.657	.371
5200	20.745	106.252	87.685	96.545	216.029	-13.061	.549
5300	20.749	106.647	88.039	98.620	215.528	-17.455	.720
5400	20.753	107.035	88.388	100.695	215.019	-21.840	.884
5500	20.757	107.416	88.730	102.770	214.498	-26.224	1.042
5600	20.761	107.790	89.067	104.846	213.974	-30.598	1.194
5700	20.765	108.157	89.399	106.923	213.439	-34.974	1.341
5800	20.768	108.518	89.725	108.999	212.895	-39.326	1.482
5900	20.771	108.873	90.047	111.076	212.344	-43.653	1.617
6000	20.774	109.223	90.364	113.154	211.786	-48.006	1.749

Dec. 31, 1960; Dec. 31, 1969

CARBON, TETRATOMIC (C_4) (IDEAL GAS) GFW = 48.0446

Point Group [$D_{\infty h}$]

ΔHf°_0 = 230.4 ± 8 kcal/mol

$S^\circ_{298.15}$ = 54.5 ± 4.0 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 232 ± 8 kcal/mol

Ground State Configuration [$^1\Sigma$]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[2150] (1)
[950] (1)
[1700] (1)
[550] (2)
[550] (2)

Bond Distance: C-C = [1.28] Å

Bond Angle: C-C-C = [180°]

σ = 2

Rotational Constant: B_0 = [0.17132] cm^{-1}

Heat of Formation

The heat of formation is obtained from the mass-spectrometric results of Drowart et al. (1) who obtained ΔHf°_{2400} = 226 ± 7 kcal/mol. This was obtained from a 2nd law analysis of the ion intensity ratio C_4^+/C^+ over a temperature range of 2200-2700°K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 4.96, yields a 2nd law entropy at 2400°K of 90.5 ± 3 eu. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of ±4.5 eu. The heats of formation at temperatures other than 2400°K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C_4 are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart et al. (1). The thermodynamic functions of C_4 were first estimated by Pitzer and Clementi (2) but the basis for this estimate has completely changed. Originally they were calculated by analogy with C_3, C_3O_2 and CO_2, but the discovery of very low bending frequencies in C_3 and C_3O_2 complicated the picture by raising the calculated entropies significantly. Sandborn (3) has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C_4 and C_5. These vibrational frequencies yield high entropies outside the limits of the second law determination. Since these frequencies are estimates based on a basically triatomic correlation we have chosen to adopt two bending frequencies of 550 cm^{-1} rather than the 200 cm^{-1} and 440 cm^{-1} estimated by Sandborn. In addition we have assumed that the ground state arising from a π^2 term is $^1\Sigma$ and not $^3\Sigma$ as assumed by Pitzer and Clementi. The basis for both these changes is to make the functions conform to the only available measured data. Use of the present table will yield values for the vapor pressure of C_4 in excellent agreement with the measurements in the 2000-3000°K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn (3) and the bond length is estimated from C_3.

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Tetramethylsilane $(Si(CH_3)_4)$

(Ideal Gas) Mol. Wt. = 88.230

INTERIM TABLE

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	33.120	86,300	86,300	.000	- 68.500	- 35.456	25,989
300	33,240	86,505	86,301	,061	- 68,542	- 35,252	25,680
400	40,080	96,988	87,684	3,722	- 70,538	- 23,846	13,028
500	46,310	106,617	90,520	8,048	- 72,231	- 11,973	5.233
600	51,690	115,548	93,956	12,955	- 73,609	.210	- ,077
700	56,370	123.875	97,642	18.363	- 74,703	12.606	- 3.936
800	60,470	131.677	101,414	24,210	- 75.530	25,141	- 6,868
900	64,090	139,012	105.188	30,442	- 76,128	37,765	- 9,170
1000	67,260	145,933	108,920	37,013	- 76,518	50,436	- 11,022
1100	70,040	152,477	112,585	43,881	- 76,726	63,146	- 12,545
1200	72,480	156,678	116.170	51,010	- 76,783	75.866	- 13.816
1300	74,620	164,566	119,668	58,367	- 76,720	88,583	- 14,891
1400	76,480	170,165	123,077	65.924	- 76.557	101.296	- 15,812
1500	78,000	175,496	126,395	73.651	- 76,343	113.995	- 16,608

December 31, 1960.

Tetramethylsilane $(Si(CH_3)_4)$ (Ideal Gas)

Mol. Wt. = 88.230

ΔH_f° 298.15 = [-68.5] kcal. mole^{-1}

$S^\circ_{298.15}$ = 86.300 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Heat of Formation. ΔH_f° 298.15 was estimated.

Heat Capacity and Entropy. C_p and $S^\circ_{298.15}$ were taken from G. Janz, Y. Mikawa, and F. Behnke, private communication, March 16, 1960.

Tetracarbon Dinitride (C_4N_2)

(Ideal Gas) Mol. Wt. = 76.06

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	,000	,000	INFINITE	- 4,239	126,341	126,341	INFINITE
100	11,948	51,789	85,148	- 3,336	126,495	125,216	- 273,647
200	17,205	61,768	71,096	- 1,866	126,957	123,776	- 135,250
298	20,528	69,314	69,314	,000	127,500	122,098	- 89,496
300	20,576	69,441	69,314	,038	127,509	122,064	- 88,919
400	22,664	75,666	70,149	2,207	127,997	120,174	- 65,657
500	24,162	80,892	71,789	4,552	128,363	118,173	- 51,651
600	25,370	85,407	73,690	7,030	128,616	116,108	- 42,290
700	26,391	89,397	75,655	9,619	128,778	114,011	- 35,594
800	27,259	92,979	77,600	12,303	128,883	111,896	- 30,567
900	27,996	96,233	79,492	15,067	128,940	109,764	- 26,653
1000	28,617	99,216	81,318	17,898	128,972	107,631	- 23,522
1100	29,141	101,969	83,072	20,787	128,981	105,495	- 20,959
1200	29,582	104,524	84,754	23,724	128,974	103,364	- 18,824
1300	29,955	106,907	86,368	26,701	128,944	101,228	- 17,017
1400	30,272	109,139	87,915	29,713	128,911	99,103	- 15,470
1500	30,542	111,237	89,401	32,754	128,867	96,974	- 14,128
1600	30,773	113,215	90,828	35,820	128,817	94,845	- 12,955
1700	30,972	115,087	92,200	38,908	128,766	92,724	- 11,920
1800	31,145	116,863	93,522	42,014	128,708	90,604	- 11,000
1900	31,295	118,551	94,795	45,136	128,649	88,493	- 10,179
2000	31,426	120,159	96,023	48,272	128,588	86,382	- 9,439
2100	31,541	121,695	97,209	51,420	128,526	84,277	- 8,770
2200	31,642	123,165	98,356	54,580	128,457	82,162	- 8,162
2300	31,732	124,574	99,465	57,749	128,390	80,068	- 7,608
2400	31,813	125,926	100,540	60,926	128,316	77,967	- 7,100
2500	31,884	127,226	101,582	64,111	128,243	75,866	- 6,632
2600	31,948	128,478	102,592	67,302	128,162	73,774	- 6,201
2700	32,006	129,685	103,573	70,500	128,082	71,678	- 5,802
2800	32,058	130,849	104,527	73,703	128,001	69,598	- 5,432
2900	32,105	131,975	105,454	76,912	127,912	67,513	- 5,088
3000	32,148	133,064	106,356	80,124	127,820	65,431	- 4,766
3100	32,187	134,119	107,235	83,341	127,728	63,356	- 4,466
3200	32,222	135,142	108,091	86,561	127,629	61,279	- 4,185
3300	32,255	136,134	108,926	89,785	127,525	59,200	- 3,920
3400	32,285	137,097	109,740	93,012	127,419	57,138	- 3,673
3500	32,312	138,033	110,535	96,242	127,306	55,062	- 3,438
3600	32,337	138,944	111,312	99,475	127,191	53,003	- 3,218
3700	32,361	139,830	112,071	102,710	127,070	50,945	- 3,009
3800	32,382	140,693	112,813	105,947	126,945	48,899	- 2,812
3900	32,403	141,535	113,538	109,186	126,813	46,848	- 2,625
4000	32,421	142,356	114,249	112,427	126,678	44,800	- 2,448
4100	32,438	143,156	114,944	115,670	126,536	42,743	- 2,278
4200	32,455	143,938	115,625	118,915	126,388	40,716	- 2,119
4300	32,470	144,702	116,292	122,161	126,231	38,670	- 1,965
4400	32,484	145,449	116,947	125,409	126,072	36,635	- 1,820
4500	32,497	146,179	117,588	128,658	125,905	34,596	- 1,680
4600	32,509	146,893	118,217	131,908	125,731	32,576	- 1,548
4700	32,521	147,592	118,835	135,160	125,554	30,555	- 1,421
4800	32,532	148,277	119,441	138,412	125,364	28,543	- 1,300
4900	32,542	148,948	120,037	141,666	125,171	26,524	- 1,183
5000	32,552	149,606	120,621	144,921	124,971	24,513	- 1,071
5100	32,561	150,250	121,196	148,176	124,758	22,486	- ,964
5200	32,569	150,883	121,761	151,433	124,542	20,492	- ,861
5300	32,577	151,503	122,316	154,690	124,318	18,498	- ,763
5400	32,585	152,112	122,862	157,948	124,086	16,512	- ,668
5500	32,592	152,710	123,400	161,207	123,843	14,519	- ,577
5600	32,599	153,297	123,928	164,467	123,596	12,528	- ,489
5700	32,606	153,875	124,449	167,727	123,337	10,537	- ,404
5800	32,612	154,442	124,961	170,988	123,070	8,562	- ,323
5900	32,618	154,999	125,465	174,249	122,794	6,605	- ,245
6000	32,624	155,548	125,962	177,512	122,512	4,621	- ,168

March 31, 1961

TETRACARBON DINITRIDE (C_4N_2) (IDEAL GAS) MOL. WT. = 76.06

$\Delta H_{f0}^\circ = 126.3 \pm 0.2$ kcal. mole^{-1}

Point Group $D_{\infty h}$

$\Delta H_{f\ 298.15}^\circ = 127.5 \pm 0.2$ kcal. mole^{-1}

$S_{298.15}^\circ = 69.31 \pm 0.02$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω cm.$^{-1}$	ω cm.$^{-1}$	ω cm.$^{-1}$
2290 (1)	2241 (1)	263 (2)
2119 (1)	1154 (1)	472 (2)
692 (1)	504 (2)	107 (2)

Bond Distances C≡N 1.14 Å C-C 1.37 Å C≡C 1.19 Å

Moment of Inertia $I = 61.65 \times 10^{-39}$ g. cm.^{2} $\sigma = 2$

Heat of Formation

G. T. Armstrong and S. Marantz, J. Phys. Chem. 64, 1776 (1960), measured the heat of combustion of the liquid for which they obtain a $\Delta H_{f\ 298.15}^\circ$ of 120.6 kcal. mole^{-1} using 94.05 kcal. mole^{-1} for $\Delta H_{f\ 298.15}^\circ$ of $CO_2(g)$. They calculate the $\Delta H_{f\ 298.15}^\circ$ of $C_4N_2(g)$ with a ΔH_{vap} taken from A. J. Saggiomo, J. Org. Chem. 22, 1171 (1957).

Heat Capacities and Entropies

Bond lengths determined by F. A. Miller and R. B. Hannan Jr., J. Chem. Phys. 21, 110 (1953) from X-ray diffraction measurements on the solid. The vibrational frequencies were observed in the infra red and Raman by F. A. Miller, R. B. Hannan Jr., and L. R. Cousins, J. Chem. Phys. 23, 2127 (1955).

Carbon, Pentatomic (C_5)

(Ideal Gas) GFW = 60.05575

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.847	232.413	232.413	INFINITE
100	7.232	46.731	68.215	-2.148	233.042	228.473	-499.328
200	10.915	52.714	59.032	-1.264	233.536	223.714	-244.463
298	14.611	57.806	57.806	.000	234.000	218.791	-160.378
300	14.668	57.896	57.806	.027	234.007	218.696	-159.320
400	17.184	62.484	58.414	1.628	234.378	213.534	-116.670
500	18.964	66.520	59.640	3.440	234.595	208.295	-91.046
600	20.318	70.102	61.091	5.407	234.672	203.023	-73.951
700	21.385	73.317	62.612	7.494	234.634	197.753	-61.741
800	22.239	76.231	64.135	9.677	234.522	192.493	-52.587
900	22.927	78.891	65.629	11.936	234.346	187.243	-45.469
1000	23.484	81.337	67.079	14.258	234.138	182.021	-39.781
1100	23.940	83.597	68.479	16.630	233.895	176.819	-35.131
1200	24.314	85.697	69.828	19.043	233.628	171.646	-31.261
1300	24.624	87.656	71.124	21.490	233.330	166.490	-27.990
1400	24.883	89.490	72.371	23.966	233.026	161.367	-25.190
1500	25.101	91.215	73.571	26.466	232.706	156.259	-22.767
1600	25.286	92.841	74.725	28.985	232.375	151.166	-20.648
1700	25.444	94.378	75.836	31.522	232.042	146.101	-18.783
1800	25.579	95.837	76.907	34.073	231.698	141.056	-17.127
1900	25.696	97.223	77.940	36.637	231.352	136.033	-15.647
2000	25.798	98.543	78.938	39.212	231.002	131.025	-14.318
2100	25.886	99.804	79.901	41.796	230.651	126.041	-13.117
2200	25.965	101.010	80.834	44.389	230.289	121.058	-12.026
2300	26.033	102.164	81.736	46.989	229.929	116.111	-11.033
2400	26.095	103.275	82.611	49.595	229.560	111.167	-10.123
2500	26.149	104.342	83.459	52.207	229.192	106.238	-9.287
2600	26.198	105.368	84.282	54.825	228.815	101.328	-8.517
2700	26.241	106.358	85.081	57.447	228.437	96.426	-7.805
2800	26.281	107.313	85.858	60.073	228.058	91.550	-7.146
2900	26.316	108.236	86.614	62.703	227.668	86.682	-6.533
3000	26.349	109.129	87.350	65.336	227.276	81.826	-5.961
3100	26.378	109.993	88.066	67.972	226.882	76.988	-5.428
3200	26.405	110.831	88.765	70.612	226.482	72.159	-4.928
3300	26.429	111.644	89.446	73.253	226.073	67.331	-4.459
3400	26.452	112.433	90.110	75.897	225.662	62.537	-4.020
3500	26.472	113.200	90.759	78.544	225.244	57.733	-3.605
3600	26.491	113.946	91.393	81.192	224.822	52.954	-3.215
3700	26.508	114.672	92.012	83.842	224.392	48.190	-2.846
3800	26.525	115.379	92.618	86.493	223.958	43.442	-2.498
3900	26.540	116.069	93.210	89.147	223.517	38.701	-2.169
4000	26.553	116.741	93.790	91.801	223.071	33.969	-1.856
4100	26.566	117.397	94.358	94.457	222.617	29.235	-1.558
4200	26.578	118.037	94.914	97.114	222.154	24.537	-1.277
4300	26.590	118.662	95.459	99.773	221.683	19.831	-1.008
4400	26.600	119.274	95.994	102.432	221.207	15.139	-.752
4500	26.610	119.872	96.518	105.093	220.723	10.453	-.508
4600	26.619	120.457	97.032	107.754	220.229	5.793	-.275
4700	26.628	121.029	97.536	110.417	219.732	1.139	-.053
4800	26.636	121.590	98.032	113.080	219.220	-3.499	.159
4900	26.643	122.139	98.518	115.744	218.704	-8.137	.363
5000	26.651	122.678	98.996	118.408	218.178	-12.759	.558
5100	26.657	123.205	99.465	121.074	217.639	-17.396	.745
5200	26.664	123.723	99.927	123.740	217.095	-21.991	.924
5300	26.670	124.231	100.381	126.407	216.542	-26.574	1.096
5400	26.675	124.730	100.827	129.074	215.979	-31.150	1.261
5500	26.681	125.219	101.266	131.742	215.402	-35.723	1.420
5600	26.686	125.700	101.698	134.410	214.820	-40.287	1.572
5700	26.691	126.172	102.123	137.079	214.224	-44.854	1.720
5800	26.695	126.636	102.542	139.748	213.618	-49.391	1.861
5900	26.700	127.093	102.954	142.418	213.003	-53.900	1.997
6000	26.704	127.542	103.360	145.088	212.378	-58.441	2.129

Dec. 31, 1960; Dec. 31, 1969

CARBON, PENTATOMIC (C_5) (IDEAL GAS) GFW = 60.05575

Point Group $[D_{\infty h}]$

$S^\circ_{298.15}$ = 57.8 ± 4 gibbs/mol

Ground State Configuration $[{}^1\Sigma]$

ΔHf°_0 = 232.4 ± 6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 234 ± 6 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}	ω_i, cm^{-1}
[1920] (1)	[550] (2)
[770] (1)	[550] (2)
[2210] (1)	[550] (2)
[1430] (1)	

Bond Distance: C-C = [1.28] Å

Bond Angle: C-C-C = [180°]

Rotational Constant = B_0 = [0.085662] cm^{-1}

$\sigma = 2$

Heat of Formation

The heat of formation is obtained from the mass-spectrometric results of Drowart et al. (1) who obtained ΔHf°_{2400} = 230 ± 5 kcal/mol. This was obtained from a 2nd law analysis of the ion intensity ratio C_5^+/C^+ over a temperature range of 2200-2700°K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 6.3, yields a 2nd law entropy at 2400°K of 103.7 ± 2 eu. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of ±3.5 eu. The heats of formation at temperatures other than 2400°K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C_5 are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart et al. (1). The thermodynamic functions of C_5 were first estimated by Pitzer and Clementi (2) but the basis for this estimate has completely changed. Originally they were calculated by analogy with C_3, C_3O_2 and CO_2, but the discovery of very low bending frequencies in C_3 and C_3O_2 complicated the picture by raising the calculated entropies significantly. Sandborn (3) has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C_4 and C_5. These vibrational frequencies yield high entropies outside the limits of the second law determination. Since these frequencies are estimates, based on a basically triatomic correlation we have chosen to adopt three doubly degenerate bending frequencies of 550 cm^{-1} in place of the 130 cm^{-1}, 330 cm^{-1} and 520 cm^{-1} frequencies estimated by Sandborn. The basis for this change is to make the functions conform to the only available measured data. Use of the present tables will yield values for the vapor pressure of C_4 in excellent agreement with the measurements in the 2000-3000°K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn (3) and the bond length is estimated equal to that in C_3.

References

1. J. Drowart, R. P. Burns, G. DeMaria, M. G. Inghram, J. Chem. Phys. 31, 1131 (1959).
2. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. 81, 4477 (1959).
3. R. H. Sandborn, J. Chem. Phys. 49, 4219 (1968).

Calcium (Ca)

(Reference State) GFW = 40.08

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-1.371	.000	.000	.000
100	4.657	3.812	15.178	-1.137	.000	.000	.000
200	5.858	7.519	10.493	-.595	.000	.000	.000
298	6.279	9.932	9.932	.000	.000	.000	.000
300	6.283	9.971	9.932	.012	.000	.000	.000
400	6.432	11.802	10.181	.649	.000	.000	.000
500	6.495	13.245	10.654	1.295	.000	.000	.000
600	6.522	14.432	11.188	1.946	.000	.000	.000
700	6.532	15.438	11.725	2.599	.000	.000	.000
800	8.254	16.772	12.283	3.592	.000	.000	.000
900	8.784	17.775	12.838	4.444	.000	.000	.000
1000	9.314	18.728	13.379	5.349	.000	.000	.000
1100	9.844	19.641	13.907	6.307	.000	.000	.000
1200	7.200	22.131	14.548	9.099	.000	.000	.000
1300	7.200	22.707	15.154	9.819	.000	.000	.000
1400	7.200	23.241	15.713	10.539	.000	.000	.000
1500	7.200	23.737	16.232	11.259	.000	.000	.000
1600	7.200	24.202	16.715	11.979	.000	.000	.000
1700	7.200	24.639	17.169	12.699	.000	.000	.000
1800	4.982	45.925	17.973	50.313	.000	.000	.000
1900	4.992	46.195	19.452	50.812	.000	.000	.000
2000	5.008	46.451	20.795	51.312	.000	.000	.000
2100	5.030	46.696	22.023	51.814	.000	.000	.000
2200	5.061	46.931	23.150	52.318	.000	.000	.000
2300	5.101	47.156	24.189	52.826	.000	.000	.000
2400	5.153	47.375	25.150	53.339	.000	.000	.000
2500	5.219	47.586	26.043	53.857	.000	.000	.000
2600	5.299	47.792	26.876	54.383	.000	.000	.000
2700	5.396	47.994	27.654	54.918	.000	.000	.000
2800	5.511	48.193	28.384	55.463	.000	.000	.000
2900	5.644	48.388	29.071	56.020	.000	.000	.000
3000	5.796	48.582	29.718	56.592	.000	.000	.000
3100	5.968	48.775	30.330	57.180	.000	.000	.000
3200	6.159	48.967	30.909	57.786	.000	.000	.000
3300	6.370	49.160	31.459	58.413	.000	.000	.000
3400	6.600	49.353	31.983	59.061	.000	.000	.000
3500	6.848	49.548	32.482	59.733	.000	.000	.000
3600	7.113	49.745	32.958	60.431	.000	.000	.000
3700	7.394	49.944	33.415	61.156	.000	.000	.000
3800	7.688	50.145	33.852	61.910	.000	.000	.000
3900	7.995	50.348	34.273	62.695	.000	.000	.000
4000	8.312	50.555	34.677	63.510	.000	.000	.000
4100	8.636	50.764	35.067	64.357	.000	.000	.000
4200	8.966	50.976	35.443	65.237	.000	.000	.000
4300	9.300	51.191	35.807	66.151	.000	.000	.000
4400	9.635	51.409	36.159	67.097	.000	.000	.000
4500	9.969	51.629	36.500	68.078	.000	.000	.000
4600	10.300	51.852	36.832	69.091	.000	.000	.000
4700	10.626	52.077	37.154	70.137	.000	.000	.000
4800	10.944	52.304	37.467	71.216	.000	.000	.000
4900	11.254	52.532	37.772	72.326	.000	.000	.000
5000	11.553	52.763	38.070	73.466	.000	.000	.000
5100	11.841	52.995	38.360	74.636	.000	.000	.000
5200	12.115	53.227	38.644	75.834	.000	.000	.000
5300	12.376	53.460	38.921	77.059	.000	.000	.000
5400	12.622	53.694	39.192	78.309	.000	.000	.000
5500	12.852	53.928	39.458	79.583	.000	.000	.000
5600	13.067	54.161	39.719	80.879	.000	.000	.000
5700	13.265	54.394	39.974	82.195	.000	.000	.000
5800	13.447	54.627	40.225	83.531	.000	.000	.000
5900	13.613	54.858	40.471	84.884	.000	.000	.000
6000	13.763	55.088	40.712	86.253	.000	.000	.000

Dec. 31, 1968

CALCIUM (Ca) (REFERENCE STATE) GFW = 40.08

0	to	721°K	Crystal alpha
721	to	1112°K	Crystal beta
1112	to	1767.4°K	Liquid
1767.4	to	6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Calcium, Alpha (Ca, α)

(Crystal) GFW = 40.08

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.371	.000	.000	.000
100	4.657	3.812	15.178	- 1.137	.000	.000	.000
200	5.858	7.519	10.493	- .595	.000	.000	.000
298	6.279	9.932	9.932	.000	.000	.000	.000
300	6.283	9.971	9.932	.012	.000	.000	.000
400	6.432	11.802	10.181	.649	.000	.000	.000
500	6.495	13.245	10.654	1.295	.000	.000	.000
600	6.522	14.432	11.188	1.946	.000	.000	.000
700	6.532	15.438	11.725	2.599	.000	.000	.000
800	6.533	16.310	12.245	3.252	- .340	.030	- .008
900	6.533	17.080	12.740	3.906	- .538	.087	- .021
1000	6.533	17.768	13.209	4.559	- .790	.170	- .037
1100	6.533	18.391	13.652	5.212	- 1.095	.280	- .056
1200	6.533	18.959	14.071	5.866	- 3.233	.572	- .104
1300	6.533	19.482	14.468	6.519	- 3.300	.892	- .150
1400	6.533	19.966	14.843	7.172	- 3.367	1.217	- .190
1500	6.533	20.417	15.200	7.826	- 3.433	1.547	- .225

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$S^\circ_{298.15}$ = 9.93 ± 0.06 gibbs/mol

Tt = 721 ± 2°K

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

ΔHt° = 0.220 ± 0.05 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 42.85 ± 0.3 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity data of Griffel et al. (1), 1.8° to 4.2°K, Roberts (2), 1.5° to 20°K, and Clusius and Vaughen (3), 10° to 200°K, were fit with polynomial expressions. Up to 20°K the three sets fit the adopted curve within ±6% with a maximum deviation of 14%. This is considered excellent agreement since the heat capacity is only 0.35 gibbs/mol at 20°K. From 20° to 200°K the data of Clusius were within ±1% of the adopted polynomial. The data of Gunther (4), 22° to 62°K, generally deviated from the adopted curve by 10%. The polynomial fit of the data of Clusius was arranged to be linear in temperature at high temperatures and was extrapolated to 298°K. The data of Eastman et al. (5), 67° to 293°K, were consistently high by 5.8 to 9% over the whole range. The extrapolation of the heat capacity to 6.28 gibbs/mol at 298°K is further justified by comparison with the heat capacity of magnesium, which is almost identical to that of calcium over the whole range, if its temperature scale is multiplied by 0.75.

The heat capacity between 298° and 721°K was obtained by forcing a polynomial of the type $H = aT^2 + bT + c + d/T$ through 298° with a slope of 6.28 and also through a value of H_{721} = 2736 cal, and making a good fit of the adopted low temperature enthalpies. The choice of H_{721} = 2736 cal was made, since Zalesinski and Zulinsky (6), Jauch (7), and Eastman et al. (8) were in essential agreement in the beta-phase at this temperature. The enthalpy of transition was subtracted to give the adopted value. The individual measurements of Jauch (7) were not available, but the value at 720°K could be read from a small plot with reasonable accuracy; Eastman et al. (8) gave only an equation for their data.

There is no question that reliable measurements of the heat capacity and enthalpy are needed in the range 200° to 700°K.

Transition Data

The temperature of transition was that reported by Peterson and Fattore (9) and confirmed by Chiotti et al. (10). Earlier reports on impure specimens ranged from 718° to 737°K and were not considered. The heat of transition was measured by Chiotti et al. (10) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (11) of 0.24 ± 0.04 kcal from enthalpy data.

Sublimation Data

See Ca(g) for details.

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10. P. Chiotti, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).
11. O. Kubaschewski, Z. Elektrochem. 54, 275 (1950).

Calcium, Beta (Ca, β)

(Crystal) GFW = 40.08

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	5.594	10.151	10.151	.000	.117	-.052	.038
300	5.604	10.185	10.151	.010	.116	-.051	.037
400	6.134	11.870	10.377	.597	.065	-.038	.021
500	6.664	13.296	10.821	1.237	.059	-.034	.015
600	7.194	14.558	11.341	1.930	.101	-.026	.009
700	7.724	15.706	11.884	2.676	.194	-.006	.002
800	8.254	16.772	12.429	3.475	.000	.000	.000
900	8.784	17.775	12.968	4.327	.000	.000	.000
1000	9.314	18.728	13.496	5.232	.000	.000	.000
1100	9.844	19.641	14.014	6.190	.000	.000	.000
1200	10.374	20.520	14.520	7.200	-1.781	-.152	.028
1300	10.904	21.371	15.014	8.264	-1.437	-.299	.050
1400	11.434	22.199	15.498	9.381	-1.041	-.418	.065
1500	11.964	23.006	15.971	10.551	-.591	-.507	.074
1600	12.494	23.795	16.436	11.774	-.088	-.564	.077
1700	13.024	24.568	16.892	13.050	.468	-.588	.076
1800	13.554	25.327	17.339	14.379	-35.817	1.259	-.153
1900	14.084	26.075	17.779	15.761	-34.934	3.294	-.379
2000	14.614	26.810	18.213	17.196	-33.999	5.282	-.577

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ΔHf_0 = unknown

$S^\circ_{298.15}$ = 10.15 gibbs/mol

$\Delta Hf_{298.15}$ = 0.117 ± 0.05 kcal/mol

Tt = 721 ± 2°K

ΔHt° = 0.220 ± 0.05 kcal/mol

Tm = 1112 ± 2°K

ΔHm° = 2.04 ± 0.10 kcal/mol

Heat of Formation

Obtained from that of α-Ca by adding ΔHt and the difference in $H_{721} - H_{298}$ for α- and β-Ca.

Heat Capacity and Entropy

The enthalpy at 721°K was fixed as described on the α-Ca table. The data of Jauch (1), and Zalesinski and Zulinski (2), and Eastman et al. (3) were then fitted by an equation of the form $H = a + bT + cT^2$ where a = -1315, b = 4.014 and c = 0.00265. The values of Jauch, read from a small graph, fit within 1% generally and within 2% maximum deviation; those of Zalesinski and Zulinski fit within 0.7% with the exception of the highest point which differed by 1.8%. The data of Eastman et al. vary from 3.6% high to 0.4% low. The entropy was obtained in a manner analogous to the heat of formation.

Transition Data

See the α-Ca table for details.

Melting Data

The melting point is that reported by Peterson and Fattore (4) and confirmed by Chiotti et al. (5). Earlier reports on less pure specimens ranged from 1083° to 1122°K. The heat of melting was measured by Chiotti et al. (5) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (6) of 2.07 ± 0.1 kcal/mol from enthalpy data.

References:

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4. D. T. Peterson and V. G. Fattore, J. Phys. Chem. 65, 2062 (1961).
5. P. Chiotti, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).
6. O. Kubaschewski, Z. Elektrochem. 54, 275 (1950).

Calcium (Ca)

(Liquid) GFW = 40.08

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	7.200	12.105	12.105	.000	2.606	1.958	- 1.435
300	7.200	12.149	12.105	.013	2.607	1.953	- 1.423
400	7.200	14.221	12.387	.733	2.690	1.723	- .941
500	7.200	15.827	12.921	1.453	2.764	1.473	- .644
600	7.200	17.140	13.518	2.173	2.833	1.208	- .440
700	7.200	18.250	14.117	2.893	2.900	.932	- .291
800	7.200	19.211	14.695	3.613	2.627	.676	- .185
900	7.200	20.059	15.245	4.333	2.495	.439	- .107
1000	7.200	20.818	15.765	5.053	2.310	.220	- .048
1100	7.200	21.504	16.256	5.773	2.072	.022	- .004
1200	7.200	22.131	16.720	6.493	.000	.000	.000
1300	7.200	22.707	17.158	7.213	.000	.000	.000
1400	7.200	23.241	17.574	7.933	.000	.000	.000
1500	7.200	23.737	17.968	8.653	.000	.000	.000
1600	7.200	24.202	18.344	9.373	.000	.000	.000
1700	7.200	24.639	18.701	10.093	.000	.000	.000
1800	7.200	25.050	19.043	10.813	- 36.894	.681	- .083
1900	7.200	25.439	19.369	11.533	- 36.673	2.762	- .318
2000	7.200	25.809	19.682	12.253	- 36.453	4.832	- .528
2100	7.200	26.160	19.982	12.973	- 36.235	6.891	- .717
2200	7.200	26.495	20.271	13.693	- 36.019	8.940	- .888
2300	7.200	26.815	20.548	14.413	- 35.807	10.978	- 1.043
2400	7.200	27.121	20.816	15.133	- 35.600	13.008	- 1.185
2500	7.200	27.415	21.074	15.853	- 35.398	15.029	- 1.314
2600	7.200	27.698	21.323	16.573	- 35.204	17.042	- 1.433
2700	7.200	27.969	21.564	17.293	- 35.019	19.048	- 1.542
2800	7.200	28.231	21.798	18.013	- 34.844	21.048	- 1.643
2900	7.200	28.484	22.024	18.733	- 34.681	23.041	- 1.736
3000	7.200	28.728	22.244	19.453	- 34.533	25.029	- 1.823

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CALCIUM (Ca) (LIQUID) GFW = 40.08

Ca

$S^\circ_{298.15}$ = 12.105 gibbs/mol

Tm = 1112 ± 2°K

Tb = 1767.4 ± 15°K

$\Delta Hf^\circ_{298.15}$ = 2.606 ± 0.1 kcal/mol

ΔHm° = 2.04 ± 0.10 kcal/mol

ΔHv° = 36.9668 kcal/mol

Heat of Formation

Obtained from that of β-Ca by adding ΔHm° and the difference between $H_{1112} - H_{298}$ for β-Ca and liquid.

Heat Capacity and Entropy

The heat capacity was derived as constant from the enthalpy values of R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946, quoted by O. Kubaschewski, Z. Elektrochem. 54, 275 (1950). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data

See the β-Ca table for details.

Vaporization Data

Tb is calculated from the free energy crossovers of the Ca(ℓ) and Ca(g) tables, and ΔHv° is the difference between $\Delta Hf^\circ_{1767.4}$ for liquid and gas.

Ca

Calcium (Ca)

(Ideal Gas) GFW = 40.08

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.481	42.740	42.740	INFINITE
100	4.968	31.565	41.409	-.984	43.003	40.227	-87.917
200	4.968	35.008	37.446	-.488	42.957	37.459	-40.934
298	4.968	36.992	36.992	.000	42.850	34.782	-25.496
300	4.968	37.023	36.992	.009	42.847	34.732	-25.302
400	4.968	38.452	37.187	.506	42.707	32.047	-17.510
500	4.968	39.560	37.555	1.003	42.558	29.400	-12.851
600	4.968	40.466	37.967	1.500	42.404	26.783	-9.756
700	4.968	41.232	38.380	1.996	42.247	24.192	-7.553
800	4.968	41.895	38.779	2.493	41.751	21.653	-5.915
900	4.968	42.480	39.158	2.990	41.396	19.161	-4.653
1000	4.968	43.004	39.517	3.487	40.988	16.712	-3.652
1100	4.968	43.477	39.856	3.984	40.527	14.306	-2.842
1200	4.968	43.910	40.176	4.480	38.231	12.097	-2.203
1300	4.968	44.307	40.479	4.977	38.008	9.928	-1.669
1400	4.969	44.675	40.765	5.474	37.785	7.776	-1.214
1500	4.970	45.018	41.038	5.971	37.562	5.641	-.822
1600	4.972	45.339	41.297	6.468	37.339	3.520	-.481
1700	4.976	45.641	41.543	6.965	37.116	1.413	-.182
1800	4.982	45.925	41.779	7.463	.000	.000	.000
1900	4.992	46.195	42.004	7.962	.000	.000	.000
2000	5.008	46.451	42.220	8.462	.000	.000	.000
2100	5.030	46.696	42.428	8.964	.000	.000	.000
2200	5.061	46.931	42.627	9.468	.000	.000	.000
2300	5.101	47.156	42.819	9.976	.000	.000	.000
2400	5.153	47.375	43.004	10.489	.000	.000	.000
2500	5.219	47.586	43.183	11.007	.000	.000	.000
2600	5.299	47.792	43.357	11.533	.000	.000	.000
2700	5.396	47.994	43.525	12.068	.000	.000	.000
2800	5.511	48.193	43.688	12.613	.000	.000	.000
2900	5.644	48.388	43.847	13.170	.000	.000	.000
3000	5.796	48.582	44.001	13.742	.000	.000	.000
3100	5.968	48.775	44.152	14.330	.000	.000	.000
3200	6.159	48.967	44.300	14.936	.000	.000	.000
3300	6.370	49.160	44.444	15.563	.000	.000	.000
3400	6.600	49.353	44.585	16.211	.000	.000	.000
3500	6.848	49.548	44.725	16.883	.000	.000	.000
3600	7.113	49.745	44.861	17.581	.000	.000	.000
3700	7.394	49.944	44.996	18.306	.000	.000	.000
3800	7.688	50.145	45.129	19.060	.000	.000	.000
3900	7.995	50.348	45.260	19.845	.000	.000	.000
4000	8.312	50.555	45.390	20.660	.000	.000	.000
4100	8.636	50.764	45.518	21.507	.000	.000	.000
4200	8.966	50.976	45.646	22.387	.000	.000	.000
4300	9.300	51.191	45.772	23.301	.000	.000	.000
4400	9.635	51.409	45.898	24.247	.000	.000	.000
4500	9.969	51.629	46.023	25.228	.000	.000	.000
4600	10.300	51.852	46.147	26.241	.000	.000	.000
4700	10.626	52.077	46.271	27.287	.000	.000	.000
4800	10.944	52.304	46.394	28.366	.000	.000	.000
4900	11.254	52.532	46.517	29.476	.000	.000	.000
5000	11.553	52.763	46.640	30.616	.000	.000	.000
5100	11.841	52.995	46.762	31.786	.000	.000	.000
5200	12.115	53.227	46.884	32.984	.000	.000	.000
5300	12.376	53.460	47.006	34.209	.000	.000	.000
5400	12.622	53.694	47.128	35.459	.000	.000	.000
5500	12.852	53.928	47.249	36.733	.000	.000	.000
5600	13.067	54.161	47.370	38.029	.000	.000	.000
5700	13.265	54.394	47.492	39.345	.000	.000	.000
5800	13.447	54.627	47.613	40.681	.000	.000	.000
5900	13.613	54.858	47.733	42.034	.000	.000	.000
6000	13.763	55.088	47.854	43.403	.000	.000	.000

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Ground State Configuration $^1S_0$

ΔHf°_0 = 42.74 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 36.992 ± 0.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 42.85 ± 0.30 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	1	35730.5	5	37757.5	7	40719.9	5
15157.9	1	35818.7	7	38192.4	3	41679.0	3
15210.0	3	35896.9	9	38219.1	5	41786.0	1
15315.9	5	35835.4	5	38259.1	7	42170.6	21
20335.3	3	36547.7	1	38417.6	1	42344.0	7
20349.3	5	36554.7	3	38464.8	3	42520.0	9
20371.0	7	36575.1	5	38551.6	5	42745.0	15
21849.6	5	36731.6	3	39337.6	9	42919.0	5
23652.3	3	37298.3	5	40474.3	3	44000.0	7
31539.5	3	37748.2	3	40537.9	7	44765.0	28
33317.3	1	37751.9	5	40690.4	1	45000.0	29

Heat of Formation

The vapor pressure over solid and liquid calcium has been reported by several authors. The results of our analysis of their data are presented in the following table. By using free energy functions based on the α crystal at 298°K all the data yield $\Delta Hs^\circ_{298.15}$ (Ca, α) which is $\Delta Hf^\circ_{298.15}$ (Ca, g).

				$\Delta Hf^\circ_{298.15}$, kcal/mol		Drift
Investigator	Method	Range°K	Points	2nd Law	3rd Law	eu
(1) Pilling (1921)	Langmuir	776 - 973	6	45.9 ± 2.6	42.34 ± 1.1	-4.8 ± 3.1
(2) Ruff (1924)	B. pt.	1233 - 1380	7	94.6 ± 10.2	41.38 ± 4.9	-40.8 ± 8.0
(3) Hartmann (1929)	B. pt.	1254 - 1452	10*	45.2 ± 1.2	42.52 ± 0.4	-2.1 ± 0.9
(4) Rudberg (1934)	Knudsen	774 - 897	7	44.4 ± 1.3	46.17 ± 0.4	2.2 ± 1.6
(5) Douglas (1954)	Knudsen	807 - 918	13	47.6 ± 0.7	42.43 ± 0.5	-6.0 ± 0.9
(6) Tomlin (1954)	Knudsen	868 - 877	6	45.9 ± 1.0	42.34 ± 0.3	-4.2 ± 1.2
(7) Priselkov (1954)	Knudsen	748 - 943	11	40.3 ± 0.4	42.31 ± 0.3	2.4 ± 0.5
(8) Smith (1959)	Knudsen	844 - 964	9**	43.1 ± 0.3	43.01 ± 0.1	-0.2 ± 0.3
(9) Smith (1962)	Knudsen	844 - 965	9	42.6 ± 0.3	42.98 ± 0.1	0.5 ± 0.4
(10) Mashovets (1965)	Transpiration	1163 - 1305	7	43.5 ± 3.5	41.12 ± 0.7	-2.0 ± 2.9
(11) Muradov (1965)	Knudsen	640 - 834	9	42.2 ± 0.9	42.58 ± 0.4	0.4 ± 1.2
(12) Bohdansky (1967)	B. pt.	1313 - 2060	8	42.3 ± 0.2	42.73 ± 0.2	0.3 ± 0.1

* 1 point rejected due to statistical test ** 3 points rejected

With the exception of sets 2, 4 and 10, all the results for the third law value fall in the range 42 - 43 kcal/mol. The drifts are both positive and negative over solid and liquid, indicating the reliability of the functions within the experimental accuracies. The adopted heat of sublimation, 42.85 ± 0.3 kcal/mol, is taken as the weighted average of sets 9, 11 and 12 which have drifts less than 1 eu. Note that sets 8 and 9 are in fact the same data but the values in set 8 were read from a graph and initially contained three extra points.

Heat Capacity and Entropy

The electronic levels and quantum weights were obtained from Moore (13), and were cut off at 45000 cm^{-1}, which is approximately the ionization limit minus kT for the maximum temperature. All of the unobserved terms in the spectrum are estimated to occur between 47000 cm^{-1} and the ionization limit.

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Calcium Monochloride (CaCl)

(Ideal Gas) GFW = 75.533

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.292	-24.824	-24.824	INFINITE
100	7.244	49.066	64.976	-1.591	-24.705	-26.973	58.949
200	8.116	54.379	58.476	-.819	-24.838	-29.195	31.903
298	8.524	57.707	57.707	.000	-25.000	-31.300	22.944
300	8.529	57.760	57.707	.016	-25.004	-31.340	22.831
400	8.719	60.243	58.044	.879	-25.192	-33.424	18.262
500	8.822	62.200	58.687	1.757	-25.387	-35.458	15.499
600	8.885	63.815	59.411	2.642	-25.587	-37.453	13.642
700	8.928	65.188	60.140	3.533	-25.788	-39.415	12.306
800	8.961	66.382	60.847	4.428	-26.330	-41.319	11.288
900	8.987	67.439	61.522	5.325	-26.729	-43.169	10.483
1000	9.009	68.387	62.162	6.225	-27.182	-44.972	9.829
1100	9.028	69.247	62.768	7.127	-27.686	-46.727	9.284
1200	9.045	70.033	63.341	8.030	-30.025	-48.282	8.793
1300	9.061	70.758	63.884	8.936	-30.290	-49.793	8.371
1400	9.076	71.430	64.399	9.843	-30.555	-51.283	8.006
1500	9.091	72.056	64.889	10.751	-30.820	-52.754	7.686
1600	9.105	72.643	65.355	11.661	-31.084	-54.208	7.404
1700	9.119	73.196	65.801	12.572	-31.348	-55.644	7.154
1800	9.133	73.717	66.226	13.485	-68.504	-56.386	6.846
1900	9.147	74.212	66.633	14.399	-68.545	-55.711	6.408
2000	9.162	74.681	67.024	15.314	-68.587	-55.035	6.014
2100	9.179	75.129	67.400	16.231	-68.630	-54.356	5.657
2200	9.196	75.556	67.761	17.150	-68.674	-53.675	5.332
2300	9.215	75.965	68.109	18.070	-68.721	-52.992	5.035
2400	9.237	76.358	68.444	18.993	-68.772	-52.307	4.763
2500	9.260	76.735	68.768	19.918	-68.827	-51.620	4.513
2600	9.286	77.099	69.082	20.845	-68.888	-50.931	4.281
2700	9.315	77.450	69.385	21.775	-68.957	-50.239	4.067
2800	9.347	77.789	69.679	22.708	-69.035	-49.544	3.867
2900	9.383	78.118	69.965	23.645	-69.122	-48.846	3.681
3000	9.421	78.437	70.242	24.585	-69.222	-48.146	3.507
3100	9.463	78.746	70.511	25.529	-69.335	-47.441	3.345
3200	9.509	79.048	70.773	26.478	-69.463	-46.733	3.192
3300	9.557	79.341	71.028	27.431	-69.610	-46.021	3.048
3400	9.610	79.627	71.277	28.389	-69.773	-45.303	2.912
3500	9.665	79.906	71.520	29.353	-69.957	-44.581	2.784
3600	9.724	80.179	71.756	30.322	-70.162	-43.853	2.662
3700	9.786	80.447	71.988	31.298	-70.389	-43.118	2.547
3800	9.851	80.708	72.214	32.279	-70.641	-42.379	2.437
3900	9.918	80.965	72.435	33.268	-70.918	-41.632	2.333
4000	9.988	81.217	72.651	34.263	-71.219	-40.877	2.233
4100	10.061	81.465	72.863	35.266	-71.546	-40.115	2.138
4200	10.136	81.708	73.071	36.275	-71.901	-39.344	2.047
4300	10.213	81.947	73.275	37.293	-72.282	-38.566	1.960
4400	10.291	82.183	73.474	38.318	-72.688	-37.774	1.876
4500	10.372	82.415	73.671	39.351	-73.122	-36.978	1.796
4600	10.454	82.644	73.863	40.392	-73.581	-36.169	1.718
4700	10.537	82.870	74.052	41.442	-74.065	-35.350	1.644
4800	10.621	83.093	74.238	42.500	-74.574	-34.522	1.572
4900	10.706	83.312	74.421	43.566	-75.106	-33.681	1.502
5000	10.791	83.530	74.601	44.641	-75.660	-32.831	1.435
5100	10.877	83.744	74.779	45.724	-76.235	-31.967	1.370
5200	10.964	83.956	74.953	46.816	-76.830	-31.093	1.307
5300	11.050	84.166	75.125	47.917	-77.443	-30.209	1.246
5400	11.137	84.373	75.294	49.027	-78.073	-29.312	1.186
5500	11.223	84.578	75.461	50.145	-78.719	-28.403	1.129
5600	11.309	84.781	75.626	51.271	-79.378	-27.483	1.073
5700	11.394	84.982	75.788	52.406	-80.049	-26.551	1.018
5800	11.479	85.181	75.948	53.550	-80.731	-25.604	.965
5900	11.563	85.378	76.107	54.702	-81.421	-24.650	.913
6000	11.646	85.573	76.263	55.863	-82.120	-23.680	.863

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Ground State Configuration $^2\Sigma$

ΔHf°_0 = -25.0 ± 3 kcal/mol

$S^\circ_{298.15}$ = 57.7 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -25.0 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	16093.3	2
	16162.8	2
$B^2\Sigma$	16850.6	2
$C^2\Pi$	26498.9	2
	26574.7	2
$D[^2\Sigma]$	31107.8	2
$E[^2\Sigma]$	34266.4	2
$F^2\Pi$	35675	2
	35700	2
$G^2\Delta$	36705	2
	36710	2

ω_e = 369.8 cm^{-1} $\omega_e x_e$ = 1.31 cm^{-1} σ = 1

B_e = 0.1516 cm^{-1} α_e = [0.0007] cm^{-1} r_e = 2.439 Å

Heat of Formation

N. D. Potter (1) investigated mass spectrometrically the gaseous equilibria among Ca, CaCl, and $CaCl_2$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the equilibrium constants $K = I(CaCl^+)^2/I(Ca^+)I(CaCl_2{}^+)$ which we calculated from the reported ion intensities for the reaction $Ca(g) + CaCl_2(g) \rightarrow 2CaCl(g)$ in the temperature range 1252°-1557°K, we obtain ΔHr°_{298} = 15.81 kcal/mol by the third law method. The third law drift is -2.8 ± 3.5 eu. The heat of formation is derived as ΔHf°_{298}(CaCl, g) = -27.0 kcal/mol.

K. F. Zmbov (7) determined by mass spectrometry the heat of the above reaction as 24.4 ± 1.3 kcal/mol with a drift of 12.5 ± 9.4 eu. This yields the heat of formation, ΔHf°_{298}(CaCl, g) = -22.7 kcal/mol.

D. L. Hildenbrand (2) also determined the equilibrium constants for the reaction (a) $Ca(g) + CaCl_2(g) \rightarrow 2CaCl(g)$ and the reaction (b) $Ca(g) + AlCl(g) \rightarrow CaCl(g) + Al(g)$ by mass spectrometry in the temperature range 1219-1353°K. Third law analysis of the reported equilibrium constants gives ΔHr°_{298} = 21.08 kcal/mol and drift = -1.4 ± 1.8 eu for reaction (a); and ΔHr°_{298} = 24.20 kcal/mol and drift = 0.5 ± 1.3 eu for reaction (b). From third law ΔHr°_{298} of (a) and (b), we derived ΔHf°_{298}(CaCl, g) as -24.4 and -23.3 kcal/mol, respectively, using all JANAF functions. Hildenbrand has also derived a corrected D°_0(Ca-Cl) = 95.0 kcal/mol from a linear Birge-Sponer extrapolation of the ground state vibrational levels with correction for its ionicity. This corrected D°_0(Ca-Cl) yields the heat of formation, ΔHf°_{298}(CaCl, g) = -23.9 kcal/mol.

Ryabova and Gurvich (3) reported D°_0(Ca-Cl) = 102 ± 6 kcal/mol from flame spectra studies. This leads to ΔHf°_{298}(CaCl, g) = -30.9 kcal/mol.

D. L. Hildenbrand (6) determined the dissociation energy of $CaCl_2(g)$ by electron impact as D°_0(CaCl-Cl) = 5.04 ± 0.02 eV which, combined with JANAF ΔHf°_{298} of $CaCl_2(g)$ and Cl(g) gives ΔHf°_{298}(CaCl, g) = -23.1 kcal/mol.

A weighted average, ΔHf°_{298}(CaCl, g) = -25 ± 3 kcal/mol, is adopted in the tabulation.

Heat Capacity and Entropy

The vibrational constants (ω_e and $\omega_e x_e$), electronic levels and ground state configuration were taken from Herzberg (4). Morgan and Barrow (5) made rotational analysis of the $C^2\Pi - X^2\Sigma$ system and reported B_o = 0.1516 cm^{-1} and r_e = 2.439 Å for the ground state. The value of α_e is calculated from the Morse potential function. The F and G states were reported by Schutte (8).

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Calcium Chloride ($CaCl_2$)

(Crystal) GFW = 110.986

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.678	- 190.313	- 190.313	INFINITE
100	11.666	8.508	39.406	- 3.090	- 190.655	- 186.609	407.834
200	16.099	18.296	26.558	- 1.652	- 190.485	- 182.610	199.546
298	17.413	25.000	25.000	.000	- 190.200	- 178.805	131.067
300	17.430	25.108	25.001	.032	- 190.195	- 178.734	130.208
400	18.080	30.222	25.694	1.811	- 189.883	- 174.961	95.594
500	18.440	34.298	27.021	3.639	- 189.554	- 171.267	74.861
600	18.690	37.682	28.523	5.495	- 189.218	- 167.641	61.063
700	18.970	40.583	30.044	7.378	- 188.866	- 164.073	51.226
800	19.340	43.139	31.524	9.292	- 188.831	- 160.527	43.854
900	19.860	45.446	32.945	11.251	- 188.614	- 157.001	38.125
1000	20.500	47.570	34.302	13.268	- 188.396	- 153.501	33.548
1100	21.200	49.557	35.600	15.353	- 188.166	- 150.023	29.807
1200	21.900	51.431	36.842	17.508	- 189.703	- 146.414	26.666
1300	22.600	53.212	38.033	19.733	- 189.100	- 142.831	24.012
1400	23.300	54.913	39.178	22.028	- 188.429	- 139.296	21.745
1500	24.000	56.544	40.282	24.393	- 187.690	- 135.812	19.788
1600	24.700	58.115	41.348	26.828	- 186.883	- 132.380	18.082
1700	25.400	59.634	42.379	29.333	- 186.007	- 128.998	16.584
1800	26.100	61.105	43.379	31.908	- 221.957	- 124.992	15.176
1900	26.800	62.535	44.349	34.553	- 220.723	- 119.637	13.761
2000	27.500	63.928	45.294	37.268	- 219.423	- 114.350	12.496

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CALCIUM CHLORIDE ($CaCl_2$) (CRYSTAL) GFW = 110.986

ΔHf_0° = -190.3 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 25.0 ± 1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -190.2 ± 0.3 kcal/mol

Tm = 1045°K

ΔHm° = 6.822 ± 0.2 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 77.5 ± 2 kcal/mol

Heat of Formation

V. B. Parker (1) has selected the standard heat of formation as -190.2 kcal/mol which is adopted in the tabulation. The heat of formation was derived from two independent paths. The first path involves $\Delta Hf^\circ_{298}(Ca^{++}, \infty H_2O)$ = -129.74 kcal/mol (1), $\Delta Hf^\circ_{298}(Cl^-, \infty H_2O)$ = -39.952 kcal/mol (2) and the heat of solution of $CaCl_2$(c) in water (3, 4, 5, 6, 7). The second path involves the heats of reaction of Ca(c), CaO(c) and $CaCl_2$(c) in aqueous HCl solution (4, 8-20).

Heat Capacity and Entropy

Kelley and Moore (21) measured the low temperature heat capacities in the temperature range from 52.6° to 295.1°K and made an extrapolation to 0°K which yielded an entropy of 4.59 ± 0.4 eu at 50.12°K. We have adopted the measured heat capacities, but made our own extrapolation to 0°K by comparison with the measured heat capacities of $BaCl_2$(c) (22) and $SrCl_2$(c) (23) from 6° to 50°K. The extrapolation gives S°_{50} = 2.45 ± 1 eu, which is used in the table. Moore (24) measured high temperature enthalpy data from 403.7° to 1667°K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data are smoothly joined at 298°K. The deviations of the observed enthalpies from the adopted values are about 2% near 400-500°K and only a few tenths percent at higher temperatures. Dworkin and Bredig (25) determined drop-calorimetrically $H_{1045}-H_{298}$ = 14.3 kcal/mol, which is in very good agreement with the adopted value of 14.2 kcal/mol.

Melting Data

The adopted melting point 1045°K was determined by T. V. Tokareva (26). Dworkin and Bredig determined the heat of fusion ΔH°_{1045} = 6.78 ± 0.1 kcal/mol by drop calorimetry. Chiotti, Gartner, Stevens and Saito (27) also measured the heat of fusion ΔH°_{1055} = 6.79 ± 0.2 kcal/mol in an adiabatic calorimeter. The adopted heat of fusion, 6.822 kcal/mol, is calculated from the difference between the observed relative enthalpy of the liquid and the adopted value for the crystal at the melting point.

Sublimation Data

The heat of sublimation is calculated from the heats of formation of $CaCl_2$(c) and $CaCl_2$(g).

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Calcium Chloride ($CaCl_2$)

(Liquid) GFW = 110.986

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.413	29.608	29.608	.000	- 185.013	- 174.991	128.272
300	17.430	29.715	29.608	.032	- 185.008	- 174.929	127.436
400	18.080	34.829	30.301	1.811	- 184.696	- 171.617	93.767
500	18.440	38.905	31.628	3.639	- 184.367	- 168.383	73.600
600	18.690	42.289	33.131	5.495	- 184.031	- 165.218	60.181
700	18.970	45.191	34.651	7.378	- 183.679	- 162.111	50.613
800	24.506	48.463	36.177	9.828	- 183.108	- 159.062	43.454
900	24.506	51.349	37.706	12.279	- 182.399	- 156.099	37.906
1000	24.506	53.931	39.202	14.729	- 181.748	- 153.214	33.485
1100	24.506	56.267	40.649	17.180	- 181.152	- 150.390	29.880
1200	24.506	58.399	42.040	19.631	- 182.393	- 147.465	26.857
1300	24.506	60.361	43.375	22.081	- 181.565	- 144.588	24.308
1400	24.506	62.177	44.654	24.532	- 180.738	- 141.775	22.132
1500	24.506	63.868	45.879	26.982	- 179.914	- 139.021	20.255
1600	24.506	65.449	47.053	29.433	- 179.091	- 136.321	18.621
1700	24.506	66.935	48.180	31.884	- 178.269	- 133.672	17.185
1800	24.506	68.336	49.261	34.334	- 214.344	- 130.392	15.832
1900	24.506	69.660	50.300	36.785	- 213.304	- 125.755	14.465
2000	24.506	70.917	51.300	39.235	- 212.269	- 121.175	13.241
2100	24.506	72.113	52.263	41.686	- 211.235	- 116.647	12.140
2200	24.506	73.253	53.191	44.137	- 210.206	- 112.167	11.143
2300	24.506	74.342	54.087	46.587	- 209.183	- 107.732	10.237
2400	24.506	75.385	54.953	49.038	- 208.166	- 103.343	9.411
2500	24.506	76.386	55.790	51.488	- 207.158	- 98.997	8.654
2600	24.506	77.347	56.601	53.939	- 206.158	- 94.690	7.959
2700	24.506	78.272	57.387	56.390	- 205.170	- 90.422	7.319
2800	24.506	79.163	58.149	58.840	- 204.196	- 86.188	6.727
2900	24.506	80.023	58.888	61.291	- 203.235	- 81.992	6.179
3000	24.506	80.854	59.607	63.741	- 202.293	- 77.828	5.670

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$S^\circ_{298.15}$ = 29.608 ± 1.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -185.013 ± 0.5 kcal/mol

Tm = 1045°K

ΔHm° = 6.822 ± 0.2 kcal/mol

Tb = 2208.6°K

ΔHv° = 56.2 kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between H_{1045}-H_{298} for the crystal and the liquid.

Heat Capacity and Entropy

The constant heat capacity above the assumed glass transition at 700°K is derived from high temperature enthalpy data in a drop calorimeter from the melting point up to 1667°K by G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943). Below the glass transition point, the heat capacity is assumed to be the same as that of the crystal. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 67, 697 (1963), reported Cp(ℓ) = 23.6 gibbs/mol from enthalpy measurements in a short temperature range by drop calorimetry.

The entropy $S^\circ_{298.15}$ = 29.608 gibbs/mol is calculated in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which ΔG = 0 for $CaCl_2(\ell) \rightarrow CaCl_2(g)$. The heat of vaporization is the difference in ΔHf°_{Tb} between liquid and gas.

Calcium Chloride ($CaCl_2$)

(Ideal Gas) GFW = 110.986

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3,613	- 112,748	- 112,748	INFINITE
100	11.800	55,007	81,443	- 2,644	- 112.709	- 113,313	247,645
200	13.522	63,806	70,627	- 1,364	- 112,697	- 113,923	124,490
298	14.179	69,347	69,347	,000	- 112,700	- 114,527	83,950
300	14,187	69,435	69,347	,026	- 112,701	- 114,538	83,441
400	14.476	73,561	69,908	1,461	- 112,733	- 115,147	62,913
500	14.622	76,808	70,975	2,917	- 112,776	- 115,744	50,592
600	14.705	79,482	72,176	4,383	- 112,830	- 116,332	42,374
700	14.756	81,753	73,386	5,857	- 112,887	- 116,912	36,502
800	14.790	83,726	74,558	7,334	- 113,289	- 117,454	32,087
900	14.813	85,469	75,675	8,814	- 113.551	- 117,959	28,644
1000	14.830	87,031	76,734	10,297	- 113,867	- 118,433	25,884
1100	14.843	88,445	77,736	11,780	- 114.239	- 118,872	23,618
1200	14.853	89,737	78,683	13,265	- 116,446	- 119,123	21,695
1300	14.860	90,926	79,579	14,751	- 116,582	- 119,341	20,063
1400	14.866	92,028	80,430	16,237	- 116,720	- 119,548	18,662
1500	14.871	93,053	81,237	17,724	- 116,859	- 119,745	17,447
1600	14.875	94,013	82,006	19,211	- 117,000	- 119,933	16,382
1700	14.878	94,915	82,739	20,699	- 117,141	- 120,110	15,441
1800	14.881	95,766	83,440	22,187	- 154,178	- 119,601	14,522
1900	14.883	96,570	84,110	23,675	- 154,101	- 117,681	13,536
2000	14.885	97,334	84,752	25,163	- 154,028	- 115,767	12,650
2100	14.887	98,060	85,368	26,652	- 153,956	- 113,856	11,849
2200	14.888	98,753	85,961	28,141	- 153,889	- 111,948	11,121
2300	14.890	99,414	86,532	29,630	- 153,827	- 110,042	10,456
2400	14.891	100,048	87,082	31,119	- 153,772	- 108,140	9,847
2500	14.892	100,656	87,613	32,608	- 153,725	- 106,240	9,287
2600	14.893	101,240	88,126	34,097	- 153,687	- 104,341	8,771
2700	14.894	101,802	88,622	35,586	- 153,661	- 102,444	8,292
2800	14.894	102,344	89,102	37,076	- 153,647	- 100,546	7,848
2900	14.895	102,867	89,568	38,565	- 153,648	- 98,650	7,434
3000	14.895	103,371	90,020	40,055	- 153,666	- 96,755	7,049
3100	14.896	103,860	90,458	41,544	- 153,704	- 94,857	6,687
3200	14.896	104,333	90,885	43,034	- 153,762	- 92,958	6,349
3300	14.897	104,791	91,299	44,524	- 153,844	- 91,056	6,030
3400	14.897	105,236	91,703	46,013	- 153,950	- 89,151	5,731
3500	14.898	105,668	92,095	47,503	- 154,083	- 87,245	5,448
3600	14.898	106,087	92,478	48,993	- 154,244	- 85,331	5,180
3700	14.898	106,496	92,852	50,483	- 154,435	- 83,414	4,927
3800	14.899	106,893	93,216	51,973	- 154,657	- 81,494	4,687
3900	14.899	107,280	93,572	53,462	- 154,914	- 79,564	4,459
4000	14.899	107,657	93,919	54,952	- 155,203	- 77,629	4,241
4100	14.899	108,025	94,259	56,442	- 155,525	- 75,686	4,034
4200	14.900	108,384	94,591	57,932	- 155,883	- 73,735	3,837
4300	14.900	108,735	94,916	59,422	- 156,276	- 71,776	3,648
4400	14.900	109,077	95,234	60,912	- 156,703	- 69,802	3,467
4500	14.900	109,412	95,545	62,402	- 157,167	- 67,825	3,294
4600	14.900	109,740	95,850	63,892	- 157,663	- 65,833	3,128
4700	14.900	110,060	96,149	65,382	- 158,194	- 63,830	2,968
4800	14.901	110,374	96,442	66,872	- 158,759	- 61,819	2,815
4900	14.901	110,681	96,729	68,362	- 159,356	- 59,790	2,667
5000	14.901	110,982	97,012	69,852	- 159,983	- 57,754	2,524
5100	14.901	111,277	97,288	71,342	- 160,640	- 55,700	2,387
5200	14.901	111,566	97,560	72,833	- 161,325	- 53,635	2,254
5300	14.901	111,850	97,827	74,323	- 162,039	- 51,560	2,126
5400	14.901	112,129	98,089	75,813	- 162,778	- 49,469	2,002
5500	14.901	112,402	98,347	77,303	- 163,541	- 47,362	1,882
5600	14.901	112,671	98,601	78,793	- 164,326	- 45,245	1,766
5700	14.901	112,935	98,850	80,283	- 165,132	- 43,113	1,653
5800	14.902	113,194	99,095	81,773	- 165,957	- 40,961	1,543
5900	14.902	113,448	99,336	83,263	- 166,800	- 38,802	1,437
6000	14.902	113,699	99,573	84,754	- 167,658	- 36,623	1,334

June 30, 1970

CALCIUM CHLORIDE ($CaCl_2$) (IDEAL GAS) GFW = 110.986

$CaCl_2$

Point Group $D_{\infty h}$

ΔHf°_0 = -112.7 ± 1 kcal/mol

$S^\circ_{298.15}$ = 69.3 ± 2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -112.7 ± 1 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
217 (1)
64 (2)
402 (1)

Bond Distance: Ca-Cl = 2.51 Å

Bond Angle: Cl-Ca-Cl = 180°

σ = 2

Rotational Constant: B_o = 0.0377 cm^{-1}

Heat of Formation

Second and third law analyses of vapor pressure data are given below. The selected third law heat of vaporization is taken from Novikov's measurement (1) as ΔHv°_{298} = 72.30 kcal/mol which is combined with ΔHf°_{298} of the liquid to give $\Delta Hf^\circ_{298}(CaCl_2, g)$ = -112.7 ± 1 kcal/mol.

Third law analyses indicate zero drift for Novikov's data, positive and negative drifts for Hildenbrand's (2) and Bautista's (3) data, respectively. Their heats are in agreement within ±1 kcal. Wartenberg (4) reported there was no boiling at 1819°K at 62 mm Hg pressure, and his value (ΔHv°_{298} = 71.1 ± 0.7 kcal/mol) serves as a guide for the minimum heat of vaporization.

Investigator	Method	Temperature Range, °K	Number of Points	ΔHv°_{298}(kcal/mol) 2nd law	3rd law	Drift e.u
Bautista and Margrave (3)	Langmuir	952-993	7	75.25 (80.34)*	73.39 (78.57)*	-1.7±6.9
Hildenbrand and Potter (2)	Torsion Effusion 0.0096 cm^2 Orifice	1142-1228	12	64.99	71.24	5.3±0.4
Hildenbrand and Potter (2)	Torsion Effusion 0.015 cm^2 Orifice	1111-1281	17	68.71	71.24	2.0±0.2
Hildenbrand and Potter (2)	Torsion Effusion Combined	1111-1281	29	68.91	71.24	2.4±0.3
Dewing (5)	Knudsen Effusion	1069-1225	4	59.37	71.03	10.2±1.6
Wartenberg and Bosse (4)	Boiling Point	1819	1	---	>71.10	---
Novikov and Gavryuchenkov (1)	Boiling Point	1591-1701	5	72.25	72.30	0.0±1.2
Lukashenko and Reutova (10)	Langmuir	973-1023	6	78.0	69.01	-9.0
	Knudsen Effusion	1073-1273	6	61.8	69.78	+8.0

*Value in parentheses is the heat of sublimation.

Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by D. White and co-workers (6) in the matrix-infrared-spectrometric studies. The linear structure is consistent within experimental error with the electric-quadrupole-deflection studies (7), and electron-diffraction data (8). Hayes (9) has qualitatively rationalized the linear structure through molecular orbital theory.

The bond length was measured by Akishin and Spiridonov (8). The moment of inertia is 74.174 x 10^{-39} g cm^2.

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Calcium Monofluoride (CaF)

(Ideal Gas) GFW = 59.0784

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.182	-64.756	-64.756	INFINITE
100	6.990	46.776	61.641	-1.487	-64.642	-66.904	146.218
200	7.510	51.754	55.580	-.765	-64.813	-69.105	75.515
298	8.045	54.860	54.860	.000	-65.000	-71.173	52.171
300	8.053	54.910	54.860	.015	-65.004	-71.212	51.878
400	8.383	57.276	55.180	.838	-65.203	-73.251	40.022
500	8.579	59.169	55.795	1.687	-65.403	-75.239	32.887
600	8.702	60.745	56.493	2.552	-65.606	-77.187	28.115
700	8.784	62.093	57.199	3.426	-65.810	-79.101	24.697
800	8.844	63.270	57.886	4.308	-66.354	-80.957	22.116
900	8.888	64.314	58.543	5.194	-66.758	-82.759	20.097
1000	8.923	65.253	59.168	6.085	-67.215	-84.513	18.470
1100	8.952	66.105	59.760	6.979	-67.725	-86.219	17.130
1200	8.976	66.885	60.322	7.875	-70.069	-87.723	15.977
1300	8.997	67.604	60.855	8.774	-70.342	-89.183	14.993
1400	9.016	68.271	61.361	9.674	-70.615	-90.622	14.147
1500	9.033	68.894	61.843	10.577	-70.888	-92.042	13.410
1600	9.049	69.477	62.302	11.481	-71.161	-93.443	12.764
1700	9.064	70.026	62.740	12.387	-71.434	-94.827	12.191
1800	9.078	70.545	63.160	13.294	-108.602	-95.515	11.597
1900	9.092	71.036	63.561	14.202	-108.655	-94.786	10.903
2000	9.107	71.503	63.947	15.112	-108.708	-94.055	10.278
2100	9.121	71.948	64.317	16.023	-108.764	-93.322	9.712
2200	9.137	72.372	64.674	16.936	-108.822	-92.585	9.197
2300	9.154	72.779	65.017	17.851	-108.883	-91.845	8.727
2400	9.172	73.169	65.349	18.767	-108.948	-91.103	8.296
2500	9.191	73.543	65.669	19.685	-109.019	-90.358	7.899
2600	9.213	73.904	65.979	20.606	-109.096	-89.610	7.532
2700	9.237	74.253	66.279	21.528	-109.181	-88.859	7.193
2800	9.263	74.589	66.570	22.453	-109.275	-88.105	6.877
2900	9.292	74.914	66.852	23.381	-109.379	-87.346	6.583
3000	9.323	75.230	67.126	24.311	-109.497	-86.585	6.308
3100	9.358	75.536	67.393	25.245	-109.628	-85.819	6.050
3200	9.395	75.834	67.652	26.183	-109.774	-85.049	5.809
3300	9.435	76.124	67.904	27.125	-109.939	-84.274	5.581
3400	9.478	76.406	68.150	28.070	-110.122	-83.493	5.367
3500	9.524	76.681	68.390	29.020	-110.326	-82.706	5.164
3600	9.573	76.950	68.624	29.975	-110.552	-81.913	4.973
3700	9.624	77.213	68.852	30.935	-110.801	-81.115	4.791
3800	9.679	77.471	69.076	31.900	-111.075	-80.308	4.619
3900	9.736	77.723	69.294	32.871	-111.376	-79.497	4.455
4000	9.795	77.970	69.508	33.847	-111.701	-78.674	4.299
4100	9.856	78.213	69.718	34.830	-112.054	-77.845	4.149
4200	9.920	78.451	69.923	35.819	-112.435	-77.005	4.007
4300	9.986	78.685	70.124	36.814	-112.844	-76.157	3.871
4400	10.053	78.915	70.321	37.816	-113.280	-75.298	3.740
4500	10.122	79.142	70.514	38.824	-113.745	-74.432	3.615
4600	10.193	79.365	70.704	39.840	-114.235	-73.552	3.495
4700	10.265	79.585	70.891	40.863	-114.753	-72.662	3.379
4800	10.338	79.802	71.074	41.893	-115.298	-71.760	3.267
4900	10.412	80.016	71.255	42.931	-115.867	-70.847	3.160
5000	10.487	80.227	71.432	43.976	-116.460	-69.922	3.056
5100	10.562	80.436	71.607	45.028	-117.077	-68.987	2.956
5200	10.638	80.642	71.778	46.088	-117.715	-68.036	2.859
5300	10.715	80.845	71.947	47.156	-118.373	-67.074	2.766
5400	10.791	81.046	72.114	48.231	-119.050	-66.102	2.675
5500	10.868	81.245	72.278	49.314	-119.744	-65.115	2.587
5600	10.945	81.441	72.440	50.405	-120.454	-64.115	2.502
5700	11.021	81.635	72.600	51.503	-121.177	-63.101	2.419
5800	11.097	81.828	72.757	52.609	-121.914	-62.076	2.339
5900	11.173	82.018	72.913	53.722	-122.661	-61.039	2.261
6000	11.248	82.207	73.066	54.843	-123.417	-59.988	2.185

Dec. 31, 1968

Ground State Configuration $^2\Sigma^+$

$\Delta Hf^\circ_0 = -64.8 \pm 2$ kcal/mol

$S^\circ_{298.15} = 54.86 \pm 0.1$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -65.0 \pm 2$ kcal/mol

Electronic Levels and Quantum Weights

	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	16482	2
	16557	2
$B^2\Sigma$	18844	2
$C^2\Pi$	30256	2
	30285	2
$D^2\Sigma$	30772	2
$E^2\Sigma$	34135	2
$F^2\Pi$	37548	4

$\omega_e = 587.1$ cm^{-1} $\omega_e x_e = 2.74$ cm^{-1} $\sigma = 1$

$B_e = 0.3225$ cm^{-1} $\alpha_e = [0.0020]$ cm^{-1} $r_e = 2.01$ Å

Heat of Formation

Hastie and Margrave (1) have recently reviewed the dissociation energy of CaF and conclude that it is 127.5 ± 2.5 kcal/mol. The analysis below considers basically the same data except that all values are JANAF.

Hildenbrand and Murad (2) in a mass spectrometric determination of the equilibria among BF, BF_3, Ca, CaF and CaF_2 reported equilibrium constants for the reaction

(A) $Ca(g) + CaF_2(g) \rightarrow 2CaF(g)$.

Blue et al. (3) have also examined several equilibria mass-spectrometrically and report equilibrium constants for reaction

(B) $Ca(g) + CaF_2(c) \rightarrow 2CaF(g)$ and reaction

(C) $Ca(g) + AlF(g) \rightarrow Al(g) + CaF(g)$.

Ryabova and Gurvich (4) give a heat of dissociation from flame studies for the reaction

(D) $CaF(g) \rightarrow Ca(g) + F(g)$.

The remaining reactions considered by Hastie and Margrave (1) were not included since they involved subtracting reactions not performed simultaneously, or involve species such as SiF_2 whose heat of formation is dependent on that of CaF and CaF_2.

Reference	Range °K	Reaction	Points	ΔHr°_{298} kcal/mol 2nd law	3rd law	Drift eu	ΔHf°_{298}** kcal/mol
Hildenbrand (2)	1583 - 1734	A	15	11.5 ± 6.8	14.70 ± 1.27	2.2 ± 4.1	-65.5 ± 1.8
Blue (3)	1271 - 1351	B	9	146.9 ± 8.0	121.08 ± 1.65	-19.4 ± 6.2	-64.5 ± 1.7
Blue (3)	1271 - 1351	C	10*	34.6 ± 3.5	32.87 ± 0.47	-1.4 ± 2.7	-65.7 ± 3.2
Ryobova (4)		D		135 ± 7			-73.3 ± 7
Hildenbrand (5)	1423 - 1443	A	2		32.97		-65.6 ± 3.2

* 1 point rejected due to failure of a statistical test

** Calculated from third law value when available

The auxiliary heats of formation used were, in kcal/mol, AlF, g = -63.4, Al, g = 78, CaF_2, g = -187.5, CaF_2, c = -293.0 and Ca, g = 42.85.

We adopt a median value of $\Delta Hf^\circ_{298.15}$(CaF, g) = -65 ± 2 kcal/mol which corresponds to a heat of dissociation of 126.7 ± 2 kcal/mol.

Heat Capacity and Entropy

Herzberg (6) gives the vibrational constants and electronic levels, Harvey (7) has reported a value for B_0 which corresponds to a bond length of 2.02 Å. The Morse potential function was used to calculate α_e.

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Calcium Difluoride (CaF_2)

(Crystal) GFW = 78.0768

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°₂₉₈)/T (gibbs/mol)	H°-H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.786	-292.305	-292.305	INFINITE
100	6.840	3.190	28.770	-2.558	-293.006	-288.874	631.334
200	13.568	10.410	17.794	-1.477	-293.167	-284.636	311.036
298	16.393	16.389	16.389	.000	-293.000	-280.481	205.598
300	16.437	16.491	16.390	.030	-292.996	-280.404	204.274
400	17.654	21.422	17.054	1.747	-292.686	-276.251	150.936
500	18.217	25.424	18.340	3.542	-292.344	-272.181	118.970
600	18.766	28.793	19.809	5.391	-291.978	-268.182	97.685
700	19.381	31.731	21.306	7.297	-291.576	-264.247	82.502
800	20.057	34.363	22.777	9.269	-291.463	-260.344	71.123
900	20.782	36.767	24.200	11.311	-291.149	-256.473	62.280
1000	21.541	38.996	25.569	13.427	-290.823	-252.638	55.214
1100	22.326	41.085	26.885	15.620	-290.480	-248.836	49.439
1200	23.131	43.062	28.152	17.892	-291.897	-244.914	44.605
1300	23.950	44.946	29.372	20.246	-291.166	-241.027	40.520
1400	24.780	46.751	30.549	22.683	-290.356	-237.200	37.029
1500	29.560	49.507	31.734	26.659	-288.011	-233.503	34.021
1600	29.810	51.422	32.905	29.628	-286.677	-229.913	31.405
1700	30.060	53.237	34.048	32.621	-285.322	-226.406	29.106
1800.	30.310	54.962	35.162	35.640	-320.839	-222.300	26.991
1900	30.560	56.608	36.248	38.683	-319.219	-216.870	24.946
2000	30.810	58.182	37.306	41.752	-317.577	-211.524	23.114
2100	31.060	59.691	38.336	44.845	-315.916	-206.264	21.466
2200	31.310	61.142	39.340	47.964	-314.234	-201.082	19.976
2300	31.560	62.539	40.318	51.107	-312.534	-195.976	18.622
2400	31.810	63.887	41.273	54.276	-310.816	-190.945	17.388
2500	32.060	65.191	42.203	57.469	-309.082	-185.986	16.259
2600	32.310	66.453	43.112	60.688	-307.332	-181.097	15.223
2700	32.560	67.677	43.999	63.931	-305.569	-176.274	14.268

Dec. 31, 1968

CALCIUM DIFLUORIDE (CaF_2) (CRYSTAL) GFW = 78.0768

$S^\circ_{298.15}$ = 16.39 ± 0.08 gibbs/mol

Tt = 1424 ± 20°K (α-β)

Tm = 1691 ± 5°K

ΔHf°_0 = -292.3 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -293.0 ± 1.5 kcal/mol

ΔHt° = 1.14 ± 0.1 kcal/mol

ΔHm° = 7.10 ± 0.1 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 105.5 ± 0.8 kcal/mol

Heat of Formation

Torgeson and Sahama (1) measured the heat of solution of CaO in aqueous 20.1% HF as -54.96 ± 0.02 kcal/mol. Using ΔHf°_{298}(CaO, c) = -151.79 kcal/mol (2), $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.317 kcal/mol (3) and $\Delta Hf^\circ_{298}(HF, 4.4H_2O)$ = -76.60 kcal/mol (4), we obtain $\Delta Hf^\circ_{298}(CaF_2, c)$ = -291.6 ± 0.6 kcal/mol.

Smyshlyaev and Edeleva (5) report the solubility product of CaF_2 as 2.7 ± 0.27 x 10^{-11} in dilute HCl, which yields ΔG°_{298} = 14.42 kcal/mol for the reaction $CaF_2(c) \rightarrow Ca^{++}(\infty, aq.) + 2F^-(\infty, aq.)$. Using $\Delta Gf^\circ_{298}(Ca^{++}, \infty\ aq.)$ = -132.30 kcal/mol (2) and $\Delta Gf^\circ_{298}(F^-, \infty\ aq.)$ = -66.95 kcal/mol (4) we obtain $\Delta Gf^\circ_{298}(CaF_2, c)$ = -280.64 ± 0.6 kcal/mol, which using the adopted functions yields $\Delta Hf^\circ_{298}(CaF_2, c)$ = -293.1 ± 0.6 kcal/mol.

Vecher and Vecher (17) have measured the emf of a high temperature solid state cell and report ΔGr°_{1200} = -17.6 ± 0.2 kcal/mol for the reaction $CaO(c) + MgF_2(c) \rightarrow CaF_2(c) + MgO(c)$. This reduces to ΔHr°_{298} = -17.6 kcal/mol which, using JANAF values for MgO and MgF_2 and CaO from reference 2, yields $\Delta Hf^\circ_{298}(CaF_2, c)$ = -294.4 ± 1.3 kcal/mol.

Kohlrauch (18) reported the solubility of CaF_2 and fluorspar, which yield solubility products of 3.6 x 10^{-11} and 2.8 x 10^{-11}. From these we obtain, as above, $\Delta Hf^\circ_{298}(CaF_2, c)$ = -292.9 and -293.1 kcal/mol.

Guntz (19) made measurements on the neutralization of $Ca(OH)_2$(aq) and HF(aq) which yield $\Delta Hf^\circ_{298}(CaF_2, c)$ = -293.1 kcal/mol, according to Parker (2).

A median value of $\Delta Hf^\circ_{298}(CaF_2, c)$ = -293 ± 1.5 kcal/mol is adopted.

Heat Capacity and Entropy

Huffman and Norwood (6) have measured the low temperature heat capacity in the range 3.6° to 30°K, Eucken and Schwers (7) in the range 17° to 86°K and Todd (8) from 54° to 296.5°K. We have fitted a smooth polynomial curve through the data of references 6 and 8 and this yields S°_{298} = 16.38 ± 0.08 eu based on $S^\circ_{3.6}$ = 0.0002 eu. The values of reference 7 deviate considerably at the lowest temperatures but are in reasonable agreement at higher temperatures.

The high temperature enthalpy of calcium fluoride has been reported by Naylor (9) to 1789°K, Krestnikov and Karetnikov (10) to 1273°K, and Lyashenko (11) to 1490°K. All the data are in approximate agreement and the more extensive results of Naylor on a very pure sample are adopted. The heat capacities, below 1424°K were derived from a polynomial fit of the enthalpy data of the form $H = aT^2 + bT + c + d/T + e/T^2$.

Transition Data

The temperature of transition is that reported by Naylor (9), the large uncertainty has been assigned since at 1424°K the enthalpies indicate complete conversion to β-CaF_2, and the next lower point is at 1402°K. Evidence in support of a transition in this region comes from Lyashenko (11) whose plot indicates a break between 1273° and 1413°K. In addition, $SrCl_2$ which has the fluorite structure has a transition near the melting point. The enthalpy of transition is that reported by Naylor (9).

Melting Data

McCreary (12) reports the melting point of a 99.1% pure sample as 1687 ± 5°K. Porter and Brown (13) report 1675 ± 5°K as the melting point of 99.8% pure CaF_2 and Rogers et al. (14) obtained 1684°K as the melting point. The adopted melting point 1691 ± 5°K, for a sample of natural fluorite of high purity, was reported by Naylor (9). The heat of melting, 7100 cals, is that measured by Naylor (9). Three determinations from high temperature phase diagrams give 7250 ± 350 cals (15), 5500 cals (16) and 9800 cals (14).

Sublimation Data

See the CaF_2(g) table for details.

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Calcium Difluoride (CaF_2)

(Liquid) GFW = 78.0768

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.393	22.125	22.125	.000	- 283.477	- 272.668	199.871
300	16.437	22.227	22.126	.030	- 283.472	- 272.601	198.590
400	17.654	27.158	22.790	1.747	- 283.162	- 269.022	146.987
500	18.217	31.160	24.077	3.542	- 282.821	- 265.526	116.061
600	18.766	34.529	25.545	5.391	- 282.455	- 262.100	95.470
700	19.381	37.468	27.043	7.297	- 282.052	- 258.739	80.782
800	20.057	40.099	28.513	9.269	- 281.940	- 255.41[illegible]	69.775
900	20.782	42.503	29.936	11.311	- 281.626	- 252.11[illegible]	61.221
1000	23.880	44.732	31.305	13.426	- 281.300	- 248.[illegible]1	54.386
1100	23.880	47.008	32.631	15.814	- 280.762	- 245.632	48.803
1200	23.880	49.086	33.917	18.202	- 282.063	- 242.308	44.130
1300	23.880	50.997	35.158	20.590	- 281.298	- 239.026	40.184
1400	23.880	52.767	36.353	22.978	- 280.537	- 235.803	36.810
1500	23.880	54.414	37.503	25.366	- 279.780	- 232.633	33.895
1600	23.880	55.995	38.609	27.754	- 279.027	- 229.516	31.350
1700	23.880	57.403	39.672	30.142	- 278.277	- 226.443	29.111
1800	23.880	58.768	40.696	32.530	- 314.425	- 222.736	27.044
1900	23.880	60.059	41.681	34.918	- 313.460	- 217.669	25.038
2000	23.880	61.284	42.631	37.306	- 312.499	- 212.651	23.237
2100	23.880	62.449	43.547	39.694	- 311.543	- 207.684	21.614
2200	23.880	63.560	44.432	42.082	- 310.592	- 202.760	20.142
2300	23.880	64.622	45.287	44.470	- 309.647	- 197.879	18.803
2400	23.880	65.638	46.113	46.858	- 308.710	- 193.040	17.579
2500	23.880	66.613	46.914	49.246	- 307.781	- 188.240	16.456
2600	23.880	67.549	47.690	51.634	- 306.862	- 183.476	15.423
2700	23.880	68.451	48.442	54.022	- 305.954	- 178.747	14.469
2800	23.880	69.319	49.172	56.410	- 305.058	- 174.053	13.585
2900	23.880	70.157	49.882	58.798	- 304.177	- 169.387	12.765
3000	23.880	70.967	50.571	61.186	- 303.314	- 164.758	12.003
3100	23.880	71.750	51.242	63.574	- 302.468	- 160.152	11.291
3200	23.880	72.508	51.894	65.962	- 301.643	- 155.574	10.625
3300	23.880	73.243	52.530	68.350	- 300.841	- 151.023	10.002
3400	23.880	73.955	53.150	70.738	- 300.062	- 146.494	9.417
3500	23.880	74.648	53.754	73.126	- 299.310	- 141.986	8.866
3600	23.880	75.320	54.344	75.514	- 298.585	- 137.501	8.347
3700	23.880	75.975	54.920	77.902	- 297.890	- 133.037	7.858
3800	23.880	76.612	55.482	80.290	- 297.226	- 128.589	7.396
3900	23.880	77.232	56.032	82.678	- 296.596	- 124.163	6.958
4000	23.880	77.836	56.570	85.066	- 295.997	- 119.748	6.543

Dec. 31, 1968

CALCIUM DIFLUORIDE (CaF_2) (LIQUID) GFW = 78.0768

$S^\circ_{298.15}$ = 22.125 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −283.477 ± 1.5 kcal/mol

Tm = 1691 ± 5°K

ΔHm° = 7.10 ± 0.1 kcal/mol

Tb = 2806.5 ± 30°K

ΔHv° = 73.78 ± 0.8 kcal/mol

Heat of Formation

The heat of formation is obtained from that of the crystal by adding the heat of melting and the difference between $H_{1691} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the heat content measurements of B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). The heat capacity is constant in the real liquid range but at 1000°K a glass transition is assumed below which it follows that of the crystal. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which ΔG = 0 for the vaporization process. The heat of vaporization is the difference in ΔHf°_{Tb} between liquid and gas.

Calcium Difluoride (CaF_2)

(Ideal Gas) GFW = 78.0768

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.025	-187.044	-187.044	INFINITE
100	9.365	53.694	75.485	-2.179	-187.127	-188.046	410.974
200	11.121	60.738	66.501	-1.153	-187.343	-188.878	206.396
298	12.253	65.412	65.412	.000	-187.500	-189.597	138.978
300	12.268	65.488	65.412	.023	-187.503	-189.611	138.131
400	12.875	69.110	65.902	1.283	-187.650	-190.290	103.970
500	13.209	72.022	66.844	2.589	-187.797	-190.933	83.457
600	13.408	74.449	67.915	3.920	-187.949	-191.546	69.770
700	13.534	76.526	69.001	5.268	-188.105	-192.133	59.987
800	13.619	78.339	70.057	6.626	-188.606	-192.668	52.635
900	13.678	79.947	71.068	7.991	-188.969	-193.155	46.904
1000	13.721	81.391	72.030	9.361	-189.389	-193.598	42.311
1100	13.753	82.700	72.941	10.735	-189.865	-193.997	38.544
1200	13.778	83.898	73.805	12.111	-192.178	-194.197	35.368
1300	13.797	85.001	74.624	13.490	-192.422	-194.355	32.674
1400	13.812	86.024	75.402	14.870	-192.669	-194.495	30.362
1500	13.825	86.978	76.143	16.252	-192.918	-194.616	28.356
1600	13.835	87.870	76.848	17.635	-193.170	-194.722	26.598
1700	13.843	88.709	77.521	19.019	-193.424	-194.810	25.045
1800	13.851	89.501	78.165	20.404	-230.575	-194.205	23.580
1900	13.857	90.250	78.782	21.789	-230.613	-192.183	22.106
2000	13.862	90.961	79.373	23.175	-230.654	-190.158	20.780
2100	13.866	91.637	79.941	24.562	-230.699	-188.134	19.579
2200	13.870	92.282	80.487	25.949	-230.749	-186.106	18.488
2300	13.874	92.899	81.014	27.336	-230.805	-184.075	17.491
2400	13.877	93.489	81.521	28.723	-230.869	-182.042	16.577
2500	13.879	94.056	82.011	30.111	-230.940	-180.006	15.736
2600	13.881	94.600	82.485	31.499	-231.021	-177.967	14.959
2700	13.884	95.124	82.944	32.887	-231.113	-175.924	14.240
2800	13.885	95.629	83.388	34.276	-231.216	-173.879	13.572
2900	13.887	96.116	83.818	35.664	-231.335	-171.827	12.949
3000	13.889	96.587	84.236	37.053	-231.471	-169.776	12.368
3100	13.890	97.043	84.642	38.442	-231.624	-167.717	11.824
3200	13.891	97.484	85.036	39.831	-231.798	-165.652	11.313
3300	13.892	97.911	85.420	41.220	-231.995	-163.583	10.834
3400	13.893	98.326	85.794	42.610	-232.214	-161.506	10.381
3500	13.894	98.729	86.157	43.999	-232.461	-159.420	9.955
3600	13.895	99.120	86.512	45.388	-232.735	-157.329	9.551
3700	13.896	99.501	86.858	46.778	-233.038	-155.231	9.169
3800	13.897	99.871	87.196	48.168	-233.372	-153.123	8.807
3900	13.897	100.232	87.525	49.557	-233.741	-151.010	8.462
4000	13.898	100.584	87.847	50.947	-234.140	-148.881	8.135
4100	13.899	100.927	88.162	52.337	-234.574	-146.745	7.822
4200	13.899	101.262	88.470	53.727	-235.043	-144.597	7.524
4300	13.900	101.589	88.771	55.117	-235.547	-142.437	7.239
4400	13.900	101.909	89.066	56.507	-236.087	-140.265	6.967
4500	13.901	102.221	89.355	57.897	-236.663	-138.083	6.706
4600	13.901	102.527	89.638	59.287	-237.273	-135.886	6.456
4700	13.901	102.826	89.916	60.677	-237.919	-133.674	6.216
4800	13.902	103.118	90.188	62.067	-238.599	-131.447	5.985
4900	13.902	103.405	90.455	63.457	-239.313	-129.208	5.763
5000	13.902	103.686	90.716	64.848	-240.058	-126.954	5.549
5100	13.903	103.961	90.973	66.238	-240.836	-124.687	5.343
5200	13.903	104.231	91.226	67.628	-241.644	-122.398	5.144
5300	13.903	104.496	91.474	69.018	-242.481	-120.096	4.952
5400	13.903	104.756	91.717	70.409	-243.345	-117.784	4.767
5500	13.904	105.011	91.957	71.799	-244.235	-115.448	4.587
5600	13.904	105.262	92.192	73.190	-245.149	-113.098	4.414
5700	13.904	105.508	92.423	74.580	-246.086	-110.730	4.246
5800	13.904	105.749	92.651	75.970	-247.044	-108.347	4.083
5900	13.905	105.987	92.875	77.361	-248.021	-105.950	3.925
6000	13.905	106.221	93.096	78.751	-249.017	-103.534	3.771

Dec. 31, 1968

CALCIUM DIFLUORIDE (CaF_2) (IDEAL GAS) GFW = 78.0768

Point Group = C_{2v}

ΔHf°_0 = -187 ± 2 kcal/mol

$S^\circ_{298.15}$ = 65.41 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -187.5 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
484 (1)
163 (1)
554 (1)

Bond Distance: Ca-F = 2.1 Å

σ = 2

Bond Angle: F-Ca-F = 135 ± 7°

Product of the Moments of Inertia: $I_AI_BI_C = 1.2836 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The heat of formation is obtained from that of the crystal by adding $\Delta Hs^\circ_{298.15}$. The vapor pressure data of five authors was analysed by 2nd and 3rd law methods to give $\Delta Hs^\circ_{298.15}$ as listed below. Note that the drifts are small and both positive and negative confirming the correctness of the functions used.

Reference	Range °K	Points	$\Delta Hs^\circ_{298.15}$ kcal/mol 2nd law	3rd law	Drift eu
Freeman (1)	1463 - 1668	9	106.2 ± 3.7	105.66 ± 0.9	-0.2 ± 2.3
Blue et al. (2)	1246 - 1498	6	99.6 ± 2.5	106.00 ± 1.0	4.1 ± 2.0
Schulz and Searcy (3)	1421 - 1689	34	102.4 ± 0.3	104.00 ± 0.2	1.0 ± 0.2
Pottie (4)	1823	1		106.4	
Ruff and LeBoucher (5)	2086 - 2208	7	106.7 ± 4.8	105.22 ± 0.5	-0.7 ± 2.2
Blue et al (2) *	1242 - 1669	19	104.7 ± 0.5		

* This set was not analysed by the third law since the absolute pressures were adjusted by the authors to match their weight loss values.

A median value of 105.5 ± 0.5 kcal/mol is adopted for the heat of sublimation which yields $\Delta Hf^\circ_{298.15}(CaF_2, g)$ = -187.5 ± 2 kcal/mol.

Heat Capacity and Entropy

The bond length was measured by Akishin and Spiridonov (6), but the diffraction patterns were interpreted as indicating a linear molecule. The vibrational frequencies and bond angle are those reported by Calder (7) using matrix isolation spectroscopy and isotopically enriched materials.

The individual moments are $I_A = 2.092 \times 10^{-39}$, $I_B = 2.3749 \times 10^{-38}$, and $I_C = 2.5840 \times 10^{-38}\ g\ cm^2$.

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Calcium Monohydroxide Unipositive Ion ($CaOH^+$)

(Ideal Gas) GFW = 57.08682

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.993	55.380	55.380	.000	87.700	84.620	-62.028
300	11.009	55.448	55.380	.020	87.704	84.600	-61.631
400	11.667	58.714	55.821	1.157	87.999	83.522	-45.635
500	12.056	61.362	56.673	2.345	88.322	82.367	-36.003
600	12.312	63.584	57.644	3.564	88.660	81.145	-29.557
700	12.506	65.497	58.633	4.805	89.004	79.864	-24.935
800	12.673	67.179	59.598	6.064	89.015	78.564	-21.463
900	12.828	68.680	60.525	7.340	89.173	77.248	-18.758
1000	12.976	70.040	61.410	8.630	89.282	75.917	-16.592
1100	13.118	71.283	62.252	9.935	89.344	74.577	-14.817
1200	13.253	72.430	63.053	11.253	87.576	73.387	-13.366
1300	13.379	73.496	63.815	12.585	87.883	72.190	-12.136
1400	13.497	74.492	64.543	13.929	88.195	70.972	-11.079
1500	13.605	75.427	65.238	15.284	88.509	69.731	-10.160
1600	13.705	76.308	65.902	16.649	88.824	68.468	-9.352
1700	13.796	77.142	66.539	18.025	89.142	67.187	-8.638
1800	13.879	77.933	67.150	19.408	52.564	66.566	-8.082
1900	13.954	78.685	67.738	20.800	53.104	67.331	-7.745
2000	14.023	79.403	68.303	22.199	53.642	68.065	-7.438
2100	14.085	80.088	68.848	23.604	54.178	68.772	-7.157
2200	14.141	80.745	69.374	25.016	54.710	69.455	-6.900
2300	14.193	81.375	69.882	26.432	55.237	70.112	-6.662
2400	14.240	81.980	70.374	27.854	55.759	70.750	-6.443
2500	14.282	82.562	70.850	29.280	56.272	71.362	-6.238
2600	14.322	83.123	71.311	30.711	56.778	71.957	-6.048
2700	14.357	83.664	71.759	32.144	57.271	72.532	-5.871
2800	14.390	84.187	72.193	33.582	57.752	73.087	-5.705
2900	14.420	84.692	72.616	35.022	58.219	73.629	-5.549
3000	14.446	85.182	73.026	36.466	58.669	74.150	-5.402
3100	14.473	85.656	73.426	37.912	59.101	74.659	-5.263
3200	14.497	86.116	73.815	39.360	59.513	75.156	-5.133
3300	14.518	86.562	74.195	40.811	59.901	75.638	-5.009
3400	14.538	86.996	74.565	42.264	60.265	76.110	-4.892
3500	14.557	87.417	74.926	43.719	60.603	76.572	-4.781
3600	14.574	87.828	75.279	45.175	60.913	77.024	-4.676
3700	14.590	88.227	75.624	46.634	61.193	77.465	-4.576
3800	14.605	88.617	75.960	48.093	61.442	77.904	-4.480
3900	14.619	88.996	76.290	49.554	61.657	78.333	-4.390
4000	14.632	89.366	76.612	51.017	61.839	78.756	-4.303
4100	14.644	89.728	76.928	52.481	61.987	79.177	-4.220
4200	14.656	90.081	77.237	53.946	62.100	79.598	-4.142
4300	14.666	90.426	77.539	55.412	62.177	80.013	-4.067
4400	14.676	90.763	77.836	56.879	62.219	80.428	-3.995
4500	14.686	91.093	78.127	58.347	62.223	80.836	-3.926
4600	14.694	91.416	78.412	59.816	62.194	81.256	-3.861
4700	14.703	91.732	78.692	61.286	62.129	81.671	-3.798
4800	14.711	92.042	78.967	62.757	62.029	82.086	-3.737
4900	14.718	92.345	79.237	64.228	61.897	82.505	-3.680
5000	14.725	92.643	79.502	65.700	61.731	82.927	-3.625
5100	14.732	92.934	79.763	67.173	61.534	83.353	-3.572
5200	14.738	93.220	80.019	68.647	61.307	83.783	-3.521
5300	14.744	93.501	80.271	70.121	61.052	84.220	-3.473
5400	14.749	93.777	80.518	71.595	60.769	84.655	-3.426
5500	14.755	94.047	80.762	73.071	60.461	85.103	-3.382
5600	14.760	94.313	81.001	74.546	60.127	85.548	-3.339
5700	14.765	94.575	81.237	76.023	59.774	86.012	-3.298
5800	14.769	94.831	81.469	77.499	59.398	86.473	-3.258
5900	14.774	95.084	81.698	78.976	59.003	86.943	-3.221
6000	14.778	95.332	81.923	80.454	58.591	87.423	-3.184

June 30, 1970

CALCIUM MONOHYDROXIDE UNIPOSITIVE ION ($CaOH^+$) (IDEAL GAS) GFW = 57.08682

Point Group [$C_{\infty v}$]

ΔHf_0° = 88.5 ± 15 kcal/mol

$S^\circ_{298.15}$ = [55.4 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 87.7 ± 15 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[733] (1)
[320] (2)
[3600] (1)

Bond Distance: Ca-O = [1.82] Å O-H = [0.96] Å

Bond Angle: Ca-O-H = [180°] σ = 1

Rotational Constant: B_0 = [0.3926] cm^{-1}

Heat of Formation

D. E. Jensen (1) determined the heat of reaction ΔHr_0° = 35 ± 10 kcal/mol for $Ca(g) + OH(g) \rightarrow CaOH^+(g) + e^-$ in atmospheric pressure hydrogen-nitrogen-oxygen flames using the microwave cavity resonance method. This value was calculated assuming a bent model for $CaOH^+$; the value is not significantly changed, within the uncertainty, by the change in configuration. Combining ΔHr° with JANAF heats of formation of Ca(g) and OH(g) and electron, we obtain $\Delta Hf^\circ_{298}(CaOH^+, g)$ = 87.7 kcal/mol, which is adopted in the table. This corresponds to an ionization potential of 6.11 eV.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CsOH, RbOH are linear (2, 3, 4). This evidence also confirms the prediction of A. D. Walsh (5) that "HAB" molecules with 10 or less valence electrons ($CaOH^+$ has 8 valence electrons) will be linear in their ground state. The molecule of $CaOH^+$ has an isoelectronic structure of KOH.

The bond distances O-H and Ca-O are assumed to be the same as those in $H_2O(g)$ and CaO(g), respectively (6, 7). The moment of inertia is 7.1294 x 10^{-39} g cm^2.

The Ca-O stretching frequency 733 cm^{-1} is estimated from those of CaO(g) (7, 9) and CaF(g) (8). The O-H stretching frequency, 3600 cm^{-1}, is estimated from those of $H_2O(g)$ (6) and $Ca(OH)_2(g)$ (10). The bending vibrational frequency, 320 cm^{-1}, is estimated by comparison with those of NaOH, CsOH, RbOH (2, 4).

The enthalpy change between 0° and 298°K is 2.630 kcal/mol.

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4. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July 1968.
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Calcium Monohydroxide (CaOH)

(Ideal Gas) GFW = 57.08737

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.633	-52.512	-52.512	INFINITE
100	7.821	46.495	65.686	-1.919	-52.759	-51.738	117.445
200	9.843	52.591	57.730	-1.028	-53.059	-54.600	59.664
298	10.993	56.757	56.757	.000	-53.300	-55.303	40.538
300	11.009	56.825	56.757	.020	-53.305	-55.316	40.298
400	11.667	60.091	57.198	1.157	-53.507	-55.955	30.573
500	12.056	62.740	58.050	2.345	-53.681	-56.546	24.716
600	12.312	64.962	59.022	3.564	-53.840	-57.104	20.800
700	12.506	66.875	60.010	4.805	-53.992	-57.636	17.995
800	12.673	68.556	60.975	6.064	-54.478	-58.117	15.877
900	12.828	70.058	61.903	7.340	-54.817	-58.552	14.218
1000	12.976	71.417	62.787	8.630	-55.205	-58.946	12.883
1100	13.118	72.660	63.629	9.935	-55.640	-59.300	11.782
1200	13.253	73.808	64.430	11.253	-57.905	-59.460	10.829
1300	13.379	74.873	65.193	12.585	-58.094	-59.582	10.017
1400	13.497	75.869	65.920	13.929	-58.279	-59.690	9.318
1500	13.606	76.804	66.615	15.284	-58.462	-59.784	8.710
1600	13.705	77.686	67.280	16.650	-58.644	-59.866	8.177
1700	13.797	78.519	67.916	18.025	-58.823	-59.936	7.705
1800	13.880	79.310	68.528	19.409	-95.896	-59.316	7.202
1900	13.957	80.063	69.115	20.801	-95.854	-57.285	6.589
2000	14.028	80.781	69.681	22.200	-95.812	-55.257	6.038
2100	14.093	81.467	70.226	23.606	-95.773	-53.230	5.540
2200	14.153	82.124	70.752	25.018	-95.736	-51.205	5.087
2300	14.210	82.754	71.260	26.436	-95.704	-49.182	4.673
2400	14.264	83.360	71.751	27.860	-95.677	-47.158	4.294
2500	14.315	83.943	72.228	29.289	-95.658	-45.139	3.946
2600	14.365	84.506	72.689	30.723	-95.646	-43.117	3.624
2700	14.413	85.049	73.137	32.162	-95.644	-41.098	3.327
2800	14.461	85.574	73.572	33.606	-95.654	-39.077	3.050
2900	14.508	86.082	73.994	35.054	-95.675	-37.054	2.792
3000	14.554	86.575	74.405	36.507	-95.713	-35.033	2.552
3100	14.601	87.053	74.806	37.965	-95.765	-33.010	2.327
3200	14.648	87.517	75.196	39.428	-95.837	-30.985	2.116
3300	14.695	87.968	75.576	40.895	-95.929	-28.957	1.918
3400	14.743	88.408	75.947	42.367	-96.042	-26.927	1.731
3500	14.791	88.836	76.309	43.844	-96.179	-24.891	1.554
3600	14.840	89.253	76.663	45.325	-96.341	-22.852	1.387
3700	14.889	89.661	77.009	46.812	-96.530	-20.807	1.229
3800	14.939	90.058	77.347	48.303	-96.746	-18.757	1.079
3900	14.989	90.447	77.678	49.799	-96.993	-16.704	.936
4000	15.039	90.827	78.002	51.301	-97.268	-14.642	.800
4100	15.089	91.199	78.319	52.807	-97.574	-12.572	.670
4200	15.139	91.563	78.630	54.319	-97.912	-10.494	.546
4300	15.190	91.920	78.935	55.835	-98.282	-8.409	.427
4400	15.240	92.270	79.234	57.357	-98.682	-6.315	.314
4500	15.289	92.613	79.528	58.883	-99.117	-4.212	.205
4600	15.339	92.950	79.816	60.414	-99.580	-2.095	.100
4700	15.388	93.280	80.099	61.951	-100.076	.030	-.001
4800	15.436	93.604	80.377	63.492	-100.602	2.165	-.099
4900	15.483	93.923	80.650	65.038	-101.157	4.310	-.192
5000	15.529	94.236	80.919	66.588	-101.740	6.467	-.283
5100	15.575	94.544	81.183	68.144	-102.352	8.640	-.370
5200	15.620	94.847	81.443	69.703	-102.989	10.820	-.455
5300	15.663	95.145	81.698	71.268	-103.651	13.019	-.537
5400	15.705	95.438	81.950	72.836	-104.338	15.222	-.616
5500	15.746	95.727	82.198	74.409	-105.045	17.445	-.693
5600	15.786	96.011	82.442	75.985	-105.774	19.676	-.768
5700	15.825	96.291	82.683	77.566	-106.520	21.924	-.841
5800	15.862	96.566	82.920	79.150	-107.285	24.185	-.911
5900	15.897	96.838	83.153	80.738	-108.066	26.458	-.980
6000	15.932	97.105	83.384	82.330	-108.861	28.745	-1.047

June 30, 1970

CALCIUM MONOHYDROXIDE (CaOH) (IDEAL GAS) GFW = 57.08737

Point Group [$C_{\infty v}$] ΔHf°_0 = -52.5 ± 5 kcal/mol

$S^\circ_{298.15}$ = [56.8 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -53.3 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[16000]	[2]
[16100]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[733] (1)
[320] (2)
[3600] (1)

Bond Distance: Ca-O = [1.82] Å O-H = [0.96] Å

Bond Angle: Ca-O-H = [180°] σ = 1

Rotational Constant: B_o = [0.3926] cm^{-1}

Heat of Formation

Cotton and Jenkins (1) determined the equilibrium constants in the temperature range 1570°K-2030°K for the reaction $Ca(g) + H_2O(g) \rightarrow CaOH(g) + H(g)$ by atomic absorption spectroscopy in a fuel-rich hydrogén-nitrogen-oxygen flame. Using all JANAF functions, third law analyses of the data give ΔHr°_{298} = 13.8 kcal/mol and the drift 1.9 ± 2.9 eu. This leads to the heat of formation, ΔHf°_{298}(CaOH, g) = -53.3 kcal/mol which is adopted in the tabulation. The bond dissociation energy, D°_0(Ca-OH), is 104.6 kcal/mol.

Ryabova and Gurvich (2) reported the bond dissociation energy D°_0(Ca-OH) as 100 kcal/mol. Schofield and Sugden (3) found $D^\circ_0(Ca\text{-}(OH)_2)$ as 217 ± 12 kcal/mol. Using the relation D°_0(M-X)/D°_0(X-M-X) = 0.47 suggested by Kent, McDonald and Margrave (4), we obtain D°_0(Ca-OH) = 102 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CsOH and RbOH are linear (5, 6, 7). This evidence also confirms the prediction of A. D. Walsh (8), that "HAB" molecules with 10 or less valence electrons (CaOH has 9 valence electrons) will be linear in their ground state.

The ground state is assumed to be $^2\Sigma$ by analogy with isoelectronic CaF (9). The electronic levels are estimated from band spectra of CaOH reported by Gaydon (14).

The bond distances O-H and Ca-O are assumed to be the same as those in $H_2O(g)$ and CaO(g), respectively (10, 11). The moment of inertia is 7.1295 x 10^{-39} g cm^2.

The O-H stretching frequency, 3600 cm^{-1}, is estimated from those of $H_2O(g)$ (10) and $Ca(OH)_2(g)$ (12). The bending frequency, 320 cm^{-1}, is estimated by comparison with those of NaOH, CsOH and RbOH (5, 7). The Ca-O stretching frequency, 733 cm^{-1}, is estimated to be the same as that of CaO(g) observed by Hultin and Lagerqvist (11) and Brewer and Hauge (13).

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11. M. Hultin and Lagerqvist, Arkiv Fysik, 2, 471 (1950).
12. O. Oehler and H. H. Günthard, J. Chem. Phys. 51, 4714 (1969).
13. L. Brewer and R. Hauge, J. Mol. Spectry. 25, 330 (1968).
14. A. G. Gaydon, Proc. Roy. Soc. (London) A231, 437 (1955).

Chlorine, Monatomic (Cl)

(Ideal Gas) At. Wt. = 35.457

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 1.499	28.520	28.520	INFINITE
100	4.969	33.955	43.977	- 1,002	28.669	27.531	- 60.166
200	5.038	37.412	39.927	- .503	28.805	26.338	- 28.780
298	5.219	39.456	39.456	.000	28.922	25.102	- 18.400
300	5.223	39.488	39.456	.010	28.924	25.079	- 18.269
400	5.370	41.013	39.663	.540	29.040	23.779	- 12.992
500	5.436	42.220	40.058	1.081	29.154	22.451	- 9.813
600	5.445	43.212	40.503	1.625	29.264	21.100	- 7.685
700	5.424	44.050	40.952	2.169	29.368	19.731	- 6.160
800	5.389	44.772	41.385	2.710	29.466	18.347	- 5.012
900	5.351	45.405	41.797	3.247	29.558	16.952	- 4.116
1000	5.314	45.967	42.187	3.780	29.644	15.547	- 3.398
1100	5.280	46.472	42.554	4.310	29.725	14.133	- 2.808
1200	5.249	46.930	42.900	4.836	29.801	12.713	- 2.315
1300	5.221	47.349	43.226	5.359	29.873	11.286	- 1.897
1400	5.197	47.735	43.534	5.880	29.941	9.853	- 1.538
1500	5.175	48.092	43.827	6.399	30.006	8.416	- 1.226
1600	5.156	48.426	44.104	6.915	30.068	6.975	- .953
1700	5.140	48.738	44.367	7.430	30.128	5.530	- .711
1800	5.125	49.031	44.616	7.943	30.184	4.080	- .495
1900	5.112	49.308	44.858	8.455	30.239	2.629	- .302
2000	5.101	49.570	45.087	8.966	30.292	1.174	- .128
2100	5.091	49.819	45.306	9.476	30.343	- .283	.029
2200	5.081	50.055	45.517	9.984	30.393	- 1.742	.173
2300	5.073	50.281	45.719	10.492	30.440	- 3.204	.304
2400	5.066	50.497	45.914	10.999	30.487	- 4.668	.425
2500	5.059	50.703	46.101	11.505	30.532	- 6.133	.536
2600	5.053	50.902	46.282	12.011	30.575	- 7.601	.639
2700	5.048	51.092	46.457	12.516	30.617	- 9.069	.734
2800	5.043	51.276	46.626	13.020	30.658	- 10.540	.823
2900	5.038	51.453	46.789	13.524	30.698	- 12.013	.905
3000	5.034	51.623	46.947	14.028	30.737	- 13.487	.982
3100	5.031	51.788	47.101	14.531	30.775	- 14.960	1.055
3200	5.027	51.948	47.250	15.034	30.812	- 16.436	1.122
3300	5.024	52.103	47.395	15.537	30.848	- 17.914	1.186
3400	5.021	52.253	47.535	16.039	30.883	- 19.392	1.246
3500	5.018	52.398	47.672	16.541	30.917	- 20.871	1.303
3600	5.016	52.539	47.805	17.043	30.950	- 22.352	1.357
3700	5.013	52.677	47.935	17.544	30.982	- 23.833	1.408
3800	5.011	52.810	48.062	18.045	31.013	- 25.314	1.456
3900	5.009	52.941	48.185	18.546	31.044	- 26.798	1.502
4000	5.007	53.067	48.306	19.047	31.073	- 28.281	1.545
4100	5.006	53.191	48.423	19.548	31.102	- 29.765	1.587
4200	5.004	53.312	48.538	20.048	31.130	- 31.249	1.626
4300	5.002	53.429	48.651	20.548	31.157	- 32.736	1.664
4400	5.001	53.544	48.761	21.049	31.184	- 34.222	1.700
4500	5.000	53.657	48.868	21.549	31.209	- 35.709	1.734
4600	4.998	53.767	48.973	22.049	31.234	- 37.196	1.767
4700	4.997	53.874	49.077	22.548	31.258	- 38.683	1.799
4800	4.996	53.979	49.178	23.048	31.281	- 40.173	1.829
4900	4.995	54.082	49.277	23.548	31.305	- 41.660	1.858
5000	4.994	54.183	49.374	24.047	31.326	- 43.149	1.886
5100	4.993	54.282	49.469	24.546	31.347	- 44.641	1.913
5200	4.992	54.379	49.563	25.046	31.368	- 46.130	1.939
5300	4.991	54.474	49.654	25.545	31.388	- 47.620	1.964
5400	4.990	54.567	49.744	26.044	31.407	- 49.112	1.988
5500	4.990	54.659	49.833	26.543	31.425	- 50.601	2.011
5600	4.989	54.749	49.920	27.042	31.443	- 52.094	2.033
5700	4.988	54.837	50.005	27.541	31.460	- 53.585	2.054
5800	4.988	54.924	50.090	28.039	31.476	- 55.077	2.075
5900	4.987	55.009	50.172	28.538	31.492	- 56.570	2.095
6000	4.986	55.093	50.254	29.037	31.507	- 58.064	2.115

March 31, 1961

CHLORINE, MONATOMIC (Cl) (IDEAL GAS) AT. WT. = 35.457

ΔH°_{f0} = 28.52 ± 2 (± 0.03) kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 28.922 ± 2 (± 0.03) kcal. mole^{-1}

Ground State Configuration $^2P_{3/2}$

$S^\circ_{298.15}$ = 39.46 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_1 cm.$^{-1}$	g_1	ϵ_1 cm.$^{-1}$	g_1	ϵ_1 cm.$^{-1}$	g_1	ϵ_1 cm.$^{-1}$	g_1
0	4	84,480.91	4	94,477.93	5	95,608.3	4
882.5	2	84,684.27	2	94,659.28	6	95,696.49	8
71,954	6	84,115.68	6	94,969.43	2	95,782.41	6
72,484.2	4	84,117.38	4	94,727.91	8	95,893.16	4
72,822.64	2	84,643.69	6	94,822.75	6	95,991.18	2
74,221.44	4	84,984.04	4	95,309.43	4	96,650.	44
74,861.24	2	85,239.98	2	95,530.51	2	97,438.78	48
82,914.54	6	85,438.04	4	95,140.05	6	99,088.57	52
83,126.59	4	85,913.44	2	95,176.	8	99,647.21	38
83,360.55	2	85,730.68	4	95,396.31	6	99,839.67	20
83,889.64	8	94,309.67	4	95,702.01	4	100,330.38	40
84,127.90	6	94,464.5	2	95,593.28	2	101,261.61	38

Heat of Formation

Bands in the visible for the $^3\Pi \leftarrow {}^1\Sigma$ transitions have been observed by A. Elliott, Proc. Roy. Soc. 127A, 638 (1930), who also lists the work of former contributors. C. F. Goodeve and B. A. Stephens, Trans. Far. Soc. 32, 1517 (1936) have measured several lines in the same system. These data lead to a convergence limit of 20,831 ± 20 cm.$^{-1}$ From which the dissociation energy is obtained assuming excited and normal Cl atoms as the dissociation products of the A state. The assigned accuracy estimation reflects the uncertain knowledge of the products. The value in parenthesis is a precision measure and would apply if the dissociation products were those assumed. See R. G. Aikin and N. S. Baylis, Trans. Far. Soc. 33, 1333 (1937) for further details on the dissociation products.

Heat Capacity and Entropy

The electronic energy levels are listed by C. E. Moore, Nat. Bur. Stands. Circ. 467, (1949).

Chlorine Unipositive Ion (Cl^+)

(Ideal Gas) Mol. Wt. = 35.45245

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100							
200							
298	5.487	40.021	40.021	.000	330.600	325.125	- 238.311
300	5.491	40.055	40.021	.010	330.612	325.090	- 236.817
400	5.646	41.660	40.239	.568	331.252	323.154	- 176.554
500	5.666	42.924	40.654	1.135	331.889	321.055	- 140.326
600	5.622	43.954	41.121	1.700	332.516	318.829	- 116.128
700	5.555	44.815	41.589	2.258	333.132	316.499	- 98.811
800	5.486	45.552	42.039	2.810	333.738	314.082	- 85.799
900	5.422	46.195	42.466	3.356	334.335	311.589	- 75.660
1000	5.365	46.763	42.868	3.895	334.925	309.029	- 67.535
1100	5.317	47.272	43.246	4.429	335.507	306.412	- 60.876
1200	5.276	47.733	43.601	4.959	336.084	303.742	- 55.316
1300	5.241	48.154	43.935	5.485	336.655	301.022	- 50.604
1400	5.212	48.541	44.250	6.007	337.222	298.261	- 46.558
1500	5.188	48.900	44.549	6.527	337.786	295.458	- 43.046
1600	5.168	49.234	44.831	7.045	338.347	292.617	- 39.968
1700	5.151	49.547	45.099	7.561	338.905	289.743	- 37.247
1800	5.139	49.841	45.355	8.075	339.460	286.834	- 34.825
1900	5.129	50.119	45.598	8.589	340.015	283.896	- 32.654
2000	5.122	50.381	45.831	9.101	340.567	280.930	- 30.697
2100	5.118	50.631	46.054	9.613	341.118	277.932	- 28.923
2200	5.117	50.869	46.267	10.125	341.668	274.911	- 27.309
2300	5.118	51.097	46.472	10.637	342.216	271.863	- 25.832
2400	5.121	51.315	46.669	11.149	342.765	268.793	- 24.476
2500	5.126	51.524	46.859	11.661	343.312	265.700	- 23.226
2600	5.133	51.725	47.043	12.174	343.859	262.585	- 22.071
2700	5.141	51.919	47.220	12.688	344.406	259.449	- 21.000
2800	5.151	52.106	47.391	13.202	344.952	256.293	- 20.004
2900	5.162	52.287	47.557	13.718	345.497	253.117	- 19.074
3000	5.174	52.462	47.717	14.235	346.043	249.920	- 18.206
3100	5.186	52.632	47.873	14.753	346.589	246.707	- 17.392
3200	5.199	52.797	48.024	15.272	347.134	243.478	- 16.628
3300	5.213	52.957	48.171	15.793	347.679	240.231	- 15.909
3400	5.227	53.113	48.314	16.315	348.224	236.967	- 15.231
3500	5.241	53.265	48.454	16.838	348.769	233.685	- 14.591
3600	5.256	53.412	48.589	17.363	349.314	230.393	- 13.986
3700	5.270	53.557	48.722	17.889	349.859	227.077	- 13.412
3800	5.285	53.697	48.851	18.417	350.405	223.755	- 12.868
3900	5.299	53.835	48.977	18.946	350.951	220.414	- 12.351
4000	5.313	53.969	49.100	19.477	351.495	217.059	- 11.859
4100	5.326	54.101	49.220	20.009	352.042	213.687	- 11.390
4200	5.339	54.229	49.338	20.542	352.588	210.311	- 10.943
4300	5.352	54.355	49.453	21.077	353.135	206.916	- 10.516
4400	5.365	54.478	49.566	21.612	353.682	203.513	- 10.108
4500	5.377	54.599	49.677	22.149	354.229	200.088	- 9.717
4600	5.388	54.717	49.785	22.688	354.778	196.660	- 9.343
4700	5.400	54.833	49.891	23.227	355.327	193.217	- 8.984
4800	5.410	54.947	49.995	23.768	355.876	189.758	- 8.639
4900	5.420	55.059	50.097	24.309	356.426	186.293	- 8.309
5000	5.430	55.168	50.198	24.852	356.976	182.819	- 7.991
5100	5.439	55.276	50.296	25.395	357.528	179.326	- 7.684
5200	5.448	55.381	50.393	25.939	358.080	175.833	- 7.390
5300	5.456	55.485	50.488	26.485	358.633	172.320	- 7.105
5400	5.463	55.587	50.582	27.031	359.187	168.799	- 6.831
5500	5.470	55.688	50.674	27.577	359.741	165.266	- 6.567
5600	5.477	55.786	50.764	28.125	360.295	161.724	- 6.311
5700	5.483	55.883	50.853	28.673	360.850	158.178	- 6.065
5800	5.489	55.979	50.941	29.221	361.406	154.613	- 5.826
5900	5.494	56.073	51.027	29.770	361.962	151.040	- 5.595
6000	5.499	56.165	51.112	30.320	362.519	147.467	- 5.371

June 30, 1965

CHLORINE UNIPOSITIVE ION (Cl^+) (IDEAL GAS) MOL. WT. = 35.45245

Ground State Configuration $^3P_2$

$\Delta H^\circ_{f\ 0}$ = 328.7 ± .5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 40.021 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 330.6 ± .5 kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1	$\mathcal{E}_1$, cm.$^{-1}$	g_1
0.0	5	27900.0	1
697.0	3	93366.6	5
996.0	1	93998.7	3
11652.0	5	94332.8	1

Heat of Formation.

The heat of formation was calculated from the equation: $Cl(g) - e^- \rightarrow Cl^+(g)$ with the JANAF auxiliary value for Cl(g); using an I.P. = 1.04991 X 10^5 cm^{-1} (300.206 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, loc. cit. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.526 kcal./mole.

Chlorine Uninegative Ion (Cl^-)

(Ideal Gas) Mol. Wt. = 35.45355

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	4.968	36.628	36.628	.000	-55.900	-57.389	42.066
300	4.968	36.658	36.628	.009	-55.907	-57.398	41.813
400	4.968	38.088	36.823	.506	-56.322	-57.834	31.597
500	4.968	39.196	37.191	1.003	-56.749	-58.162	25.421
600	4.968	40.102	37.603	1.500	-57.184	-58.404	21.272
700	4.968	40.868	38.016	1.996	-57.622	-58.572	18.286
800	4.968	41.531	38.415	2.493	-58.065	-58.678	16.029
900	4.968	42.116	38.794	2.990	-58.510	-58.727	14.260
1000	4.968	42.640	39.153	3.487	-58.958	-58.728	12.834
1100	4.968	43.113	39.492	3.984	-59.406	-58.684	11.659
1200	4.968	43.546	39.812	4.481	-59.856	-58.599	10.672
1300	4.968	43.943	40.115	4.977	-60.307	-58.474	9.830
1400	4.968	44.312	40.401	5.474	-60.759	-58.318	9.103
1500	4.968	44.654	40.674	5.971	-61.212	-58.127	8.469
1600	4.968	44.975	40.933	6.468	-61.666	-57.906	7.909
1700	4.968	45.276	41.179	6.965	-62.121	-57.657	7.412
1800	4.968	45.560	41.415	7.461	-62.576	-57.381	6.967
1900	4.968	45.829	41.640	7.958	-63.032	-57.081	6.565
2000	4.968	46.084	41.856	8.455	-63.489	-56.756	6.202
2100	4.968	46.326	42.063	8.952	-63.947	-56.407	5.870
2200	4.968	46.557	42.262	9.449	-64.406	-56.038	5.567
2300	4.968	46.778	42.454	9.945	-64.865	-55.645	5.287
2400	4.968	46.989	42.638	10.442	-65.326	-55.235	5.030
2500	4.968	47.192	42.817	10.939	-65.788	-54.805	4.791
2600	4.968	47.387	42.989	11.436	-66.251	-54.357	4.569
2700	4.968	47.575	43.155	11.933	-66.715	-53.894	4.362
2800	4.968	47.755	43.316	12.430	-67.180	-53.407	4.168
2900	4.968	47.930	43.472	12.926	-67.646	-52.910	3.987
3000	4.968	48.098	43.624	13.423	-68.114	-52.391	3.817
3100	4.968	48.261	43.771	13.920	-68.584	-51.859	3.656
3200	4.968	48.419	43.913	14.417	-69.055	-51.316	3.505
3300	4.968	48.572	44.052	14.914	-69.528	-50.754	3.361
3400	4.968	48.720	44.187	15.410	-70.001	-50.177	3.225
3500	4.968	48.864	44.319	15.907	-70.476	-49.588	3.096
3600	4.968	49.004	44.447	16.404	-70.953	-48.984	2.974
3700	4.968	49.140	44.572	16.901	-71.431	-48.363	2.857
3800	4.968	49.272	44.694	17.398	-71.910	-47.735	2.745
3900	4.968	49.401	44.813	17.895	-72.391	-47.092	2.639
4000	4.968	49.527	44.929	18.391	-72.872	-46.436	2.537
4100	4.968	49.650	45.043	18.888	-73.355	-45.770	2.440
4200	4.968	49.770	45.154	19.385	-73.839	-45.096	2.347
4300	4.968	49.887	45.263	19.882	-74.324	-44.406	2.257
4400	4.968	50.001	45.369	20.379	-74.809	-43.704	2.171
4500	4.968	50.112	45.473	20.875	-75.295	-42.987	2.088
4600	4.968	50.222	45.575	21.372	-75.782	-42.268	2.008
4700	4.968	50.328	45.675	21.869	-76.269	-41.529	1.931
4800	4.968	50.433	45.774	22.366	-76.758	-40.786	1.857
4900	4.968	50.536	45.870	22.863	-77.246	-40.036	1.786
5000	4.968	50.636	45.964	23.359	-77.734	-39.272	1.716
5100	4.968	50.734	46.057	23.856	-78.223	-38.491	1.649
5200	4.968	50.831	46.147	24.353	-78.712	-37.712	1.585
5300	4.968	50.925	46.237	24.850	-79.202	-36.916	1.522
5400	4.968	51.018	46.324	25.347	-79.691	-36.113	1.462
5500	4.968	51.109	46.411	25.844	-80.181	-35.301	1.403
5600	4.968	51.199	46.495	26.340	-80.670	-34.481	1.346
5700	4.968	51.287	46.579	26.837	-81.160	-33.659	1.290
5800	4.968	51.373	46.660	27.334	-81.649	-32.813	1.236
5900	4.968	51.458	46.741	27.831	-82.140	-31.969	1.184
6000	4.968	51.542	46.820	28.328	-82.630	-31.120	1.133

June 30, 1965

CHLORINE UNINEGATIVE ION (Cl^-) (IDEAL GAS) MOL. WT. = 35.45355

Ground State Configuration $^1S_0$

$\Delta H_f^\circ{}_0 = -54.8 \pm .5$ kcal. mole^{-1}

$S^\circ_{298.15} = 36.628$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -55.9 \pm .5$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1
0.0	1
93143.8	5
93750.639	3
94553.707	1
95399.870	3

Heat of Formation.

The heat of formation was calculated from the equation: $Cl(g) + e^- \rightarrow Cl^-(g)$ with the JANAF auxiliary values for Cl(g); using the measured electron affinity = 3.613 e.v. (83.316 kcal/mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963). Other calculated values for the electron affinity are: 3.70 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960) and 3.56 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Argon. The electronic levels above 1 X 10^5 cm.$^{-1}$ were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.481 kcal/mole.

Cesium Chloride (CsCl)

(Crystal) GFW = 168.358

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.976	-105.875	-105.875	INFINITE
100	10.538	11.424	34.894	-2.347	-106.107	-103.679	226.589
200	11.981	19.294	25.314	-1.204	-105.968	-101.300	110.696
298	12.534	24.183	24.183	.000	-105.840	-99.038	72.597
300	12.541	24.261	24.183	.023	-105.838	-98.996	72.119
400	13.070	27.941	24.682	1.304	-106.235	-96.567	52.761
500	13.600	30.915	25.640	2.637	-106.077	-94.167	41.160
600	14.125	33.441	26.735	4.024	-105.867	-91.803	33.439
700	14.650	35.658	27.854	5.462	-105.607	-89.479	27.937
800	15.220	38.871	29.043	7.863	-104.390	-87.266	23.840
900	15.338	40.671	30.237	9.391	-104.046	-85.145	20.676
1000	15.460	42.293	31.362	10.930	-119.774	-82.244	17.974
1100	15.580	43.772	32.424	12.482	-119.167	-78.520	15.600
1200	15.700	45.133	33.427	14.046	-118.550	-74.852	13.632
1300	15.820	46.394	34.377	15.622	-117.922	-71.236	11.976
1400	15.940	47.571	35.278	17.210	-117.284	-67.669	10.564
1500	16.060	48.675	36.135	18.810	-116.634	-64.147	9.346
1600	16.180	49.715	36.951	20.422	-115.975	-60.670	8.287
1700	16.310	50.700	37.731	22.047	-115.305	-57.233	7.358
1800	16.430	51.636	38.478	23.684	-114.625	-53.837	6.537
1900	16.550	52.527	39.194	25.333	-113.936	-50.478	5.806
2000	16.670	53.379	39.882	26.994	-113.241	-47.156	5.153

June 30, 1968

CESIUM CHLORIDE (CsCl) (CRYSTAL) GFW = 168.358

$\Delta Hf^\circ_0 = -105.88 \pm 0.2$ kcal/mol

$S^\circ_{298.15} = 24.183 \pm 0.005$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -105.84 \pm 0.2$ kcal/mol

$Tt(\alpha \rightarrow \beta) = 743°K$

$\Delta Ht^\circ = 0.90$ kcal/mol

$Tm = 918°K$

$\Delta Hm^\circ = 3.8$ kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 48.74 kcal/mol

Heat of Formation

The heat of solution (ΔHsoln) of CsCl(c) in water has been measured by Forcrand (1, 2), Haigh (3), Samoilov (4, 6), and Rodnikova (5). Based on their results, Parker (7) derived the corresponding $\Delta Hsoln^\circ_{298.15}(\infty\ H_2O)$ values as 4.30, 4.32, 4.08, 4.25, 4.18 and 4.18 kcal/mol. Borob'ev (8) determined the same quantity and reported $\Delta Hsoln^\circ_{298}(CsCl, \infty\ H_2O) = 4.20 \pm 0.04$ kcal/mol. Using this value, 4.20 kcal/mol, and $\Delta Hf^\circ_{298} = -61.69$ (9) and -39.952 kcal/mol (10) for $Cs^+(\infty\ H_2O)$ and $Cl^-(\infty\ H_2O)$, respectively, we evaluate $\Delta Hf^\circ_{298}(CsCl, c) = -105.84 \pm 0.2$ kcal/mol,which is adopted.

Heat Capacity and Entropy

Taylor (11) measured the low temperature heat capacities, 7.19 - 299.38°K, with an adiabatic calorimeter; the sample purity was >99.95 per cent. Employing these data we derive the value $S^\circ_{298} = 24.183$ eu based on $S^\circ_{7.19} = 0.031$ eu.

The high temperature enthalpies, 385.2 - 904.9°K, were measured by Kaylor (21, 12, 13), using a Bunsen ice calorimeter and a CsCl sample of 99.8 per cent purity. The heat capacities derived from the reported enthalpy data at temperatures 385.2 - 740.5°K appear too low (less than the adopted Cp's systematically by 0.9 gibbs/mol) to join smoothly with the low temperature data at 298°K. The Cp values derived from the measured enthalpy data in the temperature range 760 - 920°K increase rapidly from 14.46 to 16.3 gibbs/mol. In order to rationalize this situation, we adopt the high temperature heat capacities, 298 - 743°K, for CsCl(α) obtained by linear extrapolation of the low temperature data. The Cp values for CsCl(β) are adjusted such that the rate of increase in heat capacities is linear and less rapid than the original one, and the total enthalpy remains essentially unchanged. The discrepancy between the high and low temperature Cp for CsCl(α) may be caused by the incomplete β → α phase conversion involved. In order to resolve this discrepancy, independent enthalpy measurements using a high purity sample with composition well characterized before and after each drop experiment seem necessary.

Transition Data

The temperature of transition (in °K) has been reported by many investigators as 718 (14), 752 (15), 745 (16), 742 (21), 742.5 (12), 743 (20), and 733 (17), using different methods and samples of different purity. The value adopted is 743°K.

The heat of transition (in kcal/mol) was reported to be 1.8 (14), 1.55 (18), 1.4 (19), 0.80 (21), 0.58 (12), 0.90 (13), and 1.1 (17). A median value 0.90 kcal/mol is tentatively adopted.

Melting Data

See CsCl(ℓ) table for details.

Heat of Sublimation

ΔHs°_{298} is calculated as the difference between ΔHf°_{298} for CsCl(g) and CsCl(c).

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Cesium Chloride (CsCl)

(Liquid) GFW = 168.358

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.500	24.309	24.309	.000	- 103.840	- 97.076	71.159
300	18.500	24.423	24.309	.034	- 103.827	- 97.034	70.689
400	18.500	29.746	25.035	1.884	- 103.654	- 94.708	51.746
500	18.500	33.874	26.405	3.734	- 102.980	- 92.550	40.453
600	18.500	37.247	27.940	5.584	- 102.306	- 90.526	32.974
700	18.500	40.098	29.478	7.434	- 101.635	- 88.616	27.667
800	18.500	42.569	30.963	9.284	- 100.968	- 86.803	23.713
900	18.500	44.748	32.376	11.134	- 100.302	- 85.071	20.658
1000	18.500	46.697	33.713	12.984	- 115.720	- 82.594	18.051
1100	18.500	48.460	34.975	14.834	- 114.815	- 79.325	15.760
1200	18.500	50.070	36.166	16.684	- 113.912	- 76.138	13.867
1300	18.500	51.551	37.294	18.534	- 113.010	- 73.027	12.277
1400	18.500	52.922	38.362	20.384	- 112.110	- 69.986	10.925
1500	18.500	54.198	39.375	22.234	- 111.210	- 67.008	9.763
1600	18.500	55.392	40.339	24.084	- 110.313	- 64.091	8.754
1700	18.500	56.514	41.258	25.934	- 109.417	- 61.229	7.871
1800	18.500	57.571	42.135	27.784	- 108.525	- 58.421	7.093
1900	18.500	58.571	42.974	29.634	- 107.635	- 55.660	6.402
2000	18.500	59.520	43.778	31.484	- 106.750	- 52.948	5.786
2100	18.500	60.423	44.549	33.334	- 105.871	- 50.280	5.233
2200	18.500	61.283	45.291	35.184	- 104.999	- 47.654	4.734
2300	18.500	62.106	46.004	37.034	- 104.133	- 45.065	4.282
2400	18.500	62.893	46.691	38.884	- 103.278	- 42.516	3.872
2500	18.500	63.648	47.355	40.734	- 102.434	- 40.002	3.497
2600	18.500	64.374	47.995	42.584	- 101.601	- 37.521	3.154
2700	18.500	65.072	48.615	44.434	- 100.783	- 35.072	2.839
2800	18.500	65.745	49.215	46.284	- 99.982	- 32.652	2.549
2900	18.500	66.394	49.796	48.134	- 99.197	- 30.262	2.281
3000	18.500	67.021	50.360	49.984	- 98.433	- 27.898	2.032

June 30, 1968

CESIUM CHLORIDE (CsCl) (LIQUID) GFW = 168.358

$S^\circ_{298.15}$ = 24.309 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -103.84 ± 2.0 kcal/mol

Tm = 918°K

ΔHm° = 3.8 ± 1 kcal/mol

Tb = 1597.3°K

ΔHv° = 27.52 kcal/mol of liquid (to equilibrium mixture)

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{918} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The enthalpies of CsCl(ℓ) at temperatures 923.6 - 1168.0°K were measured with a Bunsen ice calorimeter by Kaylor (1, 2). Dworkin (3) derived the heat capacity of CsCl(ℓ) as 18.5 gibbs/mol from enthalpy data at temperatures 918 - 980°K. This value is adopted since it is in agreement with the enthalpy values reported by Kaylor et al. The heat capacity at temperatures above 1168 and below 923.6°K is assumed to be 18.5 gibbs/mol. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting temperature (in °K) of CsCl(c) has been determined by many investigators as 904 ± 3 (4), 919 (5), 912 (6), 911 (7), 918 (8), 916 (9), and 919 (13). The cause of the discrepancies is probably due to the difference in purity of the samples. The melting temperature adopted is 918°K.

The heat of melting (in kcal/mol) was reported to be 4.84 (14), 4.97 (15), 4.58 (10), 4.96 (11), and 4.79 (2), which were obtained calorimetrically. Using a modification of Kelley's method of obtaining heat of melting from freezing point data on binary systems involving CsCl (16), we derive the value of ΔHm° as 3.6 - 4.0 kcal/mol, based on the following systems: CsCl-NaCl (5), CsCl-CuCl (6), CsCl-AgCl (6), CsCl-LiCl (8), and $CsCl-Cs_3(PO_3)_3$ (12). The heat of melting for CsCl(c) is tentatively adopted as 3.8 kcal/mol. The ΔHm° values obtained calorimetrically are not used due to the uncertainties of the state of the sample before and after the enthalpy measurements.

Vaporization Data

Tb is the temperature at which the calculated total pressures of CsCl(g) and $Cs_2Cl_2(g)$ equal one atmosphere. The vapor composition at Tb is derived as CsCl 80.4 per cent and Cs_2Cl_2 19.6 per cent. The boiling point of CsCl(ℓ) has been determined by several investigators as 1562 (17), 1572 (18), and 1576 (19). The heat required to vaporize one mole of liquid to the above vapor mixture at Tb is ΔHv°.

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Cesium Chloride (CsCl)

(Ideal Gas) GFW = 168.358

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.421	-56.880	-56.880	INFINITE
100	7.933	51.915	68.865	-1.695	-57.015	-58.636	128.148
200	8.633	57.685	61.978	-.859	-57.183	-60.193	65.776
298	8.832	61.175	61.175	.000	-57.400	-61.628	45.174
300	8.834	61.230	61.175	.016	-57.405	-61.654	44.915
400	8.922	63.785	61.523	.905	-58.194	-62.863	34.347
500	8.974	65.782	62.182	1.800	-58.474	-63.998	27.974
600	9.011	67.421	62.923	2.699	-58.752	-65.076	23.704
700	9.041	68.812	63.667	3.602	-59.028	-66.108	20.640
800	9.067	70.021	64.388	4.507	-59.306	-67.102	18.331
900	9.090	71.091	65.074	5.415	-59.582	-68.059	16.527
1000	9.112	72.049	65.725	6.325	-75.940	-68.166	14.898
1100	9.134	72.919	66.340	7.237	-75.972	-67.386	13.388
1200	9.154	73.715	66.922	8.152	-76.004	-66.605	12.130
1300	9.174	74.448	67.473	9.068	-76.036	-65.820	11.065
1400	9.194	75.129	67.996	9.986	-76.068	-65.034	10.152
1500	9.214	75.764	68.492	10.907	-76.097	-64.244	9.360
1600	9.233	76.359	68.966	11.829	-76.128	-63.453	8.667
1700	9.252	76.919	69.417	12.753	-76.158	-62.659	8.055
1800	9.271	77.449	69.849	13.680	-76.189	-61.865	7.511
1900	9.290	77.950	70.262	14.608	-76.221	-61.067	7.024
2000	9.309	78.427	70.659	15.538	-76.257	-60.269	6.586
2100	9.328	78.882	71.039	16.470	-76.295	-59.469	6.189
2200	9.347	79.317	71.406	17.403	-76.340	-58.667	5.828
2300	9.366	79.732	71.759	18.339	-76.389	-57.862	5.498
2400	9.385	80.131	72.100	19.277	-76.445	-57.055	5.196
2500	9.404	80.515	72.429	20.216	-76.512	-56.247	4.917
2600	9.422	80.884	72.747	21.157	-76.588	-55.434	4.660
2700	9.441	81.240	73.055	22.100	-76.677	-54.619	4.421
2800	9.460	81.584	73.353	23.045	-76.781	-53.800	4.199
2900	9.478	81.916	73.643	23.992	-76.899	-52.977	3.992
3000	9.497	82.238	73.924	24.941	-77.036	-52.150	3.799
3100	9.516	82.549	74.197	25.892	-77.194	-51.318	3.618
3200	9.534	82.852	74.463	26.844	-77.376	-50.481	3.448
3300	9.553	83.145	74.722	27.799	-77.582	-49.637	3.287
3400	9.572	83.431	74.974	28.755	-77.815	-48.786	3.136
3500	9.590	83.709	75.219	29.713	-78.081	-47.930	2.993
3600	9.609	83.979	75.459	30.673	-78.380	-47.064	2.857
3700	9.628	84.243	75.693	31.635	-78.716	-46.189	2.728
3800	9.646	84.500	75.921	32.598	-79.093	-45.305	2.606
3900	9.665	84.750	76.144	33.564	-79.514	-44.410	2.489
4000	9.683	84.995	76.362	34.531	-79.982	-43.504	2.377
4100	9.702	85.235	76.576	35.501	-80.500	-42.587	2.270
4200	9.721	85.469	76.785	36.472	-81.073	-41.656	2.168
4300	9.739	85.698	76.990	37.445	-81.702	-40.711	2.069
4400	9.758	85.922	77.190	38.420	-82.388	-39.747	1.974
4500	9.776	86.141	77.386	39.396	-83.136	-38.772	1.883
4600	9.795	86.356	77.579	40.375	-83.945	-37.776	1.795
4700	9.813	86.567	77.768	41.355	-84.817	-36.762	1.709
4800	9.832	86.774	77.954	42.338	-85.752	-35.731	1.627
4900	9.851	86.977	78.136	43.322	-86.749	-34.678	1.547
5000	9.869	87.176	78.315	44.308	-87.807	-33.605	1.469
5100	9.888	87.372	78.490	45.296	-88.922	-32.509	1.393
5200	9.906	87.564	78.663	46.285	-90.095	-31.392	1.319
5300	9.925	87.753	78.833	47.277	-91.319	-30.252	1.247
5400	9.944	87.938	78.999	48.270	-92.591	-29.089	1.177
5500	9.962	88.121	79.164	49.265	-93.905	-27.899	1.109
5600	9.981	88.301	79.325	50.263	-95.257	-26.688	1.042
5700	9.999	88.478	79.484	51.262	-96.642	-25.452	.976
5800	10.018	88.652	79.641	52.262	-98.053	-24.189	.911
5900	10.036	88.823	79.795	53.265	-99.485	-22.905	.848
6000	10.055	88.992	79.947	54.270	-100.931	-21.594	.787

June 30, 1968

CESIUM CHLORIDE (CsCl) (IDEAL GAS) GFW = 168.358

Ground State Configuration $^1\Sigma^+$

$\Delta Hf^\circ_0 = -56.9 \pm 1$ kcal/mol

$S^\circ_{298.15} = 61.175 \pm 0.005$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -57.4 \pm 1$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

$\omega_e = 213.08 \pm 0.05$ cm^{-1} $\omega_e x_e = 0.733 \pm 0.008$ cm^{-1} $\sigma = 1$

$B_e = 0.07134$ cm^{-1} $\alpha_e = 0.000332$ cm^{-1} $r_e = 2.906$ Å

Heat of Formation

The total pressures of CsCl(g) and Cs_2Cl_2(g) over CsCl(c) and CsCl(ℓ) in the temperature range 605 - 1577°K have been determined by manometric, transpiration and Knudsen effusion methods by many investigators. Based on the reported results, the partial pressures of CsCl(g) and Cs_2Cl_2(g) are calculated using the derived free energy functions for CsCl(c), CsCl(ℓ), CsCl(g) and Cs_2Cl_2(g), and the heats of sublimation and vaporization which are adjusted so that the sum of the calculated partial pressures of CsCl(g) and Cs_2Cl_2(g) approaches the measured total pressures, and the evaluated second and third law ΔHr°_{298} values are in reasonable agreement. The results obtained are presented in the table below. The value of ΔHf°_{298}(CsCl, g) adopted is -57.4 ± 1 kcal/mol.

Gaydon (10) reported D_0(Cs-Cl) = 4.6 ± 0.2eV or 106.08 ± 4.61 kcal/mol. Using this D_0 value and ΔHf°_0 = 18.683 and 28.52 kcal/mol for Cs(g) and Cl(g), we evaluate ΔHf°_{298} = -59.4 ± 4.6 kcal/mol for CsCl(g), which is in fair agreement with the adopted value.

	Investigator	Reaction*	Method	Temperature, °K	No. of Points	ΔHr°_{298}, kcal/mol Second Law	Third Law	Drift eu	ΔHf°_{298}** kcal/mol
1.	Niwa (1938)	1	A	793-893	11	46.81±0.35	49.92	3.7±0.4	-55.92
2.	Cogin (1948)	1	A	690-891	28	47.80±0.31	47.88	0.1±0.4	-57.96
3.	Treadwell (1953)	1	B	784-905	10	47.08±0.26	49.17	2.5±0.3	-56.67
4.	Nesmeyanov (1960)	1	A	605-851	16	45.26±0.38	48.74	4.7±0.5	-57.10
5.	Wartenberg (1921)	2	C	1335-1577	9	49.36±0.50	46.27	-2.1±0.3	-57.57
6.	Ruff (1921)	2	C	1259-1568	7	51.61±1.08	46.17	-3.8±0.8	-57.67
7.	Fiock (1926)	2	C	1098-1293	9	47.57±0.08	46.52	-0.9±0.1	-57.32
8.	Kangro (1938)	2	B	1133-1263	3	48.73±2.09	47.00	-1.4±1.7	-56.84
9.	Schrier (1961)	2	C	1165-1387	10	47.46±0.08	46.36	-0.9±0.1	-57.48
16.	Murgulescu (1967)	1	A	1174-1353	10	47.97±0.15	46.54	-1.1±0.1	-57.30

*1 CsCl(c) = CsCl(g); 2 CsCl(ℓ) = CsCl(g); A = Knudsen effusion; B = transpiration; and C = manometric.

**Calculation based on the third law ΔHr°_{298} value.

Heat Capacity and Entropy

Clouser (11) studied the pure rotational spectra of CsCl(g) in the 0.96 - 3 mm range of the microwave region with the molecular-beam spectrometer, and derived the values of B_e, α_e, ω_e, $\omega_e x_e$ and r_e, which are adopted and corrected to the average isotopic species.

The Cs-Cl bond distance was measured as 3.06 ± 0.03 Å by the electron diffraction method by Maxwell (12), which is not used. Similar values of B_e and α_e were reported by Honig (13) and Rice (14), determined from microwave and infrared spectra, respectively. Barrow (15) gave ω_e = 240 cm^{-1}(CsCl^{35}) which is significantly different from the adopted value 214.22 cm^{-1} for CsCl^{35} and the value 209 ± 6 cm^{-1} reported by Rice (14). The moment of inertia is 3.924 x 10^{-38} g cm^2.

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Copper Monochloride (CuCl)

(Crystal) Mol. Wt. = 98.993

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	11.600	20.800	20.800	.000	- 33.000	- 28.898	21.183
300	11.656	20.872	20.800	.022	- 32.997	- 28.873	21.034
400	13.600	24.540	21.287	1.301	- 32.729	- 27.535	15.044
500	14.300	27.656	22.258	2.699	- 32.374	- 26.275	11.485
600	14.700	30.300	23.384	4.149	- 31.991	- 25.092	9.140
700	15.000	32.589	24.539	5.635	- 31.589	- 23.972	7.484
800	15.220	34.607	25.674	7.146	- 31.178	- 22.914	6.260
900	15.389	36.410	26.768	8.677	- 30.759	- 21.905	5.319
1000	15.540	38.039	27.815	10.224	- 30.338	- 20.944	4.577
1100	15.662	39.526	28.813	11.784	- 29.912	- 20.025	3.979
1200	15.777	40.894	29.764	13.356	- 29.486	- 19.146	3.487
1300	15.884	42.161	30.669	14.939	- 29.058	- 18.301	3.077
1400	15.983	43.342	31.533	16.532	- 31.815	- 17.388	2.714
1500	16.075	44.447	32.357	18.135	- 31.415	- 16.371	2.385

Mar. 31, 1966

COPPER MONOCHLORIDE (CuCl) (CRYSTAL) MOL. WT. = 98.993

$S^\circ_{298.15}$ = 20.8 ± 1.0 cal. deg.$^{-1}$ mole^{-1}

T_m = 703°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -33.0 ± 0.4 kcal. mole^{-1}

ΔH°_m = 2.445 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 54.77 ± 0.5 kcal. mole^{-1} of monomer

$\Delta H^\circ_{s\ 298.15}$ = 37.2 ± 0.2 kcal. mole^{-1} of trimer

Heat of Formation.

There have been three calorimetric determinations of the heat of formation. Thomsen, "Thermochemische Unterschungen", Barth, Leipzig (1882-1886) reported -32.875 kcal. mole^{-1}. Berthelot, Ann. Chim. Phys. 20, 504 (1880) reported -35.6 kcal. mole^{-1} and H. V. Wartenberg and H. Werth, Z. physik. Chem. A 151, 109 (1930) reported -32.1 ± 0.4 kcal. mole^{-1}. In addition, values of the heat of formation have been derived from several sets of equilibrium data. A. A. Noyes and M. Chow, J. Am. Chem. Soc. 40, 739 (1918) from a study of cell potentials derived a ΔH_r = 7.19 kcal. for the reaction $Cu(c) + HCl(\infty aq) \rightarrow CuCl(c) + 1/2\ H_2(g)$ which yields $\Delta H^\circ_{f\ 298}(CuCl)$ = -32.76 kcal. mole^{-1}. Several investigators have studied the reaction $2CuCl(c) + H_2(g) \rightarrow 2Cu(c) + 2HCl(g)$ and its reverse reaction. These include A. B. Bagdasarian, Trans. Am. Electrochem. Soc. 51, 449 (1927) who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 kcal. mole^{-1}; A. F. Kapustinsky, J. Am. Chem. Soc. 58, 460 (1936) who obtained similarly 20.1 and 21.8 kcal. mole^{-1}; S. A. Shchukarev and M. A. Oranskaya, Z. Obshchei. Khim. 24, 1926 (1954) obtained 25.4 and 21.5 kcal. mole^{-1} for the 2nd and 3rd law heat of reaction. These yield values for $\Delta H^\circ_{f\ 298}(CuCl)$ ranging from -32.1 to -34.8. M. Watanabe, Bull. Inst. Phys. Chem. Res. 9, 94 (1929) from cell studies reports $\Delta H^\circ_{f\ 298}$ (CuCl) = -34.6 kcal. mole^{-1}. A value of $\Delta H^\circ_{f\ 298}$ can also be obtained from $\Delta H^\circ_f\ (CuCl)_3(g)$, which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of CuCl(c) to trimer determined by D. W. Magee, Doctoral Thesis, Ohio State University (1955) [See trimer table], we obtain $\Delta H^\circ_{f\ 298}$ CuCl(c) = -33.01 ± 0.3 kcal. mole^{-1}. A weighted average of -33.0 ± 0.4 kcal. mole^{-1} was adopted.

Heat Capacity and Entropy.

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted $\Delta H^\circ_{f\ 298}$. A weighted average of 20.8 ± 1 cal/(mol-deg) was adopted for S°_{298} CuCl(c). The enthalpy and heat capacity above 298°K. have been reported by A. N. Krestovnikov and G. A. Karetnikov, Jour. Gen. Chem. (USSR) 6, 955 (1936). However these values were not adopted since they do not give reasonable heat capacities and other data by these workers is not in agreement with established values. Heat capacities equal to those of AgCl, as given by K. K. Kelley, U. S. Bureau of Mines Bulletin 584, Washington 1960, were adopted here above 298°K.

Melting Data.

The temperature and heat of melting were those selected by K. K. Kelley, U. S. Bur. Mines Bulletin 393 (1936), from phase studies. The heat of melting was reported by Krestovnikov and Karetnikov loc. cit. as 2.54 kcal. mole^{-1}.

Sublimation Data.

The heat of sublimation was calculated from the adopted heats of formation at 298° for the reaction $x\ CuCl(c) \rightarrow (CuCl)_x(g)$ where x = 1 or 3. See the respective gas tables for details.

Copper Monochloride (CuCl)

(Liquid) Mol. Wt. = 98.993

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	16.000	22.407	22.407	.000	-31.350	-27.727	20.325
300	16.000	22.506	22.407	.030	-31.339	-27.705	20.183
400	16.000	27.109	23.035	1.630	-30.751	-26.584	14.525
500	16.000	30.679	24.220	3.230	-30.193	-25.606	11.192
600	16.000	33.596	25.547	4.830	-29.661	-24.739	9.011
700	16.000	36.063	26.878	6.430	-29.145	-23.960	7.481
800	16.000	38.199	28.162	8.030	-28.645	-23.254	6.353
900	16.000	40.084	29.384	9.630	-28.157	-22.609	5.490
1000	16.000	41.770	30.540	11.230	-27.682	-22.019	4.812
1100	16.000	43.294	31.631	12.830	-27.216	-21.474	4.267
1200	16.000	44.687	32.662	14.430	-26.762	-20.974	3.820
1300	16.000	45.967	33.637	16.030	-26.317	-20.508	3.448
1400	16.000	47.153	34.561	17.630	-29.067	-19.977	3.118
1500	16.000	48.257	35.437	19.230	-28.670	-19.342	2.818
1600	16.000	49.290	36.271	20.830	-28.274	-18.734	2.559
1700	16.000	50.260	37.066	22.430	-27.879	-18.148	2.333
1800	16.000	51.174	37.824	24.030	-27.484	-17.586	2.135
1900	16.000	52.039	38.550	25.630	-27.090	-17.047	1.961
2000	16.000	52.860	39.245	27.230	-26.698	-16.529	1.806
2100	16.000	53.641	39.912	28.830	-26.305	-16.031	1.668
2200	16.000	54.385	40.553	30.430	-25.914	-15.550	1.545
2300	16.000	55.096	41.170	32.030	-25.524	-15.088	1.434
2400	16.000	55.777	41.765	33.630	-25.134	-14.643	1.333
2500	16.000	56.430	42.338	35.230	-24.746	-14.211	1.242
2600	16.000	57.058	42.892	36.830	-24.359	-13.799	1.160
2700	16.000	57.662	43.428	38.430	-23.973	-13.401	1.085
2800	16.000	58.243	43.947	40.030	-23.588	-13.013	1.016
2900	16.000	58.805	44.450	41.630	-95.863	-11.321	.853
3000	16.000	59.347	44.937	43.230	-95.326	-8.413	.613

Mar. 31, 1966

COPPER MONOCHLORIDE (CuCl) (LIQUID) MOL. WT. = 98.993

$S^\circ_{298.15}$ = 22.4 ± 1 cal. deg.$^{-1}$ mole^{-1}

T_m = 703°K.

T_b = [1485]°K. (to equilibrium mixture)

$\Delta H^\circ_{f\ 298.15}$ = -31.35 ± 0.4 kcal. mole^{-1}

ΔH°_m = 2.445 kcal. mole^{-1}

ΔH°_v = [5.18] kcal. mole^{-1} (to equilibrium mixture)

Heat of Formation.

Calculated from $\Delta H^\circ_{f\ 298}$ of the crystal plus ΔH°_m and the difference between $H_{T_m}-H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated to be constant at 8 cal. deg.$^{-1}$ gm. atom^{-1}. The entropy was calculated in a manner analogous to that of the heat of formation.

Boiling Data.

The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm. of monomer and 0.979 atm. of trimer.

Copper Monochloride (CuCl)

(Ideal Gas) Mol. Wt. = 98.993

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.264	21.798	21.798	INFINITE
100	7.146	48.171	63.821	-1.565	21.988	19.669	-42.987
200	7.972	53.387	57.425	-.808	21.903	17.374	-18.985
298	8.428	56.667	56.667	.000	21.770	15.178	-11.126
300	8.433	56.719	56.667	.016	21.767	15.137	-11.027
400	8.657	59.179	57.001	.871	21.611	12.950	-7.076
500	8.778	61.125	57.638	1.744	21.441	10.805	-4.723
600	8.854	62.733	58.357	2.625	21.255	8.695	-3.167
700	8.905	64.101	59.082	3.514	21.059	6.618	-2.066
800	8.942	65.293	59.786	4.406	20.851	4.567	-1.248
900	8.972	66.348	60.457	5.302	20.635	2.545	-.618
1000	8.996	67.295	61.094	6.200	20.409	.546	-.119
1100	9.017	68.153	61.698	7.101	20.175	-1.428	.284
1200	9.036	68.938	62.269	8.004	19.932	-3.381	.616
1300	9.053	69.662	62.810	8.908	19.681	-5.313	.893
1400	9.069	70.334	63.324	9.814	16.237	-7.125	1.112
1500	9.084	70.960	63.812	10.722	15.942	-8.784	1.280
1600	9.098	71.547	64.278	11.631	15.647	-10.424	1.424
1700	9.112	72.099	64.722	12.541	15.353	-12.043	1.548
1800	9.126	72.620	65.146	13.453	15.059	-13.645	1.657
1900	9.139	73.114	65.552	14.367	14.767	-15.233	1.752
2000	9.151	73.583	65.942	15.281	14.473	-16.804	1.836
2100	9.164	74.030	66.317	16.197	14.182	-18.361	1.911
2200	9.176	74.456	66.677	17.114	13.890	-19.902	1.977
2300	9.188	74.864	67.024	18.032	13.598	-21.432	2.036
2400	9.201	75.256	67.359	18.951	13.307	-22.951	2.090
2500	9.212	75.632	67.683	19.872	13.016	-24.454	2.138
2600	9.224	75.993	67.995	20.794	12.725	-25.946	2.181
2700	9.236	76.341	68.298	21.717	12.434	-27.427	2.220
2800	9.248	76.678	68.591	22.641	12.143	-28.899	2.256
2900	9.260	77.002	68.876	23.567	-60.806	-29.035	2.188
3000	9.271	77.316	69.152	24.493	-60.942	-27.936	2.035
3100	9.283	77.621	69.420	25.421	-61.091	-26.836	1.892
3200	9.294	77.916	69.681	26.350	-61.252	-25.728	1.757
3300	9.306	78.202	69.935	27.280	-61.427	-24.615	1.630
3400	9.317	78.480	70.182	28.211	-61.612	-23.496	1.510
3500	9.329	78.750	70.423	29.143	-61.811	-22.373	1.397
3600	9.340	79.013	70.658	30.077	-62.021	-21.242	1.290
3700	9.352	79.269	70.888	31.011	-62.244	-20.106	1.188
3800	9.363	79.519	71.111	31.947	-62.477	-18.967	1.091
3900	9.375	79.762	71.330	32.884	-62.722	-17.817	.998
4000	9.386	79.999	71.544	33.822	-62.977	-16.661	.910
4100	9.397	80.231	71.753	34.761	-63.240	-15.499	.826
4200	9.409	80.458	71.958	35.701	-63.514	-14.334	.746
4300	9.420	80.679	72.158	36.643	-63.795	-13.156	.669
4400	9.431	80.896	72.354	37.585	-64.084	-11.977	.595
4500	9.443	81.108	72.546	38.529	-64.379	-10.791	.524
4600	9.454	81.316	72.735	39.474	-64.681	-9.598	.456
4700	9.465	81.519	72.919	40.420	-64.990	-8.394	.390
4800	9.477	81.719	73.101	41.367	-65.302	-7.189	.327
4900	9.488	81.914	73.278	42.315	-65.620	-5.972	.266
5000	9.499	82.106	73.453	43.265	-65.941	-4.753	.208
5100	9.510	82.294	73.625	44.215	-66.265	-3.522	.151
5200	9.522	82.479	73.793	45.167	-66.593	-2.293	.096
5300	9.533	82.660	73.959	46.120	-66.924	-1.053	.043
5400	9.544	82.839	74.121	47.073	-67.257	.189	-.008
5500	9.556	83.014	74.282	48.028	-67.591	1.445	-.057
5600	9.567	83.186	74.439	48.984	-67.928	2.705	-.106
5700	9.578	83.356	74.594	49.942	-68.265	3.962	-.152
5800	9.589	83.522	74.746	50.900	-68.605	5.240	-.197
5900	9.601	83.686	74.897	51.860	-68.946	6.518	-.241
6000	9.612	83.848	75.044	52.820	-69.288	7.794	-.284

Mar. 31, 1966

COPPER MONOCHLORIDE (CuCl) (IDEAL GAS) MOL. WT. = 98.993

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 56.667 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0$ = 21.80 ± 0.4 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 21.77 ± 0.4 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	1

ω_e = 414.9 cm.$^{-1}$

B_e = 0.1761 cm.$^{-1}$

$\omega_e x_e$ = 1.577 cm.$^{-1}$

α_e = 0.0001 cm.$^{-1}$

σ = 1

r_e = 2.050 Å

Heat of Formation.

The heat of formation was obtained from the equilibrium data of L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950). They studied the reaction $x\ Cu(c) + x\ HCl(g) \rightarrow Cu_xCl_x(g) + x/2\ H_2(g)$ by measuring the amount of CuCl formed when various ratios of $HCl:H_2$ were passed over heated copper. Brewer and Lofgren analysed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressures were subjected to second and third law analysis and gave $\Delta H_{r\ 298}$ = 46.85 ± 3.2 and 43.83 ± 0.4 kcal. mole^{-1} respectively. The 3rd law value yields $\Delta H^\circ_{f\ 298}$ CuCl(g) = 21.77 ± 0.4 kcal. mole^{-1}, which was adopted.

Heat Capacity and Entropy.

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for $^{65}Cu^{35}Cl$ given by R. K. Asundi, P. R. Rao and J. K. Brody, Nature 192, 444 (1961). The rotational constants were in good agreement with those reported by A. Lagerqvist and V. Lazarova-Girsamov for $Cu^{63}Cl^{35}$, Naturwissenschaften 48, 68 (1961).

Chlorine Monofluoride (ClF)

(Ideal Gas) Mol. Wt. = 54.4514

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.129	- 12.117	- 12.117	INFINITE
100	6.961	44.228	58.569	- 1.434	- 12.120	- 12.249	26.768
200	7.201	49.102	52.750	- .730	- 12.126	- 12.376	13.524
298	7.668	52.064	52.064	.000	- 12.140	- 12.497	9.160
300	7.677	52.111	52.064	.014	- 12.140	- 12.499	9.105
400	8.067	54.376	52.370	.803	- 12.152	- 12.616	6.893
500	8.334	56.207	52.960	1.623	- 12.161	- 12.731	5.565
600	8.513	57.743	53.633	2.466	- 12.169	- 12.844	4.678
700	8.639	59.065	54.316	3.324	- 12.175	- 12.956	4.045
800	8.729	60.225	54.984	4.193	- 12.183	- 13.068	3.570
900	8.798	61.258	55.625	5.069	- 12.189	- 13.179	3.200
1000	8.851	62.187	56.235	5.952	- 12.196	- 13.288	2.904
1100	8.894	63.033	56.815	6.839	- 12.203	- 13.397	2.662
1200	8.930	63.808	57.366	7.730	- 12.211	- 13.505	2.459
1300	8.960	64.524	57.890	8.625	- 12.219	- 13.612	2.288
1400	8.986	65.189	58.388	9.522	- 12.227	- 13.719	2.142
1500	9.010	65.810	58.862	10.422	- 12.235	- 13.825	2.014
1600	9.031	66.392	59.315	11.324	- 12.245	- 13.931	1.903
1700	9.051	66.940	59.747	12.228	- 12.254	- 14.035	1.804
1800	9.069	67.458	60.161	13.134	- 12.265	- 14.141	1.717
1900	9.086	67.949	60.559	14.042	- 12.275	- 14.244	1.638
2000	9.102	68.416	60.940	14.951	- 12.287	- 14.349	1.568
2100	9.117	68.860	61.306	15.862	- 12.298	- 14.452	1.504
2200	9.132	69.284	61.660	16.775	- 12.311	- 14.553	1.446
2300	9.146	69.691	62.000	17.689	- 12.324	- 14.655	1.393
2400	9.160	70.080	62.329	18.604	- 12.338	- 14.755	1.344
2500	9.173	70.454	62.646	19.521	- 12.354	- 14.856	1.299
2600	9.186	70.814	62.953	20.439	- 12.370	- 14.955	1.257
2700	9.199	71.161	63.251	21.358	- 12.388	- 15.054	1.218
2800	9.211	71.496	63.540	22.278	- 12.406	- 15.153	1.183
2900	9.224	71.820	63.820	23.200	- 12.426	- 15.252	1.149
3000	9.236	72.133	64.091	24.123	- 12.447	- 15.351	1.118
3100	9.248	72.436	64.356	25.047	- 12.470	- 15.447	1.089
3200	9.260	72.729	64.613	25.973	- 12.494	- 15.540	1.061
3300	9.271	73.014	64.863	26.899	- 12.519	- 15.634	1.035
3400	9.283	73.291	65.107	27.827	- 12.546	- 15.728	1.011
3500	9.295	73.561	65.345	28.756	- 12.574	- 15.824	.988
3600	9.306	73.823	65.577	29.686	- 12.603	- 15.915	.966
3700	9.318	74.078	65.803	30.617	- 12.634	- 16.006	.945
3800	9.329	74.326	66.024	31.549	- 12.666	- 16.095	.926
3900	9.340	74.569	66.240	32.483	- 12.699	- 16.188	.907
4000	9.351	74.806	66.451	33.417	- 12.734	- 16.278	.889
4100	9.363	75.037	66.658	34.353	- 12.769	- 16.367	.872
4200	9.374	75.262	66.860	35.290	- 12.806	- 16.451	.856
4300	9.385	75.483	67.058	36.228	- 12.842	- 16.538	.841
4400	9.396	75.699	67.252	37.167	- 12.881	- 16.623	.826
4500	9.407	75.910	67.442	38.107	- 12.919	- 16.708	.811
4600	9.418	76.117	67.628	39.048	- 12.958	- 16.792	.798
4700	9.429	76.320	67.811	39.991	- 12.998	- 16.876	.785
4800	9.440	76.518	67.990	40.934	- 13.038	- 16.955	.772
4900	9.451	76.713	68.166	41.879	- 13.079	- 17.036	.760
5000	9.462	76.904	68.339	42.824	- 13.120	- 17.118	.748
5100	9.472	77.092	68.509	43.771	- 13.161	- 17.200	.737
5200	9.483	77.276	68.676	44.719	- 13.202	- 17.277	.726
5300	9.494	77.455	68.840	45.668	- 13.244	- 17.351	.715
5400	9.505	77.634	69.001	46.617	- 13.286	- 17.433	.706
5500	9.516	77.808	69.160	47.569	- 13.327	- 17.505	.696
5600	9.527	77.980	69.316	48.521	- 13.369	- 17.583	.686
5700	9.537	78.149	69.469	49.474	- 13.412	- 17.661	.677
5800	9.548	78.315	69.620	50.428	- 13.453	- 17.733	.668
5900	9.559	78.478	69.769	51.383	- 13.495	- 17.808	.660
6000	9.570	78.639	69.915	52.340	- 13.537	- 17.881	.651

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CHLORINE MONOFLUORIDE (ClF) (IDEAL GAS) MOL. WT. = 54.4514

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 52.064 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -12.12 ± 0.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -12.14 ± 0.6 kcal. mole^{-1}

Electronic Levels and Quantum Weight

State	ϵ_1, cm.$^{-1}$	g_1
$^1\Sigma^+$	0	1
$^3\pi^+_0$	19,592	1
$^3\pi_1$	19,592	2
$^3\pi_2$	19,592	2

ω_e = 784.39 cm.$^{-1}$

B_e = 0.51403 cm.$^{-1}$

$\omega_e x_e$ = 6.20 cm.$^{-1}$

α_e = 0.004329 cm.$^{-1}$

σ = 1

r_e = 1.62813 Å

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = -12.14 kcal. mole^{-1} was calculated from the dissociation energy (D°_0 = 58.99) obtained from the visible band spectra measured by H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 359 (1947) and A. L. Wahrhaftig, J. Chem. Phys. 10, 248 (1941). The convergence limit of 21,512 ± 20 cm.$^{-1}$ for the A state leads to the selected D°_0 assuming that the products are Cl($^2P_{1/2}$) and F($^2P_{3/2}$) or to D°_0 = 60.36 assuming Cl($^2P_{3/2}$) and F($^2P_{1/2}$). Calorimetric values bracket the two possibilities but more weight was given to the results of Wicke.

	Method	Reaction	Observation	$\Delta H^\circ_{f\ 298}$ kcal. mole^{-1}
1	Spectroscopic	$ClF = Cl(^2P_{1/2}) + F(^2P_{3/2})$	$D^\circ_0 = 58.99$	-12.14
2	Spectroscopic	$ClF = Cl(^2P_{3/2}) + F(^2P_{1/2})$	$D^\circ_0 = 60.36$	-13.51
3	Calorimetric	$1/2\ Cl_2 + 1/2\ F_2 = ClF$	$\Delta H^\circ_{293} = -11.6 \pm 0.1$	-11.6
4	Explosion method	$1/2\ Cl_2 + 1/2\ F_2 = ClF$	$\Delta H^\circ_0 = -11.7 \pm 0.5$	-11.7
5a	Calorimetric	$NaCl + ClF = NaF + Cl_2$	$\Delta H^\circ_{290} = -24.5 \pm 0.5$	-14.34*
5b	Calorimetric	$NaCl + 0.5\ F_2 = NaF + 0.5\ Cl_2$	$\Delta H^\circ_{290} = -39.5 \pm 0.5$	-15.0**

Sources

1,2 H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 359 (1947).
3 E. Wicke, Nachr. Acad. Wiss. Gottigen Math-Physik Klasse p. 89 (1946).
4 E. Wicke and H. Friz, Z Electrochem 57, 9 (1953).
5a, 5b H. Schmitz and H. J. Schumacher, Z. Naturforsch 2a, 362 (1947).

*Based on $\Delta H^\circ_{f\ 298}$(NaCl(c)) = -98.26 and $\Delta H^\circ_{f\ 298}$(NaF(c)) = -137.1 kcal. mole^{-1}

**Based on the difference between the two calorimetric reactions of reference 5a, 5b.

Heat Capacity and Entropy.

The rotational constants were obtained from the microwave spectrum by D. A. Gilbert, A. Roberts and P. A. Griswold, Phys. Rev. 76, 1723 (1949) and by D. A. Gilbert and A. Roberts Phys. Rev. 77, 742 (1950). The vibrational constants were obtained from the analysis vibration-rotation fine structure in the infrared by A. H. Nielsen and E. A. Jones, J. Chem. Phys. 19, 1117 (1951).

The rotational and vibrational constants were adjusted to Cl^{35} = 75.4% and Cl^{37} = 24.6%.

Dilithium Chloride Fluoride (Li_2ClF)

(Ideal Gas) Mol. Wt. = 68.34 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-3,208	-179,046	-179,046	INFINITE
100	8,538	51,450	75,430	-2,398	-179,170	-179,671	392,651
200	12,399	58,597	65,327	-1,346	-179,711	-179,963	196,645
298	15,019	64,037	64,037	,000	-180,200	-179,980	131,922
300	15,054	64,130	64,037	,028	-180,209	-179,979	131,108
400	16,635	68,692	64,649	1,617	-180,661	-179,832	98,251
500	17,591	72,519	65,851	3,334	-182,611	-179,422	78,421
600	18,195	75,782	67,241	5,125	-183,096	-178,736	65,101
700	18,595	78,620	68,668	6,966	-183,520	-177,977	55,564
800	18,869	81,121	70,071	8,840	-183,905	-177,159	48,395
900	19,066	83,356	71,426	10,737	-184,274	-176,293	42,808
1000	19,212	85,373	72,721	12,652	-184,629	-175,387	38,329
1100	19,320	87,209	73,956	14,579	-184,973	-174,446	34,658
1200	19,404	88,894	75,132	16,515	-185,311	-173,475	31,593
1300	19,475	90,450	76,251	18,459	-185,642	-172,475	28,994
1400	19,524	91,895	77,317	20,409	-185,969	-171,450	26,763
1500	19,570	93,244	78,335	22,364	-186,289	-170,402	24,826
1600	19,606	94,508	79,306	24,322	-186,604	-169,331	23,128
1700	19,632	95,697	80,236	26,284	-257,010	-165,586	21,287
1800	19,663	96,820	81,126	28,249	-256,957	-160,208	19,451
1900	19,680	97,884	81,981	30,217	-256,902	-154,832	17,809
2000	19,701	98,894	82,801	32,186	-256,850	-149,463	16,332
2100	19,714	99,856	83,591	34,157	-256,801	-144,098	14,996
2200	19,731	100,773	84,351	36,129	-256,755	-138,730	13,781
2300	19,740	101,650	85,084	38,102	-256,709	-133,367	12,672
2400	19,753	102,491	85,792	40,077	-256,669	-128,006	11,656
2500	19,761	103,297	86,476	42,053	-256,634	-122,644	10,721
2600	19,770	104,073	87,138	44,029	-256,603	-117,288	9,858
2700	19,776	104,819	87,779	46,007	-256,579	-111,930	9,060
2800	19,785	105,538	88,401	47,985	-256,560	-106,572	8,318
2900	19,790	106,233	89,004	49,964	-256,552	-101,216	7,627
3000	19,794	106,903	89,589	51,943	-256,550	-95,859	6,983
3100	19,800	107,553	90,158	53,923	-256,560	-90,500	6,380
3200	19,805	108,181	90,712	55,903	-256,579	-85,144	5,815
3300	19,809	108,791	91,250	57,884	-256,611	-79,788	5,284
3400	19,811	109,382	91,775	59,864	-256,653	-74,425	4,784
3500	19,815	109,956	92,286	61,846	-256,708	-69,067	4,313
3600	19,818	110,515	92,785	63,827	-256,778	-63,705	3,867
3700	19,821	111,058	93,271	65,809	-256,861	-58,344	3,446
3800	19,824	111,586	93,746	67,792	-256,959	-52,969	3,046
3900	19,827	112,101	94,211	69,774	-257,074	-47,602	2,667
4000	19,829	112,603	94,664	71,757	-257,206	-42,231	2,307
4100	19,831	113,093	95,108	73,740	-257,355	-36,852	1,964
4200	19,832	113,571	95,542	75,723	-257,523	-31,474	1,638
4300	19,834	114,038	95,966	77,706	-257,710	-26,090	1,326
4400	19,836	114,493	96,382	79,690	-257,916	-20,698	1,028
4500	19,838	114,939	96,790	81,674	-258,145	-15,306	,743
4600	19,840	115,375	97,189	83,658	-258,396	-9,907	,471
4700	19,842	115,802	97,580	85,642	-258,670	-4,506	,210
4800	19,843	116,220	97,964	87,626	-258,970	,904	-,041
4900	19,844	116,629	98,341	89,610	-259,297	6,323	-,282
5000	19,845	117,030	98,711	91,595	-259,650	11,751	-,514
5100	19,846	117,423	99,074	93,579	-260,035	17,182	-,736
5200	19,847	117,808	99,430	95,564	-260,451	22,624	-,951
5300	19,848	118,186	99,781	97,549	-260,900	28,068	-1,157
5400	19,849	118,557	100,125	99,533	-261,384	33,522	-1,357
5500	19,849	118,921	100,464	101,518	-261,907	38,993	-1,549
5600	19,850	119,279	100,796	103,503	-262,468	44,462	-1,735
5700	19,850	119,630	101,124	105,488	-263,070	49,954	-1,915
5800	19,851	119,976	101,446	107,473	-263,718	55,453	-2,089
5900	19,851	120,315	101,763	109,458	-264,409	60,958	-2,258
6000	19,852	120,649	102,075	111,444	-265,150	66,481	-2,421

December 31, 1960.

ClFLi$_2$

DILITHIUM CHLORIDE FLUORIDE (Li_2ClF) (Ideal Gas)

Mol. Wt. = 68.34

$\Delta H^\circ_{f\ 298.15}$ = [-180.2] kcal. mole^{-1}

$S^\circ_{298.15}$ = [64.037] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ from National Bureau of Standards Report No. 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine (Revised)", January, 1959. C_p from R. R. Koppang, C. M. Sherwood, and G. S. Bahn, Marquardt Corp., Van Nuys, Calif., "Some Provisional Tables of Species Thermodynamic Properties", October, 1959.

ClFLi$_2$

Magnesium Chloride Fluoride (MgClF)

(Ideal Gas) Mol. Wt. = 78.7634

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	- 2.947	- 135.599	- 135.599	INFINITE
100	9.089	51.367	72.543	- 2.118	- 135.622	- 136.237	297.745
200	10.794	58.216	63.814	- 1.120	- 135.896	- 136.863	149.557
298	11.929	62.756	62.756	.000	- 136.000	- 137.215	100.581
300	11.945	62.830	62.756	.022	- 136.003	- 137.222	99.966
400	12.619	66.367	63.234	1.253	- 136.186	- 137.602	75.182
500	13.015	69.229	64.156	2.537	- 136.375	- 137.933	60.290
600	13.259	71.625	65.207	3.851	- 136.580	- 138.226	50.349
700	13.418	73.682	66.274	5.186	- 136.803	- 138.482	43.236
800	13.526	75.481	67.315	6.533	- 137.056	- 138.707	37.893
900	13.603	77.079	68.313	7.890	- 137.344	- 138.896	33.728
1000	13.659	78.515	69.262	9.253	- 139.789	- 138.870	30.350
1100	13.701	79.819	70.164	10.621	- 140.117	- 138.764	27.570
1200	13.733	81.013	71.019	11.993	- 140.471	- 138.626	25.247
1300	13.759	82.113	71.830	13.368	- 140.852	- 138.456	23.277
1400	13.779	83.134	72.602	14.745	- 171.624	- 137.778	21.508
1500	13.796	84.085	73.336	16.123	- 171.651	- 135.359	19.722
1600	13.809	84.976	74.036	17.504	- 171.679	- 132.940	18.159
1700	13.821	85.813	74.704	18.885	- 171.708	- 130.515	16.779
1800	13.830	86.604	75.344	20.268	- 171.739	- 128.094	15.553
1900	13.838	87.352	75.956	21.651	- 171.770	- 125.667	14.455
2000	13.845	88.062	76.544	23.035	- 171.804	- 123.240	13.467
2100	13.851	88.737	77.108	24.420	- 171.838	- 120.811	12.573
2200	13.856	89.382	77.652	25.806	- 171.875	- 118.380	11.760
2300	13.861	89.998	78.175	27.192	- 171.913	- 115.946	11.017
2400	13.865	90.588	78.680	28.578	- 171.954	- 113.514	10.337
2500	13.869	91.154	79.168	29.965	- 171.997	- 111.079	9.710
2600	13.872	91.698	79.639	31.352	- 172.042	- 108.639	9.132
2700	13.874	92.221	80.096	32.739	- 172.091	- 106.198	8.596
2800	13.877	92.726	80.538	34.126	- 172.141	- 103.759	8.099
2900	13.879	93.213	80.967	35.514	- 172.195	- 101.314	7.635
3000	13.881	93.684	81.383	36.902	- 172.253	- 98.873	7.203
3100	13.883	94.139	81.787	38.291	- 172.314	- 96.425	6.798
3200	13.885	94.580	82.180	39.679	- 172.381	- 93.977	6.418
3300	13.886	95.007	82.562	41.067	- 172.451	- 91.525	6.061
3400	13.888	95.421	82.934	42.456	- 172.526	- 89.067	5.725
3500	13.889	95.824	83.297	43.845	- 172.608	- 86.615	5.408
3600	13.890	96.215	83.650	45.234	- 172.695	- 84.153	5.109
3700	13.891	96.596	83.995	46.623	- 172.789	- 81.693	4.825
3800	13.892	96.966	84.332	48.012	- 172.889	- 79.228	4.557
3900	13.893	97.327	84.660	49.401	- 172.997	- 76.766	4.302
4000	13.894	97.679	84.981	50.791	- 173.112	- 74.296	4.059
4100	13.895	98.022	85.295	52.180	- 173.237	- 71.825	3.829
4200	13.895	98.357	85.602	53.570	- 173.370	- 69.353	3.609
4300	13.896	98.684	85.903	54.959	- 173.512	- 66.874	3.399
4400	13.897	99.003	86.197	56.349	- 173.664	- 64.387	3.198
4500	13.897	99.316	86.485	57.739	- 173.826	- 61.906	3.007
4600	13.898	99.621	86.767	59.128	- 173.998	- 59.415	2.823
4700	13.898	99.920	87.044	60.518	- 174.182	- 56.922	2.647
4800	13.899	100.213	87.315	61.908	- 174.378	- 54.426	2.478
4900	13.899	100.499	87.581	63.298	- 174.585	- 51.921	2.316
5000	13.900	100.780	87.842	64.688	- 174.805	- 49.417	2.160
5100	13.900	101.055	88.099	66.078	- 175.037	- 46.910	2.010
5200	13.900	101.325	88.351	67.468	- 175.283	- 44.391	1.866
5300	13.901	101.590	88.598	68.858	- 175.543	- 41.871	1.727
5400	13.901	101.850	88.841	70.248	- 175.817	- 39.353	1.593
5500	13.902	102.105	89.080	71.638	- 176.105	- 36.820	1.463
5600	13.902	102.355	89.315	73.028	- 176.409	- 34.284	1.338
5700	13.902	102.601	89.545	74.418	- 176.728	- 31.740	1.217
5800	13.902	102.843	89.773	75.809	- 177.062	- 29.197	1.100
5900	13.903	103.081	89.996	77.199	- 177.415	- 26.646	.987
6000	13.903	103.314	90.216	78.589	- 177.783	- 24.087	.877

Dec. 31, 1960; Mar. 31, 1966

MAGNESIUM CHLORIDE FLUORIDE (MgClF) (IDEAL GAS) MOL. WT. = 78.7634

Point Group C_{2v}

$\Delta H_{f\ 0}^\circ$ = [-135.6 ± 5] kcal. mole^{-1}

$S^\circ_{298.15}$ = [62.76] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = [-136.0 ± 5] kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[719](1)
[205](1)
[453](1)

Bond Distance: Mg-Cl = [2.18] Å Mg-F = [1.77] Å

Bond Angle: Cl-Mg-F = [170]°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.5643 X 10^{-115}] g.^{3} cm.^{6}

Heat of Formation.

The heat of formation is based on an estimated $\Delta H_{r\ 298}^\circ$ = 0 for the reaction $MgCl_2(g) + MgF_2(g) \rightarrow 2MgClF(g)$, using $\Delta H_{f\ 298.15}^\circ$ = -95.85 and -176.2 kcal. mole^{-1} for $MgCl_2(g)$ and $MgF_2(g)$, respectively.

Heat Capacity and Entropy.

The bond angle is taken to be the value we have adopted for $MgCl_2(g)$. The Mg-Cl and Mg-F bond distances are assumed to be the same as those in $MgCl_2(g)$ and $MgF_2(g)$. The vibration frequencies are the averages of those for $MgCl_2(g)$ and $MgF_2(g)$. The three principal moments of inertia are: I_A = 0.0977 X 10^{-39}, I_B = 39.956 X 10^{-39} and I_C = 40.054 X 10^{-39} g. cm.^{2}

Perchloryl Fluoride (ClO_3F)

(Ideal Gas) Mol. Wt. = 102.457

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-3.178	-3.034	-3.034	INFINITE
100	8.462	54.278	78.032	-2.375	-3.996	1.097	-2.397
200	12.073	61.160	67.968	-1.362	-4.715	6.493	-7.095
298	15.517	66.653	66.653	.000	-5.120	12.090	-8.861
300	15.573	66.749	66.653	.029	-5.125	12.196	-8.884
400	18.152	71.602	67.297	1.722	-5.298	18.002	-9.835
500	20.000	75.863	68.593	3.635	-5.312	23.831	-10.416
600	21.319	79.633	70.125	5.704	-5.226	29.653	-10.801
700	22.271	82.994	71.728	7.886	-5.076	35.455	-11.069
800	22.967	86.016	73.328	10.150	-4.884	41.231	-11.263
900	23.487	88.753	74.893	12.474	-4.665	46.983	-11.408
1000	23.883	91.249	76.405	14.843	-4.426	52.710	-11.519
1100	24.189	93.540	77.860	17.248	-4.175	58.410	-11.604
1200	24.430	95.655	79.256	19.679	-3.914	64.090	-11.672
1300	24.624	97.619	80.594	22.132	-3.649	69.746	-11.725
1400	24.780	99.449	81.876	24.602	-3.382	75.380	-11.767
1500	24.909	101.164	83.106	27.087	-3.112	80.998	-11.801
1600	25.016	102.775	84.285	29.584	-2.843	86.596	-11.828
1700	25.105	104.294	85.418	32.090	-2.574	92.179	-11.850
1800	25.181	105.731	86.507	34.604	-2.311	97.744	-11.867
1900	25.246	107.094	87.555	37.125	-2.051	103.297	-11.881
2000	25.301	108.391	88.564	39.653	-1.795	108.833	-11.892
2100	25.349	109.626	89.538	42.185	-1.544	114.359	-11.901
2200	25.391	110.807	90.478	44.723	-1.300	119.871	-11.908
2300	25.428	111.936	91.387	47.264	-1.060	125.374	-11.913
2400	25.461	113.019	92.266	49.808	-.828	130.868	-11.917
2500	25.489	114.059	93.117	52.356	-.605	136.347	-11.919
2600	25.515	115.059	93.942	54.906	-.386	141.823	-11.921
2700	25.538	116.023	94.742	57.458	-.176	147.289	-11.922
2800	25.558	116.952	95.518	60.013	.027	152.747	-11.922
2900	25.577	117.849	96.273	62.570	.223	158.199	-11.922
3000	25.593	118.716	97.007	65.129	.411	163.641	-11.921
3100	25.608	119.556	97.721	67.689	.593	169.082	-11.920
3200	25.622	120.369	98.416	70.250	.767	174.513	-11.918
3300	25.635	121.158	99.093	72.813	.935	179.937	-11.916
3400	25.646	121.923	99.753	75.377	1.095	185.360	-11.914
3500	25.657	122.667	100.398	77.942	1.249	190.776	-11.912
3600	25.666	123.390	101.026	80.508	1.396	196.192	-11.910
3700	25.675	124.093	101.640	83.075	1.537	201.600	-11.907
3800	25.683	124.778	102.240	85.643	1.673	207.009	-11.905
3900	25.691	125.445	102.827	88.212	1.803	212.404	-11.902
4000	25.698	126.096	103.400	90.782	1.926	217.803	-11.900
4100	25.704	126.730	103.961	93.352	2.043	223.200	-11.897
4200	25.711	127.350	104.511	95.922	2.156	228.592	-11.894
4300	25.716	127.955	105.049	98.494	2.264	233.986	-11.892
4400	25.721	128.546	105.577	101.066	2.366	239.370	-11.889
4500	25.726	129.124	106.093	103.638	2.464	244.755	-11.886
4600	25.731	129.690	106.600	106.211	2.558	250.143	-11.884
4700	25.735	130.243	107.097	108.784	2.646	255.525	-11.881
4800	25.739	130.785	107.585	111.358	2.731	260.904	-11.879
4900	25.743	131.316	108.064	113.932	2.812	266.277	-11.876
5000	25.747	131.836	108.534	116.507	2.889	271.652	-11.873
5100	25.750	132.346	108.996	119.082	2.961	277.029	-11.871
5200	25.753	132.846	109.450	121.657	3.030	282.399	-11.868
5300	25.756	133.336	109.896	124.232	3.097	287.779	-11.866
5400	25.759	133.818	110.335	126.808	3.158	293.140	-11.863
5500	25.762	134.290	110.766	129.384	3.220	298.518	-11.861
5600	25.765	134.755	111.190	131.960	3.274	303.881	-11.859
5700	25.767	135.211	111.608	134.537	3.327	309.248	-11.857
5800	25.769	135.659	112.019	137.114	3.378	314.621	-11.855
5900	25.771	136.099	112.423	139.691	3.425	319.982	-11.852
6000	25.773	136.533	112.821	142.268	3.470	325.349	-11.850

March 31, 1961

PERCHLORYL FLUORIDE (ClO_3F) (IDEAL GAS) MOL. WT. = 102.457

ΔH°_{f0} = -3.03 ± 0.7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -5.12 ± 0.68 kcal. mole^{-1}

Point Group C_{3v}

S°_{298} = 66.65 ± 0.02 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω cm.$^{-1}$	ω cm.$^{-1}$
1061 (1)	1315 (2)
715 (1)	589 (2)
549 (1)	405 (2)

Bond Lengths and Angles F-Cl = [1.63] Å O-Cl = [1.46] Å ∢ F-Cl-O = [95° 10'] ∢ O-Cl-O = [119° 12']

= 3

Moments of Inertia $I_A = I_B = 1.595 \times 10^{-38}$ gm. cm.^{2} $I_C = [1.685 \times 10^{-38}]$ gm. cm.^{2}

Heat of Formation

C. A. Neugebauer and J. L. Margrave, J. Am. Chem. Soc. 79, 1338 (1957), measured the heat of reaction of perchloryl fluoride and hydrogen.

ClO_3F (g) + $4H_2$ (g) = HF (aq., 0.6M) + HCl (aq., 0.6M) + $3H_2O$ (l)

The necessary, additional thermal data for the calculation of the heat of formation was obtained by them from N. B. S., Circ. 500. V. H. Dibeler, R. M. Reese and D. E. Mann, J. Chem. Phys. 27, 176 (1957) obtain a value of -5.3 ± 4 kcal. mole^{-1} from the observed appearance potential of Cl^+.

Heat Capacities and Entropies

The assignment of D. R. Lide and D. E. Mann, J. Chem. Phys. 25, 1128 (1956), based upon the infra red spectra of the gas is supported by the Raman measurements of F. X. Powell and E. R. Lippincott, J. Chem. Phys. 32, 1883 (1960).

The value of the spectroscopic constant B was obtained by R. P. Madden and W. S. Benedict from a high resolution infra red spectrograph. The Cl-F bond distance was estimated assuming a single covalent bond with no ionic character as evidenced by the low dipole momenent obtained by A. A. Maryott and S. J. Kreidler, J. Chem. Phys. 27, 1221 (1957). Electron spin resonance results are explained by S. Brownstein, Can. J. Chem. 38, 1597 (1960), on the basis of a low dipole moment. The Cl-O distance was estimated to be that found in the Chlorate ion, L. Pauling, "The Nature of the Chemical Bond", 3rd ed. Cornell Univ. Press, Ithaca, 1960. The resulting values of the bond angles and I_C are consistent with the measured I_B and the assumed bond lengths.

A calorimetric entropy of 60.17 cal. deg.$^{-1}$ mole^{-1} at 226.48°K was obtained by J. K. Koehler and W. F. Giauque, J. Am. Chem. Soc. 80, 2659 (1958) for the ideal gas. If the lattice doesn't discriminate between F and O atoms then at 0°K a residual entropy of 2.75 cal. deg.$^{-1}$ mole^{-1} exists and the third law entropy would be 62.92 cal. deg.$^{-1}$ mole^{-1}. This value may be compared with 62.64 obtained statistically. The difference 0.3 cal. deg.$^{-1}$ mole^{-1} is within the range found for other molecules and explained on the basis of some discrimination in the lattice, see Koehler and Giauque, loc. cit. for references.

Phosphoryl Difluoride Chloride ($POClF_2$)

(Ideal Gas) Mol. Wt. = 120.432

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.393	- 226.287	- 226.287	INFINITE
100	9.119	58.627	84.368	- 2.574	- 226.961	- 224.269	490.116
200	13.155	66.184	73.486	- 1.460	- 227.565	- 221.331	241.847
298	16.453	72.081	72.081	.000	- 228.000	- 218.172	159.917
300	16.507	72.183	72.081	.030	- 228.007	- 218.111	158.886
400	18.960	77.287	72.760	1.811	- 228.300	- 214.764	117.336
500	20.684	81.715	74.119	3.798	- 228.482	- 211.358	92.380
600	21.889	85.599	75.715	5.930	- 228.595	- 207.922	75.732
700	22.743	89.041	77.378	8.164	- 228.673	- 204.470	63.835
800	23.360	92.120	79.031	10.471	- 249.157	- 206.320	56.361
900	23.817	94.899	80.643	12.831	- 248.961	- 200.976	48.801
1000	24.161	97.427	82.197	15.231	- 248.746	- 195.656	42.759
1100	24.427	99.743	83.688	17.661	- 248.517	- 190.359	37.819
1200	24.636	101.878	85.116	20.114	- 248.278	- 185.082	33.706
1300	24.802	103.857	86.483	22.586	- 248.032	- 179.825	30.230
1400	24.937	105.700	87.790	25.074	- 247.781	- 174.587	27.253
1500	25.047	107.424	89.042	27.573	- 247.527	- 169.367	24.676
1600	25.138	109.044	90.242	30.082	- 247.272	- 164.166	22.423
1700	25.215	110.570	91.393	32.600	- 247.016	- 158.977	20.437
1800	25.279	112.013	92.499	35.125	- 246.761	- 153.808	18.674
1900	25.335	113.381	93.563	37.656	- 246.507	- 148.649	17.098
2000	25.382	114.682	94.586	40.192	- 246.255	- 143.507	15.681
2100	25.423	115.922	95.573	42.732	- 246.005	- 138.376	14.400
2200	25.459	117.105	96.525	45.276	- 245.760	- 133.257	13.237
2300	25.490	118.237	97.445	47.823	- 245.516	- 128.148	12.176
2400	25.518	119.323	98.334	50.374	- 245.277	- 123.051	11.205
2500	25.542	120.365	99.194	52.927	- 245.042	- 117.962	10.312
2600	25.564	121.367	100.028	55.482	- 244.811	- 112.884	9.488
2700	25.583	122.332	100.836	58.039	- 244.585	- 107.814	8.726
2800	25.600	123.263	101.621	60.599	- 244.363	- 102.752	8.020
2900	25.616	124.162	102.383	63.159	- 244.146	- 97.696	7.362
3000	25.630	125.030	103.123	65.722	- 243.935	- 92.654	6.749
3100	25.643	125.871	103.844	68.285	- 243.727	- 87.613	6.176
3200	25.655	126.685	104.545	70.850	- 243.526	- 82.582	5.640
3300	25.665	127.475	105.228	73.416	- 243.329	- 77.555	5.136
3400	25.675	128.241	105.893	75.983	- 243.138	- 72.533	4.662
3500	25.684	128.986	106.542	78.551	- 242.951	- 67.518	4.216
3600	25.692	129.709	107.176	81.120	- 242.769	- 62.507	3.795
3700	25.700	130.413	107.795	83.690	- 242.592	- 57.503	3.396
3800	25.707	131.099	108.399	86.260	- 242.419	- 52.501	3.019
3900	25.713	131.767	108.989	88.831	- 242.253	- 47.507	2.662
4000	25.719	132.418	109.567	91.403	- 242.090	- 42.517	2.323
4100	25.724	133.053	110.132	93.975	- 241.932	- 37.530	2.000
4200	25.730	133.673	110.685	96.547	- 241.779	- 32.545	1.693
4300	25.734	134.278	111.227	99.121	- 241.628	- 27.565	1.401
4400	25.739	134.870	111.758	101.694	- 241.484	- 22.586	1.122
4500	25.743	135.448	112.278	104.268	- 241.343	- 17.616	.856
4600	25.747	136.014	112.788	106.843	- 241.203	- 12.647	.601
4700	25.751	136.568	113.288	109.418	- 241.070	- 7.677	.357
4800	25.754	137.110	113.778	111.993	- 240.939	- 2.711	.123
4900	25.757	137.641	114.260	114.569	- 240.811	2.252	- .100
5000	25.760	138.162	114.733	117.144	- 240.688	7.209	- .315
5100	25.763	138.672	115.197	119.721	- 240.567	12.164	- .521
5200	25.766	139.172	115.653	122.297	- 240.449	17.119	- .719
5300	25.768	139.663	116.102	124.874	- 240.334	22.074	- .910
5400	25.771	140.145	116.543	127.451	- 240.223	27.017	- 1.093
5500	25.773	140.618	116.976	130.028	- 240.113	31.972	- 1.270
5600	25.775	141.082	117.402	132.605	- 240.008	36.915	- 1.441
5700	25.777	141.538	117.822	135.183	- 239.905	41.859	- 1.605
5800	25.779	141.987	118.235	137.761	- 239.804	46.803	- 1.764
5900	25.781	142.427	118.641	140.339	- 239.706	51.738	- 1.916
6000	25.783	142.861	119.041	142.917	- 239.611	56.681	- 2.064

March 31, 1963

PHOSPHORYL DIFLUORIDE CHLORIDE ($POClF_2$) (IDEAL GAS) MOL. WT. = 120.432

Point Group C_s

$S^\circ_{298.15}$ = 72.081 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = [-226] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-228] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
274 (1)	424 (2)	948 (2)
410 (1)	618 (1)	1358 (1)
	895 (1)	

Bond Distance: P-Cl = 2.01 ± 0.04 Å P-F = 1.51 ± 0.03 Å P-O = 1.55 ± 0.03 Å

Bond Angle: F-P-F = F-P-Cl = 103° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 4.2790825 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ of $POClF_2$ was estimated to be -228 kcal. mole^{-1} from the $\Delta H^\circ_{f\ 298.15}$ of POF_3 by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-F) and D(P-Cl) values were taken from E. Neale and L. T. D. Williams, J. Chem. Soc., 2485 (1955) Part I and E. Neale, L. T. D. Williams and V. T. Moores, J. Chem. Soc., 422 (1956) Part II.

Essentially the same $\Delta H^\circ_{f\ 298.15}$ may be obtained by assuming a $\Delta H_r = 0$ for the following reaction:

$$POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$$

Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 60, 1836 (1938) and by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the F-P-F and F-P-Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of Brockway and Beach's data by Q. Williams et al., indicates that the angles in POF_2Cl, $POFCl_2$, $POCl_3$, and POF_3 should be 103° rather than the reported 106° ± 3°. The principal moments of inertia calculated from these parameters were $I_A = 3.24319 \times 10^{-38}$ g. cm.^{3}, $I_B = 1.87015 \times 10^{-38}$ g. cm.^{3}, and $I_C = 3.13496$ g. cm.$^3 \times 10^{-38}$.

The Raman spectra and vibrational frequencies for POF_2Cl were reported by M. L. Delwaulle and F. Francois, Compt. Rend. 222, 550 (1946). The frequencies were reassigned by M. L. Delwaulle and F. Francois in J. Chim. Phys. 46, 87 (1949).

Chlorine Trifluoride (ClF_3)

(Ideal Gas) Mol. Wt. = 92.4482

T, °K.	C°_p (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH°_f (kcal. mole^{-1})	ΔF°_f (kcal. mole^{-1})	Log K_P
0	.000	.000	INFINITE	- 3.262	- 36.970	- 36.970	INFINITE
100	8.872	54.430	78.926	- 2.450	- 37.551	- 34.630	75.680
200	12.582	61.712	68.598	- 1.377	- 37.889	- 31.552	34.477
298	15.260	67.279	67.279	.000	- 37.970	- 28.418	20.830
300	15.298	67.374	67.280	.028	- 37.970	- 28.360	20.659
400	16.875	72.012	67.901	1.644	- 37.924	- 25.160	13.746
500	17.798	75.885	69.122	3.382	- 37.824	- 21.980	9.607
600	18.366	79.184	70.531	5.192	- 37.696	- 18.823	6.856
700	18.734	82.045	71.976	7.048	- 37.555	- 15.688	4.898
800	18.984	84.564	73.395	8.935	- 37.410	- 12.576	3.435
900	19.162	86.811	74.763	10.843	- 37.262	- 9.480	2.302
1000	19.291	88.837	76.071	12.766	- 37.113	- 6.402	1.399
1100	19.389	90.680	77.316	14.700	- 36.965	- 3.338	.663
1200	19.464	92.370	78.501	16.643	- 36.818	- .286	.052
1300	19.523	93.931	79.629	18.592	- 36.674	2.752	- .463
1400	19.570	95.379	80.703	20.547	- 36.532	5.780	- .902
1500	19.608	96.731	81.727	22.506	- 36.392	8.798	- 1.282
1600	19.640	97.997	82.705	24.468	- 36.257	11.806	- 1.613
1700	19.666	99.189	83.640	26.434	- 36.123	14.807	- 1.903
1800	19.688	100.314	84.535	28.402	- 35.993	17.795	- 2.161
1900	19.707	101.379	85.394	30.371	- 35.866	20.782	- 2.390
2000	19.723	102.390	86.218	32.343	- 35.742	23.762	- 2.596
2100	19.737	103.353	87.012	34.316	- 35.622	26.730	- 2.782
2200	19.749	104.271	87.775	36.290	- 35.506	29.698	- 2.950
2300	19.759	105.149	88.512	38.265	- 35.393	32.661	- 3.103
2400	19.768	105.990	89.223	40.242	- 35.284	35.617	- 3.243
2500	19.776	106.797	89.910	42.219	- 35.180	38.569	- 3.372
2600	19.784	107.573	90.574	44.197	- 35.079	41.517	- 3.490
2700	19.790	108.320	91.218	46.176	- 34.982	44.462	- 3.599
2800	19.796	109.040	91.841	48.155	- 34.888	47.401	- 3.700
2900	19.801	109.734	92.447	50.135	- 34.800	50.342	- 3.794
3000	19.806	110.406	93.034	52.115	- 34.717	53.270	- 3.881
3100	19.810	111.055	93.605	54.096	- 34.637	56.204	- 3.962
3200	19.814	111.684	94.160	56.077	- 34.562	59.134	- 4.038
3300	19.817	112.294	94.700	58.059	- 34.492	62.060	- 4.110
3400	19.820	112.886	95.227	60.041	- 34.425	64.984	- 4.177
3500	19.823	113.460	95.739	62.023	- 34.364	67.911	- 4.240
3600	19.826	114.019	96.240	64.005	- 34.306	70.832	- 4.300
3700	19.829	114.562	96.727	65.988	- 34.253	73.752	- 4.356
3800	19.831	115.091	97.204	67.971	- 34.204	76.671	- 4.409
3900	19.833	115.606	97.669	69.954	- 34.161	79.585	- 4.460
4000	19.835	116.108	98.124	71.938	- 34.120	82.504	- 4.508
4100	19.837	116.598	98.568	73.921	- 34.085	85.416	- 4.553
4200	19.838	117.076	99.003	75.905	- 34.054	88.330	- 4.596
4300	19.840	117.543	99.429	77.889	- 34.024	91.246	- 4.637
4400	19.841	117.999	99.846	79.873	- 34.002	94.159	- 4.677
4500	19.843	118.445	100.254	81.857	- 33.981	97.068	- 4.714
4600	19.844	118.881	100.655	83.841	- 33.964	99.981	- 4.750
4700	19.845	119.308	101.047	85.826	- 33.952	102.893	- 4.784
4800	19.846	119.726	101.432	87.811	- 33.942	105.805	- 4.817
4900	19.847	120.135	101.809	89.795	- 33.937	108.719	- 4.849
5000	19.848	120.536	102.180	91.780	- 33.934	111.628	- 4.879
5100	19.849	120.929	102.544	93.765	- 33.935	114.536	- 4.908
5200	19.850	121.314	102.901	95.750	- 33.939	117.456	- 4.936
5300	19.851	121.692	103.252	97.735	- 33.947	120.368	- 4.963
5400	19.852	122.063	103.597	99.720	- 33.958	123.273	- 4.989
5500	19.853	122.428	103.936	101.705	- 33.972	126.186	- 5.014
5600	19.853	122.785	104.269	103.691	- 33.989	129.102	- 5.038
5700	19.854	123.137	104.597	105.676	- 34.011	132.011	- 5.061
5800	19.855	123.482	104.920	107.661	- 34.033	134.927	- 5.084
5900	19.855	123.822	105.237	109.647	- 34.060	137.831	- 5.105
6000	19.856	124.155	105.550	111.632	- 34.090	140.750	- 5.127

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

CHLORINE TRIFLUORIDE (ClF_3) (IDEAL GAS) MOL. WT. = 92.4482

Point Group C_{2v}

$S^\circ_{298.15}$ = 67.279 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -36.97 ± 0.7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -37.97 ± 0.7 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
752 (1)	703 (1)
528 (1)	434 (1)
326 (1)	364 (1)

Bond Distance: Cl-F_1 = Cl-F_3 = 1.698 Å Cl-F_2 = 1.598 Å

Bond Angle: F_1-Cl-F_2 = F_2-Cl-F_3 = 87° 29' F_3-Cl-F_1 = 185° 02' σ = 2

Product of Moments of Inertia: $I_AI_BI_C = 2.6923061 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = -37.97 kcal. mole^{-1} was calculated from $\Delta H^\circ_{r\ 298}$ = 25.83 kcal. mole^{-1} obtained by third law analysis of the equilibrium data of H. Schmitz and H. T. Schumacher, Z. Naturforsch 2a, 362 (1947) for the reaction $ClF_3(g) = ClF(g) + F_2(g)$. Similar values are obtained from the equilibrium data of K. Schäfer and E. Wicke, Z. Elektrochemie 52, 205-209 (1948). Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation (kcal. mole^{-1})	3rd Law Drift (e.u.)	ΔHf°_{298} (kcal. mole^{-1})
1a	K_p(523-623°K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta H^\circ_{r\ 298} = 25.83$	0.8 ± 0.3	-37.97
2a	K_p(733°K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta H^\circ_{r\ 298} = 25.77$	---	-37.91
2b	K_p(570-680°K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta H^\circ_{r\ 298} = 26.12$	6 ± 3	-38.26
1b	Calorimetric	$3NaCl + ClF_3 \rightarrow 3NaF + 2Cl_2$	$\Delta H^\circ_{r\ 291} = -76.5$		-40.02
1c	Calorimetric	$NaCl + 0.5\ F_2 = NaF + 0.5\ Cl_2$	$\Delta H^\circ_{r\ 291} = -39.5$		-42.0*
3	Calorimetric	$3NaCl + ClF_3 \rightarrow 3NaF + 2Cl_2$	$\Delta H^\circ_{r\ 298} = -86.8$		-29.7
4	Calorimetric	$0.5\ F_2 + NaCl \rightarrow NaF + 0.5\ Cl_2$	$\Delta H^\circ_{r\ 293} = -39.3$		-31.1**
5	Flow reaction	$0.5\ Cl_2(g) + 1.5\ F_2(g) = ClF_3(g)$	$\Delta H_{r\ 473} = -26.4$		-26.4

*From combination of 1b and 1c. **From combination of 3 and 4.

Sources

1 H. Schmitz and H. J. Schumacher Z. Naturforsch. 2a, 362 (1947).
2a (Hot wire) K. Schafer and E. Wicke, Z. Elektrochem. 52, 205 (1948).
2b (From the Graph) K. Schafer and E. Wicke, Z. Elektrochem. 52, 205 (1948).
3 H. v. Wartenberg Z. anorg. allgem. Chem. 258, 356 (1949).
4 H. v. Wartenberg and O. Fitzner, A. anorg. allgem. Chem. 151, 313 (1926).
5 C. F. Swinehart, private communication from the Harshaw Chemical Co., March, 1963.

Heat Capacity and Entropy.

The structural constants were obtained from the microwave study of D. F. Smith, J. Chem. Phys. 21, 609 (1953). The planar distorted "T" structure is similar to that derived from X-ray studies of the solid by R. D. Burbank and F. N. Bensey, J. Chem. Phys. 21, 602 (1953). Fundamental frequencies are taken from the infrared and Raman spectra of H. H. Claassen, B. Weinstock and J. G. Malm, J. Chem. Phys. 28, 285 (1958). These data confirm the "T" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claassen, et al., loc. cit., calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by J. W. Grisard, H. A. Bernhardt and G. D. Oliver, J. Am. Chem. Soc. 73, 5725 (1951) from measurements of heat capacity (14-285°K.) and vapor pressure (226-303°K.). The entropy at the normal boiling point becomes $S^\circ_{284.91}$ = 67.04 cal. deg.$^{-1}$ mole^{-1} when a non-ideality correction consistent with the dimer-monomer vapor equilibrium is applied. The corresponding statistical entropy, $S^\circ_{284.91}$ = 66.59 cal. deg.$^{-1}$ mole^{-1}, is consistent with the third law value within the probable error in the entropy of the liquid and the entropy of vaporization. The three principal moments of inertia are: $I_A = 6.1114 \times 10^{-39}$, $I_B = 1.81545 \times 10^{-38}$ and $I_C = 2.42659 \times 10^{-38}$ g. cm.^{2}

Chlorotrifluorosilane (ClSiF$_3$)

(Ideal Gas) Mol. Wt. = 120.547 **INTERIM TABLE**

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-3.971	-313.953	-313.953	INFINITE
100	11.114	57.526	88.368	-3.084	-314.521	-311.820	681.450
200	15.857	66.799	75.394	-1.719	-314.844	-308.974	337.615
298	18.971	73.751	73.751	.000	-315.000	-306.057	224.335
300	19.018	73.868	73.751	.035	-315.002	-306.002	222.912
400	21.095	79.646	74.525	2.048	-315.068	-302.989	165.538
500	22.431	84.507	76.048	4.230	-315.073	-299.969	131.110
600	23.305	88.680	77.814	6.519	-315.039	-296.950	108.159
700	23.894	92.319	79.632	8.881	-314.983	-293.940	91.768
800	24.305	95.538	81.423	11.292	-314.915	-290.939	79.477
900	24.601	98.419	83.154	13.738	-314.843	-287.945	69.919
1000	24.821	101.023	84.813	16.210	-314.771	-284.961	62.275
1100	24.987	103.397	86.396	18.701	-314.699	-281.984	56.022
1200	25.117	105.577	87.905	21.206	-314.627	-279.012	50.813
1300	25.219	107.591	89.342	23.723	-314.558	-276.046	46.405
1400	25.301	109.463	90.714	26.249	-314.491	-273.087	42.629
1500	25.368	111.211	92.022	28.783	-314.427	-270.132	39.356
1600	25.423	112.850	93.274	31.322	-314.365	-267.180	36.493
1700	25.469	114.393	94.471	33.867	-326.410	-264.124	33.954
1800	25.507	115.850	95.619	36.416	-326.314	-260.467	31.623
1900	25.540	117.230	96.720	38.968	-326.218	-256.810	29.538
2000	25.568	118.540	97.778	41.524	-326.123	-253.157	27.662
2100	25.593	119.788	98.797	44.082	-326.032	-249.513	25.966
2200	25.614	120.980	99.779	46.642	-325.943	-245.872	24.424
2300	25.632	122.119	100.725	49.205	-325.856	-242.232	23.016
2400	25.649	123.210	101.640	51.769	-325.773	-238.601	21.727
2500	25.663	124.257	102.523	54.334	-325.693	-234.969	20.540
2600	25.676	125.264	103.379	56.901	-325.616	-231.342	19.445
2700	25.687	126.233	104.207	59.469	-325.541	-227.716	18.431
2800	25.698	127.168	105.011	62.039	-325.469	-224.096	17.491
2900	25.707	128.069	105.791	64.609	-325.401	-220.476	16.615
3000	25.715	128.941	106.548	67.180	-325.336	-216.863	15.798
3100	25.723	129.784	107.284	69.752	-325.274	-213.246	15.033
3200	25.729	130.601	108.000	72.325	-325.216	-209.631	14.316
3300	25.736	131.393	108.697	74.898	-325.161	-206.020	13.643
3400	25.741	132.161	109.376	77.472	-325.109	-202.409	13.010
3500	25.747	132.908	110.037	80.046	-325.061	-198.801	12.413
3600	25.751	133.633	110.683	82.621	-419.991	-194.721	11.821
3700	25.756	134.339	111.313	85.196	-419.888	-188.466	11.132
3800	25.760	135.026	111.928	87.772	-419.789	-182.211	10.479
3900	25.764	135.695	112.529	90.348	-419.695	-175.967	9.860
4000	25.767	136.347	113.116	92.925	-419.603	-169.715	9.272
4100	25.770	136.983	113.690	95.502	-419.515	-163.471	8.713
4200	25.773	137.604	114.252	98.079	-419.431	-157.222	8.181
4300	25.776	138.211	114.802	100.656	-419.349	-150.983	7.673
4400	25.779	138.803	115.341	103.234	-419.272	-144.743	7.189
4500	25.781	139.383	115.869	105.812	-419.199	-138.509	6.727
4600	25.783	139.949	116.386	108.390	-419.129	-132.268	6.284
4700	25.786	140.504	116.894	110.969	-419.062	-126.033	5.860
4800	25.788	141.047	117.391	113.547	-418.998	-119.794	5.454
4900	25.789	141.579	117.879	116.126	-418.939	-113.564	5.065
5000	25.791	142.100	118.359	118.705	-418.882	-107.331	4.691
5100	25.793	142.610	118.829	121.284	-418.830	-101.107	4.333
5200	25.795	143.111	119.291	123.864	-418.781	-94.872	3.987
5300	25.796	143.603	119.745	126.444	-418.734	-88.641	3.655
5400	25.797	144.085	120.192	129.023	-418.692	-82.420	3.336
5500	25.799	144.558	120.630	131.603	-418.653	-76.188	3.027
5600	25.800	145.023	121.062	134.183	-418.619	-69.964	2.730
5700	25.801	145.480	121.486	136.763	-418.589	-63.734	2.444
5800	25.802	145.929	121.904	139.343	-418.559	-57.512	2.167
5900	25.803	146.370	122.315	141.923	-418.535	-51.287	1.900
6000	25.804	146.803	122.719	144.504	-418.516	-45.068	1.642

December 31, 1960.

Chlorotrifluorosilane (ClSiF$_3$) (Ideal Gas)

Mol. Wt. = 120.547

ΔH_f° 298.15 = [-315 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = [73.8 ± 4] cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$
[870] (1)
[550] (1)
[275] (1)
[900] (2)
[400] (2)
[200] (2)

Moments of Inertia: I_A = [19.9 X 10^{-39}] g. cm.^{2} σ = 3

I_B = [33.9 X 10^{-39} g. cm.^{2}] I_C = [33.9 X 10^{-39}] g. cm.^{2}

Heat of Formation. ΔH_f° 298.15 was estimated in Henderson and Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. The molecular constants were estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Chlorine Pentafluoride (ClF_5)

(Ideal Gas) GFW = 130.445

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.285	-54.913	-54.913	INFINITE
100	10.087	56.580	91.062	-3.448	-56.162	-49.388	107.938
200	17.926	65.999	76.216	-2.043	-56.870	-42.282	46.204
298	23.223	74.241	74.241	.000	-57.000	-35.080	25.714
300	23.296	74.385	74.242	.043	-56.999	-34.944	25.457
400	26.295	81.539	75.197	2.537	-56.845	-27.609	15.085
500	28.013	87.608	77.088	5.260	-56.567	-20.332	8.887
600	29.058	92.815	79.286	8.117	-56.224	-13.116	4.777
700	29.732	97.348	81.550	11.059	-55.848	-5.960	1.861
800	30.188	101.350	83.779	14.057	-55.459	1.138	-.311
900	30.510	104.926	85.934	17.092	-55.058	8.189	-1.989
1000	30.746	108.153	87.997	20.156	-54.654	15.194	-3.321
1100	30.922	111.092	89.965	23.240	-54.249	22.159	-4.403
1200	31.058	113.789	91.840	26.339	-53.842	29.088	-5.298
1300	31.165	116.279	93.625	29.450	-53.439	35.984	-6.049
1400	31.250	118.592	95.327	32.571	-53.038	42.847	-6.689
1500	31.319	120.750	96.950	35.700	-52.640	49.684	-7.239
1600	31.376	122.773	98.502	38.835	-52.246	56.491	-7.716
1700	31.423	124.677	99.986	41.975	-51.856	63.277	-8.135
1800	31.463	126.474	101.408	45.119	-51.472	70.034	-8.503
1900	31.496	128.176	102.773	48.267	-51.090	76.777	-8.831
2000	31.525	129.792	104.084	51.418	-50.714	83.500	-9.124
2100	31.550	131.331	105.345	54.572	-50.343	90.197	-9.387
2200	31.571	132.799	106.560	57.728	-49.978	96.881	-9.624
2300	31.590	134.203	107.731	60.886	-49.617	103.550	-9.840
2400	31.607	135.548	108.862	64.046	-49.263	110.200	-10.035
2500	31.622	136.839	109.956	67.207	-48.916	116.835	-10.214
2600	31.635	138.079	111.014	70.370	-48.573	123.461	-10.378
2700	31.646	139.273	112.038	73.534	-48.235	130.074	-10.529
2800	31.656	140.424	113.032	76.699	-47.903	136.670	-10.668
2900	31.666	141.535	113.996	79.865	-47.579	143.260	-10.796
3000	31.674	142.609	114.932	83.032	-47.262	149.826	-10.915
3100	31.682	143.648	115.841	86.200	-46.949	156.391	-11.026
3200	31.689	144.654	116.726	89.369	-46.644	162.947	-11.129
3300	31.695	145.629	117.587	92.538	-46.345	169.492	-11.225
3400	31.701	146.575	118.426	95.708	-46.051	176.030	-11.315
3500	31.706	147.494	119.243	98.878	-45.766	182.562	-11.400
3600	31.711	148.387	120.041	102.049	-45.484	189.085	-11.479
3700	31.715	149.256	120.818	105.220	-45.211	195.594	-11.553
3800	31.719	150.102	121.578	108.392	-44.943	202.101	-11.623
3900	31.723	150.926	122.320	111.564	-44.684	208.592	-11.689
4000	31.727	151.729	123.045	114.737	-44.428	215.088	-11.752
4100	31.730	152.513	123.754	117.909	-44.181	221.567	-11.811
4200	31.733	153.278	124.448	121.083	-43.939	228.045	-11.866
4300	31.736	154.024	125.127	124.256	-43.700	234.525	-11.920
4400	31.739	154.754	125.793	127.430	-43.472	240.990	-11.970
4500	31.741	155.467	126.444	130.604	-43.247	247.449	-12.018
4600	31.743	156.165	127.083	133.778	-43.027	253.906	-12.063
4700	31.745	156.848	127.709	136.952	-42.815	260.359	-12.107
4800	31.747	157.516	128.323	140.127	-42.606	266.812	-12.148
4900	31.749	158.171	128.925	143.302	-42.404	273.256	-12.188
5000	31.751	158.812	129.517	146.477	-42.208	279.695	-12.225
5100	31.753	159.441	130.097	149.652	-42.016	286.123	-12.261
5200	31.754	160.057	130.667	152.827	-41.830	292.569	-12.296
5300	31.756	160.662	131.228	156.003	-41.649	298.998	-12.329
5400	31.757	161.256	131.778	159.179	-41.475	305.410	-12.361
5500	31.759	161.839	132.320	162.354	-41.304	311.838	-12.391
5600	31.760	162.411	132.852	165.530	-41.140	318.260	-12.421
5700	31.761	162.973	133.375	168.706	-40.981	324.677	-12.449
5800	31.762	163.525	133.890	171.883	-40.824	331.095	-12.476
5900	31.763	164.068	134.397	175.059	-40.676	337.497	-12.502
6000	31.764	164.602	134.896	178.235	-40.532	343.906	-12.527

June 30, 1966

CHLORINE PENTAFLUORIDE (ClF_5) (IDEAL GAS) GFW = 130.445

Point Group C_{4v}

$S^\circ_{298.15}$ = 74.241 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [-54.9 ± 15] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-57 ± 15] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
712 (1)	488 (1)	732 (2)
541 (1)	346 (1)	[440](2)
486 (1)	375 (1)	302 (2)

Bond Distance: $(Cl\text{-}F)_{basal}$ = 1.72 Å $(Cl\text{-}F)_{axial}$ = 1.62 Å

Bond Angle: F-I-F = 90°

σ = 4

Product of Moments of Inertia: $I_AI_BI_C = 2.47289 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation.

The heat of formation was estimated by assuming that the ratio [A.B.E.(ClF) - A.B.E.(ClF_3)]/[A.B.E.(ClF_3) - A.B.E.(ClF_5)] was equal to [A.B.E.(BrF) - A.B.E.(BrF_3)]/[A.B.E.(BrF_3) - A.B.E.(BrF_5)], where A.B.E. represents average bond energy. All values were taken from these tables. A.B.E.(ClF_5) was thus calculated to be 36 kcal/mol which leads to ΔHf° = -57 ± 15 kcal/mol.

Heat Capacity and Entropy.

G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965), have reported the infrared spectra of the gas and the Raman spectra of the liquid. Their assignments have been adopted here, including one frequency ν_8 obtained from a valence force-field treatment. The values are consistent with those for IF_5(g) and BrF_5(g). D. F. Smith, Science 141, 1039 (1963), had previously reported three infrared bands. The structure of the molecule has not been determined but the spectra can only be interpreted assuming C_{4v} symmetry; this is in accord with IF_5 and BrF_5(g). Begun et al. assumed a square pyramidal structure with the chlorine in the base of the pyramid. There is some evidence that the chlorine may not lie in the basal plane but this would not appreciably affect the calculations. The structure adopted was that given by Begun et al. The individual moments of inertia are $I_A = I_B = 25.7380 \times 10^{-39}\ g\ cm^2$ and $I_C = 37.3298 \times 10^{-39}\ g\ cm^2$.

Iron Monochloride (FeCl)

(Ideal Gas) Mol. Wt. = 91.300

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.480	59.692	59.692	INFINITE
100	8.232	52.018	69.431	- 1.741	59.977	57.181	- 124.964
200	8.821	57.954	62.363	- .882	60.054	54.340	- 59.377
298	9.136	61.537	61.537	.000	60.000	51.543	- 37.781
300	9.141	61.593	61.537	.017	59.998	51.491	- 37.509
400	9.366	64.257	61.898	.943	59.884	48.671	- 26.591
500	9.478	66.361	62.588	1.886	59.725	45.886	- 20.056
600	9.516	68.093	63.365	2.836	59.511	43.137	- 15.712
700	9.520	69.560	64.148	3.788	59.235	40.429	- 12.622
800	9.515	70.831	64.906	4.740	58.876	37.765	- 10.316
900	9.512	71.952	65.628	5.691	58.406	35.154	- 8.536
1000	9.514	72.954	66.311	6.643	57.753	32.602	- 7.125
1100	9.522	73.861	66.957	7.595	56.882	30.134	- 5.987
1200	9.532	74.690	67.567	8.547	56.221	27.725	- 5.049
1300	9.545	75.453	68.145	9.501	55.901	25.365	- 4.264
1400	9.559	76.161	68.693	10.456	55.565	23.029	- 3.595
1500	9.572	76.821	69.213	11.413	55.216	20.716	- 3.018
1600	9.584	77.439	69.708	12.371	54.851	18.428	- 2.517
1700	9.595	78.021	70.180	13.330	54.180	16.168	- 2.078
1800	9.605	78.569	70.631	14.290	53.694	13.948	- 1.693
1900	9.612	79.089	71.062	15.251	49.522	11.938	- 1.373
2000	9.619	79.582	71.476	16.212	48.970	9.973	- 1.090
2100	9.623	80.052	71.873	17.174	48.414	8.036	- .836
2200	9.627	80.499	72.255	18.137	47.854	6.129	- .609
2300	9.630	80.927	72.623	19.100	47.289	4.243	- .403
2400	9.631	81.337	72.978	20.063	46.720	2.383	- .217
2500	9.632	81.730	73.320	21.026	46.145	.550	- .048
2600	9.633	82.108	73.651	21.989	45.566	- 1.264	.106
2700	9.633	82.472	73.971	22.952	44.981	- 3.056	.247
2800	9.632	82.822	74.281	23.916	44.391	- 4.822	.376
2900	9.632	83.160	74.581	24.879	43.795	- 6.570	.495
3000	9.631	83.487	74.873	25.842	43.194	- 8.298	.604
3100	9.631	83.802	75.156	26.805	42.588	- 10.000	.705
3200	9.630	84.108	75.431	27.768	- 41.449	- 10.244	.700
3300	9.629	84.405	75.698	28.731	- 41.603	- 9.270	.614
3400	9.629	84.692	75.958	29.694	- 41.767	- 8.286	.533
3500	9.628	84.971	76.212	30.657	- 41.940	- 7.300	.456
3600	9.628	85.242	76.459	31.620	- 42.122	- 6.304	.383
3700	9.628	85.506	76.700	32.582	- 42.314	- 5.308	.314
3800	9.628	85.763	76.935	33.545	- 42.515	- 4.310	.248
3900	9.629	86.013	77.165	34.508	- 42.725	- 3.296	.185
4000	9.629	86.257	77.389	35.471	- 42.947	- 2.287	.125
4100	9.630	86.495	77.608	36.434	- 43.176	- 1.266	.067
4200	9.631	86.727	77.823	37.397	- 43.417	- .243	.013
4300	9.632	86.953	78.032	38.360	- 43.667	.792	- .040
4400	9.634	87.175	78.238	39.323	- 43.928	1.826	- .091
4500	9.636	87.391	78.439	40.287	- 44.199	2.869	- .139
4600	9.638	87.603	78.636	41.251	- 44.478	3.920	- .186
4700	9.640	87.810	78.829	42.214	- 44.770	4.977	- .231
4800	9.642	88.013	79.018	43.179	- 45.071	6.039	- .275
4900	9.645	88.212	79.203	44.143	- 45.383	7.106	- .317
5000	9.648	88.407	79.386	45.108	- 45.705	8.178	- .357
5100	9.651	88.598	79.564	46.072	- 46.037	9.260	- .397
5200	9.654	88.786	79.740	47.038	- 46.379	10.345	- .435
5300	9.658	88.969	79.912	48.003	- 46.732	11.443	- .472
5400	9.661	89.150	80.082	48.969	- 47.096	12.542	- .508
5500	9.665	89.327	80.248	49.936	- 47.469	13.653	- .542
5600	9.669	89.501	80.412	50.902	- 47.853	14.766	- .576
5700	9.673	89.673	80.573	51.869	- 48.247	15.881	- .609
5800	9.678	89.841	80.731	52.837	- 48.651	17.017	- .641
5900	9.682	90.006	80.887	53.805	- 49.065	18.151	- .672
6000	9.687	90.169	81.040	54.773	- 49.488	19.296	- .703

June 30, 1965

IRON MONOCHLORIDE (FeCl) (IDEAL GAS) MOL. WT. = 91.300

Ground State Configuration $^6\Sigma$

$S^\circ_{298.15}$ = [61.537] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 60 ± 20 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 60 ± 20 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	6
[200]	[8]
[1000]	[8]
[4000]	[8]

ω_e = 404.92 cm.$^{-1}$

B_e = [0.17795] cm.$^{-1}$

$\omega_e x_e$ = 1.19 cm.$^{-1}$

α_e = [0.00075] cm.$^{-1}$

σ = 1

r_e = [2.09]

Heat of Formation.

The dissociation energy (D_0°) of FeCl(g) was reported as 3 ± 2 e.v. (69 ± 46 kcal. mole^{-1}) by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The corresponding $\Delta H^\circ_{f\ 298.15}$ (FeCl, g) was evaluated to be 56 ± 46 kcal. mole^{-1}. By comparing D(Fe-O) = 101 kcal. mole^{-1} in FeO(g) with the coördinate bond energies obtained in organic complexes and iron carbonyl halides of E(Fe-O) = 59.4 and E(Fe-Cl) = 37.3 kcal. mole^{-1}, reported by M. M. Jones, B. J. Yow and W. R. May, Inorg. Chem. 1, 166 (1962), the D(Fe-Cl) in FeCl(g) was estimated as 101 x (37.3/59.4) = 63.3 kcal. mole^{-1}, yielding $\Delta H^\circ_{f\ 298.15}$ (FeCl, g) = 64 kcal. mole^{-1}. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for FeCl(g) is 60 ± 20 kcal. mole^{-1}.

Heat Capacity and Entropy.

The ground state configuration, ω_e and $\omega_e x_e$ (corrected to the average isotopic species) were obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950. The Fe-Cl bond distance was assumed to be the same as that in $FeCl_2$(g). Hence the values of B_e and α_e were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe^+(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961). The total 30 for the quantum weight was obtained from the ground multiplet of Fe^+ and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels. The principal moment of inertia is 1.5728 x 10^{-38} g. cm.^{2}

Hydrogen Chloride (HCl)

(Ideal Gas) Mol. Wt. = 36.465

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.065	-22.019	-22.019	INFINITE
100	6.959	37.041	50.835	-1.379	-22.063	-22.289	48.709
200	6.961	41.865	45.282	-.683	-22.029	-22.535	24.624
298	6.964	44.645	44.645	.000	-22.063	-22.778	16.696
300	6.964	44.688	44.646	.013	-22.064	-22.782	16.596
400	6.973	46.693	44.919	.710	-22.129	-23.012	12.573
500	7.004	48.252	45.435	1.408	-22.207	-23.224	10.151
600	7.069	49.534	46.014	2.112	-22.288	-23.420	8.530
700	7.167	50.630	46.597	2.823	-22.366	-23.602	7.368
800	7.289	51.595	47.163	3.546	-22.440	-23.774	6.494
900	7.423	52.461	47.704	4.281	-22.505	-23.936	5.812
1000	7.559	53.250	48.220	5.030	-22.562	-24.093	5.265
1100	7.693	53.977	48.711	5.793	-22.611	-24.243	4.816
1200	7.819	54.652	49.178	6.569	-22.652	-24.390	4.442
1300	7.936	55.283	49.624	7.356	-22.688	-24.534	4.124
1400	8.043	55.875	50.049	8.155	-22.718	-24.675	3.852
1500	8.141	56.433	50.456	8.965	-22.744	-24.813	3.615
1600	8.229	56.961	50.847	9.783	-22.769	-24.950	3.408
1700	8.310	57.463	51.221	10.610	-22.790	-25.086	3.225
1800	8.382	57.940	51.581	11.445	-22.809	-25.221	3.062
1900	8.449	58.395	51.928	12.287	-22.826	-25.353	2.916
2000	8.509	58.830	52.262	13.135	-22.843	-25.486	2.785
2100	8.564	59.246	52.585	13.988	-22.859	-25.618	2.666
2200	8.614	59.646	52.897	14.847	-22.875	-25.750	2.558
2300	8.660	60.030	53.199	15.711	-22.891	-25.880	2.459
2400	8.703	60.399	53.491	16.579	-22.906	-26.007	2.368
2500	8.742	60.755	53.775	17.451	-22.924	-26.137	2.285
2600	8.778	61.099	54.050	18.327	-22.940	-26.266	2.208
2700	8.812	61.431	54.317	19.207	-22.958	-26.394	2.136
2800	8.844	61.752	54.577	20.090	-22.977	-26.521	2.070
2900	8.874	62.063	54.830	20.976	-22.997	-26.647	2.008
3000	8.902	62.364	55.076	21.864	-23.018	-26.773	1.950
3100	8.928	62.656	55.316	22.756	-23.040	-26.897	1.896
3200	8.953	62.940	55.549	23.650	-23.064	-27.021	1.845
3300	8.976	63.216	55.778	24.546	-23.090	-27.144	1.798
3400	8.999	63.484	56.000	25.445	-23.116	-27.266	1.753
3500	9.020	63.745	56.218	26.346	-23.145	-27.387	1.710
3600	9.041	64.000	56.431	27.249	-23.175	-27.509	1.670
3700	9.061	64.248	56.638	28.154	-23.207	-27.629	1.632
3800	9.079	64.490	56.842	29.061	-23.240	-27.749	1.596
3900	9.098	64.726	57.041	29.970	-23.276	-27.866	1.562
4000	9.115	64.956	57.236	30.881	-23.313	-27.981	1.529
4100	9.132	65.182	57.427	31.793	-23.351	-28.101	1.498
4200	9.148	65.402	57.614	32.707	-23.392	-28.216	1.468
4300	9.164	65.617	57.798	33.623	-23.433	-28.329	1.440
4400	9.180	65.828	57.978	34.540	-23.476	-28.441	1.413
4500	9.195	66.035	58.155	35.459	-23.521	-28.559	1.387
4600	9.210	66.237	58.328	36.379	-23.566	-28.667	1.362
4700	9.224	66.435	58.499	37.301	-23.612	-28.775	1.338
4800	9.238	66.629	58.666	38.224	-23.660	-28.885	1.315
4900	9.252	66.820	58.831	39.148	-23.708	-28.993	1.293
5000	9.265	67.007	58.992	40.074	-23.757	-29.102	1.272
5100	9.278	67.191	59.151	41.001	-23.807	-29.208	1.252
5200	9.291	67.371	59.308	41.930	-23.858	-29.313	1.232
5300	9.304	67.548	59.461	42.859	-23.910	-29.416	1.213
5400	9.316	67.722	59.613	43.790	-23.962	-29.521	1.195
5500	9.329	67.893	59.762	44.723	-24.015	-29.622	1.177
5600	9.341	68.061	59.908	45.656	-24.068	-29.724	1.160
5700	9.353	68.227	60.053	46.591	-24.123	-29.828	1.144
5800	9.365	68.390	60.195	47.527	-24.177	-29.928	1.128
5900	9.376	68.550	60.335	48.464	-24.233	-30.027	1.112
6000	9.388	68.707	60.474	49.402	-24.289	-30.121	1.097

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1964

HYDROGEN CHLORIDE (HCl) (IDEAL GAS) MOL. WT. = 36.465

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 44.645 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -22.019 ± 0.05 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -22.063 ± 0.05 kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 2989.59 cm.$^{-1}$

B_e = 10.5884 cm.$^{-1}$

$\omega_e x_e$ = 52.06 cm.$^{-1}$

α_e = 0.3037 cm.$^{-1}$

σ = 1

r_e = 1.2746 Å

Heat of Formation.

The selected value, Rossini's flow calorimetric measurement (1) of the direct combination of the elements, is essentially the same as that in the revised version (2) of NBS Circular 500. JANAF analyses of the more recent measurements are summarized below, while the earlier measurements have been reviewed by Rossini (1).

Experimenters	Date	Method	$\Delta H^\circ_{f\ 298.15}$ (kcal. mole^{-1})	References
Johnson, Ambrose	1963	Comparison of HCl, H_2SO_4 and SO_2 by solution calorimetry	-22.14 ± 0.12	2,3,4,5,6,7,8,9,10
Lacher, et al.	1949-52	Catalytic combination in flow calorimeter	-22.10 ± 0.12	11,12
Roth, Richter	1934	Direct combination in bomb calorimeter	-21.90 ± 0.05	13
von Wartenberg, Hanisch	1932	Direct combination in flow calorimeter	-21.90 ± 0.01	14
Rossini	1932	Direct combination in flow calorimeter	-22.063 ± 0.012	1
- - -	1922-63	ΔF°_f from e.m.f. and ΔS°_f from statistical mechanics	-22.02 ± 0.03	15,16,17,18,19,20
Lewis	1906	Equilibria for reaction HCl(g) + 1/4 O_2(g) = 1/2 H_2O(g) + 1/2 Cl_2(g)	-22.30 ± 0.44	21

The direct combination values of Roth-Richter (13) and von Wartenberg - Hanisch (14) are 0.7% less negative than that of Rossini; however, all of the other methods favor the more negative value. The Roth - Richter value may be affected by errors in the measurement of the extent of reaction by HCl titration (9,22), since a set of experiments based on determination of the amount of H_2 gave a value of -22.02 kcal. mole^{-1}.

Rossini's value is confirmed by a variety of independent methods. The solution calorimetry (3), though it is related through a complex reaction scheme, is based on species which are now quite well known. E.m.f. measurements (15,16,17,18, 19,20) give $\Delta F^\circ_{f\ 298.15}$ = -22.733; assuming an uncertainty of 1.0 mv. in E°, this leads to $\Delta H^\circ_{f\ 298.15}$ = -22.02 ± 0.03 when combined with the statistical entropies. The equilibria of Lewis (625-692°K) give $\Delta H^\circ_{f\ 298.15}$ = -22.20 ± 0.44 (second law) and -22.30 ± 0.04 (third law).

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Heat Capacity and Entropy.

Spectroscopic constants for HCl^{35} and HCl^{37} were selected from the work of E. K. Plyler, E. D. Tidwell, Z. Elektrochem. 64, 717 (1960) and C. Haeusler, P. Barchewitz, Compt. rend. 246, 3040 (1958). The values were adjusted to 75.53% HCl^{35}.

Hypochlorous Acid (HClO)

(Ideal Gas) Mol. Wt. = 52.465

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.440	-21.294	-21.294	INFINITE
100	7.954	47.566	64.019	-1.645	-21.585	-20.787	45.428
200	8.248	53.139	57.337	-.840	-21.782	-19.918	21.765
298	8.884	56.546	56.546	.000	-22.000	-18.958	13.896
300	8.897	56.601	56.547	.016	-22.004	-18.939	13.796
400	9.553	59.253	56.904	.940	-22.198	-17.887	9.773
500	10.090	61.445	57.599	1.923	-22.356	-16.790	7.339
600	10.509	63.323	58.400	2.954	-22.488	-15.664	5.705
700	10.844	64.969	59.223	4.022	-22.598	-14.517	4.532
800	11.125	66.436	60.035	5.121	-22.695	-13.358	3.649
900	11.370	67.761	60.821	6.246	-22.778	-12.185	2.959
1000	11.589	68.970	61.576	7.394	-22.849	-11.004	2.405
1100	11.787	70.084	62.300	8.563	-22.911	-9.816	1.950
1200	11.967	71.118	62.992	9.751	-22.964	-8.623	1.570
1300	12.131	72.082	63.655	10.956	-23.011	-7.427	1.248
1400	12.279	72.987	64.289	12.177	-23.051	-6.226	.972
1500	12.413	73.839	64.898	13.411	-23.088	-5.023	.732
1600	12.534	74.644	65.482	14.659	-23.122	-3.818	.522
1700	12.643	75.407	66.044	15.918	-23.152	-2.609	.335
1800	12.742	76.132	66.584	17.187	-23.181	-1.401	.170
1900	12.831	76.824	67.105	18.466	-23.209	-.189	.022
2000	12.911	77.484	67.608	19.753	-23.237	1.022	-.112
2100	12.983	78.116	68.093	21.048	-23.264	2.236	-.233
2200	13.049	78.721	68.562	22.349	-23.293	3.451	-.343
2300	13.108	79.303	69.017	23.657	-23.322	4.667	-.443
2400	13.162	79.862	69.457	24.971	-23.354	5.886	-.536
2500	13.211	80.400	69.884	26.289	-23.389	7.103	-.621
2600	13.256	80.919	70.299	27.613	-23.424	8.325	-.700
2700	13.296	81.420	70.701	28.940	-23.463	9.546	-.773
2800	13.334	81.904	71.093	30.272	-23.505	10.770	-.841
2900	13.368	82.373	71.474	31.607	-23.549	11.996	-.904
3000	13.399	82.826	71.845	32.945	-23.597	13.221	-.963
3100	13.428	83.266	72.206	34.287	-23.648	14.449	-1.019
3200	13.454	83.693	72.558	35.631	-23.703	15.678	-1.071
3300	13.479	84.107	72.902	36.978	-23.761	16.910	-1.120
3400	13.502	84.510	73.238	38.327	-23.822	18.143	-1.166
3500	13.523	84.902	73.565	39.678	-23.888	19.378	-1.210
3600	13.542	85.283	73.886	41.031	-23.957	20.616	-1.252
3700	13.560	85.654	74.199	42.386	-24.030	21.856	-1.291
3800	13.577	86.016	74.505	43.743	-24.106	23.097	-1.328
3900	13.593	86.369	74.805	45.102	-24.186	24.340	-1.364
4000	13.607	86.713	75.098	46.462	-24.270	25.585	-1.398
4100	13.621	87.050	75.385	47.823	-24.357	26.832	-1.430
4200	13.634	87.378	75.667	49.186	-24.447	28.081	-1.461
4300	13.646	87.699	75.943	50.550	-24.540	29.333	-1.491
4400	13.657	88.013	76.214	51.915	-24.636	30.587	-1.519
4500	13.667	88.320	76.479	53.281	-24.736	31.842	-1.546
4600	13.677	88.620	76.740	54.648	-24.837	33.103	-1.573
4700	13.687	88.914	76.996	56.016	-24.943	34.365	-1.598
4800	13.695	89.203	77.247	57.385	-25.050	35.626	-1.622
4900	13.704	89.485	77.494	58.755	-25.159	36.891	-1.645
5000	13.711	89.762	77.737	60.126	-25.271	38.156	-1.668
5100	13.719	90.034	77.975	61.498	-25.385	39.430	-1.690
5200	13.726	90.300	78.210	62.870	-25.501	40.700	-1.710
5300	13.732	90.562	78.440	64.243	-25.619	41.977	-1.731
5400	13.739	90.818	78.667	65.616	-25.739	43.249	-1.750
5500	13.745	91.071	78.890	66.991	-25.860	44.531	-1.769
5600	13.750	91.318	79.110	68.365	-25.985	45.809	-1.788
5700	13.756	91.562	79.326	69.741	-26.110	47.091	-1.805
5800	13.761	91.801	79.540	71.116	-26.238	48.380	-1.823
5900	13.766	92.036	79.749	72.493	-26.367	49.665	-1.840
6000	13.770	92.268	79.956	73.870	-26.497	50.956	-1.856

June 30, 1961

HYPOCHLOROUS ACID (HClO) (IDEAL GAS) MOL. WT. = 52.465

$\Delta H^\circ_{f0} = [-21] \pm 3$ kcal. mole^{-1}

Point Group C_s

$\Delta H^\circ_{f\ 298.15} = [-22] \pm 3$ kcal. mole^{-1}

$S^\circ_{298.15} = 56.546$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$

739 (1)
1242 (1)
3626 (1)

O-H distance = 0.96 ± 0.01 Å   O-Cl distance = 1.72 ± 0.04 Å   H-O-Cl angle = 104° ± 3° $\sigma = 1$

Product of moments of inertia = 4.54×10^{-117} g.^{3} cm.^{6}

Heat of Formation

I. E. Flis, K. P. Mishchenko, and N. V. Pakhomova, Zhur. Neorg. Khim. 3, 1772, 1781 (1958), report the following heats of reaction:

$ClO^-(aq) + H^+(aq) \rightarrow HOCl(aq)$ $\Delta H_{r\ 298.15} = -5.64 \pm 0.03$ kcal.

$ClO^-(aq) + H_2O_2(aq) \rightarrow Cl^-(aq) + H_2O(l) + O_2(g)$ $\Delta H_{r\ 298.15} = -36.93 \pm 0.05$ kcal.

If the following auxiliary heats of formation are used:

$Cl^-(aq)$ $\Delta H^\circ_{f\ 298.15} = -40.02$ kcal. mole^{-1} (National Bureau of Standards Circ. 500, 1952)

$H_2O(l)$ $\Delta H^\circ_{f\ 298.15} = -68.32$ kcal. mole^{-1} (National Bureau of Standards Circ. 500, 1952)

$H_2O_2(aq)$ $\Delta H^\circ_{f\ 298.15} = -45.70 \pm 0.02$ kcal. mole^{-1} (P. A. Giguère, B. G. Morissette, A. W. Olmos, and O. Knop, Can. J. Chem. 33, 804 (1955), consistent with $\Delta H^\circ_{f\ 298.15}$ of $H_2O_2(g)$ in this compilation)

then $\Delta H_{f\ 298.15}$ for HOCl(aq) is found to be -31.35 kcal. mole^{-1}. From the heats of solution in water of other weak acids, $\Delta H_{solution}$ for HClO is estimated to be -8 ± 3 kcal. mole^{-1}. These heats yield -23 ± 3 kcal. mole^{-1} for $\Delta H^\circ_{f\ 298.15}$ of HOCl(g). By averaging the heats of formation of $H_2O(g)$ and $Cl_2O(g)$, $\Delta H^\circ_{f\ 298.15}$ of HOCl(g) is estimated to be -20 ± 5 kcal. mole^{-1}. The value -22 ± 3 kcal. mole^{-1} is adopted here.

Heat Capacity and Entropy

The frequencies are from K. Hedberg and R. M. Badger, J. Chem. Phys. 19, 508 (1951), and the molecular dimensions from L. V. Gurvich and M. M. Novikov, Optics and Spectroscopy (English translation) 7, 70 (1959).

Chlorosilane (H_3SiCl)

(Ideal Gas) Mol. Wt. = 66.571

INTERIM TABLE

T, °K.	cal. mole⁻¹deg.⁻¹ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole⁻¹ $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-2,733	-45,844	-45,844	INFINITE
100	8,021	49,624	68,995	-1,937	-46,599	-45,554	99,553
200	9,638	55,559	60,918	-1,072	-47,276	-44,265	48,369
298	12,199	59,885	59,885	,000	-48,000	-42,633	31,249
300	12,245	59,960	59,885	,023	-48,013	-42,600	31,032
400	14,487	63,803	60,394	1,364	-48,637	-40,697	22,235
500	16,256	67,233	61,425	2,904	-49,121	-38,654	16,895
600	17,691	70,328	62,655	4,604	-49,479	-36,525	13,304
700	18,880	73,147	63,955	6,434	-49,731	-34,344	10,722
800	19,871	75,734	65,268	8,373	-49,895	-32,135	8,778
900	20,696	78,124	66,565	10,403	-49,993	-29,907	7,262
1000	21,384	80,341	67,834	12,508	-50,037	-27,673	6,048
1100	21,957	82,407	69,066	14,676	-50,039	-25,436	5,053
1200	22,437	84,339	70,259	16,896	-50,008	-23,200	4,225
1300	22,839	86,181	71,412	19,160	-49,953	-20,968	3,525
1400	23,179	87,856	72,527	21,462	-49,882	-18,741	2,926
1500	23,468	89,466	73,603	23,795	-49,800	-16,519	2,407
1600	23,714	90,988	74,642	26,154	-49,713	-14,304	1,954
1700	23,926	92,433	75,647	28,536	-61,725	-11,984	1,541
1800	24,109	93,805	76,618	30,938	-61,588	-9,065	1,101
1900	24,267	95,113	77,557	33,357	-61,448	-6,150	,707
2000	24,406	96,362	78,466	35,791	-61,307	-3,242	,354
2100	24,527	97,555	79,347	38,238	-61,168	-,343	,036
2200	24,634	98,699	80,201	40,696	-61,030	2,550	-,253
2300	24,729	99,796	81,029	43,164	-60,893	5,439	-,517
2400	24,813	100,850	81,833	45,641	-60,760	8,320	-,758
2500	24,888	101,865	82,614	48,126	-60,632	11,194	-,978
2600	24,955	102,842	83,374	50,619	-60,505	14,065	-1,182
2700	25,016	103,785	84,112	53,117	-60,383	16,930	-1,370
2800	25,070	104,696	84,831	55,622	-60,264	19,789	-1,545
2900	25,120	105,577	85,531	58,131	-60,149	22,649	-1,707
3000	25,165	106,429	86,214	60,645	-60,038	25,500	-1,858
3100	25,205	107,255	86,879	63,164	-59,930	28,349	-1,999
3200	25,242	108,056	87,529	65,686	-59,828	31,198	-2,131
3300	25,277	108,833	88,162	68,212	-59,730	34,043	-2,254
3400	25,308	109,588	88,782	70,742	-59,635	36,881	-2,371
3500	25,336	110,322	89,387	73,274	-59,548	39,718	-2,480
3600	25,363	111,036	89,978	75,809	-154,439	43,024	-2,612
3700	25,387	111,731	90,557	78,346	-154,300	48,508	-2,865
3800	25,410	112,409	91,123	80,886	-154,165	53,988	-3,105
3900	25,431	113,069	91,677	83,428	-154,038	59,462	-3,332
4000	25,450	113,713	92,220	85,972	-153,915	64,936	-3,548
4100	25,468	114,342	92,752	88,518	-153,797	70,405	-3,753
4200	25,485	114,956	93,273	91,066	-153,685	75,878	-3,948
4300	25,501	115,556	93,785	93,615	-153,579	81,334	-4,134
4400	25,516	116,142	94,286	96,166	-153,477	86,796	-4,311
4500	25,529	116,716	94,778	98,718	-153,383	92,251	-4,480
4600	25,542	117,277	95,261	101,272	-153,292	97,717	-4,642
4700	25,554	117,826	95,735	103,827	-153,207	103,172	-4,797
4800	25,566	118,364	96,201	106,383	-153,127	108,628	-4,946
4900	25,576	118,892	96,659	108,940	-153,052	114,079	-5,088
5000	25,586	119,408	97,109	111,498	-152,982	119,529	-5,224
5100	25,596	119,915	97,551	114,057	-152,917	124,981	-5,356
5200	25,605	120,412	97,986	116,617	-152,858	130,426	-5,481
5300	25,613	120,900	98,414	119,178	-152,803	135,879	-5,603
5400	25,621	121,379	98,835	121,740	-152,754	141,320	-5,719
5500	25,629	121,849	99,249	124,302	-152,709	146,768	-5,832
5600	25,636	122,311	99,656	126,866	-152,671	152,207	-5,940
5700	25,643	122,765	100,058	129,429	-152,637	157,658	-6,045
5800	25,649	123,211	100,453	131,994	-152,608	163,096	-6,145
5900	25,655	123,649	100,843	134,559	-152,584	168,545	-6,243
6000	25,661	124,081	101,226	137,125	-152,566	173,978	-6,337

December 31, 1960.

Chlorosilane (H_3SiCl) (Ideal Gas)

Mol. Wt. = 66.571

ΔH_f° 298.15 = [-48 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = 59.9 ± 2 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$
2201 (1)
949 (1)
551 (1)
2195 (2)
954.4(2)
664 (2)

Moments of Inertia: I_A = .9784 X 10^{-39} g. cm.^{2} σ= 3

I_B = 12.6749 X 10^{-39} g. cm.^{2} I_C = 12.6749 X 10^{-39} g. cm.^{2}

Heat of Formation. ΔH_f° 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in C. B. Henderson and R. S. Scheffee, Atlantic Res. Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960. Moments of inertia were calculated using the constants found in C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

Ammonium Chloride (NH_4Cl)

(Crystal) Mol. Wt. = 53.49158

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-5.425	-74.424	-74.424	INFINITE
100	9.000	5.868	39.148	/-3.328	-74.538	-66.082	144.416
200	16.040	14.281	24.653	-2.074	-75.202	-57.336	62.651
298	20.660	22.672	22.672	-.000	-75.180	-48.563	35.596
300	20.780	22.800	22.672	.038	-75.182	-48.398	35.256
400	24.610	29.312	23.534	2.311	-75.060	-39.479	21.569
500	21.630	36.647	25.432	5.607	-73.940	-30.704	13.420
600	24.300	40.826	27.653	7.904	-73.834	-22.062	8.036
700	26.960	44.772	29.819	10.467	-73.478	-13.457	4.201
800	29.610	48.545	31.926	13.296	-72.876	-4.923	1.345
900	32.260	52.189	33.976	16.392	-72.028	3.524	-.856
1000	34.550	55.710	35.974	19.735	-70.955	11.861	-2.592
1100	36.500	59.096	37.923	23.290	-69.694	20.084	-3.990
1200	38.200	62.351	39.824	27.033	-68.270	28.186	-5.133
1300	39.000	65.433	41.677	30.884	-66.764	36.162	-6.079
1400	40.870	68.397	43.480	34.883	-65.135	44.018	-6.871
1500	42.000	71.259	45.237	39.033	-63.385	51.757	-7.541

Dec. 31, 1960; Sept. 30, 1965

AMMONIUM CHLORIDE (NH_4Cl) (CRYSTAL) MOL. WT. = 53.49158 ClH_4N

$S^\circ_{298.15}$ = 22.7 ± 1.0 cal. deg.$^{-1}$ mole^{-1}

T_{t_2} = 242.6 °K.

T_{t_1} = 457.7 °K.

T_m = 793.2°K.

T_d = 612°K.

$\Delta H^\circ_{f\ 0}$ = -74.42 ± 0.20 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -75.18 ± 0.20 kcal. mole^{-1}

$\Delta H^\circ_{t_2}$ = 0.25 kcal. mole^{-1}

$\Delta H^\circ_{t_1}$ = 0.944 kcal. mole^{-1}

Heat of Formation.

The equilibrium pressures for the reaction $NH_4Cl(c) = NH_3(g) + HCl(g)$, at 320-626°K., have been measured by many investigators. A. Smits and W. de Lange, J. Chem. Soc., 2944 (1928), using the densi-tensimeter, determined the vapor pressure of $NH_4Cl(c)$ and the density of the saturated vapor simultaneously. The results obtained indicate that within the range 527-626°K. the saturated vapor completely dissociates into gaseous NH_3 and HCl. Based on this conclusion, the reported vapor pressure data were employed to evaluate the heat of dissociation of $NH_4Cl(c)$ by both the second and third law methods. The results are presented as follows.

Investigator	Temperature, °K.	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	Drift, e.u.
Smith and Calvert (1)	521.6-619.1	43.18 ± 0.08	42.11	-2.0 ± 0.2
Smits and Lange (2)	527.9-625.6	42.16 ± 0.22	42.14	-0.2 ± 0.4
Braune and Knoke (3)	525.4-615.0	42.02 ± 0.06	42.20	0.2 ± 0.1
Rodebush and Michalek (4)	471.3-557.0	42.43 ± 0.09	42.08	-0.3 ± 0.2
Wagner and Neumann (5)	319.0-352.7	43.83 ± 0.38	42.17	-4.9 ± 1.1
Markowitz and Boryta (6)	503.4-611.4	41.27 ± 0.38	42.12	1.3 ± 0.8

(1) A. Smith and R. P. Calvert, J. Am. Chem. Soc. 36, 1363 (1914), using isoteniscope.
(2) A. Smits and W. D. Lange, J. Chem. Soc. 2944 (1928), using densi-tensimeter.
(3) H. Braune and S. Knoke, Z. phys. Chem. 135, 49 (1928), Spiral Manometer.
(4) W. H. Rodebush and J. C. Michalek, J. Am. Chem. Soc. 51, 748 (1929), glass diaphragm manometer.
(5) H. Wagner and K. Neumann, Z. phys. Chem. 28, 51 (1961), torsion-effusion method.
(6) M. M. Markowitz and D. A. Boryta, J. Phys. Chem. 66, 1477 (1962), differential thermal analysis.

The value of $\Delta H^\circ_{r\ 298.15}$ adopted is 42.15 ± 0.10 kcal. mole^{-1}, yielding $\Delta H^\circ_{f\ 298.15}$ (NH_4Cl, c) = -75.8 ± 0.20 kcal. mole^{-1}. The corresponding $\Delta H^\circ_{r\ 298.15}$ value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS2, National Bureau of Standards, is 42.06 kcal. mole^{-1}.

Heat Capacity and Entropy.

The heat capacities (20.1-523.2°K.) of $NH_4Cl(c)$ have been measured by the following investigators: (1) R. Ewald, Ann. Physik, 44, 1213 (1914), 138-301°K; (2) F. Simon, ibid., 68, 241 (1922), 20.1-290.8°K; (3) H. Klinkhardt, ibid., 84, 167 (1927), 323.2-523.2°K.; (4) F. Simon, C. v. Simon and M. Ruhemann, Z. phys. Chem. 129, 339 (1927), 204.5-275.8°K; (5) W. T. Ziegler and C. E. Messer, J. Am. Chem. Soc., 63, 2694 (1941), 107.2-320.2; (6) R. Extermann and J. Weigle, Helv. Phys. Acta, 15, 455 (1942), 228.2-248.2°K; and (7) M. M. Popov and G. L. Galchenko, J. Gen. Chem., USSR, 21, 2489 (1951), 373.2-523.2°K. These C_p data were plotted and a smooth C_p curve was drawn and adopted. The C_p values above 523°K. were obtained by graphical extrapolation of the previous C_p curve. $S^\circ_{298.15}$ was derived from the adopted low temperature data, based on $S^\circ_{20.1}$ = 0.114 e.u.

Transition Data.

There are two transitions reported in the literature. The low temperature transition data (T_{t_2} and $\Delta H^\circ_{t_2}$) were derived based on the heat capacity (107-320°K.) data reported by W. T. Ziegler and C. E. Messer, loc. cit., in which the other T_{t_2} values given by previous investigators were reviewed. The high temperature transition data (T_{t_1} and $\Delta H^\circ_{t_1}$) were taken from H. Klinkhardt, loc. cit. However, $\Delta H^\circ_{t_1}$ = 1030 and $\Delta H^\circ_{463.5}$ = 1059.1 ± 8.0 cal. mole^{-1} were reported by E. C. Scheffer, Proc. Acad. Sci. Amsterdam, 24, 1513 (1915/16), and M. M. Popov and G. L. Galchenko, loc. cit., respectively. M. M. Markowitz and D. A. Boryta, loc. cit. determined T_{t_1} to be 459.5 ± 0.5°K.

Melting Temperature.

T_m was obtained from H. Rassow, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Decomposition Temperature.

The value of T_d was calculated as the temperature at which the vapor pressure of the decomposition products (NH_3 and HCl) equals 1 atm. By differential thermal analysis, T_d for $NH_4Cl(c)$ was determined to be 611.4°K. by M. M. Markowitz and D. A. Boryta, loc. cit.

ClH_4N

Ammonium Perchlorate (NH_4ClO_4)

(Crystal) Mol. Wt. = 117.497

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-6.032	-66.391	-66.391	INFINITE
100	19.030	17.422	67.672	-5.025	-69.021	-53.416	116.736
200	25.630	32.844	46.654	-2.762	-70.036	-37.389	40.855
298	30.610	44.020	44.020	.000	-70.690	-21.217	15.552
300	30.700	44.210	44.021	.057	-70.699	-20.911	15.233
400	35.540	53.704	45.283	3.369	-70.961	-4.264	2.329
500	40.380	62.154	47.825	7.164	-70.803	12.401	-5.420
600	47.220	74.739	51.542	13.918	-67.750	28.592	-10.414
700	52.060	82.381	55.407	18.882	-66.549	44.561	-13.912
800	56.900	89.649	59.236	24.330	-64.923	60.324	-16.479
900	61.740	96.630	63.006	30.262	-62.868	75.863	-18.421
1000	66.580	103.386	65.709	36.678	-60.376	91.148	-19.920
1100	71.599	109.972	70.343	43.592	-57.434	106.161	-21.091
1200	76.000	116.395	73.914	50.977	-54.064	120.889	-22.016
1300	79.784	122.632	77.423	58.772	-50.328	135.318	-22.748
1400	82.951	128.664	80.869	66.914	-46.284	149.449	-23.329
1500	85.500	134.477	84.250	75.341	-41.998	163.284	-23.789

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1962

ClH_4NO_4

AMMONIUM PERCHLORATE (NH_4ClO_4) (CRYSTAL) MOL. WT. = 117.497

ΔH_f° 298.15 = -70.69 ± 0.30 kcal. mole^{-1}

$S^\circ_{298.15}$ = 44.02 ± 0.04 cal. deg.$^{-1}$ mole^{-1}

T_t = 513.15°K

ΔH_t° = 2.3 ± 0.2 kcal. mole^{-1}

T_d = [513]°K.

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Research Natl. Bur. Standards 65A, 67 (1961), and M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960), have derived the heat of formation for NH_4ClO_4(c) from solution-calorimetric measurements. Their values are -70.74 ± 0.32 and -70.63 kcal. mole^{-1}, respectively. The mean of these is adopted here.

Heat Capacity and Entropy.

B. H. Justice and E. F. Westrum, private communication, April 1961, have measured the heat capacity from 5° to 350°K. The C_p values above 350°K were extrapolated. From the partial molar entropies of NH_4^+(aq) and ClO_4^-(aq) and the entropy of solution, Birky and Hepler, loc. cit., calculated a value of 43.6 cal. deg.$^{-1}$ mole^{-1} for $S^\circ_{298.15}$. The fair agreement of this value with that derived from C_p suggests that there is no residual entropy at 0°K, as there would be if the NH_4^+ ion had a random orientation.

Transition and Decomposition Data.

T_t and ΔH_t° were obtained (under a pressure of NH_3) by M. M. Markowitz, Foote Mineral Company, Exton, Pennsylvania (private communication, September 20, 1962). T_d was estimated from the report by M. M. Markowitz, loc. cit.

Mercury Monochloride (HgCl)

(Ideal Gas) Mol. Wt. = 236.067 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.353	19.727	19.727	INFINITE
100	7.523	53.156	69.599	-1.644	19.677	17.511	-38.267
200	8.393	58.686	62.893	-.841	19.503	15.411	-16.839
298	8.705	62.105	62.105	.000	18.750	13.595	-9.965
300	8.709	62.159	62.105	.016	18.747	13.563	-9.881
400	8.849	64.685	62.448	.895	18.549	11.866	-6.483
500	8.928	66.669	63.101	1.784	18.360	10.217	-4.466
600	8.981	68.302	63.836	2.680	18.172	8.606	-3.134
700	9.021	69.690	64.576	3.580	3.958	8.597	-2.684
800	9.054	70.896	65.292	4.484	3.922	9.262	-2.530
900	9.083	71.964	65.975	5.390	3.888	9.933	-2.412
1000	9.109	72.923	66.623	6.300	3.854	10.605	-2.318
1100	9.133	73.792	67.236	7.212	3.820	11.282	-2.242
1200	9.157	74.588	67.816	8.127	3.788	11.962	-2.178
1300	9.179	75.322	68.365	9.043	3.756	12.644	-2.126
1400	9.201	76.003	68.887	9.962	3.727	13.330	-2.081
1500	9.222	76.638	69.382	10.884	3.699	14.017	-2.042
1600	9.243	77.234	69.855	11.807	3.671	14.704	-2.008
1700	9.264	77.795	70.305	12.732	3.645	15.397	-1.979
1800	9.285	78.325	70.736	13.660	3.620	16.086	-1.953
1900	9.305	78.828	71.149	14.589	3.597	16.782	-1.930
2000	9.325	79.305	71.545	15.521	3.574	17.476	-1.910
2100	9.345	79.761	71.926	16.454	3.553	18.170	-1.891
2200	9.365	80.196	72.292	17.390	3.533	18.866	-1.874
2300	9.385	80.613	72.645	18.327	3.514	19.565	-1.859
2400	9.405	81.013	72.985	19.267	3.497	20.265	-1.845
2500	9.425	81.397	73.314	20.208	3.479	20.962	-1.832
2600	9.445	81.767	73.632	21.152	3.463	21.662	-1.821
2700	9.465	82.124	73.940	22.097	3.448	22.363	-1.810
2800	9.485	82.469	74.238	23.045	3.433	23.062	-1.800
2900	9.504	82.802	74.528	23.994	3.420	23.766	-1.791
3000	9.524	83.124	74.809	24.946	3.406	24.465	-1.782
3100	9.544	83.437	75.082	25.899	3.393	25.168	-1.774
3200	9.564	83.740	75.348	26.854	3.380	25.871	-1.767
3300	9.583	84.035	75.607	27.812	3.368	26.575	-1.760
3400	9.603	84.321	75.859	28.771	3.358	27.278	-1.753
3500	9.622	84.600	76.105	29.732	3.347	27.981	-1.747
3600	9.642	84.871	76.345	30.696	3.337	28.685	-1.741
3700	9.662	85.136	76.579	31.661	3.327	29.389	-1.736
3800	9.681	85.394	76.807	32.628	3.318	30.095	-1.731
3900	9.701	85.645	77.031	33.597	3.310	30.800	-1.726
4000	9.720	85.891	77.249	34.568	3.302	31.505	-1.721
4100	9.740	86.131	77.463	35.541	3.295	32.207	-1.717
4200	9.760	86.366	77.672	36.516	3.289	32.912	-1.713
4300	9.779	86.596	77.877	37.493	3.285	33.618	-1.709
4400	9.799	86.821	78.078	38.472	3.281	34.324	-1.705
4500	9.818	87.042	78.274	39.453	3.278	35.030	-1.701
4600	9.838	87.258	78.467	40.436	3.277	35.733	-1.698
4700	9.857	87.469	78.657	41.420	3.276	36.444	-1.695
4800	9.877	87.677	78.842	42.407	3.277	37.144	-1.691
4900	9.896	87.881	79.025	43.396	3.279	37.853	-1.688
5000	9.916	88.081	79.204	44.386	3.283	38.559	-1.685
5100	9.936	88.278	79.380	45.379	3.288	39.267	-1.683
5200	9.955	88.471	79.553	46.373	3.293	39.972	-1.680
5300	9.975	88.661	79.723	47.370	3.300	40.675	-1.677
5400	9.994	88.847	79.890	48.368	3.309	41.378	-1.675
5500	10.014	89.031	80.055	49.369	3.319	42.084	-1.672
5600	10.033	89.211	80.217	50.371	3.330	42.791	-1.670
5700	10.053	89.389	80.376	51.375	3.342	43.495	-1.668
5800	10.072	89.564	80.533	52.382	3.355	44.197	-1.665
5900	10.092	89.737	80.687	53.390	3.368	44.898	-1.663
6000	10.111	89.906	80.840	54.400	3.384	45.603	-1.661

December 31, 1961

MERCURY MONOCHLORIDE (HgCl) (IDEAL GAS) MOL. WT. = 236.067

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 62.105 cal deg^{-1} mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 18.75 ± 2.3 kcal mole^{-1}

Electronic Levels and Multiplicities

ε, cm^{-1}	g_i
0	2

ω_e = 290.94 cm^{-1} $\omega_e x_e$ = 1.5844 cm^{-1} σ = 1

B_e = [0.1121] cm^{-1} α_e = [0.0007] cm^{-1} r_e = 2.23 Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 23 ± 2.3 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from K. Wieland Zeits. f. Elektrochemie 64, 761 (1960) were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. Bond length given by G. Herzberg (loc. cit.).

Iodine Monochloride (ICl)

(Crystal) Mol. Wt. = 162.3574

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.907	-8.699	-8.699	INFINITE
100	9.619	10.921	34.181	-2.326	-8.833	-6.937	15.159
200	11.840	18.406	24.571	-1.233	-8.690	-5.085	5.557
298	13.200	23.405	23.405	.000	-8.466	-3.362	2.464
300	13.223	23.487	23.405	.024	-8.461	-3.330	2.426
400	14.387	27.453	23.938	1.406	-10.081	-1.597	.872
500	15.387	30.773	24.982	2.896	-14.779	.961	-.420
600	16.287	33.659	26.192	4.480	-14.077	4.044	-1.473
700	17.086	36.231	27.446	6.150	-13.296	7.004	-2.187
800	17.785	38.559	28.692	7.894	-12.446	9.846	-2.690
900	18.383	40.690	29.908	9.703	-11.533	12.578	-3.054
1000	18.880	42.653	31.086	11.567	-10.569	15.206	-3.323

Mar. 31, 1962; Sept. 30, 1963; Sept. 30, 1965

IODINE MONOCHLORIDE (ClI) (CRYSTAL) MOL. WT. = 162.3574

$S^\circ_{298.15}$ = 23.405 cal. mole^{-1} deg.$^{-1}$

T°_m = 300.53°K.

$\Delta H^\circ_{f\ 0}$ = -8.699 ± 0.025 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -8.466 ± 0.025 kcal. mole^{-1}

ΔH°_m = 2.773 ± 0.002 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 12.650 kcal. mole^{-1}

Heat of Formation.

The heat of formation is that adopted by G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965) from an analysis of the equilibrium data of J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939). This yielded a heat of formation of ICl(g), from which the heat of formation of ICl(c) was calculated by using the heat of vaporization determined by Calder and Giauque loc. cit.

Heat Capacity and Entropy.

The heat capacity has been measured by Calder and Giauque loc. cit. from 17-322°K. The entropy was calculated based on S_{15} = 0.592 cal. mole^{-1} deg.$^{-1}$ Above 300° the heat capacity data was extrapolated smoothly.

Melting Data.

All data were measured by Calder and Giauque loc. cit.

Iodine Monochloride (ICl)

(Liquid)   Mol. Wt. = 162.3574

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	24.560	32.544	32.544	-.000	-5.720	-3.341	2.449
300	24.582	32.696	32.544	.045	-5.694	-3.326	2.423
400	23.500	39.649	33.501	2.459	-6.281	-2.676	1.462
500	22.500	44.785	35.267	4.759	-10.169	-1.436	.627
600	21.500	48.799	37.200	6.959	-8.852	.185	-.067
700	20.500	52.038	39.096	9.059	-7.641	1.594	-.498
800	19.500	54.710	40.886	11.059	-6.534	2.837	-.775
900	18.500	56.949	42.550	12.959	-5.531	3.947	-.958
1000	17.500	58.847	44.088	14.759	-4.631	4.950	-1.082

Mar. 31, 1962; Sept. 30, 1963; Sept. 30, 1965

IODINE MONOCHLORIDE (ClI)   (LIQUID)   MOL. WT. = 162.3574

$S^\circ_{298.15}$ = 32.544 cal. mole^{-1} deg.$^{-1}$ ΔH_f° 298.15 = -5.72 ± 0.03 kcal. mole^{-1}

T_m° = 300.53°K. ΔH_m° = 2.773 ± 0.002 kcal. mole^{-1}

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m° and the difference between $H_{300.53}-H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity from 300.53 to 317.76°K. has been measured by G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965). Above 318°K. it was extrapolated in a smooth manner. The entropy was obtained in a manner analogous to the heat of formation.

Iodine Monochloride (ICl)

(Ideal Gas) Mol. Wt. = 162.3574

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.284	4.574	4.574	INFINITE
100	7.213	50.547	66.382	-1.584	4.559	2.493	-5.449
200	8.076	55.831	59.911	-.816	4.377	.497	-.543
298	8.497	59.145	59.145	.000	4.184	-1.368	1.003
300	8.502	59.198	59.145	.016	4.180	-1.402	1.022
400	8.700	61.674	59.482	.877	2.040	-3.164	1.729
500	8.808	63.628	60.122	1.753	-3.272	-3.959	1.731
600	8.873	65.240	60.845	2.637	-3.270	-4.097	1.492
700	8.918	66.611	61.573	3.527	-3.269	-4.235	1.322
800	8.952	67.805	62.279	4.420	-3.269	-4.374	1.195
900	8.978	68.860	62.953	5.317	-3.270	-4.511	1.095
1000	9.000	69.808	63.592	6.216	-3.270	-4.650	1.016
1100	9.019	70.666	64.196	7.117	-3.271	-4.788	.951
1200	9.036	71.452	64.769	8.020	-3.273	-4.926	.897
1300	9.052	72.176	65.311	8.924	-3.274	-5.064	.851
1400	9.066	72.847	65.826	9.830	-3.276	-5.200	.812
1500	9.080	73.473	66.315	10.737	-3.278	-5.339	.778
1600	9.094	74.059	66.781	11.646	-3.281	-5.474	.748
1700	9.106	74.611	67.225	12.556	-3.283	-5.611	.721
1800	9.119	75.132	67.650	13.467	-3.286	-5.749	.698
1900	9.131	75.625	68.057	14.380	-3.289	-5.884	.677
2000	9.143	76.094	68.447	15.293	-3.293	-6.023	.658
2100	9.155	76.540	68.822	16.208	-3.296	-6.158	.641
2200	9.167	76.967	69.183	17.124	-3.300	-6.296	.625
2300	9.178	77.374	69.530	18.042	-3.304	-6.430	.611
2400	9.190	77.765	69.865	18.960	-3.309	-6.566	.598
2500	9.201	78.141	70.189	19.880	-3.315	-6.704	.586
2600	9.212	78.502	70.502	20.800	-3.321	-6.839	.575
2700	9.223	78.849	70.804	21.722	-3.328	-6.972	.564
2800	9.234	79.185	71.098	22.645	-3.336	-7.106	.555
2900	9.246	79.509	71.382	23.569	-3.345	-7.241	.546
3000	9.257	79.823	71.658	24.494	-3.354	-7.377	.537
3100	9.268	80.127	71.927	25.420	-3.365	-7.512	.530
3200	9.279	80.421	72.188	26.348	-3.377	-7.644	.522
3300	9.290	80.707	72.441	27.276	-3.390	-7.777	.515
3400	9.300	80.984	72.689	28.205	-3.404	-7.909	.508
3500	9.311	81.254	72.929	29.136	-3.418	-8.042	.502
3600	9.322	81.516	73.164	30.068	-3.434	-8.172	.496
3700	9.333	81.772	73.394	31.000	-3.451	-8.305	.491
3800	9.344	82.021	73.617	31.934	-3.468	-8.437	.485
3900	9.355	82.264	73.836	32.869	-3.487	-8.567	.480
4000	9.366	82.501	74.050	33.805	-3.506	-8.698	.475
4100	9.376	82.732	74.259	34.742	-3.526	-8.825	.470
4200	9.387	82.958	74.463	35.681	-3.546	-8.954	.466
4300	9.398	83.179	74.663	36.620	-3.567	-9.084	.462
4400	9.409	83.396	74.859	37.560	-3.589	-9.214	.458
4500	9.419	83.607	75.051	38.502	-3.611	-9.339	.454
4600	9.430	83.814	75.240	39.444	-3.633	-9.465	.450
4700	9.441	84.017	75.424	40.388	-3.654	-9.593	.446
4800	9.452	84.216	75.605	41.332	-3.677	-9.720	.443
4900	9.462	84.411	75.783	42.278	-3.699	-9.844	.439
5000	9.473	84.602	75.957	43.225	-3.721	-9.969	.436
5100	9.484	84.790	76.129	44.173	-3.742	-10.095	.433
5200	9.495	84.974	76.297	45.121	-3.765	-10.218	.429
5300	9.505	85.155	76.463	46.071	-3.786	-10.342	.426
5400	9.516	85.333	76.625	47.022	-3.808	-10.466	.424
5500	9.527	85.508	76.785	47.975	-3.828	-10.591	.421
5600	9.537	85.680	76.942	48.928	-3.849	-10.718	.418
5700	9.548	85.848	77.097	49.882	-3.870	-10.835	.415
5800	9.559	86.015	77.249	50.837	-3.890	-10.960	.413
5900	9.570	86.178	77.399	51.794	-3.909	-11.081	.410
6000	9.580	86.339	77.547	52.751	-3.929	-11.201	.408

Mar. 31, 1962; Sept. 30, 1963; Dec. 31, 1963; Sept. 30, 1965

IODINE MONOCHLORIDE (ClI) (IDEAL GAS) MOL. WT. = 162.3574

$\Delta H^\circ_{f\ 0} = 4.574 \pm 0.025$ kcal. mole^{-1}

$S^\circ_{298.15} = 59.145$ cal. mole^{-1} deg.$^{-1}$

$\Delta H^\circ_{f\ 298.15} = 4.184 \pm 0.025$ kcal. mole^{-1}

Ground State Configuration $^1\Sigma^+$

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	1

$\omega_e = 382.18$ cm.$^{-1}$

$\omega_e x_e = 1.450$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.11298$ cm.$^{-1}$

$\alpha_e = 0.0005275$ cm.$^{-1}$

$r_e = 2.327$ Å

Heat of Formation.

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Standards, 55, 147 (1955) from which they adopt $D_0^\circ = 49.64$ kcal. mole^{-1}. J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939) studied the equilibria $NOCl = NO + 1/2\ Cl_2$ and $NO + ICl = NOCl + 1/2\ I_2(g)$ from which the equilibrium constant of $ICl = 1/2\ Cl_2 + 1/2\ I_2(g)$ can be obtained. G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965) have used 3rd law analysis to obtain $D_0^\circ = 49.578 \pm 0.025$ kcal. mole^{-1}. This value was adopted yielding $\Delta H^\circ_{f\ 298} = 4.184 \pm 0.025$ kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular and vibrational constants were obtained from G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York 1950. The values were then adjusted for the normal isotopic abundance of chlorine.

Potassium Chloride (KCl)

(Crystal)   Mol. Wt. = 74.555

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.717	-104.297	-104.297	INFINITE
100	9.369	7.594	30.087	-2.249	-104.594	-102.243	223.452
200	11.577	14.969	20.833	-1.173	-104.498	-99.919	109.186
298	12.258	19.731	19.731	-.000	-104.370	-97.700	71.616
300	12.268	19.807	19.732	.023	-104.368	-97.659	71.144
400	12.700	23.398	20.218	1.272	-104.848	-95.329	52.085
500	13.086	26.274	21.151	2.561	-104.728	-92.963	40.634
600	13.460	28.693	22.212	3.889	-104.561	-90.624	33.010
700	13.863	30.797	23.291	5.254	-104.350	-88.317	27.574
800	14.359	32.679	24.349	6.664	-104.095	-86.044	23.506
900	15.036	34.407	25.372	8.132	-103.784	-83.805	20.351
1000	16.006	36.038	26.357	9.681	-103.403	-81.606	17.835
1100	17.200	37.622	27.310	11.343	-121.827	-78.425	15.582
1200	18.200	39.163	28.234	13.115	-121.002	-74.515	13.571
1300	19.000	40.652	29.132	14.977	-120.088	-70.677	11.882
1400	19.600	42.084	30.006	16.908	-119.106	-66.913	10.446
1500	20.000	43.451	30.857	18.890	-118.074	-63.221	9.211

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CHLORIDE (KCl)   (CRYSTAL)   MOL. WT. = 74.555

$\Delta H_{f\,0}^\circ = -104.30$ kcal. mole^{-1}

$S_{298.15}^\circ = 19.73 \pm 0.04$ cal. deg.$^{-1}$ mole^{-1} $\Delta H_{f\,298.15}^\circ = -104.37 \pm 0.06$ kcal. mole^{-1}

$T_m = 1044$°K. $\Delta H_m^\circ = 6.282$ kcal. mole^{-1}

Heat of Formation.

The heat of formation was calculated from the heat of hydrolysis of K(c), the heats of solution of HCl(g) and KCl(c), and the standard heat of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the heat of formation for HCl(g), are summarized below.

Source	Reaction	$\Delta H_{r\,298.15}^\circ$ (kcal.)
1,2,3,4	$K(c) + H_2O(l) \rightarrow KOH(\infty H_2O) + 1/2\ H_2(g)$	-46.966 ± 0.05
5,2,6	$HCl(g) \rightarrow HCl(\infty H_2O)$	-17.88 ± 0.015
7	$KCl(\infty H_2O) \rightarrow KCl(c)$	-4.115 ± 0.010
7	$KOH(\infty H_2O) + HCl(\infty H_2O) \rightarrow KCl(\infty H_2O) + H_2O(l)$	-13.345 ± 0.025

1. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1957).
2. S. R. Gunn, UCRL-7992, Livermore, Calif., Jul 1964.
3. C. E. Messer, L. G. Fasolino, and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955).
4. E. E. Ketchen and W. E. Wallace, J. Am. Chem. Soc. 76, 4736 (1954).
5. C. E. Vanderzee and J. D. Nutter, J. Phys. Chem. 67, 2521 (1963).
6. S. R. Gunn and L. G. Green, J. Chem. Eng. Data 8, 180 (1963).
7. V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS2, U. S. Government Printing Office, Washington, D.C., 1965.

Heat Capacity and Entropy.

Low temperature heat capacities were obtained from the data (2.8-275°K.) of W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 467 (1957). Previous measurements scatter around the selected values and are in good agreement. These include P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov, and G. G. Mirskaya (12-298°K.), Zhur. Fiz. Khim. 28, 645 (1954); K. Clusius, J. Goldman, and A. Perlick (10-273°K.), Z. Naturforsch. 4a, 429 (1949); and J. C. Southard and R. A. Nelson (17-285°K.), J. Am. Chem. Soc. 55, 4865 (1933). For other less extensive data see the review by K. K. Kelley and E. G. King, USBM Bulletin 592, 1961. The entropy is based on the extrapolation $S_{2.8}^\circ = 0.0006$ cal./deg.-mole.

High temperature values are based on enthalpy data (373-1038°K.) from T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (673-933°K.) of S. M. Skuratov and S. A. Lapushkin, J. Gen. Chem. (USSR) 21, 2485 (1951) and the adiabatic heat capacities (334-721°K.) of A. Mustajoki, Ann. Acad. Scient. Fennicae, Series A, I, 98, 7 (1951).

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of $T_m = 1043$° and 1045°K. have been reported by E. Aukrust, B. Bjørge, H. Flood, and T. Forland, Ann. New York Acad. Sci. 79, 830 (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 62, 604 (1958), respectively. The heat of melting is confirmed by $\Delta H_m^\circ = 6.34$ kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960) and $\Delta H_m^\circ = 6.4$ and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

Potassium Chloride (KCl)

(Liquid) Mol. Wt. = 74.555

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	17.590	20.714	20.714	.000	- 100.810	- 94.433	69.221
300	17.590	20.823	20.714	.033	- 100.798	- 94.394	68.766
400	17.590	25.883	21.404	1.792	- 100.768	- 92.244	50.400
500	17.590	29.808	22.707	3.551	- 100.178	- 90.180	39.418
600	17.590	33.015	24.166	5.310	- 99.580	- 88.236	32.140
700	17.590	35.727	25.629	7.069	- 98.976	- 86.394	26.973
800	17.590	38.076	27.041	8.828	- 98.372	- 84.639	23.122
900	17.590	40.147	28.385	10.587	- 97.770	- 82.957	20.145
1000	17.590	42.001	29.655	12.346	- 97.179	- 81.344	17.778
1100	17.590	43.677	30.855	14.105	- 115.505	- 78.764	15.649
1200	17.590	45.208	31.988	15.864	- 114.693	- 75.460	13.743
1300	17.590	46.616	33.060	17.623	- 113.882	- 72.225	12.142
1400	17.590	47.919	34.075	19.382	- 113.072	- 69.049	10.779
1500	17.590	49.133	35.039	21.141	- 112.263	- 65.933	9.606
1600	17.590	50.268	35.956	22.900	- 111.455	- 62.870	8.588
1700	17.590	51.334	36.829	24.659	- 110.649	- 59.858	7.695
1800	17.590	52.340	37.663	26.418	- 109.843	- 56.895	6.908
1900	17.590	53.291	38.461	28.177	- 109.040	- 53.975	6.208
2000	17.590	54.193	39.225	29.936	- 108.239	- 51.096	5.584

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CHLORIDE (KCl) (LIQUID) MOL. WT. = 74.555

$S^\circ_{298.15}$ = 20.71 cal. deg.$^{-1}$ mole^{-1}

T_m = 1044°K.

T_b = 1710°K. (to equilibrium vapor)

T_b = [1750°K.] (to monomer only)

$\Delta H^\circ_{f\ 298.15}$ = -100.81 kcal. mole^{-1}

ΔH°_m = 6.282 kcal. mole^{-1}

ΔH°_v = 29.7 kcal. mole^{-1} (equilibrium vapor)

ΔH°_v = [37.14] kcal. mole^{-1} (monomer)

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH°_m and the difference between $(H^\circ_{1044}-H^\circ_{298})$ for the crystal and liquid.

Heat Capacity and Entropy.

The constant heat capacity, 17.59 cal./deg.-mole, was derived from enthalpy data (1053-1173°K.) of T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. This value was extrapolated above and below the experimental range. A lower value of 16.7 cal./deg.-mole was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964, from enthalpy data (1050-1110°K.) obtained in a heat of melting study. The entropy of the liquid was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of T_m = 1043° and 1045°K. have been reported by E. Aukrust, B. Björge, H. Flood, and T. Forland, Ann. New York Acad. Sci. <u>79</u>, 830 (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. <u>62</u>, 604 (1958), respectively. The heat of melting is confirmed by ΔH°_m = 6.34 kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. <u>64</u>, 269 (1960) and ΔH°_m = 6.4 and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

Vaporization Data.

T_b (to equilibrium vapor) is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and K_2Cl_2(g). This value may be compared with boiling points of 1688° and 1690°K. observed respectively by O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. <u>117</u>, 147 (1921), and H. von Wartenburg and P. Albrecht, Z. Elektrochem. <u>27</u>, 162 (1921). ΔH°_v (equilibrium vapor) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 22.3 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal. T_b (to monomer only) is taken as the temperature at which the calculated free energy change is zero for KCl(l) → KCl(g), while ΔH°_v (monomer) is the corresponding heat of reaction.

Data on vapor pressures and dimer-monomer equilibrium are reviewed on the tables for KCl(g) and K_2Cl_2(g), respectively.

Potassium Chloride (KCl)

(Ideal Gas) Mol. Wt. = 74.555

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.362	-50.882	-50.882	INFINITE
100	7.576	48.122	64.639	-1.652	-50.936	-52.638	115.040
200	8.430	53.687	57.907	-.844	-51.109	-54.274	59.307
298	8.723	57.116	57.116	.000	-51.310	-55.787	40.893
300	8.726	57.170	57.117	.016	-51.314	-55.814	40.661
400	8.857	59.701	57.461	.896	-52.163	-57.166	31.234
500	8.930	61.685	58.114	1.786	-52.443	-58.384	25.520
600	8.979	63.318	58.850	2.681	-52.708	-59.547	21.690
700	9.015	64.705	59.589	3.581	-52.964	-60.666	18.941
800	9.046	65.911	60.306	4.484	-53.215	-61.750	16.869
900	9.072	66.978	60.989	5.390	-53.467	-62.801	15.250
1000	9.097	67.935	61.637	6.298	-53.726	-63.826	13.949
1100	9.119	68.803	62.249	7.209	-72.901	-63.798	12.676
1200	9.141	69.598	62.829	8.122	-72.935	-62.969	11.468
1300	9.162	70.330	63.378	9.037	-72.968	-62.138	10.446
1400	9.182	71.010	63.899	9.955	-72.999	-61.303	9.570
1500	9.202	71.644	64.395	10.874	-73.030	-60.466	8.810
1600	9.221	72.238	64.867	11.795	-73.060	-59.626	8.145
1700	9.240	72.798	65.317	12.718	-73.090	-58.787	7.558
1800	9.259	73.327	65.747	13.643	-73.118	-57.946	7.036
1900	9.278	73.828	66.160	14.570	-73.147	-57.102	6.568
2000	9.297	74.304	66.555	15.499	-73.176	-56.255	6.147
2100	9.316	74.758	66.935	16.429	-73.205	-55.408	5.766
2200	9.335	75.192	67.300	17.362	-73.236	-54.560	5.420
2300	9.353	75.607	67.653	18.296	-73.268	-53.710	5.104
2400	9.372	76.006	67.992	19.232	-73.303	-52.861	4.814
2500	9.390	76.389	68.321	20.171	-73.341	-52.009	4.547
2600	9.408	76.758	68.638	21.110	-73.382	-51.153	4.300
2700	9.427	77.113	68.945	22.052	-73.428	-50.299	4.071
2800	9.445	77.456	69.243	22.996	-73.481	-49.440	3.859
2900	9.463	77.788	69.532	23.941	-73.539	-48.580	3.661
3000	9.482	78.109	69.813	24.888	-73.604	-47.720	3.476
3100	9.500	78.420	70.085	25.838	-73.678	-46.854	3.303
3200	9.518	78.722	70.351	26.788	-73.762	-45.987	3.141
3300	9.536	79.015	70.609	27.741	-73.855	-45.119	2.988
3400	9.555	79.300	70.860	28.696	-73.961	-44.247	2.844
3500	9.573	79.577	71.105	29.652	-74.080	-43.371	2.708
3600	9.591	79.847	71.345	30.610	-74.215	-42.490	2.579
3700	9.609	80.110	71.578	31.570	-74.366	-41.608	2.458
3800	9.627	80.367	71.806	32.532	-74.536	-40.723	2.342
3900	9.646	80.617	72.029	33.496	-74.727	-39.829	2.232
4000	9.664	80.862	72.246	34.461	-74.941	-38.933	2.127
4100	9.682	81.101	72.459	35.429	-75.181	-38.031	2.027
4200	9.700	81.334	72.668	36.398	-75.451	-37.120	1.932
4300	9.718	81.562	72.872	37.369	-75.751	-36.202	1.840
4400	9.736	81.786	73.072	38.341	-76.087	-35.279	1.752
4500	9.755	82.005	73.268	39.316	-76.460	-34.346	1.668
4600	9.773	82.220	73.461	40.292	-76.873	-33.410	1.587
4700	9.791	82.430	73.649	41.270	-77.330	-32.457	1.509
4800	9.809	82.636	73.834	42.250	-77.834	-31.495	1.434
4900	9.827	82.839	74.016	43.232	-78.389	-30.526	1.362
5000	9.845	83.038	74.194	44.216	-78.995	-29.547	1.292
5100	9.863	83.233	74.370	45.201	-79.656	-28.546	1.223
5200	9.881	83.424	74.542	46.188	-80.375	-27.535	1.157
5300	9.900	83.613	74.711	47.178	-81.152	-26.517	1.093
5400	9.918	83.798	74.878	48.168	-81.990	-25.479	1.031
5500	9.936	83.980	75.042	49.161	-82.888	-24.423	.970
5600	9.954	84.159	75.203	50.156	-83.847	-23.351	.911
5700	9.972	84.336	75.362	51.152	-84.867	-22.267	.854
5800	9.990	84.509	75.518	52.150	-85.947	-21.155	.797
5900	10.008	84.680	75.672	53.150	-87.084	-20.027	.742
6000	10.026	84.849	75.823	54.152	-88.277	-18.881	.688

Dec. 31, 1961; Mar. 31, 1966

ClK

POTASSIUM CHLORIDE (KCl) (IDEAL GAS) MOL. WT. = 74.555

Ground State Configuration $^1\Sigma$

$\Delta H_f^\circ{}_0 = -50.88$ kcal. mole^{-1}

$S^\circ_{298.15} = 57.12$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -51.31 \pm 0.1$ kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_i, cm.$^{-1}$	g_i
0	1

$\omega_e = 278.6$ cm.$^{-1}$ $\omega_e x_e = 1.157$ cm.$^{-1}$ $\sigma = 1$

$B_e = 0.127536$ cm.$^{-1}$ $\alpha_e = 0.0007799$ $r_e = 2.6667$ Å

Heat of Formation.

The heat of formation was calculated from that of the liquid based on $\Delta H_v^\circ{}_{298.15} = 49.5$ kcal./mole as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values (source 5) are based on temperature variation of ion intensity. These same five studies were used in selection of $\Delta H_r^\circ{}_{298.15} = 45.0$ kcal./mole for the dimer-monomer equilibrium (see K_2Cl_2).

The resulting tables were tested by comparison with total pressure data over the range 819-1691°K. Dimer-monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below (sources 6-11). The results are consistent except near the boiling point where the observed pressures (sources 10 and 11) are 6-18 percent larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the torsion effusion data of source 6.

Source	Method	No. of Points	Temp. Range °K.	$\Delta H^\circ_{vap\ 298}$ 2nd Law kcal./mole	$\Delta H^\circ_{vap\ 298}$ 3rd Law kcal./mole	Drift eu
1. Datz (1960)	PVT + Vap. Press.(a)	15	1310-1404	51.04±0.40	49.67	-1.0±0.4
2. Schrier (1961)	Trans. + Vap. Press.	10	1253-1352	50.75±0.80	49.49	-1.0±0.6
3. Beusman (1957)	Trans. + Vap. Press.(b)	5	1261-1372	50.26±0.77	49.28	-0.8±0.6
4. Barton et al. (1959)	Trans. + Vap. Press.	7	1250-1473	49.67±0.66	49.46	-0.1±0.5
5. Milne et al. (1960)	Mass Spectrometry	-	774-1016	49.6 ±1.8	—	—
6. Pugh et al. (1958)	Total Vap. Press.	137	819-945	49.5	49.57	0.06
7. Dietz (1936)	Total Vap. Press.	9	847-936	49.0	49.95	1.0±0.6
8. Fiock et al. (1926)	Total Vap. Press.	9	1179-1378	50.3	49.44	-0.8±0.2
9. Novikov et al. (1961)	Total Vap. Press.	9	1170-1466	51.0	49.42	-1.2±0.2
10. Ruff et al. (1921)	Total Vap. Press.	7	1393-1688	53.6	49.48	-2.7±0.4
11. Wartenburg et al. (1921)	Total Vap. Press.	16	1389-1691	50.2	49.22	-0.8±0.5

(a) Total vapor pressure from sources 2,3 and 8. (b) 1235°K. was omitted.

1. S. Datz, ORNL-2933, Oak Ridge, Tenn., May 1960.
2. E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.
3. C. Beusman, ORNL-2323, Oak Ridge, Tenn., Jun 1957.
4. J. L. Barton and H. Bloom, J. Phys. Chem. 63, 1785 (1959); 60, 1413 (1956).
5. T. A. Milne and H. M. Klein, AFOSR TN 60-512, Menlo Park, Calif., Jun 1960.
6. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958).
7. V. Dietz, J. Chem. Phys. 4, 575 (1936).
8. E. F. Fiock and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).
9. G. I. Novikov and O. G. Polyachenok, Russ. J. Inorg. Chem. 6, 996 (1961).
10. O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. 117, 149 (1921).
11. H. von Wartenburg and P. Albrecht, Z. elektrochem. 27, 162 (1921).

Heat Capacity and Entropy.

Rotational and vibrational constants are based on the microwave studies of P. L. Clouser and W. Gordy, Phys. Rev. 134, A863 (1964). Earlier microwave data of A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, Phys. Rev. 96, 629 (1954) and electric resonance data of C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, Phys. Rev. 91, 1395 (1953) are in excellent agreement. Infrared spectra of S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957) yield $\omega_e = 281 \pm 6$ cm.$^{-1}$ which is also in good agreement. The constants were adjusted to a natural isotopic composition of 24.47% ^{37}Cl and 6.8% ^{41}K.

ClK

Potassium Perchlorate ($KClO_4$)

(Crystal) Mol. Wt. = 138.557

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 5.036	- 100.896	- 100.896	INFINITE
100	15.520	14.198	56.248	- 4.205	- 102.256	- 92.261	201.626
200	21.130	26.835	38.580	- 2.349	- 102.740	- 82.041	89.646
298	26.865	36.100	36.100	.000	- 102.800	- 71.790	52.621
300	27.000	36.267	36.101	.050	- 102.797	- 71.597	52.156
400	33.100	44.927	37.240	3.075	- 102.923	- 61.143	33.405
500	36.800	52.755	39.575	6.590	- 102.039	- 50.793	22.200
600	39.500	65.466	42.624	13.705	- 97.595	- 40.804	14.862
700	41.615	71.715	46.341	17.762	- 96.249	- 31.443	9.816
800	43.600	77.403	49.874	22.023	- 94.738	- 22.289	6.089
900	45.288	82.638	53.227	26.469	- 93.077	- 13.330	3.237
1000	46.800	87.489	56.414	31.075	- 91.293	- 4.563	.997
1100	48.138	92.013	59.447	35.823	- 108.309	5.043	- 1.002
1200	49.300	96.253	62.339	40.697	- 106.078	15.251	- 2.777
1300	50.440	100.245	65.103	45.684	- 103.753	25.267	- 4.248
1400	51.507	104.022	67.749	50.782	- 101.332	35.101	- 5.479
1500	52.500	107.610	70.288	55.983	- 98.823	44.760	- 6.521

June 30, 1963

POTASSIUM PERCHLORATE ($KClO_4$) (CRYSTAL) MOL. WT. = 138.557

$\Delta H^\circ_{f\ 0}$ = -100.9 kcal. mole^{-1}

$S^\circ_{298.15}$ = 36.1 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -102.8 ± 1.0 kcal. mole^{-1}

T_t = 572.7°K.

ΔH°_t = 3.29 kcal. mole^{-1}

T_m = 798°K.

ΔH°_m = Unknown

Heat of Formation.

The heat of decomposition of $KClO_4(c)$ to $KCl(c)$ and $O_2(g)$ was measured by W. H. Johnson and A. A. Gilliland, J. Res. Natl. Bur. Std. 65A, 63 (1961), yielding $\Delta H^\circ_{f\ 298.15}$ = -103.22 ± 0.15 kcal. mole^{-1}. K. A. Hofmann and P. H. Marin, Sitzber. preuss. Akad. Wiss. Physik. math. Kl. 448 (1932), burned a mixture of paraffin and potassium perchlorate and obtained $\Delta E_{298.15}$ = -1.73 kcal. mole^{-1} for the constant volume process corresponding to the reaction: $KClO_4(c) = KCl(c) + 2O_2(g)$. Correction of their value for $\Delta(PV)$ gives $\Delta H^\circ_{r\ 298.15}$ = -0.55 kcal. mole^{-1} which agrees reasonably well to the corresponding value, -0.96 ± 0.10 kcal. mole^{-1}, reported by W. H. Johnson and A. A. Gilliland, loc. cit. However, for the same reaction, $\Delta H^\circ_{r\ 298.15}$ = -2.55 ± 0.18 kcal. mole^{-1} was determined by S. M. Skuratov, A. F. Vorob'ev and N. M. Privalova, Russ. J. Inorg. Chem. 7, 343 (1962). They measured this quantity by two different methods which gave concordant results. The value of $\Delta H^\circ_{f\ 298.15}$ reported was -101.9 ± 0.2 kcal. mole^{-1}. The value used here is the average of these four results. M. Berthelot and P. Vieille, Ann. chim. et phys. [5] 27, 225 (1882) determined the difference between the heat of explosion of ammonium picrate and that of an ammonium picrate-potassium perchlorate mixture, and also the difference between the heat of explosion of potassium picrate and that of a potassium picrate-potassium perchlorate mixture. They obtained ΔH°_r = 7.5 kcal. mole^{-1} for the reaction $KClO_4(c) = KCl(c) + 2O_2(g)$. From that the value of $\Delta H^\circ_{f\ 298.15}$ was calculated to be -111.9 kcal. mole^{-1}. This value was not used.

Heat Capacity and Entropy.

The low temperature heat capacities (12.53-298.07°K.) were measured by W. M. Latimer and J. E. Ahlberg, J. Am. Chem. Soc. 52, 549 (1930). The heat capacities above 298°K. were estimated by comparison with those of $NaClO_4(c)$. $S^\circ_{298.15}$ was reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961), based on the low temperature heat capacities measured by W. M. Latimer and J. E. Ahlberg, loc. cit., using $S^\circ_{12.59}$ (extrap.) = 0.14 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_t and ΔH°_t were obtained from the National Bureau of Standards, Circ. 500, "Selected Values of Chemical Thermodynamic Properties," by F. D. Rossini, et al., 1952.

Temperature of Melting.

T_m was taken from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

Lithium Chloride (LiCl)
(Crystal) Mol. Wt. = 42.397

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.224	-97.600	-97.600	INFINITE
100	8.679	3.247	23.574	-2.033	-97.878	-95.768	209.290
200	10.361	9.810	15.191	-1.076	-97.722	-93.720	102.408
298	11.479	14.173	14.173	.000	-97.578	-91.786	67.278
300	11.495	14.244	14.173	.021	-97.575	-91.751	66.837
400	12.182	17.652	14.633	1.207	-97.425	-89.831	49.079
500	12.749	20.432	15.523	2.454	-98.023	-87.874	38.408
600	13.287	22.804	16.544	3.756	-97.868	-85.857	31.272
700	13.810	24.892	17.590	5.111	-97.652	-83.873	26.185
800	14.325	26.769	18.622	6.518	-97.380	-81.923	22.379
900	14.833	28.486	19.624	7.976	-97.058	-80.009	19.428
1000	15.337	30.075	20.590	9.485	-96.687	-78.134	17.075
1100	15.839	31.560	21.521	11.043	-96.265	-76.299	15.158
1200	16.338	32.960	22.416	12.652	-95.794	-74.505	13.569
1300	16.838	34.287	23.279	14.311	-95.272	-72.752	12.230
1400	17.336	35.553	24.111	16.020	-94.700	-71.040	11.089
1500	17.831	36.766	24.914	17.778	-94.078	-69.372	10.107
1600	18.323	37.933	25.692	19.586	-93.405	-67.746	9.253
1700	18.817	39.059	26.445	21.443	-127.730	-64.836	8.335
1800	19.311	40.148	27.176	23.349	-126.776	-61.162	7.426
1900	19.805	41.205	27.887	25.305	-125.773	-57.543	6.619
2000	20.298	42.234	28.579	27.310	-124.723	-53.980	5.898

June 30, 1962

LITHIUM CHLORIDE (LiCl) (CRYSTAL) MOL. WT. = 42.397

ΔH_f° 298.15 = -97.578 ± 0.273 kcal mole^{-1}

$S^\circ_{298.15}$ = 14.173 ± 0.015 cal deg^{-1} mole^{-1}

T_m = 883 ± 2°K

ΔH_m = 4.74 ± 0.10 kcal mole^{-1}

Heat of Formation

The heat of formation was obtained as follows:

		ΔH_{298}(kcal mole^{-1})
(1)	$LiOH\cdot 100H_2O + HCl\cdot 100H_2O \rightarrow LiCl\cdot 201H_2O$ T. W. Richards and A. W. Rowe J. Am. Chem. Soc. 44, 684 (1922).	-13.704 ± 0.014
(2)	$Li(c) + 100H_2O(\ell) \rightarrow LiOH\cdot 100H_2O + 1/2\ H_2(g)$ S. R. Gunn and L. G. Green J. Am. Chem. Soc. 80, 4782 (1958).	-53.142 ± .019
(3)	$LiOH\cdot 1000H_2O \rightarrow LiOH\cdot 100H_2O + 900H_2O(\ell)$ T. W. Richards and A. W. Rowe, J. Am. Chem. Soc. 43, 770 (1921).	0.153 ± 0.040
(4)	$1/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow HCl(g)$ JANAF Tables.	-21.97 ± 0.09
(5)	$HCl(g) + 100H_2O(\ell) \rightarrow HCl\cdot 100H_2O$ C. M. Slansky, J. Am. Chem. Soc. 62, 2430 (1940), and J. M. Sturtevant, J. Am. Chem. Soc. 62, 3265 (1940).	-17.575 ± 0.100
(6)	$LiCl\cdot 201H_2O \rightarrow LiCl(c) + 201H_2O(\ell)$ E. Lange and F. Dürr, Z. phys. Chem. 121, 361 (1926).	8.660 ± 0.010
	(1) + (2) + (3) + (4) + (5) + (6) gives $Li(c) + 1/2\ Cl_2(g) \rightarrow LiCl(c)$	-97.578 ± 0.273

A direct calorimetric determination by H. Siemonsen and U. Siemonsen, Z. Electrochem. 56, 643 (1952) gave -94.8 ± 0.6 kcal mole^{-1}. However, the solution route was thought to be inherently more accurate and was adopted.

Heat Capacity and Entropy

The heat capacity between 15° and 325°K has been measured by D. A. Shirley, J. Am. Chem. Soc. 82, 3841 (1960) and by F. L. Oetting, W. E. Hatton and G. C. Sinke, unpublished work, Thermal Laboratory, Dow Chemical Company. The two sets of data are in substantial agreement and were plotted together and used to evaluate the entropy at 298°. The extrapolation to 0°K was done assuming a T^3 law and yielded S_{15} = 0.019 e.u. Above 298° T. B. Douglas, J. L. Dever and A. W. Harman, quoted in Natl. Bur. Standards Report 6297, have made enthalpy measurements to 1200°K. E. N. Rodigina, K. Z. Gomelski, and V. F. Luginina, Zhur. Neorg. Khim. 4, 975 (1959) also made enthalpy determinations to 1100°K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Melting and Transition Data

The melting point has been reported as follows: 880°K., Douglas et. al., loc. cit.; 883°K., Rodigina et al., loc. cit.; 883°K., H. M. Haendler, P. S. Bennett, and C. M. Wheeler, J. Electrochem. Soc. 106, 264 (1959); 879°K., H. Flood, O. Fykse and S. Urnes, Z. Electrochem. 59, 364 (1955); 879°K., H. von Wartenberg and H. Schulz, Z. Electrochem. 27, 568 (1921). The highest value of 883°K. was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas et al. yield a heat of fusion of 4.718 kcal mole^{-1}, those of Rodigina et al., 4.669 kcal mole^{-1}. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960) report a value of 4.76 ± 0.10 kcal mole^{-1} and quote 4.83 kcal mole^{-1} from a private communication from D. F. Smith. The average value ΔH_m = 4.74 ± 0.10 kcal mole^{-1} was adopted.

A transition at 838°K has been reported by Kislova andd Bergman, Russ. J. Inorg. Chem. 5, 1210 (1960) but is not supported by the enthalpy measurements quoted above.

Lithium Chloride (LiCl)

(Liquid) Mol. Wt. = 42.397

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	11,479	18,745	18,745	,000	- 93,394	- 88,965	65,210
300	11,495	18,816	18,745	,021	- 93,391	- 88,938	64,788
400	12,182	22,224	19,205	1,207	- 93,241	- 87,476	47,792
500	12,749	25,004	20,095	2,454	- 93,839	- 85,976	37,578
600	16,179	27,435	21,116	3,792	- 93,649	- 84,417	30,747
700	15,953	29,912	22,201	5,398	- 93,181	- 82,917	25,886
800	15,727	32,028	23,300	6,982	- 92,732	- 81,481	22,259
900	15,501	33,867	24,374	8,544	- 92,307	- 80,100	19,450
1000	15,275	35,489	25,406	10,082	- 91,905	- 78,766	17,214
1100	15,049	36,934	26,390	11,599	- 91,525	- 77,471	15,391
1200	14,822	38,234	27,324	13,092	- 91,170	- 76,210	13,879
1300	14,596	39,411	28,209	14,563	- 90,836	- 74,977	12,604
1400	14,370	40,485	29,048	16,011	- 90,525	- 73,768	11,515
1500	14,143	41,468	29,844	17,437	- 90,235	- 72,582	10,575
1600	13,914	42,374	30,599	18,840	- 89,967	- 71,413	9,754
1700	13,691	43,211	31,316	20,220	- 124,768	- 68,933	8,862
1800	13,467	43,987	31,999	21,578	- 124,363	- 65,659	7,972
1900	13,242	44,709	32,649	22,913	- 123,981	- 62,407	7,178
2000	13,015	45,382	33,269	24,226	- 123,623	- 59,177	6,466

June 30, 1962

LITHIUM CHLORIDE (LiCl) (LIQUID) MOL. WT. = 42.397

$\Delta H_f^\circ{}_{298.15} = -93.394$ kcal. mole^{-1}

$S^\circ_{298.15} = 18.745$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 883 \pm 2$°K

$\Delta H_m = 4.74 \pm 0.10$ kcal. mole^{-1}

T_b(equilibrium mixture) = 1656°K

T_b(monomeric gas) = 1701°K

Heat of Formation.

Obtained from that of the crystal by adding ΔH_m and $H_{883}-H_{298}$(c) and subtracting $H_{883}-H_{298}$(l).

Heat Capacity and Entropy.

The heat capacity from the melting point to 1100°K and 1200°K has been reported by E. N. Rodigina, K. Z. Gomelski, and V. F. Luginina, Zhur. Neorg. Khim. 4, 975 (1959) and T. B. Douglas, J. L. Dever, and A. W. Harman, quoted in Natl. Bur. of Standards Report 6297. The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H_T-H_{293.15} = 18.000T - 1.5 \times 10^{-3}T^2 - 2279$ cal. mole^{-1}, which fits to ± 0.3%. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy was calculated from that of the crystal in a manner analogous to the heat of formation.

Melting.

See table for crystal.

Boiling.

The equilibrium boiling point was taken from H. von Wartenburg and H. Schultz, Z. Electrochem. 27, 568 (1921) and the boiling point of the monomeric gas is defined as the temperature at which it reaches 1 atm. pressure. This was obtained from the free energy crossover between liquid and monomeric gas. The heat of vaporization to the monomeric gas was found from the tables to be 38.8 kcal. mole^{-1}.

Lithium Chloride (LiCl)

(Ideal Gas) Mol. Wt. = 42.397

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.166	-46.742	-46.742	INFINITE
100	6.978	42.859	57.562	-1.470	-46.516	-48.366	105.700
200	7.412	47.800	51.575	-.755	-46.601	-50.197	54.850
298	7.946	50.864	50.864	.000	-46.778	-51.926	38.061
300	7.954	50.913	50.864	.015	-46.782	-51.958	37.850
400	8.312	53.255	51.181	.829	-47.003	-53.651	29.312
500	8.534	55.135	51.790	1.673	-48.004	-55.208	24.130
600	8.677	56.705	52.482	2.534	-48.291	-56.620	20.623
700	8.775	58.050	53.184	3.407	-48.557	-57.988	18.104
800	8.847	59.227	53.867	4.288	-48.811	-59.319	16.204
900	8.901	60.272	54.522	5.175	-49.059	-60.617	14.719
1000	8.945	61.212	55.145	6.068	-49.304	-61.889	13.525
1100	8.981	62.067	55.736	6.964	-49.544	-63.135	12.543
1200	9.012	62.849	56.296	7.864	-49.782	-64.361	11.721
1300	9.040	63.572	56.828	8.766	-50.017	-65.566	11.022
1400	9.064	64.243	57.334	9.672	-50.248	-66.753	10.420
1500	9.087	64.869	57.816	10.579	-50.477	-67.925	9.896
1600	9.108	65.456	58.275	11.489	-50.702	-69.080	9.435
1700	9.128	66.009	58.714	12.401	-85.972	-68.893	8.856
1800	9.147	66.531	59.134	13.315	-86.010	-67.886	8.242
1900	9.165	67.026	59.537	14.230	-86.048	-66.877	7.692
2000	9.182	67.497	59.923	15.148	-86.086	-65.868	7.197
2100	9.199	67.945	60.294	16.067	-86.123	-64.858	6.750
2200	9.215	68.373	60.652	16.987	-86.162	-63.844	6.342
2300	9.232	68.783	60.997	17.910	-86.199	-62.828	5.970
2400	9.247	69.177	61.329	18.834	-86.238	-61.811	5.628
2500	9.263	69.554	61.651	19.759	-86.279	-60.792	5.314
2600	9.278	69.918	61.962	20.686	-86.320	-59.773	5.024
2700	9.294	70.268	62.263	21.615	-86.365	-58.752	4.755
2800	9.309	70.607	62.555	22.545	-86.411	-57.727	4.506
2900	9.324	70.934	62.838	23.477	-86.462	-56.703	4.273
3000	9.338	71.250	63.113	24.410	-86.515	-55.675	4.056
3100	9.353	71.556	63.381	25.344	-86.574	-54.645	3.852
3200	9.368	71.854	63.641	26.280	-86.636	-53.615	3.662
3300	9.382	72.142	63.894	27.218	-86.704	-52.582	3.482
3400	9.397	72.422	64.141	28.157	-86.776	-51.545	3.313
3500	9.411	72.695	64.382	29.097	-86.854	-50.510	3.154
3600	9.425	72.960	64.616	30.039	-86.939	-49.470	3.003
3700	9.440	73.219	64.845	30.982	-87.030	-48.429	2.860
3800	9.454	73.471	65.069	31.927	-87.127	-47.382	2.725
3900	9.468	73.716	65.287	32.873	-87.232	-46.334	2.596
4000	9.482	73.956	65.501	33.820	-87.344	-45.285	2.474
4100	9.496	74.191	65.710	34.769	-87.464	-44.232	2.358
4200	9.511	74.420	65.915	35.720	-87.592	-43.178	2.247
4300	9.525	74.644	66.115	36.672	-87.728	-42.118	2.141
4400	9.539	74.863	66.312	37.625	-87.872	-41.053	2.039
4500	9.553	75.077	66.504	38.579	-88.027	-39.989	1.942
4600	9.567	75.287	66.693	39.535	-88.191	-38.920	1.849
4700	9.581	75.493	66.878	40.493	-88.365	-37.848	1.760
4800	9.595	75.695	67.059	41.451	-88.550	-36.773	1.674
4900	9.609	75.893	67.238	42.412	-88.747	-35.691	1.592
5000	9.623	76.087	67.413	43.373	-88.955	-34.605	1.512
5100	9.636	76.278	67.585	44.336	-89.177	-33.513	1.436
5200	9.650	76.465	67.754	45.300	-89.413	-32.420	1.362
5300	9.664	76.649	67.920	46.266	-89.663	-31.325	1.292
5400	9.678	76.830	68.083	47.233	-89.929	-30.221	1.223
5500	9.692	77.008	68.244	48.202	-90.212	-29.111	1.157
5600	9.706	77.183	68.402	49.172	-90.511	-28.001	1.093
5700	9.720	77.354	68.557	50.143	-90.830	-26.881	1.031
5800	9.734	77.524	68.711	51.116	-91.169	-25.754	.970
5900	9.748	77.690	68.861	52.090	-91.528	-24.625	.912
6000	9.761	77.854	69.010	53.065	-91.909	-23.486	.855

June 30, 1962

LITHIUM CHLORIDE (LiCl) (IDEAL GAS) MOL. WT. = 42.397

$\Delta H_{f0}^\circ = -46.742$ kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -46.778 \pm 3.0$ kcal. mole^{-1}

Ground State Configuration $^1\Sigma$

$S_{298.15}^\circ = 50.864$ cal. deg.$^{-1}$ mole^{-1}

$\omega_e = 641.1 \pm 3.0$ cm.$^{-1}$

$\omega_e x_e = 4.2 \pm 0.3$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.7053$ cm.$^{-1}$

$\alpha_e = 0.0067$ cm.$^{-1}$

$r_e = 2.022$ Å

Heat of Formation.

W. Klemperer, W. G. Norris, A. Büchler and A. G. Emslie, J. Chem. Phys. 33, 1534 (1960) quote a private communication from W. H. Evans at the National Bureau of Standards giving $D_0^\circ = 4.85$ e.v., which corresponds to $\Delta H_{f0}^\circ = -45.3 \pm 2.4$ kcal. mole^{-1}. A third law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) in conjunction with the relative concentration of monomer, dimer, and trimer at 870°K from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956) and 27, 981 (1957) leads to a monomer heat of sublimation at 298° of 52.56 kcal. mole^{-1}, this gives $\Delta H_{f\ 298.15}^\circ = -45.02$ kcal. mole^{-1}. These values lead, however, to partial vapor pressures of the monomer which are less than half of the total vapor pressure near the boiling point. From the data of Miller and Kusch loc. cit. it would be expected that the monomer would be the predominant species near the boiling point, a fact also substantiated by the work of C. Beusman, AEC Report ORNL-2323 (1957), on the average molecular weight of the vapor. Thus it was decided to change the heat of sublimation so as to give the correct normal boiling point and vapor pressures in the region 1400-1600°K and to approximate the relative concentrations of monomer, dimer, and trimer as found by Miller and Kusch at 870°K. A monomer heat of sublimation at 298° of 50.8 kcal. mole^{-1} was chosen, which gives $\Delta H_{f\ 298.15}^\circ = -46.778$ kcal. mole^{-1}. The normal boiling point was taken as 1656°K as determined by H. von Wartenburg and H. Schulz, Z. Electrochem 27, 568 (1921) and the boiling point of LiCl(g) was found as 1701°K from the free energy crossover between liquid and gas.

Heat Capacity and Entropy.

The spectroscopic constants were taken from Klemperer et al. loc. cit. The value of α_e was calculated from the value of a_1 given by the Rittner potential function and the equation given by Klemperer et al. The value of r_e was taken from the Natl. Bur. of Standards Report 6297 (1959).

Lithium Hypochlorite (LiClO)

(Ideal Gas) Mol. Wt. = 58.397 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	,000	,000	INFINITE	-2,594	-2,755	-2,755	INFINITE
100	8,035	51,578	69,559	-1,798	-2,773	-3,427	7,489
200	9,061	57,415	62,166	-,950	-3,076	-3,972	4,340
298	10,268	61,264	61,264	,000	-3,400	-4,342	3,183
300	10,289	61,328	61,264	,019	-3,406	-4,348	3,167
400	11,240	64,425	61,680	1,098	-3,718	-4,614	2,521
500	11,915	67,010	62,495	2,258	-4,768	-4,727	2,066
600	12,387	69,227	63,436	3,474	-5,077	-4,689	1,708
700	12,720	71,163	64,405	4,731	-5,349	-4,603	1,437
800	12,960	72,878	65,359	6,015	-5,598	-4,480	1,224
900	13,137	74,415	66,281	7,320	-5,836	-4,326	1,050
1000	13,270	75,806	67,165	8,641	-6,066	-4,145	,906
1100	13,372	77,076	68,009	9,973	-6,290	-3,942	,783
1200	13,453	78,243	68,814	11,315	-6,511	-3,719	,677
1300	13,517	79,323	69,581	12,663	-6,728	-3,477	,585
1400	13,568	80,326	70,314	14,018	-6,944	-3,219	,503
1500	13,610	81,264	71,013	15,377	-7,157	-2,947	,429
1600	13,645	82,143	71,681	16,740	-7,368	-2,658	,363
1700	13,675	82,971	72,321	18,106	-42,625	-1,030	,132
1800	13,699	83,754	72,935	19,474	-42,655	1,419	-,172
1900	13,720	84,495	73,524	20,845	-42,685	3,870	-,445
2000	13,738	85,199	74,090	22,218	-42,717	6,320	-,691
2100	13,754	85,870	74,635	23,593	-42,754	8,771	-,913
2200	13,768	86,510	75,161	24,969	-42,792	11,227	-1,115
2300	13,780	87,122	75,667	26,346	-42,833	13,683	-1,300
2400	13,790	87,709	76,157	27,725	-42,879	16,140	-1,470
2500	13,800	88,272	76,630	29,104	-42,929	18,602	-1,626
2600	13,808	88,814	77,089	30,485	-42,983	21,063	-1,770
2700	13,815	89,335	77,533	31,866	-43,042	23,528	-1,904
2800	13,822	89,837	77,963	33,248	-43,107	25,995	-2,029
2900	13,828	90,323	78,381	34,630	-43,178	28,462	-2,145
3000	13,833	90,791	78,787	36,013	-43,254	30,935	-2,253
3100	13,838	91,245	79,182	37,397	-43,339	33,411	-2,355
3200	13,842	91,685	79,565	38,781	-43,429	35,887	-2,451
3300	13,847	92,111	79,939	40,165	-43,527	38,367	-2,541
3400	13,850	92,524	80,303	41,550	-43,632	40,851	-2,626
3500	13,854	92,925	80,658	42,935	-43,745	43,337	-2,706
3600	13,857	93,316	81,004	44,321	-43,868	45,825	-2,782
3700	13,860	93,695	81,342	45,707	-43,998	48,317	-2,854
3800	13,862	94,065	81,672	47,093	-44,137	50,819	-2,923
3900	13,865	94,425	81,995	48,479	-44,286	53,319	-2,988
4000	13,867	94,776	82,310	49,866	-44,445	55,822	-3,050
4100	13,869	95,119	82,618	51,253	-44,612	58,332	-3,109
4200	13,871	95,453	82,920	52,640	-44,792	60,845	-3,166
4300	13,873	95,779	83,215	54,027	-44,981	63,360	-3,220
4400	13,874	96,098	83,504	55,414	-45,181	65,885	-3,272
4300	13,876	96,410	83,788	56,802	-45,393	68,411	-3,322
4600	13,878	96,715	84,065	58,189	-45,617	70,942	-3,370
4700	13,879	97,014	84,338	59,577	-45,853	73,477	-3,417
4800	13,880	97,306	84,605	60,965	-46,104	76,016	-3,461
4900	13,882	97,592	84,867	62,353	-46,368	78,565	-3,504
5000	13,883	97,872	85,124	63,741	-46,646	81,120	-3,546
5100	13,884	98,147	85,377	65,130	-46,940	83,677	-3,586
5200	13,885	98,417	85,625	66,518	-47,250	86,242	-3,624
5300	13,886	98,682	85,869	67,907	-47,577	88,810	-3,662
5400	13,887	98,941	86,109	69,295	-47,922	91,387	-3,698
5500	13,888	99,196	86,344	70,684	-48,287	93,971	-3,734
5600	13,888	99,446	86,576	72,073	-48,671	96,559	-3,768
5700	13,889	99,692	86,804	73,462	-49,076	99,158	-3,802
5800	13,890	99,934	87,028	74,851	-49,505	101,762	-3,834
5900	13,891	100,171	87,249	76,240	-49,955	104,375	-3,866
6000	13,891	100,404	87,466	77,629	-50,430	106,993	-3,897

December 31, 1960.

LITHIUM HYPOCHLORITE (LiClO) (Ideal Gas)

Mol. Wt. = 58.397

ΔH_f° 298.15 = [-3.4 ± 20] kcal. mole^{-1}

$S^\circ_{298.15}$ = [61.264] cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω cm.$^{-1}$
[1150](1).
[500](1)
[700](1)

Li-O-Cl angle 115°, Li-O dist. 1.82 Å, O-Cl dist. 1.73 Å $\sigma = 1$.

Data from D. L. Hildenbrand, Aeronutronic Division of Ford Motor Company, Newport Beach, Calif., "Tables of Thermodynamic Data for Performance Calculations", September, 1959.

Lithium Perchlorate ($LiClO_4$)
(Crystal) Mol. Wt. = 106.397

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	25.100	30.000	30.000	.000	-91.000	-60.706	44.497
300	25.200	30.156	30.000	.047	-90.998	-60.519	44.086
400	31.000	38.181	31.056	2.850	-90.652	-50.398	27.535
500	34.300	45.499	33.228	6.136	-90.673	-40.336	17.630
600	36.500	51.964	35.822	9.685	-89.781	-30.349	11.054
700	38.333	57.733	38.548	13.430	-88.732	-20.525	6.408
800	39.800	62.952	41.277	17.340	-87.553	-10.863	2.968
900	41.150	67.719	43.954	21.389	-86.268	-1.352	.328
1000	42.300	72.116	46.553	25.563	-84.885	8.011	-1.751
1100	43.325	76.197	49.065	29.645	-83.417	17.229	-3.423
1200	44.200	80.005	51.486	34.223	-81.873	26.311	-4.792
1300	45.140	83.580	53.819	38.690	-80.257	35.261	-5.928
1400	46.073	86.960	56.066	43.251	-78.561	44.084	-6.881
1500	47.000	90.170	58.234	47.904	-76.786	52.783	-7.690

Dec. 31, 1960; June 30, 1963; Mar. 31, 1964

LITHIUM PERCHLORATE ($LiClO_4$) (CRYSTAL) MOL. WT. = 106.397

$\Delta H_{f\ 0}^\circ$ = Unknown

$S_{298.15}^\circ$ = [30 ± 1] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = -91.0 ± 0.7 kcal. mole^{-1}

T_m = 509°K.

ΔH_m° = [7] kcal. mole^{-1}

Heat of Formation.

The heats of reaction (ΔH_r°) involving $LiClO_4(c)$ has been determined by several investigators as follows:

Investigator	Chemical Reaction	$\Delta H_{r\ 298.15}^\circ$, kcal. mole^{-1}	$\Delta H_{f\ 298.15}^\circ$, kcal. mole^{-1}
Gilliland and Johnson(1)	$LiClO_4(c) + KCl(c) \rightarrow LiCl(c) + KClO_4(c)$	-5.86 ± 0.06	-90.34
Markowitz, et al.(2)	$LiOH(225H_2O) + HClO_4(225H_2O) \rightarrow LiClO_4(451H_2O) + H_2O(l)$	-13.54 ± 0.09	-91.7
Birky and Hepler(3)	$LiClO_4(c) \rightarrow Li^+(aq.) + ClO_4^-(aq.)$	-6.31 ± 0.13	-91.11

(1) A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961).

(2) M. M. Markowitz, R. F. Harris and H. Stewart, Jr., J. Phys. Chem. 63, 1325 (1959).

(3) M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960).

The adopted value, $\Delta H_{f\ 298.15}^\circ$ = -91.0 kcal. mole^{-1}, for $LiClO_4(c)$ is the weighted average of the three values listed.

Heat Capacity and Entropy.

Heat capacities and $S_{298.15}^\circ$ were estimated by comparison with those of $KClO_4(c)$.

Melting Data.

T_m was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910). The value of $\Delta H_{m\ 509}^\circ$ was estimated by comparison with the value, $\Delta H_{m\ 528}^\circ$ = 5.4 kcal. mole^{-1}, for $NaClO_3(c)$ reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

Lithium Perchlorate ($LiClO_4$)

(Liquid) Mol. Wt. = 106.397

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	38.500	39.245	39.245	- .000	- 85.684	- 58.146	42.620
300	38.500	39.483	39.246	.071	- 85.657	- 57.976	42.234
400	38.500	50.559	40.756	3.921	- 84.265	- 48.962	26.750
500	38.500	59.150	43.607	7.771	- 83.722	- 40.210	17.575
600	38.500	66.169	46.801	11.621	- 82.529	- 31.620	11.517
700	38.500	72.104	50.002	15.471	- 81.374	- 23.228	7.252
800	38.500	77.245	53.094	19.321	- 80.255	- 15.001	4.098
900	38.500	81.780	56.034	23.171	- 79.169	- 6.908	1.677
1000	38.500	85.836	58.815	27.021	- 78.110	1.065	- .233
1100	38.500	89.506	61.441	30.871	- 77.075	8.931	- 1.774
1200	38.500	92.855	63.921	34.721	- 76.059	16.705	- 3.042
1300	38.500	95.937	66.267	38.571	- 75.060	24.395	- 4.101
1400	38.500	98.790	68.489	42.421	- 74.075	32.008	- 4.996
1500	38.500	101.447	70.599	46.271	- 73.103	39.551	- 5.762

Dec. 31, 1960; Mar. 31, 1964

LITHIUM PERCHLORATE ($LiClO_4$) (LIQUID) MOL. WT. = 106.397

$S^\circ_{298.15}$ = [39.245] cal. deg.$^{-1}$ mole^{-1}

T_m = 509°K.

$\Delta H^\circ_{f\ 298.15}$ = [-85.574] cal. deg.$^{-1}$ mole^{-1}

ΔH°_m = [7] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$(l) was obtained from $\Delta H^\circ_{f\ 298.15}$(c) by adding ΔH°_m and the difference between $H^\circ_{370.6}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p for $LiClO_4$(l) was estimated by comparison with that for $NaClO_3$(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature (T_m) was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910). The value of $\Delta H^\circ_{m\ 509}$ was estimated by comparison with the value, $\Delta H^\circ_{m\ 528}$ = 5.4 kcal. mole^{-1}, for $NaClO_3$(c) reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

Magnesium Monochloride (MgCl)

(Ideal Gas) Mol. Wt. = 59.765

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	-2.237	-10.344	-10.344	INFINITE
100	7.077	47.399	62.801	-1.540	-10.152	-12.405	27.111
200	7.830	52.531	56.508	-.795	-10.329	-14.713	16.078
298	8.324	55.760	55.760	.000	-10.400	-16.751	12.279
300	8.330	55.812	55.760	.015	-10.403	-16.791	12.232
400	8.587	58.247	56.091	.863	-10.585	-18.894	10.323
500	8.730	60.180	56.722	1.729	-10.787	-20.946	9.156
600	8.819	61.780	57.436	2.607	-11.013	-22.959	8.363
700	8.878	63.145	58.156	3.492	-11.260	-24.930	7.784
800	8.922	64.333	58.856	4.382	-11.537	-26.865	7.339
900	8.956	65.386	59.524	5.276	-11.849	-28.762	6.984
1000	8.983	66.331	60.158	6.173	-14.318	-30.442	6.653
1100	9.007	67.188	60.759	7.073	-14.669	-32.038	6.365
1200	9.027	67.973	61.328	7.974	-15.045	-33.602	6.120
1300	9.046	68.696	61.867	8.878	-15.445	-35.132	5.906
1400	9.063	69.367	62.379	9.783	-46.236	-36.151	5.643
1500	9.079	69.993	62.866	10.691	-46.278	-35.429	5.162
1600	9.094	70.580	63.330	11.599	-46.321	-34.706	4.741
1700	9.109	71.131	63.773	12.509	-46.362	-33.976	4.368
1800	9.123	71.652	64.196	13.421	-46.403	-33.247	4.037
1900	9.136	72.146	64.602	14.334	-46.442	-32.515	3.740
2000	9.150	72.615	64.991	15.248	-46.482	-31.781	3.473
2100	9.163	73.062	65.365	16.164	-46.521	-31.047	3.231
2200	9.175	73.488	65.724	17.081	-46.560	-30.307	3.011
2300	9.188	73.896	66.071	17.999	-46.599	-29.566	2.809
2400	9.200	74.288	66.405	18.918	-46.637	-28.827	2.625
2500	9.212	74.664	66.728	19.839	-46.676	-28.086	2.455
2600	9.225	75.025	67.040	20.761	-46.715	-27.338	2.298
2700	9.237	75.373	67.342	21.684	-46.755	-26.592	2.153
2800	9.249	75.710	67.635	22.608	-46.795	-25.848	2.018
2900	9.261	76.034	67.919	23.534	-46.836	-25.096	1.891
3000	9.272	76.349	68.195	24.460	-46.879	-24.349	1.774
3100	9.284	76.653	68.463	25.388	-46.924	-23.596	1.664
3200	9.296	76.948	68.724	26.317	-46.971	-22.845	1.560
3300	9.308	77.234	68.977	27.247	-47.020	-22.089	1.463
3400	9.319	77.512	69.224	28.179	-47.072	-21.329	1.371
3500	9.331	77.782	69.465	29.111	-47.128	-20.574	1.285
3600	9.343	78.045	69.700	30.045	-47.188	-19.812	1.203
3700	9.354	78.301	69.929	30.980	-47.252	-19.049	1.125
3800	9.366	78.551	70.152	31.916	-47.320	-18.288	1.052
3900	9.377	78.794	70.371	32.853	-47.394	-17.524	.982
4000	9.389	79.032	70.584	33.791	-47.473	-16.757	.916
4100	9.400	79.264	70.793	34.731	-47.559	-15.989	.852
4200	9.412	79.491	70.998	35.671	-47.652	-15.222	.792
4300	9.423	79.712	71.198	36.613	-47.752	-14.446	.734
4400	9.435	79.929	71.394	37.556	-47.858	-13.668	.679
4500	9.446	80.141	71.586	38.500	-47.974	-12.889	.626
4600	9.457	80.349	71.774	39.445	-48.097	-12.109	.575
4700	9.469	80.552	71.959	40.391	-48.229	-11.322	.526
4800	9.480	80.752	72.140	41.339	-48.372	-10.538	.480
4900	9.492	80.948	72.317	42.287	-48.524	-9.750	.435
5000	9.503	81.139	72.492	43.237	-48.685	-8.953	.391
5100	9.515	81.328	72.663	44.188	-48.858	-8.163	.350
5200	9.526	81.513	72.832	45.140	-49.042	-7.361	.309
5300	9.537	81.694	72.997	46.093	-49.237	-6.554	.270
5400	9.549	81.872	73.160	47.047	-49.445	-5.748	.233
5500	9.560	82.048	73.320	48.003	-49.665	-4.939	.196
5600	9.571	82.220	73.477	48.959	-49.898	-4.123	.161
5700	9.583	82.390	73.632	49.917	-50.144	-3.304	.127
5800	9.594	82.556	73.785	50.876	-50.404	-2.478	.093
5900	9.605	82.721	73.935	51.836	-50.679	-1.652	.061
6000	9.617	82.882	74.083	52.797	-50.967	-.819	.030

Dec. 31, 1960; Mar 31, 1966

MAGNESIUM MONOCHLORIDE (MgCl) (IDEAL GAS) MOL. WT. = 59.765

Ground State Configuration $^2\Sigma$

$S^\circ_{298.15}$ = 55.760 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -10.34 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -10.4 ± 10 kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_1, cm.$^{-1}$	g_1
0	2

ω_e = 462.4 cm.$^{-1}$

$\omega_e x_e$ = 2.02 cm.$^{-1}$

σ = 1

B_e = [0.2417] cm.$^{-1}$

α_e = [0.0014] cm.$^{-1}$

r_e = 2.199 Å

Heat of Formation.

The heat of formation is calculated from D_0° = 3.2 e.v. reported by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York, 1950. D_0° = 2.7 ± 0.7 e.v. reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London, 1953, yields $\Delta H^\circ_{f\ 298}$ (MgCl, g) = 1.0 ± 16 kcal. mole^{-1}.

Heat Capacity and Entropy.

Spectroscopic constants were reported by Herzberg loc. cit. and adjusted for natural isotopic abundance. The bond length was reported by E. Morgan and R. F. Barrow, Nature 192, 1182, (1961). B_e and α_e were estimated by the method suggested by Herzberg loc. cit. The moment of inertia (I) is 11.578 X 10^{-39} g. cm.^{2}

Magnesium Monochloride Unipositive Ion ($MgCl^+$)

(Ideal Gas) GFW = 59.76445

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.472	54.600	54.600	.000	156.000	148.508	-108.859
300	8.477	54.652	54.600	.016	156.006	148.461	-108.154
400	8.693	57.124	54.935	.875	156.334	145.895	-79.713
500	8.813	59.078	55.575	1.751	156.638	143.251	-62.615
600	8.887	60.691	56.297	2.636	156.917	140.546	-51.194
700	8.940	62.066	57.026	3.528	157.172	137.797	-43.022
800	8.980	63.262	57.732	4.424	157.398	135.013	-36.884
900	9.013	64.322	58.406	5.324	157.588	132.204	-32.104
1000	9.044	65.273	59.046	6.227	155.622	129.556	-28.314
1100	9.077	66.136	59.652	7.133	155.775	126.941	-25.221
1200	9.115	66.928	60.226	8.042	155.904	124.314	-22.641
1300	9.165	67.659	60.770	8.956	156.010	121.676	-20.456
1400	9.230	68.341	61.287	9.876	125.731	119.512	-18.657
1500	9.314	68.980	61.778	10.803	126.205	119.051	-17.346
1600	9.420	69.585	62.248	11.739	126.687	118.557	-16.194
1700	9.549	70.159	62.696	12.687	127.181	118.036	-15.175
1800	9.702	70.709	63.126	13.650	127.687	117.482	-14.264
1900	9.879	71.239	63.539	14.629	128.211	116.903	-13.447
2000	10.076	71.750	63.937	15.626	128.751	116.293	-12.708
2100	10.291	72.247	64.321	16.644	129.311	115.654	-12.036
2200	10.521	72.731	64.692	17.685	129.893	114.992	-11.423
2300	10.761	73.204	65.052	18.749	130.496	114.301	-10.861
2400	11.008	73.667	65.402	19.837	131.124	113.584	-10.343
2500	11.256	74.122	65.741	20.951	131.775	112.838	-9.864
2600	11.502	74.568	66.072	22.088	132.449	112.069	-9.420
2700	11.742	75.006	66.395	23.251	133.145	111.273	-9.007
2800	11.972	75.438	66.710	24.436	133.863	110.448	-8.621
2900	12.191	75.862	67.019	25.645	134.601	109.600	-8.260
3000	12.394	76.278	67.320	26.874	135.358	108.723	-7.920
3100	12.582	76.688	67.616	28.123	136.131	107.822	-7.601
3200	12.752	77.090	67.906	29.390	136.919	106.898	-7.301
3300	12.903	77.485	68.190	30.673	137.719	105.948	-7.017
3400	13.037	77.872	68.469	31.970	138.529	104.976	-6.748
3500	13.151	78.252	68.743	33.280	139.347	103.974	-6.492
3600	13.248	78.624	69.013	34.600	140.171	102.954	-6.250
3700	13.328	78.988	69.277	35.929	140.998	101.907	-6.019
3800	13.391	79.344	69.537	37.265	141.827	100.840	-5.800
3900	13.440	79.693	69.793	38.606	142.655	99.749	-5.590
4000	13.474	80.033	70.045	39.952	143.479	98.638	-5.389
4100	13.496	80.366	70.293	41.301	144.299	97.505	-5.197
4200	13.506	80.692	70.537	42.651	145.113	96.355	-5.014
4300	13.506	81.009	70.776	44.002	145.919	95.184	-4.838
4400	13.497	81.320	71.013	45.352	146.717	93.999	-4.669
4500	13.480	81.623	71.245	46.701	147.502	92.789	-4.506
4600	13.456	81.919	71.474	48.048	148.278	91.567	-4.350
4700	13.427	82.208	71.699	49.392	149.040	90.325	-4.200
4800	13.393	82.490	71.921	50.733	149.788	89.067	-4.055
4900	13.355	82.766	72.140	52.070	150.522	87.797	-3.916
5000	13.313	83.036	72.355	53.404	151.240	86.510	-3.781
5100	13.269	83.299	72.567	54.733	151.943	85.203	-3.651
5200	13.223	83.556	72.776	56.057	152.628	83.893	-3.526
5300	13.176	83.807	72.981	57.377	153.297	82.564	-3.405
5400	13.127	84.053	73.184	58.693	153.948	81.219	-3.287
5500	13.078	84.294	73.384	60.003	154.579	79.869	-3.174
5600	13.029	84.529	73.581	61.308	155.191	78.500	-3.064
5700	12.981	84.759	73.775	62.609	155.785	77.133	-2.957
5800	12.932	84.984	73.966	63.904	156.359	75.743	-2.854
5900	12.884	85.205	74.155	65.195	156.912	74.350	-2.754
6000	12.837	85.421	74.341	66.481	157.445	72.946	-2.657

June 30, 1968

MAGNESIUM MONOCHLORIDE UNIPOSITIVE ION ($MgCl^+$) (IDEAL GAS) GFW = 59.76445

Ground State Configuration $[^1\Sigma]$

ΔHf°_0 = 156 ± 20 kcal/mol

$S^\circ_{298.15}$ = [54.6 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 156 ± 20 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^3\pi_u$	[9000]	6
$^1\pi_u$	[11000]	2
$^3\Sigma_g^-$	[20000]	3
$^1\Delta$	[25000]	2
$^1\Sigma^+$	[30000]	1

ω_e = [400] cm^{-1} $\omega_e x_e$ = [2] cm^{-1} σ = 1

B_e = [0.2415] cm^{-1} α_e = [0.00164] cm^{-1} r_e = [2.2] Å

Heat of Formation

The ionization potential of MgCl(g) was reported to be 7.2, 7.5 ± 0.5, and 7 ± 1 eV by Krasnov (1), Hildenbrand (9), and Beckett (2), respectively. The corresponding heats of formation at 298°K for $MgCl^+$(g) are derived as 156, 163, and 151 kcal/mol, using ΔHf°_0(MgCl, g) = -10.34 kcal/mol from the JANAF MgCl(g) table (March 31, 1966). The value of ΔHf°_{298} for $MgCl^+$(g) is tentatively selected as 156 ± 20 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as NaCl(g) which is isoelectronic with $MgCl^+$(g). The six electronic states are obtained from Fougere (3). The corresponding electronic levels are estimated by comparison with the isoelectronic molecules BeS (4), BeO (5, 6), and MgO (5, 7). The bond distance is estimated by the method suggested by Krasnov (8). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for MgCl(g) and NaCl(g). B_e and α_e are calculated by the method recommended by Herzberg (5). The moment of inertia is 1.159 x 10^{-38} g cm^2. The enthalpy at 0°K is -2.27 kcal/mol.

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Nitrosyl Chloride (NOCl)

(Ideal Gas)   Mol. Wt. = 65.4591

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	- 2.713	12.828	12.828	INFINITE
100	8.367	52.217	71.347	- 1.913	12.578	13.598	- 29.716
200	9.731	58.445	67.995	- 1.910	11.529	13.778	- 15.055
298	10.680	62.527	62.527	.000	12.370	15.800	- 11.581
300	10.694	62.593	62.527	.020	12.369	15.821	- 11.525
400	11.311	65.757	62.954	1.121	12.352	16.975	- 9.275
500	11.790	68.334	63.781	2.277	12.364	18.131	- 7.925
600	12.196	70.521	64.726	3.477	12.396	19.282	- 7.023
700	12.535	72.427	65.693	4.714	12.441	20.426	- 6.377
800	12.827	74.120	66.642	5.982	12.496	21.562	- 5.890
900	13.069	75.645	67.559	7.277	12.559	22.692	- 5.510
1000	13.273	77.033	68.438	8.595	12.629	23.814	- 5.204
1100	13.446	78.306	69.278	9.931	12.703	24.929	- 4.953
1200	13.597	79.483	70.080	11.283	12.781	26.037	- 4.742
1300	13.726	80.577	70.846	12.649	12.862	27.138	- 4.562
1400	13.841	81.598	71.578	14.028	12.946	28.233	- 4.407
1500	13.943	82.557	72.278	15.417	13.033	29.321	- 4.272
1600	14.035	83.459	72.949	16.816	13.121	30.406	- 4.153
1700	14.120	84.313	73.593	18.224	13.212	31.483	- 4.047
1800	14.195	85.122	74.211	19.640	13.303	32.555	- 3.953
1900	14.266	85.891	74.806	21.063	13.396	33.625	- 3.868
2000	14.335	86.625	75.379	22.493	13.490	34.685	- 3.790
2100	14.396	87.326	75.931	23.929	13.585	35.741	- 3.719
2200	14.458	87.997	76.464	25.372	13.680	36.794	- 3.655
2300	14.515	88.641	76.980	26.821	13.777	37.843	- 3.596
2400	14.570	89.260	77.479	28.275	13.874	38.888	- 3.541
2500	14.623	89.856	77.962	29.735	13.970	39.926	- 3.490
2600	14.675	90.430	78.430	31.200	14.068	40.965	- 3.443
2700	14.724	90.985	78.885	32.670	14.166	41.997	- 3.399
2800	14.771	91.521	79.327	34.144	14.263	43.027	- 3.358
2900	14.820	92.041	79.756	35.624	14.361	44.051	- 3.320
3000	14.866	92.544	80.174	37.108	14.458	45.073	- 3.283
3100	14.910	93.032	80.581	38.597	14.556	46.092	- 3.249
3200	14.957	93.506	80.978	40.090	14.653	47.108	- 3.217
3300	14.997	93.967	81.364	41.588	14.751	48.120	- 3.187
3400	15.044	94.415	81.742	43.090	14.849	49.133	- 3.158
3500	15.083	94.852	82.110	44.597	14.947	50.136	- 3.130
3600	15.126	95.277	82.470	46.107	15.044	51.143	- 3.105
3700	15.169	95.692	82.822	47.622	15.143	52.145	- 3.080
3800	15.210	96.098	83.166	49.141	15.243	53.140	- 3.056
3900	15.251	96.493	83.502	50.664	15.343	54.138	- 3.034
4000	15.292	96.880	83.832	52.191	15.443	55.129	- 3.012
4100	15.333	97.258	84.155	53.722	15.545	56.121	- 2.991
4200	15.371	97.628	84.471	55.257	15.648	57.108	- 2.972
4300	15.411	97.990	84.782	56.796	15.752	58.097	- 2.953
4400	15.454	98.345	85.086	58.340	15.858	59.079	- 2.934
4500	15.491	98.693	85.384	59.887	15.964	60.058	- 2.917
4600	15.530	99.033	85.677	61.438	16.074	61.044	- 2.900
4700	15.570	99.368	85.965	62.993	16.184	62.017	- 2.884
4800	15.608	99.696	86.248	64.552	16.297	62.991	- 2.868
4900	15.647	100.018	86.525	66.115	16.412	63.961	- 2.853
5000	15.688	100.335	86.799	67.681	16.529	64.929	- 2.838
5100	15.721	100.646	87.067	69.252	16.648	65.896	- 2.824
5200	15.766	100.952	87.331	70.826	16.771	66.860	- 2.810
5300	15.798	101.252	87.591	72.404	16.895	67.825	- 2.797
5400	15.838	101.548	87.847	73.986	17.022	68.781	- 2.784
5500	15.878	101.839	88.098	75.572	17.152	69.743	- 2.771
5600	15.911	102.125	88.346	77.161	17.283	70.696	- 2.759
5700	15.951	102.407	88.591	78.754	17.418	71.648	- 2.747
5800	16.002	102.685	88.831	80.352	17.557	72.602	- 2.736
5900	16.027	102.959	89.068	81.954	17.698	73.544	- 2.724
6000	16.066	103.228	89.302	83.558	17.841	74.496	- 2.713

June 30, 1961; Dec. 31, 1965

NITROSYL CHLORIDE (NOCl)   (IDEAL GAS)   MOL. WT. = 65.4591

Point Group C_s

$S^\circ_{298.15}$ = 62.53 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 12.83 ± 0.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 12.37 ± 0.2 kcal. mole^{-1}

Vibrational Frequencies & Degeneracies

ω, cm.$^{-1}$
1800 (1)
594.9 (1)
331.5 (1)

Bond Distance: N-Cl = 1.95 ± 0.06 Å   N-O = 1.17 ± 0.06 Å

Bond Angle: Cl-N-O = 114 ± 3°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.278778 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constants for the reaction $2NOCl(g) = 2NO(g) + Cl_2(g)$ have been measured in the temperature range from 372° to 491°K. by C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1938). Using the reported equilibrium constants, the heat of reaction ($\Delta H^\circ_{r\ 298}$) has been calculated by both the second and the third law methods, as 18.33 ± 0.1 kcal. mole^{-1} and 18.42 ± 0.1 kcal. mole^{-1}, respectively. The third law value is adopted to calculate the heat of formation of nitrosyl chloride (g) as $\Delta H^\circ_{f\ 298}$ = 12.37 ± 0.2 kcal. mole^{-1}.

Heat Capacity and Entropy.

The selected bond distances and angle were obtained from the microwave measurements by J. D. Rogers and D. Williams, J. Chem. Phys. 34, 2195 (1961). J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. 59, 2629 (1937), reported the bond distance N-Cl = 1.95 Å and the angle O-N-Cl = 116° by the electron diffraction method. These two are in good agreement. The three principal moments of inertia are I_A = 0.9895 X 10^{-39}, I_B = 14.6885 X 10^{-39} and I_C = 15.6780 X 10^{-39} g. cm.^{2} The selected vibrational frequencies which were obtained from the infrared spectrum by L. Landau and W. H. Fletcher, J. Mol. Spectry. 4, 276 (1960), have been modified to natural isotopic mixture. W. G. Burns and J. J. Bernstein, J. Chem. Phys. 18, 1669 (1950), reported the vibrational frequencies as 1799, 592 and 332 cm.$^{-1}$

J. S. Gordon, J. Chem. Eng. Data 7, 82 (1962), has calculated the thermodynamic functions from 298.15° to 6000°K. by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from Landau and Fletcher, loc. cit., and J. D. Rogers, W. J. Pietenpol and D. Williams, Phys. Rev. 83, 431 (1951). These calculated functions have been adopted in the tabulation. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions.

Nitryl Chloride (NO_2Cl)

(Ideal Gas) Mol. Wt. = 81.4585

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.916	4.192	4.192	INFINITE
100	8.441	53.818	74.938	- 2.112	3.590	6.525	- 14.261
200	10.744	60.355	66.133	- 1.156	3.154	9.644	- 10.538
298	12.712	65.030	65.030	.000	2.900	12.889	- 9.447
300	12.744	65.108	65.030	.024	2.897	12.951	- 9.434
400	14.254	68.991	65.549	1.377	2.775	16.324	- 8.918
500	15.408	72.302	66.577	2.863	2.752	19.716	- 8.617
600	16.291	75.193	67.777	4.450	2.794	23.106	- 8.416
700	16.966	77.757	69.023	6.114	2.877	26.485	- 8.269
800	17.485	80.058	70.261	7.838	2.988	29.849	- 8.154
900	17.886	82.141	71.467	9.607	3.119	33.200	- 8.062
1000	18.200	84.043	72.631	11.412	3.263	36.534	- 7.984
1100	18.448	85.790	73.749	13.245	3.414	39.853	- 7.918
1200	18.648	87.404	74.820	15.100	3.571	43.159	- 7.860
1300	18.809	88.903	75.847	16.973	3.731	46.452	- 7.809
1400	18.942	90.302	76.830	18.861	3.892	49.731	- 7.763
1500	19.052	91.613	77.772	20.761	4.053	53.000	- 7.722
1600	19.144	92.845	78.676	22.671	4.214	56.259	- 7.684
1700	19.222	94.008	79.544	24.589	4.375	59.508	- 7.650
1800	19.288	95.109	80.378	26.515	4.531	62.745	- 7.618
1900	19.345	96.153	81.181	28.446	4.685	65.977	- 7.589
2000	19.394	97.147	81.955	30.383	4.836	69.197	- 7.561
2100	19.436	98.094	82.701	32.325	4.984	72.412	- 7.536
2200	19.474	98.999	83.422	34.270	5.125	75.619	- 7.512
2300	19.506	99.865	84.118	36.220	5.265	78.821	- 7.489
2400	19.535	100.696	84.791	38.172	5.399	82.017	- 7.468
2500	19.561	101.494	85.444	40.126	5.526	85.205	- 7.448
2600	19.584	102.262	86.076	42.084	5.650	88.390	- 7.429
2700	19.604	103.001	86.689	44.043	5.768	91.571	- 7.412
2800	19.622	103.715	87.284	46.004	5.880	94.745	- 7.395
2900	19.639	104.404	87.863	47.967	5.988	97.918	- 7.379
3000	19.654	105.070	88.426	49.932	6.089	101.086	- 7.364
3100	19.668	105.714	88.973	51.898	6.186	104.253	- 7.349
3200	19.680	106.339	89.506	53.866	6.276	107.412	- 7.336
3300	19.691	106.945	90.025	55.834	6.361	110.570	- 7.322
3400	19.702	107.533	90.531	57.804	6.441	113.728	- 7.310
3500	19.711	108.104	91.025	59.774	6.516	116.880	- 7.298
3600	19.720	108.659	91.508	61.746	6.587	120.037	- 7.287
3700	19.728	109.200	91.978	63.718	6.652	123.185	- 7.276
3800	19.735	109.726	92.439	65.692	6.713	126.335	- 7.266
3900	19.742	110.239	92.888	67.665	6.770	129.480	- 7.256
4000	19.748	110.738	93.329	69.640	6.822	132.628	- 7.246
4100	19.754	111.226	93.759	71.615	6.870	135.772	- 7.237
4200	19.760	111.702	94.181	73.591	6.915	138.914	- 7.228
4300	19.765	112.167	94.594	75.567	6.957	142.060	- 7.220
4400	19.770	112.622	94.998	77.544	6.994	145.198	- 7.212
4500	19.774	113.066	95.395	79.521	7.028	148.339	- 7.204
4600	19.778	113.501	95.784	81.499	7.061	151.482	- 7.197
4700	19.782	113.926	96.165	83.477	7.089	154.622	- 7.190
4800	19.786	114.343	96.540	85.455	7.116	157.759	- 7.183
4900	19.789	114.751	96.907	87.434	7.140	160.892	- 7.176
5000	19.793	115.151	97.268	89.413	7.162	164.029	- 7.169
5100	19.796	115.542	97.622	91.392	7.182	167.174	- 7.164
5200	19.799	115.927	97.971	93.372	7.201	170.306	- 7.157
5300	19.801	116.304	98.313	95.352	7.217	173.446	- 7.152
5400	19.804	116.674	98.650	97.332	7.232	176.579	- 7.146
5500	19.807	117.038	98.981	99.313	7.246	179.718	- 7.141
5600	19.809	117.395	99.306	101.294	7.257	182.848	- 7.136
5700	19.811	117.745	99.627	103.275	7.268	185.985	- 7.131
5800	19.813	118.090	99.942	105.256	7.277	189.125	- 7.126
5900	19.815	118.428	100.253	107.237	7.285	192.259	- 7.121
6000	19.817	118.762	100.558	109.219	7.292	195.392	- 7.117

Dec. 31, 1962; Dec. 31, 1965

NITRYL CHLORIDE (NO_2Cl) (IDEAL GAS) MOL. WT. = 81.4585

Point Group C_{2v}

$S^\circ_{298.15}$ = 65.0 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = 4.20 ± 0.4 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 2.90 ± 0.4 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1293 (1)	1685 (1)
794 (1)	411 (1)
367 (1)	651 (1)

Bond Distance: N-Cl = 1.83 Å N-O = 1.21 Å

Bond Angle: O-N-O = 129.5° O-N-Cl = 115.25°

σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = 2.36698 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

The selected heat of formation was obtained from the recalculation of the heat of reaction $ClNO_2 + NO = ClNO + NO_2$ which has been measured calorimetrically as -9.27 kcal. mole^{-1} by J. Ray and R. Ogg, Jr., J. Chem. Phys. 31, 168 (1959). Not only the thermal effects of $2NO_2 = N_2O_4$ but also $NO + NO_2 = N_2O_3$ (a minor one) have been considered in calculation. Using all JANAF auxiliary data for ClNO, NO, NO_2, N_2O_3 and N_2O_4, the recalculation gives $\Delta H_f^\circ{}_{298}$ = 2.90 ± 0.4 kcal. mole^{-1} for $NO_2Cl(g)$. For the reaction $ClNO + N_2O_5 = ClNO_2 + 2NO_2$ also measured by Ray and Ogg, loc. cit., the recalculation gives $\Delta H_f^\circ{}_{298}$ (NO_2Cl, g) = 2.56 ± 0.4 kcal. mole^{-1}.

H. Martin and E. Koehlein, Z. physik.Chem. 17, 375 (1958), have determined kinetically the heat of reaction, $\Delta H_r^\circ{}_{273.15}$ = 3.10 kcal. mole^{-1}, for the reaction $NO_2 + NOCl = NO + NO_2Cl$ which gives $\Delta H_f^\circ{}_{298}$ = 1.90 ± 1 kcal. mole^{-1} for $NO_2Cl(g)$. H. Cordes and H. Johnston, J. Am. Chem. Soc., 76, 4264 (1954), have also determined kinetically the $\Delta H_r^\circ{}_0$ = 29.5 kcal. mole^{-1} for the reaction $NO_2Cl = NO_2 + Cl$ which gives $\Delta H_f^\circ{}_{298}$ = 6.3 ± 0.3 kcal. mole^{-1}.

Heat Capacity and Entropy.

The selected bond distances and bond angles were obtained from microwave spectrum studies by L. Clayton, Q. Williams and T. L. Weatherly, J. Chem. Phys. 30, 1328 (1959). D. J. Millen and K. M. Sinnott, J. Chem. Soc. 350 (1958), reported bond distance N-Cl = 1.840 Å, N-O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by R. Ryason and M. K. Wilson, J. Chem. Phys. 22, 2000 (1954). However, the assignment of the fundamental frequencies has been revised by R. E. Dodd, J. A. Rolfe and L. A. Woodward, Trans. Faraday Soc. 52, 145 (1956), and Y. Morino and T. Tanaka, J. Mol. Spectry. 16, 179 (1965). Morino and Tanaka's assignment was adopted. The three principal moments of inertia are I_A = 6.3658 X 10^{-39}, I_B = 16.3609 X 10^{-39} and I_C = 22.7267 X 10^{-39} g. cm.^{2}

Sodium Chloride (NaCl)

(Crystal) Mol. Wt. = 58.448

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.536	-98.158	-98.158	INFINITE
100	8.349	5.670	27.281	-2.161	-98.454	-96.192	210.218
200	11.203	12.573	18.319	-1.149	-98.389	-93.943	102.651
298	12.072	17.236	17.236	.000	-98.260	-91.788	67.279
300	12.080	17.311	17.236	.022	-98.257	-91.748	66.835
400	12.512	20.848	17.716	1.253	-98.786	-89.546	48.923
500	12.892	23.681	18.635	2.523	-98.683	-87.246	38.133
600	13.259	26.064	19.679	3.831	-98.531	-84.972	30.950
700	13.672	28.138	20.743	5.177	-98.330	-82.729	25.828
800	14.176	29.995	21.785	6.568	-98.076	-80.516	21.995
900	14.787	31.699	22.793	8.015	-97.764	-78.339	19.022
1000	15.503	33.293	23.764	9.529	-97.388	-76.200	16.653
1100	16.330	34.809	24.700	11.120	-96.941	-74.104	14.722
1200	17.200	36.268	25.604	12.797	-119.654	-71.593	13.038
1300	17.960	37.676	26.479	14.557	-118.842	-67.621	11.367
1400	18.530	39.029	27.327	16.382	-117.966	-63.714	9.946
1500	18.940	40.322	28.151	18.257	-117.041	-59.870	8.723

Dec. 31, 1960; Sept. 30, 1964

SODIUM CHLORIDE (NaCl) (CRYSTAL) MOL. Wt. = 58.448

$\Delta H_f^\circ{}_0 = -98.16 \pm 0.08$ kcal. mole^{-1}

$S^\circ_{298.15} = 17.24 \pm 0.05$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -98.26 \pm 0.08$ kcal. mole^{-1}

$T_m = 1073.8 \pm 1.0$°K.

$\Delta H_m^\circ = 6.73 \pm 0.04$ kcal. mole^{-1}

Heat of Formation.

The heat of formation is based on $\Delta H_f^\circ{}_{298.15} = -57.39$ and -39.95 kcal. mole^{-1} for $Na^+(\infty H_2O)$ and $Cl^-(\infty H_2O)$, respectively, and on the heat of solution $\Delta H^\circ_\infty{}_{298.15} = 0.922$ kcal. mole^{-1} for NaCl. These values were reported in a private communication from D. D. Wagman, National Bureau of Standards, June, 1964.

Heat Capacity and Entropy.

The low temperature values are based on the heat capacities (3-266°K) reported by T.H.K. Barron, A. J. Leadbetter, J. A. Morrison, Proc. Roy. Soc. (London) A279 (1376), 62 (1964). The earlier work of K. Clusius, J. Goldman, A. Perlick, Z. Naturforsch. 4a, 424 (1949), results in a slightly higher entropy ($S^\circ_{298.15} = 17.33$ cal. deg.$^{-1}$ mole^{-1}) but a lower heat capacity at room temperature ($C_p^\circ{}_{298.15} = 11.9$ cal. deg.$^{-1}$ mole^{-1}). The high temperature values have been obtained by reanalysis of the enthalpies (672 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963), using the new value for $C_p^\circ{}_{298.15}$. The resulting tables agree within ± 0.1 kcal. with the enthalpies (812 - 1058°K) of W. A. Roth, W. Bertram, Z. Elektrochem. 35, 38 (1929). The enthalpies (540 - 1037°K) of A. Magnus, Physik. Zeitschr. 14, 5 (1913), agree well at the lower temperatures but are about 0.3 kcal. smaller near the melting point.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of $T_m = 1073$°K. and $\Delta H_m^\circ = 6.69 \pm 0.06$ kcal. mole^{-1} were reported by A. S. Dworkin, M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

Sodium Chloride (NaCl)

(Liquid) Mol. Wt. = 58.448

ClNa

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	12.072	22.719	22.719	.000	- 92.237	- 87.400	64.063
300	12.080	22.794	22.719	.022	- 92.234	- 87.370	63.646
400	12.512	26.331	23.199	1.253	- 92.763	- 85.716	46.831
500	12.892	29.164	24.118	2.523	- 92.660	- 83.964	36.699
600	13.259	31.547	25.162	3.831	- 92.508	- 82.239	29.954
700	13.672	33.621	26.226	5.177	- 92.307	- 80.544	25.146
800	18.260	35.478	27.268	6.568	- 92.053	- 78.879	21.548
900	17.890	37.609	28.301	8.377	- 91.379	- 77.273	18.763
1000	17.330	39.467	29.327	10.140	- 90.754	- 75.740	16.552
1100	16.750	41.091	30.324	11.843	- 90.195	- 74.268	14.755
1200	16.330	42.529	31.283	13.495	- 112.933	- 72.385	13.183
1300	16.120	43.827	32.199	15.117	- 112.259	- 69.034	11.605
1400	16.030	45.018	33.072	16.724	- 111.601	- 65.734	10.261
1500	16.000	46.123	33.906	18.325	- 110.950	- 62.480	9.103
1600	16.000	47.156	34.702	19.925	- 110.301	- 59.271	8.096
1700	16.000	48.126	35.464	21.525	- 109.651	- 56.100	7.212
1800	16.000	49.041	36.193	23.125	- 109.004	- 52.970	6.431
1900	16.000	49.906	36.893	24.725	- 108.357	- 49.873	5.736
2000	16.000	50.727	37.564	26.325	- 107.712	- 46.813	5.115
2100	16.000	51.508	38.210	27.925	- 107.067	- 43.787	4.557
2200	16.000	52.252	38.832	29.525	- 106.424	- 40.787	4.052
2300	16.000	52.963	39.431	31.125	- 105.781	- 37.818	3.593
2400	16.000	53.644	40.009	32.725	- 105.141	- 34.875	3.176
2500	16.000	54.297	40.567	34.325	- 104.502	- 31.962	2.794

Dec. 31, 1960; Sept. 30, 1964

SODIUM CHLORIDE (NaCl) (LIQUID) MOL. WT. = 58.448

$S^\circ_{298.15}$ = [22.719] cal. deg.$^{-1}$ mole^{-1}

T_m = 1073.8 ± 1.0°K.

ΔH°_f 298.15 = [-92.237] kcal. mole^{-1}

ΔH°_m = 6.73 ± 0.04 kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_f(l)$ was obtained from $\Delta H^\circ_f(c)$ by addition of ΔH°_m and the difference between $(H^\circ_{1073.8} - H^\circ_{298.15})$ for the crystal and liquid.

Heat Capacity and Entropy.

These were obtained by analysis of the enthalpies (1076 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963). The heat capacity was extrapolated to a constant value of 16.0 at the higher temperatures. A glass transition was assumed at 800°K. and below this temperature C_p° was taken equal to that of the crystal.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of T_m = 1073°K. and ΔH°_m = 6.69 ± 0.06 kcal. mole^{-1} were reported by A. S. Dworkin, M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

ClNa

Sodium Chloride (NaCl)

(Ideal Gas) Mol. Wt. = 58.448

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.298	-43.020	-43.020	INFINITE
00	7.265	46.224	62.193	-1.507	-42.989	-44.783	97.869
200	8.148	51.557	55.669	-.822	-43.162	-46.513	50.825
298	8.553	54.897	54.897	.000	-43.360	-48.117	35.269
300	8.558	54.950	54.897	.016	-43.364	-48.146	35.073
400	8.749	57.441	55.236	.882	-44.256	-49.653	27.128
500	8.854	59.406	55.880	1.763	-44.543	-50.969	22.277
600	8.921	61.026	56.607	2.652	-44.810	-52.228	19.023
700	8.969	62.405	57.339	3.546	-45.060	-53.446	16.686
800	9.006	63.605	58.049	4.445	-45.299	-54.627	14.923
900	9.037	64.668	58.726	5.347	-45.532	-55.779	13.544
1000	9.064	65.622	59.369	6.252	-45.764	-56.906	12.436
1100	9.088	66.487	59.977	7.160	-46.001	-58.010	11.525
1200	9.110	67.278	60.553	8.070	-69.481	-58.632	10.678
1300	9.131	68.008	61.099	8.982	-69.517	-57.727	9.704
1400	9.152	68.686	61.617	9.896	-69.552	-56.819	8.869
1500	9.171	69.318	62.110	10.812	-69.586	-55.909	8.145
1600	9.190	69.910	62.579	11.730	-69.619	-54.995	7.512
1700	9.209	70.468	63.027	12.650	-69.649	-54.079	6.952
1800	9.227	70.995	63.455	13.572	-69.680	-53.163	6.455
1900	9.245	71.494	63.865	14.496	-69.709	-52.243	6.009
2000	9.263	71.969	64.258	15.421	-69.739	-51.324	5.608
2100	9.280	72.421	64.636	16.348	-69.767	-50.404	5.245
2200	9.298	72.853	65.000	17.277	-69.795	-49.480	4.915
2300	9.315	73.267	65.351	18.208	-69.822	-48.557	4.614
2400	9.332	73.664	65.689	19.140	-69.849	-47.631	4.337
2500	9.350	74.045	66.015	20.074	-69.876	-46.706	4.083
2600	9.367	74.412	66.331	21.010	-69.903	-45.777	3.848
2700	9.384	74.766	66.637	21.948	-69.932	-44.850	3.630
2800	9.401	75.108	66.934	22.887	-69.962	-43.922	3.428
2900	9.418	75.438	67.221	23.828	-69.993	-42.989	3.240
3000	9.435	75.757	67.501	24.770	-70.026	-42.057	3.064
3100	9.451	76.067	67.772	25.715	-70.061	-41.126	2.899
3200	9.468	76.367	68.036	26.661	-70.099	-40.191	2.745
3300	9.485	76.659	68.293	27.608	-70.141	-39.256	2.600
3400	9.502	76.942	68.543	28.558	-70.185	-38.319	2.463
3500	9.519	77.218	68.787	29.509	-70.235	-37.380	2.334
3600	9.536	77.486	69.025	30.461	-70.289	-36.440	2.212
3700	9.552	77.748	69.257	31.416	-70.347	-35.502	2.097
3800	9.569	78.003	69.484	32.372	-70.411	-34.558	1.987
3900	9.586	78.252	69.706	33.330	-70.483	-33.616	1.884
4000	9.602	78.495	69.922	34.289	-70.561	-32.669	1.785
4100	9.619	78.732	70.134	35.250	-70.648	-31.718	1.691
4200	9.636	78.964	70.342	36.213	-70.744	-30.771	1.601
4300	9.653	79.191	70.545	37.177	-70.849	-29.816	1.515
4400	9.669	79.413	70.744	38.143	-70.967	-28.861	1.433
4500	9.686	79.630	70.939	39.111	-71.096	-27.899	1.355
4600	9.703	79.843	71.130	40.081	-71.239	-26.939	1.280
4700	9.719	80.052	71.318	41.052	-71.398	-25.975	1.208
4800	9.736	80.257	71.502	42.024	-71.574	-25.009	1.139
4900	9.752	80.458	71.683	42.999	-71.769	-24.033	1.072
5000	9.769	80.655	71.860	43.975	-71.985	-23.057	1.008
5100	9.786	80.849	72.035	44.953	-72.222	-22.077	.946
5200	9.802	81.039	72.206	45.932	-72.485	-21.091	.886
5300	9.819	81.226	72.374	46.913	-72.775	-20.101	.829
5400	9.836	81.410	72.540	47.896	-73.095	-19.106	.773
5500	9.852	81.590	72.703	48.880	-73.447	-18.101	.719
5600	9.869	81.768	72.863	49.866	-73.833	-17.094	.667
5700	9.885	81.943	73.021	50.854	-74.255	-16.078	.616
5800	9.902	82.115	73.176	51.843	-74.716	-15.052	.567
5900	9.919	82.284	73.329	52.834	-75.219	-14.015	.519
6000	9.935	82.451	73.480	53.827	-75.764	-12.974	.473

Dec. 31, 1960; Dec. 31, 1964

SODIUM CHLORIDE (NaCl) (IDEAL GAS) MOL. WT. = 58.448

Ground State Configuration $^1\Sigma$

$S^\circ_{298.15}$ = 54.90 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -43.02 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -43.36 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 363.62 cm.$^{-1}$

B_e = 0.21691 cm.$^{-1}$

$\omega_e x_e$ = 1.72 cm.$^{-1}$

α_e = 0.001598 cm.$^{-1}$

σ = 1

r_e = 2.3606 Å

Heat of Formation.

The heat of formation is based on a heat of sublimation $\Delta H^\circ_{s\ 298.15}$ = 54.9 kcal. mole^{-1} obtained from the more consistent sets of vapor pressure data by correction for the presence of dimer. Observed vapor pressures were converted to monomer pressures by use of dimer-monomer ratios calculated from JANAF free energy functions and $\Delta H^\circ_{r\ 298.15}$ = 48.6 kcal. for the reaction $(NaCl)_2(g) \rightarrow 2NaCl(g)$. Higher polymeric species were neglected. Analyses of the resulting monomer pressures are summarized below.

Source	Temperature Range (°K)	Heat of Sublimation $\Delta H^\circ_{s\ 298.15}$(kcal. mole^{-1})	
		2nd Law	3rd Law
Nesmeyanov & Sazonov(1)	743 - 948*	54.35	54.94
Zimm & Mayer(2)	760 - 897*	55.15	54.91
Mayer & Wintner(3)	890 - 944*	49.6	55.37
Niwa(4)	883 - 973*	52.6	55.03
Barton & Bloom(5)	1340 - 1540**	56.67	54.68
Fiock & Rodebush(6)	1250 - 1428**	56.65	54.98
Wartenberg & Albrecht(7)	1429 - 1720**	60.0	54.45
Ruff & Mugdan(8) .	1433 - 1723**	59.5	54.44

*Knudsen effusion measurements over crystal **total pressures over liquid

1) A. N. Nesmeyanov, L. A. Sazonov, Zhur. Neorg. Khim. 2, 946 (1957).
2) B. H. Zimm, J. E. Mayer, J. Chem. Phys. 12, 362 (1944).
3) J. E. Mayer, J. H. Wintner, J. Chem. Phys. 6, 301 (1938).
4) K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser.III, 2 201 (1938).
5) J. L. Barton, H. Bloom, J. Phys. Chem. 60, 1413 (1956).
6) E. F. Fiock, W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).
7) H. von Wartenberg, P. Albrecht, Z. Elektrochem. 27, 162 (1921).
8) O. Ruff, S. Mugdan, Z. anorg. allgem. Chem. 117, 147 (1921).

Heat Capacity and Entropy.

The molecular constants are based on molecular beam studies of the rotational spectra by Clouser and Gordy, Bull. Am. Phys. Soc. 8, 326 (1963) and on microwave studies by Honig, Mandel, Stitch and Townes, Phys. Rev. 96, 629 (1954). The infrared spectra of Rice and Klemperer, J. Chem. Phys. 27, 573 (1957) give a frequency in close agreement (366 cm.$^{-1}$).

Sodium Perchlorate ($NaClO_4$)

(Crystal) Mol. Wt. = 122.448

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	26.600	34.000	34.000	.000	-91.480	-60.785	44.555
300	26.700	34.165	34.001	.049	-91.476	-60.595	44.141
400	32.500	42.622	35.115	3.003	-91.704	-50.300	27.482
500	35.900	50.258	37.395	6.431	-90.905	-40.034	17.498
600	38.300	62.774	40.297	13.487	-86.515	-30.065	10.951
700	40.267	68.829	43.948	17.417	-85.285	-20.752	6.479
800	42.000	74.322	47.406	21.532	-83.904	-11.628	3.176
900	43.400	79.350	50.680	25.803	-82.396	-2.681	.651
1000	44.700	83.991	53.782	30.209	-80.782	6.092	-1.331
1100	45.900	88.309	56.727	34.740	-79.073	14.694	-2.919
1200	47.000	92.350	59.529	39.386	-100.513	23.598	-4.298
1300	48.060	96.155	62.201	44.139	-98.422	33.857	-5.692
1400	49.060	99.753	64.756	48.996	-96.242	43.950	-6.861
1500	50.000	103.170	67.204	53.949	-93.981	53.886	-7.851

June 30, 1963

SODIUM PERCHLORATE ($NaClO_4$) (CRYSTAL) MOL. WT. = 122.448

$\Delta H_{f\ 0}^\circ$ = Unknown

$S_{298.15}^\circ$ = [34] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -91.48 \pm 0.22$ kcal. mole^{-1}

T_t = 581°K.

ΔH_t° = [3.34] kcal. mole^{-1}

T_m = 755°K.

ΔH_m° = Unknown

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961) measured the heat of solution of $NaClO_4(c)$ and gave $\Delta H_{f\ 298.15}^\circ = -91.48 \pm 0.22$ kcal. mole^{-1} for $NaClO_4(c)$. The heat of dilution of $NaClO_4(c)$ was measured by C. E. Vanderzee and J. A. Swanson, J. Phys. Chem. 67, 285 (1963). The data led to $\Delta H_{f\ 298.15}^\circ = -91.464$ kcal. mole^{-1} which agrees very well with the data reported by A. A. Gilliland and W. H. Johnson, loc. cit. The value of $\Delta H_{f\ 298.15}^\circ$ was reported to be -92.18 kcal. mole^{-1} in the National Bureau of Standards Circ. 500, "Selected Values of Chemical Thermodynamic Properties," 1952, based upon the data prior to 1950. A. F. Vorob'ev, et al., Proc. Acad. Sci. USSR, 135, 1439 (1960) measured the heat of decomposition of $NaClO_4(c)$ into $NaCl(c)$ and $O_2(g)$ and gave $\Delta H_{f\ 298.15}^\circ = -90.68 \pm 0.3$ kcal. mole^{-1} for $NaClO_4(c)$. The value reported by A. A. Gilliland and W. H. Johnson, loc. cit. was used.

Heat Capacity and Entropy.

Heat capacities and $S_{298.15}^\circ$ were estimated by comparison with those for $NaClO_3(c)$ and $KClO_4(c)$, respectively.

Transition Data.

T_t was reported in the National Bureau of Standards, Circ. 500, loc. cit. ΔH_t° was estimated from that for $KClO_4(c)$.

Temperature of Melting.

T_m was obtained from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

Chlorine Monoxide (ClO)

(Ideal Gas) Mol. Wt. = 51.457

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H_{298}^\circ$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.115	24.211	24.211	INFINITE
100	6.959	46.371	60.573	- 1.420	24.199	23.898	- 52.226
200	7.125	51.225	54.820	- .719	24.200	23.594	- 25.781
298	7.540	54.145	54.145	.000	24.192	23.298	- 17.077
300	7.548	54.191	54.145	.014	24.192	23.292	- 16.968
400	7.942	56.419	54.446	.789	24.197	22.992	- 12.562
500	8.229	58.224	55.027	1.599	24.214	22.690	- 9.917
600	8.429	59.743	55.689	2.432	24.236	22.383	- 8.153
700	8.571	61.054	56.364	3.283	24.258	22.072	- 6.891
800	8.676	62.205	57.024	4.145	24.279	21.758	- 5.944
900	8.754	63.232	57.658	5.017	24.298	21.442	- 5.207
1000	8.816	64.158	58.262	5.895	24.316	21.123	- 4.616
1100	8.865	65.000	58.837	6.780	24.333	20.803	- 4.133
1200	8.906	65.773	59.383	7.668	24.347	20.482	- 3.730
1300	8.941	66.488	59.903	8.561	24.360	20.159	- 3.389
1400	8.971	67.151	60.397	9.456	24.372	19.835	- 3.096
1500	8.998	67.771	60.868	10.355	24.382	19.511	- 2.843
1600	9.022	68.353	61.318	11.256	24.390	19.186	- 2.621
1700	9.044	68.900	61.748	12.159	24.398	18.861	- 2.425
1800	9.064	69.418	62.160	13.065	24.404	18.535	- 2.250
1900	9.083	69.909	62.555	13.972	24.407	18.209	- 2.094
2000	9.100	70.375	62.934	14.881	24.409	17.882	- 1.954
2100	9.117	70.819	63.299	15.792	24.410	17.556	- 1.827
2200	9.133	71.244	63.651	16.704	24.407	17.229	- 1.711
2300	9.148	71.650	63.990	17.619	24.404	16.903	- 1.606
2400	9.163	72.040	64.317	18.534	24.398	16.578	- 1.510
2500	9.178	72.414	64.634	19.451	24.389	16.251	- 1.421
2600	9.192	72.774	64.940	20.370	24.379	15.927	- 1.339
2700	9.206	73.122	65.237	21.290	24.366	15.602	- 1.263
2800	9.219	73.457	65.524	22.211	24.350	15.278	- 1.192
2900	9.232	73.780	65.803	23.133	24.332	14.954	- 1.127
3000	9.245	74.094	66.074	24.057	24.312	14.631	- 1.066
3100	9.256	74.397	66.338	24.982	24.289	14.309	- 1.009
3200	9.271	74.691	66.595	25.909	24.263	13.986	- .955
3300	9.283	74.976	66.844	26.836	24.235	13.666	- .905
3400	9.295	75.254	67.087	27.765	24.205	13.347	- .858
3500	9.308	75.523	67.325	28.696	24.173	13.026	- .813
3600	9.320	75.786	67.556	29.627	24.139	12.710	- .772
3700	9.332	76.041	67.782	30.559	24.102	12.393	- .732
3800	9.344	76.290	68.003	31.493	24.065	12.076	- .695
3900	9.356	76.533	68.218	32.428	24.025	11.761	- .659
4000	9.368	76.770	68.429	33.364	23.983	11.447	- .625
4100	9.379	77.002	68.635	34.302	23.941	11.134	- .593
4200	9.391	77.228	68.837	35.240	23.897	10.821	- .563
4300	9.403	77.449	69.035	36.180	23.852	10.512	- .534
4400	9.415	77.665	69.229	37.121	23.806	10.202	- .507
4500	9.426	77.877	69.419	38.063	23.759	9.892	- .480
4600	9.438	78.084	69.605	39.006	23.712	9.587	- .455
4700	9.449	78.287	69.787	39.950	23.664	9.280	- .432
4800	9.461	78.486	69.966	40.896	23.616	8.974	- .409
4900	9.472	78.682	70.142	41.843	23.568	8.669	- .387
5000	9.484	78.873	70.315	42.790	23.519	8.364	- .366
5100	9.495	79.061	70.485	43.739	23.471	8.064	- .346
5200	9.506	79.245	70.651	44.689	23.423	7.761	- .326
5300	9.518	79.427	70.815	45.641	23.376	7.462	- .308
5400	9.529	79.605	70.976	46.593	23.328	7.159	- .290
5500	9.541	79.780	71.135	47.546	23.281	6.863	- .273
5600	9.552	79.952	71.291	48.501	23.235	6.563	- .256
5700	9.563	80.121	71.444	49.457	23.188	6.263	- .240
5800	9.574	80.287	71.595	50.414	23.143	5.971	- .225
5900	9.586	80.451	71.744	51.372	23.098	5.673	- .210
6000	9.597	80.612	71.890	52.331	23.054	5.380	- .196

June 30, 1961

CHLORINE MONOXIDE (ClO) (IDEAL GAS) MOL. WT. = 51.457

$D_0 = 63.33 \pm 0.03$ kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 24.19 \pm 0.05$ kcal. mole^{-1}

Ground State Configuration $^2\Pi_{3/2}$

$S^\circ_{298.15} = 54.145$ cal. deg.$^{-1}$ mole^{-1}

Electronic Level and Multiplicity

ϵ_1, cm.$^{-1}$	g_1
0	4

$\omega_e = 866 \pm 26$ cm.$^{-1}$

$\omega_e x_e = 7.5$ cm.$^{-1}$

$D_e = 2.(2) \times 10^{-6}$ cm.$^{-1}$

$\sigma = 1$

$B_e = 0.643(3)$

$\alpha_e = [0.0069]$ cm.$^{-1}$

$r_e = 1.546$ Å

Heat of Formation

R. A. Durie and D. A. Ramsay, Can. J. Phys. 36, 35 (1958) and G. Herzberg and D. A. Ramsay, Disc. Faraday Soc. 9, 80 (1950) report $D_0 = 22152 \pm 10$ cm.$^{-1}$ and $D_0 = 22141$ cm.$^{-1}$ respectively, and these values have been averaged.

Heat Capacity and Entropy

The spectroscopic constants are for the natural mixture of isotopes and are based on measurements by Durie and Ramsay, loc. cit., and by G. Porter, Disc. Faraday Soc. 9, 60 (1950). α_e has been estimated by the method given by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, Inc., New York, 1950, p. 108.

Titanium Oxide Chloride (TiOCl)

(Ideal Gas) Mol. Wt. = 99.357

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.902	-57.998	-57.998	INFINITE
100	8.756	51.462	73.018	-2.156	-58.092	-58.707	128.298
200	11.049	58.318	64.084	-1.153	-58.248	-59.262	64.755
298	12.346	62.992	62.992	.000	-58.380	-59.726	43.779
300	12.365	63.069	62.992	.023	-58.382	-59.735	43.515
400	13.170	66.745	63.488	1.303	-58.493	-60.169	32.873
500	13.671	69.742	64.449	2.647	-58.590	-60.576	26.476
600	13.993	72.266	65.547	4.031	-58.690	-60.963	22.205
700	14.208	74.440	66.666	5.442	-58.802	-61.335	19.149
800	14.357	76.347	67.759	6.871	-58.925	-61.689	16.852
900	14.464	78.045	68.809	8.312	-59.061	-62.025	15.061
1000	14.543	79.573	69.811	9.762	-59.211	-62.347	13.625
1100	14.602	80.962	70.762	11.220	-59.375	-62.654	12.448
1200	14.649	82.235	71.666	12.682	-60.503	-62.907	11.456
1300	14.685	83.409	72.525	14.149	-60.693	-63.099	10.607
1400	14.714	84.498	73.341	15.619	-60.897	-63.277	9.878
1500	14.738	85.514	74.119	17.092	-61.113	-63.440	9.243
1600	14.758	86.466	74.862	18.567	-61.342	-63.586	8.685
1700	14.774	87.361	75.571	20.043	-61.582	-63.719	8.191
1800	14.788	88.206	76.250	21.522	-61.834	-63.839	7.751
1900	14.800	89.006	76.900	23.001	-62.100	-63.941	7.355
2000	14.810	89.765	77.524	24.481	-66.052	-63.939	6.987
2100	14.819	90.488	78.125	25.963	-66.280	-63.826	6.642
2200	14.826	91.178	78.702	27.445	-66.513	-63.705	6.328
2300	14.833	91.837	79.259	28.928	-66.747	-63.571	6.040
2400	14.838	92.468	79.797	30.412	-66.985	-63.428	5.776
2500	14.844	93.074	80.316	31.896	-67.227	-63.275	5.531
2600	14.848	93.656	80.818	33.380	-67.471	-63.113	5.305
2700	14.852	94.217	81.304	34.865	-67.719	-62.941	5.094
2800	14.856	94.757	81.774	36.351	-67.971	-62.758	4.898
2900	14.859	95.278	82.231	37.837	-68.225	-62.567	4.715
3000	14.862	95.782	82.675	39.323	-68.484	-62.369	4.543
3100	14.865	96.269	83.105	40.809	-68.746	-62.158	4.382
3200	14.867	96.741	83.524	42.296	-69.011	-61.945	4.230
3300	14.869	97.199	83.932	43.782	-69.280	-61.717	4.087
3400	14.871	97.643	84.328	45.269	-69.552	-61.486	3.952
3500	14.873	98.074	84.715	46.757	-69.827	-61.247	3.824
3600	14.875	98.493	85.092	48.244	-172.567	-59.552	3.615
3700	14.877	98.901	85.460	49.732	-172.868	-56.407	3.332
3800	14.878	99.297	85.819	51.219	-173.186	-53.254	3.063
3900	14.879	99.684	86.169	52.707	-173.521	-50.095	2.807
4000	14.881	100.061	86.512	54.195	-173.871	-46.929	2.564
4100	14.882	100.428	86.847	55.683	-174.236	-43.749	2.332
4200	14.883	100.787	87.174	57.172	-174.615	-40.564	2.111
4300	14.884	101.137	87.495	58.660	-175.008	-37.366	1.899
4400	14.885	101.479	87.809	60.148	-175.415	-34.159	1.697
4500	14.886	101.814	88.116	61.637	-175.834	-30.943	1.503
4600	14.886	102.141	88.418	63.125	-176.265	-27.718	1.317
4700	14.887	102.461	88.713	64.614	-176.708	-24.484	1.138
4800	14.888	102.774	89.003	66.103	-177.162	-21.240	.967
4900	14.888	103.081	89.287	67.592	-177.626	-17.991	.802
5000	14.889	103.382	89.566	69.080	-178.100	-14.730	.644
5100	14.890	103.677	89.840	70.569	-178.583	-11.455	.491
5200	14.890	103.966	90.109	72.058	-179.074	-8.173	.343
5300	14.891	104.250	90.373	73.547	-179.573	-4.877	.201
5400	14.891	104.528	90.632	75.037	-180.079	-1.580	.064
5500	14.892	104.801	90.887	76.526	-180.592	1.734	-.069
5600	14.892	105.070	91.138	78.015	-181.113	5.048	-.197
5700	14.893	105.333	91.385	79.504	-181.638	8.373	-.321
5800	14.893	105.592	91.628	80.993	-182.169	11.715	-.441
5900	14.893	105.847	91.867	82.483	-182.705	15.062	-.558
6000	14.894	106.097	92.102	93.972	-183.245	18.424	-.671

Sept. 30, 1963

TITANIUM OXIDE CHLORIDE (TiOCl) (IDEAL GAS) MOL. WT. = 99.357

Point Group [$C_{\infty v}$]

$\Delta H^\circ_{f\ 0}$ = [-58.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [62.992] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-58.4] kcal. mole^{-1}

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[880] (1)
[230] (2)
[490] (1)

Bond Distances: O=Ti = [1.62] Å Ti-F = [2.17] Å

Bond Angles: O=Ti-Cl = [180°]

σ = 1

Rotational Constant: B_0 = [0.09225] cm.$^{-1}$

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as -58 kcal. mole^{-1} by J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: $I_A = I_C = 30.34 \times 10^{-39}$ g. cm.^{2}

Chlorine Dioxide (ClO_2)

(Ideal Gas) Mol. Wt. = 67.457

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.582	25.590	25.590	INFINITE
100	8.085	51.762	69.612	-1.785	25.326	26.560	-58.043
200	8.997	57.623	62.293	-.934	25.134	27.872	-30.455
298	10.037	61.453	61.453	.000	25.000	29.232	-21.427
300	10.057	61.515	61.453	.019	24.998	29.259	-21.314
400	11.011	64.544	61.860	1.074	24.928	30.691	-16.768
500	11.744	67.084	62.657	2.213	24.909	32.135	-14.046
600	12.279	69.275	63.582	3.416	24.922	33.580	-12.231
700	12.669	71.199	64.535	4.664	24.953	35.020	-10.933
800	12.957	72.910	65.477	5.946	24.995	36.455	-9.958
900	13.176	74.450	66.390	7.253	25.042	37.885	-9.199
1000	13.346	75.847	67.267	8.580	25.095	39.310	-8.591
1100	13.480	77.125	68.106	9.921	25.148	40.728	-8.091
1200	13.590	78.303	68.907	11.275	25.204	42.142	-7.675
1300	13.681	79.395	69.673	12.639	25.259	43.552	-7.321
1400	13.756	80.411	70.404	14.011	25.314	44.956	-7.018
1500	13.824	81.363	71.103	15.390	25.369	46.357	-6.754
1600	13.882	82.257	71.772	16.775	25.423	47.755	-6.523
1700	13.933	83.100	72.414	18.166	25.477	49.150	-6.318
1800	13.979	83.898	73.030	19.562	25.527	50.540	-6.136
1900	14.021	84.655	73.622	20.962	25.575	51.929	-5.973
2000	14.059	85.375	74.192	22.366	25.621	53.313	-5.826
2100	14.095	86.062	74.741	23.774	25.665	54.698	-5.692
2200	14.126	86.718	75.271	25.185	25.705	56.079	-5.571
2300	14.159	87.347	75.782	26.599	25.744	57.458	-5.460
2400	14.189	87.950	76.277	28.017	25.779	58.838	-5.358
2500	14.217	88.530	76.755	29.437	25.809	60.213	-5.264
2600	14.244	89.088	77.219	30.860	25.838	61.589	-5.177
2700	14.270	89.626	77.669	32.286	25.863	62.965	-5.096
2800	14.295	90.146	78.105	33.714	25.885	64.338	-5.022
2900	14.320	90.648	78.529	35.145	25.904	65.711	-4.952
3000	14.344	91.134	78.941	36.578	25.919	67.084	-4.887
3100	14.367	91.604	79.342	38.013	25.932	68.457	-4.826
3200	14.389	92.061	79.732	39.451	25.942	69.828	-4.769
3300	14.411	92.504	80.113	40.891	25.949	71.198	-4.715
3400	14.433	92.934	80.483	42.333	25.953	72.569	-4.664
3500	14.454	93.353	80.845	43.778	25.956	73.939	-4.617
3600	14.475	93.761	81.198	45.224	25.955	75.311	-4.572
3700	14.496	94.157	81.543	46.673	25.953	76.682	-4.529
3800	14.517	94.544	81.880	48.123	25.948	78.055	-4.489
3900	14.537	94.922	82.210	49.576	25.943	79.423	-4.451
4000	14.557	95.290	82.532	51.031	25.934	80.794	-4.414
4100	14.577	95.650	82.848	52.488	25.924	82.167	-4.380
4200	14.600	96.001	83.157	53.946	25.913	83.539	-4.347
4300	14.616	96.345	83.460	55.407	25.901	84.912	-4.315
4400	14.636	96.681	83.756	56.870	25.887	86.283	-4.285
4500	14.655	97.010	84.047	58.335	25.872	87.655	-4.257
4600	14.674	97.333	84.332	59.801	25.856	89.032	-4.230
4700	14.693	97.648	84.612	61.269	25.839	90.406	-4.204
4800	14.712	97.958	84.887	62.740	25.822	91.779	-4.179
4900	14.731	98.262	85.157	64.212	25.805	93.150	-4.154
5000	14.750	98.559	85.422	65.686	25.786	94.525	-4.131
5100	14.768	98.852	85.683	67.162	25.767	95.901	-4.109
5200	14.787	99.139	85.939	68.639	25.748	97.274	-4.088
5300	14.806	99.420	86.190	70.119	25.729	98.655	-4.068
5400	14.824	99.697	86.438	71.601	25.710	100.025	-4.048
5500	14.843	99.969	86.682	73.084	25.691	101.407	-4.029
5600	14.861	100.237	86.921	74.569	25.671	102.780	-4.011
5700	14.879	100.500	87.157	76.056	25.652	104.157	-3.993
5800	14.898	100.759	87.389	77.545	25.633	105.539	-3.977
5900	14.916	101.014	87.618	79.036	25.615	106.914	-3.960
6000	14.934	101.265	87.844	80.528	25.597	108.293	-3.944

March 31, 1961

CHLORINE DIOXIDE (ClO_2) (IDEAL GAS) MOL. WT. = 67.457

$\Delta H_{f0}^\circ = 25.6 \pm 1.5$ kcal. mole^{-1}

Point Group C_{2v}

$\Delta H_{f\ 298.15}^\circ = 25 \pm 1.5$ kcal. mole^{-1}

$S_{298.15}^\circ = 61.453$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
945.3 (1)
447.4 (1)
1109 (1)

Electronic Level and Multiplicity

ϵ_1, cm.$^{-1}$	g_1
0	2

No α_1 available. $\sigma = 2$

Rotational constants: $A_{000} = 1.6006$ cm.$^{-1}$, $B_{000} = 0.33283$ cm.$^{-1}$, $C_{000} = 0.27553$ cm.$^{-1}$

$X_{11} = -4.4$ cm.$^{-1}$

$X_{22} = 0$

$g_{22} = 0$

$X_{33} = -2.0$ cm.$^{-1}$

$X_{12} = -3.0$ cm.$^{-1}$

$X_{23} = -13$ cm.$^{-1}$

$X_{31} = -14.4$ cm.$^{-1}$

Heat of Formation

W. H. Evans, T. R. Munson, and D. D. Wagman, J. Research Natl. Bur. Standards 55, 147 (1955), have evaluated the available data and chosen the above value.

Heat Capacity and Entropy

J. S. Gordon, private communication, February, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from J. B. Coon and E. Ortiz, J. Molec. Spectros. 1, 81 (1957). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

CIP

Phosphorus Monochloride (PCl)

(Ideal Gas) Mol. Wt. = 66.432

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.231	34.727	34.727	INFINITE
100	7.066	48.496	63.846	-1.535	34.983	32.542	-71.117
200	7.799	53.612	57.575	-.793	35.046	30.064	-32.850
298	8.298	56.829	56.829	.000	35.000	27.625	-20.249
300	8.305	56.881	56.830	.015	34.999	27.580	-20.091
400	8.566	59.310	57.159	.860	34.896	25.121	-13.725
500	8.712	61.238	57.789	1.725	34.763	22.692	-9.918
600	8.801	62.835	58.500	2.601	34.603	20.292	-7.391
700	8.861	64.197	59.219	3.484	34.415	17.921	-5.595
800	8.904	65.383	59.917	4.372	13.777	10.269	-2.805
900	8.937	66.433	60.584	5.265	13.788	9.830	-2.387
1000	8.964	67.376	61.217	6.160	13.797	9.389	-2.052
1100	8.986	68.232	61.816	7.057	13.805	8.948	-1.778
1200	9.005	69.015	62.384	7.957	13.812	8.505	-1.549
1300	9.022	69.736	62.922	8.858	13.818	8.064	-1.356
1400	9.038	70.405	63.433	9.761	13.824	7.621	-1.190
1500	9.052	71.029	63.919	10.666	13.830	7.178	-1.046
1600	9.066	71.614	64.382	11.571	13.834	6.734	-.920
1700	9.079	72.164	64.824	12.479	13.839	6.291	-.809
1800	9.091	72.683	65.246	13.387	13.844	5.846	-.710
1900	9.103	73.175	65.650	14.297	13.849	5.403	-.621
2000	9.114	73.642	66.038	15.208	13.852	4.957	-.542
2100	9.126	74.087	66.411	16.120	13.857	4.512	-.470
2200	9.137	74.512	66.770	17.033	13.860	4.068	-.404
2300	9.148	74.918	67.115	17.947	13.864	3.622	-.344
2400	9.158	75.308	67.449	18.862	13.866	3.176	-.289
2500	9.169	75.682	67.771	19.779	13.870	2.732	-.239
2600	9.179	76.042	68.082	20.696	13.872	2.285	-.192
2700	9.190	76.388	68.383	21.615	13.873	1.839	-.149
2800	9.200	76.723	68.675	22.534	13.874	1.395	-.109
2900	9.210	77.046	68.958	23.455	13.875	.949	-.071
3000	9.220	77.358	69.233	24.376	13.875	.503	-.037
3100	9.230	77.661	69.500	25.299	13.874	.058	.004
3200	9.241	77.954	69.760	26.222	13.871	-.390	.027
3300	9.250	78.239	70.012	27.147	13.869	-.834	.055
3400	9.260	78.515	70.258	28.072	13.865	-1.279	.082
3500	9.270	78.783	70.498	28.999	13.861	-1.725	.108
3600	9.280	79.045	70.732	29.926	13.856	-2.171	.132
3700	9.290	79.299	70.960	30.855	13.851	-2.616	.155
3800	9.300	79.547	71.183	31.784	13.845	-3.061	.176
3900	9.310	79.789	71.400	32.715	13.838	-3.504	.196
4000	9.319	80.025	71.613	33.646	13.831	-3.951	.216
4100	9.329	80.255	71.821	34.579	13.824	-4.395	.234
4200	9.339	80.480	72.024	35.512	13.815	-4.838	.252
4300	9.349	80.700	72.224	36.447	13.807	-5.285	.269
4400	9.358	80.915	72.419	37.382	13.799	-5.724	.284
4500	9.368	81.125	72.610	38.318	13.790	-6.170	.300
4600	9.378	81.331	72.797	39.256	13.783	-6.616	.314
4700	9.388	81.533	72.981	40.194	13.774	-7.057	.328
4800	9.397	81.731	73.161	41.133	13.766	-7.501	.342
4900	9.407	81.924	73.338	42.073	13.758	-7.941	.354
5000	9.417	82.115	73.512	43.015	13.751	-8.384	.366
5100	9.426	82.301	73.682	43.957	13.744	-8.827	.378
5200	9.436	82.484	73.850	44.900	13.738	-9.271	.390
5300	9.446	82.664	74.014	45.844	13.731	-9.714	.401
5400	9.455	82.841	74.176	46.789	13.726	-10.157	.411
5500	9.465	83.014	74.335	47.735	13.721	-10.596	.421
5600	9.474	83.185	74.492	48.682	13.717	-11.040	.431
5700	9.484	83.353	74.646	49.630	13.713	-11.482	.440
5800	9.494	83.518	74.797	50.579	13.710	-11.924	.449
5900	9.503	83.680	74.946	51.529	13.708	-12.368	.458
6000	9.513	83.840	75.093	52.479	13.706	-12.808	.466

June 30, 1963; Dec. 31, 1963

PHOSPHORUS MONOCHLORIDE (PCl) (IDEAL GAS) MOL. WT. = 66.432

Ground State Configuration [$^3\Sigma$]

$S^\circ_{298.15}$ = [56.8] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [34.7] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [35.0] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	[3]

ω_e = [472] cm.$^{-1}$

$\omega_e x_e$ = [1.89] cm.$^{-1}$

σ = 1

B_e = [0.2443]

α_e = [0.00098]

r_e = [2.04] Å

Heat of Formation.

The selected $\Delta H^\circ_{f\ 298.15}$ was calculated by assuming that the second and third bonds in $PCl_3(g)$ are of equal strength, and that the first bond has a strength 20% greater than the other two. These assumptions were used by C. B. Henderson and R. S. Scheffee, Survey of Thermochemical Data, Atlantic Research Corporation, Alexandria, Virginia, January 1960. The selected $\Delta H^\circ_{f\ 298.15}$ was calculated using these bond strengths and auxiliary data from JANAF Tables.

A $\Delta H^\circ_{f\ 298.15}$, 40 kcal. mole^{-1}, estimated by C. J. O'Brien and J. R. Perrin, The Marquardt Corporation and J. Perrine, Olin Mathieson Chemical Corp., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules," WSS/CI Paper 59-4, October, 1959, when adjusted to the red V phosphorus reference state becomes [44.2] kcal. mole^{-1}.

A. A. Sandoval, H. C. Moser, and R. W. Kiser, J. Phys. Chem. 67, 124, (1963) have calculated a $\Delta H^\circ_{f\ 298.15}$ for PCl from an appearance potential. They selected the process $PCl_3 \rightarrow Cl^+ + e^- + PCl + Cl$ to explain this potential rather than the process $PCl_3 \rightarrow Cl^+ + e^- + P + Cl_2$. The reason for their selection was a calculated $\Delta H_f^+(Cl)$, 10 kcal. lower than the literature value (See National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" Circular 500). Use of the JANAF $\Delta H^\circ_{f\ 298.15}$ for PCl_3 eliminates this difference. Therefore, the process of the reported appearance potential would apparently be the second process which does not involve the neutral PCl radical.

Heat Capacity and Entropy.

The molecular constants were estimated by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, April 25, 1963.

CIP

Lead Monochloride (PbCl)

(Ideal Gas) Mol. Wt. = 242.67 INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.340	3.901	3.901	INFINITE
100	7.460	53.389	69.716	-1.633	3.835	1.636	-3.574
200	8.335	58.873	63.055	-.836	3.668	-.497	.543
298	8.658	62.272	62.272	.000	3.500	-2.506	1.837
300	8.662	62.325	62.272	.016	3.497	-2.543	1.852
400	8.805	64.839	62.613	.890	3.304	-4.527	2.474
500	8.881	66.813	63.263	1.775	3.089	-6.462	2.824
600	8.929	68.436	63.994	2.666	2.855	-8.349	3.041
700	8.964	69.816	64.730	3.560	1.441	-10.006	3.124
800	8.991	71.014	65.442	4.458	1.175	-11.624	3.175
900	9.013	72.075	66.121	5.358	.916	-13.208	3.207
1000	9.034	73.025	66.765	6.261	.665	-14.764	3.226
1100	9.054	73.887	67.374	7.165	.422	-16.295	3.237
1200	9.075	74.676	67.950	8.071	.187	-17.804	3.242
1300	9.098	75.403	68.496	8.980	-.041	-19.294	3.243
1400	9.125	76.078	69.013	9.891	-.267	-20.767	3.242
1500	9.154	76.709	69.506	10.805	-.490	-22.222	3.238
1600	9.188	77.301	69.974	11.722	-.714	-23.664	3.232
1700	9.225	77.859	70.422	12.643	-.937	-25.090	3.225
1800	9.267	78.387	70.850	13.567	-1.162	-26.506	3.218
1900	9.311	78.890	71.260	14.496	-1.387	-27.908	3.210
2000	9.358	79.368	71.654	15.430	-1.614	-29.298	3.201
2100	9.408	79.826	72.032	16.368	-44.291	-29.124	3.031
2200	9.459	80.265	72.396	17.311	-44.427	-28.400	2.821
2300	9.512	80.687	72.748	18.260	-44.579	-27.667	2.629
2400	9.565	81.093	73.087	19.214	-44.747	-26.928	2.452
2500	9.618	81.484	73.415	20.173	-44.935	-26.183	2.289
2600	9.671	81.862	73.733	21.137	-45.139	-25.428	2.137
2700	9.723	82.228	74.041	22.107	-45.359	-24.666	1.997
2800	9.774	82.583	74.339	23.082	-45.598	-23.895	1.865
2900	9.824	82.927	74.630	24.062	-45.851	-23.115	1.742
3000	9.871	83.261	74.912	25.047	-46.118	-22.327	1.626
3100	9.917	83.585	75.186	26.036	-46.398	-21.530	1.518
3200	9.961	83.901	75.454	27.030	-46.691	-20.723	1.415
3300	10.003	84.208	75.714	28.028	-46.993	-19.906	1.318
3400	10.043	84.507	75.969	29.031	-47.304	-19.079	1.226
3500	10.080	84.799	76.217	30.037	-47.624	-18.247	1.139
3600	10.115	85.083	76.459	31.046	-47.949	-17.401	1.056
3700	10.148	85.361	76.696	32.060	-48.278	-16.548	.977
3800	10.179	85.632	76.928	33.076	-48.610	-15.686	.902
3900	10.208	85.897	77.154	34.096	-48.945	-14.814	.830
4000	10.235	86.155	77.376	35.118	-49.281	-13.938	.762
4100	10.261	86.408	77.593	36.143	-49.616	-13.050	.696
4200	10.284	86.656	77.806	37.170	-49.951	-12.153	.632
4300	10.305	86.898	78.015	38.199	-50.284	-11.252	.572
4400	10.325	87.135	78.219	39.231	-50.614	-10.336	.513
4500	10.344	87.368	78.420	40.264	-50.941	-9.420	.457
4600	10.361	87.595	78.617	41.300	-51.264	-8.492	.403
4700	10.377	87.818	78.810	42.336	-51.583	-7.561	.352
4800	10.391	88.037	79.000	43.375	-51.898	-6.618	.301
4900	10.404	88.251	79.187	44.415	-52.207	-5.673	.253
5000	10.416	88.461	79.370	45.456	-52.512	-4.722	.206
5100	10.427	88.668	79.551	46.498	-52.811	-3.761	.161
5200	10.438	88.870	79.728	47.541	-53.105	-2.795	.117
5300	10.447	89.069	79.902	48.585	-53.394	-1.824	.075
5400	10.456	89.265	80.074	49.630	-53.679	-.849	.034
5500	10.464	89.457	80.243	50.676	-53.958	.131	-.005
5600	10.471	89.645	80.409	51.723	-54.232	1.117	-.044
5700	10.478	89.831	80.573	52.771	-54.502	2.104	-.081
5800	10.484	90.013	80.734	53.819	-54.768	3.105	-.117
5900	10.490	90.192	80.893	54.868	-55.030	4.102	-.152
6000	10.495	90.369	81.049	55.917	-55.288	5.105	-.186

June 30, 1962

Lead Monochloride (PbCl) (Ideal Gas)

Mol. Wt. = 242.67

ΔH_f° 298.15 = 3.5 ± 7.2 kcal. mole^{-1}

$S^\circ_{298.15}$ = 62.272 cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi$

Electronic Level and Multiplicity

ϵ , cm.$^{-1}$	g_1
0	2
[8266]	2

ω_e = 303.8 cm.$^{-1}$ $\omega_e x_e$ = 0.88 cm.$^{-1}$ σ = 1

B_e = [0.1029] cm.$^{-1}$ α_e = [0.00048] cm.$^{-1}$

Heat of Formation. ΔH_f° 298.15 was calculated from the dissociation energy of PbCl(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e, and $\omega_e x_e$ were given by Herzberg, loc. cit. B_e, α_e, and ϵ were estimated by J. S. Gordon, Astrosystems, Inc., private communication, May, 1962.

Silicon Monochloride (SiCl)

(Ideal Gas) GFW = 63.539

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.363	45.203	45.203	INFINITE
100	7.826	47.854	64.232	-1.638	45.516	43.080	-94.151
200	8.297	53.451	57.590	-.828	45.682	40.565	-44.328
298	8.552	56.815	56.815	.000	45.700	38.046	-27.888
300	8.556	56.868	56.815	.016	45.699	37.998	-27.682
400	8.711	59.352	57.153	.880	45.641	35.438	-19.363
500	8.805	61.307	57.795	1.756	45.547	32.899	-14.380
600	8.866	62.918	58.518	2.640	45.428	30.380	-11.066
700	8.909	64.288	59.247	3.529	45.293	27.882	-8.705
800	8.941	65.480	59.954	4.421	45.143	25.404	-6.940
900	8.967	66.535	60.627	5.317	44.981	22.948	-5.572
1000	8.988	67.481	61.266	6.214	44.808	20.508	-4.482
1100	9.006	68.338	61.871	7.114	44.624	18.087	-3.593
1200	9.023	69.123	62.443	8.016	44.431	15.682	-2.856
1300	9.038	69.845	62.985	8.919	44.228	13.294	-2.235
1400	9.052	70.516	63.499	9.823	44.015	10.923	-1.705
1500	9.065	71.141	63.988	10.729	43.793	8.568	-1.248
1600	9.077	71.726	64.453	11.636	43.561	6.227	-.851
1700	9.089	72.277	64.898	12.545	31.327	4.007	-.515
1800	9.101	72.797	65.322	13.454	31.131	2.406	-.292
1900	9.113	73.289	65.729	14.365	30.936	.815	-.094
2000	9.124	73.757	66.118	15.277	30.740	-.764	.084
2100	9.135	74.202	66.493	16.189	30.545	-2.335	.243
2200	9.146	74.627	66.853	17.103	30.350	-3.897	.387
2300	9.156	75.034	67.200	18.019	30.156	-5.449	.518
2400	9.167	75.424	67.534	18.935	29.962	-6.992	.637
2500	9.177	75.798	67.858	19.852	29.767	-8.529	.746
2600	9.188	76.159	68.170	20.770	29.573	-10.056	.845
2700	9.199	76.506	68.472	21.690	29.378	-11.578	.937
2800	9.209	76.840	68.765	22.610	29.183	-13.089	1.022
2900	9.220	77.164	69.049	23.531	28.988	-14.596	1.100
3000	9.230	77.476	69.325	24.454	28.792	-16.097	1.173
3100	9.241	77.779	69.593	25.377	28.596	-17.591	1.240
3200	9.252	78.073	69.853	26.302	28.400	-19.076	1.303
3300	9.263	78.358	70.107	27.228	28.203	-20.556	1.361
3400	9.275	78.634	70.353	28.155	28.007	-22.030	1.416
3500	9.286	78.903	70.594	29.083	27.809	-23.502	1.468
3600	9.298	79.165	70.828	30.012	-64.349	-22.706	1.378
3700	9.310	79.420	71.057	30.942	-64.448	-21.548	1.273
3800	9.322	79.668	71.280	31.874	-64.546	-20.388	1.173
3900	9.335	79.911	71.499	32.807	-64.646	-19.225	1.077
4000	9.348	80.147	71.712	33.741	-64.745	-18.058	.987
4100	9.361	80.378	71.921	34.677	-64.845	-16.893	.900
4200	9.375	80.604	72.125	35.613	-64.945	-15.723	.818
4300	9.389	80.825	72.324	36.552	-65.043	-14.549	.739
4400	9.404	81.041	72.520	37.491	-65.142	-13.372	.664
4500	9.419	81.252	72.712	38.432	-65.239	-12.192	.592
4600	9.435	81.459	72.900	39.375	-65.335	-11.013	.523
4700	9.451	81.663	73.084	40.319	-65.431	-9.830	.457
4800	9.467	81.862	73.265	41.265	-65.525	-8.648	.394
4900	9.484	82.057	73.442	42.213	-65.618	-7.460	.333
5000	9.502	82.249	73.616	43.162	-65.709	-6.276	.274
5100	9.520	82.437	73.788	44.113	-65.799	-5.082	.218
5200	9.539	82.622	73.956	45.066	-65.887	-3.891	.164
5300	9.558	82.804	74.121	46.021	-65.973	-2.699	.111
5400	9.578	82.983	74.283	46.978	-66.057	-1.505	.061
5500	9.598	83.159	74.443	47.936	-66.140	-.310	.012
5600	9.619	83.332	74.600	48.897	-66.221	.890	-.035
5700	9.641	83.502	74.755	49.860	-66.300	2.089	-.080
5800	9.664	83.670	74.907	50.826	-66.377	3.291	-.124
5900	9.687	83.836	75.057	51.793	-66.452	4.488	-.166
6000	9.710	83.999	75.205	52.763	-66.526	5.692	-.207

Dec. 31, 1960; Sept. 30, 1967

SILICON MONOCHLORIDE (SiCl) (IDEAL GAS) GFW = 63.539

Ground State Configuration $^2\Pi_r$

$\Delta Hf^\circ_0 = 45.2 \pm 15$ kcal/mol

$S^\circ_{298.15} = 56.82$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 45.7 \pm 15$ kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	207.2	2
A $^2\Sigma^+$	22993.5	2
B $^2\Sigma^+$	34192	2
B' $^2\Delta_i$	35618	4
C $^2\Pi$	41245	4
D $^2\Pi$	44940	4

$\omega_e = 533.75$ cm^{-1} $\omega_e x_e = 2.27$ cm^{-1} $\sigma = 1$

$B_e = 0.25416$ cm^{-1} $\alpha_e = 0.00161$ cm^{-1} $r_e = 2.058$ Å

Heat of Formation

The adopted value is based on $D^\circ_0 = 90 \pm 15$ kcal/mol which is calculated from $D^\circ_0/D''(\mathrm{LBX}) = 1.01$ and $D''(\mathrm{LBX}) = 89$ kcal/mol. The latter value comes from linear Birge-Sponer extrapolation of ground state vibrational constants obtained by Verma (1) from the B'-X system. The ratio $D^\circ_0/D''(\mathrm{LBX}) = 1.01$ is calculated from an empirical relationship proposed by Hildenbrand (9): $D^\circ_0/D''(\mathrm{LBX}) = 0.365(r_x/r_e) + 0.448$ and $r_x = 14.40/(\mathrm{IP}-\mathrm{EA})$, where IP is the ionization potential of the more electropositive element and EA is the electron affinity of the more electronegative element. A similar calculation using $\omega_e''x_e'' = 2.1$ cm^{-1} obtained from the B-X system (2) would give $D^\circ_0 = 98$ kcal/mol. These values for D°_0 may be compared with average (per bond) heats of atomization of 101 kcal/mol for $SiCl_2$ and 94 kcal/mol for $SiCl_4$.

Gaydon (3) selected $D^\circ_0 = 76 \pm 12$ kcal/mol on the assumption that $D^\circ_0/D''(\mathrm{LBX}) = 0.8$, but Ovcharenko (4) suggested that this was too low by comparison with $D^\circ_0 = 117$ kcal/mol obtained from the B' state. The latter value is calculated from D'(LBX) = 33 kcal/mol and presumes that Si(^{1}D) is the excited atomic product. The B and C states could also correlate to give values fairly consistent with $D^\circ_0 = 117$. This interpretation seems unlikely, however, because it would involve a crossing of the potential curves for the B and B' states. Since the potential curves may be distorted due to the close proximity of the B and B' states, it seems preferable to obtain D°_0 from constants for the ground state.

Heat Capacity and Entropy

Electronic levels of the B and C states are taken from the B-X and C-X systems reported by Ovcharenko et al. (5, 6). The A level is that assigned by Sanii (10) from analysis of the A-X system. The D level is that derived by Herzberg (7) from data of Jevons (8), but it is assigned as $^2\Pi$ as suggested by Verma (1). The B' level is from Verma and is confirmed by the earlier analysis of Ovcharenko (4). All vibrational and rotational constants for the ground state are those obtained by Verma (1) from the B'-X system. Values only slightly different were obtained from the B-X system by Ovcharenko (5, 6). The adopted constants are adjusted to the natural isotopic abundances of Si and Cl.

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Titanium Monochloride (TiCl)

(Ideal Gas) GFW = 83.353

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.314	36.835	36.835	INFINITE
100	7.230	50.812	66.943	-1.613	37.054	34.427	-75.240
200	8.187	56.128	60.331	-.841	37.005	31.809	-34.759
298	8.915	59.538	59.538	.000	36.900	29.277	-21.460
300	8.927	59.593	59.538	.017	36.898	29.229	-21.294
400	9.491	62.243	59.896	.939	36.787	26.691	-14.583
500	9.883	64.406	60.588	1.909	36.685	24.178	-10.568
600	10.135	66.232	61.380	2.911	36.586	21.685	-7.899
700	10.285	67.806	62.189	3.932	36.483	19.210	-5.998
800	10.370	69.186	62.979	4.966	36.363	16.750	-4.576
900	10.416	70.410	63.738	6.005	36.222	14.307	-3.474
1000	10.442	71.509	64.461	7.048	36.054	11.880	-2.596
1100	10.458	72.505	65.148	8.093	35.861	9.473	-1.882
1200	10.470	73.416	65.799	9.140	34.706	7.121	-1.297
1300	10.481	74.254	66.418	10.187	34.588	4.827	-.811
1400	10.494	75.031	67.006	11.236	34.456	2.542	-.397
1500	10.509	75.756	67.565	12.286	34.308	.267	-.039
1600	10.526	76.434	68.098	13.338	34.143	-1.996	.273
1700	10.545	77.073	68.608	14.391	33.959	-4.249	.546
1800	10.564	77.676	69.095	15.447	33.754	-6.491	.788
1900	10.585	78.248	69.562	16.504	33.528	-8.720	1.003
2000	10.606	78.792	70.010	17.564	28.832	-10.784	1.178
2100	10.628	79.310	70.440	18.625	28.586	-12.759	1.328
2200	10.649	79.805	70.855	19.689	28.341	-14.723	1.463
2300	10.669	80.278	71.254	20.755	28.098	-16.674	1.584
2400	10.689	80.733	71.640	21.823	27.855	-18.614	1.695
2500	10.708	81.170	72.012	22.893	27.613	-20.546	1.796
2600	10.725	81.590	72.373	23.965	27.372	-22.468	1.889
2700	10.742	81.995	72.722	25.038	27.131	-24.380	1.973
2800	10.758	82.386	73.060	26.113	26.891	-26.284	2.052
2900	10.772	82.764	73.388	27.189	26.651	-28.177	2.123
3000	10.786	83.129	73.707	28.267	26.411	-30.064	2.190
3100	10.798	83.483	74.016	29.347	26.171	-31.942	2.252
3200	10.810	83.826	74.318	30.427	25.930	-33.816	2.309
3300	10.821	84.159	74.611	31.509	25.689	-35.677	2.363
3400	10.831	84.482	74.896	32.591	25.448	-37.532	2.413
3500	10.840	84.796	75.175	33.675	25.206	-39.383	2.459
3600	10.849	85.102	75.446	34.759	-76.662	-40.961	2.487
3700	10.857	85.399	75.711	35.844	-76.877	-39.967	2.361
3800	10.864	85.689	75.970	36.930	-77.105	-38.970	2.241
3900	10.871	85.971	76.223	38.017	-77.346	-37.960	2.127
4000	10.878	86.246	76.470	39.105	-77.602	-36.946	2.019
4100	10.884	86.515	76.712	40.193	-77.870	-35.927	1.915
4200	10.891	86.777	76.948	41.282	-78.151	-34.903	1.816
4300	10.897	87.034	77.180	42.371	-78.445	-33.871	1.722
4400	10.903	87.284	77.407	43.461	-78.749	-32.829	1.631
4500	10.909	87.589	77.629	44.552	-79.065	-31.782	1.544
4600	10.915	87.769	77.847	45.643	-79.390	-30.725	1.460
4700	10.921	88.004	78.060	46.735	-79.726	-29.663	1.379
4800	10.927	88.234	78.270	47.827	-80.072	-28.596	1.302
4900	10.933	88.459	78.476	48.920	-80.426	-27.522	1.228
5000	10.939	88.680	78.677	50.013	-80.788	-26.436	1.156
5100	10.945	88.897	78.876	51.108	-81.157	-25.345	1.086
5200	10.952	89.109	79.070	52.203	-81.534	-24.246	1.019
5300	10.959	89.318	79.262	53.298	-81.918	-23.145	.954
5400	10.966	89.523	79.450	54.394	-82.309	-22.028	.892
5500	10.973	89.724	79.635	55.491	-82.703	-20.907	.831
5600	10.980	89.922	79.817	56.589	-83.104	-19.785	.772
5700	10.987	90.117	79.996	57.687	-83.509	-18.648	.715
5800	10.995	90.308	80.172	58.786	-83.918	-17.506	.660
5900	11.003	90.496	80.345	59.886	-84.331	-16.358	.606
6000	11.011	90.681	80.516	60.987	-84.748	-15.205	.554

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

TITANIUM MONOCHLORIDE (TiCl) (IDEAL GAS) GFW = 83.353

Ground State Configuration $[^4\Sigma]$

$\Delta Hf^\circ_0 = [36.8 \pm 10.0]$ kcal/mol

$S^\circ_{298.15} = 59.54 \pm 2.0$ gibbs/mol

$\Delta Hf^\circ_{298.15} = [36.9 \pm 10.0]$ kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$\omega_e = 379.7\ cm^{-1}$ $\omega_e x_e = 3.41\ cm^{-1}$ $\sigma = 1$

$B_e = [0.146]\ cm^{-1}$ $\alpha_e = [0.0013]\ cm^{-1}$ $r_e = [2.3]$ Å

Heat of Formation

The heat of formation, ΔHf°_{298}, of TiCl (g) is calculated from the dissociation energy, D°_0, which is estimated as 105 kcal/mol. This estimate is obtained from the relation $D(TiCl_4) < D^\circ_0(TiCl) < D(TiCl_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave (1).

Extrapolations of the vibrational levels reported by Shenyavskaya (2), Rao (3) and Mace and Packer (4) yield values of the dissociation energy which are very low when considered with respect to bond energy relations.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, $\omega_e x_e$, were reported by Shenyavskaya et al. (2). The interatomic distance is estimated from Guggenheimer's relation (5). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+ (6). α_e is estimated from the Morse potential function.

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Tungsten Monochloride (WCl)

(Ideal Gas) GFW = 219.303

T, °K	gibbs/mol Cp°	S°	−(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.240	132.346	132.346	INFINITE
100	7.082	54.196	69.617	- 1.542	132.540	129.607	- 283.257
200	7.842	59.335	63.316	- .796	132.443	126.704	- 138.455
298	8.327	62.567	62.567	.000	132.300	123.917	- 90.834
300	8.334	62.619	62.567	.015	132.297	123.865	- 90.235
400	8.582	65.054	62.898	.863	132.140	121.077	- 66.154
500	8.718	66.985	63.529	1.728	131.978	118.330	- 51.722
600	8.802	68.583	64.242	2.604	131.809	115.616	- 42.113
700	8.859	69.944	64.962	3.488	131.632	112.932	- 35.259
800	8.904	71.130	65.660	4.376	131.444	110.272	- 30.125
900	8.945	72.181	66.327	5.268	131.250	107.638	- 26.138
1000	8.985	73.126	66.961	6.165	131.045	105.025	- 22.953
1100	9.027	73.984	67.561	7.065	130.833	102.433	- 20.351
1200	9.071	74.771	68.129	7.970	130.613	99.862	- 18.187
1300	9.117	75.499	68.669	8.880	130.386	97.308	- 16.359
1400	9.164	76.177	69.181	9.794	130.151	94.771	- 14.794
1500	9.211	76.810	69.669	10.713	129.909	92.254	- 13.441
1600	9.257	77.406	70.134	11.636	129.659	89.752	- 12.260
1700	9.303	77.969	70.578	12.564	129.401	87.265	- 11.219
1800	9.349	78.502	71.004	13.497	129.137	84.794	- 10.295
1900	9.394	79.009	71.412	14.434	128.865	82.337	- 9.471
2000	9.439	79.492	71.804	15.375	128.584	79.897	- 8.731
2100	9.484	79.953	72.181	16.321	128.295	77.470	- 8.062
2200	9.530	80.395	72.545	17.272	127.998	75.055	- 7.456
2300	9.578	80.820	72.895	18.228	127.694	72.656	- 6.904
2400	9.627	81.229	73.234	19.188	127.382	70.270	- 6.399
2500	9.679	81.623	73.562	20.153	127.061	67.896	- 5.935
2600	9.734	82.004	73.879	21.124	126.733	65.536	- 5.509
2700	9.792	82.372	74.187	22.100	126.393	63.190	- 5.115
2800	9.854	82.729	74.486	23.082	126.030	60.858	- 4.750
2900	9.918	83.076	74.776	24.071	125.637	58.533	- 4.411
3000	9.986	83.414	75.058	25.066	125.209	56.227	- 4.096
3100	10.057	83.742	75.333	26.068	124.732	53.934	- 3.802
3200	10.131	84.063	75.601	27.078	124.203	51.657	- 3.528
3300	10.208	84.376	75.862	28.095	123.613	49.399	- 3.272
3400	10.287	84.681	76.117	29.119	122.955	47.164	- 3.032
3500	10.368	84.981	76.366	30.152	122.216	44.943	- 2.806
3600	10.450	85.274	76.609	31.193	121.369	42.747	- 2.595
3700	10.533	85.561	76.847	32.242	112.084	40.624	- 2.400
3800	10.616	85.843	77.080	33.299	111.812	38.697	- 2.226
3900	10.700	86.120	77.309	34.365	111.548	36.777	- 2.061
4000	10.783	86.392	77.532	35.439	111.290	34.862	- 1.905
4100	10.865	86.659	77.752	36.522	111.040	32.955	- 1.757
4200	10.946	86.922	77.967	37.612	110.796	31.053	- 1.616
4300	11.025	87.181	78.178	38.711	110.560	29.155	- 1.482
4400	11.102	87.435	78.386	39.817	110.331	27.266	- 1.354
4500	11.177	87.685	78.590	40.931	110.109	25.381	- 1.233
4600	11.250	87.932	78.790	42.053	109.894	23.499	- 1.116
4700	11.319	88.175	78.987	43.181	109.685	21.623	- 1.005
4800	11.385	88.414	79.181	44.316	109.482	19.751	- .899
4900	11.449	88.649	79.372	45.458	109.285	17.885	- .798
5000	11.508	88.881	79.560	46.606	109.095	16.022	- .700
5100	11.565	89.109	79.745	47.760	108.910	14.164	- .607
5200	11.617	89.334	79.927	48.919	108.730	12.309	- .517
5300	11.666	89.556	80.107	50.083	108.555	10.454	- .431
5400	11.712	89.775	80.284	51.252	108.384	8.603	- .348
5500	11.754	89.990	80.458	52.425	108.218	6.759	- .269
5600	11.792	90.202	80.630	53.603	108.056	4.915	- .192
5700	11.827	90.411	80.800	54.784	107.897	3.071	- .118
5800	11.858	90.617	80.968	55.968	107.741	1.236	- .047
5900	11.886	90.820	81.133	57.155	107.589	- .597	.022
6000	11.911	91.020	81.296	58.345	- 86.465	- .347	.013

June 30, 1967

TUNGSTEN MONOCHLORIDE (WCl) (IDEAL GAS) GFW = 219.303

Ground State Configuration [$^2\Delta$]

ΔHf°_0 = [132.3 ± 10] kcal/mol

$S^\circ_{298.15}$ = [62.6] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [132.3 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[5000]	[2]
[15000]	[20]

ω_e = [455.4] cm^{-1}

$\omega_e x_e$ = [1.46] cm^{-1}

σ = 1

B_e = [0.11105] cm^{-1}

α_e = [0.00042] cm^{-1}

r_e = [2.26] Å

Heat of Formation

The heat of formation, ΔHf°_{298}(WCl,g) = 132.3 kcal/mol, is calculated from the bond dissociation energy, D°_{298}(W-Cl) = 100 ± 10 kcal/mol. This estimated D°_{298} is obtained from the average bond dissociation energy for $WCl_x(g) \rightarrow W(g) + xCl(g)$ where x = 2,4,5,6, using all JANAF values.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WCl_6(g). This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D^\circ_0 + 0.5\ \omega_e) = 0.0032$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is 25.20 x 10^{-39} g cm^2.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g). See WF(g) table (March 31, 1967) for details.

Zirconium Monochloride (ZrCl)

(Ideal Gas) GFW = 126.673

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.249	49.269	49.269	INFINITE
100	7.107	52.333	67.846	-1.551	49.407	46.766	-102.207
200	7.895	57.503	61.507	-.801	49.268	44.172	-48.269
298	8.366	60.754	60.754	.000	49.100	41.707	-30.572
300	8.372	60.806	60.754	.015	49.097	41.661	-30.350
400	8.612	63.251	61.086	.866	48.909	39.211	-21.424
500	8.761	65.189	61.720	1.735	48.701	36.810	-16.089
600	8.888	66.798	62.436	2.617	48.471	34.453	-12.549
700	9.021	68.178	63.160	3.513	48.221	32.135	-10.033
800	9.162	69.392	63.864	4.422	47.954	29.856	-8.156
900	9.309	70.479	64.540	5.345	47.671	27.610	-6.705
1000	9.453	71.468	65.184	6.284	47.373	25.397	-5.550
1100	9.591	72.375	65.797	7.236	47.060	23.214	-4.612
1200	9.720	73.215	66.381	8.201	45.879	21.112	-3.845
1300	9.836	73.998	66.937	9.179	45.712	19.055	-3.203
1400	9.940	74.731	67.468	10.168	45.544	17.011	-2.656
1500	10.031	75.420	67.975	11.167	45.374	14.979	-2.182
1600	10.110	76.070	68.461	12.174	45.199	12.958	-1.770
1700	10.178	76.685	68.927	13.189	45.021	10.950	-1.408
1800	10.235	77.268	69.374	14.209	44.836	8.950	-1.087
1900	10.283	77.823	69.804	15.235	44.645	6.962	-.801
2000	10.323	78.351	70.218	16.266	44.446	4.983	-.545
2100	10.355	78.856	70.618	17.300	44.240	3.015	-.314
2200	10.382	79.338	71.003	18.337	39.021	1.233	-.123
2300	10.403	79.800	71.376	19.376	38.800	-.478	.045
2400	10.420	80.243	71.736	20.417	38.581	-2.182	.199
2500	10.433	80.669	72.085	21.460	38.362	-3.876	.339
2600	10.443	81.078	72.423	22.504	38.143	-5.561	.467
2700	10.451	81.473	72.751	23.548	37.924	-7.238	.586
2800	10.458	81.853	73.069	24.594	37.704	-8.906	.695
2900	10.462	82.220	73.379	25.640	37.483	-10.567	.796
3000	10.466	82.575	73.679	26.686	37.262	-12.221	.890
3100	10.469	82.918	73.972	27.733	37.039	-13.866	.978
3200	10.471	83.250	74.257	28.780	36.815	-15.505	1.059
3300	10.473	83.573	74.534	29.827	36.590	-17.136	1.135
3400	10.474	83.885	74.804	30.874	36.363	-18.760	1.206
3500	10.476	84.189	75.068	31.922	36.135	-20.379	1.273
3600	10.478	84.484	75.326	32.970	35.907	-21.990	1.335
3700	10.479	84.771	75.577	34.018	35.677	-23.595	1.394
3800	10.481	85.051	75.823	35.066	35.446	-25.195	1.449
3900	10.483	85.323	76.063	36.114	35.213	-26.787	1.501
4000	10.486	85.588	76.298	37.162	34.980	-28.374	1.550
4100	10.488	85.847	76.527	38.211	34.746	-29.955	1.597
4200	10.491	86.100	76.752	39.260	34.511	-31.531	1.641
4300	10.494	86.347	76.973	40.309	34.276	-33.101	1.682
4400	10.498	86.588	77.188	41.359	34.040	-34.663	1.722
4500	10.502	86.824	77.400	42.409	33.803	-36.223	1.759
4600	10.506	87.055	77.607	43.459	33.567	-37.777	1.795
4700	10.510	87.281	77.811	44.510	33.330	-39.324	1.829
4800	10.515	87.502	78.010	45.561	-108.063	-40.186	1.830
4900	10.519	87.719	78.206	46.613	-108.404	-38.766	1.729
5000	10.524	87.932	78.399	47.665	-108.750	-37.343	1.632
5100	10.530	88.140	78.588	48.718	-109.101	-35.910	1.539
5200	10.535	88.345	78.773	49.771	-109.456	-34.471	1.449
5300	10.541	88.545	78.956	50.825	-109.815	-33.027	1.362
5400	10.546	88.743	79.135	51.879	-110.177	-31.575	1.278
5500	10.552	88.936	79.312	52.934	-110.542	-30.115	1.197
5600	10.558	89.126	79.485	53.990	-110.909	-28.650	1.118
5700	10.564	89.313	79.656	55.046	-111.280	-27.180	1.042
5800	10.570	89.497	79.824	56.102	-111.652	-25.698	.968
5900	10.576	89.678	79.990	57.160	-112.026	-24.215	.897
6000	10.582	89.856	80.153	58.218	-112.402	-22.723	.828

June 30, 1961; Sept. 30, 1964; Dec. 31, 1969

ZIRCONIUM MONOCHLORIDE (ZrCl) (IDEAL GAS) GFW = 126.673

Ground State Configuration $[^4\Sigma]$

$\Delta Hf°_0$ = 49.3 ± 5 kcal/mol

$S°_{298.15}$ = [60.8 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = 49.1 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

ω_e = [437] cm^{-1} $\omega_e x_e$ = [1.1] cm^{-1} σ = 1

B_e = [0.1248] cm^{-1} α_e = [0.00042] cm^{-1} r_e = [2.3] Å

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction $ZrCl_3(g) + ZrCl(g) = 2\ ZrCl_2(g)$ in the temperature range 1978-2274°K, second and third law analyses give the heats of reaction at 298°K as -10.36 and -12.83 kcal/mol, respectively. The third law drift is 1.4 ± 2.5 eu. Based on the third law $\Delta Hr°_{298}$ and $\Delta Hf°_{298}(ZrCl_2, g)$ = -44.5 kcal/mol (2), and $\Delta Hf°_{298}(ZrCl_3, g)$ = -125.3 kcal/mol (3), we obtain $\Delta Hf°_{298}(ZrCl, g)$ = 49.1 kcal/mol which is adopted in the tabulation.

Farber et al. (4) also studied mass spectrometrically the reaction $Zr(c) + Cl(g) \rightarrow ZrCl(g)$. They reported a second law heat of reaction, $\Delta Hr°_{298}$ = 8.7 ± 1.4 kcal/mol. Using the equilibrium constants K = I(ZrCl)/I(Cl) which we calculated from their reported ion intensities of run 3 in the temperature range 1667-1896°K, we obtain $\Delta Hr°_{298}$ = 20.3 kcal/mol by the third law method. The third law drift is 6.1 ± 2.4 eu. The heat of formation is derived as $\Delta Hf°_{298}(ZrCl, g)$ = 49.2 kcal/mol.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $ZrCl_4(g)$. The bond distance is then used with Guggenheimer's relation (5) for polar molecules to calculate the fundamental vibrational frequency ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D°_0 + 0.5\,\omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is 22.425×10^{-39} g cm^2.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by Moore (6). The electronic levels and the quantum weights are estimated to be the same as those of ZrF(g).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF $ZrCl_2(g)$ table dated Dec. 31, 1969.
3. JANAF $ZrCl_3(g)$ table dated Dec. 31, 1969.
4. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
5. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
6. C. E. Moore, "Atomic Energy Levels," Vol. II., Natl. Bur. Std. Circ. 467, 1952.

Chlorine, Diatomic (Cl_2)
(Reference State - Ideal Gas) Mol. Wt. = 70.906

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.194	.000	.000	.000
100	7.001	45.150	60.130	-1.498	.000	.000	.000
200	7.576	50.156	54.016	-.772	.000	.000	.000
298	8.111	53.289	53.289	.000	.000	.000	.000
300	8.119	53.339	53.289	.015	.000	.000	.000
400	8.437	55.724	53.612	.845	.000	.000	.000
500	8.624	57.628	54.231	1.698	.000	.000	.000
600	8.741	59.212	54.933	2.567	.000	.000	.000
700	8.821	60.565	55.643	3.445	.000	.000	.000
800	8.878	61.747	56.334	4.331	.000	.000	.000
900	8.922	62.796	56.995	5.221	.000	.000	.000
1000	8.956	63.737	57.623	6.115	.000	.000	.000
1100	8.985	64.592	58.218	7.012	.000	.000	.000
1200	9.010	65.375	58.782	7.912	.000	.000	.000
1300	9.032	66.097	59.318	8.814	.000	.000	.000
1400	9.051	66.767	59.826	9.718	.000	.000	.000
1500	9.069	67.392	60.310	10.624	.000	.000	.000
1600	9.086	67.978	60.771	11.532	.000	.000	.000
1700	9.102	68.530	61.211	12.441	.000	.000	.000
1800	9.117	69.050	61.633	13.352	.000	.000	.000
1900	9.133	69.544	62.036	14.264	.000	.000	.000
2000	9.149	70.013	62.423	15.179	.000	.000	.000
2100	9.166	70.459	62.795	16.094	.000	.000	.000
2200	9.184	70.886	63.154	17.012	.000	.000	.000
2300	9.203	71.295	63.499	17.931	.000	.000	.000
2400	9.223	71.687	63.832	18.852	.000	.000	.000
2500	9.245	72.064	64.154	19.776	.000	.000	.000
2600	9.268	72.427	64.465	20.701	.000	.000	.000
2700	9.293	72.777	64.766	21.629	.000	.000	.000
2800	9.319	73.116	65.058	22.560	.000	.000	.000
2900	9.346	73.443	65.342	23.493	.000	.000	.000
3000	9.374	73.760	65.617	24.429	.000	.000	.000
3100	9.403	74.068	65.885	25.368	.000	.000	.000
3200	9.432	74.367	66.145	26.310	.000	.000	.000
3300	9.461	74.658	66.399	27.255	.000	.000	.000
3400	9.490	74.941	66.646	28.202	.000	.000	.000
3500	9.518	75.216	66.887	29.153	.000	.000	.000
3600	9.546	75.485	67.122	30.106	.000	.000	.000
3700	9.573	75.747	67.352	31.062	.000	.000	.000
3800	9.598	76.002	67.576	32.020	.000	.000	.000
3900	9.622	76.252	67.795	32.981	.000	.000	.000
4000	9.645	76.496	68.010	33.945	.000	.000	.000
4100	9.666	76.734	68.220	34.910	.000	.000	.000
4200	9.685	76.967	68.425	35.878	.000	.000	.000
4300	9.702	77.195	68.626	36.847	.000	.000	.000
4400	9.718	77.419	68.824	37.818	.000	.000	.000
4500	9.732	77.637	69.017	38.791	.000	.000	.000
4600	9.743	77.851	69.207	39.764	.000	.000	.000
4700	9.754	78.061	69.393	40.739	.000	.000	.000
4800	9.762	78.266	69.576	41.715	.000	.000	.000
4900	9.768	78.468	69.755	42.692	.000	.000	.000
5000	9.774	78.665	69.931	43.669	.000	.000	.000
5100	9.778	78.859	70.105	44.646	.000	.000	.000
5200	9.783	79.049	70.275	45.624	.000	.000	.000
5300	9.787	79.235	70.442	46.603	.000	.000	.000
5400	9.790	79.418	70.607	47.582	.000	.000	.000
5500	9.792	79.598	70.768	48.561	.000	.000	.000
5600	9.794	79.774	70.928	49.540	.000	.000	.000
5700	9.795	79.947	71.084	50.520	.000	.000	.000
5800	9.797	80.118	71.239	51.499	.000	.000	.000
5900	9.797	80.285	71.391	52.479	.000	.000	.000
6000	9.798	80.450	71.540	53.459	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965.

CHLORINE, DIATOMIC (Cl_2) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 70.906

Ground State Configuration $^1\Sigma^+$

$\Delta H^\circ_{f\ 0} = 0$

$S^\circ_{298.15} = 53.29 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298} = 0$

Electronic Levels and Multiplicities

State	ϵ cm.$^{-1}$	g_1
$^1\Sigma^+$	0	1
$^3\Pi_0^+$	18,147 ± 500	1
$^3\Pi_1$	17,841 ± 500	2
$^3\Pi_2$	17,560 ± 500	2

$\omega_e = 561.1$ cm.$^{-1}$

$\omega_e x_e = 4.0$ cm.$^{-1}$

$\sigma = 2$

$B_e = 0.2408$ cm.$^{-1}$

$\alpha_e = 0.0017$ cm.$^{-1}$

$r_e = 1.986$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for Cl_2(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here were calculated by R. L. Potter, J. Chem. Phys. 31, 1100 (1959) using a direct summation over the energy levels not including those of non-bonding states. The functions are for the naturally occurring isotopic composition.

The absorption spectrum of chlorine has been observed by A. Elliott, Proc. Roy. Soc. A 127, 638 (1930); C. F. Goodeve and B. A. Stephens, Trans. Faraday Soc. 32, 1517 (1936); H. Stammreich, R. Forneris and Y. Tavares, Spectrochim. Acta, 17, 775 (1961); Y. V. Rao and P. Venkateswarlu, J. Mol. Spectr. 9, 173 (1962); and A. E. Douglas, C. K. Moller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963). There is disagreement over the vibrational assignments. The listed ground state spectroscopic constants for the naturally occurring isotopic composition are based upon the abundances given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The molecular structure of gaseous chlorine was determined by the sector-microphotometer method of electron diffraction by S. Shibata, J. Phys. Chem. 67, 2256 (1963). The value of r_e(Cl-Cl) was found to be 1.986 Å. The other r_e values, 1.983 - 1.989 Å, were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., 1950; W. G. Richards and R. F. Barrow, Proc. Chem. Soc., 297 (1962), and L. S. Bartell and K. Kuchitsu, presented at the International Conference on Magnetism and Crystallography, 1961, quoted by S. Shibata, loc. cit.

Cesium Chloride, Dimeric (Cs_2Cl_2)

(Ideal Gas) GFW = 336.716

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.990	-156.808	-156.808	INFINITE
100	17.135	71.227	108.595	-3.737	-157.277	-157.258	343.686
200	19.083	83.899	93.388	-1.898	-157.446	-157.172	171.750
298	19.507	91.614	91.614	.000	-157.700	-156.991	115.078
300	19.511	91.734	91.614	.036	-157.707	-156.986	114.364
400	19.667	97.372	92.382	1.996	-159.101	-156.361	85.431
500	19.740	101.769	93.836	3.967	-159.481	-155.632	68.027
600	19.780	105.372	95.467	5.943	-159.858	-154.825	56.395
700	19.804	108.423	97.106	7.922	-160.237	-153.957	48.067
800	19.820	111.069	98.689	9.904	-160.621	-153.035	41.807
900	19.831	113.404	100.197	11.886	-161.007	-152.062	36.926
1000	19.839	115.494	101.624	13.870	-193.559	-149.407	32.653
1100	19.844	117.385	102.972	15.854	-193.464	-144.995	28.808
1200	19.849	119.112	104.246	17.838	-193.374	-140.593	25.605
1300	19.852	120.700	105.452	19.823	-193.285	-136.198	22.897
1400	19.855	122.172	106.594	21.809	-193.199	-131.812	20.577
1500	19.857	123.542	107.679	23.794	-193.114	-127.428	18.566
1600	19.859	124.823	108.711	25.780	-193.034	-123.053	16.808
1700	19.860	126.027	109.694	27.766	-192.957	-118.680	15.257
1800	19.861	127.162	110.633	29.752	-192.886	-114.314	13.880
1900	19.862	128.236	111.532	31.738	-192.820	-109.948	12.647
2000	19.863	129.255	112.393	33.725	-192.764	-105.589	11.538
2100	19.864	130.224	113.219	35.711	-192.719	-101.232	10.535
2200	19.865	131.148	114.013	37.697	-192.689	-96.878	9.624
2300	19.865	132.031	114.777	39.684	-192.671	-92.521	8.791
2400	19.866	132.877	115.514	41.671	-192.673	-88.167	8.029
2500	19.866	133.688	116.225	43.657	-192.699	-83.813	7.327
2600	19.867	134.467	116.912	45.644	-192.747	-79.456	6.679
2700	19.867	135.217	117.576	47.630	-192.825	-75.097	6.079
2800	19.867	135.939	118.219	49.617	-192.935	-70.735	5.521
2900	19.868	136.637	118.842	51.604	-193.079	-66.368	5.002
3000	19.868	137.310	119.446	53.591	-193.264	-61.996	4.516
3100	19.868	137.962	120.033	55.578	-193.494	-57.617	4.062
3200	19.868	138.592	120.603	57.564	-193.776	-53.231	3.635
3300	19.869	139.204	121.158	59.551	-194.110	-48.833	3.234
3400	19.869	139.797	121.697	61.538	-194.502	-44.423	2.855
3500	19.869	140.373	122.223	63.525	-194.962	-40.005	2.498
3600	19.869	140.933	122.735	65.512	-195.494	-35.570	2.159
3700	19.869	141.477	123.234	67.499	-196.103	-31.118	1.838
3800	19.869	142.007	123.721	69.486	-196.796	-26.650	1.533
3900	19.869	142.523	124.197	71.473	-197.582	-22.161	1.242
4000	19.870	143.026	124.661	73.460	-198.467	-17.653	.965
4100	19.870	143.517	125.115	75.447	-199.455	-13.122	.699
4200	19.870	143.995	125.559	77.434	-200.556	-8.566	.446
4300	19.870	144.463	125.993	79.421	-201.772	-3.982	.202
4400	19.870	144.920	126.418	81.408	-203.108	.638	-.032
4500	19.870	145.366	126.834	83.395	-204.570	5.281	-.256
4600	19.870	145.803	127.242	85.382	-206.158	9.963	-.473
4700	19.870	146.230	127.641	87.369	-207.876	14.682	-.683
4800	19.870	146.649	128.033	89.356	-209.723	19.434	-.885
4900	19.870	147.058	128.417	91.343	-211.699	24.231	-1.081
5000	19.870	147.460	128.794	93.330	-213.799	29.066	-1.270
5100	19.870	147.853	129.164	95.317	-216.019	33.947	-1.455
5200	19.870	148.239	129.527	97.304	-218.356	38.870	-1.634
5300	19.870	148.618	129.884	99.291	-220.800	43.838	-1.808
5400	19.871	148.989	130.234	101.278	-223.344	48.854	-1.977
5500	19.871	149.354	130.578	103.265	-225.976	53.922	-2.143
5600	19.871	149.712	130.917	105.252	-228.688	59.033	-2.304
5700	19.871	150.063	131.250	107.239	-231.469	64.193	-2.461
5800	19.871	150.409	131.577	109.226	-234.305	69.410	-2.615
5900	19.871	150.749	131.899	111.213	-237.188	74.667	-2.766
6000	19.871	151.083	132.216	113.200	-240.101	79.980	-2.913

June 30, 1968

CESIUM CHLORIDE, DIMERIC (Cs_2Cl_2) (IDEAL GAS) GFW = 336.716

Point Group [D_{2h}]

$\Delta Hf°_0$ = -156.8 ± 2.5 kcal/mol

$S°_{298.15}$ = [91.6 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = -157.7 ± 2.5 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[140] (1)	[76] (1)
[67] (1)	[151] (1)
[141] (1)	[156] (1)

Bond Distance: Cs-Cl = [3.18] Å

Bond Angle: Cl-Cs-Cl = [93.2°]

σ = [4]

Product of the Moments of Inertia: $I_A I_B I_C$ = [3.6076 x 10^{-111}] g^3 cm^6

Heat of Formation

Datz (1) studied the molecular association equilibrium in cesium chloride vapors by measuring the temperature dependence of the molecular weight of gaseous CsCl. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element was a fused silica manometer containing Au(ℓ). Based on the reported results, we derive the equilibrium constants for the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ in the temperature range 1224 - 1418°K. The enthalpy change of this reaction is evaluated by the second and third law method as 39.3 ± 1.1 and 42.9 ± 0.6 kcal/mol, respectively. The drift in the third law value is equivalent to an entropy error of 2.7 ± 0.8 eu. Using the third law ΔHr° and $\Delta Hf°_{298}$(CsCl, g) = -57.4 kcal/mol, we obtain $\Delta Hf°_{298}$ = -157.7 ± 2.5 kcal/mol for $Cs_2Cl_2(g)$, which is adopted.

Schrier (2) determined the vapor pressures of molten cesium chloride at temperatures between 1155 and 1387°K by the boiling point or manometric method. The vapor analysis was performed using the transpiration method. An inert gas, N_2, was passed over the CsCl sample at a given temperature. The salt vapor entrained by the carrier gas was collected, weighed and analyzed. The data obtained were combined with the boiling point measurements to yield the average molecular weight of the vapor. Association into dimer was postulated. The mole fraction in the vapor and the partial pressure of CsCl(g) and $Cs_2Cl_2(g)$ were calculated. The equilibrium constants, 1209 - 1350°K, for dissociation of the Cs_2Cl_2 dimer were derived. Using the reported equilibrium constants, we evaluate the enthalpy change ($\Delta Hr°_{298}$) of the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ to be 34.1 ± 2.9 and 43.2 ± 0.9 kcal/mol by the second and third law methods. Based on the third law $\Delta Hr°_{298}$ value and $\Delta Hf°_{298}$(CsCl, g) = -57.4 kcal/mol, we obtain $\Delta Hf°_{298}$ = -158.0 kcal/mol for $Cs_2Cl_2(g)$, which is in agreement with the adopted value.

Miller and Kusch (3) made an analysis of the velocity distribution of the CsCl molecules which escape through an ideal aperture from an isothermal enclosure. They found that there was no definite evidence that any species other than diatomic molecules were present in the beams in measurable amounts, in other words, the dimerization must be small, e.g. <1.5 per cent. However, according to our calculation the concentration of dimer is 15 - 34 per cent in the temperature range 600 - 900°K, and 33 - 20 per cent at the temperatures 1000 - 1600°K.

Heat Capacity and Entropy

The molecular structure is assumed to be planar, having D_{2h} symmetry. Based on the bond distances of Cs-Cs and Cl-Cl estimated by Berkowitz (4), the Cs-Cl bond distance and Cl-Cs-Cl bond angle are calculated. The vibrational frequencies were calculated by Berkowitz (5), on the basis of the potential function for an ionic model. The three principal moments of inertia are: $I_A = 2.105 \times 10^{-37}$, $I_B = 6.272 \times 10^{-38}$, and $I_C = 2.732 \times 10^{-37}$ g cm^2.

References

1. S. Datz, Oak Ridge National Laboratory, ORNL-2933, Oak Ridge, Tennessee, May 1960.
2. E. E. Schrier, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1961.
3. R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
4. J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).
5. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

Copper Dichloride ($CuCl_2$)

(Crystal) Mol. Wt. = 134.446

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. $mole^{-1} deg.^{-1}$			kcal. $mole^{-1}$			
0	.000	.000	INFINITE	- 3.581	- 49.392	- 49.392	INFINITE
100	11.180	9.804	39.924	- 3.012	- 49.683	- 45.905	100.326
200	15.690	19.246	27.366	- 1.624	- 49.497	- 42.183	46.095
298	17.180	25.833	25.833	.000	- 49.200	- 38.655	28.335
300	17.190	25.939	25.833	.032	- 49.194	- 38.590	28.112
400	17.940	30.994	26.517	1.791	- 48.862	- 35.104	19.180
500	18.470	35.057	27.832	3.612	- 48.510	- 31.704	13.858
600	18.830	38.458	29.327	5.478	- 48.146	- 28.378	10.337
700	19.110	41.382	30.845	7.376	- 47.771	- 25.112	7.840
800	19.332	43.949	32.326	9.298	- 47.392	- 21.902	5.983
900	19.516	46.236	33.747	11.240	- 47.007	- 18.738	4.550
1000	19.687	48.301	35.101	13.201	- 46.618	- 15.618	3.413
1100	19.838	50.185	36.388	15.177	- 46.225	- 12.538	2.491
1200	19.983	51.917	37.611	17.168	- 45.830	- 9.493	1.729
1300	20.122	53.522	38.774	19.173	- 45.431	- 6.480	1.089
1400	20.256	55.018	39.881	21.192	- 48.214	- 3.397	.530
1500	20.384	56.420	40.938	23.224	- 47.838	- .210	.031

Mar. 31, 1966

COPPER DICHLORIDE ($CuCl_2$) (CRYSTAL) MOL. WT. = 134.446

$S^\circ_{298.15}$ = 25.833 cal. $deg.^{-1}$ $mole^{-1}$

T_d = [766]°K.

$\Delta H^\circ_{f\ 0}$ = -49.39 ± 1.5 kcal. $mole^{-1}$

$\Delta H^\circ_{f\ 298.15}$ = -49.2 ± 1.5 kcal. $mole^{-1}$

Heat of Formation.

S. A. Shchukarev and M. A. Oranskaya, Zhur. Obshchei Khim. 24, 1926 (1954) have reported equilibrium constants for the dissociation $CuCl_2(c) \rightarrow CuCl(c/l) + 0.5\ Cl_2(g)$, which are in general agreement with earlier reports by F. Ephraim, Ber. 50, 1069 (1917) and D. I. Tarasenkov, A. I. Grigorovich and A. V. Boroslovskaya, Collected Works of the Central State Institute for Non-Ferrous Metallurgy, Part 1, 1, 69 (1929). These data were subjected to third law analysis which revealed a significant trend of 13 ± 0.5 cal. $deg.^{-1}$ mole, indicating that equilibrium conditions were not reached. However an average value of $\Delta H_{r\ 298}$ = 16.5 ± 1.9 kcal. $mole^{-1}$ yields a heat of formation of $CuCl_2(c)$ = -49.5 ± 2.5 kcal. $mole^{-1}$ which is in good agreement with the adopted value taken from Natl. Bureau Std. Circular 500, Washington, 1952.

Heat Capacity and Entropy.

The low temperature heat capacity has been measured from 11-300°K. by J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962). The integration of this data from S_{10} = 0.111 cal. $deg.^{-1}$ $mole^{-1}$ gave S_{298} = 25.833 cal. $deg.^{-1}$ $mole^{-1}$. The heat capacity above 298° was obtained by smooth extrapolation of the above data, since the heat capacities of A. N. Krestovnikov and G. A. Karetnikov, Journ. Gen. Chem. (USSR) 6, 955 (1936) were not compatible with the low temperature data.

Decomposition Data.

The temperature of decomposition was estimated from the table for $CuCl_2(c)$, $CuCl(l)$ and $Cl_2(g)$ so that the pressure of Cl_2 is 1 atm.

Phosphoryl Fluoride Dichloride ($POCl_2F$)

(Ideal Gas) Mol. Wt. = 136.889

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.927	- 177.779	- 177.779	INFINITE
100	10.644	60.497	91.125	- 3.063	- 178.410	- 175.681	383.932
200	15.843	69.590	78.193	- 1.721	- 178.797	- 172.782	188.799
298	18.958	76.548	76.548	.000	- 179.000	- 169.782	124.448
300	19.003	76.666	76.549	.035	- 179.002	- 169.725	123.639
400	20.951	82.420	77.320	2.040	- 179.101	- 166.615	91.030
500	22.223	87.242	78.836	4.203	- 179.131	- 163.490	71.458
600	23.083	91.374	80.589	6.471	- 179.126	- 160.362	58.409
700	23.685	94.981	82.393	8.811	- 179.112	- 157.235	49.089
800	24.117	98.173	84.170	11.202	- 199.522	- 159.423	43.550
900	24.435	101.033	85.887	13.631	- 199.264	- 154.425	37.498
1000	24.674	103.620	87.533	16.087	- 198.997	- 149.458	32.662
1100	24.859	105.981	89.105	18.564	- 198.724	- 144.518	28.712
1200	25.004	108.150	90.603	21.057	- 198.446	- 139.602	25.424
1300	25.119	110.156	92.031	23.564	- 198.165	- 134.709	22.646
1400	25.212	112.022	93.393	26.080	- 197.883	- 129.838	20.268
1500	25.289	113.764	94.693	28.606	- 197.601	- 124.987	18.210
1600	25.352	115.398	95.937	31.138	- 197.320	- 120.156	16.412
1700	25.405	116.936	97.127	33.676	- 197.039	- 115.339	14.827
1800	25.450	118.390	98.269	36.218	- 196.761	- 110.544	13.421
1900	25.488	119.767	99.364	38.765	- 196.484	- 105.759	12.164
2000	25.521	121.075	100.417	41.316	- 196.212	- 100.993	11.036
2100	25.549	122.321	101.431	43.869	- 195.941	- 96.239	10.015
2200	25.574	123.510	102.408	46.426	- 195.676	- 91.498	9.089
2300	25.596	124.647	103.350	48.984	- 195.413	- 86.768	8.244
2400	25.615	125.737	104.260	51.545	- 195.156	- 82.050	7.471
2500	25.632	126.783	105.140	54.107	- 194.903	- 77.342	6.761
2600	25.647	127.789	105.992	56.671	- 194.654	- 72.645	6.106
2700	25.660	128.757	106.818	59.236	- 194.412	- 67.957	5.500
2800	25.672	129.690	107.618	61.803	- 194.174	- 63.277	4.939
2900	25.683	130.592	108.395	64.371	- 193.941	- 58.605	4.416
3000	25.693	131.462	109.149	66.940	- 193.715	- 53.945	3.930
3100	25.702	132.305	109.883	69.509	- 193.494	- 49.288	3.475
3200	25.710	133.121	110.596	72.080	- 193.280	- 44.642	3.049
3300	25.717	133.912	111.291	74.651	- 193.070	- 39.999	2.649
3400	25.724	134.680	111.967	77.223	- 192.867	- 35.363	2.273
3500	25.730	135.426	112.627	79.796	- 192.669	- 30.735	1.919
3600	25.736	136.151	113.271	82.369	- 192.477	- 26.109	1.585
3700	25.741	136.856	113.898	84.943	- 192.290	- 21.491	1.269
3800	25.746	137.543	114.512	87.518	- 192.107	- 16.876	.971
3900	25.750	138.211	115.111	90.092	- 191.931	- 12.267	.687
4000	25.754	138.863	115.697	92.668	- 191.759	- 7.665	.419
4100	25.758	139.499	116.269	95.243	- 191.592	- 3.065	.163
4200	25.762	140.120	116.830	97.819	- 191.430	1.532	- .080
4300	25.765	140.726	117.379	100.396	- 191.270	6.124	- .311
4400	25.768	141.319	117.916	102.972	- 191.116	10.717	- .532
4500	25.771	141.898	118.443	105.549	- 190.966	15.298	- .743
4600	25.774	142.464	118.959	108.127	- 190.817	19.880	- .944
4700	25.776	143.019	119.465	110.704	- 190.673	24.461	- 1.137
4800	25.779	143.561	119.961	113.282	- 190.533	29.037	- 1.322
4900	25.781	144.093	120.448	115.860	- 190.394	33.612	- 1.499
5000	25.783	144.614	120.926	118.438	- 190.258	38.180	- 1.669
5100	25.785	145.124	121.396	121.016	- 190.126	42.749	- 1.832
5200	25.787	145.625	121.857	123.595	- 189.994	47.313	- 1.988
5300	25.789	146.116	122.310	126.174	- 189.866	51.876	- 2.139
5400	25.790	146.598	122.755	128.753	- 189.740	56.431	- 2.284
5500	25.792	147.072	123.193	131.332	- 189.614	60.995	- 2.424
5600	25.793	147.536	123.624	133.911	- 189.492	65.546	- 2.558
5700	25.795	147.993	124.047	136.491	- 189.372	70.098	- 2.688
5800	25.796	148.442	124.464	139.070	- 189.252	74.653	- 2.813
5900	25.797	148.883	124.874	141.650	- 189.135	79.197	- 2.933
6000	25.799	149.316	125.278	144.230	- 189.020	83.748	- 3.050

March 31, 1963

PHOSPHORYL FLUORIDE DICHLORIDE ($POCl_2F$) (IDEAL GAS) MOL. WT. = 136.889

Point Group C_s

$S^\circ_{298.15}$ = 76.548 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = [-178] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-179] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
207 (1)	372 (1)	620 (1)
254 (1)	386 (1)	894 (1)
330 (1)	547 (1)	1331 (1)

Bond Distance: P-Cl = 1.99 ± 0.04 Å P-F = 1.50 ± 0.03 Å P-O = 1.54 ± 0.03 Å

Bond Angle: Cl-P-Cl = F-P-Cl = 103° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 4.70732540 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ of $POFCl_2$ was estimated to be -179 kcal. mole^{-1} from the $\Delta H^\circ_{f\ 298.15}$ of $POCl_3$ by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-F) and D(P-Cl) values were taken from E. Neale and L. T. D. Williams, J. Chem. Soc., 2485 (1955) Part I and E. Neale, L. T. D. Williams, and V. T. Moores, J. Chem. Soc. 422 (1956) Part II.

Essentially the same $\Delta H^\circ_{f\ 298.15}$ may be obtained by assuming a $\Delta H_r = 0$ for the following reaction:

$$POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$$

Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. <u>60</u>, 1836 (1938) and by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., <u>20</u>, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the F-P-F and F-P-Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of their data by Q. Williams et al. indicates that the angles in POF_2Cl, $POFCl_2$, $POCl_3$, and POF_3 should be 103° rather than the reported 106° ± 3°. The principal moments of inertia calculated from these parameters were $I_A = 2.69184 \times 10^{-38}$, $I_B = 3.79516 \times 10^{-38}$, and $I_C = 4.60780 \times 10^{-38}$.

The Raman spectra and vibrational frequencies for $POFCl_2$ were reported by M. L. Delwaulle and F. Francois, Compt. Rend. <u>222</u>, 550 (1946). These frequency assignments are summarized in J. Chim. Phys. <u>46</u>, 87 (1949) by M. L. Delwaulle and F. Francois.

Iron Dichloride ($FeCl_2$)

(Crystal) Mol. Wt. = 126.753

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.889	-82.320	-82.320	INFINITE
100	12.164	10.703	43.476	-3.277	-82.512	-78.917	172.465
200	16.906	21.138	29.828	-1.738	-82.116	-75.452	82.446
298	18.323	28.190	28.190	.000	-81.700	-72.270	52.973
300	18.340	28.303	28.190	.034	-81.692	-72.211	52.604
400	19.041	33.681	28.919	1.905	-81.277	-69.115	37.761
500	19.512	37.983	30.316	3.834	-80.876	-66.120	28.900
600	19.863	41.572	31.001	5.803	-80.506	-63.204	23.021
700	20.166	44.657	33.508	7.804	-80.172	-60.348	18.840
800	20.437	47.368	35.074	9.835	-79.895	-57.537	15.718
900	20.675	49.789	36.577	11.891	-79.705	-54.753	13.295
1000	20.878	51.978	38.009	13.969	-79.678	-51.985	11.361
1100	21.036	53.976	39.371	16.065	-79.854	-49.203	9.775
1200	21.165	55.812	40.666	18.175	-79.807	-46.424	8.455
1300	21.262	57.510	41.897	20.296	-79.411	-43.658	7.339
1400	21.340	59.088	43.069	22.427	-79.023	-40.921	6.388
1500	21.393	60.563	44.187	24.563	-78.646	-38.215	5.568
1600	21.435	61.945	45.254	26.705	-78.281	-35.531	4.853
1700	21.467	63.245	46.275	28.850	-78.220	-32.862	4.225
1800	21.488	64.473	47.252	30.998	-77.974	-30.202	3.667
1900	21.499	65.635	48.189	33.147	-81.414	-27.368	3.148
2000	21.500	66.738	49.089	35.297	-81.235	-24.531	2.680

June 30, 1965

IRON DICHLORIDE ($FeCl_2$) (CRYSTAL) MOL. WT. = 126.753

$S^\circ_{298.15}$ = 28.190 cal. deg.$^{-1}$ mole^{-1}

T_m = 950°K.

$\Delta H^\circ_{f\ 0}$ = -82.32 ± 0.12 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -81.70 ± 0.12 kcal. mole^{-1}

ΔH°_m = 10.28 ± 0.05 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 46.2 ± 0.7 kcal. mole^{-1}

Heat of Formation.

The enthalpy change, $\Delta H^\circ_{r\ 298.15}$ = -4.06 ± 0.05 kcal. mole^{-1}, for the reaction $Fe(\alpha) + 2(HCl\cdot 12.731\ H_2O)\ (l) = FeCl_2(c) + H_2(g) + 25.462\ H_2O\ (l)$ was reported by M. F. Koehler and J. P. Coughlin, J. Phys. Chem. 63, 605 (1959). The value of $\Delta H^\circ_{f\ 298.15}(FeCl_2, c)$ was then derived. The enthalpy change, $\Delta H^\circ_{r\ 298.15}$ = -19.5 ± 0.2 kcal. mole^{-1}, for the reaction $FeCl_2(c) = Fe^{++}(aq.) + 2\ Cl^-\ (aq.)$ was determined by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952), yielding $\Delta H^\circ_{f\ 298.15}$ = -81.4 ± 0.2 kcal. mole^{-1} which is in agreement with the adopted value reported by M. F. Koehler and J. P. Coughlin. The equilibrium constants for the reaction $FeCl_2(c) + H_2(g) = Fe\ (c) + 2HCl\ (g)$ were determined by W. Kangro and E. Petersen, Z. Anorg. Chem. 261, 157 (1950). By use of the second and third law methods the enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of this reaction was evaluated as 37.81 ± 0.68 and 38.24 kcal. mole^{-1}, respectively. Based on the third law value for $\Delta H^\circ_{r\ 298.15}$, the value of $\Delta H^\circ_{f\ 298.15}(FeCl_2, c)$ was derived to be -82.37 kcal. mole^{-1} which is in reasonable agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (53.2-295.0°K.) heat capacities were determined by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 1264 (1943). The high temperature (670.5-941.0°K.) heat capacities were measured by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 941.0°K. were obtained by graphical extrapolation. The C_p values, 60-500°C., were also reported by F. L. Oetting and N. W. Gregory, J. Phys. Chem. 65, 138 (1961) which are in good agreement with those determined by G. E. Moore, loc. cit. $S^\circ_{298.15}$ was derived from the smoothed C_p values, using $S^\circ_{53.2}$ = 4.930 e.u. The $S^\circ_{298.15}$ value was determined by E. F. Westrum, Jr. quoted by L. E. Wilson and N. W. Gregory in J. Phys. Chem. 62, 437 (1958). The entropy at 298° is assumed to include the uncoupling energy of Fe^{++} which is calculated to be 3.2 e.u. which corresponds to R ln 5.

Melting Data.

T_m and ΔH°_m were taken from G. E. Moore, loc. cit.

Heat of Sublimation.

The difference between $\Delta H^\circ_{f\ 298.15}$ for $FeCl_2(g)$ and $FeCl_2(c)$ is $\Delta H^\circ_{s\ 298.15}$. The former was obtained by the second and third law analyses on the equilibrium pressure data as described in $FeCl_2(g)$ table.

Iron Dichloride ($FeCl_2$)

(Liquid) Mol. Wt. = 126.753

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	24.420	33.432	33.432	- .000	- 74.411	- 66.544	48.776
300	24.420	33.583	33.432	.045	- 74.392	- 66.495	48.439
400	24.420	40.608	34.390	2.487	- 73.406	- 64.014	34.974
500	24.420	46.057	36.199	4.929	- 72.492	- 61.772	26.999
600	24.420	50.510	38.224	7.371	- 71.649	- 59.709	21.748
700	24.420	54.274	40.255	9.813	- 70.874	- 57.782	18.039
800	24.420	57.535	42.216	12.255	- 70.186	- 55.961	15.287
900	24.420	60.411	44.081	14.697	- 69.610	- 54.217	13.165
1000	24.420	62.984	45.845	17.139	- 69.219	- 52.532	11.480
1100	24.420	65.312	47.510	19.581	- 69.049	- 50.867	10.106
1200	24.420	67.436	49.084	22.023	- 68.670	- 49.236	8.967
1300	24.420	69.391	50.572	24.465	- 67.953	- 47.646	8.010
1400	24.420	71.201	51.981	26.907	- 67.254	- 46.110	7.198
1500	24.420	72.886	53.319	29.349	- 66.571	- 44.624	6.501
1600	24.420	74.462	54.592	31.791	- 65.906	- 43.183	5.898
1700	24.420	75.942	55.805	34.233	- 65.548	- 41.775	5.370
1800	24.420	77.338	56.963	36.675	- 65.008	- 40.393	4.904
1900	24.420	78.658	58.070	39.117	- 68.155	- 38.853	4.469
2000	24.420	79.911	59.131	41.559	- 67.684	- 37.326	4.079
2100	24.420	81.102	60.149	44.001	- 67.217	- 35.818	3.727
2200	24.420	82.238	61.128	46.443	- 66.757	- 34.333	3.411
2300	24.420	83.324	62.069	48.885	- 66.302	- 32.871	3.123
2400	24.420	84.363	62.977	51.327	- 65.853	- 31.427	2.862
2500	24.420	85.360	63.852	53.769	- 65.411	- 30.001	2.623
2600	24.420	86.318	64.698	56.211	- 64.974	- 28.595	2.403
2700	24.420	87.239	65.516	58.653	- 64.544	- 27.203	2.202
2800	24.420	88.127	66.308	61.095	- 64.121	- 25.825	2.016
2900	24.420	88.984	67.075	63.537	- 63.704	- 24.467	1.844
3000	24.420	89.812	67.819	65.979	- 63.294	- 23.121	1.684

IRON DICHLORIDE ($FeCl_2$) (LIQUID) MOL. WT. = 126.753

$S^\circ_{298.15}$ = 33.432 cal. deg.$^{-1}$ mole^{-1}

T_m = 950°K.

T_b = 1347°K.

$\Delta H^\circ_{f\ 298.15}$ = -74.411 ± 0.13 kcal. mole^{-1}

ΔH°_m = 10.28 ± 0.05 kcal. mole^{-1}

ΔH°_v = 29.83 kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}(FeCl_2,\ l)$ was obtained from $\Delta H^\circ_{f\ 298.15}(FeCl_2,\ c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity (950-1100°K.) for $FeCl_2(l)$ was reported as 24.42 cal. deg.$^{-1}$ mole^{-1} by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). A constant C_p was assumed for all the other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH°_m were taken from G. M. Moore, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change (ΔF°_r) for the reaction $FeCl_2(l) = FeCl_2(g)$ approaches zero. The corresponding enthalpy change (ΔH°_r) at T_b is the heat of vaporization (ΔH°_v).

Cl_2Fe

Iron Dichloride ($FeCl_2$)

(Ideal Gas)   Mol. Wt. = 126.753

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.394	-35.625	-35.625	INFINITE
100	10.380	55.044	80.642	-2.560	-35.595	-36.434	79.622
200	13.088	63.128	70.018	-1.378	-35.556	-37.290	40.747
298	14.830	68.710	68.710	.000	-35.500	-38.151	27.964
300	14.854	68.802	68.711	.027	-35.499	-38.168	27.804
400	15.667	73.206	69.305	1.560	-35.422	-39.069	21.346
500	15.897	76.734	70.451	3.141	-35.369	-39.988	17.478
600	15.892	79.633	71.747	4.732	-35.377	-40.911	14.901
700	15.826	82.078	73.053	6.318	-35.458	-41.829	13.059
800	15.759	84.187	74.316	7.897	-35.633	-42.730	11.673
900	15.708	86.040	75.518	9.470	-35.926	-43.599	10.587
1000	15.675	87.693	76.654	11.039	-36.408	-44.430	9.710
1100	15.654	89.186	77.726	12.606	-37.113	-45.193	8.979
1200	15.642	90.548	78.739	14.170	-37.612	-45.912	8.361
1300	15.635	91.799	79.696	15.734	-37.773	-46.596	7.833
1400	15.631	92.958	80.603	17.297	-37.953	-47.268	7.379
1500	15.627	94.036	81.463	18.860	-38.149	-47.927	6.983
1600	15.624	95.045	82.280	20.423	-38.363	-48.573	6.634
1700	15.619	95.992	83.059	21.985	-38.885	-49.197	6.324
1800	15.614	96.884	83.803	23.547	-39.225	-49.793	6.045
1900	15.606	97.728	84.514	25.108	-43.253	-50.184	5.772
2000	15.598	98.529	85.195	26.668	-43.664	-50.542	5.523
2100	15.588	99.289	85.848	28.227	-44.080	-50.873	5.294
2200	15.576	100.014	86.475	29.785	-44.504	-51.187	5.085
2300	15.564	100.706	87.079	31.343	-44.933	-51.482	4.892
2400	15.551	101.369	87.661	32.898	-45.371	-51.759	4.713
2500	15.538	102.003	88.222	34.453	-45.816	-52.014	4.547
2600	15.524	102.612	88.764	36.006	-46.268	-52.253	4.392
2700	15.509	103.198	89.288	37.558	-46.728	-52.477	4.247
2800	15.495	103.762	89.795	39.108	-47.197	-52.680	4.112
2900	15.480	104.305	90.286	40.656	-47.674	-52.867	3.984
3000	15.465	104.830	90.762	42.204	-48.158	-53.039	3.864
3100	15.451	105.337	91.224	43.750	-48.651	-53.193	3.750
3200	15.436	105.827	91.672	45.294	-132.578	-51.887	3.544
3300	15.422	106.302	92.109	46.837	-132.625	-49.366	3.269
3400	15.408	106.762	92.533	48.378	-132.684	-46.841	3.011
3500	15.394	107.208	92.946	49.918	-132.755	-44.317	2.767
3600	15.380	107.642	93.348	51.457	-132.838	-41.787	2.537
3700	15.367	108.063	93.740	52.994	-132.933	-39.256	2.319
3800	15.354	108.473	94.122	54.530	-133.040	-36.729	2.112
3900	15.342	108.871	94.496	56.065	-133.159	-34.185	1.916
4000	15.330	109.259	94.860	57.599	-133.291	-31.647	1.729
4100	15.318	109.638	95.216	59.131	-133.434	-29.105	1.551
4200	15.307	110.007	95.563	60.662	-133.591	-26.562	1.382
4300	15.295	110.367	95.904	62.193	-133.758	-24.010	1.220
4400	15.285	110.718	96.236	63.722	-133.938	-21.452	1.065
4500	15.274	111.062	96.562	65.250	-134.131	-18.900	.918
4600	15.264	111.397	96.881	66.776	-134.335	-16.331	.776
4700	15.255	111.726	97.193	68.302	-134.552	-13.766	.640
4800	15.245	112.047	97.499	69.827	-134.780	-11.194	.510
4900	15.236	112.361	97.799	71.351	-135.021	-8.615	.384
5000	15.227	112.669	98.094	72.875	-135.272	-6.037	.264
5100	15.219	112.970	98.382	74.397	-135.535	-3.445	.148
5200	15.211	113.266	98.666	75.918	-135.811	-.855	.036
5300	15.203	113.555	98.944	77.439	-136.098	1.744	-.072
5400	15.195	113.839	99.217	78.959	-136.397	4.349	-.176
5500	15.188	114.118	99.486	80.478	-136.707	6.959	-.276
5600	15.181	114.392	99.749	81.997	-137.028	9.568	-.373
5700	15.174	114.660	100.009	83.514	-137.362	12.189	-.467
5800	15.167	114.924	100.264	85.031	-137.706	14.823	-.559
5900	15.160	115.183	100.514	86.548	-138.061	17.451	-.646
6000	15.154	115.438	100.761	88.063	-138.428	20.092	-.732

June 30, 1965

IRON DICHLORIDE ($FeCl_2$)   (IDEAL GAS)   MOL. WT. = 126.753

Point Group $[D_{\infty h}]$

$S^\circ_{298.15}$ = [68.71] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0$ = -35.63 ± 2.0 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -35.50 ± 2.0 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	[5]
[800]	[10]
[3000]	[5]
[5000]	[5]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
327 (1)
[135] (2)
492 (1)

Bond Distance: Fe-Cl = [2.09] Å

Bond Angle: Cl-Fe-Cl = [180]°

Rotational Constant: B_0 = [0.05442] cm.$^{-1}$

Heat of Formation.

The equilibrium pressures for the reactions: (1) $FeCl_2(l) = FeCl_2(g)$; (2) $FeCl_2(c) = FeCl_2(g)$; and (3) $Fe(c) + 2HCl(g) = FeCl_2(g) + H_2(g)$ were determined by several investigators. Using the reported data, the corresponding enthalpy changes ($\Delta H_r^\circ{}_{298.15}$) for these reactions were evaluated by both the second and third law methods. Hence the respective $\Delta H_f^\circ{}_{298.15}$ values for $FeCl_2(g)$ were derived, based on the third law values for $\Delta H_r^\circ{}_{298.15}$. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H_f^\circ{}_{298.15}$ kcal. mole^{-1}
Beusman[1]	(1)	980.2-1167.2	37.07 ± 0.61	38.42	-35.45 ± 0.30
Schoonmaker and Porter[2]	(2)	621.0- 701.0	45.61 ± 0.10	46.14	-35.56 ± 0.20
H. Schäfer, et at.[3]	(1)	981.0-1107.0	38.95 ± 0.10	37.77	-36.10 ± 0.30
Schäfer and Krehl[4]	(1)	980.7-1106.7	40.56 ± 1.45	37.76	-36.11 ± 0.50
C. G. Maier[5]	(1)	972.1-1268.0	38.68 ± 0.16	37.95	-35.92 ± 0.30
Schäfer and Krehl[4]	(3)	1205.2-1373.2	4.10 ± 0.13	8.01	-36.13 ± 0.50

[1] C. Beusman, "Activities in the KCl-$FeCl_2$ and LiCl-$FeCl_2$ Systems", ORNL-2323, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1957.[2]

[2] R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 29, 116 (1958).

[3] H Schäfer, L. Bayer, G. Breil, K. Etzel and K. Krehl, Z. anorg. allgem. Chem. 278, 300 (1955).

[4] H. Schäfer and K. Krehl, Z. anorg. allgem. Chem. 268, 35 (1952).

The value of $\Delta H_f^\circ{}_{298.15}$ for $FeCl_2(g)$ adopted is -35.5 ± 2.0 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle, and two vibrational frequencies (ν_1 and ν_3) were obtained from L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The electronic levels and quantum weights were estimated by comparison with the electronic levels in $Fe^{++}(g)$ reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961). The total 25 for the quantum weight was obtained from the ground multiplet of Fe^{++} and was split arbitrarily. The bending frequency (ν_2) was derived such that the calculated free energy functions are consistent with the experimental equilibrium data. In other words, the free energy functions were adjusted by choosing a proper value for ν_2 in order to make the second and third law values of ΔH_r° for the reactions in reasonable agreement. The moment of inertia (I) is 5.1426 x 10^{-38} g. cm.$^{-1}$

Cl_2Fe

Dichlorosilane (SiH_2Cl_2)

(Ideal Gas) Mol. Wt. = 101.02 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.194	- 73.220	- 73.220	INFINITE
100	9.183	56.063	79.654	- 2.359	- 73.904	- 72.465	158.365
200	11.896	63.181	69.765	- 1.317	- 74.466	- 70.816	77.381
298	14.831	68.498	68.498	.000	- 75.000	- 68.909	50.509
300	14.879	68.590	68.499	.027	- 75.010	- 68.871	50.170
400	17.076	73.191	69.111	1.632	- 75.437	- 66.757	36.473
500	18.649	77.179	70.335	3.422	- 75.749	- 64.549	28.213
600	19.837	80.689	71.774	5.349	- 75.964	- 62.288	22.687
700	20.774	83.820	73.275	7.381	- 76.103	- 59.997	18.731
800	21.531	86.645	74.773	9.498	- 76.179	- 57.690	15.759
900	22.148	89.218	76.237	11.683	- 76.211	- 55.376	13.446
1000	22.655	91.578	77.655	13.924	- 76.207	- 53.061	11.596
1100	23.073	93.758	79.021	16.211	- 76.176	- 50.748	10.082
1200	23.420	95.781	80.334	18.536	- 76.123	- 48.438	8.821
1300	23.710	97.667	81.596	20.893	- 76.055	- 46.133	7.755
1400	23.954	99.434	82.807	23.277	- 75.977	- 43.836	6.843
1500	24.161	101.093	83.972	25.683	- 75.893	- 41.543	6.052
1600	24.336	102.658	85.091	28.108	- 75.806	- 39.255	5.362
1700	24.487	104.138	86.168	30.549	- 87.820	- 36.863	4.739
1800	24.617	105.542	87.206	33.004	- 87.688	- 33.873	4.113
1900	24.729	106.876	88.207	35.472	- 87.553	- 30.886	3.552
2000	24.827	108.147	89.172	37.950	- 87.418	- 27.906	3.049
2100	24.913	109.360	90.105	40.437	- 87.286	- 24.934	2.595
2200	24.989	110.521	91.007	42.932	- 87.154	- 21.968	2.182
2300	25.056	111.633	91.879	45.434	- 87.024	- 19.007	1.806
2400	25.115	112.701	92.725	47.943	- 86.896	- 16.053	1.462
2500	25.169	113.727	93.545	50.457	- 86.773	- 13.104	1.145
2600	25.216	114.716	94.340	52.977	- 86.650	- 10.160	.854
2700	25.259	115.668	95.112	55.500	- 86.533	- 7.220	.584
2800	25.297	116.587	95.863	58.028	- 86.418	- 4.286	.335
2900	25.332	117.476	96.593	60.560	- 86.305	- 1.355	.102
3000	25.363	118.335	97.303	63.094	- 86.197	1.572	- .114
3100	25.392	119.167	97.995	65.632	- 86.091	4.497	- .317
3200	25.418	119.974	98.670	68.173	- 85.989	7.420	- .507
3300	25.442	120.756	99.327	70.716	- 85.892	10.338	- .685
3400	25.464	121.516	99.969	73.261	- 85.797	13.252	- .852
3500	25.485	122.255	100.595	75.809	- 85.707	16.162	- 1.009
3600	25.503	122.973	101.207	78.358	- 180.597	19.542	- 1.186
3700	25.520	123.672	101.804	80.909	- 180.454	25.101	- 1.483
3800	25.536	124.352	102.389	83.462	- 180.315	30.655	- 1.763
3900	25.551	125.016	102.961	86.016	- 180.182	36.202	- 2.029
4000	25.565	125.663	103.520	88.572	- 180.053	41.751	- 2.281
4100	25.577	126.294	104.068	91.129	- 179.927	47.293	- 2.521
4200	25.589	126.911	104.604	93.688	- 179.806	52.840	- 2.749
4300	25.600	127.513	105.130	96.247	- 179.691	58.369	- 2.966
4400	25.610	128.102	105.646	98.808	- 179.578	63.905	- 3.174
4500	25.620	128.678	106.151	101.369	- 179.473	69.433	- 3.372
4600	25.629	129.241	106.647	103.932	- 179.369	74.970	- 3.562
4700	25.638	129.792	107.134	106.495	- 179.270	80.499	- 3.743
4800	25.646	130.332	107.611	109.059	- 179.176	86.025	- 3.917
4900	25.653	130.861	108.080	111.624	- 179.085	91.548	- 4.083
5000	25.660	131.379	108.541	114.190	- 178.998	97.071	- 4.243
5100	25.667	131.887	108.994	116.756	- 178.917	102.592	- 4.396
5200	25.673	132.386	109.439	119.323	- 178.839	108.109	- 4.543
5300	25.679	132.875	109.877	121.891	- 178.765	113.631	- 4.685
5400	25.685	133.355	110.307	124.459	- 178.695	119.143	- 4.822
5500	25.690	133.826	110.730	127.028	- 178.629	124.662	- 4.953
5600	25.695	134.289	111.147	129.597	- 178.569	130.169	- 5.080
5700	25.700	134.744	111.557	132.167	- 178.512	135.689	- 5.202
5800	25.704	135.191	111.960	134.737	- 178.459	141.196	- 5.320
5900	25.709	135.630	112.358	137.308	- 178.410	146.712	- 5.434
6000	25.713	136.063	112.749	139.879	- 178.366	152.212	- 5.544

December 31, 1960.

Dichlorosilane (SiH_2Cl_2) (Ideal Gas)

Mol. Wt. = 101.02

ΔH_f° 298.15 = [-80 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = 68.531 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{2v}

Vibrational Frequencies and Degeneracies

, cm.$^{-1}$		
2200 (1)	188 (1)	610 (1)
953 (1)	710 (1)	877 (1)
531 (1)	2200 (1)	592 (1)

Si-H distance = 1.48 Å all angles = [109° 28']

Si-Cl distance = 2.05 Å = 2

Product of Moments of Inertia: $I_AI_BI_C$ = 7.9175 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation. ΔH_f° 298.15 taken from Henderson and Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Va., January, 1960.

Heat Capacity and Entropy. Molecular constants taken from Janz and Mikawa, Bull. Chem. Soc. Japan 34, 1485 (1961).

Mercury Dichloride ($HgCl_2$)

(Crystal) Mol. Wt. = 271.524

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	17.664	34.535	34.535	.000	- 55.000	- 43.991	32.245
300	17.680	34.644	34.535	.033	- 54.994	- 43.922	31.996
400	18.400	39.838	35.239	1.840	- 54.678	- 40.278	22.006
500	18.935	44.002	36.588	3.707	- 54.316	- 36.718	16.049
600	19.520	47.503	38.123	5.628	- 53.913	- 33.236	12.106
700	20.064	50.555	39.686	7.608	- 67.486	- 28.255	8.821
800	20.480	53.263	41.217	9.637	- 66.840	- 22.694	6.200
900	20.946	55.702	42.693	11.708	- 66.155	- 17.215	4.180
1000	21.393	57.932	44.107	13.826	- 65.428	- 11.818	2.583
1100	21.818	59.991	45.458	15.986	- 64.662	- 6.493	1.290
1200	22.220	61.907	46.750	18.188	- 63.857	- 1.241	.226
1300	22.601	63.701	47.986	20.430	- 63.014	3.943	- .663
1400	22.960	65.389	49.169	22.708	- 62.136	9.062	- 1.415
1500	23.320	66.985	50.304	25.022	- 61.225	14.116	- 2.057

March 31, 1962

MERCURY DICHLORIDE ($HgCl_2$) (Crystal)

Mol. Wt. = 271.524

ΔH_f° 298.15 = -55.000 ± 1.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = [34.535] ± 1.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 550°K

ΔH_m = 4.64 ± 0.05 kcal. mole^{-1}

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952).

Heat Capacity and Entropy. C_p was determined from the heat content data of L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) and R. Ewald, Ann. d. Physik u. Chem. (4) 44, 1213 (1914). Above 550° the curve was smoothly extrapolated. The entropy was estimated by adjusting the value to give the best fit of the melting, sublimation, and vaporization data.

Melting. T_m was taken from National Bureau of Standards Circular 500 (loc. cit.) ΔH_m was given by L. E. Topol and L. D. Ransom (loc. cit.).

Mercury Dichloride ($HgCl_2$)

(Liquid) Mol. Wt. = 271.524

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	17.664	40.721	40.721	.000	- 51.404	- 42.239	30.961
300	17.680	40.830	40.721	.033	- 51.398	- 42.182	30.728
400	24.400	46.550	41.447	2.041	- 50.881	- 39.165	21.398
500	24.400	51.995	43.032	4.481	- 49.946	- 36.344	15.885
600	24.400	56.444	44.908	6.921	- 49.024	- 33.711	12.279
700	24.400	60.205	46.832	9.361	- 62.137	- 29.661	9.260
800	24.400	63.463	48.711	11.801	- 61.080	- 25.094	6.855
900	24.400	66.337	50.513	14.241	- 60.026	- 20.658	5.016
1000	24.400	68.908	52.226	16.681	- 58.977	- 16.341	3.571
1100	24.400	71.233	53.850	19.121	- 57.931	- 12.128	2.410
1200	24.400	73.356	55.389	21.561	- 56.888	- 8.011	1.459
1300	24.400	75.309	56.847	24.001	- 55.847	- 3.980	.669
1400	24.400	77.118	58.231	26.441	- 54.807	- .028	.004
1500	24.400	78.801	59.547	28.881	- 53.770	3.848	- .561

March 31, 1962

Cl_2Hg

MERCURY DICHLORIDE ($HgCl_2$) (Liquid)

Mol. Wt. = 271.524

ΔH_f° 298.15 = -51.404 ± 1.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = [40.721] ± 1.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 550°K

ΔH_m = 4.64 ± 0.05 kcal. mole^{-1}

T_b = 577°K

ΔH_v = 14.079 ± 0.25 kcal. mole^{-1}

Heat of Formation. Calculated from $\Delta H_f^\circ(c)$.

Heat Capacity and Entropy. The heat capacity was estimated to conform with the bromide and iodide, the value given by L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) was discounted. A glass type transition was assumed at 367°K below which the heat capacity was equal to that of the crystal. The entropy was obtained from $S^\circ(c)$, the entropy of fusion and the estimated heat capacity.

Fusion and Vaporization. T_m and T_b were taken from National Bureau of Standards (U.S.) Circular 500 (1952). ΔH_m was given by L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) and ΔH_v was obtained from the data of E. B. R. Prideaux, J. Chem. Soc. (London) 97, 2033 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Cl_2Hg

Mercury Dichloride ($HgCl_2$)

(Ideal Gas) Mol. Wt. = 271.524 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.476	-34.014	-34.014	INFINITE
100	11.099	56.705	82.117	-2.541	-34.188	-34.450	75.288
200	13.015	65.049	71.680	-1.326	-34.311	-34.660	37.873
298	13.889	70.433	70.433	.000	-34.965	-34.659	25.404
300	13.900	70.519	70.433	.026	-34.966	-34.657	25.246
400	14.299	74.579	70.984	1.438	-35.045	-34.541	18.871
500	14.504	77.794	72.036	2.879	-35.109	-34.407	15.038
600	14.621	80.450	73.223	4.336	-35.170	-34.261	12.479
700	14.694	82.710	74.421	5.802	-49.257	-32.534	10.157
800	14.742	84.675	75.583	7.274	-49.168	-30.152	8.237
900	14.776	86.414	76.691	8.750	-49.078	-27.779	6.745
1000	14.800	87.972	77.743	10.229	-48.990	-25.419	5.555
1100	14.818	89.383	78.738	11.710	-48.903	-23.065	4.582
1200	14.831	90.673	79.679	13.192	-48.818	-20.721	3.774
1300	14.842	91.861	80.571	14.676	-48.733	-18.383	3.090
1400	14.851	92.961	81.417	16.161	-48.648	-16.050	2.505
1500	14.858	93.986	82.222	17.646	-48.566	-13.725	2.000
1600	14.863	94.945	82.987	19.132	-48.485	-11.406	1.558
1700	14.868	95.846	83.717	20.619	-48.404	-9.088	1.168
1800	14.872	96.696	84.415	22.106	-48.325	-6.781	.823
1900	14.875	97.500	85.083	23.593	-48.246	-4.472	.514
2000	14.878	98.263	85.723	25.081	-48.170	-2.171	.237
2100	14.880	98.989	86.337	26.569	-48.094	.126	-.013
2200	14.883	99.681	86.928	28.057	-48.021	2.420	-.240
2300	14.884	100.343	87.497	29.545	-47.949	4.712	-.448
2400	14.886	100.976	88.046	31.034	-47.877	7.002	-.638
2500	14.888	101.584	88.575	32.522	-47.810	9.285	-.812
2600	14.889	102.168	89.087	34.011	-47.743	11.568	-.972
2700	14.890	102.730	89.582	35.500	-47.679	13.849	-1.121
2800	14.891	103.272	90.061	36.989	-47.618	16.125	-1.259
2900	14.892	103.794	90.526	38.478	-47.558	18.402	-1.387
3000	14.893	104.299	90.977	39.968	-47.501	20.674	-1.506
3100	14.893	104.787	91.414	41.457	-47.448	22.945	-1.618
3200	14.894	105.260	91.840	42.946	-47.398	25.216	-1.722
3300	14.895	105.719	92.253	44.436	-47.350	27.485	-1.820
3400	14.895	106.163	92.656	45.925	-47.304	29.753	-1.912
3500	14.896	106.595	93.048	47.415	-47.262	32.016	-1.999
3600	14.896	107.015	93.430	48.904	-47.223	34.283	-2.081
3700	14.897	107.423	93.803	50.394	-47.186	36.546	-2.159
3800	14.897	107.820	94.166	51.884	-47.151	38.808	-2.232
3900	14.898	108.207	94.522	53.373	-47.120	41.071	-2.301
4000	14.898	108.584	94.868	54.863	-47.091	43.333	-2.367
4100	14.898	108.952	95.207	56.353	-47.063	45.588	-2.430
4200	14.899	109.311	95.539	57.843	-47.038	47.848	-2.490
4300	14.899	109.662	95.863	59.333	-47.014	50.107	-2.547
4400	14.899	110.004	96.181	60.823	-46.992	52.368	-2.601
4500	14.899	110.339	96.492	62.313	-46.972	54.624	-2.653
4600	14.899	110.666	96.796	63.802	-46.954	56.880	-2.702
4700	14.900	110.987	97.095	65.292	-46.937	59.143	-2.750
4800	14.900	111.301	97.388	66.782	-46.921	61.393	-2.795
4900	14.900	111.608	97.675	68.272	-46.906	63.654	-2.839
5000	14.900	111.909	97.956	69.762	-46.891	65.910	-2.881
5100	14.900	112.204	98.233	71.253	-46.876	68.170	-2.921
5200	14.901	112.493	98.504	72.742	-46.865	70.425	-2.960
5300	14.901	112.777	98.771	74.232	-46.854	72.677	-2.997
5400	14.901	113.056	99.033	75.723	-46.842	74.930	-3.032
5500	14.901	113.329	99.290	77.213	-46.832	77.187	-3.067
5600	14.901	113.597	99.543	78.703	-46.823	79.443	-3.100
5700	14.901	113.861	99.792	80.193	-46.815	81.696	-3.132
5800	14.901	114.120	100.037	81.683	-46.808	83.951	-3.163
5900	14.901	114.375	100.278	83.173	-46.803	86.200	-3.193
6000	14.902	114.626	100.515	84.663	-46.798	88.457	-3.222

March 31, 1962

MERCURY DICHLORIDE ($HgCl_2$) (Ideal Gas)

Mol. Wt. = 271.524

ΔH_f° 298.15 = -34.965 ± 1.5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 70.433 cal. deg.$^{-1}$ mole^{-1}

Point Group $D_{\infty h}$

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
360 (1)
70 (2)
413 (1)

Hg-Cl distance = 2.31 Å

Moment of Inertia = 62.822 X 10^{-39} g. cm.^{2} σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952 was combined with the 3rd law heat of sublimation at 298°K from the data of K. Niwa and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III, 2, 183 (1938); R. Ruf and W. D. Treadwell, Helv. Chim. Acta 37, 1941 (1954) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is a weighted average of the values given by H. Braune and S. Knoke Naturwiss. 21, 349 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton Trans. Farad. Soc. 33, 852, 1937; L. R. Maxwell and V. M. Mosley Phys. Rev. 57, 21 (1940) and P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).

Mercury Monochloride, Dimeric (Hg_2Cl_2)

(Crystal) Mol. Wt. = 472.134 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-5.611	-62.269	-62.269	INFINITE
100	18.940	22.033	66.485	-4.445	-62.621	-58.526	127.903
200	22.820	36.586	48.202	-2.323	-62.454	-54.480	59.530
298	24.371	46.017	46.017	.000	-63.319	-50.315	36.880
300	24.390	46.168	46.017	.045	-63.312	-50.234	36.594
400	25.340	53.318	46.986	2.533	-62.977	-45.922	25.090
500	26.130	59.060	48.845	5.107	-62.559	-41.705	18.228
600	26.800	63.884	50.960	7.755	-62.079	-37.580	13.688
700	27.380	68.060	53.111	10.464	-89.599	-30.395	9.489
800	27.920	71.752	55.215	13.230	-88.714	-21.998	6.009
900	28.400	75.069	57.240	16.046	-87.781	-13.714	3.330
1000	28.840	78.084	59.176	18.909	-86.805	-5.536	1.210
1100	29.240	80.852	61.022	21.813	-85.791	2.543	-.505
1200	29.600	83.412	62.783	24.755	-84.743	10.526	-1.917
1300	29.916	85.794	64.462	27.732	-83.663	18.422	-3.097
1400	30.189	88.021	66.066	30.737	-82.555	26.232	-4.095
1500	30.420	90.112	67.600	33.768	-81.423	33.966	-4.949

December 31, 1961

MERCURY MONOCHLORIDE, DIMERIC (Hg_2Cl_2) (CRYSTAL) MOL. WT. = 472.134

$\Delta H_f^\circ{}_{298.15} = -63.319 \pm 0.05$ kcal mole^{-1} $S^\circ_{298.15} = 46.017$ cal deg^{-1} mole^{-1}

$T_{sub.} = 655$ °K (decomp.)

Heat of Formation

Based on the average free energy of formation, -50.315 kcal mole^{-1}, as measured by R. H. Gerke, J. Am. Chem. Soc. 44, 1684 (1922) and G. J. Hills and D. J. G. Ives, J. Chem. Soc. (London) 318, (1951), and the entropy of formation.

Heat Capacity

The data of F. Pollitzer, Zeits. f. Electrochemie 19, 513 (1913), from 22-199°K was treated by K. K. Kelley, U. S. Bureau of Mines Bulletin 592 (1960). The heat capacities listed by Kelley were raised by 0.06 to match the entropy data of Gerke (loc. cit.). Data above room temperature were obtained by smooth extrapolation.

Entropy

A mean value of the entropy of formation of -46.614 e.u. was adopted from the cell measurements of R. H. Gerke (loc. cit.).

Sublimation

The vapor pressure over mercurous chloride reaches 1 atmosphere at 655°K according to A. Smith and A. W. C. Menzies, J. Am. Chem. Soc. 32, 1541 (1910). At this point the vapor is dissociated into Hg(g) and $HgCl_2$(g).

Cl_2K_2

Potassium Chloride, Dimeric (K_2Cl_2)

(Ideal Gas) Mol. Wt. = 149.110

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.812	-146.852	-146.852	INFINITE
100	16.145	64.482	100.978	-3.650	-147.219	-147.446	322.243
200	18.714	76.700	86.062	-1.872	-147.402	-147.597	161.286
298	19.327	84.309	84.309	.000	-147.620	-147.652	108.231
300	19.333	84.429	84.310	.036	-147.625	-147.652	107.564
400	19.564	90.027	85.071	1.982	-149.137	-147.392	80.531
500	19.673	94.405	86.516	3.945	-149.513	-146.912	64.215
600	19.733	97.998	88.139	5.915	-149.864	-146.357	53.311
700	19.770	101.043	89.771	7.891	-150.198	-145.746	45.504
800	19.793	103.684	91.348	9.869	-150.530	-145.089	39.637
900	19.810	106.017	92.851	11.849	-150.864	-144.388	35.062
1000	19.822	108.105	94.274	13.831	-151.218	-143.652	31.395
1100	19.830	109.994	95.619	15.813	-189.407	-140.829	27.980
1200	19.837	111.720	96.889	17.797	-189.317	-136.415	24.845
1300	19.842	113.308	98.092	19.781	-189.229	-132.013	22.193
1400	19.846	114.779	99.232	21.765	-189.143	-127.613	19.921
1500	19.849	116.148	100.315	23.750	-189.058	-123.220	17.953
1600	19.852	117.429	101.345	25.735	-188.975	-118.833	16.232
1700	19.854	118.633	102.327	27.720	-188.895	-114.454	14.714
1800	19.856	119.767	103.264	29.706	-188.816	-110.075	13.365
1900	19.858	120.841	104.161	31.691	-188.743	-105.703	12.159
2000	19.859	121.860	105.021	33.677	-188.672	-101.334	11.073
2100	19.860	122.829	105.846	35.663	-188.605	-96.969	10.092
2200	19.861	123.753	106.639	37.649	-188.547	-92.607	9.200
2300	19.862	124.635	107.403	39.635	-188.494	-88.246	8.385
2400	19.863	125.481	108.138	41.622	-188.448	-83.890	7.639
2500	19.864	126.292	108.848	43.608	-188.416	-79.536	6.953
2600	19.864	127.071	109.534	45.594	-188.391	-75.176	6.319
2700	19.865	127.820	110.198	47.581	-188.380	-70.825	5.733
2800	19.865	128.543	110.840	49.567	-188.387	-66.472	5.188
2900	19.866	129.240	111.463	51.554	-188.407	-62.115	4.681
3000	19.866	129.913	112.067	53.540	-188.445	-57.762	4.208
3100	19.866	130.565	112.653	55.527	-188.505	-53.404	3.765
3200	19.867	131.196	113.223	57.514	-188.586	-49.044	3.350
3300	19.867	131.807	113.777	59.500	-188.693	-44.684	2.959
3400	19.867	132.400	114.316	61.487	-188.827	-40.318	2.592
3500	19.868	132.976	114.841	63.474	-188.991	-35.950	2.245
3600	19.868	133.536	115.352	65.461	-189.189	-31.571	1.917
3700	19.868	134.080	115.851	67.447	-189.425	-27.191	1.606
3800	19.868	134.610	116.338	69.434	-189.702	-22.806	1.312
3900	19.868	135.126	116.813	71.421	-190.024	-18.408	1.032
4000	19.869	135.629	117.277	73.408	-190.397	-14.001	.765
4100	19.869	136.120	117.731	75.395	-190.825	-9.589	.511
4200	19.869	136.598	118.174	77.382	-191.316	-5.160	.268
4300	19.869	137.066	118.608	79.369	-191.870	-.723	.037
4400	19.869	137.523	119.033	81.355	-192.501	3.731	-.185
4500	19.869	137.969	119.449	83.342	-193.209	8.202	-.398
4600	19.869	138.406	119.856	85.329	-194.001	12.682	-.603
4700	19.869	138.833	120.255	87.316	-194.885	17.189	-.799
4800	19.869	139.252	120.647	89.303	-195.866	21.709	-.988
4900	19.870	139.661	121.031	91.290	-196.952	26.258	-1.171
5000	19.870	140.063	121.407	93.277	-198.144	30.816	-1.347
5100	19.870	140.456	121.777	95.264	-199.450	35.420	-1.518
5200	19.870	140.842	122.140	97.251	-200.875	40.036	-1.683
5300	19.870	141.220	122.496	99.238	-202.421	44.681	-1.842
5400	19.870	141.592	122.846	101.225	-204.091	49.353	-1.997
5500	19.870	141.956	123.191	103.212	-205.887	54.065	-2.148
5600	19.870	142.314	123.529	105.199	-207.807	58.809	-2.295
5700	19.870	142.666	123.862	107.186	-209.852	63.583	-2.438
5800	19.870	143.012	124.189	109.173	-212.020	68.398	-2.577
5900	19.870	143.351	124.511	111.160	-214.307	73.259	-2.714
6000	19.870	143.685	124.828	113.147	-216.710	78.160	-2.847

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CHLORIDE, DIMERIC (K_2Cl_2) (IDEAL GAS) MOL. WT. = 149.110

Point Group D_{2h}

$S^\circ_{298.15}$ = [84.3] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -146.85 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -147.62 ± 1.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[219](1)	[104](1)
[108](1)	[184](1)
[180](1)	[100](1)

Bond Distance: Cl-K = [2.932] Å

Bond Angle: Cl-K-Cl = [100.8°]

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.873 X 10^{-112}] g.^{3} cm.^{6}

Heat of Formation.

The heat of formation is calculated from that of KCl(g) using $\Delta H^\circ_{r\ 298}$ = 45.0 kcal./mole for $K_2Cl_2(g) \rightarrow 2KCl(g)$ as selected from data analyses summarized below. The three experimental techniques include PVT measurements (source 1), combination of total vapor pressure and transpiration data (sources 2,3,4), and mass spectrometric studies of the variation of ion intensities with temperature (source 5). The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820-1500°K.; however, near the boiling point they are lower by 6-18 percent [see KCl(g)]. Knudsen effusion data and transpiration data over KCl(c) have been reviewed by A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958). These data suggest negligible dimer formation when combined with the total vapor pressures of Pugh and Barrow but significant dimer formation when combined with the lower (20-30 percent) total pressures of V. Dietz, J. Chem. Phys. 4, 575 (1936). Calculated dimer formation (22 mole percent at 900°K.) agrees with the latter combination but calculated total pressures agree with those of Pugh & Barrow. Velocity distribution studies of R. C. Miller and P. Kusch, J. Chem. Phys. 27, 981 (1957); 25, 860 (1956) suggest about 10 mole percent of dimer at 900°K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	No. of Points	Temp. Range °K.	ΔH°_{r} 298 2nd Law kcal./mole	3rd Law kcal./mole	Drift eu
1. Datz (1960)	PVT data	15	1310-1404	46.70±2.1	46.01	-0.5±1.6
2. Schrier (1961)	Trans. + Vap. Press.	10	1253-1352	46.24±3.5	44.98	-1.0±2.7
3. Beusman (1957)	Trans. + Vap. Press.	5	1261-1372	43.0 ±4.5	44.16	0.7±3.4
4. Barton et al. (1959)	Trans. + Vap. Press.	7	1250-1473	42.54±2.9	45.21	2.2±2.3
5. Milne et al. (1960)	Mass Spectrometry	—	774-1016	41.9 ±3	—	—

1. S. Datz, ORNL-2933, Oak Ridge, Tenn., May 1960.
2. E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.
3. C. Beusman, ORNL-2323, Oak Ridge, Tenn., Jun 1957.
4. J. L. Barton and H. Bloom, J. Phys. Chem. 63, 1785 (1959); 60, 1413 (1956).
5. T. A. Milne and H. M. Klein, AFOSR TN 60-512, Menlo Park, Calif., Jun 1960.

Heat Capacity and Entropy.

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960); 29, 1386 (1958). The sixth fundamental was arbitrarily lowered from 206 to 100 cm.$^{-1}$ since the resulting entropy increase (1.4 eu at 1300°K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer-dimer vapor, P. A. Akishin and N. G. Rambidi, Zhur. Neorg. Khim. 4, 718 (1959) have derived the bond distance and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 eu. Principal moments of inertia for the Berkowitz structure are I_A = 45.31 X 10^{-39}, I_B = 60.13 X 10^{-39}, and I_C = 105.45 X 10^{-39} g. cm.^{2}

Cl_2K_2

Lithium Chloride, Dimeric $(LiCl)_2$

(Ideal Gas) Mol. Wt. = 84.794 **INTERIM TABLE**

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.701	- 142.353	- 142.353	INFINITE
100	9.920	53.937	82.597	- 2.866	- 142.457	- 142.980	312.468
200	14.975	62.525	70.511	- 1.597	- 142.789	- 143.366	156.656
298	17.255	68.993	68.993	.000	- 143.056	- 143.591	105.250
300	17.283	69.099	68.993	.032	- 143.061	- 143.595	104.604
400	18.316	74.231	69.686	1.818	- 143.347	- 143.730	78.527
500	18.844	78.381	71.023	3.679	- 145.175	- 143.637	62.780
600	19.146	81.845	72.546	5.580	- 145.569	- 143.290	52.191
700	19.333	84.812	74.092	7.504	- 145.923	- 142.884	44.608
800	19.456	87.402	75.597	9.444	- 146.253	- 142.428	38.908
900	19.542	89.699	77.039	11.394	- 146.575	- 141.930	34.464
1000	19.604	91.761	78.409	13.352	- 146.891	- 141.397	30.901
1100	19.650	93.632	79.710	15.314	- 147.202	- 140.832	27.979
1200	19.685	95.343	80.942	17.281	- 147.511	- 140.241	25.540
1300	19.713	96.920	82.111	19.251	- 147.815	- 139.623	23.472
1400	19.735	98.382	83.222	21.224	- 148.116	- 138.981	21.695
1500	19.752	99.744	84.278	23.198	- 148.414	- 138.319	20.152
1600	19.767	101.019	85.285	25.174	- 148.708	- 137.634	18.799
1700	19.779	102.218	86.246	27.151	- 219.094	- 134.277	17.262
1800	19.789	103.349	87.165	29.130	- 219.020	- 129.288	15.697
1900	19.797	104.419	88.046	31.109	- 218.947	- 124.302	14.297
2000	19.805	105.434	88.890	33.089	- 218.878	- 119.325	13.039
2100	19.811	106.401	89.701	35.070	- 218.810	- 114.351	11.900
2200	19.816	107.322	90.481	37.051	- 218.747	- 109.377	10.865
2300	19.821	108.203	91.233	39.033	- 218.684	- 104.407	9.920
2400	19.825	109.047	91.957	41.015	- 218.629	- 99.440	9.055
2500	19.829	109.857	92.657	42.998	- 218.578	- 94.474	8.259
2600	19.832	110.634	93.334	44.981	- 218.532	- 89.513	7.524
2700	19.835	111.383	93.989	46.965	- 218.494	- 84.552	6.844
2800	19.838	112.104	94.623	48.948	- 218.464	- 79.590	6.212
2900	19.840	112.800	95.238	50.932	- 218.445	- 74.632	5.624
3000	19.842	113.473	95.834	52.916	- 218.433	- 69.672	5.075
3100	19.844	114.124	96.414	54.901	- 218.435	- 64.712	4.562
3200	19.846	114.754	96.977	56.885	- 218.447	- 59.755	4.081
3300	19.848	115.365	97.525	58.870	- 218.473	- 54.795	3.629
3400	19.849	115.957	98.059	60.855	- 218.511	- 49.831	3.203
3500	19.850	116.532	98.578	62.840	- 218.563	- 44.874	2.802
3600	19.852	117.092	99.085	64.825	- 218.631	- 39.908	2.423
3700	19.853	117.636	99.579	66.810	- 218.714	- 34.945	2.064
3800	19.854	118.165	100.061	68.795	- 218.813	- 29.972	1.724
3900	19.855	118.681	100.532	70.781	- 218.928	- 25.000	1.401
4000	19.856	119.183	100.992	72.766	- 219.063	- 20.029	1.094
4100	19.856	119.674	101.442	74.752	- 219.214	- 15.050	.802
4200	19.857	120.152	101.881	76.738	- 219.386	- 10.072	.524
4300	19.858	120.620	102.312	78.723	- 219.576	- 5.085	.258
4400	19.859	121.076	102.733	80.709	- 219.785	- .089	.004
4500	19.859	121.522	103.146	82.695	- 220.018	4.904	- .238
4600	19.860	121.959	103.550	84.681	- 220.271	9.905	- .471
4700	19.860	122.386	103.946	86.667	- 220.548	14.908	- .693
4800	19.861	122.804	104.335	88.653	- 220.850	19.918	- .907
4900	19.861	123.214	104.716	90.639	- 221.179	24.940	- 1.112
5000	19.862	123.615	105.090	92.625	- 221.532	29.969	- 1.310
5100	19.862	124.008	105.457	94.612	- 221.915	35.007	- 1.500
5200	19.863	124.394	105.817	96.598	- 222.328	40.049	- 1.683
5300	19.863	124.772	106.171	98.584	- 222.775	45.091	- 1.859
5400	19.863	125.143	106.519	100.570	- 223.254	50.151	- 2.030
5500	19.864	125.508	106.861	102.557	- 223.770	55.223	- 2.194
5600	19.864	125.866	107.197	104.543	- 224.323	60.292	- 2.353
5700	19.864	126.217	107.528	106.529	- 224.917	65.382	- 2.507
5800	19.865	126.563	107.853	108.516	- 225.553	70.485	- 2.656
5900	19.865	126.903	108.173	110.502	- 226.233	75.591	- 2.800
6000	19.865	127.236	108.488	112.489	- 226.960	80.718	- 2.940

June 30, 1962

Lithium Chloride, Dimeric $(LiCl)_2$ (Ideal Gas)

Mol. Wt. = 84.794

ΔH_f° 298.15 = -143.056 ± 3.0 kcal. mole^{-1}

$S_{298.15}^\circ$ = [68.993] cal. deg.$^{-1}$ mole^{-1}

Point Group = D_{2h}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[330] (1)	[356] (1)
[296] (1)	335 (1)
[385] (1)	460 (1)

Bond Lengths and Angles

Li-Li distance = 2.62 Å

Li-Cl distance = 2.23 Å

ClLiCl angle = 108 ± 4° σ = 4

Moment of Inertia $I_AI_BI_C = 6418 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation. A heat of sublimation at 298° of 52.1 kcal. mole^{-1} was chosen to fit the vapor pressure data and relative concentrations of monomer, dimer and trimer as described in the table for LiCl(g). This value is in reasonable agreement with the value of 53.5 kcal. mole^{-1} from a 3rd law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) and the relative concentrations of monomer, dimer, and trimer from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956). Also a value of 54.1 kcal. mole^{-1} was found by T. A. Milne and H. M. Klein, J. Chem. Phys. 33, 1628 (1960), from mass spectrometer studies.

Heat Capacity and Entropy. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), observed two bands in the infra-red spectrum and made tentative assignments. The remaining four frequencies were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), from a reasonable model. The bond lengths and angles were determined from the electron diffraction experiments of S. H. Bauer, T. Ino and R. F. Porter, J. Chem. Phys. 33, 685 (1960).

Magnesium Dichloride ($MgCl_2$)

(Crystal) Mol. Wt. = 95.218

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.288	- 153.248	- 153.248	INFINITE
100	9.630	6.204	35.079	- 2.888	- 153.703	- 149.577	326.884
200	15.195	14.977	22.926	- 1.590	- 153.688	- 145.545	159.037
298	17.060	21.422	21.422	.000	- 153.350	- 141.519	103.731
300	17.088	21.527	21.422	.032	- 153.344	- 141.446	103.038
400	18.095	26.596	22.106	1.796	- 153.024	- 137.528	75.138
500	18.677	30.701	23.428	3.636	- 152.679	- 133.692	58.434
600	19.090	34.144	24.934	5.525	- 152.328	- 129.928	47.324
700	19.420	37.111	26.467	7.451	- 151.973	- 126.222	39.406
800	19.730	39.725	27.964	9.409	- 151.626	- 122.569	33.483
900	20.040	42.067	29.403	11.397	- 151.289	- 118.956	28.885
1000	20.350	44.194	30.777	13.417	- 153.082	- 115.200	25.176
1100	20.654	46.148	32.087	15.467	- 152.731	- 111.430	22.138
1200	20.951	47.958	33.335	17.547	- 152.378	- 107.692	19.612
1300	21.242	49.646	34.526	19.657	- 152.023	- 103.982	17.480
1400	21.526	51.231	35.663	21.795	- 182.033	- 99.820	15.582
1500	21.805	52.726	36.751	23.962	- 181.269	- 93.975	13.691
1600	22.076	54.142	37.794	26.156	- 180.480	- 88.182	12.045
1700	22.342	55.488	38.796	28.377	- 179.665	- 82.435	10.597
1800	22.601	56.772	39.759	30.624	- 178.826	- 76.741	9.317
1900	22.854	58.001	40.687	32.897	- 177.961	- 71.092	8.177
2000	23.100	59.180	41.582	35.195	- 177.075	- 65.491	7.156

Dec. 31, 1960; Dec. 31, 1965

MAGNESIUM DICHLORIDE ($MgCl_2$) (CRYSTAL) MOL. WT. = 95.218

$S^\circ_{298.15} = 21.422$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 987$°K.

$\Delta H^\circ_{f\ 0} = -153.25 \pm 0.11$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -153.35 \pm 0.11$ kcal. mole^{-1}

$\Delta H_m = 10.30 \pm 0.05$ kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15} = 57.5 \pm 1.5$ kcal. mole^{-1}

Heat of Formation.

The adopted $\Delta H^\circ_{f\ 298.15} = -153.35 \pm 0.11$ kcal. mole^{-1} is from heat of solution measurements reported by C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943). Shomate and Huffmans heat of solution of Mg in 1 M HCl ($\Delta H = -111.322 \pm 0.041$ kcal. mole^{-1}) has been substantiated for calibration purposes by S. R. Gunn and B. B. Cunningham, J. Am. Chem. Soc., 79, 1563 (1957) ($\Delta H = -111.3$ kcal. mole^{-1}) and by E. F. Westrum Jr. and L. Eyring, J. Am. Chem. Soc., 74, 2045 (1952) ($\Delta H = -111.27$ kcal. mole^{-1}). Auxilliary heat of dilution and heat of formation data for HCl were taken from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS 2, Nat'l. Bur. Stds., April 1965 and from D. D. Wagman et al., N.B.S. Technical Note 270-1, Oct. 1965.

Heat Capacity and Entropy.

High temperature heat content data by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943) were joined by Shomate correlation with low temperature heat capacity data reported by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 1264 (1943). C_p(c) above T_m is a linear extrapolation from 700°K. $S^\circ_{298.15}$ is derived from the low temperature data and is based on $S^\circ_{53.6} = 2.006$ cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

$\Delta H_m = 10.30 \pm 0.05$ kcal. mole^{-1} is taken from heat content measurements of Moore loc. cit. $T_m = 987$°K. is from National Bureau of Standards Circular 500, 1952.

Sublimation Data.

The value of $\Delta H^\circ_{s\ 298.15}$ was derived by 2nd and 3rd law analyses of vapor pressure data. See the $MgCl_2(g)$ table for details.

Magnesium Dichloride ($MgCl_2$)

(Liquid) Mol. Wt. = 95.218

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	17.060	30.949	30.949	.000	- 143.779	- 134.789	98.798
300	17.088	31.055	30.949	.032	- 143.773	- 134.733	98.148
400	18.095	36.123	31.633	1.796	- 143.453	- 131.768	71.991
500	18.677	40.228	32.955	3.636	- 143.108	- 128.884	56.332
600	19.090	43.634	34.459	5.505	- 142.777	- 126.072	45.919
700	22.000	46.807	35.995	7.569	- 142.284	- 123.321	38.501
800	22.000	49.745	37.534	9.769	- 141.695	- 120.654	32.959
900	22.000	52.336	39.038	11.969	- 141.146	- 118.056	28.667
1000	22.000	54.654	40.485	14.169	- 142.759	- 115.337	25.206
1100	22.000	56.751	41.870	16.369	- 142.258	- 112.621	22.375
1200	22.000	58.665	43.191	18.569	- 141.785	- 109.948	20.023
1300	22.000	60.426	44.450	20.769	- 141.340	- 107.313	18.040
1400	22.000	62.056	45.650	22.969	- 171.288	- 104.231	16.270
1500	22.000	63.574	46.795	25.169	- 170.491	- 99.469	14.492
1600	22.000	64.994	47.889	27.369	- 169.696	- 94.762	12.943
1700	22.000	66.328	48.935	29.569	- 168.902	- 90.101	11.583
1800	22.000	67.585	49.936	31.769	- 168.110	- 85.489	10.379
1900	22.000	68.775	50.897	33.969	- 167.318	- 80.920	9.307
2000	22.000	69.903	51.819	36.169	- 166.530	- 76.392	8.347
2100	22.000	70.977	52.706	38.369	- 165.742	- 71.908	7.483
2200	22.000	72.000	53.560	40.569	- 164.957	- 67.456	6.701
2300	22.000	72.978	54.383	42.769	- 164.173	- 63.040	5.990
2400	22.000	73.914	55.177	44.969	- 163.391	- 58.660	5.341
2500	22.000	74.812	55.945	47.169	- 162.613	- 54.313	4.748
2600	22.000	75.675	56.687	49.369	- 161.836	- 49.995	4.202
2700	22.000	76.506	57.406	51.569	- 161.063	- 45.711	3.700
2800	22.000	77.306	58.103	53.769	- 160.293	- 41.453	3.235
2900	22.000	78.078	58.778	55.969	- 159.526	- 37.222	2.805
3000	22.000	78.824	59.434	58.169	- 158.764	- 33.019	2.405

Dec. 31, 1960; Dec. 31, 1965

MAGNESIUM DICHLORIDE ($MgCl_2$) (LIQUID) MOL. WT. = 95.218

$S^\circ_{298.15}$ = 30.949 cal. deg.$^{-1}$ mole^{-1}

T_m = 987°K.

T_b = [1710]°K.

$\Delta H^\circ_{f\ 298.15}$ = -143.779 kcal. mole^{-1}

ΔH°_m = 10.30 ± 0.05 kcal. mole^{-1}

ΔH°_v = [37.34] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}(l)$ was calculated from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A constant $C_p(l)$ = 22.0 cal. deg.$^{-1}$ mole^{-1} over the temperature range 1006-1428°K. is from the high temperature heat content data of G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). This constant value was assumed to hold from an assumed glass transition of 660°K. to 3000°K. $C_p(l)$ below 660°K. is taken to be that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See $MgCl_2(c)$ table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction $MgCl_2(l) = MgCl_2(g)$ approaches zero. The difference between ΔH°_f for $MgCl_2(l)$ and $MgCl_2(g)$ at T_b is ΔH°_v.

Magnesium Dichloride ($MgCl_2$)

(Ideal Gas) GFW = 95.218

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.414	-93.824	-93.824	INFINITE
100	11.096	52.626	77.676	-2.505	-93.765	-94.285	206.060
200	12.783	60.901	67.408	-1.302	-93.850	-94.892	103.693
298	13.646	66.184	66.184	.000	-93.800	-95.315	69.868
300	13.658	66.268	66.184	.025	-93.801	-95.324	69.444
400	14.115	70.267	66.726	1.416	-93.854	-95.826	52.357
500	14.368	73.446	67.763	2.842	-93.923	-96.309	42.097
600	14.519	76.080	68.936	4.286	-94.017	-96.779	35.252
700	14.615	78.326	70.121	5.743	-94.131	-97.230	30.357
800	14.680	80.282	71.272	7.208	-94.277	-97.665	26.681
900	14.725	82.014	72.371	8.679	-94.457	-98.077	23.816
1000	14.758	83.567	73.414	10.153	-96.796	-98.287	21.481
1100	14.783	84.975	74.402	11.630	-97.018	-98.427	19.556
1200	14.802	86.262	75.338	13.109	-97.266	-98.545	17.947
1300	14.816	87.447	76.224	14.590	-97.540	-98.640	16.583
1400	14.828	88.546	77.065	16.073	-128.205	-98.234	15.335
1500	14.838	89.569	77.865	17.556	-128.125	-96.096	14.001
1600	14.846	90.527	78.627	19.040	-128.046	-93.964	12.835
1700	14.852	91.427	79.354	20.525	-127.967	-91.834	11.806
1800	14.858	92.276	80.048	22.010	-127.890	-89.712	10.893
1900	14.862	93.080	80.713	23.496	-127.812	-87.592	10.075
2000	14.866	93.842	81.351	24.983	-127.737	-85.478	9.341
2100	14.870	94.568	81.963	26.470	-127.662	-83.368	8.676
2200	14.873	95.260	82.552	27.957	-127.590	-81.259	8.072
2300	14.876	95.921	83.119	29.444	-127.519	-79.154	7.521
2400	14.878	96.554	83.666	30.932	-127.449	-77.053	7.017
2500	14.880	97.161	84.193	32.420	-127.383	-74.956	6.553
2600	14.882	97.745	84.703	33.908	-127.318	-72.858	6.124
2700	14.883	98.307	85.197	35.396	-127.257	-70.766	5.728
2800	14.885	98.848	85.675	36.885	-127.198	-68.675	5.360
2900	14.886	99.370	86.138	38.373	-127.143	-66.586	5.018
3000	14.887	99.875	86.588	39.862	-127.092	-64.500	4.699
3100	14.888	100.363	87.024	41.351	-127.045	-62.414	4.400
3200	14.889	100.836	87.448	42.839	-127.004	-60.331	4.120
3300	14.890	101.294	87.861	44.328	-126.967	-58.247	3.858
3400	14.891	101.738	88.263	45.817	-126.935	-56.162	3.610
3500	14.892	102.170	88.654	47.307	-126.909	-54.085	3.377
3600	14.892	102.590	89.035	48.796	-126.890	-52.002	3.157
3700	14.893	102.998	89.407	50.285	-126.878	-49.920	2.949
3800	14.893	103.395	89.770	51.774	-126.872	-47.842	2.752
3900	14.894	103.782	90.124	53.264	-126.873	-45.764	2.565
4000	14.894	104.159	90.470	54.753	-126.884	-43.683	2.387
4100	14.895	104.527	90.809	56.242	-126.903	-41.604	2.218
4200	14.895	104.886	91.140	57.732	-126.930	-39.526	2.057
4300	14.896	105.236	91.464	59.222	-126.966	-37.445	1.903
4400	14.896	105.578	91.780	60.711	-127.012	-35.357	1.756
4500	14.896	105.913	92.091	62.201	-127.068	-33.276	1.616
4600	14.897	106.241	92.395	63.690	-127.134	-31.189	1.482
4700	14.897	106.561	92.693	65.180	-127.210	-29.102	1.353
4800	14.897	106.875	92.985	66.670	-127.298	-27.015	1.230
4900	14.897	107.182	93.272	68.160	-127.397	-24.923	1.112
5000	14.898	107.483	93.553	69.649	-127.508	-22.831	.998
5100	14.898	107.778	93.829	71.139	-127.630	-20.738	.889
5200	14.898	108.067	94.100	72.629	-127.765	-18.638	.783
5300	14.898	108.351	94.366	74.119	-127.913	-16.538	.682
5400	14.899	108.629	94.628	75.609	-128.074	-14.439	.584
5500	14.899	108.903	94.885	77.098	-128.250	-12.330	.490
5600	14.899	109.171	95.138	78.588	-128.439	-10.223	.399
5700	14.899	109.435	95.386	80.078	-128.643	-8.110	.311
5800	14.899	109.694	95.630	81.568	-128.861	-5.993	.226
5900	14.899	109.949	95.871	83.058	-129.096	-3.872	.143
6000	14.900	110.199	96.108	84.548	-129.346	-1.750	.064

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1969

MAGNESIUM DICHLORIDE ($MgCl_2$) (IDEAL GAS) GFW = 95.218

Point Group $D_{\infty h}$

$\Delta Hf°_0$ = -93.82 ± 0.5 kcal/mol

$S°_{298.15}$ = 66.184 ± 0.5 gibbs/mol

$\Delta Hf°_{298.15}$ = -93.80 ± 0.5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
590 (1)
88 (2)
[273] (1)

Bond Distance: Mg-Cl = 2.18 Å

Bond Angle: Cl-Mg-Cl = 180°

Rotational Constant: B_0 = 0.05003 cm^{-1}

σ = 2

Heat of Formation

Analysis of vapor pressure data on $MgCl_2$ is clouded by conflicting evidence for the amount of dimer in the vapor. Berkowitz and Marquart (1) by mass spectrometer studies found about 2% dimer at 920°K and derived ΔH_D = -39.2 kcal/mol and ΔS_D = -29.9 gibbs/mol. Schrier and Clark (2) from gas transpiration data calculated about 30% dimer in the saturated vapor at 1300°K, with ΔH_D = -32.0 kcal/mol and ΔS_D = -18.8 gibbs/mol. Thermodynamic functions for the gaseous monomer adopted here are clearly not compatible with large amounts of dimer and it is assumed for the present that the mass spectrometer results are correct.

Several vapor pressure studies have been published and third law analyses are given below. Berkowitz and Marquart (1) gave a single point while the remaining publications gave only equations but not individual points. Total pressures calculated from the equations were corrected for dimer.

Source	Method	Temperature Range (°K)	$\Delta Hs°_{298}$(kcal/mol) 3rd law
Berkowitz and Marquart (1)	Mass spectrometer	920	58.10
Schrier and Clark (2)	Boiling Point	1208-1413	59.55-59.68
Hildenbrand et al. (3)	Torsion-effusion	802-985	59.55-59.19
Hildenbrand et al. (4)	Torsion-effusion	800-970	59.53-59.38
Fischer et al. (5)	"Bell" method (total vapor pressures)	1136-1435	59.30-59.56

The selected value for $\Delta Hs°_{298}$ is 59.55 kcal/mol which is combined with $\Delta Hf°_{298}$ of the crystal to give $\Delta Hf°_{298}(g)$ = -93.80 kcal/mol.

Heat Capacity and Entropy

White, Mann, and co-workers (6) by matrix infrared spectroscopy determined the molecule to be linear with the asymmetric stretching frequency at 590 cm^{-1} and the doubly degenerate bending frequency at 88 cm^{-1}. The symmetric stretching frequency was estimated as 273 cm^{-1}. The asymmetric stretching was observed by Buchler and Klemperer (7) at 597 cm^{-1} and by Randall et al. (8) at 598 cm^{-1}, both by infrared spectroscopy of the vapor at high temperature. Electric deflection experiments by Klemperer and co-workers as summarized by Hayes (9) and the electron diffraction data of Akishin and Spiridonov (10) agree with the linear structure within their error limits of about 20°. The Mg-Cl bond length was determined as 2.18 Å by Akishin and Spiridonov (10).

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Molybdenum Dioxydichloride (MoO_2Cl_2)

(Ideal Gas) GFW = 198.845

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.398	-150.333	-150.333	INFINITE
100	12.763	62.512	96.872	-3.436	-150.878	-148.307	324.124
200	17.752	73.084	82.493	-1.882	-151.187	-145.598	159.102
298	20.368	80.705	80.705	.000	-151.300	-142.825	104.694
300	20.405	80.831	80.705	.038	-151.301	-142.773	104.010
400	22.034	86.942	81.527	2.166	-151.304	-139.927	76.453
500	23.081	91.979	83.129	4.425	-151.245	-137.088	59.921
600	23.773	96.253	84.969	6.770	-151.155	-134.265	48.906
700	24.244	99.955	86.851	9.173	-151.051	-131.458	41.043
800	24.576	103.215	88.697	11.615	-150.945	-128.668	35.150
900	24.817	106.125	90.475	14.085	-150.837	-125.888	30.570
1000	24.996	108.749	92.173	16.576	-150.733	-123.122	26.908
1100	25.133	111.138	93.790	19.083	-150.636	-120.366	23.914
1200	25.239	113.330	95.328	21.601	-150.552	-117.618	21.421
1300	25.323	115.353	96.792	24.130	-150.483	-114.877	19.313
1400	25.390	117.232	98.186	26.665	-150.434	-112.140	17.506
1500	25.446	118.986	99.515	29.207	-150.406	-109.405	15.940
1600	25.491	120.630	100.783	31.754	-150.402	-106.672	14.571
1700	25.529	122.176	101.997	34.305	-150.421	-103.937	13.362
1800	25.561	123.637	103.159	36.860	-150.469	-101.202	12.288
1900	25.588	125.019	104.273	39.417	-150.544	-98.461	11.326
2000	25.612	126.332	105.344	41.977	-150.650	-95.721	10.460
2100	25.632	127.583	106.373	44.540	-150.783	-92.972	9.676
2200	25.650	128.775	107.365	47.104	-150.953	-90.214	8.962
2300	25.665	129.916	108.320	49.669	-151.158	-87.450	8.310
2400	25.679	131.008	109.243	52.237	-151.403	-84.670	7.710
2500	25.691	132.057	110.135	54.805	-151.706	-81.888	7.159
2600	25.701	133.065	110.998	57.375	-152.070	-79.085	6.648
2700	25.711	134.035	111.833	59.945	-152.510	-76.272	6.174
2800	25.719	134.970	112.643	62.517	-153.033	-73.438	5.732
2900	25.727	135.873	113.428	65.089	-160.272	-70.566	5.318
3000	25.734	136.745	114.191	67.662	-160.588	-67.468	4.915
3100	25.740	137.589	114.932	70.236	-160.910	-64.357	4.537
3200	25.746	138.406	115.653	72.810	-161.240	-61.241	4.183
3300	25.751	139.199	116.355	75.385	-161.576	-58.110	3.848
3400	25.756	139.967	117.038	77.960	-161.919	-54.966	3.533
3500	25.760	140.714	117.704	80.536	-162.268	-51.822	3.236
3600	25.764	141.440	118.353	83.112	-162.623	-48.657	2.954
3700	25.768	142.146	118.987	85.689	-162.984	-45.486	2.687
3800	25.771	142.833	119.605	88.266	-163.350	-42.305	2.433
3900	25.774	143.502	120.209	90.843	-163.722	-39.115	2.192
4000	25.777	144.155	120.800	93.421	-164.100	-35.916	1.962
4100	25.780	144.792	121.377	95.998	-164.483	-32.707	1.743
4200	25.782	145.413	121.942	98.577	-164.869	-29.490	1.535
4300	25.785	146.020	122.495	101.155	-165.260	-26.261	1.335
4400	25.787	146.612	123.037	103.733	-165.656	-23.022	1.144
4500	25.789	147.192	123.567	106.312	-166.055	-19.777	.961
4600	25.791	147.759	124.087	108.891	-166.456	-16.522	.785
4700	25.792	148.313	124.596	111.470	-166.862	-13.258	.616
4800	25.794	148.856	125.096	114.050	-167.269	-9.985	.455
4900	25.796	149.388	125.586	116.629	-167.680	-6.706	.299
5000	25.797	149.909	126.068	119.209	-309.105	-1.087	.048
5100	25.799	150.420	126.540	121.789	-309.793	5.089	-.218
5200	25.800	150.921	127.004	124.368	-310.512	11.263	-.473
5300	25.801	151.413	127.460	126.949	-311.256	17.462	-.720
5400	25.802	151.895	127.908	129.529	-312.029	23.667	-.958
5500	25.803	152.368	128.349	132.109	-312.824	29.895	-1.188
5600	25.804	152.833	128.782	134.689	-313.643	36.131	-1.410
5700	25.805	153.290	129.208	137.270	-314.482	42.377	-1.625
5800	25.806	153.739	129.627	139.850	-315.338	48.659	-1.834
5900	25.807	154.180	130.039	142.431	-316.211	54.934	-2.035
6000	25.808	154.614	130.445	145.012	-317.098	61.239	-2.231

June 30, 1970

MOLYBDENUM DIOXYDICHLORIDE (MoO_2Cl_2) (IDEAL GAS) GFW = 198.845

Point Group C_{2v}

$S°_{298.15}$ = 80.70 ± 1.30 gibbs/mol

Ground State Quantum Weight = 1

$ΔHf°_0$ = -150.3 ± 3.5 kcal/mol

$ΔHf°_{298.15}$ = -151.3 ± 3.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
972 (1)	134 (1)	156 (1)
453 (1)	233 (1)	437 (1)
347 (1)	996 (1)	287 (1)

Bond Distance: Mo-O = 1.75 ± 0.10 Å Mo-Cl = 2.28 ± 0.03 Å

Bond Angle: O-Mo-O = 109.5° Cl-Mo-Cl = 113° σ = 2

O-Mo-O plane perpendicular to Cl-Mo-Cl plane

Product of Moments of Inertia: $I_AI_BI_C = 1.0986 \times 10^{-112}\ g^3\ cm^6$.

Heat of Formation

Graham and Hepler (1) determined calorimetrically ΔHr° = -65.3 ± 0.5 kcal/mol for the reaction:

$$MoO_2Cl_2(c) + 4\ NaOH(\infty\ H_2O) \rightarrow Na_2MoO_4(\infty\ H_2O) + 2\ NaCl(\infty\ H_2O) + 2\ H_2O(\ell).$$

Combining this result with the following heat of formation data; $ΔHf°(Na_2MoO_4, \infty\ H_2O)$ = -353.4 ± 0.4 kcal/mol (2); $ΔHf°(NaCl, \infty\ H_2O)$ = -97.33 ± 0.09 kcal/mol (3); $ΔHf°(NaOH, \infty\ H_2O)$ = -112.46 ± 0.1 kcal/mol (5); $ΔHf°(H_2O, \ell)$ = -68.315 kcal/mol (6); we derive $ΔHf°(MoO_2Cl_2, c)$ = -169.6 ± 1.0 kcal/mol.

Shchukarev et al. (7) measured the heats of solution of $MoO_3(c)$, $MoO_2Cl_2(c)$ and NaCl(c) in NaOH(aq) and derived ΔHr = -45.56 ± 0.5 kcal/mol for the reaction $MoO_2Cl_2(c) + 2NaOH \cdot 77\ H_2O \rightarrow MoO_3(c) + 2NaCl(c) + H_2O(\ell)$. Using JANAF auxiliary data (9) we obtain $ΔHf°_{298}(MoO_2Cl_2, c)$ = -172.86 ± 1.0 kcal/mol.

The two investigations differ only in the heat of solution of $MoO_2Cl_2(c)$, both samples were better than 99.9% pure, and multiple determinations on two different samples were employed in each case. We adopt an average of the two values, -171.2 ± 1.7 kcal/mol for $ΔHf°_{298}(MoO_2Cl_2, c)$. Shchukarev et al. (10) reported an equation for the vapor pressure over the solid from which we have calculated a 2nd law $ΔHs°_{298}$ = 19.9 kcal/mol with an estimated uncertainty of ±2 kcal/mol, a ΔCp correction of -4.1 gibbs/mol was used (11). Thus, our adopted value is $ΔHf°_{298}(MoO_2Cl_2, g)$ = -151.3 ± 3.5 kcal/mol.

Shchukarev et al. (8) report equilibrium constants for the reaction $MoO_2Cl_2(g) + 0.5\ O_2(g) \rightleftarrows MoO_3(c) + Cl_2(g)$. Shchukarev et al. (10) and Hultgren and Brewer (12) reported equilibrium data for the reaction $MoO_3(c) + 2HCl(g) \rightleftarrows MoO_2Cl_2(g) + H_2O(g)$. Second and third law analyses of these equilibrium data give the following results:

Investigator		No. of Points	$ΔHr_{298}$, kcal/mol		Drift, gibbs/mol	$-ΔHf°(MoO_2Cl_2, g)$ kcal/mol *
			2nd law	3rd law		
Shchukarev et al. (8)		7	-15.6	-30.11±2.0	-15.0	148.0 ± 3.0
Shchukarev et al. (10)		Equation	12.1	13.8±1.0	2.95	150.6 ± 1.2
Hultgren and Brewer (12)	Set I	5	27.2	15.2±1.7	-21.37	149.2 ± 2.0
	Set II	5	26.5	15.4±3.2	-21.75	149.4 ± 3.5

*Third law values

These equilibrium data are in agreement with the adopted heat of formation but are suspect because of the significant drifts and because the range of validity of the equation (10) is estimated.

Heat Capacity and Entropy

The molecular structural data are from the compilation of Sutton (13). Infrared data (14, 15, 16) for vapor phase MoO_2Cl_2 have indicated that the molecule possesses a distorted tetrahedral structure by reason of the similarity of its spectra to that of CrO_2Cl_2. Individual moments of inertia are $I_A = 53.397 \times 10^{-39}$, $I_B = 63.898 \times 10^{-39}$, and $I_C = 32.200 \times 10^{-39}\ g\ cm^2$.

The vibrational frequencies 972, 996, 453, and 437 have been observed in the infrared vapor phase spectra of MoO_2Cl_2 by Barraclough and Stals (14). These frequencies were assigned to the symmetric and asymmetric Mo-O and Mo-Cl stretches, respectively. Similar infrared data for these four frequencies have been reported by Iorns and Stafford (15) and Ward and Stafford (16). The rest of the frequencies are from the infrared and Raman studies of crystalline MoO_2Cl_2 by Adams and Churchill (17). Assignments are made by comparison with data reported for $CrO_2Cl_2(\ell)$ by Miller et al. (18).

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Sodium Chloride, Dimeric ($(NaCl)_2$)

(Ideal Gas) Mol. Wt. = 116.896

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.409	-134.433	-134.433	INFINITE
100	13.734	59.381	93.590	-3.421	-134.786	-135.067	295.175
200	17.720	70.436	79.452	-1.803	-135.063	-135.229	147.764
298	18.831	77.757	77.757	.000	-135.300	-135.262	99.145
300	18.843	77.873	77.757	.035	-135.304	-135.260	98.532
400	19.278	83.362	78.503	1.944	-136.913	-135.100	73.811
500	19.487	87.689	79.923	3.883	-137.309	-134.598	58.830
600	19.603	91.253	81.523	5.838	-137.665	-134.022	48.815
700	19.674	94.281	83.134	7.802	-137.991	-133.392	41.645
800	19.720	96.911	84.696	9.772	-138.297	-132.713	36.254
900	19.752	99.235	86.185	11.746	-138.593	-131.995	32.051
1000	19.775	101.318	87.596	13.722	-138.891	-131.248	28.683
1100	19.792	103.203	88.930	15.701	-139.201	-130.471	25.921
1200	19.804	104.926	90.192	17.680	-186.002	-128.748	23.447
1300	19.814	106.512	91.387	19.661	-185.917	-123.981	20.842
1400	19.822	107.980	92.521	21.643	-185.833	-119.219	18.610
1500	19.829	109.348	93.598	23.626	-185.750	-114.464	16.677
1600	19.834	110.628	94.622	25.609	-185.669	-109.714	14.985
1700	19.839	111.831	95.600	27.593	-185.586	-104.967	13.494
1800	19.842	112.965	96.533	29.577	-185.507	-100.229	12.169
1900	19.845	114.038	97.426	31.561	-185.429	-95.491	10.983
2000	19.848	115.056	98.283	33.546	-185.355	-90.761	9.917
2100	19.850	116.024	99.105	35.531	-185.279	-86.036	8.953
2200	19.852	116.947	99.895	37.516	-185.208	-81.309	8.077
2300	19.854	117.830	100.656	39.501	-185.138	-76.589	7.277
2400	19.856	118.675	101.389	41.486	-185.072	-71.868	6.544
2500	19.857	119.486	102.097	43.472	-185.008	-67.158	5.871
2600	19.858	120.264	102.781	45.458	-184.949	-62.440	5.248
2700	19.859	121.014	103.442	47.444	-184.895	-57.733	4.673
2800	19.860	121.736	104.083	49.430	-184.848	-53.024	4.139
2900	19.861	122.433	104.703	51.416	-184.805	-48.314	3.641
3000	19.862	123.106	105.306	53.402	-184.771	-43.609	3.177
3100	19.862	123.758	105.891	55.388	-184.744	-38.908	2.743
3200	19.863	124.388	106.459	57.374	-184.726	-34.201	2.336
3300	19.864	124.999	107.011	59.361	-184.718	-29.496	1.953
3400	19.864	125.592	107.549	61.347	-184.719	-24.793	1.594
3500	19.865	126.168	108.073	63.333	-184.734	-20.087	1.254
3600	19.865	126.728	108.583	65.320	-184.760	-15.384	.934
3700	19.865	127.272	109.081	67.306	-184.800	-10.681	.631
3800	19.866	127.802	109.567	69.293	-184.853	-5.972	.343
3900	19.866	128.318	110.041	71.280	-184.925	-1.267	.071
4000	19.866	128.821	110.504	73.266	-185.015	3.445	-.188
4100	19.867	129.312	110.957	75.253	-185.123	8.159	-.435
4200	19.867	129.790	111.400	77.240	-185.254	12.872	-.670
4300	19.867	130.258	111.833	79.226	-185.407	17.592	-.894
4400	19.868	130.714	112.257	81.213	-185.587	22.317	-1.108
4500	19.868	131.161	112.672	83.200	-185.795	27.046	-1.313
4600	19.868	131.598	113.079	85.187	-186.033	31.772	-1.509
4700	19.868	132.025	113.477	87.173	-186.306	36.512	-1.698
4800	19.868	132.443	113.868	89.160	-186.617	41.254	-1.878
4900	19.868	132.853	114.251	91.147	-186.969	46.011	-2.052
5000	19.869	133.254	114.627	93.134	-187.365	50.770	-2.219
5100	19.869	133.648	114.997	95.121	-187.809	55.537	-2.380
5200	19.869	134.034	115.359	97.108	-188.306	60.311	-2.535
5300	19.869	134.417	115.715	99.095	-188.862	65.098	-2.684
5400	19.869	134.783	116.065	101.081	-189.481	69.898	-2.829
5500	19.869	135.148	116.408	103.068	-190.167	74.702	-2.968
5600	19.869	135.506	116.746	105.055	-190.923	79.524	-3.103
5700	19.870	135.858	117.078	107.042	-191.756	84.358	-3.234
5800	19.870	136.203	117.405	109.029	-192.670	89.216	-3.362
5900	19.870	136.543	117.727	111.016	-193.671	94.084	-3.485
6000	19.870	136.877	118.043	113.003	-194.760	98.970	-3.605

Dec. 31, 1964

SODIUM CHLORIDE, DIMERIC (Na_2Cl_2) (IDEAL GAS) MOL. WT. = 116.896

Point Group D_{2h}

$S^\circ_{298.15}$ = [77.8] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0} = -134.4 \pm 2$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -135.3 \pm 2$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[265] (1)	[155] (1)
[159] (1)	[222] (1)
[226] (1)	[260] (1)

Bond Distance: Cl-Na = [2.624] Å

Bond Angle: Cl-Na-Cl = [108.4°]

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = [6.849 \times 10^{-113}]$ g.^{3} cm.^{6}

Heat of Formation.

An analysis is given below of the more extensive measurements relating to the dimer dissociation, $(NaCl)_2(g) \rightarrow 2NaCl(g)$. The mass spectrometric studies suggest that higher polymeric species may be neglected. Velocity distribution analyses are consistent with this procedure. When reduced to 298.15°K, the observed heats of dissociation of the dimer show a range of more than 7 kcal., reflecting the considerable uncertainty involved in such measurements. A value of $\Delta H^\circ_{r\ 298}$ = 48.6 kcal. was selected for the dissociation; combining this with $\Delta H^\circ_{s\ 298}$ = 54.9 kcal. mole^{-1} for sublimation to the monomer leads to $\Delta H^\circ_{s\ 298}$ = 61.2 kcal. mole^{-1} for sublimation to the dimer.

Source	Method	T	$\Delta H^\circ_{r\ T}$ (kcal. mole^{-1})	$\Delta H^\circ_{r\ 298}$ (kcal. mole^{-1}) 2nd Law	3rd Law
1	Molecular weight from vapor pressures	1350	51.0	52.8	52.0
2	Molecular weight from P-V-T measurements	1337	50.6	52.4	54.1
3	Double oven effusion with mass spectrometer	1002	47.4	48.6	—
4	Knudsen effusion with mass spectrometer	870	47.3	48.3	—
5	Knudsen effusion with mass spectrometer	930	44.5	45.6	—
6	Velocity distribution analysis	940	49.8	50.9	—
7	Velocity distribution analysis	980	46.6	47.8	—

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Heat Capacity and Entropy.

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), 29, 1386 (1958). Electron diffraction studies by Akishin and Rambidi, Z. physik. Chem. (Leipzig) 213, 111 (1960) gave a similar bond angle (108°) and a slightly shorter bond distance (2.50 Å); however, interpertation of the diffraction pattern was complicated by uncertainty in the monomer-dimer ratio for the vapor. Principal moments of inertia for the Berkowitz structure are $I_A = 18.01 \times 10^{-39}$, $I_B = 53.31 \times 10^{-39}$ and $I_C = 71.32 \times 10^{-39}$ g. cm.^{2}

Dichlorine Monoxide (Cl_2O)

(Ideal Gas) Mol. Wt. = 86.9054

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.795	21.436	21.436	INFINITE
100	8.484	53.356	73.241	-1.989	21.185	22.445	-49.051
200	10.099	59.722	65.026	-1.061	21.052	23.763	-25.965
298	11.427	64.019	64.019	.000	21.000	25.106	-18.402
300	11.447	64.090	64.019	.021	21.000	25.131	-18.307
400	12.280	67.508	64.480	1.211	21.004	26.509	-14.483
500	12.777	70.306	65.374	2.466	21.041	27.882	-12.187
600	13.086	72.665	66.397	3.760	21.088	29.246	-10.652
700	13.287	74.698	67.441	5.080	21.141	30.602	-9.554
800	13.424	76.482	68.462	6.416	21.192	31.948	-8.727
900	13.521	78.069	69.443	7.763	21.242	33.290	-8.084
1000	13.592	79.497	70.378	9.119	21.290	34.626	-7.567
1100	13.645	80.795	71.267	10.481	21.336	35.958	-7.144
1200	13.686	81.984	72.111	11.848	21.379	37.285	-6.790
1300	13.719	83.081	72.914	13.218	21.418	38.609	-6.490
1400	13.745	84.099	73.677	14.591	21.456	39.929	-6.233
1500	13.766	85.048	74.403	15.967	21.490	41.248	-6.009
1600	13.783	85.937	75.097	17.344	21.521	42.564	-5.814
1700	13.797	86.773	75.759	18.723	21.550	43.880	-5.641
1800	13.809	87.562	76.393	20.103	21.574	45.191	-5.487
1900	13.820	88.309	77.001	21.485	21.596	46.505	-5.349
2000	13.829	89.018	77.584	22.867	21.614	47.814	-5.225
2100	13.836	89.693	78.145	24.251	21.630	49.123	-5.112
2200	13.843	90.337	78.684	25.635	21.640	50.431	-5.010
2300	13.848	90.952	79.205	27.019	21.647	51.742	-4.916
2400	13.853	91.542	79.706	28.404	21.650	53.049	-4.831
2500	13.858	92.107	80.191	29.790	21.648	54.358	-4.752
2600	13.862	92.651	80.660	31.176	21.643	55.666	-4.679
2700	13.865	93.174	81.114	32.562	21.632	56.975	-4.612
2800	13.869	93.678	81.554	33.949	21.616	58.287	-4.549
2900	13.871	94.165	81.980	35.336	21.596	59.595	-4.491
3000	13.874	94.635	82.394	36.723	21.571	60.906	-4.437
3100	13.876	95.090	82.796	38.111	21.541	62.218	-4.386
3200	13.878	95.531	83.188	39.498	21.506	63.528	-4.339
3300	13.880	95.958	83.568	40.886	21.466	64.843	-4.294
3400	13.882	96.372	83.939	42.275	21.422	66.160	-4.253
3500	13.884	96.775	84.300	43.663	21.372	67.472	-4-213
3600	13.885	97.166	84.652	45.051	21.318	68.793	-4.176
3700	13.887	97.546	84.995	46.440	21.260	70.115	-4.141
3800	13.888	97.917	85.330	47.829	21.198	71.432	-4.108
3900	13.889	98.277	85.658	49.217	21.132	72.758	-4.077
4000	13.890	98.629	85.978	50.606	21.061	74.081	-4.047
4100	13.891	98.972	86.290	51.995	20.987	75.407	-4.019
4200	13.892	99.307	86.596	53.385	20.910	76.732	-3.993
4300	13.893	99.634	86.896	54.774	20.830	78.063	-3.967
4400	13.894	99.953	87.189	56.163	20.747	79.399	-3.944
4500	13.894	100.265	87.476	57.553	20.661	80.732	-3.921
4600	13.895	100.571	87.757	58.942	20.574	82.067	-3.899
4700	13.896	100.870	88.033	60.332	20.484	83.405	-3.878
4800	13.896	101.162	88.304	61.721	20.392	84.745	-3.858
4900	13.897	101.449	88.569	63.111	20.298	86.085	-3.839
5000	13.898	101.729	88.829	64.501	20.203	87.431	-3.821
5100	13.898	102.005	89.085	65.890	20.107	88.776	-3.804
5200	13.899	102.275	89.336	67.280	20.010	90.122	-3.788
5300	13.899	102.539	89.583	68.670	19.912	91.475	-3.772
5400	13.899	102.799	89.825	70.060	19.812	92.823	-3.757
5500	13.900	103.054	90.063	71.450	19.712	94.180	-3.742
5600	13.900	103.305	90.297	72.840	19.611	95.528	-3.728
5700	13.901	103.551	90.528	74.230	19.510	96.881	-3.714
5800	13.901	103.792	90.754	75.620	19.408	98.250	-3.702
5900	13.901	104.030	90.977	77.010	19.305	99.604	-3.689
6000	13.902	104.264	91.197	78.400	19.202	100.967	-3.678

Dec. 31, 1960; Dec. 31, 1965

DICHLORINE MONOXIDE (Cl_2O) (IDEAL GAS) MOL. WT. = 86.9054

Point Group C_{2v}

$S^\circ_{298.15}$ = 64.019 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 21.4 ± 0.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 21.0 ± 0.6 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
640 (1)
300 (1)
686 (1)

Bond Distance: Cl-O = 1.701 ± 0.02 Å

Bond Angle: Cl-O-Cl = 110.8 ± 1°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 1.171535 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

V. A. Kustodina, K. P. Mishchenko and I. E. Flis, Zh. Prikl. Khim. 35, 1374 (1962) (Source 1) derived the heat of formation of Cl_2O dissolved in CCl_4 from solution calorimetry at 278, 283, 298 and 308°K. The heat of formation in CCl_4 was interpolated to 285°K. D. M. Yost and R. C. Felt, J. Am. Chem. Soc. 56, 68 (1934) (Source 2) measured the partial vapor pressures of Cl_2O above its CCl_4 solution at 273 and 298°K which yield the heat of solution -6.59 kcal. mole^{-1} at 285°K. The $\Delta H^\circ_{f\ 298.15}$ = 21.0 kcal. mole^{-1} was calculated from these two values. J. I. Wallace and C. F. Goodeve, Trans. Faraday Soc. 27, 648 (1931) (Source 3) obtained the heat of explosion of $Cl_2O(g)$: their data give $\Delta H^\circ_{f\ 298.15}$ $Cl_2O(g)$ = 21.4 kcal. mole^{-1} which is in very good agreement with the above. Also P. Günther and K. Wekua, Z. Physik Chem. 154, 193 (1931) (Source 4) measured the heat of explosion; their data give $\Delta H^\circ_{f\ 298.15}$ $Cl_2O(g)$ = 24.7 kcal. mole^{-1}.

Source	Reaction	T, °K	ΔH°_T kcal. mole^{-1}	$\Delta H^\circ_{f\ 298.15}$ kcal. mole^{-1}
1	$Cl_2(g) + 1/2\ O_2(g) \rightarrow Cl_2O(\text{in } CCl_4)$	285	14.38	——
2	$Cl_2O(\text{in } CCl_4) \rightarrow Cl_2O(g)$	285	6.59	21.0
3	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2\ O_2(g)$	298	-21.4	21.4
4	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2\ O_2(g)$	298	-24.7	24.7

Heat Capacity and Entropy.

The vibrational frequencies were obtained from M. M. Rochkind and G. C. Pimentel, J. Chem. Phys. 42, 1361 (1965). The infrared spectrum of $Cl_2O(g)$ has been investigated previously beginning with the work of C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. (London) A142, 192 (1933). K. Hedberg, J. Chem. Phys. 19, 509 (1951) proposed stretching frequencies at 688 cm.$^{-1}$ (ν_1) and 969 cm.$^{-1}$ (ν_3) but left the bending frequency unknown. Previous evidence concerning the bending mode (ν_2)* was shown by Hedberg (loc. cit.) to be spurious. Rochkind and Pimentel (loc. cit.) present infrared studies of Cl_2O gas and condensed phases which reveal the bending frequency and require reassignment of the stretching fundamentals. The bond distance and bond angle were obtained from J. D. Dunitz and K. Hedberg, J. Am. Chem. Soc. 72, 3108 (1950).

The three principal moments of inertia are: I_A = 2.022 X 10^{-39}, I_B = 2.30806 X 10^{-38}, and I_C = 2.51026 X 10^{-38} g. cm.^{2}

*G. B. B. M. Sutherland and W. B. Penny, Proc. Roy. Soc. (London) A156, 678 (1936).

Titanium Oxide Dichloride ($TiOCl_2$)

(Ideal Gas) Mol. Wt. = 134.814

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.993	- 130.002	- 130.002	INFINITE
100	12.291	60.411	90.818	- 3.041	- 130.241	- 129.491	282.989
200	15.642	70.130	78.226	- 1.619	- 130.338	- 128.698	140.628
298	17.197	76.697	76.697	.000	- 130.390	- 127.878	93.733
300	17.219	76.803	76.697	.032	- 130.391	- 127.863	93.143
400	18.102	81.889	77.384	1.802	- 130.426	- 127.015	69.395
500	18.630	85.990	78.709	3.641	- 130.455	- 126.158	55.141
600	18.961	89.418	80.216	5.521	- 130.494	- 125.295	45.636
700	19.179	92.358	81.745	7.429	- 130.547	- 124.425	38.845
800	19.329	94.930	83.236	9.355	- 130.616	- 123.547	33.750
900	19.436	97.213	84.665	11.293	- 130.700	- 122.657	29.784
1000	19.515	99.265	86.024	13.241	- 130.799	- 121.759	26.609
1100	19.574	101.128	87.314	15.196	- 130.915	- 120.851	24.010
1200	19.620	102.833	88.537	17.156	- 131.995	- 119.893	21.834
1300	19.656	104.405	89.698	19.120	- 132.140	- 118.878	19.984
1400	19.685	105.863	90.801	21.087	- 132.290	- 117.853	18.397
1500	19.709	107.222	91.851	23.056	- 132.471	- 116.815	17.019
1600	19.728	108.494	92.852	25.028	- 132.656	- 115.764	15.812
1700	19.745	109.691	93.807	27.002	- 132.854	- 114.702	14.745
1800	19.758	110.820	94.722	28.977	- 133.065	- 113.629	13.796
1900	19.770	111.888	95.597	30.954	- 133.289	- 112.541	12.945
2000	19.780	112.903	96.437	32.931	- 137.201	- 111.351	12.167
2100	19.788	113.868	97.245	34.909	- 137.391	- 110.053	11.453
2200	19.796	114.789	98.021	36.889	- 137.585	- 108.747	10.803
2300	19.802	115.669	98.770	38.868	- 137.783	- 107.430	10.208
2400	19.808	116.512	99.491	40.849	- 137.984	- 106.107	9.662
2500	19.813	117.320	100.188	42.830	- 138.191	- 104.775	9.159
2600	19.817	118.098	100.862	44.812	- 138.400	- 103.435	8.694
2700	19.821	118.846	101.515	46.793	- 138.616	- 102.086	8.263
2800	19.825	119.567	102.147	48.776	- 138.836	- 100.728	7.862
2900	19.828	120.262	102.759	50.758	- 139.060	- 99.363	7.488
3000	19.831	120.935	103.354	52.741	- 139.290	- 97.992	7.138
3100	19.834	121.585	103.932	54.725	- 139.524	- 96.608	6.811
3200	19.836	122.215	104.493	56.708	- 139.763	- 95.224	6.503
3300	19.838	122.825	105.040	58.692	- 140.008	- 93.826	6.214
3400	19.840	123.417	105.571	60.676	- 140.256	- 92.424	5.941
3500	19.842	123.992	106.090	62.660	- 140.510	- 91.016	5.683
3600	19.844	124.551	106.595	64.644	- 243.230	- 88.152	5.351
3700	19.845	125.095	107.087	66.629	- 243.512	- 83.839	4.952
3800	19.947	125.624	107.568	68.613	- 243.812	- 79.519	4.573
3900	19.848	126.140	108.038	70.598	- 244.131	- 75.192	4.213
4000	19.849	126.642	108.497	72.583	- 244.466	- 70.859	3.871
4100	19.850	127.133	108.945	74.568	- 244.816	- 66.514	3.545
4200	19.851	127.611	109.384	76.553	- 245.183	- 62.163	3.235
4300	19.852	128.078	109.813	78.538	- 245.564	- 57.800	2.938
4400	19.853	128.534	110.234	80.523	- 245.959	- 53.425	2.654
4500	19.854	128.981	110.645	82.509	- 246.368	- 49.045	2.382
4600	19.855	129.417	111.049	84.494	- 246.788	- 44.655	2.121
4700	19.856	129.844	111.444	86.480	- 247.222	- 40.255	1.872
4800	19.856	130.262	111.832	88.465	- 247.667	- 35.848	1.632
4900	19.857	130.671	112.212	90.451	- 248.123	- 31.433	1.402
5000	19.858	131.073	112.585	92.436	- 248.588	- 27.008	1.180
5100	19.858	131.466	112.952	94.422	- 249.063	- 22.568	.967
5200	19.859	131.851	113.311	96.408	- 249.546	- 18.122	.762
5300	19.859	132.230	113.665	98.394	- 250.038	- 13.664	.563
5400	19.860	132.601	114.012	100.380	- 250.537	- 9.203	.372
5500	19.860	132.965	114.353	102.366	- 251.043	- 4.724	.188
5600	19.861	133.323	114.689	104.352	- 251.556	- .248	.010
5700	19.861	133.675	115.019	106.338	- 252.074	4.239	- .163
5800	19.861	134.020	115.344	108.324	- 252.598	8.746	- .330
5900	19.862	134.360	115.663	110.310	- 253.127	13.254	- .491
6000	19.862	134.693	115.977	112.297	- 253.660	17.780	- .648

Sept. 30, 1963

TITANIUM OXIDE DICHLORIDE ($TiOCl_2$) (IDEAL GAS) MOL. WT. = 134.814

Point Group [C_{2v}]

$\Delta H^\circ_{f\ 0}$ = [-130.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [76.697] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-130.4] kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[455] (1)	[250] (1)
[849] (1)	[250] (1)
[120] (1)	[180] (1)

Bond Distances: O=Ti = [1.62] Å Ti-Cl = [2.20] Å

Bond Angles: O=Ti-Cl = [120°] σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [4.628 X 10^{-113}] g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as -130 kcal. mole^{-1} by J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: I_A = 42.72 X 10^{-39} g. cm.^{2}, I_B = 17.88 X 10^{-39} g. cm.^{2}, and I_C = 60.60 X 10^{-39} g. cm.^{2}

Tungsten Dioxydichloride (WO_2Cl_2)

(Crystal) GFW = 286.7548

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.954	48.000	48.000	.000	- 186.500	- 167.985	123.136
300	25.000	48.155	48.000	.046	- 186.493	- 167.871	122.294
400	27.500	55.689	49.011	2.671	- 185.998	- 161.733	88.367
500	30.000	62.096	51.002	5.547	- 185.307	- 155.742	68.075
600	32.400	67.781	53.333	8.669	- 184.420	- 149.909	54.604
700	34.550	72.945	55.771	12.022	- 183.344	- 144.240	45.034
800	36.100	77.664	58.217	15.557	- 182.126	- 138.738	37.901
900	37.250	81.986	60.622	19.228	- 180.801	- 133.391	32.392
1000	38.000	85.953	62.959	22.994	- 179.410	- 128.197	28.0

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN DIOXYDICHLORIDE (WO_2Cl_2) (CRYSTAL) GFW = 286.7548

Cl_2O_2W

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [48.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -186.5 ± 1.4 kcal/mol

Td = 642°K

Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov[1] measured calorimetrically the heats of reaction (1) and (2) at 298°K as -67.3 ± 0.2 and -13.6 ± 0.11 kcal/mol, respectively. The reactions are given as follows:

(1) $WO_2Cl_2(c) + 4\ NaOH(16.3H_2O) \rightarrow Na_2WO_4(80{,}000\ H_2O) + 2\ NaCl(40{,}000\ H_2O) + 2\ H_2O(l)$

(2) $H_2WO_4(c) + 2\ NaOH(16.3\ H_2O) \rightarrow Na_2WO_4(20{,}000\ H_2O) + 2\ H_2O(l)$.

Based on these data and the heats of dilution for NaOH(aq)[2], NaCl(aq)[2] and Na_2WO_4(aq)[3], we obtain ΔHr°_{298} = 53.77 ± 1.0 kcal/mol for $WO_2Cl_2(c) + 2\ OH^-(\infty H_2O) \rightarrow H_2WO_4(c) + 2\ Cl^-(\infty H_2O)$. This leads to $\Delta Hf^\circ_{298}(WO_2Cl_2,\ c)$ = -186.5 kcal/mol using $\Delta Hf^\circ_{298}(H_2WO_4,\ c)$ = -270.5 ± 0.4 kcal/mol[5].

Heat Capacity and Entropy.

Cp_{300} = 25.0 gibbs/mol is estimated using Kopp's rule. Heat capacities at higher temperature are estimated from those of $WO_2(c)$, $WO_3(c)$, $WCl_6(c)$. The entropy, S°_{298} = 48.0 eu, is calculated from $\Delta S^\circ_{598.6}$ = 32.27 ± 1.3 eu for $WO_2Cl_2(c) \rightarrow WO_2Cl_2(g)$. The value of $\Delta S^\circ_{598.6}$ is obtained from the second law analysis of the vapor pressure data given by S. A. Shchukarev and A. V. Suvorov[4].

Temperature of Decomposition.

Shchukarev and Suvorov[4] found that $WO_2Cl_2(c)$ does not melt but decomposes. The saturated vapor over $WO_2Cl_2(c)$ consists mainly of $WOCl_4(g)$ which will disproportionate to form $WO_2Cl_2(g)$ and $WCl_6(g)$. The estimated Td is derived by interpolation to one atmosphere in the total pressures of $WOCl_4(g)$, $WO_2Cl_2(g)$ reported by Shchukarev and Suvorov[4].

References.

1. S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NSRDS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed ΔH°dil = 0 for $Na_2WO_4(20{,}000\ H_2O) \rightarrow Na_2WO_4(80{,}000\ H_2O)$.
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al, Zh. Neorg. Khim. 3, 2630 (1958); 5, 1650 (1960), have been revised and they are not used here.
5. JANAF H_2WO_4(c) table dated Mar. 31, 1967.

Tungsten Dioxydichloride (WO_2Cl_2)

(Ideal Gas) GFW = 286.7548

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.661	-159.703	-159.703	INFINITE
100	14.105	65.365	101.387	-3.602	-160.190	-157.842	344.964
200	18.548	76.692	86.404	-1.942	-160.432	-155.384	169.795
298	20.841	84.563	84.563	.000	-160.500	-152.886	112.069
300	20.874	84.692	84.564	.039	-160.500	-152.840	111.344
400	22.334	90.912	85.402	2.204	-160.465	-150.290	82.114
500	23.287	96.006	87.029	4.489	-160.365	-147.756	64.584
600	23.922	100.312	88.893	6.851	-160.238	-145.246	52.906
700	24.358	104.034	90.796	9.267	-160.099	-142.757	44.571
800	24.665	107.308	92.660	11.718	-159.965	-140.292	38.326
900	24.888	110.226	94.452	14.197	-159.832	-137.838	33.472
1000	25.054	112.858	96.163	16.694	-159.710	-135.402	29.592
1100	25.181	115.252	97.791	19.206	-159.598	-132.978	26.420
1200	25.279	117.447	99.339	21.729	-159.498	-130.561	23.778
1300	25.358	119.474	100.811	24.261	-159.411	-128.153	21.545
1400	25.421	121.355	102.212	26.800	-159.337	-125.752	19.631
1500	25.472	123.111	103.548	29.345	-159.277	-123.355	17.973
1600	25.514	124.756	104.822	31.894	-159.232	-120.961	16.523
1700	25.550	126.304	106.041	34.448	-159.200	-118.569	15.243
1800	25.580	127.765	107.207	37.004	-159.186	-116.180	14.106
1900	25.605	129.149	108.326	39.563	-159.187	-113.790	13.089
2000	25.627	130.463	109.400	42.125	-159.205	-111.401	12.173
2100	25.646	131.714	110.433	44.689	-159.238	-109.010	11.345
2200	25.662	132.907	111.428	47.254	-159.292	-106.619	10.592
2300	25.676	134.048	112.387	49.821	-159.360	-104.222	9.903
2400	25.689	135.141	113.312	52.389	-159.447	-101.820	9.272
2500	25.700	136.190	114.207	54.959	-159.553	-99.421	8.691
2600	25.710	137.198	115.072	57.529	-159.676	-97.010	8.154
2700	25.719	138.169	115.909	60.101	-159.823	-94.599	7.657
2800	25.727	139.104	116.721	62.673	-160.004	-92.177	7.195
2900	25.734	140.007	117.509	65.246	-160.227	-89.754	6.764
3000	25.740	140.880	118.273	67.820	-160.498	-87.319	6.361
3100	25.746	141.724	119.016	70.394	-160.829	-84.876	5.984
3200	25.752	142.541	119.739	72.969	-161.226	-82.419	5.629
3300	25.756	143.334	120.442	75.545	-161.695	-79.951	5.295
3400	25.761	144.103	121.126	78.120	-162.247	-77.464	4.979
3500	25.765	144.850	121.794	80.697	-162.892	-74.965	4.681
3600	25.769	145.576	122.444	83.273	-163.658	-72.441	4.398
3700	25.772	146.282	123.079	85.850	-172.875	-69.848	4.126
3800	25.775	146.969	123.699	88.428	-173.090	-67.059	3.857
3900	25.778	147.639	124.304	91.005	-173.312	-64.268	3.601
4000	25.781	148.291	124.895	93.583	-173.540	-61.468	3.358
4100	25.783	148.928	125.474	96.162	-173.771	-58.664	3.127
4200	25.786	149.549	126.040	98.740	-174.008	-55.854	2.906
4300	25.788	150.156	126.593	101.319	-174.248	-53.036	2.696
4400	25.790	150.749	127.136	103.898	-174.493	-50.215	2.494
4500	25.792	151.328	127.667	106.477	-174.742	-47.388	2.301
4600	25.794	151.895	128.188	109.056	-174.993	-44.551	2.117
4700	25.795	152.450	128.698	111.635	-175.249	-41.712	1.940
4800	25.797	152.993	129.198	114.215	-175.506	-38.869	1.770
4900	25.798	153.525	129.689	116.795	-175.766	-36.023	1.607
5000	25.800	154.046	130.171	119.375	-176.028	-33.169	1.450
5100	25.801	154.557	130.645	121.955	-176.292	-30.305	1.299
5200	25.802	155.058	131.109	124.535	-176.558	-27.443	1.153
5300	25.803	155.550	131.566	127.115	-176.826	-24.573	1.013
5400	25.804	156.032	132.014	129.695	-177.096	-21.700	.878
5500	25.805	156.506	132.455	132.276	-177.365	-18.817	.748
5600	25.806	156.971	132.889	134.857	-177.637	-15.937	.622
5700	25.807	157.427	133.316	137.437	-177.911	-13.050	.500
5800	25.808	157.876	133.735	140.018	-178.184	-10.146	.382
5900	25.809	158.317	134.148	142.599	-178.459	-7.247	.268
6000	25.810	158.751	134.554	145.180	-372.639	-2.259	.082

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN DIOXYDICHLORIDE (WO_2Cl_2) (IDEAL GAS) GFW = 286.7548

Point Group [C_{2v}]

$\Delta Hf^\circ_0 = -159.7 \pm 6$ kcal/mol

$S^\circ_{298.15} = [84.6]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -160.5 \pm 6$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
984 (1)	[400] (1)	[150] (1)
972 (1)	[300] (1)	[100] (1)
[400] (1)	[300] (1)	[100] (1)

Bond Distance : W-Cl = [2.26] Å   W-O = [1.81] Å

Bond Angle: Cl-W-Cl = [113°]   O-W-O = [109.47°]   O-W-Cl = [90°]   σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C = [1.165 \times 10^{-112}]\ g^3\ cm^6$

Heat of Formation.

The adopted heat of formation, $\Delta Hf^\circ_{298}(WO_2Cl_2,g) = -160.5$ kcal/mol, is obtained from $\Delta Hr^\circ_{298} = 26.0$ kcal/mol for $WO_2Cl_2(c) \rightarrow WO_2Cl_2(g)$. The latter is calculated by the third law method from the partial pressures of $WO_2Cl_2(g)$ given by S. A. Shchukarev and A. V. Suvorov[6]. Second law analysis gives $\Delta Hr^\circ_{598.6} = 24.1 \pm 0.8$ kcal/mol ($\Delta Hr^\circ_{298} = 26.0$ kcal/mol). These reported partial vapor pressures of $WO_2Cl_2(g)$ were derived by the optical tensimetric method from total pressures over $WO_2Cl_2(c)$ considering the species $WOCl_4(g)$, $WO_2Cl_2(g)$ and $WCl_6(g)$. Since the decomposition of $WO_2Cl_2(c)$ was very complicated, we tentatively assign 6 kcal/mol uncertainty to the adopted heat of formation.

Shchukarev and Suvorov[6] have also derived a log Kp equation for the disproportionation process, $2\ WOCl_4(g) = WO_2Cl_2(g) + WCl_6(g)$. Third law analysis gives $\Delta Hr^\circ_{298} = 10.3$ kcal/mol for the above process. This leads to ΔHf°_{298} (WO_2Cl_2, g) = -145.7 ± 16 kcal/mol. The second law ΔHr°_{590} is 11.0 kcal/mol ($\Delta Hr^\circ_{298} = 10.1$ kcal/mol). The drift in the third law analysis is 0.3 eu.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a distorted tetrahedron of C_{2v} symmetry, similar to that of $MoO_2Cl_2(g)$[1], and $CrO_2Cl_2(g)$[2]. The bond distances W-O and W-Cl are estimated to be the same as those in $WO_3(g)$ and $WCl_6(g)$, respectively. The bond angles are assumed to be the same as those in $MoO_2Cl_2(g)$[1]. The three principal moments of inertia are $I_A = 6.419 \times 10^{-38}$, $I_B = 5.342 \times 10^{-38}$ and $I_C = 3.397 \times 10^{-38}$ g cm^2.

The vibrational frequencies, 984 cm^{-1} and 972 cm^{-1}, were observed in the infrared spectra by C. G. Barraclough and J. Stals[3]. They tentatively assigned these two as the symmetric and asymmetric W-O stretching frequencies. The rest of the frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $CrO_2Cl_2(g)$[4,5]. They are not listed in point group order.

References.

1. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.
2. K. J. Palmer, J. Am. Chem. Soc. 60, 2360 (1938).
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Lead Dichloride ($PbCl_2$)

(Crystal) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.049	-86.412	-86.412	INFINITE
100	13.810	14.987	47.347	-3.236	-86.723	-82.823	181.000
200	16.620	25.697	34.072	-1.675	-86.486	-79.000	86.323
298	17.483	32.500	32.500	.000	-86.201	-75.386	55.257
300	17.500	32.608	32.500	.032	-86.196	-75.319	54.867
400	18.490	37.777	33.198	1.831	-85.879	-71.740	39.195
500	19.491	42.010	34.549	3.730	-85.506	-68.248	29.830
600	20.480	45.691	36.103	5.729	-85.066	-64.835	23.615
700	21.480	48.883	37.702	7.827	-85.716	-61.313	19.142
800	22.360	51.814	39.286	10.023	-85.127	-57.866	15.808
900	23.160	54.494	40.829	12.299	-84.455	-54.498	13.233
1000	23.960	56.976	42.321	14.655	-83.699	-51.210	11.191
1100	24.760	59.297	43.760	17.091	-82.859	-48.001	9.536
1200	25.560	61.486	45.146	19.607	-81.934	-44.871	8.172
1300	26.360	63.563	46.484	22.203	-80.926	-41.823	7.031
1400	27.160	65.546	47.775	24.879	-79.839	-38.857	6.065
1500	27.960	67.447	49.024	27.635	-78.673	-35.968	5.240
1600	28.760	69.277	50.233	30.471	-77.432	-33.162	4.529
1700	29.560	71.045	51.405	33.387	-76.114	-30.432	3.912
1800	30.360	72.757	52.544	36.383	-74.723	-27.788	3.374
1900	31.160	74.420	53.652	39.459	-73.257	-25.219	2.901
2000	31.960	76.038	54.731	42.615	-71.719	-22.730	2.484
2100	32.760	77.617	55.783	45.851	-112.556	-18.768	1.953
2200	33.560	79.159	56.811	49.167	-110.778	-14.344	1.425
2300	34.360	80.669	57.815	52.563	-108.942	-10.000	.950
2400	35.160	82.148	58.799	56.039	-107.049	-5.738	.523
2500	35.960	83.600	59.762	59.595	-105.102	-1.559	.136

March 31, 1962

Lead Dichloride ($PbCl_2$) (Crystal)

Mol. Wt. = 278.12

$\Delta H_f^\circ{}_{298.15} = -86.20 \pm 0.07$ kcal. mole^{-1}

$S^\circ_{298.15} = 32.5 \pm 0.5$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_s^\circ{}_{298.15} = 45.59 \pm 0.70$ kcal. mole^{-1}

$T_m = 768°K$

$\Delta H_m^\circ = 5.70$ kcal. mole^{-1}

Heat of Formation. Recalculated from the data reported by E. J. Salstrom, J. Am. Chem. Soc. 55, 2426 (1933) and A. Wachter, J. Am. Chem. Soc. 54, 2271 (1932).

Heat Capacity, Entropy and Melting Data. C_p (15.8° to 205.5°K.) reported by W. Nernst, Ann. Physik, 36, 395 (1911) and adjusted so that $S^\circ_{298.15}$ is equal to the value reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961). C_p above 298.15°K. obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) and joined smoothly to the low temperature heat capacity curve by graphical extrapolation. T_m and ΔH_m° obtained from M. Blanc and G. Petit, Compt. rend. 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of E. D. Eastman and L. H. Duschak, U. S. Bur. Mines Tech. Paper 225 (1919), C. G. Maier, U. S. Bur. Mines Tech. Paper 360, 28 (1925), H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922), and W. Jahn-Held and K. Jellinek, Z. Elektrochem. 43, 491 (1937), which are in good agreement. Vapor pressure was also measured by F. Völmer, Physik. Z. 30, 590 (1929), J. L. Barton and H. Bloom, J. Phys. Chem. 60, 1413 (1956), B. Greiner and K. Jellinek, Z. physik. Chem. A165, 97 (1933), and K. Niwa, M. Sato and M. Yosiyama, J. Faculty Sci. Hokkaido Imp. Univ. Ser. III, 3, 17 (1940).

Lead Dichloride ($PbCl_2$)

(Liquid) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	17,485	38,336	38,336	,000	-81,488	-72,413	53,078
300	17,500	38,444	38,336	,032	-81,483	-72,357	52,710
400	18,490	43,613	39,034	1,831	-81,166	-69,362	37,896
500	19,490	47,846	40,385	3,730	-80,793	-66,453	29,045
600	24,900	52,178	41,987	6,114	-79,968	-63,653	23,184
700	24,900	56,016	43,724	8,604	-80,226	-60,816	18,987
800	24,900	59,341	45,473	11,094	-79,343	-58,104	15,872
900	24,900	62,274	47,180	13,584	-78,457	-55,501	13,477
1000	24,900	64,897	48,823	16,074	-77,567	-52,999	11,582
1100	24,900	67,270	50,394	18,564	-76,673	-50,586	10,050
1200	24,900	69,437	51,892	21,054	-75,774	-48,253	8,788
1300	24,900	71,430	53,319	23,544	-74,872	-45,996	7,732
1400	24,900	73,275	54,679	26,034	-73,971	-43,810	6,839
1500	24,900	74,993	55,977	28,524	-73,071	-41,685	6,073
1600	24,900	76,600	57,216	31,014	-72,176	-39,623	5,412
1700	24,900	78,110	58,401	33,504	-71,284	-37,613	4,835
1800	24,900	79,533	59,536	35,994	-70,399	-35,661	4,330
1900	24,900	80,879	60,624	38,484	-69,519	-33,754	3,882
2000	24,900	82,156	61,669	40,974	-68,647	-31,894	3,485
2100	24,900	83,371	62,674	43,464	-110,230	-28,526	2,969
2200	24,900	84,530	63,641	45,954	-109,278	-24,659	2,449
2300	24,900	85,637	64,574	48,444	-108,348	-20,832	1,979
2400	24,900	86,696	65,474	50,934	-107,441	-17,045	1,552
2500	24,900	87,713	66,343	53,424	-106,560	-13,299	1,163
2600	24,900	88,689	67,184	55,914	-105,701	-9,585	,806
2700	24,900	89,629	67,998	58,404	-104,865	-5,904	,478
2800	24,900	90,535	68,787	60,894	-104,054	-2,253	,176
2900	24,900	91,408	69,552	63,384	-103,263	1,368	-,103
3000	24,900	92,252	70,294	65,874	-102,493	4,963	-,362

March 31, 1962

Lead Dichloride ($PbCl_2$) (Liquid)

Mol. Wt. = 278.12

$\Delta H_f^\circ{}_{298.15}$ = [-81.49] kcal. mole^{-1}

$S^\circ_{298.15}$ = [38.336] cal. deg.$^{-1}$ mole^{-1}

T_m = 768°K

ΔH_m° = 5.70 kcal. mole^{-1}

T_b = 1226°K

ΔH_v° = 26.81 ± 0.70 kcal. mole^{-1}

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy and Melting Data. C_p reported by M. Bizouard and F. Pauty, Compt. rend. 252, 511 (1961). T_m and ΔH_m° obtained from M. Blanc and G. Petit, Compt. rend. 248, 1305 (1959). A glass transition temperature of 520°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v° calculated from ΔH_s° 298.15 and functions for condensed and gaseous states.

Lead Dichloride ($PbCl_2$)

(Ideal Gas) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-3.446	-40.218	-40.218	INFINITE
100	11.084	63.059	88.077	-2.502	-40.398	-41.304	90.267
200	12.821	71.390	77.839	-1.290	-40.510	-42.162	46.070
298	13.370	76.630	76.630	.000	-40.610	-42.953	31.484
300	13.377	76.713	76.630	.025	-40.612	-42.967	31.300
400	13.599	80.596	77.158	1.375	-40.744	-43.733	23.893
500	13.708	83.643	78.161	2.741	-40.904	-44.463	19.434
600	13.769	86.148	79.290	4.115	-41.089	-45.156	16.447
700	13.806	88.274	80.425	5.494	-42.458	-45.628	14.245
800	13.830	90.119	81.524	6.876	-42.683	-46.066	12.584
900	13.847	91.749	82.571	8.260	-42.903	-46.475	11.285
1000	13.859	93.208	83.563	9.645	-43.118	-46.861	10.241
1100	13.868	94.530	84.501	11.031	-43.328	-47.226	9.382
1200	13.875	95.737	85.388	12.418	-43.532	-47.570	8.663
1300	13.880	96.848	86.227	13.806	-43.732	-47.899	8.052
1400	13.884	97.876	87.023	15.194	-43.933	-48.213	7.526
1500	13.888	98.834	87.779	16.583	-44.134	-48.510	7.068
1600	13.890	99.731	88.498	17.972	-44.340	-48.796	6.665
1700	13.893	100.573	89.184	19.361	-44.549	-49.066	6.307
1800	13.895	101.367	89.839	20.751	-44.764	-49.327	5.989
1900	13.896	102.118	90.456	22.140	-44.985	-49.574	5.702
2000	13.898	102.831	91.066	23.530	-45.213	-49.809	5.443
2100	13.899	103.509	91.643	24.920	-87.896	-48.482	5.045
2200	13.900	104.156	92.197	26.310	-88.044	-46.603	4.629
2300	13.901	104.774	92.730	27.700	-88.214	-44.714	4.249
2400	13.902	105.365	93.245	29.090	-88.407	-42.818	3.899
2500	13.902	105.933	93.741	30.480	-88.626	-40.916	3.577
2600	13.903	106.478	94.220	31.870	-88.867	-39.002	3.278
2700	13.904	107.003	94.684	33.261	-89.130	-37.079	3.001
2800	13.904	107.509	95.133	34.651	-89.419	-35.145	2.743
2900	13.905	107.996	95.568	36.041	-89.728	-33.202	2.502
3000	13.905	108.468	95.991	37.432	-90.057	-31.248	2.276
3100	13.905	108.924	96.400	38.822	-90.406	-29.282	2.064
3200	13.906	109.365	96.799	40.213	-90.773	-27.305	1.865
3300	13.906	109.793	97.186	41.604	-91.155	-25.314	1.676
3400	13.906	110.208	97.563	42.994	-91.552	-23.312	1.498
3500	13.907	110.611	97.930	44.385	-91.962	-21.302	1.330
3600	13.907	111.003	98.288	45.776	-92.382	-19.274	1.170
3700	13.907	111.384	98.637	47.166	-92.813	-17.238	1.018
3800	13.907	111.755	98.977	48.557	-93.249	-15.190	.874
3900	13.907	112.116	99.309	49.948	-93.693	-13.129	.736
4000	13.908	112.468	99.634	51.338	-94.143	-11.060	.604
4100	13.908	112.812	99.951	52.729	-94.595	-8.978	.479
4200	13.908	113.147	100.261	54.120	-95.050	-6.884	.358
4300	13.908	113.474	100.565	55.511	-95.506	-4.782	.243
4400	13.908	113.794	100.862	56.902	-95.962	-2.661	.132
4500	13.908	114.107	101.153	58.292	-96.419	-.540	.026
4600	13.908	114.412	101.438	59.683	-96.873	1.598	-.076
4700	13.908	114.711	101.717	61.074	-97.325	3.742	-.174
4800	13.909	115.004	101.991	62.465	-97.775	5.899	-.269
4900	13.909	115.291	102.259	63.856	-98.222	8.064	-.360
5000	13.909	115.572	102.523	65.247	-98.665	10.235	-.447
5100	13.909	115.847	102.781	66.638	-99.104	12.420	-.532
5200	13.909	116.118	103.035	68.028	-99.540	14.613	-.614
5300	13.909	116.382	103.284	69.419	-99.972	16.811	-.693
5400	13.909	116.642	103.529	70.810	-100.400	19.019	-.770
5500	13.909	116.898	103.770	72.201	-100.824	21.234	-.844
5600	13.909	117.148	104.007	73.592	-101.243	23.456	-.915
5700	13.909	117.395	104.240	74.983	-101.660	25.681	-.985
5800	13.909	117.636	104.468	76.374	-102.072	27.927	-1.052
5900	13.909	117.874	104.694	77.765	-102.482	30.167	-1.117
6000	13.909	118.108	104.915	79.156	-102.888	32.418	-1.181

March 31, 1962

Lead Dichloride ($PbCl_2$) (Ideal Gas)

Mol. Wt. = 278.12

ΔH_f° 298.15 = -40.61 ± 0.70 kcal. mole^{-1}

$S^\circ_{298.15}$ = [76.630]

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
[240] (1)
[70] (1)
[300] (1)

Pb-Cl distance = 2.46 ± 0.02 Å ClPbCl angle = 95° σ = 2

I_A = 24.229 X 10^{-39} g. cm.^{2} I_B = 38.741 X 10^{-39} g. cm.^{2}

$I_C = I_A + I_B$ = 62.970 X 10^{-39} g. cm.^{2}

Heat of Formation. Calculated from ΔH_f° 298.15 for $PbCl_2$(c) and ΔH_s° 298.15.

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the vibrational frequencies for the mercury dihalides.

Silicon Dichloride ($SiCl_2$)

(Ideal Gas) GFW = 98.992

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.006	-39.343	-39.343	INFINITE
100	9.196	55.703	77.418	-2.172	-39.269	-40.232	87.927
200	11.103	62.685	68.450	-1.153	-39.257	-41.205	45.027
298	12.269	67.360	67.360	.000	-39.300	-42.154	30.900
300	12.284	67.436	67.360	.023	-39.301	-42.172	30.722
400	12.893	71.063	67.850	1.285	-39.376	-43.118	23.559
500	13.224	73.979	68.794	2.592	-39.466	-44.043	19.251
600	13.420	76.408	69.866	3.925	-39.570	-44.949	16.373
700	13.543	78.487	70.953	5.274	-39.684	-45.836	14.311
800	13.626	80.301	72.011	6.633	-39.811	-46.708	12.760
900	13.684	81.910	73.023	7.998	-39.948	-47.561	11.549
1000	13.726	83.354	73.985	9.369	-40.095	-48.400	10.578
1100	13.757	84.664	74.897	10.743	-40.253	-49.223	9.780
1200	13.781	85.862	75.762	12.120	-40.421	-50.031	9.112
1300	13.800	86.966	76.581	13.499	-40.599	-50.825	8.544
1400	13.815	87.989	77.360	14.880	-40.787	-51.604	8.056
1500	13.827	88.942	78.101	16.262	-40.986	-52.370	7.630
1600	13.837	89.835	78.807	17.645	-41.196	-53.122	7.256
1700	13.845	90.674	79.480	19.029	-53.409	-53.754	6.911
1800	13.852	91.466	80.124	20.414	-53.585	-53.770	6.529
1900	13.858	92.215	80.741	21.800	-53.761	-53.774	6.185
2000	13.863	92.926	81.333	23.186	-53.940	-53.770	5.876
2100	13.868	93.602	81.901	24.572	-54.119	-53.758	5.595
2200	13.872	94.248	82.448	25.959	-54.300	-53.737	5.338
2300	13.875	94.864	82.974	27.347	-54.481	-53.707	5.103
2400	13.879	95.455	83.482	28.735	-54.664	-53.668	4.887
2500	13.882	96.021	83.972	30.123	-54.850	-53.624	4.688
2600	13.885	96.566	84.446	31.511	-55.037	-53.571	4.503
2700	13.889	97.090	84.905	32.900	-55.226	-53.512	4.331
2800	13.893	97.595	85.349	34.289	-55.418	-53.442	4.171
2900	13.897	98.083	85.780	35.678	-55.612	-53.370	4.022
3000	13.902	98.554	86.198	37.068	-55.808	-53.291	3.882
3100	13.907	99.010	86.604	38.458	-56.007	-53.204	3.751
3200	13.914	99.452	86.999	39.850	-56.207	-53.108	3.627
3300	13.921	99.880	87.382	41.241	-56.411	-53.008	3.511
3400	13.930	100.296	87.756	42.634	-56.615	-52.901	3.400
3500	13.940	100.700	88.120	44.027	-56.823	-52.792	3.297
3600	13.952	101.092	88.475	45.422	-148.992	-50.415	3.061
3700	13.965	101.475	88.821	46.818	-149.103	-47.674	2.816
3800	13.980	101.847	89.159	48.215	-149.215	-44.933	2.584
3900	13.996	102.211	89.489	49.614	-149.329	-42.187	2.364
4000	14.015	102.565	89.812	51.014	-149.445	-39.438	2.155
4100	14.035	102.912	90.127	52.417	-149.560	-36.690	1.956
4200	14.058	103.250	90.435	53.822	-149.675	-33.937	1.766
4300	14.083	103.581	90.737	55.229	-149.789	-31.179	1.585
4400	14.109	103.905	91.033	56.638	-149.904	-28.417	1.411
4500	14.138	104.223	91.323	58.050	-150.017	-25.653	1.246
4600	14.169	104.534	91.606	59.466	-150.126	-22.889	1.087
4700	14.202	104.839	91.885	60.884	-150.236	-20.120	.936
4800	14.237	105.138	92.158	62.306	-150.342	-17.354	.790
4900	14.274	105.432	92.426	63.732	-150.445	-14.579	.650
5000	14.313	105.721	92.689	65.161	-150.545	-11.809	.516
5100	14.353	106.005	92.947	66.594	-150.641	-9.027	.387
5200	14.396	106.284	93.201	68.032	-150.733	-6.250	.263
5300	14.441	106.558	93.450	69.474	-150.821	-3.473	.143
5400	14.487	106.829	93.695	70.920	-150.906	-.693	.028
5500	14.534	107.095	93.937	72.371	-150.986	2.090	-.083
5600	14.583	107.357	94.174	73.827	-151.061	4.874	-.190
5700	14.633	107.616	94.408	75.288	-151.132	7.659	-.294
5800	14.685	107.871	94.637	76.754	-151.198	10.448	-.394
5900	14.738	108.122	94.864	78.225	-151.260	13.230	-.490
6000	14.791	108.371	95.087	79.701	-151.317	16.020	-.584

Dec. 31, 1960; Dec. 31, 1969

SILICON DICHLORIDE ($SiCl_2$) (IDEAL GAS) GFW = 98.992 Cl_2Si

Point Group C_{2v} $\Delta Hf^\circ_0 = -39.34 \pm 1$ kcal/mol

$S^\circ_{298.15} = 67.36 \pm 0.5$ gibbs/mol $\Delta Hf^\circ_{298.15} = -39.3 \pm 1.0$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[28300]	[1]
[23000]	[3]	[29950]	[1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
513 (1)
[190] (1)
502 (1)

Bond Distance: Si-Cl = [2.04] Å

Bond Angle: Cl-Si-Cl = [106°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = [5.709 \times 10^{-114}]\ g^3\ cm^6$

Heat of Formation

The adopted value is derived from $\Delta Hr^\circ = 78.5 \pm 2$ kcal/mol at 298.15 K for the reaction $Si(c) + SiCl_4(g) \rightarrow 2\ SiCl_2(g)$. JANAF analyses of equilibrium data for this reaction are summarized below. Three sets of data (1, 2, 6) yield average values of ΔHr° (3rd law) which agree within 0.5 kcal/mol and values of ΔSr° (2nd law) which are in reasonable agreement with the JANAF functions. Two of the equilibrium studies used flow techniques while the third used a static technique. A median value of ΔHr° is adopted. Its uncertainty is estimated by assuming that the JANAF entropy for $SiCl_2(g)$ may be too low by 0.7 gibbs/mol at 1400 K. The adopted value corresponds to ΔH°_0 atom = 203.0 kcal/mol and an average bond energy of 101.5 kcal/mol.

Two other flow studies (3, 4) yield large entropy errors, suggesting that there are temperature-dependent errors in Kp. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino (5) gave Kp values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but ΔHr° (3rd law) is lower by 5 kcal/mol.

Source	Date	Method	Input	Range	Entropy Test[a]	ΔHr°_{298}, kcal/mol	
				T, °K	δ, gibbs/mol	2nd Law	3rd Law
Schäfer (1)	1967	Flow	Equation	1273-1473	1.6 ± 1	80.6 ± 1	78.35
Teichmann (2)	1966	Flow	Equation	1223-1573	1.7 ± 0.8	80.8 ± 1.1	78.49
Chechentsev (3)	1965	Flow	Data	1473-1573	36 ± 6	132 ± 9	76.4
Antipin (4)	1954	Flow	Data	1273-1673	26 ± 3	114 ± 4	75.4
Ishino (5)	1965	Static	Data	1448-1573	-2.1 ± 1.4	70.2 ± 2.1	73.4
Schäfer (6)	1953	Static	Equation	1400-1593	0.6 ± 0.9	79.8 ± 1.4	78.84

[a] δ = ΔSr° (2nd law) - ΔSr° (JANAF functions); where equations are used as input, the uncertainties are those given by the original authors.

Heat Capacity and Entropy

The point group is assumed to be the same as that of CF_2 and SiF_2. The Si-Cl bond length and Cl-Si-Cl bond angle are estimated to be intermediate between those in HSiCl and H_2SiCl_2. Comparisons with CF_2, SiF_2, H_2CF_2 and H_2SiF_2 confirm that the estimated angle is reasonable. Further confirmation of the structure comes from analysis of isotopic splittings in the infrared spectra of matrix-isolated $SiCl_2$. Milligan and Jacox (7) deduced angles of 90 to 120° from alternative assignments for the two stretching vibrations. Observations on argon matrices gave 502 and 513 cm^{-1} for these vibrations, but it was not possible to decide which is the symmetric mode. Principal moments of inertia are $I_A = 31.25 \times 10^{-39}$, $I_B = 5.035 \times 10^{-39}$, and $I_C = 36.29 \times 10^{-39}\ g\ cm^2$.

Milligan and Jacox (7) also observed an unstructured absorption in the ultraviolet spectrum. This is the region in which gas-phase emission studies (8) showed features tentatively ascribed to $SiCl_2$. Vibrational spacings of about 250 and 540 cm^{-1} were associated (8) with the ground state; however, this analysis should be reviewed in the light of the matrix spectra. Meanwhile, we estimate that the bending mode should be similar to that in H_2SiCl_2, probably 190 ± 40 cm^{-1}.

The ground state is assumed to be $^1A_1$ as suggested by Hückel-molecular-orbital calculations (9). Singlet excited states (8, 10) are included near 28000 and 30000 cm^{-1}, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie et al. (10) that the continuous spectrum near 23000 cm^{-1} is due to a triplet excited state.

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Titanium Dichloride ($TiCl_2$)

(Crystal) GFW = 118.806

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.179	-123.033	-123.033	INFINITE
100	9.029	6.206	34.146	-2.794	-123.478	-119.387	260.919
200	14.700	14.602	22.347	-1.549	-123.417	-115.292	125.986
298	16.690	20.876	20.876	.000	-123.200	-111.352	81.623
300	16.706	20.979	20.876	.031	-123.195	-111.279	81.066
400	17.541	25.902	21.542	1.744	-122.930	-107.346	58.651
500	18.280	29.897	22.826	3.536	-122.637	-103.483	45.232
600	18.732	33.270	24.293	5.387	-122.321	-99.682	36.309
700	19.184	36.192	25.788	7.282	-121.990	-95.935	29.952
800	19.636	38.783	27.254	9.223	-121.645	-92.237	25.198
900	20.088	41.127	28.667	11.210	-121.284	-88.581	21.510
1000	20.540	43.262	30.021	13.241	-120.911	-84.969	18.570
1100	20.992	45.240	31.315	15.318	-120.520	-81.392	16.171
1200	21.444	47.086	32.554	17.439	-121.051	-77.815	14.172
1300	21.896	48.821	33.739	19.606	-120.500	-74.235	12.480
1400	22.348	50.460	34.875	21.819	-119.920	-70.698	11.036
1500	22.800	52.017	35.966	24.076	-119.314	-67.203	9.791
1600	23.252	53.503	37.016	26.379	-118.682	-63.748	8.708
1700	23.704	54.926	38.028	28.726	-118.027	-60.334	7.756
1800	24.156	56.294	39.005	31.119	-117.350	-56.961	6.916
1900	24.608	57.612	39.950	33.558	-116.650	-53.624	6.168
2000	25.060	58.886	40.865	36.041	-120.380	-50.172	5.482

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

TITANIUM DICHLORIDE ($TiCl_2$) (CRYSTAL) GFW = 118.806

ΔHf°_0 = -123.0 ± 4.0 kcal/mol

$S^\circ_{298.15}$ = 20.88 ±.1.0 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -123.2 ± 4.0 kcal/mol

Ts = [1581.5]°K

ΔHs° = [59.4] kcal/mol

Heat of Formation

The heat of formation of $TiCl_2(c)$ has been measured calorimetrically. The chosen value of ΔHf°_{298} is the average of two such determinations. Values of ΔHf°_{298} are also calculated from the heats of reaction for the processes (A) $2TiCl_3(c) = TiCl_2(c) + TiCl_4(g)$, (B) $3TiCl_2(c) = 2TiCl_3(g) + Ti(c)$, and (C) $2TiCl_2(c) = TiCl_4(g) + Ti(c)$. These heats of reaction are combined with auxiliary JANAF values for the heats of formation of $TiCl_3(c)$, $TiCl_4(g)$, $TiCl_3(c)$ and Ti(c). The following table summarizes the data used to calculate ΔHf°_{298}.

Source	Reac.	Method	No. Pts.	Range T°K	$\Delta Hr^\circ_{298.15}$ Second Law	$\Delta Hr^\circ_{298.15}$ Third Law	Drift eu	ΔHf°_{298}* kcal/mol
Clifton and MacWood (1)		Calorimetric						-123.4, -123.8
Krieve et al. (2)		Calorimetric						-122.4
Farber and Darnell (3)	A	Effusion	11	615-732	36.0±1.4	38.9	4.2±2.1	-123.7
Sanderson and MacWood (4)	A	Knudsen	22**	593-720	35.6±0.8	39.6	6.1±1.3	-123.0
Sanderson and MacWood (4)	A	Static	15***	679-821	38.5±0.5	35.9	-3.4±0.7	-126.7
Farber and Darnell (5)	B	Effusion	13	798-893	94.4±1.9	112.6	21.4±2.2	-123.1
Farber and Darnell (5)	C	Effusion	11	794-894	51.5±1.4	63.0	13.6±1.7	-122.7
Hartman and Rinds (6)	A	Effusion	20	815-974	38.6±0.5	35.7	-3.3±0.5	-126.9
Skinner and Ruehrwein (7)	A	Manometric	5	802-928	37.6±0.5	36.0	-1.9±0.6	-126.9

*Calculated values based on third law $\Delta Hr^\circ_{298.15}$.

**Four points rejected due to failure of a statistical test.

***Two points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The heat capacity of $TiCl_2(c)$ has been measured by Kim and Stout (8) over the range 6° to 300°K. They calculated the adopted value of S°_{298} from their measurements based on S°_6 = 0.017 eu. The heat capacity above 300°K is estimated by graphical extrapolation. The large uncertainty on S°_{298} is due to the possibility of sizeable electronic contributions to the heat capacity below 6°K which would account for the rather low value of S°_{298} reported by Kim and Stout (8).

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of $TiCl_2(c)$ and $TiCl_2(g)$. The temperature of sublimation is taken as the point at which ΔGr° = 0 for the process $TiCl_2(c) = TiCl_2(g)$. These values are hypothetical since $TiCl_2$ would be decomposed to $TiCl_3(g)$ and $TiCl_4(g)$ below this temperature.

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Titanium Dichloride ($TiCl_2$)

(Ideal Gas) GFW = 118.806

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.237	-56.591	-56.591	INFINITE
100	9.829	53.355	77.894	-2.454	-56.638	-57.261	125.145
200	12.686	61.206	67.729	-1.305	-56.673	-57.869	63.236
298	13.743	66.500	66.500	.000	-56.700	-58.455	42.848
300	13.756	66.585	66.500	.025	-56.701	-58.466	42.592
400	14.218	70.614	67.046	1.427	-56.747	-59.047	32.262
500	14.452	73.814	68.091	2.862	-56.811	-59.615	26.058
600	14.585	76.462	69.271	4.314	-56.894	-60.169	21.917
700	14.668	78.717	70.464	5.777	-56.995	-60.707	18.95
800	14.724	80.679	71.621	7.247	-57.121	-61.230	16.727
900	14.766	82.416	72.725	8.721	-57.273	-61.734	14.991
1000	14.803	83.974	73.774	10.200	-57.452	-62.222	13.599
1100	14.842	85.386	74.766	11.682	-57.656	-62.688	12.455
1200	14.885	86.680	75.706	13.168	-58.822	-63.098	11.492
1300	14.937	87.873	76.596	14.659	-58.947	-63.450	10.667
1400	14.997	88.982	77.442	16.156	-59.083	-63.791	9.958
1500	15.068	90.019	78.246	17.659	-59.231	-64.122	9.343
1600	15.146	90.994	79.013	19.170	-59.391	-64.442	8.802
1700	15.232	91.915	79.745	20.689	-59.564	-64.752	8.324
1800	15.324	92.788	80.445	22.216	-59.753	-65.053	7.899
1900	15.419	93.619	81.117	23.754	-59.954	-65.341	7.516
2000	15.516	94.412	81.762	25.300	-64.621	-65.465	7.154
2100	15.613	95.172	82.383	26.857	-64.829	-65.503	6.817
2200	15.709	95.900	82.981	28.423	-65.031	-65.531	6.510
2300	15.803	96.601	83.558	29.998	-65.225	-65.548	6.228
2400	15.893	97.275	84.115	31.583	-65.411	-65.557	5.970
2500	15.980	97.926	84.655	33.177	-65.591	-65.560	5.731
2600	16.062	98.554	85.177	34.779	-65.764	-65.556	5.510
2700	16.140	99.162	85.684	36.389	-65.932	-65.545	5.305
2800	16.213	99.750	86.176	38.007	-66.095	-65.527	5.115
2900	16.282	100.320	86.654	39.632	-66.253	-65.503	4.936
3000	16.346	100.873	87.119	41.263	-66.408	-65.476	4.770
3100	16.407	101.410	87.571	42.901	-66.559	-65.441	4.614
3200	16.464	101.932	88.012	44.544	-66.708	-65.405	4.467
3300	16.517	102.440	88.441	46.194	-66.853	-65.360	4.329
3400	16.567	102.933	88.860	47.848	-66.996	-65.311	4.198
3500	16.615	103.414	89.269	49.507	-67.138	-65.263	4.075
3600	16.660	103.883	89.669	51.171	-168.903	-64.942	3.943
3700	16.702	104.340	90.059	52.839	-169.013	-62.054	3.665
3800	16.743	104.786	90.441	54.511	-169.134	-59.166	3.403
3900	16.783	105.221	90.814	56.187	-169.267	-56.266	3.153
4000	16.821	105.647	91.180	57.868	-169.411	-53.367	2.916
4100	16.857	106.063	91.538	59.551	-169.567	-50.464	2.690
4200	16.892	106.469	91.889	61.239	-169.733	-47.560	2.475
4300	16.927	106.867	92.232	62.930	-169.909	-44.651	2.269
4400	16.960	107.257	92.569	64.624	-170.095	-41.732	2.073
4500	16.992	107.638	92.900	66.322	-170.290	-38.814	1.885
4600	17.023	108.012	93.224	68.022	-170.493	-35.887	1.705
4700	17.053	108.378	93.543	69.726	-170.704	-32.958	1.533
4800	17.082	108.738	93.856	71.433	-170.923	-30.027	1.367
4900	17.110	109.090	94.163	73.143	-171.149	-27.090	1.208
5000	17.137	109.436	94.465	74.855	-171.381	-24.146	1.05
5100	17.163	109.776	94.762	76.570	-171.618	-21.197	.908
5200	17.188	110.109	95.054	78.288	-171.861	-18.244	.767
5300	17.212	110.437	95.341	80.008	-172.110	-15.293	.631
5400	17.235	110.759	95.624	81.730	-172.364	-12.329	.499
5500	17.256	111.075	95.902	83.455	-172.620	-9.360	.372
5600	17.276	111.386	96.175	85.181	-172.882	-6.396	.250
5700	17.295	111.692	96.445	86.910	-173.146	-3.419	.131
5800	17.313	111.993	96.710	88.640	-173.414	-.436	.016
5900	17.330	112.289	96.972	90.372	-173.685	2.546	-.094
6000	17.345	112.581	97.230	92.106	-173.958	5.534	-.202

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

TITANIUM DICHLORIDE ($TiCl_2$) (IDEAL GAS) GFW = 118.806

Point Group [$D_{\infty h}$]

ΔHf°_0 = -56.6 ± 3 kcal/mol

$S^\circ_{298.15}$ = [66.5 ± 3.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -56.7 ± 3 kcal/mol

Ground State Quantum Weight = 3

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[279] (1)
[196] (2)
[439] (1)

Bond Distance: Ti-Cl = [2.3] Å

Bond Angle: Cl-Ti-Cl = [180°] σ = 2

Rotational Constant: B_0 = [0.0449] cm^{-1}

Heat of Formation

Gross and Levi (1) have measured the equilibrium $2TiCl_3(g) + Ti(c) \rightarrow 3TiCl_2(g)$ at 1723°K and obtain ΔGr°_{1723} = 21.7 kcal/mol from four measurements. This yields $\Delta Hf^\circ_{298}(TiCl_2, g)$ = -56.7 ± 3 kcal/mol. They discuss the measurements of Farber and Darnell (2), on the vapor pressure of $TiCl_2(c)$, and show that the results are probably in error due to disproportionation of $TiCl_3(g)$ on condensation. In the work of Skinner and Ruehrwein (3) on the reaction $2NaCl(g) + Ti(c) = 2Na(g) + TiCl_2(g)$, Gross and Levi indicate that the basic assumption, of conversion to $TiCl_2$ only, is erroneous. In the third law analysis of both these data sets significant drifts are obtained which tends to confirm the above arguments.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(c)$ reported by Benzinger and Rundle (4). The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to correspond to the inverted states of $NiCl_2(g)$ (5). The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (6, 7, 8, 9).

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Tungsten Dichloride (WCl_2)

(Crystal) GFW = 254.756

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.600	31.200	31.200	.000	-61.500	-52.587	38.547
300	18.610	31.315	31.200	.034	-61.492	-52.532	38.269
400	19.133	36.740	31.937	1.922	-61.023	-49.616	27.109
500	19.656	41.065	33.344	3.861	-60.538	-46.819	20.465
600	20.179	44.696	34.941	5.853	-60.026	-44.123	16.072
700	20.702	47.845	36.564	7.897	-59.481	-41.514	12.961
800	21.225	50.644	38.153	9.993	-58.904	-38.989	10.651
900	21.750	53.174	39.683	12.142	-58.287	-36.534	8.872
1000	22.273	55.493	41.150	14.343	-57.634	-34.153	7.464
1100	22.796	57.640	42.553	16.596	-56.942	-31.839	6.326
1200	23.319	59.646	43.894	18.902	-56.211	-29.588	5.389
1300	23.842	61.533	45.179	21.260	-55.441	-27.400	4.606
1400	24.365	63.319	46.412	23.670	-54.632	-25.274	3.945
1500	24.888	65.018	47.596	26.133	-53.783	-23.205	3.381
1600	25.411	66.641	48.736	28.648	-52.895	-21.196	2.895
1700	25.934	68.197	49.835	31.215	-51.968	-19.241	2.474
1800	26.457	69.694	50.897	33.835	-51.001	-17.345	2.106
1900	26.980	71.139	51.925	36.507	-49.994	-15.502	1.783
2000	27.503	72.536	52.921	39.231	-48.950	-13.712	1.498

Sept. 30, 1962; Dec. 31, 1966

TUNGSTEN DICHLORIDE (WCl_2) (CRYSTAL) GFW = 254.756

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [31.2] gibbs/mol

$\Delta Hf^\circ_{298.15} = -61.5 \pm 3$ kcal/mol

Td = 862°K

Heat of Formation.

The heat of formation, ΔHf°_{298} $(WCl_2,c) = -61.5 \pm 3$ kcal/mol, is derived from the heat of combustion, $\Delta Hc^\circ = -140 \pm 3$ kcal/mol for $WCl_2(c) + 3/2\ O_2(g) \rightarrow WO_3(c) + Cl_2(g)$, reported by S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zhur. Neorg. Khim. 5, 1650 (1960). The value of ΔHc° was determined calorimetrically, but no further information about the combustion process was given in the paper.

Heat Capacity and Entropy.

Cp_{298} = 6.2 gibbs/g-atom and Cp_{900} = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 900°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy, S°_{298} = 31.2 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952. S. A. Shchukarev et al., loc. cit., have estimated ΔSr° = -30 eu for $W(c) + Cl_2(g) = WCl_2(c)$ which leads to S°_{298} (WCl_2,c) = 31.1 eu, using JANAF auxiliary data.

Temperature of Decomposition.

The decomposition temperature is obtained by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by S. A. Shchukarev, G. I. Novikov, and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2,78 (1959). Decomposition pressure data for Cl:W ratios less than two suggest that the decomposition reaction is not simple.

Tungsten Dichloride (WCl_2)

(Ideal Gas) GFW = 254.756

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol -(G°-H°298)/T	kcal/mol H°-H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.496	-3.113	-3.113	INFINITE
100	11.163	60.190	85.603	-2.541	-3.010	-4.285	9.364
200	13.005	68.546	75.171	-1.325	-3.000	-5.566	6.082
298	13.877	73.925	73.925	.000	-3.000	-6.825	5.003
300	13.887	74.011	73.925	.026	-3.000	-6.849	4.990
400	14.290	78.068	74.476	1.437	-3.008	-8.132	4.443
500	14.497	81.281	75.526	2.877	-3.022	-9.411	4.113
600	14.617	83.936	76.713	4.334	-3.045	-10.686	3.893
700	14.695	86.195	77.910	5.799	-3.079	-11.957	3.733
800	14.756	88.162	79.072	7.272	-3.125	-13.224	3.613
900	14.814	89.903	80.180	8.750	-3.179	-14.482	3.517
1000	14.881	91.467	81.232	10.235	-3.242	-15.735	3.439
1100	14.960	92.889	82.228	11.727	-3.311	-16.982	3.374
1200	15.056	94.195	83.172	13.228	-3.385	-18.221	3.318
1300	15.168	95.404	84.067	14.739	-3.462	-19.453	3.270
1400	15.295	96.533	84.917	16.262	-3.540	-20.682	3.229
1500	15.434	97.593	85.727	17.798	-3.618	-21.903	3.191
1600	15.582	98.594	86.500	19.349	-3.694	-23.120	3.158
1700	15.735	99.543	87.240	20.915	-3.768	-24.330	3.128
1800	15.890	100.447	87.949	22.496	-3.840	-25.539	3.101
1900	16.043	101.310	88.629	24.093	-3.908	-26.740	3.076
2000	16.192	102.137	89.284	25.705	-3.976	-27.940	3.053
2100	16.333	102.930	89.915	27.331	-4.042	-29.137	3.032
2200	16.465	103.693	90.524	28.971	-4.109	-30.333	3.013
2300	16.587	104.428	91.113	30.624	-4.175	-31.522	2.995
2400	16.697	105.136	91.682	32.288	-4.244	-32.708	2.978
2500	16.794	105.819	92.234	33.963	-4.317	-33.892	2.963
2600	16.879	106.480	92.770	35.647	-4.394	-35.074	2.948
2700	16.951	107.118	93.289	37.338	-4.484	-36.252	2.934
2800	17.011	107.736	93.794	39.036	-4.596	-37.426	2.921
2900	17.059	108.334	94.285	40.740	-4.740	-38.601	2.909
3000	17.095	108.913	94.763	42.448	-4.924	-39.763	2.897
3100	17.122	109.474	95.229	44.159	-5.161	-40.923	2.885
3200	17.138	110.017	95.683	45.872	-5.458	-42.070	2.873
3300	17.146	110.545	96.125	47.586	-5.823	-43.209	2.862
3400	17.146	111.057	96.557	49.301	-6.264	-44.334	2.850
3500	17.139	111.554	96.978	51.015	-6.798	-45.449	2.838
3600	17.126	112.036	97.390	52.728	-7.449	-46.541	2.825
3700	17.107	112.505	97.792	54.440	-16.549	-47.570	2.810
3800	17.084	112.961	98.185	56.150	-16.647	-48.408	2.784
3900	17.057	113.405	98.570	57.857	-16.751	-49.242	2.759
4000	17.026	113.836	98.946	59.561	-16.861	-50.073	2.736
4100	16.993	114.256	99.314	61.262	-16.975	-50.903	2.713
4200	16.957	114.665	99.675	62.959	-17.096	-51.729	2.692
4300	16.919	115.064	100.028	64.653	-17.221	-52.554	2.671
4400	16.880	115.452	100.374	66.343	-17.352	-53.370	2.651
4500	16.840	115.831	100.714	68.029	-17.489	-54.191	2.632
4600	16.799	116.201	101.046	69.711	-17.630	-55.005	2.613
4700	16.758	116.562	101.373	71.389	-17.777	-55.814	2.595
4800	16.716	116.914	101.693	73.062	-17.930	-56.622	2.578
4900	16.674	117.258	102.007	74.732	-18.087	-57.424	2.561
5000	16.633	117.595	102.315	76.397	-18.249	-58.229	2.545
5100	16.591	117.924	102.618	78.058	-18.415	-59.026	2.529
5200	16.550	118.246	102.916	79.716	-18.585	-59.821	2.514
5300	16.510	118.560	103.208	81.369	-18.761	-60.610	2.499
5400	16.470	118.869	103.495	83.018	-18.941	-61.402	2.485
5500	16.431	119.171	103.777	84.663	-19.125	-62.185	2.471
5600	16.393	119.466	104.055	86.304	-19.313	-62.965	2.457
5700	16.355	119.756	104.328	87.941	-19.506	-63.749	2.444
5800	16.319	120.040	104.596	89.575	-19.701	-64.518	2.431
5900	16.283	120.319	104.860	91.205	-19.901	-65.290	2.418
6000	16.248	120.592	105.120	92.832	-214.008	-63.972	2.330

Sept. 30, 1962; Dec. 31, 1966

TUNGSTEN DICHLORIDE (WCl_2) (IDEAL GAS) GFW = 254.756

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [74] gibbs/mol

Ground State Quantum Weight = [5]

ΔHf°_0 = [-3 ± 25] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-3 ± 25] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[5]
[5600]	[10]
[8900]	[10]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
[360]	(1)
[60]	(2)
[423]	(1)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [180]°

Rotational Constant: B_o = [0.04655] cm^{-1}

σ = [2]

Heat of Formation.

The value of $\Delta Hf^\circ_{298}(WCl_2,g)$ = -3 ± 25 kcal/mol is calculated from the heat of formation of the crystal plus the heat of sublimation, ΔHs°_{298} = 58.5 ± 25 kcal/mol. The latter is estimated from the heats of sublimation of $TiCl_2$, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The uncertainty covers the difference between the heats of sublimation among the above compounds and also the possible error in transference from the first row transition metal dichlorides to tungsten dichloride.

S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960), have also estimated the heat of sublimation as 102 kcal/mol.

Heat Capacity and Entropy.

The molecular configuration of $WCl_2(g)$ is assumed to be linear. The bond distance is estimated to be the same as that in $WCl_6(g)$. The ground state configuration ($^5\Sigma$), the low lying electronic levels and their quantum weights are assumed to be the same as those for $CrCl_2(g)$, observed by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).

The vibrational frequencies are calculated from a valence force field model. The stretching force constant, K_1, is estimated to be the same as that of $HgCl_2(g)$, 2.7 millidyne/Å. The bending force constant is assumed to be one hundredth of the stretching force constant. The moment of inertia is $I = 6.013 \times 10^{-38}$ g cm^2.

Zirconium Dichloride ($ZrCl_2$)

(Crystal) GFW = 162.126

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	
0							
100							
200							
298	17.350	26.300	26.300	.000	-103.000	-92.176	67.567
300	17.378	26.407	26.300	.032	-102.994	-92.109	67.101
400	18.168	31.521	26.992	1.812	-102.667	-88.529	48.370
500	18.700	35.634	28.323	3.656	-102.327	-85.034	37.168
600	19.130	39.082	29.836	5.548	-101.982	-81.608	29.726
700	19.530	42.062	31.375	7.481	-101.633	-78.240	24.428
800	19.868	44.692	32.878	9.451	-101.282	-74.922	20.468
900	20.206	47.052	34.324	11.455	-100.930	-71.648	17.399
1000	20.536	49.199	35.706	13.493	-100.575	-68.414	14.952
1100	20.720	51.165	37.023	15.556	-100.226	-65.215	12.957
1200	20.900	52.975	38.278	17.637	-100.741	-61.996	11.291
1300	21.080	54.656	39.474	19.737	-100.237	-58.787	9.883
1400	21.180	56.222	40.615	21.850	-99.733	-55.617	8.682
1500	21.250	57.686	41.705	23.971	-99.234	-52.483	7.647
1600	21.300	59.059	42.747	26.099	-98.742	-49.383	6.745
1700	21.350	60.352	43.745	28.231	-98.257	-46.311	5.954
1800	21.400	61.573	44.702	30.369	-97.780	-43.271	5.254
1900	21.450	62.732	45.620	32.511	-97.311	-40.254	4.630
2000	21.500	63.833	46.504	34.659	-96.850	-37.264	4.072

June 30, 1962; Dec. 31, 1969

ZIRCONIUM DICHLORIDE ($ZrCl_2$) (CRYSTAL) GFW = 162.126

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [26.3 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-103.0 ± 10] kcal/mol

Tm = [1000]°K

ΔHm° = [6.4 ± 3] kcal/mol

$\Delta Hs^\circ_{298.15}$ = [58.5 ± 10] kcal/mol

Heat of Formation

The value of $\Delta Hf^\circ_{298}(ZrCl_2, c)$ = -103.0 kcal/mol is calculated from the estimated ΔHs°_{298} = 58.5 kcal/mol for $ZrCl_2(c) + ZrCl_2(g)$, using $\Delta Hf^\circ_{298}(ZrCl_2, g)$ = -44.5 kcal/mol (1). The estimated ΔHs°_{298} is obtained as an average of the heats of sublimation at 298°K for $TiCl_2$, VCl_2, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by L. Brewer, G. R. Somayajulu and E. Brackett (2).

Heat Capacity and Entropy

The heat capacities of $ZrCl_2(c)$ are estimated based on the assumption that $Cp(ZrCl_2, c) = 1/2[Cp(ZrCl_4, c) + Cp(Zr, c)]$. The entropy, S°_{298}, is also estimated in a manner similar to that of the heat capacity.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (3) and the heat of melting was also estimated by A. Glassner (4).

References

1. JANAF $ZrCl_2(g)$ table dated Dec. 31, 1969.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, New York, 1949.
4. A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K," ANL Report 5750, Argonne National Laboratory.

Zirconium Dichloride ($ZrCl_2$)

(Liquid) GFW = 162.126

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	21.750	29.278	29.278	.000	-98.372	-88.436	64.825
300	21.750	29.413	29.278	.040	-98.358	-88.374	64.381
400	21.750	35.670	30.132	2.215	-97.636	-85.157	46.528
500	21.750	40.523	31.743	4.390	-96.965	-82.116	35.893
600	21.750	44.489	33.546	6.565	-96.337	-79.206	28.851
700	21.750	47.841	35.355	8.740	-95.746	-76.398	23.853
800	21.750	50.746	37.102	10.915	-95.190	-73.673	20.126
900	21.750	53.307	38.763	13.090	-94.667	-71.015	17.245
1000	21.750	55.599	40.334	15.265	-94.175	-68.414	14.952
1100	21.750	57.672	41.817	17.440	-93.714	-65.860	13.085
1200	21.750	59.564	43.218	19.615	-94.135	-63.296	11.528
1300	21.750	61.305	44.544	21.790	-93.556	-60.750	10.213
1400	21.750	62.917	45.799	23.965	-92.990	-58.247	9.093
1500	21.750	64.418	46.991	26.140	-92.437	-55.785	8.128
1600	21.750	65.822	48.125	28.315	-91.898	-53.359	7.289
1700	21.750	67.140	49.205	30.490	-91.370	-50.965	6.552
1800	21.750	68.383	50.236	32.665	-90.856	-48.605	5.901
1900	21.750	69.559	51.222	34.840	-90.354	-46.270	5.322
2000	21.750	70.675	52.167	37.015	-89.866	-43.963	4.808

June 30, 1962; Dec. 31, 1969

ZIRCONIUM DICHLORIDE ($ZrCl_2$) (LIQUID) GFW = 162.126

$S°_{298.15}$ = [29.278] gibbs/mol

$\Delta Hf°_{298.15}$ = [-98.372] kcal/mol

Tm = [1000]°K

ΔHm° = [6.4 ± 3] kcal/mol

Tb = [1565.3]°K

ΔHv° = [45.0] kcal/mol

Heat of Formation

The $\Delta Hf°_{298}(ZrCl_2, \ell)$ is calculated from $\Delta Hf°_{298}(ZrCl_2, c)$ by adding ΔHm° and the difference between $H_{1000} - H°_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (1), and the heat of melting was also estimated by A. Glassner (2).

Vaporization Data

Tb is the temperature at which the Gibbs energy change approaches zero for the process $ZrCl_2(\ell) \rightarrow ZrCl_2(g)$. The difference between ΔHf° for $ZrCl_2(\ell)$ and $ZrCl_2(g)$ at Tb is ΔHv°.

References

1. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, New York, 1949.
2. A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K," ANL Report 5750, Argonne National Laboratory.

Zirconium Dichloride ($ZrCl_2$)

(Ideal Gas) GFW = 162.126

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.404	-44.389	-44.389	INFINITE
100	10.856	56.357	81.450	-2.509	-44.402	-45.188	98.758
200	12.856	64.565	71.132	-1.313	-44.458	-45.951	50.213
298	13.785	69.896	69.896	.000	-44.500	-46.674	34.213
300	13.796	69.981	69.896	.026	-44.500	-46.688	34.012
400	14.231	74.017	70.443	1.429	-44.550	-47.410	25.903
500	14.457	77.219	71.489	2.865	-44.618	-48.117	21.032
600	14.587	79.868	72.671	4.318	-44.712	-48.809	17.779
700	14.668	82.123	73.865	5.781	-44.833	-49.483	15.449
800	14.724	84.085	75.022	7.250	-44.983	-50.137	13.697
900	14.766	85.822	76.128	8.725	-45.160	-50.771	12.329
1000	14.803	87.380	77.176	10.204	-45.364	-51.385	11.230
1100	14.841	88.792	78.169	11.686	-45.596	-51.975	10.327
1200	14.885	90.086	79.109	13.172	-46.706	-52.493	9.560
1300	14.937	91.279	80.000	14.663	-46.811	-52.971	8.905
1400	14.997	92.388	80.845	16.160	-46.923	-53.440	8.342
1500	15.067	93.425	81.650	17.663	-47.042	-53.901	7.853
1600	15.146	94.400	82.417	19.173	-47.168	-54.355	7.425
1700	15.232	95.321	83.149	20.692	-47.296	-54.798	7.045
1800	15.323	96.194	83.850	22.220	-47.429	-55.237	6.707
1900	15.419	97.025	84.521	23.757	-47.565	-55.666	6.403
2000	15.516	97.818	85.166	25.304	-47.705	-56.089	6.129
2100	15.613	98.578	85.787	26.860	-47.847	-56.506	5.881
2200	15.709	99.306	86.385	28.426	-52.996	-56.738	5.636
2300	15.803	100.007	86.962	30.002	-53.139	-56.903	5.407
2400	15.893	100.681	87.520	31.587	-53.275	-57.064	5.196
2500	15.980	101.332	88.059	33.180	-53.406	-57.220	5.002
2600	16.062	101.960	88.582	34.783	-53.528	-57.369	4.822
2700	16.140	102.568	89.089	36.393	-53.646	-57.516	4.656
2800	16.213	103.156	89.581	38.010	-53.760	-57.656	4.500
2900	16.282	103.726	90.059	39.635	-53.868	-57.794	4.355
3000	16.346	104.279	90.524	41.267	-53.972	-57.928	4.220
3100	16.407	104.816	90.976	42.904	-54.074	-58.058	4.093
3200	16.463	105.338	91.417	44.548	-54.172	-58.186	3.974
3300	16.517	105.845	91.846	46.197	-54.268	-58.309	3.862
3400	16.567	106.339	92.265	47.851	-54.361	-58.429	3.756
3500	16.614	106.820	92.674	49.510	-54.453	-58.549	3.656
3600	16.660	107.289	93.074	51.174	-54.542	-58.663	3.561
3700	16.702	107.746	93.464	52.842	-54.630	-58.777	3.472
3800	16.743	108.192	93.846	54.514	-54.716	-58.889	3.387
3900	16.783	108.627	94.219	56.191	-54.800	-58.996	3.306
4000	16.821	109.053	94.565	57.871	-54.884	-59.103	3.229
4100	16.857	109.469	94.943	59.555	-54.965	-59.209	3.156
4200	16.892	109.875	95.294	61.242	-55.046	-59.312	3.086
4300	16.927	110.273	95.637	62.933	-55.124	-59.413	3.020
4400	16.960	110.663	95.974	64.628	-55.200	-59.509	2.956
4500	16.992	111.044	96.305	66.325	-55.276	-59.609	2.895
4600	17.023	111.418	96.630	68.026	-55.348	-59.704	2.837
4700	17.053	111.784	96.948	69.730	-55.419	-59.796	2.781
4800	17.082	112.144	97.261	71.436	-196.646	-59.208	2.696
4900	17.110	112.496	97.568	73.146	-196.817	-56.339	2.513
5000	17.137	112.842	97.870	74.858	-196.992	-53.473	2.337
5100	17.163	113.182	98.167	76.573	-197.169	-50.598	2.168
5200	17.188	113.515	98.459	78.291	-197.348	-47.722	2.006
5300	17.212	113.843	98.746	80.011	-197.530	-44.846	1.849
5400	17.235	114.165	99.029	81.733	-197.714	-41.963	1.698
5500	17.256	114.481	99.307	83.458	-197.899	-39.076	1.553
5600	17.276	114.792	99.581	85.185	-198.084	-36.187	1.412
5700	17.295	115.098	99.850	86.913	-198.273	-33.298	1.277
5800	17.313	115.399	100.116	88.644	-198.460	-30.397	1.145
5900	17.330	115.695	100.377	90.376	-198.649	-27.501	1.019
6000	17.345	115.987	100.635	92.109	-198.840	-24.598	.896

June 30, 1962; Dec. 31, 1969

ZIRCONIUM DICHLORIDE ($ZrCl_2$) (IDEAL GAS) GFW = 162.126

Point Group = [$D_{\infty h}$] ΔHf_0° = -44.4 ± 5 kcal/mol

$S_{298.15}^\circ$ = [69.9 ± 3] gibbs/mol $\Delta Hf_{298.15}^\circ$ = -44.5 ± 5 kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[346] (1)
[92] (2)
[461] (1)

Bond Distance: Zr-Cl = [2.3] Å

Bond Angle: Cl-Zr-Cl = [180°] σ = [2]

Rotational Constant: B_0 = [0.04494] cm^{-1}

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction $ZrCl_4(g) + ZrCl_2(g) \rightarrow 2ZrCl_3(g)$ in the temperature range 1673-2110°K, second and third law analyses give the heat of reaction at 298°K as -15.8 and +1.7 kcal/mol, respectively. The third law drift is 8.9 ± 3.7 eu. Based on the third law heat of reaction and $\Delta Hf_{298}^\circ(ZrCl_4, g)$ = -207.77 kcal/mol (2) and $\Delta Hf_{298}^\circ(ZrCl_3, g)$ = -125.3 kcal/mol (3), we obtain $\Delta Hf_{298}^\circ(ZrCl_2, g)$ = -44.5 kcal/mol which is adopted in the tabulation.

Farber et al. (4) also studied mass spectrometrically the reaction (a) $Zr(c) + ZrCl_4(g) \rightarrow 2ZrCl_2(g)$ and the reaction (b) $Zr(c) + 2Cl(g) \rightarrow ZrCl_2(g)$. They reported second law heats of reaction as ΔHr_{298}° = 28.8 ± 1.8 kcal/mol for reaction (a); and -141.1 ± 2.2 kcal/mol for reaction (b). Third law analysis of the equilibrium constants which were calculated from their ion intensities of run 3 (the only available values) gives $\Delta Hf_{298}^\circ(ZrCl_2, g)$ = -43.4 kcal/mol. See JANAF $ZrCl_3(g)$ table (3) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that other transition metal dichlorides are linear (5, 6, 7, 8, 9, 10) even though some fluorides are bent (11). The bond distance is assumed to be the same as that of $ZrCl_4(g)$. The electronic levels and quantum weights are estimated to be the same as those of $TiCl_2(g)$ (12).

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 2.5 millidyne/Å and the bending force constant 0.05 millidyne/Å. The moment of inertia is 62.2817×10^{-39} g cm^2.

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford, Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF $ZrCl_4(g)$ table dated Dec. 31, 1969.
3. JANAF $ZrCl_3(g)$ table dated Dec. 31, 1969.
4. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
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10. K. R. Thompson and K. D. Carlson, J. Chem. Phys. 49, 4379 (1968).
11. J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Chem. Phys. 51, 2648 (1969).
12. JANAF $TiCl_2(g)$ table dated Dec. 31, 1968.

Copper Monochloride, Trimeric ($(CuCl)_3$)
(Ideal Gas) Mol. Wt. = 296.979

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-6.865	-61.789	-61.789	INFINITE
100	21.756	73.790	127.517	-5.373	-61.825	-61.708	134.863
200	27.780	91.104	105.304	-2.840	-61.817	-61.594	67.307
298	29.773	102.631	102.631	.000	-61.800	-61.489	45.073
300	29.795	102.815	102.632	.055	-61.800	-61.488	44.794
400	30.621	111.515	103.812	3.081	-61.810	-61.384	33.539
500	31.028	118.397	106.065	6.166	-61.853	-61.271	26.781
600	31.256	124.076	108.607	9.281	-61.940	-61.148	22.273
700	31.396	128.905	111.171	12.414	-62.059	-61.005	19.047
800	31.488	133.104	113.656	15.559	-62.215	-60.848	16.623
900	31.552	136.817	116.027	18.711	-62.399	-60.664	14.731
1000	31.598	140.144	118.275	21.869	-62.616	-60.462	13.214
1100	31.632	143.157	120.402	25.030	-62.858	-60.234	11.967
1200	31.657	145.910	122.415	28.195	-63.131	-59.986	10.925
1300	31.678	148.445	124.321	31.361	-63.430	-59.710	10.038
1400	31.694	150.793	126.129	34.530	-73.311	-59.106	9.227
1500	31.707	152.980	127.847	37.700	-73.750	-58.078	8.462
1600	31.717	155.027	129.483	40.871	-74.191	-57.020	7.789
1700	31.726	156.950	131.042	44.043	-74.632	-55.929	7.190
1800	31.733	158.764	132.532	47.216	-75.076	-54.817	6.656
1900	31.740	160.480	133.959	50.390	-75.520	-53.679	6.175
2000	31.745	162.108	135.326	53.564	-75.968	-52.517	5.739
2100	31.750	163.657	136.638	56.739	-76.416	-51.335	5.342
2200	31.754	165.134	137.900	59.914	-76.868	-50.129	4.980
2300	31.757	166.546	139.115	63.090	-77.321	-48.905	4.647
2400	31.760	167.897	140.286	66.266	-77.776	-47.660	4.340
2500	31.763	169.194	141.417	69.442	-78.236	-46.391	4.056
2600	31.765	170.440	142.509	72.618	-78.697	-45.109	3.792
2700	31.767	171.638	143.566	75.795	-79.163	-43.808	3.546
2800	31.769	172.794	144.590	78.972	-79.632	-42.488	3.316
2900	31.771	173.909	145.581	82.149	-298.079	-37.185	2.802
3000	31.773	174.986	146.544	85.326	-298.091	-28.187	2.053
3100	31.774	176.028	147.478	88.503	-298.143	-19.189	1.353
3200	31.775	177.036	148.386	91.681	-298.235	-10.183	.695
3300	31.776	178.014	149.269	94.858	-298.371	-1.183	.078
3400	31.777	178.963	150.129	98.036	-298.543	7.826	-.503
3500	31.778	179.884	150.966	101.214	-298.760	16.835	-1.051
3600	31.779	180.779	151.782	104.392	-299.012	25.861	-1.570
3700	31.780	181.650	152.577	107.570	-299.305	34.888	-2.061
3800	31.781	182.497	153.353	110.748	-299.634	43.924	-2.526
3900	31.782	183.323	154.111	113.926	-300.001	52.969	-2.968
4000	31.782	184.128	154.852	117.104	-300.402	62.022	-3.389
4100	31.783	184.912	155.575	120.282	-300.831	71.093	-3.790
4200	31.783	185.678	156.283	123.461	-301.294	80.168	-4.172
4300	31.784	186.426	156.975	126.639	-301.784	89.261	-4.537
4400	31.784	187.157	157.653	129.817	-302.300	98.358	-4.885
4500	31.785	187.871	158.317	132.996	-302.840	107.464	-5.219
4600	31.785	188.570	158.967	136.174	-303.401	116.586	-5.539
4700	31.786	189.253	159.604	139.353	-303.986	125.728	-5.846
4800	31.786	189.923	160.229	142.531	-304.587	134.877	-6.141
4900	31.786	190.578	160.841	145.710	-305.205	144.042	-6.425
5000	31.787	191.220	161.442	148.889	-305.838	153.215	-6.697
5100	31.787	191.850	162.033	152.067	-306.483	162.409	-6.960
5200	31.787	192.467	162.612	155.246	-307.144	171.602	-7.212
5300	31.788	193.072	163.181	158.425	-307.816	180.810	-7.456
5400	31.788	193.667	163.740	161.604	-308.496	190.032	-7.691
5500	31.788	194.250	164.289	164.782	-309.186	199.278	-7.919
5600	31.788	194.823	164.830	167.961	-309.885	208.530	-8.138
5700	31.789	195.385	165.361	171.140	-310.591	217.785	-8.350
5800	31.789	195.938	165.883	174.319	-311.308	227.072	-8.556
5900	31.789	196.482	166.397	177.498	-312.029	236.362	-8.755
6000	31.789	197.016	166.903	180.677	-312.759	245.655	-8.948

Mar. 31, 1966

COPPER MONOCHLORIDE TRIMERIC ($(CuCl)_3$) (IDEAL GAS) MOL. WT. = 296.979

Point Group D_{3h}

$S^\circ_{298.15}$ = [102.63] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -61.8 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -61.8 ± 0.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[80](2)

Bond Distance: Cu-Cl = 2.16 Å

Bond Angle: Cl-Cu-Cl = 150° Cu-Cl-Cu = 90°

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 2.02847 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. D. W. Magee, Doctoral Thesis, Ohio State University (1955), measured both vapor pressure by torsion effusion and vapor density in the range 533-644°K. and found only trimer present. The 2nd and 3rd law analyses gave $\Delta H^\circ_{s\ 298} = 37.37 \pm 0.04$ and 37.24 ± 0.02 kcal. mole^{-1} with a drift of -0.25 ± 0.07 cal. deg.$^{-1}$ mole^{-1}. R. A. J. Shelton, Trans. Faraday Soc. 57, 2113 (1961) using Knudsen effusion in the range 547-657°K. obtained $\Delta H^\circ_{s\ 298} = 40.35 \pm 1.4$ and 37.42 ± 0.4 kcal. mole^{-1} with a drift of -4.9 cal. deg.$^{-1}$ mole^{-1}. P. I. Fedorov and M. N. Shakhova, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 4, 550 (1961), using transport methods obtained vapor pressures over the liquid from 751-1057°K. Using 2nd and 3rd law analysis these gave $\Delta H^\circ_{s\ 298} = 38.6 \pm 1.0$ and 39.27 ± 0.5 kcal. mole^{-1}.

L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950) obtained equilibrium constants for the reaction $3Cu(c) + 3HCl(g) \rightarrow Cu_3Cl_3(g) + 1.5\ H_2(g)$. Second and third law analysis of these constants gave $\Delta H_{r\ 298} = 3.9 \pm 0.6$ and 4.39 ± 0.3 kcal. mole^{-1} which leads to $\Delta H^\circ_f = -61.8 \pm 0.5$ kcal. mole^{-1}. This was the value adopted since it is dependent only on HCl(g) and does not involve three times the uncertainty of CuCl(c) as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.

Heat Capacity and Entropy.

The structure of the trimer has been investigated by C-H. Wong and V. Schomaker, J. Phys. Chem. 61, 358 (1957). They conclude that the molecule is planar with D_{3h} symmetry and a Cu-Cl bond length of 2.16 Å. They also state that a very large amplitude of the symmetric in-plane bending appears plausible from the diffraction pattern. The infra-red spectrum has been investigated by W. Klemperer, S. A. Rice and R. S. Berry, J. Am. Chem. Soc. 79, 1810 (1957). They observed one strong absorption with a maximum at 350 cm.$^{-1}$; they attribute this to bond stretching motion of type E'. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra-red active E' mode would be close to the observed 350 cm.$^{-1}$ and this was estimated as 300 cm.$^{-1}$. The in-plane bending is the third E' mode and since this has a very large amplitude it was estimated as 60 cm.$^{-1}$ By analogy with other D_{3h} rings the A_2' mode was assumed to be in the same region as the E' stretches and was taken to be 250 cm.$^{-1}$ The $2A'_1$ stretches were estimated as 100 and 150 cm.$^{-1}$, while the out of plane A_2'' was taken as 200 cm.$^{-1}$ and the E" as 80 cm.$^{-1}$. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The individual moments of inertia were $I_A = I_B = 100.472 \times 10^{-39}$ g. cm.^{2}, $I_C = 200.944 \times 10^{-39}$ g. cm.^{2}

Trichlorofluorosilane ($FSiCl_3$)
(Ideal Gas) Mol. Wt. = 153.461

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.592	-200.490	-200.490	INFINITE
100	13.167	61.098	97.418	-3.632	-200.986	-198.197	433.138
200	18.843	72.211	82.191	-1.996	-201.063	-195.354	213.462
298	21.530	80.295	80.295	.000	-201.000	-192.565	141.147
300	21.566	80.428	80.295	.040	-200.999	-192.512	140.238
400	23.023	86.852	81.161	2.276	-200.900	-189.697	103.641
500	23.871	92.088	82.839	4.625	-200.785	-186.910	81.694
600	24.398	96.491	84.758	7.040	-200.662	-184.146	67.072
700	24.743	100.279	86.711	9.498	-200.538	-181.404	56.634
800	24.980	103.600	88.619	11.985	-200.414	-178.679	48.811
900	25.148	106.552	90.450	14.492	-200.295	-175.969	42.729
1000	25.272	109.208	92.195	17.013	-200.182	-173.271	37.867
1100	25.366	111.622	93.853	19.545	-200.075	-170.587	33.891
1200	25.438	113.832	95.428	22.085	-199.972	-167.909	30.579
1300	25.495	115.871	96.923	24.632	-199.873	-165.241	27.778
1400	25.540	117.762	98.344	27.184	-199.779	-162.583	25.379
1500	25.577	119.525	99.698	29.740	-199.689	-159.930	23.301
1600	25.608	121.177	100.990	32.299	-199.601	-157.280	21.482
1700	25.633	122.730	102.223	34.861	-211.621	-154.528	19.865
1800	25.655	124.196	103.404	37.426	-211.500	-151.177	18.355
1900	25.673	125.583	104.535	39.992	-211.380	-147.827	17.003
2000	25.688	126.901	105.620	42.560	-211.261	-144.485	15.788
2100	25.702	128.154	106.664	45.130	-211.146	-141.150	14.689
2200	25.713	129.350	107.668	47.701	-211.032	-137.820	13.690
2300	25.724	130.493	108.636	50.272	-210.921	-134.493	12.779
2400	25.733	131.588	109.570	52.845	-210.811	-131.174	11.944
2500	25.741	132.639	110.471	55.419	-210.706	-127.856	11.177
2600	25.748	133.649	111.344	57.993	-210.602	-124.546	10.469
2700	25.754	134.621	112.188	60.568	-210.501	-121.237	9.813
2800	25.759	135.557	113.006	63.144	-210.402	-117.933	9.205
2900	25.764	136.461	113.799	65.720	-210.306	-114.635	8.639
3000	25.769	137.335	114.569	68.297	-210.213	-111.338	8.111
3100	25.773	138.180	115.317	70.874	-210.122	-108.040	7.616
3200	25.777	138.998	116.045	73.452	-210.034	-104.747	7.154
3300	25.780	139.791	116.752	76.029	-209.950	-101.459	6.719
3400	25.783	140.561	117.441	78.608	-209.866	-98.171	6.310
3500	25.786	141.309	118.113	81.186	-209.786	-94.890	5.925
3600	25.789	142.035	118.767	83.765	-304.685	-91.137	5.532
3700	25.791	142.742	119.405	86.344	-304.548	-85.207	5.033
3800	25.794	143.429	120.029	88.923	-304.416	-79.279	4.559
3900	25.796	144.100	120.637	91.503	-304.286	-73.362	4.111
4000	25.798	144.753	121.232	94.082	-304.160	-67.439	3.685
4100	25.799	145.390	121.814	96.662	-304.035	-61.523	3.279
4200	25.801	146.011	122.382	99.242	-303.914	-55.604	2.893
4300	25.803	146.619	122.939	101.822	-303.797	-49.701	2.526
4400	25.804	147.212	123.484	104.403	-303.681	-43.791	2.175
4500	25.805	147.792	124.018	106.983	-303.569	-37.890	1.840
4600	25.807	148.359	124.541	109.564	-303.459	-31.982	1.519
4700	25.808	148.914	125.053	112.144	-303.351	-26.081	1.213
4800	25.809	149.457	125.556	114.725	-303.247	-20.182	.919
4900	25.810	149.989	126.049	117.306	-303.145	-14.287	.637
5000	25.811	150.511	126.533	119.887	-303.045	-8.389	.367
5100	25.812	151.022	127.008	122.468	-302.950	-2.503	.107
5200	25.813	151.523	127.475	125.050	-302.856	3.390	-.142
5300	25.813	152.015	127.934	127.631	-302.765	9.281	-.383
5400	25.814	152.497	128.384	130.212	-302.676	15.163	-.614
5500	25.815	152.971	128.827	132.794	-302.590	21.054	-.837
5600	25.816	153.436	129.262	135.375	-302.509	26.933	-1.051
5700	25.816	153.893	129.690	137.957	-302.430	32.821	-1.258
5800	25.817	154.342	130.111	140.539	-302.351	38.699	-1.458
5900	25.818	154.783	130.526	143.120	-302.277	44.581	-1.651
6000	25.818	155.217	130.934	145.702	-302.207	50.450	-1.838

December 31, 1960.

TRICHLOROFLUOROSILANE ($FSiCl_3$) (IDEAL GAS) MOL. WT. = 153.461

Point Group C_{3v}

$\Delta H^\circ_{f\ 298.15}$ = [-201 ± 15] kcal mole^{-1}

$S^\circ_{298.15}$ = [80.3 ± 4] cal deg^{-1} mole^{-1}

Vibrational Levels and Multiplicities

ω, cm^{-1}
[925] (1)
[350] (1)
[500] (2)
[270] (2)
[200] (2)

Product of the Moments of Inertia: $I_AI_BI_C$ = [142,900 x 10^{-117}] g^3 cm^6

σ = 3

All data from C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Iron Trichloride ($FeCl_3$)

(Crystal) Mol. Wt. = 162.206

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.710	- 95.804	- 95.804	INFINITE
100	13.923	13.127	52.582	- 3.946	- 96.194	- 90.582	197.957
200	20.607	25.303	36.055	- 2.150	- 95.902	- 85.055	92.940
298	23.100	34.019	34.019	.000	- 95.460	- 79.824	58.510
300	23.150	34.162	34.020	.043	- 95.451	- 79.727	58.078
400	25.500	41.141	34.955	2.475	- 94.890	- 74.567	40.739
500	28.650	47.131	36.800	5.165	- 94.154	- 69.564	30.405
600	29.500	52.382	38.970	8.047	- 93.306	- 64.726	23.575
700	30.750	57.029	41.225	11.063	- 92.395	- 60.034	18.743
800	31.500	61.188	43.465	14.179	- 91.477	- 55.476	15.154
900	31.900	64.924	45.645	17.351	- 90.615	- 51.026	12.390
1000	32.000	68.291	47.744	20.547	- 89.918	- 46.669	10.199
1100	32.000	71.341	49.753	23.747	- 89.438	- 42.363	8.416
1200	32.000	74.126	51.670	26.947	- 88.751	- 38.120	6.942
1300	32.000	76.687	53.497	30.147	- 87.727	- 33.942	5.706
1400	32.000	79.058	55.239	33.347	- 86.722	- 29.841	4.658
1500	32.000	81.266	56.902	36.547	- 85.734	- 25.814	3.761

June 30, 1965

IRON TRICHLORIDE ($FeCl_3$) (CRYSTAL) MOL. WT. = 162.206

$S^\circ_{298.15} = 34.019$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 577$°K.

$\Delta H^\circ_{f\ 0} = -95.80 \pm 0.20$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -95.46 \pm 0.20$ kcal. mole^{-1}

$\Delta H^\circ_m = 10.30$ kcal. mole^{-1}

ΔH°_s (to dimer) = 34.52 kcal. mole^{-1}

Heat of Formation.

The enthalpy change, $\Delta H^\circ_{r\ 298.15} = -24.49 \pm 0.07$ kcal. mole^{-1}, for the reaction Fe( ) + 3(HCl·12.731 H_2O)(l) + 1/2(H_2O_2·12.580 H_2O)(l) = $FeCl_3$(c) + H_2(g) + 45.483 H_2O(l) was determined by M. F. Koehler and J. P. Coughlin, J. Phys. Chem. 63, 605 (1959). This leads to $\Delta H^\circ_{f\ 298.15} = -95.46 \pm 0.20$ kcal. mole^{-1} for $FeCl_3$(c), using $\Delta H^\circ_{f\ 298.15} = -38.9 \pm 0.05$ and -45.68 ± 0.01 kcal mole^{-1} for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, National Bureau of Standards Circular 500, 1952. From $\Delta H^\circ_{r\ 298.15} = -38.0 \pm 0.2$ kcal. mole^{-1} for the reaction $FeCl_3$(c) = Fe^{+++}(aq.) reported by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952), the value of $\Delta H^\circ_{f\ 298.15}$ ($FeCl_3$, c) was calculated as -93.26 ± 0.2 kcal. mole^{-1}. The former $\Delta H^\circ_{f\ 298.15}$ value is adopted.

The equilibrium pressures of the reaction 2 $FeCl_2$(c) + Cl_2(g) = 2$FeCl_3$(c), in the temperature range of 435.7-482.2°K., were measured by H. Schäfer and E. Oehler, Z. anorg. allgem. Chem. 271, 206 (1953). Using the reported partial pressures for Cl_2(g), the enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of the reaction was evaluated as -27.49 ± 0.44 and -27.21 kcal. mole^{-1} by the second and third law methods, respectively. Based on the third law value for $\Delta H^\circ_{r\ 298.15}$, the value of $\Delta H^\circ_{f\ 298.15}$($FeCl_3$, c) was derived to be -95.36 ± 0.12 kcal. mole^{-1} which is in good agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (51-298.16°K.) heat capacities and high temperature (339.6-560.9°K.) heat content of $FeCl_3$(c) were determined by S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. 73, 4184 (1951). The low temperature C_p and the derived high temperature C_p were plotted. The two C_p curves were joined smoothly at 298°K. The C_p values above 560.9°K. were obtained by graphical extrapolation. The value of $S^\circ_{298.15}$ was derived from the low temperature data reported by S. S. Todd and J. P. Coughlin, loc. cit., using $S^\circ_{51} = 6.29$ cal. deg.$^{-1}$ mole^{-1}. The value of S°_{51} was selected to make the second and third law values of ΔH°_r, derived from the equilibrium data reported by H. Schäfer and E. Oehler, loc. cit., in good agreement. The difference in S°_{51} between the selected value, 6.29, and the reported value, 4.50 cal. deg.$^{-1}$ mole^{-1}, by S. S. Todd and J. P. Coughlin, loc. cit., is assumed to be the magnetic entropy remaining at 51°K. which was unaccounted for in the report.

Melting Data.

T_m and ΔH°_m were obtained from S. S. Todd and J. P. Coughlin, loc. cit.

Heat of Sublimation.

The difference between $\Delta H^\circ_{f\ 298.15}$ for Fe_2Cl_6(g) and 2$FeCl_3$(c) is the heat of sublimation at 298.15°K. The former is obtained by the second and third law analyses of related equilibrium data. See Fe_2Cl_6(g) table for details.

Iron Trichloride ($FeCl_3$)

(Liquid) Mol. Wt. = 162.206

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	32.000	47.955	47.955	.000	- 86.713	- 75.232	55.144
300	32.000	48.153	47.956	.059	- 86.687	- 75.161	54.752
400	32.000	57.359	49.211	3.259	- 85.358	- 71.522	39.076
500	32.000	64.499	51.581	6.459	- 84.113	- 68.207	29.812
600	32.000	70.334	54.235	9.659	- 82.946	- 65.138	23.725
700	32.000	75.266	56.896	12.859	- 81.852	- 62.257	19.437
800	32.000	79.539	59.465	16.059	- 80.849	- 59.529	16.262
900	32.000	83.309	61.909	19.259	- 79.960	- 56.918	13.821
1000	32.000	86.680	64.221	22.459	- 79.258	- 54.399	11.888
1100	32.000	89.730	66.403	25.659	- 78.779	- 51.931	10.317
1200	32.000	92.514	68.465	28.859	- 78.092	- 49.526	9.020
1300	32.000	95.076	70.415	32.059	- 77.068	- 47.188	7.933
1400	32.000	97.447	72.262	35.259	- 76.063	- 44.926	7.013
1500	32.000	99.655	74.015	38.459	- 75.075	- 42.738	6.227

June 30, 1965

IRON TRICHLORIDE ($FeCl_3$) (LIQUID) MOL. WT. = 162.206

$S^\circ_{298.15}$ = 47.955 cal. deg.$^{-1}$ mole^{-1}

T_m = 577°K.

T_b = 605°K.

$\Delta H^\circ_{f\ 298.15}$ = -86.713 kcal. mole^{-1}

ΔH°_m = 10.30 kcal. mole^{-1}

ΔH°_v(to dimer) = 10.46 kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}(FeCl_3,\ l)$ was obtained from $\Delta H^\circ_{f\ 298.15}(FeCl_3,\ c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for $FeCl_3(l)$ was taken from S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. 73, 4184 (1951) and assumed as constant between 298.15° and 1500°K. The entropy ($S^\circ_{298.15}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH°_m were reported by S. S. Todd and J. P. Coughlin, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change (ΔF°_r) of the reaction $2FeCl_3(l) = Fe_2Cl_6(g)$ approaches zero. The corresponding enthalpy change at T_b is the heat of vaporization (ΔH°_v).

Iron Trichloride ($FeCl_3$)

(Ideal Gas) Mol. Wt. = 162.206

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-4.353	-60.487	-60.487	INFINITE
100	13.511	64.295	97.744	-3.345	-60.633	-60.138	131.425
200	17.298	75.058	83.910	-1.770	-60.562	-59.666	65.197
298	18.572	82.243	82.243	.000	-60.500	-59.242	43.423
300	18.586	82.358	82.243	.034	-60.499	-59.234	43.150
400	19.117	87.787	82.980	1.923	-60.482	-58.817	32.134
500	19.379	92.084	84.386	3.849	-60.510	-58.397	25.524
600	19.526	95.632	85.973	5.795	-60.598	-57.968	21.114
700	19.616	98.649	87.574	7.752	-60.746	-57.519	17.957
800	19.675	101.272	89.126	9.717	-60.978	-57.044	15.583
900	19.716	103.592	90.607	11.687	-61.320	-56.532	13.727
1000	19.746	105.671	92.011	13.660	-61.845	-55.976	12.233
1100	19.767	107.554	93.340	15.636	-62.589	-55.348	10.996
1200	19.784	109.275	94.597	17.613	-63.125	-54.673	9.957
1300	19.797	110.859	95.788	19.592	-63.322	-53.960	9.071
1400	19.807	112.326	96.918	21.573	-63.536	-53.230	8.309
1500	19.816	113.693	97.991	23.554	-63.767	-52.487	7.647
1600	19.823	114.972	99.013	25.536	-64.016	-51.727	7.065
1700	19.828	116.174	99.987	27.518	-64.572	-50.943	6.549
1800	19.833	117.308	100.918	29.501	-64.947	-50.133	6.087
1900	19.837	118.380	101.809	31.485	-69.008	-49.111	5.649
2000	19.841	119.398	102.664	33.469	-69.453	-48.056	5.251
2100	19.844	120.366	103.484	35.453	-69.901	-46.974	4.888
2200	19.846	121.289	104.272	37.437	-70.358	-45.872	4.557
2300	19.848	122.171	105.031	39.422	-70.819	-44.748	4.252
2400	19.850	123.016	105.763	41.407	-71.288	-43.605	3.971
2500	19.852	123.827	106.470	43.392	-71.765	-42.442	3.710
2600	19.854	124.605	107.152	45.378	-72.247	-41.259	3.468
2700	19.855	125.355	107.813	47.363	-72.738	-40.061	3.243
2800	19.856	126.077	108.452	49.349	-73.236	-38.838	3.031
2900	19.857	126.773	109.072	51.334	-73.742	-37.601	2.834
3000	19.858	127.447	109.673	53.320	-74.257	-36.349	2.648
3100	19.859	128.098	110.257	55.306	-74.779	-35.074	2.473
3200	19.860	128.728	110.825	57.292	-158.735	-32.340	2.209
3300	19.861	129.339	111.376	59.278	-158.812	-28.389	1.880
3400	19.862	129.932	111.914	61.264	-158.899	-24.434	1.571
3500	19.862	130.508	112.437	63.250	-158.999	-20.483	1.279
3600	19.863	131.068	112.946	65.236	-159.112	-16.521	1.003
3700	19.863	131.612	113.444	67.223	-159.235	-12.558	.742
3800	19.864	132.142	113.929	69.209	-159.371	-8.598	.494
3900	19.864	132.658	114.402	71.195	-159.519	-4.623	.259
4000	19.865	133.161	114.865	73.182	-159.681	-.653	.036
4100	19.865	133.651	115.317	75.168	-159.852	3.328	-.177
4200	19.865	134.130	115.760	77.155	-160.037	7.306	-.380
4300	19.866	134.597	116.192	79.141	-160.233	11.296	-.574
4400	19.866	135.054	116.616	81.128	-160.441	15.288	-.759
4500	19.866	135.500	117.030	83.115	-160.662	19.282	-.936
4600	19.867	135.937	117.437	85.101	-160.892	23.285	-1.106
4700	19.867	136.364	117.835	87.088	-161.136	27.295	-1.269
4800	19.867	136.782	118.225	89.075	-161.390	31.306	-1.425
4900	19.867	137.192	118.608	91.061	-161.657	35.323	-1.575
5000	19.867	137.594	118.984	93.048	-161.933	39.339	-1.719
5100	19.868	137.987	119.353	95.035	-162.220	43.374	-1.859
5200	19.868	138.373	119.715	97.022	-162.519	47.407	-1.992
5300	19.868	138.751	120.070	99.008	-162.830	51.446	-2.121
5400	19.868	139.123	120.420	100.995	-163.152	55.489	-2.246
5500	19.868	139.487	120.763	102.982	-163.483	59.547	-2.366
5600	19.869	139.845	121.101	104.969	-163.826	63.601	-2.482
5700	19.869	140.197	121.433	106.956	-164.180	67.659	-2.594
5800	19.869	140.542	121.759	108.943	-164.544	71.742	-2.703
5900	19.869	140.882	122.080	110.930	-164.919	75.810	-2.808
6000	19.869	141.216	122.397	112.916	-165.304	79.898	-2.910

June 30, 1965

Cl_3Fe

IRON TRICHLORIDE ($FeCl_3$) (IDEAL GAS) MOL. WT. = 162.206

Point Group $[D_{3h}]$

$S^\circ_{298.15}$ = [82.243] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [6]

$\Delta H^\circ_{f\ 0}$ = -60.5 ± 1.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -60.5 ± 1.2 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[350] (1)
[160] (1)
[310] (2)
[130] (2)

Bond Distance: Fe-Cl = [2.17] Å

Bond Angle: Cl-Fe-Cl = [120]°

σ = [6]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.43769 x 10^{-112}] g.^{3} cm.^{6}

Heat of Formation.

The equilibrium pressures for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ were determined by Kangro and Bernstorff[1] and Schäfer[2], respectively. Using their vapor pressure data the corresponding values of $\Delta H^\circ_{r\ 298.15}$ for that reaction were evaluated by both the second and third law methods. Based on the third law values for $\Delta H^\circ_{r\ 298.15}$, the heats of formation ($\Delta H^\circ_{f\ 298.15}$) for $FeCl_3(g)$ were derived. The results obtained are presented as follows.

Investigator	Temperature, °K.	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H^\circ_{f\ 298.15}$, kcal. mole^{-1}
Kangro and Bernstorff[1]	760.2-1014.2	34.99 ± 0.44	35.73	-60.34 ± 0.30
Schäfer[2]	673.2-1073.2	34.81 ± 0.02	34.93	-60.74 ± 0.20

[1] W. Kangro and H. Bernstorff, Z. anorg. allgem. Chem. 263, 316 (1950).

[2] H. Schäfer, Z. anorg. allgem. Chem. 259, 53 (1949).

The adopted value of $\Delta H^\circ_{f\ 298.15}$($FeCl_3$ g) is -60.5 ± 1.2 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that of $AlCl_3(g)$ due to the similarities in structure between $Fe_2Cl_6(g)$ and $Al_2Cl_6(g)$. The Fe-Cl bond distance was estimated by comparison with those for $Fe_2Cl_6(g)$ reported by E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., 4, 910 (1963) and O. Hassel and H. Viervoll, Acta Chem. Scand. 1, 149 (1947). Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of $\Delta H^\circ_{r\ 298.15}$, derived from the vapor pressure data, for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ are in reasonable agreement. The three principal moments of inertia are: $I_A = I_B$ = 4.15794 x 10^{-38} and I_C = 8.31588 x 10^{-38} g. cm.^{2}

Cl_3Fe

Trichlorosilane ($HSiCl_3$)

(Ideal Gas) Mol. Wt. = 135.469 **INTERIM TABLE**

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.859	-110.800	-110.800	INFINITE
100	11.182	59.271	88.849	-2.958	-111.386	-109.230	238.711
200	15.113	68.274	76.456	-1.636	-111.730	-106.936	116.848
298	16.041	74.892	74.892	.000	-112.000	-104.524	76.614
300	16.086	75.004	74.892	.033	-112.005	-104.477	76.108
400	19.999	80.490	75.627	1.945	-112.193	-101.937	55.693
500	21.238	85.095	77.073	4.011	-112.306	-99.359	43.428
600	22.099	89.047	78.747	6.180	-112.363	-96.763	35.244
700	22.737	92.504	80.470	8.423	-112.380	-94.162	29.397
800	23.230	95.573	82.170	10.723	-112.363	-91.560	25.012
900	23.620	98.333	83.815	13.066	-112.326	-88.962	21.602
1000	23.934	100.838	85.394	15.444	-112.273	-86.367	18.875
1100	24.190	103.132	86.904	17.851	-112.208	-83.781	16.645
1200	24.401	105.246	88.346	20.281	-112.133	-81.199	14.788
1300	24.576	107.206	89.722	22.730	-112.053	-78.624	13.217
1400	24.722	109.033	91.037	25.195	-111.969	-76.058	11.873
1500	24.845	110.743	92.294	27.674	-111.883	-73.496	10.708
1600	24.950	112.350	93.498	30.163	-111.797	-70.938	9.689
1700	25.039	113.865	94.652	32.663	-123.814	-68.277	8.777
1800	25.116	115.299	95.759	35.171	-123.687	-65.018	7.894
1900	25.183	116.659	96.824	37.686	-123.559	-61.760	7.104
2000	25.241	117.952	97.848	40.207	-123.431	-58.510	6.393
2100	25.292	119.185	98.835	42.734	-123.306	-55.267	5.751
2200	25.337	120.362	99.787	45.265	-123.181	-52.031	5.169
2300	25.376	121.489	100.706	47.801	-123.057	-48.798	4.637
2400	25.411	122.570	101.595	50.341	-122.936	-45.574	4.150
2500	25.443	123.608	102.455	52.883	-122.818	-42.351	3.702
2600	25.471	124.607	103.288	55.429	-122.702	-39.137	3.290
2700	25.496	125.568	104.095	57.977	-122.589	-35.924	2.908
2800	25.518	126.496	104.879	60.528	-122.478	-32.717	2.554
2900	25.539	127.392	105.640	63.081	-122.369	-29.515	2.224
3000	25.557	128.258	106.379	65.636	-122.263	-26.315	1.917
3100	25.574	129.096	107.099	68.192	-122.160	-23.115	1.630
3200	25.590	129.908	107.799	70.751	-122.059	-19.920	1.360
3300	25.604	130.696	108.481	73.310	-121.963	-16.730	1.108
3400	25.617	131.461	109.146	75.871	-121.868	-13.543	.870
3500	25.629	132.203	109.794	78.434	-121.777	-10.361	.647
3600	25.640	132.926	110.426	80.997	-216.665	-6.708	.407
3700	25.650	133.628	111.044	83.561	-216.518	-.877	.052
3800	25.659	134.312	111.647	86.127	-216.376	4.950	-.285
3900	25.668	134.979	112.237	88.693	-216.237	10.769	-.603
4000	25.676	135.629	112.814	91.260	-216.102	16.590	-.906
4100	25.683	136.263	113.378	93.828	-215.969	22.405	-1.194
4200	25.690	136.882	113.930	96.397	-215.840	28.224	-1.469
4300	25.697	137.487	114.471	98.966	-215.716	34.024	-1.729
4400	25.703	138.077	115.001	101.536	-215.593	39.832	-1.978
4500	25.709	138.655	115.520	104.107	-215.475	45.632	-2.216
4600	25.714	139.220	116.029	106.678	-215.360	51.439	-2.444
4700	25.719	139.773	116.529	109.250	-215.247	57.239	-2.661
4800	25.724	140.315	117.019	111.822	-215.139	63.035	-2.870
4900	25.728	140.845	117.499	114.394	-215.032	68.829	-3.070
5000	25.732	141.365	117.972	116.967	-214.929	74.623	-3.262
5100	25.736	141.875	118.435	119.541	-214.831	80.410	-3.446
5200	25.740	142.374	118.891	122.115	-214.734	86.198	-3.623
5300	25.743	142.865	119.339	124.689	-214.642	91.989	-3.793
5400	25.746	143.346	119.779	127.263	-214.551	97.769	-3.957
5500	25.750	143.818	120.211	129.838	-214.464	103.557	-4.115
5600	25.753	144.282	120.637	132.413	-214.382	109.332	-4.267
5700	25.755	144.738	121.056	134.989	-214.303	115.119	-4.414
5800	25.758	145.186	121.468	137.564	-214.226	120.894	-4.555
5900	25.761	145.627	121.874	140.140	-214.152	126.676	-4.692
6000	25.763	146.060	122.273	142.716	-214.083	132.441	-4.824

December 31, 1960.

Trichlorosilane ($HSiCl_3$) (Ideal Gas)

Mol. Wt. = 135.469

ΔH_f° 298.15 = -119.6 kcal. mole⁻¹

$S^\circ_{298.15}$ = 74.924 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

, cm.⁻¹

2274 (1)	810 (2)
497 (1)	600 (2)
250 (1)	179 (2)

Si-H dist. = 1.48 all angles = [109° 28']

Si-Cl dist. = 2.02 = 3

Product of Moments of Inertia: $I_A I_B I_C = 75.642 \times 10^{-114}$ g.³ cm.⁶

Heat of Formation. ΔH_f° 298.15 was calculated from heats of reaction reported by E. Wolf, Z. Anorg. u. Allgem Chem. 313, 228 (1961) for the equation

$SiHCl_3(g) + 5NaOH(c) \rightleftarrows Na_2SiO_3(c) + 3NaCl(c) + 2H_2O(l)$

Heat Capacity and Entropy. Molecular constants were found in Janz and Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961). Vibrational frequencies can also be found in Henderson and Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1960.

Lithium Chloride, Trimeric ((LiC

(Ideal Gas) Mol. Wt. = 127.19 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.872	- 238.400	- 238.400	INFINITE
100	13.535	59.745	98.842	- 3.910	- 238.846	- 237.515	519.064
200	20.141	71.324	82.331	- 2.201	- 239.539	- 235.912	257.780
298	24.380	80.223	80.223	.000	- 240.134	- 234.000	171.519
300	24.441	80.374	80.223	.045	- 240.144	- 233.963	170.434
400	26.976	87.786	81.218	2.628	- 240.670	- 231.821	126.655
500	28.462	93.979	83.167	5.406	- 243.425	- 229.321	100.231
600	29.376	99.255	85.420	8.301	- 243.972	- 226.446	82.479
700	29.969	103.831	87.731	11.270	- 244.420	- 223.491	69.774
800	30.372	107.861	90.000	14.289	- 244.807	- 220.476	60.228
900	30.657	111.456	92.188	17.341	- 245.163	- 217.412	52.792
1000	30.065	114.697	94.279	20.418	- 245.497	- 214.311	46.835
1100	31.021	117.646	96.272	23.512	- 245.812	- 211.177	41.955
1200	31.142	120.351	98.167	26.621	- 246.117	- 208.017	37.883
1300	31.236	122.848	99.971	29.740	- 246.409	- 204.830	34.433
1400	31.312	125.165	101.689	32.867	- 246.693	- 201.619	31.473
1500	31.373	127.328	103.327	36.002	- 246.966	- 198.391	28.904
1600	31.424	129.354	104.891	39.141	- 247.232	- 195.142	26.654
1700	31.466	131.260	106.386	42.286	- 352.632	- 187.894	24.154
1800	31.501	133.060	107.819	45.434	- 352.341	- 178.209	21.636
1900	31.531	134.764	109.192	48.586	- 352.048	- 168.538	19.385
2000	31.556	136.382	110.512	51.740	- 351.760	- 158.891	17.362
2100	31.578	137.922	111.781	54.897	- 351.473	- 149.259	15.533
2200	31.598	139.392	113.003	58.056	- 351.191	- 139.634	13.871
2300	31.614	140.797	114.181	61.217	- 350.909	- 130.024	12.355
2400	31.629	142.142	115.318	64.379	- 350.637	- 120.427	10.966
2500	31.642	143.434	116.417	67.542	- 350.372	- 110.839	9.689
2600	31.654	144.675	117.480	70.707	- 350.112	- 101.265	8.512
2700	31.664	145.870	118.510	73.873	- 349.865	- 91.701	7.422
2800	31.673	147.022	119.507	77.040	- 349.628	- 82.140	6.411
2900	31.682	148.133	120.475	80.208	- 349.408	- 72.593	5.471
3000	31.689	149.207	121.415	83.376	- 349.197	- 63.050	4.593
3100	31.696	150.247	122.329	86.545	- 349.009	- 53.512	3.772
3200	31.702	151.253	123.217	89.715	- 348.833	- 43.986	3.004
3300	31.708	152.229	124.081	92.886	- 348.679	- 34.461	2.282
3400	31.713	153.175	124.923	96.057	- 348.542	- 24.936	1.603
3500	31.717	154.095	125.744	99.228	- 348.426	- 15.428	.963
3600	31.722	154.988	126.544	102.400	- 348.334	- 5.911	.359
3700	31.726	155.857	127.324	105.573	- 348.263	3.596	- .212
3800	31.729	156.704	128.086	108.746	- 348.217	13.112	- .754
3900	31.733	157.528	128.831	111.919	- 348.195	22.622	- 1.268
4000	31.736	158.331	129.558	115.092	- 348.202	32.126	- 1.755
4100	31.739	159.115	130.270	118.266	- 348.233	41.636	- 2.219
4200	31.741	159.880	130.965	121.440	- 348.296	51.140	- 2.661
4300	31.744	160.627	131.647	124.614	- 348.385	60.652	- 3.083
4400	31.746	161.356	132.314	127.788	- 348.503	70.176	- 3.485
4500	31.748	162.070	132.967	130.963	- 348.656	79.688	- 3.870
4600	31.751	162.768	133.607	134.138	- 348.840	89.208	- 4.238
4700	31.752	163.451	134.235	137.313	- 349.059	98.729	- 4.591
4800	31.754	164.119	134.851	140.489	- 349.316	108.254	- 4.929
4900	31.756	164.774	135.455	143.664	- 349.613	117.794	- 5.254
5000	31.758	165.415	136.047	146.840	- 349.946	127.340	- 5.566
5100	31.759	166.044	136.629	150.016	- 350.323	136.896	- 5.866
5200	31.760	166.661	137.201	153.192	- 350.747	146.453	- 6.155
5300	31.762	167.266	137.763	156.368	- 351.221	156.008	- 6.433
5400	31.763	167.860	138.315	159.544	- 351.742	165.585	- 6.701
5500	31.764	168.443	138.857	162.720	- 352.320	175.176	- 6.961
5600	31.765	169.015	139.390	165.897	- 352.952	184.760	- 7.210
5700	31.767	169.577	139.915	169.074	- 353.645	194.371	- 7.452
5800	31.768	170.130	140.431	172.250	- 354.403	203.999	- 7.687
5900	31.768	170.673	140.939	175.427	- 355.226	213.628	- 7.913
6000	31.769	171.207	141.439	178.604	- 356.119	223.284	- 8.133

June 30, 1962

Lithium Chloride, Trimeric $(LiCl)_3$ (Ideal Gas)

Mol. Wt. = 127.19
ΔH_f° 298.15 = -240.134 ± 5 kcal. mole^{-1}
$S^\circ_{298.15}$ = [80.223] cal. deg.$^{-1}$ mole^{-1}
Point Group = D_{3h}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	
[650]	(6)
[220]	(6)

Bond distances and angles Li-Cl distance = [2.2] Å
LiClLi angle [120°] Plane cyclic structure $\sigma = 6$

Moment of Inertia $I_AI_BI_C = 2.675 \times 10^{-112}$ g.^{3} cm.^{6}

Heat of Formation. The heat of sublimation at 298° was chosen so as to give the correct ratio of monomer, dimer and trimer at 870°K. The value used was 52.6 kcal. mole^{-1} which compares very well with the value 53.6 kcal. mole^{-1} obtained from a third law analysis of the data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) in conjunction with the relative concentrations of monomer, dimer, and trimer at 870°K from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1950).

Heat Capacity and Entropy. The postulated structure, bond lengths and frequencies were all taken from D. L. Hildenbrand, A. M. Saul P. R. Basford, S. E. Stephanon, L. Larson and A. Uyehara, Aeronutronic Tenth Quarterly Report on Contract NOrd 17980 Report C-898 (1960).

Phosphoryl Chloride ($POCl_3$)

(Ideal Gas) Mol. Wt. = 153.346

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.273	-128.714	-128.714	INFINITE
100	11.959	60.063	93.684	-3.362	-129.302	-126.304	276.024
200	17.430	70.215	79.544	-1.866	-129.545	-123.194	134.613
298	20.296	77.767	77.767	.000	-129.631	-120.055	87.998
300	20.335	77.893	77.768	.038	-129.631	-119.995	87.412
400	21.979	83.988	78.587	2.160	-129.642	-116.780	63.803
500	23.007	89.011	80.185	4.413	-129.605	-113.568	49.638
600	23.690	93.270	82.020	6.750	-129.550	-110.366	40.199
700	24.163	96.960	83.896	9.144	-129.495	-107.173	33.459
800	24.500	100.209	85.736	11.578	-149.872	-109.300	29.858
900	24.748	103.110	87.509	14.041	-149.587	-104.243	25.313
1000	24.935	105.720	89.202	16.526	-149.296	-99.222	21.684
1100	25.079	108.111	90.814	19.027	-149.001	-94.230	18.721
1200	25.191	110.298	92.348	21.541	-148.704	-89.264	16.256
1300	25.280	112.310	93.807	24.064	-148.406	-84.322	14.175
1400	25.353	114.195	95.197	26.596	-148.107	-79.403	12.395
1500	25.412	115.946	96.523	29.134	-147.810	-74.506	10.855
1600	25.461	117.587	97.789	31.678	-147.513	-69.629	9.510
1700	25.502	119.132	98.999	34.226	-147.218	-64.767	8.326
1800	25.537	120.591	100.159	36.778	-146.925	-59.928	7.276
1900	25.567	121.973	101.271	39.334	-146.634	-55.100	6.338
2000	25.592	123.285	102.339	41.892	-146.348	-50.293	5.495
2100	25.614	124.534	103.366	44.452	-146.063	-45.497	4.735
2200	25.633	125.726	104.356	47.014	-145.785	-40.714	4.044
2300	25.650	126.866	105.310	49.578	-145.508	-35.944	3.415
2400	25.665	127.958	106.231	52.144	-145.237	-31.187	2.840
2500	25.678	129.006	107.121	54.711	-144.971	-26.439	2.311
2600	25.689	130.013	107.982	57.280	-144.709	-21.704	1.824
2700	25.700	130.983	108.816	59.849	-144.453	-16.978	1.374
2800	25.709	131.917	109.625	62.420	-144.204	-12.259	.957
2900	25.717	132.820	110.409	64.991	-143.959	-7.552	.569
3000	25.725	133.692	111.171	67.563	-143.721	-2.854	.208
3100	25.732	134.535	111.911	70.136	-143.490	1.839	-.130
3200	25.738	135.352	112.631	72.709	-143.265	6.521	-.445
3300	25.744	136.144	113.331	75.284	-143.046	11.200	-.742
3400	25.749	136.913	114.014	77.858	-142.833	15.872	-1.020
3500	25.754	137.660	114.679	80.433	-142.626	20.533	-1.282
3600	25.758	138.385	115.327	83.009	-142.425	25.194	-1.529
3700	25.762	139.091	115.960	85.585	-142.230	29.848	-1.763
3800	25.766	139.778	116.578	88.161	-142.039	34.496	-1.984
3900	25.769	140.447	117.181	90.738	-141.855	39.141	-2.193
4000	25.773	141.100	117.771	93.315	-141.677	43.776	-2.392
4100	25.776	141.736	118.348	95.893	-141.501	48.410	-2.580
4200	25.778	142.357	118.912	98.470	-141.332	53.040	-2.760
4300	25.781	142.964	119.464	101.048	-141.166	57.664	-2.931
4400	25.783	143.557	120.005	103.626	-141.004	62.293	-3.094
4500	25.785	144.136	120.535	106.205	-140.846	66.907	-3.249
4600	25.788	144.703	121.054	108.784	-140.688	71.522	-3.398
4700	25.790	145.258	121.563	111.362	-140.536	76.136	-3.540
4800	25.791	145.801	122.063	113.942	-140.386	80.742	-3.676
4900	25.793	146.332	122.553	116.521	-140.238	85.351	-3.807
5000	25.795	146.853	123.033	119.100	-140.092	89.951	-3.932
5100	25.796	147.364	123.505	121.680	-139.947	94.555	-4.052
5200	25.798	147.865	123.969	124.259	-139.804	99.148	-4.167
5300	25.799	148.357	124.425	126.839	-139.663	103.742	-4.278
5400	25.800	148.839	124.872	129.419	-139.523	108.330	-4.384
5500	25.802	149.312	125.312	131.999	-139.383	112.926	-4.487
5600	25.803	149.777	125.745	134.580	-139.245	117.505	-4.586
5700	25.804	150.234	126.171	137.160	-139.109	122.086	-4.681
5800	25.805	150.683	126.590	139.740	-138.971	126.674	-4.773
5900	25.806	151.124	127.002	142.321	-138.836	131.247	-4.861
6000	25.807	151.558	127.407	144.901	-138.702	135.828	-4.947

June 30, 1962

PHOSPHORYL CHLORIDE ($POCl_3$) (IDEAL GAS) MOL. WT. = 153.346

$\Delta H_{f\,0}^\circ$ = -128.7 ± 0.4 kcal. mole^{-1}

$\Delta H_{f\,298.15}^\circ$ = -129.6 ± 0.4 kcal. mole^{-1}

Point Group C_{3v}

$S_{298.15}^\circ$ = 77.77 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1290 (1)	486 (1)	337 (1)
581 (2)	267 (2)	193 (2)

P-O distance = 1.45 ± 0.03 Å

P-Cl distance = 1.99 ± .02 Å

Cl-P-Cl angle = 103.6 ± 2°

I_A = 422.3 X 10^{-40} g. cm.^{2}

I_B = 419.2 X 10^{-40} g. cm.^{2}

I_C = 578.7 X 10^{-40} g. cm.^{2}

σ = 3

Heat of Formation.

The $\Delta H_{f\,298.15}^\circ$ for $POCl_3(g)$ was derived from the $\Delta H_{f\,298.15}^\circ$ of $POCl_3(l)$ and the $\Delta H_{v\,298.15}^\circ$. The $\Delta H_{f\,298.15}^\circ$ of the $POCl_3(l)$ was calculated from the heat of hydrolysis observed by T. Charnley and H. A. Skinner, J. Chem. Soc., 450, (1953) for the reaction:

$POCl_3(l) + (n + 3)H_2O(l) \rightarrow [H_3PO_4 + 3HCl]$ in n $H_2O(l)$

The auxiliary thermochemical data, on the heats of formation of water and aqueous solutions of HCl and of H_3PO_4, were taken from the National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Circular 500, and were adjusted for consistency with JANAF Tables. The heat of vaporization was measured and corrected to 298.15°K by J. B. Ott and W. F. Giauque, J. Am. Chem. Soc., 82, 1308 (1960). A correction was made for the change in phosphorus reference state [white (α) → red(V)].

Heat Capacity and Entropy.

The molecular constants are from the microwave spectral data of Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952). In order to determine the structure Williams et al. (loc. cit.) assumed the P-Cl distance equal to 1.99 Å. This was the smallest value allowed (2.02 ± 0.03 Å) by the electron diffraction work of L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 60, 1836 (1938).

Ott and Giauque (loc. cit.) have given the moments of inertia obtained from a weighted average of the isotopic species. $I_A \neq I_B$ due to isotopic loss of symmetry. The $S_{298.15}^\circ$ calculated from calorimetric data by Ott and Giauque (loc. cit.) was 77.75 cal. deg.$^{-1}$ mole^{-1} and the $S_{298.15}^\circ$, calculated from the spectral data was 77.77 cal. deg.$^{-1}$ mole^{-1}.

Phosphorus Trichloride (PCl_3)

(Ideal Gas) GFW = 137.3328

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.808	-64.455	-64.455	INFINITE
100	11.106	59.007	88.146	-2.914	-64.696	-63.675	139.161
200	15.045	68.027	75.976	-1.590	-64.779	-62.614	68.421
298	17.108	74.467	74.467	.000	-64.800	-61.545	45.114
300	17.135	74.573	74.467	.032	-64.800	-61.525	44.821
400	18.173	79.661	75.154	1.803	-64.807	-60.432	33.019
500	18.731	83.782	76.480	3.651	-64.809	-59.338	25.936
600	19.057	87.228	77.992	5.541	-64.823	-58.243	21.215
700	19.263	90.182	79.528	7.458	-64.856	-57.144	17.841
800	19.401	92.764	81.024	9.392	-85.335	-61.350	16.760
900	19.497	95.055	82.458	11.337	-85.161	-58.361	14.172
1000	19.566	97.113	83.823	13.290	-84.987	-55.395	12.106
1100	19.618	98.980	85.117	15.250	-84.814	-52.444	10.420
1200	19.658	100.689	86.345	17.214	-84.643	-49.509	9.017
1300	19.689	102.264	87.509	19.181	-84.473	-46.588	7.832
1400	19.714	103.724	88.616	21.151	-84.304	-43.679	6.819
1500	19.734	105.085	89.669	23.124	-84.136	-40.783	5.942
1600	19.751	106.359	90.673	25.098	-83.971	-37.899	5.177
1700	19.764	107.557	91.631	27.074	-83.807	-35.022	4.502
1800	19.776	108.687	92.548	29.051	-83.644	-32.159	3.905
1900	19.786	109.756	93.425	31.029	-83.483	-29.300	3.370
2000	19.794	110.771	94.268	33.008	-83.327	-26.455	2.891
2100	19.801	111.737	95.077	34.988	-83.169	-23.615	2.458
2200	19.807	112.659	95.855	36.968	-83.017	-20.783	2.065
2300	19.813	113.539	96.605	38.949	-82.865	-17.957	1.706
2400	19.818	114.383	97.328	40.931	-82.717	-15.138	1.379
2500	19.822	115.192	98.027	42.913	-82.572	-12.324	1.077
2600	19.826	115.969	98.702	44.895	-82.431	-9.518	.800
2700	19.829	116.718	99.355	46.878	-82.293	-6.717	.544
2800	19.832	117.439	99.988	48.861	-82.159	-3.918	.306
2900	19.835	118.135	100.602	50.844	-82.028	-1.128	.085
3000	19.837	118.807	101.198	52.828	-81.903	1.659	-.121
3100	19.839	119.458	101.776	54.811	-81.782	4.443	-.313
3200	19.841	120.088	102.339	56.795	-81.666	7.221	-.493
3300	19.843	120.698	102.886	58.780	-81.553	9.999	-.662
3400	19.845	121.291	103.419	60.764	-81.445	12.773	-.821
3500	19.846	121.866	103.938	62.749	-81.342	15.539	-.970
3600	19.848	122.425	104.443	64.733	-81.243	18.307	-1.111
3700	19.849	122.969	104.937	66.718	-81.148	21.071	-1.245
3800	19.850	123.498	105.418	68.703	-81.056	23.832	-1.371
3900	19.851	124.014	105.888	70.688	-80.969	26.594	-1.490
4000	19.852	124.516	106.348	72.673	-80.887	29.348	-1.603
4100	19.853	125.007	106.797	74.659	-80.806	32.102	-1.711
4200	19.854	125.485	107.236	76.644	-80.731	34.856	-1.814
4300	19.855	125.952	107.666	78.629	-80.657	37.603	-1.911
4400	19.856	126.409	108.087	80.615	-80.586	40.361	-2.005
4500	19.856	126.855	108.499	82.600	-80.519	43.104	-2.093
4600	19.857	127.291	108.903	84.586	-80.451	45.848	-2.178
4700	19.858	127.718	109.299	86.572	-80.387	48.597	-2.260
4800	19.858	128.136	109.687	88.558	-80.325	51.338	-2.337
4900	19.859	128.546	110.068	90.543	-80.264	54.086	-2.412
5000	19.859	128.947	110.441	92.529	-80.203	56.825	-2.484
5100	19.860	129.340	110.808	94.515	-80.144	59.567	-2.553
5200	19.860	129.726	111.168	96.501	-80.085	62.305	-2.619
5300	19.861	130.104	111.522	98.487	-80.028	65.040	-2.682
5400	19.861	130.475	111.869	100.473	-79.972	67.776	-2.743
5500	19.861	130.840	112.211	102.460	-79.915	70.516	-2.802
5600	19.862	131.198	112.547	104.446	-79.859	73.246	-2.859
5700	19.862	131.549	112.877	106.432	-79.805	75.977	-2.913
5800	19.862	131.895	113.202	108.418	-79.749	78.714	-2.966
5900	19.863	132.234	113.522	110.404	-79.695	81.441	-3.017
6000	19.863	132.568	113.836	112.391	-79.642	84.176	-3.066

Dec. 31, 1960; Sept. 30, 1962, June 30, 1970

PHOSPHORUS TRICHLORIDE (PCl_3) (IDEAL GAS) GFW = 137.3328

Point Group C_{3v}

$\Delta Hf^\circ_0 = -64.5 \pm 1.3$ kcal/mol

$S^\circ_{298.15} = 74.47 \pm 0.10$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -64.8 \pm 1.3$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
510 (1)	507 (2)
259 (1)	187 (2)

Bond Distance: P-Cl = 2.039 ± 0.0014 Å

Bond Angle: Cl-P-Cl = 100.27 ± 0.09°

$\sigma = 3$

Product of Moments of Inertia: $I_A I_B I_C = 6.0517 \times 10^{-113}$ g^3 cm^6.

Heat of Formation

Neale and Williams (1) measured the heat of hydrolysis of liquid phosphorus trichloride and reported a $\Delta H_r = -67.5 \pm 0.3$ kcal/mol for the following reaction:

$$PCl_3(\ell) + (X_2 + 3)\ H_2O \rightarrow H_3PO_3(aq) + 3\ HCl(aq)$$

with X_2 in range 4500 to 7500. Combining this result with heat of formation data for aqueous H_3PO_3, -229.4 kcal/mol (2, 5, 16), H_2O (2), and aqueous HCl (2), we derive $\Delta Hf^\circ(PCl_3, \ell) = -76.7$ kcal/mol. Charnley and Skinner (3) made an independent investigation of the hydrolysis of liquid phosphorus trichloride and obtained enthalpy data in very good agreement with Neale and Williams' results. Their results lead to $\Delta Hf(PCl_3, \ell) = -76.5$ kcal/mol when combined with heat of formation data (2, 5, 16).

Neale and Williams (4) also investigated the hydrolysis of liquid phosphorus trichloride in aqueous bromine solution with the formation of phosphoric acid rather than phosphorus acid which results when hydrolysis occurs in water. They reported a $\Delta H_r = -137.9$ kcal/mol for the following reaction:

$$PCl_3(\ell) + Br_2(aq) + (X_2 + 4)H_2O \rightarrow H_3PO_4(aq) + 3HCl(aq) + 2\ HBr(aq)$$

with X_2 in range 3500 to 6300. Combining this result with the following heat of formation data:

$\Delta Hf^\circ(H_3PO_4 \cdot 1\ H_2O) = -306.4 \pm 0.5$ kcal/mol (5)

$\Delta Hf^\circ(Br_2(aq)) = -0.2$ kcal/mol (6)

HCl(aq) and HBr(aq) (2)

along with dilution data for $H_3PO_4(aq)$ (2), we derive $\Delta Hf^\circ_{298}(PCl_3, \ell) = -77.0$ kcal/mol

The heat of formation from white phosphorus of gaseous PCl_3, $\Delta Hf^\circ(PCl_3, g) = -69.0 \pm 1.1$ kcal/mol, is calculated from the heat of formation of the liquid, $\Delta Hf(PCl_3, \ell) = -76.7 \pm 1.0$ kcal/mol, an average value of the three results given above, and the heat of vaporization of PCl_3. The heat of vaporization of the liquid, $\Delta Hv_{298} = 7.7 \pm 0.1$ kcal/mol, is determined from a second law analysis of the combined vapor pressure data of Nisel'son and Seryakov (7) and Regnault (8). The smoothed vapor pressure data of Regnault as reported by Stull (9) were used. Converting to the P(red, V) standard state with a $\Delta H_{trans} = 4.2 \pm 0.2$ kcal/mol (10), we derive $\Delta Hf^\circ_{298}(PCl_3, g) = -64.8 \pm 1.3$ kcal/mol.

An independent value for the heat of formation can be obtained from the work of Duus and Mykytiuk (17) on the reaction $1.5CaF_2 + PCl_3(g) \rightarrow 1.5CaCl_2 + PF_3(g)$. The authors report $\Delta H_{630} = -2.97$ kcal. From a reexamination of their technique we believe that this heat evolution is likely to be too small, perhaps by 100%. The analytical results indicate that the reaction is 99% complete or better; thus, we can use this with JANAF entropies to calculate $\Delta Hr_{298} \leq -3.55$ kcal. Finch et al. (18) have reported $\Delta Hf^\circ(CaF_2, c) - \Delta Hf^\circ(CaCl_2, c) = -100.87 \pm 0.02$ kcal/mol; thus, we obtain $\Delta Hf^\circ_{298}(PCl_3, g) \geq -70.1 \pm 2.0$ kcal/mol from $\Delta Hf^\circ_{298}(PF_3, g) = -224.9 \pm 0.9$ kcal/mol. This value is not adopted because of the lack of calorimeter calibration, but it offers an attractive possibility for further study.

Heat Capacity and Entropy

The molecular structure and bond length given above for PCl_3 are from the electron diffraction studies of Hedberg and Iwasahi (11). The adopted values are in good agreement within experimental error with the following structural data reported by Kisliuk and Townes (12) from microwave studies: $r_{P-Cl} = 2.043 \pm 0.003$ Å, the angle Cl-P-Cl = 100°6' ± 20'. The vibrational frequencies are from the recent infrared and Raman studies of Frankiss and Miller (13) and are in excellent agreement with those of Müller et. al (14) and Davis and Oetjen (15). Individual moments of inertia calculated from the electron diffraction data are: $I_A = I_B = 32.393 \times 10^{-39}$ g cm^3, and $I_C = 57.673 \times 10^{-39}$ g cm^2.

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Thiophosphoryl Chloride ($PSCl_3$)
(Ideal Gas) Mol. Wt. = 169.412 **INTERIM TABLE**

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-4.541	-86.135	-86.135	INFINITE
100	12.977	61.673	97.545	-3.587	-86.488	-85.431	186.700
200	16.573	72.586	82.488	-1.980	-86.673	-84.295	92.109
298	21.474	80.604	80.604	.000	-86.800	-83.100	60.911
300	21.513	80.737	80.604	.040	-86.802	-83.076	60.518
400	23.069	87.161	81.470	2.277	-87.442	-81.798	44.690
500	23.943	92.412	83.149	4.631	-87.876	-80.335	35.113
600	24.469	96.827	85.071	7.054	-88.215	-78.794	28.699
700	24.807	100.626	87.028	9.519	-88.500	-77.178	24.095
800	25.036	103.955	88.940	12.012	-122.244	-82.122	22.434
900	25.196	106.913	90.776	14.524	-121.941	-77.123	18.727
1000	25.313	109.574	92.525	17.050	-121.636	-72.161	15.770
1100	25.401	111.991	94.186	19.585	-121.330	-67.230	13.357
1200	25.469	114.205	95.764	22.129	-121.023	-62.325	11.350
1300	25.522	116.245	97.262	24.679	-120.715	-57.444	9.657
1400	25.564	118.138	98.686	27.233	-120.409	-52.588	8.209
1500	25.596	119.903	100.042	29.791	-120.104	-47.756	6.958
1600	25.627	121.556	101.336	32.353	-119.799	-42.942	5.865
1700	25.650	123.111	102.571	34.916	-119.496	-38.145	4.904
1800	25.670	124.577	103.754	37.482	-119.195	-33.371	4.052
1900	25.686	125.966	104.887	40.050	-118.894	-28.607	3.290
2000	25.701	127.284	105.974	42.620	-118.598	-23.866	2.608
2100	25.713	128.538	107.019	45.190	-118.302	-19.138	1.992
2200	25.724	129.734	108.024	47.762	-118.010	-14.421	1.433
2300	25.733	130.878	108.993	50.335	-117.719	-9.719	.923
2400	25.741	131.973	109.928	52.909	-117.432	-5.030	.458
2500	25.749	133.024	110.831	55.483	-117.148	-.351	.031
2600	25.755	134.034	111.704	58.058	-116.867	4.315	-.363
2700	25.761	135.006	112.549	60.634	-116.590	8.968	-.726
2800	25.766	135.943	113.368	63.211	-116.318	13.615	-1.063
2900	25.771	136.848	114.162	65.787	-116.049	18.250	-1.375
3000	25.775	137.721	114.933	68.365	-115.786	22.877	-1.666
3100	25.776	138.566	115.682	70.942	-115.526	27.495	-1.938
3200	25.782	139.385	116.410	73.520	-115.273	32.102	-2.192
3300	25.785	140.178	117.118	76.099	-115.022	36.705	-2.431
3400	25.788	140.948	117.808	78.677	-114.777	41.302	-2.655
3500	25.791	141.696	118.480	81.256	-114.537	45.883	-2.865
3600	25.793	142.422	119.135	83.836	-114.300	50.465	-3.064
3700	25.795	143.129	119.774	86.415	-114.070	55.040	-3.251
3800	25.797	143.817	120.397	88.995	-113.841	59.606	-3.428
3900	25.799	144.487	121.006	91.574	-113.619	64.170	-3.596
4000	25.801	145.140	121.602	94.154	-113.401	68.726	-3.755
4100	25.802	145.777	122.184	96.735	-113.184	73.274	-3.906
4200	25.804	146.399	122.753	99.315	-112.974	77.821	-4.049
4300	25.805	147.006	123.310	101.895	-112.765	82.356	-4.186
4400	25.807	147.600	123.855	104.476	-112.560	86.900	-4.316
4500	25.808	148.180	124.389	107.057	-112.359	91.428	-4.440
4600	25.809	148.747	124.913	109.637	-112.157	95.951	-4.558
4700	25.810	149.302	125.426	112.218	-111.958	100.475	-4.672
4800	25.811	149.845	125.929	114.800	-111.763	104.989	-4.780
4900	25.812	150.378	126.422	117.381	-111.568	109.512	-4.884
5000	25.813	150.899	126.907	119.962	-111.376	114.017	-4.983
5100	25.814	151.410	127.382	122.543	-111.184	118.527	-5.079
5200	25.815	151.911	127.849	125.125	-110.992	123.029	-5.171
5300	25.815	152.403	128.308	127.706	-110.803	127.524	-5.258
5400	25.816	152.886	128.758	130.288	-110.615	132.019	-5.343
5500	25.817	153.359	129.201	132.869	-110.427	136.515	-5.424
5600	25.817	153.825	129.637	135.451	-110.241	141.000	-5.502
5700	25.818	154.282	130.065	138.033	-110.056	145.480	-5.578
5800	25.818	154.731	130.487	140.615	-109.870	149.967	-5.651
5900	25.819	155.172	130.901	143.196	-109.685	154.438	-5.720
6000	25.820	155.606	131.309	145.778	-109.502	158.921	-5.788

Dec. 31, 1960; Sept. 30, 1962

Thiophosphoryl Chloride ($PSCl_3$) (Ideal Gas)

Mol. Wt. = 169.412

ΔH_f° 298.15 = [-86.8] kcal. mole^{-1}

$S^\circ_{298.15}$ = 80.60 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
169 (2)	[247] (2)	247 (1)
431 (1)	540 (2)	751 (1)

Bond distance P-S = 1.85 ± 0.02 Å P-Cl = 2.02 ± 0.01 Å σ = 3

Cl-P-Cl angle = 100.5° ± 1° $I_AI_BI_C$ = 2.0690 X 10^{-112} g.^{3} cm.^{6}

Heat of Formation. ΔH_f° 298 was estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corporation, Alexandria, Virginia, "Survey of Thermochemical Data," January 1960. Henderson and Scheffee (loc. cit.) use white(α) phosphorus as a reference state. Their estimated ΔH_f° 298 was adjusted to the Red (V) phosphorus reference state [see white(α) phosphorus sheet.]

Heat Capacity and Entropy. J. S. Ziomek and E. A. Piotrowski, J. Chem. Phys. 34, 1087 (1961) have chosen the most probable values for the wave numbers from the infrared spectral data of G. Cilento, D. A. Ramsey, and R. N. Jones, J. Am. Chem. Soc. 71, 2753 (1949), and the Raman spectral data of A. Simon and G. Schulze, Naturwissenschaften 25, 669 (1937); V. N. Thatte, Nature 138, 468 (1936); H. Gerding and R. Westrick, Rec. trav. chim. 61, 842 (1942); and M. Delwaulle and F. Francois, Compt. Rend. 220, 817 (1945). Ziomek and Piotrowski (loc. cit.) found their normal coordinate treatments gave the listed wave numbers as fundamentals and lent support for the 247 cm.$^{-1}$ band missing from the Raman spectral data. The structure (bond distances and angles) was determined from microwave data by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys. 20, 164 (1952).

Silicon Trichloride ($SiCl_3$)

(Ideal Gas) GFW = 134.445

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.807	-95.747	-95.747	INFINITE
100	11.322	60.745	89.740	-2.900	-95.948	-95.158	207.967
200	14.916	69.794	77.660	-1.573	-95.991	-94.346	103.096
298	16.931	76.168	76.168	.000	-96.000	-93.536	68.564
300	16.958	76.272	76.168	.031	-96.000	-93.521	68.130
400	18.030	81.314	76.848	1.786	-95.997	-92.695	50.646
500	18.623	85.407	78.163	3.622	-95.985	-91.869	40.156
600	18.975	88.836	79.664	5.503	-95.976	-91.048	33.164
700	19.200	91.779	81.190	7.413	-95.968	-90.227	28.170
800	19.350	94.353	82.678	9.341	-95.969	-89.409	24.425
900	19.456	96.639	84.104	11.281	-95.975	-88.586	21.512
1000	19.533	98.693	85.462	13.231	-95.991	-87.766	19.181
1100	19.590	100.557	86.751	15.187	-96.015	-86.943	17.274
1200	19.634	102.264	87.974	17.148	-96.049	-86.117	15.684
1300	19.669	103.837	89.134	19.114	-96.091	-85.288	14.338
1400	19.696	105.296	90.237	21.082	-96.144	-84.454	13.184
1500	19.719	106.655	91.287	23.053	-96.207	-83.617	12.183
1600	19.737	107.928	92.288	25.025	-96.282	-82.775	11.307
1700	19.752	109.126	93.243	27.000	-108.359	-81.821	10.519
1800	19.765	110.255	94.157	28.976	-108.399	-80.259	9.745
1900	19.776	111.324	95.033	30.953	-108.440	-78.693	9.052
2000	19.785	112.338	95.873	32.931	-108.485	-77.126	8.428
2100	19.793	113.304	96.680	34.910	-108.528	-75.559	7.864
2200	19.800	114.225	97.457	36.890	-108.575	-73.989	7.350
2300	19.806	115.105	98.205	38.870	-108.624	-72.414	6.881
2400	19.811	115.948	98.927	40.851	-108.674	-70.837	6.451
2500	19.816	116.757	99.624	42.832	-108.729	-69.261	6.055
2600	19.820	117.534	100.298	44.814	-108.785	-67.681	5.689
2700	19.824	118.282	100.950	46.796	-108.844	-66.100	5.350
2800	19.827	119.003	101.582	48.779	-108.908	-64.513	5.035
2900	19.830	119.699	102.195	50.762	-108.975	-62.928	4.742
3000	19.833	120.372	102.790	52.745	-109.046	-61.341	4.469
3100	19.835	121.022	103.368	54.728	-109.121	-59.750	4.212
3200	19.838	121.652	103.929	56.712	-109.200	-58.154	3.972
3300	19.840	122.262	104.476	58.696	-109.284	-56.557	3.746
3400	19.842	122.855	105.007	60.680	-109.370	-54.956	3.533
3500	19.843	123.430	105.526	62.664	-109.462	-53.360	3.332
3600	19.845	123.989	106.031	64.648	-201.519	-49.495	3.005
3700	19.846	124.532	106.523	66.633	-201.519	-45.271	2.674
3800	19.848	125.062	107.004	68.618	-201.522	-41.051	2.361
3900	19.849	125.577	107.474	70.603	-201.531	-36.827	2.064
4000	19.850	126.080	107.933	72.587	-201.544	-32.603	1.781
4100	19.851	126.570	108.382	74.573	-201.559	-28.384	1.513
4200	19.852	127.048	108.820	76.558	-201.578	-24.161	1.257
4300	19.853	127.516	109.250	78.543	-201.599	-19.936	1.013
4400	19.854	127.972	109.670	80.528	-201.623	-15.707	.780
4500	19.854	128.418	110.082	82.514	-201.649	-11.481	.558
4600	19.855	128.855	110.485	84.499	-201.675	-7.256	.345
4700	19.856	129.282	110.880	86.485	-201.705	-3.026	.141
4800	19.857	129.700	111.268	88.470	-201.735	1.197	-.054
4900	19.857	130.109	111.649	90.456	-201.767	5.430	-.242
5000	19.858	130.510	112.022	92.442	-201.799	9.653	-.422
5100	19.858	130.903	112.388	94.428	-201.830	13.890	-.595
5200	19.859	131.289	112.748	96.413	-201.864	18.120	-.762
5300	19.859	131.667	113.101	98.399	-201.897	22.347	-.921
5400	19.860	132.039	113.449	100.385	-201.932	26.577	-1.076
5500	19.860	132.403	113.790	102.371	-201.966	30.811	-1.224
5600	19.861	132.761	114.126	104.357	-202.001	35.043	-1.368
5700	19.861	133.112	114.456	106.343	-202.037	39.274	-1.506
5800	19.861	133.458	114.780	108.329	-202.072	43.513	-1.640
5900	19.862	133.797	115.100	110.316	-202.109	47.740	-1.768
6000	19.862	134.131	115.414	112.302	-202.146	51.978	-1.893

Dec. 31, 1969

SILICON TRICHLORIDE ($SiCl_3$) (IDEAL GAS) GFW = 134.445

Point Group C_{3v} $\Delta Hf^\circ_0 = -95.7 \pm 10$ kcal/mol

$S^\circ_{298.15} = 76.17 \pm 1.5$ gibbs/mol $\Delta Hf^\circ_{298.15} = -96 \pm 10$ kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
470 (1)	582 (2)
[240] (1)	[175] (2)

Bond Distance: Si-Cl = [2.02] Å

Bond Angle: Cl-Si-Cl = 110.9° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = [7.5469 \times 10^{-113}]\ g^3\ cm^6$

Heat of Formation

The adopted value is derived from an average bond energy of ΔH°_0atom/3 = 96 ± 3 kcal/mol. This value is estimated by comparison of average bond energies for MX_n where M = C or Si, X = F or Cl, and n = 2, 3 or 4. These comparisons suggest that the average bond energy for $SiCl_3$ should be bracketed by those for $SiCl_4$ and $SiCl_2$, i.e. 94.3 and 101.5 kcal/mol, respectively. Alternative estimates from linear plots of $\Delta Hf^\circ(SiCl_n)$ versus ΔHf° for SiF_n, CCl_n, and CF_n yield -98, -96, and -86 kcal/mol for ΔHf° of $SiCl_3$ at 298.15°K. These agree with the adopted value of -96 ± 10 kcal/mol, which corresponds to ΔH°_0atom = 288 ± 10 kcal/mol.

Kerr et al. (1) reported relative rates for several reactions of $SiCl_3$, but the authors state that no absolute activation energies are known for reactions of this radical. This precludes derivation of thermochemical values from the kinetic studies. Recently, however, Vurzel et al. (4) reported studies of the decomposition of $SiCl_4$ by adiabatic compression. Rate constants, as reported in Chemical Abstracts, led to an activation energy of 88 ± 5 kcal/mol for $SiCl_4 \rightarrow SiCl_3 + Cl$. The activation energy for recombination should be very close to zero, so ΔHr = 88 ± 5 compared with the adopted result of 86 ± 10 at room temperature. Steele et al. (2) derived an average value of $D(Cl_3Si\text{-}H) = 93 \pm 4$ kcal/mol from an interpretation of electron impact studies on several molecules. Using $\Delta Hf^\circ(Cl_3SiH, g) = -122.6$ kcal/mol (3), we calculate $\Delta Hf^\circ(SiCl_3) = -82$ kcal/mol and estimate the uncertainty as about 10 kcal/mol.

Heat Capacity and Entropy

Jacox and Milligan (5) studied the formation of $SiCl_3$ by photolysis of $HSiCl_3$ trapped in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of 72 ± 5° between the threefold axis and each of the Si-Cl bonds. This yields a bond angle of 110.9° which is similar to that of $HSiCl_3$. Non-planarity of $SiCl_3$ is consistent with the electron-spin-resonance studies of Roncin (6).

We adopt the results of Jacox (5) and estimate the bond length and two bending vibrations by analogy with $HSiCl_3$. Similar analogies are reliable for SiF_3 and CF_3. The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacox (5) observed unstructured absorptions corresponding to excitation energies of 30000-34500 cm^{-1} and 41000-46000 cm^{-1}. Principal moments of inertia are $I_A = 65.18 \times 10^{-39}$ and $I_B = I_C = 34.03 \times 10^{-39}\ g\ cm^2$.

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Titanium Trichloride ($TiCl_3$)

(Crystal) GFW = 154.259

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 5.000	- 173.057	- 173.057	INFINITE
100	13.011	10.600	54.440	- 4.384	- 173.619	- 167.710	366.529
200	24.361	22.626	35.636	- 2.562	- 173.344	- 161.849	176.860
298	23.222	33.401	33.401	.000	- 172.500	- 156.442	114.675
300	23.230	33.545	33.401	.043	- 172.491	- 156.343	113.896
400	23.652	40.286	34.318	2.387	- 172.009	- 151.034	82.521
500	24.038	45.606	36.062	4.772	- 171.550	- 145.843	63.748
600	24.390	50.020	38.031	7.194	- 171.098	- 140.744	51.266
700	24.677	53.602	40.020	9.647	- 170.647	- 135.722	42.374
800	24.958	57.115	41.954	12.129	- 170.204	- 130.763	35.723
900	25.235	60.071	43.806	14.639	- 169.766	- 125.858	30.563
1000	25.503	62.744	45.568	17.176	- 169.334	- 121.005	26.446
1100	25.769	65.187	47.242	19.739	- 168.905	- 116.191	23.085
1200	26.034	67.440	48.833	22.329	- 169.417	- 111.381	20.285
1300	26.297	69.535	50.345	24.946	- 168.867	- 106.567	17.916
1400	26.559	71.493	51.787	27.589	- 168.309	- 101.796	15.891
1500	26.820	73.334	53.162	30.258	- 167.744	- 97.065	14.142

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968

TITANIUM TRICHLORIDE ($TiCl_3$) (CRYSTAL) GFW = 154.259

ΔHf°_0 = -173.1 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 33.4 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -172.5 ± 1.0 kcal/mol

Tt = 220.1°K

ΔHt° = 0 kcal/mol

Ts = [1104.1]°K

ΔHs° = [39.71] kcal/mol

Heat of Formation

The heat of formation, ΔHf°_{298}, of $TiCl_3(c)$ has been measured by several investigators. The results of these measurements are as follows.

Investigators	Method	ΔHf°_{298} kcal/mol
Schaffer et al. (1954) (1)	Calorimetric, $TiCl_4 + Hg = TiCl_3 + 1/2Hg_2Cl_2$	-171.9, -172.4
Clifton and MacWood (1956) (2)	Solution calorimetric	-172.4
Johnson et al. (1956) (3)	Calorimetric, $TiCl_4(l) + HI(g) = TiCl_3(c) + HCl(g) + 1/2I_2$	-172.5
Krieve et al. (1956) (4)	Solution calorimetric	-171.3
Krieve and Mason (1956) (5)	Equilibrium, $TiCl_3(c) + HCl(g) = TiCl_4(g) + 1/2H_2(g)$	-172.9
Altman et al. (1956) (6)	Equilibrium, $Ti(c) + 3TiCl_4(l) = 4TiCl_3(c)$	-169.4, -171.0
Head (1960) (7)	Equilibrium, $2TiCl_4(2) + H_2(g) = 2TiCl_3(c) + 2HCl(g)$ $TiCl_4(l) + Hg(l) = 1/2Hg_2Cl_2(c) + TiCl_3(c)$ $TiCl_4(l) + Ag(c) = AgCl(c) + TiCl_3(c)$	-172.3

The chosen value of -172.5 ± 1.0 kcal/mol is that reported by Johnson et al. (3).

Heat Capacity and Entropy

The heat capacity and entropy of $TiCl_3(c)$ has been measured over the temperature range 54° to 1000°K by King et al. (8). The value of S°_{298} is calculated from these data based on S°_{51} = 4.29 eu.

Transition Data

A second order transition at 220.1°K was observed by King et al. (8). The heat capacity at this temperature is in excess of 146.8 gibbs/mol. King et al. measured the value of $H^\circ_{240} - H^\circ_{200}$ as 1.213 kcal/mol.

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of $TiCl_3(c)$ and $TiCl_3(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which ΔGr = 0 for the process $TiCl_3(c) = TiCl_3(g)$.

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Titanium Trichloride ($TiCl_3$)

(Ideal Gas) GFW = 154.259

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.675	-128.132	-128.132	INFINITE
100	10.094	60.859	89.124	-2.827	-128.462	-127.578	278.821
200	14.601	69.305	77.214	-1.582	-128.764	-126.564	138.303
298	17.344	75.703	75.703	.000	-128.900	-125.455	91.961
300	17.380	75.811	75.704	.032	-128.901	-125.433	91.378
400	18.796	81.027	76.405	1.849	-128.948	-124.269	67.897
500	19.531	85.309	77.771	3.769	-128.953	-123.097	53.806
600	19.924	88.908	79.335	5.744	-128.948	-121.927	44.412
700	20.139	91.997	80.929	7.748	-128.947	-120.758	37.702
800	20.261	94.695	82.485	9.769	-128.965	-119.588	32.670
900	20.333	97.086	83.977	11.799	-129.006	-118.412	28.754
1000	20.377	99.231	85.397	13.834	-129.075	-117.234	25.621
1100	20.406	101.175	86.744	15.873	-129.171	-116.044	23.056
1200	20.424	102.951	88.022	17.915	-130.231	-114.808	20.909
1300	20.437	104.586	89.234	19.958	-130.255	-113.522	19.085
1400	20.445	106.101	90.385	22.002	-130.296	-112.234	17.520
1500	20.450	107.512	91.481	24.047	-130.355	-110.942	16.164
1600	20.452	108.832	92.524	26.092	-130.435	-109.644	14.977
1700	20.453	110.072	93.520	28.137	-130.536	-108.340	13.928
1800	20.452	111.241	94.473	30.183	-130.662	-107.033	12.996
1900	20.450	112.346	95.384	32.228	-130.812	-105.714	12.160
2000	20.448	113.395	96.259	34.273	-135.438	-104.236	11.390
2100	20.445	114.393	97.099	36.317	-135.616	-102.672	10.685
2200	20.443	115.344	97.907	38.362	-135.798	-101.100	10.043
2300	20.440	116.253	98.685	40.406	-135.983	-99.517	9.456
2400	20.437	117.122	99.435	42.450	-136.170	-97.926	8.917
2500	20.434	117.957	100.159	44.493	-136.363	-96.330	8.421
2600	20.431	118.758	100.859	46.536	-136.557	-94.725	7.962
2700	20.429	119.529	101.537	48.579	-136.756	-93.112	7.537
2800	20.426	120.272	102.193	50.622	-136.960	-91.491	7.141
2900	20.423	120.989	102.829	52.665	-137.167	-89.863	6.772
3000	20.421	121.681	103.445	54.707	-137.379	-88.230	6.428
3100	20.418	122.351	104.045	56.749	-137.595	-86.587	6.104
3200	20.416	122.999	104.627	58.790	-137.817	-84.941	5.801
3300	20.413	123.627	105.193	60.832	-138.043	-83.282	5.516
3400	20.410	124.236	105.744	62.873	-138.272	-81.617	5.246
3500	20.407	124.828	106.281	64.914	-138.508	-79.952	4.992
3600	20.404	125.403	106.804	66.954	-240.373	-78.010	4.736
3700	20.401	125.962	107.315	68.995	-240.588	-73.497	4.341
3800	20.398	126.506	107.812	71.035	-240.820	-68.984	3.967
3900	20.395	127.036	108.299	73.074	-241.070	-64.453	3.612
4000	20.392	127.552	108.774	75.114	-241.338	-59.922	3.274
4100	20.388	128.055	109.238	77.153	-241.620	-55.384	2.952
4200	20.384	128.547	109.692	79.191	-241.920	-50.841	2.646
4300	20.381	129.026	110.136	81.230	-242.233	-46.290	2.353
4400	20.377	129.495	110.570	83.267	-242.561	-41.724	2.078
4500	20.373	129.953	110.996	85.305	-242.903	-37.159	1.805
4600	20.369	130.400	111.413	87.342	-243.255	-32.579	1.548
4700	20.365	130.838	111.822	89.379	-243.621	-27.994	1.302
4800	20.360	131.267	112.222	91.415	-243.999	-23.406	1.066
4900	20.356	131.687	112.615	93.451	-244.387	-18.805	.839
5000	20.351	132.098	113.001	95.486	-244.784	-14.197	.621
5100	20.347	132.501	113.379	97.521	-245.190	-9.578	.410
5200	20.342	132.896	113.751	99.555	-245.606	-4.953	.208
5300	20.338	133.284	114.116	101.589	-246.030	-.328	.014
5400	20.333	133.664	114.474	103.623	-246.462	4.316	-.175
5500	20.329	134.037	114.827	105.656	-246.899	8.968	-.356
5600	20.324	134.403	115.173	107.689	-247.344	13.616	-.531
5700	20.319	134.763	115.513	109.721	-247.795	18.280	-.701
5800	20.314	135.118	115.848	111.752	-248.251	22.957	-.865
5900	20.310	135.463	116.178	113.784	-248.713	27.633	-1.024
6000	20.305	135.805	116.502	115.814	-249.179	32.320	-1.177

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

TITANIUM TRICHLORIDE ($TiCl_3$) (IDEAL GAS) GFW = 154.259

Point Group = C_{3v}

ΔHf°_0 = -128.1 ± 1.5 kcal/mol

$S^\circ_{298.15}$ = [75.7 ± 1.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -128.9 ± 1.5 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[530] (1)	[590] (2)
[275] (1)	[260] (2)

Bond Distance: Ti-Cl = [2.3] Å

Bond Angle: Cl-Ti-Cl = [100°] σ = 3

Products of the Moments of Inertia: $I_AI_BI_C = [1.33 \times 10^{-112}]\ g^3\ cm^6$

Heat of Formation

The heat of formation of $TiCl_3(g)$ is calculated from the heats of reaction for the processes, (A) $3TiCl_4(g) + Ti(c) = 4TiCl_3(g)$ and (B) $TiCl_3(c) = TiCl_3(g)$, combined with auxiliary JANAF heats of formation for $TiCl_4(g)$, $TiCl_3(c)$ and Ti(c). Equilibrium measurements of reaction (A) have been reported by Gross and Levi (1). Vapor pressure measurements for reaction (B) have been reported by Sanderson and MacWood (2) and by Farber and Darnell (3). Second and third law analyses of these data yield the following results.

Source	Reaction	No. Points	Range, T°K	ΔHr°_{298}, kcal/mol Second Law	Third Law	Drift, eu	ΔHf°_{298}*
Gross and Levi (1)	A	3	1223		31.6 ± 2.0		-128.5
Sanderson and MacWood (2)	B	9**	628-823	42.8 ± 1.1	42.8	-0.1 ± 1.5	-129.3
Farber and Darnell	B	8	636-732	45.3 ± 2.1	45.8	0.8 ± 3.1	-126.2

*Calculation based on third law ΔHr°_{298}.

**One point rejected due to failure of statistical test.

The chosen value of ΔHf°_{298} is -128.9 kcal/mol. This value is the average of the first two determinations.

Heat Capacity and Entropy

The interatomic distance is estimated from that of the solid, given as 2.46 Å by Natta et al. (4), and from comparisons of bond distances of crystal and gas phase tetrahalides of titanium. The pyramidal bond angle is estimated assuming $TiCl_3(g)$ similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 4.28 \times 10^{-38}\ g\ cm^2$ and $I_C = 7.26 \times 10^{-38}\ g\ cm^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3} (5).

References

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2. B. S. Sanderson and G. E. MacWood, J. Phys. Chem. 60, 314 (1956).
3. M. Farber and A. J. Darnell, J. Phys. Chem. 59, 156 (1955).
4. G. Natta, P. Corradini, and G. Allegia, J. Polym. Sci. 51, 399 (1961).
5. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Trichloride ($ZrCl_3$)

(Crystal) GFW = 197.579

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	22.990	34.850	34.850	.000	-170.700	-154.481	113.238
300	23.019	34.992	34.850	.043	-170.691	-154.381	112.466
400	24.069	41.768	35.767	2.400	-170.201	-149.017	81.419
500	24.730	47.212	37.529	4.841	-169.691	-143.779	62.846
600	25.235	51.767	39.533	7.340	-169.173	-138.646	50.502
700	25.664	55.690	41.567	9.886	-168.651	-133.599	41.712
800	26.064	59.143	43.553	12.472	-168.126	-128.628	35.140
900	26.433	62.234	45.460	15.097	-167.598	-123.722	30.044
1000	26.788	65.038	47.279	17.759	-167.067	-118.877	25.981
1100	27.050	67.604	49.012	20.451	-166.537	-114.083	22.666
1200	27.300	69.968	50.661	23.168	-166.866	-109.287	19.904
1300	27.550	72.163	52.232	25.911	-166.170	-104.516	17.571
1400	27.800	74.215	53.730	28.679	-165.463	-99.800	15.579
1500	28.000	76.139	55.160	31.469	-164.748	-95.134	13.861
1600	28.200	77.953	56.528	34.279	-164.028	-90.517	12.364
1700	28.370	79.668	57.840	37.108	-163.301	-85.942	11.049
1800	28.550	81.295	59.098	39.954	-162.571	-81.415	9.885
1900	28.650	82.841	60.307	42.814	-161.840	-76.924	8.848
2000	28.750	84.313	61.471	45.684	-161.114	-72.475	7.920

June 30, 1961; June 30, 1962; June 30, 1964; Dec. 31, 1969

ZIRCONIUM TRICHLORIDE ($ZrCl_3$) (CRYSTAL) GFW = 197.579

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [34.8 ± 3] gibbs/mol

$\Delta Hf_{298.15}$ = [-170.7 ± 15] kcal/mol

Ts = [1045.9]°K

$\Delta Hs^\circ_{298.15}$ = [45.4] kcal/mol

Heat of Formation

Turnbull and Watts (1) determined the equilibrium pressures for the disproportionation of $ZrCl_3(c)$ in the temperature range from 613°K to 723°K by a modified dew point technique. Third law and second law analyses of their vapor pressure-temperature equation give the same heat of reaction ΔHr°_{298} = 30.7 kcal/mol for $2ZrCl_3(c) + ZrCl_2(c) + ZrCl_4(g)$. The adopted value, $\Delta Hf^\circ_{298}(ZrCl_3, c) = -170.7$ kcal/mol, is calculated from the heat of reaction at 298°K, and $\Delta Hf^\circ_{298}(ZrCl_4, g) = -207.77$ kcal/mol (2) and $\Delta Hf^\circ_{298}(ZrCl_2, c) = -103$ kcal/mol (3). The assigned uncertainty, ±15 kcal/mol is mainly due to the uncertainty in the heat of formation of $ZrCl_2(c)$, and also the dew point technique used.

Heat Capacity and Entropy

The heat capacities of $ZrCl_3(c)$ are estimated from the Cp values of $ZrCl_4(c)$ by deduction of one Cl atom Cp contributions which are calculated as 1/4[Cp($ZrCl_4$, c) - Cp(Zr, c)]. The S°_{298} is calculated as 34.85 eu based on the assumption that $S^\circ_{298}(ZrCl_3, c) = S^\circ_{298}(ZrCl_4, c) - 1/4[S^\circ_{298}(ZrCl_4, c) - S^\circ_{298}(Zr, c)]$.

Heat of Sublimation

The heat of sublimation is calculated from the difference in the heats of formation of gas and crystal at 298°K. The sublimation temperature is taken as the point at which ΔGr = 0 for $ZrCl_3(c) = ZrCl_3(g)$.

References

1. A. G. Turnbull and J. A. Watts, Aust. J. Chem. 16, 947 (1963).
2. JANAF $ZrCl_4(g)$ table dated Dec. 31, 1969.
3. JANAF $ZrCl_2(c)$ table dated Dec. 31, 1969.

Zirconium Trichloride ($ZrCl_3$)

(Ideal Gas) GFW = 197.579

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.210	-124.898	-124.898	INFINITE
100	12.921	63.812	96.054	-3.224	-125.168	-124.442	271.967
200	16.648	74.098	82.691	-1.719	-125.278	-123.661	135.131
298	18.170	81.070	81.070	.000	-125.300	-122.862	90.060
300	18.189	81.182	81.070	.034	-125.300	-122.846	89.494
400	18.969	86.531	81.794	1.895	-125.307	-122.028	66.673
500	19.487	90.823	83.185	3.819	-125.313	-121.207	52.980
600	19.874	94.412	84.765	5.788	-125.326	-120.385	43.850
700	20.169	97.498	86.369	7.791	-125.346	-119.560	37.328
800	20.389	100.207	87.932	9.819	-125.379	-118.732	32.436
900	20.551	102.618	89.433	11.867	-125.429	-117.898	28.630
1000	20.669	104.790	90.862	13.928	-125.498	-117.059	25.583
1100	20.756	106.764	92.219	15.999	-125.589	-116.211	23.089
1200	20.817	108.573	93.507	18.078	-126.556	-115.302	20.999
1300	20.860	110.241	94.731	20.162	-126.519	-114.366	19.227
1400	20.889	111.788	95.895	22.250	-126.492	-113.431	17.707
1500	20.907	113.230	97.003	24.340	-126.477	-112.499	16.391
1600	20.915	114.579	98.060	26.431	-126.476	-111.568	15.239
1700	20.917	115.847	99.069	28.523	-126.486	-110.633	14.223
1800	20.913	117.043	100.035	30.614	-126.511	-109.702	13.320
1900	20.906	118.173	100.960	32.705	-126.549	-108.765	12.511
2000	20.895	119.245	101.848	34.795	-126.603	-107.828	11.783
2100	20.882	120.265	102.701	36.884	-126.670	-106.889	11.124
2200	20.868	121.236	103.521	38.972	-131.756	-105.769	10.507
2300	20.853	122.163	104.312	41.058	-131.849	-104.584	9.938
2400	20.838	123.050	105.074	43.142	-131.946	-103.396	9.416
2500	20.823	123.901	105.810	45.225	-132.049	-102.205	8.935
2600	20.808	124.717	106.522	47.307	-132.155	-101.008	8.491
2700	20.793	125.502	107.210	49.387	-132.267	-99.809	8.079
2800	20.779	126.258	107.877	51.465	-132.385	-98.603	7.696
2900	20.765	126.987	108.524	53.543	-132.507	-97.396	7.340
3000	20.752	127.691	109.151	55.618	-132.635	-96.185	7.007
3100	20.740	128.371	109.760	57.693	-132.769	-94.967	6.695
3200	20.728	129.029	110.352	59.767	-132.908	-93.746	6.403
3300	20.717	129.667	110.928	61.839	-133.054	-92.519	6.127
3400	20.707	130.285	111.488	63.910	-133.203	-91.287	5.868
3500	20.697	130.885	112.034	65.980	-133.359	-90.055	5.623
3600	20.688	131.468	112.565	68.049	-133.520	-88.813	5.392
3700	20.679	132.035	113.084	70.118	-133.685	-87.569	5.172
3800	20.670	132.586	113.590	72.185	-133.855	-86.323	4.965
3900	20.662	133.123	114.084	74.252	-134.030	-85.067	4.767
4000	20.654	133.646	114.567	76.318	-134.210	-83.810	4.579
4100	20.647	134.156	115.038	78.383	-134.392	-82.549	4.400
4200	20.639	134.653	115.499	80.447	-134.580	-81.284	4.230
4300	20.632	135.139	115.950	82.510	-134.770	-80.013	4.067
4400	20.626	135.613	116.392	84.573	-134.964	-78.733	3.911
4500	20.619	136.077	116.824	86.636	-135.161	-77.457	3.762
4600	20.613	136.530	117.248	88.697	-135.359	-76.171	3.619
4700	20.607	136.973	117.663	90.758	-135.560	-74.880	3.482
4800	20.601	137.407	118.069	92.819	-276.921	-72.907	3.320
4900	20.596	137.831	118.468	94.879	-277.230	-68.649	3.062
5000	20.590	138.248	118.860	96.938	-277.547	-64.393	2.815
5100	20.585	138.655	119.244	98.997	-277.868	-60.123	2.576
5200	20.580	139.055	119.621	101.055	-278.198	-55.849	2.347
5300	20.575	139.447	119.992	103.113	-278.530	-51.574	2.127
5400	20.570	139.831	120.355	105.170	-278.868	-47.288	1.914
5500	20.565	140.209	120.713	107.227	-279.211	-42.994	1.708
5600	20.561	140.579	121.064	109.283	-279.556	-38.699	1.510
5700	20.556	140.943	121.410	111.339	-279.907	-34.399	1.319
5800	20.552	141.301	121.750	113.394	-280.259	-30.082	1.134
5900	20.548	141.652	122.084	115.449	-280.615	-25.770	.955
6000	20.544	141.997	122.413	117.504	-280.975	-21.446	.781

June 30, 1961; Dec. 31, 1961; June 30, 1964; Dec. 31, 1969

ZIRCONIUM TRICHLORIDE ($ZrCl_3$) (IDEAL GAS) GFW = 197.579

Point Group: [C_{3v}] ΔHf°_0 = -124.9 ± 5 kcal/mol

$S^\circ_{298.15}$ = [81.0 ± 3] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -125.3 ± 5 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[490] (1)	[333] (2)
[185] (1)	[131] (2)

Bond Distance: Zr-Cl = [2.3] Å

Bond Angle: Cl-Zr-Cl = [100°] σ = [3]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.53104 x 10^{-112}] g^3 cm^6

Heat of Formation

Potter (1) investigated mass spectrometrically the equilibrium $CaCl(g) + ZrCl_4(g) \rightarrow CaCl_2(g) + ZrCl_3(g)$ in the temperature range 1163-1557°K. Ion intensities were measured 2.5 eV above threshold and they were used in the calculation of equilibrium constants. Using the reported equilibrium constants, the heats of reaction at 298°K are evaluated by the third law and second law methods as -3.69 and -16.67 kcal/mol, respectively. The third law drift is 9.31 ± 1.25 eu. Using the third law ΔHr°_{298} = -3.69 kcal/mol, $\Delta Hf^\circ_{298}(ZrCl_4, g)$ = -207.77 kcal/mol (2), $\Delta Hf^\circ_{298}(CaCl, g)$ = -28.8 kcal/mol (3) and $\Delta Hf^\circ_{298}(CaCl_2, g)$ = -115.0 kcal/mol (4), we obtain $\Delta Hf^\circ_{298}(ZrCl_3, g)$ = -125.3 kcal/mol, which is adopted in the tabulation.

Farber et al. (5) also studied mass spectrometrically the reaction $Zr(c) + 3ZrCl_4(g) \rightarrow 4ZrCl_3(g)$ in the temperature range from 1579°K to 1729°K. They reported a second law heat of reaction as ΔHr°_{298} = 59.2 ± 1.6 kcal/mol. Since the attainment of equilibrium was questionable in their studies, the heat of reaction obtained from the third law method is generally more reliable. Using their reported ion intensities of run 3 (temperature range from 1667°K to 1896°K, five points), we have calculated the equilibrium constants $K_1 = (I_{ZrCl_2})^2/(I_{ZrCl_3})(I_{ZrCl})$ for reaction (1) $ZrCl_3(g) + ZrCl(g) \rightarrow 2ZrCl_2(g)$; and $K_2 = (I_{ZrCl_3})^2/(I_{ZrCl_4})(I_{ZrCl_2})$ for reaction (2) $ZrCl_4(g) + ZrCl_2 \rightarrow 2ZrCl_3(g)$. Third law analyses of the equilibrium constants give ΔHr°_{298} = -11.0 kcal/mol for reaction (1) and its drift 4.1 ± 1.7 eu; and ΔHr°_{298} = 1.4 kcal/mol for reaction (2) and its drift 11.1 ± 1.2 eu. Using the third law heats of reaction, and $\Delta Hf^\circ_{298}(ZrCl, g)$ = 49.1 kcal/mol (6) and $\Delta Hf^\circ_{298}(ZrCl_4, g)$ = -207.77 kcal/mol (2), we obtain $\Delta Hf^\circ_{298}(ZrCl_3, g)$ = -124.9 kcal/mol and $\Delta Hf^\circ_{298}(ZrCl_2, g)$ = -43.4 kcal/mol which are in good agreement with the values adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be a pyramid similar to the group VA trichlorides. The bond distance is assumed to be the same as that of $ZrCl_4(g)$. The three principal moments of inertia are $I_A = I_B$ = 45.9145 x 10^{-39} and I_C = 72.6247 x 10^{-39} g cm^2. The electronic levels are estimated as three times higher than those of $TiCl_3(g)$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by C. E. Moore (7). The quantum weights are assumed to be the same as those of $TiCl_3(g)$.

Vibrational frequencies are calculated from the estimated force constants by the valence force method (8). The force constants are estimated from those of PCl_3, $AsCl_3$ and $SbCl_3$ listed by Herzberg (8).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF $ZrCl_4(g)$ table, dated Dec. 31, 1969.
3. The heat of formation and the free energy functions of CaCl(g) are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
4. The heat of formation and the free energy functions of $CaCl_2(g)$ are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
5. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
6. JANAF ZrCl(g) table, dated Dec. 31, 1969.
7. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std. Circ. 467.
8. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc. New York, 1945.

Magnesium Dichloride, Dimeric (Mg_2Cl_4)

(Ideal Gas) GFW = 190.436

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.787	-228.107	-228.107	INFINITE
100	21.881	71.415	124.789	-5.337	-228.357	-226.014	493.954
200	27.529	88.672	102.748	-2.815	-228.411	-223.870	244.634
298	29.543	100.098	100.098	.000	-228.100	-221.509	162.370
300	29.567	100.281	100.099	.055	-228.097	-221.468	161.339
400	30.458	108.924	101.271	3.061	-227.979	-219.279	119.808
500	30.911	115.775	103.511	6.132	-227.898	-217.110	94.899
600	31.170	121.435	106.040	9.237	-227.869	-214.959	78.299
700	31.331	126.253	108.592	12.363	-227.885	-212.805	66.441
800	31.437	130.444	111.067	15.502	-227.968	-210.649	57.546
900	31.511	134.152	113.430	18.649	-228.123	-208.474	50.624
1000	31.564	137.474	115.671	21.803	-232.595	-205.917	45.003
1100	31.603	140.485	117.792	24.962	-232.834	-203.241	40.380
1200	31.634	143.236	119.800	28.123	-233.127	-200.539	36.523
1300	31.657	145.769	121.701	31.288	-233.472	-197.809	33.256
1400	31.676	148.116	123.505	34.455	-294.601	-194.092	30.299
1500	31.691	150.302	125.220	37.623	-294.239	-186.925	27.235
1600	31.704	152.347	126.852	40.793	-293.879	-179.785	24.558
1700	31.714	154.270	128.409	43.964	-293.520	-172.660	22.197
1800	31.723	156.083	129.896	47.136	-293.164	-165.564	20.102
1900	31.730	157.798	131.320	50.308	-292.808	-158.482	18.230
2000	31.736	159.426	132.685	53.482	-292.458	-151.422	16.547
2100	31.742	168.974	133.995	56.656	-292.108	-144.383	15.026
2200	31.746	162.451	135.256	59.830	-291.764	-137.353	13.645
2300	31.750	168.862	136.469	63.005	-291.421	-130.339	12.385
2400	31.754	165.214	137.639	66.180	-291.082	-123.345	11.232
2500	31.757	166.510	138.768	69.356	-290.750	-116.365	10.173
2600	31.760	167.756	139.859	72.531	-290.421	-109.392	9.195
2700	31.763	168.954	140.914	75.708	-290.098	-102.438	8.292
2800	31.765	170.110	141.937	78.884	-289.782	-95.494	7.454
2900	31.767	171.224	142.927	82.061	-289.471	-88.560	6.674
3000	31.769	172.301	143.889	85.237	-289.171	-81.640	5.947
3100	31.770	173.343	144.822	88.414	-288.878	-74.726	5.268
3200	31.772	174.352	145.729	91.591	-288.595	-67.825	4.632
3300	31.773	175.329	146.611	94.769	-288.321	-60.929	4.035
3400	31.774	176.278	147.470	97.946	-288.058	-54.035	3.473
3500	31.776	177.199	148.306	101.123	-287.809	-47.166	2.945
3600	31.777	178.094	149.121	104.301	-287.571	-40.287	2.446
3700	31.778	178.965	149.916	107.479	-287.347	-33.419	1.974
3800	31.778	179.812	150.692	110.657	-287.135	-26.562	1.528
3900	31.779	180.638	151.449	113.834	-286.940	-19.710	1.105
4000	31.780	181.442	152.189	117.012	-286.762	-12.858	.703
4100	31.781	182.227	152.912	120.190	-286.600	-6.016	.321
4200	31.781	182.993	153.619	123.369	-286.455	.821	-.043
4300	31.782	183.741	154.311	126.547	-286.329	7.659	-.389
4400	31.783	184.471	154.988	129.725	-286.221	14.505	-.720
4500	31.783	185.186	155.651	132.903	-286.135	21.334	-1.036
4600	31.784	185.884	156.301	136.082	-286.066	28.168	-1.338
4700	31.784	186.568	156.938	139.260	-286.020	35.001	-1.628
4800	31.784	187.237	157.562	142.438	-285.998	41.829	-1.905
4900	31.785	187.892	158.174	145.617	-285.997	48.662	-2.170
5000	31.785	188.534	158.775	148.795	-286.019	55.490	-2.425
5100	31.786	189.164	159.365	151.974	-286.064	62.318	-2.671
5200	31.786	189.781	159.944	155.152	-286.136	69.155	-2.906
5300	31.786	190.387	160.513	158.331	-286.233	75.988	-3.133
5400	31.787	190.981	161.071	161.510	-286.356	82.817	-3.352
5500	31.787	191.564	161.621	164.688	-286.508	89.660	-3.563
5600	31.787	192.137	162.160	167.867	-286.687	96.495	-3.766
5700	31.787	192.699	162.691	171.046	-286.896	103.342	-3.962
5800	31.788	193.252	163.213	174.225	-287.133	110.189	-4.152
5900	31.788	193.796	163.727	177.403	-287.405	117.043	-4.336
6000	31.788	194.330	164.233	180.582	-287.706	123.896	-4.513

Dec. 31, 1969

MAGNESIUM DICHLORIDE, DIMERIC (Mg_2Cl_4) (IDEAL GAS) GFW = 190.436

Point Group: [D_{2h}]

$\Delta Hf_0^\circ = -228.11 \pm 7$ kcal/mol

$S^\circ_{298.15} = [100.098 \pm 5]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -228.10 \pm 7$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[500] (1)	[240] (1)	[130] (2)
[400] (1)	[200] (1)	[100] (2)
295 (1)	[150] (1)	[80] (2)

Bond Distance: Mg-Cl = [2.18] Å, Mg-Cl'(ring) = [2.3] Å

Bond Angles: Cl'-Mg-Cl'(in ring) = [90°], Cl-Mg-Cl' = [135°]

σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 1.3313 \times 10^{-111}$ g^3 cm^6

Heat of Formation

References relative to the monomer-dimer ratio in magnesium chloride vapor are given in the discussion for monomeric ideal gas. The selected best value for the heat of dimerization at 900°K is -39.2 kcal/mol. Combined with heat of formation data for the monomer and the heat capacity of the dimer, this yields $\Delta Hf^\circ_{298.15} = -228.10$ kcal/mol.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was assumed, with the outer Mg-Cl distance the same as in $MgCl_2$ and the ring Mg-Cl distance slightly larger. The ring was taken to be square, and the Cl-Mg-Cl' angle 135°. This structure gives individual moments of inertia of $I_A = 31.12 \times 10^{-39}$ g cm^2, $I_B = 191.86 \times 10^{-39}$ g cm^2 and $I_C = I_A + I_B$.

A reasonable set of frequencies was estimated by comparison with $MgCl_2$ monomer and other dimer molecules. The single observed frequency is from A. Buchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958), who erroneously ascribed it to the bending mode of the monomer. The estimated values were adjusted until the entropy of dimerization at 900°K was -29.9 gibbs/mol, as selected in the discussion for ideal monomeric gas. The calculated thermodynamic properties of monomer and dimer give total vapor pressures in good agreement with experiment and yield a boiling point for magnesium chloride of 1624°K at one atmosphere pressure.

Molybdenum Tetrachloride ($MoCl_4$)

(Crystal) GFW = 237.752

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	31.000	53.500	53.500	.000	-114.000	-96.136	70.470
300	31.000	53.692	53.501	.057	-113.984	-96.026	69.955
400	32.300	62.788	54.732	3.222	-113.069	-90.177	49.270
500	33.600	70.135	57.100	6.517	-112.096	-84.564	36.963
600	34.900	76.376	59.805	9.942	-111.040	-79.155	28.832
700	36.200	81.852	62.572	13.497	-109.884	-73.931	23.082
800	37.600	86.779	65.294	17.187	-108.618	-68.882	18.818
900	38.900	91.285	67.935	21.015	-107.228	-63.995	15.540
1000	39.900	95.436	70.481	24.956	-105.741	-59.273	12.954
1100	40.800	99.282	72.926	28.992	-104.173	-54.700	10.868
1200	41.600	102.868	75.274	33.113	-102.538	-50.276	9.156
1300	42.200	106.222	77.527	37.304	-100.852	-45.988	7.731
1400	42.700	109.368	79.690	41.549	-99.133	-41.832	6.530
1500	43.200	112.331	81.768	45.844	-97.387	-37.799	5.507

Dec. 31, 1968

Cl_4Mo

MOLYBDENUM TETRACHLORIDE ($MoCl_4$) (CRYSTAL) GFW = 237.752

$\Delta Hf°_0$ = Unknown

$S°_{298.15}$ = [53.5 ± 3] gibbs/mol

$\Delta Hf°_{298.15}$ = -114 ± 2 kcal/mol

Tm = 590°K

$\Delta Hm°$ = [4 ± 2] kcal/mol

Heat of Formation

The adopted $\Delta Hf°_{298}$ = -114 kcal/mol was determined by Shchukarev et al. (1) by solution calorimetry. The authors measured the heat of solution of $MoCl_4$ in the aqueous solvent $FeCl_3$ + HCl and obtained the heat of formation from a comparison with the heat of solution of $MoCl_5$ measured in the same solvent.

The decomposition pressures of $2MoCl_5(c) = 2MoCl_4(c) + Cl_2(g)$ (80 - 150°C) were measured manometrically by Saeki and Matsuzaki (2). From the reported data we evaluate the enthalpy change for the above reaction by third law analysis. Based on $\Delta Hf°_{298}(MoCl_5, c)$ = -126 kcal/mol and the third law $\Delta Hr°_{298}$ = 24.132 kcal/mol, we obtain $\Delta Hf°_{298}(MoCl_4, c)$ = -113.94 kcal/mol, which is in very good agreement with the value reported by Shchukarev et al. (1).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of $WCl_4(c)$. The estimated $S°_{298}$ = 53.5 eu is based on the assumption that the entropy difference between $MoCl_4(c)$ and $MoCl_5(c)$ is about the same as that between $WCl_4(c)$ and $WCl_5(c)$. The entropy obtained from the second law analysis of the data of Saeki and Matsuzaki (2) agrees with the adopted one within the error of the vapor pressure data.

Melting Data

See liquid table.

References

1. S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Russ. J. Inorg. Chem. (English Transl.) 5, 802 (1960).
2. Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155-8 (1965).

Molybdenum Tetrachloride ($MoCl_4$)

(Liquid) GFW = 237.752

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	35.000	58.682	58.682	.000	-110.621	-94.302	69.125
300	35.000	58.899	58.683	.065	-110.597	-94.202	68.626
400	35.000	68.967	60.055	3.565	-109.347	-88.927	48.588
500	35.000	76.777	62.648	7.065	-108.169	-83.959	36.698
600	35.000	83.159	65.551	10.565	-107.038	-79.223	28.857
700	35.000	88.554	68.461	14.065	-105.937	-74.675	23.315
800	35.000	93.228	71.272	17.565	-104.861	-70.285	19.201
900	35.000	97.350	73.945	21.065	-103.799	-66.024	16.03
1000	35.000	101.038	76.473	24.565	-102.753	-61.886	13.525
1100	35.000	104.373	78.860	28.065	-101.721	-57.848	11.493
1200	35.000	107.419	81.115	31.565	-100.707	-53.906	9.818
1300	35.000	110.220	83.247	35.065	-99.712	-50.046	8.414
1400	35.000	112.814	85.268	38.565	-98.738	-46.262	7.222
1500	35.000	115.229	87.186	42.065	-97.787	-42.546	6.199

Dec. 31, 1968

MOLYBDENUM TETRACHLORIDE ($MoCl_4$) (LIQUID) GFW = 237.752

$S^\circ_{298.15}$ = [58.682] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-110.621 ± 2] kcal/mol

Tm = 590°K

ΔHm° = [4 ± 2] kcal/mol

Tb = [680]°K

ΔHv° = [14.7] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between H°_{590} - H°_{298} for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

Tm is taken from V. Gutmann, "Halogen Chemistry," Vol. 3, Academic Press, New York, 1967. ΔHm° is estimated such that the derived ΔGf° for $MoCl_4(\ell)$ yields a reasonable boiling point which is expected to be between 600 and 700°K from comparisons with related compounds.

Vaporization Data

Tb is the temperature at which the Gibbs energy change (ΔGr°) of the following process $MoCl_4(\ell) = MoCl_4(g)$ approaches zero. The difference between ΔHf° for $MoCl_4(\ell)$ and $MoCl_4(g)$ at Tb is the heat of vaporization.

Molybdenum Tetrachloride ($MoCl_4$)

(Ideal Gas) GFW = 237.752

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.321	-91.837	-91.837	INFINITE
100	16.547	66.724	108.140	-4.142	-92.167	-89.641	195.910
200	21.386	79.888	90.959	-2.214	-92.132	-87.116	95.196
298	23.448	88.869	88.869	.000	-92.000	-84.681	62.073
300	23.473	89.014	88.869	.043	-91.998	-84.636	61.658
400	24.412	95.911	89.803	2.443	-91.848	-82.205	44.915
500	24.893	101.416	91.594	4.911	-91.702	-79.811	34.88
600	25.168	105.981	93.622	7.415	-91.567	-77.445	28.209
700	25.339	109.874	95.673	9.941	-91.440	-75.102	23.448
800	25.452	113.266	97.664	12.481	-91.324	-72.778	19.882
900	25.531	116.268	99.568	15.030	-91.213	-70.464	17.111
1000	25.587	118.961	101.375	17.587	-91.110	-68.167	14.898
1100	25.630	121.402	103.086	20.148	-91.017	-65.876	13.088
1200	25.663	123.634	104.707	22.712	-90.939	-63.595	11.582
1300	25.691	125.689	106.243	25.280	-90.876	-61.319	10.309
1400	25.714	127.594	107.701	27.850	-90.832	-59.047	9.218
1500	25.735	129.369	109.087	30.423	-90.808	-56.777	8.272
1600	25.756	131.030	110.407	32.997	-90.808	-54.509	7.446
1700	25.777	132.592	111.666	35.574	-90.828	-52.237	6.716
1800	25.799	134.066	112.870	38.153	-90.874	-49.968	6.067
1900	25.823	135.462	114.023	40.734	-90.942	-47.690	5.486
2000	25.848	136.787	115.128	43.317	-91.040	-45.414	4.963
2100	25.875	138.049	116.190	45.904	-91.159	-43.132	4.489
2200	25.904	139.253	117.211	48.493	-91.310	-40.841	4.057
2300	25.935	140.405	118.195	51.084	-91.492	-38.542	3.662
2400	25.967	141.510	119.143	53.680	-91.708	-36.232	3.299
2500	26.000	142.571	120.059	56.278	-91.977	-33.918	2.965
2600	26.035	143.591	120.945	58.880	-92.302	-31.587	2.65
2700	26.070	144.574	121.802	61.485	-92.697	-29.247	2.367
2800	26.106	145.523	122.632	64.094	-93.171	-26.887	2.099
2900	26.141	146.440	123.437	66.706	-100.355	-24.493	1.846
3000	26.177	147.326	124.219	69.322	-100.611	-21.874	1.594
3100	26.213	148.185	124.978	71.941	-100.870	-19.244	1.357
3200	26.247	149.018	125.717	74.564	-101.131	-16.609	1.134
3300	26.282	149.826	126.435	77.191	-101.394	-13.962	.925
3400	26.315	150.611	127.135	79.821	-101.658	-11.305	.727
3500	26.347	151.375	127.816	82.454	-101.927	-8.651	.540
3600	26.378	152.117	128.481	85.090	-102.197	-5.977	.363
3700	26.408	152.840	129.130	87.729	-102.470	-3.300	.195
3800	26.437	153.545	129.763	90.372	-102.743	-.619	.036
3900	26.464	154.232	130.382	93.017	-103.020	2.076	-.116
4000	26.490	154.903	130.986	95.664	-103.301	4.773	-.261
4100	26.514	155.557	131.578	98.315	-103.580	7.477	-.399
4200	26.537	156.196	132.156	100.967	-103.864	10.187	-.530
4300	26.559	156.821	132.723	103.622	-104.147	12.904	-.656
4400	26.580	157.432	133.277	106.279	-104.432	15.637	-.777
4500	26.599	158.029	133.821	108.938	-104.719	18.364	-.892
4600	26.617	158.614	134.353	111.599	-105.004	21.100	-1.002
4700	26.634	159.187	134.876	114.261	-105.292	23.847	-1.109
4800	26.649	159.747	135.388	116.925	-105.580	26.596	-1.211
4900	26.664	160.297	135.891	119.591	-105.868	29.357	-1.309
5000	26.677	160.836	136.384	122.258	-247.168	34.448	-1.506
5100	26.689	161.364	136.869	124.926	-247.728	40.094	-1.718
5200	26.701	161.883	137.345	127.596	-248.316	45.740	-1.922
5300	26.712	162.391	137.813	130.266	-248.931	51.397	-2.119
5400	26.721	162.891	138.273	132.938	-249.570	57.070	-2.310
5500	26.730	163.381	138.725	135.611	-250.230	62.757	-2.494
5600	26.739	163.863	139.169	138.284	-250.911	68.452	-2.671
5700	26.746	164.336	139.607	140.958	-251.613	74.153	-2.843
5800	26.753	164.801	140.037	143.633	-252.328	79.888	-3.010
5900	26.759	165.259	140.461	146.309	-253.060	85.613	-3.171
6000	26.765	165.709	140.878	148.985	-253.805	91.366	-3.328

Dec. 31, 1968

MOLYBDENUM TETRACHLORIDE ($MoCl_4$) (IDEAL GAS) GFW = 237.752

Point Group T_d

ΔHf°_0 = -91.8 ± 3 kcal/mol

$S^\circ_{298.15}$ = [88.9] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -92.0 ± 3 kcal/mol

Ground State Quantum Weight = [3]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[390] (1)	[410] (3)
[120] (2)	[120] (3)

Electronic Levels and Quantum Weights

ϵ_i, cm	g_i
0	(3)
[10000]	(3)
[30000]	(3)

Bond Distance: Mo-Cl = [2.27] Å

Bond Angle: Cl-Mo-Cl = [109.47°] σ = [12]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.2929 x 10^{-112}] g^3 cm^6

Heat of Formation

S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Zh. Neorg. Khim. 5, 1650-4 (1960), derived the value $\Delta Hf^\circ_{298}(MoCl_4, g)$ = -89 kcal/mol from the decomposition pressures of $2MoCl_3(c) = MoCl_2(c) + MoCl_4(g)$, 480-600°C, measured by a transpiration method. However, this ΔHf°_{298} value is adjusted to be -92 ± 3 kcal/mol, in order to obtain a reasonable boiling point (see the $MoCl_4(\ell)$ table).

Heat Capacity and Entropy

Vibrational frequencies and quantum weights are estimated by comparison with those of $WCl_4(g)$. The molecular configuration is assumed to be tetrahedral similar to those of $WCl_4(g)$, $SiCl_4(g)$, $TiCl_4(g)$ and $PbCl_4(g)$. The bond distance is estimated to be the same as that of $MoCl_5(g)$. The three principal moments of inertia are $I_A = I_B = I_C = 80.89 \times 10^{-39}$ g cm^2. The low lying electronic levels are estimated to be 0, 10000, and 30000, all triplets, by comparison with those of $WCl_4(g)$.

Tungsten Oxytetrachloride $(WOCl_4)$

(Crystal) GFW = 341.6614

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	34.954	41.300	41.300	.000	- 160.400	- 131.305	96.249
300	35.000	41.516	41.301	.065	- 160.383	- 131.125	95.524
400	37.500	51.928	42.703	3.690	- 159.362	- 121.522	66.397
500	40.000	60.564	45.435	7.565	- 158.160	- 112.196	49.041
600	42.500	68.088	48.596	11.695	- 156.756	- 103.131	37.566
700	44.350	74.786	51.868	16.043	- 155.174	- 94.317	29.447
800	45.600	80.796	55.115	20.545	- 153.476	- 85.741	23.423
900	46.300	86.208	58.274	25.141	- 151.709	- 77.377	18.790
1000	46.900	91.118	61.317	29.801	- 149.904	- 69.215	15.127

Sept. 30, 1962; Mar. 31, 1967

Cl_4OW

TUNGSTEN OXYTETRACHLORIDE $(WOCl_4)$ (CRYSTAL) GFW = 341.6614

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = [41.3 ± 4] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -160.4 ± 2 kcal/mol

Tm = 484°K ΔHm° = 10.846 ± 3 kcal/mol

Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov[1] measured calorimetrically the heats of reaction (1) and (2) at 298°K as -131.5 ± 0.3 and -13.6 ± 0.11 kcal/mol, respectively. The reactions are given as follows:

(1) $WOCl_4(c) + 6\ NaOH(16.3\ H_2O) \rightarrow Na_2WO_4(190{,}000\ H_2O) + 4\ NaCl(50{,}000\ H_2O) + 3\ H_2O(l)$

(2) $H_2WO_4(c) + 2\ NaOH(16.3\ H_2O) \rightarrow Na_2WO_4(20{,}000\ H_2O) + 2\ H_2O(l)$

Based on these data and the heats of dilution for NaOH(aq)[2], and $Na_2WO_4(aq)$[3], we obtain ΔHr°_{298} = -118.0 ± 1.6 kcal/mol for $WOCl_4(c) + 4OH^-(\infty H_2O) \rightarrow H_2WO_4(c) + 4Cl^-(\infty H_2O) + H_2O(l)$. This leads to $\Delta Hr^\circ_{298}(WOCl_4,c)$ = -160.4 ± 2 kcal/mol, using $\Delta Hf^\circ_{298}(H_2WO_4,c)$ = -270.5 ± 0.4 kcal/mol[5].

Heat Capacity and Entropy.

Cp_{300} = 35.0 gibbs/mol is estimated using Kopp's rule. Since the melting point of $WOCl_4(c)$ is approximately 500°K, which is relatively low for oxygen to reach its maximum contribution, we estimate Cp_{500} = 40.0 gibbs/mol based on the values for $WO_2(c)$, $WO_3(c)$ and $WCl_6(c)$.

The entropy, S°_{298} = 41.3 eu, is calculated from ΔS°_{457} = 44.5 eu for $WOCl_4(c) \rightarrow WOCl_4(g)$ obtained from the second law analysis of the vapor pressure equation given by S. A. Shchukarev and A. V. Suvorov[4]. See $WOCl_4(g)$ table (Mar. 31, 1967) for details.

It is surprising that this entropy is smaller than the corresponding value for $WOF_4(c)$. See $WOF_4(c)$ table (Mar. 31, 1967) for details.

Melting Data.

Tm is calculated as the temperature at which the gibbs energies of formation of crystal and liquid are equal. The difference between the heats of formation of crystal and liquid at the melting point is ΔHm°. This ΔHm° is derived from 2nd law analyses of the vapor pressure equation determined by Shchukarev and Suvorov[4]. See $WOCl_4(l,g)$ tables (Mar. 31, 1967) for details.

References.

1. S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NSRDS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed ΔH°dil = 0 ± 0.5 kcal/mol for $Na_2WO_4(20{,}000\ H_2O) \rightarrow Na_2WO_4(190{,}000\ H_2O)$.
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al, Zh. Neorg. Khim. 1, 357 (1956), 3, 2630 (1958) 5, 1650 (1960), have been revised and they are not used here.
5. JANAF $H_2WO_4(c)$ table dated Mar. 31, 1967.

Tungsten Oxytetrachloride ($WOCl_4$)

(Liquid) GFW = 341.6614

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	43.500	60.600	60.600	.000	- 150.711	- 127.370	93.365
300	43.500	60.869	60.601	.080	- 150.678	- 127.226	92.684
400	43.500	73.383	62.307	4.430	- 148.933	- 119.679	65.387
500	43.500	83.090	65.529	8.780	- 147.255	- 112.554	49.197
600	43.500	91.021	69.137	13.130	- 145.632	- 105.767	38.526
700	43.500	97.727	72.754	17.480	- 144.048	- 99.249	30.987
800	43.500	103.535	76.247	21.830	- 142.502	- 92.957	25.395
900	43.500	108.659	79.569	26.180	- 140.981	- 86.854	21.091
1000	43.500	113.242	82.711	30.530	- 139.486	- 80.921	17.685

Mar. 31, 1967

TUNGSTEN OXYTETRACHLORIDE ($WOCl_4$) (LIQUID) GFW = 341.6614

$S^\circ_{298.15}$ = [60.6 ± 4] gibbs/mol

Tm = 484°K

Tb = 493°K

$\Delta Hf^\circ_{298.15}$ = -150.711 kcal/mol

ΔHm° = 10.846 ± 3 kcal/mol

ΔHv° = 10.5 kcal/mol

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WOCl_4, l)$ = -150.711 kcal/mol, is calculated from that of the gas by subtracting the heat of vaporization ΔHv°_{298} = 13.643 kcal/mol. The latter is obtained by the third law method from the vapor pressure equation given by S. A. Shchukarev* and A. V. Surorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Second law analysis gives $\Delta Hv^\circ_{501.9}$ = 10.32 kcal/mol (ΔHv°_{298} = 13.643 kcal/mol) and the boiling point Tb = 493°K. *Earlier data reported by Shchukarev et al, Zh. Neorg. Khim. 1, 357 (1956); 3, 2630(1958); and 5, 1650 (1960), have been revised and they are not used here.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.

The entropy, S°_{298} = 60.6 eu, is calculated from $\Delta S^\circ_{501.9}$ = 20.9 eu for $WOCl_4(l) \rightarrow WOCl_4(g)$ obtained from the second law analysis of the vapor pressure equation given by Shchukarev and Suvorov, loc. cit.

Melting Data.

See $WOCl_4(c)$ table (Mar. 31, 1967) for details.

Vaporization Data.

Tb is calculated as the temperature at which the Gibbs energies of formation of liquid and gas are equal. The difference between the heats of formation of liquid and gas at the boiling point is ΔHv°.

Tungsten Oxytetrachloride ($WOCl_4$)

(Ideal Gas) GFW = 341.6614

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-5.323	-135.776	-135.776	INFINITE
100	15.252	67.706	110.135	-4.243	-136.591	-132.033	288.557
200	22.002	80.618	92.323	-2.341	-136.969	-127.296	139.103
298	25.367	90.097	90.097	.000	-137.068	-122.522	89.811
300	25.414	90.254	90.097	.047	-137.069	-122.432	89.191
400	27.395	97.859	91.121	2.696	-137.024	-117.557	64.230
500	28.531	104.115	93.113	5.501	-136.891	-112.703	49.262
600	29.436	109.412	95.399	8.408	-136.711	-107.881	39.296
700	29.981	113.993	97.736	11.380	-136.505	-103.092	32.187
800	30.362	118.022	100.025	14.398	-136.291	-98.336	26.864
900	30.637	121.615	102.228	17.449	-136.069	-93.603	22.730
1000	30.842	124.854	104.331	20.523	-135.850	-88.897	19.428
1100	30.998	127.802	106.333	23.614	-135.635	-84.214	16.732
1200	31.119	130.504	108.236	26.722	-135.428	-79.547	14.488
1300	31.215	132.999	110.046	29.839	-135.230	-74.899	12.592
1400	31.292	135.315	111.769	32.964	-135.041	-70.266	10.969
1500	31.354	137.476	113.412	36.096	-134.865	-65.644	9.564
1600	31.406	139.501	114.980	39.235	-134.700	-61.034	8.337
1700	31.449	141.407	116.479	42.377	-134.547	-56.433	7.255
1800	31.486	143.205	117.914	45.524	-134.409	-51.844	6.295
1900	31.517	144.909	119.290	48.674	-134.283	-47.258	5.436
2000	31.543	146.526	120.612	51.827	-134.175	-42.681	4.664
2100	31.566	148.065	121.883	54.983	-134.079	-38.109	3.966
2200	31.586	149.534	123.107	58.141	-134.002	-33.544	3.332
2300	31.604	150.939	124.287	61.300	-133.939	-28.977	2.753
2400	31.619	152.284	125.425	64.461	-133.893	-24.412	2.223
2500	31.633	153.575	126.526	67.624	-133.866	-19.854	1.736
2600	31.645	154.816	127.590	70.789	-133.854	-15.292	1.285
2700	31.656	156.011	128.621	73.953	-133.867	-10.734	.869
2800	31.665	157.162	129.620	77.119	-133.914	-6.169	.481
2900	31.674	158.273	130.589	80.286	-134.002	-1.609	.121
3000	31.682	159.347	131.529	83.454	-134.135	2.960	-.216
3100	31.689	160.386	132.444	86.622	-134.335	7.532	-.531
3200	31.695	161.392	133.333	89.791	-134.599	12.111	-.827
3300	31.701	162.368	134.198	92.961	-134.936	16.700	-1.106
3400	31.707	163.314	135.040	96.132	-135.354	21.306	-1.370
3500	31.712	164.234	135.861	99.303	-135.869	25.913	-1.618
3600	31.716	165.127	136.662	102.474	-136.504	30.549	-1.855
3700	31.720	165.996	137.443	105.646	-145.591	35.246	-2.082
3800	31.724	166.842	138.206	108.818	-145.677	40.133	-2.308
3900	31.728	167.666	138.951	111.991	-145.771	45.027	-2.523
4000	31.731	168.469	139.678	115.164	-145.872	49.920	-2.728
4100	31.734	169.253	140.390	118.337	-145.976	54.813	-2.922
4200	31.737	170.018	141.087	121.510	-146.087	59.709	-3.107
4300	31.740	170.765	141.768	124.684	-146.201	64.611	-3.284
4400	31.742	171.494	142.436	127.858	-146.321	69.521	-3.453
4500	31.744	172.208	143.089	131.033	-146.445	74.420	-3.614
4600	31.746	172.905	143.730	134.207	-146.570	79.336	-3.769
4700	31.748	173.588	144.358	137.382	-146.700	84.251	-3.918
4800	31.750	174.256	144.974	140.557	-146.833	89.164	-4.060
4900	31.752	174.911	145.578	143.732	-146.968	94.083	-4.196
5000	31.754	175.553	146.171	146.907	-147.104	98.998	-4.327
5100	31.755	176.182	146.754	150.083	-147.241	103.926	-4.454
5200	31.757	176.798	147.325	153.258	-147.381	108.855	-4.575
5300	31.758	177.403	147.887	156.434	-147.522	113.781	-4.692
5400	31.760	177.997	148.439	159.610	-147.665	118.709	-4.804
5500	31.761	178.579	148.982	162.786	-147.807	123.653	-4.914
5600	31.762	179.152	149.516	165.962	-147.951	128.579	-5.018
5700	31.763	179.714	150.041	169.138	-148.097	133.511	-5.119
5800	31.764	180.266	150.557	172.315	-148.241	138.467	-5.218
5900	31.765	180.809	151.065	175.491	-148.388	143.409	-5.312
6000	31.766	181.343	151.565	178.668	-342.439	150.440	-5.480

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRACHLORIDE ($WOCl_4$) (IDEAL GAS) GFW = 341.6614

Point Group [C_{2v}]

ΔHf°_0 = -135.8 ± 5 kcal/mol

$S^\circ_{298.15}$ = [90.1] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -137.0 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[1000] (1)	[350] (1)	[200] (1)
[1000] (1)	[350] (1)	[200] (1)
[480] (1)	[300] (1)	[100] (1)
[480] (1)	[300] (1)	[100] (1)

Bond Distance: W-Cl = [2.26] Å W-O = [1.81] Å

Bond Angle: Cl*-W-O* = Cl*-W-Cl* = [120°]
Cl*-W-Cl** = Cl**-W-O* = [90°]
Cl**-W-Cl** = [180°] σ = [2]
*Equatorial **Axial

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.873×10^{-112}] g^3 cm^6

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WOCl_4,g)$ = -137.0 kcal/mol, is calculated from ΔHr°_{298} = 23.4 kcal/mol for $WOCl_4(c) \rightarrow WOCl_4(g)$. The latter is obtained by the third law method from the vapor pressure equation given by S. A. Shchukarev* and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Second law analysis gives $\Delta Hr^\circ_{457.2}$ = 21.9 kcal/mol (ΔHr°_{298} = 23.4 kcal/mol).

*Earlier data reported by Shchukarev et al., Zh. Neorg. Khim 1, 357 (1956), 3, 2630 (1956), 5, 1650 (1960), have been revised and they are not used here.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $SOF_4(g)$, reported by P. L. Goggin, H. L. Roberts and L. A. Woodward[1]. The bond distances W-O and W-Cl are estimated to be the same as those in $WO_3(g)$ and $WCl_6(g)$, respectively. The three principal moments of inertia are $I_A = 8.260 \times 10^{-38}$, $I_B = 1.052 \times 10^{-37}$ and $I_C = 6.757 \times 10^{-38}$ g cm^2.

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $SOF_4(g)$[1], $MoOCl_4(g)$[2], $WO_2Cl_2(g)$[3], $CrO_2Cl_2(g)$[4,5], $WO_3(g)$[6], and $WCl_6(g)$[6]. The frequencies are not listed in point group order.

References.

1. P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. 57, 1877 (1961).
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4. F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
5. H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta 1959, 438 (1959).
6. JANAF $WO_3(g)$ table (Sept. 30, 1966), $WCl_6(g)$ table (Dec. 31, 1966).

Lead Tetrachloride ($PbCl_4$)

(Ideal Gas) Mol. Wt. = 349.04 INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-5.663	-74.631	-74.631	INFINITE
100	16.018	68.470	112.093	-4.362	-75.155	-72.084	157.532
200	22.499	82.582	94.084	-2.300	-75.138	-68.998	75.393
298	24.125	91.919	91.919	.000	-75.000	-66.013	48.386
300	24.143	92.068	91.919	.045	-74.997	-65.957	48.047
400	24.835	99.121	92.876	2.498	-74.856	-62.966	34.401
500	25.180	104.704	94.703	5.000	-74.733	-60.007	26.228
600	25.374	109.313	96.765	7.529	-74.632	-57.071	20.787
700	25.493	113.234	98.845	10.073	-75.714	-53.961	16.847
800	25.572	116.644	100.861	12.626	-75.654	-50.859	13.893
900	25.626	119.659	102.785	15.186	-75.588	-47.763	11.598
1000	25.665	122.361	104.610	17.751	-75.517	-44.676	9.764
1100	25.694	124.809	106.337	20.319	-75.442	-41.596	8.264
1200	25.717	127.046	107.971	22.890	-75.362	-38.522	7.015
1300	25.734	129.105	109.518	25.462	-75.280	-35.455	5.960
1400	25.748	131.012	110.986	28.036	-75.199	-32.396	5.057
1500	25.759	132.789	112.381	30.612	-75.119	-29.340	4.275
1600	25.768	134.452	113.709	33.188	-75.046	-26.291	3.591
1700	25.776	136.014	114.976	35.765	-74.976	-23.242	2.988
1800	25.782	137.488	116.186	38.343	-74.914	-20.204	2.453
1900	25.787	138.882	117.344	40.922	-74.857	-17.164	1.974
2000	25.792	140.205	118.454	43.501	-74.811	-14.129	1.544
2100	25.796	141.463	119.520	46.080	-117.220	-9.545	.993
2200	25.799	142.663	120.545	48.660	-117.096	-4.422	.439
2300	25.802	143.810	121.532	51.240	-116.995	.700	-.067
2400	25.805	144.908	122.483	53.820	-116.919	5.816	-.530
2500	25.807	145.962	123.402	56.401	-116.871	10.927	-.955
2600	25.809	146.974	124.289	58.982	-116.846	16.039	-1.348
2700	25.811	147.948	125.147	61.563	-116.847	21.149	-1.712
2800	25.813	148.887	125.978	64.144	-116.876	26.263	-2.050
2900	25.814	149.793	126.784	66.725	-116.927	31.374	-2.364
3000	25.816	150.668	127.566	69.307	-117.001	36.488	-2.658
3100	25.817	151.514	128.325	71.888	-117.098	41.606	-2.933
3200	25.818	152.334	129.062	74.470	-117.216	46.726	-3.191
3300	25.819	153.129	129.779	77.052	-117.352	51.854	-3.434
3400	25.820	153.899	130.478	79.634	-117.504	56.986	-3.663
3500	25.821	154.648	131.158	82.216	-117.674	62.114	-3.878
3600	25.821	155.375	131.820	84.798	-117.856	67.259	-4.083
3700	25.822	156.083	132.466	87.380	-118.051	72.404	-4.277
3800	25.823	156.771	133.097	89.962	-118.254	77.552	-4.460
3900	25.823	157.442	133.713	92.544	-118.468	82.710	-4.635
4000	25.824	158.096	134.314	95.127	-118.689	87.867	-4.801
4100	25.824	158.734	134.902	97.709	-118.915	93.033	-4.959
4200	25.825	159.356	135.477	100.292	-119.146	98.205	-5.110
4300	25.825	159.964	136.039	102.874	-119.380	103.380	-5.254
4400	25.826	160.557	136.590	105.457	-119.615	108.572	-5.393
4500	25.826	161.136	137.129	108.039	-119.853	113.753	-5.524
4600	25.526	161.705	137.657	110.622	-120.088	118.950	-5.651
4700	25.827	162.261	138.175	113.205	-120.323	124.149	-5.773
4800	25.827	162.804	138.682	115.787	-120.558	129.352	-5.889
4900	25.827	163.337	139.180	118.370	-120.790	134.564	-6.002
5000	25.828	163.859	139.668	120.953	-121.018	139.773	-6.109
5100	25.828	164.370	140.147	123.536	-121.242	144.997	-6.213
5200	25.828	164.872	140.618	126.119	-121.463	150.222	-6.313
5300	25.829	165.364	141.080	128.701	-121.683	155.445	-6.410
5400	25.829	165.846	141.535	131.284	-121.898	160.676	-6.503
5500	25.829	166.320	141.981	133.867	-122.109	165.913	-6.592
5600	25.829	166.786	142.420	136.450	-122.315	171.148	-6.679
5700	25.829	167.243	142.851	139.033	-122.520	176.382	-6.763
5800	25.829	167.692	143.276	141.616	-122.719	181.640	-6.844
5900	25.830	168.134	143.693	144.199	-122.917	186.881	-6.922
6000	25.830	168.568	144.104	146.782	-123.111	192.135	-6.998

June 30, 1962

Lead Tetrachloride ($PbCl_4$) (Ideal Gas)

Mol. Wt. = 349.04

ΔH_f° 298.15 = [-75] kcal. mole^{-1}

$S^\circ_{298.15}$ = 91.9 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
326 (1)
83 (2)
341 (3)
99 (3)

Pb-Cl distance = 2.43 Å   Cl-Pb-Cl angle = 109° 28'

$I_AI_BI_C$ = 7.9660 X 10^{-112} g.^{3} cm.^{6} σ = 12

Heat of Formation. ΔH_f° 298.15 was estimated from the value of ΔH_f° 298.15 for $PbCl_2(g)$, using the relation between ΔH_f° 298.15 for dihalides and that for tetrahalides of titanium and zirconium as reference.

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Silicon Tetrachloride ($SiCl_4$)

(Ideal Gas) GFW = 169.898

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.638	-156.581	-156.581	INFINITE
100	13.672	59.770	96.201	-3.643	-157.042	-153.897	336.343
200	18.787	70.994	80.966	-1.994	-157.126	-150.705	164.683
298	21.573	79.070	79.070	.000	-157.100	-147.558	108.163
300	21.610	79.204	79.071	.040	-157.099	-147.498	107.452
400	23.133	85.651	79.940	2.285	-157.021	-144.309	78.847
500	23.989	90.914	81.625	4.645	-156.911	-141.142	61.693
600	24.505	95.337	83.551	7.071	-156.791	-138.000	50.266
700	24.835	99.141	85.513	9.539	-156.664	-134.878	42.111
800	25.057	102.473	87.429	12.035	-156.540	-131.777	36.000
900	25.214	105.433	89.268	14.549	-156.418	-128.686	31.249
1000	25.328	108.096	91.020	17.076	-156.303	-125.613	27.453
1100	25.413	110.514	92.684	19.613	-156.195	-122.549	24.348
1200	25.479	112.728	94.263	22.158	-156.095	-119.495	21.763
1300	25.530	114.770	95.763	24.709	-156.003	-116.449	19.577
1400	25.571	116.663	97.189	27.264	-155.921	-113.409	17.704
1500	25.604	118.429	98.547	29.823	-155.849	-110.375	16.082
1600	25.632	120.082	99.842	32.384	-155.789	-107.346	14.663
1700	25.654	121.637	101.079	34.949	-167.730	-104.211	13.397
1800	25.674	123.104	102.262	37.515	-167.636	-100.479	12.200
1900	25.690	124.492	103.396	40.083	-167.542	-96.748	11.129
2000	25.704	125.810	104.484	42.653	-167.452	-93.025	10.165
2100	25.716	127.065	105.529	45.224	-167.361	-89.308	9.294
2200	25.726	128.261	106.536	47.796	-167.275	-85.594	8.503
2300	25.735	129.405	107.505	50.369	-167.190	-81.881	7.780
2400	25.743	130.501	108.441	52.943	-167.108	-78.172	7.119
2500	25.750	131.552	109.344	55.518	-167.031	-74.470	6.510
2600	25.756	132.562	110.218	58.093	-166.956	-70.768	5.949
2700	25.762	133.534	111.064	60.669	-166.886	-67.072	5.429
2800	25.767	134.471	111.883	63.245	-166.822	-63.372	4.946
2900	25.771	135.375	112.678	65.822	-166.761	-59.681	4.498
3000	25.775	136.249	113.449	68.400	-166.705	-55.992	4.079
3100	25.779	137.094	114.198	70.977	-166.656	-52.303	3.687
3200	25.782	137.912	114.926	73.555	-166.612	-48.613	3.320
3300	25.785	138.706	115.635	76.134	-166.573	-44.925	2.975
3400	25.788	139.476	116.325	78.712	-166.539	-41.237	2.651
3500	25.791	140.223	116.997	81.291	-166.512	-37.558	2.345
3600	25.793	140.950	117.652	83.871	-258.449	-31.613	1.919
3700	25.795	141.657	118.292	86.450	-258.333	-25.313	1.495
3800	25.797	142.345	118.916	89.030	-258.220	-19.020	1.094
3900	25.799	143.015	119.525	91.609	-258.115	-12.725	.713
4000	25.801	143.668	120.120	94.189	-258.015	-6.434	.352
4100	25.802	144.305	120.703	96.770	-257.917	-.150	.008
4200	25.804	144.927	121.272	99.350	-257.825	6.134	-.319
4300	25.805	145.534	121.829	101.930	-257.735	12.418	-.631
4400	25.806	146.127	122.375	104.511	-257.649	18.705	-.929
4500	25.807	146.707	122.909	107.091	-257.567	24.984	-1.213
4600	25.809	147.274	123.433	109.672	-257.484	31.261	-1.485
4700	25.810	147.829	123.946	112.253	-257.406	37.541	-1.746
4800	25.811	148.373	124.449	114.834	-257.329	43.810	-1.995
4900	25.811	148.905	124.943	117.415	-257.254	50.089	-2.234
5000	25.812	149.426	125.427	119.996	-257.179	56.354	-2.463
5100	25.813	149.938	125.903	122.578	-257.103	62.633	-2.684
5200	25.814	150.439	126.370	125.159	-257.030	68.902	-2.896
5300	25.815	150.931	126.829	127.741	-256.957	75.164	-3.099
5400	25.815	151.413	127.279	130.322	-256.886	81.429	-3.296
5500	25.816	151.887	127.722	132.904	-256.814	87.696	-3.485
5600	25.817	152.352	128.158	135.485	-256.743	93.957	-3.667
5700	25.817	152.809	128.587	138.067	-256.673	100.216	-3.842
5800	25.818	153.258	129.008	140.649	-256.602	106.484	-4.012
5900	25.818	153.699	129.423	143.230	-256.534	112.734	-4.176
6000	25.819	154.133	129.831	145.812	-256.465	118.996	-4.334

Dec. 31, 1960; March 31, 1964; Sept. 30, 1967

SILICON TETRACHLORIDE ($SiCl_4$) (IDEAL GAS) GFW = 169.898

Point Group T_d

$S^\circ_{298.15}$ = 79.07 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -156.58±0.6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -157.1±0.6 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
425±1 (1)	620±1 (3)
149±2 (2)	220±4 (3)

Bond Distance: Si-Cl = 2.0173±0.0034 Å

Bond Angle: Cl-Si-Cl = 109° 28'

σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 2.60708 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The adopted value is calculated from ΔHv_{298} = 7.09 kcal/mol (see below) and ΔHf°_{298} = -164.18 kcal/mol for the liquid. The latter is derived from the calorimetric study of Schäfer (1) using ΔHf°_{298} (AgCl, c) = -30.37 kcal/mol (2). Both $SiCl_4(\ell)$ and Si(c) were reacted with AgF+HF(aq) to obtain the overall reaction. Other calorimetric studies (3-7) of $SiCl_4(\ell)$ yield values which differ by up to 7 kcal/mol, but each study appears to involve a final state which is not well known or not well defined. Results are summarized below for the overall experimental reactions. Data of Beezer (3) are combined with those of Good (8) for $[H_2SiF_6, 41HF, 174H_2O]$ by neglecting the unknown heat of dilution between the two calorimetric solutions. Data of Wolfe (4) involve a questionable conversion of Na_2SiO_3(calorimetric sol) → Na_2SiO_3(c). The aqueous hydrolysis reactions (5-7) yield SiO_2(colloidal soln) which appears to be an ill-defined state judging by the variation in the observed heats. ΔHf° for this colloidal solution is taken as -214.4 kcal/mol (2).

Source	Reaction	ΔHr°_{298} kcal/mol	$\Delta Hf^\circ_{298}(SiCl_4, \ell)$ kcal/mol
1. Schäfer (1964)	$SiCl_4(\ell)+4Ag(c) = Si(c)+4AgCl(c)$	42.7±0.4	-164.18
3. Beezer (1964)	$SiCl_4(\ell)+185HF(4.335H_2O) = 4HCl(11H_2O)+[H_2SiF_6, 179HF, 758H_2O]$	-97.0±0.4	-169.9
4. Wolf (1961)	$SiCl_4(\ell)+13NaOH(27.8H_2O) = Na_2SiO_3(c)+4NaCl(c)+3H_2O(\ell)+7NaOH(52.14H_2O)$	-129.3±0.8	-167.3
5. Ring (1966)	$SiCl_4(\ell)+2H_2O(\ell) = 4HCl(500H_2O)+SiO_2$(colloidal soln)	-79.8±0.3	-157.2
6. Andrianov (1953)	$SiCl_4(\ell)+2H_2O(\ell) = 4HCl(600H_2O)+SiO_2$(colloidal soln)	-76.6	-160.4
7. Roth (1928)	$SiCl_4(\ell)+2H_2O(\ell) = 4HCl(aq)+SiO_2$(colloidal soln)	-70.1	-166.9

Heat Capacity and Entropy

The bond distance r_g is from the precise electron diffraction study of Morino (9). Earlier data gave values of 2.00 to 2.02 Å. Vibrational frequencies are from the Raman and infrared spectra of the vapor reported by Morino (10). Infrared data of Smith (11) confirm that ν_3 is about 12 cm^{-1} larger in the vapor than in the liquid. The moments of inertia are $I_A = I_B = I_C = 6.3883 \times 10^{-38}\ g\ cm^2$.

Vaporization Data

Vapor pressure data ranging from 20° below Tm (supercooled liquid) to 10° above Tb are in reasonable agreement as summarized below. The analysis is based on fugacities calculated from vapor pressures by the approximation of Pitzer (19) using Tc = 506°K (20), Pc = 37.1 atm (21) and ω = 0.26. At 298.15°K the calculated f/P is 0.982 compared with 0.984 observed by Wood (22). The analysis also presumes a linear variation of the liquid phase Cp based on 33.3 gibbs/mol at 210°K and 34.2 at 300°K. The latter value is from data of Vold (17) since earlier data (77-294°K) of Latimer (18) appear to have a large positive bias below Tm. The Cp at 210°K assumes Latimer's value to have about 1 percent bias by analogy with his data for $CCl_4(\ell)$.

Source	No. of Points	Range, T°K	ΔSv°_{298}, eu	ΔHv°_{298}, kcal/mol
Combined 14, 15, 22	-	275-341	21.45 ± 0.04	7.09 ± 0.01
12. Balk (1964)	-	183-204	22.13	7.19
13. King (1962)	6	303-323	20.85 ± 0.13	6.89 ± 0.04
14. Nisel'son (1960)	12	298-341	21.48 ± 0.09	7.10 ± 0.03
15. Jenkins (1954)	6	275-330	21.40 ± 0.05	7.08 ± 0.01
16. Kearby (1936)	13	273-333	21.55 ± 0.08	7.13 ± 0.03

References

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Titanium Tetrachloride ($TiCl_4$)

(Crystal) GFW = 189.712

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.437	-195.704	-195.704	INFINITE
100	20.191	22.096	74.536	-5.244	-196.037	-189.020	413.103
200	26.859	38.329	52.654	-2.865	-195.568	-182.158	199.053
298	30.943	49.927	49.927	.000	-194.807	-175.733	128.816
300	31.000	50.119	49.928	.057	-194.791	-175.614	127.935
400	33.350	59.380	51.174	3.282	-193.844	-169.361	92.535
500	34.800	66.994	53.600	6.697	-192.781	-163.361	71.405

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (CRYSTAL) GFW = 189.712

$\Delta Hf°_0 = -195.7 \pm 1.0$ kcal/mol

$S°_{298.15} = 49.93 \pm 0.1$ gibbs/mol

$\Delta Hf°_{298.15} = -194.807 \pm 1.0$ kcal/mol

Tm = 249.05°K

$\Delta Hm° = 2.382$ kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf°_{298}$, of $TiCl_4(c)$ is calculated from the corresponding quantity for $TiCl_4(\ell)$ and the values of $H°_{249.05} - H°_{298.15}$ for both crystal and liquid.

Heat Capacity and Entropy

The heat capacity of $TiCl_4(c)$ has been reported by Latimer (1) and by Furukawa (2). The data from the latter investigation are adopted. These data lead to a value of 44.5 eu for $S°_{249.05}$. This compares with Latimer's value (1) of 43.8 eu for the same quantity. The heat capacity of the solid is extrapolated to a value of 18R at 600°K, based on the known heat capacities of $TiBr_4(c)$ and $TiI_4(c)$. The hypothetical entropy at 298°K is based on the integration of the extrapolated curve and the value at the melting point.

Melting Data

The triple point is reported to be 249.05°K, with a measured heat of fusion of 2.382 kcal/mol, by Furukawa (2). Latimer (1) reported values of 248.0°K and 2.233 kcal/mol for these quantities. The former data are adopted.

References

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Titanium Tetrachloride ($TiCl_4$)

(Liquid) GFW = 189.712

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200	34.584	46.498	63.496	- 3.400	- 193.496	- 181.719	198.573
298	34.704	60.326	60.326	.000	- 192.200	- 176.226	129.177
300	34.709	60.541	60.327	.064	- 192.177	- 176.127	128.308
400	34.936	70.557	61.691	3.547	- 190.972	- 170.961	93.408
500	35.153	78.376	64.274	7.051	- 189.820	- 166.091	72.598
600	35.370	84.805	67.176	10.577	- 188.698	- 161.452	58.809
700	35.586	90.273	70.095	14.125	- 187.592	- 156.999	49.017
800	35.803	95.039	72.921	17.694	- 186.505	- 152.704	41.717
900	36.020	99.269	75.618	21.285	- 185.430	- 148.542	36.071
1000	36.237	103.075	78.177	24.898	- 184.369	- 144.503	31.581

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (LIQUID) GFW = 189.712

$S^\circ_{298.15}$ = 60.326 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -192.2 ± 0.9 kcal/mol

Tm = 249.05°K

ΔHm° = 2.382 kcal/mol

Tb = 409°K

ΔHv° = 8.55 kcal/mol

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298.15}$, of $TiCl_4(\ell)$ is calculated from that of $TiCl_4(g)$ and the value of $\Delta Hv^\circ_{298.15}$. The value of ΔHv°_{298} is determined from second and third law analyses of fugacity as follows.

				ΔHv°_{298}			
Source	Method	Range	No. Pts.	2nd Law	3rd Law	Drift, eu	ΔHf°_{298}
1. Pike and Foster (1959)(1)	Manometric	363-415	18*	9.82±0.02	9.83	0.0±0.1	-192.2
2. Seryakov et al. (1960)(2)	Manometric	358-412	8	9.79±0.03	9.84	0.1±0.1	-192.2
3. Schafer et al. (1953) (3)	Isoteniscope	313-358	17*	9.86±0.02	9.82	-0.1±0.0	-192.2
4. Schafer et al. (1953) (3)	Isoteniscope	313-357	16**	9.80±0.01	9.82	0.0±0.0	-192.2
5. Schafer et al. (1953) (3)	Isoteniscope	313-357	16	9.91±0.02	9.83	-0.2±0.1	-192.2
6. Schafer et al. (1953) (3)	Isoteniscope	312-359	17	9.90±0.02	9.83	-0.2±0.1	-192.2
7. Weed (1957) (4)	Manometric	298-319	***	9.79±0.01	9.82	0.1±0.0	-192.2
8. Weed (1957) (4)	Manometric	298-319	***	9.81±0.01	9.82	0.0±0.0	-192.2
9. Weed (1957) (4)	Spectra	250-302	***	9.69±0.01	9.80	0.4±0.0	-192.2

* two points rejected due to failure of a statistical test

** three points rejected due to failure of a statistical test

*** selected points from extensive data

Third law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures. Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the $TiCl_4(g)$ table. The conversion to fugacity was made using Pitzer's method for normal fluids (5). The calculation was carried out using the value of 45.7 atm for the critical pressure, P_c, reported by Minzer (6) and estimated values of 643 ± 15°K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, ω. Schafer et al. (7) reported a calorimetric determination of ΔHv°_{298}. Their value of 9.9 ± 0.2 kcal/mol was used to check the reliability of their equipment, assuming that the vapor pressure data (3) gave a more accurate determination of ΔHv°_{298}. The adopted value of ΔHv°_{298} is 9.82 ± 0.02 kcal/mol.

Heat Capacity and Entropy

The entropy and heat capacity of $TiCl_4(\ell)$ has been measured by Furukawa (8). His reported values are adopted.

Melting Data

See $TiCl_4(c)$ table for details.

Vaporization Data

The boiling temperature, Tb, is taken as the temperature at which Kp = 1 for the reaction $TiCl_4(\ell) = TiCl_4(g)$. The vapor pressure data are discussed above.

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Titanium Tetrachloride ($TiCl_4$)

(Ideal Gas) GFW = 189.712

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.166	-182.026	-182.026	INFINITE
100	16.117	63.412	103.421	-4.001	-182.387	-179.501	392.299
200	20.582	76.098	86.822	-2.145	-182.441	-176.584	192.962
298	22.852	84.793	84.793	.000	-182.400	-173.721	127.341
300	22.881	84.935	84.794	.042	-182.399	-173.667	126.516
400	24.008	91.690	85.707	2.393	-182.326	-170.767	93.303
500	24.610	97.118	87.464	4.827	-182.244	-167.886	73.383
600	24.962	101.639	89.461	7.307	-182.168	-165.022	60.109
700	25.183	105.504	91.483	9.815	-182.102	-162.171	50.632
800	25.330	108.877	93.451	12.341	-182.058	-159.328	43.526
900	25.433	111.867	95.334	14.879	-182.036	-156.486	38.000
1000	25.507	114.551	97.124	17.427	-182.040	-153.650	33.580
1100	25.563	116.985	98.821	19.980	-182.070	-150.808	29.963
1200	25.605	119.211	100.428	22.539	-183.063	-147.927	26.941
1300	25.639	121.262	101.953	25.101	-183.019	-145.001	24.377
1400	25.665	123.163	103.401	27.666	-182.991	-142.078	22.179
1500	25.686	124.934	104.778	30.234	-182.980	-139.156	20.275
1600	25.704	126.592	106.090	32.803	-182.990	-136.233	18.609
1700	25.719	128.151	107.343	35.375	-183.019	-133.308	17.138
1800	25.731	129.622	108.540	37.947	-183.074	-130.385	15.831
1900	25.741	131.013	109.686	40.521	-183.151	-127.453	14.660
2000	25.750	132.334	110.786	43.095	-187.705	-124.366	13.590
2100	25.758	133.590	111.842	45.671	-187.809	-121.198	12.613
2200	25.765	134.789	112.858	48.247	-187.919	-118.024	11.725
2300	25.770	135.934	113.837	50.824	-188.030	-114.842	10.912
2400	25.776	137.031	114.781	53.401	-188.145	-111.657	10.168
2500	25.780	138.083	115.692	55.979	-188.265	-108.468	9.482
2600	25.784	139.094	116.573	58.557	-188.387	-105.274	8.849
2700	25.788	140.068	117.425	61.135	-188.515	-102.076	8.262
2800	25.791	141.006	118.250	63.714	-188.648	-98.870	7.717
2900	25.794	141.911	119.051	66.294	-188.784	-95.661	7.209
3000	25.796	142.785	119.827	68.873	-188.927	-92.450	6.735
3100	25.799	143.631	120.582	71.453	-189.075	-89.230	6.291
3200	25.801	144.450	121.315	74.033	-189.229	-86.010	5.874
3300	25.803	145.244	122.028	76.613	-189.389	-82.779	5.482
3400	25.804	146.014	122.722	79.193	-189.553	-79.543	5.113
3500	25.806	146.762	123.398	81.774	-189.724	-76.311	4.765
3600	25.807	147.489	124.058	84.355	-291.525	-72.802	4.420
3700	25.809	148.197	124.700	86.935	-291.679	-66.724	3.941
3800	25.810	148.885	125.328	89.516	-291.849	-60.648	3.488
3900	25.811	149.555	125.940	92.097	-292.038	-54.556	3.057
4000	25.812	150.209	126.539	94.679	-292.245	-48.464	2.648
4100	25.813	150.846	127.124	97.260	-292.468	-42.369	2.258
4200	25.814	151.468	127.696	99.841	-292.709	-36.270	1.887
4300	25.815	152.076	128.256	102.423	-292.963	-30.163	1.533
4400	25.816	152.669	128.804	105.004	-293.233	-24.041	1.194
4500	25.817	153.249	129.341	107.586	-293.517	-17.925	.871
4600	25.817	153.817	129.867	110.168	-293.811	-11.793	.560
4700	25.818	154.372	130.383	112.749	-294.120	-5.657	.263
4800	25.819	154.916	130.888	115.331	-294.440	.480	-.022
4900	25.819	155.448	131.384	117.913	-294.771	6.629	-.296
5000	25.820	155.969	131.870	120.495	-295.110	12.783	-.559
5100	25.820	156.481	132.348	123.077	-295.457	18.949	-.812
5200	25.821	156.982	132.817	125.659	-295.814	25.119	-1.056
5300	25.821	157.474	133.278	128.241	-296.180	31.286	-1.290
5400	25.822	157.957	133.730	130.823	-296.553	37.472	-1.517
5500	25.822	158.431	134.175	133.406	-296.930	43.666	-1.735
5600	25.823	158.896	134.612	135.988	-297.315	49.853	-1.946
5700	25.823	159.353	135.042	138.570	-297.706	56.054	-2.149
5800	25.823	159.802	135.465	141.152	-298.101	62.271	-2.346
5900	25.824	160.243	135.882	143.735	-298.501	68.483	-2.537
6000	25.824	160.677	136.291	146.317	-298.906	74.706	-2.721

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE ($TiCl_4$) (IDEAL GAS) GFW = 189.712

Point Group T_d

$\Delta Hf°_0$ = -182.0 ± 0.9 kcal/mol

$S°_{298}$ = 84.8 ± 0.7 gibbs/mol

$\Delta Hf°_{298.15}$ = -182.4 ± 0.9 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
388 (1)	498.5 (3)
111 (2)	131 (3)

Bond Distance: Ti-Cl = 2.185 Å

Bond Angle: Cl-Ti-Cl = 109° 28'

σ = 12

Product of the Moments of Inertia: $I_A I_B I_C = 4.2092 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The heat of formation, $\Delta Hf°_{298}$, of $TiCl_4(g)$ and $TiCl_4(\ell)$ has been measured by several investigators. The results of these measurements are as follows.

Investigators	Method	Reaction	$\Delta Hf°_{298}$, kcal/mol $TiCl_4(\ell)$	 $TiCl_4(g)$
Johnson et al. (1959) (1)	Calorimetric	$Ti(c)+2Cl_2(g) = TiCl_4(g)$	(-192.2)	-182.4±0.7
Farber and Darnell (1955) (2)	Equilibrium	$TiO_2(c)+4HCl(g) = TiCl_4(g)+2H_2O(g)$	(-192.7)	-182.9±0.5
Skinner and Ruehrwein (1955) (3)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.3±3.0	(-180.5)
Gross et al.(1957) (4)	Calorimetric	$Ti(c)+xCl_2(\ell) = [TiCl_4+(x-2)Cl_2]$ soln	-191.5±0.3	(-181.7)
Krieve et al. (1956) (5)	Calorimetric	$Ti(c)+xCl_2(g) = [TiCl_4+(x-2)Cl_2]$ soln	-190.0±0.4	(-180.2)
Thomsen (1882) (6)		$TiCl_4(\ell)+2H_2O(\ell) = 4HCl_{(0.002\ m)}+TiO_2(c)$	-194.5	(-184.7)

The chosen value of $\Delta Hf°_{298}$ is that reported by Johnson et al. (1). This investigation has the advantage of being independent of the heat of vaporization of chlorine and any heats of solution in deriving the value of the heat of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura et al. (7). The tetrahedral structure was established by the Raman work of Bhagavantam (8). The vibrational frequencies determined from the infrared and Raman spectra of $TiCl_4$ by Hawkins and Carpenter (9) are adjusted downward 8 cm^{-1} for ν_2 and ν_4 so that the heats of vaporization determined by both second and third law methods are in agreement. See $TiCl_4(\ell)$ table for details. The principal moments of inertia are: $I_A = I_B = I_C = 74.943 \times 10^{-39}\ g\ cm^2$.

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Tungsten Tetrachloride (WCl_4)

(Crystal) GFW = 325.662

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	31.000	47.400	47.400	.000	-105.900	-85.929	62.987
300	31.030	47.592	47.401	.057	-105.884	-85.805	62.509
400	32.335	56.697	48.633	3.226	-104.964	-79.250	43.300
500	33.640	64.053	51.004	6.524	-103.973	-72.934	31.879
600	34.945	70.302	53.712	9.954	-102.892	-66.826	24.341
700	36.250	75.786	56.482	13.513	-101.710	-60.906	19.016
800	37.555	80.712	59.208	17.204	-100.424	-55.166	15.071
900	38.840	85.212	61.850	21.025	-99.025	-49.590	12.042
1000	39.920	89.361	64.397	24.965	-97.527	-44.177	9.655
1100	40.840	93.211	66.843	29.004	-95.946	-38.920	7.733
1200	41.570	96.797	69.192	33.126	-94.299	-33.807	6.157
1300	42.170	100.148	71.445	37.313	-92.602	-28.834	4.847
1400	42.700	103.293	73.609	41.557	-90.863	-23.994	3.746
1500	43.170	106.255	75.688	45.851	-89.089	-19.279	2.809
1600	43.600	109.055	77.687	50.190	-87.285	-14.683	2.006
1700	44.000	111.710	79.611	54.570	-85.454	-10.198	1.311
1800	44.400	114.237	81.465	58.990	-83.598	-5.829	.708
1900	44.760	116.647	83.253	63.448	-81.717	-1.556	.179
2000	45.100	118.952	84.981	67.942	-79.818	2.614	-.286

Sept. 30, 1962; Dec. 31, 1966

TUNGSTEN TETRACHLORIDE (WCl_4) (CRYSTAL) GFW = 325.662

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [47.4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -105.9 ± 15 kcal/mol

Td = [771]°K

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WCl_4,c)$ = -105.9 kcal/mol, is calculated from ΔHr°_{298} = 58.9 kcal/mol for $3WCl_4(c) = WCl_2(c) + 2WCl_5(g)$. The value of ΔHr°_{298} is calculated by the third law method from decomposition pressure data in the temperature range from 354°C to 436°C reported by S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔHr°_{298} = 73.6 ± 7.9 kcal/mol and the third law drift is -24 ± 12 eu,which would correspond to a total entropy discrepancy of -8 ± 4 eu per mole of WCl_4. This entropy discrepancy is probably within the combined uncertainty of the data and the estimated entropies for the three species. S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz i Khim., No. 2, 78 (1959), have shown that decomposition pressures are essentially independent of the composition in the solid phase until $WCl_4(c)$ is almost completely decomposed to $WCl_2(c)$. This is consistent with the assumption of solid phase activities of unity which we have used in the equilibrium analysis.

Heat Capacity and Entropy.

Cp_{298} = 6.2 gibbs/g-atom and Cp_{700} = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 700°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy of $WCl_4(c)$, S°_{298} = 47.4 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952.

Temperature of Decomposition.

Td is calculated as the temperature at which the gibbs energy change of the reaction $3\ WCl_4(c) = WCl_2(c) + 2\ WCl_5(g)$ approaches zero. We have also derived an approximate value of decomposition temperature, Td = 744°K, by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The difference between the two decomposition temperatures is related to the second law entropy and the adopted entropy.

Tungsten Tetrachloride (WCl_4)

(Ideal Gas) GFW = 325.662

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.405	-80.128	-80.128	INFINITE
100	16.901	68.151	110.128	-4.198	-80.469	-78.024	170.521
200	21.673	81.550	92.734	-2.237	-80.440	-75.575	82.585
298	23.629	90.624	90.624	.000	-80.300	-73.216	53.669
300	23.652	90.770	90.624	.044	-80.297	-73.172	53.306
400	24.526	97.709	91.564	2.458	-80.132	-70.822	38.696
500	24.971	103.235	93.365	4.935	-79.962	-68.514	29.947
600	25.224	107.812	95.402	7.446	-79.800	-66.239	24.128
700	25.381	111.713	97.461	9.977	-79.646	-63.991	19.979
800	25.485	115.110	99.459	12.521	-79.507	-61.767	16.874
900	25.557	118.116	101.368	15.073	-79.377	-59.556	14.462
1000	25.609	120.811	103.180	17.631	-79.261	-57.361	12.536
1100	25.648	123.254	104.896	20.194	-79.156	-55.177	10.963
1200	25.678	125.487	106.520	22.760	-79.065	-53.001	9.653
1300	25.703	127.543	108.059	25.330	-78.985	-50.831	8.546
1400	25.725	129.449	109.520	27.901	-78.919	-48.669	7.598
1500	25.745	131.225	110.908	30.475	-78.865	-46.510	6.777
1600	25.765	132.887	112.230	33.050	-78.825	-44.355	6.059
1700	25.785	134.449	113.492	35.627	-78.797	-42.197	5.425
1800	25.806	135.924	114.698	38.207	-78.781	-40.049	4.863
1900	25.829	137.320	115.852	40.789	-78.776	-37.894	4.359
2000	25.854	138.645	116.959	43.373	-78.787	-35.741	3.906
2100	25.880	139.907	118.022	45.959	-78.808	-33.590	3.496
2200	25.909	141.112	119.044	48.549	-78.843	-31.440	3.123
2300	25.939	142.264	120.029	51.141	-78.889	-29.280	2.782
2400	25.971	143.369	120.978	53.737	-78.947	-27.122	2.470
2500	26.004	144.429	121.895	56.335	-79.021	-24.961	2.182
2600	26.038	145.450	122.782	58.938	-79.104	-22.796	1.916
2700	26.073	146.433	123.640	61.543	-79.208	-20.629	1.670
2800	26.108	147.382	124.471	64.152	-79.340	-18.454	1.440
2900	26.144	148.299	125.277	66.765	-79.508	-16.282	1.227
3000	26.180	149.186	126.059	69.381	-79.720	-14.098	1.027
3100	26.215	150.045	126.819	72.001	-79.987	-11.908	.840
3200	26.250	150.878	127.558	74.624	-80.316	-9.708	.663
3300	26.284	151.686	128.277	77.251	-80.713	-7.493	.496
3400	26.317	152.471	128.977	79.881	-81.186	-5.264	.338
3500	26.349	153.235	129.659	82.514	-81.752	-3.030	.189
3600	26.380	153.977	130.324	85.150	-82.433	-.767	.047
3700	26.410	154.700	130.973	87.790	-91.561	1.560	-.092
3800	26.438	155.405	131.607	90.432	-91.685	4.075	-.234
3900	26.465	156.092	132.226	93.077	-91.812	6.601	-.370
4000	26.491	156.763	132.831	95.725	-91.942	9.122	-.498
4100	26.515	157.417	133.423	98.376	-92.071	11.650	-.621
4200	26.539	158.056	134.002	101.028	-92.205	14.181	-.738
4300	26.560	158.681	134.569	103.683	-92.338	16.715	-.850
4400	26.581	159.292	135.124	106.340	-92.473	19.256	-.956
4500	26.600	159.889	135.667	108.999	-92.610	21.794	-1.058
4600	26.618	160.474	136.200	111.660	-92.745	24.339	-1.156
4700	26.635	161.047	136.723	114.323	-92.882	26.889	-1.250
4800	26.650	161.608	137.235	116.987	-93.020	29.433	-1.340
4900	26.664	162.157	137.738	119.653	-93.158	31.993	-1.427
5000	26.678	162.696	138.232	122.320	-93.295	34.545	-1.510
5100	26.690	163.225	138.717	124.988	-93.431	37.104	-1.590
5200	26.702	163.743	139.193	127.658	-93.567	39.667	-1.667
5300	26.712	164.252	139.661	130.329	-93.704	42.225	-1.741
5400	26.722	164.751	140.121	133.000	-93.841	44.794	-1.813
5500	26.731	165.242	140.574	135.673	-93.976	47.363	-1.882
5600	26.739	165.723	141.019	138.347	-94.110	49.933	-1.949
5700	26.747	166.197	141.456	141.021	-94.246	52.495	-2.013
5800	26.754	166.662	141.887	143.696	-94.379	55.081	-2.076
5900	26.760	167.119	142.310	146.372	-94.513	57.659	-2.136
6000	26.766	167.569	142.728	149.048	-288.551	62.323	-2.270

Sept. 30, 1962; Dec. 31, 1966

TUNGSTEN TETRACHLORIDE (WCl_4) (IDEAL GAS) GFW = 325.662

Point Group [T_d] $\Delta Hf^\circ_0 = -80.1 \pm 8$ kcal/mol

$S^\circ_{298.15}$ = [90.6] gibbs/mol $\Delta Hf^\circ_{298.15} = -80.3 \pm 8$ kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i cm^{-1}	g_i
0	[3]
[10000]	[3]
[30000]	[3]

Vibrational Frequencies and Degeneracies

ω cm^{-1}		ω cm^{-1}	
[380]	(1)	[390]	(3)
[110]	(2)	[115]	(3)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [109.47]° σ = [12]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.154 x 10^{-112}] g^3 cm^6

Heat of Formation.

The heat of formation, ΔHf°_{298} (WCl_4,g) = -80.3 kcal/mol, is calculated from ΔHr° = 37.7 kcal/mol for $WCl_6(g) \rightarrow WCl_4(g) + Cl_2(g)$. The value of ΔHr°_{298} is calculated by the third law method from the equation for log Kp given by S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). The second law ΔHr°_{298} is 43.6 kcal/mol and the third law drift is -9.6 eu.

Heat Capacity and Entropy.

The molecular configuration is assumed to be tetrahedral similar to those of $SiCl_4$, $TiCl_4$, VCl_4, $GeCl_4$, $ZrCl_4$, $SnCl_4$, $PbCl_4$. The bond distance is estimated to be the same as that in $WCl_6(g)$. The three principal moments of inertia are: $I_A = I_B = I_C = 80.18 \times 10^{-39}$ g cm^2.

All vibrational frequencies are estimated from those of $SiCl_4$, $TiCl_4$, VCl_4, $GeCl_4$, $SnCl_4$ and $PbCl_4$ given by Kazuo Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, 1963.

If it is considered that the metal atoms are effectively ionized, then the W^{4+} will have 2 d electrons in a field of chloride ions. The electronic splitting would be roughly the inverse of that in $NiCl_2(g)$, as given by D. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966), where Ni has a d^8 configuration. By analogy with the splitting in $NiCl_2$, the low lying electronic levels are estimated to be 10000 cm^{-1} and 30000 cm^{-1}, both triplets.

Zirconium Tetrachloride ($ZrCl_4$)

(Crystal) GFW = 233.032

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.957	-234.418	-234.418	INFINITE
100	18.640	16.852	66.682	-4.983	-235.048	-227.368	496.912
200	25.880	32.445	45.905	-2.692	-234.735	-219.772	240.156
298	28.630	43.360	43.360	.000	-234.170	-212.545	155.799
300	28.660	43.537	43.361	.053	-234.158	-212.410	154.741
400	29.970	51.982	44.503	2.991	-233.503	-205.259	112.148
500	30.760	58.759	46.699	6.030	-232.921	-198.276	86.666
600	31.340	64.420	49.193	9.136	-232.131	-191.432	69.729
700	31.820	69.288	51.724	12.294	-231.435	-184.704	57.667
800	32.260	73.566	54.192	15.499	-230.735	-178.077	48.648
900	32.660	77.389	56.561	18.745	-230.031	-171.536	41.655
1000	33.040	80.850	58.820	22.030	-229.323	-165.076	36.077

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) (CRYSTAL) GFW = 233.032

$\Delta Hf^\circ_0 = -234.42 \pm 0.28$ kcal/mol

$S^\circ_{298.15} = 43.36 \pm 0.7$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -234.17 \pm 0.28$ kcal/mol

Tm = 710°K

ΔHm = 12 ± 3 kcal/mol

Ts = 606.8°K

$\Delta Hs^\circ_{298.15} = 26.4 \pm 0.3$ kcal/mol

Heat of Formation

Gal'chenko et al. (1) determined the heat of formation of $ZrCl_4(c)$ by the direct chlorination of the highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. Their value, $\Delta Hf^\circ_{298}(ZrCl_4,\ c) = -234.17 \pm 0.28$ kcal/mol, is adopted in the tabulation.

Gross et al. (2) measured calorimetrically $\Delta Hr^\circ_{298} = -225.89$ kcal/mol for $Zr(c) + 2Cl_2(\ell) \rightarrow ZrCl_4(c)$. Corrections for the difference in heat content between liquid and gaseous chlorine at 25°C and 1 atm led to the value of standard heat of formation, $\Delta Hf^\circ_{298}(ZrCl_4,\ c) = -234.7 \pm 0.4$ kcal/mol, which is in good agreement with the value adopted. Siemonsen and Siemonsen (3) also measured the heat of formation by direct chlorination of the metal in an enameled bomb calorimeter. However, they did not report their detailed experimental procedure, neither the purity of their sample, nor the corrections. The value was given as $\Delta Hf^\circ_{298} = -231.9 \pm 0.5$ kcal/mol.

Heat Capacity and Entropy

Todd (4) measured the low temperature heat capacities from 52.6 to 296.7°K, and made an extrapolation to 0°K which yielded an entropy of 8.12 eu at 51°K. We have adopted the measured heat capacities, but have made our own extrapolation to 0°K, based on the ratio of the measured heat capacities of ZrF_4 (5), TiF_4 (6), and $TiCl_4$ (7) from 6° to 50°K. This extrapolation gives $S^\circ_{50} = 6.758 \pm 0.7$ eu which is used in the table. Coughlin and King (8) measured high temperature enthalpy data from 335.9° to 566.8°K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities and adopted in the table.

Melting Data

The melting point, 710°K, has been observed by Rahlfs and Fischer (9), Palko et al. (10), Denisova et al. (11, 12).

Palko et al. derived the heat of melting as 9 ± 2.5 kcal/mol from their vapor pressure data. Denisova et al. (11, 12) determined thermographically the heat of melting as 14 ± 3 kcal/mol and also determined the heat of vaporization at 710°K as 10.4 kcal/mol which combined with the heat of sublimation at 710°K (23.8 kcal/mol) gives the heat of melting as 13.4 kcal/mol. A weighted average 12 ± 3 kcal/mol is adopted for the heat of melting.

Heat of Sublimation

Several investigators have measured the vapor pressure of $ZrCl_4(c)$ by the static method. Second and third law analyses for the vapor pressure data are summarized below:

Source	No. of Points	Temperature Range (°K)	ΔHs°_{298} (kcal/mol) 2nd law	3rd law	ΔSs°_{298} (eu)	Drift (eu)
Rahlfs and Fischer (9)	11	535-607	27.516	26.379	46.57	-1.95±0.75
Palko et al. (10)	86*	500-689	26.255	26.435	44.573	0.05±0.24
Denisova et al. (11)	17**	626-708	26.515	26.376	44.91	-0.29±0.51

* 4 points rejected due to failure of a statistical test.

** 1 point rejected due to failure of a statistical test.

The third law value, $\Delta Hs^\circ_{298} = 26.4$ kcal/mol, is adopted in the tabulation.

The sublimation temperature is obtained from the Gibbs free energy crossover between solid and gas. Rahlfs and Fischer (9) reported the sublimation temperature as 604°K.

Since the sublimation temperature is lower than the melting point, the liquid phase is thermodynamically unstable at normal conditions.

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Zirconium Tetrachloride ($ZrCl_4$)

(Ideal Gas) GFW = 233.032

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-5.401	-207.462	-207.462	INFINITE
100	16.965	65.649	107.339	-4.169	-207.834	-205.034	448.101
200	21.485	78.974	90.076	-2.220	-207.863	-202.207	220.961
298	23.486	87.980	87.980	.000	-207.770	-199.448	146.199
300	23.511	88.125	87.980	.043	-207.768	-199.396	145.260
400	24.430	95.031	88.915	2.446	-207.648	-196.624	107.430
500	24.904	100.538	90.708	4.915	-207.536	-193.881	84.745
600	25.176	105.105	92.738	7.420	-207.447	-191.158	69.629
700	25.345	108.999	94.790	9.947	-207.382	-188.450	58.837
800	25.456	112.391	96.782	12.487	-207.347	-185.749	50.744
900	25.534	115.395	98.687	15.037	-207.339	-183.049	44.450
1000	25.590	118.088	100.494	17.593	-207.360	-180.351	39.416
1100	25.631	120.529	102.207	20.154	-207.410	-177.647	35.295
1200	25.663	122.760	103.828	22.719	-208.341	-174.887	31.851
1300	25.688	124.816	105.364	25.287	-208.271	-172.102	28.933
1400	25.708	126.720	106.822	27.857	-208.214	-169.322	26.432
1500	25.724	128.494	108.209	30.428	-208.171	-166.545	24.266
1600	25.737	130.155	109.529	33.001	-208.142	-163.772	22.370
1700	25.748	131.716	110.789	35.576	-208.123	-160.996	20.697
1800	25.757	133.188	111.993	38.151	-208.120	-158.226	19.211
1900	25.765	134.580	113.145	40.727	-208.129	-155.451	17.881
2000	25.772	135.902	114.250	43.304	-208.154	-152.680	16.684
2100	25.777	137.160	115.311	45.881	-208.190	-149.907	15.601
2200	25.782	138.359	116.332	48.459	-213.245	-146.954	14.598
2300	25.787	139.505	117.315	51.038	-213.304	-143.937	13.677
2400	25.790	140.603	118.262	53.617	-213.367	-140.919	12.832
2500	25.794	141.656	119.177	56.196	-213.436	-137.900	12.055
2600	25.797	142.667	120.061	58.775	-213.507	-134.876	11.337
2700	25.799	143.641	120.917	61.355	-213.583	-131.852	10.673
2800	25.802	144.579	121.745	63.935	-213.665	-128.821	10.055
2900	25.804	145.485	122.548	66.516	-213.750	-125.791	9.480
3000	25.806	146.359	123.327	69.096	-213.842	-122.759	8.943
3100	25.807	147.206	124.084	71.677	-213.939	-119.720	8.440
3200	25.809	148.025	124.820	74.257	-214.043	-116.680	7.969
3300	25.810	148.819	125.535	76.838	-214.152	-113.634	7.526
3400	25.812	149.590	126.231	79.420	-214.264	-110.585	7.108
3500	25.813	150.338	126.909	82.001	-214.385	-107.538	6.715
3600	25.814	151.065	127.570	84.582	-214.510	-104.480	6.343
3700	25.815	151.773	128.215	87.164	-214.640	-101.421	5.991
3800	25.816	152.461	128.844	89.745	-214.775	-98.363	5.657
3900	25.817	153.132	129.458	92.327	-214.915	-95.295	5.340
4000	25.818	153.785	130.058	94.909	-215.061	-92.226	5.039
4100	25.818	154.423	130.645	97.490	-215.210	-89.156	4.752
4200	25.819	155.045	131.218	100.072	-215.364	-86.082	4.479
4300	25.820	155.652	131.779	102.654	-215.520	-83.002	4.219
4400	25.820	156.246	132.329	105.236	-215.680	-79.912	3.969
4500	25.821	156.826	132.867	107.818	-215.844	-76.830	3.731
4600	25.821	157.394	133.394	110.400	-216.008	-73.738	3.503
4700	25.822	157.949	133.910	112.983	-216.175	-70.640	3.285
4800	25.822	158.493	134.417	115.565	-357.502	-66.863	3.044
4900	25.823	159.025	134.914	118.147	-357.778	-60.800	2.712
5000	25.823	159.547	135.401	120.729	-358.060	-54.740	2.393
5100	25.824	160.058	135.879	123.312	-358.346	-48.666	2.085
5200	25.824	160.560	136.349	125.894	-358.639	-42.590	1.790
5300	25.824	161.052	136.811	128.477	-358.937	-36.514	1.506
5400	25.825	161.534	137.264	131.059	-359.240	-30.428	1.231
5500	25.825	162.008	137.710	133.641	-359.547	-24.332	.967
5600	25.825	162.474	138.148	136.224	-359.855	-18.238	.712
5700	25.826	162.931	138.579	138.807	-360.169	-12.141	.466
5800	25.826	163.380	139.002	141.389	-360.484	-6.024	.287
5900	25.826	163.821	139.419	143.972	-360.802	.084	-.003
6000	25.826	164.255	139.830	146.554	-361.124	6.206	-.226

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

ZIRCONIUM TETRACHLORIDE ($ZrCl_4$) (IDEAL GAS) GFW = 233.032

Point Group = T_d $\Delta Hf_0^\circ = -207.46 \pm 0.2$ kcal/mol

$S^\circ_{298.15} = 88.0 \pm 0.2$ gibbs/mol $\Delta Hf^\circ_{298.15} = -207.77 \pm 0.2$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
376 (1)	418 (3)
99 (2)	110 (3)

Bond Distance: Zr-Cl = 2.32 ± 0.02 Å

Bond Angle: Cl-Zr-Cl = 109°28' σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 6.03177 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

The heat of formation of gaseous $ZrCl_4$, $\Delta Hf^\circ_{298} = -207.77 \pm 0.2$ kcal/mol, is calculated from the heat of formation of the crystal and the heat of sublimation derived from vapor pressure data. (See JANAF $ZrCl_4$(c) table dated Dec. 31, 1969).

Hildenbrand et al. (1) determined the equilibrium constants by the transpiration method for the reaction:

$$ZrO_2(c) + 4HCl(g) \rightarrow ZrCl_4(g) + 2H_2O(g)$$

Second and third law analyses for their data are given below:

Series	No. of Points	Temp. Range (°K)	ΔHr°_{298}(kcal/mol) 2nd law	ΔHr°_{298}(kcal/mol) 3rd law	Drift (eu)	$\Delta Hf^\circ_{298}(g)$* (kcal/mol)
I	10	1171-1375	28.853	29.321	0.29±0.34	-205.6
II	9	1169-1374	31.397	30.007	-1.08±0.47	-205.0

*Derived from third law ΔHr°_{298} and $\Delta Hf^\circ_{298}(ZrO_2, c) = -262.3$ kcal/mol, $\Delta Hf^\circ_{298}(HCl, g) = -22.063$ kcal/mol and $\Delta Hf^\circ_{298}(H_2O, g) = -57.796$ kcal/mol.

The derived heat of formation is in fair agreement with the value adopted.

Heat Capacity and Entropy

Spiridonov et al. (2) measured the bond distance Zr-Cl = 2.32 ± 0.02 Å in the vapor phase by electron diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton (3) and Kimura et al. (4). The three principal moments of inertia are $I_A = I_B = I_C = 84.4942 \times 10^{-39}\ g\ cm^2$.

Wilmshurst (5) observed one fundamental vibrational frequency ($\nu_3 = 421\ cm^{-1}$) in the infrared spectrum of $ZrCl_4$ vapor, and made reasonable estimates ($\nu_1 = 388$, $\nu_2 = 102$ and $\nu_4 = 112\ cm^{-1}$) for the three remaining unobserved fundamentals, based on observed overtone and combination bands. Godnev et al. (6) calculated the four fundamental vibrational frequencies (382, 108, 423 and 114 cm^{-1}) from data for related group IV halides through the use of a 5-parameter potential function. Büchler et al. (7) also found in the infrared spectrum the vibrational frequency, $\nu_3 = 423\ cm^{-1}$. Delwaulle and Francois (8) observed the symmetric stretching vibration ν_1 at 383 cm^{-1} from the Raman spectrum of $ZrCl_4$ in PCl_5 and $POCl_3$, both of which form complexes with $ZrCl_4$. Bobovich (9) reported the symmetric stretching vibration ν_1 at 315 cm^{-1} from a partially polarized band in his Raman spectrometric studies.

Pontrelli (10) observed in the Raman spectrum all four fundamental vibrational frequencies (376, 99, 418 and 110 cm^{-1}) which are adopted in the tabulation.

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Molybdenum Pentachloride ($MoCl_5$)

(Crystal) GFW = 273.205

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	37.200	57.000	57.000	.000	- 126.000	- 101.236	74.208
300	37.220	57.230	57.001	.069	- 125.980	- 101.083	73.639
400	40.000	68.320	58.494	3.931	- 124.783	- 92.960	50.791
500	42.700	77.538	61.405	8.066	- 123.396	- 85.159	37.223
600	45.400	85.569	64.777	12.476	- 121.790	- 77.658	28.287
700	47.500	92.733	68.268	17.126	- 119.978	- 70.443	21.993
800	49.000	99.178	71.736	21.954	- 118.017	- 63.502	17.348
900	50.100	105.016	75.114	26.911	- 115.942	- 56.808	13.795
1000	50.900	110.337	78.374	31.962	- 113.792	- 50.355	11.005
1100	51.580	115.221	81.505	37.088	- 111.583	- 44.117	8.765
1200	52.080	119.732	84.505	42.272	- 109.335	- 38.084	6.936
1300	52.420	123.915	87.378	47.498	- 107.065	- 32.239	5.420
1400	52.650	127.809	90.128	52.752	- 104.789	- 26.568	4.147
1500	52.800	131.447	92.763	58.025	- 102.518	- 21.059	3.068

Dec. 31, 1968

MOLYBDENUM PENTACHLORIDE ($MoCl_5$) (CRYSTAL) GFW = 273.205

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = [57 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -126 ± 2 kcal/mol

Tm = 467°K

ΔH°_m = [4.5 ± 1.5] kcal/mol

Heat of Formation

The heat of formation is obtained from S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960). The authors derived the $\Delta Hf^\circ_{298}(MoCl_5, c)$ = -126 kcal/mol by measuring the heat of solution of $MoCl_5$ in NaOH(aq), which was compared with the heats of solution of MoO_3 and NaCl measured in the same solvent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of $WCl_5(c)$. S°_{298} is estimated as 57 eu from the vapor pressure data for $MoCl_5(c) + MoCl_5(g)$ measured by S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.) 26, 2335 (1956).

Melting Data

See liquid table.

Molybdenum Pentachloride ($MoCl_5$)

(Liquid) GFW = 273.205

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	42.000	65.441	65.441	.000	- 121.921	- 99.673	73.062
300	42.000	65.701	65.442	.078	- 121.891	- 99.535	72.511
400	42.000	77.783	67.089	4.278	- 120.356	- 92.318	50.440
500	42.000	87.156	70.200	8.478	- 118.905	- 85.477	37.362
600	42.000	94.813	73.683	12.678	- 117.508	- 78.922	28.747
700	42.000	101.287	77.176	16.878	- 116.146	- 72.600	22.667
800	42.000	106.896	80.549	21.078	- 114.813	- 66.473	18.159
900	42.000	111.843	83.756	25.278	- 113.496	- 60.507	14.693
1000	42.000	116.268	86.790	29.478	- 112.197	- 54.691	11.953
1100	42.000	120.271	89.655	33.678	- 110.914	- 49.002	9.736
1200	42.000	123.925	92.360	37.878	- 109.650	- 43.431	7.910
1300	42.000	127.287	94.919	42.078	- 108.406	- 37.963	6.382
1400	42.000	130.400	97.344	46.278	- 107.184	- 32.590	5.088
1500	42.000	133.297	99.645	50.478	- 105.986	- 27.304	3.978

Dec. 31, 1968

MOLYBDENUM PENTACHLORIDE ($MoCl_5$) (LIQUID) GFW = 273.205

$S^\circ_{298.15}$ = [65.441] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-121.9205] kcal/mol

Tm = 467°K

ΔHm° = [4.5 ± 1.5] kcal/mol

Tb = 537°K

ΔHv° = [12.0] kcal/mol

Heat of Formation

The heat of formation is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and estimated as 42 gibbs/mol or 7 gibbs/g-atm. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm is taken from S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and V. K. Moksimov, Russ. J. Inorg. Chem. (English Transl.) 4, 935 (1959). ΔHm° is estimated by comparison with that of $WCl_5(c)$.

Vaporization Data

Tb is the temperature at which the difference between the Gibbs energy of formation for $MoCl_5(\ell)$ and $MoCl_5(g)$ approaches zero. The difference between $\Delta Hf^\circ_{537}(MoCl_5, \ell)$ and $\Delta Hf^\circ_{537}(MoCl_5, g)$ is ΔHv°.

Molybdenum Pentachloride ($MoCl_5$)

(Ideal Gas) GFW = 273.205

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-6.165	-106.584	-106.584	INFINITE
100	18.497	68.762	118.232	-4.947	-107.223	-102.644	224.328
200	25.708	84.166	97.581	-2.683	-107.215	-98.039	107.132
298	28.556	95.043	95.043	.000	-107.000	-93.578	68.595
300	28.590	95.220	95.043	.053	-106.996	-93.495	68.111
400	29.868	103.642	96.183	2.984	-106.730	-89.035	48.646
500	30.522	110.384	98.372	6.006	-106.456	-84.642	36.997
600	30.895	115.985	100.854	9.079	-106.187	-80.304	29.251
700	31.126	120.766	103.365	12.181	-105.923	-76.012	23.732
800	31.280	124.933	105.806	15.301	-105.669	-71.758	19.603
900	31.389	128.624	108.140	18.435	-105.418	-67.532	16.399
1000	31.470	131.935	110.357	21.578	-105.176	-63.338	13.843
1100	31.536	134.938	112.457	24.729	-104.942	-59.165	11.755
1200	31.594	137.685	114.447	27.885	-104.722	-55.014	10.019
1300	31.648	140.216	116.333	31.047	-104.516	-50.880	8.554
1400	31.701	142.563	118.124	34.215	-104.326	-46.761	7.300
1500	31.754	144.752	119.827	37.388	-104.155	-42.655	6.215
1600	31.809	146.803	121.449	40.566	-104.005	-38.560	5.267
1700	31.866	148.733	122.998	43.750	-103.873	-34.471	4.431
1800	31.924	150.556	124.479	46.939	-103.764	-30.394	3.690
1900	31.983	152.284	125.897	50.134	-103.674	-26.317	3.027
2000	32.042	153.926	127.258	53.336	-103.611	-22.249	2.431
2100	32.102	155.491	128.565	56.543	-103.567	-18.186	1.893
2200	32.162	156.985	129.824	59.756	-103.553	-14.119	1.403
2300	32.220	158.416	131.036	62.975	-103.566	-10.052	.955
2400	32.278	159.789	132.205	66.200	-103.614	-5.983	.545
2500	32.334	161.108	133.335	69.431	-103.712	-1.916	.168
2600	32.389	162.377	134.428	72.667	-103.866	2.162	-.182
2700	32.441	163.600	135.486	75.908	-104.088	6.240	-.505
2800	32.492	164.781	136.511	79.155	-104.390	10.335	-.807
2900	32.540	165.922	137.506	82.407	-111.401	14.455	-1.089
3000	32.586	167.026	138.472	85.663	-111.485	18.794	-1.369
3100	32.630	168.095	139.410	88.924	-111.571	23.139	-1.631
3200	32.671	169.132	140.323	92.189	-111.661	27.484	-1.877
3300	32.710	170.138	141.211	95.458	-111.755	31.836	-2.108
3400	32.746	171.115	142.076	98.731	-111.849	36.193	-2.326
3500	32.780	172.064	142.919	102.007	-111.951	40.540	-2.531
3600	32.812	172.988	143.742	105.287	-112.053	44.904	-2.726
3700	32.841	173.888	144.545	108.569	-112.161	49.266	-2.910
3800	32.868	174.764	145.328	111.855	-112.270	53.627	-3.084
3900	32.893	175.618	146.094	115.143	-112.385	57.999	-3.250
4000	32.916	176.451	146.843	118.433	-112.504	62.368	-3.408
4100	32.936	177.264	147.575	121.726	-112.624	66.738	-3.557
4200	32.955	178.058	148.291	125.021	-112.749	71.112	-3.700
4300	32.972	178.834	148.992	128.317	-112.876	75.490	-3.837
4400	32.986	179.592	149.679	131.615	-113.005	79.881	-3.968
4500	32.999	180.333	150.352	134.914	-113.138	84.260	-4.092
4600	33.011	181.059	151.012	138.215	-113.270	88.646	-4.212
4700	33.020	181.769	151.659	141.516	-113.406	93.040	-4.326
4800	33.028	182.464	152.293	144.819	-113.544	97.431	-4.436
4900	33.035	183.145	152.916	148.122	-113.683	101.833	-4.542
5000	33.040	183.813	153.527	151.426	-254.835	108.560	-4.745
5100	33.044	184.467	154.128	154.730	-255.247	115.842	-4.964
5200	33.047	185.109	154.717	158.034	-255.690	123.120	-5.175
5300	33.049	185.738	155.297	161.339	-256.159	130.404	-5.377
5400	33.049	186.356	155.866	164.644	-256.655	137.703	-5.573
5500	33.049	186.962	156.426	167.949	-257.172	145.014	-5.762
5600	33.047	187.558	156.977	171.254	-257.711	152.328	-5.945
5700	33.045	188.143	157.518	174.558	-258.273	159.645	-6.121
5800	33.042	188.717	158.051	177.863	-258.848	166.998	-6.293
5900	33.038	189.282	158.576	181.167	-259.442	174.335	-6.458
6000	33.033	189.837	159.092	184.470	-260.049	181.699	-6.618

Dec. 31, 1968

MOLYBDENUM PENTACHLORIDE ($MoCl_5$) (IDEAL GAS) GFW = 273.205

Point Group D_{3h}

ΔHf°_0 = -106.6 ± 1 kcal/mol

$S^\circ_{298.15}$ = [95 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -107.0 ± 1 kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[490] (1)	[350] (2)
[400] (1)	[170] (2)
[410] (1)	[100] (2)
[150] (1)	[190] (2)

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	(2)
[7000]	(2)
[14000]	(2)

Bond Distance: Mo-Cl = 2.27 ± 0.02 Å

Bond Angles: Cl*-Mo-Cl* = 120° Cl*-Mo-Cl** = 90° Cl**-Mo-Cl** = 180° σ = 6

* Equatorial ** Axial

Product of the Moments of Inertia: $I_AI_BI_C = 1.02576 \times 10^{-111}\ g^3\ cm^6$

Heat of Formation

The adopted ΔHf°_{298} = -107.0 kcal/mol is obtained from the vapor pressure data for $MoCl_5(c) = MoCl_5(g)$ measured by Shchukarev et al. (1) and Saeki and Matsuzaki (2).

Source	Method	Reaction	Temperature Range, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second law	Third law	Drift e.u.	ΔHf°_{298}* kcal/mol
Shchukarev	Transpiration	$MoCl_5(c) = MoCl_5(g)$	343 - 435	19.04 ± 0.45	19.18	0.3	-106.82
Saeki	Manometric	$MoCl_5(c) = MoCl_5(g)$	298 - 474	16.79 ± 0.06	18.94	5.6	-107.06

* Calculation based on third law ΔHr°_{298}.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of $NbCl_5$ obtained from infrared and Raman spectra by Carlson (3). Structure, bond distance and bond angle are taken from Ewens et al. (4). The three principal moments of inertia are $I_A = I_B = 106.1682 \times 10^{-39}$ and $I_C = 91.0024 \times 10^{-39}\ g\ cm^2$. The electronic levels are estimated to be 0, 7000 and 14000 cm^{-1}, all doublets, by comparison with those of $WCl_5(g)$.

Sources

1. S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.) 26, 2335-9 (1956).
2. Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155-8 (1965).
3. G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).
4. R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358-62 (1938).

Phosphorus Pentachloride (PCl_5)

(Ideal Gas) Mol. Wt. = 208.260

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-5.462	-81.027	-81.027	INFINITE
100	15.058	64.014	107.923	-4.391	-81.800	-76.755	167.739
200	22.874	77.094	89.385	-2.458	-81.988	-71.604	78.242
298	26.743	87.043	87.043	.000	-81.913	-66.519	48.758
300	26.792	87.209	87.043	.050	-81.909	-66.423	48.387
400	28.698	95.208	88.121	2.835	-81.732	-61.287	33.484
500	29.717	101.732	90.211	5.760	-81.510	-56.200	24.564
600	30.313	107.207	92.600	8.764	-81.280	-51.160	18.634
700	30.688	111.910	95.031	11.816	-81.056	-46.158	14.411
800	30.939	116.025	97.403	14.898	-101.272	-46.499	12.702
900	31.114	119.680	99.679	18.001	-100.830	-39.677	9.634
1000	31.240	122.965	101.846	21.119	-100.386	-32.909	7.192
1100	31.335	125.947	103.904	24.248	-99.941	-26.183	5.202
1200	31.407	128.677	105.856	27.385	-99.496	-19.498	3.551
1300	31.464	131.193	107.710	30.529	-99.052	-12.848	2.160
1400	31.509	133.527	109.471	33.678	-98.608	-6.233	.973
1500	31.546	135.702	111.148	36.830	-98.166	.350	-.051
1600	31.576	137.739	112.747	39.987	-97.727	6.902	-.943
1700	31.601	139.654	114.274	43.145	-97.289	13.433	-1.727
1800	31.622	141.461	115.735	46.307	-96.853	19.930	-2.420
1900	31.640	143.171	117.134	49.470	-96.419	26.411	-3.038
2000	31.655	144.794	118.477	52.634	-95.992	32.861	-3.591
2100	31.668	146.339	119.767	55.801	-95.563	39.292	-4.089
2200	31.679	147.812	121.009	58.968	-95.142	45.704	-4.540
2300	31.689	149.221	122.205	62.136	-94.722	52.098	-4.950
2400	31.698	150.570	123.359	65.306	-94.307	58.472	-5.324
2500	31.706	151.864	124.473	68.476	-93.898	64.830	-5.667
2600	31.712	153.107	125.551	71.647	-93.492	71.171	-5.982
2700	31.718	154.304	126.594	74.818	-93.094	77.495	-6.272
2800	31.724	155.458	127.604	77.990	-92.702	83.810	-6.541
2900	31.729	156.571	128.584	81.163	-92.315	90.104	-6.790
3000	31.733	157.647	129.535	84.336	-91.936	96.386	-7.021
3100	31.737	158.688	130.459	87.510	-91.564	102.658	-7.237
3200	31.741	159.695	131.357	90.684	-91.200	108.916	-7.438
3300	31.744	160.672	132.230	93.858	-90.842	115.166	-7.627
3400	31.747	161.620	133.081	97.032	-90.491	121.406	-7.804
3500	31.750	162.540	133.910	100.207	-90.149	127.628	-7.969
3600	31.752	163.435	134.717	103.382	-89.812	133.848	-8.125
3700	31.755	164.305	135.505	106.558	-89.483	140.057	-8.272
3800	31.757	165.151	136.274	109.733	-89.158	146.254	-8.411
3900	31.759	165.976	137.025	112.909	-88.842	152.450	-8.543
4000	31.761	166.780	137.759	116.085	-88.533	158.629	-8.667
4100	31.762	167.565	138.477	119.261	-88.226	164.802	-8.784
4200	31.764	168.330	139.178	122.437	-87.928	170.970	-8.896
4300	31.766	169.078	139.865	125.614	-87.632	177.127	-9.002
4400	31.767	169.808	140.537	128.791	-87.341	183.292	-9.104
4500	31.768	170.522	141.196	131.967	-87.056	189.432	-9.200
4600	31.769	171.220	141.841	135.144	86.769	195.571	-9.291
4700	31.771	171.903	142.473	138.321	-86.489	201.711	-9.379
4800	31.772	172.572	143.093	141.498	-86.212	207.835	-9.463
4900	31.773	173.227	143.702	144.676	-85.936	213.967	-9.543
5000	31.774	173.869	144.299	147.853	-85.661	220.080	-9.619
5100	31.774	174.498	144.885	151.030	-85.387	226.198	-9.693
5200	31.775	175.115	145.460	154.208	-85.115	232.304	-9.763
5300	31.776	175.721	146.025	157.386	-84.846	238.400	-9.830
5400	31.777	176.315	146.581	160.563	-84.576	244.496	-9.895
5500	31.778	176.898	147.127	163.741	-84.307	250.594	-9.957
5600	31.778	177.470	147.664	166.919	-84.039	256.674	-10.017
5700	31.779	178.033	148.191	170.096	-83.773	262.751	-10.074
5800	31.779	178.586	148.711	173.274	-83.505	268.836	-10.130
5900	31.780	179.129	149.222	176.452	-83.239	274.901	-10.182
6000	31.781	179.663	149.725	179.630	-82.974	280.975	-10.234

Dec. 31, 1960; Sept. 30, 1962

PHOSPHORUS PENTACHLORIDE (PCl_5) (IDEAL GAS) MOL. WT. = 208.260

$\Delta H_f^\circ{}_0 = -81.0 \pm 1.0$ kcal. mole⁻¹ $\Delta H_f^\circ{}_{298.15} = -81.9 \pm 1.0$ kcal. mole⁻¹

Point Group D_{3h} $S^\circ_{298.15} = 87.0$ cal. deg.⁻¹ mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹	ω, cm.⁻¹	ω, cm.⁻¹
394 (1)	394 (1)	465 (1)
[176](1)	592 (2)	335 (2)
100 (2)	280 (2)	

Bond angles: $Cl_{(equatorial)}-P-Cl_{(equatorial)} = 120°$ $Cl_{(axial)}-P-Cl_{(axial)} = 180°$ $Cl_{(axial)}-P-Cl_{(equatorial)} = 90°$

Bond distance: $P-Cl_{(equatorial)} = 2.04$ Å $P-Cl_{(axial)} = 2.19$ Å

Product of moment of inertia: $I_AI_BI_C = 6.3873 \times 10^{-112}$ g.³ cm.⁶ $\sigma = 6$

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was calculated from the $\Delta H_r^\circ{}_{298.15}$ for the reaction: $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$. Third law calculations using experimental equilibrium constants, and free energy functions from JANAF Tables gave a $\Delta H_r{}_{298.15} = -20.884$ kcal. mole⁻¹. This ΔH_r° is the average of (1) $\Delta H_r^\circ{}_{298.15} = -20.766 \pm 0.26$ kcal. mole⁻¹ and (2) $\Delta H_r^\circ{}_{298.15} = -21.001 \pm 0.24$ kcal. mole⁻¹. The first, $\Delta H_r^\circ(1)$, was obtained from eleven experimental equilibrium constants measured by C. Holland, Z. Electrochem 18, 234 (1912) as corrected by W. Nernst, Z. Electrochem. 22, 37 (1916). The second, $\Delta H_r^\circ(2)$, was obtained from thirteen experimental equilibrium constants measured by W. Fischer and O. Jübermann, Z. anorg. u. allgem. Chim. 235, 337 (1938).

For the same reaction, $PCl_3(g) + Cl_2(g) = PCl_5(g)$, a third law calculation by D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941) gave a $\Delta H_0^\circ = -21.320 \pm 0.107$ kcal. mole⁻¹. With a new assignment of fundamental frequencies J. K. Wilmshurst and H. J. Bernstein, J. Chem. Phys. 27, 661 (1957) reported a $\Delta E_0^\circ = -20.525 \pm 0.16$ kcal. mole⁻¹.

The $\Delta H_f^\circ{}_{298.15}$ values corresponding to these heats of reaction are:

$\Delta H_f^\circ{}_{298.15}$	Source
-82.9 kcal. mole⁻¹	D. P. Stevenson and D. M. Yost (loc. cit.).
-82.1 kcal. mole⁻¹	J. K. Wilmshurst and H. J. Bernstein (loc. cit.).
-81.9 kcal. mole⁻¹	Calculated using free energy functions from JANAF Tables.

Heat Capacity and Entropy.

The fundamental vibrational frequencies were assigned by Wilmshurst and Bernstein (loc. cit.) from their infrared and Raman spectral data, except the frequency, 176 cm.⁻¹, which they calculated. Electron diffraction data of M. Rouault, Ann. phys. 14, 78 (1940) and Sargent and Schomaker, (quoted in) J. Chem. Phys. 9, 403 (1941), show the free PCl_5 molecule to be a trigonal bipyramid of D_{3h} symmetry. The bond lengths were calculated from force constants and Badger's rule by Wilmshurst and Bernstein (loc. cit.). Their values are in good agreement with the electron diffraction bond lengths of M. Rouault, (loc. cit.). The calculated moments of inertia are $I_A = I_B = 93.2177 \times 10^{-39}$ g. cm.² and $I_C = 73.5053 \times 10^{-39}$ g. cm.²

Tungsten Pentachloride (WCl_5)
(Crystal) GFW = 361.115

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	37.200	52.000	52.000	.000	- 122.600	- 96.056	70.411
300	37.255	52.230	52.001	.069	- 122.580	- 95.892	69.857
400	40.018	63.326	53.495	3.933	- 121.380	- 87.172	47.629
500	42.781	72.553	56.408	8.073	- 119.973	- 78.777	34.434
600	45.400	80.591	59.782	12.485	- 118.344	- 70.687	25.748
700	47.450	87.751	63.276	17.133	- 116.513	- 62.587	19.634
800	49.000	94.194	66.745	21.959	- 114.534	- 55.363	15.124
900	50.100	100.032	70.124	26.917	- 112.443	- 48.088	11.677
1000	50.900	105.355	73.385	31.970	- 110.279	- 41.055	8.973
1100	51.580	110.239	76.516	37.095	- 108.061	- 34.240	6.803
1200	52.080	114.750	79.517	42.279	- 105.802	- 27.628	5.032
1300	52.420	118.933	82.390	47.505	- 103.517	- 21.207	3.565
1400	52.650	122.826	85.141	52.759	- 101.220	- 14.961	2.335
1500	52.800	126.464	87.776	58.032	- 98.920	- 8.879	1.294

Dec. 31, 1962; Dec. 31, 1966

TUNGSTEN PENTACHLORIDE (WCl_5) (CRYSTAL) GFW = 361.115

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [52.0] gibbs/mol

$\Delta Hf^\circ_{298.15} = -122.6 \pm 10$ kcal/mol

Tm = 526°K

$\Delta Hm^\circ = 4.917 \pm 1$ kcal/mol

$\Delta Hs^\circ_{298.15}$ = 24.0 kcal/mol

Heat of Formation.

The heat of formation, ΔHf°_{298} (WCl_5,c) = -122.6 kcal/mol, is calculated from that of the gas less the heat of sublimation, ΔHs°_{298} = 24.0 kcal/mol. The latter is calculated by the third law method from partial pressures of WCl_5(g) derived from the total pressure data* of S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4 Ser. Fiz. i Khim., No. 1, 120 (1959). Dimer pressures, calculated from the same authors' dimer-monomer dissociation data, are subtracted from the total pressures in order to obtain the monomer pressures. Analyses of the monomer pressures over both crystal and liquid give similar results and the average values for ΔHs°_{298} are 20.6 (second law) and 24.0 kcal/mol (third law) with a drift of about 7 eu.

*Earlier data reported by Shchukarev et al., Zhur. Neorg. Khim. 1, 357 (1956); 3, 2630 (1958), have been revised and are not used here.

Heat Capacity and Entropy.

Cp_{298} = 6.2 gibbs/g-atom and Cp_{526} = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 526°, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S°_{298} = 52 eu, is estimated by comparison with those of WCl_2 (c), WCl_4 (c) and WCl_6 (c).

Melting Data.

The melting point was determined from vapor pressure data by Shchukarev et al., loc. cit. The heat of melting is the difference at the melting point between the second law heats of vaporization and sublimation derived from total vapor pressure data of Shchukarev et al., loc. cit.

Heat of Sublimation.

See the heat of formation of WCl_5(g) for details.

Tungsten Pentachloride (WCl_5)

(Liquid) GFW = 361.115

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	43.500	59.393	59.393	.000	- 118.400	- 94,060	68.948
300	43.500	59.662	59,394	.080	- 118.368	- 93,910	68.413
400	43.500	72.176	61.100	4.430	- 116.682	- 86.014	46.996
500	43.500	81.883	64.322	8.780	- 115.066	- 78.535	34,327
600	43.500	89.814	67.930	13.130	- 113.499	- 71.376	25,999
700	43.500	96.520	71.547	17.480	- 111.965	- 64.477	20.131
800	43.500	102.328	75.040	21.830	- 110.463	- 57.799	15.790
900	43.500	107.452	78.362	26.180	- 108.980	- 51.303	12.458
1000	43.500	112.035	81.504	30.530	- 107.519	- 44.975	9.829
1100	43.500	116.181	84.471	34.880	- 106.076	- 38.791	7.707
1200	43.500	119.966	87.274	39.230	- 104.651	- 32.736	5.962
1300	43.500	123.446	89.924	43.580	- 103.242	- 26.801	4.506
1400	43.500	126.671	92.435	47.930	- 101.849	- 20.973	3.274
1500	43.500	129.673	94.819	52.280	- 100.472	- 15.245	2.221

Dec. 31, 1962; Dec. 31, 1966

TUNGSTEN PENTACHLORIDE (WCl_5) (LIQUID) GFW = 361.115

$S^\circ_{298.15}$ = [59.393] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -118.4 kcal/mol

Tm = 526°K

ΔHm° = 4.917 ± 1 kcal/mol

Tb = 561.4°K

ΔHv° = 16.266 kcal/mol

Heat of Formation.

The heat of formation, ΔHf°_{298} (WCl_5,l) = -118.4 kcal/mol, is calculated from that of WCl_5(c) by adding the heat of melting and the difference between $H^\circ_{526} - H^\circ_{298}$ for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom.

The entropy of WCl_5(l), $S^\circ_{298.15}$ = 59.393 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See WCl_5(c) table for details.

Vaporization Data.

The boiling point, 561.4°K, is calculated as the temperature at which the gibbs energy of formation for both WCl_5(l) and WCl_5(g) are equal. The difference in the heats of formation of WCl_5(l) and WCl_5(g) at the boiling point is the heat of vaporization. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva[1] revised their previous data[2] and derived the boiling point as 561.2°K from their vapor pressure measurements.

References:

1. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959).
2. S. A. Shchukarev and G. I. Novikov, Zhur. Neorg. Khim. 1, 357 (1956).

Tungsten Pentachloride (WCl_5)

(Ideal Gas) GFW = 361.115

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.273	-98.199	-98.199	INFINITE
100	19.093	70.239	120.387	-5.015	-98.837	-94.343	206.187
200	26.024	85.961	99.494	-2.707	-98.824	-89.825	98.156
298	28.736	96.935	96.935	.000	-98.600	-85.454	62.639
300	28.769	97.113	96.936	.053	-98.595	-85.372	62.194
400	29.979	105.576	98.082	2.998	-98.315	-81.007	44.260
500	30.596	112.339	100.280	6.030	-98.016	-76.713	33.531
600	30.947	117.951	102.771	9.108	-97.721	-72.480	26.401
700	31.166	122.740	105.290	12.215	-97.431	-68.297	21.323
800	31.311	126.911	107.737	15.339	-97.154	-64.156	17.527
900	31.413	130.605	110.077	18.476	-96.885	-60.045	14.581
1000	31.490	133.919	112.298	21.621	-96.629	-55.968	12.232
1100	31.553	136.924	114.402	24.773	-96.383	-51.915	10.315
1200	31.608	139.671	116.395	27.931	-96.150	-47.882	8.720
1300	31.660	142.204	118.284	31.095	-95.927	-43.869	7.375
1400	31.711	144.552	120.078	34.263	-95.716	-39.873	6.224
1500	31.763	146.741	121.783	37.437	-95.515	-35.890	5.229
1600	31.817	148.793	123.408	40.616	-95.325	-31.922	4.360
1700	31.873	150.723	124.958	43.800	-95.144	-27.960	3.595
1800	31.930	152.547	126.441	46.991	-94.973	-24.017	2.916
1900	31.988	154.275	127.861	50.186	-94.811	-20.076	2.309
2000	32.047	155.917	129.223	53.388	-94.661	-16.146	1.764
2100	32.107	157.482	130.532	56.596	-94.518	-12.226	1.272
2200	32.166	158.977	131.791	59.810	-94.388	-8.313	.826
2300	32.224	160.408	133.004	63.029	-94.266	-4.400	.418
2400	32.281	161.781	134.175	66.254	-94.156	-.494	.045
2500	32.337	163.100	135.306	69.485	-94.059	3.404	-.298
2600	32.392	164.369	136.399	72.722	-93.971	7.303	-.614
2700	32.444	165.593	137.458	75.964	-93.902	11.194	-.906
2800	32.494	166.773	138.484	79.211	-93.861	15.092	-1.178
2900	32.543	167.915	139.479	82.462	-93.857	18.975	-1.430
3000	32.588	169.019	140.446	85.719	-93.897	22.866	-1.666
3100	32.632	170.088	141.385	88.980	-93.992	26.759	-1.887
3200	32.673	171.125	142.298	92.245	-94.150	30.655	-2.094
3300	32.712	172.131	143.187	95.515	-94.377	34.561	-2.289
3400	32.748	173.108	144.052	98.788	-94.680	38.475	-2.473
3500	32.782	174.057	144.896	102.064	-95.078	42.395	-2.647
3600	32.814	174.981	145.719	105.344	-95.592	46.332	-2.813
3700	32.843	175.881	146.522	108.627	-104.555	50.329	-2.973
3800	32.870	176.757	147.306	111.912	-104.515	54.512	-3.135
3900	32.894	177.611	148.073	115.201	-104.479	58.701	-3.290
4000	32.917	178.444	148.821	118.491	-104.448	62.884	-3.436
4100	32.938	179.257	149.554	121.784	-104.418	67.064	-3.575
4200	32.956	180.051	150.271	125.079	-104.393	71.244	-3.707
4300	32.973	180.827	150.972	128.375	-104.369	75.424	-3.833
4400	32.987	181.585	151.659	131.673	-104.349	79.613	-3.954
4500	33.000	182.327	152.333	134.972	-104.332	83.784	-4.069
4600	33.012	183.052	152.993	138.273	-104.314	87.968	-4.179
4700	33.021	183.762	153.640	141.575	-104.300	92.153	-4.285
4800	33.029	184.457	154.275	144.877	-104.287	96.329	-4.386
4900	33.036	185.139	154.898	148.181	-104.276	100.509	-4.483
5000	33.041	185.806	155.509	151.484	-104.265	104.687	-4.576
5100	33.045	186.460	156.110	154.789	-104.253	108.873	-4.666
5200	33.048	187.102	156.699	158.093	-104.244	113.051	-4.751
5300	33.049	187.732	157.279	161.398	-104.236	117.222	-4.834
5400	33.050	188.349	157.849	164.703	-104.229	121.405	-4.914
5500	33.049	188.956	158.409	168.008	-104.221	125.585	-4.990
5600	33.048	189.551	158.960	171.313	-104.214	129.760	-5.064
5700	33.045	190.136	159.501	174.618	-104.209	133.928	-5.135
5800	33.042	190.711	160.035	177.922	-104.202	138.116	-5.204
5900	33.038	191.276	160.559	181.226	-104.198	142.289	-5.271
6000	33.034	191.831	161.076	184.530	-298.099	148.553	-5.411

Dec. 31, 1962; Dec. 31, 1966

TUNGSTEN PENTACHLORIDE (WCl_5) (IDEAL GAS) GFW = 361.116

Point Group [D_{3h}] ΔHf°_0 = -98.2 ± 8 kcal/mol

$S^\circ_{298.15}$ = [96.9] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -98.6 ± 8 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[480] (1)	[350] (2)
[400] (1)	[150] (2)
[380] (1)	[100] (2)
[130] (1)	[180] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl*-W-Cl* = [120]° Cl*-W-Cl** = [90]° Cl**-W-Cl** = [180]° σ = [6]

* Equatorial ** Axial

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.98 x 10^{-112}] g^3 cm^6

Heat of Formation.

The heat of formation, ΔHf°_{298} (WCl_5,g) = -98.6 kcal/mol, is calculated from ΔHr°_{298} = 19.4 kcal/mol for $WCl_6(g) \rightarrow WCl_5(g) + 1/2\ Cl_2(g)$. The value of ΔHr°_{298} is calculated by the third law method from the equation for log Kp given by S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). The second law ΔHr°_{298} is 24.6 kcal/mol and the third law drift is -8.5 eu.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $MoCl_5$ determined by electron diffraction by R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938). The bond distance is estimated to be the same as that in $WCl_6(g)$. The three principal moments of inertia are: $I_A = I_B = 105.23 \times 10^{-39}$ and $I_C = 90.20 \times 10^{-39}$ g cm^2.

All vibrational frequencies are estimated from those of $SbCl_5$, PCl_5, $NbCl_5$ and $TaCl_5$ obtained from infrared and Raman spectra by G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).

If it is considered that the metal atoms are effectively ionized, then the W^{5+} will have a single d electron in a field of chloride ions. The electronic splitting would be roughly the inverse of that in $CuCl_2(g)$ as given by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966), where Cu has a d^9 configuration. By analogy with the splitting in $CuCl_2$, the low lying electronic levels are estimated to be 7000 cm^{-1} and 14000 cm^{-1}, both doublets.

Iron Trichloride, Dimeric ($(FeCl_3)_2$)

(Ideal Gas) Mol. Wt. = 324.412

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-9.667	-157.335	-157.335	INFINITE
100	31.628	87.361	163.422	-7.606	-157.583	-152.469	333.206
200	39.240	112.184	132.091	-3.981	-156.965	-147.587	161.268
298	41.508	128.350	128.350	.000	-156.400	-143.110	104.897
300	41.533	128.607	128.351	.077	-156.390	-143.028	104.191
400	42.446	140.698	129.993	4.282	-155.927	-138.647	75.750
500	42.891	150.222	133.121	8.551	-155.567	-134.368	58.729
600	43.139	158.066	136.644	12.853	-155.332	-130.153	47.406
700	43.290	164.728	140.192	17.175	-155.222	-125.968	39.327
800	43.390	170.516	143.629	21.510	-155.281	-121.791	33.270
900	43.458	175.631	146.906	25.852	-155.561	-117.587	28.553
1000	43.508	180.212	150.011	30.201	-156.208	-113.341	24.769
1100	43.544	184.361	152.948	34.554	-157.296	-108.992	21.654
1200	43.572	188.151	155.726	38.909	-157.967	-104.583	19.046
1300	43.594	191.639	158.356	43.268	-157.960	-100.134	16.833
1400	43.611	194.871	160.851	47.628	-157.990	-95.684	14.936
1500	43.625	197.880	163.220	51.990	-158.052	-91.233	13.292
1600	43.637	200.696	165.475	56.353	-158.151	-86.775	11.852
1700	43.646	203.342	167.626	60.717	-158.864	-82.296	10.579
1800	43.654	205.836	169.680	65.082	-159.214	-77.782	9.444
1900	43.661	208.197	171.645	69.448	-166.938	-72.875	8.382
2000	43.666	210.437	173.529	73.814	-167.429	-67.917	7.421
2100	43.671	212.567	175.338	78.181	-167.927	-62.927	6.549
2200	43.676	214.599	177.077	82.549	-168.441	-57.916	5.753
2300	43.679	216.540	178.751	86.916	-168.967	-52.879	5.024
2400	43.683	218.399	180.364	91.284	-169.506	-47.821	4.354
2500	43.686	220.183	181.922	95.653	-170.061	-42.739	3.736
2600	43.688	221.896	183.426	100.021	-170.628	-37.635	3.163
2700	43.690	223.545	184.882	104.390	-171.211	-32.512	2.632
2800	43.692	225.134	186.291	108.760	-171.810	-27.358	2.135
2900	43.694	226.667	187.657	113.129	-172.424	-22.192	1.672
3000	43.696	228.149	188.982	117.498	-173.055	-17.004	1.239
3100	43.698	229.581	190.269	121.868	-173.702	-11.786	.831
3200	43.699	230.969	191.519	126.238	-341.216	-3.667	.250
3300	43.700	232.313	192.735	130.608	-340.971	6.879	-.456
3400	43.701	233.618	193.919	134.978	-340.748	17.418	-1.120
3500	43.702	234.885	195.071	139.348	-340.551	27.940	-1.745
3600	43.703	236.116	196.194	143.718	-340.378	38.476	-2.336
3700	43.704	237.313	197.289	148.089	-340.227	48.998	-2.894
3800	43.705	238.479	198.358	152.459	-340.101	59.503	-3.422
3900	43.706	239.614	199.401	156.830	-339.999	70.031	-3.924
4000	43.706	240.721	200.421	161.200	-339.925	80.535	-4.400
4100	43.707	241.800	201.417	165.571	-339.869	91.049	-4.853
4200	43.708	242.853	202.391	169.942	-339.842	101.553	-5.284
4300	43.708	243.882	203.344	174.313	-339.836	112.063	-5.695
4400	43.709	244.887	204.277	178.683	-339.855	122.577	-6.088
4500	43.709	245.869	205.190	183.054	-339.899	133.078	-6.463
4600	43.710	246.829	206.085	187.425	-339.961	143.600	-6.822
4700	43.710	247.770	206.962	191.796	-340.051	154.112	-7.166
4800	43.710	248.690	207.822	196.167	-340.162	164.625	-7.495
4900	43.711	249.591	208.665	200.538	-340.298	175.148	-7.812
5000	43.711	250.474	209.492	204.909	-340.454	185.661	-8.115
5100	43.712	251.340	210.304	209.281	-340.629	196.191	-8.407
5200	43.712	252.189	211.102	213.652	-340.830	206.719	-8.688
5300	43.712	253.021	211.885	218.023	-341.054	217.248	-8.958
5400	43.712	253.838	212.654	222.394	-341.300	227.785	-9.218
5500	43.713	254.640	213.410	226.765	-341.566	238.332	-9.470
5600	43.713	255.428	214.154	231.137	-341.853	248.868	-9.712
5700	43.713	256.202	214.884	235.508	-342.164	259.408	-9.946
5800	43.713	256.962	215.603	239.879	-342.494	269.986	-10.173
5900	43.714	257.709	216.311	244.251	-342.846	280.536	-10.391
6000	43.714	258.444	217.007	248.622	-343.219	291.113	-10.603

June 30, 1965

IRON TRICHLORIDE, DIMERIC (Fe_2Cl_6) (IDEAL GAS) MOL. WT. = 324.412

Point Group D_{2h}

$S^\circ_{298.15}$ = [128.35] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -157.34 ± 2.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -156.40 ± 2.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
[300] (1)	[110] (1)	[230] (1)
[200] (1)	[350] (1)	[85] (1)
[120] (1)	[100] (1)	[70] (1)
[95] (1)	[18] (1)	[260] (1)
[35] (1)	[310] (1)	[110] (1)
[250] (1)	[110] (1)	[90] (1)

Bond Distance: Fe-Cl = 2.11 ± 0.03 Å Fe-Cl_{bridge} = 2.28 ± 0.03 Å

Bond Angle: Cl-Fe-Cl = 128 ± 3° Cl_{bridge}-Fe-Cl_{bridge} = 92 ± 3° $\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 7.35910 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation.

The vaporization of $FeCl_3(c)$ is complex. It involves three possible chemical reactions, i.e. (1) $2FeCl_3(c) = Fe_2Cl_6(g)$; (2) $FeCl_3(c) = FeCl_3(g)$; and (3) $2FeCl_3(c) = 2FeCl_2(c) + Cl_2(g)$. Although these equilibria have been studied previously by many investigators, a review of their reported data reveals inconsistencies and errors. At room temperature the main vapor species present above $FeCl_3(c)$ is $Fe_2Cl_6(g)$, a dimer of $FeCl_3(g)$. As temperature increases, the dimer gradually decomposes into monomers ($FeCl_3$, g). Simultaneously, part of $FeCl_3(c)$ also decomposes into $FeCl_2(c)$ and $Cl_2(g)$. Therefore in order to obtain the partial pressure of $Fe_2Cl_6(g)$, the partial pressures of other vapor species, e.g. $Cl_2(g)$ and $FeCl_3(g)$, must be known and deducted from the observed total pressures. However, only few investigators made such corrections. The total pressures above $FeCl_3(c)$, at 500-600°K., have been determined by Maier[1] and Johnstone et al.[2], respectively. The partial pressures of $Fe_2Cl_6(g)$ were evaluated by the subtraction of the calculated equilibrium pressures of Cl_2 (g), obtained from reaction (3), from the reported total pressures. The partial pressures of $FeCl_3(g)$ were found to be insignificant at these temperatures. Using the partial pressures obtained for $Fe_2Cl_6(g)$, the enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of reaction (1) was derived by both the second and third law methods. Then the value of $\Delta H^\circ_{f\ 298.15}$ (Fe_2Cl_6, g) was calculated. The results are given in the table.

Wilson and Gregory[3] have investigated the vaporization and thermal decomposition equilibria of $FeCl_3(c)$ by gas saturation flow and diaphragm gage techniques. Using the partial pressures for $Fe_2Cl_6(g)$, calculated from an equation, the values of $\Delta H^\circ_{r\ 298.15}$ and $\Delta H^\circ_{f\ 298.15}$ were also evaluated and listed in the table. Based on the total pressures measured by Stirnemann[4] and Sano[5], the equations for the pressures of $Fe_2Cl_6(g)$ and $Cl_2(g)$ in equilibrium with $FeCl_3(c)$ and $FeCl_2(c)$ as a function of temperature were reported by Wilson and Gregory[3]. The corresponding values of $\Delta H^\circ_{r\ 298.15}$ and $\Delta H^\circ_{f\ 298.15}$ were hence calculated. A brief summary and discussion of results of some other previous investigators were also given in the same report.

		$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1}		$\Delta H^\circ_{f\ 298.15}$*
Investigator	Temperature, °K.	Second Law Value	Third Law Value	kcal. mole^{-1}
Maier[1]	489.6-591.5	32.18 ± 0.40	34.67	-156.25 ± 0.50
Johnstone, et al.[2]	505.2-562.2	34.81 ± 0.49	34.50	-156.42 ± 0.50
Wilson and Gregory[3]	463.4-577.2	34.46	34.45	-156.47 ± 0.40
Stirnemann[4]	526.2-574.2	35.04	34.49	-156.43 ± 0.50
Sano[5]	513.2-569.2	30.67	34.76	-156.16 ± 0.50

*Based on the third law values for $\Delta H^\circ_{r\ 298.15}$.

[1] C. G. Maier, U. S. Bur. Mines Tech. Paper 360 (1925).

[2] H. F. Johnstone, H. C. Weingartner and W. E. Winsche, J. Am. Chem. Soc. 64, 241 (1942).

[3] L. E. Wilson and N. W. Gregory, J. Phys. Chem. 62, 433 (1958).

[4] E. Stirnemann, Neues Jahrb. Mineral., Geol., Palaont., 52A, 334 (1925).

[5] K. Sano, J. Chem. Soc. Japan, 59, 1073 (1938).

The value of $\Delta H^\circ_{f\ 298.15}$ for $Fe_2Cl_6(g)$ is selected as -156.4 ± 2.0 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., 4, 910 (1963). The vibrational frequencies were estimated by comparison with those for $Al_2Cl_6(g)$ such that the values of ΔH° derived from the equilibrium data by the second and third law methods are in reasonable agreement. The three principal moments of inertia are: $I_A = 2.79395 \times 10^{-37}$, $I_B = 1.16349 \times 10^{-37}$ and $I_C = 2.26383 \times 10^{-37}$ g. cm.^{2}

Molybdenum Hexachloride ($MoCl_6$)

(Crystal) GFW = 308.658

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	41.900	61.000	61.000	.000	-125.000	-93.484	68.526
300	42.000	61.260	61.001	.078	-124.978	-93.289	67.961
400	46.000	73.890	62.696	4.478	-123.658	-82.918	45.304
500	50.000	84.597	66.030	9.283	-122.028	-72.913	31.870
600	53.300	94.031	69.926	14.463	-120.086	-63.267	23.045
700	54.900	102.378	73.979	19.879	-117.947	-53.966	16.849
800	55.700	109.767	77.999	25.414	-115.722	-44.980	12.288
900	55.900	116.340	81.901	30.995	-113.469	-36.269	8.807
1000	56.000	122.235	85.645	36.590	-111.222	-27.815	6.079
1100	56.100	127.577	89.218	42.195	-108.982	-19.582	3.891
1200	56.200	132.463	92.621	47.810	-106.753	-11.554	2.104
1300	56.300	136.965	95.861	53.435	-104.535	-3.711	.624
1400	56.367	141.140	98.948	59.069	-102.331	3.962	-.619
1500	56.400	145.031	101.892	64.708	-100.147	11.479	-1.672

MOLYBDENUM HEXACHLORIDE ($MoCl_6$) (CRYSTAL) GFW = 308.658

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = [61.0 ± 4.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-125 ± 10] kcal/mol

Ts = [527]°K

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. 10, 576-8 (1965), assumed that the equilibrium $MoCl_6(c) = MoCl_5(g) + 1/2\ Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, ΔH°_T = 4 kcal/mol and ΔS°_T = 8 eu, of the equilibrium $MoCl_6(c) = MoCl_5(c) + 1/2\ Cl_2(g)$, from which they obtained the $\Delta Hf^\circ_{298}(MoCl_6, c) = -125$ kcal/mol.

Heat Capacity and Entropy

The adopted heat capacity is the same as that of $WCl_6(\alpha, c)$, since the heat capacities of W and Mo are almost the same. The entropy is estimated from that of $MoCl_5(c)$ by the addition of 4 eu due to one extra chlorine atom in the molecule.

Vaporization Data

The sublimation point is calculated from the free energy crossover between crystal and gas. However, it should be noted that $MoCl_6(c)$ is unstable with respect to $MoCl_5(c)$ at all temperatures and thus sublimation could occur only under an atmosphere of Cl_2.

Molybdenum Hexachloride ($MoCl_6$)

(Ideal Gas) GFW = 308.658

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-7.423	-104.745	-104.745	INFINITE
100	22.631	68.215	128.458	-6.024	-105.551	-98.660	215.621
200	31.337	87.085	103.343	-3.252	-105.398	-91.790	100.304
298	34.446	100.272	100.272	.000	-105.000	-85.193	62.448
300	34.482	100.485	100.273	.064	-104.992	-85.071	61.974
400	35.815	110.612	101.644	3.587	-104.549	-78.497	42.889
500	36.482	118.683	104.273	7.805	-104.106	-72.034	31.486
600	36.859	125.371	107.248	10.874	-103.675	-65.660	23.917
700	37.092	131.072	110.254	14.572	-103.254	-59.358	18.533
800	37.244	136.035	113.173	18.290	-102.846	-53.118	14.511
900	37.350	140.428	115.962	22.020	-102.444	-46.924	11.395
1000	37.427	144.368	118.609	25.759	-102.053	-40.779	8.912
1100	37.483	147.938	121.116	29.504	-101.673	-34.669	6.888
1200	37.526	151.201	123.489	33.255	-101.308	-28.595	5.208
1300	37.560	154.206	125.737	37.009	-100.961	-22.550	3.791
1400	37.587	156.991	127.872	40.767	-100.633	-16.531	2.581
1500	37.609	159.585	129.900	44.527	-100.328	-10.533	1.535
1600	37.626	162.013	131.832	48.288	-100.049	-4.557	.622
1700	37.641	164.294	133.675	52.052	-99.791	1.408	-.181
1800	37.654	166.446	135.437	55.817	-99.562	7.350	-.892
1900	37.664	168.482	137.123	59.582	-99.358	13.290	-1.529
2000	37.673	170.414	138.740	63.349	-99.187	19.211	-2.099
2100	37.681	172.252	140.292	67.117	-99.040	25.124	-2.615
2200	37.687	174.006	141.785	70.885	-98.930	31.034	-3.083
2300	37.693	175.681	143.222	74.654	-98.853	36.942	-3.510
2400	37.698	177.285	144.609	78.424	-98.816	42.848	-3.902
2500	37.703	178.824	145.947	82.194	-98.837	48.747	-4.262
2600	37.707	180.303	147.240	85.965	-98.918	54.656	-4.594
2700	37.710	181.726	148.491	89.735	-99.076	60.561	-4.902
2800	37.714	183.098	149.702	93.507	-99.318	66.482	-5.189
2900	37.717	184.421	150.877	97.278	-106.276	72.425	-5.458
3000	37.719	185.700	152.017	101.050	-106.312	78.584	-5.725
3100	37.721	186.937	153.123	104.822	-106.357	84.750	-5.975
3200	37.724	188.134	154.199	108.594	-106.411	90.913	-6.209
3300	37.726	189.295	155.245	112.367	-106.473	97.083	-6.430
3400	37.727	190.421	156.263	116.139	-106.542	103.257	-6.637
3500	37.729	191.515	157.254	119.912	-106.622	109.419	-6.832
3600	37.730	192.578	158.221	123.685	-106.708	115.599	-7.018
3700	37.732	193.612	159.164	127.458	-106.803	121.777	-7.193
3800	37.733	194.618	160.083	131.231	-106.904	127.952	-7.359
3900	37.734	195.598	160.982	135.005	-107.013	134.139	-7.517
4000	37.735	196.554	161.859	138.778	-107.132	140.322	-7.667
4100	37.736	197.485	162.717	142.552	-107.253	146.507	-7.810
4200	37.737	198.395	163.555	146.326	-107.383	152.695	-7.946
4300	37.738	199.283	164.376	150.099	-107.517	158.887	-8.076
4400	37.739	200.150	165.179	153.873	-107.656	165.095	-8.200
4500	37.740	200.998	165.966	157.647	-107.801	171.287	-8.319
4600	37.740	201.828	166.736	161.421	-107.946	177.489	-8.433
4700	37.741	202.640	167.492	165.195	-108.097	183.700	-8.542
4800	37.742	203.434	168.232	168.969	-108.251	189.906	-8.647
4900	37.742	204.212	168.959	172.744	-108.407	196.126	-8.748
5000	37.743	204.975	169.671	176.518	-249.577	204.669	-8.946
5100	37.743	205.722	170.371	180.292	-250.008	213.770	-9.161
5200	37.744	206.455	171.058	184.066	-250.470	222.865	-9.367
5300	37.744	207.174	171.732	187.841	-250.959	231.966	-9.565
5400	37.745	207.880	172.395	191.615	-251.475	241.083	-9.757
5500	37.745	208.572	173.047	195.390	-252.012	250.214	-9.943
5600	37.746	209.252	173.687	199.164	-252.571	259.346	-10.121
5700	37.746	209.920	174.317	202.939	-253.152	268.481	-10.294
5800	37.746	210.577	174.937	206.714	-253.746	277.656	-10.462
5900	37.747	211.222	175.546	210.488	-254.360	286.811	-10.624
6000	37.747	211.857	176.146	214.263	-254.986	295.997	-10.782

Dec. 31, 1968

MOLYBDENUM HEXACHLORIDE ($MoCl_6$) (IDEAL GAS) GFW = 308.658

Point Group O_h

ΔHf°_0 = [-104.7 ± 20] kcal/mol

$S^\circ_{298.15}$ = [100.3 ± 4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-105.0 ± 20] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[347] (1)	[144] (3)
[326] (2)	[171] (3)
[390] (3)	[106] (3)

Bond Distance: Mo-Cl = [2.26] Å

Bond Angle: Cl-Mo-Cl = [90°] σ = 24

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.7396 x 10^{-111}] g^3 cm^6

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. 10, 576-82 (1965), assumed that the equilibrium $MoCl_6(c)$ = $MoCl_5(g)$ + 1/2 $Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, ΔH°_T = 2.5 kcal/mol and ΔS°_T = 10 eu of the equilibrium $MoCl_6(g)$ = $MoCl_5(g)$ + 1/2 $Cl_2(g)$, from which they obtained the ΔHf°_{298}($MoCl_6$, g) = -105 kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of MoF_6 and WF_6, given by K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York - London, 1963, and WCl_6 given by J. C. Evans and G. Y. S. Lo, J. Mol. Spectrosc. 26, 147 (1968).

Structure, bond distance and bond angle are estimated to be the same as those of WCl_6. The three principal moments of inertia are $I_A = I_B = I_C$ = 120.2684 x 10^{-39} g cm^2.

Tungsten Hexachloride, Alpha (α-WCl_6)
(Crystal) GFW = 396.568

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	41.926	57.000	57.000	.000	-141.900	-108.903	79.828
300	42.000	57.260	57.001	.078	-141.878	-108.699	79.187
400	46.000	69.890	58.696	4.478	-140.557	-97.831	53.452
500	50.000	82.807	62.251	10.278	-137.917	-87.441	38.221
600	53.100	92.224	66.478	15.448	-135.965	-77.525	28.238
700	54.820	100.551	70.763	20.852	-133.816	-67.953	21.216
800	55.650	107.935	74.957	26.382	-131.577	-58.699	16.036
900	55.950	114.510	78.993	31.965	-129.306	-49.723	12.074
1000	56.000	120.408	82.845	37.563	-127.044	-41.004	8.962
1100	56.000	125.745	86.506	43.163	-124.799	-32.509	6.459
1200	56.000	130.618	89.982	48.763	-122.574	-24.218	4.411
1300	56.000	135.100	93.283	54.363	-120.366	-16.110	2.708
1400	56.000	139.250	96.420	59.963	-118.175	-8.173	1.276
1500	56.000	143.114	99.405	65.563	-116.001	-.392	.057

Dec. 31, 1962; Dec. 31, 1966

Cl_6W

TUNGSTEN HEXACHLORIDE, ALPHA (α-WCl_6) (CRYSTAL) GFW = 396.568

$S^\circ_{298.15}$ = [57.0] gibbs/mol

Tt ($\alpha_1 \rightarrow \alpha_2$) = 450 ± 10°K

Tt ($\alpha_2 \rightarrow \beta$) = 503° ± 3°K

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = -141.9 ± 6 kcal/mol

ΔHt° ($\alpha_1 \rightarrow \alpha_2$) = [1.0] kcal/mol

ΔHt° ($\alpha_2 \rightarrow \beta$) = 3.77 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 23.9 kcal/mol

Heat of Formation.

S. A. Shchukarev, I. V. Vasilkova and G. I. Novikov, Zh. Neorg. Khim. 3, 2642 (1958), have measured calorimetrically the heat of solution of WCl_6(c) and also of H_2WO_4(c) in a 12% solution of NaOH as -188.0 ± 0.3 and -13.6 ± 0.11 kcal/mol, respectively. Based on these data and a heat of dilution value for Na_2WO_4 which is essentially zero, we obtain ΔHr°_{298} = -174.4 ± 0.3 kcal/mol for WCl_6(c) + 6NaOH(16.3H_2O) → H_2WO_4(c) + 6NaCl(2200$0H_2O$) + 2H_2O(l). This reaction gives ΔHf°_{298}(WCl_6,c) = -141.9 ± 6 kcal/mol, using a revised ΔHf°_{298}(H_2WO_4,c) = -270.5 kcal/mol, and other auxiliary data from JANAF Tables and from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS2, Natl. Bur. Std., Washington, D.C., April, 1965. The authors have suggested a possible uncertainty of the order of 5 kcal/mol due to the slowness of the dissolution of WCl_6(c).

Heat Capacity and Entropy.

J. R. Welty[1] has measured the enthalpy changes for WCl_6(α,c) in the temperature range from 406° to 502.4°K by drop calorimetry. Few points were measured in the region of the $\alpha_1 \rightarrow \alpha_2$ transition and no attempt was made to investigate the phase present at the conclusion of the drop. Thus, these data appear to be inadequate to define the heat capacities of the α_1 and α_2 phases. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy, S°_{298} = 57.0 eu, is calculated from that of the gas using ΔS°_{298} = 43.155 eu from the vaporization and sublimation data given in the WCl_6(g) table (December 31, 1966).

Transition Data.

Transition temperatures and heats of transition have been reported by the following investigators, and their results are summarized as follows:

		$\alpha_1 \rightarrow \alpha_2$ transition		$\alpha_2 \rightarrow \beta$ transition	
Investigator	Method	Temperature (°K)	ΔHt° (kcal/mol)	Temperature (°K)	ΔHt° (kcal/mol)
Ketelaar[2] et al.	Vapor pressure	441	-	500	3.4
Stevenson[3]	Cooling curve	458	-	503	-
	Vapor pressure	-	-	503	1.9
Welty[1]	Drop calorimetric	-	-	504	3.4
Shchukarev[4] et al.	Vapor pressure	-	-	504	3.4
Dobrotin[5]	Approximate calorimetric	-	-	493 ± 10	5.5

The adopted ΔH°_{450} ($\alpha_1 \rightarrow \alpha_2$) and ΔH°_{503} ($\alpha_2 \rightarrow \beta$) are calculated as 1.0 and 3.77 kcal/mol, respectively, based on the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is given.

Melting Data.

See WCl_6 (β,c) table (December 31, 1966).

Heat of Sublimation.

See WCl_6(g) table (December 31, 1966) for detailed information about sublimation data.

References:

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).
3. F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Fiz. i Khim. No. 1, 95 (1964).

Tungsten Hexachloride, Beta (β - WCl_6)

(Crystal) GFW = 396.568

		gibbs/mol		kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	45.000	67.066	67.066	.000	-136.921	-106.925	78.378
300	45.000	67.344	67.067	.083	-136.894	-106.739	77.759
400	45.000	80.290	68.832	4.583	-135.473	-96.906	52.947
500	45.000	90.332	72.165	9.083	-134.133	-87.419	38.211
600	45.000	98.536	75.897	13.583	-132.851	-78.197	28.483
700	45.000	105.473	79.640	18.083	-131.606	-69.187	21.601
800	45.000	111.482	83.253	22.583	-130.397	-60.357	16.489
900	45.000	116.782	86.689	27.083	-129.209	-51.670	12.547
1000	45.000	121.523	89.940	31.583	-128.045	-43.120	9.424
1100	45.000	125.812	93.009	36.083	-126.900	-34.683	6.891
1200	45.000	129.728	95.908	40.583	-125.775	-26.350	4.799
1300	45.000	133.330	98.650	45.083	-124.667	-18.110	3.045
1400	45.000	136.664	101.248	49.583	-123.576	-9.953	1.554
1500	45.000	139.769	103.714	54.083	-122.502	-1.875	.273

Dec. 31, 1966

TUNGSTEN HEXACHLORIDE, BETA (β-WCl_6) (CRYSTAL) GFW = 396.568

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [67.066] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-136.921] kcal/mol

$Tt\ (\alpha_2 \rightarrow \beta)$ = 503 ± 3°K

$\Delta Ht\ (\alpha_2 \rightarrow \beta)$ = 3.77 kcal/mol

Tm = 555 ± 2°K

ΔHm° = 1.60 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 18.921 kcal/mol

Heat of Formation.

The heat of formation, ΔHf°_{298} (WCl_6,β,c) = -136.921 kcal/mol, is calculated from that of $WCl_6(\alpha,c)$ by adding the heat of $\alpha_2 \rightarrow \beta$ transition and the difference between $H^\circ_{503} - H^\circ_{298.15}$ for $WCl_6(\alpha,c)$ and $WCl_6(\beta,c)$.

Heat Capacity and Entropy.

J. R. Welty[1] has measured the enthalpy changes for $WCl_6(\beta,c)$ in the temperature range from 508° to 553°K by drop calorimetry. Because of the short temperature range, poor distribution of points, and lack of identification of the phase present at the conclusion of each drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are consistent with the enthalpy data within their probable uncertainty.

The entropy of $WCl_6(\beta,c)$, $S^\circ_{298.15}$ = 67.066 eu, is calculated in a manner analogous to that of the heat of formation.

Transition Data.

See $WCl_6(\alpha,c)$ table (Dec. 31, 1966).

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized as follows:

Investigator	Method	Melting Point (°K)	ΔHm° (kcal/mol)
Ketelaar[2] et al.	Vapor pressure	557	2.3
Stevenson[3]	Cooling curve	555	-
	Vapor pressure	555	1.5
Welty[1]	Drop calorimetric	556	1.6
Shchukarev[4] et al.	Vapor pressure	564	2.0
Dobrotin[5] et al.	Approximate calorimetric	545 ± 12	4.2

The adopted heat of melting, ΔH°_{555} = 1.6 kcal/mol, is calculated from the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is available.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for $WCl_6(\beta,c)$ and $WCl_6(g)$.

References.

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).
3. T. D. Stevenson, Ph.D. Thesis, Oregon State University, (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No.4, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Ser. Fiz. i Khim., No. 1, 95 (1964).

Tungsten Hexachloride (WCl_6)

(Liquid) GFW = 396.568

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	48.000	68.085	68.085	.000	-136.091	-106.399	77.992
300	48.000	68.382	68.086	.089	-136.058	-106.215	77.378
400	48.000	82.191	69.969	4.889	-134.337	-96.531	52.742
500	48.000	97.902	73.524	9.689	-132.697	-87.269	38.145
600	48.000	101.653	77.505	14.489	-131.115	-78.332	28.532
700	48.000	109.052	81.497	19.289	-129.570	-69.657	21.748
800	48.000	115.462	85.351	24.089	-128.061	-61.205	16.720
900	48.000	121.115	89.017	28.889	-126.573	-52.934	12.854
1000	48.000	126.173	92.484	33.689	-125.109	-44.834	9.799
1100	48.000	130.747	95.758	38.489	-123.664	-36.876	7.327
1200	48.000	134.924	98.850	43.289	-122.239	-29.050	5.291
1300	48.000	138.766	101.775	48.089	-120.831	-21.341	3.588
1400	48.000	142.323	104.546	52.889	-119.440	-13.740	2.145
1500	48.000	145.635	107.176	57.689	-118.066	-6.238	.909

Dec. 31, 1962; Dec. 31, 1966

Cl_6W

TUNGSTEN HEXACHLORIDE (WCl_6) (LIQUID) GFW = 396.568

$S^\circ_{298.15}$ = [68.085] gibbs/mol

Tm = 555 ± 2°K

Tb = 613.6°K

$\Delta Hf^\circ_{298.15}$ = -136.091 kcal/mol

ΔHm° = 1.60 kcal/mol

ΔHv° = 14.319 kcal/mol

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298.15}(WCl_6,l)$ = -136.091 kcal/mol, is calculated from that of $WCl_6(\beta,c)$ by adding the heat of melting and the difference between $H^\circ_{555} - H^\circ_{298.15}$ for $WCl_6(\beta,c)$ and $WCl_6(l)$.

Heat Capacity and Entropy.

J. R. Welty, Ph.D. Thesis, Oregon State University (1962), has measured the enthalpy changes for $WCl_6(l)$ in the temperature range from 560° to 603°K by drop calorimetry. Since the temperature range was very short and no attempt was made to investigate the phase present at the conclusion of the drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy of $WCl_6(l)$, $S^\circ_{298.15}$ = 68.085 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See $WCl_6(\beta,c)$ table dated Dec. 31, 1966.

Vaporization Data.

The boiling point, 613.6°K, is calculated as the temperature at which the gibbs energies of formation for both $WCl_6(l)$ and $WCl_6(g)$ are equal. The difference in the heats of formation of $WCl_6(l)$ and $WCl_6(g)$ at the boiling point is the heat of vaporization.

J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943), have determined the boiling point and the heat of vaporization as 609.7°K and 15.24 kcal/mol, respectively, from vapor pressure measurements. S. A. Shchukarev and A. V. Suvorov revised their previous data[2,3] and gave the boiling point and the heat of vaporization as 616.2°K and 14.7 kcal/mol, respectively, from their vapor pressure measurements.

See $WCl_6(g)$ table, dated Dec. 31, 1966, for detailed information about vaporization data.

References:

1. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
2. S. A. Shchukarev and G. I. Novikov, Zh. Neorg. Khim. 1, 357 (1956).
3. S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and A. K. Baev, Zh. Neorg. Khim. 3, 2630 (1958).

Tungsten Hexachloride (WCl$_6$)

(Ideal Gas) GFW = 396.568

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-7.359	-117.588	-117.588	INFINITE
100	22.253	68.286	128.247	-5.996	-118.469	-111.523	243.733
200	31.228	86.997	103.221	-3.245	-118.376	-104.569	114.268
298	34.402	100.155	100.155	.000	-118.000	-97.870	71.740
300	34.439	100.368	100.156	.064	-117.992	-97.745	71.207
400	35.793	110.486	101.526	3.584	-117.551	-91.063	49.754
500	36.468	118.553	104.152	7.200	-117.095	-84.492	36.931
600	36.850	125.239	107.126	10.868	-116.645	-78.014	28.416
700	37.085	130.938	110.130	14.565	-116.203	-71.610	22.358
800	37.239	135.901	113.048	18.282	-115.777	-65.272	17.831
900	37.346	140.294	115.836	22.012	-115.359	-58.981	14.323
1000	37.423	144.233	118.482	25.750	-114.957	-52.742	11.527
1100	37.481	147.802	120.988	29.496	-114.566	-46.539	9.246
1200	37.524	151.065	123.360	33.246	-114.191	-40.370	7.352
1300	37.558	154.070	125.609	37.000	-113.829	-34.234	5.755
1400	37.585	156.855	127.742	40.758	-113.480	-28.125	4.391
1500	37.607	159.449	129.770	44.517	-113.147	-22.040	3.211
1600	37.625	161.876	131.702	48.279	-112.828	-15.975	2.182
1700	37.640	164.158	133.545	52.042	-112.523	-9.928	1.276
1800	37.653	166.310	135.306	55.807	-112.233	-3.906	.474
1900	37.663	168.346	136.992	59.573	-111.956	2.110	-.243
2000	37.672	170.278	138.608	63.339	-111.700	8.106	-.886
2100	37.680	172.116	140.160	67.107	-111.454	14.088	-1.466
2200	37.687	173.869	141.653	70.875	-111.229	20.059	-1.993
2300	37.693	175.544	143.090	74.644	-111.017	26.027	-2.473
2400	37.698	177.149	144.476	78.414	-110.822	31.980	-2.912
2500	37.702	178.688	145.814	82.184	-110.648	37.924	-3.315
2600	37.706	180.167	147.107	85.954	-110.489	43.866	-3.687
2700	37.710	181.590	148.358	89.725	-110.355	49.798	-4.031
2800	37.713	182.961	149.570	93.496	-110.256	55.734	-4.350
2900	37.716	184.285	150.744	97.268	-110.198	61.653	-4.646
3000	37.719	185.563	151.883	101.040	-110.190	67.581	-4.923
3100	37.721	186.800	152.990	104.812	-110.244	73.505	-5.182
3200	37.723	187.998	154.065	108.584	-110.366	79.432	-5.425
3300	37.725	189.159	155.111	112.356	-110.563	85.368	-5.654
3400	37.727	190.285	156.129	116.129	-110.840	91.314	-5.870
3500	37.729	191.378	157.121	119.902	-111.217	97.260	-6.073
3600	37.730	192.441	158.087	123.675	-111.714	103.227	-6.267
3700	37.732	193.475	159.030	127.448	-120.665	109.253	-6.453
3800	37.733	194.481	159.950	131.221	-120.616	115.463	-6.641
3900	37.734	195.462	160.848	134.994	-120.576	121.677	-6.819
4000	37.735	196.417	161.725	138.768	-120.544	127.888	-6.987
4100	37.736	197.349	162.582	142.541	-120.516	134.094	-7.148
4200	37.737	198.258	163.421	146.315	-120.496	140.303	-7.301
4300	37.738	199.146	164.242	150.089	-120.479	146.512	-7.447
4400	37.739	200.014	165.045	153.863	-120.468	152.728	-7.586
4500	37.740	200.862	165.831	157.636	-120.464	158.928	-7.719
4600	37.740	201.691	166.602	161.410	-120.459	165.142	-7.846
4700	37.741	202.503	167.357	165.184	-120.460	171.354	-7.968
4800	37.742	203.297	168.098	168.959	-120.463	177.559	-8.084
4900	37.742	204.076	168.824	172.733	-120.470	183.771	-8.197
5000	37.743	204.838	169.537	176.507	-120.477	189.978	-8.304
5100	37.743	205.586	170.236	180.281	-120.484	196.191	-8.407
5200	37.744	206.318	170.923	184.056	-120.493	202.406	-8.507
5300	37.744	207.037	171.598	187.830	-120.506	208.608	-8.602
5400	37.745	207.743	172.261	191.605	-120.518	214.816	-8.694
5500	37.745	208.436	172.912	195.379	-120.531	221.030	-8.783
5600	37.745	209.116	173.552	199.154	-120.543	227.233	-8.868
5700	37.746	209.784	174.182	202.928	-120.559	233.434	-8.950
5800	37.746	210.440	174.802	206.703	-120.571	239.661	-9.031
5900	37.746	211.085	175.411	210.477	-120.587	245.868	-9.108
6000	37.747	211.720	176.011	214.252	-314.506	254.162	-9.258

Dec. 31, 1962; Dec. 31, 1966

TUNGSTEN HEXACHLORIDE (WCl$_6$) (IDEAL GAS) GFW = 396.568

Point Group O_h
$S^\circ_{298.15}$ = [100.2] gibbs/mol
Ground State Quantum Weight = 1

ΔHf°_0 = -117.6 ± 6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -118.0 ± 6 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[360] (1)	[140] (3)
[340] (2)	[180] (3)
375 (3)	[120] (3)

Bond Distance: W-Cl = 2.26 Å
Bond Angle: Cl-W-Cl = 90° σ = 24
Product of the Moments of Inertia: $I_A I_B I_C = 1.7396 \times 10^{-111}\ g^3\ cm^6$

Heats of Formation.

The heat of formation of WCl$_6$(g), ΔHf°_{298} = -118.0 kcal/mol, is calculated from that of the crystal plus the adopted heat of sublimation, ΔHs°_{298} = 23.9 kcal/mol for $WCl_6(\alpha,c) \rightarrow WCl_6(g)$. The latter was obtained from third law analysis of the vapor pressure data [1,2,3,4], using all JANAF functions (Dec. 31, 1966).

Investigator	Phase Studied	Temp. range (°K)	No. of Points	ΔHs°_{298} (kcal/mol) 2nd law	3rd law	Drift (eu)	$\Delta Hf^\circ_{298}(WCl_6,g)$*** (kcal/mol)
Stevenson[1]	α, c	462 - 502	38	20.9 ± 0.5	23.74	6.2 ± 1.0	-118.16
	β*, c	503 - 551	15	23.1 ± 0.2	23.89	1.5 ± 0.3	-118.01
	l*	557 - 598	13	24.2 ± 0.1	23.89	-0.6 ± 0.1	-118.01
Shchukarev[2] et al.	α, c	**	-	22.0	23.80	4.0	-118.10
	β*, c		-	23.8	23.98	0.4	-117.92
	l*		-	24.1	23.98	-0.2	-117.92
Ketelaar[3] et al.	α, c	425 - 500	21	23.1 ± 0.1	23.94	1.7 ± 0.4	-117.96
	β*, c	504 - 554	21	24.4 ± 0.1	23.91	-0.8 ± 0.1	-117.99
	l*	523 - 635	21	24.4 ± 0.1	23.85	-1.0 ± 0.1	-118.05
Vernon[4]	α, c	298 - 423	4	16.1 ± 4.1	21.02	10.8 ± 12.8	-120.88

A. A. Vernon[4] has also determined the equilibrium constants in the temperature range from 1360° to 1600°K for the decomposition of WCl$_6$(g) to W(c) and Cl$_2$(g) by reaction of the sample with a hot tungsten filament in a vacuum bulb. Using the reported equilibrium constants, the heat of formation of WCl$_6$(g) at 298°K is calculated by the second and third law method as -131.8 ± 2.9 kcal/mol and -135.2 kcal/mol, respectively. The third law drift is 2.4 ± 1.9 eu. Unfortunately, the reported equilibrium constants may be seriously in error, since atomic chlorine is the main species at the pressure and temperature studied.

* Enthalpy changes are converted to ΔHs°_{298} for $WCl_6(\alpha, c) \rightarrow WCl_6(g)$.

** Vapor pressure equations for the crystal (α,β) and the liquid to gas are given.

*** The third law ΔHs°_{298} is used in calculation.

References:

1. F. D. Stevenson, Ph.D Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
2. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Previous vapor pressure measurements, cited in Zh. Neorg. Khim. 1, 357 (1956) and 3, 2630 (1958), have been revised and are not used as references here.
3. J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).
4. A. A. Vernon, J. Am. Chem. Soc. 59, 1832 (1937).

Cl_6W

Heat Capacity and Entropy.

R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938), have determined the octahedral structure for WCl$_6$(g) by electron diffraction and found the bond length to be 2.26A.

The vibrational frequency of ν_3, 375 cm^{-1}, was observed in the infrared spectra by J. C. Evans, The Dow Chemical Company, private communication, Dec. 1, 1966. The values of ν_1, ν_2 and ν_5 (360, 340 and 180 cm^{-1}, respectively) are estimated, based on those of the aqueous ion $PtCl_6^{2-}$ reported by L. A. Woodward and J. A. Creighton, Spectrochim. Acta 17, 594 (1961). The values of ν_4 and ν_6 (140 and 120 cm^{-1}, respectively) are estimated by comparison with those of WF$_6$(g).

The three principal moments of inertia are $I_A = I_B = I_C = 120.2684 \times 10^{-39}$ g cm^2.

Tungsten Pentachloride, Dimeric (W_2Cl_{10})

(Ideal Gas) GFW = 722.230

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 14.438	- 208.690	- 208.690	INFINITE
100	47.951	108.851	223.358	- 11.451	- 209.495	- 197.345	431.298
200	58.922	146.124	176.176	- 6.010	- 208.644	- 185.489	202.692
298	62.969	170.521	170.521	.000	- 207.600	- 174.346	127.799
300	63.017	170.911	170.522	.117	- 207.580	- 174.140	126.861
400	64.828	189.319	173.020	6.520	- 206.505	- 163.157	89.145
500	65.754	203.895	177.788	13.053	- 205.439	- 152.441	66.632
600	66.283	215.934	183.172	19.658	- 204.401	- 141.939	51.701
700	66.612	226.178	188.602	26.304	- 203.387	- 131.609	41.090
800	66.830	235.088	193.868	32.976	- 202.411	- 121.427	33.172
900	66.981	242.969	198.894	39.667	- 201.454	- 111.357	27.041
1000	67.090	250.032	203.661	46.371	- 200.528	- 101.401	22.161
1100	67.171	256.430	208.172	53.084	- 199.628	- 91.533	18.186
1200	67.233	262.278	212.441	59.805	- 198.757	- 81.744	14.888
1300	67.281	267.661	216.484	66.531	- 197.913	- 72.027	12.109
1400	67.320	272.649	220.320	73.261	- 197.097	- 62.375	9.737
1500	67.351	277.295	223.965	79.994	- 196.310	- 52.779	7.690
1600	67.377	281.642	227.435	86.731	- 195.551	- 43.234	5.906
1700	67.398	285.728	230.745	93.469	- 194.820	- 33.731	4.336
1800	67.416	289.580	233.908	100.210	- 194.118	- 24.281	2.948
1900	67.431	293.226	236.935	106.953	- 193.441	- 14.857	1.709
2000	67.444	296.685	239.837	113.696	- 192.803	- 5.475	.598
2100	67.455	299.976	242.623	120.441	- 192.187	3.871	- .403
2200	67.465	303.114	245.302	127.187	- 191.609	13.189	- 1.310
2300	67.473	306.113	247.881	133.934	- 191.057	22.494	- 2.137
2400	67.480	308.985	250.367	140.682	- 190.538	31.769	- 2.893
2500	67.487	311.740	252.768	147.430	- 190.058	41.017	- 3.586
2600	67.493	314.387	255.087	154.179	- 189.606	50.255	- 4.224
2700	67.498	316.934	257.331	160.929	- 189.202	59.470	- 4.814
2800	67.502	319.389	259.504	167.679	- 188.865	68.681	- 5.361
2900	67.506	321.758	261.610	174.429	- 188.610	77.862	- 5.868
3000	67.510	324.046	263.653	181.180	- 188.451	87.051	- 6.342
3100	67.514	326.260	265.637	187.931	- 188.413	96.229	- 6.784
3200	67.517	328.403	267.565	194.683	- 188.507	105.413	- 7.199
3300	67.519	330.481	269.440	201.434	- 188.749	114.604	- 7.590
3400	67.522	332.497	271.265	208.187	- 189.149	123.807	- 7.958
3500	67.524	334.454	273.043	214.939	- 189.746	133.010	- 8.306
3600	67.527	336.356	274.775	221.691	- 190.581	142.250	- 8.636
3700	67.529	338.207	276.465	228.444	- 208.320	151.601	- 8.955
3800	67.530	340.007	278.114	235.197	- 208.057	161.322	- 9.278
3900	67.532	341.762	279.723	241.950	- 207.809	171.045	- 9.585
4000	67.534	343.471	281.296	248.703	- 207.576	180.756	- 9.876
4100	67.535	345.139	282.832	255.457	- 207.347	190.455	- 10.152
4200	67.536	346.766	284.335	262.210	- 207.134	200.153	- 10.415
4300	67.538	348.356	285.806	268.964	- 206.925	209.844	- 10.665
4400	67.539	349.908	287.245	275.718	- 206.726	219.550	- 10.905
4500	67.540	351.426	288.655	282.472	- 206.537	229.220	- 11.132
4600	67.541	352.911	290.035	289.226	- 206.348	238.904	- 11.351
4700	67.542	354.363	291.389	295.980	- 206.169	248.594	- 11.560
4800	67.543	355.785	292.715	302.734	- 205.995	258.257	- 11.759
4900	67.544	357.178	294.017	309.489	- 205.825	267.936	- 11.950
5000	67.544	358.542	295.294	316.243	- 205.656	277.599	- 12.134
5100	67.545	359.880	296.547	322.998	- 205.486	287.270	- 12.310
5200	67.546	361.192	297.778	329.752	- 205.322	296.930	- 12.480
5300	67.546	362.478	298.986	336.507	- 205.162	306.579	- 12.642
5400	67.547	363.741	300.174	343.261	- 205.003	316.232	- 12.799
5500	67.548	364.980	301.341	350.016	- 204.843	325.896	- 12.950
5600	67.548	366.197	302.488	356.771	- 204.683	335.532	- 13.095
5700	67.549	367.393	303.616	363.526	- 204.528	345.157	- 13.234
5800	67.549	368.568	304.726	370.281	- 204.368	354.821	- 13.370
5900	67.550	369.722	305.818	377.036	- 204.213	364.458	- 13.500
6000	67.550	370.858	306.893	383.791	- 591.866	378.262	- 13.778

Dec. 31, 1966

TUNGSTEN PENTACHLORIDE, DIMERIC (W_2Cl_{10}) (IDEAL GAS) GFW = 722.230

Point Group [D_{2h}]

$S^\circ_{298.15}$ = [170] gibbs/mol

Ground State Quantum Weight = [3]

ΔHf°_0 = -208.7 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -207.6 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[500] (2)	[150] (2)	[90] (2)
[400] (2)	[125] (4)	[80] (2)
[350] (2)	[100] (6)	[60] (4)
[250] (2)		[40] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl*-W-Cl* = [90]° W-Cl*$_{bridge}$-W = [90]° σ = [4]

Cl**-W-Cl** = [180]° Cl*-W-Cl** = [90]°

*Equatorial **Axial

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.638] x 10^{-110} g^3 cm^6

Heat of Formation.

The heat of formation, ΔHf°_{298} (W_2Cl_{10},g) = -207.6 kcal/mol, is calculated from ΔHr°_{298} = 10.4 kcal/mol for W_2Cl_{10}(g) = 2 WCl_5(g), using all JANAF functions (Dec. 31, 1966). The value of ΔHr°_{298} is obtained from third law analysis of the partial pressures of WCl_5(g) and W_2Cl_{10}(g) derived from PVT data determined by S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔHr°_{298} is 10.4 ± 0.3 kcal/mol.

Heat Capacity and Entropy.

The molecular configuration is estimated by analogy with that of Mo_2Cl_{10} reported by D. Z. Sands and A. Zalkin, Acta Cryst. 12, 723 (1959). Chlorine atoms are placed octahedrally around two tungsten atoms and these two octahedra share one common edge with six chlorine and two tungsten atoms in a plane. The bond length is estimated to be the same as that in WCl_6(g). The three principal moments of inertia are I_A = 210.5 x 10^{-39}, I_B = 576.8 x 10^{-39} and I_C = 546.8 x 10^{-39} g cm^2.

All vibrational frequencies are estimated, based on those of WCl_5, $(AlCl_3)_2$ and Cs_2Cl_2, such that $S^\circ_{607}(W_2Cl_{10},g)$ = 216.65 eu. This entropy is derived from ΔS°_{607} = 19.92 ± 0.5 eu for $W_2Cl_{10}(g)$ = $2WCl_5(g)$, obtained by second law analysis of the data of Shchukarev et al., loc. cit. The frequencies are not in point group order.

Cobalt (Co)

(Reference State) GFW = 58.9332

T, °K	C_p° (gibbs/mol)	S° (gibbs/mol)	$-(G^\circ-H^\circ_{298})/T$ (gibbs/mol)	$H^\circ-H^\circ_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 1.139	.000	.000	.000
100	3.330	1.840	11.990	- 1.015	.000	.000	.000
200	5.340	4.920	7.710	- .558	.000	.000	.000
298	5.930	7.180	7.180	.000	.000	.000	.000
300	5.937	7.217	7.180	.011	.000	.000	.000
400	6.340	8.980	7.418	.625	.000	.000	.000
500	6.740	10.439	7.880	1.279	.000	.000	.000
600	7.090	11.699	8.414	1.971	.000	.000	.000
700	7.420	12.817	8.964	2.897	.000	.000	.000
800	7.750	13.975	9.529	3.557	.000	.000	.000
900	8.250	14.916	10.075	4.356	.000	.000	.000
1000	8.840	15.815	10.605	5.210	.000	.000	.000
1100	9.520	16.688	11.118	6.127	.000	.000	.000
1200	10.330	17.548	11.618	7.115	.000	.000	.000
1300	11.630	18.424	12.108	8.211	.000	.000	.000
1400	10.570	19.337	12.592	9.443	.000	.000	.000
1500	9.500	20.021	13.065	10.435	.000	.000	.000
1600	9.150	20.622	13.519	11.365	.000	.000	.000
1700	9.030	21.172	13.953	12.272	.000	.000	.000
1800	9.680	23.889	14.407	17.067	.000	.000	.000
1900	9.680	24.413	14.920	18.035	.000	.000	.000
2000	9.680	24.909	15.407	19.003	.000	.000	.000
2100	9.680	25.381	15.871	19.971	.000	.000	.000
2200	9.680	25.832	16.314	20.939	.000	.000	.000
2300	9.680	26.262	16.737	21.907	.000	.000	.000
2400	9.680	26.674	17.143	22.875	.000	.000	.000
2500	9.680	27.069	17.532	23.843	.000	.000	.000
2600	9.680	27.449	17.906	24.811	.000	.000	.000
2700	9.680	27.814	18.266	25.779	.000	.000	.000
2800	9.680	28.166	18.613	26.747	.000	.000	.000
2900	9.680	28.506	18.949	27.715	.000	.000	.000
3000	9.680	28.834	19.273	28.683	.000	.000	.000
3100	9.680	29.151	19.586	29.651	.000	.000	.000
3200	6.300	57.569	20.151	119.737	.000	.000	.000
3300	6.308	57.763	21.288	120.368	.000	.000	.000
3400	6.319	57.952	22.364	120.999	.000	.000	.000
3500	6.333	58.135	23.383	121.632	.000	.000	.000
3600	6.351	58.314	24.351	122.266	.000	.000	.000
3700	6.372	58.488	25.271	122.902	.000	.000	.000
3800	6.396	58.658	26.148	123.540	.000	.000	.000
3900	6.423	58.825	26.983	124.181	.000	.000	.000
4000	6.453	58.988	27.781	124.825	.000	.000	.000
4100	6.487	59.147	28.544	125.472	.000	.000	.000
4200	6.523	59.304	29.275	126.122	.000	.000	.000
4300	6.563	59.456	29.975	126.777	.000	.000	.000
4400	6.605	59.609	30.647	127.435	.000	.000	.000
4500	6.650	59.758	31.292	128.098	.000	.000	.000
4600	6.697	59.905	31.913	128.765	.000	.000	.000
4700	6.746	60.050	32.510	129.437	.000	.000	.000
4800	6.798	60.192	33.085	130.114	.000	.000	.000
4900	6.852	60.333	33.640	130.797	.000	.000	.000
5000	6.907	60.472	34.175	131.485	.000	.000	.000
5100	6.965	60.609	34.692	132.178	.000	.000	.000
5200	7.024	60.745	35.192	132.878	.000	.000	.000
5300	7.085	60.879	35.675	133.583	.000	.000	.000
5400	7.147	61.012	36.143	134.295	.000	.000	.000
5500	7.210	61.144	36.596	135.013	.000	.000	.000
5600	7.275	61.275	37.036	135.737	.000	.000	.000
5700	7.340	61.404	37.462	136.468	.000	.000	.000
5800	7.406	61.532	37.876	137.205	.000	.000	.000
5900	7.474	61.659	38.278	137.949	.000	.000	.000
6000	7.541	61.786	38.669	138.700	.000	.000	.000

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COBALT (Co) (REFERENCE STATE) GFW = 58.9332

0 to 700°K Crystal alpha
700 to 1768°K Crystal beta
1768 to 3170°K Liquid
3170 to 6000°K Ideal Monatomic gas

See crystal, liquid and monatomic gas tables for details.

Cobalt (Co)

(Crystal) GFW = 58.9332

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.139	.000	.000	.000
100	3.330	1.840	11.990	-1.015	.000	.000	.000
200	5.340	4.920	7.710	-.558	.000	.000	.000
298	5.930	7.180	7.180	.000	.000	.000	.000
300	5.937	7.217	7.180	.011	.000	.000	.000
400	6.340	8.980	7.418	.625	.000	.000	.000
500	6.740	10.439	7.880	1.279	.000	.000	.000
600	7.090	11.699	8.414	1.971	.000	.000	.000
700	7.420	12.817	8.964	2.697	.000	.000	.000
800	7.750	13.975	9.529	3.557	.000	.000	.000
900	8.250	14.916	10.075	4.356	.000	.000	.000
1000	8.840	15.815	10.605	5.210	.000	.000	.000
1100	9.520	16.688	11.118	6.127	.000	.000	.000
1200	10.330	17.548	11.618	7.115	.000	.000	.000
1300	11.630	18.424	12.108	8.211	.000	.000	.000
1400	10.570	19.337	12.592	9.443	.000	.000	.000
1500	9.500	20.021	13.065	10.435	.000	.000	.000
1600	9.150	20.622	13.519	11.365	.000	.000	.000
1700	9.030	21.172	13.953	12.272	.000	.000	.000
1800	9.000	21.688	14.368	13.176	-3.891	.070	-.009
1900	9.000	22.175	14.766	14.076	-3.959	.293	-.034
2000	9.000	22.636	15.148	14.976	-4.027	.519	-.057
2100	9.000	23.075	15.516	15.876	-4.095	.747	-.078
2200	9.000	23.494	15.869	16.776	-4.163	.980	-.097
2300	9.000	23.894	16.209	17.676	-4.231	1.215	-.115
2400	9.000	24.277	16.537	18.576	-4.299	1.453	-.132
2500	9.000	24.645	16.854	19.476	-4.367	1.693	-.148

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COBALT (Co) (CRYSTAL) GFW = 58.9332

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 7.18 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Tt = [700°] K

ΔHt° = 0.108 kcal/mol

Tm = 1768°K

ΔHm° = 3.87 ± 0.06 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 101.5 ± 0.5 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity of Co(c) is adopted from Hultgren et al. (1). Their selected values are based on the data from nineteen investigations. The entropy values are based on S°_1 = 0.0011 eu. The heat capacity has a maximum value of 13.14 gibbs/mol at the Curie point (1394°K).

Transition Data

The exact nature of the α(hcp)-β(fcc) transition is yet to be clearly elucidated. Three investigations (2,3,4) indicate that it is not a simple time- and temperature-dependent phenomenon. Crystalline cobalt exists as pure β-phase above 700°K whereas mixtures of alpha and beta cobalt commonly coexist in varying proportions below this temperature. The values of Tt° and ΔHt° are those selected by Hultgren et al. (1).

Melting Data

The temperature and heat of melting are those selected by Hultgren et al. (1).

Heat of Sublimation

The heat of sublimation is calculated from the data of Edwards et al. (5). See Co(g) table for details.

References

1. R. Hultgren, R. L. Orr and K. K. Kelley "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif., (1966).
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4. P. R. Rao, Proc. Indian Acad. Sci. Sect. A, 61, 230 (1965).
5. J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 73, 4729 (1951).

Cobalt (Co)

(Liquid) GFW = 58.9332

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.930	9.793	9.793	.000	4.303	3.524	-2.583
300	5.937	9.830	9.793	.011	4.303	3.519	-2.564
400	6.340	11.593	10.031	.625	4.303	3.258	-1.780
500	6.740	13.052	10.493	1.279	4.303	2.997	-1.310
600	7.090	14.312	11.027	1.971	4.303	2.735	-.996
700	7.380	15.426	11.577	2.694	4.300	2.473	-.772
800	7.750	16.434	12.122	3.450	4.195	2.228	-.609
900	8.250	17.375	12.654	4.249	4.196	1.982	-.481
1000	8.840	18.274	13.172	5.103	4.195	1.736	-.379
1100	9.520	19.148	13.675	6.020	4.196	1.490	-.296
1200	9.560	19.978	14.166	6.974	4.162	1.246	-.227
1300	9.600	20.745	14.643	7.932	4.024	1.007	-.169
1400	9.640	21.458	15.105	8.894	3.754	.785	-.122
1500	9.680	22.124	15.551	9.860	3.728	.574	-.084
1600	9.680	22.749	15.981	10.828	3.766	.363	-.050
1700	9.680	23.336	16.397	11.796	3.827	.148	-.019
1800	9.680	23.889	16.798	12.764	.000	.000	.000
1900	9.680	24.412	17.185	13.732	.000	.000	.000
2000	9.680	24.909	17.559	14.700	.000	.000	.000
2100	9.680	25.381	17.920	15.668	.000	.000	.000
2200	9.680	25.832	18.270	16.636	.000	.000	.000
2300	9.680	26.262	18.608	17.604	.000	.000	.000
2400	9.680	26.674	18.935	18.572	.000	.000	.000
2500	9.680	27.069	19.253	19.540	.000	.000	.000
2600	9.680	27.449	19.561	20.508	.000	.000	.000
2700	9.680	27.814	19.860	21.476	.000	.000	.000
2800	9.680	28.166	20.150	22.444	.000	.000	.000
2900	9.680	28.506	20.433	23.412	.000	.000	.000
3000	9.680	28.834	20.707	24.380	.000	.000	.000
3100	9.680	29.151	20.974	25.348	.000	.000	.000
3200	9.680	29.459	21.235	26.316	-89.118	.836	-.057
3300	9.680	29.757	21.489	27.284	-88.781	3.641	-.241
3400	9.680	30.045	21.736	28.252	-88.444	6.437	-.414
3500	9.680	30.326	21.977	29.220	-88.109	9.222	-.576
3600	9.680	30.599	22.213	30.188	-87.775	11.999	-.728
3700	9.680	30.864	22.443	31.156	-87.443	14.766	-.872
3800	9.680	31.122	22.668	32.124	-87.113	17.524	-1.008
3900	9.680	31.374	22.888	33.092	-86.786	20.273	-1.136
4000	9.680	31.619	23.104	34.060	-86.462	23.014	-1.257

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COBALT (Co) (LIQUID) GFW = 58.9332

$S^\circ_{298.15}$ = 9.79 gibbs/mol

Tm = 1768°K

Tb = 3170.29°K

$\Delta Hf^\circ_{298.15}$ = 4.303 ± 0.1 kcal/mol

ΔHm° = 3.87 ± 0.06 kcal/mol

ΔHv° = 89.219 kcal/mol

Heat of Formation

The heat of formation (ΔHf°_{298}) of Co(ℓ) is obtained from that of the crystal by adding ΔHm° and the differences between H_{1768}-H_{298} for crystal and liquid.

Heat Capacity and Entropy

The heat capacity of Co(ℓ) selected by Hultgren et al. (1) is used at temperatures above 1768°K. The heat capacities at temperatures below the melting point are estimated by assuming a glass transition at 1100°K and heat capacities similar to those of the crystal below 1100°K.

Melting Data

See Co(c) table for details.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K so that the free energy functions calculated by integration of the crystal liquid data and by statistical methods from the gas phase are equal at the boiling point.

Reference

1. R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif. (1966).

Cobalt (Co)

(Ideal Gas) GFW = 58.9332

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.520	101.119	101.119	INFINITE
100	4.970	37.290	47.521	- 1.023	101.492	97.947	- 214.063
200	5.127	40.764	43.369	- .521	101.537	94.368	- 103.121
298	5.503	42.879	42.879	.000	101.500	90.857	- 66.600
300	5.510	42.913	42.879	.010	101.499	90.791	- 66.141
400	5.857	44.546	43.100	.579	101.455	87.227	- 47.659
500	6.077	45.881	43.527	1.177	101.399	83.677	- 36.575
600	6.188	47.000	44.015	1.791	101.321	80.140	- 29.191
700	6.236	47.958	44.512	2.413	101.216	76.617	- 23.921
800	6.259	48.793	44.996	3.038	100.981	73.127	- 19.977
900	6.274	49.531	45.459	3.664	100.809	69.655	- 16.915
1000	6.291	50.193	45.900	4.292	100.583	66.205	- 14.469
1100	6.309	50.793	46.318	4.922	100.298	62.780	- 12.473
1200	6.329	51.343	46.714	5.554	99.940	59.386	- 10.816
1300	6.347	51.850	47.090	6.188	99.477	56.023	- 9.418
1400	6.363	52.321	47.447	6.824	98.881	52.703	- 8.227
1500	6.375	52.761	47.787	7.461	98.526	49.417	- 7.200
1600	6.383	53.172	48.111	8.099	98.234	46.153	- 6.304
1700	6.386	53.559	48.420	8.737	97.965	42.906	- 5.516
1800	6.385	53.924	48.716	9.376	93.809	39.745	- 4.826
1900	6.381	54.270	48.999	10.014	93.479	36.751	- 4.227
2000	6.374	54.597	49.271	10.652	93.149	33.774	- 3.691
2100	6.365	54.908	49.532	11.289	92.818	30.813	- 3.207
2200	6.355	55.203	49.783	11.925	92.486	27.868	- 2.768
2300	6.343	55.486	50.025	12.560	92.153	24.938	- 2.370
2400	6.332	55.755	50.258	13.193	91.819	22.023	- 2.005
2500	6.322	56.014	50.483	13.826	91.483	19.122	- 1.672
2600	6.312	56.261	50.701	14.458	91.147	16.234	- 1.365
2700	6.304	56.499	50.911	15.089	90.810	13.359	- 1.081
2800	6.298	56.729	51.115	15.719	90.472	10.497	- .819
2900	6.294	56.950	51.312	16.348	90.134	7.647	- .576
3000	6.293	57.163	51.504	16.978	89.795	4.808	- .350
3100	6.295	57.369	51.690	17.607	89.456	1.981	- .140
3200	6.300	57.569	51.870	18.237	.000	.000	.000
3300	6.308	57.763	52.046	18.867	.000	.000	.000
3400	6.319	57.952	52.217	19.498	.000	.000	.000
3500	6.333	58.135	52.383	20.131	.000	.000	.000
3600	6.351	58.314	52.546	20.765	.000	.000	.000
3700	6.372	58.488	52.704	21.401	.000	.000	.000
3800	6.396	58.658	52.858	22.040	.000	.000	.000
3900	6.423	58.825	53.009	22.680	.000	.000	.000
4000	6.453	58.988	53.157	23.324	.000	.000	.000
4100	6.487	59.147	53.301	23.971	.000	.000	.000
4200	6.523	59.304	53.442	24.622	.000	.000	.000
4300	6.563	59.458	53.580	25.276	.000	.000	.000
4400	6.605	59.609	53.715	25.934	.000	.000	.000
4500	6.650	59.758	53.848	26.597	.000	.000	.000
4600	6.697	59.905	53.978	27.264	.000	.000	.000
4700	6.746	60.050	54.106	27.937	.000	.000	.000
4800	6.798	60.192	54.231	28.614	.000	.000	.000
4900	6.852	60.333	54.354	29.296	.000	.000	.000
5000	6.907	60.472	54.475	29.984	.000	.000	.000
5100	6.965	60.609	54.594	30.678	.000	.000	.000
5200	7.024	60.745	54.711	31.377	.000	.000	.000
5300	7.085	60.879	54.826	32.083	.000	.000	.000
5400	7.147	61.012	54.939	32.794	.000	.000	.000
5500	7.210	61.144	55.051	33.512	.000	.000	.000
5600	7.275	61.275	55.161	34.236	.000	.000	.000
5700	7.340	61.404	55.269	34.967	.000	.000	.000
5800	7.406	61.532	55.376	35.704	.000	.000	.000
5900	7.474	61.659	55.482	36.448	.000	.000	.000
6000	7.541	61.786	55.586	37.199	.000	.000	.000

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COBALT, MONATOMIC (Co) (IDEAL GAS) GFW = 58.9332

Ground State Configuration $^4F_{9/2}$

$S°_{298.15}$ = 42.88 gibbs/mol

$\Delta Hf°_0$ = 101.1 ± 0.5 kcal/mol

$\Delta Hf°_{298.15}$ = 101.5 ± 0.5 kcal/mol

Electronic Levels and Multiplicities

ε_i cm^{-1}	g_i	ε_i cm^{-1}	g_i	ε_i cm^{-1}	g_i	ε_i cm^{-1}	g_i	ε_i cm^{-1}	g_i	ε_i cm^{-1}	g_i
0	10	5076	4	15774	4	18775	2	23184	10	29488	36
816	8	7442	8	16196	2	20501	4	23208	8	30107	20
1407	6	8461	6	16467	10	21216	2	24466	42	33100	144
1809	4	13796	6	17234	8	21780	12	25590	30	42245	268
3483	10	14036	4	16471	4	22475	10	25987	54	48000	694
4143	8	14399	2	16778	6	21921	6	27983	10	55000	782
4690	6	15184	6	18390	4	23153	4	28975	28	[18000]	24

Heat of Formation

The heat of formation is the heat of sublimation at 298°K. The adopted value is that reported by Edwards et al. (1). Their value is used because their vapor pressure measurements for Fe (1) and Cu (2) have proved to be very reliable. The results obtained by Vintaikin and Tomash (3) are rejected because their vapor pressure data for Fe (4) resulted in a value for the heat of sublimation which was higher than the accepted value [see JANAF Fe(g) Table for details]. The remaining vapor pressure data are rejected either because the drift was too large or because there were not enough points. Second and third law analyses of the available vapor pressure data gave the following results, with reaction A corresponding to Co(c) = Co(g) and reaction B corresponding to Co(ℓ) = Co(g).

					$\Delta Hr°_{298.15}$			
Source	Reaction	Method	No. Pts.	Range, T°K	2nd Law	3rd Law	Drift, eu	$\Delta Hf°_{298}$**
Edwards (1)	A	Langmuir	9	1363-1522	101.0 ± 1.0	101.54	+0.4 ± 0.7	101.54
Kornev (5)	A	Knudsen	8*	1323-1523	98.8 ± 0.8	95.37	-2.4 ± 0.6	95.37
Dancy (6)	B	Langmuir	1	1823	--	90.51	--	94.82
Ruff (7)	B	Boiling Pt.	1	2648	--	99.35	--	103.66
Nesmeyanov (8)	A	Knudsen	3	1391-1540	82.4 ± 2.4	82.31	-0.1 ± 1.6	82.31
Nesmeyanov (9)	A	Knudsen	12*	1345-1541	91.7 ± 2.4	83.19	-5.9 ± 1.7	83.19
Vintaikin (3)	A	Knudsen	Eqn.	1373-1523	102.9	103.34	+0.3	103.34

*One point rejected due to failure of a statistical test.

**Calculation based on third law $\Delta Hr°_{298}$.

Heat Capacity and Entropy

The electronic levels are taken from Moore (10). Levels above 25,000 cm^{-1} are averaged. Unobserved levels below 20,000 cm^{-1} are estimated.

References

1. J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 73, 4729 (1951).
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5. Iu. V. Kornev and V. N. Golubkin Dokl. Akad. Nauk SSSR 99, 565 (1954).
6. T. E. Dancy, J. Iron Steel Inst. (London) 167, 160 (1951).
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8. An. N. Nesmeyanov and D. D. Man, Dokl. Akad. Nauk SSSR 123, 1064 (1959).
9. An. N. Nesmeyanov and D. D. Man, Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, No. 1 (1960).
10. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467 (1949).

Cobalt Unipositive Ion (Co^+)

(Ideal Gas) GFW = 58.9327

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	5.323	42.599	42.599	.000	284.341	272.293	-199.596
300	5.329	42.632	42.599	.010	284.349	272.219	-198.311
400	5.642	44.209	42.812	.559	284.781	268.110	-146.488
500	5.870	45.495	43.224	1.135	285.200	263.894	-115.348
600	6.015	46.579	43.695	1.730	285.600	259.595	-94.557
700	6.115	47.514	44.175	2.337	285.977	255.229	-79.686
800	6.201	48.336	44.645	2.953	286.230	250.828	-68.523
900	6.287	49.071	45.097	3.577	286.552	246.383	-59.830
1000	6.375	49.738	45.528	4.210	286.828	241.904	-52.868
1100	6.460	50.350	45.939	4.852	287.050	237.401	-47.167
1200	6.538	50.915	46.330	5.502	287.208	232.880	-42.413
1300	6.604	51.441	46.703	6.159	287.266	228.348	-38.389
1400	6.656	51.932	47.059	6.822	287.194	223.819	-34.940
1500	6.693	52.393	47.400	7.490	287.367	219.287	-31.950
1600	6.717	52.826	47.726	8.160	287.603	214.740	-29.332
1700	6.728	53.233	48.038	8.833	287.864	210.179	-27.020
1800	6.728	53.618	48.337	9.505	284.240	205.671	-24.972
1900	6.719	53.982	48.625	10.178	284.442	201.301	-23.155
2000	6.704	54.326	48.901	10.849	284.642	196.920	-21.518
2100	6.683	54.652	49.167	11.518	284.839	192.529	-20.037
2200	6.660	54.963	49.424	12.186	285.036	188.128	-18.689
2300	6.634	55.258	49.671	12.850	285.229	183.719	-17.457
2400	6.606	55.540	49.910	13.512	285.420	179.302	-16.328
2500	6.578	55.809	50.140	14.171	285.608	174.877	-15.288
2600	6.551	56.067	50.363	14.828	285.793	170.443	-14.327
2700	6.523	56.313	50.579	15.482	285.976	166.003	-13.437
2800	6.497	56.550	50.788	16.133	286.156	161.557	-12.610
2900	6.472	56.778	50.991	16.781	286.333	157.104	-11.840
3000	6.448	56.997	51.188	17.427	286.508	152.645	-11.120
3100	6.425	57.208	51.378	18.071	286.680	148.179	-10.447
3200	6.404	57.411	51.564	18.712	197.732	144.545	-9.872
3300	6.383	57.608	51.744	19.351	198.237	142.874	-9.462
3400	6.364	57.798	51.919	19.989	198.741	141.190	-9.076
3500	6.347	57.983	52.090	20.624	199.240	139.489	-8.710
3600	6.330	58.161	52.256	21.258	199.736	137.775	-8.364
3700	6.315	58.334	52.418	21.890	200.229	136.047	-8.036
3800	6.300	58.503	52.576	22.521	200.719	134.306	-7.724
3900	6.287	58.666	52.730	23.151	201.205	132.552	-7.428
4000	6.275	58.825	52.880	23.779	201.685	130.785	-7.146
4100	6.263	58.980	53.027	24.404	202.162	129.007	-6.877
4200	6.252	59.131	53.171	25.031	202.634	127.218	-6.620
4300	6.242	59.278	53.311	25.656	203.101	125.416	-6.374
4400	6.233	59.421	53.448	26.280	203.564	123.604	-6.139
4500	6.225	59.561	53.583	26.903	204.020	121.781	-5.914
4600	6.217	59.698	53.714	27.525	204.472	119.949	-5.699
4700	6.209	59.831	53.843	28.146	204.918	118.107	-5.492
4800	6.203	59.962	53.969	28.767	205.359	116.256	-5.293
4900	6.196	60.090	54.093	29.387	205.793	114.394	-5.102
5000	6.191	60.215	54.214	30.006	206.220	112.524	-4.918
5100	6.185	60.337	54.333	30.625	206.643	110.647	-4.742
5200	6.180	60.458	54.449	31.243	207.058	108.760	-4.571
5300	6.176	60.575	54.564	31.861	207.468	106.867	-4.407
5400	6.172	60.691	54.676	32.478	207.870	104.964	-4.248
5500	6.168	60.804	54.786	33.095	208.265	103.054	-4.095
5600	6.165	60.915	54.895	33.712	208.655	101.138	-3.947
5700	6.162	61.024	55.002	34.328	209.037	99.214	-3.804
5800	6.160	61.131	55.106	34.944	209.413	97.285	-3.666
5900	6.158	61.237	55.209	35.560	209.782	95.349	-3.532
6000	6.156	61.340	55.311	36.176	210.143	93.405	-3.402

Sept. 30, 1967

COBALT UNIPOSITIVE ION (Co^+) (IDEAL GAS) GFW = 58.9327

Ground State Configuration $^3F_4$

$S^\circ_{298.15}$ = 42.6 ± 0.1 gibbs/mol

ΔHf°_0 = 282.50 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 284.34 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	9	13261	5	27484	7
950	7	13405	3	28112	5
1597	5	13594	1	27585	3
3351	11	17772	7	41738	25
4029	9	18032	5	45972	35
4561	7	18339	3	47667	69
4950	5	24075	5	49865	48
5205	3	24268	3	52230	15
9813	9	24412	1	56011	5
10708	7	24887	5	62670	58
11322	5	26000	4	84127	131

Heat of Formation

The heat of formation, ΔHf°_{298}, is calculated from the equation $Co(g) - e^- \rightarrow Co^+(g)$ with the JANAF auxiliary value for Co(g); using an ionization potential of 63438 cm^{-1} (181.377 kcal/mol) obtained from C. E. Moore, "Atomic Energy Levels," Vol. II, U. S. Natl. Bur. Std. Circ. 467, 1949. The value of $H^\circ_0 - H^\circ_{298}$ is -1.504 kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, loc. cit. Levels above 30,000 cm^{-1} are averaged.

Cobalt Difluoride (CoF_2)

(Crystal) GFW = 96.9300

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.978	-160.229	-160.229	INFINITE
100	8.005	5.976	32.192	-2.622	-160.692	-157.036	343.201
200	13.763	13.563	21.032	-1.494	-160.721	-153.341	167.563
298	16.470	19.605	19.605	.000	-160.500	-149.760	109.777
300	16.501	19.707	19.605	.031	-160.494	-149.694	109.052
400	18.096	24.701	20.275	1.770	-160.139	-146.144	79.849
500	18.864	28.830	21.586	3.622	-159.748	-142.691	62.370
600	19.309	32.312	23.091	5.533	-159.361	-139.316	50.746
700	19.602	35.312	24.627	7.479	-158.992	-136.005	42.463
800	19.814	37.944	26.131	9.450	-158.747	-132.730	36.260
900	19.979	40.287	27.576	11.440	-158.432	-129.497	31.446
1000	20.115	42.400	28.954	13.445	-158.166	-126.298	27.602
1100	20.231	44.322	30.265	15.463	-157.957	-123.122	24.462
1200	20.334	46.087	31.511	17.491	-157.814	-119.960	21.848
1300	20.429	47.719	32.696	19.529	-157.775	-116.809	19.637
1400	20.516	49.236	33.824	21.576	-157.867	-113.654	17.742
1500	20.599	50.654	34.899	23.632	-157.714	-110.501	16.100
1600	20.678	51.986	35.926	25.696	-157.495	-107.361	14.665
1700	20.753	53.242	36.908	27.768	-157.248	-104.234	13.400
1800	20.827	54.430	37.849	29.847	-160.886	-101.054	12.270
1900	20.899	55.558	38.751	31.933	-160.692	-97.735	11.242
2000	20.969	56.632	39.619	34.026	-160.494	-94.425	10.318

June 30, 1970

COBALT DIFLUORIDE (CoF_2) (CRYSTAL) GFW = 96.9300

ΔHf°_0 = -160.2 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 19.60 ± 0.10 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -160.5 ± 1.0 kcal/mol

Tm = 1400°K

ΔHm° = 14.058 ± 3.0 kcal/mol

ΔHs° = 75.3 ± 3.0 kcal/mol

Heat of Formation

Heus and Egan (1) measured the electromotive force of a solid state galvanic cell which involved the reactions

$Al(c) + 3/2\ CoF_2(c) \rightarrow AlF_3(c) + 3/2\ Co(c)$. E_{873} = 1.611 volts

$Mg(c) + CoF_2(c) \rightarrow MgF_2(c) + Co(c)$. E_{873} = 2.231 volts

Combining these results with auxiliary thermodynamic data (2) for the reactants and products, we derive ΔHf°(CoF_2, c) = -160.2 and -159.5 kcal/mol.

Several equilibrium studies (3, 4, 5) involving CoF_2(c) have been reported in the literature. Second and third law analyses of these equilibrium data are summarized below, auxiliary data for CoO(c) and $CoCl_2$(c) are from (6).

Reference	Chemical Reaction	Temp. Range °K	Points	ΔHr_{298} kcal/mol 2nd law	ΔHr_{298} kcal/mol 3rd law	Drift gibbs/mol	*ΔHf°(CoF_2, c) kcal/mol
(3)	$CoF_2(c) + 2HCl(g) \rightleftarrows CoCl_2(c) + 2HF(g)$	588-805	3	4.1	1.75±0.4	-1.7±0.1	-162.6±2.0
(4)	$CoF_2(c) + H_2(g) \rightleftarrows Co(c) + 2HF(g)$	673-873	3	35.2	31.5±1.0	-4.2±3.5	-161.8±2.0
(5)	$CoF_2(c) + H_2O(g) \rightleftarrows CoO(c) + 2HF(g)$	773-1023	5	30.2	31.1±0.2	0.9±0.3	-160.45±1.0

*Third law values except for the first reaction.

We note that Heus and Egan (1), in the same paper, measured $\Delta Hf^\circ_{298}(AlF_3, c)$ = -360.2 kcal in excellent agreement with the JANAF value (2). Domange (5) also measured similar equilibria for MgF_2 and CaF_2, which were very consistent with the JANAF heats of formation (2). Jellinek and Rudat (4) reported similar equilibria for PbF_2(c), which show excellent consistency with the JANAF heat of formation (2). Thus, it is apparent that these three sets are probably quite reliable, and we adopt $\Delta Hf^\circ_{298.15}(CoF_2, c)$ = -160.5 ± 1 kcal/mol.

Heat Capacity and Entropy

Catalano and Stout (7) measured low temperature heat capacities in the temperature range 10° to 300°K. Heat capacity data above 300°K are calculated from the high temperature (468-1400°K) enthalpy data of Binford et al. (8). Both sets of data were smoothed by computer and joined at 298.15°K.

The value of $S^\circ_{298.15}$ is obtained from the low temperature heat capacity data of Catalano and Stout (7) and is based on S_{10} = 0.013 gibbs/mol.

Melting Data

Tm = 1400°K is from the high temperature enthalpy studies of Binford et al. (8). ΔHm is calculated from their enthalpy data. Premelting of the sample is assumed to be responsible for the rapid rise in the enthalpy near the melting point. This enthalpy is included in ΔHm.

Heat of Sublimation

Kana'an et al. (9) made sublimation studies of CoF_2 using Knudsen and Langmuir techniques over the temperature range 972°-1241°K. Second and third law analyses of these sublimation pressures are summarized below.

Method	Temp. Range °K	No. of Points	ΔHs°_{298} kcal/mol 2nd law	ΔHs°_{298} kcal/mol 3rd law	Drift gibbs/mol
Knudsen	1058-1242	17	75.0	75.1±0.1	0.1±0.2
Langmuir	972-1032	8	72.8	75.5±0.2	2.6±1.4

The selected value is ΔHs°_{298} = 75.3 ± 3.0 kcal/mol.

References

1. R. J. Heus and J. J. Egan, Z. Phys. Chem., 49, 38 (1966).
2. JANAF Thermochemical Tables; AlF_3 dated 6-30-70; MgF_2 dated 3-31-66; PbF_2 dated 6-30-69; CaF_2 dated 12-31-68.
3. K. Jellinek and R. Koop, Z. Phys. Chem., A145, 305 (1929).
4. K. Jellinek and A. Rudat, Z. Anorg. Chem., 175, 281 (1928).
5. L. Domange, Ann. Chim., 7, 225 (1937).
6. U. S. Natl. Bur. Std. Techn. Note 270-4, 1969.
7. E. Catalano and J. W. Stout, J. Chem. Phys., 23, 1803 (1955).
8. J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., 71, 2404 (1967).
9. A. S. Kana'an, G. Besenbruch, and J. L. Margrave, J. Inorg. Nucl. Chem., 28, 1035 (1966).

Cobalt Difluoride (CoF_2)
(Liquid) GFW = 96.9300

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	25.000	20.611	20.611	.000	- 152.412	- 141.972	104.068
300	25.000	20.766	20.611	.046	- 152.391	- 141.908	103.380
400	25.000	27.958	21.592	2.546	- 151.275	- 138.583	75.718
500	25.000	33.536	23.444	5.046	- 150.236	- 135.532	59.241
600	25.000	38.094	25.517	7.546	- 149.260	- 132.684	48.330
700	25.000	41.948	27.596	10.046	- 148.337	- 129.995	40.586
800	25.000	45.286	29.604	12.546	- 147.563	- 127.421	34.810
900	25.000	48.231	31.513	15.046	- 146.738	- 124.952	30.343
1000	25.000	50.865	33.319	17.546	- 145.977	- 122.574	26.788
1100	25.000	53.248	35.024	20.046	- 145.286	- 120.268	23.895
1200	25.000	55.423	36.634	22.546	- 144.671	- 118.020	21.494
1300	25.000	57.424	38.158	25.046	- 144.170	- 115.821	19.471
1400	25.000	59.277	39.601	27.546	- 143.809	- 113.654	17.742
1500	25.000	61.002	40.971	30.046	- 143.212	- 111.520	16.248
1600	25.000	62.615	42.274	32.546	- 142.557	- 109.429	14.947
1700	25.000	64.131	43.515	35.046	- 141.882	- 107.378	13.804
1800	25.000	65.560	44.701	37.546	- 145.099	- 105.300	12.785
1900	25.000	66.911	45.834	40.046	- 144.491	- 103.105	11.860
2000	25.000	68.194	46.921	42.546	- 143.886	- 100.941	11.030
2100	25.000	69.413	47.963	45.046	- 143.284	- 98.810	10.283
2200	25.000	70.576	48.964	47.546	- 142.685	- 96.707	9.607
2300	25.000	71.688	49.928	50.046	- 142.088	- 94.629	8.992
2400	25.000	72.752	50.857	52.546	- 141.494	- 92.579	8.430
2500	25.000	73.772	51.754	55.046	- 140.903	- 90.553	7.916
2600	25.000	74.753	52.620	57.546	- 140.314	- 88.550	7.443
2700	25.000	75.696	53.457	60.046	- 139.727	- 86.570	7.007
2800	25.000	76.605	54.268	62.546	- 139.142	- 84.613	6.604
2900	25.000	77.483	55.053	65.046	- 138.560	- 82.674	6.230
3000	25.000	78.330	55.815	67.546	- 137.981	- 80.760	5.883

June 30, 1970

COBALT DIFLUORIDE (CoF_2) (LIQUID) GFW = 96.9300

$S^\circ_{298.15}$ = 20.61 ± 2.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -152.412 ± 4.0 kcal/mol

Tm = 1400°K

ΔHm° = 14.058 ± 3.0 kcal/mol

Tb = [2012]°K

ΔHv° = [48.0] kcal/mol

Heat of Formation

ΔHf°(ℓ) is calculated from ΔHf°(c) by adding the heat of melting and the difference in (H_{1400}-H_{298}) between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid CoF_2 is estimated by comparison with those for $FeCl_2$(ℓ), MgF_2(ℓ), and PbF_2(ℓ) and is assumed constant in the temperature range 298°-3000°K. Binford et al. (1) reported Cp = 30.3 gibbs/mol for liquid CoF_2 at 1444°K. This value is based on only two enthalpy points near the melting point and appears high in comparison with heat capacities for other liquid metal dihalides. Therefore, the value is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the CoF_2(c) table for details.

Vaporization Data

Tb is the temperature at which the Gibbs energy change for the process CoF_2(ℓ) → CoF_2(g) approaches zero. The difference between the heat of formation of the gas and liquid at Tb is ΔHv°.

Reference

1. J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., 71, 2404 (1967).

Cobalt Difluoride (CoF_2)

(Ideal Gas) GFW = 96.9300

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.093	-85.044	-85.044	INFINITE
100	9.821	54.359	76.666	-2.231	-85.001	-86.183	188.353
200	11.369	61.706	67.516	-1.162	-85.089	-87.337	95.438
298	12.239	66.421	66.421	.000	-85.200	-88.418	64.812
300	12.252	66.497	66.422	.023	-85.202	-88.439	64.427
400	12.793	70.102	66.909	1.277	-85.332	-89.498	48.899
500	13.126	72.996	67.847	2.574	-85.496	-90.522	39.567
600	13.341	75.409	68.912	3.899	-85.695	-91.509	33.332
700	13.494	77.478	69.991	5.241	-85.930	-92.459	28.867
800	13.613	79.288	71.042	6.596	-86.301	-93.360	25.505
900	13.713	80.897	72.050	7.963	-86.609	-94.223	22.881
1000	13.803	82.347	73.008	9.338	-86.973	-95.051	20.773
1100	13.885	83.666	73.918	10.723	-87.397	-95.839	19.041
1200	13.960	84.877	74.781	12.115	-87.890	-96.584	17.590
1300	14.029	85.998	75.602	13.515	-88.489	-97.286	16.355
1400	14.093	87.040	76.382	14.921	-89.222	-97.935	15.288
1500	14.150	88.014	77.125	16.333	-89.713	-98.540	14.357
1600	14.202	88.929	77.835	17.751	-90.140	-99.115	13.538
1700	14.250	89.791	78.513	19.173	-90.543	-99.662	12.812
1800	14.293	90.607	79.162	20.601	-94.832	-100.119	12.156
1900	14.331	91.381	79.785	22.032	-95.293	-100.399	11.549
2000	14.366	92.117	80.383	23.467	-95.753	-100.655	10.999
2100	14.397	92.819	80.959	24.905	-96.213	-100.890	10.500
2200	14.425	93.489	81.513	26.346	-96.673	-101.102	10.044
2300	14.450	94.131	82.048	27.790	-97.132	-101.292	9.625
2400	14.473	94.746	82.565	29.236	-97.592	-101.464	9.240
2500	14.493	95.337	83.064	30.684	-98.053	-101.616	8.883
2600	14.510	95.906	83.547	32.134	-98.514	-101.749	8.553
2700	14.526	96.454	84.015	33.586	-98.975	-101.864	8.245
2800	14.539	96.983	84.468	35.040	-99.436	-101.963	7.959
2900	14.551	97.493	84.909	36.494	-99.900	-102.044	7.690
3000	14.561	97.987	85.337	37.950	-100.365	-102.113	7.439
3100	14.569	98.464	85.752	39.406	-100.831	-102.163	7.202
3200	14.576	98.927	86.157	40.864	-190.416	-101.362	6.923
3300	14.582	99.375	86.551	42.321	-190.549	-98.579	6.529
3400	14.586	99.811	86.934	43.780	-190.682	-95.789	6.157
3500	14.589	100.234	87.308	45.239	-190.820	-92.994	5.807
3600	14.591	100.645	87.673	46.698	-190.960	-90.197	5.476
3700	14.592	101.044	88.029	48.157	-191.105	-87.396	5.162
3800	14.592	101.434	88.377	49.616	-191.254	-84.590	4.865
3900	14.591	101.813	88.716	51.075	-191.409	-81.784	4.583
4000	14.590	102.182	89.048	52.534	-191.568	-78.969	4.315
4100	14.588	102.542	89.373	53.993	-191.733	-76.153	4.059
4200	14.585	102.894	89.691	55.452	-191.903	-73.332	3.816
4300	14.581	103.237	90.002	56.910	-192.080	-70.505	3.583
4400	14.577	103.572	90.307	58.368	-192.264	-67.677	3.362
4500	14.573	103.900	90.605	59.825	-192.455	-64.845	3.149
4600	14.568	104.220	90.898	61.282	-192.652	-62.006	2.946
4700	14.563	104.533	91.184	62.739	-192.857	-59.164	2.751
4800	14.557	104.840	91.466	64.195	-193.069	-56.315	2.564
4900	14.551	105.140	91.742	65.650	-193.291	-53.464	2.385
5000	14.545	105.434	92.013	67.105	-193.520	-50.609	2.212
5100	14.539	105.722	92.279	68.559	-193.757	-47.751	2.046
5200	14.532	106.004	92.540	70.013	-194.003	-44.882	1.886
5300	14.526	106.281	92.796	71.466	-194.257	-42.010	1.732
5400	14.519	106.552	93.049	72.918	-194.522	-39.140	1.584
5500	14.512	106.818	93.297	74.370	-194.794	-36.259	1.441
5600	14.505	107.080	93.540	75.821	-195.076	-33.372	1.302
5700	14.498	107.337	93.780	77.271	-195.368	-30.482	1.169
5800	14.491	107.589	94.016	78.720	-195.668	-27.587	1.039
5900	14.483	107.836	94.248	80.169	-195.978	-24.689	.915
6000	14.476	108.080	94.477	81.617	-196.298	-21.783	.793

June 30, 1970

COBALT DIFLUORIDE (CoF_2) (IDEAL GAS) GFW = 96.9300

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [66.42 ± 3.0] gibbs/mol

Ground State Configuration [$^4\Sigma$]

ΔHf°_0 = -85.0 ± 3.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -85.2 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	4
[300]	[4]
[4000]	[4]
[9000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[600] (1)
[151] (1)
762 (1)

Bond Distance: Co-F = [1.72] Å

Bond Angle: F-Co-F = [165°]

Product of Moments of Inertia: $I_AI_BI_C = 6.5424 \times 10^{-116}\ g^3\ cm^6$

σ = 2

Heat of Formation

The heat of formation of gaseous CoF_2, ΔHf°_{298} = -88.1 ± 7.0 kcal/mol, is calculated from the heat of formation of the crystal, ΔHf°_{298} = -163.4 ± 4.0 kcal/mol, and the heat of sublimation, ΔHs°_{298} = 75.3 ± 3.0 kcal/mol. The sublimation value is determined from a third law analysis of the vapor pressure data for CoF_2 reported by Kana'an et al. (1). See CoF_2(c) table for details.

Heat Capacity and Entropy

Büchler et al. (2) investigated the deflection of a molecular beam of CoF_2(g) by an electric field and found that within the sensitivity of the apparatus the molecule was nonpolar and consequently possessed a linear structure. Hastie et al. (3) recently investigated the infrared absorption spectra of several transition metal difluorides through the use of matrix isolation techniques. Isotopic shift measurements for matrix isolated NiF_2, ZnF_2, and CuF_2 in neon and argon indicated that these species were slightly bent. Based upon these results, the authors estimated the F-Co-F angle as 165°. This value is adopted here. The bond length was estimated by Brewer et al. (4). Individual moments of inertia are $I_A = 0.1925 \times 10^{-39}$, $I_B = 18.341 \times 10^{-39}$, and $I_C = 18.533 \times 10^{-39}\ g\ cm^2$.

Hastie et al. (3) isolated CoF_2 in neon and argon matrices and observed the ν_3 fundamental at 762 cm^{-1}. They also calculated $\nu_1 = 600\ cm^{-1}$ by a valence force field method and estimated ν_2 as 151 cm^{-1} by applying the variation in the frequencies for the chlorides of Co, Ni, Cu, and Zn to the fluorides. The electronic levels and quantum weights are estimated by comparison with the electronic energy levels for Co^{++}(g) ion (5) and those for $CoCl_2$(g) observed by Hougen et al. (6).

References

1. A. S. Kana'an, G. Besenbruch, and J. L. Margrave, J. Inorg. Nucl. Chem., 28, 1035 (1966).
2. A. Büchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys., 40, 3471 (1964).
3. J. W. Hastie, R. H. Hauge, and J. L. Margrave, High Temperature Science, 1, 76 (1969).
4. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev., 63, 111 (1963).
5. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. II, 1952.
6. J. T. Hougen, G. E. Leroi, and T. C. James, J. Chem. Phys., 34, 1670 (1961).

Cesium (Cs)

(Reference State) GFW = 132.905

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.844	.000	.000	.000
100	6.169	13.134	26.443	-1.331	.000	.000	.000
200	6.645	17.556	21.007	-.690	.000	.000	.000
298	7.695	20.351	20.351	.000	.000	.000	.000
300	7.733	20.399	20.351	.014	.000	.000	.000
400	7.533	24.249	21.059	1.276	.000	.000	.000
500	7.446	25.920	21.871	2.025	.000	.000	.000
600	7.409	27.274	22.662	2.767	.000	.000	.000
700	7.395	28.415	23.405	3.507	.000	.000	.000
800	7.393	29.402	24.094	4.247	.000	.000	.000
900	7.399	30.273	24.733	4.986	.000	.000	.000
1000	4.968	47.954	26.148	21.807	.000	.000	.000
1100	4.968	48.428	28.152	22.303	.000	.000	.000
1200	4.969	48.860	29.860	22.800	.000	.000	.000
1300	4.971	49.258	31.337	23.297	.000	.000	.000
1400	4.975	49.627	32.630	23.795	.000	.000	.000
1500	4.981	49.970	33.775	24.292	.000	.000	.000
1600	4.992	50.292	34.797	24.791	.000	.000	.000
1700	5.008	50.595	35.718	25.291	.000	.000	.000
1800	5.031	50.882	36.552	25.793	.000	.000	.000
1900	5.062	51.154	37.314	26.297	.000	.000	.000
2000	5.102	51.415	38.012	26.805	.000	.000	.000
2100	5.154	51.665	38.657	27.318	.000	.000	.000
2200	5.218	51.906	39.253	27.837	.000	.000	.000
2300	5.295	52.140	39.809	28.362	.000	.000	.000
2400	5.385	52.367	40.327	28.896	.000	.000	.000
2500	5.491	52.589	40.813	29.440	.000	.000	.000
2600	5.613	52.807	41.270	29.995	.000	.000	.000
2700	5.752	53.021	41.702	30.563	.000	.000	.000
2800	5.908	53.233	42.110	31.146	.000	.000	.000
2900	6.085	53.444	42.497	31.745	.000	.000	.000
3000	6.282	53.653	42.865	32.363	.000	.000	.000
3100	6.502	53.863	43.217	33.002	.000	.000	.000
3200	6.747	54.073	43.553	33.665	.000	.000	.000
3300	7.018	54.285	43.875	34.353	.000	.000	.000
3400	7.317	54.498	44.184	35.069	.000	.000	.000
3500	7.647	54.715	44.482	35.817	.000	.000	.000
3600	8.008	54.936	44.769	36.600	.000	.000	.000
3700	8.403	55.160	45.047	37.420	.000	.000	.000
3800	8.831	55.390	45.316	38.281	.000	.000	.000
3900	9.294	55.625	45.577	39.187	.000	.000	.000
4000	9.790	55.867	45.831	40.141	.000	.000	.000
4100	10.318	56.115	46.079	41.146	.000	.000	.000
4200	10.876	56.370	46.321	42.206	.000	.000	.000
4300	11.461	56.633	46.558	43.323	.000	.000	.000
4400	12.069	56.903	46.790	44.499	.000	.000	.000
4500	12.694	57.182	47.018	45.737	.000	.000	.000
4600	13.331	57.468	47.242	47.036	.000	.000	.000
4700	13.972	57.761	47.463	48.403	.000	.000	.000
4800	14.612	58.062	47.680	49.832	.000	.000	.000
4900	15.242	58.370	47.895	51.325	.000	.000	.000
5000	15.855	58.684	48.108	52.880	.000	.000	.000
5100	16.443	59.004	48.318	54.495	.000	.000	.000
5200	16.999	59.328	48.527	56.168	.000	.000	.000
5300	17.516	59.657	48.734	57.894	.000	.000	.000
5400	17.989	59.989	48.939	59.670	.000	.000	.000
5500	18.411	60.323	49.143	61.490	.000	.000	.000
5600	18.780	60.658	49.346	63.350	.000	.000	.000
5700	19.091	60.994	49.547	65.244	.000	.000	.000
5800	19.343	61.328	49.747	67.166	.000	.000	.000
5900	19.536	61.660	49.946	69.111	.000	.000	.000
6000	19.668	61.990	50.144	71.071	.000	.000	.000

June 30, 1968

CESIUM (Cs) (REFERENCE STATE) GFW = 132.905

0	to	301.55°K	Crystal
301.55	to	951.6°K	Liquid
951.6	to	6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Cesium (Cs)

(Crystal) GFW = 132.905

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.844	.000	.000	INFINITE
100	6.169	13.134	26.443	-1.331	.000	.000	.000
200	6.645	17.556	21.007	-.690	.000	.000	.000
298	7.695	20.351	20.351	.000	.000	.000	.000
300	7.733	20.399	20.351	.014	.000	.000	.000
400	8.620	22.775	20.669	.842	-.434	.156	-.085
500	8.890	24.733	21.292	1.720	-.305	.289	-.126
600	8.970	26.361	22.005	2.614	-.153	.394	-.144
700	8.990	27.746	22.729	3.512	.005	.473	-.148
800	8.995	28.947	23.433	4.411	.164	.528	-.144
900	9.000	30.006	24.106	5.311	.325	.565	-.137
1000	9.000	30.955	24.744	6.211	-15.596	1.404	-.307

June 30, 1968

CESIUM (Cs) (CRYSTAL) GFW = 132.905

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 20.351 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Tm = 301.55 ± 0.01°K

ΔHm° = 0.499 ± 0.001 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 18.32 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 0.19-301.55°K, have been measured by Dauphinee (1), McCollum (2), Martin (3), Lien (4), Filby (5), and Morgan (6). The adopted values are derived based on the Cp data reported by Filby (5) and Lien (4). Lien measured the heat capacities in the temperature range 0.1874 to 1.20°K in the adiabatic demagnetization cryostat and at higher temperatures, 1.2 to 4.09°K, in the liquid-helium temperature cryostat. The Cs sample was obtained from a commercial source of 99.8 per cent purity. Filby determined the Cp values in the temperature ranges 0.4-1.5°K, 3-26°K and 20-320°K, using commercial samples of 99.9 per cent purity. These two sets of measurements are joined smoothly at 4°K. $S^\circ_{298.15}$ is derived from the adopted heat capacities, based on $S^\circ_{0.20}$ = 0.0002 eu.

Dauphinee (1) determined the heat capacities of Cs(c) employing a sample badly contaminated with oxygen. In the temperature range of approximately 100 to 200°K, an anomaly of Cp curve somewhat similar to those found for sodium and potassium was reported. This anomaly was not observed by Filby who used the higher purity cesium sample. The Cp values reported by Dauphinee are lower than the adopted ones by about 0.5 to 1.5 per cent in the temperatures 55 to 220°K; above 270°K his reported heat capacities are unreasonably high. Therefore the data are not adopted for evaluation. McCollum (2) calculated the Debye θ values from the measured low temperature heat capacities and plotted them, since no numerical data were reported these were not used. The low temperature Cp values determined by Martin (3) and Morgan (6) are in good agreement with the adopted ones.

Melting Data

See Cs(ℓ) table for details.

Heat of Sublimation

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Cs(g) and Cs(c).

References

1. T. M. Dauphinee, D. L. Martin and H. Preston-Thomas, Proc. Roy. Soc. (London) A233, 214 (1955), 20-320°K.
2. D. C. McCollum, Jr. and H. B. Silsbee, Phys. Rev. 127, 119 (1962), 1.3-12°K.
3. B. D. Martin, D. A. Zych and C. V. Heer, Phys. Rev. 135, A671 (1964), 0.36-1.63°K.
4. W. H. Lien and N. E. Phillips, Phys. Rev. 133, A1370 (1964), 0.19-4.09°K.
5. J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) A284, 83 (1965), 0.7-320°K.
6. J. A. Morgan and J. C. Thompson, J. Chem. Phys. 47, 4607 (1967), 2.1-4.2°K.

Cesium (Cs)

(Liquid) GFW = 132.905

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	7.753	22.005	22.005	.000	.499	.006	-.004
300	7.747	22.053	22.005	.014	.499	.003	-.002
400	7.533	24.250	22.306	.777	.000	.000	.000
500	7.446	25.920	22.869	1.526	.000	.000	.000
600	7.409	27.274	23.494	2.268	.000	.000	.000
700	7.395	28.415	24.117	3.008	.000	.000	.000
800	7.393	29.402	24.718	3.748	.000	.000	.000
900	7.399	30.273	25.287	4.487	.000	.000	.000
1000	7.409	31.053	25.826	5.228	-16.080	.821	-.179
1100	7.422	31.760	26.334	5.969	-15.835	2.500	-.497
1200	7.437	32.407	26.813	6.712	-15.589	4.155	-.757
1300	7.454	33.003	27.267	7.457	-15.341	5.791	-.974
1400	7.472	33.556	27.696	8.203	-15.093	7.406	-1.156
1500	7.491	34.072	28.104	8.951	-14.842	9.005	-1.312

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CESIUM (Cs) (LIQUID) GFW = 132.905

$S^\circ_{298.15}$ = 22.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0.499 kcal/mol

Tm = 301.55 ± 0.01°K

ΔHm° = 0.499 ± 0.001 kcal/mol

Tb = 951.6°K

ΔHv° = 16.198 kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{301.55} - H^\circ_{298}$ for Cs(c) and Cs(ℓ).

Heat Capacity and Entropy

The enthalpies of Cs(ℓ) have been measured by Tepper et al. (1), Achener (2), and Lemmon et al. (3), using drop calorimetry. Lemmon et al. used a cesium sample of 99.994 per cent purity and encapsulated in Nb-1Zr alloy. They found that Cs(ℓ) does not behave as a normal liquid from about 100-300°C. The thermal conductivity measurements of Cs(ℓ) show a change of slope at about 200°C and its electrical resistivity also shows scatter in this region. The heat capacities, 301.55-1435.2°K, derived from the reported enthalpies (corrected for vapor condensation), are consistent with the low temperature heat capacity data on Cs(c) at 298°K and are adopted.

Tepper et al. measured the enthalpies in the temperature range 351.1-1238°K. The reported enthalpy values are considerably higher, over 20 per cent, at the lower end of the measured temperature range than the adopted ones. However, the agreement becomes better at the higher temperature end. Achener determined the enthalpies of Cs(ℓ) at the temperatures 340.1-1175.7°K. Using the reported enthalpies, the average heat capacity is derived to be 9.75 gibbs/mol, which is unreasonably high by comparison with those for the other alkali metals. The above two sets of data are not used for evaluation. The enthalpies of Cs(ℓ), 773-1423°K, were also measured by Shapiro (4 and quoted by 3). The derived constant heat capacity, 7.60 gibbs/mol, is in reasonable agreement with the adopted ones.

Heat capacities of Cs(ℓ), 301.55-373.2°K, were reported by Filby (5), 301.55-320°K, Dauphinee (6), 310-320°K, and Rengade (7), 301.7-373.2°K. The values obtained are consistent with the adopted ones.

$S^\circ_{298.15}$ is derived in a manner analogous to that of the heat of formation.

Melting Data

The melting point and heat of melting have been determined by many investigators. The results reported are presented in the table below. The adopted Tm and ΔHm° are obtained from (5). The two determinations of fraction melted against temperature are in very good agreement with one another and lead to a linear plot of reciprocal fraction melted against temperature thus indicating that the major impurity is solid insoluble. This is confirmed by a graph of excess heat capacity against the reciprocal of $(T_0-T)^2$, where T_0 is the melting point, which indicates an impurity (mainly oxygen) concentration of 0.06 atomic per cent.

Tm, °K	ΔHm°, kcal/mol	References
299.52	0.496	M. Eckardt and E. Graefe, Z. Anorg. Chem. 23, 378 (1900).
301.35	-	A. Guntz and W. Broniewski, J. Chim. Phys. 7, 474 (1909).
301.60±0.05	0.500	E. Rengade (7).
301.75	-	J. H. Boer, J. Broos and H. Emmens, Z. Anorg. Chem. 191, 118 (1930).
301.45	-	E. Rinck, Compt. Rend. 199, 1217 (1934).
301.95±0.1	-	L. Losana, Gazz. Chim. Ital. 65, 855 (1935).
301.75	-	J. B. Taylor and J. Langmuir, Phys. Rev. 51, 759 (1937).
301.79±0.17	-	K. Clusius and H. Stern, Z. Angew. Physik 6, 194 (1954).
-	0.510	W. D. Weatherford, Jr., et al., WADD Tech. Rept. 61-96, November 1961.
301.67	0.470	A. W. Lemmon et al. (3).
301.55±0.01	0.499±0.01	J. D. Filby and D. L. Martin (5).

Vaporization Data

Tb is the temperature at which the Gibbs energy change (ΔGr°) for the reaction Cs(ℓ) = Cs(g) approaches zero. The difference between ΔHf°(Cs, g) and ΔHf°(Cs, ℓ) at Tb is ΔHv°. Due to the presence of dimer (Cs_2) in the vapor (see Cs(g) and Cs_2(g) tables for details), the real boiling point of Cs(ℓ) is calculated to be 941.3°K at which the vapor mixture contains 0.835 mol of monomer/mol of Cs(ℓ) vaporized, or 9.0 per cent of dimer. The corresponding heat of vaporization is evaluated as 15.26 kcal/mol of vapor mixture.

References

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3. A. W. Lemmon, Jr., H. W. Deem, E. A. Eldridge, E. H. Hall, J. Matolich, Jr., and J. F. Walling, "The Specific Heat, Thermal Conductivity, and Viscosity of Liquid Cesium," BATT-4673-T7, Battelle Memorial Institute, February 1964.
4. A. Shapiro and C. J. Meisl, General Electric Company, Flight Propulsion Laboratory Department Report No. R60FPD358-A, Nov. 9, 1960.
5. J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) A284, 83 (1965).
6. T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. (London) A233, 214 (1955).
7. E. Rengade, Compt. Rend. 156, 1897 (1913); Bull. Soc. Chim. France 15, 130 (1914).

Cesium (Cs)

(Ideal Gas) GFW = 132.905

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.481	18.683	18.683	INFINITE
100	4.968	36.515	46.359	- .984	18.667	16.328	- 35.686
200	4.968	39.959	42.397	- .488	18.522	14.042	- 15.344
298	4.968	41.942	41.942	.000	18.320	11.883	- 8.710
300	4.968	41.973	41.942	.009	18.315	11.843	- 8.628
400	4.968	43.402	42.137	.506	17.550	9.889	- 5.403
500	4.968	44.511	42.505	1.003	17.298	8.002	- 3.498
600	4.968	45.417	42.917	1.500	17.053	6.167	- 2.246
700	4.968	46.182	43.330	1.996	16.809	4.372	- 1.365
800	4.968	46.846	43.729	2.493	16.566	2.611	- .713
900	4.968	47.431	44.109	2.990	16.324	.882	- .214
1000	4.968	47.954	44.468	3.487	.000	.000	.000
1100	4.968	48.428	44.806	3.984	.000	.000	.000
1200	4.969	48.860	45.127	4.480	.000	.000	.000
1300	4.971	49.258	45.429	4.977	.000	.000	.000
1400	4.975	49.627	45.716	5.475	.000	.000	.000
1500	4.981	49.970	45.988	5.972	.000	.000	.000
1600	4.992	50.292	46.247	6.471	.000	.000	.000
1700	5.008	50.595	46.494	6.971	.000	.000	.000
1800	5.031	50.882	46.730	7.473	.000	.000	.000
1900	5.062	51.154	46.956	7.977	.000	.000	.000
2000	5.102	51.415	47.172	8.485	.000	.000	.000
2100	5.154	51.665	47.380	8.998	.000	.000	.000
2200	5.218	51.906	47.581	9.517	.000	.000	.000
2300	5.295	52.140	47.774	10.042	.000	.000	.000
2400	5.385	52.367	47.960	10.576	.000	.000	.000
2500	5.491	52.589	48.141	11.120	.000	.000	.000
2600	5.613	52.807	48.316	11.675	.000	.000	.000
2700	5.752	53.021	48.487	12.243	.000	.000	.000
2800	5.908	53.233	48.652	12.826	.000	.000	.000
2900	6.085	53.444	48.814	13.425	.000	.000	.000
3000	6.282	53.653	48.972	14.043	.000	.000	.000
3100	6.502	53.863	49.126	14.682	.000	.000	.000
3200	6.747	54.073	49.278	15.345	.000	.000	.000
3300	7.018	54.285	49.426	16.033	.000	.000	.000
3400	7.317	54.498	49.572	16.749	.000	.000	.000
3500	7.647	54.715	49.716	17.497	.000	.000	.000
3600	8.008	54.936	49.858	18.280	.000	.000	.000
3700	8.403	55.160	49.998	19.100	.000	.000	.000
3800	8.831	55.390	50.137	19.961	.000	.000	.000
3900	9.294	55.625	50.275	20.867	.000	.000	.000
4000	9.790	55.867	50.411	21.821	.000	.000	.000
4100	10.318	56.115	50.548	22.826	.000	.000	.000
4200	10.876	56.370	50.683	23.886	.000	.000	.000
4300	11.461	56.633	50.818	25.003	.000	.000	.000
4400	12.069	56.903	50.954	26.179	.000	.000	.000
4500	12.694	57.182	51.089	27.417	.000	.000	.000
4600	13.331	57.468	51.224	28.718	.000	.000	.000
4700	13.972	57.761	51.360	30.083	.000	.000	.000
4800	14.612	58.062	51.497	31.513	.000	.000	.000
4900	15.242	58.370	51.634	33.005	.000	.000	.000
5000	15.855	58.684	51.772	34.560	.000	.000	.000
5100	16.443	59.004	51.910	36.176	.000	.000	.000
5200	16.999	59.328	52.050	37.848	.000	.000	.000
5300	17.516	59.657	52.190	39.574	.000	.000	.000
5400	17.989	59.989	52.332	41.350	.000	.000	.000
5500	18.411	60.323	52.474	43.170	.000	.000	.000
5600	18.780	60.658	52.617	45.030	.000	.000	.000
5700	19.091	60.994	52.761	46.924	.000	.000	.000
5800	19.343	61.328	52.906	48.846	.000	.000	.000
5900	19.536	61.660	53.052	50.791	.000	.000	.000
6000	19.668	61.990	53.198	52.751	.000	.000	.000

June 30, 1968

CESIUM (Cs) (IDEAL GAS) GFW = 132.905

Ground State Configuration $^2S_{1/2}$

$\Delta Hf°_0$ = 18.68 ± 0.5 kcal/mol

$S°_{298.15}$ = 41.942 ± 0.01 gibbs/mol

$\Delta Hf°_{298.15}$ = 18.32 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.00	2	22588.89	4	28445.78	72
11178.24	2	22631.83	6	29428.78	38
11732.35	4	24317.17	2	30172.46	28
14499.49	4	24472.29	8	[29148.23]	[66]
14597.08	6	24472.46	6	[29678.98]	[96]
18535.51	2	25764.23	6	[30042.54]	[130]
21765.65	2	26616.40	26	[30302.39]	[168]
21946.66	4	27363.68	34		

Heat of Formation

The total pressures of Cs(g) and Cs_2(g) over Cs(c) and Cs(ℓ) in the temperature range 238.6 to 1268.3°K have been measured, using the boiling point method, by Bonilla (4), Tepper (3) and Achener (2); using the static method, by Kröner (10), Scott (7) and Stone (1); and the positive ion method by Taylor (6). Füchtbauer (8) and Hackspill (9) have determined the vapor pressures of Cs(ℓ) by a spectroscopic method and P-V-T relationships, respectively. Based on the reported total pressures, the partial pressures of Cs(g) and Cs_2(g) are evaluated by use of dimer-monomer ratios calculated from JANAF free energy functions and $\Delta Hr°_{298.15}$ = 11.24 kcal/mol for the reaction Cs_2(g) = 2Cs(g). The value of $\Delta Hr°_{298.15}$ is adopted such that the derived monomer partial pressures give consistent second and third law heats of vaporization. The results are presented in the table below.

Stone et al. (1) measured the vapor pressures of Cs(ℓ) at temperatures 920-1682°K and pressures 0.811-33.53 atm in both the saturation and superheat regions, using a static method and a refractory metal apparatus with a diaphragm as a null-point detector. These vapor pressures reported at temperatures 920-1267.3°K and total pressure below 10 atm are used for evaluation and are reasonably represented by a mixture of monomer and dimer ideal gases. The value of $\Delta Hf°_{298}$(Cs, g) is adopted as 18.32±0.5 kcal/mol which is derived based on the vapor pressures reported by Stone et al. The results obtained are in reasonable agreement with the values derived from the other vapor pressure sets.

		No. of	$\Delta Hr°_{298}$, kcal/mol			
Investigator	Temperature, °K	Points	Second Law	Third Law	Drift, eu	$\Delta Hf°_{298}$, kcal/mol*
1. Stone (1966)	920.6-1267.7	79	18.19±0.02	17.82	-0.37±0.02	18.32
2. Achener (1964)	751.5-1144.3	15	18.15±0.04	17.88	-0.30±0.05	18.38
3. Tepper (1963)	729.1-1268.3	21	18.11±0.02	17.86	-0.27±0.02	18.36
4. Bonilla (1962)	674.3-1199.2	41	18.16±0.03	17.76	-0.42±0.03	18.26
5. Weathford (1961)	722.2-1277.8	11	18.01±0.01	18.09	0.08±0.01	18.59
6. Taylor (1937)	238.6-298.5	8	18.41±0.03	18.35	-0.22±0.11	18.35
	303.3-345.8	6	17.75±0.10	17.86	0.32±0.31	18.36
7. Scott (1924)	321.4-386.6	8	17.28±0.28	17.13	-0.43±0.79	17.63
8. Füchtbauer (1921)	464.1-505.5	4	17.20±0.74	18.10	1.86±1.54	18.60
9. Hackspill (1913)	503.2-670.2	10	18.33±0.47	18.00	-0.56±0.80	18.50
10. Kröner (1913)	522.7-628.7	12	18.67±0.44	18.10	-1.00±0.76	18.60

*Calculation based on the third law $\Delta Hr°_{298}$ and $\Delta Hf°_{298}$ = 0 and 0.499 kcal/mol for Cs(c) and Cs(ℓ), respectively.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights ($n \leqslant 10$) are obtained from Moore (11). The electronic levels above 25000 cm^{-1} are average values calculated from those given by Moore. The missing electronic levels, where quantum number n = 7, 8, 9 and 10, and the corresponding quantum weights are estimated according to the method recommended by Gurvich (12). The calculated values at 6000°K, e.g. Cp = 19.668 gibbs/mol and S° = 61.990 eu, are not significantly different from the corresponding values, Cp = 19.650 gibbs/mol and S° = 61.871 eu, obtained from using all the electronic levels reported by Moore for calculation without cutting or adding any levels.

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Cesium Unipositive Ion (Cs^+)

(Ideal Gas) GFW = 132.90445

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	4.968	40.565	40.565	.000	108.100	100.586	- 73.732
300	4.968	40.596	40.565	.009	108.104	100.539	- 73.243
400	4.968	42.025	40.760	.506	107.836	98.147	- 53.625
500	4.968	43.133	41.128	1.003	108.081	95.696	- 41.829
600	4.968	44.039	41.540	1.500	108.333	93.196	- 33.946
700	4.968	44.805	41.953	1.996	108.585	90.652	- 28.303
800	4.968	45.468	42.352	2.493	108.839	88.073	- 24.060
900	4.968	46.054	42.731	2.990	109.094	85.462	- 20.753
1000	4.968	46.577	43.090	3.487	93.267	83.643	- 18.280
1100	4.968	47.050	43.429	3.984	93.765	82.658	- 16.423
1200	4.968	47.483	43.749	4.480	94.261	81.627	- 14.866
1300	4.968	47.880	44.052	4.977	94.757	80.553	- 13.542
1400	4.968	48.249	44.339	5.474	95.253	79.441	- 12.401
1500	4.968	48.591	44.611	5.971	95.750	78.295	- 11.408
1600	4.968	48.912	44.870	6.467	96.244	77.115	- 10.533
1700	4.968	49.213	45.116	6.964	96.738	75.904	- 9.758
1800	4.968	49.497	45.352	7.461	97.229	74.664	- 9.065
1900	4.968	49.766	45.577	7.958	97.719	73.398	- 8.443
2000	4.968	50.020	45.793	8.455	98.205	72.106	- 7.879
2100	4.968	50.263	46.000	8.951	98.685	70.788	- 7.367
2200	4.968	50.494	46.199	9.448	99.160	69.448	- 6.899
2300	4.968	50.715	46.391	9.945	99.528	68.086	- 6.470
2400	4.968	50.926	46.575	10.442	100.088	66.706	- 6.074
2500	4.968	51.129	46.754	10.939	100.538	65.305	- 5.709
2600	4.968	51.324	46.926	11.435	100.976	63.887	- 5.370
2700	4.968	51.511	47.092	11.932	101.402	62.454	- 5.055
2800	4.968	51.692	47.253	12.429	101.813	61.003	- 4.762
2900	4.968	51.866	47.409	12.926	102.207	59.540	- 4.487
3000	4.968	52.035	47.561	13.423	102.583	58.060	- 4.230
3100	4.968	52.198	47.708	13.919	102.937	56.570	- 3.988
3200	4.968	52.355	47.850	14.416	103.268	55.071	- 3.761
3300	4.968	52.508	47.989	14.913	103.574	53.560	- 3.547
3400	4.968	52.657	48.124	15.410	103.851	52.041	- 3.345
3500	4.968	52.801	48.256	15.907	104.097	50.513	- 3.154
3600	4.968	52.941	48.384	16.403	104.307	48.979	- 2.973
3700	4.968	53.077	48.509	16.900	104.481	47.437	- 2.802
3800	4.968	53.209	48.631	17.397	104.614	45.896	- 2.640
3900	4.968	53.338	48.750	17.894	104.702	44.350	- 2.485
4000	4.968	53.464	48.866	18.390	104.740	42.800	- 2.338
4100	4.968	53.587	48.980	18.887	104.729	41.250	- 2.199
4200	4.968	53.706	49.091	19.384	104.663	39.705	- 2.066
4300	4.968	53.823	49.200	19.881	104.540	38.159	- 1.939
4400	4.968	53.937	49.306	20.378	104.358	36.620	- 1.819
4500	4.968	54.049	49.410	20.874	104.112	35.080	- 1.704
4600	4.968	54.158	49.512	21.371	103.805	33.551	- 1.594
4700	4.968	54.265	49.612	21.868	103.434	32.027	- 1.489
4800	4.968	54.370	49.710	22.365	102.999	30.510	- 1.389
4900	4.968	54.472	49.806	22.862	102.500	29.007	- 1.294
5000	4.968	54.573	49.901	23.358	101.937	27.514	- 1.203
5100	4.968	54.671	49.993	23.855	101.316	26.029	- 1.115
5200	4.968	54.767	50.084	24.352	100.637	24.561	- 1.032
5300	4.968	54.862	50.174	24.849	99.905	23.104	- .953
5400	4.968	54.955	50.261	25.346	99.123	21.661	- .877
5500	4.968	55.046	50.347	25.842	98.296	20.236	- .804
5600	4.968	55.136	50.432	26.339	97.429	18.820	- .734
5700	4.968	55.223	50.515	26.836	96.529	17.430	- .668
5800	4.968	55.310	50.597	27.333	95.601	16.048	- .605
5900	4.968	55.395	50.678	27.830	94.650	14.684	- .544
6000	4.968	55.478	50.757	28.326	93.683	13.340	- .486

June 30, 1968

CESIUM UNIPOSITIVE ION (Cs^+) (IDEAL GAS) GFW = 132.90445

Ground State Configuration $^1S_0$

ΔHf°_0 = 108.5 ± 1 kcal/mol

$S^\circ_{298.15}$ = 40.565 ± 0.0005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 108.1 ± 1 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

Heat of Formation

The ionization potential of Cs(g) was reported as 3.893 eV or 89.776 kcal/mol by C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1958. Based on this data we derived $\Delta Hf^\circ_{298.15}$ = 108.1 ± 1 kcal/mol for $Cs^+(g)$.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights were reported by Moore, loc. cit. However, the lowest electronic level above ground state is given as 107392.33 cm^{-1} which is so high that the evaluated thermodynamic properties of $Cs^+(g)$ will not be affected if we disregard all of these higher levels for calculation. Therefore we do not use them. The $H^\circ-H^\circ_{298}$ value at 0°K is -1.481 kcal/mol.

Cesium Fluoride (CsF)

(Crystal) GFW = 151.9034

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	12.420	21.100	21.100	.000	-132.570	-125.571	92.046
300	12.430	21.177	21.100	.023	-132.568	-125.528	91.447
400	12.850	24.810	21.593	1.287	-132.951	-123.034	67.223
500	13.280	27.724	22.537	2.593	-132.797	-120.573	52.702
600	13.710	30.183	23.611	3.943	-132.606	-118.144	43.034
700	14.130	32.328	24.707	5.335	-132.379	-115.751	36.139
800	14.550	34.242	25.781	6.769	-132.118	-113.394	30.978
900	14.970	35.980	26.819	8.245	-131.819	-111.071	26.972
1000	15.380	37.579	27.816	9.763	-147.565	-107.963	23.595
1100	15.740	39.063	28.772	11.320	-146.950	-104.031	20.669
1200	16.000	40.444	29.688	12.907	-146.308	-100.158	18.241
1300	16.180	41.732	30.565	14.517	-145.647	-96.338	16.196
1400	16.290	42.935	31.406	16.141	-144.974	-92.571	14.451
1500	16.370	44.062	32.213	17.774	-144.294	-88.851	12.946
1600	16.430	45.121	32.987	19.414	-143.610	-85.178	11.635
1700	16.470	46.118	33.730	21.059	-142.924	-81.547	10.484
1800	16.490	47.060	34.445	22.707	-142.239	-77.957	9.465
1900	16.500	47.952	35.133	24.357	-141.555	-74.403	8.558
2000	16.500	48.798	35.795	26.007	-140.877	-70.886	7.746

June 30, 1968

CESIUM FLUORIDE (CsF) (CRYSTAL) GFW = 151.9034

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [21.1 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -132.57 ± 0.5 kcal/mol

Tm = 976°K

ΔHm° = 5.19 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 47.37 kcal/mol

Heat of Formation

The enthalpy of solution (ΔHsoln) of CsF(c) in water at 298.15°K has been carefully determined with an adiabatic calorimeter by Somsen (1). Based on the reported value, $\Delta Hsoln^\circ_{298}$ = -8.62 ± 0.04 kcal/mol and ΔHf°_{298} = -61.69 (2) and -79.5 kcal/mol (3) for $Cs^+(\infty\ H_2O)$ and $F^-(\infty\ H_2O)$, respectively, the heat of formation for CsF(c) is calculated to be -132.57 kcal/mol which is adopted.

The value, $\Delta Hsoln^\circ_{298}$ = -8.81 ± 0.2 kcal/mol for CsF(c), was reported by Parker (4), which is in agreement with the value measured by Somsen (1).

Heat Capacity and Entropy

The heat capacities of CsF(c) are estimated according to the method of Kristov (5), based on $H^\circ_{976} - H^\circ_{298}$ = 9.4 kcal/mol reported by Dworkin (6). The entropy (S°_{298}) is estimated such that the calculated and observed vapor pressures are in good agreement (see CsF(g) and Cs_2F_2(g) tables for details).

Melting Data

Tm and ΔHm° are obtained from Bredig (7) and Dworkin (8). Bukhalova (9) reported Tm = 958°K,which is not adopted.

Heat of Sublimation

ΔHs°_{298} is calculated as the difference between ΔHf°_{298} for CsF(g) and CsF(c).

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Cesium Fluoride (CsF)

(Liquid) GFW = 151.9034

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	17.700	21.534	21.534	.000	-129.983	-123.114	90.245
300	17.700	21.644	21.535	.033	-129.971	-123.071	89.657
400	17.700	26.736	22.229	1.803	-129.848	-120.701	65.948
500	17.700	30.685	23.540	3.573	-129.231	-118.487	51.791
600	17.700	33.913	25.008	5.343	-128.619	-116.395	42.397
700	17.700	36.641	26.480	7.113	-128.014	-114.406	35.719
800	17.700	39.005	27.901	8.883	-127.417	-112.503	30.735
900	17.700	41.089	29.253	10.653	-126.824	-110.674	26.875
1000	17.700	42.954	30.531	12.423	-142.318	-108.091	23.623
1100	17.700	44.641	31.739	14.193	-141.490	-104.708	20.803
1200	17.700	46.181	32.879	15.963	-140.665	-101.400	18.467
1300	17.700	47.598	33.957	17.733	-139.844	-98.161	16.502
1400	17.700	48.910	34.979	19.503	-139.025	-94.986	14.828
1500	17.700	50.131	35.949	21.273	-138.208	-91.868	13.385
1600	17.700	51.273	36.871	23.043	-137.394	-88.806	12.130
1700	17.700	52.346	37.750	24.813	-136.583	-85.794	11.030
1800	17.700	53.358	38.590	26.583	-135.776	-82.831	10.057
1900	17.700	54.315	39.392	28.353	-134.972	-79.910	9.192
2000	17.700	55.223	40.161	30.123	-134.174	-77.032	8.418
2100	17.700	56.086	40.899	31.893	-133.382	-74.196	7.722
2200	17.700	56.910	41.609	33.663	-132.597	-71.396	7.093
2300	17.700	57.697	42.291	35.433	-131.820	-68.631	6.521
2400	17.700	58.450	42.949	37.203	-131.053	-65.900	6.001
2500	17.700	59.173	43.583	38.973	-130.297	-63.202	5.525
2600	17.700	59.867	44.196	40.743	-129.554	-60.532	5.088
2700	17.700	60.535	44.789	42.513	-128.824	-57.891	4.686
2800	17.700	61.178	45.363	44.283	-128.111	-55.278	4.315
2900	17.700	61.800	45.919	46.053	-127.415	-52.688	3.971
3000	17.700	62.400	46.459	47.823	-126.739	-50.124	3.652

June 30, 1968

CESIUM FLUORIDE (CsF) (LIQUID) GFW = 151.9034

$S^\circ_{298.15}$ = [21.534] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -129.983 kcal/mol

Tm = 976°K

ΔHm° = 5.19 kcal/mol

Tb = 1504°K

ΔHv° = 27.6 kcal/mol of liquid

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{976} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

Dworkin (1) measured the heat capacity of CsF(ℓ) at the melting point to be 17.7 gibbs/mol which is adopted and assumed to be constant in the temperature range 298 - 3000°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See CsF(c) for details.

Vaporization Data

Tb is the temperature at which the calculated vapor pressures of CsF(g) and $Cs_2F_2(g)$ equal one atmosphere. The vapor composition at Tm is calculated as CsF 80.3 per cent and Cs_2F_2 19.7 per cent. The heat required to vaporize one mole of liquid to the above vapor mixture at Tm is ΔHv°.

Tb has been observed as 1524 and 1526°K by Wartenberg (1) and Ruff (2), respectively, which are in fair agreement with the calculated one, 1504°K.

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
2. O. Ruff, G. Schmidt and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922).

Cesium Fluoride (CsF)

(Ideal Gas) GFW = 151.9034

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.304	-84.605	-84.605	INFINITE
100	7.291	49.399	65.419	-1.602	-84.764	-86.355	188.729
200	8.176	54.754	58.876	-.824	-84.977	-87.862	96.011
298	8.565	58.107	58.102	.000	-85.200	-89.233	65.410
300	8.570	58.155	58.102	.016	-85.205	-89.258	65.024
400	8.750	60.648	58.441	.883	-85.985	-90.403	49.394
500	8.848	62.612	59.086	1.763	-86.257	-91.477	39.985
600	8.909	64.231	59.812	2.651	-86.527	-92.495	33.691
700	8.952	65.608	60.544	3.544	-86.800	-93.468	29.182
800	8.985	66.806	61.254	4.441	-87.076	-94.403	25.790
900	9.012	67.865	61.931	5.341	-87.353	-95.301	23.142
1000	9.035	68.816	62.573	6.244	-103.714	-95.349	20.839
1100	9.056	69.678	63.180	7.148	-103.751	-94.510	18.777
1200	9.075	70.467	63.755	8.055	-103.790	-93.668	17.059
1300	9.093	71.194	64.299	8.963	-103.830	-92.823	15.605
1400	9.110	71.869	34.816	9.873	-103.872	-91.975	14.358
1500	9.126	72.498	65.308	10.785	-103.912	-91.123	13.277
1600	9.142	73.087	65.776	11.699	-103.955	-90.270	12.330
1700	9.158	73.642	66.222	12.614	-103.999	-89.413	11.495
1800	9.173	74.166	66.649	13.530	-104.046	-88.555	10.752
1900	9.187	74.662	67.058	14.448	-104.094	-87.692	10.087
2000	9.202	75.134	67.450	15.368	-104.146	-86.827	9.488
2100	9.217	75.583	67.827	16.289	-104.203	-85.960	8.946
2200	9.231	76.012	68.189	17.211	-104.266	-85.091	8.453
2300	9.245	76.423	68.538	18.135	-104.335	-84.217	8.002
2400	9.260	76.817	68.875	19.060	-104.412	-83.341	7.589
2500	9.274	77.195	69.200	19.987	-104.500	-82.461	7.209
2600	9.288	77.559	69.515	20.915	-104.599	-81.578	6.857
2700	9.302	77.910	69.819	21.844	-104.710	-80.689	6.531
2800	9.316	78.248	70.114	22.775	-104.835	-79.798	6.229
2900	9.329	78.576	70.401	23.707	-104.977	-78.900	5.946
3000	9.343	78.892	70.678	24.641	-105.138	-78.000	5.682
3100	9.357	79.199	70.948	25.576	-105.319	-77.092	5.435
3200	9.371	79.496	71.211	26.512	-105.524	-76.179	5.203
3300	9.385	79.784	71.466	27.450	-105.754	-75.258	4.984
3400	9.399	80.065	71.715	28.389	-106.011	-74.330	4.778
3500	9.412	80.337	71.957	29.330	-106.301	-73.393	4.583
3600	9.426	80.603	72.194	30.272	-106.624	-72.449	4.398
3700	9.440	80.861	72.425	31.215	-106.985	-71.494	4.223
3800	9.453	81.113	72.650	32.160	-107.386	-70.529	4.056
3900	9.467	81.359	72.870	33.106	-107.833	-69.555	3.898
4000	9.481	81.599	73.085	34.053	-108.326	-68.566	3.746
4100	9.494	81.833	73.296	35.002	-108.871	-67.566	3.602
4200	9.508	82.062	73.502	35.952	-109.470	-66.552	3.463
4300	9.522	82.286	73.704	36.903	-110.126	-65.522	3.330
4400	9.535	82.505	73.901	37.856	-110.841	-64.476	3.203
4500	9.549	82.719	74.095	38.811	-111.617	-63.415	3.080
4600	9.563	82.929	74.285	39.766	-112.456	-62.334	2.962
4700	9.576	83.135	74.471	40.723	-113.359	-61.234	2.847
4800	9.590	83.337	74.653	41.681	-114.326	-60.115	2.737
4900	9.603	83.535	74.833	42.641	-115.356	-58.975	2.630
5000	9.617	83.729	75.009	43.602	-116.448	-57.813	2.527
5100	9.631	83.920	75.181	44.564	-117.600	-56.631	2.427
5200	9.644	84.107	75.351	45.528	-118.809	-55.422	2.329
5300	9.658	84.291	75.518	46.493	-120.071	-54.191	2.235
5400	9.671	84.471	75.682	47.460	-121.383	-52.938	2.143
5500	9.685	84.649	75.844	48.427	-122.738	-51.657	2.053
5600	9.698	84.823	76.003	49.397	-124.133	-50.351	1.965
5700	9.712	84.995	76.159	50.367	-125.562	-49.021	1.880
5800	9.726	85.164	76.313	51.339	-127.018	-47.665	1.796
5900	9.739	85.331	76.464	52.312	-128.498	-46.286	1.715
6000	9.753	85.494	76.613	53.287	-129.992	-44.879	1.635

June 30, 1968

CESIUM FLUORIDE (CsF) (IDEAL GAS) GFW = 151.9034

Ground State Configuration $^1\Sigma^+$

ΔHf°_0 = -84.6 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 58.10 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -85.2 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 353 ± 4 cm^{-1}

B_e = 0.18437 cm^{-1}

$\omega_e x_e$ = 1.23 cm^{-1}

α_e = 0.001105 cm^{-1}

σ = 1

r_e = 2.345 Å

Heat of Formation

The vapor pressures of CsF(c) and CsF(ℓ) were measured by the manometric method (A) by Wartenberg (1), Ruff (2) and Cantor (3); the torsion-fiber effusion method (B) by Pugh (4); and the Knudsen effusion method (C) by Scheer (5). Based on the reported total pressures, the corresponding partial pressures of CsF(g) and Cs_2F_2(g) were evaluated using the adjusted heats of vaporization and Gibbs free energy functions such that the calculated and observed total pressures are in reasonable agreement, and the derived enthalpy changes by the second and third law methods are consistent. The results obtained are presented in the table below. The value of ΔHf°_{298}(CsF, g) is adopted as -82.5 ± 0.5 kcal/mol.

The dissociation energy (D_0) of CsF(g) has been reported using the spectroscopic convergence limit as 5.65eV(130.3 kcal/mol) and 5.5eV(126.8 kcal/mol) by Herzberg (6) and Gaydon (9), respectively. Based on the above two D_0 values, and ΔHf°_0 = 18.68 and 18.36 for Cs(g) and F(g), we obtain the corresponding value for ΔHf°_{298}(CsF, g) as -93.86 and -90.39 kcal/mol, which are not adopted.

Investigators	Reaction*	Method	ΔHr°_{298}, kcal/mol Second Law	ΔHr°_{298}, kcal/mol Third Law	Drift eu	ΔHf°_{298}, kcal/mol**
1. Wartenberg (1921)	2	A	45.39±0.15	44.98	-0.28±0.10	-85.00
2. Ruff (1922)	2	A	44.78±1.70	44.94	0.11±1.18	-85.04
3. Cantor (1958)	2	A	44.83	44.89	0.05±0.04	-85.09
4. Pugh (1958)	1	B	48.52±0.03	47.57	-1.18±0.04	-85.00
5. Scheer (1962)	1	C	48.43±0.27	46.61	-2.35±0.35	-85.96

*1 represents the reaction CsF(c) = CsF(g); 2, the reaction CsF(ℓ) = CsF(g).

**Calculation based on the third law ΔHr°_{298}, and ΔHf°_{298} = -132.57 and -129.983 kcal/mol for CsF(c) and CsF(ℓ), respectively.

Heat Capacity and Entropy

The ground state configuration was reported by Herzberg (6). The molecular constants are obtained from Honig (7), who observed the microwave spectra of CsF(g) at temperatures of about 700°C. Based on the J = 1 → 2 transition, the molecular constants are derived. The vibrational frequency (ω_e) has been reported, from different kinds of spectra, in the range 270 - 385 cm^{-1} by many investigators, e.g. radiofrequency, infrared, ultraviolet, microwave, etc. The value of ω_e adopted was reported by Baikov (8), who also reviewed the ω_e values obtained by the earlier investigators.

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), 1391 - 1524°K, 6 points. Two data points at 1228 and 1319°K are not adopted for evaluation due to the inconsistency with the other data.
2. O. Ruff, G. Schmidt and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922), 1306 - 1528°K, 7 points.
3. S. Cantor and F. Blankenship, "Vapor Pressure of the Alkali Fluorides," Oak Ridge National Laboratory, Oak Ridge, Tennessee, September 1958, 1009 - 1380°K, 7 points calculated using the given vapor pressure equation.
4. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958), 753 - 856°K, 6 points.
5. M. D. Scheer and J. Fine, J. Chem. Phys. 36, 1647 (1962), 677 - 878°K, 32 points. Evaluation based on the reported data points.
6. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
7. A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 96, 629 (1954).
8. V. I. Baikov and K. P. Vasilevskii, Opt. Spectry. (USSR) (English Transl.) 22, 198 (1967).
9. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Cesium Monoxide (CsO)
(Ideal Gas) GFW = 148.9044

T, °K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.361	15.520	15.520	INFINITE
100	7.569	52.061	68.567	-1.651	15.371	13.548	-29.609
200	8.424	57.621	61.839	-.844	15.189	11.798	-12.892
298	8.719	61.049	61.049	.000	15.000	10.171	-7.456
300	8.722	61.103	61.049	.016	14.996	10.141	-7.388
400	8.854	63.632	61.393	.896	14.258	8.723	-4.766
500	8.927	65.616	62.046	1.785	14.033	7.365	-3.219
600	8.976	67.249	62.781	2.680	13.808	6.053	-2.205
700	9.013	68.635	63.521	3.580	13.579	4.779	-1.492
800	9.043	69.841	64.237	4.483	13.343	3.536	-.966
900	9.069	70.907	64.920	5.388	13.102	2.326	-.565
1000	9.093	71.864	65.568	6.296	-3.224	1.962	-.429
1100	9.115	72.732	66.180	7.207	-3.229	2.482	-.493
1200	9.137	73.526	66.760	8.119	-3.238	3.001	-.547
1300	9.157	74.258	67.309	9.034	-3.249	3.522	-.592
1400	9.177	74.937	67.829	9.951	-3.862	4.042	-.631
1500	9.196	75.571	68.325	10.869	-3.276	4.565	-.665
1600	9.216	76.165	68.796	11.790	-3.293	5.088	-.695
1700	9.235	76.724	69.246	12.712	-3.311	5.612	-.722
1800	9.253	77.253	69.677	13.637	-3.333	6.137	-.745
1900	9.272	77.753	70.089	14.563	-3.358	6.665	-.767
2000	9.290	78.230	70.484	15.491	-3.388	7.193	-.786
2100	9.309	78.683	70.864	16.421	-3.424	7.723	-.804
2200	9.327	79.117	71.229	17.353	-3.467	8.254	-.820
2300	9.345	79.532	71.581	18.287	-3.516	8.788	-.835
2400	9.363	79.930	71.921	19.222	-3.576	9.325	-.849
2500	9.381	80.312	72.249	20.159	-3.647	9.863	-.862
2600	9.399	80.681	72.566	21.098	-3.729	10.405	-.875
2700	9.417	81.036	72.873	22.039	-3.825	10.951	-.886
2800	9.435	81.379	73.171	22.982	-3.937	11.500	-.898
2900	9.453	81.710	73.460	23.926	-4.065	12.054	-.908
3000	9.471	82.031	73.740	24.872	-4.214	12.613	-.919
3100	9.489	82.342	74.012	25.820	-4.383	13.177	-.929
3200	9.507	82.643	74.277	26.770	-4.577	13.745	-.939
3300	9.525	82.936	74.535	27.722	-4.797	14.320	-.948
3400	9.543	83.221	74.787	28.675	-5.045	14.904	-.958
3500	9.561	83.498	75.032	29.630	-5.325	15.494	-.967
3600	9.579	83.767	75.271	30.587	-5.640	16.093	-.977
3700	9.597	84.030	75.504	31.546	-5.992	16.702	-.987
3800	9.614	84.286	75.732	32.507	-6.385	17.322	-.996
3900	9.632	84.536	75.954	33.469	-6.822	17.950	-1.006
4000	9.650	84.780	76.172	34.433	-7.308	18.591	-1.016
4100	9.668	85.019	76.385	35.399	-7.845	19.245	-1.026
4200	9.686	85.252	76.593	36.367	-8.436	19.912	-1.036
4300	9.703	85.480	76.797	37.336	-9.083	20.596	-1.047
4400	9.721	85.703	76.997	38.307	-9.790	21.293	-1.058
4500	9.739	85.922	77.193	39.280	-10.557	22.008	-1.069
4600	9.757	86.136	77.385	40.255	-11.387	22.743	-1.081
4700	9.775	86.346	77.573	41.232	-12.280	23.494	-1.092
4800	9.792	86.552	77.758	42.210	-13.236	24.266	-1.105
4900	9.810	86.754	77.940	43.190	-14.256	25.055	-1.118
5000	9.828	86.953	78.118	44.172	-15.336	25.868	-1.131
5100	9.846	87.147	78.293	45.156	-16.476	26.705	-1.144
5200	9.864	87.339	78.465	46.141	-17.673	27.561	-1.158
5300	9.881	87.527	78.634	47.129	-18.921	28.445	-1.173
5400	9.899	87.712	78.801	48.118	-20.218	29.349	-1.188
5500	9.917	87.893	78.965	49.109	-21.558	30.281	-1.203
5600	9.935	88.072	79.126	50.101	-22.937	31.234	-1.219
5700	9.952	88.248	79.284	51.095	-24.349	32.214	-1.235
5800	9.970	88.421	79.440	52.092	-25.787	33.221	-1.252
5900	9.988	88.592	79.594	53.089	-27.248	34.249	-1.269
6000	10.006	88.760	79.745	54.089	-28.721	35.306	-1.286

Dec. 31, 1968

CESIUM MONOXIDE (CsO) (IDEAL GAS) GFW = 148.9044

Ground State Configuration $[^2\pi]$

ΔHf°_0 = [15.5 ± 10] kcal/mol

$S^\circ_{298.15}$ = [61 ± 1] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [15.0 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]

ω_e = [280] cm^{-1}

$\omega_e x_e$ = [1.0] cm^{-1}

σ = 1

B_e = [0.198] cm^{-1}

α_e = [0.001] cm^{-1}

r_e = [2.40] Å

Heat of Formation

The heat of formation is estimated from three calculated values. The methods of estimation are described as follows. Brewer and Margrave (1) suggested that the ΔHf value for MO(g) from the gaseous ions can be taken as the mean of the corresponding ΔHf values for the the alkali fluoride and chloride with a maximum uncertainty of 10 kcal/mol. Adopting ΔHr°_{298} = -131.1 and -109.6 kcal/mol for the reaction $Cs^+(g) + F^-(g) = CsF(g)$ and $Cs^+(g) + Cl^-(g) = CsCl(g)$, respectively, we obtain ΔHr°_{298} = -120.4 kcal/mol for $Cs^+(g) + O^-(g) = CsO(g)$ which leads to ΔHf°_{298}(CsO, g) = 12.0 kcal/mol. The ΔHf°_{298} values of the above species used for calculation are taken from the respective JANAF Thermochemical Tables.

Based on the assumption that D(Cs-O) = 1/2[D(Cs_2) + D(O_2)], we derive D_{298}(Cs-O) = 65.2 kcal/mol and ΔHf°_{298} = 12.7 kcal/mol for CsO(g).

Adopting the Cs-O bond energy as half of the atomization energy of Cs_2O, we calculate D(Cs-O) = 60 ± 10 kcal/mol and ΔHf°_{298}(CsO, g) = 17 ± 10 kcal/mol.

The heat of formation for CsO(g) is tentatively selected as 15 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of the isoelectronic molecule OH(g). ω_e is estimated from those of LiO(g), CsF(g), and CsCl(g). The bond distance is taken from that in CsOH(g) reported by Lide and Kuczkowski (2). $\omega_e x_e$ is estimated by comparison with those of the other alkali oxides. The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg (3). The moment of inertia is 1.413×10^{-38} g cm^2.

References

1. L. Brewer and J. L. Margrave, J. Phys. Chem. 59, 421 (1955).
2. D. R. Lide, Jr. and R. L. Kuczkowski, J. Chem. Phys. 46, 4768 (1967).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Cesium, Dimeric (Cs_2)

(Ideal Gas) GFW = 265.810

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.635	26.453	26.453	INFINITE
100	8.942	58.007	75.921	-1.791	26.271	23.097	-50.478
200	9.046	64.243	68.698	-.891	25.889	20.063	-21.923
298	9.112	67.867	67.867	.000	25.400	17.301	-12.682
300	9.114	67.923	67.867	.017	25.389	17.251	-12.567
400	9.176	70.554	68.225	.931	23.779	14.957	-8.172
500	9.237	72.608	68.904	1.852	23.202	12.818	-5.603
600	9.297	74.297	69.666	2.779	22.645	10.795	-3.932
700	9.357	75.735	70.433	3.711	22.097	8.864	-2.767
800	9.416	76.988	71.176	4.650	21.556	7.009	-1.915
900	9.476	78.101	71.884	5.595	21.023	5.224	-1.269
1000	9.536	79.102	72.557	6.545	-11.669	5.138	-1.123
1100	9.597	80.014	73.194	7.502	-11.704	6.822	-1.355
1200	9.659	80.852	73.798	8.465	-11.735	8.507	-1.549
1300	9.723	81.627	74.371	9.434	-11.760	10.195	-1.714
1400	9.791	82.350	74.915	10.409	-11.781	11.883	-1.855
1500	9.861	83.028	75.434	11.392	-11.792	13.575	-1.978
1600	9.937	83.667	75.928	12.382	-11.800	15.266	-2.085
1700	10.017	84.272	76.402	13.380	-11.802	16.958	-2.180
1800	10.103	84.847	76.855	14.385	-11.801	18.649	-2.264
1900	10.195	85.396	77.290	15.400	-11.794	20.342	-2.340
2000	10.294	85.921	77.709	16.425	-11.785	22.033	-2.408
2100	10.400	86.426	78.112	17.459	-11.777	23.723	-2.469
2200	10.512	86.912	78.501	18.505	-11.769	25.413	-2.525
2300	10.632	87.382	78.877	19.562	-11.762	27.104	-2.575
2400	10.758	87.837	79.241	20.631	-11.761	28.793	-2.622
2500	10.891	88.279	79.593	21.714	-11.766	30.482	-2.665
2600	11.030	88.709	79.936	22.810	-11.780	32.172	-2.704
2700	11.175	89.128	80.268	23.920	-11.806	33.864	-2.741
2800	11.325	89.537	80.592	25.045	-11.847	35.555	-2.775
2900	11.479	89.937	80.908	26.185	-11.905	37.250	-2.807
3000	11.638	90.329	81.215	27.341	-11.985	38.947	-2.837
3100	11.800	90.713	81.515	28.513	-12.091	40.646	-2.866
3200	11.964	91.090	81.809	29.701	-12.229	42.348	-2.892
3300	12.130	91.461	82.096	30.906	-12.400	44.057	-2.918
3400	12.297	91.826	82.376	32.127	-12.611	45.771	-2.942
3500	12.465	92.184	82.651	33.365	-12.869	47.492	-2.966
3600	12.631	92.538	82.921	34.620	-13.180	49.219	-2.988
3700	12.797	92.886	83.186	35.891	-13.549	50.959	-3.010
3800	12.961	93.230	83.446	37.179	-13.983	52.709	-3.031
3900	13.122	93.568	83.701	38.483	-14.491	54.470	-3.052
4000	13.280	93.903	83.952	39.804	-15.078	56.246	-3.073
4100	13.434	94.232	84.198	41.139	-15.753	58.037	-3.094
4200	13.585	94.558	84.441	42.490	-16.522	59.844	-3.114
4300	13.731	94.879	84.680	43.856	-17.390	61.672	-3.135
4400	13.873	95.197	84.916	45.236	-18.362	63.523	-3.155
4500	14.009	95.510	85.148	46.630	-19.444	65.395	-3.176
4600	14.141	95.819	85.376	48.038	-20.638	67.294	-3.197
4700	14.267	96.125	85.602	49.458	-21.948	69.220	-3.219
4800	14.388	96.426	85.824	50.891	-23.373	71.175	-3.241
4900	14.503	96.724	86.044	52.336	-24.914	73.160	-3.263
5000	14.613	97.018	86.260	53.792	-26.568	75.179	-3.286
5100	14.718	97.309	86.474	55.258	-28.332	77.231	-3.310
5200	14.817	97.596	86.685	56.735	-30.201	79.317	-3.334
5300	14.911	97.879	86.894	58.221	-32.167	81.443	-3.358
5400	15.000	98.158	87.100	59.717	-34.223	83.605	-3.384
5500	15.085	98.434	87.303	61.221	-36.359	85.807	-3.410
5600	15.164	98.707	87.504	62.734	-38.566	88.047	-3.436
5700	15.239	98.976	87.703	64.254	-40.834	90.329	-3.463
5800	15.310	99.242	87.900	65.782	-43.150	92.651	-3.491
5900	15.377	99.504	88.094	67.316	-45.506	95.012	-3.519
6000	15.439	99.763	88.287	68.857	-47.885	97.414	-3.548

June 30, 1968

CESIUM, DIMERIC (Cs_2) (IDEAL GAS) GFW = 265.810

Ground State Configuration ${}^1\Sigma_g^+$

$S^\circ_{298.15}$ = [67.87] gibbs/mol

ΔHf°_0 = 26.45 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 25.40 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
${}^1\Sigma_g^+$	0	1
${}^1\Sigma_\mu^+$	9000	1
${}^1\Pi_\mu$	13043.87	2
$[{}^1\Sigma_\mu^+]$	16066.03	[1]
$[{}^1\Pi_\mu]$	16175.80	[2]

ω_e = 41.99 cm^{-1}

B_e = [0.01263] cm^{-1}

$\omega_e x_e$ = 0.08005 cm^{-1}

α_e = [0.000035] cm^{-1}

σ = 2

r_e = [4.48] Å

Heat of Formation

The vapor pressures of Cs(g) and Cs_2(g) over Cs(ℓ) have been measured by many investigators (see Cs(g) table for details). For internal consistency, the vapor pressures determined at temperatures 980-1684°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-V-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHr°_{298} = 11.24 kcal/mol for the reaction $Cs_2(g) = 2Cs(g)$, the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction $Cs_2(g) = 2Cs(g)$ is calculated by the second and third law methods. The results are presented in the table below. The value of $\Delta Hf^\circ_{298}(Cs_2, g)$ is adopted as 25.40 ± 1.0 kcal/mol.

The D_0(Cs-Cs) was reported as 0.45 eV or 10.38 kcal/mol by Gaydon (5) and Herzberg (3), yielding ΔHf°_{298} = 25.93 ± 0.92 kcal/mol for Cs_2(g) which is in agreement with the adopted value, within the experimental uncertainty.

Expt. No.	No. of Points	Temperature, °K	Pressure, atm	ΔHr°_{298}, kcal/mol Second Law	ΔHr°_{298}, kcal/mol Third Law	Drift eu	ΔHf°_{298}* kcal/mol
28 (1)	23	1151-1680	4.7-7.5	12.39±0.10	11.63	-0.55±0.07	25.01
30 (1)	24	980-1684	1.1-2.0	10.90±0.16	11.24	0.25±0.12	25.40
38 (1)	19	1100-1657	3.2-5.2	12.28±0.22	11.22	-0.77±0.16	25.42
1-6, 8, 10 (2)	54	955-1375	1.0-5.4	12.35±0.70	11.47	-0.74±0.58	25.17

*Calculation based on the third law ΔHr°_{298} and ΔHf°_{298}(Cs, g) = 18.32 kcal/mol.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights, ω_{e_1} and $\omega_e x_e$ are obtained from Herzberg (3). The second electronic level is reported as 8800-11000 cm^{-1} and the value 9000 cm^{-1} is chosen for calculation. The last two electronic states are estimated by comparison with those for K_2(g) given by (3). The bond distance r_e is calculated from ω based on the method suggested by Guggenheimer (4). The values of B_e and α_e are calculated (3). The moment of inertia is 2.2145×10^{-37} g cm^2.

References

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Cesium Fluoride, Dimeric (Cs_2F_2)

(Ideal Gas) GFW = 303.8068

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.606	-211.548	-211.548	INFINITE
100	14.917	65.063	100.445	-3.538	-212.201	-212.011	463.350
200	18.239	76.707	85.904	-1.840	-212.485	-211.695	231.329
298	19.093	84.179	84.179	.000	-212.740	-211.258	154.856
300	19.103	84.297	84.179	.035	-212.747	-211.249	153.894
400	19.430	89.844	84.933	1.964	-214.112	-210.367	114.939
500	19.586	94.198	86.366	3.916	-214.465	-209.392	91.525
600	19.672	97.777	87.979	5.879	-214.818	-208.342	75.889
700	19.725	100.814	89.601	7.849	-215.179	-207.234	64.701
800	19.759	103.450	91.171	9.823	-215.551	-206.076	56.297
900	19.782	105.779	92.667	11.801	-215.927	-204.868	49.749
1000	19.799	107.864	94.084	13.780	-248.475	-201.978	44.142
1100	19.812	109.752	95.424	15.760	-248.379	-197.331	39.206
1200	19.821	111.476	96.691	17.742	-248.288	-192.694	35.094
1300	19.829	113.063	97.890	19.725	-248.202	-188.064	31.616
1400	19.835	114.533	99.027	21.708	-248.122	-183.443	28.637
1500	19.839	115.901	100.107	23.691	-248.044	-178.824	26.055
1600	19.843	117.182	101.135	25.676	-247.972	-174.213	23.796
1700	19.847	118.385	102.114	27.660	-247.906	-169.604	21.804
1800	19.849	119.519	103.050	29.645	-247.847	-165.002	20.034
1900	19.852	120.593	103.945	31.630	-247.794	-160.399	18.450
2000	19.854	121.611	104.803	33.615	-247.752	-155.800	17.025
2100	19.855	122.580	105.627	35.601	-247.722	-151.205	15.736
2200	19.857	123.503	106.419	37.586	-247.708	-146.610	14.564
2300	19.858	124.386	107.181	39.572	-247.707	-142.013	13.494
2400	19.859	125.231	107.915	41.558	-247.727	-137.418	12.514
2500	19.860	126.042	108.624	43.544	-247.770	-132.822	11.611
2600	19.861	126.821	109.309	45.530	-247.837	-128.222	10.778
2700	19.862	127.570	109.972	47.516	-247.932	-123.619	10.006
2800	19.862	128.293	110.613	49.502	-248.059	-119.014	9.289
2900	19.863	128.990	111.235	51.488	-248.221	-114.399	8.621
3000	19.864	129.663	111.838	53.475	-248.423	-109.785	7.998
3100	19.864	130.314	112.424	55.461	-248.669	-105.159	7.414
3200	19.865	130.945	112.993	57.448	-248.965	-100.525	6.866
3300	19.865	131.556	113.546	59.434	-249.314	-95.882	6.350
3400	19.865	132.149	114.085	61.421	-249.720	-91.225	5.864
3500	19.866	132.725	114.609	63.407	-250.194	-86.555	5.405
3600	19.866	133.285	115.120	65.394	-250.738	-81.873	4.970
3700	19.866	133.829	115.618	67.380	-251.360	-77.173	4.558
3800	19.867	134.359	116.105	69.367	-252.065	-72.454	4.167
3900	19.867	134.875	116.579	71.354	-252.863	-67.720	3.795
4000	19.867	135.378	117.043	73.340	-253.759	-62.960	3.440
4100	19.867	135.869	117.496	75.327	-254.759	-58.180	3.101
4200	19.868	136.347	117.939	77.314	-255.871	-53.372	2.777
4300	19.868	136.815	118.373	79.301	-257.098	-48.536	2.467
4400	19.868	137.272	118.797	81.287	-258.448	-43.670	2.169
4500	19.868	137.718	119.213	83.274	-259.922	-38.774	1.883
4600	19.868	138.155	119.620	85.261	-261.524	-33.842	1.608
4700	19.868	138.582	120.019	87.248	-263.257	-28.872	1.343
4800	19.869	139.000	120.410	89.235	-265.119	-23.865	1.087
4900	19.869	139.410	120.793	91.221	-267.113	-18.818	.839
5000	19.869	139.812	121.170	93.208	-269.232	-13.730	.600
5100	19.869	140.205	121.539	95.195	-271.473	-8.601	.369
5200	19.869	140.591	121.902	97.182	-273.832	-3.421	.144
5300	19.869	140.969	122.258	99.169	-276.299	1.804	-.074
5400	19.869	141.341	122.608	101.156	-278.869	7.070	-.286
5500	19.869	141.705	122.952	103.143	-281.528	12.392	-.492
5600	19.869	142.063	123.290	105.130	-284.270	17.761	-.693
5700	19.869	142.415	123.622	107.117	-287.082	23.181	-.889
5800	19.869	142.761	123.949	109.104	-289.951	28.649	-1.080
5900	19.870	143.100	124.271	111.091	-292.869	34.163	-1.265
6000	19.870	143.434	124.588	113.078	-295.819	39.733	-1.447

June 30, 1968

CESIUM FLUORIDE, DIMERIC (Cs_2F_2) (IDEAL GAS) GFW = 303.8068

Point Group [D_{2h}]

ΔHf_0° = -211.55 ± 2.0 kcal/mol

$S^\circ_{298.15}$ = [84 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -212.74 ± 2.0 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[200] (1)	[120] (1)
[110] (1)	[220] (1)
[210] (1)	[230] (1)

Bond Distance: Cs-F = [2.35] Å

Bond Angle: F-Cs-F = [85°] Cs-F-Cs = [95°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.126 x 10^{-112}] g^3 cm^6

Heat of Formation

Evidence from the velocity distribution in molecular beams (1) has shown that alkali halide vapors contain significant amounts of polymeric species. Using the same method Eisenstadt (2) determined the molecular composition of CsF vapor in the temperature range 838 - 919°K. Based on the reported equilibrium constants for the reaction $(CsF)_2(g) = 2CsF(g)$, we evaluate the enthalpy change (ΔHr°_{298}) by the second and third law methods to be 40.53 ± 1.75 and 42.34 ± 0.26 kcal/mol, respectively. Employing ΔHf°_{298} = 42.34 and ΔHf°_{298}(CsF, g) = -85.2 kcal/mol, we obtained ΔHf°_{298} = -212.74 kcal/mol for Cs_2F_2(g), which is adopted.

Heat Capacity and Entropy

The Cs_2F_2 molecule is assumed to have a rhombic configuration of symmetry D_{2h} as Cs_2Cl_2(3). The Cs-F bond distance is taken as the same as that in CsF(g). The bond angles and vibrational frequencies are estimated by comparison with those of the other dimeric alkali halides (3, 4). The three principal moments of inertia are: I_A = 1.590 x 10^{-38}, I_B = 1.325 x 10^{-37} and I_C = 1.484 x 10^{-37} g cm^2.

References

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Dicesium Monoxide (Cs_2O)

(Ideal Gas) GFW = 281.8094

T, °K	Cp°	gibbs/mol S°	−(G°−H°298)/T	H°−H°298	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.331	-20.606	-20.606	INFINITE
100	10.503	62.790	87.229	-2.444	-21.091	-22.674	49.554
200	12.564	70.834	77.191	-1.272	-21.549	-24.072	26.304
298	13.238	75.998	75.998	.000	-22.000	-25.218	18.485
300	13.245	76.079	75.998	.024	-22.010	-25.238	18.386
400	13.521	79.933	76.521	1.365	-23.549	-25.905	14.154
500	13.657	82.966	77.518	2.724	-24.053	-26.436	11.555
600	13.732	85.464	78.640	4.094	-24.545	-26.865	9.786
700	13.779	87.584	79.770	5.470	-25.038	-27.212	8.496
800	13.809	89.426	80.864	6.849	-25.538	-27.491	7.510
900	13.830	91.054	81.908	8.231	-26.041	-27.703	6.727
1000	13.845	92.512	82.897	9.615	-58.712	-26.219	5.730
1100	13.856	93.832	83.832	11.000	-58.739	-22.968	4.563
1200	13.865	95.038	84.716	12.386	-58.771	-19.714	3.590
1300	13.872	96.148	85.553	13.773	-58.806	-16.458	2.767
1400	13.877	97.176	86.347	15.161	-58.847	-13.201	2.061
1500	13.881	98.134	87.101	16.548	-58.889	-9.938	1.448
1600	13.885	99.030	87.819	17.937	-58.937	-6.673	.912
1700	13.888	99.872	88.504	19.325	-58.989	-3.405	.438
1800	13.890	100.666	89.158	20.714	-59.049	-.134	.016
1900	13.892	101.417	89.783	22.103	-59.115	3.142	-.361
2000	13.894	102.129	90.383	23.493	-59.192	6.420	-.702
2100	13.895	102.807	90.958	24.882	-59.281	9.703	-1.010
2200	13.897	103.454	91.512	26.272	-59.385	12.989	-1.290
2300	13.898	104.071	92.045	27.661	-59.504	16.282	-1.547
2400	13.899	104.663	92.558	29.051	-59.643	19.580	-1.783
2500	13.900	105.230	93.054	30.441	-59.805	22.883	-2.000
2600	13.900	105.775	93.533	31.831	-59.991	26.195	-2.202
2700	13.901	106.300	93.996	33.221	-60.206	29.514	-2.389
2800	13.902	106.806	94.444	34.611	-60.453	32.841	-2.563
2900	13.902	107.293	94.879	36.002	-60.735	36.179	-2.727
3000	13.903	107.765	95.301	37.392	-61.057	39.526	-2.879
3100	13.903	108.221	95.710	38.782	-61.423	42.885	-3.023
3200	13.904	108.662	96.108	40.173	-61.840	46.255	-3.159
3300	13.904	109.090	96.495	41.563	-62.308	49.639	-3.287
3400	13.904	109.505	96.872	42.953	-62.836	53.040	-3.409
3500	13.905	109.908	97.238	44.344	-63.428	56.456	-3.525
3600	13.905	110.300	97.596	45.734	-64.093	59.891	-3.636
3700	13.905	110.681	97.944	47.125	-64.833	63.346	-3.742
3800	13.906	111.052	98.284	48.515	-65.657	66.822	-3.843
3900	13.906	111.413	98.616	49.906	-66.572	70.319	-3.941
4000	13.906	111.765	98.941	51.297	-67.586	73.841	-4.034
4100	13.906	112.108	99.258	52.687	-68.703	77.391	-4.125
4200	13.906	112.443	99.568	54.078	-69.931	80.967	-4.213
4300	13.907	112.771	99.871	55.469	-71.274	84.576	-4.299
4400	13.907	113.090	100.168	56.859	-72.737	88.218	-4.382
4500	13.907	113.403	100.458	58.250	-74.325	91.893	-4.463
4600	13.907	113.709	100.743	59.641	-76.039	95.608	-4.542
4700	13.907	114.008	101.022	61.031	-77.884	99.359	-4.620
4800	13.907	114.300	101.296	62.422	-79.856	103.151	-4.697
4900	13.907	114.587	101.564	63.813	-81.958	106.982	-4.772
5000	13.908	114.868	101.827	65.204	-84.185	110.861	-4.846
5100	13.908	115.144	102.086	66.594	-86.533	114.787	-4.919
5200	13.908	115.414	102.339	67.985	-88.997	118.755	-4.991
5300	13.908	115.679	102.589	69.376	-91.568	122.777	-5.063
5400	13.908	115.938	102.833	70.767	-94.239	126.844	-5.134
5500	13.908	116.194	103.074	72.157	-96.999	130.965	-5.204
5600	13.908	116.444	103.311	73.548	-99.840	135.134	-5.274
5700	13.908	116.690	103.543	74.939	-102.749	139.356	-5.343
5800	13.908	116.932	103.772	76.330	-105.715	143.632	-5.412
5900	13.908	117.170	103.997	77.721	-108.727	147.954	-5.481
6000	13.908	117.404	104.219	79.112	-111.770	152.333	-5.549

Dec. 31, 1968

DICESIUM MONOXIDE (Cs_2O) (IDEAL GAS) GFW = 281.8094

Point Group C_{2v}

ΔHf°_0 = -20.6 ± 10 kcal/mol

$S^\circ_{298.15}$ = [76 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -22.0 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[290] (1)
[130] (1)
[300] (1)

Bond Distance: Cs-O = [2.4] Å

Bond Angle: Cs-O-Cs = [105°]

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.415 x 10^{-112}] g^3cm^6

Heat of Formation

The appearance potentials of CsOH and Cs_2O ions were investigated by Emel'yanov et al. (1), using the electron-impact method with a mass spectrometer fitted with a heated ion source and a Pt effusion chamber. The heat of atomization of Cs_2O was derived as 117 ± 9 kcal/mol. Based on this value we calculate the heat of formation (ΔHf°_{298}) of Cs_2O to be -22 ± 10 kcal/mol, employing ΔHf°_0 = 18.68 and 58.99 kcal/mol for Cs(g) and O(g), respectively. Brewer and Mastick (2) calculated theoretically the stability of gaseous alkali oxides according to ionic models and gave the heats of formation from gaseous atoms for Cs_2O(g) as -24 kcal/mol. The ΔHf°_{298} value is evaluated to be 72.2 kcal/mol which is not adopted.

Heat Capacity and Entropy

The molecular structure of Cs_2O(g) has been determined to be nonlinear by Büchler et al. (3), using electric-deflection method. The Cs-O bond distance is assumed to be the same as that in CsOH(g) reported by Lide and Kuczkowski (4). The bond angle is estimated by comparison with that in the H_2O molecule. Three vibrational frequencies are estimated from those for H_2O(g). The three principal moments of inertia are: $I_A = 5.350 \times 10^{-39}$, $I_B = 1.600 \times 10^{-37}$, and $I_C = 1.6535 \times 10^{-37}$ g cm^2.

References

1. A. M. Emel'yanov, A. V. Gusarov, L. N. Gorokhov, and N. A. Sadovnikova, Teor. Eksp. Khim. 3, 226 (1967).
2. L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951).
3. A. Büchler and J. L. Stauffer and W. Klemperer, J. Chem. Phys. 46, 605 (1967).
4. D. R. Lide, Jr. and R. L. Kuczkowski, J. Chem. Phys. 46, 4768 (1967).

Copper (Cu)

(Reference State) At. Wt. = 63.54

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.195	.000	.000	.000
100	3.826	2.392	12.749	-1.036	.000	.000	.000
200	5.399	5.661	8.437	-.555	.000	.000	.000
298	5.843	7.913	7.913	.000	.000	.000	.000
300	5.846	7.949	7.913	.011	.000	.000	.000
400	6.077	9.665	8.146	.608	.000	.000	.000
500	6.250	11.040	8.591	1.224	.000	.000	.000
600	6.394	12.193	9.098	1.857	.000	.000	.000
700	6.516	13.188	9.613	2.502	.000	.000	.000
800	6.620	14.064	10.116	3.159	.000	.000	.000
900	6.725	14.850	10.599	3.826	.000	.000	.000
1000	6.822	15.564	11.060	4.504	.000	.000	.000
1100	6.910	16.218	11.500	5.190	.000	.000	.000
1200	6.998	16.823	11.918	5.886	.000	.000	.000
1300	7.086	17.387	12.318	6.590	.000	.000	.000
1400	7.500	20.263	12.772	10.488	.000	.000	.000
1500	7.500	20.780	13.288	11.238	.000	.000	.000
1600	7.500	21.264	13.772	11.988	.000	.000	.000
1700	7.500	21.719	14.226	12.738	.000	.000	.000
1800	7.500	22.148	14.654	13.488	.000	.000	.000
1900	7.500	22.553	15.060	14.238	.000	.000	.000
2000	7.500	22.938	15.444	14.988	.000	.000	.000
2100	7.500	23.304	15.810	15.738	.000	.000	.000
2200	7.500	23.653	16.158	16.488	.000	.000	.000
2300	7.500	23.986	16.491	17.238	.000	.000	.000
2400	7.500	24.305	16.810	17.988	.000	.000	.000
2500	7.500	24.612	17.116	18.738	.000	.000	.000
2600	7.500	24.906	17.410	19.488	.000	.000	.000
2700	7.500	25.189	17.693	20.238	.000	.000	.000
2800	7.500	25.462	17.966	20.988	.000	.000	.000
2900	5.892	51.236	18.686	94.396	.000	.000	.000
3000	6.010	51.438	19.774	94.991	.000	.000	.000
3100	6.131	51.637	20.799	95.598	.000	.000	.000
3200	6.253	51.834	21.766	96.217	.000	.000	.000
3300	6.375	52.028	22.680	96.849	.000	.000	.000
3400	6.496	52.220	23.546	97.492	.000	.000	.000
3500	6.616	52.410	24.368	98.148	.000	.000	.000
3600	6.732	52.598	25.149	98.815	.000	.000	.000
3700	6.846	52.784	25.894	99.494	.000	.000	.000
3800	6.954	52.968	26.604	100.184	.000	.000	.000
3900	7.059	53.150	27.282	100.885	.000	.000	.000
4000	7.158	53.330	27.931	101.596	.000	.000	.000
4100	7.251	53.508	28.553	102.316	.000	.000	.000
4200	7.339	53.684	29.149	103.046	.000	.000	.000
4300	7.421	53.858	29.722	103.784	.000	.000	.000
4400	7.498	54.029	30.272	104.530	.000	.000	.000
4500	7.568	54.198	30.802	105.283	.000	.000	.000
4600	7.633	54.365	31.312	106.043	.000	.000	.000
4700	7.693	54.530	31.805	106.810	.000	.000	.000
4800	7.747	54.693	32.280	107.582	.000	.000	.000
4900	7.797	54.853	32.739	108.359	.000	.000	.000
5000	7.842	55.011	33.183	109.141	.000	.000	.000
5100	7.884	55.167	33.612	109.927	.000	.000	.000
5200	7.921	55.320	34.028	110.718	.000	.000	.000
5300	7.955	55.471	34.431	111.512	.000	.000	.000
5400	7.987	55.620	34.822	112.309	.000	.000	.000
5500	8.016	55.767	35.202	113.109	.000	.000	.000
5600	8.043	55.912	35.570	113.912	.000	.000	.000
5700	8.069	56.054	35.929	114.717	.000	.000	.000
5800	8.094	56.195	36.277	115.526	.000	.000	.000
5900	8.118	56.334	36.616	116.336	.000	.000	.000
6000	8.142	56.470	36.945	117.149	.000	.000	.000

Dec. 31, 1965

COPPER (Cu) (REFERENCE STATE) AT. WT. = 63.54

0	to 1356.6°K.	Crystal
1356.6	to 2848°K.	Liquid
2848	to 6000°K.	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Copper (Cu)

(Crystal) At. Wt. = 63.54

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.195	.000	.000	INFINITE
100	3.826	2.392	12.749	- 1.036	.000	.000	.001
200	5.399	5.661	8.437	- .555	.000	.000	.000
298	5.843	7.913	7.913	.000	.000	.000	.000
300	5.846	7.949	7.913	.011	.000	.000	.000
400	6.077	9.665	8.146	.608	.000	.000	.000
500	6.250	11.040	8.591	1.224	.000	.000	.000
600	6.394	12.193	9.098	1.857	.000	.000	.000
700	6.516	13.188	9.613	2.502	.000	.000	.000
800	6.620	14.064	10.116	3.159	.000	.000	.000
900	6.725	14.850	10.599	3.826	.000	.000	.000
1000	6.822	15.564	11.060	4.504	.000	.000	.000
1100	6.910	16.218	11.500	5.190	.000	.000	.000
1200	6.998	16.823	11.918	5.886	.000	.000	.000
1300	7.086	17.387	12.318	6.590	.000	.000	.000
1400	7.174	17.915	12.699	7.303	- 3.185	.102	- .016
1500	7.262	18.413	13.063	8.025	- 3.213	.337	- .049
1600	7.350	18.885	13.413	8.755	- 3.233	.574	- .078
1700	7.438	19.333	13.748	9.495	- 3.243	.813	- .105
1800	7.526	19.761	14.070	10.243	- 3.245	1.052	- .128
1900	7.614	20.170	14.380	11.000	- 3.238	1.290	- .148
2000	7.702	20.563	14.680	11.766	- 3.222	1.528	- .167

Dec. 31, 1965

COPPER (Cu) (CRYSTAL) AT. WT. = 63.54

$\Delta H^\circ_{f\ 0} = 0$ kcal. mole^{-1}

$S^\circ_{298.15} = 7.913 \pm 0.04$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 0$ kcal. mole^{-1}

$T_m = 1356.6$°K.

$\Delta H^\circ_m = 3.17 \pm 0.15$ kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15} = 81 \pm 0.4$ kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature specific heat of copper has been measured by several workers and generally there is good agreement. The selected values lie close to the determinations of J. A. Kok and W. H. Keesom (1.2-20°K), Physica 3, 1035 (1936); D. L. Martin (20-300°K), Can. J. Phys. 38, 17 (1960); C. B. Satterthwaite, R. S. Craig and W. E. Wallace, J. Am. Chem. Soc. 76, 232 (1954), and S. M. Dockerty, Can. J. Research 9, 84 (1933) and 15A, 59 (1937). Several other workers have reported values of C_p slightly higher than the adopted values especially W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. 63, 1897 (1941), however these measurements were not used for reasons discussed by Martin. The heat capacity above room temperature has been determined directly by several workers, the values of R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Solids 26, 607 (1965) join well with the low temperature data and are adopted. These values lie within 1% of the values adpoted by R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York,1963. Several determinations of the solid enthalpy are also in good agreement with selected heat capacity curve. For references to these determinations refer to Hultgren et al. loc. cit.

Melting Data.

The melting point of copper is well established and the recent determination of W. Heyne, Exptl. Tech. Physik. 12, 87 (1964) is adopted. The heat of fusion was obtained from the calculated enthalpy of the solid at the melting point and the liquid enthalpy measurements of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The liquid enthalpies of I. B. Fieldhouse, J. C. Hedge, J. I. Lang and T. E. Waterman, ASTIA Doc. No. A. D. 150954 are somewhat higher than the adopted values.

Sublimation Data.

See Cu(g) for details.

Copper (Cu)

(Liquid) At. Wt. = 63.54

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	7.500	8.663	8.663	.000	2.224	2.000	- 1.466
300	7.500	8.709	8.663	.014	2.227	1.999	- 1.456
400	7.500	10.867	8.957	.764	2.380	1.899	- 1.038
500	7.500	12.541	9.513	1.514	2.514	1.763	- .771
600	7.500	13.908	10.135	2.264	2.631	1.602	- .583
700	7.500	15.064	10.759	3.014	2.736	1.423	- .444
800	7.500	16.066	11.361	3.764	2.829	1.227	- .335
900	7.500	16.949	11.934	4.514	2.912	1.023	- .248
1000	7.500	17.739	12.475	5.264	2.984	.809	- .177
1100	7.500	18.454	12.987	6.014	3.048	.588	- .117
1200	7.500	19.107	13.470	6.764	3.102	.361	- .066
1300	7.500	19.707	13.927	7.514	3.148	.132	- .022
1400	7.500	20.263	14.360	8.264	.000	.000	.000
1500	7.500	20.780	14.771	9.014	.000	.000	.000
1600	7.500	21.264	15.162	9.764	.000	.000	.000
1700	7.500	21.719	15.534	10.514	.000	.000	.000
1800	7.500	22.148	15.890	11.264	.000	.000	.000
1900	7.500	22.553	16.230	12.014	.000	.000	.000
2000	7.500	22.938	16.556	12.764	.000	.000	.000
2100	7.500	23.304	16.869	13.514	.000	.000	.000
2200	7.500	23.653	17.169	14.264	.000	.000	.000
2300	7.500	23.986	17.458	15.014	.000	.000	.000
2400	7.500	24.305	17.737	15.764	.000	.000	.000
2500	7.500	24.611	18.006	16.514	.000	.000	.000
2600	7.500	24.906	18.266	17.264	.000	.000	.000
2700	7.500	25.189	18.517	18.014	.000	.000	.000
2800	7.500	25.461	18.760	18.764	.000	.000	.000
2900	7.500	25.725	18.996	19.514	- 72.658	1.324	- .100
3000	7.500	25.979	19.224	20.264	- 72.503	3.874	- .282
3100	7.500	26.225	19.446	21.014	- 72.360	6.417	- .452
3200	7.500	26.463	19.662	21.764	- 72.229	8.958	- .612
3300	7.500	26.694	19.871	22.514	- 72.111	11.491	- .761
3400	7.500	26.918	20.075	23.264	- 72.004	14.023	- .901
3500	7.500	27.135	20.274	24.014	- 71.910	16.552	- 1.034
3600	7.500	27.346	20.467	24.764	- 71.827	19.080	- 1.158
3700	7.500	27.552	20.656	25.514	- 71.756	21.602	- 1.276
3800	7.500	27.752	20.840	26.264	- 71.696	24.125	- 1.387
3900	7.500	27.947	21.020	27.014	- 71.647	26.645	- 1.493
4000	7.500	28.136	21.195	27.764	- 71.608	29.168	- 1.594

Dec. 31, 1965

COPPER (Cu) (LIQUID) AT. WT. = 63.54

$S^\circ_{298.15}$ = 8.663 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 2.224 kcal. mole^{-1}

T°_m = 1356.6°K.

ΔH°_m = 3.17 ± 0.15 kcal. mole^{-1}

T°_b = 2848°K.

ΔH°_v = 72.743 kcal. mole^{-1}

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH°_m and the difference between $H_{1356.6}-H_{298}$ for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was calculated from the enthalpy data of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The entropy was obtained in a manner analagous to the heat of formation.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Copper (Cu)

(Ideal Gas) At. Wt. = 63.54

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.481	80.714	80.714	INFINITE
100	4.968	34.317	44.161	-.984	81.052	77.859	-170.153
200	4.968	37.760	40.198	-.488	81.067	74.648	-81.567
298	4.968	39.744	39.744	.000	81.000	71.510	-52.415
300	4.968	39.775	39.744	.009	80.998	71.450	-52.049
400	4.968	41.204	39.939	.506	80.898	68.282	-37.306
500	4.968	42.313	40.307	1.003	80.779	65.142	-28.472
600	4.968	43.218	40.719	1.500	80.643	62.028	-22.592
700	4.968	43.984	41.132	1.996	80.494	58.937	-18.400
800	4.968	44.648	41.531	2.493	80.334	55.867	-15.261
900	4.968	45.233	41.911	2.990	80.164	52.819	-12.826
1000	4.968	45.756	42.269	3.487	79.983	49.791	-10.881
1100	4.969	46.230	42.608	3.984	79.794	46.781	-9.294
1200	4.970	46.662	42.928	4.481	79.595	43.788	-7.974
1300	4.972	47.060	43.231	4.978	79.388	40.813	-6.861
1400	4.977	47.429	43.518	5.475	75.987	37.955	-5.925
1500	4.985	47.772	43.790	5.973	75.735	35.247	-5.135
1600	4.997	48.094	44.049	6.472	75.484	32.556	-4.447
1700	5.016	48.398	44.296	6.973	75.235	29.881	-3.841
1800	5.041	48.685	44.532	7.476	74.988	27.221	-3.305
1900	5.074	48.959	44.758	7.981	74.743	24.572	-2.826
2000	5.116	49.220	44.975	8.491	74.503	21.939	-2.397
2100	5.168	49.471	45.183	9.005	74.267	19.316	-2.010
2200	5.229	49.713	45.383	9.525	74.037	16.705	-1.659
2300	5.300	49.947	45.577	10.051	73.813	14.103	-1.340
2400	5.380	50.174	45.763	10.585	73.597	11.511	-1.048
2500	5.468	50.395	45.944	11.127	73.389	8.932	-.781
2600	5.565	50.612	46.120	11.679	73.191	6.355	-.534
2700	5.668	50.823	46.290	12.241	73.003	3.791	-.307
2800	5.778	51.032	46.456	12.813	72.825	1.229	-.096
2900	5.892	51.236	46.617	13.396	.000	.000	.000
3000	6.010	51.438	46.774	13.991	.000	.000	.000
3100	6.131	51.637	46.928	14.598	.000	.000	.000
3200	6.253	51.834	47.078	15.218	.000	.000	.000
3300	6.375	52.028	47.225	15.849	.000	.000	.000
3400	6.496	52.220	47.369	16.493	.000	.000	.000
3500	6.616	52.410	47.511	17.148	.000	.000	.000
3600	6.732	52.598	47.649	17.816	.000	.000	.000
3700	6.846	52.784	47.786	18.495	.000	.000	.000
3800	6.954	52.968	47.920	19.185	.000	.000	.000
3900	7.059	53.150	48.051	19.885	.000	.000	.000
4000	7.158	53.330	48.181	20.596	.000	.000	.000
4100	7.251	53.508	48.309	21.317	.000	.000	.000
4200	7.339	53.684	48.435	22.046	.000	.000	.000
4300	7.421	53.858	48.559	22.784	.000	.000	.000
4400	7.498	54.029	48.681	23.530	.000	.000	.000
4500	7.568	54.198	48.802	24.284	.000	.000	.000
4600	7.633	54.365	48.921	25.044	.000	.000	.000
4700	7.693	54.530	49.039	25.810	.000	.000	.000
4800	7.747	54.693	49.155	26.582	.000	.000	.000
4900	7.797	54.853	49.269	27.359	.000	.000	.000
5000	7.842	55.011	49.383	28.141	.000	.000	.000
5100	7.884	55.167	49.495	28.928	.000	.000	.000
5200	7.921	55.320	49.605	29.718	.000	.000	.000
5300	7.955	55.471	49.714	30.512	.000	.000	.000
5400	7.987	55.620	49.822	31.309	.000	.000	.000
5500	8.016	55.767	49.929	32.109	.000	.000	.000
5600	8.043	55.912	50.035	32.912	.000	.000	.000
5700	8.069	56.054	50.139	33.718	.000	.000	.000
5800	8.094	56.195	50.242	34.526	.000	.000	.000
5900	8.118	56.334	50.344	35.337	.000	.000	.000
6000	8.142	56.470	50.445	36.150	.000	.000	.000

Dec. 31, 1965

COPPER (Cu) (IDEAL GAS) AT. WT. = 63.54

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 39.744 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 80.714 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 81.0 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.0	2	44406.3	6	54784.0	4	57948.7	4
11202.6	6	44544.2	4	55027.7	2	57893.1	4
13245.4	4	44915.6	2	55387.7	4	57895.1	6
30535.3	2	43726.2	6	55391.3	6	57905.2	6
30783.7	4	44963.2	8	55426.3	8	57908.7	8
39018.7	6	45821.0	2	55429.8	6	58568.9	2
40114.0	4	45879.3	4	56030.0	8	59249.5	4
40943.7	2	46172.8	4	58119.3	6	59250.7	6
40909.1	10	46598.4	6	56343.7	4	59275.3	4
41153.4	8	49383.0	4	58364.7	2	59323.2	2
41562.9	6	49383.3	2	56651.5	6	59647.9	2
42302.5	4	49935.2	4	58690.9	4	60070.0	16
43137.2	2	49942.1	6	56671.4	2	60595.0	16
43514.0	8	52848.8	2	57419.3	2	61150.0	26

Heat of Formation.

The heat of sublimation has been determined by second and third law analysis of the vapor pressure data of a large number of investigators. The results are summarized below:

Ref.	Range°K.	Method	Points	$\Delta H^\circ_{subl.\ 298.15}$ kcal. mole^{-1} 2nd law	3rd law	Drift cal. deg.$^{-1}$ mole^{-1}
1.	1242-1340	Knudsen	6	80.6 ± 0.2	81.39 ± 0.04	0.3 ± 0.2
1.	1370-1563	Knudsen	10*	83.0 ± 0.6	81.34 ± 0.2	-1.0 ± 0.5
2.	1367-1523	Langmuir	8	79.8 ± 1.6	80.20 ± 0.3	0.3 ± 1.2
3.	1605-1879	Transport	21*	79.7 ± 0.6	80.55 ± 0.25	0.5 ± 0.4
4.	1192-1360	Knudsen	13	80.6 ± 4.0	81.16 ± 1.2	0.4 ± 3.1
5.	1143-1292	Langmuir	5	81.3 ± 1.0	80.61 ± 0.2	-0.6 ± 0.8
6.	1475-1707	Knudsen	8	83.2 ± 1.3	81.05 ± 0.4	-1.4 ± 0.8
7.	987-1330	Knudsen	14	80.5 ± 2.3	82.14 ± 1.7	2.7 ± 2.0
8.	1356-1466	Langmuir	5	79.1 ± 2.3	79.96 ± 0.3	1.1 ± 1.8
8.	1268-1320	Langmuir	7*	92.5 ± 3.3	81.26 ± 0.5	-8.9 ± 2.6
9.	1429-1640	Knudsen	9	76.6 ± 1.0	80.30 ± 0.4	2.3 ± 0.6
10.	1419-1463	Knudsen	7	63.0 ± 11.7	81.84 ± 0.8	12.9 ± 8.2
11.	1083	Transport	1		79.2	
12.	2138-2643	Boiling	4	93.5 ± 4.3	77.25 ± 2.8	-6.3 ± 1.7
13.	2378-2573	Boiling	5	120.0 ± 8.0	76.1 ± 2.8	-18.0 ± 3.3
14.	2253-2583	Boiling	3	76.3 ± 13.8	75.0 ± 2.0	-0.9 ± 5.9
15.	1768-2116	Boiling	6	66.2 ± 2.5	73.5 ± 1.3	3.5 ± 1.3

*1 Point rejected due to failure of statistical test.

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The first eight references may be considered to have reasonable drifts and second and third law agreement. The three Langmuir values are grouped closely together at about 80.3 kcal. mole^{-1}. The Knudsen values all lie a little higher averaging 81.4 kcal. mole^{-1}, the single transport determination is at 80.55 kcal. mole^{-1}. If the evaporation coefficient is not unity in the Langmuir experiments then one would observe lower pressures and higher heats of sublimation, thus it appears that the coefficient must be unity and that all techniques are measuring valid heats of sublimation. A value of 81 ± 0.5 kcal. mole^{-1} was chosen weighted toward the more precise Knudsen work of Hersh.

Heat Capacity and Entropy.

The electronic ground state configuration and higher electronic levels were taken from C. E. Moore "Atomic Energy Levels", Natl. Bur. Stds. Circular 467, Washington 1952.

Copper Unipositive Ion (Cu^+)

(Ideal Gas) At. Wt. = 63.53945

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	38.367	38.367	.000	260.668	250.101	- 183.320
300	4.968	38.397	38.367	.009	260.675	250.035	- 182.142
400	4.968	39.827	38.562	.506	261.072	246.428	- 134.636
500	4.968	40.935	38.930	1.003	261.450	242.724	- 106.089
600	4.968	41.841	39.342	1.500	261.811	238.944	- 87.031
700	4.968	42.607	39.755	1.996	262.158	235.105	- 73.400
800	4.968	43.270	40.154	2.493	262.495	231.217	- 63.162
900	4.968	43.855	40.533	2.990	262.822	227.288	- 55.190
1000	4.968	44.379	40.892	3.487	263.138	223.322	- 48.805
1100	4.968	44.852	41.231	3.984	263.446	219.327	- 43.574
1200	4.968	45.285	41.551	4.481	263.744	215.302	- 39.210
1300	4.968	45.682	41.854	4.977	264.032	211.254	- 35.513
1400	4.968	46.050	42.140	5.474	261.128	207.286	- 32.357
1500	4.968	46.393	42.413	5.971	261.372	203.430	- 29.638
1600	4.968	46.714	42.672	6.468	261.616	199.558	- 27.257
1700	4.968	47.015	42.918	6.965	261.860	195.674	- 25.154
1800	4.968	47.299	43.154	7.461	262.102	191.773	- 23.283
1900	4.969	47.568	43.379	7.958	262.346	187.859	- 21.608
2000	4.969	47.823	43.595	8.455	262.590	183.932	- 20.098
2100	4.970	48.065	43.802	8.952	262.834	179.993	- 18.731
2200	4.971	48.296	44.001	9.449	263.078	176.044	- 17.488
2300	4.973	48.517	44.193	9.946	263.321	172.080	- 16.351
2400	4.976	48.729	44.377	10.444	263.566	168.108	- 15.308
2500	4.981	48.932	44.556	10.942	263.811	164.128	- 14.347
2600	4.987	49.128	44.728	11.440	264.056	160.134	- 13.460
2700	4.996	49.316	44.894	11.939	264.302	156.135	- 12.638
2800	5.008	49.498	45.055	12.439	264.549	152.124	- 11.873
2900	5.024	49.674	45.212	12.941	192.139	149.428	- 11.261
3000	5.044	49.845	45.363	13.444	192.544	147.946	- 10.777
3100	5.069	50.010	45.510	13.950	192.940	146.455	- 10.325
3200	5.099	50.172	45.654	14.458	193.326	144.952	- 9.899
3300	5.136	50.329	45.793	14.970	193.703	143.434	- 9.499
3400	5.180	50.483	45.929	15.486	194.072	141.905	- 9.121
3500	5.232	50.634	46.061	16.006	194.433	140.365	- 8.764
3600	5.291	50.782	46.190	16.532	194.789	138.816	- 8.427
3700	5.359	50.928	46.316	17.065	195.140	137.253	- 8.107
3800	5.436	51.072	46.439	17.604	195.486	135.686	- 7.803
3900	5.522	51.214	46.560	18.152	195.830	134.109	- 7.515
4000	5.617	51.355	46.678	18.709	196.172	132.520	- 7.240
4100	5.721	51.495	46.794	19.276	196.516	130.924	- 6.979
4200	5.835	51.634	46.907	19.853	196.860	129.324	- 6.729
4300	5.958	51.773	47.019	20.443	197.209	127.712	- 6.491
4400	6.090	51.912	47.129	21.045	197.562	126.089	- 6.263
4500	6.231	52.050	47.236	21.661	197.921	124.459	- 6.044
4600	6.380	52.189	47.343	22.292	198.289	122.821	- 5.835
4700	6.537	52.328	47.447	22.938	198.665	121.176	- 5.634
4800	6.702	52.467	47.550	23.600	199.052	119.525	- 5.442
4900	6.872	52.607	47.652	24.278	199.450	117.865	- 5.257
5000	7.049	52.747	47.753	24.974	199.860	116.200	- 5.079
5100	7.230	52.889	47.852	25.688	200.285	114.518	- 4.907
5200	7.416	53.031	47.950	26.420	200.723	112.833	- 4.742
5300	7.605	53.174	48.047	27.171	201.177	111.136	- 4.583
5400	7.796	53.318	48.144	27.941	201.647	109.432	- 4.429
5500	7.989	53.463	48.239	28.731	202.134	107.721	- 4.280
5600	8.182	53.608	48.334	29.539	202.635	106.002	- 4.137
5700	8.374	53.755	48.427	30.367	203.155	104.271	- 3.998
5800	8.565	53.902	48.521	31.214	203.690	102.532	- 3.863
5900	8.754	54.050	48.613	32.080	204.243	100.787	- 3.733
6000	8.940	54.199	48.705	32.965	204.812	99.026	- 3.607

Dec. 31, 1965

COPPER UNIPOSITIVE ION (Cu^+) (IDEAL GAS) AT. WT. = 63.53945

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 38.367 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 258.9 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 260.668 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.0	1	68694.7	39
21928.6	7	72095.4	42
22847.0	5	85388.8	5
23998.3	3	88505.7	9
26264.5	5	95565.7	9

Heat of Formation.

The heat of formation was obtained from the dissociation limit of Cu(g) which was given as 62317.2 cm.$^{-1}$ (or 178.187 kcal. mole^{-1}) by C. E. Moore "Atomic Energy Levels", Nat. Bur. Stds. Circ. 467, Washington 1952. This value applies to 0°K., the enthalpy of Cu, Cu^+ and e^- between 298°K. and zero are all 1.481 kcal. mole^{-1}, thus at 298°K. the dissociation energy is 179.668 kcal. mole^{-1}. The heat of formation was then obtained from the reaction $Cu(g) \rightarrow Cu^+ + e^-$ as $\Delta H^\circ_{f\ 298.15}$ = 260.668 ± 0.5 kcal. mole^{-1}, the uncertainty is that due to Cu(g).

Heat Capacity and Entropy.

The ground state configuration and higher electronic levels were taken from C. E. Moore, loc. cit. Levels above 100,000 cm.$^{-1}$ were not included since they do not affect the thermodynamic function, levels above 30,000 cm.$^{-1}$ were averaged.

Copper Monofluoride (CuF)

(Crystal) GFW = 82.5384

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	10.720	15.500	15.500	.000	- 46.000	- 41.040	30.083
300	10.790	15.567	15.500	.020	- 45.998	- 41.010	29.875
400	12.950	18.997	15.953	1.218	- 45.782	- 39.374	21.513
500	13.820	21.987	16.869	2.559	- 45.461	- 37.808	16.526
600	14.350	24.556	17.941	3.969	- 45.100	- 36.311	13.226
700	14.700	26.796	19.050	5.423	- 44.716	- 34.875	10.889
800	14.920	28.774	20.144	6.904	- 44.325	- 33.497	9.151
900	15.060	30.540	21.203	8.404	- 43.930	- 32.167	7.811
1000	15.150	32.132	22.217	9.915	- 43.540	- 30.881	6.749
1100	15.190	33.578	23.185	11.432	- 43.155	- 29.634	5.888
1200	15.220	34.901	24.107	12.952	- 42.779	- 28.422	5.176
1300	15.240	36.120	24.985	14.475	- 42.411	- 27.240	4.579
1400	15.250	37.250	25.821	16.000	- 45.238	- 25.985	4.056
1500	15.250	38.302	26.619	17.525	- 44.919	- 24.621	3.587

June 30, 1966

COPPER MONOFLUORIDE (CuF) (CRYSTAL) GFW = 82.5384

$S^\circ_{298.15}$ = [15.5 ± 0.5] gibbs/mol

Tm = Unknown

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = [-46 ± 10] kcal/mol

ΔHm° = Unknown

$\Delta Hs^\circ_{298.15}$ = [58] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) for CuF(c) is not available from literature at the present time. The lattice energy (U_o) for CuF(c) has been calculated to be 209, 213 and 232 kcal/mol, based on the assumption of ionic bonding in CuF(c), by Pauling, Zachariasen and Ebert and Woitinek, respectively (see T. C. Waddington, Trans. Faraday Soc. 55, 1531 (1959) for details). The corresponding enthalpy change for the reaction CuF(c) = Cu^+(g) + F^-(g) was evaluated as 210.18, 214.18 and 233.18 kcal/mol. Using $\Delta Hf^\circ_{298.15}$ = 260.67 kcal/mol for Cu^+(g) and -62.2 kcal/mol for F^-(g), the values of $\Delta Hf^\circ_{298.15}$ (CuF, c) were calculated to be -11.7, -15.7 and -34.7 kcal/mol. However, based on $\Delta Hf^\circ_{298.15}$(CuF, g) = 12 ± 9 kcal/mol which was measured, the values of $\Delta Hs^\circ_{298.15}$ would be 23.7, 27.7 and 46.7 kcal/mol which seem to be too small. By comparison with those for KF(c) and HgF(c), the value of $\Delta Hs^\circ_{298.15}$ was estimated as 58 kcal/mol. From this $\Delta Hs^\circ_{298.15}$ value and $\Delta Hf^\circ_{298.15}$ (CuF, g), the heat of formation for CuF(c) was derived.

Heat Capacity and Entropy.

The heat capacities, 298.15-1000°K, and $S^\circ_{298.15}$ were estimated by comparison with those for CuCl(c), NaCl(c) and NaF(c). The Cp values above 1000°K were obtained by graphical extrapolation.

Heat of Sublimation.

The value of $\Delta Hs^\circ_{298.15}$ was estimated by comparison with those for KF(c) and HgF(c).

Copper Monofluoride (CuF)

(Ideal Gas) GFW = 82.5384

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.171	12.079	12.079	INFINITE
100	6.980	6.076	60.836	-1.476	12.268	9.934	-21.710
200	7.446	51.030	54.823	-.759	12.154	7.634	-8.343
298	7.983	54.109	54.109	.000	12.000	5.449	-3.994
300	7.992	54.158	54.109	.015	11.997	5.408	-3.940
400	8.342	56.509	54.427	.833	11.833	3.237	-1.768
500	8.555	58.396	55.038	1.679	11.659	1.107	-.484
600	8.693	59.968	55.733	2.541	11.473	-.985	.359
700	8.786	61.316	56.436	3.416	11.277	-3.046	.951
800	8.855	62.494	57.121	4.298	11.069	-5.079	1.388
900	8.907	63.540	57.778	5.186	10.852	-7.084	1.720
1000	8.948	64.481	58.402	6.079	10.624	-9.066	1.981
1100	8.983	65.335	58.994	6.976	10.389	-11.023	2.190
1200	9.013	66.118	59.555	7.875	10.144	-12.959	2.360
1300	9.039	66.840	60.088	8.778	9.891	-14.873	2.500
1400	9.063	67.511	60.595	9.683	6.445	-16.667	2.602
1500	9.084	68.137	61.077	10.590	6.147	-18.308	2.667
1600	9.105	68.724	61.537	11.500	5.849	-19.929	2.722
1700	9.124	69.277	61.976	12.411	5.551	-21.531	2.768
1800	9.143	69.799	62.396	13.325	5.254	-23.115	2.807
1900	9.161	70.294	62.799	14.240	4.957	-24.684	2.839
2000	9.179	70.764	63.185	15.157	4.660	-26.235	2.867
2100	9.197	71.212	63.557	16.076	4.364	-27.772	2.890
2200	9.216	71.640	63.915	16.996	4.068	-29.295	2.910
2300	9.235	72.051	64.260	17.919	3.773	-30.807	2.927
2400	9.256	72.444	64.593	18.843	3.479	-32.304	2.942
2500	9.279	72.822	64.914	19.770	3.185	-33.786	2.954
2600	9.303	73.187	65.225	20.699	2.893	-35.261	2.964
2700	9.330	73.538	65.527	21.631	2.602	-36.721	2.972
2800	9.359	73.878	65.819	22.565	2.313	-38.173	2.979
2900	9.391	74.207	66.103	23.503	-70.633	-38.289	2.886
3000	9.426	74.526	66.378	24.443	-70.764	-37.173	2.708
3100	9.465	74.836	66.646	25.388	-70.903	-36.051	2.542
3200	9.507	75.137	66.907	26.337	-71.052	-34.922	2.385
3300	9.552	75.430	67.161	27.289	-71.211	-33.792	2.238
3400	9.602	75.716	67.408	28.247	-71.376	-32.655	2.099
3500	9.655	75.995	67.649	29.210	-71.552	-31.513	1.968
3600	9.712	76.268	67.885	30.178	-71.733	-30.367	1.844
3700	9.773	76.535	68.115	31.153	-71.921	-29.216	1.726
3800	9.837	76.796	68.340	32.133	-72.116	-28.057	1.614
3900	9.905	77.053	68.560	33.120	-72.316	-26.899	1.507
4000	9.976	77.304	68.776	34.114	-72.520	-25.728	1.406
4100	10.050	77.552	68.987	35.115	-72.728	-24.559	1.309
4200	10.128	77.795	69.194	36.124	-72.938	-23.380	1.217
4300	10.207	78.034	69.396	37.141	-73.149	-22.194	1.128
4400	10.289	78.270	69.595	38.166	-73.363	-21.011	1.044
4500	10.374	78.502	69.791	39.199	-73.575	-19.820	.963
4600	10.460	78.731	69.983	40.241	-73.787	-18.624	.885
4700	10.547	78.957	70.171	41.291	-73.999	-17.422	.810
4800	10.636	79.180	70.357	42.350	-74.207	-16.213	.738
4900	10.726	79.400	70.539	43.418	-74.413	-15.003	.669
5000	10.816	79.617	70.718	44.495	-74.616	-13.786	.603
5100	10.906	79.832	70.895	45.581	-74.815	-12.567	.539
5200	10.997	80.045	71.069	46.677	-75.010	-11.347	.477
5300	11.087	80.255	71.240	47.781	-75.201	-10.120	.417
5400	11.177	80.463	71.409	48.894	-75.388	-8.892	.360
5500	11.266	80.669	71.576	50.016	-75.568	-7.657	.304
5600	11.354	80.873	71.740	51.147	-75.745	-6.420	.251
5700	11.440	81.075	71.902	52.287	-75.916	-5.184	.199
5800	11.525	81.275	72.062	53.435	-76.082	-3.942	.149
5900	11.609	81.472	72.219	54.592	-76.243	-2.691	.100
6000	11.690	81.668	72.375	55.757	-76.400	-1.448	.053

June 30, 1966

COPPER MONOFLUORIDE (CuF) (IDEAL GAS) GFW = 82.5384

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 54.11 gibbs/mol

ΔHf°_0 = 12 ± 9 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 12 ± 9 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 621.89 cm^{-1} $\omega_e x_e$ = 3.941 cm^{-1} σ = 1

B_e = 0.3794 cm^{-1} α_e = 0.004586 cm^{-1} r_e = 1.743 Å

Heat of Formation.

Based on spectroscopic data, the dissociation energy (D°_0) of CuF (g) was selected as 3.0 ± 1.0 eV by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953. Using $\Delta Hf^\circ_{298.15}$ = 18.36 and 80.71 kcal/mol for F(g) and Cu(g), respectively, the value of $\Delta Hf^\circ_{298.15}$ for CuF (g) was calculated to be 30 ± 23 kcal/mol.

Values of the dissociation energy for CuF(g) have been derived by R. A. Kent, J. D. McDonald, and J. L. Margrave, J. Phys. Chem. 70, 874 (1966), as 3.63 ± 0.2 to 4.1 ± 0.5 eV, based on mass spectrometric studies of CuF_2 sublimation from a Knudsen cell, the appearance potential of CuF^+ ion from CuF_2 in both reducing and nonreducing systems, and a theoretical calculation assuming an ionic model like that used by E. S. Rittner, J. Chem. Phys. 19, 1030 (1951). Until further data are available, a value D (CuF) = 3.8 ± 0.5 eV was recommended. Using this dissociation energy for CuF (g), the heat of formation (298.15°K) for CuF(g) was evaluated to be 12 ± 9 kcal/mol which is adopted here.

Heat Capacity and Entropy.

The values of ground state configuration, ω_e, $\omega_e x_e$, B_e, α_e and r_e were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950, and corrected to the average isotopic species.

Copper Difluoride (CuF_2)

(Crystal) GFW = 101.5368

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.770	16.400	16.400	.000	- 131.200	- 119.286	87.439
300	16.780	16.504	16.400	.031	- 131.194	- 119.213	86.846
400	17.460	21.424	17.067	1.743	- 130.849	- 115.270	62.980
500	18.140	25.394	18.347	3.523	- 130.492	- 111.416	48.700
600	18.800	28.760	19.809	5.371	- 130.109	- 107.636	39.207
700	19.410	31.704	21.302	7.281	- 129.695	- 103.922	32.446
800	19.980	34.334	22.770	9.251	- 129.248	- 100.272	27.393
900	20.490	36.718	24.189	11.275	- 128.767	- 96.679	23.477
1000	20.940	38.900	25.553	13.348	- 128.257	- 93.140	20.356
1100	21.300	40.914	26.859	15.460	- 127.723	- 89.655	17.813
1200	21.580	42.780	28.109	17.605	- 127.171	- 86.218	15.702
1300	21.750	44.514	29.305	19.772	- 126.611	- 82.827	13.924
1400	21.860	46.130	30.450	21.953	- 129.235	- 79.378	12.391
1500	21.918	47.641	31.546	24.142	- 128.707	- 75.836	11.049
1600	21.960	49.057	32.597	26.336	- 128.178	- 72.330	9.880
1700	21.987	50.389	33.604	28.534	- 127.648	- 68.854	8.852
1800	22.000	51.646	34.572	30.733	- 127.121	- 65.412	7.942
1900	22.000	52.835	35.502	32.933	- 126.595	- 61.997	7.131
2000	22.000	53.964	36.397	35.133	- 126.072	- 58.610	6.405

June 30, 1966

COPPER DIFLUORIDE (CuF_2) (CRYSTAL) GFW = 101.5368

$\Delta Hf°_0$ = Unknown

$S°_{298.15}$ = [16.4] gibbs/mol

$\Delta Hf°_{298.15} = -131.2 \pm 0.8$ kcal/mol

Tm = 1043°K

$\Delta Hm°$ = [9.4] kcal/mol

$\Delta Hs°_{298.15} = 62.5 \pm 0.6$ kcal/mol

Heat of Formation.

The chemical equilibrium for the reaction (1) $CuF_2(c) + H_2(g) = Cu(c) + 2HF(g)$ has been studied by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928). The equilibrium gas phase composition was found to be HF 4.3% and H_2 95.7%, at 423°K. From this data the enthalpy change ($\Delta Hr°_{298.15}$) of the reaction was evaluated. The equilibrium for the reaction (2) $CuF_2(c) + H_2O(g) = CuO(c) + 2HF(g)$ was investigated by L. Domange, Compt. rend. 200, 239 (1935). Based on the equilibrium data reported, the $\Delta Hr°_{298.15}$ value for the reaction was derived. The results obtained are presented as follows.

		$\Delta Hr°_{298.15}$, kcal/mol			
Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift eu	$\Delta Hf°_{298.15}$ kcal/mol
(1)	423	—	22.38	—	-152.0
(2)	473.15-723.15	23.06 ± 1.33	22.15	-1.67 ± 1.96	-131.2

Using the third law values for $\Delta Hr°_{298.15}$, the corresponding $\Delta Hf°_{298.15}$ (CuF_2, c) values were calculated. The adopted heat of formation for $CuF_2(c)$ is -131.2 ± 0.8 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 298.15-1000°K, and $S°_{298.15}$ were estimated by comparison with those for $CuCl_2(c)$, $CaF_2(c)$ and $CaCl_2(c)$, respectively. The Cp values above 1000°K were obtained by graphical extrapolation.

Melting Data.

Tm was reported by H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, Jr., J. Am. Chem. Soc. 76 2178 (1954). Tm for $CuF_2(c)$ in HF(g) or $N_2(g)$ was found to be 950 ± 5°C or 785 ± 10°C, respectively, by H. von Wartenberg, Z. anorg. allgem. Chem. 241, 381 (1939). Heat of melting was estimated by comparison with those for other related compounds.

Heat of Sublimation.

See $CuF_2(g)$ table for details.

Copper Difluoride (CuF_2)

(Liquid) GFW = 101.5368

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	22.500	20.584	20.584	.000	− 124.300	− 113.633	83.295
300	22.500	20.723	20.584	.042	− 124.283	− 113.568	82.734
400	22.500	27.196	21.467	2.292	− 123.400	− 110.130	60.172
500	22.500	32.217	23.134	4.542	− 122.573	− 106.909	46.730
600	22.500	36.319	25.000	6.792	− 121.788	− 103.851	37.828
700	22.500	39.787	26.871	9.042	− 121.034	− 100.920	31.509
800	22.500	42.792	28.677	11.292	− 120.307	− 98.099	26.799
900	22.500	45.442	30.396	13.542	− 119.600	− 95.364	23.158
1000	22.500	47.813	32.021	15.792	− 118.913	− 92.709	20.262
1100	22.500	49.957	33.556	18.042	− 118.241	− 90.121	17.905
1200	22.500	51.915	35.005	20.292	− 117.584	− 87.594	15.953
1300	22.500	53.716	36.376	22.542	− 116.941	− 85.120	14.310
1400	22.500	55.383	37.675	24.792	− 119.496	− 82.594	12.893
1500	22.500	56.936	38.908	27.042	− 118.907	− 79.979	11.653
1600	22.500	58.388	40.080	29.292	− 118.322	− 77.404	10.573
1700	22.500	59.752	41.198	31.542	− 117.740	− 74.863	9.624
1800	22.500	61.038	42.265	33.792	− 117.162	− 72.359	8.786
1900	22.500	62.254	43.285	36.042	− 116.586	− 69.884	8.039
2000	22.500	63.408	44.263	38.292	− 116.013	− 67.439	7.369

COPPER DIFLUORIDE (CuF_2) (LIQUID) GFW = 101.5368

$S^\circ_{298.15}$ = [20.584] gibbs/mol

Tm = 1043°K

Tb = [1722]°K

$\Delta Hf^\circ_{298.15}$ = [-124.30] kcal/mol

ΔHm° = [9.4] kcal/mol

ΔHv° = [43.98] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) was obtained from $\Delta Hf^\circ_{298.15}$ (CuF_2, c) by adding ΔHm° and the difference between $H^\circ_{1043}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated based on an assumption that the average heat capacity for $CuF_2(l)$ is 7.5 gibbs/atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $CuF_2(c)$ table for details.

Vaporization Data.

Tb is the temperature at which the free energy change for the reaction $CuF_2(l) = CuF_2(g)$ becomes zero. The difference between ΔHf° for liquid and gas at Tb is ΔHv°.

Copper Difluoride (CuF_2)
(Ideal Gas) GFW = 101.5368

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.920	- 68.315	- 68.315	INFINITE
100	8.999	49.386	70.986	- 2.160	- 68.409	- 69.039	150.884
200	11.016	56.302	62.056	- 1.151	- 68.581	- 69.600	76.055
298	12.340	60.966	60.966	.000	- 68.700	- 70.073	51.365
300	12.360	61.042	60.966	.023	- 68.702	- 70.082	51.055
400	13.199	64.723	61.462	1.304	- 68.788	- 70.528	38.535
500	13.709	67.727	62.424	2.652	- 68.863	- 70.954	31.014
600	14.029	70.257	63.524	4.040	- 68.940	- 71.365	25.995
700	14.240	72.437	64.645	5.454	- 69.022	- 71.763	22.405
800	14.384	74.348	65.741	6.886	- 69.113	- 72.149	19.710
900	14.488	76.049	66.794	8.329	- 69.213	- 72.523	17.611
1000	14.564	77.579	67.797	9.782	- 69.323	- 72.885	15.929
1100	14.624	78.970	68.751	11.242	- 69.441	- 73.235	14.550
1200	14.673	80.245	69.656	12.707	- 69.569	- 73.575	13.400
1300	14.717	81.421	70.516	14.176	- 69.707	- 73.902	12.424
1400	14.758	82.513	71.335	15.650	- 73.038	- 74.117	11.570
1500	14.801	83.533	72.114	17.128	- 73.221	- 74.189	10.809
1600	14.846	84.490	72.858	18.610	- 73.404	- 74.249	10.142
1700	14.895	85.391	73.569	20.097	- 73.585	- 74.294	9.551
1800	14.949	86.244	74.250	21.589	- 73.765	- 74.332	9.025
1900	15.008	87.054	74.903	23.087	- 73.941	- 74.359	8.553
2000	15.072	87.825	75.530	24.591	- 74.114	- 74.374	8.127
2100	15.141	88.562	76.133	26.102	- 74.283	- 74.384	7.741
2200	15.213	89.268	76.714	27.620	- 74.448	- 74.385	7.389
2300	15.289	89.946	77.275	29.145	- 74.608	- 74.378	7.068
2400	15.367	90.599	77.816	30.677	- 74.764	- 74.368	6.772
2500	15.447	91.227	78.340	32.218	- 74.914	- 74.344	6.499
2600	15.528	91.835	78.848	33.767	- 75.058	- 74.320	6.247
2700	15.610	92.422	79.340	35.324	- 75.196	- 74.286	6.013
2800	15.692	92.992	79.817	36.889	- 75.328	- 74.253	5.796
2900	15.772	93.544	80.281	38.462	- 148.113	- 72.887	5.493
3000	15.852	94.080	80.732	40.043	- 148.080	- 70.296	5.121
3100	15.929	94.601	81.171	41.632	- 148.052	- 67.703	4.773
3200	16.005	95.108	81.599	43.229	- 148.031	- 65.109	4.447
3300	16.078	95.601	82.016	44.833	- 148.018	- 62.518	4.140
3400	16.148	96.082	82.422	46.444	- 148.011	- 59.927	3.852
3500	16.215	96.551	82.819	48.063	- 148.012	- 57.334	3.580
3600	16.280	97.009	83.207	49.687	- 148.020	- 54.744	3.323
3700	16.341	97.456	83.586	51.318	- 148.036	- 52.154	3.081
3800	16.398	97.893	83.957	52.955	- 148.059	- 49.563	2.850
3900	16.453	98.319	84.320	54.598	- 148.090	- 46.971	2.632
4000	16.503	98.736	84.675	56.246	- 148.127	- 44.375	2.425
4100	16.551	99.145	85.023	57.899	- 148.171	- 41.785	2.227
4200	16.595	99.544	85.364	59.556	- 148.223	- 39.187	2.039
4300	16.636	99.935	85.698	61.218	- 148.279	- 36.587	1.860
4400	16.673	100.318	86.026	62.883	- 148.344	- 33.992	1.688
4500	16.708	100.693	86.348	64.552	- 148.413	- 31.395	1.525
4600	16.739	101.060	86.664	66.224	- 148.488	- 28.791	1.368
4700	16.767	101.421	86.974	67.900	- 148.569	- 26.191	1.218
4800	16.792	101.774	87.279	69.578	- 148.654	- 23.581	1.074
4900	16.815	102.120	87.578	71.258	- 148.745	- 20.973	.935
5000	16.834	102.460	87.872	72.941	- 148.840	- 18.365	.803
5100	16.851	102.794	88.162	74.625	- 148.940	- 15.759	.675
5200	16.866	103.121	88.446	76.311	- 149.045	- 13.143	.552
5300	16.878	103.443	88.726	77.998	- 149.154	- 10.533	.434
5400	16.888	103.758	89.001	79.686	- 149.268	- 7.917	.320
5500	16.896	104.068	89.273	81.376	- 149.384	- 5.295	.210
5600	16.902	104.373	89.540	83.065	- 149.507	- 2.675	.104
5700	16.906	104.672	89.802	84.756	- 149.632	- .053	.002
5800	16.908	104.966	90.061	86.446	- 149.763	2.574	- .097
5900	16.908	105.255	90.316	88.137	- 149.897	5.202	- .193
6000	16.907	105.539	90.568	89.828	- 150.036	7.830	- .285

June 30, 1966

COPPER DIFLUORIDE (CuF_2) (IDEAL GAS) GFW = 101.5368

Point Group $D_{\infty h}$

ΔHf_0° = -68.3 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = [60.97] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -68.7 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
[9000]	[4]
[18000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[608](1)
[205](2)
768 (1)

Bond Distance: Cu-F = [1.72] Å

Bond Angle: F-Cu-F = [180]°

σ = 2

Rotational Constant: B_o = [0.14996] cm^{-1}

Heat of Formation.

The vapor pressures of $CuF_2(c)$, at temperatures from 897 to 1026°K, have been determined by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Based on these data, the heat of sublimation ($\Delta Hs^\circ_{298.15}$) of $CuF_2(c)$ was derived to be 62.45 ± 0.5 and 62.50 kcal/mol by the second and third law method, respectively. From the values of $\Delta Hs^\circ_{298.15}$ and $\Delta Hf^\circ_{298.15}$ for $CuF_2(c)$, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $CuF_2(g)$ was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The ground state electronic configuration, $^2\Sigma$, was obtained from A. Büchler, J. L. Stauffer and W. Klemperer, Interim Tech. Rept. No. 6, Apr. 30, 1964, Arthur D. Little, Inc., Cambridge, Mass. The other electronic levels and quantum weights were assumed from those for $CuCl_2(g)$ reported by J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961). The vibrational frequency, ν_3, was determined by P. H. Kasai, E. B. Whipple and W. Weltner, Jr., J. Chem. Phys. 44, 2581 (1966). The other two frequencies, ν_1 and ν_3, were calculated by Valence Force Treatment described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is I = 1.86649 X 10^{-38} g cm^2.

Copper Dihydroxide $(Cu(OH)_2)$

(Crystal) GFW = 97.55474

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	22.750	25.900	25.900	.000	- 107.640	- 89.088	65.303
300	22.760	26.041	25.900	.042	- 107.635	- 88.973	64.817
400	23.780	32.728	26.805	2.369	- 107.310	- 82.800	45.240
500	24.800	38.144	28.548	4.798	- 106.927	- 76.715	33.532
600	25.820	42.756	30.541	7.329	- 106.484	- 70.713	25.757
700	26.800	46.812	32.581	9.962	- 105.976	- 64.790	20.228
800	27.620	50.447	34.591	12.685	- 105.414	- 58.946	16.103
900	28.200	53.735	36.538	15.477	- 104.815	- 53.172	12.912
1000	28.600	56.729	38.410	18.318	- 104.197	- 47.468	10.374
1100	28.860	59.467	40.202	21.192	- 103.574	- 41.824	8.310
1200	29.040	61.987	41.914	24.088	- 102.956	- 36.239	6.600
1300	29.130	64.315	43.548	26.997	- 102.352	- 30.703	5.162
1400	29.170	66.475	45.110	29.912	- 104.953	- 25.111	3.920
1500	29.200	68.489	46.602	32.830	- 104.422	- 19.427	2.831

June 30, 1966

COPPER DIHYDROXIDE $(Cu(OH)_2)$ (CRYSTAL) GFW = 97.55474

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [25.9] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -107.64 ± 2.0 kcal/mol

Td = 433°K

Heat of Formation.

The enthalpy change (ΔHr°_{433}) for the reaction $Cu(OH)_2(c) = CuO(c) + H_2O(g)$ has been determined by L. V. My, Bull. soc. chim. France, No. 3, 545 (1964). Based on the reported value, ΔHr°_{433} = 12 kcal/mol, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $Cu(OH)_2(c)$ was derived as -107.64 kcal/mol, using $\Delta Hf^\circ_{298.15}$ = -37.250 and -57.798 kcal/mol for CuO(c) and $H_2O(g)$, respectively, which was adopted here.

The free energy change ($\Delta Gr^\circ_{298.15}$) of the reaction $Cu(OH)_2(c) = Cu^{++}(aq) + 2\ OH^-(aq)$ was evaluated to be 26.36 and 26.26 kcal/mol, based on the solubility product for $Cu(OH)_2(c)$ reported by (1) E. S. Ganelina, Zh. prikl. Khim. 37, 1358 (1964) and (2) N. P. Zhuk, Zh. Fiz. Khim. 28, 1523 (1954), respectively. Using values of $S^\circ_{298.15}$ and $\Delta Hf^\circ_{298.15}$ for Cu^{++} (aq) and OH^-(aq) from "Selective Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1, 1965, by D. D. Wagman and co-workers, the corresponding enthalpy change $\Delta Hr^\circ_{298.15}$) and heat of formation ($\Delta Hf^\circ_{298.15}$) for $Cu(OH)_2(c)$ were derived. The results obtained are presented as follows.

Chemical Reaction	$\Delta Hr^\circ_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol	Reference
$Cu(OH)_2(c) = Cu^{++}(aq) + 2\ OH^-(aq)$	10.06	-104.61	(1)
$Cu(OH)_2(c) = Cu^{++}(aq) + 2\ OH^-(aq)$	9.97	-104.52	(2)
$CuO(c) + H_2O(l) = Cu(OH)_2(c)$	-1.9	-107.5	(3)
$CuO(c) + H_2O(l) = Cu(OH)_2(c)$	0.3	-105.3	(4)

The heats of solution of CuO(c) and $Cu(OH)_2(c)$ in HNO_3(aq.) have been determined by (3) de Forcrand, Compt. rend. 157, 441 (1913) to be -16.38 and -14.46 kcal/mol, respectively. From these data the enthalpy change for the reaction $CuO(c) + H_2O(l) = Cu(OH)_2(c)$ was derived as -1.9 kcal/mol. For the same reaction, the enthalpy change was reported to be 0.3 kcal/mol by (4) P. Sabatier, Compt. rend. 125, 301 (1897). Based on $\Delta Hf^\circ_{298.15}$ = -37.25 and -68.315 kcal/mol for CuO(c) and $H_2O(l)$, respectively, the heat of formation for $Cu(OH)_2(c)$ was evaluated. The results obtained are presented in the above table.

Heat Capacity and Entropy.

The heat capacities, 298.15-700°K, were estimated by comparison with those for CuO(c), CaO(c) and $Ca(OH)_2(c)$. The Cp values above 700°K were obtained by graphical extrapolation. $S^\circ_{298.15}$ was estimated such that the derived ΔGf° $(Cu(OH)_2, c)$ = ΔGf° (CuO, c) + ΔGf° (H_2O, g) at 433°K.

Decomposition Temperature.

Td is the temperature at which the Gibbs energy change for the reaction $Cu(OH)_2(c) = CuO(c) + H_2O(g)$ equals zero.

Copper Monoxide (CuO)

(Crystal) GFW = 79.5394

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.695	-36.713	-36.713	INFINITE
100	3.945	2.335	17.732	-1.540	-37.063	-34.988	76.466
200	8.321	6.460	11.058	-.920	-37.272	-32.810	35.853
298	10.066	10.183	10.183	.000	-37.250	-30.622	22.446
300	10.094	10.245	10.183	.019	-37.249	-30.581	22.278
400	11.244	13.323	10.595	1.091	-37.129	-28.374	15.503
500	11.960	15.914	11.406	2.254	-36.948	-26.204	11.454
600	12.500	18.145	12.348	3.478	-36.734	-24.076	8.770
700	12.980	20.108	13.319	4.752	-36.494	-21.984	6.864
800	13.430	21.871	14.280	6.073	-36.229	-19.930	5.445
900	13.870	23.478	15.214	7.438	-35.938	-17.909	4.349
1000	14.310	24.962	16.115	8.847	-35.621	-15.923	3.480
1100	14.750	26.347	16.983	10.300	-35.273	-13.970	2.776
1200	15.190	27.649	17.818	11.797	-34.896	-12.050	2.195
1300	15.630	28.882	18.622	13.338	-34.488	-10.161	1.708
1400	16.070	30.057	19.397	14.923	-37.233	-8.206	1.281
1500	16.510	31.180	20.146	16.552	-36.789	-6.147	.896
1600	16.950	32.260	20.869	18.225	-36.305	-4.121	.563
1700	17.390	33.301	21.570	19.942	-35.779	-2.125	.273
1800	17.830	34.307	22.250	21.703	-35.212	-.160	.019
1900	18.270	35.283	22.910	23.508	-34.605	1.770	-.204
2000	18.710	36.231	23.553	25.357	-33.956	3.668	-.401

June 30, 1966

COPPER MONOXIDE (CuO) (CRYSTAL) GFW = 79.5394

$\Delta Hf^\circ_0 = -36.71$ kcal/mol

$S^\circ_{298.15} = 10.18 \pm 0.1$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -37.25 \pm 0.5$ kcal/mol

Td = 1395°K

Heat of Formation.

The more consistent data relative to the heat of formation are reviewed below. The selected value of -37.25 kcal/mol was derived from $\Delta Hf^\circ_{298} = -40.7$ kcal/mol for $Cu_2O(c)$ and $\Delta Hr^\circ_{298} = 33.80$ kcal/mol for $2CuO(c) = Cu_2O(c) + 0.5\ O_2$. Four different sets of oxygen dissociation pressure measurements yield heats of reaction in close agreement with each other and with the aqueous calorimetry of Thomsen. Thomsen's data may be reduced to the heat of reduction of CuO(c) with H_2 by combining heats of reaction for $CuO + H_2SO_4$, $Fe + H_2SO_4$, and $Fe + CuSO_4(aq)$. Direct calorimetric measurement of the heat of reduction by von Wartenberg and Werth yields $\Delta Hf^\circ_{298} = -38.04 \pm 0.2$ when corrected for incomplete condensation of water. Direct measurement is difficult and this value may correspond to incomplete reduction. The value of -33.02 reported by Wöhler and Jochum, Z. physik. Chem. 167A, 169 (1933), is unreasonable. Equilibrium constants derived from Balesdent and Chiche yield -37.6 kcal/mol by third law analysis, but a serious entropy error is present. This is no doubt due to uncertainties in the activity of Cu in Cu-Au alloys. Other data have been reviewed by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Author	Method	Reaction**	Temp.	No. of Points	ΔHr°_{298}(kcal/mol) 2nd Law	3rd Law	Drift (eu)	ΔHr°_{298}* (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-31.15		—	-37.16
2. Wartenberg et al. (1932)	Calorimetry	A	295	—	-30.27±0.2		—	-38.04
3. Balesdent (1955)	Equilibrium Data	B	1011-1156	32	68.2 ±0.7	75.18	6.4±0.7	-37.59
4. Assayag (1955)	Kp	C	1047-1342	11	33.28±0.15	33.81	0.4±0.1	-37.25
5. Becker (1927)	Kp	C	1193-1293	6	33.84±0.27	33.80	0.0±0.2	-37.25
6. Roberts et al. (1921)	Kp	C	1189-1358	20	33.96±0.07	33.76	-0.1±0.1	-37.23
7. Foote et al. (1908)	Kp	C	1223-1323	7	33.19±0.17	33.74	0.4±0.1	-37.22
8. Combined 4,5,6,7	Kp	C	1047-1358	45	33.70±0.10	33.77	0.04±0.09	-37.24

*Based on third law where possible.

**Reaction A: $CuO(c) + H_2 = Cu(c) + H_2O(l)$ B: $2CuO(c) = 2Cu(c) + O_2$

C: $2CuO(c) = Cu_2O(c) + 0.5\ O_2$

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3. D. Balesdent, Compt. rend. 240, 760 (1955); 1884 (1955); P. Chiche, Ann. chim. 7, 361 (1952).
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Heat Capacity and Entropy.

Low temperature values are based on data (15-297°K) from J. Hu and H. L. Johnston, J. Am. Chem. Soc. 75, 2471 (1953). Earlier data from R. W. Millar (71-302°K), J. Am. Chem. Soc. 51, 215 (1929), are in satisfactory agreement, while those of K. Clusius and P. Harteck (30-200°K), Z. physik. Chem. 134, 243 (1928), are higher by several percent. A small anomaly in the heat capacity is observed in the region 210-230°K. Magnetic measurements of M. O'Keefe and F. S. Stone, Phys. Chem. Solids 23, 261 (1962), and neutron diffraction studies of B. N. Brockhouse, Phys. Rev. 94, 781 (1954), suggest that this is a Néel point associated with antiferromagnetism. The entropy was obtained from the heat capacities based on $S^\circ_{15} = 0.016$ eu.

High temperature values are based on specific heats (373-1273°K) obtained from a dynamic method by D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 5800 b (1963). Enthalpy data (523-1253°K) of Wöhler and Jochum, loc. cit., lead to a value for S°_{1200} lower by about 0.25 eu, but this is inconsistent with the equilibrium data for $2CuO = Cu_2O + 0.5\ O_2$.

Temperature of Decomposition.

T_d is calculated as the temperature at which ΔF equals zero for $2CuO(c) = Cu_2O(c) + 0.5\ O_2(g)$.

Copper Monoxide (CuO)

(Ideal Gas) GFW = 79.5394

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.333	58.800	58.800	INFINITE
100	7.573	47.222	63.437	-1.622	59.005	56.592	-123.681
200	8.245	52.723	56.843	-.824	58.973	54.183	-59.208
298	8.522	56.072	56.072	.000	58.900	51.847	-38.005
300	8.526	56.124	56.072	.016	58.898	51.803	-37.738
400	8.689	58.601	56.408	.877	58.807	49.451	-27.019
500	8.791	60.552	57.049	1.752	58.700	47.125	-20.598
600	8.862	62.161	57.771	2.634	58.572	44.821	-16.326
700	8.921	63.532	58.498	3.524	58.428	42.541	-13.282
800	8.982	64.727	59.204	4.419	58.267	40.281	-11.004
900	9.049	65.789	59.878	5.320	58.094	38.043	-9.238
1000	9.126	66.746	60.517	6.229	57.911	35.825	-7.830
1100	9.211	67.620	61.124	7.146	57.723	33.626	-6.681
1200	9.301	68.425	61.699	8.071	57.528	31.443	-5.727
1300	9.394	69.174	62.246	9.006	57.331	29.278	-4.922
1400	9.486	69.873	62.766	9.950	53.945	27.229	-4.251
1500	9.575	70.531	63.262	10.903	53.712	25.328	-3.690
1600	9.658	71.151	63.736	11.865	53.485	23.443	-3.202
1700	9.735	71.739	64.189	12.835	53.264	21.573	-2.773
1800	9.805	72.298	64.624	13.812	53.047	19.716	-2.394
1900	9.867	72.829	65.042	14.795	52.833	17.869	-2.055
2000	9.922	73.337	65.444	15.785	52.622	16.035	-1.752
2100	9.969	73.822	65.832	16.779	52.414	14.211	-1.479
2200	10.009	74.287	66.206	17.778	52.207	12.397	-1.231
2300	10.043	74.733	66.567	18.781	52.002	10.590	-1.006
2400	10.071	75.161	66.916	19.787	51.797	8.795	-.801
2500	10.094	75.572	67.254	20.795	51.591	7.008	-.613
2600	10.112	75.968	67.582	21.805	51.385	5.229	-.440
2700	10.127	76.350	67.899	22.817	51.178	3.458	-.280
2800	10.138	76.719	68.208	23.831	50.970	1.695	-.132
2900	10.147	77.075	68.508	24.845	-21.898	1.262	-.095
3000	10.154	77.419	68.799	25.860	-21.954	2.063	-.150
3100	10.159	77.752	69.082	26.876	-22.024	2.865	-.202
3200	10.162	78.075	69.358	27.892	-22.108	3.670	-.251
3300	10.165	78.387	69.627	28.908	-22.206	4.475	-.296
3400	10.167	78.691	69.889	29.925	-22.318	5.285	-.340
3500	10.169	78.986	70.145	30.941	-22.445	6.098	-.381
3600	10.170	79.272	70.395	31.958	-22.584	6.917	-.420
3700	10.172	79.551	70.638	32.976	-22.736	7.738	-.457
3800	10.174	79.822	70.876	33.993	-22.902	8.564	-.493
3900	10.176	80.086	71.109	35.010	-23.079	9.393	-.526
4000	10.178	80.344	71.337	36.028	-23.269	10.228	-.559
4100	10.182	80.595	71.560	37.046	-23.468	11.069	-.590
4200	10.186	80.841	71.778	38.064	-23.678	11.914	-.620
4300	10.190	81.080	71.991	39.083	-23.897	12.767	-.649
4400	10.196	81.315	72.201	40.102	-24.126	13.619	-.676
4500	10.202	81.544	72.406	41.122	-24.361	14.479	-.703
4600	10.209	81.768	72.607	42.143	-24.604	15.346	-.729
4700	10.217	81.988	72.804	43.164	-24.855	16.217	-.754
4800	10.226	82.203	72.998	44.186	-25.110	17.096	-.778
4900	10.235	82.414	73.188	45.209	-25.371	17.975	-.802
5000	10.245	82.621	73.374	46.233	-25.636	18.862	-.824
5100	10.256	82.824	73.558	47.258	-25.906	19.758	-.847
5200	10.268	83.023	73.738	48.285	-26.179	20.651	-.868
5300	10.281	83.219	73.915	49.312	-26.455	21.555	-.889
5400	10.294	83.411	74.089	50.341	-26.734	22.462	-.909
5500	10.307	83.600	74.260	51.371	-27.015	23.378	-.929
5600	10.322	83.786	74.428	52.402	-27.298	24.297	-.948
5700	10.337	83.969	74.594	53.435	-27.582	25.218	-.967
5800	10.352	84.149	74.757	54.470	-27.869	26.151	-.985
5900	10.368	84.326	74.918	55.506	-28.156	27.086	-1.003
6000	10.384	84.500	75.076	56.543	-28.445	28.022	-1.021

Sept. 30, 1966; June 30, 1970

COPPER MONOXIDE (CuO) (IDEAL GAS) GFW = 79.5394

Symmetry Number = 1

$S^\circ_{298.15}$ = 56.07 ± 0.1 gibbs/mol

ΔHf°_0 = 58.8 ± 8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 58.9 ± 8 kcal/mol

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^2\Pi$	0	2	1.726	0.4446	[0.0034]	632	[3.5]
	269	2					
$A^2\Pi$	4460	2		[0.4420]	[0.0040]	633	4.5
	4735	2					
$B^2\Sigma$	20953	2		[0.4426]	[0.0052]	637	6.5
$C^2\Pi$	23550	4		0.4213	[0.0046]	[610]	[5.0]

Heat of Formation

The heat of formation is calculated from that of the crystal, ΔHs°_{298} = 96.1 kcal/mol, which was obtained by 3rd law analysis of the sublimation pressure at 1273°K reported by Mack et al. (1). They employed a transpiration method and analysed for copper (in minute amounts) by its catalytic effect on the oxidation rate of sodium sulfite. The resulting pressure is only 100 times the predicted pressure of Cu(g) over CuO(c). Three pressures were reported but not used in the range 873-1173°K, since these yield a much smaller value for the heat of vaporization and imply a high dissociation energy.

Some estimates of D°_0 CuO obtained by different methods are given below. These estimates along with a correlation of D°_0 values for MnO, FeO, NiO and ZnO favor D°_0 = 82 ± 10, close to the value adopted.

Method	kcal/mol ΔHs°_{298}	D°_0	ΔHf°_{298}
Mack et al. (1) Transpiration	96.1	80.8	58.9
Arithmetic mean of D°_0 for O_2 and Cu_2		82	57.7
Geometric mean of D°_0 for O_2 and Cu_2		73	66.7
Linear Birge Sponer extrapolation of $A^2\Pi$ state		76±12	63.7±12

Heat Capacity and Entropy

The visible spectrum of CuO has been extensively investigated, but only very recently has significant progress been made in its analysis. Antic-Jovanovic et al. (2) were able to obtain a vibrational analysis of the major band system by use of O^{18} isotope studies. Shirk and Bass (3) recently reported absorption and fluorescence spectra in inert-gas matrices which allows assignment of the ground state and the first two excited states. They have strong evidence for the lower state of the blue system being the ground state and also for the second system, which corresponds to the red-orange system, originating in the upper state of the blue system. Thus, it is probable that the B state is $^2\Sigma$ and the X and A states are both $^2\Pi$ with very similar molecular constants, which serves to confuse the analysis of the spectra. It also appears likely that the 4182Å band analysed by Lagerqvist and Uhler (4) is a $^2\Pi$-$^2\Pi$ transition terminating in the ground state; thus we adopt their rotational constants for the X and C states. The vibrational frequencies and anharmonicities for the A and B states were from Antic-Jovanovic (2), as well as the vibrational interval for the ground state. The anharmonicity for the ground state was chosen so as to provide a reasonable Birge-Sponer extrapolation of the dissociation energy. The values of the α_e were estimated from the Morse potential function relations. The rotational constants were assumed to be nearly constant. The values of the splitting in the electronic levels in the X and A states are from Antic-Jovanovic (2), and are roughly confirmed by Shirk and Bass (3).

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states.

References

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2. A. Antic-Jovanovic, D. S. Pesic and A. G. Gaydon, Proc. Roy. Soc. (London) 307A, 399 (1968).
3. J. S. Shirk and A. M. Bass, J. Chem. Phys. 52, 1894 (1970).
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Copper Sulfate ($CuSO_4$)

(Crystal) GFW = 159.6016

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.030	-181.662	-181.662	INFINITE
100	10.449	7.808	43.361	-3.555	-182.898	-174.864	382.166
200	18.405	17.726	28.119	-2.078	-183.687	-166.489	181.931
298	23.630	26.112	26.112	.000	-184.030	-157.960	115.788
300	23.730	26.259	26.113	.044	-184.033	-157.798	114.956
400	27.470	33.617	27.091	2.611	-184.584	-149.023	81.422
500	30.400	40.076	29.055	5.510	-184.701	-140.113	61.243
600	32.580	45.820	31.379	8.664	-184.547	-131.205	47.792
700	34.160	50.966	33.816	12.005	-184.207	-122.315	38.188
800	35.300	55.606	36.255	15.481	-196.809	-114.775	31.355
900	36.100	59.811	38.643	19.052	-195.971	-104.569	25.393
1000	36.750	63.649	40.954	22.695	-195.101	-94.458	20.644
1100	37.300	67.178	43.180	26.398	-194.205	-84.439	16.776
1200	37.790	70.445	45.318	30.153	-193.286	-74.500	13.568
1300	38.230	73.488	47.369	33.955	-192.347	-64.638	10.867
1400	38.630	76.336	49.337	37.798	-194.577	-54.749	8.547
1500	39.010	79.014	51.227	41.680	-193.635	-44.796	6.527
1600	39.370	81.543	53.044	45.599	-192.668	-34.903	4.768
1700	39.710	83.940	54.791	49.553	-191.677	-25.072	3.223
1800	40.050	86.220	56.474	53.541	-190.667	-15.302	1.858
1900	40.370	88.394	58.098	57.562	-189.636	-5.586	.643
2000	40.690	90.472	59.665	61.615	-188.584	4.072	-.445

June 30, 1966

COPPER SULFATE ($CuSO_4$) (CRYSTAL) GFW = 159.6016

$S^\circ_{298.15}$ = 26.11 ± 0.1 gibbs/mol

Td = 1078°K

ΔHf°_0 = -181.66 ± 0.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -184.03 ± 0.2 kcal/mol

Heat of Formation.

The heat of solution ($\Delta Hr^\circ_{298.15}$) of CuO(c) in sulfuric acid to form $CuSO_4$(c) has been measured by L. H. Adami and E. G. King, U. S. Bur. Mines RI 6617, 1965. From the reported value, ΔHr° = -5.61 ± 0.09 kcal/mol for the reaction $CuO(c) + H_2SO_4(7.068\ H_2O) = CuSO_4(c) + H_2O(l)$, the heat of formation ($\Delta Hf^\circ_{298.15}$ for $CuSO_4$(c) was evaluated as -184.03 kcal/mol, using $\Delta Hf^\circ_{298.15}$ = -37.25, -209.49 and -68.315 kcal/mol for CuO(c), $H_2SO_4(7.068\ H_2O)$ and $H_2O(l)$, respectively. See $Fe_2(SO_4)_3$(c) table for the sources of the last two $\Delta Hf^\circ_{298.15}$ values.

The equilibrium pressures for the following chemical reactions: (A) $2CuSO_4(c) = CuO\cdot CuSO_4(c) + SO_3(g)$, (B) $3Cu(c) + CuSO_4(c) = 2Cu_2O(c) + SO_2(g)$, and (C) $4CuSO_4(c) + Cu_2O(c) = 3CuO\cdot CuSO_4(c) + SO_2(g)$, were determined by several investigators. For reaction (A), the partial pressures of SO_3(g) at different temperatures were calculated from the measured total pressures exerted by SO_3(g), SO_2(g) and O_2(g) produced by the reaction $SO_3(g) = SO_2(g) + 1/2\ O_2(g)$. From these vapor pressure data, the corresponding enthalpy changes ($\Delta Hr^\circ_{298.15}$) for the three reactions were evaluated by the second and third law methods. The results obtained are presented in the following table. The value of $\Delta Hf^\circ_{298.15}$ ($CuSO_4$, c) adopted was -184.03 ± 0.2 kcal/mol.

Investigator	Reaction	Temperature, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$ kcal/mol
Wöhler, et al. (1)	(A)	819.15-1004.15	25.90±3.60	47.45	22± 4	-181.87
Reinders and Goudriaan (2)	(A)	953.15-1053.15	56.54±0.77	51.96	-4.55±0.79	-184.13
	(C)	825.15- 921.15	42.84±1.38	42.34	-0.55±1.57	-184.42
Ingraham (3)	(A)	880.15-1071.75	51.59±0.41	51.75	0.07±0.43	-184.02
Randall et al. (4)	(B)	525.1 - 608.1	31.71±0.76	32.27	0.84±1.30	-184.62

(1) L. Wöhler, W. Plüddemann and P. Wöhler, Ber. Deut. Chem. Gesell. 41, 703 (1908).

(2) W. Reinders and F. Goudriaan, Z. anorg. allgem. Chem. 126, 85 (1923).

(3) T. R. Ingraham, Trans. Met. Soc. AIME, 233, 259 (1965).

(4) M. Randall, R. F. Nielsen and G. H. West, Ind. Eng. Chem. 23, 388 (1931). In this report, the high temperature equilibrium reactions of copper were critically reviewed.

Heat Capacity and Entropy.

The low temperature heat capacities, 52.67-296.29°K, were obtained from W. W. Weller, U. S. Bur. Mines RI 6669, 1965. The high temperature heat capacities were measured by H. Schottky, Z. phys. Chem. 64, 415 (1908), 282°C; R. Ewald, Ann. Physik., 44, 1213 (1914), 275-373°K; A. N. Krestovnikov and E. J. Feigina, J. Gen. Chem. USSR, 6, 1481 (1936), 288-873°K; and D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk SSSR, No. 12 79-84 (1963), 373-1273°K. The heat capacities below 51°K were obtained from J. W. Stout, J. Chem. Phys. 9, 285 (1941). In that paper, the Cp values, 15-58°K, were plotted as function of temperature and the Cp curve shows a maximum at 34.8°K. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve was drawn. The entropy above the normal Cp curve is reported to be 0.48 eu, rather than a magnetic entropy of Rln2 = 1.377 eu. Apparently the magnetic entropy increases gradually above 40°K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

The Cp values above 298.15°K were extrapolated smoothly by comparison with those for $MnSO_4$(c) (see $FeSO_4$(c) table for details). The adopted Cp values are close to the average of the reported Cp values.

The value of $S^\circ_{298.15}$ was derived using the low temperature Cp data reported by W. W. Weller, loc. cit., based on S°_{51} = 2.851 eu evaluated from Cp data determined by J. W. Stout, loc. cit.

Decomposition Temperature.

Td is the temperature at which the total pressure of the gaseous decomposition products equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $CuSO_4$(c), determined by T. R. Ingraham, loc. cit.

Copper, Diatomic (Cu_2)
(Ideal Gas)   GFW = 127.080

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.373	116.017	116.017	INFINITE
100	7.640	48.700	65.302	-1.660	116.412	112.020	-244.820
200	8.471	54.304	58.538	-.847	116.263	107.667	-117.653
298	8.744	57.745	57.745	.000	116.000	103.502	-75.869
300	8.747	57.799	57.745	.016	115.994	103.424	-75.344
400	8.868	60.334	58.090	.898	115.682	99.280	-54.244
500	8.935	62.321	58.745	1.788	115.340	95.220	-41.620
600	8.981	63.954	59.481	2.684	114.970	91.229	-33.230
700	9.015	65.341	60.222	3.584	114.580	87.304	-27.258
800	9.044	66.547	60.939	4.487	114.169	83.434	-22.793
900	9.069	67.614	61.622	5.392	113.740	79.618	-19.334
1000	9.092	68.570	62.270	6.301	113.293	75.851	-16.577
1100	9.113	69.438	62.883	7.211	112.831	72.129	-14.331
1200	9.134	70.232	63.463	8.123	112.351	68.448	-12.466
1300	9.154	70.964	64.012	9.038	111.858	64.811	-10.896
1400	9.173	71.643	64.533	9.954	104.978	61.414	-9.587
1500	9.192	72.276	65.028	10.872	104.396	58.322	-8.498
1600	9.211	72.870	65.500	11.792	103.816	55.269	-7.549
1700	9.229	73.429	65.950	12.714	103.238	52.253	-6.718
1800	9.247	73.957	66.380	13.638	102.662	49.272	-5.982
1900	9.265	74.458	66.793	14.564	102.088	46.319	-5.328
2000	9.284	74.933	67.188	15.491	101.515	43.401	-4.743
2100	9.302	75.387	67.567	16.420	100.944	40.508	-4.216
2200	9.320	75.820	67.933	17.351	100.375	37.645	-3.740
2300	9.338	76.234	68.285	18.284	99.808	34.806	-3.307
2400	9.357	76.632	68.624	19.219	99.243	31.990	-2.913
2500	9.376	77.015	68.952	20.156	98.680	29.202	-2.553
2600	9.395	77.383	69.270	21.094	98.118	26.434	-2.222
2700	9.414	77.738	69.577	22.035	97.559	23.687	-1.917
2800	9.435	78.080	69.874	22.977	97.001	20.964	-1.636
2900	9.455	78.412	70.163	23.922	-48.870	20.904	-1.575
3000	9.477	78.733	70.443	24.868	-49.114	23.315	-1.699
3100	9.500	79.044	70.716	25.817	-49.379	25.734	-1.814
3200	9.523	79.346	70.981	26.768	-49.666	28.165	-1.924
3300	9.548	79.639	71.239	27.722	-49.976	30.600	-2.027
3400	9.573	79.925	71.490	28.678	-50.306	33.045	-2.124
3500	9.600	80.203	71.735	29.636	-50.660	35.500	-2.217
3600	9.628	80.473	71.974	30.598	-51.032	37.970	-2.305
3700	9.657	80.738	72.207	31.562	-51.426	40.445	-2.389
3800	9.687	80.995	72.435	32.529	-51.839	42.937	-2.469
3900	9.719	81.248	72.658	33.499	-52.271	45.432	-2.546
4000	9.752	81.494	72.876	34.473	-52.719	47.945	-2.620
4100	9.786	81.735	73.089	35.450	-53.182	50.470	-2.690
4200	9.822	81.971	73.298	36.430	-53.662	53.006	-2.758
4300	9.859	82.203	73.502	37.414	-54.154	55.552	-2.823
4400	9.897	82.430	73.702	38.402	-54.658	58.105	-2.886
4500	9.936	82.653	73.899	39.394	-55.172	60.671	-2.947
4600	9.976	82.872	74.091	40.389	-55.697	63.250	-3.005
4700	10.017	83.087	74.281	41.389	-56.231	65.842	-3.062
4800	10.059	83.298	74.466	42.393	-56.771	68.451	-3.117
4900	10.103	83.506	74.649	43.401	-57.317	71.063	-3.170
5000	10.147	83.711	74.828	44.413	-57.869	73.686	-3.221
5100	10.191	83.912	75.004	45.430	-58.424	76.328	-3.271
5200	10.237	84.110	75.177	46.452	-58.984	78.972	-3.319
5300	10.283	84.306	75.348	47.478	-59.546	81.624	-3.366
5400	10.329	84.498	75.515	48.508	-60.110	84.297	-3.412
5500	10.376	84.688	75.680	49.543	-60.675	86.978	-3.456
5600	10.423	84.876	75.843	50.583	-61.241	89.668	-3.499
5700	10.471	85.061	76.003	51.628	-61.806	92.362	-3.541
5800	10.519	85.243	76.161	52.678	-62.374	95.078	-3.583
5900	10.567	85.423	76.316	53.732	-62.940	97.805	-3.623
6000	10.615	85.601	76.469	54.791	-63.507	100.527	-3.662

Sept. 30, 1966

Ground State Configuration [$^1\Sigma$] ΔHf_0° = 116.0 kcal/mol

$S_{298.15}$ = 57.74 gibbs/mol $\Delta Hf_{298.15}^\circ$ = 116.0 ± 3 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[1]
20433	[1]
21758	[1]

$\omega_e = 265.34\ \text{cm}^{-1}$ $\omega_e x_e = 1.015\ \text{cm}^{-1}$ $\sigma = 2$

$B_e = 0.10776\ \text{cm}^{-1}$ $\alpha_e = 0.000608\ \text{cm}^{-1}$ $r_e = 2.219\text{Å}$

Heat of Formation.

The heat of formation was calculated from that of Cu(g) using ΔHr_{298}° = 46.0 kcal/mol for $Cu_2(g) \rightarrow 2\ Cu(g)$ obtained by third law analysis of the mass spectrometric data of Ackerman et al. Earlier studies of mass spectra and of the electronic band spectra yield values in reasonable agreement as shown below. The selected ΔHr° corresponds to D_0° = 1.97 eV compared with the linear Birge-Sponer extrapolation of 2.1 eV.

Source	Method	Range °K	ΔHr_{298}° (kcal/mol) 2nd law	3rd law	Drift eu	ΔHf_{298}° kcal/mol
1. Ackerman et al. (1960)	Mass Spect.	1549-1709	47.8 ± 2.6	45.99	-1.0 ± 1.6	116.0
2. Schissel (1957)	Mass Spect.	1575-1720	50.3 ± 3.7	46.76	-2.1 ± 2.3	115.0
3. Drowart et al. (1956)	Mass Spect.	1440-1560	-	46.5	-	115.5
4. Kleman et al. (1954)	Band Spectra	-	-	49	-	113

1. M. Ackerman, F. E. Stafford and J. Drowart, J. Chem. Phys. 33, 1784 (1960). Dimer-monomer pressure ratio obtained from intensity ratio using factor 0.705.
2. P. Schissel, J. Chem. Phys. 26, 1276 (1957). Point at 1730°K omitted. Dimer-monomer pressure ratio obtained from intensity ratio using factor 0.588.
3. J. Drowart and R. E. Honig, J. Chem. Phys. 25, 581 (1956).
4. B. Kleman and S. Lindkvist, Arkiv Fysik 8, 333 (1954).

Heat Capacity and Entropy.

Molecular constants, except for $\omega_e x_e$, were taken from the rotational analysis of bands of the B-X system given by D. N. Travis and R. F. Barrow, Proc. Chem. Soc. (London), 44 (1962). The value for $\omega_e x_e$ was obtained from the earlier study of Kleman and Lindquist, loc. cit., who showed by means of the vibrational isotope effect that the emitter was Cu_2. The spectroscopic characters of the ground and excited states are uncertain, but Travis and Barrow indicate that the transition is probably $^1\Sigma^+_u - {}^1\Sigma^+_g$ for the B-X system. Vibrational and rotational constants were adjusted for 30.91% ^{65}Cu.

Dicopper Monoxide (Cu_2O)

(Crystal) GFW = 143.0794

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.037	-40.309	-40.309	INFINITE
100	9.506	8.902	34.082	-2.518	-40.455	-38.798	84.792
200	12.893	16.598	23.537	-1.388	-40.635	-37.069	40.507
298	15.199	22.213	22.213	.000	-40.700	-35.299	25.875
300	15.230	22.307	22.213	.028	-40.700	-35.266	25.691
400	16.580	26.893	22.829	1.626	-40.652	-33.459	18.281
500	17.410	30.687	24.032	3.327	-40.548	-31.671	13.843
600	18.040	33.919	25.417	5.101	-40.418	-29.909	10.894
700	18.620	36.743	26.838	6.934	-40.264	-28.167	8.794
800	19.220	39.269	28.237	8.826	-40.085	-26.454	7.227
900	19.850	41.568	29.592	10.779	-39.873	-24.780	6.013
1000	20.520	43.694	30.897	12.797	-39.624	-23.094	5.047
1100	21.220	45.683	32.152	14.884	-39.329	-21.456	4.263
1200	21.920	47.559	33.358	17.041	-38.988	-19.846	3.614
1300	22.620	49.341	34.520	19.268	-38.597	-18.265	3.071
1400	23.320	51.043	35.640	21.565	-44.528	-16.514	2.578
1500	24.020	52.676	36.721	23.932	-44.097	-14.529	2.117
1600	24.720	54.249	37.768	26.369	-43.598	-12.574	1.718
1700	25.420	55.768	38.782	28.876	-43.032	-10.650	1.369
1800	26.120	57.241	39.767	31.453	-42.400	-8.762	1.064
1900	26.820	58.672	40.725	34.100	-41.700	-6.914	.795
2000	27.520	60.066	41.657	36.817	-40.933	-5.103	.558
2100	28.220	61.425	42.566	39.604	-40.099	-3.330	.347
2200	28.920	62.754	43.454	42.461	-39.198	-1.600	.159
2300	29.620	64.055	44.321	45.388	-38.229	.086	-.008
2400	30.320	65.331	45.170	48.385	-37.193	1.728	-.157
2500	31.020	66.582	46.002	51.452	-36.090	3.333	-.291

June 30, 1966

DICOPPER MONOXIDE (Cu_2O) (CRYSTAL) GFW = 143.0794

ΔHf°_0 = -40.31 kcal/mol

$S^\circ_{298.15}$ = 22.21 ± 0.08 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -40.7 ± 0.5 kcal/mol

Tm = 1509°K

ΔHm° = 13.58 ± 2 kcal/mol

Heat of Formation.

Summarized below are the more consistent results for the heat of formation. The selected value of -40.7 kcal/mol is based on data from Thomsen and from Ishakawa and Kimura. More recent equilibrium data yield essentially the same average for ΔHf but the separate values scatter by about ±0.7 kcal/mol and significant entropy errors are apparent.

Thomsen obtained values of -40.80, -40.87 and -41.51 from aqueous calorimetry using three different paths. He favored the first path which may be recalculated by combination of the heats of reaction of $Cu_2O + H_2SO_4$, $Fe + H_2SO_4$ and $Fe + CuSO_4(aq)$ to yield the heat of reduction of Cu_2O with H_2. Direct measurements of the heat of reduction reported by L. Wöhler and N. Jochum, Z. physik. Chem. 167A, 169 (1933), appear to be unreliable since they lead to -43.0 for the heat of formation. The cell data of Ishakawa and Kimura show very little drift and are in excellent agreement with Thomsen.

Author	Method	Reaction**	Temp. (°K)	No. of Points	ΔHr°_{298} (kcal/mol) 2nd Law	ΔHr°_{298} (kcal/mol) 3rd Law	Drift (eu)	ΔHf°_{298}* (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-27.61		—	-40.70
2. Hill et al.(1958)	Fused salt Emf	B	987	1		-41.38	—	-41.38
3. Kiukkola et al.(1957)	Emf vs. Fe/Fe_xO	B	1073-1323	4	-43.03±0.56	-40.42	2.1±0.5	-40.42
	Emf vs. Fe_yO/Fe_3O_4	B	1073-1323	4	-44.14±0.10	-40.36	3.1±0.1	-40.36
4. Balesdent (1955)	Equilibrium data	C	1011-1156	28	36.03±1.1	41.20	4.7±1.0	-41.20
5. Makolkin (1942)	Aqueous Emf	D	288- 308	3	29.46±0.7	28.30	-4.0±2.5	-40.02
6. Maier (1929)	Aqueous Emf	D	298-318	7	29.94±0.4	28.07	-6.2±1.3	-40.24
7. Ishakawa et al.(1927)	Aqueous Emf	D	273-318	5	27.42±0.04	27.63	0.7±0.1	-40.69

*Based on 3rd law values wherever possible.

**Reaction A: $Cu_2O(c) + H_2 = 2Cu + H_2O(l)$, B: $2Cu + 0.5\ O_2 = Cu_2O(c)$

C: $Cu_2O(c) = 2Cu + 0.5\ O_2$, D: $2Cu + H_2O(l) = Cu_2O(c) + H_2$.

1. J. Thomsen, "Thermochemische Untersuchungen," vol. III, Barth, Leipzig, 1883.
2. D. G. Hill, B. Porter and A. S. Gillespie, Jr., J. Electrochem. Soc. 105, 408 (1958).
3. K. Kiukkola, C. Wagner, J. Electrochem. Soc. 104, 379 (1957).
4. D. Balesdent, Compt. rend. 240, 760 (1955); 1884 (1955).
5. I. A. Makolkin, J. Phys. Chem. (U.S.S.R.) 16, 13 (1942); cf. Chem. Abs. 37, 2641 (1943).
6. C. G. Maier, J. Am. Chem. Soc. 51, 194 (1929).
7. F. Ishakawa and G. Kimura, "Sexagint, Yikichi Osaka," pp. 255-69, Chem. Inst. Kyoto Imp. Univ., Kyoto, Japan, 1927; cf. Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Heat Capacity and Entropy.

Low temperature values are based on data from L. V. Gregor (2.8-21°K), J. Phys. Chem. 66, 1645 (1962) and from J. Hu and H. L. Johnston (15-300°K), J. Am. Chem. Soc. 73, 4550 (1951). Earlier data by R. W. Millar (76-291°K), J. Am. Chem. Soc. 51, 215 (1929) are in satisfactory agreement. The entropy was obtained from the heat capacities based on $S^\circ_{2.8}$ = 0.0015 eu.

High temperature values were obtained from specific heats (373-1273°K) determined with a dynamic method by D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 79 (1963). Enthalpy data (543-1223°K) from Wöhler and Jochum, loc. cit., yield for S°_{1000} a value about 0.4 eu higher, but this is inconsistent with extensive equilibrium data for $2CuO(c) = Cu_2O(c) + 0.5\ O_2$ [see CuO(c)].

Melting Data.

For details see $Cu_2O(l)$.

Dicopper Monoxide (Cu_2O)

(Liquid) GFW = 143.0794

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.000	22.901	22.901	.000	-32.029	-26.833	19.669
300	24.000	23.049	22.901	.044	-32.013	-26.801	19.525
400	24.000	29.954	23.843	2.444	-31.163	-25.194	13.765
500	24.000	35.309	25.620	4.844	-30.360	-23.794	10.400
600	24.000	39.685	27.611	7.244	-29.604	-22.554	8.215
700	24.000	43.385	29.607	9.644	-28.883	-21.435	6.692
800	24.000	46.589	31.534	12.044	-28.196	-20.420	5.578
900	24.000	49.416	33.367	14.444	-27.537	-19.487	4.732
1000	24.000	51.945	35.100	16.844	-26.906	-18.627	4.071
1100	24.000	54.232	36.737	19.244	-26.298	-17.828	3.542
1200	24.000	56.321	38.284	21.644	-25.714	-17.086	3.112
1300	24.000	58.242	39.746	24.044	-25.150	-16.389	2.755
1400	24.000	60.020	41.131	26.444	-30.978	-15.531	2.425
1500	24.000	61.676	42.446	28.844	-30.514	-14.446	2.105
1600	24.000	63.225	43.697	31.244	-30.052	-13.390	1.829
1700	24.000	64.680	44.889	33.644	-29.593	-12.361	1.589
1800	24.000	66.052	46.027	36.044	-29.138	-11.360	1.379
1900	24.000	67.349	47.115	38.444	-28.685	-10.385	1.195
2000	24.000	68.580	48.158	40.844	-28.235	-9.433	1.031
2100	24.000	69.751	49.159	43.244	-27.788	-8.503	.885
2200	24.000	70.868	50.120	45.644	-27.344	-7.596	.755
2300	24.000	71.935	51.046	48.044	-26.902	-6.711	.638
2400	24.000	72.956	51.938	50.444	-26.463	-5.842	.532
2500	24.000	73.936	52.798	52.844	-26.027	-4.989	.436
2600	24.000	74.877	53.629	55.244	-25.593	-4.156	.349
2700	24.000	75.783	54.433	57.644	-25.162	-3.340	.270
2800	24.000	76.656	55.211	60.044	-24.733	-2.539	.198
2900	24.000	77.498	55.965	62.444	-169.623	.894	-.067
3000	24.000	78.312	56.697	64.844	-168.890	6.762	-.493

June 30, 1966

Cu_2O

DICOPPER MONOXIDE (Cu_2O) (LIQUID) GFW = 143.0794

$S^\circ_{298.15}$ = 22.901 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -32.029 kcal/mol

Tm = 1509°K

ΔHm° = 13.58 ± 2 kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔHm° and the difference between ($H^\circ_{1509}-H^\circ_{298}$) for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated on the basis of 8 gibbs per g atom, giving a value of 24 gibbs/mol which is essentially the same as that of the crystal at the melting point. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

Tm is the value recommended by S. J. Schneider, NBS Monograph 68, U. S. Govt. Printing Office, Washington, D.C., October, 1963, based on pressure-temperature-composition studies of H. S. Roberts and F. H. Smyth, J. Am. Chem. Soc. 43, 1061 (1921). The heat of melting was selected as 13.58 kcal/mol, corresponding to ΔSm° = 3 eu per g atom. A value of 13.4 kcal/mol has been derived from the Cu_2O-CuCl phase diagram by K. K. Kelley, USBM Bulletin 393, U. S. Govt. Printing Office, Washington, 1936. Another value may be obtained from oxygen dissociation pressures for the system $Cu_2O(l)$-CuO(c) determined by Roberts and Smyth, loc. cit. Equilibrium constants may be obtained for the reaction $2CuO(c) = Cu_2O(l) + 0.5\ O_2$ by assuming the activity of Cu_2O in the melt to be equal to its mole fraction. Based on the mole fractions given by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931), the equilibrium data yield ΔH°_m = 15.8 ± 0.8 kcal/mol by second law analysis of all points or 12.9 ± 1.6 by omission of 4 points at high pressure and low mole fraction. These results appear to be consistent with the selected value within the approximations involved.

Cu_2O

Copper Oxide Sulfate ($CuO.CuSO_4$)

(Crystal) GFW = 239.141

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	33.710	37.600	37.600	.000	- 221.700	- 189.390	138.827
300	33.800	37.809	37.601	.062	- 221.702	- 189.191	137.825
400	38.800	48.253	38.991	3.705	- 222.130	- 178.339	97.440
500	42.300	57.304	41.769	7.768	- 222.065	- 167.390	73.166
600	44.890	65.255	45.034	12.133	- 221.710	- 156.485	57.000
700	46.800	72.324	48.437	16.721	- 221.157	- 145.631	45.468
800	48.310	78.674	51.827	21.478	- 233.534	- 136.159	37.197
900	49.600	84.440	55.135	26.374	- 232.445	- 124.050	30.123
1000	50.800	89.728	58.333	31.395	- 231.289	- 112.065	24.492
1100	51.900	94.622	61.413	36.530	- 230.066	- 100.204	19.909
1200	53.000	99.185	64.372	41.775	- 228.777	- 88.454	16.110
1300	54.090	103.471	67.217	47.131	- 227.417	- 76.813	12.913
1400	55.050	107.515	69.952	52.588	- 232.363	- 65.079	10.159
1500	56.000	111.345	72.585	58.140	- 230.936	- 53.181	7.748

COPPER OXIDE SULFATE ($CuO \cdot CuSO_4$) (CRYSTAL) GFW = 239.141

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [37.6 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -221.7 ± 0.3 kcal/mol

Td = 1138.4°K

Heat of Formation.

The equilibrium pressures for the following reactions: (A) $CuO \cdot CuSO_4(c) = 2CuO(c) + SO_3(g)$ and $SO_3(g) = SO_2(g) + 0.5\ O_2(g)$, and (B) $CuO \cdot CuSO_4(c) + Cu_2O(c) = 4CuO(c) + SO_2(g)$, were determined by (1) W. Reinders and F. Goudriaan, Z. anorg. allgem. Chem. 126, 85 (1923), and (2) T. R. Ingraham, Trans. Met. Soc. AIME, 233, 359 (1965). Using the reported vapor pressures, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reference	Reaction	Temperature, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$* kcal/mol
(1)	A**	1013 - 1093	53.03 ± 2.53	52.43	-0.7 ± 2.4	-221.5
(1)	B	917 - 1027	41.72 ± 1.42	42.43	0.5 ± 1.4	-221.7
(2)	A**	969 - 1138	50.92 ± 0.16	52.57	1.5 ± 0.2	-221.7

* Based on the third law value for $\Delta Hr^\circ_{298.15}$.

** Partial pressures were calculated from JANAF Values for the SO_3 - SO_2 equilibrium.

The value of $\Delta Hf^\circ_{298.15}$ ($CuO \cdot CuSO_4$, c) adopted is -221.7 ± 0.3 kcal/mol.

Heat Capacity and Entropy.

The heat capacities were calculated as the sum of those for CuO(c) and $CuSO_4$(c). The value of $S^\circ_{298.15}$ was estimated by comparison with those for CuO(c) and $CuSO_4$(c), and adjusted so that, using the derived free energy functions, the second and third law values for $\Delta Hr^\circ_{298.15}$ agree reasonably.

Decomposition Temperature.

Td is the temperature at which the total pressure of the gaseous decomposition products of reaction (A) equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $CuO \cdot CuSO_4$(c), determined by T. R. Ingraham, loc. cit.

Fluorine, Monatomic (F)

(Ideal Gas) Mol. Wt. = 18.9984

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.558	18.357	18.357	INFINITE
100	5.068	32.116	42.710	-1.059	18.508	17.331	-37.875
200	5.403	35.746	38.415	-.534	18.684	16.089	-17.580
298	5.437	37.917	37.917	.000	18.860	14.777	-10.832
300	5.436	37.951	37.917	.010	18.863	14.752	-10.746
400	5.361	39.505	38.129	.550	19.018	13.358	-7.298
500	5.282	40.693	38.528	1.082	19.147	11.927	-5.213
600	5.218	41.650	38.971	1.607	19.256	10.472	-3.814
700	5.169	42.450	39.412	2.126	19.349	9.001	-2.810
800	5.133	43.138	39.836	2.641	19.431	7.517	-2.053
900	5.105	43.741	40.237	3.153	19.505	6.023	-1.462
1000	5.083	44.277	40.615	3.663	19.572	4.522	-.988
1100	5.066	44.761	40.970	4.170	19.633	3.013	-.599
1200	5.052	45.201	41.305	4.676	19.691	1.500	-.273
1300	5.041	45.605	41.620	5.180	19.744	-.018	.003
1400	5.032	45.978	41.918	5.684	19.794	-1.540	.240
1500	5.025	46.325	42.201	6.187	19.841	-3.065	.447
1600	5.018	46.649	42.469	6.689	19.886	-4.594	.627
1700	5.013	46.954	42.724	7.191	19.929	-6.126	.788
1800	5.009	47.240	42.967	7.692	19.969	-7.660	.930
1900	5.005	47.511	43.199	8.192	20.007	-9.197	1.058
2000	5.001	47.767	43.421	8.693	20.044	-10.733	1.173
2100	4.999	48.011	43.634	9.193	20.079	-12.273	1.277
2200	4.996	48.244	43.838	9.692	20.112	-13.816	1.372
2300	4.994	48.466	44.034	10.192	20.144	-15.358	1.459
2400	4.992	48.678	44.224	10.691	20.175	-16.902	1.539
2500	4.990	48.882	44.406	11.190	20.203	-18.448	1.613
2600	4.988	49.078	44.582	11.689	20.231	-19.995	1.681
2700	4.987	49.266	44.752	12.188	20.257	-21.542	1.744
2800	4.986	49.447	44.916	12.687	20.282	-23.090	1.802
2900	4.985	49.622	45.076	13.185	20.306	-24.639	1.857
3000	4.984	49.791	45.230	13.683	20.327	-26.191	1.908
3100	4.983	49.954	45.380	14.182	20.349	-27.740	1.956
3200	4.982	50.113	45.525	14.680	20.369	-29.294	2.001
3300	4.981	50.266	45.666	15.178	20.387	-30.845	2.043
3400	4.980	50.415	45.804	15.676	20.405	-32.399	2.082
3500	4.980	50.559	45.938	16.174	20.421	-33.950	2.120
3600	4.979	50.699	46.068	16.672	20.436	-35.502	2.155
3700	4.978	50.836	46.195	17.170	20.450	-37.059	2.189
3800	4.978	50.968	46.319	17.668	20.463	-38.610	2.220
3900	4.977	51.098	46.440	18.166	20.474	-40.169	2.251
4000	4.977	51.224	46.558	18.663	20.485	-41.723	2.280
4100	4.977	51.347	46.673	19.161	20.494	-43.279	2.307
4200	4.976	51.467	46.786	19.659	20.502	-44.835	2.333
4300	4.976	51.584	46.896	20.156	20.510	-46.390	2.358
4400	4.975	51.698	47 004	20.654	20.515	-47.944	2.381
4500	4.975	51.810	47.110	21.151	20.520	-49.502	2.404
4600	4.975	51.919	47.213	21.649	20.524	-51.056	2.426
4700	4.975	52.026	47.314	22.146	20.527	-52.612	2.446
4800	4.974	52.131	47.413	22.644	20.529	-54.169	2.466
4900	4.974	52.233	47.511	23.141	20.529	-55.722	2.485
5000	4.974	52.334	47.606	23.639	20.529	-57.281	2.504
5100	4.974	52.432	47.700	24.136	20.527	-58.837	2.521
5200	4.973	52.529	47.792	24.633	20.524	-60.393	2.538
5300	4.973	52.624	47.882	25.131	20.521	-61.950	2.554
5400	4.973	52.717	47.971	25.628	20.515	-63.509	2.570
5500	4.973	52.808	48.058	26.125	20.510	-65.062	2.585
5600	4.973	52.898	48.144	26.623	20.503	-66.619	2.600
5700	4.973	52.986	48.228	27.120	20.494	-68.175	2.614
5800	4.972	53.072	48.310	27.617	20.486	-69.728	2.627
5900	4.972	53.157	48.392	28.114	20.475	-71.284	2.640
6000	4.972	53.241	48.472	28.612	20.464	-72.842	2.653

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

Ground State Configuration $^2P_{3/2}$

$S^\circ_{298.15}$ = 37.917 cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0$ = 18.36 ± 0.40 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 18.86 ± 0.40 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0	4	116,597.23	14	128,346.36	80
404	2	117,465.88	22	132,786.07	16
103,327.14	18	118,627.73	10	133,531.81	22
115,918.7	6	123,118.7	12	134,978.71	88

Heat of Formation.

The dissociation energy (D_o) of fluorine has been discussed by numerous investigators for many years. Until about fifteen years ago, high values of $D_o(F_2)$, about 63 kcal. mole^{-1}, were widely accepted. These values were obtained from extrapolations of the spectroscopic data for the halogens, e.g. D_o = 63.3 kcal. mole^{-1} was reported by H. V. Wartenberg, G. Sprenger and J. Taylor, Z. physik. Chem., Bodenstein-Festband, 61 (1931). However, meanwhile many indirect determinations as well as estimation have been carried out, which yield appreciably lower values. In 1950 the available data were examined critically by M. G. Evans, E. Warhurst and E. Whittle, J. Chem. Soc. 1524 (1950) and shown to support a value, $D_o(F_2)$ = 37 ± 8 kcal. mole^{-1}. The indirect determinations include (1) the thermal conductivity measurements by E. U. Franck and E. Wicke, Z. Elektrochem. 55, 643 (1951); (2) the explosion method by H. Friz. Dissert., Göttingen, 1952; (3) estimation by use of the relations between D_o and the vibrational frequencies by A. Eucken and E. Wicke, Naturwiss., 37, 233 (1950); and (4) spectroscopic data on the dissociation energy of diatomic fluorides. Recently more direct methods have been used to determine $D_o(F_2)$. They gave similar values. The D_o values reported by the previous investigators have been reviewed by L. Haar and C. W. Beckett, National Bureau of Standards Report 1435 (1952), and E. Wicke and H. Friz. Z. Elecktrochem. 57, 9 (1953).

The low bond dissociation energy of $F_2(g)$ has been attributed to the repulsion between the unshared electrons on the bound fluorine atoms by K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948), or to the absence in fluorine of strengthening of the bond by hybridization of the p- or d- orbitals as may take place in the higher halogens by R. S. Mulliken, J. Am. Chem. Soc. 77, 884 (1955). M. G. Brown, Trans. Faraday Soc. 55, 9 (1959) suggests that the observed low D_o value results from the large energy required to promote the F atoms to the valence state from which the bond may be formed.

The equilibrium pressures for the reaction $F_2(g) \rightarrow 2F(g)$ have been measured by several investigators. Using the reported equilibrium constants, the dissociation energy, $D_{298.15}$, was evaluated by both the second and third law methods. The results obtained are presented as follows.

	$D_{298.15}$, kcal. mole^{-1}		
Temperature, °K.	2nd Law Value	3rd Law Value	Reference
759 - 1115	36.91 ± 0.41	37.76	1
810 - 860	56.7 ∓ 18.2	33.1	2
513 - 790	34.4 ∓ 1.8	38.0	3
723 - 820	41.8 ∓ 0.2	—	4

1. R. N. Doescher, J. Chem. Phys. 20, 330 (1952).
2. P. W. Gilles and J. L. Margrave, J. Chem. Phys. 21, 381 (1953).
3. H. Wise, J. Phys. Chem. 58, 389 (1954).
4. M. Farber, et al. "Study of Rocket Engine Exhaust Products", Thirteenth Quarterly Report, June 1 - Oct. 31, 1964, Maremont Corporation, Pasadena, California.

By use of H_2-F_2 mixture explosion method, $D_o(F_2)$ was reported as 37 ± 2 kcal. mole^{-1} by E. Wicke and H. Friz. loc. cit. K. L. Wray and D. F. Hornig, J. Chem. Phys. 24, 1271 (1956), using shock wave method, obtained D_o = 31.0 ± 4.3 kcal. mole^{-1}. The continuous absorption electronic spectrum of $F_2(g)$ and the Raman displacement for the 0 → 1 vibrational transition have been used by A. L. G. Rees, J. Chem. Phys. 26, 1567 (1957) to compute the potential energy curve for the repulsive $_1\Pi_u$ state dissociating to two normal F(g). This curve is consistent with the value, D_o = 37.1 ± 0.85 kcal. mole^{-1}. The absorption spectrum of $F_2(g)$ has been observed in the vacuum UV region by R. P. Iczkowski and J. L. Margrave, J. Chem. Phys. 30, 403 (1959). From a progression of bands at 874A, the value, D_o = 37.5 ± 2 kcal. mole^{-1} is deduced.

The F_2 dissociation energy is selected as 37.72 ± 0.80 kcal. mole^{-1}, yielding $\Delta H_f^\circ{}_{298.15}(F, g)$ = 18.86 ± 0.40 kcal. mole^{-1}.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weights were taken from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Fluorine Uninegative Ion (F^-)

(Ideal Gas)   Mol. Wt. = 18.99895

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	34.768	34.768	.000	-62.200	-63.857	46.806
300	4.968	34.799	34.768	.009	-62.207	-63.867	46.525
400	4.968	36.228	34.963	.506	-62.592	-64.363	35.164
500	4.968	37.337	35.331	1.003	-62.996	-64.759	28.305
600	4.968	38.242	35.743	1.500	-63.412	-65.073	23.702
700	4.968	39.008	36.156	1.996	-63.837	-65.315	20.391
800	4.968	39.672	36.555	2.493	-64.270	-65.498	17.892
900	4.968	40.257	36.934	2.990	-64.708	-65.625	15.935
1000	4.968	40.780	37.293	3.487	-65.151	-65.703	14.359
1100	4.968	41.254	37.632	3.984	-65.597	-65.738	13.060
1200	4.968	41.686	37.952	4.481	-66.045	-65.731	11.971
1300	4.968	42.084	38.255	4.977	-66.496	-65.686	11.042
1400	4.968	42.452	38.542	5.474	-66.950	-65.607	10.241
1500	4.968	42.795	38.814	5.971	-67.406	-65.495	9.542
1600	4.968	43.115	39.073	6.468	-67.863	-65.351	8.926
1700	4.968	43.416	39.320	6.965	-68.322	-65.180	8.379
1800	4.968	43.700	39.555	7.461	-68.783	-64.982	7.889
1900	4.968	43.969	39.781	7.958	-69.245	-64.760	7.449
2000	4.968	44.224	39.996	8.455	-69.708	-64.511	7.049
2100	4.968	44.466	40.203	8.952	-70.174	-64.239	6.685
2200	4.968	44.697	40.403	9.449	-70.640	-63.946	6.352
2300	4.968	44.918	40.594	9.945	-71.107	-63.630	6.046
2400	4.968	45.130	40.779	10.442	-71.576	-63.297	5.764
2500	4.968	45.332	40.957	10.939	-72.047	-62.941	5.502
2600	4.968	45.527	41.129	11.436	-72.519	-62.567	5.259
2700	4.968	45.715	41.295	11.933	-72.991	-62.178	5.033
2800	4.968	45.896	41.456	12.430	-73.465	-61.769	4.821
2900	4.968	46.070	41.612	12.926	-73.939	-61.342	4.623
3000	4.968	46.238	41.764	13.423	-74.416	-60.898	4.436
3100	4.968	46.401	41.911	13.920	-74.893	-60.439	4.261
3200	4.968	46.559	42.054	14.417	-75.372	-59.968	4.095
3300	4.968	46.712	42.193	14.914	-75.851	-59.480	3.939
3400	4.968	46.860	42.328	15.410	-76.331	-58.976	3.791
3500	4.968	47.004	42.459	15.907	-76.813	-58.457	3.650
3600	4.968	47.144	42.587	16.404	-77.296	-57.926	3.516
3700	4.968	47.280	42.712	16.901	-77.780	-57.378	3.389
3800	4.968	47.413	42.834	17.398	-78.265	-56.824	3.268
3900	4.968	47.542	42.953	17.895	-78.752	-56.255	3.152
4000	4.968	47.668	43.070	18.391	-79.238	-55.670	3.042
4100	4.968	47.790	43.183	18.888	-79.727	-55.071	2.935
4200	4.968	47.910	43.294	19.385	-80.217	-54.468	2.834
4300	4.968	48.027	43.403	19.882	-80.707	-53.849	2.737
4400	4.968	48.141	43.510	20.379	-81.199	-53.219	2.643
4500	4.968	48.253	43.614	20.875	-81.691	-52.578	2.553
4600	4.968	48.362	43.716	21.372	-82.184	-51.925	2.467
4700	4.968	48.469	43.816	21.869	-82.679	-51.262	2.384
4800	4.968	48.573	43.914	22.366	-83.175	-50.583	2.303
4900	4.968	48.676	44.010	22.863	-83.672	-49.904	2.226
5000	4.968	48.776	44.104	23.359	-84.170	-49.210	2.151
5100	4.968	48.875	44.197	23.856	-84.669	-48.507	2.079
5200	4.968	48.971	44.288	24.353	-85.169	-47.791	2.009
5300	4.968	49.066	44.377	24.850	-85.670	-47.068	1.941
5400	4.968	49.159	44.465	25.347	-86.173	-46.337	1.875
5500	4.968	49.250	44.551	25.844	-86.676	-45.594	1.812
5600	4.968	49.339	44.636	26.340	-87.180	-44.835	1.750
5700	4.968	49.427	44.719	26.837	-87.685	-44.080	1.690
5800	4.968	49.514	44.801	27.334	-88.191	-43.311	1.632
5900	4.968	49.598	44.881	27.831	-88.699	-42.529	1.575
6000	4.968	49.682	44.961	28.328	-89.208	-41.748	1.521

June 30, 1965

FLUORINE UNINEGATIVE ION (F^-)   (IDEAL GAS)   MOL. WT. = 18.99895

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 34.768 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -61.1 ± .5 kcal/mole

$\Delta H^\circ_{f\ 298.15}$ = -62.2 ± .5 kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1
0.00	1

Heat of Formation.

The heat of formation was calculated from the equation: $F(g) + e^- \rightarrow F^-(g)$ with the JANAF auxiliary value for F(g); using the measured electron affinity = 3.448 e.v. (79.511 kcal/mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963). Other calculated values for the electron affinity are: 3.37 reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 3.08 e.v. E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, 133, A1274 (1964); 3.50 e.v. B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Neon. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.481 kcal/mole.

Iron Monofluoride (FeF)

(Ideal Gas) Mol. Wt. = 74.8454

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.167	11.363	11.363	INFINITE
100	6.978	49.406	64.122	-1.472	11.608	8.849	-19.337
200	7.421	54.350	58.129	-.756	11.552	6.097	-6.662
298	7.950	57.417	57.417	.000	11.400	3.450	-2.529
300	7.959	57.467	57.418	.015	11.397	3.400	-2.477
400	8.306	59.808	57.735	.829	11.200	.764	-.417
500	8.518	61.686	58.343	1.672	10.964	-1.819	.795
600	8.652	63.252	59.035	2.531	10.677	-4.349	1.584
700	8.743	64.593	59.735	3.401	10.333	-6.827	2.131
800	8.807	65.765	60.417	4.278	9.909	-9.252	2.527
900	8.854	66.805	61.070	5.161	9.378	-11.616	2.821
1000	8.891	67.740	61.691	6.049	8.666	-13.913	3.041
1100	8.921	68.589	62.280	6.939	7.736	-16.122	3.203
1200	8.946	69.366	62.839	7.833	7.018	-18.264	3.326
1300	8.967	70.083	63.369	8.728	6.639	-20.355	3.422
1400	8.985	70.748	63.872	9.626	6.244	-22.416	3.499
1500	9.002	71.369	64.352	10.525	5.835	-24.450	3.562
1600	9.017	71.950	64.809	11.426	5.409	-26.455	3.613
1700	9.030	72.497	65.245	12.329	4.678	-28.427	3.654
1800	9.043	73.014	65.662	13.232	4.129	-30.360	3.686
1900	9.055	73.503	66.062	14.137	-.105	-32.075	3.689
2000	9.067	73.968	66.446	15.043	-.718	-33.743	3.687
2100	9.078	74.410	66.815	15.950	-1.336	-35.377	3.682
2200	9.088	74.833	67.170	16.859	-1.958	-36.984	3.674
2300	9.099	75.237	67.512	17.768	-2.584	-38.563	3.664
2400	9.108	75.624	67.842	18.678	-3.215	-40.114	3.653
2500	9.118	75.996	68.161	19.590	-3.850	-41.636	3.640
2600	9.128	76.354	68.469	20.502	-4.489	-43.137	3.626
2700	9.137	76.699	68.767	21.415	-5.133	-44.612	3.611
2800	9.146	77.031	69.057	22.330	-5.780	-46.061	3.595
2900	9.155	77.352	69.337	23.245	-6.432	-47.487	3.579
3000	9.164	77.663	69.609	24.161	-7.088	-48.893	3.562
3100	9.173	77.964	69.874	25.077	-7.749	-50.276	3.544
3200	9.182	78.255	70.132	25.995	-91.838	-50.192	3.428
3300	9.190	78.538	70.382	26.914	-92.044	-48.890	3.238
3400	9.199	78.812	70.626	27.833	-92.258	-47.577	3.058
3500	9.208	79.079	70.864	28.754	-92.480	-46.261	2.889
3600	9.216	79.338	71.095	29.675	-92.710	-44.933	2.728
3700	9.225	79.591	71.322	30.597	-92.948	-43.605	2.576
3800	9.233	79.837	71.543	31.520	-93.195	-42.270	2.431
3900	9.241	80.077	71.758	32.443	-93.451	-40.924	2.293
4000	9.250	80.311	71.969	33.368	-93.716	-39.576	2.162
4100	9.258	80.540	72.175	34.293	-93.989	-38.218	2.037
4200	9.266	80.763	72.377	35.220	-94.272	-36.856	1.918
4300	9.274	80.981	72.575	36.147	-94.564	-35.482	1.803
4400	9.283	81.194	72.768	37.074	-94.866	-34.107	1.694
4500	9.291	81.403	72.958	38.003	-95.178	-32.725	1.589
4600	9.299	81.607	73.144	38.933	-95.499	-31.329	1.488
4700	9.307	81.807	73.326	39.863	-95.832	-29.931	1.392
4800	9.315	82.003	73.505	40.794	-96.173	-28.522	1.299
4900	9.323	82.196	73.680	41.726	-96.526	-27.115	1.209
5000	9.332	82.384	73.852	42.659	-96.889	-25.694	1.123
5100	9.340	82.569	74.021	43.592	-97.263	-24.269	1.040
5200	9.348	82.750	74.188	44.527	-97.647	-22.830	.959
5300	9.356	82.928	74.351	45.462	-98.042	-21.386	.882
5400	9.364	83.103	74.511	46.398	-98.449	-19.938	.807
5500	9.372	83.275	74.669	47.335	-98.865	-18.480	.734
5600	9.380	83.444	74.824	48.272	-99.293	-17.015	.664
5700	9.388	83.610	74.977	49.210	-99.731	-15.542	.596
5800	9.396	83.774	75.127	50.150	-100.180	-14.061	.530
5900	9.404	83.934	75.275	51.090	-100.639	-12.573	.466
6000	9.412	84.093	75.421	52.030	-101.109	-11.079	.404

Sept. 30, 1965

IRON MONOFLUORIDE (FeF) (IDEAL GAS) MOL. WT. = 74.8454

Ground State Configuration $[^6\Sigma]$

$\Delta H^\circ_{f\ 0}$ = [11.4 ± 5.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [57.4] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [11.4 ± 5.0] kcal. mole

Electronic Levels and Quantum Weight

ϵ, cm.$^{-1}$	g_1
0	[6]

ω_e = [630.0] cm.$^{-1}$

$\omega_e x_e$ = [2.7] cm.$^{-1}$

σ = 1

B_e = [0.3670] cm.$^{-1}$

α_e = [0.0017] cm.$^{-1}$

r_e = [1.8] Å

Heat of Formation.

The Dissociation energy (D_o) of FeF(g) was estimated as 4.64 ± 0.22 e.v. or 107 ± 5 kcal. mole^{-1} by J. L. Margrave, "Optical Spectra and Molecular Parameters of Light Element Molecules", Progress Report No. 8, Jan. 1 to Mar 31, 1965, William Marsh Rice University, Houston, Texas. From the value of D° (Fe-F) the heat of formation ($\Delta H^\circ_{f\ 298.15}$) for FeF(g) was derived to be 11.4 ± 5.0 kcal. mole^{-1}.

Heat Capacity and Entropy.

The ground state configuration and bond distance (r_e) were estimated by comparison with those for FeCl(g). The value of B_e was calculated using the relationship $B_e = \frac{2.79889 \times 10^{-39}}{I}$ where I = moment of inertia of FeF(g), and α_e was estimated by comparison with those for AlF(g), AlCl(g) and FeCl(g). The value of ω_e was derived from the bond distance, reduced mass and number of valence electrons according to the method given by K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946), and the $\omega_e x_e$ was estimated from those for AlF(g), AlCl(g) and FeCl(g). The moment of inertia is 7.6259 X 10^{-39} g. cm.^{2}

Hydrogen Fluoride (HF)

(Ideal Gas) GFW = 20.00637

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.055	-65.128	-65.128	INFINITE
100	6.962	33.902	47.698	-1.380	-65.180	-65.316	142.747
200	6.962	38.728	42.145	-.683	-65.135	-65.474	71.547
298	6.964	41.508	41.508	.000	-65.140	-65.641	48.116
300	6.964	41.551	41.508	.013	-65.141	-65.644	47.822
400	6.967	43.555	41.781	.709	-65.176	-65.807	35.955
500	6.972	45.110	42.297	1.406	-65.232	-65.959	28.831
600	6.986	46.382	42.875	2.104	-65.300	-66.098	24.076
700	7.015	47.461	43.455	2.804	-65.377	-66.225	20.676
800	7.063	48.400	44.016	3.508	-65.459	-66.341	18.124
900	7.129	49.236	44.550	4.217	-65.544	-66.446	16.135
1000	7.210	49.991	45.057	4.934	-65.628	-66.542	14.543
1100	7.303	50.683	45.537	5.660	-65.712	-66.629	13.238
1200	7.402	51.322	45.993	6.395	-65.792	-66.709	12.149
1300	7.504	51.919	46.426	7.140	-65.870	-66.782	11.227
1400	7.606	52.479	46.839	7.896	-65.945	-66.849	10.436
1500	7.705	53.007	47.233	8.661	-66.018	-66.910	9.749
1600	7.800	53.507	47.609	9.437	-66.089	-66.969	9.147
1700	7.891	53.983	47.970	10.221	-66.157	-67.020	8.616
1800	7.977	54.436	48.317	11.015	-66.223	-67.071	8.143
1900	8.058	54.870	48.650	11.816	-66.287	-67.115	7.720
2000	8.133	55.285	48.972	12.626	-66.348	-67.157	7.339
2100	8.204	55.683	49.282	13.443	-66.408	-67.197	6.993
2200	8.270	56.067	49.582	14.267	-66.467	-67.233	6.679
2300	8.331	56.436	49.872	15.097	-66.524	-67.266	6.392
2400	8.389	56.791	50.153	15.933	-66.580	-67.296	6.128
2500	8.442	57.135	50.425	16.774	-66.637	-67.327	5.886
2600	8.493	57.467	50.690	17.621	-66.691	-67.352	5.661
2700	8.540	57.789	50.947	18.473	-66.746	-67.376	5.454
2800	8.584	58.100	51.197	19.329	-66.800	-67.400	5.261
2900	8.625	58.402	51.440	20.189	-66.853	-67.418	5.081
3000	8.664	58.695	51.677	21.054	-66.907	-67.439	4.913
3100	8.701	58.980	51.908	21.922	-66.960	-67.456	4.756
3200	8.736	59.256	52.133	22.794	-67.014	-67.471	4.608
3300	8.768	59.526	52.353	23.669	-67.067	-67.484	4.469
3400	8.800	59.788	52.568	24.548	-67.121	-67.496	4.339
3500	8.829	60.043	52.778	25.429	-67.176	-67.505	4.215
3600	8.857	60.293	52.983	26.313	-67.231	-67.513	4.099
3700	8.884	60.536	53.184	27.200	-67.287	-67.520	3.988
3800	8.910	60.773	53.381	28.090	-67.343	-67.525	3.884
3900	8.934	61.005	53.573	28.982	-67.402	-67.531	3.784
4000	8.958	61.231	53.762	29.877	-67.460	-67.532	3.690
4100	8.981	61.453	53.947	30.774	-67.520	-67.534	3.600
4200	9.002	61.669	54.128	31.673	-67.580	-67.533	3.514
4300	9.023	61.881	54.306	32.574	-67.642	-67.531	3.432
4400	9.043	62.089	54.480	33.478	-67.705	-67.529	3.354
4500	9.063	62.292	54.652	34.383	-67.769	-67.526	3.279
4600	9.082	62.492	54.820	35.290	-67.834	-67.518	3.208
4700	9.100	62.687	54.985	36.199	-67.901	-67.510	3.139
4800	9.118	62.879	55.148	37.110	-67.968	-67.500	3.073
4900	9.135	63.067	55.308	38.023	-68.037	-67.489	3.010
5000	9.152	63.252	55.465	38.937	-68.107	-67.479	2.950
5100	9.168	63.433	55.619	39.853	-68.178	-67.466	2.891
5200	9.184	63.612	55.771	40.771	-68.251	-67.450	2.835
5300	9.200	63.787	55.921	41.690	-68.324	-67.432	2.781
5400	9.215	63.959	56.068	42.611	-68.400	-67.419	2.729
5500	9.230	64.128	56.213	43.533	-68.476	-67.399	2.678
5600	9.244	64.295	56.356	44.457	-68.555	-67.379	2.630
5700	9.259	64.458	56.496	45.382	-68.634	-67.356	2.583
5800	9.272	64.619	56.635	46.308	-68.715	-67.333	2.537
5900	9.286	64.778	56.772	47.236	-68.797	-67.310	2.493
6000	9.300	64.934	56.907	48.166	-68.880	-67.285	2.451

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1968

HYDROGEN FLUORIDE (HF) (IDEAL GAS) GFW = 20.00637

Ground State Configuration $^1\Sigma^+$

ΔHf°_0 = -65.13 ± 0.2 kcal/mol

$S_{298.15}$ = 41.508 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -65.14 ± 0.2 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	1

ω_e = 4138.32 cm^{-1} $\omega_e x_e$ = 89.88^{-1} σ = 1

B_e = 20.9557 cm^{-1} α_e = 0.798^{-1} r_e = 0.9168 Å

Heat of Formation

The selected value is obtained from a least squares, simultaneous solution (1) for the heats of formation of HF(g), HF(50 H_2O) and five closely related fluorides. Other results, based on 23 selected observations relating the 7 variables, are as follows in kcal/mol: HF(50 H_2O), -76.78 ± 0.1; NaF(c), -137.52 ± 0.2; BF_3(g), -271.42 ± 0.4; CF_4(g), -223.04 ± 0.3; NF_3(g), -31.43 ± 0.3; and C_2F_4(polymer), -198.2 ± 0.7. The ± values are approximate estimates of the overall uncertainty including systematic error. Further details of the simultaneous solution are given in (1).

The values given above require the use of certain auxiliary data; e.g., the value for NaF(c) presumes ΔH°_σsoln = 0.23 ± 0.01 and $\Delta Hf^\circ_{298.15}[Na^+(\infty\ H_2O)]$ = -57.47 ± 0.04 kcal/mol. Use of these auxiliary data leads to $\Delta Hf^\circ_{298.15}$ = -79.82 kcal/mol for HF(∞ H_2O) and F^-(∞ H_2O); however, values for HF(n H_2O) should be obtained from that of HF(50 H_2O) by use of $[\phi_L(n) - \phi_L(50)]$ taken from the tables of Parker (2). This procedure should be reliable except in dilute solutions (n > 1000) where the equilibria $HF \rightarrow H^+ + F^-$ and $HF + F^- \rightarrow HF_2^-$ yield an overall ΔH of about 3 kcal/mol. Parker (2) used thermodynamic data for these equilibria in order to calculate ϕ_L for the dilute solutions, but recent data (3-5) suggest that minor changes in the calculations may be desirable. For this reason the simultaneous solution includes $\phi_L(50)$ = 3184 ± 300 cal/mol (2) as an "observation" rather than as a fixed value. The result of the simultaneous solution is smaller by only 150 cal/mol, suggesting that $\phi_L(50)$ does not contain a major inconsistency.

Heat Capacity and Entropy

The ground state configuration is that deduced from UV spectra by Johns and Barrow (6). The excited state near 85000 cm^{-1} is omitted since its contribution to the thermodynamic functions in negligible. High-resolution studies of the vibration-rotation spectrum were reported by Mann et al. (7) and subsequently confirmed by others (8, 9). The analysis of Webb and Rao (9) is adopted for this table.

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Hypofluorous Acid (HFO)

(Ideal Gas) Mol. Wt. = 36.00577

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.391	- 30.287	- 30.287	INFINITE
100	7.949	45.187	61.148	- 1.596	- 30.575	- 29.764	65.045
200	8.009	50.705	54.704	- .800	- 30.770	- 28.882	31.559
298	8.335	53.954	53.954	.000	- 31.000	- 27.907	20.455
300	8.344	54.006	53.954	.015	- 31.005	- 27.888	20.315
400	8.876	56.477	54.288	.876	- 31.232	- 26.814	14.650
500	9.421	58.517	54.935	1.791	- 31.435	- 25.685	11.227
600	9.904	60.278	55.682	2.758	- 31.612	- 24.518	8.930
700	10.315	61.837	56.452	3.769	- 31.766	- 23.323	7.281
800	10.668	63.238	57.214	4.819	- 31.901	- 22.109	6.040
900	10.975	64.512	57.955	5.901	- 32.020	- 20.876	5.069
1000	11.248	65.683	58.670	7.013	- 32.123	- 19.633	4.291
1100	11.490	66.766	59.358	8.150	- 32.215	- 18.379	3.651
1200	11.708	67.776	60.018	9.310	- 32.294	- 17.118	3.117
1300	11.902	68.721	60.651	10.490	- 32.366	- 15.850	2.665
1400	12.076	69.609	61.260	11.690	- 32.429	- 14.577	2.275
1500	12.232	70.448	61.844	12.905	- 32.487	- 13.299	1.938
1600	12.372	71.242	62.407	14.135	- 32.542	- 12.020	1.642
1700	12.497	71.996	62.949	15.379	- 32.592	- 10.734	1.380
1800	12.610	72.713	63.472	16.635	- 32.640	- 9.447	1.147
1900	12.711	73.398	63.976	17.901	- 32.687	- 8.158	.938
2000	12.801	74.052	64.464	19.176	- 32.732	- 6.865	.750
2100	12.883	74.679	64.936	20.461	- 32.777	- 5.572	.580
2200	12.956	75.280	65.392	21.753	- 32.824	- 4.276	.425
2300	13.023	75.857	65.835	23.052	- 32.870	- 2.976	.283
2400	13.083	76.413	66.264	24.357	- 32.918	- 1.675	.153
2500	13.138	76.948	66.681	25.668	- 32.969	- .374	.033
2600	13.188	77.464	67.086	26.984	- 33.020	.933	- .078
2700	13.233	77.963	67.479	28.306	- 33.074	2.239	- .181
2800	13.275	78.445	67.862	29.631	- 33.130	3.547	- .277
2900	13.313	78.911	68.235	30.960	- 33.189	4.862	- .366
3000	13.347	79.363	68.599	32.293	- 33.251	6.172	- .450
3100	13.379	79.801	68.953	33.630	- 33.314	7.488	- .528
3200	13.409	80.227	69.299	34.969	- 33.381	8.803	- .601
3300	13.436	80.640	69.636	36.311	- 33.451	10.123	- .670
3400	13.461	81.041	69.966	37.656	- 33.523	11.445	- .736
3500	13.484	81.432	70.288	39.004	- 33.599	12.769	- .797
3600	13.506	81.812	70.603	40.353	- 33.678	14.096	- .856
3700	13.525	82.182	70.911	41.705	- 33.761	15.425	- .911
3800	13.544	82.543	71.212	43.058	- 33.846	16.757	- .964
3900	13.561	82.895	71.507	44.413	- 33.935	18.087	- 1.014
4000	13.577	83.239	71.796	45.770	- 34.027	19.421	- 1.061
4100	13.592	83.574	72.079	47.129	- 34.123	20.760	- 1.107
4200	13.606	83.902	72.357	48.489	- 34.221	22.099	- 1.150
4300	13.620	84.222	72.629	49.850	- 34.322	23.444	- 1.191
4400	13.632	84.535	72.896	51.213	- 34.428	24.787	- 1.231
4500	13.644	84.842	73.158	52.576	- 34.536	26.131	- 1.269
4600	13.655	85.142	73.416	53.941	- 34.647	27.483	- 1.306
4700	13.665	85.436	73.668	55.307	- 34.762	28.834	- 1.341
4800	13.674	85.723	73.916	56.674	- 34.878	30.193	- 1.375
4900	13.684	86.006	74.160	58.042	- 34.998	31.544	- 1.407
5000	13.692	86.282	74.400	59.411	- 35.122	32.903	- 1.438
5100	13.700	86.553	74.635	60.781	- 35.248	34.268	- 1.468
5200	13.708	86.819	74.867	62.151	- 35.376	35.632	- 1.498
5300	13.715	87.081	75.095	63.522	- 35.508	36.999	- 1.526
5400	13.722	87.337	75.320	64.894	- 35.643	38.364	- 1.553
5500	13.729	87.589	75.540	66.267	- 35.779	39.738	- 1.579
5600	13.735	87.836	75.758	67.640	- 35.920	41.113	- 1.604
5700	13.741	88.079	75.972	69.014	- 36.063	42.492	- 1.629
5800	13.746	88.318	76.183	70.388	- 36.208	43.873	- 1.653
5900	13.752	88.553	76.390	71.763	- 36.356	45.253	- 1.676
6000	13.757	88.785	76.595	73.138	- 36.507	46.632	- 1.698

Dec. 31, 1960; Sept. 30, 1965

HYPOFLUOROUS ACID (HFO) (IDEAL GAS) MOL. WT. = 36.00577

Point Group C_s

$S^\circ_{298.15}$ = [53.954] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-30 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-31 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[1500] (1)
[1065] (1)
[3645] (1)

Bond Distance: H-O = [0.98] Å O-F = [1.41] Å

Bond Angle: H-O-F = [104]° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.2826 X 10^{-117}] g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for HFO(g) was calculated based on an estimated value for the heat of atomization i.e. ΔH°_r = 161.6 kcal. mole^{-1} for the reaction HFO(g) = H(g) + F(g) + O(g). The ΔH°_r value was assumed to be the sum of the F-O and H-O bond energies which were obtained from the corresponding bond energies in $F_2O(g)$ and $H_2O(g)$ molecules.

Heat Capacity and Entropy.

The H-O and F-O bond distances were assumed to be the same as those in the $H_2O(g)$ and $F_2O(g)$ molecules. The vibrational frequencies and H-O-F bond angle were estimated by comparison with the corresponding values for $H_2O(g)$, $F_2O(g)$ and $Cl_2O(g)$. The three principal moments of inertia are I_A = 0.1332 X 10^{-39}, I_B = 3.0366 X 10^{-39} and I_C = 3.1699 X 10^{-39} g. cm.^{2}

Fluorosilane (H_3SiF)
(Ideal Gas) Mol. Wt. = 50.114 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.617	-102.770	-102.770	INFINITE
100	7.964	47.314	65.538	-1.822	-103.525	-102.473	223.943
200	8.971	53.030	57.992	-.992	-104.225	-101.170	110.548
298	11.333	57.035	57.035	.000	-105.000	-99.505	72.936
300	11.379	57.105	57.035	.021	-105.014	-99.471	72.461
400	13.730	60.711	57.511	1.280	-105.691	-97.517	53.278
500	15.651	63.988	58.484	2.752	-106.219	-95.411	41.702
600	17.213	66.985	59.655	4.398	-106.612	-93.210	33.950
700	18.500	69.738	60.901	6.186	-106.893	-90.952	28.395
800	19.563	72.280	62.167	8.091	-107.082	-88.661	24.220
900	20.444	74.637	63.423	10.092	-107.201	-86.350	20.968
1000	21.173	76.829	64.655	12.174	-107.263	-84.030	18.364
1100	21.779	78.877	65.856	14.323	-107.282	-81.706	16.233
1200	22.285	80.794	67.022	16.527	-107.265	-79.380	14.456
1300	22.708	82.595	68.151	18.777	-107.224	-77.059	12.954
1400	23.065	84.291	69.244	21.066	-107.166	-74.739	11.667
1500	23.367	85.893	70.301	23.388	-107.097	-72.425	10.552
1600	23.625	87.410	71.323	25.738	-107.023	-70.118	9.577
1700	23.846	88.849	72.312	28.112	-119.046	-67.703	8.703
1800	24.037	90.217	73.269	30.506	-118.922	-64.689	7.854
1900	24.203	91.522	74.196	32.919	-118.793	-61.679	7.094
2000	24.347	92.767	75.094	35.346	-118.665	-58.675	6.411
2100	24.474	93.958	75.964	37.788	-118.537	-55.680	5.794
2200	24.586	95.099	76.808	40.241	-118.412	-52.690	5.234
2300	24.684	96.194	77.627	42.704	-118.287	-49.704	4.723
2400	24.772	97.247	78.423	45.177	-118.167	-46.725	4.255
2500	24.850	98.259	79.196	47.658	-118.052	-43.753	3.825
2600	24.920	99.235	79.948	50.147	-117.938	-40.781	3.428
2700	24.983	100.177	80.680	52.642	-117.828	-37.817	3.061
2800	25.040	101.087	81.393	55.143	-117.723	-34.858	2.721
2900	25.092	101.966	82.087	57.650	-117.621	-31.896	2.404
3000	25.138	102.818	82.764	60.162	-117.525	-28.945	2.109
3100	25.181	103.643	83.424	62.678	-117.431	-25.995	1.833
3200	25.219	104.443	84.069	65.198	-117.344	-23.044	1.574
3300	25.255	105.219	84.698	67.721	-117.261	-20.096	1.331
3400	25.287	105.974	85.313	70.248	-117.182	-17.155	1.103
3500	25.317	106.707	85.913	72.779	-117.110	-14.213	.887
3600	25.344	107.421	86.501	75.312	-212.017	-10.802	.656
3700	25.370	108.116	87.076	77.847	-211.895	-5.214	.308
3800	25.393	108.793	87.638	80.386	-211.777	.371	-.021
3900	25.415	109.452	88.189	82.926	-211.667	5.949	-.333
4000	25.435	110.096	88.729	85.469	-211.561	11.530	-.630
4100	25.454	110.724	89.258	88.013	-211.461	17.104	-.912
4200	25.472	111.338	89.776	90.559	-211.368	22.683	-1.180
4300	25.488	111.938	90.285	93.107	-211.280	28.249	-1.436
4400	25.503	112.524	90.784	95.657	-211.198	33.818	-1.680
4500	25.517	113.097	91.273	98.208	-211.123	39.381	-1.912
4600	25.531	113.658	91.754	100.760	-211.052	44.954	-2.136
4700	25.543	114.207	92.225	103.314	-210.987	50.518	-2.349
4800	25.555	114.745	92.689	105.869	-210.927	56.084	-2.553
4900	25.566	115.272	93.145	108.425	-210.873	61.644	-2.749
5000	25.577	115.789	93.592	110.982	-210.825	67.204	-2.937
5100	25.587	116.295	94.033	113.540	-210.782	72.766	-3.118
5200	25.596	116.792	94.465	116.100	-210.745	78.324	-3.292
5300	25.605	117.280	94.891	118.660	-210.713	83.888	-3.459
5400	25.613	117.759	95.310	121.221	-210.687	89.439	-3.620
5500	25.621	118.229	95.723	123.782	-210.665	94.999	-3.775
5600	25.628	118.690	96.129	126.345	-210.651	100.553	-3.924
5700	25.635	119.144	96.529	128.908	-210.641	106.116	-4.069
5800	25.642	119.590	96.922	131.472	-210.636	111.667	-4.208
5900	25.649	120.028	97.310	134.036	-210.638	117.229	-4.342
6000	25.655	120.459	97.693	136.601	-210.645	122.778	-4.472

December 31, 1960.

Fluorosilane (H_3SiF) (Ideal Gas)

Mol. Wt. = 50.114

ΔH_f° 298.15 = [-105 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = 57.04 ± 2 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ωcm.$^{-1}$
2206 (1)
990 (1)
872 (1)
2196 (2)
943.4(2)
728.1(2)

Moments of Inertia: $I_A = 0.9784 \times 10^{-39}$ g. cm.^{2} $\sigma = 3$
$I_B = 5.8578 \times 10^{-39}$ g. cm.^{2} $I_C = 5.8578 \times 10^{-39}$ g. cm.^{2}

Heat of Formation. ΔH_f° 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in Henderson and Scheffee, op. cit. Moments of inertia were calculated using the constants found in C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

Mercurous Fluoride (HgF)

(Ideal Gas) Mol. Wt. = 219.61

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.226	1.762	1.762	INFINITE
100	7.051	51.035	66.329	-1.529	1.703	-.476	1.041
200	7.765	56.131	60.081	-.790	1.475	-2.567	2.805
298	8.282	59.338	59.338	.000	.700	-4.352	3.190
300	8.289	59.389	59.338	.015	.696	-4.383	3.193
400	8.570	61.816	59.667	.860	.495	-6.044	3.302
500	8.731	63.747	60.297	1.725	.305	-7.658	3.347
600	8.834	65.349	61.009	2.604	.119	-9.233	3.363
700	8.905	66.716	61.729	3.491	-14.095	-9.206	2.874
800	8.956	67.909	62.429	4.384	-14.132	-8.505	2.323
900	9.001	68.967	63.097	5.282	-14.168	-7.798	1.894
1000	9.036	69.917	63.733	6.184	-14.205	-7.090	1.549
1100	9.067	70.780	64.335	7.090	-14.243	-6.376	1.267
1200	9.095	71.570	64.905	7.998	-14.280	-5.659	1.031
1300	9.121	72.299	65.446	8.909	-14.318	-4.939	.830
1400	9.145	72.976	65.960	9.822	-14.354	-4.216	.658
1500	9.166	73.607	66.449	10.738	-14.391	-3.490	.508
1600	9.189	74.200	66.915	11.655	-14.428	-2.763	.377
1700	9.210	74.758	67.360	12.575	-14.464	-2.032	.261
1800	9.231	75.285	67.786	13.497	-14.500	-1.302	.158
1900	9.251	75.784	68.194	14.421	-14.534	-.566	.065
2000	9.270	76.259	68.585	15.348	-14.568	.171	-.019
2100	9.290	76.712	68.962	16.276	-14.602	.907	-.094
2200	9.309	77.145	69.324	17.205	-14.636	1.645	-.163
2300	9.328	77.559	69.673	18.137	-14.668	2.387	-.227
2400	9.346	77.956	70.010	19.071	-14.700	3.131	-.285
2500	9.365	78.338	70.335	20.006	-14.732	3.872	-.338
2600	9.383	78.706	70.650	20.944	-14.763	4.617	-.388
2700	9.401	79.060	70.955	21.883	-14.793	5.365	-.434
2800	9.420	79.402	71.251	22.824	-14.822	6.109	-.477
2900	9.438	79.733	71.538	23.767	-14.850	6.861	-.517
3000	9.456	80.054	71.816	24.712	-14.879	7.607	-.554
3100	9.474	80.364	72.087	25.658	-14.907	8.357	-.589
3200	9.492	80.665	72.350	26.606	-14.934	9.109	-.622
3300	9.510	80.957	72.607	27.557	-14.961	9.861	-.653
3400	9.527	81.241	72.857	28.508	-14.985	10.614	-.682
3500	9.545	81.518	73.100	29.462	-15.011	11.368	-.710
3600	9.563	81.787	73.338	30.417	-15.035	12.122	-.736
3700	9.581	82.049	73.570	31.375	-15.058	12.876	-.760
3800	9.598	82.305	73.796	32.334	-15.081	13.633	-.784
3900	9.616	82.555	74.018	33.294	-15.104	14.387	-.806
4000	9.634	82.798	74.234	34.257	-15.126	15.145	-.827
4100	9.651	83.036	74.446	35.221	-15.147	15.899	-.847
4200	9.669	83.269	74.653	36.187	-15.167	16.657	-.867
4300	9.687	83.497	74.856	37.155	-15.187	17.416	-.885
4400	9.704	83.720	75.055	38.124	-15.206	18.173	-.903
4500	9.722	83.938	75.250	39.096	-15.224	18.933	-.919
4600	9.739	84.152	75.441	40.069	-15.243	19.690	-.935
4700	9.757	84.362	75.629	41.044	-15.261	20.454	-.951
4800	9.775	84.567	75.813	42.020	-15.278	21.211	-.966
4900	9.792	84.769	75.994	42.999	-15.294	21.973	-.980
5000	9.810	84.967	76.171	43.979	-15.310	22.735	-.994
5100	9.827	85.161	76.346	44.960	-15.327	23.496	-1.007
5200	9.845	85.352	76.517	45.944	-15.343	24.259	-1.020
5300	9.862	85.540	76.685	46.929	-15.359	25.019	-1.032
5400	9.880	85.725	76.851	47.917	-15.374	25.777	-1.043
5500	9.897	85.906	77.014	48.905	-15.389	26.540	-1.055
5600	9.915	86.084	77.174	49.896	-15.405	27.306	-1.066
5700	9.932	86.260	77.332	50.888	-15.420	28.070	-1.076
5800	9.950	86.433	77.488	51.882	-15.436	28.830	-1.086
5900	9.967	86.603	77.641	52.878	-15.453	29.589	-1.096
6000	9.985	86.771	77.792	53.876	-15.469	30.354	-1.106

December 31, 1961

MERCUROUS FLUORIDE (HgF) (IDEAL GAS) MOL. WT. = 219.61

Ground State Configuration $^2\Sigma$

ΔH_f° 298.15 = 0.7 ± 12.0 kcal mole^{-1}

$S_{298.15}^\circ$ = 59.338 cal deg^{-1} mole^{-1}

Electronic Levels and Multiplicities

ϵ, cm^{-1}	g_i
0	2

ω_e = 490.8 cm^{-1} $\omega_e x_e$ = 4.05 cm^{-1} σ = 1

B_e = [0.2732] cm^{-1} α_e = [0.0026] cm^{-1} r_e = [1.89] Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 32 ± 12 kcals for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg (loc. cit.). Bond length estimated by comparison of the mercurous halides with thalium and cesium halides.

Iodine Monofluoride (IF)

(Ideal Gas) Mol. Wt. = 145.9028

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.176	-22.192	-22.192	INFINITE
100	6.983	48.396	63.204	-1.481	-22.209	-24.285	53.071
200	7.473	53.359	57.169	-.762	-22.429	-26.277	28.713
298	8.021	56.451	56.451	.000	-22.648	-28.119	20.611
300	8.030	56.501	56.451	.015	-22.652	-28.153	20.508
400	8.384	58.864	56.771	.837	-24.801	-29.885	16.328
500	8.601	60.760	57.385	1.687	-30.116	-30.650	13.397
600	8.743	62.341	58.083	2.555	-30.113	-30.757	11.203
700	8.841	63.696	58.791	3.434	-30.108	-30.865	9.636
800	8.915	64.882	59.479	4.322	-30.104	-30.973	8.461
900	8.973	65.936	60.139	5.217	-30.099	-31.083	7.548
1000	9.020	66.883	60.767	6.116	-30.095	-31.192	6.817
1100	9.061	67.745	61.363	7.020	-30.090	-31.302	6.219
1200	9.097	68.535	61.928	7.928	-30.085	-31.412	5.721
1300	9.130	69.265	62.465	8.840	-30.080	-31.523	5.299
1400	9.160	69.942	62.975	9.754	-30.075	-31.634	4.938
1500	9.188	70.575	63.461	10.672	-30.069	-31.745	4.625
1600	9.215	71.169	63.924	11.592	-30.064	-31.857	4.351
1700	9.241	71.729	64.367	12.515	-30.058	-31.970	4.110
1800	9.266	72.258	64.791	13.440	-30.052	-32.084	3.895
1900	9.290	72.759	65.197	14.368	-30.046	-32.195	3.703
2000	9.313	73.236	65.587	15.298	-30.039	-32.309	3.530
2100	9.336	73.691	65.962	16.231	-30.032	-32.423	3.374
2200	9.359	74.126	66.324	17.165	-30.025	-32.538	3.232
2300	9.381	74.543	66.672	18.102	-30.018	-32.652	3.103
2400	9.403	74.942	67.008	19.042	-30.010	-32.765	2.984
2500	9.425	75.327	67.333	19.983	-30.003	-32.883	2.874
2600	9.447	75.697	67.648	20.927	-29.994	-32.997	2.774
2700	9.468	76.054	67.953	21.872	-29.986	-33.113	2.680
2800	9.490	76.398	68.248	22.820	-29.977	-33.227	2.593
2900	9.511	76.732	68.535	23.770	-29.968	-33.344	2.513
3000	9.532	77.055	68.814	24.722	-29.960	-33.464	2.438
3100	9.553	77.367	69.085	25.677	-29.950	-33.577	2.367
3200	9.574	77.671	69.348	26.633	-29.940	-33.695	2.301
3300	9.595	77.966	69.605	27.591	-29.930	-33.812	2.239
3400	9.616	78.253	69.855	28.552	-29.920	-33.932	2.181
3500	9.636	78.532	70.099	29.515	-29.909	-34.048	2.126
3600	9.657	78.804	70.337	30.479	-29.898	-34.167	2.074
3700	9.678	79.068	70.569	31.446	-29.887	-34.284	2.025
3800	9.698	79.327	70.797	32.415	-29.875	-34.404	1.979
3900	9.719	79.579	71.019	33.386	-29.863	-34.524	1.935
4000	9.739	79.825	71.236	34.359	-29.851	-34.643	1.893
4100	9.760	80.066	71.448	35.333	-29.839	-34.763	1.853
4200	9.780	80.301	71.656	36.311	-29.826	-34.881	1.815
4300	9.801	80.532	71.860	37.290	-29.812	-35.005	1.779
4400	9.821	80.757	72.059	38.271	-29.800	-35.124	1.745
4500	9.842	80.978	72.255	39.254	-29.786	-35.245	1.712
4600	9.862	81.195	72.447	40.239	-29.772	-35.368	1.680
4700	9.882	81.407	72.636	41.226	-29.758	-35.489	1.650
4800	9.903	81.615	72.821	42.215	-29.743	-35.609	1.621
4900	9.923	81.820	73.002	43.207	-29.728	-35.733	1.594
5000	9.943	82.021	73.180	44.200	-29.713	-35.858	1.567
5100	9.964	82.218	73.356	45.195	-29.698	-35.983	1.542
5200	9.984	82.411	73.528	46.193	-29.682	-36.102	1.517
5300	10.004	82.602	73.697	47.192	-29.666	-36.227	1.494
5400	10.025	82.789	73.864	48.194	-29.650	-36.351	1.471
5500	10.045	82.973	74.028	49.197	-29.633	-36.475	1.449
5600	10.065	83.154	74.189	50.203	-29.616	-36.600	1.428
5700	10.085	83.332	74.348	51.210	-29.599	-36.721	1.408
5800	10.106	83.508	74.505	52.220	-29.581	-36.849	1.388
5900	10.126	83.681	74.659	53.231	-29.563	-36.977	1.370
6000	10.146	83.851	74.811	54.245	-29.545	-37.099	1.351

Mar. 31, 1962; Dec. 31, 1965

IODINE MONOFLUORIDE (IF) (IDEAL GAS) MOL. WT. = 145.9028

Ground State Configuration $[^1\Sigma^+]$

$S^\circ_{298.15}$ = 56.451 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -22.192 ± 0.9 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -22.648 ± 0.9 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 612 cm.$^{-1}$

B_e = 0.2799 cm.$^{-1}$

$\omega_e x_e$ = 4 cm.$^{-1}$

α_e = 0.00763 cm.$^{-1}$

r_e = 1.906 Å

σ = 1

Heat of Formation.

R. A. Durie and A. G. Gaydon, J. Phys. Chem. 56, 316 (1952), have obtained the dissociation limit (from the spectra) of IF as 23570 cm.$^{-1}$ The first excited states of F and I are 404 and 7598 cm.$^{-1}$ above the ground state respectively. There are two sets of dissociation products possible: $I(^2P_{1/2}) + F(^2P_{3/2})$ or $I(^2P_{3/2}) + F(^2P_{1/2})$. When corrected to the normal atoms, the observed limit gives $D_0(IF(g))$ 2.87 ± 0.04 e.v. or 66.18 ± 0.9 kcal. mole^{-1} and 1.98 ± 0.04 e.v. or 45.66 ± 0.9 kcal. mole^{-1} for dissociation energy respectively. Durie and Gaydon, loc. cit., favored the lower value. However L. Slutsky and S. H. Bauer, J. Am. Chem. Soc. 76, 270 (1954) have pointed out a numerical error in their calculations, which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives $\Delta H^\circ_{f\ 298.15}$ = -22.648 ± 0.9 kcal. mole^{-1} for the reaction 1/2 $I_2(c)$ + 1/2 $F_2(g)$ = IF(g).

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards 55, 147 (1955) except r_e = 1.906 Å was obtained from L. G. Cole and G. W. Elverun Jr., J. Chem. Phys. 20, 1543 (1952) and ground state configuration was estimated by comparison with that for IBr and ICl from G. Herzberg,"Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

Potassium Fluoride (KF)

(Crystal) GFW = 58.1004

T, °K	gibbs/mol Cp°	S°	-(G°-H°298)/T	kcal/mol H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.390	-135.542	-135.542	INFINITE
100	7.554	4.899	25.579	-2.068	-135.982	-133.586	291.951
200	10.800	11.391	16.956	-1.113	-135.997	-131.163	143.329
298	11.707	15.905	15.905	.000	-135.900	-128.811	94.421
300	11.717	15.977	15.905	.022	-135.898	-128.767	93.807
400	12.200	19.418	16.371	1.219	-136.400	-126.293	69.003
500	12.600	22.185	17.266	2.459	-136.306	-123.777	54.103
600	12.970	24.515	18.285	3.738	-136.169	-121.283	44.177
700	13.350	26.543	19.323	5.054	-135.995	-118.815	37.096
800	13.720	28.349	20.340	6.407	-135.787	-116.375	31.792
900	14.120	29.988	21.322	7.799	-135.545	-113.963	27.674
1000	14.620	31.500	22.265	9.235	-135.273	-111.579	24.386
1100	15.260	32.923	23.170	10.727	-153.863	-108.201	21.498
1200	15.960	34.282	24.040	12.291	-153.245	-104.076	18.955
1300	16.400	35.578	24.878	13.910	-152.575	-100.006	16.812
1400	16.680	36.804	25.687	15.565	-151.870	-95.987	14.984
1500	16.850	37.961	26.467	17.242	-151.146	-92.021	13.407
1600	16.950	39.052	27.220	18.932	-150.410	-88.103	12.034
1700	17.000	40.082	27.946	20.630	-149.669	-84.232	10.829
1800	17.000	41.053	28.648	22.330	-148.928	-80.405	9.762
1900	17.000	41.972	29.325	24.030	-148.190	-76.618	8.813
2000	17.000	42.844	29.979	25.730	-147.453	-72.869	7.963

Dec. 31, 1961; Dec. 31, 1963; June 30, 1969

POTASSIUM FLUORIDE (KF) (CRYSTAL) GFW = 58.1004

ΔHf°_0 = -135.5 ± 0.1 kcal/mol

$S^\circ_{298.15}$ = 15.905 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -135.9 ± 0.1 kcal/mol

Tm = 1131°K

ΔHm° = 6.50 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 57.8 kcal/mol (to monomer)

Heat of Formation

The heat of solution of KF(c) in water has been measured by several investigators. Their results have been converted to ΔH°_∞ by Parker (5) and listed in the table below. Using $\Delta H^\circ_\infty = -4.24$, $\Delta Hf^\circ_{298}(K^+, \infty H_2O) = -60.32$ (6), and $\Delta Hf^\circ_{298}(F^-, \infty H_2O) = -79.82$ kcal/mol (7), we obtain $\Delta Hf^\circ_{298} = -135.9 \pm 0.1$ kcal/mol which is adopted.

Investigator	Temperature, °K	Concentration, molality	No. of Determinations	ΔH°_∞, kcal/mol
1. Guntz (1884)	291	0.28	1	-3.95
2. Forcrand (1911)	288	0.50	1	-4.54
3. Lange and Eichler (1927)	298	3.16 - 0.21	8	-4.24±0.4
4. Lange and Martin (1937)	298	0.31	1	-4.01

Heat Capacity and Entropy

The low temperature heat capacities, 16-323°K, were measured by Westrum and Pitzer (8). The high temperature enthalpies, 298-530°K and 291-1187°K, were determined by Westrum and Pitzer (8), and Lyashenko (9), respectively. However, the high temperature Cp values derived from both sets appear to be inconsistent with the low temperature Cp values. The heat capacities derived from the enthalpy data of Westrum and Pitzer are too high (3% at 530°K and less at lower temperatures) to be joined smoothly with their low temperature Cp's. The adopted enthalpy at 530°K is about 1.4% lower than the reported value. The heat capacity derived from the enthalpy data of Lyashenko is 2.5% lower than the adopted one at 900°K. The differences are smaller at lower temperatures. At 900°K, the adopted enthalpy is 1.3% higher than the reported value. The adopted heat capacities in the temperature range, 323-2000°K, are estimated by graphical comparison with other alkali fluorides and chlorides, and joined smoothly with the low temperature data at 298°K.

S°_{298} is derived based on the adopted low temperature heat capacities.

Melting Data

See the KF(ℓ) table.

Heat of Sublimation

The value of ΔHs°_{298} is obtained as the difference between ΔHf°_{298} for KF(c) and KF(g).

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Potassium Fluoride (KF)
(Liquid) GFW = 58.1004

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.200	16.167	16.167	.000	- 132.519	- 125.508	92.000
300	17.200	16.273	16.167	.032	- 132.507	- 125.465	91.401
400	17.200	21.222	16.842	1.752	- 132.486	- 123.101	67.259
500	17.200	25.060	18.116	3.472	- 131.913	- 120.821	52.811
600	17.200	28.196	19.542	5.192	- 131.335	- 118.656	43.221
700	17.200	30.847	20.973	6.912	- 130.756	- 116.589	36.401
800	17.200	33.144	22.354	8.632	- 130.181	- 114.605	31.309
900	17.200	35.170	23.668	10.352	- 129.611	- 112.692	27.365
1000	17.200	36.982	24.910	12.072	- 129.055	- 110.843	24.225
1100	17.200	38.621	26.083	13.792	- 147.418	- 108.024	21.462
1200	17.200	40.118	27.191	15.512	- 146.643	- 104.476	19.028
1300	17.200	41.494	28.239	17.232	- 145.872	- 100.994	16.979
1400	17.200	42.769	29.232	18.952	- 145.102	- 97.570	15.231
1500	17.200	43.956	30.175	20.672	- 144.335	- 94.201	13.725
1600	17.200	45.066	31.071	22.392	- 143.569	- 90.884	12.414
1700	17.200	46.109	31.925	24.112	- 142.806	- 87.616	11.264
1800	17.200	47.092	32.741	25.832	- 142.045	- 84.391	10.247
1900	17.200	48.022	33.521	27.552	- 141.287	- 81.209	9.341
2000	17.200	48.904	34.268	29.272	- 140.531	- 78.065	8.531
2100	17.200	49.743	34.985	30.992	- 139.778	- 74.961	7.801
2200	17.200	50.543	35.674	32.712	- 139.029	- 71.892	7.142
2300	17.200	51.308	36.337	34.432	- 138.284	- 68.858	6.543
2400	17.200	52.040	36.977	36.152	- 137.543	- 65.855	5.997
2500	17.200	52.742	37.593	37.872	- 136.808	- 62.884	5.497
2600	17.200	53.417	38.189	39.592	- 136.078	- 59.939	5.038
2700	17.200	54.066	38.765	41.312	- 135.354	- 57.026	4.616
2800	17.200	54.691	39.323	43.032	- 134.639	- 54.139	4.226
2900	17.200	55.295	39.863	44.752	- 133.931	- 51.274	3.864
3000	17.200	55.878	40.387	46.472	- 133.231	- 48.439	3.529

Dec. 31, 1961; Dec. 31, 1963; June 30, 1969

POTASSIUM FLUORIDE (KF) (LIQUID) GFW = 58.1004

$S^\circ_{298.15}$ = 16.167 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -132.519 kcal/mol

Tm = 1131°K ΔHm° = 6.50 kcal/mol

Tb = 1790°K ΔHv°(to mixture) = 33.9 kcal/mol of liquid

Heat of Formation

The $\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1131} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those of the alkali fluorides and chlorides, and is assumed to be constant in the temperature range, 298-3000°K. The Cp value, 16 gibbs/mol, derived from the enthalpy data of Lyashenko (12) appears low and is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm has been reported as 1119 (1, 2), 1129 (3, 4), 1131 (5, 6), and 1153°K (7). The value 1131°K is adopted. Kelley (8) evaluated the following freezing-point data of binary systems: KF-AlF$_3$ (9), KF-K$_2$SO$_4$ (10), KF-KCl (11), KF-K$_2$CO$_3$ (13), and KF-K$_3$PO$_4$ (14), and derived the values of ΔHm° (in kcal/mol) as 5.5, 5.55, 6.51, 7.1, and 7.1 respectively. The best value is recommended as 6.50 kcal/mol. Other reported ΔHm° values are 6.70 (7) and 6.75 ± 0.1 kcal/mol (12). The value of heat of melting is tentatively adopted as 6.50 kcal/mol.

Vaporization Data

The boiling point (Tb) is calculated to be the temperature at which the partial pressures of KF(g) and $K_2F_2(g)$ equal one atmosphere. The composition of the gaseous mixture in equilibrium with KF(ℓ) at Tb is calculated as K_2F_2 21.1% and KF 78.9%. The heat required to vaporize one mole of liquid at Tb is evaluated to be 33.9 kcal.

The experimental values for the boiling point are 1778°K (1) and 1771°K (15).

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Potassium Fluoride (KF)

(Ideal Gas) GFW = 58.1004

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.259	-77.611	-77.611	INFINITE
100	7.131	45.662	61.273	-1.561	-77.675	-79.355	173.430
200	7.949	50.862	54.892	-.806	-77.890	-80.951	88.459
298	8.420	54.135	54.135	.000	-78.100	-82.409	60.408
300	8.426	54.187	54.135	.016	-78.104	-82.436	60.055
400	8.662	56.647	54.469	.871	-78.948	-83.732	45.749
500	8.794	58.595	55.106	1.745	-79.221	-84.897	37.108
600	8.877	60.206	55.825	2.628	-79.479	-86.007	31.328
700	8.935	61.579	56.552	3.519	-79.730	-87.075	27.186
800	8.979	62.775	57.256	4.415	-79.979	-88.108	24.070
900	9.015	63.835	57.930	5.315	-80.229	-89.109	21.639
1000	9.045	64.786	58.569	6.218	-80.490	-90.083	19.688
1100	9.072	65.650	59.174	7.124	-99.667	-90.005	17.882
1200	9.096	66.440	59.747	8.032	-99.704	-89.124	16.232
1300	9.119	67.169	60.290	8.943	-99.742	-88.241	14.835
1400	9.140	67.846	60.806	9.856	-99.779	-87.354	13.637
1500	9.161	68.477	61.296	10.771	-99.817	-86.465	12.598
1600	9.181	69.069	61.764	11.688	-99.854	-85.574	11.689
1700	9.200	69.626	62.210	12.607	-99.892	-84.681	10.887
1800	9.218	70.152	62.637	13.528	-99.930	-83.786	10.173
1900	9.237	70.651	63.046	14.451	-99.969	-82.888	9.534
2000	9.255	71.126	63.438	15.375	-100.008	-81.986	8.959
2100	9.273	71.578	63.815	16.302	-100.049	-81.085	8.439
2200	9.290	72.009	64.178	17.230	-100.092	-80.181	7.965
2300	9.308	72.423	64.527	18.160	-100.137	-79.275	7.533
2400	9.325	72.819	64.864	19.091	-100.184	-78.367	7.136
2500	9.342	73.200	65.190	20.025	-100.236	-77.458	6.771
2600	9.359	73.567	65.505	20.960	-100.291	-76.543	6.434
2700	9.377	73.920	65.811	21.897	-100.350	-75.630	6.122
2800	9.394	74.262	66.106	22.835	-100.416	-74.714	5.832
2900	9.410	74.592	66.393	23.775	-100.488	-73.793	5.561
3000	9.427	74.911	66.672	24.717	-100.567	-72.874	5.309
3100	9.444	75.220	66.943	25.661	-100.654	-71.948	5.072
3200	9.461	75.521	67.206	26.606	-100.751	-71.019	4.850
3300	9.478	75.812	67.462	27.553	-100.857	-70.091	4.642
3400	9.494	76.095	67.712	28.502	-100.976	-69.157	4.445
3500	9.511	76.371	67.956	29.452	-101.108	-68.218	4.260
3600	9.528	76.639	68.193	30.404	-101.254	-67.274	4.084
3700	9.544	76.900	68.425	31.357	-101.418	-66.330	3.918
3800	9.561	77.155	68.651	32.313	-101.600	-65.380	3.760
3900	9.578	77.403	68.873	33.270	-101.804	-64.425	3.610
4000	9.594	77.646	69.089	34.228	-102.030	-63.462	3.467
4100	9.611	77.883	69.301	35.188	-102.284	-62.495	3.331
4200	9.627	78.115	69.508	36.150	-102.566	-61.521	3.201
4300	9.644	78.342	69.710	37.114	-102.879	-60.539	3.077
4400	9.661	78.564	69.909	38.079	-103.228	-59.552	2.958
4500	9.677	78.781	70.104	39.046	-103.615	-58.553	2.844
4600	9.694	78.994	70.295	40.015	-104.043	-57.549	2.734
4700	9.710	79.202	70.482	40.985	-104.516	-56.533	2.629
4800	9.727	79.407	70.666	41.957	-105.035	-55.504	2.527
4900	9.743	79.608	70.846	42.930	-105.607	-54.466	2.429
5000	9.760	79.805	71.024	43.905	-106.231	-53.419	2.335
5100	9.776	79.998	71.198	44.882	-106.911	-52.354	2.244
5200	9.793	80.188	71.369	45.861	-107.649	-51.277	2.155
5300	9.809	80.375	71.537	46.841	-108.447	-50.186	2.069
5400	9.826	80.558	71.702	47.822	-109.307	-49.082	1.986
5500	9.842	80.739	71.865	48.806	-110.229	-47.959	1.906
5600	9.859	80.916	72.025	49.791	-111.212	-46.816	1.827
5700	9.875	81.091	72.183	50.777	-112.257	-45.657	1.751
5800	9.892	81.263	72.338	51.766	-113.363	-44.480	1.676
5900	9.908	81.432	72.490	52.756	-114.527	-43.282	1.603
6000	9.924	81.599	72.641	53.747	-115.749	-42.061	1.532

Dec. 31, 1961; Mar. 31, 1964; June 30, 1969

Ground State Configuration $^1\Sigma$

$\Delta Hf_0^\circ = -77.6 \pm 0.5$ kcal/mol

$S^\circ_{298.15} = 54.135 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298} = -78.1 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	1

$\omega_e = 426.04$ cm^{-1}

$\omega_e x_e = 2.43$ cm^{-1}

$\sigma = 1$

$B_e = 0.27994$ cm^{-1}

$\alpha_e = 0.002335$ cm^{-1}

$r_e = 2.17155$ Å

Heat of Formation

The total vapor pressures of KF(g) and K_2F_2(g) over KF(c, ℓ) have been determined by many investigators using the boiling point (1, 2, 5), Knudsen-effusion (3), transpiration (4), and torsion-effusion (6) methods. A method of trial and error is employed to select the appropriate values for ΔHs°_{298}(KF, c) and ΔHv°_{298}(KF, ℓ) such that by use of these two values and ΔHr°_{298} = 50 kcal/mol for the reaction $K_2F_2(g) = 2KF(g)$ and the Gibbs energy functions for KF(c), KF(ℓ), KF(g), and K_2F_2(g), the calculated total pressures of KF(g) and K_2F_2(g) are consistent with the measured ones. Adopting $\Delta Hs^\circ_{298} = 57.8$ and ΔHv°_{298} = 54.42 kcal/mol, we evaluate the partial pressures of KF(g) and K_2F_2(g) from the reported total pressure measurements. Based on the derived partial pressures for KF(g), the enthalpy changes for the processes: A. KF(c) = KF(g), and B. KF(ℓ) = KF(g) are calculated by the second and third law methods. Using the third law ΔHr°_{298} and ΔHf°_{298} = -135.90 and -132.519 kcal/mol for KF(c) and KF(ℓ), respectively, we obtain the ΔHf°_{298} for KF(g). The results are presented in the table below.

The dissociation energy (D_0) of KF(g) has been determined as 117 ± 8 kcal/mol by flame photometry by Page and Sugden (7), and Bulewicz, Phillips, and Sugden (8), yielding ΔHf°_{298}(KF, g) = -77.6 ± 8 kcal/mol. Barrow and Caunt (9) measured the fluctuation bands in the ultraviolet absorption spectra of KF and reported the upper limit for the D_0(KF, g) value to be 121.8 kcal/mol which leads to ΔHf°_{298}(KF, g) = -81.4 kcal/mol as the lower limit. Gaydon (10) reported D_0 = 116.9 ± 4.6 kcal/mol for KF(g). The corresponding value of ΔHf°_{298} is calculated as -77.5 ± 4.6 kcal/mol.

The heat of formation for KF(g) at 298°K is adopted as -78.1 ± 0.5 kcal/mol.

Investigator	Method	Temperature, °K	No. of Points	Process	ΔHr°, kcal/mol Second Law	ΔHr°, kcal/mol Third Law	Drift eu	ΔHf°_{298} kcal/mol
1. Wartenberg (1921)	boiling point	1624-1776	5	B	54.4 ± 0.9	54.16	-0.1±0.5	-78.36
2. Ruff (1922)	boiling point	1551-1773	6	B	58.1 ± 2.5	54.14	-2.4±1.5	-78.38
3. Niwa (1938)	Knudsen-effusion	913-973	6	A	56.2 ± 0.3	55.67	-0.6±0.3	-80.23
4. Naryshkin (1939)	transpiration	1023-1108	2	A	—	57.23	—	-78.67
		1188-1233	2**	B	—	54.60	—	-77.92
5. Cantor (1958)	boiling point	1200-1500	7*	B	54.4	54.38	-0.02	-78.14
6. Pugh (1958)	torsion-effusion	910-1020	6*	A	57.7	58.12	0.47	-77.78

* Data points calculated from the given vapor pressure equation.

** Only the data point at 1233°K is adopted for evaluation.

Heat Capacity and Entropy

The rotational transition spectrum of KF(g) has been measured in the millimeter- and submillimeter-wave region with a high resolution molecular-beam absorption spectrometer by Veazey and Gordy (15). From the derived potential constants the vibrational constants were calculated. The reported values for ω_e, $\omega_e x_e$, B_e, α_e and r_e are adopted.

Other values of ω_e reported are (in cm^{-1}): 390 ± 39 (11), 405 ± 25 (9), 429 ± 3 (12), and 426 ± 4 (13). The value of $\omega_e x_e$ has been determined as 1.45 cm^{-1} by Barrow and Caunt (9), and 2.4 cm^{-1} by Ritchie and Lew (12) and Baikov and Vasilevskii (13). Using the molecular beam electric resonance method, Green and Lew (14) measured the rotational transitions between the J = 0 and J = 1 states of $K^{39}F$ and reported the following values: B_e = 0.27994 cm^{-1}, α_e = 0.002335 cm^{-1}, and r_e = 2.17144 ± 0.00005 Å which are in excellent agreement with the adopted values. By use of the same method, Grabner and Hughes (11) investigated the rotational Stark spectrum of $K^{39}F$ and reported the K-F bond distance for the zeroth vibrational state as 2.55 ± 0.06 Å.

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Lithium Fluoride (LiF)

(Crystal) GFW = 25.9374

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.547	- 146.837	- 146.837	INFINITE
100	3.063	1.161	15.761	- 1.460	- 147.217	- 145.122	317.164
200	7.840	4.945	9.375	- .886	- 147.433	- 142.919	156.174
298	9.994	8.523	8.523	.000	- 147.450	- 140.696	103.133
300	10.023	8.585	8.523	.019	- 147.449	- 140.654	102.466
400	11.124	11.641	8.932	1.084	- 147.390	- 138.396	75.616
500	11.790	14.197	9.737	2.230	- 148.065	- 136.080	59.481
600	12.330	16.395	10.667	3.437	- 147.988	- 133.689	48.696
700	12.840	18.334	11.627	4.695	- 147.855	- 131.316	40.999
800	13.320	20.080	12.576	6.003	- 147.672	- 128.966	35.232
900	13.790	21.677	13.500	7.359	- 147.445	- 126.641	30.753
1000	14.240	23.153	14.392	8.760	- 147.176	- 124.343	27.175
1100	14.700	24.532	15.252	10.208	- 146.863	- 122.075	24.254
1200	15.116	25.829	16.080	11.699	- 146.508	- 119.837	21.825
1300	15.509	27.054	16.877	13.230	- 146.114	- 117.630	19.775
1400	15.881	28.218	17.646	14.800	- 145.683	- 115.454	18.023
1500	16.230	29.325	18.388	16.406	- 145.216	- 113.311	16.509
1600	16.557	30.383	19.105	18.045	- 144.715	- 111.200	15.189
1700	16.862	31.396	19.798	19.716	- 179.230	- 107.794	13.858
1800	17.144	32.368	20.470	21.417	- 178.487	- 103.612	12.580
1900	17.405	33.302	21.121	23.144	- 177.719	- 99.472	11.442
2000	17.643	34.201	21.753	24.897	- 176.928	- 95.375	10.422
2100	17.859	35.067	22.366	26.672	- 176.116	- 91.319	9.504
2200	18.052	35.902	22.963	28.468	- 175.287	- 87.299	8.672
2300	18.224	36.709	23.543	30.282	- 174.441	- 83.319	7.917
2400	18.373	37.488	24.108	32.112	- 173.583	- 79.376	7.228
2500	18.500	38.240	24.658	33.956	- 172.713	- 75.468	6.597

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

LITHIUM FLUORIDE (LiF) (CRYSTAL) GFW = 25.9374

ΔHf°_0 = -146.84 ± 0.2 kcal/mol

$S^\circ_{298.15}$ = 8.523 ± 0.005 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -147.45 ± 0.2 kcal/mol

Tm = 1121.3 ± 1.0°K

ΔHm° = 6.474 ± 0.005 kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 66.0 kcal/mol

Heat of Formation

The heats of solution and reaction of LiF(c) in water and hydrochloric acid have been measured by many investigators. The reported ΔHsoln values are listed in the table below. Using $\Delta Hf^\circ_{298}(Li^+, \infty H_2O)$ = -66.56 kcal/mol (8), and $\Delta Hf^\circ_{298}(F^-, \infty H_2O)$ = -79.82 kcal/mol (9), we calculate the corresponding ΔHf°_{298} values for LiF(c). Based on the heat of solution of LiOH(c) in excess HF solution measured by Sinke (7), the value, ΔHf°_{298}(LiF,c) = -146.65 ± 0.5 kcal/mol is derived. The value of ΔHf°_{298} for LiF(c) is adopted as -147.45 ± 0.2 kcal/mol

Investigator	Solvent	Temperature, °K	Concentration (LiF·nH_2O)	ΔHr, kcal/mol	ΔH°_∞, kcal/mol*	ΔHf°_{298}, kcal/mol
1. de Forcrand (1911)	H_2O	288.2	unavailable	1.04	—	—
2. Kolesov-Skuratov (1961)	H_2O	294.7	3800 H_2O	1.25 ± 0.02	1.13 ± 0.05	-147.50
3. Wulff (1962)	HCl	298.2	unavailable	unavailable	1.10 ± 0.10	-147.47
4. Stephenson et al. (1964)	H_2O	298.2	2780-5560 H_2O	unavailable	1.07 ± 0.05	-147.44
5. Cox and Harrop (1964)	H_2O	298.2	60400 H_2O	1.059 ± 0.028	1.014 ± 0.055	-147.38

*The heat of dilution data of Parker (6) are used to convert ΔHr to ΔH°_∞.

Heat Capacity and Entropy

Clusius, Goldman, and Perlick (10) measured the low temperature heat capacities in the temperature range 19 to 272°K and Clusius and Eichenauer (11) from 10 to 111°K. Below 20°K a number of investigators have reported values of θ_D, and the average value of 729 ± 6 is used here. The high temperature enthalpies from 298°K to the melting point 1121.3°K were measured by Douglas and Dever (12), and Voskresenskaya et al. (13). All these data are taken and smoothed by computer up to 400°K. Above 400°K the Cp values are obtained graphically by drawing a smooth line through the data points.

S°_{298} is derived from the adopted low temperature heat capacities, based on S°_{20} = 0.064 eu.

Melting Data

See the LiF(ℓ) table for details.

Heat of Sublimation

The difference between ΔHf°_{298} for LiF(g) and LiF(c) is ΔHs°_{298}.

References

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Lithium Fluoride (LiF)

(Liquid) GFW = 25.9374

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	15.340	10.269	10.269	.000	- 143.081	- 136.847	100.311
300	15.340	10.363	10.269	.028	- 143.071	- 136.809	99.665
400	15.340	14.776	10.870	1.562	- 142.543	- 134.802	73.652
500	15.340	18.200	12.007	3.096	- 142.830	- 132.846	58.067
600	15.340	20.996	13.279	4.630	- 142.425	- 130.887	47.676
700	15.340	23.361	14.555	6.164	- 142.017	- 128.997	40.275
800	15.340	25.409	15.786	7.698	- 141.608	- 127.165	34.740
900	15.340	27.216	16.958	9.232	- 141.203	- 125.384	30.447
1000	15.340	28.832	18.066	10.766	- 140.801	- 123.648	27.023
1100	15.340	30.294	19.112	12.300	- 140.401	- 121.952	24.230
1200	15.340	31.629	20.100	13.834	- 140.004	- 120.293	21.908
1300	15.340	32.857	21.035	15.368	- 139.607	- 118.666	19.950
1400	15.340	33.994	21.921	16.902	- 139.212	- 117.070	18.275
1500	15.340	35.052	22.761	18.436	- 138.816	- 115.502	16.829
1600	15.340	36.042	23.561	19.970	- 138.421	- 113.960	15.566
1700	15.340	36.972	24.323	21.504	- 173.073	- 111.116	14.283
1800	15.340	37.849	25.050	23.038	- 172.497	- 107.487	13.051
1900	15.340	38.678	25.746	24.572	- 171.922	- 103.890	11.950
2000	15.340	39.465	26.412	26.106	- 171.349	- 100.325	10.963
2100	15.340	40.214	27.052	27.640	- 170.779	- 96.789	10.073
2200	15.340	40.927	27.666	29.174	- 170.212	- 93.278	9.266
2300	15.340	41.609	28.258	30.708	- 169.645	- 89.794	8.532
2400	15.340	42.262	28.828	32.242	- 169.083	- 86.335	7.862
2500	15.340	42.888	29.378	33.776	- 168.524	- 82.898	7.247
2600	15.340	43.490	29.909	35.310	- 167.967	- 79.485	6.681
2700	15.340	44.069	30.423	36.844	- 167.415	- 76.092	6.159
2800	15.340	44.627	30.920	38.378	- 166.865	- 72.720	5.676
2900	15.340	45.165	31.402	39.912	- 166.322	- 69.366	5.228
3000	15.340	45.685	31.870	41.446	- 165.783	- 66.033	4.810

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

LITHIUM FLUORIDE (LiF) (LIQUID) GFW = 25.9374

$S^\circ_{298.15}$ = 10.269 gibbs/mol

Tm = 1121.3 ± 1.0°K

Tb = 1990°K

$\Delta Hf^\circ_{298.15}$ = -143.081 kcal/mol

ΔHm° = 6.474 ± 0.005 kcal/mol

ΔHv°(to mixture) = 35.08 kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1121.3} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4826 (1954), and N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Shmidt, Akad. Nauk SSSR, Izvest. Sekt. Fiz. - Khim. Anal. 27, 233 (1956), have measured the enthalpies of LiF liquid to 1200 and 1400°K, respectively. Using the reported enthalpy data, a constant heat capacity is derived for each set. The adopted Cp for LiF(ℓ) is the mean of the two derived heat capacities, and is extended arbitrarily to the temperatures above Tb and below Tm. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been determined by many investigators. See the table below for details. The adopted value, 1121.3 ± 1.0°K, is that reported by Douglas and Dever, loc. cit. The heat of melting is the mean of the ΔHm° values reported by Douglas and Dever, loc. cit., and Voskresenskaya et al., loc. cit.

Tm, °K	Source
1115	H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
1115	G. Petit and A. Cremieu, Compt. Rend. 243, 360 (1956).
1119	H. Flood, V. Fykse, and S. Urnes, Z. Elektrochem. 59 364 (1955).
1120	V. P. Goryacheva, A. G. Bergman, and A. G. Kislova, Zh. Neorg. Khim. 4, 2744 (1959).
1121	H. M. Haendler, P. S. Sennett, and C. M. Wheeler, J. Electrochem. Soc. 106, 264 (1959).
1121.2	Z. A. Mateiko and G. A. Bukhalova, Zh. Neorg. Khim. 4, 1649 (1959).
1121.3	T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4826 (1954).
1123	G. A. Bukhalova and D. V. Sementsova, Russ. J. Inorg. Chem. (English Transl.) 10, 1027 (1965).

Vaporization Data

Tb is the temperature at which the partial pressures of LiF(g), Li_2F_2(g), and Li_3F_3(g), in equilibrium with LiF(ℓ), equal one atmosphere. The vapor composition at the boiling point is evaluated as LiF 69%, Li_2F_2 26.6%, and Li_3F_3 4.4%. The heat required to vaporize one mole of liquid to form 0.739 mole of vapor mixture of the above composition at Tb is calculated to be 35.08 kcal.

The value of Tb for LiF(ℓ) has been reported to be 1943 and 1949°K by O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922), and H. von Wartenberg and H. Schulz, loc. cit., respectively, which were obtained by extrapolation of their vapor pressure data, measured by the boiling point method.

Lithium Fluoride (LiF)

(Ideal Gas) GFW = 25.9374

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.109	-81.399	-81.399	INFINITE
100	6.960	40.092	54.235	-1.414	-81.171	-82.969	181.330
200	7.094	44.940	48.511	-.714	-81.261	-84.746	92.606
298	7.478	47.840	47.840	.000	-81.450	-86.418	63.346
300	7.485	47.887	47.840	.014	-81.454	-86.449	62.978
400	7.879	50.096	48.139	.783	-81.691	-88.079	48.124
500	8.178	51.888	48.715	1.586	-82.709	-89.569	39.151
600	8.391	53.399	49.373	2.415	-83.009	-90.912	33.115
700	8.546	54.705	50.044	3.263	-83.287	-92.208	28.789
800	8.660	55.854	50.699	4.123	-83.552	-93.465	25.533
900	8.747	56.879	51.330	4.994	-83.810	-94.688	22.993
1000	8.816	57.804	51.932	5.872	-84.064	-95.883	20.955
1100	8.872	58.647	52.505	6.757	-84.314	-97.053	19.283
1200	8.919	59.421	53.049	7.646	-84.561	-98.200	17.885
1300	8.959	60.137	53.567	8.540	-84.804	-99.327	16.698
1400	8.994	60.802	54.061	9.438	-85.045	-100.434	15.679
1500	9.025	61.424	54.531	10.339	-85.283	-101.525	14.792
1600	9.052	62.007	54.980	11.243	-85.517	-102.600	14.015
1700	9.078	62.556	55.410	12.149	-120.797	-102.333	13.156
1800	9.102	63.076	55.821	13.058	-120.846	-101.245	12.293
1900	9.124	63.569	56.216	13.970	-120.893	-100.153	11.520
2000	9.145	64.037	56.596	14.883	-120.942	-99.061	10.825
2100	9.165	64.484	56.961	15.798	-120.990	-97.967	10.196
2200	9.184	64.911	57.313	16.716	-121.039	-96.869	9.623
2300	9.203	65.319	57.652	17.635	-121.087	-95.770	9.100
2400	9.220	65.711	57.980	18.556	-121.138	-94.668	8.621
2500	9.238	66.088	58.296	19.479	-121.190	-93.564	8.179
2600	9.255	66.451	58.603	20.404	-121.242	-92.459	7.772
2700	9.272	66.800	58.900	21.330	-121.298	-91.350	7.394
2800	9.288	67.138	59.188	22.258	-121.354	-90.240	7.044
2900	9.304	67.464	59.468	23.188	-121.416	-89.127	6.717
3000	9.320	67.780	59.740	24.119	-121.479	-88.013	6.412
3100	9.335	68.086	60.004	25.052	-121.547	-86.896	6.126
3200	9.351	68.382	60.262	25.986	-121.618	-85.777	5.858
3300	9.366	68.670	60.512	26.922	-121.695	-84.656	5.607
3400	9.381	68.950	60.756	27.859	-121.776	-83.531	5.369
3500	9.396	69.222	60.994	28.798	-121.862	-82.406	5.146
3600	9.411	69.487	61.226	29.739	-121.954	-81.276	4.934
3700	9.426	69.745	61.453	30.680	-122.053	-80.147	4.734
3800	9.441	69.997	61.675	31.624	-122.157	-79.009	4.544
3900	9.455	70.242	61.891	32.568	-122.269	-77.874	4.364
4000	9.470	70.482	62.103	33.515	-122.388	-76.734	4.193
4100	9.484	70.716	62.310	34.462	-122.515	-75.591	4.029
4200	9.499	70.944	62.513	35.412	-122.650	-74.446	3.874
4300	9.513	71.168	62.712	36.362	-122.792	-73.295	3.725
4400	9.527	71.387	62.906	37.314	-122.944	-72.142	3.583
4500	9.542	71.601	63.097	38.268	-123.106	-70.986	3.448
4600	9.556	71.811	63.284	39.222	-123.278	-69.826	3.318
4700	9.570	72.017	63.468	40.179	-123.461	-68.664	3.193
4800	9.584	72.218	63.648	41.136	-123.655	-67.496	3.073
4900	9.598	72.416	63.825	42.096	-123.861	-66.324	2.958
5000	9.612	72.610	63.999	43.056	-124.080	-65.146	2.848
5100	9.626	72.801	64.170	44.018	-124.313	-63.965	2.741
5200	9.640	72.988	64.337	44.981	-124.561	-62.778	2.638
5300	9.654	73.172	64.502	45.946	-124.824	-61.589	2.540
5400	9.669	73.352	64.665	46.912	-125.103	-60.395	2.444
5500	9.682	73.530	64.824	47.880	-125.401	-59.192	2.352
5600	9.696	73.704	64.981	48.849	-125.716	-57.988	2.263
5700	9.710	73.876	65.136	49.819	-126.051	-56.773	2.177
5800	9.724	74.045	65.288	50.791	-126.408	-55.555	2.093
5900	9.738	74.211	65.438	51.764	-126.785	-54.332	2.013
6000	9.752	74.375	65.585	52.738	-127.186	-53.098	1.934

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

LITHIUM FLOURIDE (LiF) (Ideal Gas) GFW = 25.9374

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 47.840 ± 0.002 gibbs/mol

ΔHf°_0 = -81.40 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -81.45 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	1

ω_e = 914.33 cm^{-1}

$\omega_e x_e$ = 8.00 cm^{-1}

σ = 1

B_e = 1.3588 cm^{-1}

α_e = 0.0203 cm^{-1}

r_e = 1.5631 Å

Heat of Formation

The molecular species produced on vaporization of lithium fluoride have been studied by many investigators during the last ten years. The occurrence of dimer and trimer molecules in addition to the monomer has been established by use of mass spectrometric (4, 7, 8), torsion effusion (3, 6), molecular beam (9, 10), and transpiration (11) methods. To evaluate ΔHv°(LiF,g), we have used a trial and error variation of ΔHs° and ΔHv° for the monomer, dimer and trimer in order to obtain reasonable agreement with the observed total pressures, 997-1939°K, (1, 2, 3, 5, 6). Using, as guidelines, these total pressures and the equilibrium data for dimer and trimer (see these tables), we adopt ΔHs°_{298} = 66.0, 69.57 and 79.73 and ΔHv°_{298} = 61.63, 60.83 and 66.62 kcal/mol for LiF, Li_2F_2 and Li_3F_3, respectively. The adopted value ΔHs°_{1000} = 63.1 kcal/mol is in agreement with the reported values: 64.8 ± 2 (12), 63.6 ± 1 (6) and 63.0 ± 1.5 kcal/mol (8) at 1000°K.

A second and third law analysis of the total pressure data is given below. Monomer pressures for this analysis are obtained by deducing dimer and trimer pressures calculated from JANAF free energy functions and the adopted values of ΔHs°_{298} and ΔHv°_{298}.

The vapor pressure data reported by Eisenstadt et al. (9, 10) are too low and so not consistent with the others and are not used for evaluation. The transpiration data of Sense and Stone (11) and Knudsen-effusion data of Evseev et al. (13) are not considered for analysis because of the complications involved in converting the reported apparent pressures to the real total pressures of the gaseous mixtures containing monomer, dimer and trimer.

Herzberg (14) and Gaydon (15) reported the dissociation energies (D_0) of LiF(g) to be ≤ 6.6 and 5.95 ± 0.3 eV, respectively. Using these D_0 values, we derive ΔHf°_{298}(LiF,g) as -95.9 and -80.9 ± 6.9 kcal/mol. By use of flame-photometric method, Page and Sugden (16) and Bulewicz et al. (17) gave D_0 = 141 and 136 ± 8 kcal/mol, yielding ΔHf°_{298}(LiF,g) = -84.7 and -79.7 ± 8 kcal/mol.

Investigator	Temperature, °K	Method	Process†	No. of Points	ΔHr°_{298}, kcal/mol Second Law	Third Law	Drift eu	ΔHf°_{298} † kcal/mol
1. Wartenberg (1921)	1626-1820	boiling point	I	5	67.6 ± 2.4	61.4	-3.6 ± 1.4	-81.68
2. Ruff (1922)	1671-1939	boiling point	I	14	65.8 ± 0.7	60.8	-2.7 ± 0.4	-82.28
3. Pugh (1958)*	1020-1120	torsion-effusion	II	6	69.1	66.8	-2.2	-80.65
4. Porter (1958)	1073	mass spectrometry	II	1	—	67.7	—	-79.75
5. Cantor (1958)*	1328-1575	boiling point	I	10	64.5	61.6	-2.0	-81.48
6. Hildenbrand (1964)*	997-1119	torsion-effusion	II	24	69.9	66.8	-3.0	-80.65
	1125-1159	torsion-effusion	I	19	67.1	62.3	-4.2	-80.78

* Data points are calculated from the given vapor pressure equation.

† Process I: LiF(ℓ) = LiF(g); II: LiF(c) = LiF(g); ΔHf°_{298}(LiF,g) values are calculated based on the third law ΔHr°_{298}.

Heat Capacity and Entropy

The infrared spectrum of LiF(g) and microwave spectrum of Li^6F have been observed by Vidale (19), and Wharten and Klemperer (21), respectively. The reported vibrational and rotational constants for Li^7F(g) and Li^6F(g), are adopted and corrected to the average istopic species. Veazey and Gordy (18) measured the rotational transitions of Li^7F with a high resolution molecular-beam absorption spectrometer. By use of the electric resonance method of molecular beam spectroscopy, Braunstein and Trischka (22) observed the transitions between v = 0 and v = 1 vibrational states. The infrared spectrum of LiF(g) have also been measured by Vasilevskii and Baikov (20).

References

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Lithium Hypofluorite (LiFO)

(Ideal Gas)   Mol. Wt. = 41.9368

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.588	-21.390	-21.390	INFINITE
100	8.029	49.124	67.043	-1.792	-21.417	-22.043	48.173
200	9.004	54.938	59.676	-.948	-21.703	-22.565	24.656
298	10.285	58.775	58.775	.000	-22.000	-22.923	16.802
300	10.307	58.839	58.776	.019	-22.005	-22.929	16.703
400	11.331	61.953	59.193	1.104	-22.282	-23.194	12.672
500	12.031	64.562	60.013	2.274	-23.299	-23.315	10.191
600	12.502	66.800	60.962	3.502	-23.577	-23.291	8.483
700	12.824	68.753	61.939	4.770	-23.824	-23.225	7.251
800	13.052	70.481	62.900	6.064	-24.054	-23.124	6.317
900	13.217	72.028	63.830	7.378	-24.276	-22.994	5.583
1000	13.339	73.427	64.721	8.706	-24.494	-22.839	4.991
1100	13.433	74.703	65.571	10.045	-24.709	-22.664	4.503
1200	13.505	75.875	66.382	11.392	-24.922	-22.469	4.092
1300	13.563	76.958	67.154	12.745	-25.135	-22.255	3.741
1400	13.609	77.965	67.891	14.104	-25.346	-22.026	3.438
1500	13.646	78.905	68.594	15.467	-25.558	-21.781	3.173
1600	13.678	79.787	69.267	16.833	-25.768	-21.522	2.940
1700	13.704	80.617	69.910	18.202	-61.026	-19.922	2.561
1800	13.725	81.401	70.527	19.574	-61.057	-17.503	2.125
1900	13.744	82.144	71.119	20.947	-61.090	-15.082	1.735
2000	13.760	82.849	71.688	22.322	-61.127	-12.660	1.383
2100	13.774	83.521	72.236	23.699	-61.166	-10.237	1.065
2200	13.786	84.162	72.763	25.077	-61.211	-7.810	.776
2300	13.796	84.775	73.272	26.456	-61.257	-5.382	.511
2400	13.805	85.362	73.764	27.836	-61.310	-2.951	.269
2500	13.814	85.926	74.239	29.217	-61.368	-.519	.045
2600	13.821	86.468	74.699	30.599	-61.429	1.916	-.161
2700	13.827	86.990	75.145	31.981	-61.498	4.353	-.352
2800	13.833	87.493	75.577	33.364	-61.571	6.793	-.530
2900	13.838	87.978	75.996	34.748	-61.652	9.239	-.696
3000	13.843	88.447	76.403	36.132	-61.739	11.685	-.851
3100	13.847	88.901	76.799	37.517	-61.834	14.135	-.996
3200	13.851	89.341	77.184	38.902	-61.935	16.585	-1.133
3300	13.855	89.767	77.559	40.287	-62.046	19.040	-1.261
3400	13.858	90.181	77.924	41.673	-62.164	21.500	-1.382
3500	13.861	90.583	78.280	43.058	-62.290	23.960	-1.496
3600	13.864	90.973	78.627	44.445	-62.425	26.430	-1.604
3700	13.866	91.353	78.966	45.831	-62.570	28.898	-1.707
3800	13.868	91.723	79.297	47.218	-62.724	31.376	-1.804
3900	13.871	92.083	79.620	48.605	-62.887	33.852	-1.897
4000	13.873	92.434	79.936	49.992	-63.061	36.335	-1.985
4100	13.874	92.777	80.245	51.379	-63.246	38.822	-2.069
4200	13.876	93.111	80.548	52.767	-63.441	41.313	-2.150
4300	13.878	93.438	80.844	54.155	-63.646	43.811	-2.227
4400	13.879	93.757	81.134	55.542	-63.864	46.312	-2.300
4500	13.881	94.069	81.418	56.930	-64.094	48.818	-2.371
4600	13.882	94.374	81.696	58.319	-64.336	51.331	-2.439
4700	13.883	94.673	81.969	59.707	-64.592	53.844	-2.504
4800	13.884	94.965	82.237	61.095	-64.860	56.369	-2.566
4900	13.885	95.251	82.499	62.484	-65.144	58.897	-2.627
5000	13.886	95.532	82.757	63.872	-65.442	61.430	-2.685
5100	13.887	95.807	83.010	65.261	-65.757	63.972	-2.741
5200	13.888	96.076	83.259	66.650	-66.088	66.522	-2.796
5300	13.889	96.341	83.503	68.039	-66.437	69.073	-2.848
5400	13.890	96.600	83.744	69.428	-66.804	71.633	-2.899
5500	13.891	96.855	83.980	70.817	-67.190	74.204	-2.948
5600	13.891	97.106	84.212	72.206	-67.598	76.770	-2.996
5700	13.892	97.352	84.440	73.595	-68.026	79.353	-3.042
5800	13.893	97.593	84.665	74.984	-68.477	81.948	-3.088
5900	13.893	97.831	84.886	76.373	-68.952	84.540	-3.131
6000	13.894	98.064	85.104	77.763	-69.451	87.152	-3.174

Dec. 31, 1960; Sept. 30, 1965

LITHIUM HYPOFLUORITE (LiFO)   (IDEAL GAS)   MOL. WT. = 41.9368

Point Group C_s

$\Delta H^\circ_{f\ 0}$ = [-21 ± 10] kcal. mole⁻¹

$S^\circ_{298.15}$ = [58.775] cal. deg.⁻¹ mole⁻¹

$\Delta H^\circ_{f\ 298.15}$ = [-22 ± 10] kcal. mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[800] (1)
[500] (1)
[950] (1)

Bond Distance: Li-O = [1.59] Å   F-O = [1.41] Å

Bond Angle: F-O-Li = [104]°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.21684 X 10^{-116}] g.³ cm.⁶

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) for LiFO(g) was calculated from $\Delta H^\circ_{r\ 298.15}$ = 139 kcal. mole⁻¹ for the reaction LiFO(g) = Li(g) + F(g) + O(g) where the value of $\Delta H^\circ_{r\ 298.15}$ was estimated to be the sum of the F-O and Li-O bond energies. The values of the F-O and Li-O bond energies were obtained from those in $F_2O(g)$ and $Li_2O(g)$ molecules, respectively.

Heat Capacity and Entropy.

The F-O and Li-O bond distances were assumed to be the same as those in $F_2O(g)$ and $Li_2O(g)$ molecules, respectively. The F-O-Li bond angle and vibrational frequencies were estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are: $I_A = 5.1543 \times 10^{-39}$, $I_B = 1.2729 \times 10^{-39}$ and $I_C = 6.4272 \times 10^{-39}$ g. cm.²

Magnesium Monofluoride (MgF)

(Ideal Gas) GFW = 43.3104

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.143	-52.992	-52.992	INFINITE
100	6.965	44.892	59.371	-1.448	-52.798	-55.025	120.258
200	7.280	49.789	53.487	-.740	-53.002	-57.299	62.613
298	7.782	52.791	52.791	.000	-53.100	-59.288	43.459
300	7.790	52.839	52.791	.014	-53.104	-59.324	43.219
400	8.168	55.136	53.102	.814	-53.303	-61.371	33.532
500	8.413	56.987	53.700	1.644	-53.519	-63.363	27.696
600	8.574	58.536	54.380	2.493	-53.754	-65.311	23.789
700	8.684	59.866	55.071	3.357	-54.009	-67.215	20.986
800	8.763	61.031	55.745	4.229	-54.295	-69.084	18.873
900	8.822	62.067	56.391	5.109	-54.614	-70.914	17.220
1000	8.868	62.999	57.006	5.993	-57.091	-72.525	15.850
1100	8.905	63.846	57.590	6.882	-57.451	-74.052	14.713
1200	8.936	64.622	58.144	7.774	-57.834	-75.545	13.759
1300	8.962	65.339	58.670	8.669	-58.243	-77.004	12.946
1400	8.985	66.004	59.170	9.566	-89.044	-77.952	12.169
1500	9.005	66.624	59.647	10.465	-89.097	-77.157	11.242
1600	9.024	67.206	60.101	11.367	-89.150	-76.361	10.430
1700	9.041	67.754	60.536	12.271	-89.202	-75.559	9.714
1800	9.056	68.271	60.951	13.175	-89.256	-74.756	9.077
1900	9.071	68.761	61.349	14.082	-89.307	-73.948	8.506
2000	9.085	69.226	61.732	14.990	-89.360	-73.137	7.992
2100	9.098	69.670	62.099	15.899	-89.413	-72.327	7.527
2200	9.111	70.094	62.453	16.809	-89.466	-71.512	7.104
2300	9.123	70.499	62.794	17.721	-89.519	-70.693	6.717
2400	9.135	70.887	63.123	18.634	-89.572	-69.874	6.363
2500	9.147	71.261	63.441	19.548	-89.626	-69.055	6.037
2600	9.158	71.620	63.749	20.463	-89.680	-68.229	5.735
2700	9.169	71.965	64.047	21.380	-89.735	-67.401	5.456
2800	9.180	72.299	64.336	22.297	-89.790	-66.576	5.196
2900	9.191	72.621	64.616	23.216	-89.847	-65.742	4.954
3000	9.202	72.933	64.888	24.135	-89.906	-64.913	4.729
3100	9.212	73.235	65.152	25.054	-89.965	-64.078	4.518
3200	9.223	73.528	65.410	25.978	-90.027	-63.244	4.319
3300	9.233	73.812	65.660	26.901	-90.090	-62.407	4.133
3400	9.243	74.087	65.904	27.825	-90.157	-61.561	3.957
3500	9.254	74.356	66.141	28.749	-90.227	-60.724	3.792
3600	9.264	74.616	66.373	29.675	-90.301	-59.875	3.635
3700	9.274	74.870	66.599	30.602	-90.379	-59.029	3.487
3800	9.284	75.118	66.820	31.530	-90.461	-58.182	3.346
3900	9.294	75.359	67.036	32.459	-90.549	-57.334	3.213
4000	9.303	75.594	67.247	33.389	-90.642	-56.478	3.086
4100	9.313	75.824	67.454	34.320	-90.742	-55.624	2.965
4200	9.323	76.049	67.656	35.251	-90.849	-54.769	2.850
4300	9.333	76.268	67.853	36.184	-90.963	-53.906	2.740
4400	9.343	76.483	68.047	37.118	-91.086	-53.043	2.635
4500	9.352	76.693	68.237	38.053	-91.216	-52.177	2.534
4600	9.362	76.899	68.423	38.988	-91.356	-51.308	2.438
4700	9.372	77.100	68.605	39.925	-91.505	-50.434	2.345
4800	9.381	77.298	68.785	40.863	-91.665	-49.560	2.257
4900	9.391	77.491	68.960	41.801	-91.836	-48.679	2.171
5000	9.400	77.681	69.133	42.741	-92.017	-47.797	2.089
5100	9.410	77.867	69.302	43.681	-92.211	-46.915	2.010
5200	9.420	78.050	69.469	44.623	-92.416	-46.022	1.934
5300	9.429	78.230	69.632	45.565	-92.634	-45.127	1.861
5400	9.439	78.406	69.793	46.509	-92.865	-44.232	1.790
5500	9.448	78.579	69.951	47.453	-93.109	-43.326	1.722
5600	9.458	78.749	70.107	48.398	-93.369	-42.417	1.655
5700	9.467	78.917	70.260	49.345	-93.642	-41.504	1.591
5800	9.477	79.082	70.411	50.292	-93.930	-40.593	1.530
5900	9.486	79.244	70.559	51.240	-94.234	-39.668	1.469
6000	9.496	79.403	70.705	52.189	-94.553	-38.741	1.411

Dec. 31, 1960; June 30, 1964; Mar. 31, 1967

MAGNESIUM MONOFLUORIDE (MgF) (IDEAL GAS) GFW = 43.3104

Ground State Configuration $^2\Sigma$

ΔHf°_0 = -53.0 ± 1.3 kcal/mol

$S^\circ_{298.15}$ = 52.791 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -53.1 ± 1.3 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2

ω_e = 717.6 cm^{-1}

$\omega_e x_e$ = 3.84 cm^{-1}

σ = 1

B_e = 0.5199 cm^{-1}

α_e = [0.00386] cm^{-1}

r_e = 1.752 Å

Heat of Formation.

The equilibrium constants for the decomposition of MgF(g) into Mg(g), MgF_2(c) and MgF_2(g) were determined by T. C. Ehlert, Ph.D. Thesis, University of Wisconsin, 1963. Using this data, the heats of decomposition are evaluated by both the third and second law methods. The results are presented in the table below. The equilibrium constants for the reaction $AlF_3(g) + 2Mg(g) \rightarrow AlF(g) + 2MgF(g)$ were also reported by T. C. Ehlert, loc. cit. The heat of reaction is calculated by the third and second law methods, respectively. The dissociation energy (D°_0) of MgF(g) was reported to be 3.2 ± 0.7 and 4.2 eu by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, and G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950, respectively. The corresponding values of $\Delta Hf^\circ_{298.15}$ for MgF(g) are derived. The results are also listed in the table. The value of $\Delta Hf^\circ_{298.15}$ for MgF(g) adopted is the average of the first two $\Delta Hf^\circ_{298.15}$ values.

Investigator	Chemical Reaction	$\Delta Hr^\circ_{298.15}$ kcal/mol Third Law Value	Second Law Value	$\Delta Hf^\circ_{298.15}$ kcal/mol
T. C. Ehlert	$2MgF(g) = Mg(g) + MgF_2(g)$	-34.76 ± 0.74	-70 ± 19	-52.8 ± 1.3*
	$2MgF(g) = Mg(g) + MgF_2(c)$	-126.66 ± 0.80	-92 ± 21	-53.4 ± 1.2*
	$AlF_3(g) + 2Mg(g) = AlF(g) + 2MgF(g)$	18.66 ± 0.40	2.7 ± 3.2	-67.7 ± 1.0*
G. Herzberg	$MgF(g) \rightarrow Mg(g) + F(g)$	D°_0 = 4.2 eV		-42.6
A. G. Gaydon	$MgF(g) \rightarrow Mg(g) + F(g)$	D°_0 = 3.2 ± 0.7 eV		-19.6 ± 16.1

*Based on $\Delta Hr^\circ_{298.15}$ value by the third law method.

Heat Capacity and Entropy.

All the molecular constants are taken from G. Herzberg, loc. cit., except α_e which is estimated.

Nitrogen Monofluoride (NF)

(Ideal Gas) Mol. Wt. = 33.0051

FN

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.090	59.501	59.501	INFINITE
100	6.957	43.760	57.713	- 1.395	59.506	59.070	- 129.091
200	7.007	48.590	52.081	- .698	59.501	58.636	- 64.072
298	7.253	51.427	51.427	.000	59.500	58.212	- 42.669
300	7.259	51.472	51.427	.013	59.500	58.204	- 42.400
400	7.604	53.607	51.716	.756	59.509	57.772	- 31.563
500	7.913	55.339	52.273	1.533	59.531	57.334	- 25.060
600	8.156	56.804	52.909	2.337	59.563	56.893	- 20.722
700	8.340	58.075	53.558	3.162	59.599	56.445	- 17.622
800	8.480	59.199	54.194	4.003	59.635	55.991	- 15.295
900	8.588	60.204	54.807	4.857	59.671	55.534	- 13.485
1000	8.674	61.113	55.393	5.720	59.705	55.072	- 12.035
1100	8.743	61.943	55.951	6.591	59.736	54.607	- 10.849
1200	8.799	62.707	56.483	7.468	59.764	54.139	- 9.860
1300	8.846	63.413	56.989	8.351	59.790	53.670	- 9.022
1400	8.887	64.070	57.472	9.237	59.812	53.198	- 8.304
1500	8.922	64.684	57.932	10.128	59.833	52.726	- 7.682
1600	8.953	65.261	58.373	11.022	59.851	52.251	- 7.137
1700	8.981	65.805	58.794	11.918	59.867	51.775	- 6.656
1800	9.006	66.319	59.198	12.818	59.881	51.298	- 6.228
1900	9.029	66.806	59.586	13.719	59.894	50.823	- 5.846
2000	9.050	67.270	59.958	14.623	59.906	50.345	- 5.501
2100	9.070	67.712	60.317	15.529	59.916	49.865	- 5.189
2200	9.088	68.134	60.663	16.437	59.924	49.387	- 4.906
2300	9.106	68.539	60.997	17.347	59.932	48.907	- 4.647
2400	9.122	68.927	61.319	18.258	59.939	48.427	- 4.410
2500	9.138	69.299	61.631	19.171	59.944	47.949	- 4.191
2600	9.154	69.658	61.933	20.086	59.949	47.469	- 3.990
2700	9.169	70.004	62.225	21.002	59.953	46.989	- 3.803
2800	9.183	70.338	62.509	21.920	59.956	46.507	- 3.630
2900	9.197	70.660	62.785	22.839	59.959	46.029	- 3.469
3000	9.211	70.972	63.052	23.759	59.961	45.547	- 3.318
3100	9.224	71.274	63.313	24.681	59.963	45.067	- 3.177
3200	9.237	71.567	63.566	25.604	59.963	44.587	- 3.045
3300	9.250	71.852	63.813	26.528	59.963	44.105	- 2.921
3400	9.263	72.128	64.053	27.454	59.963	43.626	- 2.804
3500	9.276	72.397	64.288	28.381	59.962	43.145	- 2.694
3600	9.288	72.658	64.517	29.309	59.961	42.666	- 2.590
3700	9.300	72.913	64.740	30.239	59.959	42.184	- 2.492
3800	9.312	73.161	64.959	31.169	59.957	41.705	- 2.398
3900	9.324	73.403	65.172	32.101	59.954	41.224	- 2.310
4000	9.336	73.639	65.381	33.034	59.951	40.745	- 2.226
4100	9.348	73.870	65.585	33.968	59.947	40.263	- 2.146
4200	9.359	74.095	65.785	34.904	59.943	39.785	- 2.070
4300	9.371	74.316	65.981	35.840	59.940	39.304	- 1.998
4400	9.383	74.531	66.173	36.778	59.934	38.825	- 1.928
4500	9.394	74.742	66.361	37.717	59.929	38.345	- 1.862
4600	9.405	74.949	66.545	38.657	59.924	37.865	- 1.799
4700	9.417	75.151	66.726	39.598	59.918	37.386	- 1.738
4800	9.428	75.350	66.904	40.540	59.912	36.906	- 1.680
4900	9.439	75.544	67.078	41.483	59.905	36.427	- 1.625
5000	9.450	75.735	67.250	42.428	59.898	35.948	- 1.571
5100	9.461	75.922	67.418	43.373	59.891	35.467	- 1.520
5200	9.473	76.106	67.583	44.320	59.884	34.991	- 1.471
5300	9.484	76.287	67.746	45.268	59.875	34.510	- 1.423
5400	9.495	76.464	67.905	46.217	59.867	34.031	- 1.377
5500	9.506	76.638	68.063	47.167	59.858	33.557	- 1.333
5600	9.517	76.810	68.217	48.118	59.849	33.075	- 1.291
5700	9.528	76.978	68.370	49.070	59.839	32.601	- 1.250
5800	9.539	77.144	68.519	50.024	59.829	32.122	- 1.210
5900	9.550	77.307	68.667	50.978	59.818	31.643	- 1.172
6000	9.560	77.468	68.812	51.933	59.807	31.163	- 1.135

Dec. 31, 1960; June 30, 1965

NITROGEN MONOFLUORIDE (NF) (IDEAL GAS) MOL. WT. = 33.0051

Ground State Configuration [$^3\Sigma$]

$S^\circ_{298.15}$ = 51.427 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 59.5 ± 8 kcal. mole

$\Delta H^\circ_{f\ 298.15}$ = 59.5 ± 8 kcal. mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1
0	3

ν_e = 1115 cm.$^{-1}$

B_e = [.923] cm.$^{-1}$

$\nu_e x_e$ = [12.175]

α_e = [.0120]

σ = 1

r_e = [1.51 Å]

Heat of Formation.

The heat of formation was obtained by taking an average of two estimates of the dissociation energy of NF. The first estimate of 3.15 e.v. (72.4 kcal./mole) was obtained from W. C. Price, T. R. Passmore and D. M. Roessler Discussions Faraday Soc. 35, 201 - 11 (1963). The second estimate of 70.4 kcal./mole was obtained by taking one-half the dissociation energy of NF_2 (g) calculated from JANAF values. The $\Delta H_{f\ 298.15}$ for NF (g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal./mole.

Heat Capacity and Entropy.

The ν_e value was obtained from infrared studies of D. E. Milligan and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964). The r_e value was estimated from Guggenheimer's relation for single bonded molecules. [K. M. Guggenheimer, Proc. Phys. Soc. (London), 58, 456 (1946)] The anharmonicity constant x_e was estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The α_e value was then calculated using the Morse potential function; B_e was determined from the bond length. The ground state configuration was assumed to be the same as that in NBr. The prinicpal moment of inertia is 3.05247 x 10^{-39} g. cm.^{2}

FN

Nitrosyl Fluoride (ONF)

(Ideal Gas) Mol. Wt. = 49.01

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.558	-15.129	-15.129	INFINITE
100	6.015	49.752	57.371	-1.762	-15.384	-14.340	31.339
200	6.856	55.532	60.147	-.923	-15.583	-13.213	14.438
298	9.883	59.273	59.273	.000	-15.700	-12.023	8.813
300	9.899	59.335	59.274	.018	-15.702	-12.001	8.742
400	10.654	62.291	59.672	1.048	-15.761	-10.756	5.877
500	11.229	64.733	60.447	2.143	-15.786	-9.502	4.153
600	11.686	66.822	61.339	3.290	-15.790	-8.244	3.003
700	12.055	68.652	62.256	4.477	-15.780	-6.987	2.181
800	12.352	70.282	63.159	5.698	-15.763	-5.733	1.566
900	12.591	71.751	64.034	6.946	-15.740	-4.480	1.088
1000	12.784	73.088	64.873	8.215	-15.714	-3.230	.706
1100	12.941	74.314	65.676	9.501	-15.687	-1.983	.394
1200	13.069	75.446	66.444	10.802	-15.659	-.738	.134
1300	13.175	76.496	67.177	12.114	-15.632	.504	-.085
1400	13.263	77.476	67.878	13.437	-15.606	1.744	-.272
1500	13.337	78.394	68.549	14.767	-15.581	2.983	-.435
1600	13.399	79.256	69.192	16.103	-15.559	4.219	-.576
1700	13.452	80.070	69.808	17.446	-15.537	5.455	-.701
1800	13.498	80.840	70.400	18.794	-15.519	6.688	-.812
1900	13.537	81.571	70.968	20.145	-15.504	7.923	-.911
2000	13.571	82.267	71.516	21.501	-15.490	9.156	-1.000
2100	13.600	82.929	72.044	22.859	-15.480	10.387	-1.081
2200	13.626	83.563	72.553	24.221	-15.474	11.618	-1.154
2300	13.649	84.169	73.045	25.585	-15.469	12.849	-1.221
2400	13.670	84.750	73.521	26.951	-15.469	14.082	-1.282
2500	13.688	85.309	73.981	28.318	-15.473	15.311	-1.338
2600	13.704	85.846	74.427	29.688	-15.478	16.544	-1.391
2700	13.718	86.363	74.860	31.059	-15.488	17.775	-1.439
2800	13.731	86.862	75.280	32.432	-15.500	19.008	-1.484
2900	13.743	87.345	75.687	33.805	-15.517	20.242	-1.525
3000	13.754	87.811	76.084	35.180	-15.537	21.474	-1.564
3100	13.763	88.262	76.469	36.556	-15.559	22.708	-1.601
3200	13.772	88.699	76.845	37.933	-15.585	23.942	-1.635
3300	13.780	89.123	77.211	39.310	-15.614	25.178	-1.667
3400	13.788	89.534	77.567	40.689	-15.646	26.414	-1.698
3500	13.794	89.934	77.915	42.068	-15.682	27.652	-1.727
3600	13.801	90.323	78.254	43.448	-15.719	28.893	-1.754
3700	13.806	90.701	78.585	44.828	-15.760	30.131	-1.780
3800	13.812	91.069	78.909	46.209	-15.803	31.375	-1.804
3900	13.817	91.428	79.225	47.590	-15.850	32.613	-1.828
4000	13.821	91.778	79.535	48.972	-15.899	33.857	-1.850
4100	13.825	92.119	79.838	50.355	-15.951	35.101	-1.871
4200	13.829	92.452	80.134	51.737	-16.005	36.348	-1.891
4300	13.833	92.778	80.424	53.121	-16.061	37.597	-1.911
4400	13.837	93.096	80.709	54.504	-16.121	38.844	-1.929
4500	13.840	93.407	80.987	55.888	-16.182	40.093	-1.947
4600	13.843	93.711	81.261	57.272	-16.245	41.346	-1.964
4700	13.846	94.009	81.529	58.656	-16.311	42.599	-1.981
4800	13.848	94.300	81.792	60.041	-16.378	43.855	-1.997
4900	13.851	94.586	82.050	61.426	-16.448	45.108	-2.012
5000	13.853	94.866	82.304	62.811	-16.520	46.363	-2.026
5100	13.855	95.140	82.553	64.197	-16.594	47.622	-2.041
5200	13.857	95.409	82.797	65.582	-16.670	48.882	-2.054
5300	13.859	95.673	83.038	66.968	-16.747	50.146	-2.068
5400	13.861	95.932	83.274	68.354	-16.827	51.406	-2.080
5500	13.863	96.187	83.507	69.740	-16.908	52.672	-2.093
5600	13.865	96.436	83.735	71.127	-16.991	53.936	-2.105
5700	13.866	96.682	83.960	72.513	-17.076	55.204	-2.117
5800	13.868	96.923	84.182	73.900	-17.161	56.475	-2.128
5900	13.869	97.160	84.400	75.287	-17.250	57.742	-2.139
6000	13.871	97.393	84.614	76.674	-17.339	59.016	-2.150

June 30, 1961

NITROSYL FLUORIDE (ONF) (IDEAL GAS) MOL. WT. = 49.01

$\Delta H_{f0}^\circ = -15.1 \pm 0.4$ kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -15.7 \pm 0.4$ kcal. mole^{-1}

Point Group C_s

$S_{298.15}^\circ = 59.273$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
1844.03 (1)
521 (1)
765.85 (1)

Bond lengths and angles: N-O distance = 1.13 Å N-F distance = 1.52 Å O-N-F angle = 110.2°

Moments of inertia: $I_A = 8.8135 \times 10^{-40}$ g. cm.^{2} $I_B = 70.8354 \times 10^{-40}$ g. cm.^{2} $\sigma = 1$

$I_C = 79.8375 \times 10^{-40}$ g. cm.^{2}

Heat of Formation

For the reaction $2NO(g) + F_2(g) \rightarrow 2ONF(g)$, H. S. Johnston and H. J. Bertin, J. Am. Chem. Soc. 81, 6402 (1959), report $\Delta H_{r\ 298.15}^\circ = -74.8 \pm 0.8$ kcal., determined calorimetrically. This yields -15.7 ± 0.4 kcal. mole^{-1} for $\Delta H_{f\ 298.15}^\circ$.

Heat Capacity and Entropy

C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 135 (1952), report the frequencies, obtained from the infrared spectrum, and moments of inertia, obtained from the microwave spectrum.

Nitryl Fluoride (NO_2F)

(Ideal Gas) Mol. Wt. = 65.0039

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.755	-24.589	-24.589	INFINITE
100	8.110	51.770	71.350	-1.958	-25.195	-22.279	48.689
200	9.856	57.847	63.203	-1.071	-25.690	-19.159	20.935
298	11.918	62.177	62.177	.000	-26.000	-15.882	11.641
300	11.953	62.251	62.177	.022	-26.004	-15.820	11.524
400	13.626	65.929	62.668	1.305	-26.166	-12.396	6.773
500	14.903	69.114	63.645	2.734	-26.223	-8.946	3.910
600	15.876	71.921	64.795	4.275	-26.209	-5.491	2.000
700	16.620	74.426	65.995	5.902	-26.150	-2.041	.637
800	17.193	76.685	67.193	7.594	-26.060	1.395	-.381
900	17.638	78.737	68.363	9.336	-25.950	4.821	-1.171
1000	17.987	80.614	69.496	11.118	-25.824	8.234	-1.799
1100	18.265	82.342	70.586	12.931	-25.690	11.632	-2.311
1200	18.488	83.941	71.633	14.769	-25.549	15.020	-2.735
1300	18.669	85.428	72.638	16.627	-25.405	18.395	-3.092
1400	18.819	86.817	73.601	18.502	-25.258	21.759	-3.397
1500	18.942	88.120	74.526	20.390	-25.111	25.112	-3.659
1600	19.046	89.346	75.415	22.290	-24.964	28.455	-3.887
1700	19.134	90.503	76.268	24.199	-24.817	31.791	-4.087
1800	19.209	91.599	77.090	26.116	-24.674	35.115	-4.263
1900	19.273	92.639	77.881	28.040	-24.534	38.435	-4.421
2000	19.328	93.629	78.644	29.970	-24.396	41.745	-4.561
2100	19.376	94.573	79.380	31.906	-24.262	45.049	-4.688
2200	19.419	95.476	80.092	33.845	-24.134	48.344	-4.802
2300	19.456	96.340	80.779	35.789	-24.008	51.636	-4.906
2400	19.488	97.169	81.445	37.736	-23.887	54.923	-5.001
2500	19.518	97.965	82.090	39.687	-23.773	58.202	-5.088
2600	19.544	98.731	82.715	41.640	-23.662	61.480	-5.168
2700	19.567	99.469	83.322	43.595	-23.556	64.754	-5.241
2800	19.588	100.181	83.912	45.553	-23.455	68.022	-5.309
2900	19.606	100.868	84.485	47.513	-23.360	71.292	-5.372
3000	19.623	101.533	85.042	49.474	-23.270	74.552	-5.431
3100	19.639	102.177	85.584	51.437	-23.184	77.811	-5.485
3200	19.653	102.801	86.113	53.402	-23.104	81.066	-5.536
3300	19.666	103.406	86.628	55.368	-23.029	84.319	-5.584
3400	19.678	103.993	87.130	57.335	-22.958	87.573	-5.629
3500	19.688	104.564	87.620	59.303	-22.892	90.820	-5.671
3600	19.698	105.118	88.098	61.273	-22.830	94.073	-5.711
3700	19.707	105.658	88.566	63.243	-22.772	97.319	-5.748
3800	19.716	106.184	89.022	65.214	-22.719	100.564	-5.783
3900	19.724	106.696	89.469	67.186	-22.670	103.805	-5.817
4000	19.731	107.196	89.906	69.159	-22.625	107.045	-5.848
4100	19.738	107.683	90.334	71.132	-22.585	110.288	-5.879
4200	19.744	108.159	90.752	73.107	-22.547	113.527	-5.907
4300	19.750	108.623	91.163	75.081	-22.512	116.773	-5.935
4400	19.755	109.077	91.565	77.057	-22.483	120.009	-5.961
4500	19.760	109.521	91.959	79.032	-22.456	123.247	-5.985
4600	19.765	109.956	92.345	81.009	-22.432	126.486	-6.009
4700	19.770	110.381	92.724	82.985	-22.412	129.722	-6.032
4800	19.774	110.797	93.097	84.963	-22.394	132.962	-6.054
4900	19.778	111.205	93.462	86.940	-22.380	136.191	-6.074
5000	19.782	111.605	93.821	88.918	-22.368	139.427	-6.094
5100	19.785	111.996	94.173	90.896	-22.360	142.666	-6.113
5200	19.788	112.381	94.520	92.875	-22.353	145.898	-6.132
5300	19.791	112.757	94.860	94.854	-22.349	149.143	-6.150
5400	19.794	113.127	95.195	96.833	-22.349	152.371	-6.166
5500	19.797	113.491	95.525	98.813	-22.349	155.609	-6.183
5600	19.800	113.847	95.849	100.793	-22.354	158.845	-6.199
5700	19.802	114.198	96.168	102.773	-22.360	162.078	-6.214
5800	19.805	114.542	96.481	104.753	-22.367	165.321	-6.229
5900	19.807	114.881	96.790	106.734	-22.378	168.549	-6.243
6000	19.809	115.214	97.095	108.715	-22.390	171.788	-6.257

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1965

NITRYL FLUORIDE (NO_2F) (IDEAL GAS) MOL. WT. = 65.0039

Point Group C_{2v}

$S^\circ_{298.15}$ = 62.2 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -24.6 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -26.0 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1312 (1)	1793 (1)
822 (1)	570 (1)
460 (1)	742 (1)

Bond Distance: N-F = 1.40 Å N-O = 1.21 Å

Bond Angle: O-N-O = 129.5° F-N-O = 115.25°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 6.401696 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The heat of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine ($NO_2(g) + 1/2\ F_2(g) = NO_2F(g)$) has been measured calorimetrically as -33.9 kcal. mole^{-1} by J. D. Breazeale and R. O. MacLaren, "Thermochemistry of Oxygen-Fluorine Bonding" (Final Tech. Summary Report, Contract No. Nonr 3433(00), ARPA Order No. 184-62) United Technology Corporation, Sunnyvale, Calif., Mar. 1963. The heat of formation, $\Delta H^\circ_{f\ 298}$ = -26.0 kcal. mole^{-1}, for $NO_2F(g)$ was then derived. The values of $\Delta H^\circ_{f\ 298}$ = -20 ± 5 and -19 ± 2 kcal. mole^{-1} were issued in their second and third quarterly tech. reports, and have been quoted in the literature by E. Tschuikow-Roux, J. Phys. Chem. 66, 1636 (1962).

G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, 1957 quoted ΔH°_f = 26 kcal. mole^{-1} (presumably it has a minus sign) for $NO_2F(g)$ which was derived from the heat of solution measured by Nichols and Robinson, a private communication to Hetherington and Robinson.

Heat Capacity and Entropy.

D. F. Smith and D. W. Magnuson, Phys. Rev. 87, 226(1952), have measured the moments of inertia from microwave spectrum of $NO_2F(g)$. In order to calculate the bond distances, given as N-F = 1.35 Å and N-O = 1.23 Å, the bond angle O-N-O was assumed to be 125°. The selected bond distances and angle were obtained from L. Clayton, Q. Williams and T. Weatherly, J. Chem. Phys. 30, 1328 (1959). Clayton et al. assumed the bond angle O-N-O in $NO_2F(g)$ should be the same as that in $NO_2Cl(g)$, and then calculated the bond distances N-F and N-O from Smith and Magnuson's data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. 52, 145 (1956).

The three principal moments of inertia are I_A = 6.3658 X 10^{-39}, I_B = 7.3383 X 10^{-39} and I_C = 13.7041 X 10^{-39} g. cm.^{2}

Fluorine Nitrate (FNO_3)

(Ideal Gas) Mol. Wt. = 81.008

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.390	4.313	4.313	INFINITE
100	9.870	56.665	81.866	- 2.520	3.424	7.926	- 17.322
200	12.747	64.355	71.325	- 1.394	2.828	12.680	- 13.856
298	15.589	69.988	69.988	.000	2.500	17.594	- 12.896
300	15.638	70.085	69.989	.029	2.496	17.687	- 12.885
400	17.951	74.915	70.632	1.714	2.381	22.774	- 12.443
500	19.687	79.117	71.918	3.600	2.415	27.871	- 12.182
600	20.975	82.826	73.433	5.636	2.547	32.952	- 12.002
700	21.933	86.135	75.015	7.784	2.738	38.005	- 11.865
800	22.654	89.113	76.595	10.015	2.968	43.025	- 11.753
900	23.203	91.814	78.138	12.309	3.223	48.018	- 11.660
1000	23.629	94.282	79.631	14.651	3.496	52.982	- 11.579
1100	23.963	96.550	81.067	17.032	3.778	57.916	- 11.506
1200	24.229	98.647	82.446	19.442	4.067	62.825	- 11.442
1300	24.444	100.595	83.768	21.876	4.358	67.710	- 11.383
1400	24.620	102.414	85.036	24.329	4.652	72.572	- 11.328
1500	24.765	104.117	86.252	26.799	4.945	77.414	- 11.279
1600	24.886	105.720	87.419	29.281	5.236	82.235	- 11.232
1700	24.988	107.231	88.540	31.775	5.527	87.040	- 11.189
1800	25.075	108.662	89.619	34.278	5.811	91.825	- 11.149
1900	25.149	110.020	90.657	36.790	6.091	96.598	- 11.111
2000	25.213	111.312	91.658	39.308	6.367	101.353	- 11.075
2100	25.268	112.543	92.623	41.832	6.638	106.095	- 11.041
2200	25.317	113.720	93.556	44.361	6.899	110.825	- 11.009
2300	25.359	114.846	94.457	46.895	7.157	115.542	- 10.978
2400	25.397	115.926	95.329	49.433	7.408	120.251	- 10.950
2500	25.430	116.964	96.174	51.974	7.649	124.945	- 10.922
2600	25.460	117.962	96.993	54.519	7.885	129.634	- 10.896
2700	25.487	118.923	97.787	57.066	8.114	134.313	- 10.871
2800	25.510	119.850	98.559	59.616	8.335	138.982	- 10.848
2900	25.532	120.746	99.309	62.168	8.549	143.648	- 10.825
3000	25.551	121.612	100.038	64.723	8.755	148.301	- 10.803
3100	25.569	122.450	100.747	67.279	8.956	152.949	- 10.782
3200	25.585	123.262	101.438	69.836	9.148	157.590	- 10.762
3300	25.600	124.049	102.111	72.396	9.334	162.224	- 10.743
3400	25.613	124.814	102.768	74.956	9.512	166.856	- 10.725
3500	25.625	125.557	103.409	77.518	9.685	171.479	- 10.707
3600	25.637	126.279	104.034	80.081	9.852	176.103	- 10.690
3700	25.647	126.981	104.645	82.645	10.012	180.718	- 10.674
3800	25.657	127.665	105.241	85.211	10.167	185.332	- 10.659
3900	25.666	128.332	105.825	87.777	10.316	189.935	- 10.643
4000	25.674	128.982	106.396	90.344	10.459	194.538	- 10.629
4100	25.681	129.616	106.954	92.911	10.596	199.140	- 10.615
4200	25.689	130.235	107.501	95.480	10.730	203.736	- 10.601
4300	25.695	130.839	108.037	98.049	10.859	208.336	- 10.588
4400	25.701	131.430	108.562	100.619	10.982	212.922	- 10.575
4500	25.707	132.008	109.077	103.189	11.100	217.510	- 10.563
4600	25.713	132.573	109.581	105.760	11.216	222.102	- 10.552
4700	25.718	133.126	110.076	108.332	11.325	226.683	- 10.540
4800	25.723	133.667	110.562	110.904	11.432	231.266	- 10.529
4900	25.727	134.198	111.039	113.476	11.535	235.837	- 10.518
5000	25.731	134.718	111.508	116.049	11.634	240.414	- 10.508
5100	25.735	135.227	111.968	118.623	11.729	244.990	- 10.498
5200	25.739	135.727	112.420	121.196	11.822	249.561	- 10.488
5300	25.742	136.217	112.864	123.770	11.911	254.139	- 10.479
5400	25.746	136.698	113.301	126.345	11.997	258.699	- 10.470
5500	25.749	137.171	113.731	128.920	12.081	263.275	- 10.461
5600	25.752	137.635	114.154	131.495	12.160	267.837	- 10.452
5700	25.755	138.091	114.570	134.070	12.237	272.401	- 10.444
5800	25.758	138.539	114.979	136.646	12.312	276.971	- 10.436
5900	25.760	138.979	115.382	139.222	12.384	281.528	- 10.428
6000	25.763	139.412	115.779	141.798	12.453	286.093	- 10.420

March 31, 1963

FLUORINE NITRATE (FNO_3) (IDEAL GAS) MOL. WT. = 81.008

Point Group C_s

$S^\circ_{298.15}$ = [70] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = [4.3 ± 0.5] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 2.5 ± 0.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[1300] (1)	[760] (1)
[800] (1)	[980] (1)
[680] (1)	[370] (1)
[1700] (1)	[130] (1)
[450] (1)	

Bond Distance: O=N = 1.29 ± 0.05 Å N-O' = 1.39 ± 0.05 Å O'-F = 1.42 ± 0.05 Å

Bond Angle: O-N-O = 125° ± 5° F-O'-N = 105° ± 5° σ = 1

Angle between NO'F plane and O_2NO' plane = 90°.

Product of the Moments of Inertia: $I_AI_BI_C = 3.88637 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The value, 2.5 ± 0.5 kcal. mole^{-1}, for the heat of formation of FNO_3(g) was obtained from R. Anderson, et al., "Thermochemistry of Oxygen-Fluorine Bonding," UTC 2002-QT4, United Technology Corporation, Sunnyvale, California, March 1, 1961, through February 28, 1962. The value of ΔH_f° reported by O. G. Talakin, et al., Russ. J. Phys. Chem., 36, 561 (1962) was -4.2 ± 0.9 kcal. mole^{-1} at 294°K.

Heat Capacity and Entropy.

Vibrational frequencies were estimated by comparison with those of HNO_3(g) reported by A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and angles were taken from L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 13 (1937). The three principal moments of inertia are: 8.8598×10^{-39}, 1.8572×10^{-38}, and 2.3618×10^{-38} g. cm.^{2} The possible existence of restricted internal rotation in the molecule was not considered. Thus the values of C_p and S° calculated may be low.

Sodium Fluoride (NaF)

(Crystal) GFW = 41.9882

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.029	-136.953	-136.953	INFINITE
100	5.458	2.645	21.053	-1.841	-137.432	-135.093	295.246
200	9.754	8.032	13.227	-1.039	-137.567	-132.674	144.980
298	11.198	12.240	12.240	.000	-137.520	-130.280	95.498
300	11.215	12.309	12.240	.021	-137.518	-130.235	94.876
400	11.854	15.633	12.689	1.178	-138.090	-127.768	69.809
500	12.252	18.323	13.555	2.384	-138.029	-125.193	54.722
600	12.590	20.587	14.544	3.626	-137.923	-122.635	44.670
700	12.936	22.553	15.550	4.902	-137.779	-120.099	37.497
800	13.315	24.305	16.537	6.214	-137.595	-117.585	32.123
900	13.741	25.897	17.490	7.567	-137.370	-115.097	27.949
1000	14.222	27.370	18.405	8.964	-137.105	-112.636	24.617
1100	14.760	28.750	19.283	10.413	-136.799	-110.205	21.896
1200	15.360	30.059	20.127	11.918	-159.682	-107.345	19.550
1300	16.000	31.314	20.940	13.486	-159.062	-103.008	17.317
1400	16.530	32.520	21.724	15.114	-158.385	-98.722	15.411
1500	16.880	33.674	22.483	16.787	-157.665	-94.485	13.766
1600	17.000	34.768	23.217	18.482	-156.924	-90.297	12.334
1700	17.000	35.799	23.927	20.182	-156.179	-86.154	11.076
1800	17.000	36.770	24.614	21.882	-155.437	-82.058	9.963
1900	17.000	37.689	25.278	23.582	-154.696	-78.000	8.972
2000	17.000	38.561	25.920	25.282	-153.958	-73.983	8.085
2100	17.000	39.391	26.542	26.982	-153.220	-70.004	7.285
2200	17.000	40.182	27.144	28.682	-152.484	-66.058	6.562
2300	17.000	40.937	27.728	30.382	-151.750	-62.147	5.905
2400	17.000	41.661	28.293	32.082	-151.018	-58.265	5.306
2500	17.000	42.355	28.842	33.782	-150.287	-54.418	4.757
2600	17.000	43.022	29.375	35.482	-149.560	-50.596	4.253
2700	17.000	43.663	29.892	37.182	-148.834	-46.804	3.789
2800	17.000	44.281	30.395	38.882	-148.112	-43.040	3.359
2900	17.000	44.878	30.884	40.582	-147.392	-39.297	2.961
3000	17.000	45.454	31.360	42.282	-146.676	-35.584	2.592

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1968

SODIUM FLUORIDE (NaF) (CRYSTAL) GFW = 41.9882

$\Delta Hf^\circ_0 = -136.95 \pm 0.2$ kcal/mol

$S^\circ_{298.15} = 12.24 \pm 0.02$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -137.52 \pm 0.2$ kcal/mol

Tm = 1269 ± 2°K

$\Delta Hm^\circ = 7.97$ kcal/mol

$\Delta Hs^\circ_{298.15} = 68.1$ kcal/mol

Heat of Formation

The heats of solution and reaction of NaF(c) have been determined by many investigators. Incorporating their reported data with auxiliary ΔHf°_{298} values (1, 2), we calculate the corresponding values of ΔHf°_{298}(NaF, c). The results are presented in the table below. The adopted ΔHf°_{298}(NaF, c) is -137.52 ± 0.2 kcal/mol.

Investigator	Reaction*	Temperature, °K	Concentration $NaF \cdot nH_2O$	No. of determination	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
1. Guntz (1884)	A	285	400	1	0.13	-137.42
2. Latimer - Jolly (1953)	A	298	1850	2	0.23 ± 0.01	-137.52
3. Hepler et al. (1953)	A	298	1540	1	0.22 ± 0.01	-137.51
4. Davies - Benson (1965)	A	298	222	1	0.24 ± 0.01	-137.53
5. Thomsen (1882)	B	291	—	2	16.24 ± 0.15	-137.38
6. Wartenberg - Fitzner (1926)	C	293	—	1	-39.3 ± 0.1	-137.62
7. Schmitz - Schumaker (1947)	C	291	—	1	-39.5	-137.82
8. Coughlin (1958)	D	298	—	6	-1.40 ± 0.06	-137.58
9. Vórob'yev - Skuratov (1960)	E	298	—	5	-325.5 ± 2.2	-137.13

*A represents NaF(c) = NaF(n H_2O) and $\Delta Hr^\circ_{298} = \Delta H^\circ_\infty$; B, NaOH(200 H_2O) + HF(200 H_2O) = NaF(401 H_2O) + H_2O(NaF·401 H_2O); C, NaCl(c) + 1/2 F_2(g) = NaF(c) + 1/2 Cl_2(g); D, NaCl(c) + HF(5.716 H_2O) = NaF(c) + HCl(12.731 H_2O); E, 4Na(c) + CF4(g) = 4NaF(c) + C (graphite).

Heat Capacity and Entropy

The low temperature heat capacities, 0.05 - 15°K and 54.01 -295.86°K, were measured by Harrison et al. (10) and King (11), respectively. These two sets of data are joined smoothly with the high temperature heat capacities at 298°K which were derived from the enthalpy measurements, 406.1 - 1282.2°K, determined by O'Brien and Kelley (12). The Cp values above 1282.2°K are obtained by linear extrapolation. S°_{298} is calculated using the adopted low temperature heat capacities and $S^\circ_{54} = 0.555$ eu.

Frank (13) commented that the temperature measurements of O'Brien and Kelley (12) seemed to be about 20°K high at 1000° with a smaller error at lower temperatures. A correction for the assumed error in the temperature measurement was used in the previous JANAF table. However, Douglas and Ditmars (14) have questioned this correction, since new enthalpy data for AlF_3 yielded Cp values in better agreement with the original Cp values of O'Brien and Kelley than with the corrected values of Frank. The α → β transition of AlF_3(c) was found in the range 723 - 6°K, while O'Brien and Kelley selected 727°K based on a point at 728.1°K in the β region and a point at 724.9°K in the pretransition region. Frank's correction yields an error of 9° at 727°K, yet the true error appears to be negligible (≤2°) for AlF_3(c). Based on the above reasoning and the comparison of the Cp curve of NaF(c) with those of NaCl(c), LiCl(c), and LiF(c) in the temperature range 300 - 1300°K, we adopt the high temperature enthalpy data of O'Brien and Kelley without any correction.

The low temperature heat capacities in the temperature ranges 81 - 190 and 198 - 273°K were also measured by Koref (15); and high temperature enthalpies at temperatures 288 - 1073 and 290 - 1287°K were reported by Krestovnikov and Karetnikov (16), and Lyashenko (17), respectively. They are not used for evaluation.

Melting Data

See the NaF(ℓ) table for details.

Heat of Sublimation

ΔHs°_{298} is the difference between ΔHf°_{298} for NaF(g) and NaF(c).

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Sodium Fluoride (NaF)

(Liquid) GFW = 41.9882

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	11.198	17.559	17.559	.000	-130.545	-124.891	91.548
300	11.215	17.629	17.560	.021	-130.543	-124.856	90.957
400	11.854	20.953	18.008	1.178	-131.115	-122.921	67.161
500	12.252	23.642	18.875	2.384	-131.054	-120.878	52.836
600	12.590	25.906	19.863	3.626	-130.948	-118.852	43.292
700	12.936	27.873	20.870	4.902	-130.804	-116.848	36.481
800	13.315	29.624	21.856	6.214	-130.620	-114.866	31.380
900	18.290	31.217	22.809	7.567	-130.395	-112.909	27.418
1000	17.710	33.112	23.747	9.365	-129.729	-111.003	24.260
1100	17.280	34.779	24.676	11.114	-129.122	-109.162	21.688
1200	16.960	36.269	25.581	12.826	-151.799	-106.914	19.472
1300	16.700	37.616	26.456	14.508	-151.065	-103.203	17.350
1400	16.500	38.846	27.297	16.168	-150.356	-99.549	15.540
1500	16.340	39.978	28.105	17.809	-149.667	-95.944	13.979
1600	16.210	41.029	28.881	19.437	-148.994	-92.384	12.619
1700	16.100	42.008	29.624	21.052	-148.334	-88.865	11.424
1800	16.010	42.926	30.338	22.658	-147.686	-85.387	10.367
1900	15.930	43.789	31.024	24.254	-147.049	-81.942	9.426
2000	15.860	44.604	31.682	25.844	-146.421	-78.532	8.582
2100	15.800	45.377	32.316	27.427	-145.800	-75.155	7.821
2200	15.750	46.111	32.927	29.004	-145.187	-71.805	7.133
2300	15.710	46.810	33.515	30.577	-144.579	-68.483	6.507
2400	15.670	47.477	34.083	32.146	-143.978	-65.186	5.936
2500	15.640	48.117	34.632	33.712	-143.382	-61.917	5.413
2600	15.610	48.729	35.162	35.274	-142.792	-58.669	4.932
2700	15.580	49.318	35.676	36.834	-142.207	-55.445	4.488
2800	15.560	49.884	36.173	38.391	-141.628	-52.244	4.078
2900	15.540	50.430	36.655	39.946	-141.053	-49.059	3.697
3000	15.520	50.956	37.123	41.499	-140.484	-45.898	3.344
3100	15.500	51.465	37.578	43.049	-139.921	-42.755	3.014
3200	15.490	51.957	38.020	44.599	-139.362	-39.629	2.707
3300	15.470	52.433	38.449	46.147	-138.811	-36.521	2.419
3400	15.460	52.895	38.867	47.693	-138.265	-33.430	2.149
3500	15.450	53.343	39.275	49.239	-137.727	-30.351	1.895

Dec. 31, 1960; June 30, 1964; Dec. 31, 1968

SODIUM FLUORIDE (NaF) (LIQUID) GFW = 41.9882

$S^\circ_{298.15}$ = 17.559 gibbs/mol

Tm = 1269 ± 2°K

Tb = 2060°K

$\Delta Hf^\circ_{298.15}$ = -130.545 kcal/mol

ΔH°_m = 7.97 kcal/mol

ΔH°_v(to mixture) = 42.1 kcal/mol of NaF(ℓ)

Heat of Formation

ΔHf°_{298}(ℓ) is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{1269} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities of NaF(ℓ) are derived from the enthalpy data, 1287.6 - 1746.5°K, determined by O'Brien and Kelley (1). A glass transition temperature is assumed at 900°K, i.e. the heat capacities below 900°K are taken from those for NaF(c). The Cp values above 1746.5°K are obtained by extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The value of Tm has been reported as (°K): 1313 (2), 1285 (1), 1270 (3, 4, 5), 1269 (6), 1268 (7, 8, 9), 1267 (10, 11, 12), 1265 (13), 1263 (14), and 1253 (15). We select Tm = 1269°K. The value 1285°K reported by O'Brien and Kelley seems unreasonably high and is not adopted. The cause of this discrepancy is still unresolved (17). The heat of melting is calculated as the difference between the adopted enthalpies for NaF(c) and NaF(ℓ) at 1269°K. Kelley (18) derived ΔHm°_{1265} to be 5.82 - 8.43 kcal/mol, based on 13 sets of molten salts equilibrium data involving NaF. The value ΔHm°_{1285} = 8.03 kcal/mol reported by O'Brien and Kelley is not used.

Vaporization Data

Tb is the temperature at which the partial pressures of NaF(g) and Na_2F_2(g) in equilibrium with NaF(ℓ) equal one atmosphere. The vapor composition at Tb is evaluated as NaF 84.8% and Na_2F_2 15.2%. The heat required to vaporize one mole of liquid to form 0.868 mole of vapor mixture of the above composition at Tb is calculated to be 42.1 kcal/mol.

Ruff et al. (16) measured the vapor pressured of NaF(ℓ) in the temperature range of 1699 - 1974°K and reported Tb = 1978°K.

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Sodium Fluoride (NaF)

(Ideal Gas) GFW = 41.9882

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.205	-69.029	-69.029	INFINITE
100	7.016	43.787	58.875	-1.509	-69.000	-70.775	154.679
200	7.643	48.823	52.716	-.779	-69.207	-72.472	79.194
298	8.178	51.983	51.983	.000	-69.420	-74.030	54.265
300	8.185	52.034	51.983	.015	-69.424	-74.058	53.951
400	8.494	54.435	52.308	.851	-70.317	-75.516	41.260
500	8.674	56.351	52.932	1.710	-70.603	-76.782	33.561
600	8.789	57.943	53.638	2.583	-70.866	-77.992	28.409
700	8.868	59.304	54.353	3.466	-71.115	-79.161	24.715
800	8.926	60.493	55.047	4.356	-71.353	-80.294	21.935
900	8.972	61.547	55.712	5.251	-71.586	-81.397	19.766
1000	9.010	62.494	56.344	6.150	-71.819	-82.475	18.025
1100	9.043	63.354	56.943	7.053	-72.059	-83.530	16.596
1200	9.071	64.142	57.510	7.959	-95.541	-84.105	15.318
1300	9.097	64.870	58.049	8.867	-95.581	-83.150	13.979
1400	9.121	65.545	58.560	9.778	-95.621	-82.192	12.831
1500	9.144	66.175	59.047	10.691	-95.660	-81.231	11.835
1600	9.166	66.766	59.511	11.607	-95.699	-80.268	10.964
1700	9.186	67.322	59.955	12.524	-95.737	-79.302	10.195
1800	9.206	67.848	60.379	13.444	-95.775	-78.335	9.511
1900	9.226	68.346	60.785	14.366	-95.812	-77.364	8.899
2000	9.244	68.820	61.175	15.289	-95.850	-76.392	8.348
2100	9.263	69.271	61.550	16.215	-95.887	-75.420	7.849
2200	9.281	69.702	61.911	17.142	-95.924	-74.444	7.395
2300	9.299	70.115	62.258	18.071	-95.961	-73.467	6.981
2400	9.317	70.511	62.594	19.002	-95.998	-72.487	6.601
2500	9.335	70.892	62.918	19.934	-96.035	-71.509	6.251
2600	9.352	71.259	63.232	20.869	-96.073	-70.526	5.928
2700	9.370	71.612	63.536	21.805	-96.111	-69.543	5.629
2800	9.387	71.953	63.831	22.743	-96.151	-68.560	5.351
2900	9.404	72.283	64.116	23.682	-96.191	-67.570	5.092
3000	9.421	72.602	64.394	24.623	-96.235	-66.585	4.851
3100	9.438	72.911	64.664	25.566	-96.279	-65.596	4.625
3200	9.455	73.211	64.926	26.511	-96.325	-64.605	4.412
3300	9.472	73.502	65.182	27.458	-96.375	-63.613	4.213
3400	9.489	73.785	65.431	28.406	-96.428	-62.620	4.025
3500	9.506	74.060	65.673	29.355	-96.485	-61.621	3.848
3600	9.523	74.329	65.910	30.307	-96.546	-60.625	3.680
3700	9.539	74.590	66.141	31.260	-96.612	-59.629	3.522
3800	9.556	74.844	66.367	32.215	-96.683	-58.625	3.372
3900	9.573	75.093	66.587	33.171	-96.762	-57.627	3.229
4000	9.589	75.335	66.803	34.129	-96.847	-56.620	3.094
4100	9.606	75.572	67.014	35.089	-96.941	-55.612	2.964
4200	9.623	75.804	67.220	36.050	-97.044	-54.605	2.841
4300	9.639	76.031	67.423	37.013	-97.156	-53.591	2.724
4400	9.656	76.252	67.621	37.978	-97.281	-52.579	2.612
4500	9.672	76.470	67.815	38.945	-97.418	-51.559	2.504
4600	9.689	76.682	68.006	39.913	-97.570	-50.541	2.401
4700	9.705	76.891	68.192	40.882	-97.737	-49.517	2.303
4800	9.722	77.095	68.376	41.854	-97.922	-48.489	2.208
4900	9.738	77.296	68.556	42.827	-98.127	-47.454	2.117
5000	9.755	77.493	68.733	43.801	-98.354	-46.418	2.029
5100	9.771	77.686	68.906	44.778	-98.603	-45.378	1.945
5200	9.788	77.876	69.077	45.756	-98.878	-44.331	1.863
5300	9.804	78.063	69.245	46.735	-99.182	-43.278	1.785
5400	9.821	78.246	69.410	47.717	-99.516	-42.222	1.709
5500	9.837	78.427	69.572	48.700	-99.883	-41.159	1.636
5600	9.854	78.604	69.732	49.684	-100.285	-40.087	1.564
5700	9.870	78.778	69.889	50.670	-100.724	-39.007	1.496
5800	9.887	78.950	70.044	51.658	-101.203	-37.921	1.429
5900	9.903	79.119	70.196	52.648	-101.725	-36.825	1.364
6000	9.919	79.286	70.346	53.639	-102.291	-35.720	1.301

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1968

SODIUM FLUORIDE (NaF) (IDEAL GAS) GFW = 41.9882

Ground State Configuration $^1\Sigma$

ΔHf°_0 = -69.03 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 51.983 ± 0.002 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -69.42 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 536.10 ± 0.35 cm^{-1} $\omega_e x_e$ = 3.83 ± 0.14 cm^{-1} σ = 1

B_e = 0.4369 cm^{-1} α_e = 0.00456 cm^{-1} r_e = 1.9260 Å

Heat of Formation

The total pressures of NaF(g) and Na_2F_2(g), in equilibrium with NaF(c, ℓ) at temperatures 1020 - 1974°K, have been determined by many investigators, using manometric (1, 2, 5), torsion-effusion (6, 8), Knudsen-effusion (3, 7), transpiration (4), and molecular-beam velocity-selector (9, 10) methods. In order to evaluate ΔHv°(LiF, g) we have used a trial and error variation of ΔHs° and ΔHv° for the monomer and dimer such that the ΔHr°_{298} values derived by the second and third law methods are in reasonable agreement.

Incorporating ΔHs°_{298} = 68.1 and 72.7, and ΔHv°_{298} = 61.12 and 58.75 kcal/mol for NaF and Na_2F_2, respectively, with JANAF functions for NaF(c), NaF(ℓ), NaF(g) and Na_2F_2(g), we derive the partial pressures of NaF monomer from the reported total pressures. Based on the calculated partial pressures of NaF(g), the corresponding heats of vaporization are evaluated by the second and third law methods. Using the third law ΔHr°_{298} and ΔHf°_{298} = -137.52 and -130.545 kcal/mol for NaF(c) and NaF(ℓ), we obtain values of ΔHf°_{298} for NaF(g). The results are presented in the table below. The ΔHf°_{298}(NaF, g) value adopted is -69.42 kcal/mol.

The vapor pressure data reported by Miller and Kusch (9) and Eisenstadt et al. (10) are not consistent with the other sets and are not used for evaluation.

Gaydon (11) and Herzberg (12) reported D°_0 = 114.2 ± 6.9 (4.95 ± 0.3 eV) and ≤ 122.2 kcal/mol (5.3 eV), respectively. Using JANAF ΔHf°_{298} values for Na(g) and F(g), we obtain ΔHf°_{298}(NaF, g) = -70.5 ± 5.8 and ≥ -78.5 kcal/mol. Employing flame-photometric method, Bulewicz et al. (13) and Page and Sugden (14) derived D°_0 = 121 ± 7 and 119 - 120 kcal/mol for NaF(g), which lead to ΔHf°_{298}(NaF, g) = -77.3 ± 7 and -75 to -76 kcal/mol.

	Investigator	Temperature °K	Process**	No. of Points	ΔHr°_{298}, kcal/mol Second law	ΔHr°_{298}, kcal/mol Third law	Drift eu	ΔHf°_{298} kcal/mol
1.	Wartenberg - Schulz (1921)	1669 - 1830	B	5	67.76 ± 0.11	59.90	-4.5 ± 0.1	-70.65
2.	Ruff et al. (1922)	1699 - 1974	B	14	64.07 ± 0.58	59.54	-2.4 ± 0.3	-71.01
3.	Niwa (1938)	1053 - 1112	A	5	63.18 ± 1.04	66.68	3.2 ± 1.0	-70.84
4.	Sense et al. (1957)	1208 - 1265	A	7	71.26 ± 0.63	68.25	-2.4 ± 0.5	-69.27
		1274 - 1348	B	9	65.88 ± 0.76	61.14	-3.6 ± 0.6	-69.41
5.	Cantor - Blankenship (1958)	1381 - 1592	B	6*	66.13	60.84	-3.6	-69.71
6.	Pugh - Barrow (1958)	1023 - 1166	A	7*	68.13	68.14	0.0	-69.38
7.	Porter - Schoonmaker (1958)	1121	A	1	—	68.82	—	-68.70
8.	Entner - Neckel (1967)	1016 - 1236	A	6*	68.54 ± 0.10	67.74	-0.7 ± 0.1	-69.78

* Data points calculated from a given total pressure equation.

** Process A: NaF(c) = NaF(g); B: NaF(ℓ) = NaF(g).

Heat Capacity and Entropy

Veazey and Gordy (15) have measured the rotational transitions of NaF in the millimeter- and sub-millimeter-wave region with a high-resolution molecular-beam absorption spectrometer. The derived values of ω_e, $\omega_e x_e$, B_e, α_e and r_e are adopted here.

Using the molecular beam electric resonance method, Bauer and Lew (16) measured the transition between the J = 0 and J = 1 rotational levels of $Na^{23}F^{19}$ in the three lowest vibrational states. Radio-frequency transitions for $Na^{23}F^{19}$ have been observed by Hollowell et al. (19). Infrared spectra of NaF have been analyzed by Snelson and Pitzer (17), Ritchie and Lew (18), and Baikov and Vasilevskii (20). The molecular constants derived by the above authors are similar to the values adopted, except the value ω_e = 550 cm^{-1} (17) which is different from the value 536.1 cm^{-1} reported by Veazey and Gordy (15).

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Fluorine Monoxide (FO)

(Ideal Gas) GFW = 34.998

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.095	25.998	25.998	INFINITE
100	6.958	44.076	58.080	-1.400	25.998	25.695	-56.155
200	7.029	48.910	52.423	-.703	25.997	25.392	-27.747
298	7.319	51.765	51.765	.000	26.000	25.094	-18.394
300	7.326	51.810	51.765	.014	26.000	25.088	-18.277
400	7.694	53.968	52.057	.765	26.011	24.783	-13.541
500	8.007	55.720	52.619	1.550	26.027	24.474	-10.698
600	8.246	57.202	53.263	2.364	26.047	24.162	-8.801
700	8.426	58.488	53.919	3.198	26.067	23.846	-7.445
800	8.562	59.622	54.563	4.047	26.084	23.527	-6.427
900	8.667	60.637	55.182	4.909	26.101	23.206	-5.635
1000	8.750	61.554	55.774	5.780	26.116	22.884	-5.001
1100	8.818	62.392	56.338	6.658	26.129	22.559	-4.482
1200	8.875	63.161	56.875	7.543	26.141	22.236	-4.050
1300	8.923	63.874	57.387	8.433	26.151	21.909	-3.683
1400	8.965	64.537	57.874	9.328	26.160	21.582	-3.369
1500	9.002	65.156	58.339	10.226	26.168	21.257	-3.097
1600	9.035	65.738	58.783	11.128	26.173	20.929	-2.859
1700	9.066	66.287	59.209	12.033	26.179	20.601	-2.648
1800	9.093	66.806	59.617	12.941	26.181	20.272	-2.461
1900	9.119	67.298	60.008	13.852	26.182	19.944	-2.294
2000	9.144	67.767	60.384	14.765	26.182	19.615	-2.143
2100	9.167	68.213	60.747	15.680	26.180	19.288	-2.007
2200	9.189	68.640	61.096	16.598	26.175	18.959	-1.883
2300	9.210	69.049	61.433	17.518	26.170	18.631	-1.770
2400	9.230	69.442	61.758	18.440	26.162	18.303	-1.667
2500	9.250	69.819	62.073	19.364	26.151	17.975	-1.571
2600	9.269	70.182	62.378	20.290	26.139	17.649	-1.484
2700	9.287	70.532	62.674	21.218	26.126	17.324	-1.402
2800	9.306	70.870	62.961	22.147	26.110	16.998	-1.327
2900	9.324	71.197	63.239	23.079	26.093	16.674	-1.257
3000	9.341	71.514	63.510	24.012	26.073	16.346	-1.191
3100	9.359	71.820	63.773	24.947	26.053	16.024	-1.130
3200	9.376	72.118	64.029	25.884	26.030	15.699	-1.072
3300	9.393	72.406	64.278	26.822	26.006	15.378	-1.018
3400	9.410	72.687	64.522	27.762	25.980	15.056	-.968
3500	9.427	72.960	64.759	28.704	25.953	14.735	-.920
3600	9.444	73.226	64.990	29.648	25.925	14.416	-.875
3700	9.461	73.485	65.216	30.593	25.895	14.096	-.833
3800	9.478	73.737	65.437	31.540	25.865	13.781	-.793
3900	9.495	73.984	65.653	32.489	25.833	13.458	-.754
4000	9.512	74.224	65.865	33.439	25.800	13.144	-.718
4100	9.529	74.459	66.071	34.391	25.766	12.829	-.684
4200	9.547	74.689	66.274	35.345	25.732	12.513	-.651
4300	9.564	74.914	66.472	36.301	25.698	12.200	-.620
4400	9.582	75.134	66.667	37.258	25.661	11.885	-.590
4500	9.600	75.350	66.857	38.217	25.626	11.570	-.562
4600	9.618	75.561	67.044	39.178	25.589	11.260	-.535
4700	9.637	75.768	67.227	40.141	25.552	10.949	-.509
4800	9.656	75.971	67.408	41.105	25.516	10.641	-.484
4900	9.675	76.170	67.584	42.072	25.479	10.331	-.461
5000	9.694	76.366	67.758	43.040	25.442	10.019	-.438
5100	9.714	76.558	67.929	44.011	25.405	9.712	-.416
5200	9.733	76.747	68.096	44.983	25.368	9.404	-.395
5300	9.754	76.933	68.261	45.957	25.332	9.098	-.375
5400	9.774	77.115	68.424	46.934	25.295	8.790	-.356
5500	9.795	77.295	68.583	47.912	25.260	8.485	-.337
5600	9.816	77.471	68.741	48.893	25.224	8.184	-.319
5700	9.838	77.645	68.895	49.876	25.190	7.879	-.302
5800	9.860	77.817	69.048	50.860	25.156	7.573	-.285
5900	9.882	77.985	69.198	51.847	25.122	7.272	-.269
6000	9.904	78.152	69.345	52.837	25.090	6.967	-.254

Dec. 31, 1960; June 30, 1965; Dec. 31, 1966

FLUORINE MONOXIDE (FO) (IDEAL GAS) GFW = 34.998

Ground State Configuration $[^2\Pi]$

$S^\circ_{298.15}$ = 51.77 ± 0.3 gibbs/mol

ΔHf°_0 = [26 ± 10] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [26 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[29000]	[4]

ω_e = 1056 cm^{-1}

$\omega_e x_e$ = [15] cm^{-1}

σ = 1

B_e = [1.148] cm^{-1}

α_e = [0.020] cm^{-1}

r_e = [1.30] Å

Heat of Formation.

Several values have been proposed for the heat of formation of FO(g). V. H. Dibeler, R. M. Reese and J. L. Franklin, J. Chem. Phys. 27, 1296 (1957), obtained D_0(FO,g) = 24 kcal from electron impact studies. However, theoretical estimates give D_0 values in the range 45 - 56 kcal. W. C. Price, T. R. Passmore and D. M. Roessler, Discussions Faraday Soc. 35, 207 (1963), estimated 52 kcal for D_0(FO,g).

From a consideration of the central bond energies in FNNF and HNNH with that in HOOH, using all JANAF values of 101, 109 and 50 kcal, we predict the bond dissociation energy in FO-OF to be 46 ± 4 kcal, which yields D_0(FO,g) = 51 ± 2 kcal. The average F-O bond dissociation energy in F_2O(g) is 49.8 ± 0.5 kcal. Also, since there is one less antibonding electron in FO than in F_2, we should expect the F-O bond to be greater than that in F_2(38 kcal). Thus a median value of D_0(FO,g) = 51.4 ± 10 kcal is adopted here which leads to ΔHf°_{298}(FO) = 26 kcal/mol.

Heat Capacity and Entropy.

The fundamental frequency is obtained by adding $2\omega_e x_e$ to the value reported by A. Arkell, R. R. Reinhard and L. P. Larson, J. Am. Chem. Soc. 87, 1016 (1965), from matrix isolation studies. The bond length was taken equal to that in the isoelectronic molecule O_2^-(g). The value of $\omega_e x_e$ was obtained from the Morse potential function and the assumed dissociation energy. The rotational constant α_e was also estimated from the above parameters and the Morse potential curve. The $^2\Pi$ ground state is that predicted by molecular orbital theory and the first excited state would also be $^2\Pi$. By analogy with the isoelectronic O_2^-(g) states, the first excited level was estimated at 29000 cm^{-1}.

Titanium Oxide Fluoride (TiOF)

(Ideal Gas) Mol. Wt. = 82.9

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.698	- 102.996	- 102.996	INFINITE
100	7.977	49.327	69.127	- 1.980	- 103.116	- 103.742	226.717
200	10.109	55.558	60.002	- 1.069	- 103.352	- 104.275	113.941
298	11.585	59.887	59.887	.000	- 103.540	- 104.682	76.730
300	11.608	59.958	59.887	.021	- 103.543	- 104.689	76.263
400	12.618	63.447	60.356	1.236	- 103.689	- 105.049	57.393
500	13.267	66.337	61.271	2.533	- 103.810	- 105.374	46.057
600	13.690	68.796	62.326	3.882	- 103.927	- 105.676	38.490
700	13.975	70.929	63.406	5.267	- 104.051	- 105.958	33.080
800	14.173	72.809	64.466	6.674	- 104.186	- 106.222	29.017
900	14.315	74.487	65.488	8.099	- 104.331	- 106.467	25.852
1000	14.420	76.001	66.465	9.536	- 104.490	- 106.696	23.317
1100	14.500	77.379	67.395	10.982	- 104.663	- 106.910	21.240
1200	14.562	78.644	68.281	12.436	- 105.798	- 107.068	19.499
1300	14.611	79.811	69.123	13.894	- 105.998	- 107.165	18.015
1400	14.650	80.896	69.926	15.357	- 106.210	- 107.248	16.741
1500	14.682	81.907	70.691	16.824	- 106.434	- 107.314	15.635
1600	14.708	82.856	71.422	18.294	- 106.672	- 107.364	14.665
1700	14.730	83.748	72.121	19.766	- 106.921	- 107.401	13.807
1800	14.749	84.591	72.791	21.240	- 107.183	- 107.422	13.042
1900	14.764	85.388	73.433	22.715	- 107.458	- 107.427	12.356
2000	14.778	86.146	74.050	24.192	- 111.420	- 107.325	11.727
2100	14.789	86.867	74.643	25.671	- 111.659	- 107.113	11.147
2200	14.799	87.556	75.215	27.150	- 111.902	- 106.892	10.618
2300	14.808	88.214	75.766	28.631	- 112.147	- 106.657	10.134
2400	14.816	88.844	76.298	30.112	- 112.396	- 106.414	9.690
2500	14.823	89.449	76.812	31.594	- 112.648	- 106.160	9.280
2600	14.829	90.031	77.309	33.076	- 112.903	- 105.896	8.901
2700	14.834	90.590	77.791	34.560	- 113.161	- 105.621	8.549
2800	14.839	91.130	78.257	36.043	- 113.423	- 105.338	8.222
2900	14.844	91.651	78.710	37.527	- 113.688	- 105.042	7.916
3000	14.848	92.154	79.150	39.012	- 113.956	- 104.742	7.630
3100	14.851	92.641	79.577	40.497	- 114.227	- 104.427	7.362
3200	14.854	93.112	79.993	41.982	- 114.501	- 104.110	7.110
3300	14.857	93.570	80.398	43.468	- 114.778	- 103.779	6.873
3400	14.860	94.013	80.792	44.954	- 115.058	- 103.444	6.649
3500	14.863	94.444	81.175	46.440	- 115.341	- 103.098	6.437
3600	14.865	94.863	91.550	47.926	- 218.088	- 101.299	6.149
3700	14.867	95.270	81.915	49.413	- 218.396	- 98.050	5.791
3800	14.869	95.667	82.272	50.900	- 218.721	- 94.790	5.451
3900	14.871	96.053	82.620	52.387	- 219.062	- 91.528	5.129
4000	14.872	96.429	82.961	53.874	- 219.418	- 88.255	4.822
4100	14.874	96.797	83.294	55.361	- 219.790	- 84.970	4.529
4200	14.875	97.155	83.620	56.848	- 220.176	- 81.678	4.250
4300	14.877	97.505	83.939	58.336	- 220.575	- 78.374	3.983
4400	14.878	97.847	84.251	59.824	- 220.989	- 75.063	3.728
4500	14.879	98.181	84.557	61.312	- 221.415	- 71.740	3.484
4600	14.880	98.508	84.856	62.800	- 221.853	- 68.408	3.250
4700	14.881	98.828	85.150	64.288	- 222.305	- 65.069	3.026
4800	14.882	99.142	85.438	65.776	- 222.767	- 61.716	2.810
4900	14.883	99.449	85.721	67.264	- 223.240	- 58.361	2.603
5000	14.884	99.749	85.999	68.752	- 223.723	- 54.992	2.404
5100	14.885	100.044	86.271	70.241	- 224.217	- 51.613	2.212
5200	14.885	100.333	86.539	71.729	- 224.720	- 48.222	2.027
5300	14.886	100.617	86.802	73.218	- 225.231	- 44.817	1.848
5400	14.887	100.895	87.060	74.707	- 225.751	- 41.413	1.676
5500	14.887	101.168	87.314	76.195	- 226.278	- 37.991	1.510
5600	14.888	101.436	87.564	77.684	- 226.813	- 34.567	1.349
5700	14.889	101.700	87.810	79.173	- 227.355	- 31.132	1.194
5800	14.889	101.959	88.052	80.662	- 227.903	- 27.683	1.043
5900	14.890	102.213	88.290	82.151	- 228.456	- 24.227	.897
6000	14.890	102.464	88.524	83.640	- 229.015	- 20.756	.756

Sept. 30, 1963

TITANIUM OXIDE FLUORIDE (TiOF) (IDEAL GAS) MOL. WT. = 82.9

Point Group $[C_{\infty v}]$

$S^\circ_{298.15}$ = [59.887] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = [-103.0] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-103.5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[880] (1)
[300] (2)
[740] (1)

Bond Distances: Ti=O = [1.62] Å Ti-F = [1.74] Å

Bond Angle: O=Ti-F = [180°]

$\sigma = 1$

Rotational Constant: B_0 = [0.1705] cm.$^{-1}$

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as -103 kcal. mole^{-1} by J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moment was 16.419 X 10^{-39} g. cm.^{2}

Monofluorine Dioxide (FO_2)

(Ideal Gas) GFW = 50.9972

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.688	3.442	3.442	INFINITE
100	8.242	51.736	70.617	-1.888	3.200	4.201	-9.181
200	9.611	57.864	62.844	-.996	3.047	5.272	-5.761
298	10.611	61.903	61.903	.000	3.000	6.376	-4.674
300	10.626	61.968	61.903	.020	3.000	6.397	-4.660
400	11.319	65.125	62.329	1.119	3.003	7.530	-4.114
500	11.843	67.710	63.154	2.278	3.027	8.660	-3.785
600	12.247	69.907	64.101	3.483	3.062	9.783	-3.563
700	12.559	71.819	65.070	4.724	3.099	10.901	-3.403
800	12.800	73.512	66.021	5.993	3.137	12.012	-3.281
900	12.986	75.031	66.940	7.282	3.174	13.119	-3.186
1000	13.132	76.407	67.819	8.589	3.211	14.223	-3.108
1100	13.248	77.665	68.657	9.908	3.245	15.321	-3.044
1200	13.341	78.821	69.457	11.238	3.279	16.419	-2.990
1300	13.416	79.892	70.219	12.576	3.308	17.513	-2.944
1400	13.478	80.889	70.946	13.920	3.335	18.603	-2.904
1500	13.529	81.821	71.640	15.271	3.359	19.693	-2.869
1600	13.572	82.695	72.304	16.626	3.380	20.782	-2.839
1700	13.608	83.519	72.940	17.985	3.398	21.869	-2.812
1800	13.639	84.298	73.549	19.347	3.410	22.954	-2.787
1900	13.665	85.036	74.135	20.713	3.419	24.040	-2.765
2000	13.688	85.738	74.697	22.080	3.423	25.124	-2.745
2100	13.708	86.406	75.239	23.450	3.423	26.210	-2.728
2200	13.725	87.044	75.761	24.822	3.416	27.295	-2.711
2300	13.740	87.654	76.265	26.195	3.406	28.381	-2.697
2400	13.754	88.239	76.752	27.570	3.389	29.469	-2.684
2500	13.766	88.801	77.223	28.946	3.367	30.553	-2.671
2600	13.776	89.341	77.679	30.323	3.340	31.643	-2.660
2700	13.786	89.861	78.120	31.701	3.308	32.733	-2.650
2800	13.794	90.363	78.549	33.080	3.271	33.821	-2.640
2900	13.802	90.847	78.964	34.460	3.227	34.916	-2.631
3000	13.809	91.315	79.368	35.840	3.178	36.007	-2.623
3100	13.815	91.768	79.761	37.222	3.126	37.103	-2.616
3200	13.821	92.207	80.143	38.603	3.067	38.198	-2.609
3300	13.826	92.632	80.515	39.986	3.004	39.297	-2.603
3400	13.831	93.045	80.878	41.369	2.935	40.398	-2.597
3500	13.835	93.446	81.231	42.752	2.862	41.501	-2.591
3600	13.839	93.836	81.576	44.136	2.786	42.607	-2.587
3700	13.843	94.215	81.912	45.520	2.704	43.715	-2.582
3800	13.846	94.584	82.241	46.904	2.618	44.827	-2.578
3900	13.850	94.944	82.562	48.289	2.529	45.934	-2.574
4000	13.853	95.295	82.876	49.674	2.435	47.047	-2.571
4100	13.855	95.637	83.183	51.060	2.337	48.164	-2.567
4200	13.858	95.971	83.484	52.445	2.236	49.282	-2.564
4300	13.860	96.297	83.778	53.831	2.132	50.408	-2.562
4400	13.863	96.615	84.066	55.217	2.023	51.532	-2.560
4500	13.865	96.927	84.348	56.604	1.912	52.656	-2.557
4600	13.867	97.232	84.625	57.990	1.798	53.787	-2.555
4700	13.868	97.530	84.896	59.377	1.679	54.919	-2.554
4800	13.870	97.822	85.163	60.764	1.560	56.054	-2.552
4900	13.872	98.108	85.424	62.151	1.437	57.187	-2.551
5000	13.873	98.388	85.681	63.538	1.311	58.326	-2.549
5100	13.875	98.663	85.932	64.926	1.183	59.468	-2.548
5200	13.876	98.932	86.180	66.313	1.052	60.613	-2.547
5300	13.877	99.197	86.423	67.701	.920	61.761	-2.547
5400	13.878	99.456	86.662	69.089	.784	62.906	-2.546
5500	13.880	99.711	86.897	70.477	.648	64.060	-2.546
5600	13.881	99.961	87.128	71.865	.508	65.213	-2.545
5700	13.882	100.207	87.355	73.253	.366	66.366	-2.545
5800	13.883	100.448	87.579	74.641	.223	67.532	-2.545
5900	13.884	100.685	87.799	76.029	.078	68.692	-2.545
6000	13.884	100.919	88.016	77.418	.069	69.855	-2.544

Sept. 30, 1966

MONOFLUORINE DIOXIDE (FO_2) (IDEAL GAS) GFW = 50.9972

Point Group C_s

$S°_{298.15}$ = 61.9 gibbs/mol

Ground State Quantum Weight = 2

$\Delta Hf°_0$ = 3.4 ± 5 kcal/mol

$\Delta Hf°_{298.15}$ = 3.0 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
1495.0	(1)
584.5	(1)
376.0	(1)

Bond Distance: O-O = 1.22 Å O-F = 1.58 Å

Bond Angle: O-O-F = 109.5° $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 7.7504 \times 10^{-116}\ g^3cm^6$

Heat of Formation.

The heat of formation for $FO_2(g)$ is unavailable in the literature. Based on a kinetic study of the thermal decomposition of $F_2O_2(g)$ reported by H. J. Schumacher and P. Frisch, Z. physik. Chem. B24, 332 (1934), the enthalpy change for the reaction $F_2O_2(g) = F(g) + O_2F(g)$ was estimated to be + 17.3 kcal/mol by J. B. Levy and B. K. Wesley, J. Phys. Chem. 69, 408 (1965), assuming that the activation energy for the reverse reaction is negligible. From this data the value of $\Delta Hf°_{298.15}(FO_2,\ g)$ was calculated as + 3.2 kcal/mol, using $\Delta Hf°_{298.15}$ = + 4.73 kcal/mol for $F_2O_2(g)$ determined calorimetrically by A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc. 81, 6398 (1959).

Based on the assumption that the enthalpy change for the reaction $F_2O_2(g) = F(g) + O_2F(g)$ is 16.5 kcal/mol, which is half of the enthalpy change for the reaction $F_2O_2(g) = 2F(g) + O_2(g)$, the heat of formation ($\Delta Hf°_{298.15}$) for $FO_2(g)$ was derived as + 2.4 kcal/mol.

The value of $\Delta Hf°_{298.15}(FO_2,g)$ adopted is 3 ± 5 kcal/mol.

Heat Capacity and Entropy.

The vibrational frequencies for FOO(g) were assumed to be the same as those obtained from matrix isolation by P. N. Noble and G. C. Pimentel, J. Chem. Phys. 44, 3641 (1966). These authors have observed two more frequencies for isotopically substituted FOO and combined them with those observed by R. D. Spratley, J. J. Turner and G. C. Pimentel, J. Chem. Phys. 44, 2063 (1966), and performed a normal coordinate analysis. The results confirm the fact that the bond distances and angles in FOO are essentially the same as those reported for $F_2O_2(g)$ by R. H. Jackson, J. Chem. Soc., 4585 (1962). The same molecular structure for FOO was also deduced from electron spin resonance and electron paramagnetic resonance data reported by R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 44, 434 (1966) and P. H. Kasai and A. D. Kirschenbaum, J. Am. Chem. Soc. 87, 3069 (1965), respectively. Hence this molecular structure was adopted. Two vibrational frequencies, ν_1 and ν_3, for FOO molecule were also observed by A. Arkell, J. Am. Chem. Soc. 87, 4057 (1965).

The three principal moments of inertia are: $I_A = 1.1103 \times 10^{-39}$, $I_B = 7.8182 \times 10^{-39}$ and $I_C = 8.9285 \times 10^{-39}$ g cm^2.

Phosphorus Monofluoride (PF)

(Ideal Gas) Mol. Wt. = 49.975 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.117	-14.200	-14.200	INFINITE
100	6.959	45.962	60.183	-1.422	-13.944	-16.356	35.743
200	7.135	50.819	54.421	-.720	-13.910	-18.795	20.538
298	7.557	53.744	53.744	.000	-14.000	-21.177	15.522
300	7.566	53.791	53.744	.014	-14.002	-21.221	15.459
400	7.956	56.023	54.046	.791	-14.143	-23.606	12.897
500	8.277	57.831	54.628	1.601	-14.307	-25.955	11.344
600	8.430	59.350	55.291	2.435	-14.490	-28.268	10.296
700	8.566	60.661	55.967	3.286	-14.698	-30.548	9.537
800	8.664	61.811	56.627	4.147	-35.353	-38.107	10.410
900	8.737	62.836	57.261	5.017	-35.357	-38.450	9.337
1000	8.794	63.760	57.865	5.894	-35.361	-38.794	8.478
1100	8.839	64.600	58.440	6.776	-35.367	-39.138	7.776
1200	8.876	65.371	58.986	7.662	-35.372	-39.481	7.190
1300	8.907	66.082	59.505	8.551	-35.379	-39.822	6.694
1400	8.933	66.743	59.999	9.443	-35.385	-40.163	6.269
1500	8.956	67.361	60.469	10.337	-35.392	-40.503	5.901
1600	8.976	67.939	60.918	11.234	-35.400	-40.845	5.579
1700	8.994	68.484	61.347	12.132	-35.409	-41.184	5.294
1800	9.011	68.998	61.758	13.033	-35.417	-41.525	5.042
1900	9.026	69.486	62.152	13.935	-35.426	-41.863	4.815
2000	9.041	69.949	62.530	14.838	-35.436	-42.202	4.611
2100	9.054	70.391	62.894	15.743	-35.447	-42.540	4.427
2200	9.067	70.812	63.245	16.649	-35.458	-42.877	4.259
2300	9.079	71.216	63.583	17.556	-35.469	-43.215	4.106
2400	9.091	71.602	63.909	18.465	-35.482	-43.553	3.966
2500	9.102	71.974	64.224	19.374	-35.494	-43.887	3.836
2600	9.113	72.331	64.529	20.285	-35.508	-44.224	3.717
2700	9.123	72.675	64.824	21.197	-35.521	-44.558	3.607
2800	9.133	73.007	65.111	22.110	-35.535	-44.892	3.504
2900	9.143	73.328	65.389	23.023	-35.549	-45.225	3.408
3000	9.153	73.638	65.658	23.938	-35.565	-45.560	3.319
3100	9.163	73.938	65.921	24.854	-35.580	-45.892	3.235
3200	9.172	74.229	66.176	25.771	-35.597	-46.226	3.157
3300	9.181	74.511	66.424	26.688	-35.613	-46.557	3.083
3400	9.191	74.786	66.666	27.607	-35.631	-46.889	3.014
3500	9.200	75.052	66.902	28.527	-35.648	-47.218	2.948
3600	9.209	75.312	67.132	29.447	-35.666	-47.550	2.887
3700	9.218	75.564	67.356	30.368	-35.685	-47.880	2.828
3800	9.227	75.810	67.576	31.290	-35.704	-48.207	2.772
3900	9.235	76.050	67.790	32.214	-35.724	-48.536	2.720
4000	9.244	76.284	67.999	33.138	-35.744	-48.866	2.670
4100	9.253	74.512	68.204	34.062	-35.765	-49.194	2.622
4200	9.261	76.735	68.405	34.988	-35.786	-49.519	2.577
4300	9.270	76.953	68.601	35.915	-35.808	-49.848	2.533
4400	9.278	77.166	68.793	36.842	-35.831	-50.171	2.492
4500	9.287	77.375	68.981	37.770	-35.854	-50.498	2.452
4600	9.295	77.579	69.166	38.699	-35.876	-50.827	2.415
4700	9.304	77.779	69.347	39.629	-35.900	-51.150	2.378
4800	9.312	77.975	69.525	40.560	-35.925	-51.472	2.343
4900	9.320	78.167	69.699	41.492	-35.949	-51.794	2.310
5000	9.329	78.356	69.871	42.424	-35.975	-52.117	2.278
5100	9.337	78.540	70.039	43.357	-36.002	-52.443	2.247
5200	9.345	78.722	70.204	44.291	-36.028	-52.765	2.218
5300	9.353	78.900	70.367	45.226	-36.055	-53.085	2.189
5400	9.362	79.075	70.526	46.162	-36.082	-53.409	2.161
5500	9.370	79.247	70.683	47.099	-36.110	-53.727	2.135
5600	9.378	79.415	70.838	48.036	-36.139	-54.047	2.109
5700	9.386	79.582	70.990	48.974	-36.168	-54.366	2.084
5800	9.394	79.745	71.139	49.913	-36.197	-54.687	2.061
5900	9.403	79.905	71.286	50.853	-36.227	-55.006	2.037
6000	9.411	80.064	71.431	51.794	-36.258	-55.323	2.015

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Monofluoride (PF) (Ideal Gas)

Mol. Wt. = 49.975

$\Delta H_f^\circ{}_{298.16} = -14 \pm 3$ kcal. mole^{-1}

$S^\circ_{298.15} = 53.7$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^3\Sigma$

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_1
0	3

$\omega_e = 846.75$ cm.$^{-1}$ $\omega_e x_e = 4.489$ cm.$^{-1}$ $B_e = 0.5665$ cm.$^{-1}$

$\alpha_e = 0.00456$ cm.$^{-1}$ $r_e = 1.590$ Å $\sigma = 1$

Heat of Formation. $\Delta H_f^\circ{}_{298.15}$ was derived from a D_0° calculated with spectroscopic constants reported by A. E. Douglas and M. Frackowiak, Can. J. Phys. 40, 832 (1962). The D_0° value was calculated using the dissociation and spectroscopic relations given by G. Herzberg in "Spectra of Diatomic Molecules", D. van Nostrand Co., N. Y., 2nd Ed. (1950) pages 93 and 100. If the PF molecule dissociates to the ground state atoms, $P(^4S_{3/2}) + F(^2P_{3/2})$, the corresponding $\Delta H_f^\circ{}_{298.15}$ is -15 ± 3 kcal. mole^{-1}. If the dissociation is to the phosphorus ground state and the excited fluorine state, $P(^4S_{3/2}) + F(^2P_{1/2})$, the corresponding $\Delta H_f^\circ{}_{298.15}$ is -14 ± 3 kcal. mole^{-1}. The dissociation to an excited $F(^2P_{1/2})$ atom was assumed to obtain the selected $\Delta H_f^\circ{}_{298.15} = -14 \pm 3$ kcal. mole^{-1}.

The heat of formation was estimated to be -17 kcal. mole^{-1} by J. S. Gordon, "Thermodynamic Data for Combustion Products", January, 1960, Thiokol Chemical Corp. This estimate when changed from white(α) to red(V) phosphorus reference state (-13 kcal. mole^{-1}) agrees within uncertainty limits with the derived $\Delta H_f^\circ{}_{298.15}$ values.

Heat Capacity and Entropy. The molecular constants were reported by Douglas and Frackowiak (loc. cit.). They photographed and analyzed the electronic spectra of PF in the emission spectrum of a discharge through a mixture of PF_3 and He.

Phosphorus Sulfide Fluoride (PSF)

(Ideal Gas) Mol. Wt. = 82.041 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.654	- 36.684	- 35.584	INFINITE
100	8.165	56.356	74.924	- 1.856	- 36.488	- 39.644	86.638
200	9.371	62.368	67.283	- .983	- 36.676	- 42.747	46.710
298	10.621	66.350	66.350	.000	- 37.000	- 45.660	33.468
300	10.642	66.416	66.350	.020	- 37.006	- 45.713	33.300
400	11.590	69.615	66.780	1.134	- 37.909	- 48.540	26.519
500	12.228	72.275	67.520	2.327	- 38.628	- 51.114	22.341
600	12.652	74.545	68.590	3.573	- 39.257	- 53.551	19.505
700	12.942	76.518	69.585	4.853	- 39.835	- 55.863	17.440
800	13.146	78.260	70.562	6.158	- 73.871	- 64.694	17.673
900	13.293	79.817	71.506	7.481	- 73.860	- 63.546	15.430
1000	13.402	81.224	72.408	8.816	- 73.848	- 62.401	13.637
1100	13.485	82.505	73.269	10.160	- 73.833	- 61.259	12.170
1200	13.550	83.682	74.088	11.512	- 73.817	- 60.116	10.948
1300	13.601	84.768	74.869	12.870	- 73.800	- 58.973	9.914
1400	13.642	85.778	75.612	14.232	- 73.783	- 57.833	9.028
1500	13.676	86.720	76.322	15.598	- 73.767	- 56.695	8.260
1600	13.704	87.604	76.999	16.967	- 73.750	- 55.558	7.588
1700	13.727	88.435	77.648	18.338	- 73.735	- 54.420	6.996
1800	13.746	89.220	78.269	19.712	- 73.720	- 53.286	6.470
1900	13.763	89.964	78.865	21.088	- 73.705	- 52.149	5.998
2000	13.777	90.670	79.438	22.465	- 73.693	- 51.017	5.575
2100	13.789	91.343	79.989	23.843	- 73.682	- 49.884	5.191
2200	13.800	91.985	80.520	25.222	- 73.672	- 48.749	4.843
2300	13.809	92.598	81.032	26.603	- 73.663	- 47.618	4.525
2400	13.817	93.186	81.526	27.984	- 73.655	- 46.486	4.233
2500	13.825	93.750	82.004	29.366	- 73.648	- 45.352	3.965
2600	13.831	94.293	82.466	30.749	- 73.643	- 44.222	3.717
2700	13.837	94.815	82.914	32.132	- 73.640	- 43.091	3.488
2800	13.842	95.318	83.348	33.516	- 73.637	- 41.961	3.275
2900	13.847	95.804	83.769	34.901	- 73.636	- 40.828	3.077
3000	13.851	96.273	84.178	36.286	- 73.637	- 39.696	2.892
3100	13.854	96.728	84.576	37.671	- 73.638	- 38.565	2.719
3200	13.858	97.168	84.962	39.057	- 73.643	- 37.435	2.557
3300	13.861	97.594	85.339	40.442	- 73.647	- 36.304	2.404
3400	13.864	98.008	85.705	41.829	- 73.654	- 35.170	2.261
3500	13.867	98.410	86.063	43.215	- 73.562	- 34.040	2.125
3600	13.869	98.800	86.411	44.602	- 73.671	- 32.908	1.998
3700	13.871	99.180	86.751	45.989	- 73.683	- 31.775	1.877
3800	13.873	99.550	87.083	47.376	- 73.695	- 30.640	1.762
3900	13.875	99.911	87.407	48.764	- 73.710	- 29.508	1.654
4000	13.877	100.262	87.724	50.151	- 73.725	- 28.374	1.550
4100	13.879	100.605	88.034	51.539	- 73.742	- 27.241	1.452
4200	13.880	100.939	88.338	52.927	- 73.762	- 26.103	1.358
4300	13.881	101.266	88.634	54.315	- 73.781	- 24.971	1.269
4400	13.883	101.585	88.925	55.703	- 73.804	- 23.833	1.184
4500	13.884	101.897	89.210	57.092	- 73.828	- 22.697	1.102
4600	13.885	102.202	89.489	58.480	- 73.852	- 21.565	1.025
4700	13.886	102.501	89.763	59.869	- 73.879	- 20.427	.950
4800	13.887	102.793	90.031	61.257	- 73.908	- 19.289	.878
4900	13.888	103.079	90.295	62.646	- 73.937	- 18.145	.809
5000	13.889	103.360	90.553	64.035	- 73.969	- 17.009	.743
5100	13.890	103.635	90.807	65.424	- 74.003	- 15.871	.680
5200	13.891	103.905	91.056	66.813	- 74.037	- 14.730	.619
5300	13.891	104.169	91.301	68.202	- 74.073	- 13.589	.560
5400	13.892	104.429	91.542	69.591	- 74.111	- 12.449	.504
5500	13.893	104.684	91.778	70.980	- 74.150	- 11.304	.449
5600	13.893	104.934	92.011	72.370	- 74.192	- 10.161	.397
5700	13.894	105.180	92.240	73.759	- 74.235	- 9.018	.346
5800	13.895	105.422	92.465	75.149	- 74.279	- 7.874	.297
5900	13.895	105.659	92.687	76.538	- 74.324	- 6.733	.249
6000	13.896	105.893	92.905	77.928	- 74.372	- 5.582	.203

Dec. 31, 1960; Sept. 30, 1962

PHOSPHORUS SULFIDE FLUORIDE (PSF) (Ideal Gas)

Mol. Wt. = 82.041

ΔH_f° 298.15 = [-37 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = [66.35 ± 3] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$
[940] (1)
[740] (1)
[400] (1)

Product of the Moments of Inertia: $I_A I_B I_C$ = [7.999 X 10^{-114}] g.^{3} cm.^{6} $\sigma = 1$

Heat of Formation. The ΔH_f° 298.15 was estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Virginia, "Survey of Thermochemical Data," January, 1960. This estimated ΔH_f 298.15 was corrected for the change in the reference state of phosphorus from white α to red V.

Heat Capacity and Entropy. The vibrational frequencies were estimated by comparison with the corresponding frequencies of PF(g), PS(g), and PF_2(g). The vibrational levels of PF_2(g) in turn were estimated by J. S. Gordon, Thiokol Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products," January, 1960. The entropy was estimated by C. B. Henderson and R. S. Scheffee (loc. cit.). The product of the moment of inertia was derived from the estimated entropy.

Lead Monofluoride (PbF)

(Ideal Gas) Mol. Wt. = 226.21 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.215	- 8.516	- 8.516	INFINITE
100	7.033	51,377	66.568	- 1.519	- 8.591	- 10.813	23.631
200	7.705	56,444	60.364	- .784	- 8.809	- 12.949	14.149
298	8.224	59,627	59.627	.000	- 9.000	- 14.939	10.950
300	8.231	59,678	59.627	.015	- 9.004	- 14.976	10.909
400	8.517	62,089	59.954	.854	- 9.202	- 16.936	9.253
500	8.680	64,008	60.579	1.715	- 9.418	- 18.847	8.238
600	8.781	65,601	61.287	2.588	- 9.650	- 20.710	7.543
700	8.849	66,960	62.003	3.470	- 11.064	- 22.343	6.975
800	8.899	68,145	62.698	4.357	- 11.331	- 23.936	6.539
900	8.937	69,195	63.363	5.249	- 11.591	- 25.496	6.191
1000	8.968	70,138	63.994	6.144	- 11.844	- 27.028	5.907
1100	8.997	70,994	64.592	7.043	- 12.091	- 28.535	5.669
1200	9.024	71,778	65.159	7.944	- 12.329	- 30.018	5.467
1300	9.052	72,502	65.696	8.847	- 12.563	- 31.482	5.292
1400	9.081	73,174	66.206	9.754	- 12.795	- 32.930	5.140
1500	9.113	73,801	66.692	10.664	- 13.025	- 34.358	5.006
1600	9.149	74,391	67.155	11.577	- 13.256	- 35.774	4.886
1700	9.188	74,946	67.597	12.494	- 13.487	- 37.173	4.779
1800	9.230	75,473	68.020	13.415	- 13.721	- 38.562	4.682
1900	9.275	75,973	68.426	14.340	- 13.956	- 39.936	4.593
2000	9.323	76,450	68.815	15.270	- 14.193	- 41.296	4.512
2100	9.373	76,906	69.190	16.204	- 56.881	- 41.093	4.276
2200	9.424	77,343	69.550	17.144	- 57.028	- 40.339	4.007
2300	9.477	77,763	69.898	18.089	- 57.191	- 39.576	3.760
2400	9.529	78,168	70.234	19.040	- 57.372	- 38.806	3.534
2500	9.582	78,558	70.560	19.995	- 57.572	- 38.030	3.324
2600	9.635	78,935	70.875	20.956	- 57.789	- 37.243	3.130
2700	9.686	79,299	71.180	21.922	- 58.021	- 36.448	2.950
2800	9.737	79,652	71.476	22.893	- 58.271	- 35.645	2.782
2900	9.786	79,995	71.764	23.869	- 58.536	- 34.831	2.625
3000	9.833	80,327	72.044	24.850	- 58.816	- 34.010	2.478
3100	9.878	80,651	72.316	25.836	- 59.107	- 33.179	2.339
3200	9.921	80,965	72.582	26.826	- 59.412	- 32.338	2.208
3300	9.962	81,271	72.840	27.820	- 59.725	- 31.486	2.085
3400	10.001	81,569	73.093	28.818	- 60.047	- 30.625	1.968
3500	10.038	81,859	73.339	29.820	- 60.377	- 29.755	1.858
3600	10.072	82,142	73.580	30.826	- 60.712	- 28.874	1.753
3700	10.104	82,419	73.815	31.834	- 61.053	- 27.985	1.653
3800	10.134	82,689	74.045	32.846	- 61.395	- 27.085	1.558
3900	10.163	82,952	74.270	33.861	- 61.740	- 26.179	1.467
4000	10.189	83,210	74.490	34.879	- 62.086	- 25.266	1.380
4100	10.213	83,462	74.706	35.899	- 62.432	- 24.340	1.297
4200	10.235	83,708	74.917	36.921	- 62.777	- 23.405	1.218
4300	10.256	83,949	75.125	37.946	- 63.121	- 22.465	1.142
4400	10.275	84,185	75.328	38.972	- 63.462	- 21.514	1.069
4500	10.292	84,416	75.527	40.001	- 63.800	- 20.559	.998
4600	10.308	84,643	75.723	41.031	- 64.136	- 19.593	.931
4700	10.323	84,865	75.915	42.062	- 64.467	- 18.624	.866
4800	10.337	85,082	76.104	43.095	- 64.795	- 17.640	.803
4900	10.349	85,295	76.289	44.130	- 65.118	- 16.657	.743
5000	10.360	85,505	76.472	45.165	- 65.438	- 15.666	.685
5100	10.370	85,710	76.651	46.202	- 65.753	- 14.668	.629
5200	10.379	85,911	76.827	47.239	- 66.064	- 13.660	.574
5300	10.388	86,109	77.000	48.278	- 66.370	- 12.648	.522
5400	10.396	86,303	77.171	49.317	- 66.674	- 11.633	.471
5500	10.402	86,494	77.338	50.357	- 66.973	- 10.613	.422
5600	10.409	86,682	77.504	51.397	- 67.268	- 9.583	.374
5700	10.415	86,866	77.666	52.438	- 67.560	- 8.553	.328
5800	10.420	87,047	77.826	53.480	- 67.848	- 7.512	.283
5900	10.425	87,225	77.984	54.522	- 68.135	- 6.472	.240
6000	10.429	87,401	78.140	55.565	- 68.418	- 5.427	.198

June 30, 1962

Lead Monofluoride (PbF) (Ideal Gas)

Mol. Wt. = 226.21

ΔH_f° 298.15 = -9.0 ± 9.2 kcal. mole^{-1}

$S^\circ_{298.15}$ = 59.627 cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi$

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_1
0	2
8266	2

ω_e = 507.2 cm.$^{-1}$ $\omega_e x_e$ = 2.30 cm.$^{-1}$ σ = 1

B_e = [0.2397] cm.$^{-1}$ α_e = [0.0017] cm.$^{-1}$

Heat of Formation. ΔH_f° 298.15 was calculated from the dissociation energy of PbF(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ϵ, ω_e, and $\omega_e x_e$ were given by G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950. B_e and α_e were estimated by J. S. Gordon, Astrosystems, Inc., private communication, May, 1962.

Silicon Monofluoride (SiF)

(Ideal Gas) GFW = 47.0844

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.261	-5.037	-5.037	INFINITE
100	7.830	45.521	60.769	-1.525	-4.712	-7.138	15.600
200	7.616	50.870	54.643	-.755	-4.573	-9.635	10.529
298	7.803	53.937	53.937	.000	-4.600	-12.118	8.883
300	7.809	53.985	53.937	.014	-4.602	-12.165	8.862
400	8.096	56.272	54.247	.810	-4.698	-14.672	8.017
500	8.326	58.104	54.841	1.632	-4.824	-17.151	7.497
600	8.492	59.638	55.516	2.473	-4.967	-19.604	7.141
700	8.611	60.956	56.201	3.328	-5.122	-22.031	6.878
800	8.699	62.112	56.869	4.194	-5.289	-24.437	6.676
900	8.765	63.141	57.510	5.067	-5.464	-26.818	6.512
1000	8.817	64.067	58.120	5.947	-5.653	-29.181	6.378
1100	8.858	64.909	58.700	6.830	-5.850	-31.525	6.263
1200	8.893	65.682	59.250	7.718	-6.056	-33.850	6.165
1300	8.921	66.395	59.772	8.609	-6.272	-36.157	6.079
1400	8.946	67.057	60.269	9.502	-6.497	-38.448	6.002
1500	8.968	67.675	60.743	10.398	-6.732	-40.721	5.933
1600	8.987	68.254	61.194	11.296	-6.976	-42.979	5.871
1700	9.005	68.799	61.626	12.195	-19.224	-45.116	5.800
1800	9.021	69.315	62.039	13.097	-19.433	-46.633	5.662
1900	9.036	69.803	62.435	13.999	-19.643	-48.139	5.537
2000	9.050	70.267	62.815	14.904	-19.852	-49.632	5.424
2100	9.063	70.708	63.180	15.809	-20.061	-51.117	5.320
2200	9.075	71.130	63.532	16.716	-20.271	-52.591	5.224
2300	9.087	71.534	63.871	17.624	-20.480	-54.055	5.136
2400	9.099	71.921	64.199	18.534	-20.690	-55.510	5.055
2500	9.110	72.293	64.515	19.444	-20.900	-56.957	4.979
2600	9.121	72.650	64.821	20.356	-21.110	-58.395	4.909
2700	9.132	72.995	65.117	21.268	-21.320	-59.826	4.843
2800	9.142	73.327	65.405	22.182	-21.529	-61.247	4.781
2900	9.153	73.648	65.683	23.097	-21.740	-62.661	4.722
3000	9.164	73.958	65.954	24.013	-21.950	-64.071	4.668
3100	9.174	74.259	66.217	24.930	-22.160	-65.472	4.616
3200	9.185	74.550	66.473	25.847	-22.371	-66.863	4.567
3300	9.195	74.833	66.722	26.766	-22.582	-68.251	4.520
3400	9.206	75.108	66.965	27.687	-22.792	-69.631	4.476
3500	9.217	75.375	67.201	28.608	-23.003	-71.006	4.434
3600	9.229	75.635	67.432	29.530	-115.174	-70.117	4.257
3700	9.241	75.888	67.657	30.454	-115.285	-68.864	4.068
3800	9.253	76.134	67.877	31.378	-115.397	-67.607	3.888
3900	9.265	76.375	68.092	32.304	-115.509	-66.351	3.718
4000	9.278	76.610	68.302	33.231	-115.621	-65.087	3.556
4100	9.291	76.839	68.507	34.160	-115.734	-63.825	3.402
4200	9.305	77.063	68.708	35.090	-115.846	-62.558	3.255
4300	9.320	77.282	68.905	36.021	-115.957	-61.286	3.115
4400	9.335	77.496	69.098	36.954	-116.069	-60.015	2.981
4500	9.350	77.706	69.287	37.888	-116.179	-58.736	2.853
4600	9.367	77.912	69.472	38.824	-116.289	-57.460	2.730
4700	9.384	78.114	69.654	39.761	-116.399	-56.179	2.612
4800	9.401	78.311	69.832	40.700	-116.508	-54.897	2.500
4900	9.420	78.505	70.007	41.641	-116.616	-53.611	2.391
5000	9.439	78.696	70.179	42.584	-116.723	-52.327	2.287
5100	9.459	78.883	70.348	43.529	-116.829	-51.036	2.187
5200	9.479	79.067	70.514	44.476	-116.934	-49.744	2.091
5300	9.501	79.248	70.677	45.425	-117.037	-48.451	1.998
5400	9.523	79.426	70.837	46.376	-117.140	-47.159	1.909
5500	9.546	79.600	70.995	47.330	-117.242	-45.862	1.822
5600	9.570	79.773	71.150	48.286	-117.342	-44.560	1.739
5700	9.595	79.942	71.303	49.244	-117.442	-43.258	1.659
5800	9.621	80.109	71.453	50.205	-117.540	-41.956	1.581
5900	9.647	80.274	71.602	51.168	-117.637	-40.657	1.506
6000	9.674	80.436	71.747	52.134	-117.732	-39.351	1.433

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1963; Dec. 31, 1969

SILICON MONOFLUORIDE (SiF) (IDEAL GAS) GFW = 47.0844

Ground State Configuration $^2\Pi_r$

$\Delta Hf^\circ_0 = -5.0 \pm 3$ kcal/mol

$S^\circ_{298.15} = 53.937 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -4.6 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X^2\Pi_r$	0	2
	161.93	2
$A^2\Sigma^-$	22787.6	2
$^4\Sigma$	29808.4	4
$B^2\Sigma$	34638.3	2
$C^2\Delta$	39537	4
$C'^2\Pi$	41965	4
$D'^2\Pi$	46607	4
$D^2\Sigma^+$	47491	2

$\omega_e = 857.2 \pm 0.1$ cm^{-1} $\omega_e x_e = 4.74 \pm 0.03$ cm^{-1} $\sigma = 1$

$B_e = 0.58138$ cm^{-1} $\alpha_e = 0.00490$ cm^{-1} $r_e = 1.6008$ Å

Heat of Formation

Ehlert and Margrave (1) have studied mass-spectrometrically the reaction $Si(g) + SiF_2(g) \rightarrow 2SiF(g)$ by monitoring the intensities of the Si^+, SiF_2^+ and SiF^+ ions in an equilibrium system containing CaF_2 and Si. The ionization cross-sections are assumed to cancel so that equilibrium constants can be obtained directly from the ion intensities. We have analysed the above data using present JANAF functions and obtain $\Delta Hr_{298} = 23.5 \pm 3$ kcal by the third law technique with a drift of -0.8 ± 11 eu, the second law value is 23.9 ± 7 kcal. We adopt the third law value which with JANAF auxiliary data gives $\Delta Hf^\circ_{298}(SiF, g) = -4.6 \pm 3$ kcal/mol.

Johns and Barrow (2) have selected $D^\circ_0(SiF, g) = 125 \pm 10$ kcal/mol, from Birge-Sponer extrapolations of several states, this gives $\Delta Hf^\circ_0 = 0.1 \pm 10$ kcal/mol in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants of the various electronic levels have been documented by Johns and Barrow (2), Verma (3), Barrow et al. (4), and Appelblad et al. (5). The approximation involving the use of the ground state constants for all electronic levels is used since it introduces negligible error in this molecule.

References

1. T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 41, 1066 (1964).
2. J. W. C. Johns and R. F. Barrow, Proc. Phys. Soc. (London) 71, 476 (1958).
3. R. D. Verma, Can. J. Phys. 40, 586 (1962).
4. R. F. Barrow, D. Butler, J. W. C. Johns and J. L. Powell, Proc. Phys. Soc. (London) 73, 317 (1959).
5. O. Appelblad, R. F. Barrow, and R. D. Verma, J. Phys. B (Proc. Phys. Soc. (London)) Series 2, 1, 274 (1968).

Titanium Monofluoride (TiF)

(Ideal Gas) GFW = 66.8984

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.208	-16.001	-16.001	INFINITE
100	6.992	48.501	63.625	-1.512	-15.787	-18.405	40.225
200	7.602	53.498	57.438	-.788	-15.871	-21.002	22.950
298	8.446	56.692	56.692	.000	-16.000	-23.497	17.223
300	8.461	56.744	56.692	.016	-16.002	-23.543	17.151
400	9.156	59.279	57.033	.898	-16.123	-26.037	14.226
500	9.636	61.377	57.698	1.840	-16.231	-28.504	12.459
600	9.942	63.163	58.464	2.820	-16.333	-30.950	11.273
700	10.128	64.711	59.248	3.824	-16.440	-33.377	10.421
800	10.236	66.071	60.018	4.843	-16.564	-35.789	9.777
900	10.298	67.281	60.759	5.870	-16.711	-38.183	9.272
1000	10.334	68.368	61.466	6.902	-16.886	-40.560	8.864
1100	10.357	69.354	62.139	7.936	-17.086	-42.917	8.527
1200	10.373	70.256	62.779	8.973	-18.250	-45.218	8.235
1300	10.387	71.087	63.386	10.011	-18.378	-47.460	7.979
1400	10.401	71.857	63.964	11.050	-18.521	-49.693	7.757
1500	10.417	72.575	64.514	12.091	-18.680	-51.913	7.564
1600	10.433	73.248	65.039	13.134	-18.858	-54.122	7.393
1700	10.450	73.881	65.541	14.178	-19.056	-56.321	7.241
1800	10.469	74.479	66.021	15.224	-19.276	-58.508	7.104
1900	10.487	75.045	66.481	16.271	-19.518	-60.681	6.980
2000	10.506	75.584	66.923	17.321	-24.229	-62.686	6.850
2100	10.525	76.097	67.348	18.373	-24.493	-64.602	6.723
2200	10.543	76.587	67.757	19.426	-24.756	-66.507	6.607
2300	10.561	77.056	68.151	20.481	-25.018	-68.398	6.499
2400	10.577	77.506	68.531	21.538	-25.280	-70.278	6.400
2500	10.593	77.938	68.899	22.597	-25.542	-72.148	6.307
2600	10.607	78.354	69.255	23.657	-25.804	-74.008	6.221
2700	10.620	78.754	69.599	24.718	-26.065	-75.856	6.140
2800	10.633	79.141	69.933	25.781	-26.326	-77.696	6.064
2900	10.644	79.514	70.257	26.844	-26.587	-79.523	5.993
3000	10.654	79.875	70.572	27.909	-26.849	-81.346	5.926
3100	10.662	80.224	70.877	28.975	-27.110	-83.157	5.863
3200	10.670	80.563	71.175	30.042	-27.372	-84.963	5.803
3300	10.677	80.891	71.464	31.109	-27.634	-86.758	5.746
3400	10.683	81.210	71.746	32.177	-27.896	-88.545	5.692
3500	10.689	81.520	72.021	33.246	-28.160	-90.325	5.640
3600	10.694	81.821	72.289	34.315	-130.049	-91.834	5.575
3700	10.698	82.114	72.551	35.385	-130.285	-90.770	5.362
3800	10.701	82.400	72.806	36.455	-130.535	-89.701	5.159
3900	10.705	82.678	73.056	37.525	-130.800	-88.621	4.966
4000	10.707	82.949	73.300	38.595	-131.077	-87.536	4.783
4100	10.710	83.213	73.538	39.666	-131.369	-86.443	4.608
4200	10.712	83.471	73.772	40.737	-131.673	-85.346	4.441
4300	10.714	83.723	74.000	41.809	-131.990	-84.239	4.282
4400	10.717	83.970	74.224	42.880	-132.319	-83.125	4.129
4500	10.718	84.211	74.443	43.952	-132.660	-82.003	3.983
4600	10.720	84.446	74.658	45.024	-133.011	-80.871	3.842
4700	10.722	84.677	74.869	46.096	-133.374	-79.734	3.708
4800	10.724	84.902	75.076	47.168	-133.748	-78.588	3.578
4900	10.726	85.124	75.278	48.241	-134.131	-77.438	3.454
5000	10.729	85.340	75.478	49.314	-134.523	-76.275	3.334
5100	10.731	85.553	75.673	50.387	-134.924	-75.108	3.219
5200	10.733	85.761	75.865	51.460	-135.334	-73.928	3.107
5300	10.736	85.966	76.054	52.533	-135.752	-72.746	3.000
5400	10.739	86.166	76.239	53.607	-136.177	-71.552	2.896
5500	10.742	86.363	76.421	54.681	-136.608	-70.349	2.795
5600	10.745	86.557	76.601	55.756	-137.047	-69.145	2.698
5700	10.748	86.747	76.777	56.830	-137.491	-67.924	2.604
5800	10.752	86.934	76.951	57.905	-137.941	-66.701	2.513
5900	10.756	87.118	77.121	58.981	-138.396	-65.469	2.425
6000	10.760	87.299	77.289	60.056	-138.856	-64.233	2.340

June 30, 1961; June 30, 1964; Sept. 30, 1964; Dec. 31, 1967

TITANIUM MONOFLUORIDE (TiF) (IDEAL GAS) GFW = 66.8984

Ground State Configuration $[^4\Sigma]$

$\Delta Hf_0^\circ = [-16 \pm 10]$ kcal/mol

$S^\circ_{298.15} = 56.7 \pm 2.0$ gibbs/mol

$\Delta Hf^\circ_{298.15} = [-16 \pm 10]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[4]	[6000]	[4]
[1000]	[4]	[8000]	[4]
[2000]	[4]	[10000]	[4]
[4000]	[4]		

$\omega_e = [590]$ cm^{-1}

$B_e = [0.328]$ cm^{-1}

$\omega_e x_e = [6.6]$ cm^{-1}

$\alpha_e = [0.0036]$ cm^{-1}

$\sigma = 1$

$r_e = [1.95]$ Å

Heat of Formation

The heat of formation, ΔHf°_{298}, of TiF(g) is calculated from the dissociation energy, D_0°. The dissociation energy is estimated as 148 ± 6 kcal/mol using the corresponding quantity for TiF_2(g) and the relation $D(MF)/D(MF_2) = 0.46 \pm 0.02$ which Zmbov and Margrave (1) found held for other mono- and di-fluorides.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, $\omega_e x_e$, are estimated from those of the alkali and mercury monohalides. The interatomic distance, r_e, is estimated from those of TiCl(g), TiF_2(g) and TiF_3(g). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+ (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Tungsten Monofluoride (WF)

(Ideal Gas) GFW = 202.8484

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.140	92.404	92.404	INFINITE
100	6.963	52.019	66.466	-1.445	92.596	89.658	-195.948
200	7.262	56.910	60.597	-.737	92.473	86.759	-94.805
298	7.755	59.903	59.903	.000	92.300	83.990	-61.566
300	7.764	59.951	59.904	.014	92.296	83.938	-61.148
400	8.140	62.240	60.213	.811	92.119	81.178	-44.354
500	8.386	64.085	60.809	1.638	91.942	78.463	-34.296
600	8.547	65.629	61.487	2.485	91.762	75.784	-27.604
700	8.659	66.956	62.176	3.346	91.576	73.136	-22.834
800	8.743	68.118	62.847	4.216	91.380	70.514	-19.264
900	8.811	69.151	63.491	5.094	91.178	67.920	-16.493
1000	8.872	70.083	64.105	5.978	90.966	65.346	-14.281
1100	8.930	70.931	64.687	6.868	90.746	62.794	-12.476
1200	8.985	71.711	65.241	7.764	90.518	60.264	-10.975
1300	9.040	72.432	65.766	8.665	90.282	57.753	-9.709
1400	9.094	73.104	66.267	9.572	90.038	55.258	-8.626
1500	9.146	73.733	66.744	10.484	89.786	52.784	-7.691
1600	9.197	74.325	67.199	11.401	89.527	50.326	-6.874
1700	9.247	74.884	67.635	12.323	89.259	47.884	-6.156
1800	9.295	75.414	68.053	13.251	88.984	45.457	-5.519
1900	9.342	75.918	68.453	14.182	88.700	43.046	-4.951
2000	9.389	76.398	68.839	15.119	88.408	40.653	-4.442
2100	9.436	76.857	69.210	16.060	88.108	38.273	-3.983
2200	9.483	77.298	69.567	17.006	87.798	35.902	-3.567
2300	9.531	77.720	69.913	17.957	87.481	33.553	-3.188
2400	9.581	78.127	70.247	18.912	87.156	31.215	-2.843
2500	9.633	78.519	70.570	19.873	86.822	28.891	-2.526
2600	9.688	78.898	70.883	20.839	86.481	26.581	-2.234
2700	9.747	79.265	71.186	21.811	86.127	24.283	-1.966
2800	9.808	79.620	71.481	22.789	85.752	22.002	-1.717
2900	9.872	79.965	71.768	23.772	85.346	19.731	-1.487
3000	9.940	80.301	72.047	24.763	84.904	17.476	-1.273
3100	10.011	80.628	72.318	25.761	84.416	15.234	-1.074
3200	10.084	80.947	72.583	26.765	83.874	13.011	-.889
3300	10.160	81.259	72.841	27.777	83.272	10.804	-.716
3400	10.238	81.563	73.093	28.797	82.603	8.621	-.554
3500	10.319	81.861	73.340	29.825	81.852	6.456	-.403
3600	10.400	82.153	73.580	30.861	80.994	4.312	-.262
3700	10.482	82.439	73.816	31.905	71.698	2.242	-.132
3800	10.565	82.720	74.047	32.958	71.416	.369	-.021
3900	10.648	82.995	74.273	34.018	71.140	-1.496	.084
4000	10.730	83.266	74.494	35.087	70.872	-3.356	.183
4100	10.812	83.532	74.711	36.164	70.610	-5.209	.278
4200	10.892	83.793	74.924	37.249	70.356	-7.052	.367
4300	10.970	84.050	75.134	38.343	70.109	-8.891	.452
4400	11.046	84.304	75.339	39.443	69.868	-10.731	.533
4500	11.120	84.553	75.541	40.552	69.634	-12.561	.610
4600	11.192	84.798	75.740	41.667	69.406	-14.393	.683
4700	11.260	85.039	75.935	42.790	69.183	-16.199	.753
4800	11.326	85.277	76.127	43.919	68.967	-18.013	.820
4900	11.388	85.511	76.316	45.055	68.756	-19.824	.884
5000	11.447	85.742	76.502	46.197	68.550	-21.630	.945
5100	11.502	85.969	76.686	47.344	68.348	-23.434	1.004
5200	11.554	86.193	76.867	48.497	68.151	-25.231	1.060
5300	11.602	86.413	77.045	49.655	67.958	-27.021	1.114
5400	11.646	86.631	77.220	50.817	67.768	-28.817	1.166
5500	11.687	86.845	77.393	51.984	67.581	-30.602	1.216
5600	11.725	87.056	77.564	53.155	67.398	-32.386	1.264
5700	11.758	87.264	77.732	54.329	67.216	-34.170	1.310
5800	11.789	87.468	77.898	55.506	67.038	-35.941	1.354
5900	11.816	87.670	78.062	56.686	66.860	-37.714	1.397
6000	11.839	87.869	78.224	57.869	-127.219	-37.405	1.362

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN MONOFLUORIDE (WF) (IDEAL GAS) GFW = 202.8484

Ground State Configuration $[^2\Delta]$

$S°_{298.15}$ = [59.9] gibbs/mol

$\Delta Hf°_0$ = [92.4 ± 15] kcal/mol

$\Delta Hf°_{298.15}$ = [92.3 ± 15] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i cm^{-1}	g_i
0	[4]
[5000]	[2]
[15000]	[20]

ω_e = [726.5] cm^{-1} $\omega_e x_e$ = [2.9] cm^{-1} σ = 1

B_e = [0.2923] cm^{-1} α_e = [0.0015] cm^{-1} r_e = [1.83] Å

Heat of Formation.

The heat of formation, $\Delta Hf°_{298}(WF,g)$ = 92.3 kcal/mol, is calculated from the bond dissociation energy $D°_{298}(WF)$ = 130 ± 15 kcal/mol. This value of $D°_{298}$ is estimated to be slightly higher than the average bond dissociation energy of $WF_6(g)$ by analogy with the WCl_x system.

Heat Capacity and Entropy.

The bond distance is estimated to be the same as that in $WF_6(g)$. This distance is then used with Guggenheimer's relation to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheimer, Proc. Phys. Soc. 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D_0 + 0.5\ \omega_e) = 0.0042$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is 9.575×10^{-39} g cm^2.

The ground state configuration, low lying electronic levels and their quantum weights are estimated based on the tentative molecular orbital diagram for TaO given by W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. 42, 882 (1965). Using this scheme, we obtain the ground state configuration as $\pi^4\sigma^2\delta^3$, which yields a $^2\Delta$ ground state. The first excited state is assumed to have $\pi^4\sigma\delta^4$ which yields a $^2\Sigma$ state. Higher levels are considered to be formed by transition to π^* antibonding orbitals, and by analogy with TaO these are assumed to lie in the 15000 cm^{-1} region. The degeneracy of these levels is estimated roughly from the large number of possible configurations.

Zirconium Monofluoride (ZrF)

(Ideal Gas) GFW = 110.2184

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.171	20.005	20.005	INFINITE
100	6.979	50.198	64.953	-1.476	20.141	17.491	-38.227
200	7.442	55.148	58.941	-.759	19.982	14.896	-16.277
298	7.989	58.227	58.227	.000	19.800	12.439	-9.118
300	7.998	58.277	58.227	.015	19.797	12.393	-9.028
400	8.364	60.632	58.546	.834	19.608	9.954	-5.439
500	8.611	62.526	59.159	1.684	19.403	7.563	-3.306
600	8.809	64.114	59.856	2.555	19.180	5.216	-1.900
700	8.993	65.485	60.564	3.445	18.939	2.907	-.908
800	9.176	66.698	61.256	4.353	18.681	.634	-.173
900	9.355	67.789	61.923	5.280	18.408	-1.606	.390
1000	9.528	68.784	62.560	6.224	18.121	-3.814	.834
1100	9.691	69.700	63.168	7.185	17.819	-5.993	1.191
1200	9.842	70.550	63.748	8.162	16.651	-8.092	1.474
1300	9.979	71.343	64.302	9.153	16.497	-10.148	1.706
1400	10.102	72.087	64.832	10.157	16.342	-12.191	1.903
1500	10.212	72.788	65.339	11.173	16.187	-14.223	2.072
1600	10.309	73.450	65.826	12.199	16.027	-16.246	2.219
1700	10.393	74.078	66.293	13.234	15.865	-18.258	2.347
1800	10.467	74.674	66.742	14.278	15.698	-20.261	2.460
1900	10.531	75.242	67.174	15.328	15.525	-22.254	2.560
2000	10.587	75.783	67.591	16.383	15.345	-24.238	2.649
2100	10.635	76.301	67.994	17.445	15.158	-26.213	2.728
2200	10.677	76.797	68.383	18.510	9.960	-28.002	2.782
2300	10.713	77.272	68.759	19.580	9.762	-29.722	2.824
2400	10.745	77.729	69.123	20.653	9.566	-31.435	2.863
2500	10.773	78.168	69.476	21.729	9.372	-33.139	2.897
2600	10.798	78.591	69.819	22.807	9.179	-34.836	2.928
2700	10.821	78.999	70.151	23.888	8.987	-36.525	2.956
2800	10.842	79.393	70.474	24.971	8.797	-38.207	2.982
2900	10.861	79.774	70.788	26.057	8.607	-39.882	3.006
3000	10.880	80.142	71.094	27.144	8.418	-41.552	3.027
3100	10.897	80.499	71.392	28.232	8.229	-43.214	3.047
3200	10.914	80.845	71.682	29.323	8.041	-44.871	3.065
3300	10.930	81.181	71.965	30.415	7.854	-46.521	3.081
3400	10.946	81.508	72.241	31.509	7.667	-48.166	3.096
3500	10.962	81.825	72.510	32.604	7.481	-49.804	3.110
3600	10.978	82.135	72.773	33.701	7.295	-51.438	3.123
3700	10.994	82.436	73.030	34.800	7.110	-53.068	3.135
3800	11.010	82.729	73.281	35.900	6.925	-54.691	3.145
3900	11.027	83.015	73.527	37.002	6.740	-56.312	3.156
4000	11.043	83.294	73.768	38.105	6.557	-57.925	3.165
4100	11.060	83.567	74.004	39.211	6.374	-59.535	3.174
4200	11.077	83.834	74.235	40.317	6.191	-61.140	3.181
4300	11.095	84.095	74.461	41.426	6.010	-62.741	3.189
4400	11.112	84.350	74.683	42.536	5.828	-64.338	3.196
4500	11.130	84.600	74.900	43.648	5.647	-65.931	3.202
4600	11.149	84.845	75.114	44.762	5.468	-67.520	3.208
4700	11.167	85.085	75.324	45.878	5.289	-69.104	3.213
4800	11.186	85.320	75.529	46.996	-136.046	-70.001	3.187
4900	11.205	85.551	75.732	48.115	-136.328	-68.622	3.061
5000	11.224	85.778	75.930	49.237	-136.614	-67.238	2.939
5100	11.243	86.000	76.126	50.360	-136.905	-65.850	2.822
5200	11.263	86.219	76.318	51.485	-137.199	-64.451	2.709
5300	11.283	86.433	76.506	52.613	-137.495	-63.049	2.600
5400	11.302	86.644	76.692	53.742	-137.796	-61.644	2.495
5500	11.322	86.852	76.875	54.873	-138.098	-60.231	2.393
5600	11.342	87.056	77.055	56.006	-138.403	-58.810	2.295
5700	11.362	87.257	77.232	57.142	-138.710	-57.387	2.200
5800	11.383	87.455	77.407	58.279	-139.018	-55.957	2.109
5900	11.403	87.650	77.579	59.418	-139.327	-54.524	2.020
6000	11.423	87.841	77.748	60.559	-139.638	-53.084	1.934

June 30, 1961; Sept. 30, 1964; June 30, 1969

ZIRCONIUM MONOFLUORIDE (ZrF) (IDEAL GAS) GFW = 110.2184

Ground State Configuration $[{}^4\Sigma]$ $\Delta Hf^\circ_0 = [20.0 \pm 5]$ kcal/mol

$S^\circ_{298.15} = [58 \pm 2]$ gibbs/mol $\Delta Hf^\circ_{298.15} = [19.8 \pm 5]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[4]	[18000]	[4]
[3000]	[4]	[24000]	[4]
[6000]	[4]	[30000]	[4]
[12000]	[4]		

$\omega_e = [628.0]\ \text{cm}^{-1}$ $\omega_e x_e = [4.0]\ \text{cm}^{-1}$ $\sigma = 1$

$B_e = [0.29699]\ \text{cm}^{-1}$ $\alpha_e = [0.009]\ \text{cm}^{-1}$ $r_e = [1.90]\ \text{Å}$

Heat of Formation

Based on $[D(ZrF)/D(ZrF_2)] = 0.46$, as indicated by recent work on the fluorides of Groups II and IV elements (1, 2, 3, 4, 5), and $D_0(ZrF_2) = 318.1$ kcal/mol, the $D_0(ZrF)$ is calculated as 146.3 kcal/mol. Using $\Delta Hf^\circ_0(Zr,\ g) = 147.99$, $\Delta Hf^\circ_0(F,\ g) = 18.36$, and $D_0(ZrF,\ g) = 146.3$ kcal/mol, we derive $\Delta Hf^\circ_0(ZrF,\ g) = 20.0$ or $\Delta Hf^\circ_{298}(ZrF,\ g) = 19.8 \pm 5$ kcal/mol which is adopted.

The ΔHf°_{298} for ZrF(g) was evaluated as approximately 16 ± 5 kcal/mol by Murad and Hildenbrand (8), employing different $D(ZrF_2)$ value. Their value is in agreement with the adopted one, within the assigned uncertainty.

Heat Capacity and Entropy

The ground state configuration is taken from the ground state multiplet of Zr^+ (6). The electronic levels are estimated as three times higher than those of TiF(g) and the quantum weights are assumed to be the same. ω_e is taken to be approximately the same as the Zr-F stretching frequency ν_1 for $ZrF_4(g)$. B_e is calculated from the formula $B_e = (2.799076 \times 10^{-39})(I_e)^{-1}$ where $I_e = \mu r_e^2$, μ = reduced mass of ZrF(g), $r_e = 1.90$ Å which is estimated from those of ZrF_4, CF_4, CF and other related gaseous molecules. α_e is derived from B_e, ω_e, and $\omega_e x_e$ (estimated), according to the method suggested by Herzberg (7). The moment of inertia is 9.425×10^{-39} g cm^2.

References

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Fluorine, Diatomic (F_2)

(Reference State - Ideal Gas)

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.110	.000	.000	.000
100	6.959	40.695	54.846	- 1.415	.000	.000	.000
200	7.098	45.544	49.118	- .715	.000	.000	.000
298	7.490	48.447	48.447	.000	.000	.000	.000
300	7.498	48.493	48.447	.014	.000	.000	.000
400	7.900	50.707	48.746	.784	.000	.000	.000
500	8.207	52.505	49.324	1.591	.000	.000	.000
600	8.429	54.022	49.983	2.423	.000	.000	.000
700	8.591	55.334	50.656	3.274	.000	.000	.000
800	8.713	56.489	51.314	4.140	.000	.000	.000
900	8.808	57.521	51.948	5.016	.000	.000	.000
1000	8.885	58.453	52.553	5.901	.000	.000	.000
1100	8.948	59.303	53.128	6.793	.000	.000	.000
1200	9.003	60.084	53.676	7.690	.000	.000	.000
1300	9.050	60.807	54.197	8.593	.000	.000	.000
1400	9.092	61.479	54.693	9.500	.000	.000	.000
1500	9.130	62.108	55.167	10.411	.000	.000	.000
1600	9.166	62.698	55.619	11.326	.000	.000	.000
1700	9.198	63.255	56.052	12.244	.000	.000	.000
1800	9.229	63.781	56.467	13.166	.000	.000	.000
1900	9.259	64.281	56.865	14.090	.000	.000	.000
2000	9.287	64.757	57.248	15.017	.000	.000	.000
2100	9.314	65.210	57.616	15.947	.000	.000	.000
2200	9.341	65.644	57.972	16.880	.000	.000	.000
2300	9.366	66.060	58.314	17.815	.000	.000	.000
2400	9.391	66.459	58.645	18.753	.000	.000	.000
2500	9.416	66.843	58.966	19.694	.000	.000	.000
2600	9.440	67.213	59.276	20.637	.000	.000	.000
2700	9.464	67.570	59.576	21.582	.000	.000	.000
2800	9.488	67.914	59.868	22.529	.000	.000	.000
2900	9.511	68.248	60.151	23.479	.000	.000	.000
3000	9.534	68.570	60.427	24.432	.000	.000	.000
3100	9.557	68.883	60.694	25.386	.000	.000	.000
3200	9.579	69.187	60.955	26.343	.000	.000	.000
3300	9.602	69.482	61.209	27.302	.000	.000	.000
3400	9.624	69.769	61.457	28.263	.000	.000	.000
3500	9.646	70.049	61.698	29.227	.000	.000	.000
3600	9.668	70.321	61.934	30.192	.000	.000	.000
3700	9.690	70.586	62.164	31.160	.000	.000	.000
3800	9.712	70.845	62.389	32.130	.000	.000	.000
3900	9.734	71.097	62.609	33.103	.000	.000	.000
4000	9.755	71.344	62.825	34.077	.000	.000	.000
4100	9.777	71.585	63.035	35.054	.000	.000	.000
4200	9.799	71.821	63.242	36.033	.000	.000	.000
4300	9.820	72.052	63.444	37.013	.000	.000	.000
4400	9.842	72.278	63.642	37.997	.000	.000	.000
4500	9.863	72.499	63.836	38.982	.000	.000	.000
4600	9.884	72.716	64.027	39.969	.000	.000	.000
4700	9.906	72.929	64.214	40.959	.000	.000	.000
4800	9.927	73.138	64.398	41.950	.000	.000	.000
4900	9.948	73.343	64.578	42.944	.000	.000	.000
5000	9.970	73.544	64.756	43.940	.000	.000	.000
5100	9.991	73.741	64.930	44.938	.000	.000	.000
5200	10.012	73.936	65.101	45.938	.000	.000	.000
5300	10.033	74.127	65.270	46.940	.000	.000	.000
5400	10.054	74.314	65.436	47.945	.000	.000	.000
5500	10.075	74.499	65.599	48.951	.000	.000	.000
5600	10.097	74.681	65.759	49.960	.000	.000	.000
5700	10.118	74.860	65.917	50.971	.000	.000	.000
5800	10.139	75.036	66.073	51.983	.000	.000	.000
5900	10.160	75.209	66.226	52.998	.000	.000	.000
6000	10.181	75.380	66.378	54.015	.000	.000	.000

December 31, 1960.

Fluorine, Diatomic (F_2) (Reference State - Ideal Gas)

Mol. Wt. = 38.00

$\Delta H_{f\ 298.15}^\circ$ = 0 kcal. mole^{-1}

$S_{298.15}^\circ$ = 48.45 cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^1\Sigma$

ω_e = 923.1 cm.$^{-1}$

$\omega_e x_e$ = 16.04 cm.$^{-1}$

B_e = 0.8938 cm.$^{-1}$

α_e = 0.022 cm.$^{-1}$

D_e = 3.346 X 10^{-6} cm.$^{-1}$

r_e = 1.409 Å

$\sigma = 2$

Heat Capacities and Entropies. Molecular and spectroscopic constants calculated from Raman measurements of D. Andrychuk, Can. J. Phys. 29, 151 (1951), and the dissociation energy listed by J. G. Stamper and R. F. Barrow, Trans. Faraday Soc. 54, 1592 (1958).

Iron Difluoride (FeF$_2$)

(Crystal) Mol. Wt. = 93.8438

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.049	- 168.564	- 168.564	INFINITE
100	7.994	7.374	33.204	- 2.583	- 168.896	- 165.417	361.502
200	13.530	14.824	22.204	- 1.476	- 168.911	- 161.907	176.915
298	16.280	20.790	20.790	.000	- 168.700	- 158.507	116.184
300	16.300	20.891	20.790	.030	- 168.695	- 158.444	115.421
400	17.200	25.708	21.441	1.707	- 168.414	- 155.069	84.722
500	17.900	29.624	22.698	3.463	- 168.140	- 151.765	66.333
600	18.440	32.938	24.135	5.281	- 167.884	- 148.515	54.094
700	18.850	35.812	25.603	7.146	- 167.659	- 145.305	45.364
800	19.180	38.351	27.041	9.048	- 167.491	- 142.125	38.825
900	19.440	40.626	28.426	10.980	- 167.411	- 138.959	33.742
1000	19.630	42.684	29.751	12.934	- 167.499	- 135.796	29.677
1100	19.769	44.562	31.013	14.904	- 167.796	- 132.607	26.345
1200	19.880	46.287	32.215	16.887	- 167.873	- 129.410	23.568
1300	19.955	47.881	33.359	18.879	- 167.607	- 126.214	21.218
1400	20.020	49.363	34.450	20.877	- 167.355	- 123.040	19.207
1500	20.072	50.746	35.491	22.882	- 167.114	- 119.883	17.466
1600	20.120	52.043	36.485	24.892	- 166.888	- 116.743	15.946
1700	20.164	53.264	37.437	26.906	- 166.967	- 113.609	14.605
1800	20.200	54.418	38.348	28.924	- 166.862	- 110.475	13.413
1900	20.229	55.510	39.223	30.946	- 170.441	- 107.158	12.325
2000	20.250	56.549	40.064	32.970	- 170.400	- 103.830	11.345

Sept. 30, 1965

IRON DIFLUORIDE (FeF$_2$) (CRYSTAL) MOL. WT. = 93.8438

$S^\circ_{298.15}$ = 20.79 ± 0.04 cal. deg.$^{-1}$ mole^{-1}

T_m = [1373]°K.

$\Delta H^\circ_{f\ 0}$ = -168.6 ± 10 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -168.7 ± 10 kcal. mole^{-1}

ΔH°_m = [12.4] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 75.6 ± 2.0 kcal. mole^{-1}

Heat of Formation.

The equilibrium pressures for the reaction $FeF_2(c) + H_2(g) = Fe(c) + 2HF(g)$ have been measured by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928) at 773, 873 and 973°K. The enthalpy change ($\Delta H^\circ_{r\ 298.15}$) of the reaction was evaluated by the second and third law methods to be 27.19 and 39.08 kcal. mole^{-1}, respectively. Based on the third law value of $\Delta H^\circ_{r\ 298.15}$, the $\Delta H^\circ_{f\ 298.15}$ (FeF$_2$, c) was calculated to be -168.7 ± 10 kcal. mole^{-1}. The drift in the third law values of $\Delta H^\circ_{r\ 298.15}$ was evaluated to be 13.3 ± 1.8 e.u.

Heat Capacity and Entropy.

The low temperature (11.33 - 307.30°K.) heat capacities were determined by E. Catalano and J. W. Stout, J. Chem. Phys. 23, 1803 (1955). The heat capacities above 307°K. were estimated by comparison with those of FeCl$_2$(c), MgCl$_2$(c) and MgF$_2$(c). The value of $S^\circ_{298.15}$ was obtained from E. Catalano and J. W. Stout, loc. cit., in which a sharp maximum C_p of 17.8 cal. deg.$^{-1}$ mole^{-1} at 78.35°K. was reported. The $S^\circ_{298.15}$ value was based on S°_{15} = 0.039 e.u.

Melting Data.

T_m was estimated as 1100°C based on the data reported by W. Biltz and E. Rahlfs, Z. anorg. allgem. Chem. 166, 363 (1927). The value of ΔH°_m was calculated using ΔS°_m = 9 e.u. which was assumed to be the same as the corresponding value for MgF$_2$(c).

Heat of Sublimation.

The value of $\Delta H^\circ_{s\ 298.15}$ was obtained from J. L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William Marsh Rice University, Houston, Texas. See FeF$_2$(g) table for details.

Iron Difluoride (FeF_2)

(Liquid)   Mol. Wt. = 93.8438

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	23.500	21.951	21.951	.000	- 161.229	- 151.383	110.961
300	23.500	22.096	21.951	.043	- 161.211	- 151.322	110.232
400	23.500	28.857	22.873	2.393	- 160.257	- 148.171	80.953
500	23.500	34.101	24.614	4.743	- 159.389	- 145.253	63.487
600	23.500	38.385	26.563	7.093	- 158.601	- 142.500	51.903
700	23.500	42.008	28.517	9.443	- 157.891	- 139.874	43.669
800	23.500	45.146	30.404	11.793	- 157.275	- 137.345	37.519
900	23.500	47.914	32.199	14.143	- 156.777	- 134.884	32.753
1000	23.500	50.390	33.896	16.493	- 156.469	- 132.472	28.950
1100	23.500	52.630	35.499	18.843	- 156.386	- 130.071	25.842
1200	23.500	54.674	37.013	21.193	- 156.096	- 127.696	23.256
1300	23.500	56.555	38.445	23.543	- 155.472	- 125.354	21.073
1400	23.500	58.297	39.801	25.893	- 154.868	- 123.061	19.210
1500	23.500	59.918	41.089	28.243	- 154.282	- 120.809	17.601
1600	23.500	61.435	42.314	30.593	- 153.716	- 118.597	16.199
1700	23.500	62.859	43.481	32.943	- 153.459	- 116.412	14.965
1800	23.500	64.203	44.595	35.293	- 153.022	- 114.248	13.871
1900	23.500	65.473	45.661	37.643	- 156.273	- 111.919	12.873
2000	23.500	66.679	46.682	39.993	- 155.906	- 109.596	11.975
2100	23.500	67.825	47.662	42.343	- 155.546	- 107.288	11.165
2200	23.500	68.918	48.603	44.693	- 155.193	- 104.997	10.430
2300	23.500	69.963	49.509	47.043	- 154.846	- 102.725	9.761
2400	23.500	70.963	50.383	49.393	- 154.506	- 100.467	9.148
2500	23.500	71.923	51.225	51.743	- 154.173	- 98.223	8.586
2600	23.500	72.844	52.039	54.093	- 153.846	- 95.990	8.068
2700	23.500	73.731	52.826	56.443	- 153.525	- 93.771	7.590
2800	23.500	74.586	53.588	58.793	- 153.210	- 91.565	7.147
2900	23.500	75.410	54.326	61.143	- 152.902	- 89.365	6.734
3000	23.500	76.207	55.043	63.493	- 152.601	- 87.183	6.351

Sept. 30, 1965

IRON DIFLUORIDE (FeF_2)   (LIQUID)   MOL. WT. = 93.8438

$S^\circ_{298.15}$ = [21.951] cal. deg.$^{-1}$ mole^{-1}

T_m = [1373]°K.

T_b = [2110]°K.

ΔH°_f 298.15 = [-161.229] kcal. mole^{-1}

ΔH°_m = [12.4] kcal. mole^{-1}

ΔH°_v = [53.64] kcal. mole^{-1}

Heat of Formation.

The value of ΔH°_f 298.15 (FeF_2, l) was obtained from ΔH°_f 298.15 (FeF_2, c) by adding ΔH°_m and the difference between $H^\circ_{T_m} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeF_2(l) was estimated by comparison with those for $FeCl_2$(c), $MgCl_2$(c), MgF_2(c), $CaCl_2$(c) and CaF_2(c). The C_p(FeF_2, l) value was assumed to be constant in the temperature range, 298.15 - 3000°K. The entropy ($S^\circ_{298.15}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See the FeF_2(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction $FeF_2(l) = FeF_2(g)$ approaches zero. The difference between ΔH°_f for FeF_2(l) and FeF_2(g) at T_b is ΔH°_v.

Iron Difluoride (FeF_2)

(Ideal Gas) Mol. Wt. = 93.8438

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.029	-92.944	-92.944	INFINITE
100	9.216	51.319	73.890	-2.257	-92.970	-93.886	205.178
200	11.449	58.427	64.522	-1.219	-93.054	-94.770	103.555
298	13.324	63.361	63.361	.000	-93.100	-95.600	70.073
300	13.355	63.444	63.361	.025	-93.100	-95.616	69.653
400	14.673	67.482	63.903	1.432	-93.089	-96.454	52.697
500	15.365	70.841	64.965	2.938	-93.065	-97.299	42.527
600	15.647	73.672	66.186	4.491	-93.074	-98.146	35.748
700	15.723	76.091	67.433	6.061	-93.144	-98.986	30.903
800	15.714	78.191	68.649	7.633	-93.306	-99.812	27.266
900	15.679	80.040	69.814	9.203	-93.588	-100.609	24.430
1000	15.644	81.690	70.921	10.769	-94.064	-101.367	22.153
1100	15.617	83.179	71.968	12.332	-94.768	-102.058	20.276
1200	15.600	84.537	72.960	13.893	-95.267	-102.704	18.704
1300	15.591	85.786	73.899	15.452	-95.434	-103.317	17.368
1400	15.588	86.941	74.790	17.011	-95.621	-103.916	16.221
1500	15.590	88.016	75.636	18.570	-95.826	-104.501	15.225
1600	15.594	89.023	76.442	20.129	-96.051	-105.073	14.352
1700	15.599	89.968	77.210	21.689	-96.584	-105.623	13.578
1800	15.604	90.860	77.944	23.249	-96.937	-106.146	12.887
1900	15.609	91.704	78.646	24.810	-100.977	-106.463	12.245
2000	15.612	92.504	79.319	26.371	-101.399	-106.739	11.663
2100	15.613	93.266	79.965	27.932	-101.828	-106.996	11.135
2200	15.613	93.993	80.587	29.493	-102.264	-107.234	10.652
2300	15.611	94.687	81.185	31.054	-102.706	-107.450	10.210
2400	15.608	95.351	81.761	32.615	-103.155	-107.647	9.802
2500	15.603	95.988	82.318	34.176	-103.611	-107.823	9.425
2600	15.597	96.600	82.855	35.736	-104.074	-107.984	9.076
2700	15.590	97.188	83.375	37.295	-104.544	-108.124	8.752
2800	15.582	97.755	83.879	38.854	-105.020	-108.248	8.449
2900	15.573	98.302	84.367	40.412	-105.504	-108.355	8.165
3000	15.563	98.830	84.840	41.969	-105.996	-108.447	7.900
3100	15.553	99.340	85.300	43.524	-106.495	-108.519	7.650
3200	15.542	99.833	85.746	45.079	-190.426	-107.130	7.316
3300	15.530	100.311	86.180	46.633	-190.476	-104.528	6.922
3400	15.519	100.775	86.603	48.185	-190.538	-101.924	6.551
3500	15.507	101.225	87.014	49.736	-190.611	-99.317	6.201
3600	15.495	101.661	87.415	51.287	-190.694	-96.702	5.870
3700	15.482	102.086	87.806	52.835	-190.790	-94.094	5.558
3800	15.470	102.498	88.187	54.383	-190.897	-91.478	5.261
3900	15.458	102.900	88.559	55.929	-191.017	-88.860	4.979
4000	15.446	103.291	88.923	57.475	-191.147	-86.239	4.712
4100	15.434	103.672	89.278	59.019	-191.290	-83.612	4.457
4200	15.422	104.044	89.625	60.562	-191.446	-80.986	4.214
4300	15.411	104.407	89.964	62.103	-191.614	-78.352	3.982
4400	15.399	104.761	90.297	63.644	-191.795	-75.719	3.761
4500	15.388	105.107	90.622	65.183	-191.989	-73.081	3.549
4600	15.377	105.445	90.941	66.721	-192.195	-70.433	3.346
4700	15.366	105.776	91.253	68.259	-192.415	-67.786	3.152
4800	15.356	106.099	91.559	69.795	-192.647	-65.126	2.965
4900	15.345	106.416	91.859	71.330	-192.894	-62.471	2.786
5000	15.335	106.726	92.153	72.864	-193.154	-59.809	2.614
5100	15.325	107.029	92.442	74.397	-193.427	-57.140	2.448
5200	15.316	107.327	92.725	75.929	-193.714	-54.463	2.289
5300	15.306	107.618	93.003	77.460	-194.014	-51.778	2.135
5400	15.297	107.904	93.277	78.990	-194.329	-49.096	1.987
5500	15.288	108.185	93.545	80.519	-194.656	-46.403	1.844
5600	15.280	108.460	93.809	82.048	-194.997	-43.702	1.705
5700	15.271	108.731	94.068	83.575	-195.352	-41.001	1.572
5800	15.263	108.996	94.324	85.102	-195.719	-38.284	1.443
5900	15.255	109.257	94.574	86.628	-196.100	-35.573	1.318
6000	15.247	109.513	94.821	88.153	-196.494	-32.844	1.196

Sept. 30, 1965

IRON DIFLUORIDE (FeF_2) (IDEAL GAS) MOL. WT. = 93.8438

Point Group $[D_{\infty h}]$

$S^\circ_{298.15}$ = [63.4] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0 = -92.9 \pm 3.4$ kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -93.1 \pm 3.4$ kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_i, cm.$^{-1}$	g_i
0	[5]
[1000]	[10]
[4000]	[5]
[6000]	[5]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[550] (1)
[190] (2)
[714] (1)

Bond Distance: Fe-F = [1.8] Å

Bond Angle: F-Fe-F = [180]°

Rotational Constant: B_o = 0.13692 cm.$^{-1}$

$\sigma = 2$

Heat of Formation.

The rate of sublimation of $FeF_2(c)$ was measured between 965 and 1149°K. by the Knudsen technique employing the high temperature magnetic mass spectrometer by John L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William March Rice University, Houston, Texas. The only vapor species of importance is $FeF_2(g)$. From the vapor pressure data the third law heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) was reported as 75.6 ± 2.0 kcal. mole^{-1}. The sum of the values of $\Delta H^\circ_{s\ 298.15}$ and $\Delta H^\circ_{f\ 298.15}$ for $FeF_2(c)$ is the $\Delta H^\circ_{f\ 298.15}$ (FeF_2, g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The Fe-F bond distance was estimated from that in $FeF_2(c)$ reported by W. H. Baur, Acta Cryst. 11, 488 (1958). The vibrational frequencies, ω_1 and ω_3, were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The values of ω_2, electronic levels and quantum weights were estimated by comparison with those for $FeCl_2(g)$. See $FeCl_2(g)$ table for details. The moment of inertia is 2.04404×10^{-39} g. cm.^{2}

Potassium Bifluoride (KHF_2)

(Crystal) Mol. Wt. = 78.108

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.654	- 220.744	- 220.744	INFINITE
100	11.680	8.458	39.618	- 3.116	- 221.695	- 216.401	472.920
200	16.010	18.154	26.619	- 1.693	- 221.893	- 211.006	230.566
298	18.361	25.000	25.000	.000	- 221.905	- 205.653	150.741
300	18.400	25.114	25.000	.034	- 221.905	- 205.553	149.738
400	20.603	30.705	25.748	1.983	- 222.387	- 200.004	109.272
500	23.960	41.322	27.579	6.871	- 219.398	- 194.610	85.060
600	23.960	45.691	30.245	9.267	- 218.910	- 189.697	69.094
700	23.960	49.384	32.722	11.663	- 218.432	- 184.866	57.715
800	23.960	52.584	35.009	14.059	- 217.967	- 180.104	49.200
900	23.960	55.406	37.122	16.455	- 217.515	- 175.398	42.590
1000	23.960	57.930	39.079	18.851	- 217.084	- 170.743	37.314
1100	23.960	60.214	40.898	21.247	- 235.580	- 165.105	32.802
1200	23.960	62.299	42.596	23.643	- 234.945	- 158.724	28.906
1300	23.960	64.216	44.186	26.039	- 234.321	- 152.399	25.619
1400	23.960	65.992	45.681	28.435	- 233.706	- 146.119	22.809
1500	23.960	67.645	47.091	30.831	- 233.101	- 139.883	20.380
1600	23.960	69.191	48.424	33.227	- 232.506	- 133.689	18.260
1700	23.960	70.644	49.689	35.623	- 231.919	- 127.531	16.394
1800	23.960	72.013	50.892	38.019	- 231.342	- 121.409	14.740
1900	23.960	73.309	52.038	40.415	- 230.773	- 115.317	13.264
2000	23.960	74.538	53.132	42.811	- 230.211	- 109.253	11.938

June 30, 1962; Dec. 31, 1963

POTASSIUM BIFLUORIDE (KHF_2) (CRYSTAL) MOL. WT. = 78.108

$S^\circ_{298.15}$ = 25.0 ± 0.1 cal. deg. mole^{-1}

T_t = 469.8°K.

T_m = 511.8°K.

$\Delta H^\circ_{f\ 0}$ = -220.74 ± 0.35 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -221.90 ± 0.35 kcal. mole^{-1}

ΔH_t = 2.671 ± 0.01 kcal. mole^{-1}

ΔH_m = 1.582 ± 0.003 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained from the enthalpy of decomposition measurements of M. L. Davis and E. F. Westrum, J. Phys. Chem. 65, 338 (1961) who gave $\Delta H_{d\ 500}$ = 18.82 ± 0.05 kcal. mole^{-1} and the heats of formation of HF(g) and KF(c) from the JANAF Tables, in conjunction with enthalpies at 500°K. from E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949). A third law analysis of the decomposition vapor pressure by Westrum and Pitzer, loc. cit. did not agree with enthalpy of decomposition measurements, giving $\Delta H_{d\ 298}$ = 21.274 ± 0.2 kcal. mole^{-1} as compared to Davis and Westrum's value at 298°K. of 21.505 ± 0.05 kcal. mole^{-1}. As the liquid vapor pressure data, which were not used, have a large trend in the third law heat of vaporization with temperature it was suspected that the pressure measurements were in error. This is borne out somewhat by a small trend in the values over the solid in the range 480-500°K.

Heat Capacity and Entropy.

Westrum and Pitzer, loc. cit., have measured the heat capacity from 16°K. to the melting point. Their data has been used to calculate the entropy at 298° using a T^3 law extrapolation below 16°K., giving S_{16} = 0.103 e.u.

Melting and Transition Data.

The temperatures of melting and transition and the heats of melting and transition were taken from Davis and Westrum, loc. cit.

Potassium Bifluoride (KHF_2)

(Liquid) Mol. Wt. = 78.108

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	18.344	32.300	32.300	.000	- 218.243	- 204.168	149.652
300	18.400	32.414	32.300	.034	- 218.243	- 204.081	148.666
400	25.000	38.817	33.112	2.282	- 218.426	- 199.287	108.880
500	25.000	44.396	34.832	4.782	- 217.825	- 194.574	85.044
600	25.000	48.954	36.817	7.282	- 217.233	- 189.979	69.196
700	25.000	52.808	38.833	9.782	- 216.651	- 185.482	57.907
800	25.000	56.146	40.793	12.282	- 216.082	- 181.070	49.464
900	25.000	59.090	42.666	14.782	- 215.526	- 176.726	42.913
1000	25.000	61.725	44.443	17.282	- 214.991	- 172.445	37.686
1100	25.000	64.107	46.124	19.782	- 233.383	- 167.191	33.216
1200	25.000	66.283	47.714	22.282	- 232.644	- 161.204	29.358
1300	25.000	68.284	49.221	24.782	- 231.916	- 155.282	26.104
1400	25.000	70.136	50.649	27.282	- 231.197	- 149.413	23.323
1500	25.000	71.861	52.006	29.782	- 230.488	- 143.595	20.921
1600	25.000	73.475	53.298	32.282	- 229.789	- 137.826	18.825
1700	25.000	74.990	54.530	34.782	- 229.099	- 132.099	16.982
1800	25.000	76.419	55.707	37.282	- 228.417	- 126.415	15.348
1900	25.000	77.771	56.833	39.782	- 227.744	- 120.766	13.891
2000	25.000	79.053	57.912	42.282	- 227.079	- 115.151	12.582

June 30, 1962; Dec. 31, 1963

POTASSIUM BIFLUORIDE (KHF_2) (LIQUID) MOL. WT. = 78.108

$S^\circ_{298.15}$ = 32.3 cal. deg. mole^{-1}

ΔH_f° 298.15 = -218.24 ± 0.35 kcal. mole^{-1}

T_m = 511.8°K.

ΔH_m° = 1.582 ± 0.003 kcal. mole^{-1}

$T_{decomp.}$ = [751]°K.

Heat of Formation.

This was calculated from the heat of formation of the crystal, the heat of melting and $H_{511.8}-H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The entropy was determined from that of the crystal in a manner analogous to the heat of formation. The heat capacity just above the melting point was measured by E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949) and was assumed constant above the melting point. A glass type transition was assumed at 341°K. below which the heat capacity is that of the solid.

Melting.

See table for crystal.

Decomposition.

The temperature of decomposition was estimated from the free energy cross-over and is the point where the HF(g) reaches 1 atm. It should be noted that the vapor pressures over the liquid of Westrum and Pitzer, loc. cit. are apparently in error, being high by roughly 12%. A 3rd law analysis at each vapor pressure point gave an almost constant heat of reaction in the solid region but in the liquid region the value changed abruptly with temperature. The only factors which were variable were the pressure and the liquid heat capacity, a trial change of 20% in the heat capacity produced an almost negligible change in the heat of reaction. Thus the vapor pressures over the liquid appear to be in error and the decomposition point of 702°K. obtained by extrapolating to 1 atmosphere is also in error.

Difluorosilane (SiH_2F_2)

(Ideal Gas) Mol. Wt. = 68.106 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.788	-191.898	-191.898	INFINITE
100	6.366	51.705	71.552	-1.985	-192.613	-191.184	417.811
200	9.881	57.923	63.319	-1.079	-193.285	-189.506	207.073
298	12.191	62.282	62.282	.000	-194.000	-187.500	137.434
300	12.238	62.358	62.282	.023	-194.013	-187.460	136.558
400	14.621	66.212	62.792	1.368	-194.641	-185.176	101.171
500	16.597	69.695	63.830	2.933	-195.131	-182.751	79.877
600	18.172	72.866	65.076	4.674	-195.495	-180.239	65.649
700	19.425	75.765	66.399	6.556	-195.756	-177.674	55.470
800	20.428	78.427	67.738	8.551	-195.935	-175.079	47.827
900	21.236	80.881	69.064	10.635	-196.053	-172.463	41.878
1000	21.891	83.154	70.361	12.793	-196.123	-169.839	37.116
1100	22.426	85.266	71.621	15.010	-196.156	-167.209	33.220
1200	22.866	87.237	72.841	17.275	-196.160	-164.576	29.972
1300	23.231	89.082	74.020	19.580	-196.144	-161.944	27.224
1400	23.536	90.815	75.158	21.919	-196.112	-159.314	24.869
1500	23.793	92.448	76.257	24.286	-196.071	-156.687	22.828
1600	24.010	93.990	77.318	26.676	-196.025	-154.064	21.043
1700	24.196	95.452	78.342	29.087	-208.077	-151.332	19.454
1800	24.356	96.839	79.331	31.515	-207.981	-148.001	17.969
1900	24.494	98.160	80.288	33.957	-207.882	-144.671	16.640
2000	24.614	99.420	81.213	36.413	-207.781	-141.344	15.445
2100	24.726	100.623	82.109	38.880	-207.681	-138.027	14.364
2200	24.812	101.775	82.977	41.356	-207.583	-134.713	13.382
2300	24.894	102.880	83.818	43.842	-207.484	-131.400	12.485
2400	24.966	103.941	84.635	46.335	-207.389	-128.096	11.664
2500	25.030	104.962	85.428	48.835	-207.298	-124.795	10.909
2600	25.088	105.944	86.198	51.341	-207.208	-121.495	10.212
2700	25.140	106.892	86.947	53.852	-207.122	-118.201	9.567
2800	25.186	107.807	87.676	56.369	-207.038	-114.911	8.969
2900	25.229	108.692	88.385	58.889	-206.959	-111.618	8.411
3000	25.267	109.548	89.077	61.414	-206.884	-108.337	7.892
3100	25.302	110.377	89.750	63.943	-206.810	-105.053	7.406
3200	25.333	111.181	90.408	66.474	-206.743	-101.769	6.950
3300	25.362	111.961	91.049	69.009	-206.679	-98.488	6.522
3400	25.389	112.718	91.675	71.547	-206.618	-95.212	6.120
3500	25.413	113.455	92.287	74.087	-206.564	-91.934	5.740
3600	25.436	114.171	92.885	76.629	-301.488	-88.187	5.353
3700	25.456	114.866	93.470	79.174	-301.381	-82.264	4.859
3800	25.476	115.547	94.042	81.721	-301.279	-76.342	4.390
3900	25.493	116.209	94.602	84.269	-301.183	-70.428	3.947
4000	25.510	116.855	95.150	86.819	-301.091	-64.510	3.524
4100	25.525	117.485	95.687	89.371	-301.004	-58.599	3.123
4200	25.539	118.100	96.213	91.924	-300.923	-52.683	2.741
4300	25.553	118.701	96.729	94.479	-300.845	-46.777	2.377
4400	25.565	119.289	97.236	97.035	-300.774	-40.870	2.030
4500	25.577	119.864	97.732	99.592	-300.709	-34.969	1.698
4600	25.588	120.426	98.219	102.150	-300.647	-29.058	1.380
4700	25.596	120.976	98.698	104.709	-300.591	-23.155	1.077
4800	25.607	121.515	99.167	107.270	-300.538	-17.248	.785
4900	25.617	122.043	99.629	109.831	-300.492	-11.350	.506
5000	25.625	122.561	100.082	112.393	-300.450	-5.450	.238
5100	25.633	123.068	100.528	114.956	-300.413	.449	-.019
5200	25.641	123.566	100.966	117.519	-300.382	6.349	-.267
5300	25.648	124.055	101.397	120.084	-300.354	12.252	-.505
5400	25.655	124.534	101.821	122.649	-300.332	18.143	-.734
5500	25.661	125.005	102.239	125.215	-300.314	24.043	-.955
5600	25.667	125.467	102.649	127.781	-300.303	29.938	-1.168
5700	25.673	125.922	103.054	130.348	-300.296	35.840	-1.374
5800	25.678	126.368	103.452	132.916	-300.292	41.732	-1.572
5900	25.683	126.807	103.844	135.484	-300.295	47.632	-1.764
6000	25.688	127.239	104.230	138.052	-300.304	53.522	-1.949

December 31, 1960.

Difluorosilane (SiH_2F_2) (Ideal Gas)

Mol. Wt. = 68.106

ΔH_f° 298.15 = [-194 ± 15] kcal. mole^{-1}

$S_{298.15}^\circ$ = [62.576] cal. deg.$^{-1}$ mole^{-1}

Point Group C_{2v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
2245 (1)	321.7 (1)	728.2 (1)
870 (1)	2250 (1)	[905] (1)
984.8 (1)	[978] (1)	[785] (1)

Moments of Inertia: $I_A = 3.40 \times 10^{-39}$ g. cm.^{2} $\sigma = 2$

$I_B = 10.76 \times 10^{-39}$ g. cm.^{2} $I_C = 13.16 \times 10^{-39}$ g. cm.^{2}

Heat of Formation. ΔH_f° 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were taken from G. Janz and Y. Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961). Moments of inertia were found in Henderson and Scheffee, op. cit.

Mercury Difluoride (HgF_2)

(Crystal) Mol. Wt. = 238.61

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	17.891	27.800	27.800	.000	-101.000	-89.426	65.548
300	17.900	27.911	27.800	.033	-100.993	-89.355	65.092
400	18.400	33.128	28.508	1.848	-100.609	-85.532	46.730
500	18.900	37.288	29.862	3.713	-100.203	-81.809	35.757
600	19.400	40.778	31.398	5.628	-99.769	-78.171	28.473
700	19.900	43.806	32.959	7.593	-113.330	-73.037	22.802
800	20.400	46.696	34.486	9.608	-112.678	-67.325	18.391
900	20.900	48.927	35.957	11.673	-111.985	-61.696	14.981
1000	21.400	51.155	37.367	13.788	-111.252	-56.148	12.271
1100	21.900	53.218	38.716	15.953	-110.476	-50.675	10.068
1200	22.400	55.145	40.005	18.168	-109.655	-45.274	8.245
1300	22.900	56.958	41.240	20.433	-108.790	-39.943	6.715
1400	23.400	58.673	42.425	22.748	-107.878	-34.681	5.414
1500	23.900	60.305	43.563	25.113	-106.921	-29.485	4.296
1600	24.400	61.863	44.658	27.528	-105.918	-24.357	3.327
1700	24.900	63.358	45.715	29.993	-104.868	-19.289	2.480
1800	25.400	64.795	46.735	32.508	-103.772	-14.290	1.735
1900	25.900	66.182	47.722	35.073	-102.627	-9.348	1.075
2000	26.400	67.523	48.679	37.688	-101.436	-4.468	.488

March 31, 1962

F_2Hg

MERCURY DIFLUORIDE (HgF_2) (Crystal)

Mol. Wt. = 238.61

ΔH°_f 298.15 = [-101.0 ± 10.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [27.800 ± 2.0] cal. deg.$^{-1}$ mole^{-1}

T_m = 918°K

ΔH_m = [5.5 ± 1.0] kcal. mole^{-1}

Heat of Formation. Estimated by comparison of the mercurous and mercuric halides.

Heat Capacity and Entropy. The heat capacity was assumed to be a linear function of temperature and was estimated to be 7.0 cal. deg.$^{-1}$ per atom at the melting point. The entropy was estimated by comparison with the other mercuric and mercurous halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1960).

Melting. T_m was given by O. Ruff and G. Bahlau, Ber. 51, 1752 (1918). The heat of melting was from L. Brewer, paper 7, National Nuclear Energy Series 4-19B "Thermodynamics" McGraw-Hill (1950).

F_2Hg

Mercury Difluoride (HgF_2)

(Liquid) Mol. Wt. = 238.61

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	17.891	32.083	32.083	.000	- 96.772	- 86.475	63.385
300	17.900	32.194	32.083	.033	- 96.765	- 86.412	62.948
400	16.400	37.411	32.791	1.848	- 96.381	- 83.017	45.356
500	16.900	41.571	34.145	3.713	- 95.975	- 79.723	34.845
600	19.400	45.061	35.681	5.628	- 95.541	- 76.513	27.869
700	24.400	48.715	37.282	8.003	- 108.692	- 71.835	22.427
800	24.400	51.974	38.920	10.443	- 107.615	- 66.644	18.205
900	24.400	54.848	40.533	12.883	- 106.547	- 61.586	14.954
1000	24.400	57.418	42.095	15.323	- 105.489	- 56.648	12.380
1100	24.400	59.744	43.595	17.763	- 104.438	- 51.815	10.294
1200	24.400	61.867	45.031	20.203	- 103.392	- 47.077	8.573
1300	24.400	63.820	46.402	22.643	- 102.352	- 42.426	7.132
1400	24.400	65.628	47.712	25.083	- 101.315	- 37.854	5.909
1500	24.400	67.312	48.963	27.523	- 100.283	- 33.357	4.860
1600	24.400	68.886	50.159	29.963	- 99.255	- 28.931	3.952
1700	24.400	70.366	51.305	32.403	- 98.230	- 24.565	3.158
1800	24.400	71.760	52.403	34.843	- 97.209	- 20.265	2.460
1900	24.400	73.080	53.457	37.283	- 96.189	- 16.015	1.842
2000	24.400	74.331	54.469	39.723	- 95.173	- 11.821	1.292

March 31, 1962

MERCURY DIFLUORIDE (HgF_2) (Liquid)

Mol. Wt. = 238.61

ΔH_f° 298.15 = [-96.772 ± 10.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [32.083 ± 2.0] cal. deg.$^{-1}$ mole^{-1}

T_m = 918°K

ΔH_m = [5.5 ± 1.0] kcal. mole^{-1}

T_b = 920°K

ΔH_v = [22.0 ± 4.0] kcal. mole^{-1}

Heat of Formation. Calculated from ΔH_f° (crystal).

Heat Capacity and Entropy. C_p was estimated by analogy with mercuric iodide and bromide. A glass type transition was assumed at 613°K below which the heat capacity was that of HgF_2(crystal). The entropy was calculated from S°(crystal) and the estimated ΔH_m and heat capacities of crystal and liquid.

Fusion and Vaporization. T_m was given by O. Ruff and G. Bahlan, Ber. 51, 1752 (1918). T_b, ΔH_m, and ΔH_v were all taken from L. Brewer, paper 7, National Nuclear Energy Series 4-19B "Thermodynamics" McGraw-Hill (1950).

Mercury Difluoride (HgF_2)

(Ideal Gas) Mol. Wt. = 238.61

INTERIM TABLE

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-3.152	-68.994	-68.994	INFINITE
100	10.129	51.105	74.176	-2.307	-69.252	-69.404	151.674
200	11.722	58.627	64.691	-1.213	-69.475	-69.462	75.901
298	12.899	63.545	63.545	.000	-70.185	-69.269	50.773
300	12.916	63.624	63.545	.024	-70.187	-69.263	50.456
400	13.614	67.445	64.061	1.354	-70.288	-68.938	37.664
500	14.018	70.530	65.056	2.737	-70.364	-68.592	29.980
600	14.263	73.110	66.190	4.152	-70.430	-68.231	24.852
700	14.422	75.321	67.340	5.587	-84.521	-66.288	20.695
800	14.529	77.254	68.461	7.035	-84.436	-63.690	17.398
900	14.604	78.970	69.535	8.492	-84.351	-61.101	14.837
1000	14.659	80.512	70.557	9.955	-84.270	-58.523	12.790
1100	14.701	81.911	71.526	11.423	-84.191	-55.952	11.116
1200	14.732	83.192	72.446	12.895	-84.113	-53.388	9.723
1300	14.757	84.372	73.319	14.369	-84.039	-50.830	8.545
1400	14.777	85.466	74.148	15.846	-83.965	-48.278	7.536
1500	14.793	86.486	74.937	17.325	-83.894	-45.730	6.663
1600	14.807	87.441	75.689	18.805	-83.826	-43.190	5.899
1700	14.818	88.339	76.407	20.286	-83.760	-40.651	5.226
1800	14.827	89.187	77.093	21.768	-83.697	-38.120	4.628
1900	14.835	89.989	77.751	23.251	-83.634	-35.588	4.093
2000	14.842	90.750	78.382	24.735	-83.574	-33.059	3.612
2100	14.847	91.474	78.988	26.219	-83.517	-30.538	3.178
2200	14.852	92.165	79.572	27.704	-83.462	-28.017	2.783
2300	14.857	92.825	80.134	29.190	-83.408	-25.497	2.423
2400	14.861	93.457	80.676	30.676	-83.356	-22.978	2.092
2500	14.864	94.064	81.199	32.162	-83.308	-20.466	1.789
2600	14.867	94.647	81.705	33.649	-83.261	-17.953	1.509
2700	14.870	95.208	82.195	35.135	-83.217	-15.439	1.250
2800	14.872	95.749	82.670	36.623	-83.173	-12.933	1.009
2900	14.874	96.271	83.130	38.110	-83.132	-10.421	.785
3000	14.876	96.775	83.576	39.597	-83.095	-7.919	.577
3100	14.876	97.263	84.010	41.085	-83.058	-5.413	.382
3200	14.880	97.736	84.432	42.573	-83.024	-2.907	.199
3300	14.881	98.193	84.842	44.061	-82.992	-.404	.027
3400	14.883	98.638	85.241	45.549	-82.961	2.098	-.135
3500	14.884	99.069	85.630	47.038	-82.933	4.601	-.287
3600	14.885	99.489	86.009	48.526	-82.907	7.102	-.431
3700	14.886	99.896	86.379	50.015	-82.883	9.600	-.567
3800	14.887	100.293	86.740	51.503	-82.862	12.103	-.696
3900	14.888	100.680	87.092	52.992	-82.843	14.598	-.818
4000	14.889	101.057	87.437	54.481	-82.825	17.099	-.934
4100	14.889	101.425	87.773	55.970	-82.810	19.593	-1.044
4200	14.890	101.783	88.103	57.459	-82.797	22.092	-1.149
4300	14.891	102.134	88.425	58.948	-82.785	24.591	-1.250
4400	14.891	102.476	88.741	60.437	-82.777	27.086	-1.345
4500	14.892	102.811	89.049	61.926	-82.770	29.582	-1.437
4600	14.892	103.138	89.352	63.415	-82.766	32.077	-1.524
4700	14.893	103.458	89.649	64.905	-82.764	34.578	-1.608
4800	14.893	103.772	89.940	66.394	-82.764	37.073	-1.688
4900	14.894	104.079	90.225	67.883	-82.767	39.571	-1.765
5000	14.894	104.380	90.505	69.373	-82.771	42.069	-1.839
5100	14.895	104.675	90.780	70.862	-82.779	44.563	-1.910
5200	14.895	104.964	91.050	72.352	-82.789	47.064	-1.978
5300	14.895	105.248	91.316	73.841	-82.802	49.561	-2.044
5400	14.896	105.526	91.576	75.331	-82.817	52.051	-2.107
5500	14.896	105.800	91.832	76.820	-82.835	54.552	-2.168
5600	14.896	106.068	92.084	78.310	-82.856	57.054	-2.227
5700	14.897	106.332	92.332	79.800	-82.879	59.554	-2.283
5800	14.897	106.591	92.575	81.289	-82.906	62.049	-2.338
5900	14.897	106.845	92.815	82.779	-82.936	64.544	-2.391
6000	14.897	107.096	93.051	84.269	-82.968	67.045	-2.442

December 31, 1961

MERCURY DIFLUORIDE (HgF_2) (IDEAL GAS) MOL. WT. = 238.61

Point Group $D_{\infty h}$

ΔH_f° 298.15 = [-70.2 ± 10.0] kcal mole⁻¹

$S^\circ_{298.15}$ = 63.545 cal deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm⁻¹
[600] (1)
[120] (2)
[593] (1)

Hg-F distance = [1.96] Å

Moment of Inertia = [12.118 x 10^{-39}] g cm² $\sigma = 2$

Heat of Formation

Estimated by comparison with the other gaseous mercuric halides and with the crystalline mercurous mercuric fluorides.

Heat Capacity and Entropy

Vibrational constants were estimated by analogy with the other mercuric halides and the mercurous halides. The bond length was estimated by assuming the mercurous bond to be 0.965 of the mercuric bond by analogy with the mercury chlorides.

Mercury Monofluoride, Dimeric (Hg_2F_2)

(Crystal) Mol. Wt. = 439.22 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	24.000	38.400	38.400	.000	- 116.000	- 102.169	74.888
300	24.020	38.549	38.400	.044	- 115.994	- 102.083	74.364
400	25.020	45.599	39.355	2.498	- 115.632	- 97.497	53.267
500	25.910	51.280	41.190	5.045	- 115.196	- 93.013	40.654
600	26.690	56.075	43.281	7.676	- 114.695	- 88.624	32.280
700	27.370	60.241	45.413	10.380	- 142.192	- 81.180	25.344
800	27.950	63.935	47.502	13.147	- 141.285	- 72.525	19.812
900	28.430	67.255	49.515	15.966	- 140.334	- 63.985	15.537
1000	28.860	70.273	51.442	18.831	- 139.348	- 55.556	12.141
1100	29.239	73.042	53.282	21.736	- 138.329	- 47.226	9.382
1200	29.567	75.601	55.036	24.677	- 137.279	- 38.990	7.101
1300	29.845	77.979	56.711	27.648	- 136.205	- 30.842	5.185
1400	30.073	80.199	58.310	30.644	- 135.108	- 22.777	3.556
1500	30.250	82.280	59.840	33.661	- 133.996	- 14.791	2.155

March 31, 1962

MERCURY MONOFLUORIDE, DIMERIC (Hg_2F_2) (Crystal)

Mol. Wt. = 439.22

ΔH_f° 298.15 = [-116.0 ± 3.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = [38.4 ± 2.0] cal. deg.$^{-1}$ mole^{-1}

T_{sub} = [949]°K (decomp.)

Heat of Formation. A value of ΔF_f° 298.15 was obtained from the cell measurements of G. G. Koerber and T. de Vries, J. Amer. Chem. Soc. 74, 5008 (1952). This was combined with ΔS_f° from the estimated entropy.

Heat Capacity and Entropy. The heat capacity was estimated by comparison with mercurous chloride. The entropy was estimated by comparison with the other mercurous and mercuric halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1960).

Sublimation. Sublimation with decomposition to Hg(g) and $HgF_{2(g)}$ was assumed at 949°K from the free energy change of the reaction.

Potassium Difluoride Uninegative Ion (KF_2^-)

(Ideal Gas) GFW = 77.09935

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	13.627	62.561	62.561	.000	-166.000	-164.112	120.298
300	13.640	62.645	62.561	.025	-166.011	-164.100	119.547
400	14.130	66.645	63.103	1.417	-167.200	-163.263	89.203
500	14.388	69.828	64.141	2.844	-167.820	-162.208	70.901
600	14.537	72.466	65.315	4.291	-168.428	-161.028	58.654
700	14.631	74.714	66.501	5.749	-169.033	-159.745	49.875
800	14.693	76.672	67.652	7.216	-169.641	-158.379	43.267
900	14.736	78.405	68.753	8.687	-170.255	-156.934	38.109
1000	14.767	79.960	69.797	10.162	-170.883	-155.421	33.967
1100	14.790	81.368	70.786	11.640	-190.431	-152.821	30.363
1200	14.808	82.656	71.722	13.120	-190.842	-149.383	27.206
1300	14.822	83.842	72.609	14.602	-191.256	-145.910	24.530
1400	14.833	84.941	73.451	16.085	-191.674	-142.406	22.231
1500	14.842	85.964	74.252	17.569	-192.095	-138.871	20.234
1600	14.850	86.922	75.014	19.053	-192.520	-135.309	18.482
1700	14.856	87.823	75.741	20.538	-192.948	-131.722	16.934
1800	14.861	88.672	76.436	22.024	-193.378	-128.108	15.554
1900	14.865	89.476	77.102	23.511	-193.812	-124.471	14.317
2000	14.869	90.238	77.740	24.997	-194.250	-120.808	13.201
2100	14.872	90.964	78.352	26.484	-194.692	-117.126	12.189
2200	14.875	91.656	78.941	27.972	-195.139	-113.422	11.267
2300	14.878	92.317	79.509	29.459	-195.590	-109.696	10.424
2400	14.880	92.950	80.056	30.947	-196.047	-105.954	9.648
2500	14.882	.3.558	80.584	32.435	-196.512	-102.191	8.934
2600	14.883	94.142	81.094	33.924	-196.981	-98.406	8.272
2700	14.885	94.703	81.588	35.412	-197.459	-94.608	7.658
2800	14.886	95.245	82.066	36.901	-197.945	-90.791	7.087
2900	14.887	95.767	82.529	38.389	-198.440	-86.952	6.553
3000	14.888	96.272	82.979	39.878	-198.945	-83.102	6.054
3100	14.889	96.760	83.416	41.367	-199.461	-79.230	5.586
3200	14.890	97.233	83.840	42.856	-199.989	-75.345	5.146
3300	14.891	97.691	84.253	44.345	-200.530	-71.443	4.731
3400	14.892	98.135	84.655	45.834	-201.085	-67.524	4.340
3500	14.892	98.567	85.046	47.323	-201.657	-63.585	3.970
3600	14.893	98.987	85.428	48.812	-202.246	-59.630	3.620
3700	14.894	99.395	85.800	50.302	-202.854	-55.659	3.288
3800	14.894	99.792	86.163	51.791	-203.485	-51.674	2.972
3900	14.895	100.179	86.517	53.281	-204.139	-47.674	2.672
4000	14.895	100.556	86.863	54.770	-204.818	-43.649	2.385
4100	14.895	100.924	87.202	56.260	-205.527	-39.611	2.111
4200	14.896	101.283	87.533	57.749	-206.269	-35.558	1.850
4300	14.896	101.633	87.857	59.239	-207.042	-31.482	1.600
4400	14.897	101.976	88.174	60.728	-207.857	-27.393	1.361
4500	14.897	102.310	88.484	62.218	-208.709	-23.279	1.131
4600	14.897	102.638	88.788	63.708	-209.606	-19.151	.910
4700	14.897	102.958	89.086	65.198	-210.551	-14.999	.697
4800	14.898	103.272	89.379	66.687	-211.546	-10.823	.493
4900	14.898	103.579	89.665	68.177	-212.595	-6.633	.296
5000	14.898	103.880	89.947	69.667	-213.698	-2.423	.106
5100	14.898	104.175	90.223	71.157	-214.861	1.818	-.078
5200	14.899	104.464	90.494	72.647	-216.085	6.078	-.255
5300	14.899	104.748	90.760	74.136	-217.372	10.364	-.427
5400	14.899	105.027	91.022	75.626	-218.723	14.668	-.594
5500	14.899	105.300	91.279	77.116	-220.138	19.003	-.755
5600	14.899	105.568	91.532	78.606	-221.617	23.370	-.912
5700	14.899	105.832	91.780	80.096	-223.161	27.752	-1.064
5800	14.900	106.091	92.025	81.586	-224.768	32.171	-1.212
5900	14.900	106.346	92.265	83.076	-226.437	36.615	-1.356
6000	14.900	106.596	92.502	84.566	-228.166	41.088	-1.497

Dec. 31, 1968

POTASSIUM DIFLUORIDE UNINEGATIVE ION (KF_2^-) (IDEAL GAS) GFW = 77.09935

Point Group [$D_{\infty h}$]

ΔHf_0° = -165 ± 10 kcal/mol

$S^\circ_{298.15}$ = [63 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -166 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[350] (1)
[130] (2)
[500] (1)

Bond Distance: K-F = [2.17] Å

Bond Angle: F-K-F = [180°]

$\sigma = 2$

Rotational Constant: B_0 = [0.094] cm^{-1}

Heat of Formation

The heat of formation is estimated from three calculated values. The methods of calculation are described as follows. In a manner analogous to $LiF_2^-(g)$, the first reaction considered is $KF(g) + F^-(g) = KF_2^-(g)$ and the ΔHr°_{298} value is evaluated to be between 0 and 1/2(-50) = -25 kcal/mol (see $LiF_2^-(g)$ table for details), yielding $\Delta Hf^\circ_{298}(KF_2^-, g)$ between -140 and -165 kcal/mol. The ΔHf°_{298} values for the other species involved are taken from JANAF Tables.

The second reaction employed for estimation is $K_2F_2(g) = KF_2^-(g) + K^+(g)$. The enthalpy change of this reaction is calculated as ΔHr°_{298} = 1/2(50.0) + 138.8 = 163.8 kcal/mol where the KF_2^- ion is considered to be converted from $K_2F_2(g)$ by breaking one of the two dimer association bonds (ΔHr°_{298} = 50.0 kcal/mol) and one K^+-F^- ionic bond (ΔHr°_{298} = 138.8 kcal/mol). Using ΔHf°_{298} = -206.2 and 122.9 kcal/mol for $K_2F_2(g)$ and $K^+(g)$, we obtain the heat of formation for $KF_2^-(g)$ as -165 kcal/mol.

Based on an assumption that the electron affinity of $KF_2(g)$ is similar to that of F (see $LiF_2^-(g)$ table for details), i.e. ΔHr°_{298} = 83.5 kcal/mol (1) for the reaction $KF_2^-(g) = KF_2(g) + e^-(g)$, we derive $\Delta Hf^\circ_{298}(KF_2^-, g)$ = -167.7 kcal/mol. The ΔHf°_{298} for $KF_2(g)$ is calculated as -84.2 kcal/mol from the value ΔHr°_{298} = 143.3 kcal/mol for the reaction $K_2F_2(g) = KF_2(g) + K(g)$ where the ΔHr°_{298} value is calculated as the sum of two enthalpy changes, i.e. half of the heat of dimer dissociation into two monomers or 1/2(50.0) = 25.0 kcal/mol, and the heat of dissociation of KF(g) or 118.3 kcal/mol.

The value of ΔHf°_{298} for $KF_2^-(g)$ is tentatively adopted as -166 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion given by Walsh (2) that molecules with not more than 16 valency electrons are linear in their ground states. The K-F bond distance is taken to be the same as that of KF(g) reported by Veazey and Gordy (3). The vibrational frequencies are estimated from the vibrational frequency of KF(g) using the method suggested by Herzberg (4). The moment of inertia is 2.971 x 10^{-38} g cm^2. The enthalpy at 0°K is -3.293 kcal/mol.

References

1. H. O. Pritchard, Chem. Rev. 52, 529 (1953).
2. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
3. S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).
4. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, p. 172.

Potassium Fluoride, Dimeric (K_2F_2)

(Ideal Gas) GFW = 116.2008

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.381	-205.085	-205.085	INFINITE
100	13.560	58.214	92.182	-3.397	-205.624	-205.674	449.500
200	17.604	69.158	78.132	-1.795	-205.962	-205.571	224.637
298	18.768	76.444	76.444	.000	-206.200	-205.330	150.511
300	18.780	76.560	76.444	.035	-206.205	-205.325	149.579
400	19.240	82.035	77.187	1.939	-207.699	-204.765	111.878
500	19.462	86.354	78.604	3.875	-208.056	-203.991	89.164
600	19.585	89.914	80.201	5.828	-208.387	-203.145	73.995
700	19.660	92.940	81.810	7.790	-208.708	-202.245	63.144
800	19.709	95.568	83.369	9.759	-209.029	-201.302	54.993
900	19.743	97.892	84.856	11.732	-209.356	-200.315	48.643
1000	19.767	99.973	86.266	13.707	-209.708	-199.294	43.556
1100	19.785	101.858	87.599	15.685	-247.896	-196.186	38.979
1200	19.799	103.580	88.860	17.664	-247.808	-191.487	34.875
1300	19.810	105.165	90.054	19.645	-247.728	-186.799	31.404
1400	19.818	106.634	91.186	21.626	-247.644	-182.114	28.429
1500	19.825	108.001	92.262	23.608	-247.567	-177.435	25.852
1600	19.831	109.281	93.287	25.591	-247.493	-172.762	23.598
1700	19.835	110.483	94.263	27.574	-247.428	-168.095	21.610
1800	19.839	111.617	95.196	29.558	-247.358	-163.431	19.843
1900	19.843	112.690	96.089	31.542	-247.298	-158.771	18.263
2000	19.845	113.708	96.944	33.527	-247.240	-154.110	16.840
2100	19.848	114.676	97.766	35.511	-247.190	-149.456	15.554
2200	19.850	115.600	98.556	37.496	-247.148	-144.803	14.385
2300	19.852	116.482	99.316	39.481	-247.112	-140.152	13.318
2400	19.853	117.327	100.049	41.467	-247.084	-135.503	12.339
2500	19.855	118.137	100.757	43.452	-247.070	-130.856	11.439
2600	19.856	118.916	101.440	45.438	-247.063	-126.203	10.608
2700	19.857	119.666	102.101	47.423	-247.071	-121.557	9.839
2800	19.858	120.388	102.742	49.409	-247.094	-116.910	9.125
2900	19.859	121.085	103.362	51.395	-247.132	-112.255	8.460
3000	19.860	121.758	103.964	53.381	-247.187	-107.609	7.839
3100	19.861	122.409	104.549	55.367	-247.263	-102.952	7.258
3200	19.861	123.040	105.117	57.353	-247.360	-98.293	6.713
3300	19.862	123.651	105.669	59.339	-247.481	-93.637	6.201
3400	19.863	124.244	106.207	61.325	-247.630	-88.974	5.719
3500	19.863	124.820	106.730	63.312	-247.807	-84.303	5.264
3600	19.864	125.379	107.241	65.298	-248.018	-79.625	4.834
3700	19.864	125.923	107.738	67.284	-248.266	-74.948	4.427
3800	19.864	126.453	108.224	69.271	-248.555	-70.259	4.041
3900	19.865	126.969	108.698	71.257	-248.890	-65.566	3.674
4000	19.865	127.472	109.161	73.244	-249.273	-60.857	3.325
4100	19.865	127.963	109.614	75.230	-249.714	-56.142	2.993
4200	19.866	128.441	110.056	77.217	-250.216	-51.414	2.675
4300	19.866	128.909	110.489	79.203	-250.782	-46.672	2.372
4400	19.866	129.365	110.913	81.190	-251.425	-41.921	2.082
4500	19.866	129.812	111.328	83.177	-252.149	-37.148	1.804
4600	19.867	130.249	111.735	85.163	-252.952	-32.365	1.538
4700	19.867	130.676	112.133	87.150	-253.851	-27.559	1.281
4800	19.867	131.094	112.524	89.137	-254.847	-22.729	1.035
4900	19.867	131.504	112.907	91.123	-255.951	-17.882	.798
5000	19.867	131.905	113.283	93.110	-257.162	-13.017	.569
5100	19.868	132.299	113.652	95.097	-258.489	-8.117	.348
5200	19.868	132.684	114.014	97.084	-259.936	-3.193	.134
5300	19.868	133.063	114.370	99.070	-261.506	1.758	-.072
5400	19.868	133.434	114.720	101.057	-263.202	6.733	-.273
5500	19.868	133.799	115.063	103.044	-265.025	11.748	-.467
5600	19.868	134.157	115.401	105.031	-266.975	16.801	-.656
5700	19.868	134.508	115.733	107.018	-269.051	21.886	-.839
5800	19.869	134.854	116.060	109.005	-271.252	27.008	-1.018
5900	19.869	135.194	116.381	110.991	-273.575	32.172	-1.192
6000	19.869	135.527	116.698	112.978	-276.015	37.381	-1.362

June 30, 1961; Mar. 31, 1964; June 30, 1969

POTASSIUM FLUORIDE, DIMERIC (K_2F_2) (IDEAL GAS) GFW = 116.2008

Point Group D_{2h}

ΔHf°_0 = -205.1 ± 2 kcal/mol

$S^\circ_{298.15}$ = [76.4 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -206.2 ± 2 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[273] (1)	[150] (1)
[150] (1)	[255] (1)
[235] (1)	[258] (1)

Bond Distance: K-F = 2.2 Å

Bond Angles: F-K-F = [90°] K-F-K = [90°]

Product of the Moments of Inertia: $I_AI_BI_C = [2.240 \times 10^{-113}]\ g^3\ cm^6$

Heat of Formation

The equilibrium constants (K_c) for the reaction $K_2F_2(g) = 2KF(g)$, in the temperature range 974-1052°K, were determined by Eisenstadt, Rothberg, and Kusch (1). Although the reported absolute values of the vapor pressures of KF(c) are not adopted for evaluation, the reported K_c values are used to calculate the enthalpy change (ΔHr°_{298}) for the above reaction. The second law and third law values of ΔHr°_{298} are derived as 51.0 ± 1.6 and 50.0 kcal/mol, respectively. Based on the third law ΔHr°_{298} and ΔHf°_{298}(KF, g) = -78.1 kcal/mol, we obtain ΔHf°_{298} = -206.2 kcal/mol for $K_2F_2(g)$ which is tentatively adopted.

Heat Capacity and Enthalpy

The molecular structure and K-F bond distance were determined by Akishin and Rambidi (2), using electron diffraction with sector microphotometry. The bond angles are estimated by comparison with other alkali halide dimers. The vibrational frequencies are taken from Berkowitz (3) which were calculated based on an ionic model. The three principal moments of inertia are: $I_A = 3.1423 \times 10^{-38}$, $I_B = 1.5267 \times 10^{-38}$, and $I_C = 4.6690 \times 10^{-38}\ g\ cm^2$.

References

1. M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. 29, 797 (1958).
2. P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. 213, 111 (1960).
3. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

Lithium Difluoride Uninegative Ion (LiF_2^-)

(Ideal Gas) GFW = 44.93635

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	11.393	54.853	54.853	.000	-170.000	-168.349	123.403
300	11.413	54.924	54.853	.021	-170.013	-168.339	122.635
400	12.305	58.338	55.313	1.210	-170.712	-167.675	91.614
500	12.922	61.154	56.207	2.473	-172.171	-166.759	72.890
600	13.363	63.551	57.236	3.788	-172.898	-165.607	60.322
700	13.682	65.636	58.291	5.142	-173.591	-164.337	51.308
800	13.918	67.479	59.326	6.522	-174.266	-162.970	44.521
900	14.095	69.129	60.325	7.923	-174.929	-161.518	39.222
1000	14.230	70.621	61.282	9.340	-175.584	-159.993	34.966
1100	14.335	71.983	62.193	10.768	-176.233	-158.403	31.472
1200	14.418	73.234	63.062	12.206	-176.877	-156.754	28.549
1300	14.484	74.390	63.889	13.651	-177.517	-155.049	26.066
1400	14.538	75.466	64.678	15.102	-178.155	-153.297	23.931
1500	14.583	76.470	65.431	16.558	-178.790	-151.499	22.073
1600	14.619	77.413	66.151	18.019	-179.422	-149.659	20.442
1700	14.650	78.300	66.840	19.482	-215.101	-146.451	18.828
1800	14.677	79.138	67.500	20.948	-215.550	-142.399	17.290
1900	14.699	79.932	68.134	22.417	-215.999	-138.323	15.911
2000	14.718	80.687	68.743	23.888	-216.450	-134.223	14.667
2100	14.735	81.405	69.329	25.361	-216.903	-130.102	13.540
2200	14.750	82.091	69.893	26.835	-217.359	-125.958	12.513
2300	14.762	82.747	70.438	28.311	-217.814	-121.791	11.573
2400	14.774	83.376	70.964	29.788	-218.275	-117.609	10.710
2500	14.784	83.979	71.473	31.265	-218.740	-113.404	9.914
2600	14.793	84.559	71.965	32.744	-219.207	-109.182	9.178
2700	14.800	85.117	72.442	34.224	-219.678	-104.942	8.494
2800	14.808	85.656	72.904	35.704	-220.153	-100.684	7.859
2900	14.814	86.175	73.353	37.185	-220.634	-96.407	7.265
3000	14.820	86.678	73.789	38.667	-221.120	-92.116	6.711
3100	14.825	87.164	74.212	40.149	-221.613	-87.806	6.190
3200	14.830	87.635	74.624	41.632	-222.111	-83.485	5.702
3300	14.834	88.091	75.026	43.115	-222.617	-79.145	5.242
3400	14.838	88.534	75.416	44.599	-223.128	-74.789	4.807
3500	14.842	88.964	75.797	46.083	-223.648	-70.418	4.397
3600	14.845	89.382	76.169	47.567	-224.176	-66.032	4.009
3700	14.848	89.789	76.532	49.052	-224.712	-61.630	3.640
3800	14.851	90.185	76.886	50.537	-225.257	-57.213	3.290
3900	14.854	90.571	77.232	52.022	-225.812	-52.787	2.958
4000	14.856	90.947	77.570	53.508	-226.374	-48.341	2.641
4100	14.858	91.314	77.901	54.993	-226.949	-43.882	2.339
4200	14.861	91.672	78.224	56.479	-227.534	-39.414	2.051
4300	14.863	92.021	78.541	57.966	-228.127	-34.926	1.775
4400	14.864	92.363	78.851	59.452	-228.734	-30.427	1.511
4500	14.866	92.697	79.155	60.938	-229.352	-25.912	1.258
4600	14.868	93.024	79.453	62.425	-229.982	-21.386	1.016
4700	14.869	93.344	79.745	63.912	-230.626	-16.845	.783
4800	14.871	93.657	80.032	65.399	-231.283	-12.287	.559
4900	14.872	93.963	80.313	66.886	-231.956	-7.719	.344
5000	14.873	94.264	80.589	68.373	-232.642	-3.136	.137
5100	14.874	94.558	80.860	69.861	-233.345	1.462	-.063
5200	14.876	94.847	81.126	71.348	-234.066	6.074	-.255
5300	14.877	95.131	81.388	72.836	-234.804	10.699	-.441
5400	14.878	95.409	81.645	74.324	-235.561	15.335	-.621
5500	14.878	95.682	81.898	75.811	-236.339	19.990	-.794
5600	14.879	95.950	82.146	77.299	-237.136	24.660	-.962
5700	14.880	96.213	82.391	78.787	-237.956	29.339	-1.125
5800	14.881	96.472	82.631	80.275	-238.799	34.039	-1.283
5900	14.882	96.726	82.868	81.763	-239.666	38.747	-1.435
6000	14.883	96.977	83.101	83.252	-240.558	43.473	-1.583

Dec. 31, 1968

LITHIUM DIFLUORIDE UNINEGATIVE ION (LiF_2^-) (IDEAL GAS) GFW = 44.93635

Point Group [$D_{\infty h}$]

ΔHf°_0 = [-169 ± 15] kcal/mol

$S^\circ_{298.15}$ = [55 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-170 ± 15] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1300] (1)
[350] (2)
[550] (1)

Bond Distance: Li-F = [1.57] Å

Bond Angle: F-Li-F = [180°]

σ = [2]

Rotational Constant: B_0 = [0.180] cm^{-1}

Heat of Formation

Due to lack of thermal data, the heat of formation for $LiF_2^-(g)$ is arbitrarily selected from the following three estimated values. For the reaction (1) $LiF(g) + F^-(g) = LiF_2^-(g)$, we expect the enthalpy change would be between 0 to -31 kcal/mol. Comparison with the other molecules like CO_2, BOF, BeF_2, etc. having 16 valence electrons leads us to assume that the isoelectronic molecule LiF_2^- should also be quite stable. This indicates that reaction (1) is favorable or ΔHr°_{298} is negative. However, the $LiF-F^-$ bond strength is expected to be weaker than half of the two ionic bonds between Li^+ and F^- in Li_2F_2 molecule (see Li_2F_2 (g) table for the molecular structure). In other words, the ΔHr°_{298} value of reaction (1) is less negative than half of the heat of dimerization (-62.4 kcal/mol). Incorporating ΔHr°_{298} = 0 and -31 kcal/mol, respectively, for reaction (1), with ΔHf°_{298} = -81.45 and -62.2 kcal/mol for LiF(g) and $F^-(g)$, we derived the corresponding values for $\Delta Hf^\circ_{298}(LiF_2^-, g)$ as -144 and -175 kcal/mol, which are the upper and lower limits.

The electron affinities of Li and F atoms are reported as 0.7 and 3.448 eV, respectively, by Beckett and Cassidy (1). From this data we estimate that the electron affinity of $LiF_2(g)$ should be closer to that of F atom than to that of Li. Assuming ΔHr°_{298} = electron affinity of F atom = 83.5 kcal/mol for the reaction $LiF_2^-(g) = LiF_2(g) + e^-(g)$, we obtain the heat of formation for $LiF_2^-(g)$ as -177.3 kcal/mol. The $\Delta Hf^\circ_{298}(LiF_2, g)$ used for calculation is derived from an estimated ΔHr°_{298} = 169.9 kcal/mol for the decomposition of LiF dimer or $Li_2F_2(g) = LiF_2(g) + Li(g)$ as the sum of two enthalpy changes, namely, half of the heat of dissociation of the dimer and the heat of dissociation of the monomer.

The third estimated value for the heat of formation of $LiF_2^-(g)$ is calculated as follows. Based on the two heats of reaction, i.e. ΔHr°_{298} = 62.4 kcal/mol for $Li_2F_2(g) = LiF(g)$, and ΔHr°_{298} = 183.5 kcal/mol for $LiF(g) = Li^+(g) + F^-(g)$, we assume the enthalpy change of the reaction $Li_2F_2(g) = LiF_2^-(g) + Li^+(g)$ to be 1/2(62.4) + 183.5 = 214.7 kcal/mol. In other words, we consider the $LiF_2^-(g)$ molecule is formed by breaking half of the dimer dissociation bonds and one monomer dissociation bond to produce two ions. Using ΔHf°_{298} = -225.33 and 164.24 kcal/mol for $Li_2F_2(g)$ and $Li^+(g)$, we evaluate $\Delta Hf^\circ_{298}(LiF_2^-, g)$ = -174.9 kcal/mol.

From the above three estimated values, we tentatively choose $\Delta Hf^\circ_{298}(LiF_2^-, g)$ as -170 ± 15 kcal/mol.

Heat Capacity and Entropy

According to A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953), molecules with not more than 16 valence electrons are linear in their ground states. Since $LiF_2^-(g)$ has 16 valence electrons, we assume its molecular structure is linear. The Li-F bond distance is estimated by comparison with that of LiF(g) reported by Wharton et al. (2). The vibrational frequencies are estimated from those of the isoelectronic gaseous molecules, CO_2 and BeF_2. The moment of inertia is 1.555×10^{-38} g cm^2. The enthalpy at 0°K is -2.653 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, U. S. Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1203 (1963).

Lithium Fluoride, Dimeric (Li_2F_2)

(Ideal Gas) GFW = 51.8748

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.193	- 224.203	- 224.203	INFINITE
100	8.661	49.312	73.152	- 2.384	- 224.327	- 224.837	491.381
200	12.195	56.332	63.085	- 1.351	- 224.874	- 225.134	246.015
298	15.088	61.788	61.788	.000	- 225.330	- 225.161	165.047
300	15.130	61.881	61.788	.028	- 225.338	- 225.160	164.029
400	16.813	66.487	62.404	1.633	- 225.745	- 225.038	122.955
500	17.776	70.352	63.618	3.367	- 227.654	- 224.663	98.200
600	18.359	73.648	65.022	5.176	- 228.103	- 224.020	81.599
700	18.734	76.509	66.463	7.032	- 228.498	- 223.309	69.720
800	18.987	79.028	67.880	8.919	- 228.861	- 222.544	60.796
900	19.165	81.275	69.245	10.827	- 229.211	- 221.732	53.844
1000	19.295	83.301	70.551	12.750	- 229.553	- 220.883	48.274
1100	19.392	85.145	71.795	14.684	- 229.887	- 220.000	43.710
1200	19.467	86.836	72.979	16.628	- 230.216	- 219.087	39.901
1300	19.526	88.396	74.106	18.577	- 230.542	- 218.146	36.674
1400	19.572	89.845	75.179	20.532	- 230.864	- 217.180	33.903
1500	19.610	91.197	76.202	22.491	- 231.182	- 216.191	31.499
1600	19.642	92.463	77.179	24.454	- 231.496	- 215.181	29.392
1700	19.668	93.655	78.114	26.420	- 301.902	- 211.496	27.190
1800	19.689	94.780	79.009	28.387	- 301.851	- 206.178	25.033
1900	19.708	95.845	79.867	30.357	- 301.799	- 200.882	23.104
2000	19.724	96.856	80.691	32.329	- 301.750	- 195.552	21.369
2100	19.737	97.819	81.484	34.302	- 301.705	- 190.247	19.799
2200	19.749	98.737	82.248	36.276	- 301.664	- 184.938	18.372
2300	19.760	99.615	82.984	38.252	- 301.623	- 179.634	17.069
2400	19.769	100.456	83.695	40.228	- 301.591	- 174.332	15.875
2500	19.777	101.264	84.381	42.206	- 301.562	- 169.029	14.776
2600	19.784	102.039	85.046	44.184	- 301.539	- 163.730	13.763
2700	19.790	102.786	85.689	46.162	- 301.524	- 158.429	12.824
2800	19.796	103.506	86.313	48.142	- 301.513	- 153.130	11.952
2900	19.801	104.201	86.917	50.121	- 301.516	- 147.829	11.141
3000	19.806	104.872	87.505	52.102	- 301.524	- 142.530	10.383
3100	19.810	105.522	88.076	54.083	- 301.545	- 137.229	9.675
3200	19.814	106.151	88.631	56.064	- 301.575	- 131.929	9.010
3300	19.817	106.760	89.171	58.045	- 301.619	- 126.627	8.386
3400	19.820	107.352	89.697	60.027	- 301.674	- 121.321	7.798
3500	19.823	107.927	90.210	62.009	- 301.742	- 116.016	7.244
3600	19.826	108.485	90.710	63.992	- 301.824	- 110.707	6.721
3700	19.828	109.028	91.197	65.974	- 301.922	- 105.401	6.226
3800	19.830	109.557	91.674	67.957	- 302.035	- 100.080	5.756
3900	19.833	110.072	92.139	69.940	- 302.165	- 94.767	5.311
4000	19.834	110.574	92.593	71.924	- 302.311	- 89.448	4.887
4100	19.836	111.064	93.038	73.907	- 302.477	- 84.123	4.484
4200	19.838	111.542	93.473	75.891	- 302.662	- 78.798	4.100
4300	19.839	112.009	93.898	77.875	- 302.864	- 73.463	3.734
4400	19.841	112.465	94.315	79.859	- 303.088	- 68.124	3.384
4500	19.842	112.911	94.724	81.843	- 303.335	- 62.783	3.049
4600	19.843	113.347	95.124	83.827	- 303.604	- 57.435	2.729
4700	19.845	113.774	95.516	85.812	- 303.897	- 52.085	2.422
4800	19.846	114.192	95.901	87.796	- 304.216	- 46.723	2.127
4900	19.847	114.601	96.278	89.781	- 304.563	- 41.354	1.844
5000	19.848	115.002	96.649	91.766	- 304.936	- 35.975	1.572
5100	19.849	115.395	97.012	93.751	- 305.341	- 30.594	1.311
5200	19.850	115.780	97.370	95.735	- 305.779	- 25.199	1.059
5300	19.850	116.158	97.721	97.720	- 306.250	- 19.803	.817
5400	19.851	116.530	98.065	99.706	- 306.755	- 14.397	.583
5500	19.852	116.894	98.405	101.691	- 307.300	- 8.973	.357
5600	19.853	117.252	98.738	103.676	- 307.884	- 3.549	.129
5700	19.853	117.603	99.066	105.661	- 308.510	1.896	- .073
5800	19.854	117.948	99.388	107.647	- 309.180	7.348	- .277
5900	19.855	118.288	99.706	109.632	- 309.896	12.807	- .474
6000	19.855	118.621	100.018	111.617	- 310.662	18.287	- .666

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

LITHIUM FLUORIDE, DIMERIC (Li_2F_2) (IDEAL GAS) GFW = 51.8748

Point Group D_{2h}

$\Delta Hf^\circ_0 = -224.20 \pm 4.0$ kcal/mol

$S^\circ_{298.15} = 61.8 \pm 2$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -225.33 \pm 4.0$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[570] (1)	301.5 (1)
[570] (1)	571.5 (1)
[490] (1)	658.0 (1)

Bond Distances: Li-F = 1.68 Å F-F = 2.67 Å

Bond Angles: Li-F-Li = 74.76° F-Li-F = 105.24° σ = 4

Product of the Moments of Inertia: $I_AI_BI_C = 3.6766 \times 10^{-115}\ g^3cm^6$

Heat of Formation

The heat of formation (ΔHf°_{298}) is calculated based on the adopted value ΔHr°_{1000} = 61.4 kcal/mol for the reaction $Li_2F_2(g) = 2LiF(g)$ which is consistent with the literature values listed in the table below. Due to lack of knowledge of the fragmentation patterns, the relative ionization cross sections of the ionic species formed in the mass spectrometer, and the molecular constants of the LiF polymers, the evaluation of equilibrium constants used to calculate ΔHr° involves considerable uncertainty. In order to solve this problem more research work seems necessary.

	Investigator	ΔHr°_{1000}, kcal/mol	Experimental Method
1.	Berkowitz et al. (1962)	61.6 ± 2	mass spectrometry with a double-oven apparatus
2.	Buchler and Stauffer (1966)	61.3 ± 3	mass spectrometry with a two-piece Ni Knudsen cell
3.	Eisenstadt et al. (1958)	61.2	molecular-beam velocity-selector
4.	Hildenbrand et al. (1964)	60.4 ± 3	torsion effusion
5.	Akishin et al. (1959)	59.5 ± 3	mass spectrometry with a double effusion chamber
6.	Porter and Schoonmaker (1958)	65.0 *	mass spectrometry with a Mo Knudsen cell

* derived from reported vapor pressures of LiF(g) and $Li_2F_2(g)$ at 1073°K.

Heat Capacity and Entropy

The molecular structure of $Li_2F_2(g)$ was determined as D_{2h} by Buchler et al. (12), using electric deflection and mass spectrometric detection. Akishin and Rambidi (7) studied the structure of $Li_2F_2(g)$ by electron deflection with sector microphotometry and assigned the bond distances of Li-F and F-F which are adopted. Evidence for a matrix stabilized linear structure of Li_2F_2 has been obtained by extending the spectral measurements for matrix isolated lithium fluoride into the far infrared region by Redington (8) and Abramowitz et al. (9).

Klemperer and Norris (10) observed two infrared-active vibrational frequencies, 640 and 460 cm^{-1}, and assigned them as $\nu_5(B_{2u})$ and $\nu_6(B_{3u})$. The infrared absorption spectra of lithium fluoride monomer and dimer isolated in solid inert gas matrices were investigated by Linevsky (11), Snelson and Pitzer (13), and Schlick and Schnepp (14). Redington (8) obtained infrared spectra of LiF species suspended in solid Ne, O_2, CO, and CH_4 at liquid-helium temperature. The observed solvent shifts for LiF and Li_2F_2 spectra exhibit several regularities. The vibrational frequencies used for calculation are those reported by Snelson (15) who re-examined the spectrum of LiF species over the range 200 - 4000 cm^{-1}, using sample purity of 99.3%. The saturated vapor was isolated at 900°C and the superheated unsaturated vapor at 1200°C. A variety of deposition rates and matrix dilutions was tried. Based on the frequencies assigned to the isotopic species, the vibrational frequencies of the natural isotopic $Li_2F_2(g)$ are calculated. It appears that the vibrational frequencies calculated on the basis of the potential function for an ionic model by Berkowitz (16) are too low.

The three principal moments of inertia are: $I_A = 2.3970 \times 10^{-39}$, $I_B = 1.1244 \times 10^{-38}$ and $I_C = 1.3641 \times 10^{-38}$ g cm^2.

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Magnesium Difluoride (MgF_2)
(Crystal)   Mol. Wt. = 62.3083

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.370	-267.764	-267.764	INFINITE
100	5.193	2.552	24.476	-2.192	-268.435	-264.394	577.805
200	11.668	8.378	14.948	-1.314	-268.819	-260.279	284.406
298	14.720	13.683	13.683	.000	-268.700	-256.005	187.648
300	14.790	13.775	13.684	.027	-268.698	-255.927	186.434
400	16.390	18.265	14.785	1.592	-268.517	-251.695	137.513
500	17.310	22.028	15.468	3.280	-268.278	-247.516	108.184
600	17.830	25.232	16.835	5.038	-268.021	-243.388	88.650
700	18.250	28.013	18.237	6.843	-267.760	-239.302	74.710
800	18.600	30.473	19.616	8.685	-267.509	-235.256	64.266
900	18.930	32.683	20.947	10.562	-267.269	-231.238	56.150
1000	19.230	34.693	22.223	12.470	-269.165	-227.066	49.623
1100	19.520	36.539	23.441	14.408	-268.921	-222.869	44.278
1200	19.800	38.250	24.605	16.374	-268.679	-218.693	39.828
1300	20.080	39.846	25.717	18.368	-268.441	-214.537	36.065
1400	20.350	41.344	26.780	20.389	-298.571	-209.920	32.768
1500	20.610	42.757	27.799	22.437	-297.931	-203.609	29.664
1600	20.880	44.096	28.776	24.512	-297.268	-197.344	26.955
1700	21.140	45.369	29.715	26.613	-296.582	-191.118	24.569
1800	21.400	46.585	30.618	28.740	-295.874	-184.936	22.453
1900	21.660	47.749	31.489	30.893	-295.141	-178.792	20.565
2000	21.920	48.867	32.331	33.072	-294.386	-172.687	18.869
2100	22.175	49.942	33.144	35.277	-293.608	-166.624	17.340
2200	22.430	50.980	33.931	37.507	-292.808	-160.594	15.953
2300	22.686	51.982	34.694	39.763	-291.984	-154.601	14.690
2400	22.943	52.953	35.435	42.044	-291.138	-148.648	13.536
2500	23.200	53.895	36.155	44.351	-290.270	-142.730	12.477

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE (MgF_2)   (CRYSTAL)   MOL. WT. = 62.3088

$S^\circ_{298.15}$ = 13.68 ± 0.07 cal. deg.$^{-1}$ mole^{-1}

T_m = 1536°K.

$\Delta H^\circ_{f\ 0}$ = -267.8 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -268.7 ± 0.3 kcal. mole^{-1}

ΔH°_m = 13.90 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 95.5 ± 1.5 kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ for MgF_2(c) was obtained from E. Rudzitis and W. N. Hubbard, Argonne National Laboratory, Argonne, Illinois, private communication, dated June 18, 1964. This value was determined by fluorine bomb calorimetry which is considered as comparatively the best method available at the present time. The heats of reaction involving MgF_2(c) were measured by many early investigators. However, the $\Delta H^\circ_{f\ 298.15}$($MgF_2$, c) values derived are in reasonable agreement. The results are presented as follows.

Investigator	Chemical Reaction	$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1}	$\Delta H^\circ_{f\ 298.15}$, kcal. mole^{-1}
Domange(1)	$MgF_2(c) + H_2O(g) \rightarrow 2HF(g) + MgO(c)$	+51.76 ± 1.2(1)	-267.3 ± 1.3
Wartenberg(2)	$Mg(c) + 2(HF\cdot 80H_2O) \rightarrow MgF_2(c) + H_2(g) + 160H_2O(l)$	-109.5 ± 0.7	-262.1 ± 0.8
Torgeson, et al.(3)	$Mg(OH)_2(c) + 2HF(Sol.) \rightarrow MgF_2(c) + 2H_2O(l)$	-29.09	-266.5 ± 0.8
Gross, et al.(4)	$Mg(c) + PbF_2(c) \rightarrow MgF_2(c) + Pb(c)$	-109.5 ± 1.5	-269.1 ± 1.8

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Heat Capacity and Entropy.

The low temperature heat capacities, 54.22-296.5°K., were measured by S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949). The high temperature heat capacities, 298-1536°K., were obtained from the heat content measurements determined by B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). These two sets of data were joined smoothly at 298°K. $S^\circ_{298.15}$ was obtained from C_p data reported by S. S. Todd, loc. cit., using S°_{51} (extrap.) = 0.537 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m and ΔH°_m were taken from B. F. Naylor, loc. cit.

Heat of Sublimation.

The vapor pressure of MgF_2(c) has been measured by seven investigators. Using the reported data, the respective $\Delta H^\circ_{s\ 298.15}$ for MgF_2(c) were calculated (see MgF_2(g) table for detail). The adopted value was selected to be 95.5 ± 1.5 kcal. mole^{-1}.

Magnesium Difluoride (MgF_2)

(Liquid)   Mol. Wt. = 62.3088

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	22.570	15.290	15.290	- .000	- 259.557	- 247.341	181.297
300	22.570	15.430	15.290	.042	- 259.540	- 247.266	180.124
400	22.570	21.923	16.176	2.299	- 258.667	- 243.308	132.931
500	22.570	26.959	17.847	4.556	- 257.859	- 239.563	104.708
600	22.570	31.074	19.719	6.813	- 257.103	- 235.976	85.950
700	22.570	34.553	21.596	9.070	- 256.390	- 232.511	72.590
800	22.570	37.567	23.408	11.327	- 255.724	- 229.147	62.597
900	22.570	40.225	25.132	13.584	- 255.104	- 225.862	54.844
1000	22.570	42.603	26.763	15.841	- 256.651	- 222.463	48.617
1100	22.570	44.754	28.302	18.098	- 256.088	- 219.073	43.524
1200	22.570	46.718	29.756	20.355	- 255.555	- 215.731	39.288
1300	22.570	48.525	31.131	22.612	- 255.054	- 212.432	35.711
1400	22.570	50.197	32.434	24.869	- 284.948	- 208.692	32.577
1500	22.570	51.755	33.671	27.126	- 284.099	- 203.274	29.616
1600	22.570	53.211	34.847	29.383	- 283.254	- 197.915	27.033
1700	22.570	54.580	35.968	31.640	- 282.412	- 192.606	24.760
1800	22.570	55.870	37.038	33.897	- 281.574	- 187.349	22.746
1900	22.570	57.090	38.062	36.154	- 280.737	- 182.137	20.949
2000	22.570	58.248	39.042	38.411	- 279.904	- 176.967	19.337
2100	22.570	59.349	39.983	40.668	- 279.074	- 171.844	17.883
2200	22.570	60.399	40.888	42.925	- 278.247	- 166.755	16.565
2300	22.570	61.402	41.758	45.182	- 277.422	- 161.705	15.365
2400	22.570	62.363	42.596	47.439	- 276.600	- 156.693	14.268
2500	22.570	63.284	43.406	49.696	- 275.782	- 151.715	13.262
2600	22.570	64.169	44.187	51.953	- 274.966	- 146.766	12.336
2700	22.570	65.021	44.943	54.210	- 274.153	- 141.850	11.481
2800	22.570	65.842	45.675	56.467	- 273.342	- 136.968	10.690
2900	22.570	66.634	46.384	58.724	- 272.535	- 132.108	9.955
3000	22.570	67.399	47.072	60.981	- 271.733	- 127.283	9.272
3100	22.570	68.139	47.740	63.238	- 270.933	- 122.481	8.634
3200	22.570	68.856	48.388	65.495	- 270.138	- 117.705	8.038
3300	22.570	69.550	49.019	67.752	- 269.347	- 112.954	7.480
3400	22.570	70.224	49.633	70.009	- 268.561	- 108.224	6.956
3500	22.570	70.878	50.231	72.266	- 267.781	- 103.520	6.464
3600	22.570	71.514	50.813	74.523	- 267.006	- 98.836	6.000
3700	22.570	72.132	51.381	76.780	- 266.238	- 94.175	5.562
3800	22.570	72.734	51.935	79.037	- 265.476	- 89.533	5.149
3900	22.570	73.321	52.476	81.294	- 264.722	- 84.919	4.758
4000	22.570	73.892	53.004	83.551	- 263.975	- 80.315	4.388

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE (MgF_2)   (LIQUID)   MOL. WT. = 62.3088

$S^\circ_{298.15}$ = 15.290 cal. deg.$^{-1}$ mole^{-1}

T_m = 1536°K.

T_b = [2499]°K.

$\Delta H^\circ_{f\ 298.15}$ = -259.557 kcal. mole^{-1}

ΔH°_m = 13.90 kcal. mole^{-1}

ΔH°_v = [63.48] kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}(l)$ was obtained from $\Delta H^\circ_{f\ 298.15}(c)$ by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity (1691-1800°K.) was reported by B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). The same value was used for other temperatures. The entropy was obtained in a manner analogous to that of the heat or formation.

Melting Data.

T_m and ΔH°_m were obtained from B. F. Naylor, Loc. Cit.

Vaporization Data.

T_b was obtained from equilibrium calculation between the species $MgF_2(l)$, $MgF_2(g)$, and $(MgF_2)_2(g)$, i.e., the temperature at which the sum of the partial pressures of $MgF_2(g)$ and $(MgF_2)_2(g)$ equals one atmosphere. From the difference between the heats of formation of $MgF_2(l)$ and $MgF_2(g)$ at the boiling point, the heat of vaporization was calculated. At the boiling point the amount of dimeric species is negligible in comparison with that of the monomeric species.

Magnesium Difluoride (MgF_2)

(Ideal Gas) Mol. Wt. = 62.3088

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.878	-172.772	-172.772	INFINITE
100	8.842	50.659	71.252	-2.059	-172.802	-173.571	379.340
200	10.488	57.319	62.764	-1.089	-173.094	-174.342	190.512
298	11.621	61.734	61.734	.000	-173.200	-174.832	128.155
300	11.638	61.806	61.734	.022	-173.203	-174.842	127.372
400	12.364	65.262	62.200	1.225	-173.384	-175.361	95.813
500	12.815	68.073	63.102	2.485	-173.573	-175.833	76.857
600	13.103	70.437	64.133	3.782	-173.777	-176.267	64.205
700	13.295	72.472	65.182	5.103	-174.000	-176.664	55.157
800	13.427	74.256	66.207	6.439	-174.255	-177.028	48.362
900	13.522	75.844	67.192	7.787	-174.544	-177.358	43.068
1000	13.592	77.272	68.129	9.143	-176.992	-177.472	38.786
1100	13.644	78.570	69.020	10.505	-177.324	-177.506	35.267
1200	13.685	79.759	69.866	11.871	-177.682	-177.506	32.328
1300	13.717	80.856	70.670	13.242	-178.067	-177.476	29.836
1400	13.743	81.874	71.435	14.615	-208.845	-176.937	27.621
1500	13.764	82.822	72.162	15.990	-208.878	-174.654	25.447
1600	13.782	83.711	72.857	17.367	-208.913	-172.373	23.545
1700	13.796	84.547	73.520	18.746	-208.949	-170.087	21.866
1800	13.808	85.336	74.155	20.126	-208.988	-167.802	20.374
1900	13.818	86.083	74.763	21.508	-209.026	-165.512	19.038
2000	13.827	86.792	75.347	22.890	-209.068	-163.220	17.836
2100	13.835	87.467	75.908	24.273	-209.112	-160.929	16.748
2200	13.841	88.111	76.448	25.657	-209.158	-158.633	15.759
2300	13.847	88.726	76.969	27.041	-209.206	-156.333	14.855
2400	13.852	89.315	77.471	28.426	-209.256	-154.034	14.027
2500	13.857	89.881	77.956	29.812	-209.309	-151.734	13.265
2600	13.861	90.425	78.425	31.198	-209.364	-149.429	12.561
2700	13.864	90.948	78.880	32.584	-209.422	-147.122	11.909
2800	13.868	91.452	79.320	33.971	-209.481	-144.815	11.303
2900	13.870	91.939	79.747	35.357	-209.545	-142.502	10.739
3000	13.873	92.409	80.161	36.745	-209.612	-140.192	10.213
3100	13.875	92.864	80.563	38.132	-209.682	-137.877	9.720
3200	13.877	93.304	80.955	39.520	-209.756	-135.558	9.258
3300	13.879	93.732	81.335	40.908	-209.834	-133.241	8.824
3400	13.881	94.146	81.706	42.296	-209.917	-130.915	8.415
3500	13.88	94.548	82.067	43.684	-210.006	-128.589	8.029
3600	13.884	94.939	82.419	45.072	-210.100	-126.259	7.665
3700	13.886	95.320	82.763	46.461	-210.200	-123.931	7.320
3800	13.887	95.690	83.098	47.849	-210.307	-121.596	6.993
3900	13.888	96.051	83.426	49.238	-210.421	-119.266	6.683
4000	13.889	96.403	83.746	50.627	-210.542	-116.926	6.389
4100	13.890	96.746	84.059	52.016	-210.673	-114.586	6.108
4200	13.891	97.080	84.365	53.405	-210.812	-112.238	5.840
4300	13.892	97.407	84.664	54.794	-210.960	-109.888	5.585
4400	13.893	97.727	84.958	56.183	-211.119	-107.538	5.341
4500	13.894	98.039	85.245	57.573	-211.287	-105.182	5.108
4600	13.894	98.344	85.526	58.962	-211.467	-102.820	4.885
4700	13.895	98.643	85.802	60.352	-211.658	-100.456	4.671
4800	13.896	98.935	86.073	61.741	-211.862	-98.083	4.466
4900	13.896	99.222	86.338	63.131	-212.078	-95.713	4.269
5000	13.897	99.503	86.599	64.520	-212.308	-93.338	4.080
5100	13.897	99.778	86.854	65.910	-212.551	-90.962	3.898
5200	13.898	100.048	87.106	67.300	-212.808	-88.570	3.722
5300	13.898	100.313	8 .352	68.690	-213.079	-86.176	3.554
5400	13.899	100.572	87.595	70.079	-213.367	-83.783	3.391
5500	13.899	100.827	87.833	71.469	-213.669	-81.377	3.234
5600	13.899	101.078	88.067	72.859	-213.988	-78.972	3.082
5700	13.900	101.324	88.298	74.249	-214.323	-76.554	2.935
5800	13.900	101.566	88.524	75.639	-214.674	-74.140	2.794
5900	13.901	101.803	88.747	77.029	-215.044	-71.709	2.656
6000	13.901	102.037	88.967	78.419	-215.431	-69.283	2.524

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE (MgF_2) (IDEAL GAS) MOL. WT. = 62.3088

Point Group C_{2v}

$S^\circ_{298.15}$ = 61.734 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -172.8 ± 1.5 kcal. mole⁻¹

$\Delta H^\circ_{f\ 298.15}$ = -173.2 ± 1.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
478 (1)
241 (1)
834 (1)

Bond Distance: Mg-F = 1.77 ± 0.02 Å

Bond Angle: F-Mg-F = 150 ± 5°

Product of the Moments of Inertia: $I_AI_BI_C = 1.80632 \times 10^{-115}$ g.³ cm.⁶

$\sigma = 2$

Heat of Formation.

The vapor pressure of $MgF_2(g)$ over $MgF_2(c)$ and $MgF_2(l)$ has been measured by many investigators using different methods. Based on the reported vapor pressure data, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Method*	$\Delta H^\circ_{s\ 298.15}$, kcal. mole⁻¹ Second Law Value	Third Law Value	Drift cal. deg.⁻¹ mole⁻¹
Ruff and Boucher[1]	1934 - 2129	a	99.48 ± 2.56	96.19	-1.66 ± 1.31
Guenther[2]	1284 - 1530	b	95.06 ± 0.50	95.64	0.45 ± 0.33
Hammer[3]	1451 - 1533	b	93.68 ± 2.67	96.21	1.62 ± 1.79
	1568 - 1613	b	94.17 ± 6.80	96.21	1.26 ± 4.16
	1413 - 1518	c	95.73 ± 2.99	96.19	0.22 ± 2.08
	1539 - 1614	c	96.87 ± 4.35	96.09	-0.51 ± 2.74
Berkowitz and Marquart[4]	1450	c	——	94.68	——
Farber, et al.[5]	1273 - 1513	c	80.72 ± 1.11	91.58	7.75 ± 0.80
Hildenbrand, et al.[6]	1326 - 1527	c	91.80 ± 1.11	93.40	1.12 ± 0.78
	1544 - 1604	c	94.49 ± 5.00	93.95	-0.39 ± 3.17
	1425 - 1533	c	104.79	95.75	-6.14
	1540 - 1606	c	102.81	95.48	-4.65
	1200 - 1530	—	94.0	——	——
Margrave, et al.[7]	1241 - 1492	b	93.77 ± 2.5	93.07	1.69 ± 0.08

*a = Manometric method; b = Knudsen effusion method; and c = Torsion effusion method

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6 The first two sets of data were obtained from D. L. Hildenbrand, et al., Philco, Ford Motor Company, "An Experimental Program for Obtaining the Thermodynamic Properites of Propellant Combustion Products", U-1187, Third Quarterly Report, Mar. 15, 1961. The last $\Delta H^\circ_{s\ 298.15}$ value was given by D. L. Hildenbrand, private communication, March 19, 1964. The rest were reported by D. L. Hildenbrand, loc. cit., U-2289, Fifth Quarterly Technical Report, Sept. 15, 1963. These values were summarized by D. L. Hildenbrand, et al., J. Chem. Phys. 40, 2882 (1964).

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When vapor pressure data were determined above melting point, 1536°K., the heat of sublimation was derived from the heat of vaporization obtained incorporating heat of melting. All data were carefully examined and some inconsistent vapor pressure points were discarded. The best value of $\Delta H^\circ_{s\ 298.15}$ for $MgF_2(c)$ was selected as 95.5 ± 1.5 kcal. mole⁻¹. The heat of formation for $MgF_2(g)$ was calculated from the heats of formation and sublimation for $MgF_2(c)$.

Heat Capacity and Entropy.

The molecular structure of $MgF_2(g)$ has been reported to be linear by A. Büchler, J. L. Stauffer and W. Klemperer, Interim Technical Report No. 7, June 30, 1964, A. D. Little, Inc., and bent by M. J. Linevsky, First Quarterly Report, Nov. 1, 1963 - Jan. 31, 1964, General Electric Company. An intensive investigation of the matrix spectrum of $MgF_2(g)$ has been made recently by D. E. Mann and G. V. Calder, National Bureau of Standards Report 8919, July 1, 1965. The final results were presented by D. E. Mann at the ICRPG Working Group on Thermochemistry meeting on Mar. 17, 1966. The vibrational frequencies, bent structure and bond angle were confirmed by use of isotopic substitution, and were adopted here. The Mg-F bond distance was reported by P. A. Akishin, V. P. Spiridonov, G. A. Sobolev and V. A. Naumov, Zh. Fiz. Khim. 31, 461 (1957). The three principal moments of inertia are: $I_A = 5.1660 \times 10^{-40}$, $I_B = 1.8442 \times 10^{-38}$ and $I_C = 1.8959 \times 10^{-38}$ g. cm.²

Nitrogen Difluoride (NF_2)

(Ideal Gas) Mol. Wt. = 52.008

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	- 2.528	10.718	10.718	INFINITE
100	7.985	50.345	67.667	- 1.732	10.476	11.417	- 24.951
200	8.677	56.044	60.574	- .906	10.251	12.450	- 13.604
298	9.801	59.715	59.715	.000	10.100	13.564	- 9.942
300	9.822	59.775	59.715	.018	10.098	13.585	- 9.896
400	10.851	62.748	60.113	1.054	10.015	14.762	- 8.065
500	11.617	65.256	60.897	2.179	9.982	15.953	- 6.973
600	12.159	67.425	61.809	3.370	9.984	17.148	- 6.246
700	12.544	69.330	62.750	4.606	10.006	18.340	- 5.726
800	12.820	71.024	63.680	5.875	10.037	19.528	- 5.335
900	13.024	72.546	64.582	7.468	10.074	20.713	- 5.029
1000	13.177	73.927	65.449	8.478	10.113	21.892	- 4.784
1100	13.295	75.189	66.278	9.802	10.150	23.068	- 4.583
1200	13.387	76.350	67.069	11.136	10.187	24.242	- 4.415
1300	13.460	77.424	67.825	12.479	10.221	25.412	- 4.272
1400	13.519	78.424	68.547	13.828	10.253	26.579	- 4.149
1500	13.568	79.358	69.237	15.182	10.282	27.744	- 4.042
1600	13.608	80.235	69.897	16.541	10.308	28.907	- 3.948
1700	13.641	81.061	70.530	17.904	10.331	30.070	- 3.866
1800	13.670	81.842	71.137	19.269	10.350	31.228	- 3.791
1900	13.694	82.581	71.720	20.637	10.367	32.389	- 3.725
2000	13.714	83.284	72.281	22.008	10.382	33.549	- 3.666
2100	13.732	83.954	72.821	23.380	10.393	34.705	- 3.612
2200	13.748	84.593	73.341	24.754	10.401	35.862	- 3.562
2300	13.761	85.205	73.844	26.130	10.407	37.020	- 3.518
2400	13.773	85.791	74.330	27.506	10.410	38.177	- 3.476
2500	13.784	86.353	74.799	28.884	10.410	39.334	- 3.438
2600	13.793	86.894	75.254	30.263	10.407	40.491	- 3.403
2700	13.802	87.415	75.695	31.643	10.402	41.649	- 3.371
2800	13.809	87.917	76.123	33.023	10.395	42.805	- 3.341
2900	13.816	88.401	76.538	34.405	10.386	43.965	- 3.313
3000	13.822	88.870	76.941	35.787	10.372	45.120	- 3.287
3100	13.828	89.323	77.333	37.169	10.358	46.279	- 3.262
3200	13.833	89.762	77.715	38.552	10.340	47.438	- 3.240
3300	13.838	90.188	78.086	39.936	10.319	48.598	- 3.218
3400	13.842	90.601	78.448	41.320	10.297	49.759	- 3.198
3500	13.846	91.002	78.801	42.704	10.272	50.921	- 3.179
3600	13.849	91.392	79.146	44.089	10.244	52.084	- 3.162
3700	13.852	91.772	79.482	45.474	10.214	53.245	- 3.145
3800	13.855	92.141	79.810	46.859	10.182	54.410	- 3.129
3900	13.858	92.501	80.131	48.245	10.146	55.572	- 3.114
4000	13.861	92.852	80.445	49.631	10.109	56.738	- 3.100
4100	13.863	93.195	80.751	51.017	10.069	57.904	- 3.086
4200	13.865	93.529	81.052	52.404	10.027	59.071	- 3.074
4300	13.867	93.855	81.346	53.790	9.983	60.242	- 3.062
4400	13.869	94.174	81.634	55.177	9.935	61.409	- 3.050
4500	13.871	94.485	81.916	56.564	9.886	62.578	- 3.039
4600	13.873	94.790	82.192	57.951	9.834	63.751	- 3.029
4700	13.875	95.089	82.464	59.339	9.780	64.924	- 3.019
4800	13.876	95.381	82.730	60.726	9.723	66.100	- 3.009
4900	13.877	95.667	82.991	62.114	9.664	67.273	- 3.000
5000	13.879	95.947	83.247	63.502	9.602	68.450	- 2.992
5100	13.880	96.222	83.499	64.890	9.538	69.623	- 2.983
5200	13.881	96.492	83.746	66.278	9.472	70.807	- 2.976
5300	13.882	96.756	83.989	67.666	9.403	71.987	- 2.968
5400	13.883	97.016	84.228	69.054	9.332	73.164	- 2.961
5500	13.884	97.270	84.463	70.443	9.258	74.351	- 2.954
5600	13.885	97.521	84.694	71.831	9.181	75.535	- 2.948
5700	13.886	97.766	84.921	73.220	9.103	76.722	- 2.942
5800	13.887	98.008	85.144	74.608	9.022	77.109	- 2.936
5900	13.888	98.245	85.364	75.997	8.938	79.094	- 2.930
6000	13.889	98.479	85.581	77.386	8.852	80.284	- 2.924

Dec. 31, 1962; Mar. 31, 1964

NITROGEN DIFLUORIDE (NF_2) (IDEAL GAS) MOL. WT. = 52.008

Point Group = C_{2v}

$S^\circ_{298.15}$ = 59.72 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 2

$\Delta H^\circ_{f\ 0}$ = 10.7 ± 2.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 10.1 ± 2.0 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1074 (1)
573 (1)
931 (1)

Bond Distance: N-F = 1.37 Å

Bond Angle: F-N-F = 104.2°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 7.6097 X 10^{-116} gm.^{3} cm.^{6}

Heat of Formation.

C. B. Colburn and F. A. Johnson, J. Chem. Phys. 33, 1869 (1960), report the study of the dissociation reaction $N_2F_4(g) = 2NF_2(l)$ by two independent methods: (a) measurement of the pressure variation with temperature at constant volume and (b) a spectrophotometric method based on the temperature dependence of the ultraviolet absorption of the NF_2 radical. The authors give a more detailed account of their data in J. Am. Chem. Soc. 83, 3043 (1961). The contents of these articles indicate that $2NF_2(l)$ should read $2NF_2(g)$ in the above reaction. The first method gave a value of 19.85 kcal. mole^{-1} for the heat of dissociation in the temperature range 373 to 423°K. which corresponds to 19.87 kcal. mole^{-1} at 298°K. From their ΔH and ΔS data, ΔF was calculated and used in a third law evaluation of the heat of dissociation. The ΔH_{298} so calculated showed an increasing trend with increasing temperature; the average value was 22.87 kcal. mole^{-1} which is not in agreement with their value of 19.87 kcal. mole^{-1}. The spectrophotometric value of 21.7 kcal. mole^{-1} at 298°K. was obtained from the integrated Van't Hoff equation.

L. H. Piette, F. A. Johnson, K. A. Booman and C. B. Colburn, J. Chem. Phys. 35, 1481 (1961), studied the temperature dependence of the EPR spectrum of the NF_2 radical. They obtained a second law value of 19.3 kcal. mole^{-1} for the heat of dissociation. This value, however, depends upon the degree of dissociation of N_2F_4 which they calculated from the (dP/dT) measurements of Colburn and Johnson. Any error in the (dP/dT) measurements would manifest itself in like manner here.

H. E. Doorenbos and B. R. Loy, J. Chem. Phys. 39, 2393 (1963), investigated the ESR spectrum of the N_2F_4-NF_2 equilibrium from which they calculated a second law value of 19.8 kcal. mole^{-1} for the heat of dissociation. They report that at 25°C. and 13 atm. N_2F_4 is 0.022% dissociated in the vapor phase. A third law calculation using this datum and the relationship $K_p = (4\alpha^2/1-\alpha^2)P_T$, where α is the degree of dissociation of N_2F_4 and P_T is the total pressure, gave a heat of dissociation of 21.79 kcal. mole^{-1} at 298°K.; this is not in agreement with their second law value.

J. T. Herron and V. H. Dibeler, J. Research Natl. Bur. Standards 65A, 405 (1961), report thermal dissociation data for N_2F_4. From their data they calculate a second law value of 21.5 kcal. mole^{-1} for the heat of dissociation of N_2F_4. A second and third law evaluation of their data was performed in the Dow Thermal Laboratory. It was found that if the k factor, relating their measured ion abundances to partial pressures, was taken as 4.72 X 10^{-8}, a third law value was obtained that showed slight scatter but no temperature dependence. Excluding those points that showed scatter, the third law heat of dissociation at 298°K. was 22.27 kcal. mole^{-1}. A second law plot gave a heat value of 22.23 kcal. mole^{-1} at an average temperature of 400°K. or 22.25 kcal. mole^{-1} at 298°K. Those points that deviated from the chosen straight line in the second law plot showed corresponding deviations in the third law calculation. Those points lying on the second law slope gave a constant third law value.

The heat of dissociation for $N_2F_4(g) = 2NF_2(g)$ was taken to be 22.26 kcal. mole^{-1}. Utilizing the heat of formation of $N_2F_4(g)$ (see N_2F_4 table), the heat of formation of the difluoroamino radical becomes 10.1 ± 2.0 kcal. mole^{-1}. All values for the heat of dissociation fall within the limits of error assigned to the heat of formation of NF_2.

Heat Capacity and Entropy.

See table on tetrafluorohydrazine (N_2F_4) (ideal gas) for writeup.

Difluorodiazine, Cis-(N_2F_2)

(Ideal Gas) Mol. Wt. = 66.0102

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.725	17.857	17.857	INFINITE
100	8.036	51.829	71.121	-1.929	17.273	19.971	-43.644
200	9.644	57.787	63.090	-1.060	16.739	22.887	-25.009
298	11.941	62.071	62.071	.000	16.400	25.984	-19.046
300	11.982	62.145	62.071	.022	16.395	26.043	-18.972
400	13.900	65.867	62.565	1.321	16.227	29.290	-16.003
500	15.306	69.129	63.559	2.785	16.181	32.562	-14.232
600	16.318	72.014	64.732	4.369	16.221	35.837	-13.053
700	17.053	74.587	65.960	6.039	16.312	39.100	-12.207
800	17.595	76.902	67.185	7.773	16.437	42.345	-11.568
900	18.002	78.999	68.383	9.554	16.583	45.576	-11.067
1000	18.313	80.912	69.542	11.370	16.740	48.788	-10.662
1100	18.555	82.669	70.657	13.214	16.904	51.985	-10.328
1200	18.746	84.292	71.726	15.080	17.072	55.168	-10.047
1300	18.900	85.799	72.751	16.962	17.240	58.336	-9.807
1400	19.025	87.205	73.734	18.859	17.409	61.489	-9.598
1500	19.127	88.521	74.676	20.766	17.576	64.633	-9.417
1600	19.213	89.758	75.581	22.684	17.743	67.765	-9.256
1700	19.284	90.925	76.449	24.608	17.906	70.887	-9.113
1800	19.345	92.029	77.285	26.540	18.067	73.997	-8.984
1900	19.397	93.076	78.088	28.477	18.227	77.103	-8.868
2000	19.442	94.072	78.863	30.419	18.384	80.198	-8.763
2100	19.481	95.022	79.610	32.365	18.538	83.281	-8.667
2200	19.514	95.929	80.331	34.315	18.689	86.361	-8.579
2300	19.544	96.797	81.028	36.268	18.838	89.434	-8.498
2400	19.570	97.630	81.703	38.224	18.985	92.499	-8.423
2500	19.593	98.429	82.356	40.182	19.127	95.560	-8.353
2600	19.614	99.198	82.989	42.143	19.268	98.614	-8.289
2700	19.632	99.938	83.603	44.105	19.406	101.667	-8.229
2800	19.649	100.653	84.199	46.069	19.542	104.707	-8.172
2900	19.664	101.342	84.779	48.035	19.676	107.752	-8.120
3000	19.677	102.009	85.342	50.002	19.805	110.783	-8.070
3100	19.690	102.655	85.890	51.970	19.933	113.810	-8.023
3200	19.701	103.280	86.424	53.940	20.058	116.838	-7.979
3300	19.711	103.886	86.944	55.910	20.179	119.862	-7.938
3400	19.720	104.475	87.451	57.882	20.300	122.881	-7.898
3500	19.729	105.047	87.946	59.854	20.416	125.896	-7.861
3600	19.736	105.603	88.428	61.827	20.530	128.908	-7.825
3700	19.744	106.143	88.900	63.801	20.642	131.920	-7.792
3800	19.750	106.670	89.361	65.776	20.751	134.926	-7.760
3900	19.756	107.183	89.811	67.751	20.857	137.928	-7.729
4000	19.762	107.683	90.252	69.727	20.961	140.929	-7.700
4100	19.767	108.171	90.683	71.704	21.062	143.926	-7.672
4200	19.772	108.648	91.105	73.681	21.160	146.920	-7.645
4300	19.777	109.113	91.518	75.658	21.257	149.918	-7.619
4400	19.781	109.568	91.923	77.636	21.349	152.905	-7.594
4500	19.785	110.012	92.320	79.614	21.439	155.895	-7.571
4600	19.789	110.447	92.710	81.593	21.528	158.884	-7.548
4700	19.792	110.873	93.092	83.572	21.613	161.866	-7.526
4800	19.796	111.290	93.466	85.552	21.696	164.851	-7.505
4900	19.799	111.698	93.834	87.531	21.775	167.830	-7.485
5000	19.802	112.098	94.196	89.511	21.852	170.812	-7.466
5100	19.804	112.490	94.551	91.492	21.927	173.784	-7.447
5200	19.807	112.875	94.899	93.472	21.999	176.767	-7.429
5300	19.809	113.252	95.242	95.453	22.068	179.743	-7.411
5400	19.812	113.622	95.579	97.434	22.134	182.714	-7.394
5500	19.814	113.986	95.910	99.415	22.197	185.690	-7.378
5600	19.816	114.343	96.236	101.397	22.258	188.662	-7.363
5700	19.818	114.694	96.557	103.378	22.315	191.634	-7.347
5800	19.820	115.038	96.873	105.360	22.371	194.608	-7.333
5900	19.822	115.377	97.183	107.342	22.423	197.571	-7.318
6000	19.823	115.710	97.489	109.325	22.473	200.541	-7.304

Dec. 31, 1965

DIFLUORODIAZINE, Cis-(N_2F_2) (IDEAL GAS) MOL. WT. = 66.0102

Point Group C_{2v}

$S^\circ_{298.15}$ = 62.1 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 17.9 ± 1.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 16.4 ± 1.2 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
896 (1)	952 (1)
1524 (1)	573 (1)
552 (1)	737 (1)

Bond Distance: N-F = 1.384 Å N-N = 1.214 Å

Bond Angle: F-N-N = 114.5 ± 0.5°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 6.583621 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was derived from the heat of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2NH_4F(c) + 4/3\ N_2(g)$ which was measured calorimetrically by G. T. Armstrong and S. Marantz[1]. There are two isomers, the trans and the active form of difluorodiazine. The heats of formation were determined to be 19.4 and 16.4 kcal. mole^{-1} for the trans and the active isomers respectively. The active form of N_2F_2 has been interpreted here as the cis isomer which will be discussed later. The heat of isomerization has also been reported as 3.0 kcal. mole^{-1} by Armstrong and Marantz. The value, $\Delta H^\circ_{f\ 298}$ (cis N_2F_2, g) = 16.4 kcal. mole^{-1}, is adopted in the tabulation.

A. V. Pankratov et al.[2], have measured the enthalpy of reaction $N_2F_2(g) + 3KI = 2KF + N_2 + KI_3$ in acidic solution (pH = 3), and reported $\Delta H^\circ_{f\ 298}$ (active N_2F_2, g) = 25.3 ± 2.0 kcal. mole^{-1}.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal. mole^{-1} by C. B. Colburn et al.[9] The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives $\Delta H^\circ_{r\ 298}$ = 2.52 ± 0.05 kcal. mole^{-1} for the reaction cis $N_2F_2(g) \rightarrow$ trans $N_2F_2(g)$ which is in good agreement with Armstrong and Sidney's data.

Heat Capacity and Entropy.

Although the infrared spectrum[7,8] of the active form of $N_2F_2(g)$ has been interpreted as favoring the 1,1-difluorodiazine over the cis-configuration[3,4], n.m.r.[5] and microwave[6] studies definitely indicate the latter. The vibrational frequencies[7] previously assigned to the 1,1-difluorodiazine have been adopted here for the cis isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies[6]. The principal moments of inertia were: I_A = 4.2438 X 10^{-39}, I_B = 10.5129 X 10^{-39} and I_C = 14.7567 X 10^{-39} g. cm.^{2}

See the trans $N_2F_2(g)$ table for the comparison of the different physical properties between trans and cis isomers.

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(8) R. H. Sanborn, J. Chem. Phys. 34, 2188 (1961).

(9) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, J. Am. Chem. Soc. 81, 6397 (1959).

Difluorodiazine, Trans-(N_2F_2)
(Ideal Gas)   Mol. Wt. = 66.0102

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.923	20.659	20.659	INFINITE
100	8.453	51.506	72.695	- 2.119	20.083	22.813	- 49.856
200	10.774	58.062	63.860	- 1.160	19.639	25.733	- 28.118
298	12.779	62.752	62.752	.000	19.400	28.781	- 21.096
300	12.812	62.832	62.753	.024	19.397	28.839	- 21.008
400	14.392	66.744	63.275	1.387	19.293	32.006	- 17.486
500	15.583	70.090	64.312	2.889	19.285	35.186	- 15.379
600	16.473	73.014	65.523	4.494	19.346	38.362	- 13.973
700	17.139	75.605	66.782	6.176	19.449	41.524	- 12.964
800	17.641	77.928	68.033	7.916	19.580	44.668	- 12.202
900	18.026	80.029	69.251	9.701	19.730	47.795	- 11.606
1000	18.323	81.945	70.426	11.519	19.889	50.904	- 11.124
1100	18.558	83.702	71.554	13.363	20.053	53.998	- 10.728
1200	18.744	85.325	72.635	15.229	20.221	57.077	- 10.395
1300	18.895	86.832	73.670	17.111	20.389	60.142	- 10.110
1400	19.019	88.237	74.661	19.007	20.557	63.192	- 9.864
1500	19.121	89.553	75.610	20.914	20.724	66.232	- 9.650
1600	19.206	90.789	76.520	22.830	20.889	69.262	- 9.460
1700	19.277	91.956	77.394	24.755	21.053	72.280	- 9.292
1800	19.338	93.060	78.234	26.685	21.212	75.286	- 9.141
1900	19.390	94.107	79.042	28.622	21.372	78.288	- 9.005
2000	19.435	95.102	79.821	30.563	21.528	81.282	- 8.882
2100	19.474	96.052	80.571	32.509	21.682	84.262	- 8.769
2200	19.509	96.958	81.296	34.458	21.832	87.240	- 8.666
2300	19.538	97.826	81.996	36.410	21.980	90.210	- 8.571
2400	19.565	98.658	82.673	38.366	22.127	93.174	- 8.484
2500	19.588	99.457	83.328	40.323	22.268	96.131	- 8.403
2600	19.609	100.226	83.963	42.283	22.408	99.082	- 8.328
2700	19.628	100.967	84.580	44.245	22.546	102.029	- 8.258
2800	19.645	101.681	85.178	46.209	22.682	104.968	- 8.193
2900	19.660	102.370	85.759	48.174	22.815	107.910	- 8.132
3000	19.673	103.037	86.324	50.141	22.944	110.838	- 8.074
3100	19.686	103.682	86.873	52.109	23.072	113.765	- 8.020
3200	19.697	104.308	87.408	54.078	23.196	116.687	- 7.969
3300	19.707	104.914	87.930	56.048	23.317	119.608	- 7.921
3400	19.717	105.502	88.438	58.019	23.437	122.527	- 7.876
3500	19.726	106.074	88.934	59.991	23.553	125.438	- 7.832
3600	19.733	106.630	89.417	61.964	23.667	128.348	- 7.791
3700	19.741	107.171	89.890	63.938	23.779	131.253	- 7.752
3800	19.748	107.697	90.352	65.912	23.887	134.160	- 7.716
3900	19.754	108.210	90.803	67.887	23.993	137.058	- 7.680
4000	19.760	108.710	91.245	69.863	24.097	139.957	- 7.647
4100	19.765	109.198	91.676	71.839	24.197	142.851	- 7.614
4200	19.770	109.675	92.099	73.816	24.295	145.742	- 7.583
4300	19.775	110.140	92.514	75.793	24.392	148.637	- 7.554
4400	19.779	110.595	92.919	77.771	24.484	151.521	- 7.526
4500	19.783	111.039	93.317	79.749	24.574	154.408	- 7.499
4600	19.787	111.474	93.707	81.728	24.663	157.294	- 7.473
4700	19.791	111.900	94.090	83.707	24.748	160.173	- 7.448
4800	19.794	112.316	94.465	85.686	24.830	163.060	- 7.424
4900	19.797	112.724	94.833	87.665	24.909	165.936	- 7.401
5000	19.800	113.124	95.195	89.645	24.986	168.816	- 7.379
5100	19.803	113.516	95.551	91.625	25.060	171.685	- 7.357
5200	19.805	113.901	95.900	93.606	25.133	174.565	- 7.336
5300	19.808	114.278	96.243	95.586	25.201	177.439	- 7.316
5400	19.810	114.649	96.581	97.567	25.267	180.301	- 7.297
5500	19.813	115.012	96.912	99.548	25.330	183.180	- 7.279
5600	19.815	115.369	97.239	101.530	25.391	186.049	- 7.261
5700	19.817	115.720	97.560	103.511	25.448	188.919	- 7.243
5800	19.819	116.065	97.876	105.493	25.504	191.784	- 7.226
5900	19.820	116.403	98.187	107.475	25.556	194.650	- 7.210
6000	19.822	116.736	98.494	109.457	25.605	197.517	- 7.194

Dec. 31, 1965

DIFLUORODIAZINE, Trans-(N_2F_2) (IDEAL GAS) **MOL. WT. = 66.0102**

Point Group C_{2h}

$S^\circ_{298.15}$ = 62.75 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 20.7 ± 1.2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 19.4 ± 1.2 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1010 (1)	989 (1)
1636 (1)	421 (1)
592 (1)	360 (1)

Bond Distance : N-F = 1.44 Å   N-N = 1.25 Å

Bond Angle: F-N-N = 115°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 432.6784 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

G. T. Armstrong and S. Marantz, J. Chem. Phys. 38, 169 (1963) have measured calorimetrically the enthalpy of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2NH_4F(c) + 4/3\ N_2(g)$, and reported $\Delta H^\circ_{f\ 298}$ (trans N_2F_2, g) = 19.4 ± 1.2 kcal. mole^{-1} which is adopted in this tabulation.

Heat Capacity and Entropy.

The bond distances and bond angle were obtained from S. H. Bauer, J. Am. Chem. Soc. 69, 3104 (1947), by electron diffraction. The fundamental vibrational frequencies were obtained from R. H. Sanborn, J. Chem. Phys. 33, 1855 (1960) by infrared spectroscopy. The three principal moments of inertia are $I_A = 0.919 \times 10^{-39}$, $I_B = 21.2433 \times 10^{-39}$ and $I_C = 22.1623 \times 10^{-39}$ g. cm.^{2}

As pointed out by R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. 34, 2187 (1961), the trans N_2F_2 is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

Sodium Difluoride Uninegative Ion (NaF_2^-)

(Ideal Gas) GFW = 60.98715

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	13.112	59.885	59.885	.000	- 160.000	- 158.256	116.005
300	13.128	59.966	59.885	.024	- 160.011	- 158.245	115.281
400	13.769	63.840	60.409	1.372	- 161.274	- 157.513	86.061
500	14.129	66.955	61.417	2.769	- 161.922	- 156.498	68.405
600	14.346	69.551	62.562	4.194	- 162.547	- 155.354	56.588
700	14.484	71.774	63.723	5.636	- 163.158	- 154.106	48.114
800	14.578	73.715	64.853	7.089	- 163.763	- 152.772	41.735
900	14.643	75.436	65.935	8.550	- 164.365	- 151.362	36.756
1000	14.691	76.981	66.964	10.017	- 164.970	- 149.885	32.757
1100	14.727	78.383	67.939	11.488	- 165.584	- 148.349	29.474
1200	14.755	79.666	68.864	12.962	- 189.444	- 146.297	26.644
1300	14.776	80.848	69.741	14.439	- 189.863	- 142.683	23.987
1400	14.794	81.943	70.574	15.917	- 190.286	- 139.039	21.705
1500	14.808	82.964	71.366	17.397	- 190.711	- 135.363	19.722
1600	14.819	83.920	72.121	18.879	- 191.138	- 131.659	17.984
1700	14.829	84.819	72.842	20.361	- 191.567	- 127.928	16.446
1800	14.837	85.667	73.531	21.844	- 191.999	- 124.173	15.077
1900	14.843	86.469	74.191	23.328	- 192.433	- 120.393	13.848
2000	14.849	87.231	74.824	24.813	- 192.870	- 116.590	12.740
2100	14.854	87.956	75.432	26.298	- 193.309	- 112.766	11.736
2200	14.859	88.647	76.018	27.784	- 193.751	- 108.920	10.820
2300	14.863	89.307	76.581	29.270	- 194.194	- 105.053	9.982
2400	14.866	89.940	77.125	30.756	- 194.642	- 101.168	9.213
2500	14.869	90.547	77.649	32.243	- 195.092	- 97.266	8.503
2600	14.871	91.130	78.157	33.730	- 195.546	- 93.342	7.846
2700	14.874	91.691	78.648	35.217	- 196.003	- 89.404	7.237
2800	14.876	92.232	79.123	36.705	- 196.463	- 85.449	6.670
2900	14.878	92.754	79.584	38.193	- 196.926	- 81.472	6.140
3000	14.879	93.259	80.032	39.680	- 197.397	- 77.485	5.645
3100	14.881	93.747	80.466	41.168	- 197.870	- 73.481	5.180
3200	14.882	94.219	80.889	42.657	- 198.348	- 69.462	4.744
3300	14.884	94.677	81.300	44.145	- 198.833	- 65.427	4.333
3400	14.885	95.121	81.700	45.633	- 199.322	- 61.378	3.945
3500	14.886	95.553	82.089	47.122	- 199.819	- 57.309	3.579
3600	14.887	95.972	82.469	48.611	- 200.322	- 53.231	3.232
3700	14.888	96.380	82.840	50.099	- 200.834	- 49.138	2.902
3800	14.889	96.777	83.201	51.588	- 201.353	- 45.029	2.590
3900	14.889	97.164	83.554	53.077	- 201.883	- 40.914	2.293
4000	14.890	97.541	83.899	54.566	- 202.420	- 36.775	2.009
4100	14.891	97.909	84.237	56.055	- 202.970	- 32.625	1.739
4200	14.891	98.267	84.566	57.544	- 203.532	- 28.469	1.481
4300	14.892	98.618	84.889	59.033	- 204.105	- 24.291	1.235
4400	14.892	98.960	85.205	60.522	- 204.695	- 20.106	.999
4500	14.893	99.295	85.514	62.012	- 205.297	- 15.900	.772
4600	14.893	99.622	85.818	63.501	- 205.918	- 11.688	.555
4700	14.894	99.943	86.115	64.990	- 206.558	- 7.458	.347
4800	14.894	100.256	86.406	66.480	- 207.217	- 3.213	.146
4900	14.895	100.563	86.692	67.969	- 207.900	1.045	- .047
5000	14.895	100.864	86.972	69.459	- 208.605	5.314	- .232
5100	14.895	101.159	87.248	70.948	- 209.338	9.600	- .411
5200	14.896	101.448	87.518	72.438	- 210.098	13.901	- .584
5300	14.896	101.732	87.783	73.927	- 210.890	18.219	- .751
5400	14.896	102.010	88.044	75.417	- 211.715	22.545	- .912
5500	14.896	102.284	88.301	76.907	- 212.575	26.890	- 1.069
5600	14.897	102.552	88.553	78.396	- 213.473	31.257	- 1.220
5700	14.897	102.816	88.801	79.886	- 214.411	35.632	- 1.366
5800	14.897	103.075	89.045	81.376	- 215.391	40.029	- 1.508
5900	14.897	103.330	89.285	82.865	- 216.418	44.441	- 1.646
6000	14.898	103.580	89.521	84.355	- 217.490	48.868	- 1.780

Dec. 31, 1968

SODIUM DIFLUORIDE UNINEGATIVE ION (NaF_2^-) (IDEAL GAS) GFW = 60.98715

Point Group [$D_{\infty h}$] ΔHf°_0 = -159 ± 10 kcal/mol

$S^\circ_{298.15}$ = [60 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -160 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[400] (1)
[170] (2)
[650] (1)

Bond Distance: Na-F = [1.93] Å

Bond Angle: F-Na-F = [180°] σ = [2]

Rotational Constant: B_0 = [0.119] cm^{-1}

Heat of Formation

The heat of formation for $NaF_2^-(g)$ is estimated from three calculated values. The methods of calculation are described as follows. The first reaction we take into consideration is $NaF(g) + F^-(g) = NaF_2^-(g)$. In a manner analogous to $LiF_2^-(g)$ molecule (see $LiF_2^-(g)$ table for details), we assume $NaF_2^-(g)$ is stable and ΔHr°_{298} for the reaction $NaF(g) + F^-(g) = NaF_2^-(g)$ is somewhere between 0 to 1/2(-64) = -32 kcal/mol where the value -56 kcal/mol is the heat of dimerization. Based on ΔHr°_{298} = 0 and -28 kcal/mol, respectively, with JANAF ΔHf°_{298} values for the species involved, we obtain $\Delta Hf^\circ_{298}(NaF_2^-, g)$ = -132 and -164 kcal/mol as the upper and lower limits.

The heat of formation, calculated based on the reaction $NaF_2^-(g) = NaF_2(g) + e^-(g)$, is -165.8 kcal/mol, using ΔHr°_{298} and $\Delta Hf^\circ_{298}(NaF_2, g)$ estimated as 83.5 and -82.3 kcal/mol, respectively. The ΔHr°_{298} value is obtained from an assumption that the enthalpy change for removing an electron from $NaF_2^-(g)$ is comparable to that from $F^-(g)$. Due to the fact that the Na atom has smaller electronegativity (0.9) than that of the F atom (4.0), we expect that there is less possibility that the electron will associate with Na atom in the NaF_2^- molecule. Therefore we adopt the electron affinity of F(g) reported by H. O. Pritchard, Chem. Rev. 52, 529 (1953), or ΔHr°_{298} = 83.5 kcal/mol for the reaction $F^-(g) = F(g) + e^-(g)$ as the ΔHr°_{298} for $NaF_2^-(g) = NaF_2(g) + e^-(g)$. The value of ΔHf°_{298} for $NaF_2(g)$ is calculated using the enthalpy change for the reaction $Na_2F_2(g) = NaF_2(g) + Na(g)$ as 145.8 kcal/mol which is derived from the sum of two enthalpy changes, namely, half of the ΔHr°_{298} value for the dimer dissociation reaction $Na_2F_2(g) = 2NaF(g)$, and the ΔHr°_{298} for the monomer dissociation reaction $NaF(g) = Na(g) + F(g)$.

Employing ΔHr°_{298} = 63.5 kcal/mol for $Na_2F_2(g) = 2NaF(g)$ and 153.0 kcal/mol for $NaF(g) = Na^+(g) + F^-(g)$, we estimate ΔHr°_{298} = 1/2(63.5) + 153.0 = 184.7 kcal/mol for the reaction $Na_2F_2(g) = NaF_2^-(g) + Na^+(g)$, which leads to ΔHf°_{298} = 163.4 kcal/mol for $NaF_2^-(g)$. For all calculations the ΔHf°_{298} values of the chemical species involved are taken from JANAF Thermochemical Tables.

The value of ΔHf°_{298} for $NaF_2^-(g)$ is tentatively adopted as -160 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion by A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953) that molecules with not more than 16 valence electrons are linear in their ground state. The Na-F bond distance is estimated by comparison with that of NaF(g) reported by S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965). The vibrational frequencies are estimated from those for the isoelectronic molecule $SiO_2(g)$. The moment of inertia is 2.350×10^{-38} g cm^2. The enthalpy at 0°K is -3.117 kcal/mol.

Sodium Fluoride, Dimeric (Na_2F_2)

(Ideal Gas) GFW = 83.9764

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.645	-200.753	-200.753	INFINITE
100	9.945	53.939	81.929	-2.799	-201.242	-201.428	440.221
200	14.550	62.342	70.140	-1.560	-201.877	-201.346	220.021
298	16.926	68.655	68.655	.000	-202.300	-200.992	147.331
300	16.956	68.760	68.655	.031	-202.307	-200.983	146.416
400	18.092	73.812	69.336	1.790	-204.006	-200.379	109.482
500	18.687	77.920	70.655	3.632	-204.453	-199.419	87.166
600	19.031	81.360	72.161	5.519	-204.840	-198.375	72.258
700	19.245	84.311	73.691	7.434	-205.188	-197.271	61.591
800	19.388	86.891	75.183	9.366	-205.512	-196.118	53.577
900	19.487	89.180	76.613	11.310	-205.824	-194.924	47.334
1000	19.559	91.237	77.975	13.263	-206.136	-193.697	42.332
1100	19.612	93.104	79.266	15.221	-206.462	-192.440	38.234
1200	19.653	94.812	80.492	17.185	-253.275	-190.235	34.646
1300	19.685	96.387	81.655	19.152	-253.205	-184.984	31.099
1400	19.711	97.847	82.760	21.122	-253.136	-179.739	28.059
1500	19.731	99.207	83.811	23.094	-253.069	-174.498	25.424
1600	19.748	100.481	84.814	25.068	-253.004	-169.262	23.120
1700	19.762	101.679	85.771	27.043	-252.939	-164.028	21.087
1800	19.774	102.809	86.686	29.020	-252.878	-158.802	19.281
1900	19.784	103.878	87.563	30.998	-252.818	-153.576	17.665
2000	19.792	104.893	88.405	32.977	-252.762	-148.354	16.211
2100	19.800	105.859	89.213	34.956	-252.707	-143.139	14.897
2200	19.806	106.780	89.991	36.937	-252.655	-137.921	13.701
2300	19.812	107.661	90.740	38.918	-252.605	-132.708	12.610
2400	19.817	108.504	91.463	40.899	-252.560	-127.494	11.610
2500	19.821	109.313	92.161	42.881	-252.517	-122.287	10.690
2600	19.825	110.091	92.835	44.863	-252.480	-117.076	9.841
2700	19.828	110.839	93.488	46.846	-252.446	-111.870	9.055
2800	19.831	111.560	94.121	48.829	-252.418	-106.667	8.326
2900	19.834	112.256	94.735	50.812	-252.395	-101.455	7.646
3000	19.836	112.928	95.330	52.796	-252.380	-96.255	7.012
3100	19.839	113.579	95.908	54.779	-252.371	-91.052	6.419
3200	19.841	114.209	96.470	56.763	-252.370	-85.847	5.863
3300	19.842	114.819	97.017	58.747	-252.379	-80.644	5.341
3400	19.844	115.412	97.549	60.732	-252.395	-75.441	4.849
3500	19.846	115.987	98.068	62.716	-252.425	-70.228	4.385
3600	19.847	116.546	98.574	64.701	-252.465	-65.024	3.947
3700	19.848	117.090	99.067	66.686	-252.518	-59.822	3.534
3800	19.850	117.619	99.548	68.671	-252.585	-54.606	3.141
3900	19.851	118.135	100.018	70.656	-252.671	-49.402	2.768
4000	19.852	118.637	100.477	72.641	-252.772	-44.186	2.414
4100	19.853	119.128	100.926	74.626	-252.894	-38.966	2.077
4200	19.854	119.606	101.365	76.611	-253.038	-33.751	1.756
4300	19.854	120.073	101.795	78.597	-253.202	-28.524	1.450
4400	19.855	120.530	102.215	80.582	-253.397	-23.301	1.157
4500	19.856	120.976	102.627	82.568	-253.618	-18.065	.877
4600	19.857	121.412	103.031	84.553	-253.872	-12.833	.610
4700	19.857	121.839	103.427	86.539	-254.160	-7.590	.353
4800	19.858	122.257	103.815	88.525	-254.487	-2.340	.107
4900	19.858	122.667	104.195	90.511	-254.857	2.923	-.130
5000	19.859	123.068	104.569	92.496	-255.274	8.187	-.358
5100	19.859	123.461	104.935	94.482	-255.740	13.458	-.577
5200	19.860	123.847	105.295	96.468	-256.260	18.743	-.788
5300	19.860	124.225	105.649	98.454	-256.840	24.038	-.991
5400	19.861	124.596	105.996	100.440	-257.485	29.340	-1.187
5500	19.861	124.961	106.338	102.426	-258.199	34.655	-1.377
5600	19.861	125.319	106.674	104.413	-258.985	39.989	-1.561
5700	19.862	125.670	107.004	106.399	-259.850	45.338	-1.738
5800	19.862	126.016	107.329	108.385	-260.798	50.699	-1.910
5900	19.863	126.355	107.648	110.371	-261.835	56.080	-2.077
6000	19.863	126.689	107.963	112.357	-262.962	61.476	-2.239

June 30, 1964; Dec. 31, 1968

SODIUM FLUORIDE, DIMERIC (Na_2F_2) (IDEAL GAS) GFW = 83.9764

Point Group [D_{2h}]

$\Delta Hf°_0$ = [-200.8 ± 3] kcal/mol

$S°_{298.15}$ = [68.7 ± 4] gibbs/mol

$\Delta Hf°_{298.15}$ = [-202.3 ± 3] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[420] (1)	[200] (1)
[400] (1)	[425] (1)
[350] (1)	[500] (1)

Bond Distance: Na-F = 2.02 Å

Bond Angle: Na-F-Na = [85°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.6135×10^{-114}] g^3 cm^6

Heat of Formation

Although the absolute values of the vapor pressure measurements are not used for evaluation, the ratios of the numbers of dimeric and monomeric NaF molecules that effuse from the oven at the temperatures 1115 - 1191°K determined by Eisenstadt, Rothberg, and Kusch (1) by use of the electron-beam velocity-selector method are used. Based on the reported equilibrium data we evaluate the enthalpy change of the reaction (A) $Na_2F_2(g) = 2NaF(g)$ by the second and third law methods. The results are presented in the table below.

Porter and Schoonmaker (2) analyzed the vapor effusing from a Knudsen cell at 1121°K mass spectrometrically and derived the partial pressures of NaF(g) and $Na_2F_2(g)$ at that temperature. Using these reported partial pressures we calculate, by the third law method, the value $\Delta Hr°_{298}$ = 64.1 kcal/mol for reaction (A).

Sidorov et al. (3) studied the NaF - ZrF_4 system by the mass spectrometric method and derived the partial pressures of NaF(g) and $Na_2F_2(g)$ as a function of composition and temperature. Employing the data points reported at 1074 and 1167°K we obtain the third law value $\Delta Hr°_{298}$ = 62.0 ± 1.6 kcal/mol for the same reaction.

The $\Delta Hf°_{298}$ (Na_2F_2, g) is calculated based on the adopted third law value $\Delta Hr°_{298}$ = 63.5 kcal/mol for the reaction Na_2F_2 (g) = 2NaF(g), using $\Delta Hf°_{298}$(NaF, g) = -69.5 kcal/mol. Brewer and Brackett (9) reported $\Delta Hr°_{1000}$ = 56.9 kcal/mol for the above reaction. According to our tables the $\Delta Hr°_{1000}$ value is 62.5 kcal/mol.

	Investigator	Temperature, °K	No. of Points	$\Delta Hr°_{298}$, kcal/mol Second Law	Third Law	Drift eu	$\Delta Hf°_{298}$ kcal/mol
1.	Eisenstadt et al. (1958)	1115 - 1191	6	58.1 ± 2.9	63.5	4.7 ± 2.5	-202.4
2.	Porter and Schoonmaker (1958)	1121	1	—	64.1	—	-203.0
3.	Sidorov et al. (1964)	1074 - 1167	8	—	62.0 ± 1.6	—	-200.9

Heat Capacity and Entropy

The $Na_2F_2(g)$ molecule is assumed to have a rhombic structure with D_{2h} (V_h) symmetry (4, 5). The Na-F bond distance is reported by Akishin and Rambidi (5), who studied the molecular structure of alkali halide vapors by electron diffraction with sector microphotometry. The bond angle is estimated by comparison with those of the other alkali halides. Berkowitz (4, 6) has calculated the vibration frequencies of Na_2F_2 based on an ionic model. By comparison of the calculated frequencies of Li_2F_2 (6) with those of the observed ones (see Li_2F_2(g) table for details) we reestimate the vibrational frequencies for $Na_2F_2(g)$ to be higher than the ones reported by Berkowitz (6). Bauer et al. (7) used a pseudo-electrostatic model, similar to the one suggested by O'Konski and Higuchi (8), to calculate the entropies of dimerization for a number of gaseous alkali halides and estimated the six vibrational frequencies as 477, 318, 291, 477, 291, and 291 cm^{-1}. Bauer et al. calculated $\Delta S°_{1146}$ = -32.5 eu for the reaction $2NaF(g) = Na_2F_2(g)$, in reasonable agreement with the value -33.5 eu which is derived using JANAF $S°_{1146}$ values for NaF(g) and $Na_2F_2(g)$.

The three principal moments of inertia are: $I_A = 1.399 \times 10^{-38}$, $I_B = 1.422 \times 10^{-38}$, and $I_C = 2.821 \times 10^{-38}$ g cm^2.

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Oxygen Difluoride (F_2O)

(Ideal Gas) GFW = 53.9962

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.604	6.404	6.404	INFINITE
100	6.066	49.383	67.457	-1.807	6.158	7.359	-16.083
200	9.095	55.249	60.025	-.955	5.962	8.643	-9.445
298	10.349	59.118	59.118	.000	5.860	9.984	-7.318
300	10.371	59.182	59.118	.019	5.859	10.009	-7.292
400	11.373	62.311	59.538	1.109	5.823	11.400	-6.229
500	12.061	64.928	60.361	2.283	5.825	12.794	-5.592
600	12.524	67.170	61.314	3.514	5.846	14.186	-5.167
700	12.841	69.126	62.293	4.783	5.875	15.575	-4.863
800	13.065	70.856	63.257	6.079	5.906	16.957	-4.632
900	13.227	72.405	64.189	7.394	5.938	18.337	-4.453
1000	13.348	73.805	65.082	8.723	5.968	19.713	-4.308
1100	13.439	75.082	65.934	10.062	5.996	21.085	-4.189
1200	13.511	76.254	66.746	11.410	6.023	22.456	-4.090
1300	13.567	77.338	67.519	12.764	6.046	23.825	-4.005
1400	13.613	78.345	68.257	14.123	6.066	25.192	-3.933
1500	13.650	79.286	68.961	15.486	6.082	26.558	-3.870
1600	13.681	80.168	69.634	16.853	6.096	27.922	-3.814
1700	13.706	80.998	70.279	18.222	6.106	29.287	-3.765
1800	13.728	81.782	70.896	19.594	6.111	30.648	-3.721
1900	13.746	82.524	71.489	20.968	6.113	32.012	-3.682
2000	13.762	83.230	72.058	22.343	6.112	33.376	-3.647
2100	13.775	83.902	72.606	23.720	6.106	34.738	-3.615
2200	13.787	84.543	73.134	25.098	6.095	36.102	-3.586
2300	13.797	85.156	73.644	26.477	6.081	37.466	-3.560
2400	13.806	85.743	74.136	27.858	6.063	38.832	-3.536
2500	13.815	86.307	74.612	29.239	6.039	40.196	-3.514
2600	13.822	86.849	75.072	30.621	6.012	41.564	-3.494
2700	13.828	87.371	75.518	32.003	5.980	42.933	-3.475
2800	13.834	87.874	75.950	33.386	5.945	44.301	-3.458
2900	13.839	88.359	76.370	34.770	5.904	45.674	-3.442
3000	13.844	88.829	76.777	36.154	5.859	47.043	-3.427
3100	13.848	89.283	77.173	37.538	5.811	48.417	-3.413
3200	13.852	89.722	77.559	38.923	5.758	49.792	-3.401
3300	13.855	90.149	77.934	40.309	5.701	51.169	-3.389
3400	13.858	90.562	78.299	41.694	5.640	52.548	-3.378
3500	13.861	90.964	78.655	43.080	5.575	53.930	-3.368
3600	13.864	91.355	79.003	44.467	5.508	55.314	-3.358
3700	13.866	91.734	79.342	45.853	5.435	56.697	-3.349
3800	13.868	92.104	79.673	47.240	5.359	58.086	-3.341
3900	13.871	92.464	79.996	48.627	5.279	59.470	-3.333
4000	13.873	92.816	80.312	50.014	5.196	60.862	-3.325
4100	13.874	93.158	80.621	51.401	5.109	62.254	-3.318
4200	13.876	93.493	80.924	52.789	5.019	63.649	-3.312
4300	13.878	93.819	81.220	54.177	4.927	65.049	-3.306
4400	13.879	94.138	81.510	55.564	4.829	66.446	-3.300
4500	13.880	94.450	81.794	56.952	4.730	67.847	-3.295
4600	13.882	94.755	82.072	58.340	4.627	69.252	-3.290
4700	13.883	95.054	82.345	59.729	4.521	70.658	-3.286
4800	13.884	95.346	82.613	61.117	4.413	72.069	-3.281
4900	13.885	95.632	82.876	62.505	4.300	73.477	-3.277
5000	13.886	95.913	83.134	63.894	4.186	74.889	-3.273
5100	13.887	96.188	83.387	65.283	4.068	76.303	-3.270
5200	13.888	96.458	83.636	66.671	3.947	77.723	-3.267
5300	13.889	96.722	83.880	68.060	3.825	79.146	-3.264
5400	13.889	96.982	84.121	69.449	3.698	80.561	-3.260
5500	13.890	97.237	84.357	70.838	3.571	81.990	-3.258
5600	13.891	97.487	84.589	72.227	3.439	83.416	-3.255
5700	13.892	97.733	84.818	73.616	3.305	84.845	-3.253
5800	13.892	97.974	85.042	75.006	3.170	86.279	-3.251
5900	13.893	98.212	85.263	76.395	3.031	87.709	-3.249
6000	13.893	98.445	85.481	77.784	2.890	89.147	-3.247

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1964; Dec. 31, 1969

Point Group C_{2v}

ΔHf°_0 = 6.40 ± 0.38 kcal/mol

$S^\circ_{298.15}$ = 59.12 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 5.86 ± 0.38 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
928 (1)
461 (1)
831 (1)

Bond Distance: F-O = 1.412 Å

Bond Angle: F-O-F = 103°10'

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 1.01936 \times 10^{-115}$ g^3 cm^6

Heat of Formation

King and Armstrong (1) have established the heat of formation with a series of reactions in a flame calorimeter. They burned F_2O in hydrogen to give HF aqueous, in addition they burned F_2 in hydrogen and O_2 in hydrogen so that the heat of formation, 5.86 kcal/mol, is directly obtainable. This value is in good agreement with the recalculated values (1) from Wartenberg and Klinkott (2), 5.7 ± 2 kcal/mol, and Ruff and Menzel (3), 4.7 ± 2 kcal/mol but differs from that of Bisbee et al. (4), -4.06 ± 2.2 kcal/mol. There were several factors in the experiments of Bisbee that might cause a too negative heat of formation and we choose to adopt the definitive value of 5.86 kcal/mol reported by King and Armstrong.

Heat Capacity and Entropy

The structural parameters are those reported by Pierce et al. (5) for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton et al. (6) disagree but according to Pierce et al. (7) the line assignments used by Hilton are incorrect. The vibrational frequencies were reported by Jones et al. (8), several other investigators report similar values (9, 10, 11). Nebgen et al. (12) have obtained the anharmonic constants for the three vibrations. Individual moments of inertia are $I_A = 1.4396 \times 10^{-39}$, $I_B = 7.7255 \times 10^{-39}$ and $I_C = 9.1651 \times 10^{-39}$ g cm^2.

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Thionyl Difluoride (SOF_2)

(Ideal Gas) Mol. Wt. = 86.0602

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.063	-133.862	-133.862	INFINITE
100	8.650	55.063	77.606	-2.254	-134.269	-133.334	291.386
200	11.495	61.914	68.160	-1.249	-134.697	-132.224	144.480
298	13.833	66.965	66.965	.000	-135.000	-130.941	95.978
300	13.870	67.051	66.965	.026	-135.005	-130.916	95.367
400	15.508	71.280	67.531	1.500	-135.755	-129.497	70.750
500	16.622	74.868	68.649	3.110	-136.256	-127.873	55.890
600	17.389	77.971	69.950	4.813	-136.619	-126.160	45.951
700	17.928	80.694	71.294	6.580	-136.892	-124.369	38.828
800	18.317	83.115	72.623	8.393	-150.169	-123.835	33.828
900	18.605	85.290	73.912	10.240	-150.043	-120.550	29.272
1000	18.821	87.262	75.150	12.112	-149.911	-117.280	25.630
1100	18.989	89.064	76.334	14.003	-149.774	-114.025	22.654
1200	19.120	90.722	77.465	15.908	-149.634	-110.779	20.175
1300	19.224	92.257	78.544	17.826	-149.493	-107.546	18.079
1400	19.309	93.684	79.575	19.753	-149.352	-104.324	16.285
1500	19.378	95.019	80.561	21.687	-149.212	-101.115	14.732
1600	19.435	96.271	81.504	23.628	-149.073	-97.911	13.373
1700	19.483	97.451	82.408	25.574	-148.935	-94.718	12.176
1800	19.524	98.566	83.275	27.524	-148.801	-91.535	11.113
1900	19.559	99.623	84.108	29.478	-148.668	-88.356	10.163
2000	19.588	100.627	84.909	31.436	-148.539	-85.185	9.308
2100	19.614	101.583	85.680	33.396	-148.413	-82.022	8.536
2200	19.637	102.496	86.424	35.358	-148.292	-78.862	7.834
2300	19.656	103.369	87.142	37.323	-148.173	-75.708	7.194
2400	19.674	104.206	87.836	39.290	-148.058	-72.559	6.607
2500	19.689	105.010	88.507	41.258	-147.948	-69.418	6.068
2600	19.703	105.782	89.156	43.227	-147.842	-66.277	5.571
2700	19.715	106.526	89.786	45.198	-147.739	-63.142	5.111
2800	19.726	107.243	90.397	47.170	-147.640	-60.013	4.684
2900	19.735	107.935	90.990	49.143	-147.546	-56.881	4.286
3000	19.744	108.605	91.566	51.117	-147.458	-53.760	3.916
3100	19.752	109.252	92.126	53.092	-147.370	-50.636	3.570
3200	19.760	109.879	92.671	55.068	-147.290	-47.517	3.245
3300	19.766	110.488	93.202	57.044	-147.211	-44.405	2.941
3400	19.772	111.078	93.719	59.021	-147.138	-41.288	2.654
3500	19.778	111.651	94.223	60.998	-147.070	-38.176	2.384
3600	19.783	112.208	94.715	62.977	-147.002	-35.062	2.128
3700	19.788	112.750	95.195	64.955	-146.942	-31.953	1.887
3800	19.792	113.278	95.664	66.934	-146.883	-28.846	1.659
3900	19.796	113.792	96.122	68.914	-146.830	-25.745	1.443
4000	19.800	114.294	96.570	70.893	-146.779	-22.639	1.237
4100	19.804	114.782	97.008	72.874	-146.732	-19.534	1.041
4200	19.807	115.260	97.437	74.854	-146.689	-16.435	.855
4300	19.810	115.726	97.857	76.835	-146.649	-13.331	.678
4400	19.813	116.181	98.269	78.816	-146.614	-10.232	.508
4500	19.815	116.627	98.672	80.797	-146.581	-7.135	.347
4600	19.818	117.062	99.067	82.779	-146.551	-4.034	.192
4700	19.820	117.488	99.454	84.761	-146.525	-.936	.044
4800	19.822	117.906	99.834	86.743	-146.501	2.159	-.098
4900	19.824	118.314	100.207	88.725	-146.482	5.262	-.235
5000	19.826	118.715	100.573	90.708	-146.466	8.352	-.365
5100	19.828	119.108	100.933	92.691	-146.452	11.446	-.490
5200	19.830	119.493	101.286	94.673	-146.442	14.545	-.611
5300	19.831	119.870	101.633	96.656	-146.433	17.647	-.728
5400	19.833	120.241	101.974	98.640	-146.429	20.736	-.839
5500	19.834	120.605	102.310	100.623	-146.427	23.834	-.947
5600	19.835	120.962	102.640	102.606	-146.429	26.933	-1.051
5700	19.837	121.313	102.964	104.590	-146.433	30.027	-1.151
5800	19.838	121.658	103.284	106.574	-146.439	33.126	-1.248
5900	19.839	121.998	103.598	108.558	-146.448	36.210	-1.341
6000	19.840	122.331	103.907	110.542	-146.461	39.314	-1.432

Dec. 31, 1960; Sept. 30, 1965

THIONYL DIFLUORIDE (SOF_2) (IDEAL GAS) MOL. WT. = 86.0602

Point Group C_s

$S^\circ_{298.15}$ = 66.965 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-134 ± 10] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-135 ± 10] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1308 (1)	393 (1)
801 (1)	721 (1)
526 (1)	326 (1)

Bond Distance: O-S = 1.412 Å S-F = 1.585 Å

Bond Angle: O-S-F = 106° 49' F-S-F = 92° 49'

$\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 1.65545 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

From the enthalpy change, $\Delta H^\circ_{r\ 298.15}$ = 131.03 kcal. mole^{-1}, for the reaction $SO_2F_2(g) = SOF_2(g) + O(g)$, the value of $\Delta H^\circ_{f\ 298.15}$ for $SOF_2(g)$ was calculated to be -133.5 kcal. mole^{-1}, using $\Delta H^\circ_{f\ 298.15}$ = -205.0 and 59.56 kcal. mole^{-1} for $SO_2F_2(g)$ and O(g), respectively. The value of $\Delta H^\circ_{r\ 298.15}$ was assumed to be the same as that for the reaction $SO_2(g) = SO(g) + O(g)$ which was calculated based on $\Delta H^\circ_{f\ 298.15}$ = -70.95, 0.52 and 59.56 kcal. mole^{-1} for $SO_2(g)$ SO(g) and O(g), respectively. Using $\Delta H^\circ_{r\ 298.15}$ = 127.86 kcal. mole^{-1} for the reaction $SO_2F_2(g) = SOF_2(g) + O(g)$, the value of $\Delta H^\circ_{f\ 298.15}$ (SOF_2, g) was evaluated as -136.7 kcal. mole^{-1} where the $\Delta H^\circ_{r\ 298.15}$ value was assumed to be the same as the S-O bond energy in $SO_2(g)$. The value of $\Delta H^\circ_{f\ 298.15}$ (SOF_2, g) adopted is -135 ± 10 kcal. mole^{-1}.

Heat Capacity and Entropy.

The bond distances and angles were obtained from R. C. Ferguson, J. Am. Chem. Soc. 76, 850 (1954). The vibrational frequencies were taken from R. J. Gillespie and E. A. Robinson, Can. J. Chem. 39, 2171 (1961). The assignment of these vibrational frequencies was based on the previous measurements of the infrared and Raman spectra reported by J. K. O'Loane and M. K. Wilson, J. Chem. Phys. 23, 1313 (1955), P. Bender and J. M. Wood, J. Chem. Phys., 23, 1316 (1955) and D. M. Yost, Proc. Indian Acad. Sci. 8, 333 (1938). The fundamental assignment reported by J. K. O'Loane and M. K. Wilson, loc. cit., was 1333, 808, 530, (410), 748 and 390 cm.$^{-1}$ The three principal moments of inertia are: $I_A = 1.0034 \times 10^{-38}$, $I_B = 9.7421 \times 10^{-39}$ and $I_C = 1.6935 \times 10^{-38}$ g. cm.^{2}

The heat capacities of thionyl fluoride (SOF_2) have been measured, from 12° to 230°K., by E. L. Pace and B. F. Turnbull, J. Chem. Phys. 43, 1953 (1965), for a sample of 99.976 mole % purity. Incorporating them with the measured ΔH°_m, 1.506 kcal. mole^{-1} at T_m = 143.25°K., and ΔH°_v, 5.091 kcal. mole^{-1} at T_b = 228.84°K., which was derived from the measured vapor pressure of $SOF_2(l)$, the entropy of $SOF_2(g)$ at 228.84°K. was evaluated as 63.56 e.u. This value is in excellent agreement with the corresponding value, 63.522 e.u., calculated using the adopted molecular constants. This indicates the fact that the molecular constants used for the calculation of the tabulated thermodynamic functions are adequate. Hence the new vibrational frequencies suggested by Pace and Turnbull, loc. cit., were not used.

Silicon Oxide Difluoride ($SiOF_2$)

(Ideal Gas) Mol. Wt. = 82.09

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.869	- 229.953	- 229.953	INFINITE
100	8.205	53.862	74.570	- 2.071	- 230.270	- 229.419	501.370
200	10.471	60.167	65.907	- 1.148	- 230.668	- 228.412	249.585
298	12.832	64.806	64.806	.000	- 231.000	- 227.231	166.557
300	12.871	64.885	64.806	.024	- 231.006	- 227.208	165.513
400	14.656	68.847	65.334	1.405	- 231.258	- 225.902	123.421
500	15.922	72.261	66.386	2.938	- 231.448	- 224.540	98.142
600	16.818	75.248	67.619	4.577	- 231.591	- 223.145	81.276
700	17.462	77.891	68.902	6.293	- 231.705	- 221.727	69.223
800	17.932	80.255	70.176	8.064	- 231.801	- 220.296	60.179
900	18.284	82.389	71.416	9.875	- 231.887	- 218.852	53.142
1000	18.551	84.330	72.612	11.718	- 231.968	- 217.399	47.510
1100	18.758	86.108	73.759	13.584	- 232.045	- 215.940	42.901
1200	18.921	87.747	74.857	15.468	- 232.120	- 214.471	39.059
1300	19.052	89.267	75.908	17.367	- 232.195	- 212.997	35.806
1400	19.158	90.683	76.913	19.277	- 232.269	- 211.518	33.018
1500	19.245	92.008	77.876	21.198	- 232.344	- 210.033	30.600
1600	19.317	93.252	78.799	23.126	- 232.421	- 208.543	28.484
1700	19.378	94.425	79.684	25.061	- 244.601	- 206.938	26.602
1800	19.429	95.534	80.634	27.001	- 244.640	- 204.725	24.856
1900	19.473	96.586	81.351	28.946	- 244.679	- 202.506	23.292
2000	19.511	97.586	82.138	30.896	- 244.720	- 200.284	21.885
2100	19.543	98.539	82.897	32.848	- 244.763	- 198.062	20.612
2200	19.572	99.448	83.628	34.804	- 244.809	- 195.838	19.454
2300	19.597	100.319	84.335	36.763	- 244.856	- 193.611	18.396
2400	19.619	101.154	85.019	38.723	- 244.908	- 191.382	17.427
2500	19.638	101.955	85.680	40.686	- 244.963	- 189.150	16.535
2600	19.656	102.725	86.321	42.651	- 245.020	- 186.916	15.711
2700	19.671	103.467	86.943	44.617	- 245.081	- 184.680	14.948
2800	19.685	104.183	87.546	46.585	- 245.144	- 182.443	14.240
2900	19.698	104.874	88.131	48.554	- 245.212	- 180.200	13.580
3000	19.709	105.542	88.701	50.525	- 245.284	- 177.960	12.964
3100	19.719	106.189	89.254	52.496	- 245.358	- 175.714	12.387
3200	19.728	106.815	89.793	54.469	- 245.437	- 173.465	11.847
3300	19.737	107.422	90.318	56.442	- 245.519	- 171.217	11.339
3400	19.745	108.011	90.830	58.416	- 245.604	- 168.964	10.860
3500	19.752	108.584	91.329	60.391	- 336.731	- 165.117	10.310
3600	19.758	109.140	91.816	62.366	- 336.761	- 160.212	9.726
3700	19.764	109.682	92.292	64.342	- 336.795	- 155.308	9.173
3800	19.770	110.209	92.756	66.319	- 336.832	- 150.402	8.650
3900	19.775	110.722	93.211	68.296	- 336.873	- 145.500	8.153
4000	19.780	111.223	93.655	70.274	- 336.917	- 140.590	7.681
4100	19.784	111.712	94.089	72.252	- 336.967	- 135.680	7.232
4200	19.788	112.188	94.514	74.231	- 337.017	- 130.770	6.804
4300	19.792	112.654	94.931	76.210	- 337.070	- 125.855	6.396
4400	19.796	113.109	95.339	78.189	- 337.130	- 120.945	6.007
4500	19.799	113.554	95.739	80.169	- 337.189	- 116.033	5.635
4600	19.802	113.989	96.131	82.149	- 337.253	- 111.118	5.279
4700	19.805	114.415	96.515	84.130	- 337.319	- 106.200	4.938
4800	19.808	114.832	96.893	86.110	- 337.387	- 101.281	4.611
4900	19.811	115.241	97.263	88.091	- 337.459	- 96.362	4.298
5000	19.813	115.641	97.626	90.073	- 337.533	- 91.445	3.997
5100	19.815	116.033	97.984	92.054	- 337.610	- 86.521	3.707
5200	19.818	116.418	98.334	94.036	- 337.689	- 81.595	3.429
5300	19.820	116.796	98.679	96.017	- 337.770	- 76.666	3.161
5400	19.822	117.166	99.018	98.000	- 337.856	- 71.747	2.904
5500	19.823	117.530	99.351	99.982	- 337.942	- 66.815	2.655
5600	19.825	117.887	99.679	101.964	- 338.032	- 61.882	2.415
5700	19.827	118.238	100.002	103.947	- 338.125	- 56.949	2.183
5800	19.828	118.583	100.319	105.930	- 338.218	- 52.013	1.960
5900	19.830	118.922	100.631	107.912	- 338.317	- 47.085	1.744
6000	19.831	119.255	100.939	109.896	- 338.417	- 42.146	1.535

Sept. 30, 1963

SILICON OXIDE DIFLUORIDE ($SiOF_2$) (IDEAL GAS) MOL. WT. = 82.09

Point Group $[C_{2v}]$

$S^\circ_{298.15}$ = [64.806] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-230 ± 6] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-231 ± 6] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[440] (1)	[760] (1)
[490] (1)	[980] (1)
[610] (1)	[1420] (1)

Bond Distance: Si-O = [1.60] Å Si-F = [1.54] Å σ = 2

Bond Angle: F-Si-O = [120]° F-Si-F = [120]°

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.56608 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{298.15}$ was estimated by comparison with those for $SiF_4(g)$ and $SiO_2(g)$.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for $COF_2(g)$ and $TiOF_2(g)$. The vibrational frequencies for $COF_2(g)$ and $TiOF_2(g)$ were obtained from R. J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. 22, 1953 (1954), and J. S. Gordon, private communication, May 12, 1961, respectively. The bond distances of Si-O and Si-F were assumed to be the same as those for SiO(g) and $SiF_4(g)$, respectively. Point group, ground state multiplicity, and bond angles were estimated.

Titanium Oxide Difluoride ($TiOF_2$)

(Ideal Gas) Mol. Wt. = 101.9

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.245	- 219.998	- 219.998	INFINITE
100	8.967	55.237	79.531	- 2.429	- 220.367	- 219.550	479.303
200	12.457	62.529	69.314	- 1.357	- 220.793	- 218.556	238.815
298	15.005	68.016	68.016	.000	- 221.050	- 217.394	159.346
300	15.042	68.109	68.016	.028	- 221.054	- 217.371	158.347
400	16.625	72.672	68.627	1.618	- 221.209	- 216.118	118.076
500	17.588	76.494	69.829	3.332	- 221.316	- 214.833	93.849
600	18.195	79.758	71.219	5.124	- 221.407	- 213.526	77.773
700	18.597	82.595	72.646	6.965	- 221.500	- 212.206	66.251
800	18.873	85.097	74.049	8.839	- 221.601	- 210.873	57.605
900	19.070	87.332	75.403	10.737	- 221.711	- 209.524	50.877
1000	19.214	89.349	76.698	12.651	- 221.835	- 208.164	45.492
1100	19.324	91.186	77.933	14.578	- 221.974	- 206.791	41.084
1200	19.408	92.871	79.109	16.515	- 223.074	- 205.366	37.401
1300	19.475	94.427	80.228	18.459	- 223.239	- 203.883	34.274
1400	19.528	95.873	81.294	20.410	- 223.418	- 202.389	31.593
1500	19.572	97.221	82.312	22.365	- 223.609	- 200.879	29.267
1600	19.607	98.486	83.283	24.324	- 223.815	- 199.357	27.230
1700	19.637	99.675	84.213	26.286	- 224.033	- 197.822	25.430
1800	19.662	100.798	85.104	28.251	- 224.265	- 196.275	23.830
1900	19.683	101.862	95.958	30.218	- 224.510	- 194.712	22.396
2000	19.702	102.872	86.779	32.187	- 228.443	- 193.043	21.094
2100	19.717	103.834	87.568	34.158	- 228.655	- 191.268	19.905
2200	19.731	104.751	88.328	36.131	- 228.871	- 189.483	18.823
2300	19.743	105.629	89.062	38.104	- 229.091	- 187.686	17.833
2400	19.753	106.469	89.770	40.079	- 229.315	- 185.882	16.926
2500	19.763	107.276	90.454	42.055	- 229.544	- 184.068	16.090
2600	19.771	108.051	91.116	44.032	- 229.776	- 182.246	15.318
2700	19.778	108.797	91.757	46.009	- 230.013	- 180.412	14.603
2800	19.785	109.517	92.378	47.987	- 230.253	- 178.571	13.937
2900	19.791	110.211	92.981	49.966	- 230.498	- 176.718	13.317
3000	19.796	110.882	93.567	51.945	- 230.749	- 174.863	12.738
3100	19.801	111.531	94.136	53.925	- 231.001	- 172.993	12.195
3200	19.805	112.160	94.690	55.906	- 231.259	- 171.121	11.686
3300	19.809	112.770	95.228	57.886	- 231.520	- 169.236	11.207
3400	19.813	113.361	95.753	59.867	- 231.786	- 167.347	10.756
3500	19.816	113.935	96.264	61.849	- 232.055	- 165.446	10.330
3600	19.819	114.494	96.763	63.831	- 334.789	- 162.094	9.840
3700	19.822	115.037	97.249	65.813	- 335.086	- 157.293	9.290
3800	19.825	115.565	97.725	67.795	- 335.400	- 152.479	8.759
3900	19.827	116.080	98.189	69.778	- 335.733	- 147.666	8.275
4000	19.829	116.582	98.642	71.761	- 336.080	- 142.841	7.804
4100	19.831	117.072	99.086	73.744	- 336.444	- 138.004	7.356
4200	19.833	117.550	99.520	75.727	- 336.824	- 133.161	6.929
4300	19.835	118.017	99.944	77.710	- 337.217	- 128.304	6.521
4400	19.837	118.473	100.360	79.694	- 337.627	- 123.442	6.131
4500	19.838	118.918	100.768	81.678	- 338.050	- 118.569	5.758
4600	19.840	119.355	101.167	83.662	- 338.485	- 113.686	5.401
4700	19.841	119.781	101.559	85.646	- 338.936	- 108.795	5.059
4800	19.843	120.199	101.943	87.630	- 339.398	- 103.890	4.730
4900	19.844	120.608	102.320	89.614	- 339.872	- 98.983	4.415
5000	19.845	121.009	102.689	91.599	- 340.357	- 94.064	4.111
5100	19.846	121.402	103.052	93.583	- 340.854	- 89.136	3.820
5200	19.847	121.787	103.409	95.568	- 341.360	- 84.191	3.538
5300	19.848	122.165	103.759	97.553	- 341.876	- 79.234	3.267
5400	19.849	122.536	104.104	99.537	- 342.403	- 74.282	3.006
5500	19.850	122.901	104.442	101.522	- 342.936	- 69.307	2.754
5600	19.851	123.258	104.775	103.507	- 343.480	- 64.330	2.510
5700	19.851	123.610	105.102	105.492	- 344.031	- 59.343	2.275
5800	19.852	123.955	105.424	107.478	- 344.588	- 54.342	2.048
5900	19.853	124.294	105.741	109.463	- 345.153	- 49.335	1.827
6000	19.853	124.628	106.053	111.448	- 345.724	- 44.311	1.614

Sept. 30, 1963

TITANIUM OXIDE DIFLUORIDE ($TiOF_2$) (IDEAL GAS) MOL. WT. = 101.9

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [68.016] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-220] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-221] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[553] (1)	[715] (1)
[888] (1)	[300] (1)
[350] (1)	[452] (1)

Bond Distances: Ti=O = [1.62] Å Ti-F = [1.74] Å

Bond Angle: O=Ti-F = [120°] σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [4.34 X 10^{-114}] g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as -220 kcal. mole^{-1} by J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. The principal moments of inertia are: I_A = 14.3274 X 10^{-39} g. cm.^{2}, I_B = 11.6632 X 10^{-39} g. cm.^{2}, and I_C = 25.9907 X 10^{-39} g. cm.^{2}

Sulfuryl Difluoride (SO_2F_2)

(Ideal Gas) Mol. Wt. = 102.066

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.406	-203.169	-203.169	INFINITE
100	9.213	55.351	81.201	-2.585	-203.919	-200.936	439.124
200	13.238	62.984	70.286	-1.460	-204.567	-197.684	216.009
298	16.356	68.883	68.883	.000	-205.000	-194.207	142.351
300	16.406	68.985	68.884	.030	-205.007	-194.141	141.425
400	18.698	74.036	69.557	1.792	-205.825	-190.451	104.053
500	20.355	78.396	70.899	3.749	-206.344	-186.545	81.535
600	21.556	82.219	72.473	5.848	-206.689	-182.549	66.490
700	22.433	85.612	74.113	8.049	-206.917	-178.482	55.722
800	23.082	88.652	75.743	10.327	-220.128	-175.679	47.991
900	23.572	91.400	77.333	12.660	-219.923	-170.134	41.312
1000	23.947	93.904	78.866	15.037	-219.699	-164.613	35.975
1100	24.239	96.200	80.339	17.447	-219.463	-159.118	31.612
1200	24.470	98.320	81.751	19.883	-219.216	-153.642	27.981
1300	24.656	100.286	83.102	22.339	-218.965	-148.186	24.911
1400	24.807	102.119	84.395	24.813	-218.709	-142.752	22.283
1500	24.931	103.835	85.635	27.300	-218.452	-137.336	20.009
1600	25.034	105.447	86.823	29.798	-218.194	-131.936	18.021
1700	25.121	106.967	87.964	32.306	-217.935	-126.552	16.269
1800	25.195	108.405	89.060	34.822	-217.680	-121.186	14.713
1900	25.258	109.769	90.114	37.345	-217.426	-115.830	13.323
2000	25.312	111.066	91.130	39.873	-217.176	-110.490	12.073
2100	25.359	112.302	92.109	42.407	-216.929	-105.164	10.944
2200	25.400	113.483	93.054	44.945	-216.688	-99.846	9.918
2300	25.436	114.613	93.967	47.487	-216.450	-94.541	8.983
2400	25.468	115.696	94.850	50.032	-216.218	-89.244	8.126
2500	25.496	116.736	95.704	52.580	-215.992	-83.960	7.339
2600	25.521	117.737	96.533	55.131	-215.770	-78.682	6.614
2700	25.543	118.700	97.336	57.684	-215.554	-73.413	5.942
2800	25.563	119.630	98.116	60.240	-215.343	-68.155	5.319
2900	25.581	120.527	98.873	62.797	-215.139	-62.898	4.740
3000	25.598	121.395	99.609	65.356	-214.942	-57.654	4.200
3100	25.612	122.234	100.326	67.916	-214.748	-52.414	3.695
3200	25.626	123.048	101.023	70.478	-214.562	-47.181	3.222
3300	25.638	123.836	101.703	73.042	-214.379	-41.956	2.778
3400	25.649	124.602	102.365	75.606	-214.204	-36.731	2.361
3500	25.660	125.346	103.011	78.171	-214.035	-31.515	1.968
3600	25.669	126.069	103.641	80.738	-213.868	-26.299	1.597
3700	25.678	126.772	104.257	83.305	-213.710	-21.092	1.246
3800	25.686	127.457	104.859	85.873	-213.555	-15.886	.914
3900	25.693	128.124	105.447	88.442	-213.406	-10.692	.599
4000	25.700	128.775	106.022	91.012	-213.261	-5.492	.300
4100	25.707	129.409	106.585	93.582	-213.122	-.301	.016
4200	25.713	130.029	107.135	96.153	-212.987	4.888	-.254
4300	25.718	130.634	107.675	98.725	-212.855	10.078	-.512
4400	25.723	131.225	108.203	101.297	-212.731	15.258	-.758
4500	25.728	131.804	108.721	103.869	-212.610	20.439	-.993
4600	25.733	132.369	109.229	106.443	-212.491	25.618	-1.217
4700	25.737	132.923	109.728	109.016	-212.379	30.792	-1.432
4800	25.741	133.464	110.217	111.590	-212.269	35.966	-1.637
4900	25.745	133.995	110.696	114.164	-212.164	41.136	-1.835
5000	25.748	134.515	111.168	116.739	-212.063	46.300	-2.024
5100	25.752	135.025	111.630	119.314	-211.966	51.468	-2.205
5200	25.755	135.525	112.085	121.889	-211.872	56.634	-2.380
5300	25.758	136.016	112.532	124.465	-211.780	61.801	-2.548
5400	25.760	136.497	112.971	127.041	-211.694	66.954	-2.710
5500	25.763	136.970	113.403	129.617	-211.609	72.119	-2.866
5600	25.766	137.434	113.828	132.193	-211.531	77.276	-3.016
5700	25.768	137.890	114.247	134.770	-211.454	82.430	-3.160
5800	25.770	138.339	114.658	137.347	-211.379	87.590	-3.300
5900	25.772	138.779	115.063	139.924	-211.308	92.736	-3.435
6000	25.774	139.212	115.462	142.501	-211.241	97.895	-3.566

Dec. 31, 1960; Mar. 31, 1963

SULFURYL DIFLUORIDE (SO_2F_2) (IDEAL GAS) MOL. WT. = 102.066

Point Group C_{2v}

$S^\circ_{298.15}$ = 68.883 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = -203 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -205 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1269 (1)	274 (1)	539 (1)
848 (1)	360 (1)	885 (1)
553 (1)	1502 (1)	386 (1)

Bond Distance: S=0 = 1.405 ± 0.003 Å S-F = 1.530 ± 0.003 Å

Bond Angle: 0-S-0 = 123° 58' ± 12' F-S-F = 96° 7' ± 10' σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 4.4873 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was reported by R. M. Reese, V. H. Dibeler and J. L. Franklin, J. Chem. Phys. 29, 880 (1958). The value was calculated from the appearance potential of the SO_2^+ ion obtained from electron impact studies of SO_2 and SO_2F_2.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from G. R. Hunt, and M. K. Wilson, Spectrochim. Acta, 16, 570 (1960). The bond distances and bond angles were reported by D. R. Lide, Jr., D. E. Mann, and R. M. Fristrom, J. Chem. Phys., 26, 734 (1957). The entropy of sulfuryl fluoride gas has been calculated from the calorimetric data and the third law of thermodynamics to be 62.66 cal. deg.$^{-1}$ mole^{-1} at 217.78°K. by F. J. Bockhoff, R. V. Petrella, and E. L. Pace, J. Chem. Phys. 32, 799 (1960). The discrepancy between entropy value calculated from calorimetric data and that calculated from molecular and spectroscopic data (1 atm., 217.78°K) is attributed to randomness in the solid at 0°K by F. J. Bockhoff and E. L. Pace, J. Chem. Phys. 34, 3502 (1962). The vibrational frequencies reported by W. D. Perkins and M. Kent Wilson, J. Chem. Phys. 20, 1791 (1952) were 1269 (1), 848 (1), 544 (1), [300] (1), [385] (1), 1502 (1), 553 (1), 885 (1), and 539 (1) cm.$^{-1}$ The three principal moments of inertia are: 1.6567×10^{-38}, 1.6567×10^{-38}, and 1.6349×10^{-38} g. cm.^{2}

Phosphorus Difluoride (PF_2)

(Ideal Gas) Mol. Wt. = 68.975 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.668	- 104.696	- 104.696	INFINITE
100	8.216	52.151	70.837	- 1.869	- 104.683	- 105.679	230.950
200	9.437	58.201	63.145	- .989	- 104.821	- 106.628	116.512
298	10.677	62.207	62.207	.000	- 105.000	- 107.478	78.779
300	10.698	62.273	62.207	.020	- 105.003	- 107.493	78.305
400	11.640	65.488	62.639	1.140	- 105.186	- 108.294	59.166
500	12.269	68.158	63.483	2.337	- 105.367	- 109.052	47.664
600	12.687	70.434	64.457	3.586	- 105.551	- 109.772	39.982
700	12.970	72.412	65.455	4.870	- 105.751	- 110.459	34.485
800	13.169	74.158	66.436	6.178	- 126.392	- 116.428	31.805
900	13.312	75.718	67.382	7.502	- 126.380	- 115.183	27.969
1000	13.419	77.126	68.287	8.839	- 126.367	- 113.940	24.900
1100	13.499	78.409	69.150	10.185	- 126.354	- 112.699	22.390
1200	13.562	79.586	69.971	11.538	- 126.341	- 111.458	20.298
1300	13.612	80.674	70.753	12.897	- 126.329	- 110.217	18.528
1400	13.652	81.684	71.498	14.260	- 126.318	- 108.978	17.011
1500	13.684	82.627	72.209	15.627	- 126.308	- 107.738	15.697
1600	13.711	83.511	72.888	16.997	- 126.300	- 106.502	14.547
1700	13.733	84.343	73.538	18.369	- 126.294	- 105.264	13.532
1800	13.752	85.129	74.160	19.743	- 126.290	- 104.029	12.630
1900	13.768	85.873	74.757	21.119	- 126.287	- 102.791	11.823
2000	13.782	86.579	75.331	22.497	- 126.286	- 101.555	11.097
2100	13.793	87.252	75.883	23.876	- 126.287	- 100.319	10.440
2200	13.804	87.894	76.414	25.255	- 126.292	- 99.082	9.842
2300	13.813	88.508	76.927	26.636	- 126.297	- 97.845	9.297
2400	13.821	89.096	77.422	28.018	- 126.305	- 96.609	8.797
2500	13.828	99.660	77.900	29.400	- 126.315	- 95.370	8.337
2600	13.834	90.202	78.363	30.783	- 126.328	- 94.133	7.912
2700	13.839	90.725	78.811	32.167	- 126.342	- 92.893	7.519
2800	13.844	91.228	79.245	33.551	- 126.358	- 91.655	7.154
2900	13.849	91.714	79.667	34.936	- 126.376	- 90.413	6.813
3000	13.853	92.184	80.077	36.321	- 126.398	- 89.175	6.496
3100	13.856	92.638	80.474	37.707	- 126.420	- 87.933	6.199
3200	13.860	93.078	80.861	39.092	- 126.447	- 86.692	5.921
3300	13.863	93.504	81.238	40.478	- 126.474	- 85.449	5.659
3400	13.866	93.918	81.605	41.865	- 126.504	- 84.205	5.412
3500	13.868	94.320	81.963	43.252	- 126.536	- 82.959	5.180
3600	13.870	94.711	82.311	44.639	- 126.570	- 81.714	4.960
3700	13.873	95.091	82.652	46.026	- 126.607	- 80.468	4.753
3800	13.875	95.461	82.984	47.413	- 126.646	- 79.218	4.556
3900	13.876	95.821	83.308	48.801	- 126.688	- 77.971	4.369
4000	13.878	96.173	83.626	50.188	- 126.732	- 76.722	4.192
4100	13.880	96.515	83.936	51.576	- 126.778	- 75.472	4.023
4200	13.881	96.850	84.239	52.964	- 126.827	- 74.217	3.862
4300	13.882	97.177	84.536	54.352	- 126.877	- 72.966	3.708
4400	13.884	97.496	84.827	55.741	- 126.930	- 71.709	3.562
4500	13.885	97.808	85.112	57.129	- 126.986	- 70.456	3.422
4600	13.886	98.113	85.392	58.518	- 127.042	- 69.201	3.288
4700	13.887	98.412	85.666	59.906	- 127.103	- 67.942	3.159
4800	13.888	98.704	85.934	61.295	- 127.165	- 66.680	3.036
4900	13.889	98.990	86.198	62.684	- 127.229	- 65.417	2.918
5000	13.890	99.271	86.456	64.073	- 127.296	- 64.156	2.804
5100	13.891	99.546	86.710	65.462	- 127.366	- 62.897	2.695
5200	13.891	99.816	96.960	66.851	- 127.437	- 61.629	2.590
5300	13.892	100.080	87.205	68.240	- 127.511	- 60.361	2.489
5400	13.893	100.340	87.446	69.629	- 127.588	- 59.099	2.392
5500	13.893	100.595	87.682	71.019	- 127.665	- 57.826	2.298
5600	13.894	100.845	87.915	72.408	- 127.747	- 56.556	2.207
5700	13.895	101.091	88.144	73.798	- 127.830	- 55.282	2.120
5800	13.895	101.333	88.370	75.187	- 127.915	- 54.010	2.035
5900	13.896	101.570	88.591	76.577	- 128.002	- 52.738	1.953
6000	13.896	101.804	88.810	77.966	- 128.093	- 51.460	1.874

June 30, 1962

Phosphorus Difluoride (PF_2) (Ideal Gas)

Mol. Wt. = 68.975

$\Delta H_{f\ 298.15}$ = [-105 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = [62.2 ± 3] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = 2

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
[376] (1)
[775] (1)
[890] (1)

$I_AI_BI_C$ = [1.9059 x 10^{-115}] g.^{3} cm.^{6} σ = 2

Heat of Formation. $\Delta H^\circ_{f\ 298.15}$ was estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Virginia, "Survey of Thermochemical Data," January, 1960. For their estimation they assumed certain bond energies for the dissociation of PF_3(g). Bond one was assumed 20% greater than bond two and three which were assumed to be equal. $\Delta H^\circ_{f\ 298.18}$ was corrected for the change in phosphorus reference state (white α → red V).

Heat Capacity and Entropy. Molecular constants and vibrational levels were estimated by J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products," January, 1960.

Lead Difluoride (PbF_2)

(Crystal) GFW = 245.1868

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.720	27.000	27.000	.000	- 161.800	- 150.789	110.531
300	17.750	27.110	27.000	.033	- 161.793	- 150.721	109.800
400	19.290	32.427	27.715	1.885	- 161.363	- 147.092	80.367
500	20.830	36.897	29.115	3.891	- 160.837	- 143.584	62.761
600	22.370	40.831	30.746	6.051	- 160.199	- 140.190	51.064
700	23.910	45.394	32.569	8.978	- 159.993	- 136.810	42.714
800	24.300	49.529	34.463	12.053	- 158.505	- 133.623	36.504
900	24.300	52.391	36.299	14.483	- 157.665	- 130.563	31.705
1000	24.300	54.951	38.038	16.913	- 156.826	- 127.596	27.886
1100	24.300	57.267	39.683	19.343	- 155.987	- 124.715	24.778
1200	24.300	59.382	41.238	21.773	- 155.145	- 121.907	22.202
1300	24.300	61.327	42.709	24.203	- 154.304	- 119.171	20.035
1400	24.300	63.128	44.104	26.633	- 153.466	- 116.501	18.187
1500	24.300	64.804	45.429	29.063	- 152.631	- 113.888	16.593
1600	24.300	66.372	46.689	31.493	- 151.803	- 111.333	15.207
1700	24.300	67.845	47.891	33.923	- 150.980	- 108.828	13.991
1800	24.300	69.234	49.038	36.353	- 150.166	- 106.375	12.916
1900	24.300	70.548	50.136	38.783	- 149.358	- 103.964	11.959
2000	24.300	71.795	51.188	41.213	- 148.558	- 101.594	11.102

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

LEAD DIFLUORIDE (PbF_2) (CRYSTAL) GFW = 245.1868

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = [27.0 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -161.8 ± 1.0 kcal/mol

Tt_2 = 613°K

ΔHt_2° = [0.61] kcal/mol

Tt_1 = 725°K

ΔHt_1° = 0.65 kcal/mol

Tm = 1099°K

ΔHm° = 2.98 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 58.5 kcal/mol

Heat of Formation

The heats of formation at 298.15°K derived from the enthalpy changes of different chemical reactions are listed below. The adopted one is the average of the last three $\Delta Hf^\circ_{298.15}$ values, which is also in reasonable agreement with the $\Delta Hf^\circ_{298.15}$ values evaluated from (1) and (5).

Reference	Chemical Reaction	$\Delta Hr^\circ_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
1	$PbF_2(c) + H_2(g) = Pb(\ell) + 2\ HF(g)$	32.0 ± 0.56*	-161.3 ± 0.6
2	$PbF_2(c) + H_2O(g) = PbO(c) + 2\ HF(g)$	29.6 ± 2.1**	-154.5 ± 4.0
3	$Pb(c) + F_2(g) = PbF_2(c)$	-159.7 ± 0.5	-159.7 ± 0.5
4	$PbO(c) + 2\ HF(40\%\ aq) = PbF_2(c) + H_2O(\ell)$	-22.9 ± 0.3	-159.0 ± 0.5
5	$PbF_2(c) + 2\ Na(c) = Pb(c) + 2NaF(aq)$	-112.2 ± 0.2	-162.2 ± 0.4
6	$PbF_2(c) + Mg(c) = Pb(c) + MgF_2(c)$	-109.5 ± 1.5	-159.2 ± 2.0
7	$3/2\ PbF_2(c) + Al(c) = 3/2\ Pb(c) + AlF_3(c)$	-118.5 ± 0.1	-161.5 ± 1.0
8	$3/2\ PbF_2(c) + Al(c) = 3/2\ Pb(c) + AlF_3(c)$	-117.7 ± 0.6	-162.1 ± 1.0
9	$1/2\ PbF_2(c) + 1/3\ Al(c) = 1/2\ Pb(\ell) + 1/3\ AlF_3(c)$	-38.3 ± 0.8	-161.8 ± 1.0

* This is the third law value. The second law value is 32.4 ± 0.9 kcal/mol. The entropy drift is -0.5 ± 1.2 eu.

** This is the third law value. The second law value is 39.6 ± 0.7 kcal/mol. The entropy drift is -10.9 ± 0.8 eu.

Heat Capacity and Entropy

Banashek, Patsukova, and Rassonskaya (10) measured the high temperature enthalpies ($H^\circ - H^\circ_{293.16}$), for $PbF_2(c)$ in the temperature range 670-1165°K. Based on their enthalpy measurements the heat capacity of $PbF_2(\gamma)$ at temperatures 725-1099°K is derived as 24.3 ± 0.2 gibbs/mol by the least square method. The heat capacities below 725°K are estimated using their reported enthalpies at 670-725°K, which are based on a mixture of β and γ, as a guide.

The $S^\circ_{298.15}$ is estimated to be 25 eu by the method suggested by Kubaschewski and Evans (11), and adjusted to 27 eu so that the second and third law $\Delta Hr^\circ_{298.15}$ values derived from the equilibrium data reported by Jellinek and Rudat (1) are in good agreement.

Transition Data

The transition temperatures are obtained from Banashek, Patsukova, and Rassonskaya (10). The β → γ transition at 613°K was reported as either slow or irreversible and the γ → β transition at 725°K was reversible. The polymorphism of $PbF_2(c)$ has been studied by many other investigators. However, the relations between the temperature and the character of polymorphic transformation are not consistent (10).

The enthalpy difference at 725°K for $PbF_2(\gamma)$ and $PbF_2(\beta)$ is ΔHt_1°. The value of ΔHt_2° is estimated such that the generated functions yield reasonable agreement among the derived ΔHf°_{298} values (see the above table).

Melting Data

See $PbF_2(\ell)$ table.

Heat of Sublimation

The difference between $\Delta Hf^\circ_{298.15}$ for $PbF_2(g)$ and $PbF_2(c)$ is $\Delta Hs^\circ_{298.15}$.

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Lead Difluoride (PbF_2)

(Liquid) GFW = 245.1868

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.000	28.647	28.647	.000	-158.722	-148.202	108.635
300	24.000	28.796	28.648	.044	-158.704	-148.137	107.918
400	24.000	35.700	29.589	2.444	-157.726	-144.763	79.095
500	24.000	41.056	31.367	4.844	-156.806	-141.632	61.907
600	24.000	45.431	33.357	7.244	-155.928	-138.679	50.514
700	24.000	49.131	35.353	9.644	-156.249	-135.680	42.361
800	24.000	52.336	37.280	12.044	-155.436	-132.799	36.279
900	24.000	55.163	39.113	14.444	-154.626	-130.017	31.573
1000	24.000	57.691	40.847	16.844	-153.817	-127.327	27.827
1100	24.000	59.979	42.484	19.244	-153.008	-124.717	24.779
1200	24.000	62.067	44.030	21.644	-152.196	-122.180	22.252
1300	24.000	63.988	45.492	24.044	-151.385	-119.711	20.125
1400	24.000	65.766	46.878	26.444	-150.577	-117.306	18.312
1500	24.000	67.422	48.193	28.844	-149.772	-114.956	16.749
1600	24.000	68.971	49.443	31.244	-148.974	-112.662	15.389
1700	24.000	70.426	50.635	33.644	-148.181	-110.415	14.195
1800	24.000	71.798	51.773	36.044	-147.397	-108.220	13.140
1900	24.000	73.096	52.862	38.444	-146.619	-106.064	12.200
2000	24.000	74.327	53.904	40.844	-145.849	-103.948	11.359
2100	24.000	75.498	54.905	43.244	-187.537	-100.321	10.441
2200	24.000	76.614	55.867	45.644	-186.690	-96.188	9.555
2300	24.000	77.681	56.792	48.044	-185.866	-92.092	8.751
2400	24.000	78.702	57.684	50.444	-185.066	-88.032	8.016
2500	24.000	79.682	58.544	52.844	-184.292	-84.007	7.344

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

LEAD DIFLUORIDE (PbF_2) (LIQUID) GFW = 245.1868

$S^\circ_{298.15}$ = [28.647] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -158.722 kcal/mol

Tm = 1099°K

ΔHm° = 2.98 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298.15}(\ell)$ is obtained from $\Delta Hf^\circ_{298.15}(c)$ by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy

The enthalpies ($H^\circ - H^\circ_{293.16}$) of $PbF_2(\ell)$ in the temperature range 1104-1165°K were determined by Banashek, Patsukova, and Rassonskaya (1). Based on their reported results the heat capacity of $PbF_2(\ell)$ is evaluated to be 24 ± 2 gibbs/mol by the least square method. This Cp value is adopted and extended to 298 and 2500°K, respectively.

The entropy ($S^\circ_{298.15}$) is calculated in a manner analogous to that of the heat of formation.

Melting Data

Tm is taken from Banashek, Patsukova, and Rassonskaya (1). The enthalpy difference at Tm for $PbF_2(\ell)$ and $PbF_2(\gamma)$ is ΔHm°.

Other values of Tm (°K) reported are 1091 (2, 11), 1097 (3, 4, 5) and 1128 (6). Using the freezing point data of binary systems PbF_2-$PbBr_2$ (5), PbF_2-$PbCl_2$ (5, 7), PbF_2-PbI_2 (5, 8), PbF_2-PbO (9), and PbF_2-NaF (10), Kelley (3) evaluated the corresponding values of ΔHm° (kcal/mol) as 1.70, 1.70, 1.96, 3.87, and 2.47. Other reported values of ΔHm° are 3.00 (1) and 4.16 (2) kcal/mol.

Vaporization Data

From mass spectroscopic study on the vapor species in PbF_2, Zmbov, Hastie, and Margrave (4) have shown that molten PbF_2 vaporizes partly as molecular PbF_2. There is considerable disproportionation, and at 715°C the vapor composition is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb (4, 12). Tb has been reported as 1565°K (11) where the vapor is expected to be a mixture of the above species.

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Lead Difluoride (PbF_2)

(Ideal Gas) GFW = 245.1868

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.138	- 102.684	- 102.684	INFINITE
100	9.766	58.829	81.482	- 2.265	- 102.929	- 103.862	226.991
200	11.589	66.186	72.152	- 1.193	- 103.160	- 104.694	114.405
298	12.603	71.027	71.027	.000	- 103.300	- 105.416	77.272
300	12.616	71.105	71.027	.023	- 103.303	- 105.429	76.805
400	13.115	74.811	71.529	1.313	- 103.435	- 106.117	57.980
500	13.379	77.768	72.491	2.639	- 103.589	- 106.772	46.670
600	13.532	80.222	73.581	3.985	- 103.765	- 107.391	39.117
700	13.628	82.316	74.683	5.343	- 105.128	- 107.789	33.653
800	13.692	84.140	75.753	6.709	- 105.349	- 108.155	29.547
900	13.737	85.756	76.777	8.081	- 105.567	- 108.493	26.346
1000	13.769	87.205	77.748	9.456	- 105.783	- 108.806	23.780
1100	13.793	88.518	78.669	10.835	- 105.995	- 109.099	21.676
1200	13.812	89.719	79.540	12.215	- 106.203	- 109.370	19.919
1300	13.826	90.826	80.366	13.597	- 106.410	- 109.626	18.430
1400	13.838	91.851	81.151	14.980	- 106.619	- 109.866	17.151
1500	13.847	92.806	81.896	16.364	- 106.830	- 110.089	16.040
1600	13.854	93.700	82.606	17.749	- 107.047	- 110.300	15.066
1700	13.861	94.540	83.284	19.135	- 107.268	- 110.495	14.205
1800	13.866	95.332	83.931	20.521	- 107.498	- 110.682	13.439
1900	13.871	96.082	84.551	21.908	- 107.733	- 110.852	12.751
2000	13.874	96.793	85.146	23.296	- 107.975	- 111.008	12.130
2100	13.878	97.470	85.717	24.683	- 150.676	- 109.603	11.407
2200	13.881	98.116	86.266	26.071	- 150.841	- 107.644	10.693
2300	13.883	98.733	86.794	27.459	- 151.029	- 105.675	10.041
2400	13.885	99.324	87.304	28.848	- 151.240	- 103.699	9.443
2500	13.887	99.891	87.796	30.236	- 151.478	- 101.715	8.892
2600	13.889	100.436	88.272	31.625	- 151.738	- 99.719	8.382
2700	13.890	100.960	88.732	33.014	- 152.020	- 97.712	7.909
2800	13.892	101.465	89.178	34.403	- 152.326	- 95.696	7.469
2900	13.893	101.953	89.610	35.792	- 152.653	- 93.665	7.059
3000	13.894	102.424	90.030	37.182	- 153.000	- 91.628	6.675
3100	13.895	102.879	90.437	38.571	- 153.365	- 89.576	6.315
3200	13.896	103.320	90.833	39.961	- 153.748	- 87.512	5.977
3300	13.897	103.748	91.217	41.351	- 154.145	- 85.436	5.658
3400	13.898	104.163	91.592	42.740	- 154.557	- 83.346	5.357
3500	13.898	104.566	91.957	44.130	- 154.981	- 81.245	5.073
3600	13.899	104.957	92.313	45.520	- 155.414	- 79.131	4.804
3700	13.900	105.338	92.660	46.910	- 155.857	- 77.006	4.549
3800	13.900	105.709	92.998	48.300	- 156.306	- 74.867	4.306
3900	13.901	106.070	93.329	49.690	- 156.763	- 72.721	4.075
4000	13.901	106.422	93.652	51.080	- 157.223	- 70.562	3.855
4100	13.902	106.765	93.967	52.470	- 157.688	- 68.390	3.646
4200	13.902	107.100	94.276	53.860	- 158.155	- 66.204	3.445
4300	13.902	107.427	94.578	55.251	- 158.622	- 64.010	3.253
4400	13.903	107.747	94.874	56.641	- 159.092	- 61.803	3.070
4500	13.903	108.059	95.163	58.031	- 159.561	- 59.590	2.894
4600	13.903	108.365	95.447	59.421	- 160.030	- 57.361	2.725
4700	13.904	108.664	95.725	60.812	- 160.497	- 55.127	2.563
4800	13.904	108.957	95.998	62.202	- 160.963	- 52.874	2.407
4900	13.904	109.243	96.265	63.593	- 161.427	- 50.620	2.258
5000	13.904	109.524	96.527	64.983	- 161.890	- 48.355	2.114
5100	13.905	109.799	96.785	66.373	- 162.351	- 46.083	1.975
5200	13.905	110.069	97.038	67.764	- 162.808	- 43.793	1.841
5300	13.905	110.334	97.286	69.154	- 163.264	- 41.498	1.711
5400	13.905	110.594	97.530	70.545	- 163.718	- 39.201	1.587
5500	13.905	110.849	97.770	71.935	- 164.170	- 36.890	1.466
5600	13.906	111.100	98.006	73.326	- 164.619	- 34.570	1.349
5700	13.906	111.346	98.238	74.717	- 165.067	- 32.246	1.236
5800	13.906	111.588	98.466	76.107	- 165.513	- 29.908	1.127
5900	13.906	111.826	98.690	77.498	- 165.958	- 27.571	1.021
6000	13.906	112.059	98.911	78.888	- 166.402	- 25.224	.919

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

LEAD DIFLUORIDE (PbF_2) (IDEAL GAS) GFW = 245.1868

Point Group C_{2v}

ΔHf°_0 = -102.7 ± 1 kcal/mol

$S^\circ_{298.15}$ = [71 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -103.3 ± 1 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[450] (1)
[120] (1)
[450] (1)

Bond Distance: Pb-F = 2.13 ± 0.02 Å

Bond Angle: F-Pb-F = [95°] $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = [4.5690 \times 10^{-114}]\ g^3\ cm^6$

Heat of Formation

Vapor pressure data for PbF_2 have previously been interpreted on the assumption that PbF_2 was the only species present in the gas phase (1, 2). Zmbov, Hastie, and Margrave (3) have studied the vapor species over PbF_2(c, ℓ) mass spectrometrically and shown that PbF_2 vaporizes only partly as molecular PbF_2 and there is considerable disproportionation. The vapor composition at 988°K is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb (3, 4). From extrapolation of the ion intensity data from 1043 to 988°K to the temperature region in which Nesmeyanov and Iofa (2) measured the saturated vapor pressures of PbF_2(c), 792-988°K, by Knudsen effusion method, the partial pressure of PbF_2(c), at 988°K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the heat of sublimation (ΔHs°_{298}) of PbF_2(c) is derived as 58.50 kcal/mol by the third law method, yielding $\Delta Hf^\circ_{298}(PbF_2, g)$ = -103.3 ± 1 kcal/mol.

Due to lack of data on vapor compositions over PbF_2(c, ℓ) at various temperatures, the total pressure measurements reported by Wartenberg and Bosse (1), using boiling point method, and those of Nesmeyanov and Iofa (2) are not used for evaluation.

Heat Capacity and Entropy

The bond distance was determined by Akishin, Spiridonov and Khodchenkov (5). The bond angle is assumed to be the same as that in PbX_2(g) where X = Cl, Br or I (6). The vibrational frequencies are calculated by valence force method (10) using force constants estimated by comparison with those for PbF (7), CaF (7), CaF_2 (8), MgF (7), and MgF_2 (9). The value of ν_2 is in fair agreement with the value, 145 cm^{-1}, estimated by (4). The three principal moments of inertia are: $I_A = 1.5559 \times 10^{-38}$, $I_B = 1.1040 \times 10^{-38}$, and $I_C = 2.6599 \times 10^{-38}\ g\ cm^2$.

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Silicon Difluoride (SiF_2)

(Ideal Gas) GFW = 66.0828

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.678	-140.299	-140.299	INFINITE
100	8.298	51.186	69.947	-1.876	-140.256	-141.214	308.622
200	9.476	57.293	62.234	-.988	-140.349	-142.141	155.325
298	10.638	61.298	61.298	.000	-140.500	-142.990	104.816
300	10.658	61.364	61.298	.020	-140.503	-143.006	104.180
400	11.561	64.564	61.728	1.134	-140.666	-143.815	78.577
500	12.214	67.221	62.569	2.326	-140.825	-144.564	63.198
600	12.640	69.488	63.538	3.570	-140.981	-145.322	52.933
700	12.931	71.460	64.531	4.850	-141.137	-146.032	45.593
800	13.137	73.201	65.508	6.154	-141.299	-146.722	40.083
900	13.285	74.757	66.451	7.475	-141.466	-147.389	35.791
1000	13.396	76.163	67.353	8.809	-141.641	-148.038	32.354
1100	13.480	77.444	68.213	10.153	-141.824	-148.669	29.538
1200	13.545	78.619	69.032	11.505	-142.014	-149.283	27.188
1300	13.597	79.706	69.812	12.862	-142.215	-149.881	25.197
1400	13.639	80.715	70.555	14.224	-142.425	-150.462	23.488
1500	13.672	81.657	71.264	15.589	-142.646	-151.027	22.005
1600	13.700	82.540	71.941	16.958	-142.877	-151.580	20.705
1700	13.724	83.372	72.590	18.329	-155.112	-152.010	19.542
1800	13.744	84.157	73.211	19.703	-155.310	-151.823	18.434
1900	13.761	84.900	73.806	21.078	-155.509	-151.624	17.441
2000	13.775	85.606	74.379	22.455	-155.709	-151.412	16.546
2100	13.788	86.279	74.930	23.833	-155.911	-151.194	15.735
2200	13.800	86.921	75.460	25.213	-156.114	-150.965	14.997
2300	13.811	87.534	75.972	26.593	-156.319	-150.726	14.322
2400	13.821	88.122	76.466	27.975	-156.525	-150.478	13.703
2500	13.831	88.687	76.944	29.357	-156.734	-150.223	13.132
2600	13.841	89.229	77.406	30.741	-156.943	-149.958	12.605
2700	13.851	89.752	77.853	32.125	-157.154	-149.685	12.116
2800	13.862	90.256	78.287	33.511	-157.365	-149.404	11.661
2900	13.874	90.742	78.709	34.898	-157.578	-149.114	11.238
3000	13.887	91.213	79.118	36.286	-157.793	-148.823	10.842
3100	13.901	91.669	79.515	37.675	-158.008	-148.520	10.471
3200	13.917	92.110	79.902	39.066	-158.224	-148.208	10.122
3300	13.934	92.539	80.278	40.459	-158.440	-147.892	9.794
3400	13.953	92.955	80.645	41.853	-158.657	-147.569	9.486
3500	13.973	93.360	81.003	43.249	-158.875	-147.239	9.194
3600	13.996	93.754	81.351	44.648	-251.052	-144.645	8.781
3700	14.021	94.137	81.692	46.048	-251.171	-141.689	8.369
3800	14.047	94.512	82.024	47.452	-251.288	-138.727	7.979
3900	14.076	94.877	82.349	48.858	-251.407	-135.767	7.608
4000	14.107	95.234	82.667	50.267	-251.524	-132.798	7.256
4100	14.139	95.582	82.978	51.679	-251.642	-129.832	6.921
4200	14.173	95.923	83.282	53.095	-251.757	-126.859	6.601
4300	14.209	96.257	83.580	54.514	-251.870	-123.882	6.296
4400	14.247	96.584	83.871	55.937	-251.984	-120.906	6.005
4500	14.286	96.905	84.158	57.364	-252.094	-117.923	5.727
4600	14.327	97.220	84.438	58.794	-252.203	-114.941	5.461
4700	14.369	97.528	84.713	60.229	-252.311	-111.955	5.206
4800	14.413	97.831	84.984	61.668	-252.415	-108.967	4.961
4900	14.457	98.129	85.249	63.112	-252.517	-105.976	4.727
5000	14.503	98.421	85.509	64.560	-252.617	-102.988	4.502
5100	14.549	98.709	85.765	66.012	-252.715	-99.995	4.285
5200	14.596	98.992	86.017	67.469	-252.810	-96.996	4.077
5300	14.643	99.270	86.264	68.931	-252.901	-93.998	3.876
5400	14.691	99.544	86.508	70.398	-252.991	-91.004	3.683
5500	14.739	99.814	86.747	71.870	-253.077	-88.003	3.497
5600	14.787	100.081	86.983	73.346	-253.162	-84.997	3.317
5700	14.836	100.343	87.215	74.827	-253.244	-81.991	3.144
5800	14.884	100.601	87.444	76.313	-253.323	-78.987	2.976
5900	14.932	100.856	87.669	77.804	-253.400	-75.987	2.815
6000	14.979	101.107	87.891	79.299	-253.475	-72.978	2.658

Dec. 31, 1960; Sept. 30, 1963; June 30, 1968; Dec. 31, 1968

SILICON DIFLUORIDE (SiF_2) (IDEAL GAS) GFW = 66.0828

Point Group [C_{2v}]

$\Delta Hf^\circ_0 = -140.3 \pm 3$ kcal/mol

$S^\circ_{298.15} = 61.30 \pm 0.05$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -140.5 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[20000]	[3]
44109	1

Vibrational Levels and Degeneracies

ω, cm^{-1}
855 (1)
345 (1)
872 (1)

Bond Distance: Si-F = 1.5913 Å

Bond Angle: F-Si-F = 100°59'

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 3.20372 \times 10^{-115}\ g^3\ cm^6$

Heat of Formation

J. L. Margrave, A. S. Kanaan, and D. C. Pease, J. Phys. Chem. 66, 1200 (1962), have reported some approximate equilibrium constants for the reaction $Si(c) + SiF_4(g) \rightarrow 2SiF_2(g)$. These were calculated from yields of polymerized products and a knowledge of the total system pressure given in U. S. Patent No. 2,840,588 (1958). The data were subjected to third law analysis using the present JANAF functions and yielded $\Delta H_{298} = 92 \pm 10$ kcal/mol, which gives $\Delta Hf^\circ_{298}(SiF_2,\ g) = -147 \pm 5$ kcal/mol.

T. C. Ehlert and J. L. Margrave, J. Chem. Phys. 41, 1066 (1964), have reported equilibrium constants for three reactions determined mass spectrometrically.

A. $CaF_2(c) + Si(g) \rightarrow Ca(g) + SiF_2(g)$

B. $CaF_2(g) + Si(g) \rightarrow Ca(g) + SiF_2(g)$

C. $2CaF(g) + Si(g) \rightarrow 2Ca(g) + SiF_2(g)$

A 2nd and 3rd law analysis of the data is shown below.

Reaction	Range °K	Points	ΔHr°_{298} kcal/mol 2nd law	3rd law	Drift eu	ΔHf°_{298} kcal/mol
A	1395 - 1543	12	80.2 ± 14.1	88.0 ± 3.0	4.6 ± 9.7	-140.1 ± 3
B	1395 - 1543	12	-9.2 ± 14.1	-18.0 ± 3.0	-6.6 + 9.6	-140.7 ± 3
C	1395 - 1543	12	-18.6 ± 7.5	-33.6 ± 1.8	-10.2 ± 5.0	-141 ± 3

We adopt $\Delta Hf^\circ_{298.15}(SiF_2,\ g) = -140.5 \pm 3$ kcal/mol.

Heat Capacity and Entropy

The microwave, ultraviolet and infrared spectra have all been extensively studied (1, 2, 3, 4, 5, 6, 7). We have adopted the vibrational frequencies and molecular structure from V. M. Khanna et al. (1). The electronic levels are from V. M. Khanna et al. (2), with an estimated triplet level by analogy with CF_2.

The individual moments of inertia are $I_A = 2.7482 \times 10^{-39}\ g\ cm^2$, $I_B = 9.5100 \times 10^{-39}\ g\ cm^2$, and $I_C = 12.2582 \times 10^{-39}\ g\ cm^2$.

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Titanium Difluoride (TiF_2)

(Ideal Gas) GFW = 85.8968

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.871	-164.109	-164.109	INFINITE
100	8.238	49.695	71.156	-2.146	-164.213	-164.916	360.424
200	11.063	56.336	62.194	-1.171	-164.396	-165.541	180.895
298	12.638	61.081	61.081	.000	-164.500	-166.083	121.742
300	12.659	61.159	61.081	.023	-164.502	-166.093	120.999
400	13.486	64.927	61.589	1.335	-164.578	-166.610	91.032
500	13.942	67.990	62.573	2.708	-164.658	-167.111	73.044
600	14.213	70.657	63.695	4.117	-164.747	-167.593	61.046
700	14.387	72.762	64.837	5.548	-164.853	-168.059	52.470
800	14.504	74.692	65.951	6.993	-164.984	-168.509	46.035
900	14.590	76.405	67.019	8.448	-165.141	-168.940	41.024
1000	14.660	77.946	68.036	9.910	-165.328	-169.354	37.012
1100	14.722	79.346	69.001	11.379	-165.540	-169.745	33.725
1200	14.784	80.630	69.918	12.855	-166.713	-170.079	30.976
1300	14.850	81.816	70.788	14.336	-166.849	-170.354	28.639
1400	14.923	82.919	71.615	15.825	-166.996	-170.619	26.635
1500	15.002	83.951	72.404	17.321	-167.156	-170.872	24.896
1600	15.089	84.922	73.156	18.826	-167.329	-171.113	23.373
1700	15.181	85.840	73.875	20.339	-167.517	-171.345	22.028
1800	15.278	86.710	74.564	21.862	-167.721	-171.566	20.831
1900	15.378	87.539	75.226	23.395	-167.939	-171.773	19.758
2000	15.479	88.330	75.861	24.937	-172.622	-171.813	18.775
2100	15.579	89.088	76.473	26.490	-172.849	-171.768	17.876
2200	15.678	89.815	77.063	28.053	-173.069	-171.713	17.058
2300	15.775	90.514	77.633	29.626	-173.281	-171.645	16.310
2400	15.868	91.187	78.184	31.208	-173.487	-171.569	15.624
2500	15.956	91.837	78.717	32.799	-173.687	-171.486	14.991
2600	16.040	92.464	79.234	34.399	-173.880	-171.394	14.407
2700	16.120	93.071	79.735	36.007	-174.067	-171.294	13.865
2800	16.194	93.659	80.222	37.623	-174.248	-171.189	13.362
2900	16.264	94.228	80.695	39.246	-174.425	-171.073	12.892
3000	16.330	94.781	81.155	40.876	-174.598	-170.958	12.454
3100	16.391	95.317	81.604	42.512	-174.766	-170.832	12.044
3200	16.449	95.838	82.040	44.154	-174.931	-170.705	11.659
3300	16.503	96.345	82.466	45.801	-175.093	-170.569	11.296
3400	16.554	96.839	82.882	47.454	-175.251	-170.429	10.955
3500	16.602	97.319	83.287	49.112	-175.407	-170.284	10.633
3600	16.648	97.788	83.684	50.775	-277.185	-169.872	10.313
3700	16.692	98.244	84.071	52.442	-277.308	-166.891	9.858
3800	16.733	98.690	84.450	54.113	-277.442	-163.906	9.427
3900	16.773	99.125	84.821	55.788	-277.588	-160.916	9.018
4000	16.811	99.550	85.184	57.468	-277.743	-157.921	8.628
4100	16.848	99.966	85.539	59.151	-277.911	-154.924	8.258
4200	16.884	100.372	85.887	60.837	-278.090	-151.924	7.905
4300	16.918	100.770	86.229	62.527	-278.278	-148.917	7.569
4400	16.952	101.160	86.564	64.221	-278.477	-145.907	7.247
4500	16.984	101.541	86.892	65.918	-278.685	-142.892	6.940
4600	17.016	101.914	87.215	67.618	-278.902	-139.869	6.645
4700	17.046	102.281	87.532	69.321	-279.129	-136.845	6.363
4800	17.075	102.640	87.843	71.027	-279.364	-133.813	6.093
4900	17.104	102.992	88.148	72.736	-279.608	-130.782	5.833
5000	17.131	103.338	88.449	74.448	-279.859	-127.740	5.584
5100	17.157	103.678	88.744	76.162	-280.118	-124.699	5.344
5200	17.183	104.011	89.034	77.879	-280.384	-121.644	5.113
5300	17.207	104.339	89.320	79.598	-280.657	-118.591	4.890
5400	17.230	104.660	89.601	81.320	-280.937	-115.531	4.676
5500	17.251	104.977	89.878	83.044	-281.221	-112.463	4.469
5600	17.272	105.288	90.150	84.770	-281.513	-109.395	4.269
5700	17.291	105.594	90.418	86.499	-281.808	-106.315	4.076
5800	17.309	105.895	90.683	88.229	-282.109	-103.234	3.890
5900	17.325	106.191	90.943	89.960	-282.416	-100.150	3.710
6000	17.341	106.482	91.200	91.694	-282.726	-97.061	3.535

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968; Dec. 31, 1968

TITANIUM DIFLUORIDE (TiF_2) (IDEAL GAS) GFW = 85.8968

Point Group [$D_{\infty h}$]

$\Delta Hf°_0$ = -164.1 ± 10 kcal/mol

$S°_{298.15}$ = 61.1 ± 1.5 gibbs/mol

$\Delta Hf°_{298.15}$ = -164.5 ± 10 kcal/mol

Ground State Quantum Weight = 3

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[473] (1)
[283] (2)
[633] (1)

Bond Distance: Ti-F = [1.95] Å

Bond Angle: F-Ti-F = [180°]

σ = 2

Rotational Constant: B_0 = [0.1167] cm^{-1}

Heat of Formation

Zmbov and Margrave (1) have reported ion intensities and the corresponding equilibrium constants for the reaction $Ca(g) + TiF_3(g) = CaF(g) + TiF_2(g)$. Second and third law analyses of their data give a second law $\Delta Hr°_{298}$ of 7.0 kcal/mol, a third law $\Delta Hr°_{298}$ of 11.76 kcal/mol and a third law drift of 3.1 ± 3.8 eu. The heat of formation, $\Delta Hf°_{298}$, of $TiF_2(g)$ is calculated from the third law $\Delta Hr°_{298}$, above, and the JANAF heat of formation of $TiF_3(g)$, CaF(g) and Ca(g).

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2$, $TiCl_4$, and TiF_4. The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2(g)$ are estimated by assuming they correspond to the inverted states of $NiCl_2(g)$ (2). The linear configuration is assumed because experimental evidence (3) indicates that other transition metal difluorides, viz. those of Mn, Co, Ni, Cu, and Zn, are linear.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).
3. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

Zirconium Difluoride (ZrF_2)

(Crystal) GFW = 129.2168

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	15.760	18.000	18.000	.000	- 230.000	- 218.145	159.905
300	15.780	18.098	18.000	.029	- 229.996	- 218.072	158.865
400	16.700	22.766	18.631	1.654	- 229.764	- 214.130	116.995
500	17.500	26.580	19.850	3.365	- 229.511	- 210.252	91.901
600	18.200	29.834	21.250	5.151	- 229.235	- 206.426	75.190
700	18.800	32.687	22.684	7.002	- 228.941	- 202.647	63.269
800	19.270	35.228	24.096	8.906	- 228.636	- 198.912	54.340
900	19.700	37.523	25.462	10.855	- 228.325	- 195.215	47.405
1000	20.080	39.619	26.775	12.844	- 228.010	- 191.553	41.864
1100	20.380	41.547	28.031	14.868	- 227.695	- 187.923	37.337
1200	20.650	43.332	29.233	16.919	- 228.237	- 184.269	33.540
1300	20.890	44.995	30.382	18.997	- 227.756	- 180.624	30.366
1400	21.100	46.551	31.482	21.097	- 227.268	- 177.016	27.633
1500	21.230	48.011	32.536	23.213	- 226.779	- 173.443	25.271
1600	21.350	49.386	33.546	25.343	- 226.292	- 169.905	23.208
1700	21.420	50.682	34.517	27.481	- 225.810	- 166.394	21.391
1800	21.490	51.909	35.449	29.627	- 225.336	- 162.914	19.781
1900	21.500	53.071	36.346	31.777	- 224.871	- 159.459	18.342
2000	21.500	54.174	37.210	33.927	- 224.420	- 156.027	17.050

Dec. 31, 1960; June 30, 1961; June 30, 1989

ZIRCONIUM DIFLUORIDE (ZrF_2) (CRYSTAL) GFW = 129.2168

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [18 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-230 ± 15] kcal/mol

Tm = [1175 ± 150]°K

ΔHm° = [9 ± 2] kcal/mol

$\Delta Hs^\circ_{298.15}$ = [96.6] kcal/mol

Heat of Formation

More recent thermal data related to the heat of formation of $ZrF_2(c)$ is unavailable. The adopted $\Delta Hf^\circ_{298}(ZrF_2, c)$ value is taken from (1) which was estimated by Brewer (2).

Heat Capacity and Entropy

The heat capacities in the temperature range 298-2000°K are estimated by comparison with those of $ZrF_4(c)$ and Zr(c). The S°_{298} is calculated as 17.2 and 17.0 eu based on the assumptions that $S(ZrF_2) = 1/2[S(ZrF_4) + S(Zr)]$ and $S(ZrF_2) = S(ZnF_2) - S(Zn) + S(Zr)$. Using the additive entropy constants S°_{298} = 12.1 and 4.7 eu for Zr and F suggested by Kubaschewski and Evans (3), we obtain $S^\circ_{298}(ZrF_2, c) = 12.1 + 2\ (4.7) = 21.5$ eu. Based on S°_{298} = 11.5 and 3.9 eu for Zr^{4+} and F^- recommended by Kelley (4), the value $S^\circ_{298}(ZrF_2, c)$ is derived as 19.3 eu. The entropy at 298°K for $ZrF_2(c)$ is tentatively adopted as 18 ± 2 eu.

Melting Data

Both Tm and ΔHm° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of $ZrF_4(c)$ which was obtained from experimental measurements (5). Therefore these estimated values are tentatively adopted.

Heat of Sublimation

The difference between ΔHf°_{298} for $ZrF_2(g)$ and $ZrF_2(c)$ is ΔHs°_{298}.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, unpublished data, University of California, Berkeley, California.
3. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
4. K. K. Kelley, private communication, June 1960.
5. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Zirconium Difluoride (ZrF_2)

(Liquid) GFW = 129.2168

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.760	24.103	24.103	.000	- 222.502	- 212.467	155.742
300	15.780	24.201	24.103	.029	- 222.498	- 212.405	154.737
400	16.700	28.869	24.734	1.654	- 222.266	- 209.074	114.232
500	17.500	32.683	25.953	3.365	- 222.013	- 205.806	89.958
600	18.200	35.937	27.353	5.151	- 221.737	- 202.589	73.793
700	18.800	38.790	28.787	7.002	- 221.443	- 199.421	62.262
800	24.000	41.332	30.199	8.907	- 221.137	- 196.296	53.626
900	24.000	44.159	31.596	11.307	- 220.375	- 193.237	46.924
1000	24.000	46.688	32.981	13.707	- 219.649	- 190.261	41.582
1100	24.000	48.975	34.333	16.107	- 218.958	- 187.356	37.224
1200	24.000	51.063	35.641	18.507	- 219.151	- 184.461	33.595
1300	24.000	52.984	36.902	20.907	- 218.348	- 181.602	30.530
1400	24.000	54.763	38.115	23.307	- 217.560	- 178.805	27.913
1500	24.000	56.419	39.281	25.707	- 216.787	- 176.063	25.652
1600	24.000	57.968	40.401	28.107	- 216.030	- 173.374	23.682
1700	24.000	59.423	41.478	30.507	- 215.286	- 170.729	21.949
1800	24.000	60.795	42.513	32.907	- 214.558	- 168.132	20.414
1900	24.000	62.092	43.510	35.307	- 213.843	- 165.571	19.045
2000	24.000	63.323	44.470	37.707	- 213.142	- 163.048	17.817
2100	24.000	64.494	45.396	40.107	- 212.455	- 160.562	16.710
2200	24.000	65.611	46.289	42.507	- 216.785	- 157.930	15.689
2300	24.000	66.677	47.153	44.907	- 216.120	- 155.268	14.754
2400	24.000	67.699	47.988	47.307	- 215.458	- 152.637	13.900
2500	24.000	68.679	48.796	49.707	- 214.799	- 150.034	13.116
2600	24.000	69.620	49.579	52.107	- 214.142	- 147.456	12.395
2700	24.000	70.526	50.338	54.507	- 213.487	- 144.902	11.729
2800	24.000	71.399	51.075	56.907	- 212.834	- 142.375	11.113
2900	24.000	72.241	51.790	59.307	- 212.184	- 139.868	10.541
3000	24.000	73.054	52.485	61.707	- 211.537	- 137.389	10.009

Dec. 31, 1960; June 30, 1961; June 30, 1969

ZIRCONIUM DIFLUORIDE (ZrF_2) (LIQUID) GFW = 129.2168

$S^\circ_{298.15}$ = [24.103] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-222.502] kcal/mol

Tm = [1175 ± 150]°K

ΔHm° = [9 ± 2] kcal/mol

Tb = [2529]°K

ΔHv° = [69.0] kcal/mol

Heat of Formation

The $\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1175} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated from those of $ZrF_4(\ell)$, $CaF_2(\ell)$, $Zr(\ell)$, and $Ca(\ell)$, and is assumed to be constant in the temperature range 800-3000°K. A glass transition temperature is assumed at 800°K. The Cp values below 800°K are adopted from the $ZrF_2(c)$ table.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Both Tm and ΔHm° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of $ZrF_4(c)$ which was obtained from experimental measurements (1). Therefore these estimated values are tentatively adopted.

Vaporization Data

Tb is the temperature at which the Gibbs energy change of the process $ZrF_2(\ell) = ZrF_2(g)$ approaches zero. The difference between ΔHf° for $ZrF_2(\ell)$ and $ZrF_2(g)$ at Tb is ΔHv°.

Reference

1. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Zirconium Difluoride (ZrF_2)

(Ideal Gas) GFW = 129.2168

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.827	-132.796	-132.796	INFINITE
100	8.509	56.898	77.099	-2.020	-132.896	-134.181	293.253
200	10.289	63.336	68.741	-1.081	-133.183	-135.352	147.906
298	11.628	67.715	67.715	.000	-133.400	-136.368	99.960
300	11.647	67.787	67.716	.022	-133.403	-136.386	99.357
400	12.437	71.257	68.193	1.229	-133.589	-137.352	75.045
500	12.896	74.086	69.090	2.498	-133.778	-138.272	60.439
600	13.176	76.464	70.126	3.803	-133.983	-139.151	50.686
700	13.357	78.509	71.181	5.130	-134.213	-139.995	43.708
800	13.481	80.302	72.211	6.472	-134.470	-140.804	38.466
900	13.572	81.895	73.200	7.825	-134.755	-141.579	34.380
1000	13.646	83.329	74.143	9.186	-135.068	-142.321	31.104
1100	13.711	84.632	75.038	10.554	-135.409	-143.030	28.417
1200	13.776	85.828	75.888	11.928	-136.628	-143.655	26.163
1300	13.844	86.934	76.696	13.309	-136.844	-144.231	24.247
1400	13.918	87.962	77.464	14.697	-137.068	-144.791	22.603
1500	13.999	88.925	78.196	16.093	-137.299	-145.334	21.175
1600	14.086	89.831	78.896	17.497	-137.538	-145.863	19.924
1700	14.180	90.688	79.564	18.910	-137.781	-146.375	18.818
1800	14.277	91.501	80.205	20.333	-138.030	-146.875	17.833
1900	14.378	92.276	80.820	21.766	-138.282	-147.359	16.950
2000	14.479	93.016	81.411	23.209	-138.538	-147.829	16.154
2100	14.581	93.725	81.981	24.662	-138.798	-148.289	15.433
2200	14.680	94.406	82.530	26.125	-144.065	-148.558	14.758
2300	14.777	95.060	83.061	27.598	-144.327	-148.755	14.135
2400	14.870	95.691	83.574	29.080	-144.583	-148.943	13.563
2500	14.959	96.300	84.071	30.572	-144.832	-149.120	13.036
2600	15.043	96.888	84.553	32.072	-145.075	-149.286	12.549
2700	15.123	97.458	85.020	33.580	-145.312	-149.442	12.097
2800	15.198	98.009	85.474	35.096	-145.543	-149.592	11.676
2900	15.268	98.543	85.916	36.620	-145.769	-149.731	11.284
3000	15.334	99.062	86.346	38.150	-145.992	-149.867	10.918
3100	15.395	99.566	86.764	39.686	-146.210	-149.992	10.574
3200	15.453	100.056	87.172	41.229	-146.424	-150.110	10.252
3300	15.507	100.532	87.569	42.777	-146.635	-150.222	9.949
3400	15.559	100.996	87.957	44.330	-146.843	-150.328	9.663
3500	15.607	101.447	88.336	45.888	-147.049	-150.425	9.393
3600	15.653	101.888	88.707	47.451	-147.251	-150.518	9.138
3700	15.696	102.317	89.069	49.019	-147.451	-150.607	8.896
3800	15.738	102.736	89.423	50.591	-147.649	-150.688	8.667
3900	15.778	103.146	89.770	52.166	-147.847	-150.769	8.449
4000	15.816	103.546	90.109	53.746	-148.041	-150.840	8.241
4100	15.853	103.937	90.442	55.330	-148.234	-150.908	8.044
4200	15.889	104.319	90.767	56.917	-148.426	-150.970	7.856
4300	15.924	104.693	91.087	58.507	-148.616	-151.027	7.676
4400	15.957	105.060	91.400	60.101	-148.806	-151.082	7.504
4500	15.990	105.419	91.708	61.699	-148.993	-151.133	7.340
4600	16.021	105.771	92.010	63.299	-149.180	-151.179	7.183
4700	16.051	106.115	92.306	64.903	-149.364	-151.219	7.032
4800	16.081	106.454	92.598	66.510	-290.707	-150.572	6.856
4900	16.109	106.786	92.884	68.119	-290.996	-147.649	6.585
5000	16.137	107.111	93.165	69.731	-291.290	-144.722	6.326
5100	16.163	107.431	93.442	71.346	-291.588	-141.791	6.076
5200	16.188	107.745	93.714	72.964	-291.889	-138.847	5.836
5300	16.212	108.054	93.981	74.584	-292.194	-135.900	5.604
5400	16.235	108.357	94.245	76.206	-292.504	-132.953	5.381
5500	16.257	108.655	94.504	77.831	-292.816	-129.994	5.165
5600	16.277	108.948	94.759	79.458	-293.131	-127.028	4.958
5700	16.297	109.237	95.011	81.086	-293.451	-124.060	4.757
5800	16.314	109.520	95.259	82.717	-293.771	-121.085	4.563
5900	16.331	109.799	95.503	84.349	-294.095	-118.107	4.375
6000	16.346	110.074	95.743	85.983	-294.422	-115.122	4.193

Dec. 31, 1960; June 30, 1961; June 30, 1969; Dec. 31, 1969

ZIRCONIUM DIFLUORIDE (ZrF_2) (IDEAL GAS) GFW = 129.2168

Point Group C_{2v}

$\Delta Hf°_0$ = -132.8 ± 5 kcal/mol

$S°_{298.15}$ = [67.7 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = -133.4 ± 5 kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[560] (1)
[300] (1)
[670] (1)

Bond Distance: Zr-F = [1.92] Å

Bond Angle: F-Zr-F = [125°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.3968 x 10^{-114}] g^3 cm^6

Heat of Formation

Murad and Hildenbrand (1) studied the gaseous equilibria involving ZrF_4, ZrF_3, ZrF_2, Ca, and CaF, mass-spectrometrically. Ion intensities were measured 3 eV above threshold over the temperature range 1665-1747°K, and the equilibrium constants for the reaction 2 Ca(g) + ZrF_4(g) = 2 CaF(g) + ZrF_2(g) were calculated. Using the reported equilibrium constants, the enthalpy changes ($\Delta Hr°_{298}$) of this reaction are evaluated by the second and third law methods to be 15.4 and 50.9 kcal/mol, respectively. The drift in third law values is 20.4 ± 17.6 eu. Based on the third law $\Delta Hr°_{298}$ value and $\Delta Hf°_{298}$ = 42.85 ± 0.3, -65.0 ± 2, and -400.0 ± 0.5 kcal/mol for Ca(g), CaF(g), and ZrF_4(g), respectively, we obtain $\Delta Hf°_{298}$(ZrF_2, g) = -133.4 ± 5 kcal/mol, which is adopted.

Using Gibbs energy functions derived from different molecular constants for the reactants and products, Murad and Hildenbrand (1) derived a third law $\Delta Hr°_{298}$ = 42.6 ± 5 and $\Delta Hf°_{298}$(ZrF_2, g) = -141 ± 5 kcal/mol, which are in fair agreement with the adopted values.

Heat Capacity and Entropy

According to the correlations of Charkin and Dyatkina (2), the ZrF_2(g) molecule has an angular configuration. The F-Zr-F angle is estimated as 125°, which is similar to the value reported by Hastie, Hauge, and Margrave (4) for TiF_2(g). The F-Zr bond distance is estimated from that of ZrF_4(g). The vibrational frequencies are calculated based on the method suggested by Herzberg (3). The value ν_1 is calculated from the vibrational frequency (ν) of ZrF(g) by use of the relation $\nu_1 = \nu\sqrt{\frac{Zr}{Zr+F}}$ where Zr and F are gram atomic weights of zirconium and fluorine. ν_3 is derived from ν_1 using the formula $\nu_3 = \nu_1\sqrt{\frac{Zr+2F}{Zr}}$, and ν_2 is calculated as 0.44 ν_3 where the value 0.44 is estimated by comparison with the ratios of ν_2/ν_3 for other related compounds. Ground state quantum weight is taken to be the same as that of TiF_2(g). The three principal moments of inertia are: $I_A = 1.830 \times 10^{-38}$, $I_B = 3.502 \times 10^{-39}$, and $I_C = 2.180 \times 10^{-38}$ g cm^2. The electronic levels and quantum weights are estimated to be the same as those of TiF_2(g).

References

1. E. Murad and D. L. Hildenbrand, J. Chem. Phys. 45, 4751 (1966).
2. O. P. Charkin and M. E. Dyatkina, Russ. J. Struct. Chem. (English Transl.) 6, 550 (1965).
3. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.
4. J. W. Hastie, R. H. Hauge, and J. L. Margrave, J. Chem. Phys. 51, 2648 (1969).

Iron Trifluoride (FeF_3)

(Crystal) Mol. Wt. = 112.8422

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	21.750	23.500	23.500	.000	- 249.000	- 232.393	170.341
300	21.900	23.635	23.500	.040	- 248.992	- 232.290	169.215
400	23.033	30.477	24.421	2.423	- 248.390	- 226.812	123.918
500	22.865	35.584	26.162	4.711	- 247.988	- 221.467	96.799
600	23.140	39.778	28.092	7.011	- 247.665	- 216.194	78.745
700	23.440	43.367	30.024	9.340	- 247.402	- 210.969	65.864
800	23.740	46.517	31.892	11.699	- 247.210	- 205.781	56.214
900	24.040	49.330	33.676	14.088	- 247.111	- 200.608	48.712
1000	24.340	51.879	35.371	16.507	- 247.176	- 195.442	42.712
1100	24.640	54.212	36.979	18.956	- 247.440	- 190.249	37.797
1200	24.940	56.369	38.506	21.435	- 247.470	- 185.054	33.701
1300	25.240	58.377	39.959	23.944	- 247.138	- 179.865	30.237
1400	25.540	60.259	41.342	26.483	- 246.799	- 174.704	27.271
1500	25.840	62.031	42.663	29.052	- 246.449	- 169.565	24.704
1600	26.140	63.708	43.926	31.651	- 246.092	- 164.452	22.462
170C	26.440	65.302	45.137	34.280	- 246.015	- 159.355	20.485
1800	26.740	66.822	46.300	36.939	- 245.730	- 154.267	18.730
1900	27.040	68.276	47.419	39.628	- 249.104	- 149.009	17.139
2000	27.340	69.670	48.497	42.347	- 248.831	- 143.746	15.707

Sept. 30, 1965

IRON TRIFLUORIDE (FeF_3) (CRYSTAL) MOL. WT. = 112.8422

$\Delta H^\circ_{f\ 0}$ = Unknown

$S^\circ_{298.15}$ = [23.5 ± 2] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -249 ± 3 kcal. mole^{-1}

T_s = [1200]°K.

$\Delta H^\circ_{s\ 298.15}$ = [52.8] kcal. mole^{-1}

Heat of Formation.

The equilibrium pressures for the reaction $2FeF_3(c) + H_2(g) = 2FeF_2(c) + 2HF(g)$ have been measured at temperatures 623, 723 and 823°K. by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928). Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 kcal. mole^{-1} by the third and second law methods, respectively. The corresponding $\Delta H^\circ_{f\ 298.15}$ (FeF_3, c) values are calculated to be -252.4 and -249.2 kcal. mole^{-1}. The equilibrium constants for the reaction $2FeF_3(c) + 3H_2O(g) = Fe_2O_3(c) + 6HF(g)$ were determined by L. Domange, Ann. Chim., 7, 225 (1937). Based on the third law value of $\Delta H^\circ_{r\ 298.15}$, 62.0 kcal. mole^{-1}, the $\Delta H^\circ_{f\ 298.15}$ (FeF_3, c) was calculated as -237.4 kcal. mole^{-1}. The value of $\Delta H^\circ_{f\ 298.15}$ for $FeF_3(c)$ is selected to be -249 ± 3 kcal. mole^{-1}.

Heat Capacity and Entropy.

The heat capacities of $FeF_3(c)$ at temperatures 100-450°K. were determined by H. Bizette, R. Mainard and J. Picard, Comp. rend. 5508 (1965). The results were presented graphically by plotting C_p vs. T. The C_p curve shows a peak at 367°K. An antiferromagnetic transition at about 394°K. was reported by E. O. Wollan, H. R. Child, W. C. Koehler and M. K. Wilkinson, Phys. Rev. 112, 1132 (1958). The heat capacities above 450°K. and $S^\circ_{298.15}$ were estimated by comparison with those for $FeCl_3(c)$ $AlCl_3(c)$ and $AlF_3(c)$.

Sublimation Data.

The phenomenon that $FeF_3(c)$ sublimes without fusion at temperatures near 1000°C has been observed and reported by Poulenc, Ann. Chim. phys. (7), 2, 1 (1894). Based on this data the value of T_s was estimated. The value of heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) was calculated using an estimated entropy of sublimation, ΔS°_s = 40 e.u. in order to have $\Delta F_r \cong 0$ for the reaction $FeF_3(c) = FeF_3(g)$ at 1200°K.

Iron Trifluoride (FeF_3)

(Ideal Gas)   Mol. Wt. = 112.8422

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.539	- 195.499	- 195.499	INFINITE
100	10.557	58.479	85.163	- 2.668	- 195.774	- 195.371	426.963
200	13.644	66.840	74.063	- 1.445	- 196.022	- 194.867	212.930
298	15.666	72.690	72.690	.000	- 196.200	- 194.259	142.389
300	15.697	72.787	72.690	.029	- 196.203	- 194.247	141.502
400	17.027	77.500	73.323	1.670	- 196.343	- 193.573	105.758
500	17.858	81.396	74.560	3.418	- 196.481	- 192.866	84.298
600	18.389	84.702	75.982	5.232	- 196.644	- 192.128	69.979
700	18.742	87.565	77.436	7.090	- 196.852	- 191.358	59.742
800	18.986	90.084	78.863	8.977	- 197.132	- 190.557	52.055
900	19.160	92.331	80.237	10.885	- 197.514	- 189.713	46.066
1000	19.288	94.357	81.549	12.807	- 198.076	- 188.820	41.264
1100	19.385	96.200	82.799	14.741	- 198.855	- 187.851	37.321
1200	19.460	97.890	83.987	16.684	- 199.421	- 186.831	34.025
1300	19.519	99.450	85.117	18.633	- 199.650	- 185.772	31.230
1400	19.566	100.898	86.193	20.587	- 199.895	- 184.694	28.831
1500	19.605	102.250	87.219	22.546	- 200.156	- 183.600	26.749
1600	19.637	103.516	88.199	24.508	- 200.435	- 182.488	24.925
1700	19.663	104.707	89.135	26.473	- 201.022	- 181.350	23.313
1800	19.685	105.832	90.032	28.440	- 201.429	- 180.184	21.876
1900	19.704	106.897	90.891	30.410	- 205.522	- 178.807	20.567
2000	19.720	107.908	91.717	32.381	- 205.997	- 177.388	19.383
2100	19.734	108.870	92.511	34.354	- 206.480	- 175.946	18.310
2200	19.747	109.789	93.276	36.328	- 206.969	- 174.482	17.332
2300	19.757	110.667	94.013	38.303	- 207.464	- 172.994	16.437
2400	19.767	111.508	94.725	40.279	- 207.967	- 171.486	15.615
2500	19.775	112.315	95.412	42.257	- 208.477	- 169.954	14.857
2600	19.782	113.091	96.077	44.234	- 208.994	- 168.404	14.155
2700	19.789	113.837	96.721	46.213	- 209.517	- 166.830	13.503
2800	19.794	114.557	97.346	48.192	- 210.046	- 165.241	12.897
2900	19.800	115.252	97.951	50.172	- 210.584	- 163.630	12.331
3000	19.804	115.923	98.539	52.152	- 211.129	- 162.004	11.801
3100	19.809	116.572	99.110	54.133	- 211.679	- 160.354	11.304
3200	19.813	117.201	99.666	56.114	- 295.663	- 157.245	10.739
3300	19.816	117.811	100.207	58.095	- 295.765	- 152.921	10.127
3400	19.819	118.403	100.733	60.077	- 295.878	- 148.591	9.551
3500	19.822	118.977	101.246	62.059	- 296.001	- 144.254	9.007
3600	19.825	119.536	101.747	64.041	- 296.136	- 139.915	8.494
3700	19.828	120.079	102.235	66.024	- 296.281	- 135.575	8.008
3800	19.830	120.608	102.711	68.007	- 296.438	- 131.231	7.547
3900	19.832	121.123	103.177	69.990	- 296.607	- 126.881	7.110
4000	19.834	121.625	103.632	71.973	- 296.787	- 122.527	6.694
4100	19.836	122.115	104.077	73.957	- 296.979	- 118.168	6.299
4200	19.838	122.593	104.512	75.941	- 297.184	- 113.806	5.922
4300	19.839	123.060	104.938	77.924	- 297.399	- 109.433	5.562
4400	19.841	123.516	105.355	79.908	- 297.629	- 105.063	5.218
4500	19.842	123.962	105.763	81.893	- 297.870	- 100.687	4.890
4600	19.844	124.398	106.164	83.877	- 298.124	- 96.299	4.575
4700	19.845	124.825	106.556	85.861	- 298.392	- 91.909	4.274
4800	19.846	125.242	106.941	87.846	- 298.671	- 87.505	3.984
4900	19.847	125.652	107.319	89.831	- 298.965	- 83.108	3.707
5000	19.848	126.053	107.690	91.815	- 299.273	- 78.703	3.440
5100	19.849	126.446	108.053	93.800	- 299.593	- 74.293	3.184
5200	19.850	126.831	108.411	95.785	- 299.927	- 69.863	2.936
5300	19.851	127.209	108.762	97.770	- 300.274	- 65.434	2.698
5400	19.851	127.580	109.107	99.755	- 300.636	- 61.006	2.469
5500	19.852	127.945	109.446	101.740	- 301.010	- 56.565	2.248
5600	19.853	128.302	109.780	103.726	- 301.399	- 52.113	2.034
5700	19.854	128.654	110.108	105.711	- 301.802	- 47.661	1.827
5800	19.854	128.999	110.431	107.696	- 302.216	- 43.194	1.628
5900	19.855	129.338	110.748	109.682	- 302.645	- 38.729	1.435
6000	19.855	129.672	111.061	111.667	- 303.087	- 34.251	1.248

Sept. 30, 1965

IRON TRIFLUORIDE (FeF_3)   (IDEAL GAS)   MOL. WT. = 112.8422

Point Group $[D_{3h}]$

$S^\circ_{298.15}$ = [72.7] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-195.5 ± 5] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-196.2 ± 5] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[600] (1)	[800] (2)
[250] (1)	[220] (2)

Bond Distance: Fe-F = [1.9] cm.$^{-1}$

Bond Angle: F-Fe-F = [120]°

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.96723 X 10^{-114}] g.^{3} cm.^{6}

σ = [6]

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ (FeF_3, g) was calculated from $\Delta H^\circ_{s\ 298.15}$ and $\Delta H^\circ_{f\ 298.15}$ for FeF_3(c). The value $\Delta H^\circ_{s\ 298.15}$ = 65.5 kcal. mole^{-1} was derived from $\Delta H^\circ_{s\ 1200}$ (see FeF_3(c) table for details).

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were estimated by comparison with those for AlF_3(g). The vibrational frequencies were estimated by comparison with those for AlF_3(g), TiF_3(g) and ZrF_3(g). The three principal moments of inertia are: $I_A = I_B = 1.7081 \times 10^{-38}$ and $I_C = 3.4162 \times 10^{-38}$ g. cm.^{2}

Trifluorosilane ($SiHF_3$)

(Ideal Gas) Mol. Wt. = 86.098

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.249	-281.316	-281.316	INFINITE
100	9.139	53.523	77.799	-2.428	-281.981	-279.918	611.731
200	12.339	60.858	67.613	-1.351	-282.530	-277.636	303.372
298	15.120	66.317	66.317	.000	-283.000	-275.133	201.668
300	15.166	66.411	66.317	.028	-283.008	-275.084	200.389
400	17.453	71.102	66.941	1.664	-283.383	-272.382	148.816
500	19.163	75.190	68.191	3.499	-283.657	-269.600	117.836
600	20.433	78.801	69.664	5.482	-283.845	-266.769	97.166
700	21.392	82.027	71.204	7.576	-283.969	-263.912	82.393
800	22.132	84.933	72.742	9.753	-284.046	-261.042	71.310
900	22.712	87.575	74.245	11.997	-284.086	-258.162	62.687
1000	23.173	89.993	75.701	14.292	-284.103	-255.282	55.789
1100	23.545	92.219	77.103	16.628	-284.099	-252.400	50.145
1200	23.847	94.281	78.449	18.998	-284.080	-249.518	45.441
1300	24.096	96.200	79.742	21.396	-284.051	-246.639	41.462
1400	24.303	97.994	80.982	23.816	-284.014	-243.762	38.051
1500	24.476	99.677	82.173	26.255	-283.973	-240.888	35.096
1600	24.623	101.261	83.317	28.711	-283.930	-238.018	32.510
1700	24.747	102.758	84.417	31.179	-295.990	-235.040	30.215
1800	24.854	104.175	85.476	33.660	-295.904	-231.461	28.102
1900	24.947	105.522	86.496	36.150	-295.816	-227.882	26.211
2000	25.027	106.803	87.479	38.648	-295.729	-224.306	24.510
2100	25.097	108.026	88.429	41.155	-295.642	-220.740	22.972
2200	25.158	109.195	89.346	43.668	-295.558	-217.176	21.573
2300	25.212	110.315	90.234	46.186	-295.474	-213.612	20.297
2400	25.260	111.389	91.093	48.710	-295.394	-210.057	19.127
2500	25.303	112.421	91.926	51.238	-295.318	-206.503	18.052
2600	25.341	113.414	92.733	53.770	-295.243	-202.951	17.059
2700	25.376	114.371	93.517	56.306	-295.171	-199.402	16.140
2800	25.407	115.294	94.278	58.845	-295.102	-195.859	15.287
2900	25.435	116.187	95.018	61.387	-295.037	-192.312	14.492
3000	25.460	117.049	95.739	63.932	-294.977	-188.776	13.752
3100	25.483	117.884	96.440	66.479	-294.918	-185.236	13.059
3200	25.504	118.694	97.122	69.029	-294.864	-181.697	12.409
3300	25.523	119.479	97.786	71.580	-294.813	-178.160	11.798
3400	25.541	120.241	98.437	74.133	-294.766	-174.626	11.224
3500	25.557	120.982	99.071	76.688	-294.725	-171.092	10.683
3600	25.572	121.702	99.690	79.245	-389.661	-167.086	10.143
3700	25.585	122.403	100.294	81.802	-389.565	-160.906	9.504
3800	25.598	123.085	100.885	84.362	-389.474	-154.726	8.898
3900	25.610	123.750	101.463	86.922	-389.389	-148.555	8.324
4000	25.620	124.399	102.028	89.483	-389.307	-142.378	7.779
4100	25.631	125.032	102.581	92.046	-389.230	-136.208	7.260
4200	25.640	125.649	103.123	94.609	-389.157	-130.033	6.766
4300	25.649	126.253	103.654	97.174	-389.087	-123.866	6.295
4400	25.657	126.842	104.174	99.739	-389.024	-117.700	5.846
4500	25.665	127.419	104.685	102.305	-388.966	-111.539	5.417
4600	25.672	127.983	105.185	104.872	-388.910	-105.369	5.006
4700	25.679	128.535	105.676	107.440	-388.859	-99.208	4.613
4800	25.685	129.076	106.158	110.008	-388.812	-93.039	4.236
4900	25.691	129.606	106.631	112.577	-388.771	-86.881	3.875
5000	25.696	130.125	107.096	115.146	-388.733	-80.720	3.528
5100	25.702	130.634	107.552	117.716	-388.700	-74.564	3.195
5200	25.707	131.133	108.001	120.286	-388.671	-68.400	2.875
5300	25.711	131.623	108.442	122.857	-388.646	-62.239	2.566
5400	25.716	132.103	108.876	125.429	-388.626	-56.088	2.270
5500	25.720	132.575	109.302	128.000	-388.610	-49.927	1.984
5600	25.724	133.039	109.722	130.573	-388.600	-43.770	1.708
5700	25.728	133.494	110.135	133.145	-388.594	-37.608	1.442
5800	25.732	133.942	110.542	135.718	-388.590	-31.455	1.185
5900	25.735	134.381	110.942	138.292	-388.592	-25.296	.937
6000	25.738	134.814	111.336	140.865	-388.600	-19.144	.697

December 31, 1960.

Trifluorosilane ($SiHF_3$) (Ideal Gas)

Mol. Wt. = 86.098

ΔH_f° 298.15 = [-283 ± 15] kcal. mole^{-1}

$S^\circ_{298.15}$ = 66.304 cal. deg.$^{-1}$ mole^{-1}

Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$	
2315 (1)	999 (2)
859 (1)	844 (2)
425 (1)	305 (2)

Moments of Inertia: I_A = 11.7272 X 10^{-39} g. cm.^{2} σ = 3

I_B = 11.7272 X 10^{-39} g. cm.^{2} I_C = 20.8927 X 10^{-39} g. cm.^{2}

Heat of Formation. ΔH_f° 298.15 was found estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were assigned by C. Newman, S. Polo and M. Wilson, Spec. Chim. Acta 15, 793 (1959). Constants used in calculating moment of inertia came from G. Heath, L. Thomas, and J. Sheridan, Trans. Far. Soc. 50, 779 (1954).

Lithium Fluoride, Trimeric (Li_3F_3)

(Ideal Gas) GFW = 77.8122

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.883	-361.023	-361.023	INFINITE
100	13.343	55.608	94.630	-3.902	-361.442	-360.371	787.590
200	20.151	67.065	78.114	-2.210	-362.119	-359.024	392.323
298	24.498	75.997	75.997	.000	-362.620	-357.392	261.975
300	24.559	76.149	75.997	.045	-362.629	-357.360	260.337
400	27.074	83.592	76.995	2.639	-363.053	-355.537	194.256
500	28.534	89.804	78.953	5.425	-365.731	-353.382	154.463
600	29.429	95.092	81.214	8.327	-366.217	-350.863	127.802
700	30.008	99.675	83.531	11.301	-366.619	-348.274	108.736
800	30.402	103.709	85.806	14.322	-366.973	-345.630	94.422
900	30.680	107.307	87.999	17.377	-367.305	-342.941	83.277
1000	30.884	110.551	90.094	20.456	-367.623	-340.217	74.354
1100	31.037	113.502	92.090	23.552	-367.929	-337.461	67.047
1200	31.155	116.207	93.989	26.662	-368.229	-334.680	60.953
1300	31.247	118.705	95.795	29.782	-368.521	-331.872	55.793
1400	31.321	121.023	97.515	32.911	-368.808	-329.041	51.366
1500	31.381	123.186	99.156	36.046	-369.088	-326.190	47.526
1600	31.430	125.213	100.721	39.187	-369.363	-323.320	44.163
1700	31.471	127.120	102.219	42.332	-474.776	-316.451	40.682
1800	31.506	128.920	103.653	45.481	-474.501	-307.143	37.292
1900	31.535	130.624	105.028	48.633	-474.226	-297.850	34.261
2000	31.560	132.242	106.348	51.788	-473.956	-288.575	31.534
2100	31.582	133.783	107.618	54.945	-473.691	-279.318	29.069
2200	31.600	135.252	108.841	58.104	-473.431	-270.066	26.829
2300	31.617	136.657	110.020	61.265	-473.173	-260.828	24.784
2400	31.631	138.003	111.158	64.427	-472.926	-251.602	22.912
2500	31.644	139.295	112.258	67.591	-472.686	-242.384	21.189
2600	31.655	140.536	113.322	70.756	-472.453	-233.179	19.601
2700	31.665	141.731	114.352	73.922	-472.232	-223.980	18.130
2800	31.674	142.883	115.351	77.089	-472.018	-214.790	16.765
2900	31.683	143.994	116.319	80.257	-471.824	-205.604	15.495
3000	31.690	145.069	117.260	83.426	-471.638	-196.429	14.310
3100	31.696	146.108	118.174	86.595	-471.472	-187.256	13.201
3200	31.702	147.114	119.063	89.765	-471.319	-178.092	12.163
3300	31.708	148.090	119.928	92.935	-471.186	-168.931	11.188
3400	31.713	149.036	120.770	96.106	-471.070	-159.769	10.270
3500	31.718	149.956	121.591	99.278	-470.974	-150.616	9.405
3600	31.722	150.849	122.391	102.450	-470.899	-141.463	8.588
3700	31.726	151.719	123.172	105.622	-470.847	-132.317	7.816
3800	31.729	152.565	123.934	108.795	-470.818	-123.157	7.083
3900	31.733	153.389	124.679	111.968	-470.814	-114.013	6.389
4000	31.736	154.192	125.407	115.141	-470.836	-104.865	5.730
4100	31.738	154.976	126.119	118.315	-470.886	-95.713	5.102
4200	31.741	155.741	126.815	121.489	-470.965	-86.566	4.505
4300	31.744	156.488	127.496	124.663	-471.070	-77.408	3.934
4400	31.746	157.218	128.163	127.838	-471.208	-68.249	3.390
4500	31.748	157.931	128.817	131.013	-471.379	-59.092	2.870
4600	31.750	158.629	129.458	134.187	-471.584	-49.929	2.372
4700	31.752	159.312	130.086	137.363	-471.826	-40.766	1.896
4800	31.754	159.980	130.701	140.538	-472.105	-31.591	1.438
4900	31.755	160.635	131.306	143.713	-472.428	-22.409	.999
5000	31.757	161.276	131.899	146.889	-472.789	-13.216	.578
5100	31.758	161.905	132.481	150.065	-473.198	-4.023	.172
5200	31.760	162.522	133.053	153.241	-473.655	5.186	-.218
5300	31.761	163.127	133.614	156.417	-474.163	14.393	-.594
5400	31.762	163.721	134.166	159.593	-474.724	23.611	-.956
5500	31.763	164.304	134.709	162.769	-475.343	32.852	-1.305
5600	31.764	164.876	135.243	165.945	-476.020	42.090	-1.643
5700	31.766	165.438	135.768	169.122	-476.760	51.356	-1.969
5800	31.767	165.991	136.284	172.298	-477.567	60.629	-2.285
5900	31.767	166.534	136.792	175.475	-478.442	69.910	-2.590
6000	31.768	167.068	137.292	178.652	-479.392	79.217	-2.885

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

LITHIUM FLUORIDE, TRIMERIC (Li_3F_3) (IDEAL GAS) GFW = 77.8122

Point Group [D_{3h}]

$\Delta Hf°_0$ = -361.02 ± 6.0 kcal/mol

$S°_{298.15}$ = [76 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = -362.62 ± 6.0 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
280 (1)	530 (2)
[430] (1)	755 (2)
[640] (1)	245 (2)
[480] (1)	[140] (2)

Bond Distance: Li-F = [1.68] Å

Bond Angles: F-Li-F = [120°] Li-F-Li = [120°] σ = 6

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.2122 x 10^{-113}] g^3cm^6

Heat of Formation

The heat of formation ($\Delta Hf°_{298}$) is derived based on the adopted value $\Delta Hr°_{298}$ = 79.73 kcal/mol for the reaction 3LiF(c) = Li_3F_3(g), using $\Delta Hf°_{298}$(LiF, c) = -147.45 kcal/mol. The $\Delta Hr°_{298}$ value is calculated to be 73.9 kcal/mol at 1000°K, which is consistent with the values $\Delta Hs°_{1000}$ = 73.9 ± 3 and 74.9 ± 1 kcal/mol reported by Büchler and Stauffer (1) and Akishin et al. (2), respectively. Using the adopted $\Delta Hf°_{298}$ values for monomer, dimer, and trimer, we also evaluate the value $\Delta Hr°_{1073}$ = 53.8 kcal/mol for the reaction $Li_3F_3(g) = Li_2F_2(g) + LiF(g)$ which is in agreement with the value 50 < $\Delta Hr°_{1073}$ < 65 kcal/mol reported by Porter and Schoonmaker (3). Rothberg et al. (4) have determined the partial pressures of LiF monomer, dimer, and trimer in the temperature range 980 - 1070°K, using the molecular-beam velocity-selector method (5). However, the total pressures derived from these data are too low in comparison with the other reported vapor pressures. Thus their data are not adopted for evaluation.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of the BeO trimer. The Li-F bond distance is taken from that of the Li_2F_2 molecule determined by Akishin and Rambidi (6). Four vibrational frequencies, A_2'' and three E', are reported by Snelson (7) from analysis of the infrared spectra of LiF using the matrix isolation technique. The reported frequencies are corrected to the average isotopic species. The other four frequencies, E_2'' and three A', are estimated by comparison with those for the isoelectronic molecule Be_3O_3. The three principal moments of inertia are $I_A = I_B$ = 1.823 x 10^{-38} and I_C = 3.646 x 10^{-38} g cm^2.

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Nitrogen Trifluoride (NF_3)

(Ideal Gas) GFW = 71.0019

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.832	-30.061	-30.061	INFINITE
100	8.135	51.551	71.897	-2.035	-30.653	-27.795	60.746
200	10.224	57.734	63.387	-1.131	-31.147	-24.731	27.025
298	12.756	62.299	62.299	.000	-31.430	-21.515	15.771
300	12.799	62.378	62.300	.024	-31.434	-21.454	15.629
400	14.785	66.349	62.827	1.409	-31.552	-18.104	9.892
500	16.149	69.804	63.885	2.960	-31.563	-14.740	6.443
600	17.072	72.836	65.129	4.624	-31.503	-11.379	4.145
700	17.708	75.518	66.426	6.365	-31.403	-8.033	2.508
800	18.157	77.914	67.715	8.159	-31.279	-4.704	1.285
900	18.484	80.072	68.970	9.992	-31.140	-1.390	.337
1000	18.728	82.033	70.180	11.853	-30.993	1.907	-.417
1100	18.914	83.827	71.340	13.736	-30.842	5.190	-1.031
1200	19.059	85.479	72.450	15.635	-30.689	8.460	-1.541
1300	19.174	87.009	73.512	17.547	-30.537	11.717	-1.970
1400	19.266	88.434	74.528	19.469	-30.386	14.961	-2.335
1500	19.342	89.766	75.499	21.399	-30.237	18.196	-2.651
1600	19.404	91.016	76.431	23.337	-30.090	21.419	-2.926
1700	19.456	92.194	77.324	25.280	-29.945	24.635	-3.167
1800	19.500	93.307	78.181	27.227	-29.805	27.839	-3.380
1900	19.537	94.363	79.005	29.179	-29.666	31.039	-3.570
2000	19.569	95.366	79.798	31.135	-29.530	34.232	-3.741
2100	19.597	96.321	80.562	33.093	-29.398	37.414	-3.894
2200	19.621	97.233	81.300	35.054	-29.269	40.593	-4.033
2300	19.642	98.106	82.011	37.017	-29.143	43.766	-4.159
2400	19.660	98.942	82.700	38.982	-29.020	46.933	-4.274
2500	19.677	99.745	83.365	40.949	-28.903	50.095	-4.379
2600	19.691	100.517	84.010	42.917	-28.787	53.253	-4.476
2700	19.704	101.260	84.636	44.887	-28.674	56.408	-4.566
2800	19.716	101.977	85.242	46.858	-28.564	59.555	-4.648
2900	19.726	102.669	85.831	48.830	-28.458	62.704	-4.725
3000	19.736	103.338	86.404	50.803	-28.357	65.841	-4.796
3100	19.744	103.985	86.961	52.777	-28.257	68.979	-4.863
3200	19.752	104.612	87.502	54.752	-28.162	72.115	-4.925
3300	19.759	105.220	88.030	56.728	-28.070	75.247	-4.983
3400	19.766	105.810	88.544	58.704	-27.980	78.378	-5.038
3500	19.771	106.383	89.046	60.681	-27.895	81.507	-5.089
3600	19.777	106.940	89.535	62.658	-27.812	84.632	-5.138
3700	19.782	107.482	90.013	64.636	-27.733	87.753	-5.183
3800	19.787	108.010	90.480	66.615	-27.658	90.876	-5.227
3900	19.791	108.524	90.936	68.593	-27.587	93.990	-5.267
4000	19.795	109.025	91.382	70.573	-27.517	97.108	-5.306
4100	19.799	109.514	91.818	72.552	-27.453	100.222	-5.342
4200	19.802	109.991	92.245	74.532	-27.391	103.336	-5.377
4300	19.805	110.457	92.663	76.513	-27.331	106.451	-5.410
4400	19.808	110.912	93.073	78.493	-27.277	109.559	-5.442
4500	19.811	111.358	93.474	80.474	-27.225	112.666	-5.472
4600	19.814	111.793	93.868	82.456	-27.176	115.776	-5.501
4700	19.816	112.219	94.254	84.437	-27.131	118.883	-5.528
4800	19.818	112.636	94.632	86.419	-27.089	121.992	-5.554
4900	19.820	113.045	95.004	88.401	-27.051	125.096	-5.580
5000	19.822	113.446	95.369	90.383	-27.017	128.201	-5.604
5100	19.824	113.838	95.727	92.365	-26.985	131.298	-5.627
5200	19.826	114.223	96.079	94.348	-26.957	134.410	-5.649
5300	19.828	114.601	96.425	96.330	-26.932	137.513	-5.670
5400	19.829	114.971	96.765	98.313	-26.912	140.608	-5.691
5500	19.831	115.335	97.099	100.296	-26.894	143.715	-5.711
5600	19.832	115.693	97.428	102.279	-26.880	146.818	-5.730
5700	19.834	116.044	97.752	104.263	-26.870	149.921	-5.748
5800	19.835	116.389	98.070	106.246	-26.861	153.023	-5.766
5900	19.836	116.728	98.384	108.230	-26.858	156.118	-5.783
6000	19.837	117.061	98.692	110.213	-26.658	159.221	-5.800

Dec. 31, 1960; Mar. 31, 1961; Mar. 31, 1964; June 30, 1969

NITROGEN TRIFLUORIDE (NF_3) (IDEAL GAS) GFW = 71.0019

Point Group C_{3v}

$\Delta Hf^\circ_0 = -30.06 \pm 0.3$ kcal/mol

$S^\circ_{298.15} = 62.30 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -31.43 \pm 0.3$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1032 (1)
642 (1)
906 (2)
492 (2)

Bond Distance: N-F = 1.371 Å

Bond Angle: F-N-F = 102°9'

$\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = 8.855 \times 10^{-115}$ g^3 cm^6

Heat of Formation

The adopted heat of formation was obtained from a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12-31-68). The data which was considered relating directly to NF_3 was as follows.

A. $8\ NF_3(g) + 3\ C_2N_2(g) \rightarrow 6\ CF_4(g) + 7\ N_2(g)$

Walker (1) reported $\Delta Hr^\circ_{298} = -1308.8 \pm 1.3$ kcal/mol.

B. $NF_3(g) + 1.5\ H_2(g) \rightarrow 3HF(50\ H_2O) + 0.5\ N_2(g)$

Sinke (2) reported $\Delta Hr^\circ_{298} = -199.49 \pm 0.22$ kcal/mol for a final state of HF(123 H_2O); the corrected value is -199.40 ± 0.22 kcal/mol.

C. $2\ NF_3(g) + S(c, rh) \rightarrow SF_6(g) + N_2(g)$

Walker (3) reported $\Delta Hr^\circ_{298} = -228.26 \pm 0.25$ kcal/mol.

D. $NF_3(g) \rightarrow 0.5\ N_2(g) + 1.5\ F_2(g)$

Sinke (4) reported $\Delta Hr^\circ_{298} = 31.44 \pm 0.3$ kcal/mol for the above dissociation from experimental explosion of hydrogen in 10 percent and 100 percent excess NF_3.

E. $NF_3(g) + B(c, \beta) \rightarrow BF_3(g) + 0.5\ N_2(g)$

Ludwig and Cooper (5) reported $\Delta Hr^\circ_{298} = -239.46 \pm 1.2$ kcal/mol, 5 percent of the boron remained unreacted and was detected by analysis.

Further details of the simultaneous adjustment are given by Syverud (6).

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin (7) and are in good agreement with those of Pace and Pierce (8), and Wilson and Polo (9). The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii (10). The bond length and angle were from the microwave studies of Sheridan and Gordy (11), whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu (12).

The individual moments of inertia are $I_A = I_B = 7.854 \times 10^{-39}$ g cm^2 and $I_C = 14.354 \times 10^{-39}$ g cm^2.

Pierce and Pace (13) have obtained the entropy of the gas at 144.15°K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 eu is in good agreement with our calculated value of 54.56 eu.

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Trifluoramine Oxide (NOF_3)

(Ideal Gas) GFW = 87.0013

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.266	-37.027	-37.027	INFINITE
100	8.540	53.754	78.368	-2.461	-37.959	-33.252	72.672
200	12.535	60.804	67.909	-1.421	-38.864	-28.241	30.860
298	16.219	66.535	66.535	.000	-39.000	-23.042	16.891
300	16.277	66.636	66.536	.030	-39.004	-22.944	16.715
400	18.824	71.692	67.208	1.794	-39.099	-17.570	9.600
500	20.535	76.089	68.554	3.767	-39.053	-12.192	5.329
600	21.721	79.944	70.138	5.883	-38.919	-6.830	2.488
700	22.569	83.359	71.787	8.100	-38.731	-1.496	.467
800	23.191	86.416	73.428	10.390	-38.511	3.807	-1.040
900	23.658	89.175	75.027	12.733	-38.268	9.083	-2.206
1000	24.016	91.687	76.569	15.118	-38.012	14.330	-3.132
1100	24.295	93.990	78.050	17.534	-37.747	19.551	-3.884
1200	24.517	96.114	79.468	19.975	-37.476	24.749	-4.507
1300	24.695	98.083	80.825	22.436	-37.204	29.924	-5.031
1400	24.840	99.919	82.124	24.913	-36.930	35.077	-5.476
1500	24.959	101.637	83.368	27.403	-36.656	40.212	-5.859
1600	25.059	103.251	84.561	29.904	-36.384	45.326	-6.191
1700	25.142	104.773	85.706	32.414	-36.113	50.426	-6.483
1800	25.213	106.212	86.805	34.932	-35.848	55.506	-6.739
1900	25.274	107.577	87.863	37.456	-35.583	60.576	-6.968
2000	25.326	108.875	88.881	39.986	-35.323	65.632	-7.172
2100	25.372	110.111	89.863	42.521	-35.066	70.670	-7.355
2200	25.412	111.293	90.810	45.061	-34.815	75.699	-7.520
2300	25.446	112.423	91.726	47.604	-34.567	80.718	-7.670
2400	25.477	113.507	92.611	50.150	-34.325	85.726	-7.806
2500	25.504	114.547	93.468	52.699	-34.089	90.721	-7.931
2600	25.528	115.548	94.298	55.251	-33.856	95.710	-8.045
2700	25.550	116.512	95.103	57.804	-33.628	100.691	-8.150
2800	25.570	117.441	95.884	60.360	-33.405	105.659	-8.247
2900	25.587	118.339	96.643	62.918	-33.187	110.626	-8.337
3000	25.603	119.207	97.381	65.478	-32.976	115.577	-8.420
3100	25.617	120.046	98.098	68.039	-32.767	120.525	-8.497
3200	25.630	120.860	98.797	70.601	-32.565	125.467	-8.569
3300	25.642	121.649	99.478	73.165	-32.368	130.402	-8.636
3400	25.653	122.414	100.141	75.730	-32.175	135.333	-8.699
3500	25.663	123.158	100.788	78.295	-31.989	140.258	-8.758
3600	25.672	123.881	101.420	80.862	-31.805	145.179	-8.814
3700	25.681	124.585	102.036	83.430	-31.628	150.091	-8.866
3800	25.689	125.270	102.639	85.998	-31.455	155.003	-8.915
3900	25.696	125.937	103.227	88.568	-31.287	159.902	-8.961
4000	25.703	126.588	103.803	91.138	-31.123	164.804	-9.004
4100	25.709	127.223	104.367	93.708	-30.965	169.699	-9.046
4200	25.715	127.842	104.918	96.279	-30.811	174.592	-9.085
4300	25.720	128.447	105.459	98.851	-30.659	179.485	-9.122
4400	25.725	129.039	105.988	101.423	-30.515	184.367	-9.158
4500	25.730	129.617	106.507	103.996	-30.374	189.247	-9.191
4600	25.734	130.182	107.015	106.569	-30.236	194.130	-9.223
4700	25.738	130.736	107.514	109.143	-30.105	199.005	-9.254
4800	25.742	131.278	108.003	111.717	-29.976	203.882	-9.283
4900	25.746	131.809	108.484	114.291	-29.852	208.749	-9.311
5000	25.749	132.329	108.956	116.866	-29.732	213.617	-9.337
5100	25.753	132.839	109.419	119.441	-29.616	218.477	-9.362
5200	25.756	133.339	109.874	122.017	-29.504	223.347	-9.387
5300	25.758	133.829	110.321	124.592	-29.396	228.211	-9.410
5400	25.761	134.311	110.761	127.168	-29.293	233.061	-9.433
5500	25.764	134.784	111.194	129.744	-29.192	237.926	-9.454
5600	25.766	135.248	111.619	132.321	-29.097	242.781	-9.475
5700	25.769	135.704	112.038	134.898	-29.005	247.636	-9.495
5800	25.771	136.152	112.450	137.475	-28.916	252.491	-9.514
5900	25.773	136.593	112.855	140.052	-28.832	257.335	-9.532
6000	25.775	137.026	113.254	142.629	-28.751	262.187	-9.550

June 30, 1970

TRIFLUORAMINE OXIDE (NOF_3) (IDEAL GAS) GFW = 87.0013

Point Group C_{3v}

$\Delta Hf°_0 = -37.0 \pm 5.0$ kcal/mol

$S°_{298.15} = 66.54 \pm 0.05$ gibbs/mol

$\Delta Hf°_{298.15} = -39.0 \pm 5.0$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1687 (1)	887 (2)
743 (1)	528 (2)
558 (1)	398 (2)

Bond Distance: N-O = [1.15] Å N-F = 1.48 ± 0.1 Å

Bond Angle: ONF = [109° 28'] FNF = [109° 28'] σ = 3

Product of the Moments of Inertia: $I_AI_BI_C = [4.0703 \times 10^{-114}]\ g^3\ cm^6$

Heat of Formation

Bougon et al. (1) determined equilibrium constants for the reaction $NOF(g) + F_2(g) \rightleftarrows NOF_3(g)$ as a function of temperature and total pressure. Second and third law analyses of these equilibrium data are given below:

	No. of Points	Temp. Range °K	$\Delta Hr°_{298}$, kcal/mol 2nd Law	3rd Law	Drift gibbs/mol
Set I	7	533-643	-17.1	-18.7	-2.4±2.1
Set II	1	533.2		-18.2	

Set I contains their equilibrium data as a function of temperature, while Set II is their adopted equilibrium constant, Kp(553.2°K) = 0.015 ± 0.005 $atm.^{-1}$, corresponding to the lowest pressure (103 atm.) that was studied. Estimated corrections for nonideality are small and neglected. Adopting $\Delta Hr°_{298} = -18.7 \pm 1.0$ kcal/mol, we derive $\Delta Hf°(NOF_3, g) = -34.4 \pm 1.4$ kcal/mol with $\Delta Hf°(NOF, g) = -15.7 \pm 0.4$ kcal/mol (2).

Armstrong and King (3) determined $\Delta Hr_{304} = -253.7 \pm 0.6$ kcal/mol for the reaction $NOF_3(g) + 5/2\ H_2(g) + 122\ H_2O(\ell) \rightarrow 1/2\ N_2(g) + [3HF \cdot 123\ H_2O](\ell)$ in a constant pressure flame calorimeter. Combining this result with their earlier enthalpy data for reduction reactions involving $F_2(g)$ and $O_2(g)$ with $H_2(g)$, they obtained $\Delta Hf_{304}(NOF_3, g) = -44.7 \pm 1.5$ kcal/mol.

Very recently, Dibeler and Walker (4) investigated the photoionization of NOF_3 by mass spectrometry. From their ionization threshold data, they determined $\Delta Hf°_0(NOF_3, g) = -69.6 \pm 1.2$ kcal/mol.

The value for the heat of formation of gaseous NOF_3 is tentatively selected as -39.0 ± 5.0 kcal/mol.

Heat Capacity and Entropy

Several recent infrared (5, 6, and 7) and Raman (8) studies of NOF_3 have been reported in the literature. The fundamental vibrational frequencies observed in the infrared spectrum of the molecule by the various investigators are in good agreement, although the assignment of the ν_3 and ν_5 bending modes has varied. Fox et al. (6) assigned ν_3 = 558 cm^{-1} and ν_5 = 528 cm^{-1}, while Curtis et al. (7) reversed the assignments. Very recently, Abramowitz and Levin (8) investigated the Raman spectrum of polycrystalline film of NOF_3 at 78°K and assigned ν_3 = 535 cm^{-1} and ν_5 = 522 cm^{-1} consistent with the infrared work of Fox et al. (6). The fundamental vibrational frequencies and assignments given by Fox et al. (6) are adopted here.

Fox et al. (9) also investigated the nuclear magnetic resonance spectrum of NOF_3 which indicated that the molecule contained three equivalent fluorine atoms. This result, along with the general appearance of the infrared spectrum, clearly establishes that the molecule has C_{3v} symmetry. The N-O bond distance and bond angles are estimated quantities from the work of Curtis et al. (7). These estimated data have been used in calculating the N-F bond distance from the rotational constants given by Curtis et al. (7). Individual moments of inertia calculated from the structural data given above are: $I_A = I_B = 14.86 \times 10^{-39}\ g\ cm^2$, and $I_C = 18.44 \times 10^{-39}\ g\ cm^2$.

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Phosphoryl Fluoride (POF_3)

(Ideal Gas)   GFW = 103.9684

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	,000	.000	INFINITE	- 3,384	- 293,919	- 293,919	INFINITE
100	8,989	54,777	80,468	- 2,569	- 294,585	- 291,739	637,596
200	13,162	62,286	69,593	- 1,461	- 295,193	- 288,642	315,413
298	16,447	68,187	68,187	,000	- 295,600	- 285,333	209,155
300	16,499	68,289	68,188	,030	- 295,606	- 285,270	207,819
400	18,904	73,385	68,866	1,807	- 295,873	- 281,780	153,957
500	20,604	77,797	70,221	3,788	- 296,039	- 278,237	121,617
600	21,805	81,666	71,813	5,912	- 296,142	- 274,666	100,047
700	22,662	85,095	73,470	8,137	- 296,215	- 271,080	84,635
800	23,287	88,164	75,118	10,436	- 316,697	- 272,797	74,525
900	23,752	90,935	76,724	12,789	- 316,501	- 267,320	64,914
1000	24,104	93,456	78,273	15,183	- 316,287	- 261,868	57,231
1100	24,377	95,767	79,760	17,608	- 316,061	- 256,438	50,949
1200	24,591	97,898	81,184	20,056	- 315,825	- 251,027	45,718
1300	24,762	99,873	82,546	22,524	- 315,584	- 245,636	41,295
1400	24,901	101,713	83,851	25,008	- 315,338	- 240,264	37,507
1500	25,015	103,435	85,099	27,504	- 315,090	- 234,909	34,226
1600	25,110	105,053	86,296	30,010	- 314,841	- 229,574	31,358
1700	25,189	106,578	87,445	32,525	- 314,592	- 224,250	28,829
1800	25,256	108,019	88,548	35,047	- 314,346	- 218,946	26,584
1900	25,313	109,386	89,609	37,576	- 314,100	- 213,651	24,575
2000	25,362	110,686	90,631	40,110	- 313,856	- 208,371	22,770
2100	25,405	111,924	91,616	42,648	- 313,615	- 203,104	21,137
2200	25,442	113,107	92,566	45,191	- 313,379	- 197,847	19,654
2300	25,474	114,239	93,484	47,736	- 313,145	- 192,600	18,301
2400	25,503	115,324	94,371	50,285	- 312,916	- 187,365	17,062
2500	25,529	116,365	95,230	52,837	- 312,691	- 182,138	15,922
2600	25,551	117,367	96,063	55,391	- 312,471	- 176,921	14,872
2700	25,571	118,332	96,870	57,947	- 312,254	- 171,710	13,899
2800	25,589	119,262	97,653	60,505	- 312,041	- 166,509	12,997
2900	25,606	120,160	98,414	63,065	- 311,833	- 161,312	12,157
3000	25,620	121,029	99,153	65,626	- 311,632	- 156,130	11,374
3100	25,634	121,869	99,872	68,189	- 311,433	- 150,948	10,642
3200	25,646	122,683	100,573	70,753	- 311,240	- 145,776	9,956
3300	25,657	123,472	101,255	73,318	- 311,050	- 140,608	9,312
3400	25,667	124,238	101,919	75,884	- 310,867	- 135,445	8,706
3500	25,676	124,982	102,568	78,451	- 310,688	- 130,285	8,135
3600	25,685	125,706	103,200	81,019	- 310,513	- 125,134	7,597
3700	25,693	126,410	103,818	83,588	- 310,343	- 119,988	7,087
3800	25,700	127,095	104,422	86,158	- 310,177	- 114,841	6,605
3900	25,707	127,763	105,012	88,728	- 310,017	- 109,707	6,148
4000	25,713	128,414	105,589	91,299	- 309,860	- 104,574	5,714
4100	25,718	129,049	106,153	93,871	- 309,708	- 99,444	5,301
4200	25,724	129,668	106,706	96,443	- 309,561	- 94,315	4,908
4300	25,729	130,274	107,247	99,016	- 309,416	- 89,191	4,533
4400	25,733	130,865	107,777	101,589	- 309,279	- 84,070	4,176
4500	25,738	131,444	108,296	104,162	- 309,144	- 78,956	3,835
4600	25,742	132,009	108,806	106,736	- 309,012	- 73,843	3,508
4700	25,746	132,563	109,305	109,311	- 308,887	- 68,731	3,196
4800	25,749	133,105	109,796	111,885	- 308,764	- 63,619	2,897
4900	25,753	133,636	110,277	114,461	- 308,645	- 58,513	2,610
5000	25,756	134,156	110,749	117,036	- 308,532	- 53,411	2,335
5100	25,759	134,666	111,213	119,612	- 308,422	- 48,314	2,070
5200	25,762	135,167	111,669	122,188	- 308,315	- 43,212	1,816
5300	25,764	135,657	112,117	124,764	- 308,212	- 38,110	1,572
5400	25,767	136,139	112,557	127,341	- 308,115	- 33,025	1,337
5500	25,769	136,612	112,990	129,917	- 308,019	- 27,924	1,110
5600	25,771	137,076	113,416	132,494	- 307,929	- 22,834	,891
5700	25,774	137,532	113,836	135,072	- 307,842	- 17,742	,680
5800	25,776	137,981	114,248	137,649	- 307,757	- 12,654	,477
5900	25,778	138,421	114,654	140,227	- 307,677	- 7,572	,280
6000	25,779	138,855	115,054	142,805	- 307,601	- 2,483	,090

Mar. 31, 1963; Dec. 31, 1963; Dec. 31, 1969

PHOSPHORYL FLUORIDE (POF_3)   (IDEAL GAS)   GFW = 103.9684

Point Group C_{3v} $\Delta Hf^\circ_0 = -293.9 \pm 1.9$ kcal/mol

$S^\circ_{298.15} = 68.19 \pm 0.07$ gibbs/mol $\Delta Hf^\circ_{298.15} = -295.6 \pm 1.9$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
1417.7 (1)	994 (2)
872.8 (1)	483.2 (2)
473.2 (1)	335.6 (2)

Bond Distance: P-O = 1.45 ± 0.03 Å   P-F = 1.52 ± 0.02 Å

Bond Angle: F-P-F = 102.5° ± 2°   F-P-O = 115.8° ± 2° $\sigma = 3$

Product of Moments of Inertia: $I_AI_BI_C = 5.9019 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

Ebel and Bretscher (1) measured the enthalpy change for the following reaction:

$$PF_3(g) + 1/2\ O_2(g) \rightarrow POF_3(g)$$

They reported a heat of reaction of -70.6 ± 1 kcal/mol. Combining this result with the heat of formation of PF_3, $\Delta Hf^\circ_{298} = -224.9 \pm 0.9$ kcal/mol (2), we derive, $\Delta Hf^\circ_{298}(POF_3, g) = -295.6 \pm 1.9$ kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Selig and Claassen (3) and are in good agreement with the Raman and infrared studies of Gutowsky and Liehr (4). Several microwave studies (5, 6, 7, 8) of POF_3 have been reported. As pointed out by Williams et al. (7), the rotational constant calculated from their microwave studies leads to a moment of inertia, I_B, which is in disagreement with the moment of inertia calculated from the molecular constants obtained from electron-diffraction studies by Brockway and Beach (9). Since insufficient microwave data were available for an independent determination, Williams et al. (7) sought to find parameters which were consistent with both measurements. Their molecular constants are adopted for this tabulation. Individual moments of inertia are $I_A = I_B = 18.244 \times 10^{-39}\ g\ cm^2$ and $I_C = 17.731 \times 10^{-39}\ g\ cm^2$.

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Phosphorus Trifluoride (PF_3)
(Ideal Gas) GFW = 87.969

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.092	- 223.965	- 223.965	INFINITE
100	8.741	53.183	76.003	- 2.282	- 224.288	- 223.353	488.138
200	11.620	60.123	66.443	- 1.264	- 224.639	- 222.276	242.892
298	14.027	65.233	65.233	.000	- 224.900	- 221.058	162.040
300	14.066	65.320	65.233	.026	- 224.904	- 221.034	161.023
400	15.791	69.619	65.808	1.525	- 225.093	- 219.712	120.045
500	16.928	73.274	66.945	3.165	- 225.235	- 218.352	95.441
600	17.678	76.431	68.269	4.897	- 225.351	- 216.964	79.029
700	18.187	79.197	69.637	6.692	- 225.466	- 215.557	67.300
800	18.543	81.650	70.988	8.530	- 246.010	- 219.444	59.949
900	18.799	83.850	72.297	10.397	- 245.893	- 216.130	52.483
1000	18.990	85.841	73.553	12.287	- 245.769	- 212.830	46.514
1100	19.135	87.658	74.754	14.194	- 245.642	- 209.543	41.632
1200	19.247	89.328	75.900	16.113	- 245.511	- 206.267	37.566
1300	19.336	90.872	76.993	18.043	- 245.380	- 203.000	34.127
1400	19.407	92.308	78.036	19.980	- 245.248	- 199.745	31.182
1500	19.465	93.649	79.033	21.924	- 245.117	- 196.498	28.630
1600	19.513	94.906	79.986	23.873	- 244.987	- 193.263	26.399
1700	19.553	96.091	80.899	25.826	- 244.859	- 190.033	24.430
1800	19.587	97.209	81.774	27.783	- 244.733	- 186.814	22.682
1900	19.615	98.269	82.615	29.743	- 244.608	- 183.598	21.119
2000	19.640	99.276	83.423	31.706	- 244.486	- 180.390	19.712
2100	19.661	100.235	84.201	33.671	- 244.365	- 177.190	18.440
2200	19.680	101.150	84.950	35.638	- 244.249	- 173.993	17.285
2300	19.696	102.025	85.674	37.607	- 244.134	- 170.802	16.230
2400	19.710	102.863	86.373	39.577	- 244.022	- 167.618	15.264
2500	19.723	103.668	87.049	41.549	- 243.913	- 164.435	14.375
2600	19.734	104.442	87.703	43.522	- 243.808	- 161.259	13.555
2700	19.744	105.187	88.337	45.496	- 243.704	- 158.084	12.796
2800	19.753	105.905	88.951	47.470	- 243.603	- 154.916	12.092
2900	19.761	106.598	89.548	49.446	- 243.506	- 151.748	11.436
3000	19.768	107.268	90.128	51.422	- 243.413	- 148.590	10.825
3100	19.774	107.917	90.691	53.399	- 243.321	- 145.429	10.253
3200	19.780	108.545	91.239	55.377	- 243.233	- 142.274	9.717
3300	19.786	109.153	91.773	57.356	- 243.147	- 139.119	9.213
3400	19.791	109.744	92.293	59.334	- 243.066	- 135.968	8.740
3500	19.795	110.318	92.800	61.314	- 242.988	- 132.816	8.293
3600	19.799	110.876	93.294	63.293	- 242.912	- 129.670	7.872
3700	19.803	111.418	93.777	65.273	- 242.840	- 126.527	7.474
3800	19.807	111.946	94.248	67.254	- 242.770	- 123.381	7.096
3900	19.810	112.461	94.708	69.235	- 242.704	- 120.243	6.738
4000	19.813	112.962	95.158	71.216	- 242.643	- 117.104	6.398
4100	19.816	113.452	95.599	73.197	- 242.584	- 113.967	6.075
4200	19.818	113.929	96.029	75.179	- 242.528	- 110.828	5.767
4300	19.821	114.396	96.451	77.161	- 242.474	- 107.693	5.474
4400	19.823	114.851	96.864	79.143	- 242.426	- 104.558	5.193
4500	19.825	115.297	97.269	81.126	- 242.380	- 101.428	4.926
4600	19.827	115.733	97.665	83.108	- 242.336	- 98.299	4.670
4700	19.829	116.159	98.054	85.091	- 242.297	- 95.166	4.425
4800	19.831	116.576	98.436	87.074	- 242.261	- 92.032	4.190
4900	19.833	116.985	98.810	89.057	- 242.228	- 88.901	3.965
5000	19.834	117.386	99.178	91.041	- 242.198	- 85.773	3.749
5100	19.836	117.779	99.539	93.024	- 242.173	- 82.651	3.542
5200	19.837	118.164	99.893	95.008	- 242.149	- 79.519	3.342
5300	19.838	118.542	100.242	96.992	- 242.129	- 76.390	3.150
5400	19.839	118.913	100.584	98.975	- 242.114	- 73.271	2.965
5500	19.841	119.277	100.920	100.959	- 242.100	- 70.138	2.787
5600	19.842	119.634	101.251	102.944	- 242.091	- 67.012	2.615
5700	19.843	119.985	101.577	104.928	- 242.086	- 63.883	2.449
5800	19.844	120.331	101.897	106.912	- 242.081	- 60.759	2.289
5900	19.845	120.670	102.213	108.896	- 242.082	- 57.637	2.135
6000	19.846	121.003	102.523	110.881	- 242.086	- 54.509	1.985

Dec. 31, 1960; June 30, 1962; Dec. 31, 1963; Dec. 31, 1969

PHOSPHORUS TRIFLUORIDE (PF_3) (IDEAL GAS) GFW = 87.969

Point Group C_{3v}

$\Delta Hf^\circ_0 = -224.0 \pm 0.9$ kcal/mol

$S^\circ_{298.15} = 65.23 \pm 0.03$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -224.9 \pm 0.9$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
892 (1)	860 (2)
487 (1)	344 (2)

Bond Distance: P-F = 1.5700 ± 0.0012 Å F····F = 2.3643 ± 0.0028 Å

Bond Angle: F-P-F = 97.8 ± 0.2°

$\sigma = 3$

Product of Moments of Inertia: 2.0621×10^{-114} g^3 cm^6

Heat of Formation

Berthelot (1) measured the heats of hydrolysis of $PF_3(g)$ and $PCl_3(\ell)$. These results can be combined to give, ΔHr = 24.5 kcal/mol, for the reaction

$PF_3(g) + 3KCl{\cdot}157\ H_2O \rightarrow PCl_3(\ell) + 3KF{\cdot}112\ H_2O$.

Combining this result with the following heat of formation data,

$\Delta Hf^\circ_{298}(PCl_3,\ \ell) = -72.2$ kcal/mol (2)

$\Delta Hf^\circ_{298}(KCl{\cdot}157\ H_2O) = -100.0$ kcal/mol (3)

$\Delta Hf^\circ_{298}(KF{\cdot}112\ H_2O) = -138.5$ kcal/mol (3)

we derive, $\Delta Hf^\circ_{298}(PF_3,\ g) = -212.2$ kcal/mol.

Duus and Mykytink (4) reported a heat of reaction of -2.361 kcal/mol (corrected to 25°C) for the following reaction

$PCl_3(g) + 3/2\ CaF_2(c) \rightarrow PF_3(g) + 3/2\ CaCl_2(c)$.

Combining this result with the following heat of formation data,

$\Delta Hf^\circ_{298}(PCl_3,\ g) = -64.4$ kcal/mol (2)

$\Delta Hf^\circ_{298}(CaF_2,\ c) = 293.0 \pm 1.5$ kcal/mol (5)

$\Delta Hf^\circ_{298}(CaCl_2,\ c) = -190.0$ kcal/mol (3)

we derive, $\Delta Hf^\circ_{298}(PF_3,\ g) = -221.9$ kcal/mol.

Recently, Rudzitis et al. (6) measured the heat of combustion of PF_3 in fluorine in a two-chambered bomb calorimeter at 25°C. They reported a heat of combustion of -152.0 ± 0.2 kcal/mol for the reaction

$PF_3(g) + F_2(g) \rightarrow PF_5(g)$.

Combining this result with the heat of formation of PF_5, $\Delta Hf^\circ_{298}(PF_5,\ g) = -376.9 \pm 0.7$ kcal/mol (7), we derive, $\Delta Hf^\circ_{298}(PF_3,\ g) = -224.9 \pm 0.9$ kcal/mol. This result is adopted for this tabulation.

Heat Capacity and Entropy

The vibrational frequencies are those reported by Wilson and Palo (8). Several different values for the P-F bond length and F-P-F bond angle have been reported in the literature. This problem was recently discussed by Morino et al. (9), who also reported new data obtained from electron-diffraction studies. Their results are adopted for this tabulation. Individual moments of inertia calculated according to their structure are: $I_A = I_B = 10.814 \times 10^{-39}$ g cm^2 and $I_C = 17.634 \times 10^{-39}$ g cm^2.

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Thiophosphoryl Fluoride (PSF_3)

(Ideal Gas) GFW = 120.033

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.647	- 235.567	- 235.567	INFINITE
100	9.747	56.533	84.656	- 2.812	- 236.030	- 235.133	513.883
200	14.452	64.793	72.760	- 1.593	- 236.572	- 234.019	255.724
298	17.818	71.230	71.230	.000	- 237.000	- 232.670	170.552
300	17.870	71.341	71.230	.033	- 237.007	- 232.643	169.481
400	20.202	76.823	71.962	1.944	- 237.883	- 231.114	126.275
500	21.744	81.509	73.415	4.047	- 238.499	- 229.350	100.249
600	22.771	85.570	75.110	6.276	- 238.976	- 227.473	82.857
700	23.472	89.136	76.864	8.591	- 239.371	- 225.499	70.404
800	23.966	92.305	78.600	10.964	- 273.205	- 230.072	62.853
900	24.324	95.149	80.283	13.379	- 272.978	- 224.693	54.563
1000	24.590	97.726	81.901	15.826	- 272.739	- 219.342	47.937
1100	24.793	100.080	83.448	18.295	- 272.491	- 214.016	42.521
1200	24.951	102.244	84.925	20.783	- 272.236	- 208.710	38.011
1300	25.076	104.247	86.336	23.284	- 271.978	- 203.424	34.199
1400	25.176	106.109	87.682	25.797	- 271.718	- 198.161	30.934
1500	25.258	107.849	88.969	28.319	- 271.456	- 192.916	28.108
1600	25.326	109.481	90.201	30.848	- 271.195	- 187.689	25.637
1700	25.382	111.018	91.381	33.384	- 270.933	- 182.477	23.459
1800	25.430	112.470	92.512	35.924	- 270.674	- 177.284	21.525
1900	25.470	113.846	93.599	38.470	- 270.413	- 172.100	19.796
2000	25.505	115.154	94.645	41.018	- 270.156	- 166.933	18.242
2100	25.535	116.399	95.651	43.570	- 269.901	- 161.780	16.837
2200	25.561	117.587	96.621	46.125	- 269.649	- 156.636	15.560
2300	25.584	118.724	97.558	48.682	- 269.398	- 151.505	14.396
2400	25.604	119.813	98.463	51.242	- 269.151	- 146.386	13.330
2500	25.622	120.859	99.338	53.803	- 268.905	- 141.273	12.350
2600	25.638	121.864	100.185	56.366	- 268.663	- 136.174	11.446
2700	25.652	122.832	101.006	58.931	- 268.423	- 131.083	10.610
2800	25.664	123.765	101.802	61.496	- 268.186	- 126.002	9.835
2900	25.676	124.666	102.575	64.063	- 267.952	- 120.925	9.113
3000	25.686	125.537	103.326	66.632	- 267.723	- 115.862	8.441
3100	25.695	126.379	104.056	69.201	- 267.494	- 110.803	7.812
3200	25.704	127.195	104.767	71.771	- 267.272	- 105.753	7.223
3300	25.711	127.986	105.458	74.341	- 267.050	- 100.710	6.670
3400	25.718	128.754	106.132	76.913	- 266.833	- 95.670	6.150
3500	25.725	129.499	106.789	79.485	- 266.620	- 90.639	5.660
3600	25.731	130.224	107.430	82.058	- 266.407	- 85.613	5.197
3700	25.736	130.929	108.056	84.631	- 266.201	- 80.594	4.761
3800	25.741	131.615	108.667	87.205	- 265.996	- 75.578	4.347
3900	25.746	132.284	109.264	89.779	- 265.797	- 70.574	3.955
4000	25.750	132.936	109.848	92.354	- 265.600	- 65.568	3.582
4100	25.754	133.572	110.418	94.929	- 265.406	- 60.571	3.229
4200	25.758	134.193	110.977	97.505	- 265.217	- 55.574	2.892
4300	25.761	134.799	111.524	100.081	- 265.029	- 50.586	2.571
4400	25.764	135.391	112.060	102.657	- 264.848	- 45.600	2.265
4500	25.767	135.970	112.585	105.234	- 264.668	- 40.620	1.973
4600	25.770	136.536	113.099	107.810	- 264.491	- 35.647	1.694
4700	25.773	137.091	113.604	110.388	- 264.319	- 30.673	1.426
4800	25.775	137.633	114.099	112.965	- 264.150	- 25.701	1.170
4900	25.778	138.165	114.585	115.543	- 263.984	- 20.730	.925
5000	25.780	138.686	115.061	118.120	- 263.824	- 15.771	.689
5100	25.782	139.196	115.530	120.699	- 263.666	- 10.816	.464
5200	25.784	139.697	115.990	123.277	- 263.511	- 5.855	.246
5300	25.786	140.188	116.442	125.855	- 263.360	- .900	.037
5400	25.787	140.670	116.886	128.434	- 263.214	4.044	- .164
5500	25.789	141.143	117.323	131.013	- 263.069	8.997	- .358
5600	25.791	141.608	117.752	133.592	- 262.930	13.944	- .544
5700	25.792	142.064	118.175	136.171	- 262.795	18.887	- .724
5800	25.793	142.513	118.590	138.750	- 262.660	23.826	- .898
5900	25.795	142.954	119.000	141.330	- 262.530	28.757	- 1.065
6000	25.796	143.387	119.402	143.909	- 262.405	33.699	- 1.227

Mar. 31, 1963; Dec. 31, 1969

THIOPHOSPHORYL FLUORIDE (PSF_3) (IDEAL GAS) GFW = 120.033

Point Group C_{3v}

ΔHf°_0 = [-236 ± 15] kcal/mol

$S^\circ_{298.15}$ = 71.23 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-237 ± 15] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
981 (1)	945 (2)
442 (1)	275 (2)
695 (1)	402 (2)

Bond Distance: P-S = 1.87 ± 0.03 Å P-F = 1.53 ± 0.02 Å

Bond Angle: F-P-F = 100.3° ± 2° F-P-S = 117.6° ± 2° $\sigma = 3$

Product of Moments of Inertia: $I_AI_BI_C = 1.7316 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

The heat of formation of PSF_3 is calculated from the heat of formation of POF_3 and estimated P=O and P=S bond strengths. Mortimer (1) calculated several P=O and P=S bond dissociation energies from heat of reaction data reported in the literature. Some of these data are given below.

Reaction	D(P=O) kcal/mole	D(P=S) kcal/mole
ΔH oxidation PF_3 to POF_3	130.3	
ΔH oxidation $P(OEt)_3$ to $PS(OEt)_3$		81.6
ΔH oxidation PPr_3 to $PSPr_3$		82.6

Mole and McCoubrey (2) reported the following heat of reaction:

$PCl_3(\ell) + S(c) \rightarrow PSCl_3(\ell)$. ΔHr = -5.6 kcal/mol.

Combining this result with heat of vaporization data for PCl_3 (3) and $PSCl_3$ (4), along with the heat of sublimation of S (5), we derive, D(P=S) = 71 kcal/mol. Averaging this result with the two values given above, we obtain $\bar{D}$(P=S) = 78.4 kcal/mol. We assume that this result represents the enthalpy change for reaction

$PSF_3(g) \rightarrow PF_3(g) + S(g)$.

Combining this result with similar data for POF_3, namely D(P=O) = 130.3 kcal/mol and $\Delta Hf^\circ_{298}(POF_3, g) = -295.6 \pm 1.9$ kcal/mol (6), we derive, $\Delta Hf^\circ_{298}(PSF_3, g) = -237 \pm 15$ kcal/mol, from the relationship

$$\Delta Hf^\circ_{298}(PSF_3, g) = \Delta Hf^\circ_{298}(POF_3, g) + \Delta Hf^\circ_{298}(S, g) - \Delta Hf^\circ_{298}(O, g) - D(P{=}O) + D(P{=}S).$$

Heat Capacity and Entropy

Several recent infrared and Raman studies (7, 8, 9, 10) of PSF_3 have been reported. These data are in good agreement, except for the ν_1 fundamental. Dewaulle and Francois (11) assigned this fundamental to the 869 cm^{-1} band observed in their spectra. The recent work indicates that this fundamental should be assigned to the 981 cm^{-1} band. Average values of the vibrational frequencies reported by (8, 9, 10) are adopted for this tabulation. The molecular structure of this molecule was determined by Williams et al. (12) and Hawkins and Cohen (13) from microwave studies. The individual moments of inertia calculated from the constants given by Williams et al. (12) are $I_A = I_B = 3.1527 \times 10^{-38}\ g\ cm^2$ and $I_C = 1.7410 \times 10^{-38}\ g\ cm^2$.

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Silicon Trifluoride (SiF_3)

(Ideal Gas) GFW = 85.0812

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 3.202	- 262.268	- 262.268	INFINITE
100	9.250	54.836	78.618	- 2.378	- 262.551	- 261.838	572.247
200	12.145	62.195	68.694	- 1.300	- 262.803	- 261.021	285.231
298	14.250	67.454	67.454	.000	- 263.000	- 260.104	190.661
300	14.285	67.543	67.455	.026	- 263.004	- 260.086	189.473
400	15.856	71.881	68.035	1.538	- 263.154	- 259.089	141.559
500	16.932	75.542	69.180	3.181	- 263.266	- 258.059	112.798
600	17.660	78.698	70.510	4.913	- 263.350	- 257.010	93.616
700	18.162	81.460	71.881	6.705	- 263.419	- 255.947	79.910
800	18.517	83.910	73.234	8.540	- 263.483	- 254.877	69.629
900	18.776	86.107	74.545	10.406	- 263.543	- 253.796	61.630
1000	18.968	88.095	75.802	12.293	- 263.607	- 252.711	55.230
1100	19.115	89.910	77.003	14.198	- 263.676	- 251.618	49.992
1200	19.230	91.579	78.149	16.115	- 263.749	- 250.518	45.626
1300	19.320	93.122	79.242	18.043	- 263.830	- 249.412	41.930
1400	19.393	94.556	80.285	19.979	- 263.920	- 248.300	38.761
1500	19.453	95.896	81.282	21.921	- 264.019	- 247.179	36.014
1600	19.502	97.153	82.235	23.869	- 264.129	- 246.054	33.609
1700	19.543	98.337	83.148	25.821	- 276.242	- 244.814	31.473
1800	19.578	99.455	84.023	27.778	- 276.318	- 242.965	29.500
1900	19.607	100.514	84.863	29.737	- 276.395	- 241.110	27.734
2000	19.633	101.521	85.671	31.699	- 276.474	- 239.248	26.144
2100	19.654	102.479	86.449	33.663	- 276.554	- 237.387	24.705
2200	19.673	103.394	87.199	35.630	- 276.637	- 235.521	23.397
2300	19.690	104.269	87.922	37.598	- 276.722	- 233.649	22.202
2400	19.705	105.107	88.621	39.568	- 276.809	- 231.774	21.106
2500	19.718	105.912	89.296	41.539	- 276.899	- 229.897	20.098
2600	19.729	106.685	89.950	43.511	- 276.991	- 228.015	19.166
2700	19.739	107.430	90.584	45.484	- 277.086	- 226.128	18.304
2800	19.748	108.148	91.198	47.459	- 277.182	- 224.239	17.503
2900	19.757	108.841	91.795	49.434	- 277.281	- 222.344	16.756
3000	19.764	109.511	92.374	51.410	- 277.385	- 220.454	16.060
3100	19.771	110.159	92.938	53.387	- 277.489	- 218.554	15.408
3200	19.777	110.787	93.486	55.364	- 277.597	- 216.649	14.796
3300	19.783	111.396	94.019	57.342	- 277.708	- 214.743	14.222
3400	19.788	111.986	94.539	59.321	- 277.821	- 212.833	13.681
3500	19.793	112.560	95.046	61.300	- 277.938	- 210.918	13.170
3600	19.797	113.118	95.540	63.279	- 370.017	- 206.743	12.551
3700	19.801	113.660	96.023	65.259	- 370.040	- 202.208	11.944
3800	19.804	114.188	96.494	67.240	- 370.065	- 197.670	11.369
3900	19.808	114.703	96.954	69.220	- 370.096	- 193.139	10.823
4000	19.811	115.204	97.404	71.201	- 370.128	- 188.597	10.304
4100	19.814	115.694	97.844	73.182	- 370.166	- 184.063	9.811
4200	19.817	116.171	98.275	75.164	- 370.205	- 179.522	9.342
4300	19.819	116.637	98.696	77.146	- 370.245	- 174.979	8.893
4400	19.821	117.093	99.109	79.128	- 370.292	- 170.439	8.466
4500	19.824	117.538	99.514	81.110	- 370.339	- 165.895	8.057
4600	19.826	117.974	99.911	83.092	- 370.389	- 161.352	7.666
4700	19.828	118.401	100.299	85.075	- 370.444	- 156.806	7.291
4800	19.829	118.818	100.681	87.058	- 370.500	- 152.259	6.933
4900	19.831	119.227	101.055	89.041	- 370.560	- 147.710	6.588
5000	19.833	119.628	101.423	91.024	- 370.623	- 143.166	6.258
5100	19.834	120.020	101.784	93.008	- 370.688	- 138.617	5.940
5200	19.836	120.406	102.138	94.991	- 370.757	- 134.061	5.634
5300	19.837	120.783	102.486	96.975	- 370.827	- 129.507	5.340
5400	19.838	121.154	102.829	98.958	- 370.903	- 124.961	5.057
5500	19.839	121.518	103.165	100.942	- 370.980	- 120.404	4.784
5600	19.841	121.876	103.496	102.926	- 371.062	- 115.843	4.521
5700	19.842	122.227	103.821	104.910	- 371.146	- 111.282	4.267
5800	19.843	122.572	104.142	106.895	- 371.233	- 106.723	4.021
5900	19.844	122.911	104.457	108.879	- 371.324	- 102.170	3.785
6000	19.845	123.245	104.767	110.863	- 371.418	- 97.606	3.555

Sept. 30, 1963; Dec. 31, 1969; June 30, 1970

SILICON TRIFLUORIDE (SiF_3) (IDEAL GAS) GFW = 85.0812

Point Group C_{3v}

$\Delta Hf°_0$ = [-262.3 ± 5] kcal/mol

$S°_{298.15}$ = 67.45 ± 0.5 gibbs/mol

$\Delta Hf°_{298.15}$ = [-263 ± 5] kcal/mol

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
832 (1)
406 (1)
954 (2)
290 (2)

Bond Distance: Si-F = [1.56] Å

Bond Angle: F-Si-F = [109.47°]

$\sigma = 3$

Product of the Moments of Inertia: $I_AI_BI_C = 2.5135 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

The heat of formation is estimated from the assumption of a 0.5 kcal heat for the reaction:

$SiF_4(g) + SiF_2(g) \rightarrow 2SiF_3(g)$. ΔH = 0.5 kcal

$\Delta Hf°_{298}(SiF_3,\ g) = -263$ kcal/mol is derived from $\Delta Hf°_{298}(SiF_4,\ g) = -385.98$ kcal/mol and $\Delta Hf°_{298}(SiF_2,\ g) = -140.5$ kcal/mol. The above value is confirmed by the observations of Layne (1), whose total pressure data above the silicon -- magnesium fluoride system agree with those calculated from these tables.

Heat Capacity and Entropy

The bond length is estimated between those of SiF_4 and SiF_2. The vibrational frequencies are from Milligan et al. (2), and the angle is taken to be tetrahedral, since they also reported an angle of approximately 71° between the Si-F bonds and the threefold axis. The spectra of the radical were obtained in inert gas matrices and all the fundamentals were observed. The individual moments of inertia are $I_A = I_C = 11.081 \times 10^{-39}\ g\ cm^2$, $I_B = 20.472 \times 10^{-39}\ g\ cm^2$.

References

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Titanium Trifluoride (TiF_3)

(Crystal) GFW = 104.8952

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	21.994	21.000	21.000	.000	- 343.100	- 325.510	238.606
300	22.000	21.136	21.000	.041	- 343.091	- 325.402	237.055
400	22.300	27.497	21.866	2.253	- 342.652	- 319.572	174.606
500	22.970	32.545	23.513	4.516	- 342.245	- 313.850	137.184
600	23.536	36.783	25.381	6.841	- 341.834	- 308.210	112.265
700	24.128	40.455	27.278	9.224	- 341.414	- 302.638	94.488
800	24.746	43.717	29.132	11.668	- 340.979	- 297.129	81.172
900	25.390	46.669	30.919	14.174	- 340.523	- 291.674	70.828
1000	26.060	49.378	32.632	16.747	- 340.042	- 286.274	62.565
1100	26.756	51.894	34.270	19.387	- 339.528	- 280.920	55.814
1200	27.478	54.253	35.838	22.099	- 339.914	- 275.578	50.190
1300	28.226	56.482	37.341	24.884	- 339.198	- 270.245	45.432
1400	29.000	58.602	38.784	27.745	- 338.426	- 264.970	41.364
1500	29.800	60.634	40.174	30.690	- 337.593	- 259.751	37.846
1600	30.000	62.563	41.513	33.680	- 336.738	- 254.590	34.775
1700	30.200	64.388	42.806	36.690	- 335.888	- 249.481	32.073
1800	30.400	66.120	44.053	39.720	- 335.046	- 244.426	29.677
1900	30.600	67.769	45.258	42.770	- 334.209	- 239.413	27.539
2000	30.800	69.343	46.424	45.840	- 337.828	- 234.290	25.602

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968

TITANIUM TRIFLUORIDE (TiF_3) (CRYSTAL) GFW = 104.8952

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = [21.0 ± 3.0]

$\Delta Hf^\circ_{298.15}$ = -343.1 ± 10.0 kcal/mol

Ts = 1309.7 °K

ΔHs° = 52.97 kcal/mol

Heat of Formation

Blocher and Hall (1) have reported vapor pressure data for the process $1/2Hg_2F_2 + TiF_3(c) = TiF_4(g) + Hg(\ell)$. Second and third law analyses of their data give a second law ΔHr°_{298} of 23.7 kcal/mol, a third law ΔHr°_{298} of 29.864, and a third law drift of 11.9 ± 1.0 eu. The third law value is combined with the JANAF values for the heat of formation of $Hg_2F_2(c)$ and $TiF_4(g)$ to give a ΔHf°_{298} of -343.1 ± 10.0 kcal/mol. The large uncertainty on ΔHf°_{298} is assigned because Blocher and Hall were not able to identify $TiF_3(c)$ as the reaction product in the above process. They reported that the X-ray pattern of the products contained lines corresponding to $Hg_2F_2(c)$ plus others that did not correspond to $TiF_3(c)$.

Heat Capacity and Entropy

The heat capacity of $TiF_3(c)$ is estimated from the heat capacities of ZrF_4 and TiF_4. The entropy, S°_{298}, is estimated from CrF_3 and from ionic entropy contributions. Both methods give values which are within ±0.5eu of the chosen value of 21 ± 3eu.

Heat of Sublimation

The heat of sublimation is calculated from the vapor pressure data of Zmbov and Margrave (2). See $TiF_3(g)$ table for details. The sublimation temperature is taken as the point at which $\Delta Gr = 0$ for the reaction $TiF_3(c) = TiF_3(g)$.

References

1. J. N. Blocher, Jr. and E. N. Hall, J. Phys. Chem. 63, 127 (1959).
2. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).

Titanium Trifluoride (TiF_3)

(Ideal Gas) GFW = 104.8952

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.323	-283.106	-283.106	INFINITE
100	9.131	56.491	81.514	-2.502	-283.462	-282.810	618.080
200	12.794	63.937	70.971	-1.407	-283.874	-281.985	308.138
298	15.675	69.622	69.622	.000	-284.100	-281.007	205.984
300	15.718	69.719	69.622	.029	-284.103	-280.988	204.700
400	17.513	74.509	70.263	1.699	-284.206	-279.930	152.947
500	18.567	78.541	71.526	3.507	-284.254	-278.857	121.888
600	19.190	81.986	72.990	5.398	-284.278	-277.775	101.179
700	19.569	84.975	74.493	7.337	-284.301	-276.689	86.386
800	19.808	87.605	75.971	9.307	-284.340	-275.600	75.290
900	19.965	89.947	77.396	11.296	-284.401	-274.503	66.659
1000	20.074	92.057	78.758	13.298	-284.490	-273.400	59.752
1100	20.151	93.974	80.056	15.310	-284.606	-272.285	54.098
1200	20.209	95.730	81.290	17.328	-285.685	-271.120	49.378
1300	20.251	97.349	82.464	19.351	-285.731	-269.905	45.375
1400	20.284	98.851	83.581	21.378	-285.793	-268.686	41.944
1500	20.309	100.252	84.646	23.408	-285.875	-267.460	38.969
1600	20.328	101.563	85.663	25.439	-285.979	-266.229	36.365
1700	20.342	102.796	86.635	27.473	-286.105	-264.991	34.067
1800	20.353	103.959	87.565	29.508	-286.258	-263.748	32.023
1900	20.361	105.059	88.458	31.543	-286.436	-262.491	30.193
2000	20.367	106.104	89.314	33.580	-291.088	-261.070	28.528
2100	20.372	107.098	90.137	35.617	-291.296	-259.566	27.013
2200	20.376	108.046	90.930	37.654	-291.508	-258.051	25.635
2300	20.378	108.951	91.694	39.692	-291.723	-256.524	24.375
2400	20.381	109.819	92.431	41.730	-291.942	-254.989	23.220
2500	20.382	110.651	93.143	43.768	-292.165	-253.445	22.156
2600	20.383	111.450	93.832	45.806	-292.391	-251.892	21.173
2700	20.384	112.219	94.499	47.845	-292.620	-250.329	20.263
2800	20.384	112.961	95.145	49.883	-292.852	-248.760	19.417
2900	20.385	113.676	95.772	51.921	-293.089	-247.176	18.628
3000	20.385	114.367	96.380	53.960	-293.330	-245.594	17.892
3100	20.384	115.036	96.971	55.998	-293.573	-243.997	17.202
3200	20.384	115.683	97.546	58.037	-293.820	-242.396	16.555
3300	20.383	116.310	98.105	60.075	-294.070	-240.784	15.946
3400	20.382	116.918	98.650	62.113	-294.323	-239.164	15.373
3500	20.381	117.509	99.180	64.152	-294.581	-237.537	14.832
3600	20.379	118.083	99.697	66.189	-396.467	-235.639	14.305
3700	20.377	118.642	100.202	68.227	-396.703	-231.171	13.655
3800	20.376	119.185	100.694	70.265	-396.955	-226.694	13.038
3900	20.373	119.714	101.175	72.302	-397.225	-222.212	12.452
4000	20.371	120.230	101.645	74.340	-397.510	-217.718	11.896
4100	20.369	120.733	102.105	76.377	-397.812	-213.220	11.366
4200	20.366	121.224	102.554	78.413	-398.130	-208.716	10.861
4300	20.363	121.703	102.994	80.450	-398.462	-204.201	10.379
4400	20.360	122.171	103.424	82.486	-398.811	-199.680	9.918
4500	20.357	122.629	103.846	84.522	-399.172	-195.152	9.478
4600	20.353	123.076	104.259	86.557	-399.547	-190.611	9.056
4700	20.350	123.514	104.664	88.592	-399.937	-186.064	8.652
4800	20.346	123.942	105.061	90.627	-400.339	-181.507	8.264
4900	20.342	124.362	105.451	92.662	-400.754	-176.947	7.892
5000	20.338	124.773	105.833	94.696	-401.181	-172.374	7.534
5100	20.334	125.175	106.209	96.729	-401.620	-167.798	7.191
5200	20.330	125.570	106.577	98.762	-402.070	-163.202	6.859
5300	20.326	125.957	106.939	100.795	-402.530	-158.606	6.540
5400	20.322	126.337	107.295	102.828	-403.002	-154.003	6.233
5500	20.318	126.710	107.645	104.860	-403.481	-149.383	5.936
5600	20.313	127.076	107.988	106.891	-403.972	-144.762	5.650
5700	20.309	127.436	108.326	108.922	-404.470	-140.124	5.373
5800	20.305	127.789	108.659	110.953	-404.976	-135.483	5.105
5900	20.300	128.136	108.986	112.983	-405.492	-130.836	4.846
6000	20.296	128.477	109.308	115.013	-406.014	-126.180	4.596

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968

TITANIUM TRIFLUORIDE (TiF_3) (IDEAL GAS) GFW = 104.8952

Point Group = C_{3v}

ΔHf°_0 = -283.1 ± 10.0

$S^\circ_{298.15}$ = [69.6 ± 1.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -284.1 ± 10.0 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[2]
[600]	[2]
[1500]	[2]
[4000]	[2]
[10000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[800] (1)
[450] (1)
[750] (2)
[300] (2)

Bond Distance: Ti-F = [1.9] Å

Bond Angle: F-Ti-F = [100°]

σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = [7.45 x 10^{-114} g^3 cm^6

Heat of Formation

The heat of formation of $TiF_3(g)$ is calculated from that of $TiF_3(c)$ and the heat of sublimation determined from the mass spectrometric vapor pressure data of Zmbov and Margrave (1). Their data give nine points over the temperature range 759 - 865°K.

Second and third law analyses of their data give a second law ΔHs°_{298} of 61.2 ± 0.4 kcal/mol and a third law ΔHs°_{298} of 59.0 kcal/mol with an entropy drift of -2.7 ± 0.5 units. The third law value is used to calculate ΔHf°_{298}.

Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiF_4(g)$, and $TiCl_4(g)$, and $TiCl_3(g)$. The pyramidal bond angle is estimated assuming $TiF_3(g)$ similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 1.68 \times 10^{-38}$ g cm^2 and $I_C = 2.66 \times 10^{-38}$ g cm^2. The vibrational frequencies are estimated from those of PF_3 and AsF_3. The electronic levels are estimated from the levels of Ti^{+3} (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Trifluoride (ZrF_3)

(Crystal) GFW = 148.2152

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	20.000	21.000	21.000	.000	- 335.000	- 316.817	232.233
300	20.150	21.124	21.000	.037	- 334.995	- 316.705	230.719
400	21.950	27.182	21.814	2.147	- 334.663	- 310.654	169.734
500	23.150	32.215	23.405	4.405	- 334.266	- 304.699	133.184
600	24.000	36.515	25.241	6.765	- 333.833	- 298.825	108.847
700	24.600	40.261	27.124	9.195	- 333.385	- 293.026	91.487
800	25.100	43.580	28.978	11.682	- 332.930	- 287.292	78.484
900	25.450	46.557	30.769	14.210	- 332.478	- 281.614	68.385
1000	25.750	49.255	32.484	16.771	- 332.034	- 275.987	60.317
1100	25.930	51.719	34.123	19.355	- 331.604	- 270.403	53.724
1200	26.020	53.979	35.684	21.953	- 332.048	- 264.805	48.228
1300	26.100	56.065	37.173	24.559	- 331.490	- 259.224	43.579
1400	26.170	58.001	38.592	27.173	- 330.942	- 253.685	39.602
1500	26.230	59.809	39.947	29.793	- 330.405	- 248.184	36.160

June 30, 1961; June 30, 1964; June 30, 1969

ZIRCONIUM TRIFLUORIDE (ZrF_3) (CRYSTAL) GFW = 148.2152

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [21 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-335 ± 20] kcal/mol

$\Delta Hs^\circ_{298.15}$ = [70.1] kcal/mol

Heat of Formation

The heat of formation at 298°K for ZrF_3(c) was reported as -350 kcal/mol (1) which was estimated by Brewer (2). Based on this ΔHf°_{298} value, the crystal lattice energy (U) of ZrF_3(c) is calculated to be 1371 kcal/mol by the Born-Haber cycle method (3). For the evaluation of U from the relation: $\Delta Hf^\circ(ZrF_3, c) = \Sigma I_i + L - 3(E - D/2) - U$, the following values (kcal/mol) are used: ΣI_i(the sum of the successive three ionization potentials of Zr metal) = 1055 (4), L(the enthalpy of sublimation of Zr metal) = 148.3 (5), E(the electron affinity of fluorine) = 79.5 (6), and D(the enthalpy of dissociation of fluorine) = 37.7 (7). The derived value of U(ZrF_3, c) is of the same order of magnitude of the value, U(TiF_3, c) = 1376 kcal/mol, calculated by Cavell and Clark (3) using the same method.

From $\Delta Hf^\circ_{298}(ZrF_3, c)$ = -350 kcal/mol, the derived $\Delta Gf^\circ(ZrF_3, c)$ values indicate that ZrF_3(c) is thermodynamically more stable than the system ZrF_4(c) + Zr(c). For example, in the temperature range 298-1200°K, the Gibbs energy changes for the reaction 3 ZrF_4(c) + Zr(c) = 4 ZrF_3(c) are about -29 ± 1 kcal/mol. However, this product ZrF_3(c) has never been prepared successfully from this reaction in many laboratories (8). In order to make the $\Delta Gf^\circ(ZrF_3, c)$ values consistent with the experimental observations, the heat of formation of ZrF_3(c) is arbitrarily adjusted to be 15 kcal/mol less negative, or $\Delta Hf^\circ_{298}(ZrF_3, c)$ = -335 kcal/mol with uncertainty as high as ±20 kcal/mol. This value is tentatively adopted.

The Gibbs energy changes for the reaction 3 ZrF_4(g) + Zr(c) = 4 ZrF_3(c) are evaluated to be very favorable at temperatures below 900°K, e.g. ΔGr° = -93.9 and -6.7 kcal/mol at 298 and 900°K, respectively. But according to Larsen and Leddy (9), this reaction does not occur in the temperature range 473-973°K, and pressure range 5-15 atm. One possible explanation is that these heterogeneous reactants may require very high activation energy to initiate the reaction. In other words, this reaction is unfavorable at these temperatures probably due to kinetic rather than thermodynamic reasons.

Heat Capacity and Entropy

The heat capacities of ZrF_3(c) are not available in the literature. They are estimated from the Cp values of ZrF_4(c) by deduction of one F atom Cp contributions which are calculated as $1/4(Cp_{ZrF_4(c)} - Cp_{Zr(c)})$. The $S^\circ_{298.15}$ is taken to be $1/2[S^\circ_{298}(ZrF_4, c) + S^\circ_{298}(ZrF_2, c)]$ of which the value $S^\circ_{298}(ZrF_2, c)$ is estimated (see ZrF_2(c) table for details).

Heat of Sublimation

The difference between ΔHf°_{298} for ZrF_3(g) and ZrF_3(c) is ΔHs°_{298}. Actually, ZrF_3(c) is thermodynamically unstable, e.g. the Gibbs energy changes for the reaction 4 ZrF_3(c) = 3 ZrF_4(c) + Zr(c) are about -30 kcal/mol in the temperature range 298-1400°K. In other words, ZrF_3(c) decomposes into ZrF_4(c) + Zr(c) before sublimation occurs.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, private communication, University of California, Berkeley, California; cited in reference 1.
3. R. G. Cavell and H. C. Clark, J. Chem. Soc. 1965, 444 (1965).
4. C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.
5. JANAF Zr(c) table, Dec. 31, 1967.
6. U. S. Natl. Bur. Std. Rept. 8628, January 1965.
7. JANAF F(g) table, Sept. 30, 1965.
8. T. B. Douglas, private communication, Natl. Bur. Std., July 10, 1961.
9. E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956).

Zirconium Trifluoride (ZrF_3)

(Ideal Gas) GFW = 148.2152

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.610	-263.324	-263.324	INFINITE
100	10.621	58.513	85.884	-2.737	-263.706	-263.117	575.042
200	14.029	67.004	74.467	-1.492	-264.037	-262.386	286.721
298	16.212	73.047	73.047	.000	-264.200	-261.535	191.710
300	16.244	73.147	73.047	.030	-264.202	-261.519	190.516
400	17.616	78.023	73.703	1.728	-264.282	-260.610	142.391
500	18.524	82.058	74.982	3.538	-264.334	-259.687	113.509
600	19.165	85.495	76.455	5.424	-264.373	-258.753	94.251
700	19.628	88.486	77.964	7.365	-264.415	-257.813	80.493
800	19.965	91.130	79.448	9.346	-264.466	-256.868	70.173
900	20.210	93.496	80.880	11.355	-264.533	-255.914	62.144
1000	20.390	95.636	82.250	13.386	-264.619	-254.952	55.720
1100	20.523	97.586	83.557	15.432	-264.728	-253.981	50.461
1200	20.620	99.376	84.802	17.489	-265.712	-252.946	46.068
1300	20.692	101.029	85.987	19.555	-265.695	-251.882	42.345
1400	20.743	102.565	87.117	21.627	-265.688	-250.820	39.155
1500	20.779	103.997	88.195	23.703	-265.695	-249.756	36.389
1600	20.803	105.339	89.225	25.782	-265.716	-248.695	33.970
1700	20.817	106.601	90.210	27.863	-265.750	-247.628	31.835
1800	20.824	107.791	91.154	29.945	-265.801	-246.564	29.937
1900	20.825	108.917	92.060	32.028	-265.865	-245.493	28.238
2000	20.822	109.985	92.930	34.110	-265.945	-244.417	26.709
2100	20.816	111.000	93.766	36.192	-266.041	-243.341	25.325
2200	20.808	111.969	94.572	38.273	-271.157	-242.080	24.048
2300	20.798	112.893	95.348	40.354	-271.279	-240.754	22.877
2400	20.787	113.778	96.098	42.433	-271.407	-239.425	21.803
2500	20.776	114.627	96.822	44.511	-271.540	-238.091	20.814
2600	20.765	115.441	97.523	46.588	-271.677	-236.749	19.901
2700	20.753	116.225	98.201	48.664	-271.819	-235.402	19.054
2800	20.742	116.979	98.858	50.739	-271.965	-234.052	18.269
2900	20.731	117.707	99.496	52.812	-272.116	-232.692	17.536
3000	20.720	118.410	100.115	54.885	-272.273	-231.335	16.853
3100	20.710	119.089	100.716	56.956	-272.433	-229.967	16.213
3200	20.700	119.746	101.300	59.027	-272.598	-228.594	15.612
3300	20.691	120.383	101.869	61.096	-272.767	-227.217	15.048
3400	20.682	121.001	102.423	63.165	-272.940	-225.833	14.516
3500	20.673	121.600	102.962	65.233	-273.118	-224.442	14.015
3600	20.665	122.182	103.488	67.300	-273.298	-223.048	13.541
3700	20.657	122.748	104.001	69.366	-273.484	-221.651	13.092
3800	20.650	123.299	104.501	71.431	-273.674	-220.246	12.667
3900	20.643	123.835	104.990	73.496	-273.869	-218.842	12.264
4000	20.636	124.358	105.468	75.560	-274.066	-217.426	11.880
4100	20.629	124.867	105.935	77.623	-274.268	-216.009	11.514
4200	20.623	125.364	106.392	79.685	-274.474	-214.584	11.166
4300	20.617	125.850	106.839	81.747	-274.682	-213.154	10.834
4400	20.611	126.324	107.276	83.809	-274.897	-211.722	10.516
4500	20.605	126.787	107.704	85.870	-275.113	-210.286	10.213
4600	20.599	127.239	108.124	87.930	-275.334	-208.843	9.922
4700	20.594	127.682	108.536	89.989	-275.559	-207.394	9.644
4800	20.589	128.116	108.939	92.049	-416.943	-205.256	9.346
4900	20.584	128.540	109.335	94.107	-417.280	-200.841	8.958
5000	20.579	128.956	109.723	96.165	-417.626	-196.422	8.586
5100	20.574	129.364	110.104	98.223	-417.980	-192.000	8.228
5200	20.569	129.763	110.478	100.280	-418.342	-187.559	7.883
5300	20.564	130.155	110.846	102.337	-418.711	-183.116	7.551
5400	20.560	130.539	111.207	104.393	-419.090	-178.674	7.231
5500	20.556	130.916	111.562	106.449	-419.474	-174.216	6.923
5600	20.551	131.287	111.911	108.504	-419.865	-169.751	6.625
5700	20.547	131.650	112.254	110.559	-420.264	-165.281	6.337
5800	20.543	132.008	112.592	112.614	-420.666	-160.804	6.059
5900	20.540	132.359	112.924	114.668	-421.075	-156.324	5.791
6000	20.536	132.704	113.251	116.721	-421.491	-151.834	5.531

June 30, 1961; June 30, 1964; June 30, 1969; Dec. 31, 1969

ZIRCONIUM TRIFLUORIDE (ZrF_3) (IDEAL GAS) GFW = 148.2152

Point Group [C_{3v}]

$\Delta Hf°_0$ = -263.3 ± 5 kcal/mol

$S°_{298.15}$ = [73.0 ± 2] gibbs/mol

$\Delta Hf°_{298.15}$ = -264.2 ± 5 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[611] (1)	[655] (2)
[203] (1)	[240] (2)

Bond Distance: Zr-F = [1.93] Å

Bond Angle: F-Zr-F = [105°]

σ = [3]

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.8857×10^{-114}] g^3 cm^6

Heat of Formation

Murad and Hildenbrand (1) studied the gaseous equilibria involving ZrF_4, ZrF_3, ZrF_2, Ca and CaF. These species were generated at high temperatures in a graphite Knudsen cell containing powdered calcium fluoride and elemental zirconium. Ion intensities were measured 3 eV above threshold over the temperature range 1665-1747°K and the equilibrium constants were calculated for the following isomolecular reaction: $Ca(g) + ZrF_4(g) = CaF(g) + ZrF_3(g)$. Based on the reported equilibrium constants, the enthalpy change of this reaction is evaluated by the second and third law methods as -8.0 ± 25 and 28.0 ± 2 kcal/mol, respectively. The third law entropy drift is 20 ± 15 eu. Using the third law value and $\Delta Hf°_{298}$ = 42.85 ± 0.3, -400.0 ± 0.5, and -65.0 ± 2 kcal/mol for Ca(g), ZrF_4(g), and CaF(g) we obtain $\Delta Hf°_{298}(ZrF_3, g)$ = -264.2 ± 5 kcal/mol, which is adopted. Employing slightly different Gibbs energy functions and $\Delta Hf°_{298}$ values for the products and reactants, Murad and Hildenbrand (1) evaluated the third law enthalpy change of the above reaction as 29.4 ± 5 and $\Delta Hf°_{298}(ZrF_3, g)$ = -262 ± 5 kcal/mol, which are in reasonable agreement with the values adopted here.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of $TiF_3(g)$. The Zr-F bond distance is estimated by comparison with those for $ZrF_4(g)$ and $ZrF_2(g)$. The F-Zr-F bond angle is taken to be slightly larger than the F-Ti-F bond angle in the $TiF_3(g)$ molecule. The vibrational frequencies are calculated by the valence force method (2) using force constants transferred from those for the $ZrF_2(g)$ molecule. The three principal moments of inertia are: $I_A = I_B = 1.8280 \times 10^{-38}$, and $I_C = 2.9583 \times 10^{-38}$ g cm^2. The electronic levels are estimated to be three times higher than those of $TiF_3(g)$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by C. E. Moore (3). The quantum weights are assumed to be the same as those of $TiF_3(g)$.

References

1. E. Murad and D. L. Hildenbrand, J. Chem. Phys. 45, 4751 (1966).
2. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.
3. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std. Circ. 467.

Magnesium Difluoride, Dimeric ($(MgF_2)_2$)

(Ideal Gas) Mol. Wt. = 124.6176

F_4Mg_2

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.190	-409.478	-409.478	INFINITE
100	10.361	57.433	90.824	-3.339	-410.325	-407.475	890.535
200	17.222	66.733	76.520	-1.957	-411.467	-404.383	441.889
298	22.287	74.629	74.629	.000	-411.900	-400.602	293.649
300	22.361	74.767	74.629	.041	-411.909	-400.532	291.788
400	25.489	81.667	75.548	2.447	-412.271	-396.682	216.737
500	27.376	87.574	77.378	5.098	-412.518	-392.753	171.672
600	28.559	92.678	79.512	7.899	-412.719	-388.782	141.614
700	29.337	97.142	81.719	10.797	-412.909	-384.775	120.132
800	29.871	101.097	83.899	13.759	-413.129	-380.745	104.015
900	30.251	104.638	86.010	16.766	-413.396	-376.680	91.470
1000	30.530	107.841	88.035	19.805	-417.965	-372.222	81.349
1100	30.741	110.761	89.970	22.869	-418.289	-367.635	73.042
1200	30.903	113.443	91.816	25.952	-418.654	-363.014	66.114
1300	31.031	115.922	93.576	29.049	-419.069	-358.359	60.246
1400	31.134	118.225	95.256	32.157	-480.263	-352.713	55.061
1500	31.217	120.376	96.860	35.275	-479.961	-343.611	50.064
1600	31.286	122.393	98.393	38.400	-479.660	-334.535	45.695
1700	31.343	124.292	99.861	41.532	-479.358	-325.471	41.842
1800	31.391	126.085	101.269	44.669	-479.059	-316.431	38.420
1900	31.432	127.783	102.620	47.810	-478.758	-307.403	35.359
2000	31.467	129.396	103.919	50.955	-478.461	-298.389	32.606
2100	31.497	130.932	105.169	54.103	-478.167	-289.398	30.118
2200	31.523	132.398	106.373	57.254	-477.876	-280.413	27.856
2300	31.546	133.800	107.536	60.408	-477.586	-271.442	25.793
2400	31.566	135.143	108.658	63.563	-477.301	-262.489	23.903
2500	31.584	136.432	109.744	66.721	-477.021	-253.546	22.165
2600	31.600	137.671	110.794	69.880	-476.744	-244.608	20.561
2700	31.614	138.864	111.812	73.041	-476.471	-235.685	19.077
2800	31.626	140.014	112.798	76.203	-476.201	-226.777	17.701
2900	31.638	141.124	113.756	79.366	-475.938	-217.867	16.419
3000	31.648	142.196	114.686	82.530	-475.684	-208.978	15.224
3100	31.657	143.234	115.591	85.695	-475.433	-200.091	14.106
3200	31.666	144.239	116.470	88.861	-475.191	-191.213	13.059
3300	31.673	145.214	117.327	92.028	-474.956	-182.345	12.076
3400	31.680	146.160	118.161	95.196	-474.730	-173.476	11.151
3500	31.687	147.078	118.974	98.364	-474.516	-164.619	10.279
3600	31.693	147.971	119.767	101.533	-474.311	-155.765	9.456
3700	31.698	148.839	120.541	104.703	-474.119	-146.917	8.678
3800	31.703	149.685	121.297	107.873	-473.939	-138.076	7.941
3900	31.708	150.508	122.035	111.043	-473.775	-129.249	7.243
4000	31.712	151.311	122.757	114.214	-473.624	-120.412	6.579
4100	31.716	152.094	123.463	117.386	-473.492	-111.585	5.948
4200	31.720	152.858	124.154	120.558	-473.376	-102.760	5.347
4300	31.723	153.605	124.830	123.730	-473.278	-93.937	4.774
4400	31.726	154.334	125.493	126.902	-473.202	-85.113	4.228
4500	31.729	155.047	126.142	130.075	-473.145	-76.295	3.705
4600	31.732	155.745	126.778	133.248	-473.110	-67.477	3.206
4700	31.735	156.427	127.401	136.421	-473.099	-58.657	2.728
4800	31.737	157.095	128.013	139.595	-473.111	-49.833	2.269
4900	31.739	157.750	128.613	142.769	-473.149	-41.018	1.829
5000	31.742	158.391	129.202	145.943	-473.213	-32.198	1.407
5100	31.744	159.019	129.781	149.117	-473.305	-23.388	1.002
5200	31.746	159.636	130.349	152.292	-473.424	-14.556	.612
5300	31.747	160.241	130.907	155.466	-473.572	-5.725	.236
5400	31.749	160.834	131.456	158.641	-473.751	3.091	-.125
5500	31.751	161.417	131.995	161.816	-473.960	11.927	-.474
5600	31.752	161.989	132.526	164.991	-474.203	20.764	-.810
5700	31.754	162.551	133.048	168.167	-474.477	29.613	-1.135
5800	31.755	163.103	133.561	171.342	-474.784	38.452	-1.449
5900	31.757	163.646	134.067	174.518	-475.128	47.305	-1.752
6000	31.758	164.180	134.564	177.693	-475.507	56.153	-2.045

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE, DIMERIC ($(MgF_2)_2$) (IDEAL GAS) MOL. WT. = 124.6176

Point Group [D_{2h}]

$S_{298.15}^\circ$ = [74.63] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H_{f\ 0}^\circ = -409.5 \pm 3.4$ kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -411.9 \pm 3.4$ kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[430] (1)	[390] (1)
[260] (1)	[660] (1)
[330] (1)	[930] (1)
[250] (1)	[700] (1)
[720] (1)	[500] (1)
[700] (1)	[500] (1)

Bond Distance: Mg-F = [1.77] Å

Bond Angle: F-Mg-F' = [135]° Mg-F'-Mg = [90]° F'-Mg-F' = [90]°

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.5711 X 10^{-113}] g.^{3} cm.^{6}

Heat of Formation.

The enthalpy change, ΔH_r° = 30 kcal. mole^{-1}, for the reaction $MgF_2(c) + MgF_2(g) = (MgF_2)_2(g)$ was determined by J. Berkowitz and J. R. Marquart, J. Chem. Phys. 8, 1853 (1962). Hence the heat of formation for $(MgF_2)_2(g)$ was calculated.

Heat Capacity and Entropy.

The molecular structure was assumed to be planar. The two Mg atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two F atoms. The two remaining F atoms are situated outside the square on a straight line joining the two Mg atoms. The bond distance between Mg and F atom was estimated to be the same as that in the $MgF_2(g)$ molecule. Vibrational frequencies were estimated by comparison with those for MgF(g) and $(NaF)_2$. The vibrational frequencies for $(NaF)_2$ were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The three principal moments are 9.8896 X 10^{-39}, 7.02735 X 10^{-38}, and 8.01631 X 10^{-38} g. cm.^{2}

F_4Mg_2

Molybdenum Oxytetrafluoride ($MoOF_4$)

(Ideal Gas) GFW = 187.933

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.638	-298.285	-298.285	INFINITE
100	12.901	59.771	96.492	-3.672	-299.173	-294.773	644.226
200	18.843	70.613	80.982	-2.074	-299.763	-290.115	317.023
298	23.121	78.992	78.992	.000	-300.000	-285.319	209.144
300	23.185	79.135	78.993	.043	-300.003	-285.229	207.789
400	25.929	86.213	79.939	2.510	-300.021	-280.295	153.146
500	27.631	92.196	81.808	5.194	-299.932	-275.374	120.366
600	28.720	97.337	83.978	8.015	-299.784	-270.474	98.520
700	29.445	101.822	86.214	10.926	-299.607	-265.602	82.925
800	29.948	105.789	88.417	13.897	-299.419	-260.760	71.236
900	30.308	109.338	90.548	16.911	-299.222	-255.938	62.150
1000	30.575	112.546	92.590	19.956	-299.027	-251.140	54.887
1100	30.776	115.470	94.539	23.024	-298.836	-246.360	48.947
1200	30.932	118.155	96.397	26.109	-298.655	-241.597	44.001
1300	31.055	120.636	98.167	29.209	-298.490	-236.849	39.818
1400	31.154	122.941	99.855	32.320	-298.344	-232.113	36.234
1500	31.234	125.093	101.467	35.439	-298.219	-227.385	33.130
1600	31.301	127.111	103.007	38.566	-298.118	-222.667	30.415
1700	31.356	129.011	104.482	41.699	-298.041	-217.953	28.020
1800	31.402	130.804	105.895	44.837	-297.995	-213.247	25.892
1900	31.442	132.503	107.251	47.979	-297.973	-208.537	23.987
2000	31.476	134.117	108.554	51.125	-297.982	-203.830	22.273
2100	31.505	135.653	109.808	54.274	-298.022	-199.124	20.723
2200	31.530	137.119	111.017	57.426	-298.096	-194.413	19.313
2300	31.553	138.521	112.182	60.580	-298.205	-189.697	18.025
2400	31.572	139.865	113.308	63.736	-298.356	-184.974	16.844
2500	31.589	141.154	114.396	66.895	-298.562	-180.250	15.757
2600	31.605	142.393	115.449	70.054	-298.832	-175.509	14.753
2700	31.618	143.586	116.469	73.215	-299.174	-170.759	13.822
2800	31.631	144.736	117.458	76.378	-299.598	-165.998	12.957
2900	31.642	145.846	118.418	79.542	-306.738	-161.194	12.148
3000	31.652	146.919	119.351	82.706	-306.956	-156.178	11.378
3100	31.661	147.957	120.257	85.872	-307.177	-151.147	10.656
3200	31.669	148.963	121.138	89.038	-307.405	-146.111	9.979
3300	31.676	149.937	121.996	92.206	-307.639	-141.067	9.342
3400	31.683	150.883	122.832	95.374	-307.878	-136.013	8.743
3500	31.689	151.802	123.647	98.542	-308.125	-130.955	8.177
3600	31.695	152.694	124.441	101.712	-308.374	-125.886	7.642
3700	31.700	153.563	125.216	104.881	-308.632	-120.815	7.136
3800	31.705	154.408	125.974	108.052	-308.894	-115.731	6.656
3900	31.710	155.232	126.713	111.222	-309.163	-110.651	6.201
4000	31.714	156.035	127.436	114.394	-309.436	-105.555	5.767
4100	31.718	156.818	128.143	117.565	-309.716	-100.456	5.355
4200	31.721	157.582	128.835	120.737	-310.000	-95.348	4.961
4300	31.725	158.329	129.513	123.909	-310.288	-90.230	4.586
4400	31.728	159.058	130.176	127.082	-310.585	-85.112	4.228
4500	31.731	159.771	130.826	130.255	-310.884	-79.986	3.885
4600	31.734	160.469	131.462	133.428	-311.189	-74.853	3.556
4700	31.736	161.151	132.087	136.602	-311.500	-69.712	3.242
4800	31.739	161.819	132.699	139.775	-311.814	-64.558	2.939
4900	31.741	162.474	133.300	142.949	-312.135	-59.406	2.650
5000	31.743	163.115	133.890	146.124	-453.473	-51.915	2.269
5100	31.745	163.744	134.469	149.298	-454.077	-43.879	1.880
5200	31.747	164.360	135.038	152.473	-454.713	-35.828	1.506
5300	31.749	164.965	135.597	155.647	-455.379	-27.761	1.145
5400	31.750	165.558	136.147	158.822	-456.078	-19.697	.797
5500	31.752	166.141	136.687	161.997	-456.800	-11.604	.461
5600	31.753	166.713	137.218	165.173	-457.551	-3.500	.137
5700	31.755	167.275	137.740	168.348	-458.325	4.611	-.177
5800	31.756	167.827	138.254	171.524	-459.118	12.748	-.480
5900	31.758	168.370	138.760	174.699	-459.934	20.880	-.773
6000	31.759	168.904	139.258	177.875	-460.766	29.041	-1.058

June 30, 1970

MOLYBDENUM OXYTETRAFLUORIDE ($MoOF_4$) (IDEAL GAS) GFW = 187.933

Point Group [C_{4v}] ΔHf°_0 = [-298 ± 30] kcal/mol

$S^\circ_{298.15}$ = [78.99 ± 2.00] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-300 ± 30] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1045 (1)	[600] (1)	720 (2)
[300] (1)	[300] (1)	530 (2)
680 (1)	[200] (1)	[150] (2)

Bond Distance: Mo-O = [1.64] Å Mo-F = [1.82] Å

Bond Angle: O-Mo-F = [90°] F-Mo-F = [90°] σ = [4]

Product of Moments of Inertia: $I_AI_BI_C$ = [3.1468×10^{-113}] g^3 cm^6

Heat of Formation

Zmbov et al. (1) investigated the stabilities of some molybdenum and tungsten oxyfluorides by means of mass spectrometry. These studies led to heats of formation for MoO_2F_2(g), WO_2F_2(g), and WOF_4(g) which were used by the authors to develop a correlation among the heats of formation of the oxides, oxyfluorides, and fluorides of Mo and W. ΔHf°_{298} varies almost linearly with the number of oxygen atoms (1) for the series WF_6, WOF_4 and WO_2F_2. Assuming a similar variation for MoF_6, $MoOF_4$ and MoO_2F_2, we estimate ΔHf°($MoOF_4$, g) = -320 kcal/mol.

Heat of formation data (2) for MoF_6(g), MoO(g), MoO_2(g), and MoO_3(g) have been used to derive the following average bond dissociation energies:

$\overline{D}$(Mo-F) = 107 kcal/mol
$\overline{D}$(Mo-O) = 135 kcal/mol

From these data we derive ΔHf°($MoOF_4$, g) = -271 kcal/mol.

The heat of formation for $MoOF_4$ is tentatively selected as 300 ± 30 kcal/mol.

Heat Capacity and Entropy

Blanchard (3) suggested that $MoOF_4$(g) possessed C_{4v} symmetry by reason of the similarity of its infrared spectra with that of $XeOF_4$(g). X-ray diffraction studies of crystalline $MoOF_4$ by Edwards et al. (4, 5) support this view. The structure of the molecule is assumed to be square-pyramidal. The bond lengths are from the crystallographic studies of $MoOF_4$ by Edwards et al. (4, 5). Individual moments of inertia are $I_A = I_B = 27.437 \times 10^{-39}$, $I_C = 41.801 \times 10^{-39}$ g cm^2.

Blanchard (3) reported the following vibrational frequencies and assignments:

$$\nu_1 = 1045,\ \nu_7 = 720,\ \nu_3 = 680, \text{ and } \nu_8 = 530 \text{ cm}^{-1}.$$

Similar frequencies have been reported by Edwards et al. (4) from their study of the infrared spectra of gaseous $MoOF_4$. The rest of the frequencies and assignments are estimated by comparison with data for $XeOF_4$ (6).

References

1. K. F. Zmbov, O. M. Uy, and J. L. Margrave, J. Phys. Chem., 73, 3008 (1969).
2. JANAF Data.
3. S. Blanchard, Commissariat a l'Énergie Atomique report CEA-R 3194, 1967.
4. A. J. Edwards, G. R. Jones, and B. R. Steventon, Chem. Commun., 462 (1967).
5. A. J. Edwards and B. R. Steventon, J. Chem. Soc., 2503 (1968).
6. G. M. Begun, W. H. Fletcher, and D. F. Smith, J. Chem. Phys., 42, 2236 (1965).

Tetrafluorohydrazine (N_2F_4)
(Ideal Gas) Mol. Wt. = 104.016

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.710	.582	.582	INFINITE
100	9.981	57.235	85.581	-2.835	-.618	5.609	-12.258
200	14.303	65.365	73.549	-1.637	-1.523	12.219	-13.352
298	18.922	71.962	71.962	.000	-2.000	19.080	-13.985
300	19.000	72.079	71.962	.035	-2.006	19.210	-13.994
400	22.584	78.066	72.754	2.125	-2.153	26.313	-14.376
500	25.047	83.388	74.359	4.514	-2.081	33.423	-14.609
600	26.717	88.112	76.266	7.108	-1.863	40.507	-14.754
700	27.868	92.322	78.264	9.841	-1.560	47.546	-14.844
800	28.684	96.100	80.262	12.670	-1.206	54.535	-14.898
900	29.277	99.514	82.214	15.570	-.817	61.481	-14.929
1000	29.719	102.623	84.102	18.521	-.410	68.380	-14.944
1100	30.057	105.472	85.917	21.510	.007	75.239	-14.948
1200	30.320	108.099	87.657	24.530	.432	82.061	-14.945
1300	30.528	110.534	89.325	27.572	.857	88.846	-14.936
1400	30.696	112.803	90.922	30.634	1.284	95.598	-14.923
1500	30.833	114.925	92.452	33.710	1.709	102.321	-14.907
1600	30.946	116.919	93.919	36.800	2.133	109.014	-14.890
1700	31.040	118.798	95.328	39.899	2.553	115.683	-14.871
1800	31.120	120.575	96.682	43.007	2.968	122.321	-14.851
1900	31.188	122.259	97.984	46.123	3.383	128.944	-14.831
2000	31.246	123.860	99.238	49.244	3.792	135.544	-14.811
2100	31.296	125.386	100.447	52.372	4.198	142.117	-14.790
2200	31.340	126.843	101.614	55.503	4.597	148.676	-14.769
2300	31.378	128.237	102.742	58.639	4.994	155.217	-14.748
2400	31.412	129.573	103.832	61.779	5.387	161.740	-14.728
2500	31.441	130.856	104.887	64.922	5.773	168.245	-14.707
2600	31.468	132.090	105.910	68.067	6.155	174.737	-14.687
2700	31.492	133.278	106.902	71.215	6.534	181.217	-14.668
2800	31.513	134.423	107.864	74.365	6.909	187.676	-14.648
2900	31.532	135.530	108.799	77.517	7.279	194.131	-14.629
3000	31.549	136.599	109.708	80.672	7.643	200.561	-14.610
3100	31.564	137.634	110.592	83.827	8.004	206.985	-14.592
3200	31.579	138.636	111.453	86.984	8.359	213.400	-14.574
3300	31.591	139.608	112.292	90.143	8.710	219.802	-14.556
3400	31.603	140.551	113.109	93.303	9.058	226.195	-14.539
3500	31.614	141.467	113.906	96.463	9.398	232.578	-14.522
3600	31.624	142.358	114.684	99.625	9.736	238.952	-14.506
3700	31.633	143.225	115.444	102.788	10.069	245.313	-14.489
3800	31.642	144.068	116.186	105.952	10.397	251.669	-14.474
3900	31.649	144.890	116.912	109.117	10.720	258.009	-14.458
4000	31.657	145.692	117.621	112.282	11.039	264.348	-14.443
4100	31.663	146.474	118.316	115.448	11.352	270.675	-14.428
4200	31.669	147.237	118.995	118.614	11.660	276.997	-14.413
4300	31.675	147.982	119.661	121.782	11.968	283.315	-14.399
4400	31.681	148.710	120.313	124.949	12.265	289.619	-14.385
4500	31.686	149.422	120.952	128.118	12.561	295.916	-14.371
4600	31.690	150.119	121.578	131.287	12.853	302.213	-14.358
4700	31.695	150.800	122.193	134.456	13.138	308.499	-14.345
4800	31.699	151.468	122.796	137.626	13.420	314.785	-14.332
4900	31.703	152.121	123.387	140.796	13.696	321.057	-14.319
5000	31.707	152.762	123.968	143.966	13.967	327.329	-14.307
5100	31.710	153.390	124.539	147.137	14.234	333.583	-14.294
5200	31.713	154.005	125.100	150.308	14.497	339.854	-14.283
5300	31.716	154.610	125.651	153.480	14.755	346.108	-14.271
5400	31.719	155.202	126.193	156.651	15.006	352.348	-14.260
5500	31.722	155.784	126.726	159.824	15.255	358.601	-14.249
5600	31.725	156.356	127.250	162.996	15.497	364.841	-14.238
5700	31.727	156.918	127.765	166.168	15.734	371.081	-14.227
5800	31.730	157.469	128.273	169.341	15.969	377.313	-14.217
5900	31.732	158.012	128.772	172.514	16.197	383.533	-14.206
6000	31.734	158.545	129.264	175.688	16.421	389.758	-14.196

Mar. 31, 1964

TETRAFLUOROHYDRAZINE (N_2F_4) (IDEAL GAS) MOL. WT. = 104.016

Point Group = C_2

$S^\circ_{298.15}$ = 71.96 cal. deg.$^{-1}$ mole^{-1}.

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 0.6 ± 2.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -2.0 ± 2.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1010 (1)	549 (1)	946 (1)
998 (1)	390 (1)	737 (1)
933 (1)	122 (1)	519 (1)
591 (1)	959 (1)	467 (1)

Bond Distances: N-N = [1.47 Å] N-F = [1.37 Å]

Bond Angles: F-N-F = [108°] N-N-F = [104°] Dihedral Angle = [65°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.1817 X 10^{-113}] gm.^{3} cm.^{6}

Heat of Formation.

G. T. Armstrong, S. Marantz, and C. F. Coyle, National Bureau of Standards Report No. 6584, October, 1959, studied the reaction

$$N_2F_4(g) + 16/3\ NH_3(g) = 4NH_4F(s) + 5/3\ N_2(g).$$

From this reaction, they calculate the heat of formation of N_2F_4 to be -2.0 ± 2.5 kcal. mole^{-1}. The recalculated heat of formation of $NH_4F(s)$ (see NF_2 table) differs from the value quoted in Circular 500 by 0.06 kcal. mole^{-1}. This correction would make the heat of formation of tetrafluorohydrazine more negative by 0.24 kcal. mole^{-1}. In view of the large uncertainty in the heat of formation, however, this correction was not applied.

Heat Capacity and Entropy.

The fundamental frequencies were taken from the vapor phase infrared work of J. R. Durig and R. C. Lord, Spectrochim. Acta 19, 1877 (1963). The principal moments of inertia were calculated from the rotational constants reported by D. R. Lide, Jr. and D. E. Mann, J. Chem. Phys. 31, 1129 (1959). Lide and Mann calculated the bond angles for assumed values of the NN and NF distances.

The principal moments of inertia are: I_A = 1.5051 X 10^{-38} gm. cm.^{2}, I_B = 2.6315 X 10^{-38} gm. cm.^{2}, I_C = 2.9836 X 10^{-38} gm. cm.^{2}.

continued from the table nitrogen difluoride (NF_2) (ideal gas).

Heat Capacity and Entropy.

M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. 35, 1129 (1961), investigated the infrared spectrum of NF_2. They were able to assign the band center at 1074 cm.$^{-1}$ to the symmetric stretching mode ω_1. The absorption in the 930-940 cm.$^{-1}$ region was assigned to ω_3.

M. D. Harmony and R. J. Myers, J. Chem. Phys. 37, 636 (1962), performed matrix isolation experiments on NF_2. They arrived at the assignment ω_1 = 1070 cm.$^{-1}$, ω_2 = 573 cm.$^{-1}$, and ω_3 = 931 cm.$^{-1}$. The stretching frequencies for similar molecules in an N_2 matrix are about 5 cm.$^{-1}$ below the gas phase values. A comparison of the gas phase and matrix values of ω_1 show excellent agreement.

F. A. Johnson and C. B. Colburn, Inorg. Chem. 1, 431 (1962), report infrared studies on NF_2 but they draw no definite conclusions.

The gas phase value for ω_1 and the matrix values for ω_2 and ω_3 were taken to represent the fundamental vibrational frequencies of NF_2.

Harmony, Myers, Schoen, Lide, and Mann estimated the N-F distance as 1.37 Å and used this with their data to calculate an F-N-F angle of 104.2°. Using these data the moments of inertia are: I_A = 7.3728 X 10^{-39} gm. cm.^{2}, I_B = 1.2035 X 10^{-39} gm. cm.^{2}, I_C = 8.5763 X 10^{-39} gm. cm.^{2}.

Tungsten Oxytetrafluoride (WOF_4)

(Crystal) GFW = 275.843

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	31.926	42.000	42.000	.000	- 355.370	- 329.371	241.435
300	32.000	42.198	42.001	.059	- 355.356	- 329.210	239.829
400	36.000	51.951	43.304	3.459	- 354.441	- 320.623	175.180
500	39.800	60.410	45.896	7.257	- 353.224	- 312.305	136.509
600	42.700	67.937	48.954	11.390	- 351.743	- 304.256	110.825
700	44.500	74.670	52.156	15.760	- 350.085	- 296.470	92.562
800	45.900	80.715	55.354	20.288	- 348.321	- 288.933	78.933
900	46.900	86.177	58.481	24.927	- 346.483	- 281.618	68.386
1000	47.300	91.137	61.502	29.635	- 344.613	- 274.511	59.994

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (CRYSTAL) GFW = 275.843

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [42.0 ± 4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-355.37 ± 6] kcal/mol

Tm = 379°K

ΔHm° = 1.219 ± 2 kcal/mol

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WOF_4,c)$ = -355.37 kcal/mol, is calculated from that of the gas less the heat of sublimation, ΔHs°_{298} = 16.97 kcal/mol. The latter is calculated by the third law method from the vapor pressure equation determined by G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law ΔHs°_{298} is 17.01 kcal/mol.

Heat Capacity and Entropy.

The heat capacities are estimated from those of $WOCl_4(c)$, $WO_3(c)$, $WO_2(c)$, $WCl_6(c)$ and $WF_6(c,l)$.

The entropy, S°_{298} = 42.0 eu, is calculated from ΔS°_{348} = 37.0 eu for $WOF_4(c) \rightarrow WOF_4(g)$, obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

It is surprising that this entropy is larger than the corresponding value for $WOCl_4(c)$ (JANAF $WOCl_4(c)$ table dated Mar. 31, 1967). In both cases the entropies of the condensed phases are derived from the gas phase values using second law analysis of sublimation and vaporization data. The resulting entropy of melting for WOF_4, 3.2 eu, is much smaller than the value 22.4 eu for $WOCl_4$. This extreme difference may be a reflection of the uncertainty inherent in derivation of ΔS°_m as the difference between the values for sublimation and vaporization. If the values of ΔS°_m are correct, they suggest the possibility of an undiscovered solid state transition for WOF_4 similar to that observed for WF_6.

Melting Data.

Tm is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(c) \rightarrow WOF_4(l)$ approaches zero. The difference between the heats of formation for crystal and liquid at the melting point is ΔHm°.

O. Ruff, F. Eisner, and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the melting point as 383°K. Cady and Hargreaves, loc. cit., derived the melting point as 378°K, and the heat of fusion as 2.26 kcal/mol from vapor pressure equations for crystal and liquid. This second law value of ΔHm°, when corrected for ΔCp of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

Tungsten Oxytetrafluoride (WOF_4)

(Liquid) GFW = 275.843

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	43.500	42.800	42.800	.000	- 354.955	- 329.194	241.306
300	43.500	43.069	42.801	.080	- 354.920	- 329.035	239.702
400	43.500	55.583	44.507	4.430	- 353.055	- 320.690	175.217
500	43.500	65.290	47.729	8.780	- 351.285	- 312.807	136.728
600	43.500	73.221	51.337	13.130	- 349.588	- 305.271	111.195
700	43.500	79.927	54.954	17.480	- 347.950	- 298.014	93.044
800	43.500	85.735	58.447	21.830	- 346.364	- 290.992	79.495
900	43.500	90.859	61.769	26.180	- 344.815	- 284.163	69.004
1000	43.500	95.442	64.911	30.530	- 343.302	- 277.505	60.649

June 30. 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (LIQUID) GFW = 275.843

$S^\circ_{298.15}$ = [42.8 ± 4] gibbs/mol

Tm = 379°K

Tb = 460°K

$\Delta Hf^\circ_{298.15}$ = [-354.955] kcal/mol

ΔHm° = 1.219 ± 2 kcal/mol

ΔHv° = 13.4 kcal/mol

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WOF_4,l)$ = -354.955 kcal/mol, is calculated from that of the gas less the heat of vaporization, ΔHv°_{298} = 16.555 kcal/mol. The latter is calculated by the third law method from the vapor pressure equation determined by G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law ΔHv°_{298} is 16.60 kcal/mol.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.

The entropy, S°_{298} = 42.8 eu, is calculated from ΔS°_{415} = 31.2 eu for $WOF_4(l) \rightarrow WOF_4(g)$, obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

Melting Data.

See $WOF_4(c)$ table (Mar. 31, 1967).

Vaporization Data.

Tb is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(l) \rightarrow WOF_4(g)$ approaches zero. The difference between the heats of formation for liquid and gas at the boiling point is ΔHv°.

O. Ruff, F. Eisner and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the boiling point as 458°K. Cady and Hargreaves, loc. cit., derived the boiling point as 459°K, and the heat of vaporization as 14.23 kcal/mol from the vapor pressure equation for the liquid. This second law value of ΔHv°, when corrected for ΔCp of vaporization, is in good agreement with the value adopted in the tabulation.

Tungsten Oxytetrafluoride (WOF_4)

(Ideal Gas) GFW = 275.843

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 4.467	- 336.420	- 336.420	INFINITE
100	12.552	61.838	97.238	- 3.540	- 337.387	- 333.132	728.059
200	18.170	72.462	82.338	- 1.975	- 338.050	- 328.590	359.067
298	21.914	80.448	80.448	.000	- 338.400	- 323.864	237.399
300	21.975	80.583	80.448	.041	- 338.405	- 323.774	235.869
400	24.749	87.309	81.346	2.385	- 338.545	- 318.871	174.223
500	26.641	93.049	83.127	4.961	- 338.550	- 313.951	137.228
600	27.919	98.026	85.205	7.693	- 338.470	- 309.037	112.566
700	28.800	102.400	87.355	10.531	- 338.344	- 304.139	94.956
800	29.422	106.289	89.483	13.444	- 338.195	- 299.266	81.756
900	29.875	109.782	91.548	16.410	- 338.030	- 294.409	71.492
1000	30.212	112.948	93.532	19.415	- 337.862	- 289.571	63.286
1100	30.470	115.840	95.431	22.450	- 337.695	- 284.751	56.575
1200	30.670	118.500	97.244	25.507	- 337.531	- 279.943	50.985
1300	30.829	120.961	98.975	28.583	- 337.376	- 275.149	46.257
1400	30.957	123.251	100.628	31.672	- 337.229	- 270.370	42.207
1500	31.061	125.390	102.208	34.773	- 337.094	- 265.596	38.697
1600	31.147	127.398	103.720	37.884	- 336.971	- 260.836	35.629
1700	31.219	129.288	105.169	41.002	- 336.860	- 256.079	32.921
1800	31.280	131.074	106.559	44.127	- 336.765	- 251.333	30.516
1900	31.331	132.767	107.895	47.258	- 336.684	- 246.588	28.364
2000	31.376	134.375	109.179	50.393	- 336.617	- 241.845	26.428
2100	31.414	135.907	110.415	53.533	- 336.567	- 237.111	24.676
2200	31.447	137.369	111.608	56.674	- 336.535	- 232.378	23.085
2300	31.476	138.768	112.758	59.822	- 336.517	- 227.643	21.631
2400	31.502	140.108	113.870	62.971	- 336.517	- 222.908	20.299
2500	31.525	141.394	114.945	66.122	- 336.536	- 218.176	19.073
2600	31.545	142.631	115.987	69.276	- 336.570	- 213.439	17.941
2700	31.563	143.822	116.996	72.431	- 336.627	- 208.701	16.893
2800	31.579	144.970	117.974	75.588	- 336.714	- 203.962	15.920
2900	31.593	146.079	118.925	78.747	- 336.844	- 199.219	15.014
3000	31.606	147.150	119.848	81.907	- 337.023	- 194.473	14.167
3100	31.618	148.187	120.745	85.068	- 337.257	- 189.720	13.375
3200	31.629	149.191	121.618	88.231	- 337.558	- 184.956	12.632
3300	31.639	150.164	122.469	91.394	- 337.929	- 180.181	11.933
3400	31.648	151.109	123.297	94.558	- 338.382	- 175.394	11.274
3500	31.656	152.026	124.105	97.724	- 338.928	- 170.587	10.652
3600	31.664	152.918	124.893	100.890	- 339.592	- 165.768	10.063
3700	31.671	153.786	125.662	104.056	- 348.709	- 160.886	9.503
3800	31.677	154.630	126.414	107.224	- 348.824	- 155.801	8.961
3900	31.683	155.453	127.148	110.392	- 348.946	- 150.726	8.446
4000	31.688	156.256	127.865	113.560	- 349.071	- 145.643	7.958
4100	31.693	157.038	128.567	116.729	- 349.204	- 140.555	7.492
4200	31.698	157.802	129.254	119.899	- 349.341	- 135.464	7.049
4300	31.703	158.548	129.927	123.069	- 349.480	- 130.365	6.626
4400	31.707	159.277	130.586	126.239	- 349.630	- 125.274	6.222
4500	31.711	159.989	131.231	129.410	- 349.781	- 120.173	5.836
4600	31.714	160.686	131.864	132.582	- 349.937	- 115.066	5.467
4700	31.718	161.368	132.485	135.753	- 350.101	- 109.957	5.113
4800	31.721	162.036	133.093	138.925	- 350.266	- 104.842	4.774
4900	31.724	162.690	133.691	142.097	- 350.439	- 99.730	4.448
5000	31.727	163.331	134.277	145.270	- 350.616	- 94.613	4.136
5100	31.729	163.959	134.853	148.443	- 350.797	- 89.496	3.835
5200	31.732	164.576	135.419	151.616	- 350.983	- 84.369	3.546
5300	31.734	165.180	135.975	154.789	- 351.174	- 79.233	3.267
5400	31.736	165.773	136.521	157.962	- 351.371	- 74.110	2.999
5500	31.738	166.356	137.058	161.136	- 351.569	- 68.971	2.741
5600	31.740	166.927	137.586	164.310	- 351.775	- 63.826	2.491
5700	31.742	167.489	138.106	167.484	- 351.985	- 58.686	2.250
5800	31.744	168.041	138.617	170.659	- 352.197	- 53.535	2.017
5900	31.746	168.584	139.121	173.833	- 352.416	- 48.389	1.792
6000	31.747	169.118	139.616	177.008	- 546.543	- 41.154	1.499

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF_4) (IDEAL GAS) GFW = 275.843 F_4OW

Point Group [C_{2v}] ΔHf°_0 = -336.4 ± 6 kcal/mol

$S^\circ_{298.15}$ = [80.4] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -338.4 ± 6 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[1000] (1)	[700] (1)	[250] (1)
[1000] (1)	[700] (1)	[250] (1)
[900] (1)	[300] (1)	[200] (1)
[900] (1)	[300] (1)	[200] (1)

Bond Distance: W-F = [1.83] Å W-O = [1.81] Å

Bond Angle: F*-W-O* = F*-W-F* = [120°]
F**-W-F* = F**-W-O* = [90°]
F**-W-F** = [180°] σ = [2]

*Equatorial **Axial

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.868] x 10^{-113} g^3 cm^6

Heat of Formation.

The heat of formation, $\Delta Hf^\circ_{298}(WOF_4,g)$ = -338.4 kcal/mol, is the value determined mass spectrometrically by K. F. Zmbov and J. L. Margrave, Rice Univ., private communication, Mar. 1967, from equilibrium studies of $2TaF_5(g) + WO_3(c) = 2\ TaOF_3(g) + WOF_4(g)$.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $SOF_4(g)$, reported by P. L. Goggin, H. L. Roberts and L. A. Woodward.[1] The bond distances W-O and W-F are estimated to be the same as those in $WO_3(g)$ and $WF_6(g)$, respectively. The three principal moments of inertia are I_A = 3.509 x 10^{-38}, I_B = 3.698 x 10^{-38} and I_C = 2.981 x 10^{-38} g cm^2.

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $SOF_4(g)^1$, $MoOCl_4(g)^2$, $WO_2Cl_2(g)^3$, $CrO_2Cl_2(g)^{4,5}$, $WO_3(g)^6$ and $WF_6(g)^6$. These frequencies are not in point group order.

References.

1. P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. 57, 1877 (1961).
2. T. V. Iorns and F. E. Stafford, J. Am. Chem. Soc. 88, 4819 (1966).
3. C. G. Barraclough and J. Stals, Aust. J. Chem. 19, 741 (1966).
4. F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta, 1959, 709 (1959).
5. H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta, 1959, 438 (1959).
6. JANAF $WO_3(g)$ table (Sept. 30, 1966), $WF_6(g)$ table (Mar. 31, 1967).

Lead Tetrafluoride (PbF_4)

(Ideal Gas) Mol. Wt. = 283.21

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.723	- 184.859	- 184.859	INFINITE
100	14.233	60.071	97.046	- 3.697	- 185.646	- 182.634	399.128
200	19.019	71.555	81.621	- 2.013	- 185.965	- 179.464	196.100
298	21.735	79.709	79.709	.000	- 186.000	- 176.260	129.196
300	21.772	79.844	79.709	.040	- 186.000	- 176.200	128.355
400	23.250	86.331	80.584	2.299	- 185.933	- 172.940	94.486
500	24.076	91.616	82.278	4.669	- 185.850	- 169.704	74.174
600	24.571	96.053	84.214	7.103	- 185.770	- 166.481	60.638
700	24.886	99.866	86.184	9.577	- 186.868	- 163.081	50.914
800	25.098	103.204	88.108	12.077	- 186.821	- 159.687	43.622
900	25.247	106.169	89.953	14.595	- 186.769	- 156.298	37.953
1000	25.355	108.835	91.710	17.125	- 186.715	- 152.916	33.418
1100	25.436	111.256	93.379	19.665	- 186.658	- 149.539	29.709
1200	25.499	113.472	94.962	22.212	- 186.596	- 146.166	26.619
1300	25.547	115.515	96.465	24.764	- 186.536	- 142.798	24.005
1400	25.586	117.409	97.895	27.321	- 186.478	- 139.437	21.766
1500	25.618	119.176	99.255	29.881	- 186.424	- 136.076	19.825
1600	25.644	120.830	100.552	32.444	- 186.378	- 132.723	18.128
1700	25.665	122.385	101.791	35.010	- 186.337	- 129.369	16.631
1800	25.683	123.853	102.977	37.577	- 186.308	- 126.024	15.301
1900	25.699	125.242	104.112	40.146	- 186.285	- 122.674	14.110
2000	25.712	126.560	105.202	42.717	- 186.271	- 119.324	13.038
2100	25.723	127.815	106.249	45.289	- 228.717	- 114.427	11.908
2200	25.733	129.012	107.257	47.862	- 228.630	- 108.988	10.826
2300	25.742	130.156	108.228	50.435	- 228.568	- 103.549	9.839
2400	25.749	131.252	109.164	53.010	- 228.531	- 98.115	8.934
2500	25.756	132.303	110.069	55.585	- 228.523	- 92.683	8.102
2600	25.762	133.313	110.944	58.161	- 228.539	- 87.248	7.334
2700	25.767	134.286	111.790	60.737	- 228.579	- 81.811	6.622
2800	25.772	135.223	112.611	63.314	- 228.644	- 76.377	5.961
2900	25.776	136.127	113.406	65.892	- 228.732	- 70.933	5.345
3000	25.780	137.001	114.178	68.470	- 228.844	- 65.495	4.771
3100	25.783	137.847	114.928	71.048	- 228.974	- 60.048	4.233
3200	25.786	138.665	115.657	73.626	- 229.126	- 54.598	3.729
3300	25.789	139.459	116.366	76.205	- 229.293	- 49.139	3.254
3400	25.792	140.229	117.057	78.784	- 229.476	- 43.675	2.807
3500	25.794	140.976	117.730	81.363	- 229.675	- 38.205	2.386
3600	25.796	141.703	118.386	83.943	- 229.883	- 32.730	1.987
3700	25.798	142.410	119.025	86.523	- 230.104	- 27.252	1.610
3800	25.800	143.098	119.650	89.103	- 230.333	- 21.763	1.252
3900	25.802	143.768	120.260	91.683	- 230.573	- 16.277	.912
4000	25.804	144.421	120.856	94.263	- 230.817	- 10.779	.589
4100	25.805	145.059	121.438	96.843	- 231.069	- 5.276	.281
4200	25.807	145.680	122.008	99.424	- 231.324	.237	- .012
4300	25.808	146.288	122.566	102.005	- 231.581	5.754	- .292
4400	25.809	146.881	123.112	104.586	- 231.844	11.277	- .560
4500	25.810	147.461	123.646	107.167	- 232.107	16.801	- .816
4600	25.811	148.028	124.170	109.748	- 232.372	22.337	- 1.061
4700	25.812	148.584	124.684	112.329	- 232.639	27.875	- 1.296
4800	25.813	149.127	125.187	114.910	- 232.905	33.428	- 1.522
4900	25.814	149.659	125.681	117.491	- 233.173	38.977	- 1.738
5000	25.815	150.181	126.166	120.073	- 233.440	44.531	- 1.946
5100	25.816	150.692	126.642	122.654	- 233.708	50.087	- 2.146
5200	25.816	151.193	127.109	125.236	- 233.974	55.665	- 2.339
5300	25.817	151.685	127.568	127.817	- 234.241	61.240	- 2.525
5400	25.818	152.168	128.020	130.399	- 234.509	66.808	- 2.704
5500	25.818	152.641	128.463	132.981	- 234.775	72.393	- 2.877
5600	25.819	153.106	128.899	135.563	- 235.042	77.984	- 3.043
5700	25.819	153.563	129.328	138.145	- 235.310	83.574	- 3.204
5800	25.820	154.012	129.749	140.727	- 235.576	89.175	- 3.360
5900	25.820	154.454	130.164	143.309	- 235.845	94.768	- 3.510
6000	25.821	154.888	130.573	145.891	- 236.114	100.373	- 3.656

June 30, 1962

Lead Tetrafluoride (PbF_4) (Ideal Gas)

Mol. Wt. = 283.21

$\Delta H_{f\ 298.15}^\circ$ = [-186] kcal. mole^{-1}

$S^\circ_{298.15}$ = 79.7 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
564 (1)
158 (2)
570 (3)
180 (3)

Pb-F distance = 2.08 Å F-Pb-F angle = 109° 28'

$I_AI_BI_C = 4.8233 \times 10^{-113}$ g.^{3} cm.^{6} $\sigma = 12$

Heat of Formation. $\Delta H_{f\ 208.15}^\circ$ was estimated by comparison with the value of $\Delta H_{f\ 298.15}^\circ$ for $PbF_2(g)$.

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Sulfur Tetrafluoride (SF_4)

(Ideal Gas) GFW = 108.058

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.768	-185.095	-185.095	INFINITE
100	10.501	56.658	85.593	-2.894	-185.775	-183.005	399.957
200	14.757	65.244	73.396	-1.630	-186.304	-180.011	196.707
298	18.270	71.829	71.829	.000	-186.600	-176.852	129.636
300	18.325	71.943	71.830	.034	-186.604	-176.792	128.793
400	20.691	77.564	72.580	1.994	-187.283	-173.474	94.782
500	22.181	82.354	74.068	4.143	-187.686	-169.974	74.296
600	23.138	86.489	75.802	6.412	-187.938	-166.405	60.613
700	23.776	90.107	77.592	8.760	-188.092	-162.778	50.822
800	24.217	93.312	79.361	11.161	-201.248	-160.425	43.826
900	24.533	96.184	81.073	13.599	-201.000	-155.336	37.721
1000	24.767	98.781	82.716	16.065	-200.745	-150.276	32.843
1100	24.943	101.150	84.286	18.551	-200.486	-145.243	28.857
1200	25.080	103.327	85.783	21.052	-200.223	-140.231	25.540
1300	25.188	105.339	87.211	23.566	-199.960	-135.240	22.736
1400	25.274	107.208	88.573	26.089	-199.698	-130.273	20.336
1500	25.344	108.955	89.875	28.620	-199.437	-125.323	18.260
1600	25.402	110.592	91.119	31.157	-199.178	-120.391	16.445
1700	25.450	112.134	92.310	33.700	-198.920	-115.473	14.845
1800	25.491	113.590	93.452	36.247	-198.667	-110.576	13.426
1900	25.525	114.969	94.549	38.798	-198.414	-105.686	12.157
2000	25.555	116.279	95.603	41.352	-198.165	-100.810	11.016
2100	25.581	117.526	96.617	43.909	-197.920	-95.953	9.986
2200	25.603	118.717	97.595	46.468	-197.679	-91.101	9.050
2300	25.622	119.855	98.538	49.029	-197.441	-86.262	8.197
2400	25.639	120.946	99.449	51.592	-197.207	-81.433	7.415
2500	25.654	121.993	100.330	54.157	-196.977	-76.614	6.698
2600	25.668	123.000	101.183	56.723	-196.751	-71.804	6.036
2700	25.680	123.968	102.009	59.291	-196.527	-67.001	5.423
2800	25.690	124.903	102.810	61.859	-196.308	-62.212	4.856
2900	25.700	125.804	103.587	64.429	-196.093	-57.422	4.327
3000	25.709	126.676	104.343	66.999	-195.885	-52.649	3.835
3100	25.716	127.519	105.077	69.570	-195.677	-47.877	3.375
3200	25.724	128.335	105.791	72.142	-195.476	-43.112	2.944
3300	25.730	129.127	106.486	74.715	-195.277	-38.355	2.540
3400	25.736	129.895	107.163	77.288	-195.083	-33.600	2.160
3500	25.741	130.641	107.823	79.862	-194.895	-28.852	1.802
3600	25.746	131.367	108.467	82.437	-194.707	-24.109	1.464
3700	25.751	132.072	109.096	85.011	-194.528	-19.373	1.144
3800	25.755	132.759	109.710	87.587	-194.350	-14.640	.842
3900	25.759	133.428	110.309	90.162	-194.180	-9.919	.556
4000	25.763	134.080	110.895	92.739	-194.010	-5.191	.284
4100	25.766	134.716	111.469	95.315	-193.847	-.475	.025
4200	25.769	135.337	112.030	97.892	-193.688	4.240	-.221
4300	25.772	135.944	112.579	100.469	-193.531	8.953	-.455
4400	25.775	136.536	113.116	103.046	-193.383	13.659	-.678
4500	25.778	137.115	113.643	105.624	-193.236	18.361	-.892
4600	25.780	137.682	114.160	108.202	-193.093	23.061	-1.096
4700	25.782	138.236	114.666	110.780	-192.956	27.759	-1.291
4800	25.784	138.779	115.163	113.358	-192.822	32.456	-1.478
4900	25.786	139.311	115.650	115.937	-192.693	37.152	-1.657
5000	25.788	139.832	116.129	118.515	-192.570	41.836	-1.829
5100	25.790	140.343	116.599	121.094	-192.450	46.518	-1.993
5200	25.791	140.843	117.060	123.673	-192.334	51.212	-2.152
5300	25.793	141.335	117.513	126.253	-192.221	55.895	-2.305
5400	25.795	141.817	117.959	128.832	-192.116	60.567	-2.451
5500	25.796	142.290	118.397	131.412	-192.012	65.249	-2.593
5600	25.797	142.755	118.828	133.991	-191.916	69.929	-2.729
5700	25.798	143.212	119.252	136.571	-191.823	74.603	-2.860
5800	25.800	143.660	119.669	139.151	-191.732	79.277	-2.987
5900	25.801	144.101	120.079	141.731	-191.647	83.940	-3.109
6000	25.802	144.535	120.483	144.311	-191.567	88.615	-3.228

Sept. 30, 1965; Dec. 31, 1969

SULFUR TETRAFLUORIDE (SF_4) (IDEAL GAS) GFW = 108.058

Point Group C_{2v}

$\Delta Hf°_0$ = -185.1 ± 6 kcal/mol

$S°_{298.15}$ = 71.83 ± 0.10 gibbs/mol

$\Delta Hf°_{298.15}$ = -186.6 ± 6 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
891.5 (1)	171 (1)	532.2 (1)
558.4 (1)	645 (1)	728 (1)
353 (1)	867 (1)	226 (1)

Bond Distance: $(S\text{-}F)_{eq.}$ = 1.545 ± 0.003 Å
$(S\text{-}F)_{ax.}$ = 1.646 ± 0.003 Å

Bond Angle: $(F\text{-}S\text{-}F)_{eq.}$ = 101°33' ± 30'
$(F\text{-}S\text{-}F)_{ax.}$ = 186°56' ± 30'

$\sigma = 2$

Product of Moments of Inertia: $I_AI_BI_C = 6.721 \times 10^{-114}\ g^3\ cm^6$

Heat of Formation

Vaughn and Muetterties (1) reported calorimetric data for the hydrogenation of SF_4. Their experiments produced HF in amounts ranging from 5.8 to 7.5g. Roughly 1.3g should have been present as saturated, real vapor in the bomb volume of 360 ml at the final temperature of the experiment. Although the authors made allowance for this mixture of HF(ℓ) and HF(real vapor), their values appear to be quite unrealistic. More reliable corrections are readily obtained from the recent review by Vanderzee (2) of PVT and calorimetric data for HF liquid and real vapor.

We choose to reduce the data to a standard state of HF(ℓ), starting from the authors' values of the calorimeter heat capacity and the observed temperature rise. Calculated values for the heat evolved are corrected by a) an increase of ~120 cal for conversion of real vapor to liquid, b) a decrease of 113 to 175 cal for oxidation of $H_2S(g)$ to S(c) in the last three experiments, and c) an increase of 22 to 75 cal for adjustment of the reaction to 25°C from the final temperature of the experiment. At 298.15 K we obtain

$$SF_4(g) + 2H_2(g) \rightarrow 4HF(\ell) + S(c), \quad \Delta Hr° = -102.9 \pm 4 \text{ kcal/mol},$$

where the uncertainty is increased by 1.5 kcal/mol for other possible corrections which are neglected due to insufficient information.

The adopted ΔHf°, -186.6 ± 6 kcal/mol, is derived from ΔHr° using ΔHf° = -72.38 ± [0.5] kcal/mol (2, 3) for HF(ℓ). Smith (4) quoted a value of ΔHf° = -176 kcal/mol for SF_4 as determined by Nicholls (5) from hydrolysis studies. We do not have details of the hydrolysis studies, but the result presumably should be adjusted for changes in ΔHf° of aqueous HF.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Levin and Berney (6) and are in good agreement with the frequencies reported by Dodd et al. (7) except for the 353 and 171 cm^{-1} bands. The structural data are from the microwave studies of Tolles and Gwinn (8) and are in good agreement within experimental error with electron-diffraction data reported by Kimura and Bauer (9) and Ewing and Sutton (10). Individual moments of inertia calculated from the rotational constants reported by Tolles and Gwinn (8) are $I_A = 1.2552 \times 10^{-38}\ g\ cm^2$, $I_B = 2.0540 \times 10^{-38}\ g\ cm^2$, and $I_C = 2.6069 \times 10^{-38}\ g\ cm^2$.

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Silicon Tetrafluoride (SiF_4)

(Ideal Gas) Mol. Wt. = 104.09

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.659	-384.650	-384.650	INFINITE
100	9.942	52.646	80.836	-2.819	-385.264	-382.298	835.472
200	14.503	61.039	68.947	-1.582	-385.708	-379.141	414.286
298	17.565	67.433	67.433	.000	-385.980	-375.855	275.496
300	17.614	67.541	67.433	.033	-385.984	-375.793	273.752
400	19.850	72.934	68.153	1.912	-386.153	-372.367	203.442
500	21.406	77.541	69.581	3.980	-386.249	-368.910	161.243
600	22.477	81.544	71.249	6.177	-386.289	-365.437	133.104
700	23.224	85.069	72.976	8.464	-386.294	-361.960	113.004
800	23.758	88.206	74.688	10.815	-386.277	-358.486	97.929
900	24.149	91.029	76.349	13.211	-386.247	-355.013	86.205
1000	24.442	93.589	77.947	15.642	-386.211	-351.545	76.826
1100	24.667	95.929	79.477	18.098	-386.171	-348.081	69.154
1200	24.842	98.083	80.939	20.573	-386.128	-344.619	62.761
1300	24.981	100.078	82.335	23.065	-386.084	-341.161	57.352
1400	25.094	101.933	83.670	25.569	-386.040	-337.707	52.716
1500	25.185	103.668	84.946	28.083	-385.997	-334.256	48.699
1600	25.261	105.296	86.167	30.605	-385.956	-330.808	45.184
1700	25.325	106.829	87.338	33.135	-398.018	-327.252	42.069
1800	25.378	108.276	88.462	35.670	-397.940	-323.096	39.227
1900	25.424	109.651	89.541	38.210	-397.861	-318.940	36.685
2000	25.463	110.957	90.579	40.754	-397.784	-314.785	34.396
2100	25.497	112.200	91.580	43.303	-397.708	-310.640	32.327
2200	25.526	113.387	92.544	45.854	-397.636	-306.496	30.446
2300	25.552	114.522	93.475	48.408	-397.565	-302.354	28.729
2400	25.575	115.610	94.375	50.964	-397.498	-298.217	27.155
2500	25.595	116.654	95.245	53.522	-397.435	-294.080	25.707
2600	25.613	117.656	96.088	56.083	-397.373	-289.947	24.371
2700	25.629	118.625	96.905	58.645	-397.314	-285.816	23.134
2800	25.643	119.558	97.698	61.209	-397.257	-281.689	21.986
2900	25.656	120.458	98.467	63.773	-397.206	-277.560	20.916
3000	25.667	121.328	99.215	66.340	-397.158	-273.441	19.919
3100	25.678	122.170	99.942	68.907	-397.112	-269.316	18.986
3200	25.687	122.985	100.649	71.475	-397.071	-265.192	18.111
3300	25.696	123.775	101.338	74.044	-397.033	-261.074	17.289
3400	25.704	124.543	102.009	76.614	-396.998	-256.954	16.516
3500	25.711	125.288	102.664	79.185	-488.006	-251.241	15.687
3600	25.718	126.012	103.302	81.757	-487.915	-244.477	14.841
3700	25.724	126.717	103.926	84.329	-487.830	-237.718	14.041
3800	25.730	127.403	104.534	86.901	-487.750	-230.958	13.282
3900	25.735	128.072	105.129	89.475	-487.673	-224.207	12.564
4000	25.740	128.723	105.711	92.048	-487.600	-217.448	11.880
4100	25.744	129.359	106.280	94.623	-487.532	-210.695	11.231
4200	25.749	129.979	106.837	97.197	-487.468	-203.944	10.612
4300	25.753	130.585	107.382	99.772	-487.405	-197.190	10.022
4400	25.756	131.177	107.916	102.348	-487.350	-190.444	9.459
4500	25.760	131.756	108.440	104.924	-487.296	-183.700	8.921
4600	25.763	132.322	108.953	107.500	-487.247	-176.956	8.407
4700	25.766	132.876	109.456	110.076	-487.203	-170.209	7.914
4800	25.769	133.419	109.950	112.653	-487.160	-163.462	7.442
4900	25.771	133.950	110.434	115.230	-487.123	-156.717	6.990
5000	25.774	134.471	110.910	117.807	-487.090	-149.979	6.555
5100	25.776	134.981	111.377	120.385	-487.060	-143.240	6.138
5200	25.778	135.482	111.835	122.962	-487.035	-136.492	5.736
5300	25.780	135.973	112.286	125.540	-487.012	-129.749	5.350
5400	25.782	136.455	112.729	128.118	-486.996	-123.019	4.979
5500	25.784	136.928	113.165	130.697	-486.981	-116.275	4.620
5600	25.786	137.393	113.593	133.275	-486.973	-109.530	4.274
5700	25.788	137.849	114.015	135.854	-486.968	-102.788	3.941
5800	25.789	138.297	114.430	138.433	-486.965	-96.048	3.619
5900	25.791	138.738	114.838	141.012	-486.969	-89.317	3.308
6000	25.792	139.172	115.240	143.591	-486.977	-82.576	3.008

Dec. 31, 1960; Sept. 30, 1963

SILICON TETRAFLUORIDE (SiF_4) (IDEAL GAS) MOL. WT. = 104.09

Point Group T_d

$S^\circ_{298.15}$ = 67.433 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -384.65 ± 0.19 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -385.98 ± 0.19 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
800 (1)	1031 (3)
268 (2)	391 (3)

Bond Distance: Si-F = 1.54 ± 0.02 Å

Bond Angle: F-Si-F = 109° 28'

σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 7.93269 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation of $SiF_4(g)$ was measured by direct combination of the elements in a bomb calorimeter by S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 67, 815 (1963). $\Delta H^\circ_{f\ 298.15}$ was found to be -385.98 ± 0.19 kcal. mole^{-1}. Heats of the reaction between $SiF_4(g)$ and Na(c), 19% HF solution, 0.4% HF solution, a solution of NaF saturated with Na_2SiF_6, and water have been measured by A. F. Vorob'ev, V. P. Kolesov, and S. M. Skuratov, Zh. Neorg. Khim. 5, 1402 (1960). The value of $\Delta H^\circ_{f\ 298.15}$ for $SiF_4(g)$ was reported to be -372.4 ± 0.4 kcal. mole^{-1} which was not used.

Heat Capacity and Entropy.

The vibrational frequencies used were reported by E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz, and A. H. Nielsen, J. Chem. Phys. 19, 242 (1951). The values of vibrational frequencies were given as 800(1), 285(2), 1000(3), and 431(3) cm.$^{-1}$ for $SiF_4(g)$ by D. M. Yost, E. M. Lassettee, and S. T. Gross, J. Chem. Phys. 4, 325 (1936). The molecular data were obtained from L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 57, 2684 (1935). The three principal moments of inertia are: $I_A = I_B = I_C = 1.99437 \times 10^{-38}$ g. cm.^{2}

Titanium Tetrafluoride (TiF_4)

(Crystal) GFW = 123.8936

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.841	- 393.669	- 393.669	INFINITE
100	13.030	10.031	52.456	- 4.243	- 394.595	- 387.262	846.359
200	22.080	22.173	34.367	- 2.439	- 394.649	- 379.852	415.083
298	27.310	32.016	32.016	.000	- 394.200	- 372.673	273.176
300	27.390	32.185	32.017	.051	- 394.188	- 372.540	271.395
400	30.270	40.483	33.128	2.942	- 393.455	- 365.427	199.660
500	32.160	47.451	35.315	6.068	- 392.589	- 358.520	156.709
600	33.480	53.437	37.848	9.353	- 391.634	- 351.795	128.141
700	34.450	58.673	40.457	12.751	- 390.624	- 345.234	107.787
800	35.190	63.324	43.030	16.235	- 389.582	- 338.822	92.562
900	35.770	67.503	45.521	19.784	- 388.521	- 332.539	80.752
1000	36.250	71.297	47.912	23.385	- 387.454	- 326.378	71.330
1100	36.640	74.771	50.198	27.030	- 386.382	- 320.321	63.642
1200	36.960	77.973	52.381	30.711	- 386.247	- 314.324	57.246
1300	37.240	80.943	54.465	34.421	- 385.057	- 308.379	51.843
1400	37.480	83.712	56.456	38.157	- 383.864	- 302.526	47.226
1500	37.690	86.305	58.361	41.916	- 382.672	- 296.756	43.237

Sept. 30, 1961; June 30, 1964; Sept. 30, 1967

F_4Ti

TITANIUM TETRAFLUORIDE (TiF_4) (CRYSTAL) GFW = 123.8936

ΔHf°_0 = -393.67 ± 0.9 kcal/mol

$S^\circ_{298.15}$ = 32.02 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -394.2 ± 0.9 kcal/mol

Ts = 558.6°K

$\Delta Hs^\circ_{298.15}$ = 23.37 ± 0.1 kcal/mol

Heat of Formation

The heat of formation ($\Delta Hf^\circ_{298.15}$) of TiF_4(c) was measured using a fluorine bomb calorimeter by Greenberg et al. (1). Gross et al. (2) reported a value of -393.4 kcal/mol for ΔHf°_{298}. The latter measurements were not corrected for impurities in the titanium sample, thus the value reported by Greenberg et al. is adopted.

Heat Capacity and Entropy

The heat capacity of TiF_4(c) has been measured over the temperature range 6° to 304°K by Euler and Westrum (3). They obtained the value of S°_{298} based on S°_{10} = 0.11 eu. Heat capacities above 300°K are estimated from those of ZrF_4(c) (4).

Heat of Sublimation

The sublimation point is calculated as the temperature at which ΔGr° = 0 for $TiF_4(c) = TiF_4(g)$. The heat of sublimation is obtained from the data of Hall et al. (5).

References

1. E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem. 66, 1345 (1962).
2. P. Gross, C. Hayman, and D. L. Levi, XVIIth Interim. Congr. Pure Appl. Chem. Abstr. 1, 90 (1959).
3. R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. 65, 132 (1961).
4. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).
5. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 105, 275 (1958).

Titanium Tetrafluoride (TiF_4)

(Ideal Gas) GFW = 123.8936

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.508	-369.936	-369.936	INFINITE
100	14.013	56.606	91.520	-3.491	-370.443	-367.768	803.756
200	17.807	67.630	77.028	-1.880	-370.690	-364.984	398.836
298	20.357	75.243	75.243	.000	-370.800	-362.161	265.471
300	20.397	75.369	75.243	.038	-370.801	-362.107	263.795
400	22.126	81.492	76.066	2.170	-370.827	-359.202	196.259
500	23.211	86.556	77.672	4.442	-370.815	-356.299	155.738
600	23.905	90.853	79.520	6.800	-370.787	-353.398	128.725
700	24.364	94.575	81.411	9.215	-370.760	-350.502	109.431
800	24.682	97.850	83.265	11.668	-370.749	-347.610	94.963
900	24.908	100.771	85.051	14.148	-370.757	-344.717	83.709
1000	25.075	103.405	86.757	16.648	-370.791	-341.823	74.705
1100	25.201	105.801	88.381	19.162	-370.850	-338.922	67.338
1200	25.298	107.998	89.925	21.687	-371.871	-335.978	61.190
1300	25.375	110.026	91.395	24.221	-371.857	-332.987	55.980
1400	25.436	111.909	92.793	26.761	-371.860	-329.998	51.515
1500	25.486	113.665	94.127	29.308	-371.880	-327.005	47.645
1600	25.527	115.312	95.400	31.858	-371.923	-324.013	44.258
1700	25.562	116.860	96.617	34.413	-371.987	-321.016	41.269
1800	25.591	118.322	97.783	36.970	-372.079	-318.019	38.613
1900	25.615	119.706	98.901	39.531	-372.193	-315.012	36.235
2000	25.636	121.021	99.974	42.093	-376.783	-311.842	34.077
2100	25.654	122.272	101.006	44.658	-376.928	-308.594	32.116
2200	25.670	123.466	102.000	47.224	-377.078	-305.338	30.332
2300	25.684	124.607	102.959	49.792	-377.230	-302.071	28.703
2400	25.696	125.701	103.884	52.361	-377.387	-298.801	27.209
2500	25.706	126.750	104.777	54.931	-377.549	-295.523	25.835
2600	25.716	127.758	105.642	57.502	-377.714	-292.239	24.565
2700	25.724	128.729	106.479	60.074	-377.882	-288.946	23.389
2800	25.732	129.665	107.291	62.647	-378.053	-285.652	22.296
2900	25.739	130.568	108.078	65.220	-378.230	-282.343	21.278
3000	25.745	131.440	108.842	67.795	-378.411	-279.040	20.328
3100	25.750	132.285	109.585	70.369	-378.595	-275.723	19.438
3200	25.756	133.102	110.307	72.945	-378.783	-272.403	18.604
3300	25.760	133.895	111.010	75.520	-378.976	-269.075	17.820
3400	25.764	134.664	111.694	78.097	-379.171	-265.740	17.082
3500	25.768	135.411	112.361	80.673	-379.373	-262.398	16.385
3600	25.772	136.137	113.012	83.250	-481.202	-258.789	15.711
3700	25.775	136.843	113.646	85.828	-481.382	-252.611	14.921
3800	25.778	137.530	114.266	88.405	-481.580	-246.426	14.173
3900	25.781	138.200	114.871	90.983	-481.796	-240.237	13.463
4000	25.783	138.853	115.462	93.561	-482.027	-234.037	12.787
4100	25.786	139.489	116.041	96.140	-482.276	-227.836	12.145
4200	25.788	140.111	116.606	98.719	-482.541	-221.628	11.533
4300	25.790	140.718	117.160	101.297	-482.821	-215.410	10.948
4400	25.792	141.311	117.702	103.877	-483.118	-209.190	10.391
4500	25.794	141.890	118.233	106.456	-483.429	-202.963	9.857
4600	25.795	142.457	118.754	109.035	-483.754	-196.723	9.346
4700	25.797	143.012	119.264	111.615	-484.094	-190.480	8.857
4800	25.799	143.555	119.764	114.195	-484.446	-184.226	8.388
4900	25.800	144.087	120.255	116.775	-484.813	-177.970	7.938
5000	25.801	144.608	120.737	119.355	-485.192	-171.703	7.505
5100	25.802	145.119	121.210	121.935	-485.583	-165.437	7.089
5200	25.804	145.620	121.675	124.515	-485.986	-159.146	6.689
5300	25.805	146.112	122.131	127.096	-486.399	-152.858	6.303
5400	25.806	146.594	122.580	129.676	-486.826	-146.567	5.932
5500	25.807	147.068	123.021	132.257	-487.259	-140.257	5.573
5600	25.808	147.533	123.455	134.838	-487.705	-133.946	5.227
5700	25.809	147.989	123.881	137.418	-488.160	-127.620	4.893
5800	25.809	148.438	124.300	139.999	-488.622	-121.292	4.570
5900	25.810	148.880	124.713	142.580	-489.094	-114.960	4.258
6000	25.811	149.313	125.120	145.161	-489.574	-108.617	3.956

Sept. 30, 1961; June 30, 1964; Sept. 30, 1967

TITANIUM TETRAFLUORIDE (TiF_4) (IDEAL GAS) GFW = 123.8936

Point Group [T_d]

$S°_{298.15}$ = 75.24 ± 0.5 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -369.9 ± 1 kcal/mol

$\Delta Hf°_{298.15}$ = -370.8 ± 1 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[701] (1)	[750] (3)
[168] (2)	[178] (3)

Bond Distance: Ti-F = [1.80] Å

Bond Angle: F-Ti-F = [109°28']

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.02 x 10^{-113}] g^3 cm^6 σ = [12]

Heat of Formation

The heat of formation of $TiF_4(g)$ is calculated from that of the crystal and the heat of sublimation, $\Delta Hs°_{298}$, obtained from vapor pressure measurements. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 105, 275 (1958), have reported extensive vapor pressure data for the reaction $TiF_4(c) = TiF_4(g)$. Second and third law analyses of their data yielded the following results.

Method	No. Pts.	Range, T°K	$\Delta Hr°_{298}$, kcal/mol 2nd Law	$\Delta Hr°_{298}$, kcal/mol 3rd Law	Drift, eu	$\Delta Hf°_{298}$*
1. Spoon Gauge	26**	441-552	23.5 ± 0.1	23.37	-0.3 ± 0.1	-370.8
2. Ruff-Fischer	6	435-498	23.0 ± 0.4	23.40	+0.9 ± 0.9	-370.8
3. Transpiration	3	426-512	25.8 ± 2.0	23.72	-4.5 ± 4.3	-370.5
4. Rodebush	6	473-537	23.7 ± 0.6	23.39	-0.5 ± 1.2	-370.8
5. 1, 2, and 4	36***	435-552	23.4 ± 0.1	23.37	-0.1 ± 0.1	-370.8

*Calculation based on third law $\Delta Hr°_{298}$.

**Four points rejected due to failure of a statistical test.

***Eight points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The interatomic distance is obtained from a correlation of the measured values for $TiCl_4(g)$, $TiBr_4(g)$, $TiCl_6^{-2}$, and TiF_6^{-2}. The principal moments of inertia are $I_A = I_B = I_C$ = 2.724 x 10^{-38} g cm^2.

The vibrational frequencies are estimated by a valence force field treatment of estimated force constants. The force constants are estimated from a correlation with the constants of CF_4, SiF_4, CCl_4, $SiCl_4$, CBr_4, $SiBr_4$, $TiCl_4$ and $TiBr_4$. The resulting frequencies are adjusted so that calculations of $\Delta Hs°_{298}$ by both second and third law methods are in agreement.

Zirconium Tetrafluoride (ZrF_4)

(Crystal) GFW = 167.2136

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.182	-455.441	-455.441	INFINITE
100	10.060	5.481	43.591	-3.811	-456.672	-448.746	980.733
200	20.210	15.991	27.166	-2.235	-457.022	-440.614	481.480
298	24.760	25.024	25.024	.000	-456.800	-432.595	317.101
300	24.810	25.177	25.024	.046	-456.793	-432.445	315.036
400	27.120	32.663	26.029	2.653	-456.349	-424.391	231.876
500	28.610	38.883	27.996	5.444	-455.823	-416.463	182.036
600	29.630	44.195	30.264	8.359	-455.250	-408.644	148.848
700	30.350	48.820	32.591	11.360	-454.657	-400.922	125.174
800	30.930	52.911	34.881	14.424	-454.058	-393.288	107.441
900	31.510	56.587	37.092	17.546	-453.450	-385.728	93.668
1000	32.050	59.936	39.211	20.725	-452.830	-378.237	82.664
1100	32.560	63.014	41.237	23.955	-452.201	-370.809	73.673
1200	33.050	65.868	43.172	27.235	-452.411	-363.385	66.181
1300	33.550	68.533	45.021	30.565	-451.581	-355.999	59.849
1400	34.060	71.039	46.791	33.946	-450.719	-348.679	54.431

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; June 30, 1969

F_4Zr

ZIRCONIUM TETRAFLUORIDE (ZrF_4) (CRYSTAL) GFW = 167.2136

$S°_{298.15}$ = 25.024 ± 0.05 gibbs/mol

Tt(α → β) = 723°K

Tm = 1205 ± 2°K

Ts = 1179°K

$\Delta Hf°_0$ = -455.44 ± 0.25 kcal/mol

$\Delta Hf°_{298.15}$ = -456.80 ± 0.25 kcal/mol

ΔHt° = Unavailable

ΔHm° = 15.35 ± 0.10 kcal/mol

ΔHs° = 51.64 kcal/mol

$\Delta Hs°_{298.15}$ = 56.80 kcal/mol

Heat of Formation

The heat of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg, Settle, Feder, and Hubbard (1). The reported value $\Delta Hf°_{298}(ZrF_4, c)$ = -456.80 ± 0.25 kcal/mol is adopted.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307°K were determined by adiabatic calorimetry by Westrum (2). Using these low temperature Cp data the value of $S°_{298}$ is derived as 25.024 ± 0.05 eu, based on $S°_{10}$ = 0.0074 eu.

McDonald, Sinke, and Stull (3) measured the high temperature enthalpies of $ZrF_4(c)$ at temperatures 283.9 - 1225.8°K in a copper block drop calorimeter. Smith, Miller, and Taylor (4) used a Bunsen ice calorimeter for the heat-content measurements in the temperature range 273 - 1150°K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298°K, the high temperature heat capacities derived from the enthalpy data of McDonald, Sinke, and Stull (3) are adopted. The Cp values above 1200°K are obtained by smooth extrapolation.

Transition Data

Zirconium tetrafluoride has three crystal structures (α, β and γ) and one amorphous form (5). From a differential thermal analysis of $(NH_4)_3 ZrF_7$ sample, Chrétien and Gaudreau (6) found that $ZrF_4(c)$ has an α and β form with a transition temperature above 678°K. They also determined the densities of α(tetragonal) and β(monoclinic) as 4.25 ± 0.05 and 4.61 ± 0.03 gm/cc, and a transition temperature as Tt(α → β) = 723°K (7). It was observed that the α phase is unstable at all temperatures above 298°K. In reference (5), Gaudreau mentioned the methods of preparation of the four varieties of ZrF_4 and indicated that α-, γ-, and amorphous ZrF_4 transform irreversibly to β-ZrF_4 at 723 - 773°K.

The ZrF_4 sample employed by McDonald, Sinke, and Stull (3) for enthalpy measurement was prepared by disolving hafnium-free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773°K in a platinum boat in a slow current of anhydrous HF. X-ray diffraction showed only crystalline ZrF_4. Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms or a pure ZrF_4(β). Smith, Miller, and Taylor (4) obtained their ZrF_4 sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above complicated situation, we emphasize that this $ZrF_4(c)$ table is not strictly a α, β-combined phase table. However, the differences in the calculated functions are probably not significant.

Melting Data

Tm and ΔHm° are taken from McDonald, Sinke, and Stull (3). The values were obtained under conditions greater than one atmosphere.

Sublimation Data

The sublimation temperature (Ts) is calculated as the temperature at which the Gibbs energy change of the process $ZrF_4(c) = ZrF_4(g)$ approaches zero. The difference between $\Delta Hf°_{298}$ for $ZrF_4(g)$ and $ZrF_4(c)$ at 1179 and 298°K is ΔHs° and $\Delta Hs°_{298}$, respectively.

Since ths sublimation temperature is lower than the melting point, the ZrF_4 sublimes before it melts.

References

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6. A. Chrétien and B. Gaudreau, Compt. Rend. 246, 2266 (1958).
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Zirconium Tetrafluoride (ZrF_4)

(Ideal Gas) GFW = 167.2136

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.527	-398.986	-398.986	INFINITE
100	13.653	57.560	92.910	-3.535	-399.596	-396.878	867.375
200	18.119	68.546	78.169	-1.925	-399.912	-394.014	430.559
298	20.887	76.339	76.339	.000	-400.000	-391.095	286.680
300	20.927	76.468	76.339	.039	-400.000	-391.039	284.872
400	22.603	82.740	77.183	2.223	-399.979	-388.053	212.022
500	23.593	87.899	78.826	4.537	-399.930	-385.078	168.318
600	24.205	92.259	80.711	6.929	-399.880	-382.112	139.184
700	24.603	96.022	82.635	9.371	-399.846	-379.153	118.377
800	24.873	99.326	84.519	11.845	-399.837	-376.199	102.773
900	25.065	102.267	86.331	14.343	-399.853	-373.244	90.636
1000	25.205	104.916	88.059	16.856	-399.899	-370.286	80.926
1100	25.310	107.323	89.703	19.382	-399.974	-367.321	72.980
1200	25.391	109.529	91.264	21.918	-400.928	-364.296	66.347
1300	25.455	111.564	92.749	24.460	-400.886	-361.244	60.731
1400	25.506	113.453	94.161	27.008	-400.857	-358.196	55.917
1500	25.548	115.214	95.506	29.561	-400.842	-355.148	51.745
1600	25.582	116.864	96.790	32.118	-400.843	-352.104	48.095
1700	25.610	118.415	98.017	34.677	-400.858	-349.055	44.874
1800	25.634	119.880	99.191	37.239	-400.890	-346.011	42.011
1900	25.654	121.266	100.317	39.804	-400.934	-342.959	39.449
2000	25.671	122.583	101.398	42.370	-400.994	-339.905	37.143
2100	25.686	123.836	102.437	44.938	-401.069	-336.852	35.057
2200	25.699	125.031	103.437	47.507	-406.163	-333.615	33.142
2300	25.710	126.174	104.401	50.078	-406.262	-330.313	31.387
2400	25.720	127.268	105.331	52.649	-406.367	-327.010	29.778
2500	25.729	128.318	106.229	55.222	-406.474	-323.702	28.298
2600	25.737	129.327	107.098	57.795	-406.589	-320.387	26.931
2700	25.744	130.299	107.940	60.369	-406.705	-317.068	25.665
2800	25.750	131.235	108.755	62.944	-406.824	-313.748	24.489
2900	25.756	132.139	109.546	65.519	-406.949	-310.418	23.394
3000	25.761	133.012	110.314	68.095	-407.079	-307.094	22.372
3100	25.765	133.857	111.060	70.671	-407.211	-303.758	21.415
3200	25.770	134.675	111.785	73.248	-407.348	-300.417	20.518
3300	25.773	135.468	112.491	75.825	-407.489	-297.074	19.674
3400	25.777	136.237	113.178	78.403	-407.633	-293.725	18.880
3500	25.780	136.985	113.847	80.981	-407.783	-290.369	18.131
3600	25.783	137.711	114.500	83.559	-407.935	-287.011	17.424
3700	25.785	138.417	115.137	86.137	-408.093	-283.652	16.755
3800	25.788	139.105	115.759	88.716	-408.254	-280.284	16.120
3900	25.790	139.775	116.366	91.295	-408.421	-276.920	15.518
4000	25.792	140.428	116.960	93.874	-408.590	-273.542	14.946
4100	25.794	141.065	117.540	96.453	-408.765	-270.166	14.401
4200	25.796	141.687	118.107	99.033	-408.943	-266.782	13.882
4300	25.798	142.294	118.663	101.612	-409.124	-263.392	13.387
4400	25.799	142.887	119.207	104.192	-409.312	-260.003	12.914
4500	25.801	143.466	119.739	106.772	-409.502	-256.611	12.463
4600	25.802	144.034	120.261	109.352	-409.696	-253.210	12.030
4700	25.804	144.588	120.773	111.933	-409.895	-249.805	11.616
4800	25.805	145.132	121.275	114.513	-551.254	-245.711	11.188
4900	25.806	145.664	121.767	117.094	-551.565	-239.341	10.675
5000	25.807	146.185	122.250	119.674	-551.887	-232.968	10.183
5100	25.808	146.696	122.725	122.255	-552.217	-226.594	9.710
5200	25.809	147.197	123.190	124.836	-552.555	-220.197	9.255
5300	25.810	147.689	123.648	127.417	-552.901	-213.801	8.816
5400	25.811	148.171	124.098	129.998	-553.257	-207.408	8.394
5500	25.812	148.645	124.540	132.579	-553.619	-200.997	7.987
5600	25.812	149.110	124.974	135.160	-553.989	-194.579	7.594
5700	25.813	149.567	125.402	137.742	-554.366	-188.157	7.214
5800	25.814	150.016	125.822	140.323	-554.748	-181.729	6.848
5900	25.814	150.457	126.236	142.904	-555.138	-175.300	6.494
6000	25.815	150.891	126.643	145.486	-555.534	-168.859	6.151

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; June 30, 1969

ZIRCONIUM TETRAFLUORIDE (ZrF_4) (IDEAL GAS) GFW = 167.2136

Point Group Td

$\Delta Hf°_0$ = -399.0 ± 1.0 kcal/mol

$S°_{298.15}$ = [76.3 ± 1] gibbs/mol

$\Delta Hf°_{298.15}$ = -400.0 ± 1.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[630] (1)	668 (3)
[180] (2)	190 (3)

Bond Distance: Zr-F = 1.94 ± 0.02 Å

Bond Angle: F-Zr-F = 109.47°

σ = 12

Product of the Moments of Inertia: $I_AI_BI_C = 3.17347 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation

The vapor pressures of $ZrF_4(c)$ in the temperature range 617-1150°K were determined by many investigators using various methods. Based on the reported vapor pressure data, the corresponding heats of sublimation are evaluated by the second and third law methods. Using the third law $\Delta Hs°_{298}$ and $\Delta Hf°_{298}(ZrF_4, c)$ = -456.8 kcal/mol, the heats of formation at 298°K for $ZrF_4(g)$ are evaluated. The results are presented in the table below. The values of $\Delta Hf°_{298}(ZrF_4, g)$ listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies ν_1 and ν_2 are reasonable. The heat of formation at 298°K for $ZrF_4(g)$ is adopted as -400.0 kcal/mol.

Investigator	Method	Temperature, °K	No. of Points	$\Delta Hs°_{298}$, kcal/mol Second Law	Third Law	Drift eu	$\Delta Hf°_{298}$ kcal/mol
1. Lauter (1948)	unavailable	950-1150	Equn.	56.49±0.12	56.83	0.3	-399.97
2. Sense et al. (1954)	transpiration	617-881	14	60.67±0.09	57.13	-3.4±0.1	-399.67
3. Sense et al. (1957)	transpiration	900-1150	6	60.64±0.13	57.24	-3.3±0.1	-399.56
4. Cantor (1958)	quasistatic	710-808	29	56.11±0.62	56.65	0.5±0.6	-400.15
5. Hildenbrand-Theard (1961)	torsion-effusion	748-849	15	55.81±1.44	57.05	1.5±1.8	-399.75
6. Hildenbrand-Theard (1961)	torsion-effusion	735-825	10	52.59±0.39	57.09	5.7±0.5	-399.71
7. Galkin et al. (1963)	Knudsen-effusion	720-850	5	51.53±0.06	54.79	4.1±0.1	-402.01
8. Akishin et al. (1963)	mass spectrometry	700-900	5	59.25±2.34	57.30	-2.4±2.9	-399.50
9. Fischer et al. (1964)	"bell method"	1000-1150	Equn.	57.38±0.12	56.89	-0.5	-399.91
10. Sidorov et al. (1965)	mass spectrometry	769	1	—	57.58	—	-399.22

Heat Capacity and Entropy

The molecular structure of $ZrF_4(g)$ has been studied by electron diffraction by Spiridonov (11). The configuration was found to be a regular tetrahedron with interatomic distance Zr-F = 1.94 ± 0.02 Å and F-Zr-F bond angle = 109.47° which are adopted.

Employing the estimated interaction coefficients and interatomic distance Zr-F = 1.85 Å, Godnev, Aleksandrovskaia, and Rigina (12) calculated three vibrational frequencies for $ZrF_4(g)$ as ν_1 = 600 - 725, ν_2 = 150 - 200, and ν_4 = 180 ± 230 cm^{-1}. Büchler, Berkowitz, and Dugre (13) observed the infrared spectra of some group IV halides and assigned ν_3 = 668 and ν_4 = 190 ± 20 cm^{-1} for $ZrF_4(g)$. The frequency ν_3 has also been reported as 670 cm^{-1} (14). The values of ν_3 and ν_4 adopted here are those reported by Büchler, Berkowitz, and Dugre (13). The adopted ν_1 is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. ν_2 is calculated from ν_1, ν_3 and ν_4 using the relationship (15) $\frac{\nu_3\nu_4}{\nu_1\nu_2} = \sqrt{\frac{2}{3}(1+\frac{4F}{Zr})}$ where F and Zr are gram atomic weights of fluorine and zirconium, respectively. The three principal moments of inertia are $I_A = I_B = I_C = 3.166 \times 10^{-38}\ g\ cm^2$.

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Iodine Pentafluoride (IF_5)

(Ideal Gas) GFW = 221.8964

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.792	-198.780	-198.780	INFINITE
100	12.552	59.852	98.521	-3.867	-199.957	-195.039	426.258
200	20.063	71.020	82.081	-2.212	-200.641	-189.804	207.408
298	24.588	79.959	79.959	.000	-200.840	-184.431	135.191
300	24.651	80.111	79.959	.046	-200.841	-184.329	134.284
400	27.188	87.586	80.961	2.650	-202.748	-178.755	97.667
500	28.635	93.822	82.928	5.447	-207.730	-172.290	75.308
600	29.512	99.127	85.197	8.358	-207.347	-165.237	60.188
700	30.076	103.721	87.522	11.339	-206.943	-158.250	49.408
800	30.457	107.764	89.805	14.367	-206.531	-151.323	41.340
900	30.726	111.367	92.004	17.427	-206.113	-144.447	35.077
1000	30.922	114.615	94.105	20.510	-205.695	-137.618	30.076
1100	31.069	117.570	96.106	23.610	-205.279	-130.832	25.994
1200	31.182	120.278	98.009	26.723	-204.863	-124.080	22.598
1300	31.271	122.778	99.820	29.845	-204.452	-117.364	19.731
1400	31.342	125.098	101.543	32.976	-204.045	-110.681	17.278
1500	31.399	127.262	103.187	36.113	-203.642	-104.025	15.156
1600	31.446	129.290	104.755	39.256	-203.244	-97.398	13.304
1700	31.486	131.198	106.255	42.402	-202.850	-90.793	11.672
1800	31.519	132.999	107.691	45.553	-202.463	-84.217	10.225
1900	31.547	134.703	109.069	48.706	-202.080	-77.656	8.932
2000	31.571	136.322	110.391	51.862	-201.701	-71.115	7.771
2100	31.591	137.863	111.663	55.020	-201.329	-64.599	6.723
2200	31.609	139.333	112.888	58.180	-200.963	-58.097	5.771
2300	31.625	140.739	114.068	61.342	-200.600	-51.609	4.904
2400	31.639	142.085	115.208	64.505	-200.245	-45.139	4.110
2500	31.651	143.377	116.309	67.669	-199.896	-38.685	3.382
2600	31.662	144.618	117.374	70.835	-199.552	-32.242	2.710
2700	31.671	145.813	118.405	74.002	-199.213	-25.811	2.089
2800	31.680	146.965	119.405	77.169	-198.878	-19.397	1.514
2900	31.688	148.077	120.374	80.338	-198.551	-12.989	.979
3000	31.695	149.151	121.316	83.507	-198.231	-6.604	.481
3100	31.701	150.191	122.231	86.676	-197.914	-.220	.016
3200	31.707	151.197	123.120	89.847	-197.604	6.153	-.420
3300	31.712	152.173	123.986	93.018	-197.300	12.516	-.829
3400	31.717	153.120	124.829	96.189	-197.000	18.870	-1.213
3500	31.721	154.039	125.650	99.361	-196.708	25.220	-1.575
3600	31.725	154.933	126.451	102.533	-196.420	31.558	-1.916
3700	31.729	155.802	127.233	105.706	-196.138	37.884	-2.238
3800	31.732	156.648	127.996	108.879	-195.862	44.209	-2.543
3900	31.735	157.473	128.741	112.053	-195.594	50.516	-2.831
4000	31.738	158.276	129.470	115.226	-195.329	56.826	-3.105
4100	31.741	159.060	130.182	118.400	-195.072	63.126	-3.365
4200	31.744	159.825	130.879	121.574	-194.820	69.421	-3.612
4300	31.746	160.572	131.560	124.749	-194.571	75.713	-3.848
4400	31.748	161.302	132.228	127.924	-194.333	81.993	-4.073
4500	31.750	162.015	132.882	131.098	-194.098	88.268	-4.287
4600	31.752	162.713	133.523	134.274	-193.867	94.541	-4.492
4700	31.754	163.396	134.151	137.449	-193.645	100.808	-4.688
4800	31.755	164.064	134.768	140.624	-193.426	107.076	-4.875
4900	31.757	164.719	135.372	143.800	-193.215	113.335	-5.055
5000	31.759	165.361	135.966	146.976	-193.010	119.586	-5.227
5100	31.760	165.990	136.548	150.152	-192.809	125.827	-5.392
5200	31.761	166.607	137.120	153.328	-192.615	132.083	-5.551
5300	31.763	167.212	137.682	156.504	-192.426	138.329	-5.704
5400	31.764	167.805	138.235	159.680	-192.245	144.557	-5.851
5500	31.765	168.388	138.778	162.857	-192.067	150.797	-5.992
5600	31.766	168.960	139.312	166.033	-191.898	157.030	-6.128
5700	31.767	169.523	139.837	169.210	-191.734	163.261	-6.260
5800	31.768	170.075	140.353	172.387	-191.572	169.488	-6.386
5900	31.769	170.618	140.862	175.563	-191.419	175.704	-6.508
6000	31.770	171.152	141.362	178.740	-191.272	181.927	-6.627

Mar. 31, 1962; Dec. 31, 1963; Mar. 31, 1966; Dec. 31, 1969

IODINE PENTAFLUORIDE (IF_5) (IDEAL GAS) GFW = 221.8964

Point Group C_{4v}

ΔHf°_0 = -198.8 ± 0.4 kcal/mol

$S^\circ_{298.15}$ = 79.96 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -200.84 ± 0.35 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = [1.86] Å I-F(axial) = [1.75] Å

Bond Angle: F-I-F = [90°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.10383 x 10^{-113}] g^3 cm^6

σ = 4

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF_5 and IF_7, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔHf° = $-210.8_0 \pm 0.3_2$ kcal/mol for $IF_5(\ell)$ at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [≥1] and -208.8 ± [≥1.7] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3). In particular, we estimate lower limits of ±0.8 kcal/mol for ΔHf° of $HIO_3(1250\ H_2O)$ and $KIO_3(1250\ H_2O)$ by comparison with recent data (4).

ΔHf° for the ideal gas is derived from that of the liquid by use of ΔHv° = 9.96 kcal/mol at 298.15 K. ΔHv° was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF_5, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF_5, IF_5, ClF_5, and $XeOF_4$ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF_7. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are $I_A = I_B = 30.66 \times 10^{-39}$ and $I_C = 43.65 \times 10^{-39}$ g cm^2.

Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν_9 (∿200 cm^{-1}) is difficult, so we substitute the liquid value of 190 cm^{-1}. The Raman-active fundamental ν_5 is not observed for IF_5, or any of the similar molecules, so its value is taken from the calculations (7).

Osborne et al. (5) used calorimetric data at low temperatures to derive S° = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔSv° based on their vapor pressure equation, the authors obtained S° = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (82.50) is lower by 0.56 gibbs/mol. Part of this difference arises from uncertainties in ν_5, ν_9, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

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Phosphorus Pentafluoride (PF_5)
(Ideal Gas) GFW = 125.966

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.950	-374.713	-374.713	INFINITE
100	10.598	55.939	86.608	-3.067	-375.658	-370.929	810.665
200	15.576	64.732	73.580	-1.770	-376.429	-365.880	399.815
298	20.276	71.868	71.868	.000	-376.900	-360.591	264.321
300	20.352	71.994	71.869	.038	-376.906	-360.491	262.617
400	23.718	78.342	72.711	2.252	-377.150	-354.975	193.949
500	25.941	83.891	74.405	4.743	-377.247	-349.420	152.731
600	27.416	88.760	76.400	7.416	-377.256	-343.852	125.248
700	28.421	93.066	78.479	10.211	-377.221	-338.287	105.618
800	29.128	96.910	80.547	13.090	-397.590	-338.041	92.348
900	29.640	100.372	82.561	16.030	-397.276	-330.614	80.284
1000	30.021	103.515	84.502	19.014	-396.944	-323.227	70.641
1100	30.310	106.391	86.363	22.031	-396.598	-315.872	62.758
1200	30.536	109.038	88.143	25.074	-396.240	-308.548	56.194
1300	30.714	111.490	89.846	28.137	-395.879	-301.254	50.645
1400	30.857	113.771	91.475	31.215	-395.513	-293.989	45.894
1500	30.974	115.904	93.033	34.307	-395.144	-286.747	41.779
1600	31.071	117.907	94.526	37.410	-394.776	-279.536	38.183
1700	31.151	119.793	95.957	40.521	-394.408	-272.342	35.012
1800	31.219	121.575	97.331	43.639	-394.043	-265.177	32.197
1900	31.277	123.265	98.652	46.764	-393.477	-258.025	29.680
2000	31.327	124.870	99.923	49.895	-393.314	-250.894	27.416
2100	31.369	126.400	101.148	53.029	-392.954	-243.785	25.371
2200	31.407	127.860	102.329	56.168	-392.599	-236.689	23.513
2300	31.439	129.257	103.470	59.311	-392.245	-229.609	21.818
2400	31.468	130.596	104.572	62.456	-391.897	-222.548	20.266
2500	31.493	131.881	105.639	65.604	-391.552	-215.497	18.839
2600	31.516	133.116	106.672	68.754	-391.212	-208.463	17.523
2700	31.536	134.306	107.674	71.907	-390.875	-201.438	16.305
2800	31.554	135.453	108.646	75.061	-390.541	-194.430	15.176
2900	31.570	136.561	109.589	78.218	-390.213	-187.427	14.125
3000	31.584	137.631	110.506	81.375	-389.892	-180.448	13.146
3100	31.598	138.667	111.398	84.534	-389.572	-173.469	12.230
3200	31.610	139.671	112.266	87.695	-389.259	-166.504	11.372
3300	31.621	140.643	113.111	90.856	-388.949	-159.547	10.566
3400	31.631	141.588	113.935	94.019	-388.645	-152.600	9.809
3500	31.640	142.505	114.738	97.183	-388.344	-145.656	9.095
3600	31.648	143.396	115.522	100.347	-388.050	-138.727	8.422
3700	31.656	144.263	116.287	103.512	-387.761	-131.807	7.785
3800	31.663	145.108	117.034	106.678	-387.476	-124.888	7.183
3900	31.670	145.930	117.765	109.845	-387.199	-117.988	6.612
4000	31.676	146.732	118.479	113.012	-386.923	-111.087	6.070
4100	31.682	147.514	119.178	116.180	-386.655	-104.197	5.554
4200	31.687	148.278	119.861	119.348	-386.392	-97.307	5.063
4300	31.692	149.023	120.531	122.517	-386.131	-90.426	4.596
4400	31.696	149.752	121.187	125.687	-385.880	-83.552	4.150
4500	31.701	150.464	121.830	128.857	-385.631	-76.688	3.724
4600	31.705	151.161	122.460	132.027	-385.387	-69.827	3.318
4700	31.709	151.843	123.078	135.198	-385.150	-62.968	2.928
4800	31.712	152.511	123.684	138.369	-384.916	-56.110	2.555
4900	31.715	153.165	124.279	141.540	-384.689	-49.260	2.197
5000	31.719	153.805	124.863	144.712	-384.467	-42.419	1.854
5100	31.722	154.434	125.437	147.884	-384.251	-35.590	1.525
5200	31.724	155.050	126.000	151.056	-384.039	-28.747	1.208
5300	31.727	155.654	126.554	154.229	-383.832	-21.913	.904
5400	31.729	156.247	127.098	157.401	-383.633	-15.099	.611
5500	31.732	156.829	127.634	160.574	-383.434	-8.268	.329
5600	31.734	157.401	128.160	163.748	-383.247	-1.447	.056
5700	31.736	157.963	128.678	166.921	-383.063	5.371	-.206
5800	31.738	158.515	129.188	170.095	-382.882	12.182	-.459
5900	31.740	159.057	129.690	173.269	-382.707	18.985	-.703
6000	31.742	159.591	130.183	176.443	-382.539	25.794	-.940

June 30, 1963; Dec. 31, 1969

PHOSPHORUS PENTAFLUORIDE (PF_5) (IDEAL GAS) GFW = 125.966

Point Group D_{3h}

$S^\circ_{298.15}$ = 71.87 ± 0.5 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -374.7 ± 0.7 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -376.9 ± 0.7 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
817 (1)	1025 (2)
640 (1)	532.5 (2)
946.6 (1)	179 (2)
575.1 (1)	514 (2)

Bond Distance: (P-F)eq. = 1.534 ± 0.004 Å (P-F)ax = 1.577 ± 0.005 Å

Bond Angle: $F_{eq.}$-P-$F_{eq.}$ = 120° ± 0.4° $F_{eq.}$-P-$F_{ax.}$ = 74.3° ± 0.4°

Product of Moments of Inertia: $I_AI_BI_C = 1.614 \times 10^{-113}\ g^3\ cm^6$ $\sigma = 6$

Heat of Formation

Gross, Hayman, and Stuart (1) measured the heat of combustion of α-white phosphorus in fluorine at 25°C. They reported a heat of formation of -381.4 ± 0.8 kcal/mol (based on α-white phosphorus standard state) calculated from their combustion studies. Similar combustion studies were performed by O'Hare and Hubbard (2). They reported a heat of formation of -380.8 ± 0.3 kcal/mol (α-white phosphorus standard state), which is in excellent agreement with the work of Gross et al. (1). An average value of -381.1 ± 0.5 kcal/mol is adopted for this tabulation. Converting to the P(red, V) standard state with a ΔH trans = 4.2 ± 0.2 kcal/mol (3), we derive, $\Delta Hf^\circ_{298}(PF_5, g)$ = -376.9 ± 0.7 kcal/mol.

Heat Capacity and Entropy

The molecular structure and bond lengths given above for PF_5 were recently determined by Hansen and Bartell (4) from electron-diffraction studies. These results indicate that PF_5 has a trigonal bipyramid structure with nonequivalent axial and equatorial bonds. Wyatt et al. (5) determined rotational constants for PF_5 from a study of the infrared vibration-rotation band contour of the ν_4 (575 cm^{-1}) fundamental. Their analysis led to the following P-F bond lengths which are in excellent agreement with the electron-diffraction results: $r_{eq.}$ = 1.534 ± 0.024 Å and r_{ax} = 1.581 ± 0.025 Å. Individual moments of inertia, calculated from the rotational constants given by Wyatt et al. (5) and adopted for this table, are $I_A = 2.230 \times 10^{-38}\ g\ cm^2$ and $I_B = I_C = 2.690 \times 10^{-38}\ g\ cm^2$. The electron diffraction data lead to a product of moments of inertia of $1.604 \times 10^{-113}\ g^3\ cm^6$.

Several recent infrared and Raman studies (6, 7, and 8) have been reported for PF_5. These data are in good agreement except for the ν_7 fundamental. Griffiths et al. (6) originally assigned this fundamental to the 126 cm^{-1} band observed in their infrared spectra. Hoskins (9) later attributed this band to one of the pure rotational lines of hydrogen fluoride, which he felt was present in the sample as an impurity. Further work by Griffiths (10) on the pressure dependence of the infrared spectra of PF_5 indicated that the missing fundamental should be assigned to the weak band at 301 cm^{-1}. Deiters and Holmes (11) recently showed that this band is not a fundamental of PF_5 but a difference band (ν_3-ν_2). Very recently, Levin (8) investigated the Raman spectra of solid phosphorus pentafluoride and assigned the ν_7 fundamental to the 179 cm^{-1} band. Also, Beattie et al. (12) investigated the Raman spectra of PF_5 in the gas phase at 25°C and 125°C and assigned the ν_7 fundamental to 175 cm^{-1} band which is in excellent agreement with Levin's assignment (8). The fundamental vibrational frequencies of Holmes and Lord (7) are adopted along with Levin's assignment (8) of the ν_7 fundamental (179 cm^{-1}).

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Molybdenum Hexafluoride (MoF_6)

(Liquid) GFW = 209.930

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200	36.502	46.733	65.648	- 3.783	- 380.180	- 361.269	394.776
298	40.582	62.068	62.068	.000	- 379.080	- 352.214	258.180
300	40.659	62.319	62.069	.075	- 379.058	- 352.048	256.467
400	44.817	74.586	63.713	4.349	- 377.684	- 343.242	187.539
500	48.974	85.033	66.956	9.038	- 376.032	- 334.819	146.349
600	53.131	94.329	70.756	14.144	- 374.053	- 326.755	119.021
700	57.289	102.832	74.739	19.665	- 371.728	- 319.050	99.612
800	61.446	110.753	78.751	25.601	- 369.042	- 311.707	85.154
900	65.604	118.230	82.726	31.954	- 365.975	- 304.719	73.996
1000	69.761	125.358	86.635	38.722	- 362.528	- 298.095	65.149

June 30, 1970

MOLYBDENUM HEXAFLUORIDE (MoF_6) (LIQUID) GFW = 209.930

$S^\circ_{298.15}$ = 62.07 ± 0.06 gibbs/mol

Tm = 290.76°K

Tb = 307.04°K ($\ell \rightarrow$ real gas, P = 1 atm, f = 0.966 atm)

Tb = 308.0°K ($\ell \rightarrow$ ideal gas, P = f = 1 atm)

$\Delta Hf^\circ_{298.15}$ = -379.080 ± 0.3 kcal/mol

ΔHm° = 1.034 ± 0.001 kcal/mol

ΔHv = 6.512 ± 0.04 kcal/mol

ΔHv° = 6.562 kcal/mol

Heat of Formation

The adopted heat of formation, ΔHf°(MoF_6, ℓ) = -379.080 ± 0.3 kcal/mol, is calculated from the heat of formation of the gas, ΔHf°(MoF_6, g) = -372.4 ± 0.2 kcal/mol (1), and the heat of vaporization, ΔHv° = 6.680 ± 0.03 kcal/mol at 298.15°K. The value for the heat of vaporization is obtained from a third law analysis of the vapor pressure data reported by Osborne et al. (2).

Myers and Brady (3) determined calorimetrically ΔHr = -154.7 kcal/mol for the hydrolysis reaction:

$$MoF_6(\ell) + 8\ NaOH\cdot 516\ H_2O \rightarrow \begin{bmatrix} Na_2MoO_4 \\ + \\ 6\ NaF \\ + \\ 4\ H_2O \end{bmatrix} \text{ in soln.}$$

Heats of formation of Na_2MoO_4 and NaF in the final solution were determined from the following two auxiliary heat of reaction measurements:

$$MoO_3(c) + 2\ NaOH\cdot 514\ H_2O \rightarrow Na_2MoO_4\ (\text{in soln.}) + H_2O(\ell) \qquad (1)$$

$$\Delta Hr = -17.6\ \text{kcal/mol}$$

$$NaF(c) + \begin{bmatrix} NaOH\cdot 514\ H_2O \\ + \\ 0.00186\ MoO_3 \end{bmatrix} \rightarrow NaF\ (\text{in soln.}) \qquad (2)$$

$$\Delta Hr = +0.09\ \text{kcal/mol}$$

Combining these results with the following heat of formation data:

ΔHf°(MoO_3, c) = -178.1 ± 0.1 kcal/mol (4)
ΔHf°(NaF, c) = -137.52 ± 0.2 kcal/mol (5)
ΔHf°(NaOH·500 H_2O) = -112.12 kcal/mol (6)

we derive ΔHf(Na_2MoO_4, in soln.) = -351.6 kcal/mol and ΔHf(NaF, in soln.) = -137.4 kcal/mol. These data, when combined with the results for the hydrolysis of MoF_6, lead to ΔHf°(MoF_6, ℓ) = -397.6 kcal/mol. This result is not in agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity measurements for liquid MoF_6 by Osborne et al. (2) are adopted. Outside the observed range Cp was extrapolated linearly with temperature. $S^\circ_{298.15}$ is evaluated from the thermal data of Osborne et al. (2) and the third law of thermodynamics. They reported heat capacity data in the range 5°-350°K with $S_{5°K}$ = 0.024 gibbs/mol.

Melting Data

Melting point and heat of melting data for MoF_6 have been reported by several investigators. These results are summarized below.

Investigator	Method	Melting Point °K	ΔHm° kcal/mol
Osborne et al. (2)	Calorimetric	290.76 ± 0.02	1.034 ± 0.001
Brady et al. (7)	Calorimetric	290.7	1.059 ± 0.010
Cady and Hargreaves (8)	Vapor Pressure	290.55	1.00 ± 0.03*
Ruff and Ascher (9)	Vapor Pressure	290.65	1.31 ± 0.2*

* This value is the difference between the 2nd law heat of sublimation corrected for ΔCp of the process and the adopted heat of vaporization calculated at 290.76°K with ($H_{290.76}-H_{298.15}$) for the vapor and liquid.

The value $\Delta Hm^\circ_{290.76}$ = 1.034 ± 0.001 kcal/mol from Osborne et al. (2) is adopted.

Vaporization Data

Second and third law analyses of various sets of vapor pressure data (2, 8, 9) are summarized below. Corrections for nonideality of the vapor have been calculated from the second virial coefficient equation reported by Osborne et al. (2).

Investigator	Temp. Range °K	No. of Points	Boiling Point °K	ΔHv°_{298} kcal/mol	
				2nd law*	3rd law
Osborne et al. (2)	291.15 - 320.15	21	307.04	6.690	6.680
Cady and Hargreaves (8)	290.55 - 307.15	Equation	307.15	6.74	6.68
Ruff and Ascher (9)	290.65 - 294.85	4	308.15	5.99	6.68

* with ΔCp = -11.77 gibbs/mol

The value ΔHv°_{298} = 6.680 ± 0.03 ($\Delta Hv_{307.04}$ = 6.512 ± 0.04) kcal/mol, determined from the vapor pressure data of Osborne et al. (2), is adopted in the tabulation. The temperature at which ΔGv° = 0 is 308.0°K and the corresponding ΔHv° = 6.562 kcal/mol.

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Molybdenum Hexafluoride (MoF_6)
(Ideal Gas) GFW = 209.930

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.740	-370.714	-370.714	INFINITE
100	16.070	59.431	105.853	-4.642	-371.818	-365.385	798.548
200	23.949	73.216	86.257	-2.608	-372.325	-358.711	391.981
298	28.816	83.762	83.761	.000	-372.400	-352.002	258.024
300	28.887	83.940	83.762	.053	-372.400	-351.876	256.341
400	31.858	92.694	84.935	3.104	-372.249	-345.051	188.527
500	33.639	100.011	87.239	6.386	-372.004	-338.281	147.863
600	34.751	106.250	89.901	9.809	-371.708	-331.562	120.771
700	35.478	111.665	92.632	13.323	-371.390	-324.895	101.437
800	35.976	116.437	95.315	16.897	-371.066	-318.278	86.950
900	36.329	120.696	97.903	20.513	-370.736	-311.698	75.691
1000	36.588	124.537	100.377	24.160	-370.410	-305.157	66.692
1100	36.783	128.034	102.735	27.829	-370.091	-298.647	59.336
1200	36.934	131.241	104.979	31.515	-369.782	-292.165	53.211
1300	37.052	134.203	107.114	35.215	-369.492	-285.708	48.032
1400	37.147	136.952	109.149	38.925	-369.221	-279.274	43.597
1500	37.224	139.518	111.089	42.643	-368.973	-272.855	39.755
1600	37.287	141.922	112.941	46.369	-368.750	-266.457	36.396
1700	37.340	144.184	114.713	50.100	-368.552	-260.068	33.434
1800	37.384	146.320	116.410	53.837	-368.384	-253.697	30.803
1900	37.422	148.342	118.038	57.577	-368.241	-247.327	28.449
2000	37.454	150.262	119.602	61.321	-368.129	-240.964	26.331
2100	37.482	152.090	121.106	65.068	-368.048	-234.613	24.416
2200	37.506	153.835	122.554	68.817	-368.002	-228.259	22.675
2300	37.527	155.502	123.951	72.569	-367.990	-221.906	21.086
2400	37.546	157.100	125.299	76.323	-368.020	-215.553	19.629
2500	37.562	158.633	126.602	80.078	-368.107	-209.202	18.288
2600	37.577	160.106	127.862	83.835	-368.256	-202.840	17.050
2700	37.590	161.525	129.083	87.593	-368.477	-196.473	15.903
2800	37.601	162.892	130.266	91.353	-368.779	-190.100	14.838
2900	37.612	164.212	131.414	95.113	-375.799	-183.687	13.843
3000	37.621	165.487	132.529	98.875	-375.896	-177.071	12.900
3100	37.630	166.721	133.612	102.638	-375.995	-170.440	12.016
3200	37.637	167.916	134.665	106.401	-376.103	-163.807	11.187
3300	37.644	169.074	135.690	110.165	-376.216	-157.171	10.409
3400	37.651	170.198	136.689	113.930	-376.334	-150.529	9.676
3500	37.657	171.289	137.662	117.695	-376.461	-143.883	8.984
3600	37.662	172.350	138.611	121.461	-376.590	-137.233	8.331
3700	37.667	173.382	139.537	125.228	-376.727	-130.585	7.713
3800	37.672	174.387	140.441	128.994	-376.871	-123.926	7.127
3900	37.676	175.365	141.324	132.762	-377.022	-117.275	6.572
4000	37.680	176.319	142.187	136.530	-377.176	-110.609	6.043
4100	37.684	177.250	143.031	140.298	-377.339	-103.945	5.541
4200	37.687	178.158	143.856	144.066	-377.508	-97.274	5.062
4300	37.690	179.045	144.664	147.835	-377.679	-90.596	4.605
4400	37.693	179.911	145.455	151.604	-377.862	-83.920	4.168
4500	37.696	180.758	146.231	155.374	-378.047	-77.241	3.751
4600	37.698	181.587	146.990	159.144	-378.238	-70.557	3.352
4700	37.701	182.398	147.735	162.914	-378.438	-63.865	2.970
4800	37.703	183.191	148.465	166.684	-378.641	-57.162	2.603
4900	37.705	183.969	149.182	170.454	-378.853	-50.463	2.251
5000	37.707	184.730	149.885	174.225	-520.083	-41.430	1.811
5100	37.709	185.477	150.576	177.996	-520.580	-31.858	1.365
5200	37.711	186.209	151.254	181.767	-521.111	-22.262	.936
5300	37.713	186.928	151.921	185.538	-521.673	-12.660	.522
5400	37.714	187.633	152.575	189.309	-522.270	-3.063	.124
5500	37.716	188.325	153.219	193.081	-522.891	6.562	-.261
5600	37.717	189.004	153.852	196.852	-523.543	16.200	-.632
5700	37.719	189.672	154.475	200.624	-524.220	25.842	-.991
5800	37.720	190.328	155.087	204.396	-524.916	35.504	-1.338
5900	37.721	190.973	155.690	208.168	-525.637	45.160	-1.673
6000	37.722	191.607	156.283	211.940	-526.377	54.845	-1.998

June 30, 1970

MOLYBDENUM HEXAFLUORIDE (MoF_6) (IDEAL GAS) GFW = 209.930

Point Group O_h

$S^\circ_{298.15}$ = 83.76 ± 0.50 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -370.7 ± 0.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -372.4 ± 0.2 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
741 (1)	262 (3)
643 (2)	312 (3)
741 (3)	122 (3)

Bond Distance: Mo-F = 1.84 ± 0.02 Å

Bond Angle: F-Mo-F = 90°

Product of Moments of Inertia: $I_AI_BI_C = 7.771 \times 10^{-113}\ g^3\ cm^6$

σ = 24

Heat of Formation

Settle et al. (1) measured the heat of formation of gaseous MoF_6 by direct combination of its elements in a nickel bomb calorimeter. Their result was $\Delta Hf^\circ_{298}(MoF_6, g) = -372.4 \pm 0.2$ kcal/mol. This value is adopted in the tabulation.

Heat Capacity and Entropy

Tanner and Duncan (2) investigated the Raman spectra of liquid MoF_6, and their results indicated that the structure of the molecule was a regular octahedron with O_h symmetry rather than an unsymmetrical structure as reported by Braune and Pinnow (3) from electron diffraction studies. The Mo-F bond length is from the electron diffraction studies of Nazarian (4). Individual moments of inertia are $I_A = I_B = I_C = 4.268 \times 10^{-38}$ g cm^2.

Several infrared (5, 6, 7, 8) and Raman (5, 7) studies of MoF_6 have been reported. The vibrational frequencies reported for MoF_6 from these studies are in good agreement except for the infrared and Raman inactive ν_6 vibration. Burke et al. (5) and Hellberg et al. (8) derived $\nu_6 = 234\ cm^{-1}$, while Claassen et al. (7) assigned $\nu_6 = 190\ cm^{-1}$ and Gaunt (6) assigned $\nu_6 = 240\ cm^{-1}$. Weinstock and Goodman (9) recently analyzed the infrared and Raman data for MoF_6 and assigned $\nu_6 = 122\ cm^{-1}$.

Osborne et al. (10) calculated S° = 62.06 ± 0.06 gibbs/mol for liquid MoF_6 at 298.15°K from their low temperature thermal data. Combining this with ΔSv, they obtained S° = 83.75 ± 0.10 gibbs/mol for the ideal gas at 298.15°K. Accepting the assignments of Weinstock and Goodman (9), we calculate $S^\circ_{298.15}$ = 83.76 gibbs/mol, which is in excellent agreement with the thermal results. The other assignments given above for ν_6 all lead to ideal gas entropies that are lower than the thermal results. Therefore, the assignments given by Weinstock and Goodman (9) are adopted here.

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Sulfur Hexafluoride (SF_6)

(Ideal Gas) Mol. Wt. = 146.0544

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 4.053	- 288.460	- 288.460	INFINITE
100	9.280	53.312	85.652	- 3.234	- 289.890	- 282.716	617.846
200	16.505	61.798	71.637	- 1.968	- 291.117	- 275.026	300.520
298	23.224	69.713	69.713	.000	- 291.790	- 266.966	195.682
300	23.329	69.857	69.713	.043	- 291.799	- 266.813	194.364
400	27.852	77.237	70.689	2.619	- 292.632	- 258.408	141.181
500	30.705	83.783	72.667	5.558	- 293.052	- 249.802	109.183
600	32.544	89.555	75.011	8.727	- 293.236	- 241.130	87.827
700	33.772	94.670	77.461	12.047	- 293.269	- 232.416	72.560
800	34.624	99.239	79.903	15.469	- 306.270	- 224.997	61.463
900	35.235	103.354	82.284	18.963	- 305.842	- 214.862	52.173
1000	35.687	107.091	84.580	22.511	- 305.390	- 204.778	44.752
1100	36.029	110.509	86.784	26.097	- 304.923	- 194.741	38.690
1200	36.294	113.656	88.894	29.714	- 304.441	- 184.744	33.645
1300	36.503	116.569	90.913	33.354	- 303.955	- 174.786	29.383
1400	36.670	119.281	92.843	37.013	- 303.464	- 164.870	25.736
1500	36.807	121.816	94.691	40.687	- 302.971	- 154.987	22.580
1600	36.919	124.195	96.461	44.374	- 302.477	- 145.138	19.824
1700	37.013	126.436	98.159	48.070	- 301.984	- 135.317	17.395
1800	37.092	128.554	99.790	51.776	- 301.494	- 125.534	15.241
1900	37.159	130.561	101.357	55.488	- 301.004	- 115.767	13.316
2000	37.217	132.469	102.865	59.207	- 300.517	- 106.029	11.586
2100	37.266	134.286	104.318	62.931	- 300.035	- 96.322	10.024
2200	37.309	136.020	105.720	66.660	- 299.557	- 86.630	8.605
2300	37.347	137.680	107.074	70.393	- 299.082	- 76.962	7.313
2400	37.380	139.270	108.383	74.130	- 298.612	- 67.315	6.130
2500	37.410	140.797	109.649	77.869	- 298.149	- 57.689	5.043
2600	37.436	142.264	110.875	81.611	- 297.690	- 48.077	4.041
2700	37.459	143.678	112.064	85.356	- 297.234	- 38.485	3.115
2800	37.480	145.040	113.218	89.103	- 296.783	- 28.913	2.257
2900	37.498	146.356	114.338	92.852	- 296.339	- 19.348	1.458
3000	37.515	147.627	115.426	96.603	- 295.903	- 9.811	.715
3100	37.531	148.858	116.485	100.355	- 295.468	- .283	.020
3200	37.545	150.049	117.515	104.109	- 295.042	9.236	- .631
3300	37.557	151.205	118.519	107.864	- 294.620	18.735	- 1.241
3400	37.569	152.326	119.497	111.620	- 294.204	28.228	- 1.814
3500	37.579	153.416	120.450	115.378	- 293.796	37.706	- 2.354
3600	37.589	154.474	121.381	119.136	- 293.390	47.177	- 2.864
3700	37.598	155.504	122.289	122.895	- 292.994	56.630	- 3.345
3800	37.606	156.507	123.177	126.656	- 292.601	66.077	- 3.800
3900	37.614	157.484	124.044	130.417	- 292.218	75.501	- 4.231
4000	37.621	158.436	124.892	134.178	- 291.838	84.934	- 4.640
4100	37.628	159.365	125.721	137.941	- 291.465	94.345	- 5.029
4200	37.634	160.272	126.533	141.704	- 291.099	103.751	- 5.399
4300	37.639	161.158	127.328	145.468	- 290.735	113.151	- 5.751
4400	37.645	162.023	128.107	149.232	- 290.384	122.538	- 6.086
4500	37.650	162.869	128.870	152.997	- 290.035	131.916	- 6.406
4600	37.654	163.697	129.618	156.762	- 289.692	141.286	- 6.712
4700	37.659	164.507	130.352	160.527	- 289.358	150.652	- 7.005
4800	37.663	165.300	131.072	164.293	- 289.027	160.013	- 7.285
4900	37.667	166.076	131.778	168.060	- 288.704	169.372	- 7.554
5000	37.670	166.837	132.472	171.827	- 288.388	178.712	- 7.811
5100	37.674	167.583	133.153	175.594	- 288.078	188.043	- 8.058
5200	37.677	168.315	133.822	179.361	- 287.774	197.386	- 8.296
5300	37.680	169.033	134.480	183.129	- 287.475	206.713	- 8.524
5400	37.683	169.737	135.126	186.897	- 287.186	216.024	- 8.743
5500	37.685	170.428	135.762	190.666	- 286.899	225.349	- 8.954
5600	37.688	171.107	136.387	194.435	- 286.622	234.665	- 9.158
5700	37.690	171.774	137.002	198.203	- 286.352	243.971	- 9.354
5800	37.693	172.430	137.607	201.973	- 286.083	253.270	- 9.543
5900	37.695	173.074	138.203	205.742	- 285.824	262.557	- 9.725
6000	37.697	173.708	138.789	209.512	- 285.571	271.853	- 9.902

Dec. 31, 1960; Sept. 30, 1965

SULFUR HEXAFLUORIDE (SF_6) (IDEAL GAS) MOL. WT. = 146.0544

Point Group O_h

$S^\circ_{298.15}$ = 69.713 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -288.46 ± 0.24 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -291.79 ± 0.24 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
770 (1)	345 (3)
640 (2)	615 (3)
522 (3)	947 (3)

Bond Length = 1.564 Å

Bond Angle: F-S-F = 90°

σ = 24

Product of the Moments of Inertia: $I_AI_BI_C$ = 29,400 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, Preprint of Paper XIV on Fluorine Bomb Calorimetry, July, 1965, measured the enthalpy of combustion of rhombic sulfur in fluorine. Their result yields $\Delta H_f^\circ{}_{298}$ = -291.79 ± 0.24 kcal. mole^{-1}. P. Gross, C. Hayman, and D. L. Levi, XVIIth Intern. Congr. Pure and Appl. Chem., Abstr. 1, 90 (1959), reported -289.5 kcal. mole^{-1} also based on direct combination of the elements. O'Hare, Settle, and Hubbard mentioned a private communication from Dr. Gross indicating -289.5 kcal. mole^{-1} may be in error due to oxygen in the fluorine used and preliminary results of a redetermination are in better agreement with -291.79 kcal. mole^{-1}. D. M. Yost and W. H. Claussen, J. Am. Chem. Soc. 55, 887 (1933) determined -262 kcal. mole^{-1}, again by direct reaction of the elements, which now appears too low. The work of O'Hare et al., loc. cit., is adopted.

Heat Capacity and Entropy.

V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 124 (1963) measured the bond length adopted here by the electron diffraction technique. Earlier less accurate work by the same method by H. Braune and S. Knoke, Z. physik. Chem. B21, 297 (1933) and L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. USA 19, 68 (1933) is in agreement within experimental error. T. E. Morsy, Ber. Bunsenges Physik. Chem. 68, 277 (1964) reviewed the literature on Raman and infrared spectra. Frequencies given here differ slightly from his selection because more weight was given to the Raman frequencies of C. W. Gullikson, J. R. Nielsen, and A. T. Stair, Jr., J. Mol. Spectroscopy 1, 151 (1957). Calculated functions by Morsy loc. cit. are in reasonable agreement with the present work.

A. Eucken and E. Schröder, Z. physik. Chem. 41B, 307 (1938) measured low temperature thermal data from which K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961) calculated S°_{298} = 70.3 ± 0.7 cal. mole^{-1} deg.$^{-1}$ which agrees within experimental error with the spectroscopic result.

The three principal moments of inertia are $I_A = I_B = I_C$ = 3.0863 X 10^{-38} g. cm.^{2}

Tungsten Hexafluoride (WF_6)

(Liquid) GFW = 297.8404

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200	40.500	41.393	63.269	- 3.975	- 419.147	- 392.387	436.430
298	40.500	59.564	59.564	.000	- 417.870	- 389.963	285.654
300	40.500	59.815	59.565	.075	- 417.848	- 389.796	283.966
400	40.500	71.466	61.153	4.125	- 416.697	- 380.621	207.962
500	40.500	80.503	64.153	8.175	- 415.669	- 371.726	162.481
600	40.500	87.887	67.512	12.225	- 414.726	- 363.025	132.232
700	40.500	94.130	70.880	16.275	- 413.850	- 354.477	110.673
800	40.500	99.538	74.132	20.325	- 413.031	- 346.055	94.538
900	40.500	104.308	77.225	24.375	- 412.251	- 337.725	82.012
1000	40.500	108.575	80.150	28.425	- 411.510	- 329.489	72.010

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

TUNGSTEN HEXAFLUORIDE (WF_6) (LIQUID) GFW = 297.8404

$S^\circ_{298.15}$ = 59.564 ± 0.2 gibbs/mol

Tm = 275.2°K

Tb = 290.3°K

$\Delta Hf^\circ_{298.15}$ = -417.87 ± 0.5 kcal/mol

ΔHm° = 0.980 kcal/mol

ΔHv° = 6.465 ± 0.08 kcal/mol

Heat of Formation.

The adopted heat of formation, -417.87 kcal/mol, is calculated from the chosen $\Delta Hv^\circ_{290.3}$ = 6.465 ± 0.08 kcal/mol with $\Delta Hf^\circ_{298}(WF_6,g)$ = -411.5 ± 0.4 kcal/mol using all JANAF functions. The value of $\Delta Hv^\circ_{290.3}$ is obtained by corrected 2nd law analysis of vapor pressure data[6,7,8] which are given in the vaporization section of this table.

O. E. Myers and A. P. Brady[1] measured calorimetrically ΔHr°_{298} = -150.1 kcal/mol for the reaction $WF_6(l) + 8\ NaOH(500H_2O) \rightarrow Na_2WO_4(4900H_2O) + 4H_2O(l) + 6NaF(800\ H_2O)$. V. I. Spitsyn and N. N. Patsukova[2] measured calorimetrically ΔHr°_{298} = -13.8 kcal/mol for the reaction $WO_3(c) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200H_2O) + H_2O(l)$. Based on these data and auxiliary data for NaOH(aq)[3,9], NaF(aq)[3,10] and $Na_2WO_4(aq)$[4], we obtain ΔHr°_{298} = -136.2 kcal/mol for $WF_6(l) + 6\ NaOH(\infty H_2O) \rightarrow WO_3(c) + 3\ H_2O(l) + 6\ NaF(\infty H_2O)$. This leads to $\Delta Hf^\circ_{298}(WF_6,\ l)$ = -416.9 ± 1 kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy.

The heat capacity, 40.5 gibbs/mol, is obtained from a graph of the Cp versus temperature curve determined calorimetrically by E. F. Westrum, Jr.[5]

The entropy, S°_{298} = 59.564 eu, is calculated from the chosen $\Delta Hv^\circ_{290.3}$ = 6.465 kcal/mol with $S^\circ_{298}(WF_6,g)$ = 81.504 eu using all JANAF functions.

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized below. Ruff and Ascher's value, 2.40 kcal/mol, is too high because they did not know of the existence of a solid-solid transition[5] at 264.7°K with ΔHt° = 2.067 kcal/mol. Westrum's data are adopted in the tabulation.

Investigator	Method	Melting Point (°K)	ΔHm° (kcal/mol)
Westrum[5]	Calorimetric	275.2	0.980
Ruff and Ascher[7]	Vapor pressure	275.4	2.400*
Barber & Cady[8]	Warming curve	275.1	0.500
Cady & Hargreaves[6]	Vapor pressure	275.2	0.420*

*This value is the difference between the 2nd law heats of sublimation and vaporization without correction for ΔCp° for both processes.

Vaporization Data.

Second law analyses of the data[6,7,8], neglecting corrections for nonideality of the vapor, are summarized below. The value of ΔHv°_{298} = 6.37 kcal/mol ($\Delta Hv^\circ_{290.3}$ = 6.465 kcal/mol) is selected in the tabulation.

Investigator	Temp. Range (°K)	No. of Points	Boiling Point (°K)	ΔHv°_{298} * (kcal/mol)	ΔSv°_{298} * (eu)
Ruff and Ascher[7]	273 - 287.5	5	290.7 ± 0.2	6.30 ± 0.12	21.70
Barber and Cady[8]	285 - 324.5	16	290.2 ± 0.05	6.37 ± 0.01	21.94
Cady and Hargreaves[6]	275 - 290	Equation	290.3 ± 0.05	6.12	21.09

*From second law analysis using ΔCp = -12.4 gibbs/mol

References.

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2. V. I. Spitsyn and N. N. Patsukova, Russ. J. Inorg. Chem. (English Transl.) 10, 1304 (1965).
3. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NSRDS-NBS2 Natl. Bur. Std., Washington, D.C., Apr. 1965.
4. We have assumed $\Delta H^\circ dil$ = 0 for $Na_2WO_4(4200H_2O) \rightarrow Na_2WO_4(4900H_2O)$ based on the dilution data of R. L. Graham and L. G. Hepler, J. Am. Chem. Soc. 80, 3538 (1958).
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9. JANAF NaOH(c) table dated Mar. 31, 1966.
10. U.S. Natl. Bur. Std. Tech. Note 270-1, 1965.

Tungsten Hexafluoride (WF_6)

(Ideal Gas) GFW = 297.8404

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.435	-409.416	-409.416	INFINITE
100	14.228	58.272	102.965	-4.469	-410.691	-404.080	883.116
200	23.197	71.175	83.956	-2.556	-411.358	-397.154	433.990
298	28.448	81.504	81.504	.000	-411.500	-390.140	285.980
300	28.523	81.680	81.505	.053	-411.500	-390.009	284.121
400	31.652	90.354	82.666	3.075	-411.377	-382.856	209.183
500	33.508	97.634	84.952	6.341	-411.133	-375.755	164.242
600	34.660	103.853	87.597	9.754	-410.827	-368.706	134.301
700	35.412	109.256	90.313	13.260	-410.495	-361.710	112.931
800	35.925	114.020	92.985	16.828	-410.158	-354.767	96.918
900	36.289	118.274	95.563	20.440	-409.816	-347.863	84.473
1000	36.556	122.112	98.029	24.083	-409.482	-340.998	74.525
1100	36.757	125.606	100.379	27.749	-409.156	-334.167	66.393
1200	36.912	128.811	102.617	31.433	-408.838	-327.361	59.620
1300	37.033	131.771	104.747	35.130	-408.536	-320.583	53.895
1400	37.131	134.519	106.777	38.839	-408.245	-313.829	48.991
1500	37.210	137.083	108.713	42.556	-407.969	-307.091	44.743
1600	37.275	139.487	110.562	46.280	-407.709	-300.378	41.030
1700	37.329	141.748	112.330	50.010	-407.464	-293.674	37.754
1800	37.374	143.883	114.025	53.746	-407.236	-286.993	34.846
1900	37.413	145.905	115.650	57.485	-407.022	-280.317	32.244
2000	37.446	147.825	117.211	61.228	-406.825	-273.649	29.903
2100	37.475	149.653	118.713	64.974	-406.646	-267.000	27.787
2200	37.499	151.397	120.159	68.723	-406.485	-260.357	25.864
2300	37.521	153.064	121.554	72.474	-406.339	-253.713	24.108
2400	37.540	154.661	122.900	76.227	-406.212	-247.080	22.500
2500	37.557	156.194	124.201	79.982	-406.104	-240.454	21.020
2600	37.572	157.667	125.460	83.738	-406.013	-233.828	19.655
2700	37.585	159.086	126.680	87.496	-405.943	-227.205	18.391
2800	37.597	160.453	127.862	91.255	-405.904	-220.588	17.218
2900	37.608	161.772	129.008	95.016	-405.908	-213.966	16.125
3000	37.618	163.047	130.122	98.777	-405.962	-207.353	15.106
3100	37.626	164.281	131.204	102.539	-406.071	-200.733	14.152
3200	37.634	165.476	132.256	106.302	-406.247	-194.106	13.257
3300	37.641	166.634	133.281	110.066	-406.494	-187.473	12.416
3400	37.648	167.758	134.278	113.830	-406.822	-180.830	11.624
3500	37.654	168.849	135.250	117.596	-407.245	-174.170	10.876
3600	37.660	169.910	136.199	121.361	-407.786	-167.504	10.169
3700	37.665	170.942	137.124	125.127	-416.780	-160.777	9.497
3800	37.670	171.946	138.027	128.894	-416.773	-153.851	8.848
3900	37.674	172.925	138.909	132.661	-416.775	-146.941	8.234
4000	37.678	173.879	139.772	136.429	-416.779	-140.019	7.650
4100	37.682	174.809	140.615	140.197	-416.792	-133.101	7.095
4200	37.685	175.717	141.440	143.965	-416.811	-126.179	6.566
4300	37.688	176.604	142.247	147.734	-416.832	-119.255	6.061
4400	37.692	177.471	143.038	151.503	-416.865	-112.341	5.580
4500	37.694	178.318	143.813	155.272	-416.901	-105.424	5.120
4600	37.697	179.146	144.572	159.042	-416.942	-98.498	4.680
4700	37.699	179.957	145.316	162.812	-416.992	-91.574	4.258
4800	37.702	180.751	146.046	166.582	-417.045	-84.645	3.854
4900	37.704	181.528	146.762	170.352	-417.107	-77.719	3.466
5000	37.706	182.290	147.465	174.123	-417.174	-70.794	3.094
5100	37.708	183.036	148.155	177.893	-417.248	-63.874	2.737
5200	37.710	183.769	148.833	181.664	-417.327	-56.936	2.393
5300	37.712	184.487	149.499	185.435	-417.412	-50.000	2.062
5400	37.713	185.192	150.154	189.206	-417.506	-43.080	1.744
5500	37.715	185.884	150.797	192.978	-417.602	-36.139	1.436
5600	37.716	186.564	151.430	196.749	-417.708	-29.202	1.140
5700	37.718	187.231	152.052	200.521	-417.819	-22.262	.854
5800	37.719	187.887	152.664	204.293	-417.933	-15.320	.577
5900	37.720	188.532	153.267	208.065	-418.056	-8.384	.311
6000	37.721	189.166	153.860	211.837	-612.089	.643	-.023

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

TUNGSTEN HEXAFLUORIDE (WF_6) (IDEAL GAS) GFW = 297.8404

Point Group O_h

$S^\circ_{298.15}$ = 81.504 gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf^\circ_0 = -409.4 \pm 0.4$ kcal/mol

$\Delta Hf^\circ_{298.15} = -411.5 \pm 0.4$ kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
769 (1)	256 (3)
670 (2)	322 (3)
712 (3)	216 (3)

Bond Distance: W-F = 1.83 Å

Bond Angle: F-W-F = 90°

σ = 24

Product of the Moments of Inertia: $I_A I_B I_C = 7.54576 \times 10^{-113}\ g^3\ cm^6$

Heat of Formation.

P. A. G. O'Hare and W. N Hubbard, J. Phys. Chem. 70, 3353 (1966), determined the heat of formation, $\Delta Hf^\circ_{298}(WF_6,g) = -411.5 \pm 0.4$ kcal/mol, by combustion of tungsten in fluorine in a bomb calorimeter. This value is adopted in the tabulation.

Heat Capacity and Entropy.

The molecular configuration and vibrational frequencies were obtained from the infrared and Raman spectroscopic studies by J. Gaunt[1]; T. G. Burke, D. F. Smith and A. H. Nielsen[2]; K. N. Tanner and A. B. F. Duncan[3].

The bond distance was reported by H. H. Claasen[4], based on the preliminary result of V. Schomaker, M. Kimura and B. Weinstock[5] who determined the bond distance by electron diffraction. J. Gaunt[6] derived W-F = 1.89 Å from correlations with other hexafluorides and a valence force constant calculation. The three principal moments of inertia are $I_A = I_B = I_C = 4.22572 \times 10^{-38}$ g cm^2.

References.

1. J. Gaunt, Trans. Faraday Soc. 49, 1122 (1953).
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3. K. N. Tanner and A. B. F. Duncan, J. Am. Chem. Soc. 73, 1164 (1951).
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6. J. Gaunt, Trans. Faraday Soc. 50, 546 (1954).

Iodine Heptafluoride (IF_7)

(Ideal Gas) GFW = 259.8932

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.610	-226.348	-226.348	INFINITE
100	12.487	59.083	106.243	-4.716	-228.251	-219.187	479.033
200	24.727	71.685	85.817	-2.826	-229.400	-209.587	229.026
298	32.134	83.085	83.084	.000	-229.700	-199.778	146.441
300	32.235	83.284	83.085	.060	-229.701	-199.593	145.403
400	36.323	93.175	84.406	3.508	-231.534	-189.494	103.535
500	38.645	101.553	87.020	7.266	-236.362	-178.535	78.038
600	40.052	108.733	90.055	11.207	-235.782	-167.022	60.838
700	40.957	114.980	93.179	15.260	-235.156	-155.610	48.584
800	41.569	120.491	96.256	19.388	-234.510	-144.293	39.419
900	42.001	125.414	99.227	23.568	-233.848	-133.055	32.310
1000	42.315	129.856	102.071	27.785	-233.181	-121.892	26.640
1100	42.552	133.901	104.784	32.029	-232.513	-110.796	22.013
1200	42.733	137.611	107.367	36.293	-231.842	-99.758	18.168
1300	42.876	141.037	109.827	40.574	-231.177	-88.777	14.925
1400	42.990	144.219	112.171	44.867	-230.514	-77.849	12.153
1500	43.082	147.188	114.408	49.171	-229.855	-66.965	9.757
1600	43.158	149.971	116.544	53.483	-229.202	-56.129	7.667
1700	43.221	152.590	118.588	57.802	-228.554	-45.330	5.828
1800	43.274	155.062	120.547	62.127	-227.915	-34.576	4.198
1900	43.319	157.403	122.425	66.457	-227.279	-23.850	2.743
2000	43.358	159.626	124.230	70.791	-226.649	-13.157	1.438
2100	43.391	161.742	125.967	75.128	-226.027	-2.502	.260
2200	43.420	163.761	127.639	79.469	-225.414	8.127	-.807
2300	43.445	165.692	129.252	83.812	-224.805	18.732	-1.780
2400	43.467	167.541	130.809	88.157	-224.205	29.306	-2.669
2500	43.486	169.316	132.314	92.505	-223.614	39.856	-3.484
2600	43.504	171.022	133.770	96.855	-223.029	50.384	-4.235
2700	43.519	172.664	135.180	101.206	-222.451	60.892	-4.929
2800	43.533	174.247	136.548	105.558	-221.878	71.373	-5.571
2900	43.546	175.775	137.874	109.912	-221.315	81.843	-6.168
3000	43.557	177.251	139.162	114.268	-220.762	92.274	-6.722
3100	43.567	178.680	140.414	118.624	-220.213	102.703	-7.241
3200	43.576	180.063	141.632	122.981	-219.673	113.112	-7.725
3300	43.585	181.404	142.817	127.339	-219.141	123.503	-8.179
3400	43.592	182.705	143.971	131.698	-218.615	133.879	-8.606
3500	43.599	183.969	145.096	136.057	-218.099	144.247	-9.007
3600	43.606	185.197	146.193	140.418	-217.587	154.594	-9.385
3700	43.612	186.392	147.263	144.779	-217.086	164.921	-9.741
3800	43.617	187.555	148.308	149.140	-216.592	175.244	-10.079
3900	43.622	188.688	149.329	153.502	-216.108	185.540	-10.397
4000	43.627	189.793	150.327	157.864	-215.628	195.836	-10.700
4100	43.631	190.870	151.303	162.227	-215.159	206.115	-10.987
4200	43.635	191.922	152.257	166.591	-214.697	216.386	-11.260
4300	43.639	192.949	153.192	170.954	-214.239	226.649	-11.520
4400	43.643	193.952	154.107	175.319	-213.795	236.894	-11.767
4500	43.646	194.933	155.003	179.683	-213.355	247.127	-12.002
4600	43.649	195.892	155.882	184.048	-212.922	257.357	-12.227
4700	43.652	196.831	156.743	188.413	-212.500	267.576	-12.442
4800	43.655	197.750	157.588	192.778	-212.082	277.792	-12.648
4900	43.657	198.650	158.416	197.144	-211.675	287.995	-12.845
5000	43.660	199.532	159.230	201.510	-211.276	298.185	-13.034
5100	43.662	200.397	160.029	205.876	-210.883	308.358	-13.214
5200	43.664	201.244	160.813	210.242	-210.499	318.550	-13.388
5300	43.666	202.076	161.584	214.608	-210.122	328.724	-13.555
5400	43.668	202.892	162.341	218.975	-209.755	338.872	-13.715
5500	43.670	203.694	163.086	223.342	-209.393	349.035	-13.869
5600	43.671	204.481	163.818	227.709	-209.042	359.187	-14.018
5700	43.673	205.254	164.538	232.076	-208.698	369.333	-14.161
5800	43.674	206.013	165.247	236.444	-208.358	379.471	-14.299
5900	43.676	206.760	165.944	240.811	-208.029	389.593	-14.431
6000	43.677	207.494	166.631	245.179	-207.708	399.722	-14.560

Mar. 31, 1962; Mar. 31, 1963; Dec. 31, 1963; June 30, 1966; Dec. 31, 1969

IODINE HEPTAFLUORIDE (IF_7) (IDEAL GAS) GFW = 259.8932

Point Group D_{5h}

$\Delta Hf^\circ_0 = -226.35 \pm 0.6$ kcal/mol

$S^\circ_{298.15} = 83.08 \pm 0.3$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -229.7 \pm 0.6$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
676 (1)	746 (2)	510 (2)
635 (1)	425 (2)	352 (2)
670 (1)	257 (2)	310 (2)
365 (1)		[340] (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.76 Å

Bond Angle: F(eq)-I-F(ax) = 90° F(eq)-I-F(eq) = 72° $\sigma = 10$

Product of the Moments of Inertia: $I_AI_BI_C = 1.1965 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

Settle et al. (1) derived ΔHf° = -229.7 ± 0.6 kcal/mol for $IF_7(g)$ at 298.15 K from treatment of their calorimetric data on combustion of iodine in fluorine. The combustion products, consisting of mixtures of IF_5 and IF_7, were expanded, treated to remove excess fluorine, and then hydrolyzed. The solutions were analyzed for iodate and the sum of iodate plus periodate. Since the recovery of iodine was not complete (about 70 to 99%), it was necessary to try various assumptions about the form of the unrecovered iodine. Consistent results were obtained only by assigning the unrecovered iodine to IF_7, the less volatile product. This treatment indicated that IF_7 was formed in yields ranging from about 1 to 70%.

ΔHr° for the reaction $IF_7(g) \rightarrow IF_5(g) + F_2(g)$ may be checked via equilibrium data (2). Using six points read from Fig. 2 of Bernstein and Katz, we obtain ΔHr°(3rd law) = 29.36 ± 0.2 kcal/mol and ΔHr°(2nd law) = 29.53 ± 0.7 kcal/mol, both at 298.15 K. The entropy test, ΔSr°(2nd law) - ΔSr°(JANAF Functions) = 0.3 ± 1.4 gibbs/mol, indicates consistency with the JANAF functions. Combination of ΔHr°(3rd law) with ΔHf° for $IF_5(g)$ yields ΔHf°(IF_7, g) = -230.2 ± 0.6 kcal/mol. In deriving the uncertainty, we assume that ΔHr°(3rd law) is uncertain by ±0.5 kcal/mol due to an estimated uncertainty of about 1.0 gibbs/mol in the JANAF value of ΔSr° at 500 K.

Heat Capacity and Entropy

Recent evidence favors D_{5h} symmetry and a pentagonal bipyramidal structure for the heptafluoride. Claassen et al. (3) review the earlier debate about structures of lower symmetry. They provide convincing evidence of D_{5h} symmetry from the first observation of Raman spectra of the vapor state and re-examination of the infrared spectra. Their data--including five fundamentals in Raman (two polarized), five fundamentals in infrared, no coincidences between Raman and infrared, and one fundamental inactive--are consistent only with D_{5h} symmetry. This is confirmed by Falconer et al. (4) who interpret their electric-deflection experiments as indicating a symmetry-forbidden dipole moment. Extended Hückel-molecular-orbital calculations (5) also predict D_{5h} symmetry. The adopted structural parameters are from our approximate analysis of the electron-diffraction data of Thompson and Bartell (6). The authors gave a radial distribution curve and suggested only a gross (unrefined) structure because of the probable presence of a fluorocarbon impurity in their sample. Principal moments of inertia are $I_A = I_B = 46.83 \times 10^{-39}$ and $I_C = 54.57 \times 10^{-39}\ g\ cm^2$.

Observed vibrational fundamentals are from Claassen et al. (3). The inactive fundamental is estimated from the calculations of Khanna (7).

References

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2. R. B. Bernstein and J. J. Katz, J. Phys. Chem. 56, 885 (1952).
3. H. H. Claassen, E. L. Gasner and H. Selig, J. Chem. Phys 49, 1803 (1968).
4. W. E. Falconer, A. Büchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 48, 312 (1968).
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Iron (Fe)

(Reference State) At. Wt. = 55.85

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.075	.000	.000	INFINITE
100	2.880	1.465	11.190	- .972	.000	.000	.000
200	5.133	4.302	7.053	- .550	.000	.000	.000
298	5.989	6.529	6.529	- .000	.000	.000	.000
300	6.000	6.566	6.529	.011	.000	.000	.000
400	6.500	8.363	6.771	.637	.000	.000	.000
500	7.020	9.868	7.243	1.312	.000	.000	.000
600	7.580	11.197	7.793	2.042	.000	.000	.000
700	8.240	12.412	8.367	2.831	.000	.000	.000
800	9.170	13.569	8.946	3.699	.000	.000	.000
900	10.480	14.718	9.523	4.675	.000	.000	.000
1000	13.560	15.934	10.102	5.832	.000	.000	.000
1100	10.230	17.249	10.697	7.207	.000	.000	.000
1200	8.160	18.256	11.281	8.370	.000	.000	.000
1300	8.310	18.915	11.844	9.193	.000	.000	.000
1400	8.460	19.537	12.371	10.032	.000	.000	.000
1500	8.610	20.125	12.869	10.885	.000	.000	.000
1600	8.760	20.686	13.340	11.754	.000	.000	.000
1700	9.820	21.396	13.791	12.929	.000	.000	.000
1800	10.000	21.963	14.230	13.920	.000	.000	.000
1900	10.540	24.536	14.748	18.597	.000	.000	.000
2000	10.580	25.077	15.251	19.653	.000	.000	.000
2100	10.620	25.595	15.731	20.713	.000	.000	.000
2200	10.660	26.090	16.191	21.777	.000	.000	.000
2300	10.700	26.564	16.631	22.845	.000	.000	.000
2400	10.740	27.020	17.055	23.917	.000	.000	.000
2500	10.780	27.460	17.462	24.993	.000	.000	.000
2600	10.820	27.883	17.855	26.073	.000	.000	.000
2700	10.860	28.292	18.234	27.157	.000	.000	.000
2800	10.900	28.688	18.600	28.245	.000	.000	.000
2900	10.940	29.071	18.955	29.337	.000	.000	.000
3000	10.980	29.443	19.298	30.433	.000	.000	.000
3100	11.020	29.804	19.631	31.533	.000	.000	.000
3200	6.412	56.676	20.406	116.062	.000	.000	.000
3300	6.488	56.874	21.508	116.707	.000	.000	.000
3400	6.565	57.069	22.551	117.360	.000	.000	.000
3500	6.644	57.260	23.540	118.020	.000	.000	.000
3600	6.724	57.449	24.480	118.689	.000	.000	.000
3700	6.805	57.634	25.373	119.365	.000	.000	.000
3800	6.889	57.816	26.224	120.050	.000	.000	.000
3900	6.974	57.997	27.037	120.743	.000	.000	.000
4000	7.061	58.174	27.813	121.445	.000	.000	.000
4100	7.151	58.350	28.556	122.155	.000	.000	.000
4200	7.242	58.523	29.267	122.875	.000	.000	.000
4300	7.335	58.695	29.950	123.604	.000	.000	.000
4400	7.430	58.864	30.605	124.342	.000	.000	.000
4500	7.527	59.032	31.235	125.090	.000	.000	.000
4600	7.625	59.199	31.841	125.847	.000	.000	.000
4700	7.725	59.364	32.425	126.615	.000	.000	.000
4800	7.826	59.528	32.988	127.392	.000	.000	.000
4900	7.928	59.690	33.531	128.180	.000	.000	.000
5000	8.032	59.851	34.056	128.978	.000	.000	.000
5100	8.136	60.011	34.563	129.786	.000	.000	.000
5200	8.240	60.170	35.054	130.605	.000	.000	.000
5300	8.345	60.328	35.529	131.434	.000	.000	.000
5400	8.450	60.485	35.990	132.274	.000	.000	.000
5500	8.555	60.641	36.437	133.124	.000	.000	.000
5600	8.660	60.796	36.870	133.985	.000	.000	.000
5700	3.764	60.950	37.291	134.856	.000	.000	.000
5800	8.868	61.104	37.701	135.738	.000	.000	.000
5900	8.970	61.256	38.099	136.630	.000	.000	.000
6000	9.072	61.408	38.486	137.532	.000	.000	.000

Mar. 31, 1965

IRON (Fe) (REFERENCE STATE) AT. WT. = 55.85

0 to 1184°K. Crystal alpha
1184 to 1665°K. Crystal gamma
1665 to 1809°K. Crystal delta
1809 to 3145°K. Liquid
3145 to 6000°K. Ideal Monatomic gas

See crystal, liquid and monatomic gas for details.

(Crystal) At. Wt. = 55.85

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.075	.000	.000	INFINITE
100	2.880	1.465	11.190	-.972	.000	.000	.001
200	5.133	4.302	7.053	-.550	.000	.000	.000
298	5.989	6.529	6.529	-.000	.000	.000	.000
300	6.000	6.566	6.529	.011	.000	.000	.000
400	6.500	8.363	6.771	.637	.000	.000	.000
500	7.020	9.868	7.243	1.312	.000	.000	.000
600	7.580	11.197	7.793	2.042	.000	.000	.000
700	8.240	12.412	8.367	2.831	.000	.000	.000
800	9.170	13.569	8.946	3.699	.000	.000	.000
900	10.480	14.718	9.523	4.675	.000	.000	.000
1000	13.560	15.934	10.102	5.832	.000	.000	.000
1100	10.230	17.249	10.697	7.207	.000	.000	.000
1200	8.160	18.256	11.281	8.370	.000	.000	.000
1300	8.310	18.915	11.844	9.193	.000	.000	.000
1400	8.460	19.537	12.371	10.032	.000	.000	.000
1500	8.610	20.125	12.869	10.885	.000	.000	.000
1600	8.760	20.686	13.340	11.754	.000	.000	.000
1700	9.820	21.396	13.791	12.929	.000	.000	.000
1800	10.000	21.963	14.230	13.920	.000	.000	.000
1900	10.161	22.508	14.651	14.928	-3.669	.184	-.021
2000	10.300	23.033	15.057	15.951	-3.702	.386	-.042
2100	10.419	23.538	15.449	16.987	-3.726	.594	-.062
2200	10.519	24.025	15.828	18.035	-3.742	.801	-.080
2300	10.598	24.495	16.194	19.091	-3.754	1.004	-.095
2400	10.658	24.947	16.550	20.154	-3.763	1.212	-.110
2500	10.698	25.383	16.894	21.221	-3.772	1.421	-.124

Mar. 31, 1965

IRON (Fe) (CRYSTAL) AT. WT. = 55.85

$S^\circ_{298.15}$ = 6.529 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

T_{t1} = 1184°K.

T_{t2} = 1665°K.

T_m = 1809°K.

$\Delta H^\circ_{f\ 0}$ = 0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 0 kcal. mole^{-1}

ΔH°_{t1} = 0.225 kcal. mole^{-1}

ΔH°_{t2} = 0.260 kcal. mole^{-1}

ΔH°_m = 3.630 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 99.5 ± 0.4 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The heat capacity below 298°K. was obtained by smoothing graphically the data of G. Duyckaerts, Physica 6, 401 (1939) and W. H. Keesom and B. Kurrelmeyer, Physica, 6, 633 (1939) over the range 1° - 20°K; F. E. Simon and R. C. Swain, Z. Physik. Chem. 28B, 189 (1935) (30-220°K.), A. Eucken and H. Werth, Z. Anorg. Chem. 188, 152 (1930) (17-206°K.) and K. K. Kelley, J. Chem. Phys. 11, 16 (1943) (55-295°K.). This data on integration yielded $S_{298.15}$ = 6.529 starting with S_1° = 0.0003 cal. deg.$^{-1}$ mole^{-1}. The heat capacity and enthalpy data above room temperature are extensive and the heat capacities and enthalpies chosen by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York 1963, were adopted here. These values have a sharp peak in the heat capacity curve at the Curie pernt* and through this region follow closely the work of P. R. Pallister, J. Iron Steel Inst. 161, 87 (1949). This data has recently been corroborated using a pulse heating technique by D. C. Wallace, P. H. Sidles and G. C. Danielson, J. App. Phys. 31, 168 (1960). It should be noted that there is some disagreement between the heat capacities chosen and the enthalpies measured by P. D. Anderson and R. Hultgren, Trans. Met. Soc. AIME, 224, 842 (1962). The measured values lie consistently above the chosen enthalpies in the range 298-900°K. by from 30 to 60 calories, however the chosen values are considered to be the more reliable. The γ-iron heat capacities adopted here have recently been substantially confirmed by W. A. Dench and O. Kubaschewski, J. Iron Steel Inst. (London) 201, 140 (1963).

Transition Data.

The enthalpies of the α - γ transition at 1184°K. and the γ - δ transition at 1665°K. were also taken from Hultgren et al. loc. cit.

Melting Data.

The temperature and heat of melting were those adopted by Hultgren et al. loc. cit.

Heat of Sublimation.

The value adopted is from a critical second and third law analysis of the data of 14 investigators over gamma-iron and liquid iron. See the Fe(g) table for details.

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*See W. F. Giauque, G. E. Brodale, R. A. Fisher and E. W. Hornung, J. Chem. Phys. 42, 1 (1965) for the definition of "pernt".

Iron (Fe)

(Liquid) At. Wt. = 55.85

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	5.985	8.195	8.195	.000	3.138	2.641	-1.936
300	6.000	8.232	8.195	.011	3.138	2.638	-1.922
400	6.500	10.029	8.437	.637	3.138	2.472	-1.350
500	7.020	11.534	8.909	1.312	3.138	2.305	-1.008
600	7.580	12.863	9.460	2.042	3.138	2.138	-.779
700	8.240	14.078	10.034	2.831	3.138	1.972	-.616
800	9.170	15.235	10.612	3.699	3.138	1.805	-.493
900	10.480	16.384	11.189	4.675	3.138	1.639	-.398
1000	13.560	17.600	11.768	5.832	3.138	1.472	-.322
1100	10.230	18.916	12.364	7.207	3.138	1.304	-.259
1200	10.260	19.761	12.945	8.179	2.947	1.141	-.208
1300	10.300	20.584	13.502	9.207	3.152	.982	-.165
1400	10.340	21.348	14.035	10.239	3.345	.809	-.126
1500	10.380	22.063	14.547	11.275	3.528	.621	-.090
1600	10.420	22.734	15.038	12.315	3.699	.422	-.058
1700	10.460	23.367	15.509	13.359	3.568	.217	-.028
1800	10.500	23.966	15.963	14.407	3.625	.019	-.002
1900	10.540	24.535	16.399	15.459	.000	.000	.000
2000	10.580	25.077	16.819	16.515	.000	.000	.000
2100	10.620	25.594	17.225	17.575	.000	.000	.000
2200	10.660	26.089	17.617	18.639	.000	.000	.000
2300	10.700	26.564	17.995	19.707	.000	.000	.000
2400	10.740	27.020	18.362	20.779	.000	.000	.000
2500	10.780	27.459	18.717	21.855	.000	.000	.000
2600	10.820	27.883	19.062	22.935	.000	.000	.000
2700	10.860	28.292	19.396	24.019	.000	.000	.000
2800	10.900	28.687	19.721	25.107	.000	.000	.000
2900	10.940	29.071	20.037	26.199	.000	.000	.000
3000	10.980	29.442	20.344	27.295	.000	.000	.000
3100	11.020	29.803	20.643	28.395	.000	.000	.000
3200	11.060	30.153	20.935	29.499	-83.425	1.448	-.099
3300	11.100	30.494	21.220	30.607	-82.962	4.092	-.271
3400	11.140	30.826	21.497	31.719	-82.503	6.723	-.432
3500	11.180	31.150	21.768	32.835	-82.047	9.338	-.583
3600	11.220	31.465	22.033	33.955	-81.596	11.946	-.725
3700	11.260	31.773	22.292	35.079	-81.148	14.537	-.859
3800	11.300	32.074	22.546	36.207	-80.705	17.114	-.984
3900	11.340	32.368	22.794	37.339	-80.266	19.687	-1.103
4000	11.380	32.656	23.037	38.475	-79.832	22.240	-1.215
4100	11.420	32.937	23.275	39.615	-79.402	24.791	-1.321
4200	11.460	33.213	23.508	40.759	-78.978	27.324	-1.422
4300	11.500	33.483	23.737	41.907	-78.559	29.852	-1.517
4400	11.540	33.748	23.962	43.059	-78.145	32.365	-1.608
4500	11.580	34.008	24.182	44.215	-77.737	34.871	-1.693

Mar. 31, 1965

IRON (Fe) (LIQUID) AT. WT. = 55.85

$S^\circ_{298.15}$ = 8.195 cal. deg.$^{-1}$ mole^{-1}

T_m = 1809°K.

T_b = 3145.4°K.

ΔH°_f 298.15 = 3.138 kcal. mole^{-1}

ΔH°_m = 3.630 kcal. mole^{-1}

ΔH°_v = 83.679 kcal. mole^{-1}

Heat of Formation.

The ΔH°_f 298.15 was obtained from that of the crystal by adding ΔH_m and the difference between $H_{1809} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was that chosen by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York (1963).

Melting Data.

See Fe(c) for details.

Vaporization Data.

The boiling point was calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K. so that the free energy function calculated by integration of the crystal liquid data or by statistical methods from the gas phase were equal at the boiling point.

Iron (Fe)

(Ideal Gas) At. Wt. = 55.85

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.637	98.938	98.938	INFINITE
100	5.112	36.949	48.330	- 1.138	99.334	95.785	- 209.329
200	5.823	40.713	43.667	- .591	99.459	92.177	- 100.722
298	6.137	43.112	43.112	.000	99.500	88.593	- 64.937
300	6.138	43.150	43.113	.011	99.500	88.525	- 64.487
400	6.103	44.916	43.354	.675	99.488	84.867	- 46.367
500	5.949	46.263	43.806	1.228	99.416	81.219	- 35.499
600	5.785	47.332	44.308	1.815	99.273	77.592	- 28.261
700	5.643	48.213	44.805	2.386	99.055	73.994	- 23.101
800	5.529	48.959	45.279	2.944	98.745	70.433	- 19.241
900	5.441	49.605	45.724	3.493	98.318	66.919	- 16.249
1000	5.375	50.175	46.141	4.033	97.701	63.460	- 13.869
1100	5.329	50.685	46.532	4.568	96.861	60.082	- 11.937
1200	5.302	51.147	46.897	5.100	96.230	56.760	- 10.337
1300	5.291	51.571	47.241	5.629	95.936	53.483	- 8.991
1400	5.296	51.963	47.564	6.158	95.626	50.230	- 7.841
1500	5.313	52.329	47.870	6.689	95.304	46.998	- 6.847
1600	5.343	52.673	48.159	7.221	94.967	43.788	- 5.981
1700	5.383	52.998	48.434	7.758	94.329	40.605	- 5.220
1800	5.432	53.307	48.697	8.298	93.878	37.459	- 4.548
1900	5.487	53.602	48.947	8.844	89.747	34.522	- 3.971
2000	5.548	53.885	49.187	9.396	89.243	31.627	- 3.456
2100	5.613	54.157	49.417	9.954	88.741	28.761	- 2.993
2200	5.681	54.420	49.639	10.519	88.242	25.916	- 2.574
2300	5.751	54.674	49.852	11.090	87.745	23.092	- 2.194
2400	5.823	54.920	50.058	11.669	87.252	20.292	- 1.848
2500	5.895	55.159	50.257	12.255	86.762	17.514	- 1.531
2600	5.968	55.392	50.450	12.848	86.275	14.752	- 1.240
2700	6.041	55.619	50.638	13.449	85.792	12.009	- .972
2800	6.115	55.840	50.820	14.056	85.311	9.286	- .725
2900	6.189	56.056	50.996	14.672	84.835	6.578	- .496
3000	6.263	56.267	51.169	15.294	84.361	3.889	- .283
3100	6.337	56.473	51.336	15.924	83.891	1.217	- .086
3200	6.412	56.676	51.500	16.562	.000	.000	.000
3300	6.488	56.874	51.660	17.207	.000	.000	.000
3400	6.565	57.069	51.816	17.859	.000	.000	.000
3500	6.644	57.260	51.969	18.520	.000	.000	.000
3600	6.724	57.449	52.119	19.188	.000	.000	.000
3700	6.805	57.634	52.265	19.865	.000	.000	.000
3800	6.889	57.816	52.409	20.549	.000	.000	.000
3900	6.974	57.997	52.550	21.242	.000	.000	.000
4000	7.061	58.174	52.688	21.944	.000	.000	.000
4100	7.151	58.350	52.824	22.655	.000	.000	.000
4200	7.242	58.523	52.958	23.374	.000	.000	.000
4300	7.335	58.695	53.089	24.103	.000	.000	.000
4400	7.430	58.864	53.218	24.841	.000	.000	.000
4500	7.527	59.032	53.346	25.589	.000	.000	.000
4600	7.625	59.199	53.471	26.347	.000	.000	.000
4700	7.725	59.364	53.595	27.114	.000	.000	.000
4800	7.826	59.528	53.717	27.892	.000	.000	.000
4900	7.928	59.690	53.837	28.679	.000	.000	.000
5000	8.032	59.851	53.956	29.477	.000	.000	.000
5100	8.136	60.011	54.073	30.286	.000	.000	.000
5200	8.240	60.170	54.189	31.105	.000	.000	.000
5300	8.345	60.328	54.303	31.934	.000	.000	.000
5400	8.450	60.485	54.416	32.774	.000	.000	.000
5500	8.555	60.641	54.528	33.624	.000	.000	.000
5600	8.660	60.796	54.638	34.485	.000	.000	.000
5700	8.764	60.950	54.748	35.356	.000	.000	.000
5800	8.868	61.104	54.856	36.237	.000	.000	.000
5900	8.970	61.256	54.963	37.129	.000	.000	.000
6000	9.072	61.408	55.069	38.032	.000	.000	.000

Mar. 31, 1965

IRON, MONATOMIC (Fe) (IDEAL GAS) AT. WT. = 55.85

Ground State Configuration $^5D_4$

$S^\circ_{298.15}$ = 43.112 cal. mole^{-1} deg.$^{-1}$

$\Delta H^\circ_{f\ 0}$ = 98.9 ± 0.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 99.5 ± 0.4 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0	9	12561	7	19913	5	29828	163
416	7	12969	5	20020	3	35529	218
704	5	17550	7	19390	13	43022	412
888	3	17727	5	19621	11	47182	427
978	1	17927	3	19788	9	50241	426
6928	11	18378	5	20641	9	51765	405
7377	9	19553	3	20874	7	53782	433
7728	7	20038	1	21039	5	57421	482
7986	5	19351	11	21949	27		
8155	3	19563	9	22928	49		
11976	9	19757	7	25143	148		

Heat of Formation.

The heat of formation is the heat of sublimation at 298°K. which was obtained by second and third law analysis of the following vapor pressure data.

Method	Points	Ref.	$\Delta H_{s\ 298.15}$ 2nd law kcal. mole^{-1}	$\Delta H_{s\ 298.15}$ 3rd law kcal. mole^{-1}	Drift in 3rd law cal. deg.$^{-1}$ mole^{-1}
Boiling	1	1	—	105.6	—
Boiling	1	2	—	88.1	—
Transport	1	3	—	101.4	—
Langmuir	1	4	—	100.5	—
Transport	20	5*	100.0 ± 1.1	99.5	-0.2 ± 0.6
Langmuir	12	6	98.4 ± 1.8	97.3	-0.6 ± 1.2
Langmuir	12	7	101.6 ± 1.8	98.0	-1.1 ± 1.3
Langmuir	9	8*	99.4 ± 1.0	99.8	0.3 ± 0.7
Alloy activities	4	9	101.7 ± 13.5	99.1	-4.6 ± 7.5
Knudsen	6	10	110.1 ± 10.7	96.9	-8.5 ± 6.9
Langmuir	12	11*	108.8 ± 1.0	96.8	-7.9 ± 0.8
Langmuir	12	12	105.9 ± 1.2	97.2	-5.9 ± 0.9
Isotope Exchange	10	13*	95.6 ± 5.2	97.3	1.0 ± 3.6
Knudsen	—	14**	99.9	99.0	-0.6
Knudsen	—	15**	98.6	101.0	—
Langmuir	4	16	94.5 ± 0.5	96.8	1.5 ± 0.3

*1 point rejected in statistical test. **Data from equations.

1 - O. Ruff and W. Bormann, Z. Anorg. Chem. 88, 365 (1914) [2723°K.]
2 - H. C. Greenwood and M. S. B. Fellow, Proc. Roy. Soc. 83A, 483 (1910) [2723°K.]
3 - E. T. Turkdogan and L. E. Leake, Trans. Met. Soc. AIME, 218, 1136 (1960) [1873°K.]
4 - L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946) [1873°K.]
5 - J. P. Morris, G. R. Zellars, S. L. Payne and R. L. Kipp, U.S.B.M. Report Invest. 5364 (1957) [1810-1889°K.]
6 - A. L. Marshall, R. W. Dornte, and F. J. Norton, J. Am. Chem. Soc. 59, 1161 (1937) [1317-1579°K.]
7 - Ref. 6 with temperatures increased by 11 degrees suggested by Ref. 8 [1328-1590°K.]
8 - J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 75, 4729 (1951) [1389-1519°K.]
9 - R. Speiser, A. J. Jacobs and J. W. Spretnak, Trans. Met. Soc. AIME, 215, 185 (1959) [1725-1926°K]
10 - Yu. V. Kornev, Dokl. Akad. Nauk. SSSR, 93, 467 (1953) [1464-1623°K.]
11 - V. D. Burlakov, Viz. Metallov i Metalloved 5, 90 (1957) (cast specimen) [1292-1529°K.]
12 - Ref. 11 using evaporated specimens on different substrates [1302-1505°K.]
13 - I. I. Ivanov - Thesis - Inst. of Metallurgy, Acad. Sci. USSR (1957) [1260-1620°K.]
14 - K. M. Myles and A. T. Aldred, J. Phys. Chem. 68, 64 (1964) [1450-1650°K.]
15 - E. Z. Vintaikin, Dokl. Akad. Nauk. SSSR, 117, 632 (1957) [1400-1600°K.]
16 - H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. 30, 201 (1927) [1270-1580°K.]

The adopted value of 99.5 kcal. mole^{-1} is based mainly on the work of Refs. 5, 8 and 14, which have the best drift analysis and agreement between second and third law.

Heat Capacities and Entropies.

The electronic levels were taken from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949). Levels above 20,000 cm.$^{-1}$ were averaged.

Iron Dihydroxide $(Fe(OH)_2)$

(Crystal) GFW = 89.86174

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	23.200	21.000	21.000	.000	-137.200	-117.599	86.203
300	23.220	21.144	21.000	.043	-137.194	-117.478	85.583
400	24.400	27.987	21.925	2.424	-136.844	-110.958	60.625
500	25.520	33.552	23.711	4.921	-136.452	-104.530	45.690
600	26.600	38.302	25.756	7.527	-136.031	-98.186	35.764
700	27.600	42.480	27.853	10.239	-135.588	-91.912	28.696
800	28.430	46.222	29.919	13.042	-135.157	-85.705	23.413
900	29.050	49.608	31.921	15.918	-134.783	-79.545	19.316
1000	29.490	52.693	33.847	18.846	-134.557	-73.422	16.046
1100	29.760	55.517	35.690	21.810	-134.533	-67.305	13.372
1200	29.900	58.113	37.452	24.793	-134.295	-61.209	11.148
1300	29.960	60.509	39.135	27.787	-133.725	-55.142	9.270
1400	29.980	62.730	40.742	30.784	-133.189	-49.117	7.667
1500	30.000	64.799	42.277	33.783	-132.676	-43.129	6.284

June 30, 1966

IRON DIHYDROXIDE $(Fe(OH)_2)$ (CRYSTAL) GFW = 89.86174

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [21 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -137.2 ± 0.7 kcal/mol

Tm = Unknown

ΔHm° = Unknown

$\Delta Hs^\circ_{298.15}$ = 58.2 kcal/mol

Heat of Formation.

The heat of combustion of $Fe(OH)_2(c)$, according to the chemical reaction $Fe(OH)_2(c) + 1/4\ O_2(g) = 1/2\ Fe_2O_3(c) + H_2O(l)$, was determined to be -29.8 ± 0.65 kcal/mol by R. Fricke and S. Rihl, Z. anorg. allgem. chem. 251, 414 (1943). From this data the heat of formation ($\Delta Hf^\circ_{298.15}$) was evaluated to be -137.2 ± 0.7 kcal/mol. which was adopted here.

The enthalpy changes for the following three reactions were determined by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886:

Reaction	ΔHr°_{291}, kcal/mol
1. $FeCl_2(c) = FeCl_2\ (400\ H_2O)$	-17.9
2. $FeCl_2(200\ H_2O) + H_2SO_4(200\ H_2O) = FeSO_4(200\ H_2O) + 2\ HCl(100\ H_2O)$	-3.6
3. $FeSO_4(aq.) + 2KOH(aq.) = Fe(OH)_2\ (c) + K_2SO_4(aq.)$	-6.34

Using $\Delta Hf^\circ_{298.15}$ = -81.7 kcal/mol for $FeCl_2(c)$ and those for the other compounds in aqueous solution (assuming aq. = 200 H_2O in Reaction 3) obtained from D.D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, National Bureau of Standards, 1965, the heat of formation (298.15°K) for $Fe(OH)_2(c)$ was derived as -135.8 kcal/mol which agrees reasonably with the adopted value.

Heat Capacity and Entropy.

The heat capacities, 298.15 - 700°K, and $S^\circ_{298.15}$ were estimated by comparison with those for $FeCl_2(c)$, $CaCl_2(c)$ and $Ca(OH)_2(c)$. The Cp values above 700°K were obtained by graphical extrapolation of the Cp curve plotted using the above Cp values.

Heat of Sublimation.

The value of $\Delta Hs^\circ_{298.15}$ was calculated as the difference between $\Delta Hf^\circ_{298.15}$ for $Fe(OH)_2(g)$ and $Fe(OH)_2(c)$.

Iron Dihydroxide $(Fe(OH)_2)$

(Ideal Gas) GFW = 89.86174

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.396	-77.222	-77.222	INFINITE
100	8.787	54.182	80.037	-2.586	-77.968	-76.661	167.542
200	13.193	61.525	69.027	-1.501	-78.604	-75.101	82.066
298	17.090	67.577	67.577	.000	-79.000	-73.286	53.720
300	17.145	67.683	67.577	.032	-79.005	-73.251	53.363
400	19.362	72.953	68.281	1.869	-79.199	-71.300	38.956
500	20.585	77.416	69.673	3.871	-79.302	-69.312	30.296
600	21.397	81.245	71.291	5.973	-79.385	-67.306	24.516
700	22.039	84.593	72.957	8.145	-79.482	-65.285	20.383
800	22.588	87.573	74.601	10.377	-79.622	-63.251	17.279
900	23.067	90.261	76.194	12.661	-79.840	-61.190	14.859
1000	23.485	92.714	77.725	14.989	-80.214	-59.100	12.916
1100	23.846	94.970	79.192	17.356	-80.787	-56.957	11.316
1200	24.156	97.058	80.595	19.756	-81.132	-54.780	9.977
1300	24.419	99.002	81.937	22.185	-81.127	-52.584	8.840
1400	24.643	100.820	83.221	24.639	-81.130	-50.388	7.866
1500	24.833	102.527	84.452	27.113	-81.146	-48.191	7.021
1600	24.993	104.135	85.632	29.604	-81.179	-45.995	6.283
1700	25.128	105.654	86.766	32.110	-81.517	-43.787	5.629
1800	25.242	107.094	87.856	34.629	-81.675	-41.564	5.047
1900	25.339	108.461	88.904	37.158	-85.524	-39.145	4.503
2000	25.420	109.763	89.915	39.696	-85.757	-36.701	4.010
2100	25.490	111.005	90.890	42.242	-86.000	-34.239	3.563
2200	25.548	112.192	91.832	44.794	-86.256	-31.769	3.156
2300	25.598	113.329	92.742	47.351	-86.522	-29.288	2.783
2400	25.641	114.420	93.622	49.913	-86.801	-26.793	2.440
2500	25.677	115.467	94.475	52.479	-87.094	-24.289	2.123
2600	25.707	116.475	95.302	55.048	-87.397	-21.770	1.830
2700	25.734	117.445	96.104	57.621	-87.713	-19.239	1.557
2800	25.756	118.382	96.883	60.195	-88.043	-16.699	1.303
2900	25.775	119.286	97.640	62.772	-88.384	-14.141	1.066
3000	25.792	120.160	98.377	65.350	-88.739	-11.576	.843
3100	25.806	121.006	99.093	67.930	-89.104	-8.997	.634
3200	25.818	121.825	99.791	70.511	-172.908	-4.962	.339
3300	25.828	122.620	100.470	73.093	-172.836	.282	-.019
3400	25.837	123.391	101.133	75.677	-172.779	5.527	-.355
3500	25.844	124.140	101.780	78.261	-172.738	10.770	-.673
3600	25.851	124.868	102.411	80.845	-172.714	16.016	-.972
3700	25.856	125.577	103.028	83.431	-172.705	21.256	-1.256
3800	25.861	126.266	103.630	86.017	-172.711	26.500	-1.524
3900	25.865	126.938	104.219	88.603	-172.734	31.743	-1.779
4000	25.868	127.593	104.796	91.190	-172.773	36.983	-2.021
4100	25.871	128.232	105.359	93.777	-172.827	42.230	-2.251
4200	25.873	128.855	105.912	96.364	-172.898	47.476	-2.470
4300	25.875	129.464	106.452	98.951	-172.985	52.727	-2.680
4400	25.877	130.059	106.982	101.539	-173.087	57.970	-2.879
4500	25.878	130.641	107.501	104.127	-173.206	63.219	-3.070
4600	25.879	131.209	108.011	106.714	-173.340	68.487	-3.254
4700	25.880	131.766	108.510	109.302	-173.492	73.742	-3.429
4800	25.880	132.311	109.000	111.890	-173.657	79.006	-3.597
4900	25.881	132.844	109.481	114.478	-173.839	84.269	-3.759
5000	25.881	133.367	109.954	117.067	-174.036	89.534	-3.914
5100	25.881	133.880	110.418	119.655	-174.250	94.810	-4.063
5200	25.881	134.382	110.874	122.243	-174.479	100.086	-4.206
5300	25.881	134.875	111.322	124.831	-174.723	105.377	-4.345
5400	25.881	135.359	111.763	127.419	-174.984	110.654	-4.478
5500	25.881	135.834	112.196	130.007	-175.258	115.951	-4.607
5600	25.881	136.300	112.623	132.595	-175.550	121.245	-4.732
5700	25.880	136.758	113.042	135.183	-175.855	126.547	-4.852
5800	25.880	137.208	113.455	137.771	-176.176	131.862	-4.969
5900	25.879	137.651	113.861	140.359	-176.511	137.169	-5.081
6000	25.879	138.086	114.261	142.947	-176.860	142.490	-5.190

June 30, 1966; Dec. 31, 1966

IRON DIHYDROXIDE $(Fe(OH)_2)$ (IDEAL GAS) GFW = 89.86174

Point Group $[C_{2h}]$

$S^\circ_{298.15}$ = [67.58] gibbs/mol

ΔHf°_0 = [-77.2 ± 0.5] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-79.0 ± 0.5] kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1
0	[5]
[700]	[10]
[2500]	[5]
[4000]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[2300] (1)	[450] (1)	[800] (1)
[750] (1)	[320] (1)	[700] (1)
[400] (1)	[2600] (1)	[570] (1)

Bond Distance: Fe-O = [1.8] Å O-H = [0.96] Å

Bond Angle: O-Fe-O = [180]° Fe-O-H = [105]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.368 x 10^{-116}] g^3 cm^6

Heat of Formation.

The equilibrium constants, at temperatures between 1300 and 1460°C, for the chemical reaction $Fe(c) + 2H_2O(g) = Fe(OH)_2(g) + H_2(g)$, were determined by G. R. Belton and F. D. Richardson, Trans. Faraday Soc. 58, 1562 (1962). Using these data, the enthalpy change ($\Delta Hr^\circ_{298.15}$) of the reaction is evaluated to be 35.53 ± 3.0 and 36.57 kcal/mol by the second and third law method, respectively. Based on the third law value for $\Delta Hr^\circ_{298.15}$, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $Fe(OH)_2(g)$ is calculated to be -79 ± 0.5 kcal/mol.

Heat Capacity and Entropy.

The molecular structure is assumed to be the same as that for $B(OH)_2(g)$. The Fe-O bond distance is taken from FeO(g). The O-H bond distance and Fe-O-H bond angle are estimated from those for $H_2O(g)$. The vibrational frequencies, and electronic levels and quantum weights are obtained by comparison with those for $B(OH)_2(g)$ and $FeCl_2(g)$, respectively. These values are adjusted to give reasonable second and third law agreements. The three principal moments of inertia are: $I_A = 2.658 \times 10^{-40}$, $I_B = 1.864 \times 10^{-38}$ and $I_C = 1.890 \times 10^{-38}$ g cm^2.

Iron Trihydroxide ($Fe(OH)_3$)

(Crystal) GFW = 106.86911

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.300	25.000	25.000	.000	- 199.000	- 168.634	123.612
300	24.400	25.151	25.000	.045	- 199.005	- 168.446	122.713
400	28.200	32.714	26.006	2.683	- 199.100	- 158.238	86.457
500	31.000	39.312	28.021	5.645	- 198.958	- 148.034	64.706
600	33.600	45.205	30.403	8.882	- 198.634	- 137.877	50.222
700	35.400	50.523	32.904	12.333	- 198.192	- 127.784	39.896
800	37.000	55.357	35.413	15.956	- 197.693	- 117.762	32.171
900	38.300	59.792	37.879	19.723	- 197.191	- 107.799	26.177
1000	39.400	63.887	40.277	23.610	- 196.779	- 97.891	21.394
1100	40.250	67.684	42.598	27.594	- 196.517	- 88.010	17.486
1200	40.900	71.215	44.838	31.653	- 195.994	- 78.174	14.237
1300	41.400	74.509	46.995	35.769	- 195.103	- 68.391	11.498
1400	41.750	77.591	49.071	39.927	- 194.210	- 58.678	9.160
1500	42.000	80.480	51.070	44.115	- 193.331	- 49.026	7.143

June 30, 1966

IRON TRIHYDROXIDE ($Fe(OH)_3$) (CRYSTAL) GFW = 106.86911

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [25 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -199 ± 3 kcal/mol

Tm = Unknown

ΔHm° = Unknown

Heat of Formation.

P. Schindler, W. Michaelis and W. Feitknecht, Helv. Chim. Acta, 46, 444 (1963), investigated the solubility of aged $Fe(OH)_3$ precipitates by determining the Fe^{+++} and H^+ ion concentration of solution in contact with the solid phase. The ion concentration was measured by the EMF method at the constant ionic strength 3M $NaClO_4$(solution). The precipitates were investigated by X-ray and electron miscroscope methods. The equilibrium constant was derived as $\log [Fe^{+++}] [H^+]^{-3} = \log K = 3.55 \pm 0.1$ for amorphous inactive hydroxide at 25°C. From these data the quantity log Ks = -39.1 ± 0.2 was evaluated where Ks is the solubility product of $Fe(OH)_3$. The Gibbs energy change ($\Delta Gr^\circ_{298.15}$) of the reaction $Fe(OH)_3(c) = Fe^{+++}(aq) + 3OH^-(aq)$ was calculated to be 53.34 ± 0.27 kcal/mol. Using $S_{298.15}$ = 70.1 and -2.57 gibbs/mol for Fe^{+++}(aq) and OH^-(aq), respectively, and an estimated $S^\circ_{298.15}(Fe(OH)_3, c)$ = 25 gibbs/mol, the enthalpy change ($\Delta Hr^\circ_{298.15}$) of the reaction is calculated to be 22.69 kcal/mol, according to the relationship $\Delta H = \Delta F + T\Delta S$. The entropy values for Fe^{+++} and OH^- ions were obtained from "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1 by D. D. Wagman and co-workers, 1965, respectively. Based on $\Delta Hf^\circ_{298.15}(Fe^{+++}, aq) = -11.4$ and $\Delta Hf^\circ_{298.15}(OH^-, aq) = -54.97$ kcal/mol, taken from the same sources, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $Fe(OH)_3$(c) was evaluated to be -199 ± 3 kcal/mol, which was adopted here.

The divergent values for solubility product (SP) of $Fe(OH)_3$ found in the literature may be due not only to the various forms of precipitate, but also to the tendency to form colloidal solutions. The SP values for $Fe(OH)_3$ were also reported by Evans and Pryor, J. Chem. Soc. S157 (1949); Kriukor and Awsejewitsch, Z. Elektrochem. 39, 884 (1933); Ruff and Hirsch, Z. Anorg. Chem. 146, 338 (1925); Britton, J. Chem. Soc. 2148 (1925); and Jellinek and Gorden, Z. Phys. Chem. 112, 207 (1924).

The enthalpy changes (ΔHr°_{291}) for the reactions: (1) $FeCl_3(aq) + 3NaOH(aq) = Fe(OH)_3(c) + 3NaCl(aq)$ and (2) $FeCl_3(c) = FeCl_3(aq)$ were determined to be -24.50 and -31.68 kcal/mol, respectively, by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886. Assuming the aqueous solutions all contain 200 mol of H_2O, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $Fe(OH)_3$ was calculated as -196.9 kcal/mol from Reactions (1) and (2). The $\Delta Hf^\circ_{298.15}$ values for NaOH(aq) and NaCl(aq) were obtained from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS-2, National Bureau of Standards, 1965, and JANAF $\Delta Hf^\circ_{298.15}$ values for NaOH(c) and NaCl(c).

Heat Capacity and Entropy.

The heat capacities, 298.15 - 1000°K, were estimated by comparison with those for $B_2O_3(c)$, $Fe_2O_3(c)$ and $B(OH)_3(c)$. The Cp values above 1000°K were obtained by graphical extrapolation. The $S^\circ_{298.15}(Fe(OH)_3, c)$ value was estimated by comparison with that for $B(OH)_3(c)$.

Iron Diiodide (FeI_2)

(Crystal) GFW = 309.6558

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	20.000	40.000	40.000	.000	- 25.000	- 26.703	19.574
300	20.000	40.124	40.000	.037	- 24.998	- 26.714	19.461
400	20.060	45.886	40.786	2.040	- 28.793	- 27.161	14.840
500	20.120	50.368	42.270	4.049	- 38.982	- 25.793	11.274
600	20.178	54.042	43.935	6.064	- 38.594	- 23.194	8.449
700	22.800	57.588	45.633	8.368	- 37.978	- 20.673	6.454
800	26.500	60.874	47.332	10.834	- 37.281	- 18.244	4.984
900	30.182	64.217	49.022	13.676	- 36.319	- 15.920	3.866
1000	32.700	67.542	50.708	16.833	- 35.224	- 13.713	2.997
1100	33.745	70.716	52.385	20.164	- 34.175	- 11.607	2.306
1200	34.000	73.665	54.037	23.554	- 32.857	- 9.619	1.752
1300	34.000	76.387	55.653	26.954	- 31.189	- 7.750	1.303
1400	34.000	78.907	57.225	30.354	- 29.540	- 6.008	.938
1500	34.000	81.252	58.749	33.754	- 27.906	- 4.386	.639

Sept. 30, 1966

IRON DIIODIDE (FeI_2) (CRYSTAL) GFW = 309.6558

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [40 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −25 ± 4 kcal/mol

Tt = 650°K

ΔHt° = 0.2 kcal/mol

Tm = 860 ± 2°K

ΔHm° = [10.7] kcal/mol

$\Delta Hs^\circ_{298.15}$ (to monomer) = [46] kcal/mol

$\Delta Hs^\circ_{298.15}$ (to dimer) = [52] kcal/mol

Heat of Formation.

The chemical equilibrium of the decomposition of $FeI_2(c)$, 771.15 — 858.15°K, has been studied by W. E. Zaugg and N. W. Gregory, J. Phys. Chem 70, 486 (1966). Using the reported partial pressures for $I_2(g)$, the enthalpy change ($\Delta Hr^\circ_{298.15}$) for the reaction $FeI_2(c) = Fe(c) + I_2(g)$ was evaluated by both the second and third law methods to be 39.79 ± 1.0 and 39.69 ± 0.3 kcal/mol, respectively. Based on the third law $\Delta Hr^\circ_{298.15}$ value, the heat of formation ($\Delta Hf^\circ_{298.15}$) for $FeI_2(c)$ was calculated as -25 kcal/mol which was adopted here.

The enthalpy change for the reaction $FeI_2(c) = Fe^{++}(aq) + 2\ I^-\ (aq)$ was determined to be -19.46 ± 0.03 kcal/mol by P. Paoletti, A. Sabatini and A. Vacca, Trans. Faraday Soc. 61, 2417 (1965), using a solution calorimetric method. Adopting $\Delta Hf^\circ_{298.15}$ = -21.3 and -13.19 kcal/mol for $Fe^{++}(aq)$ and I^- (aq), respectively, the value of $\Delta Hf^\circ_{298.15}$ (FeI_2, c) was derived as -28.22 ± 1 kcal/mol. The value of $\Delta Hf^\circ_{298.15}$ (I^-, aq) was taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, National Bureau of Standards, 1965. The value of $\Delta Hf^\circ_{298.15}$ (Fe^{++}, aq) was derived from heats of solution and formation for $FeCl_2(c)$.

The heats of solution of Fe(c), $I_2(c)$ and $FeI_2(c)$ in aqueous Br_2-KBr solution were measured by W. Hieber and A. Woerner, Z. Elektrochem. 40, 287 (1934), using an ice calorimeter. From the results obtained the heat of formation for $FeI_2(c)$ was reported as -30.1 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 343.15 — 773.15°K, were measured by F. L. Oetting and N. W. Gregory, J. Phys. Chem. 65, 173 (1961). The Cp values at temperatures below 343.15 and above 773.15°K were estimated by graphical extrapolation. The low temperature heat capacities, 11-130°K, were determined by G. Miljutin and E. A. Parfenowa, Phys. Trans. Ukrain, Acad. Sci. 9, 81 (1940). These data appear to be inadequate for the derivation of the entropy at 298.15°K. The value of $S^\circ_{298.15}$ adopted was calculated from the entropy change, $\Delta Sr^\circ_{298.15}$ = 28.7 eu, for the decomposition reaction $FeI_2(c) = Fe(c) + I_2(g)$, obtained by the second law analysis of the equilibrium pressure data reported by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 486 (1966).

Transition Data.

A minor transition in the vicinity of 370°C (360-385°C) has been reported by F. L. Oetting and N. W. Gregory, loc. cit. Subsequent studies by T. J. Wydeven, Ph. D. Thesis, University of Washington, Seattle, Wash., 1964, have shown the magnitude of the transition to be sensitive to trace amounts of impurities, but the nature of the transition has not been clearly established. A magnetic transition at 10°K was reported by H. Bizette, C. Terrier and B. Tsai, Compt. rend. 245, 507 (1957). The ΔHt° value was evaluated from the heat capacity - temperature plot given by F. L. Oetting and N. W. Gregory, loc. cit.

Melting Data.

Tm was reported by W. Fischer and R. Gewehr, Z. anorg. allgem. Chem. 222, 303 (1935). ΔHm° was estimated by comparison with that for $FeBr_2(c)$.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ (to monomer) is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for $FeI_2(g)$ and $FeI_2(c)$. $\Delta Hs^\circ_{298.15}$ (to dimer) was calculated as the difference between those for $Fe_2I_4(g)$ and 2 $FeI_2(c)$.

Iron Diiodide (FeI_2)
(Liquid) GFW = 309.6558

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	27.000	46.720	46.720	.000	-16.969	-20.676	15.156
300	27.000	46.887	46.720	.050	-16.954	-20.699	15.079
400	27.000	54.654	47.779	2.750	-20.052	-21.928	11.981
500	27.000	60.679	49.779	5.450	-29.550	-21.517	9.405
600	27.000	65.602	52.018	8.150	-28.477	-20.013	7.290
700	27.000	69.764	54.264	10.850	-27.465	-18.684	5.833
800	27.000	73.369	56.432	13.550	-26.534	-17.493	4.779
900	27.000	76.549	58.494	16.250	-25.714	-16.413	3.986
1000	27.000	79.394	60.444	18.950	-25.076	-15.417	3.369
1100	27.000	81.967	62.285	21.650	-24.658	-14.467	2.874
1200	27.000	84.317	64.075	24.350	-24.030	-13.574	2.472
1300	27.000	86.478	65.670	27.050	-23.062	-12.741	2.142
1400	27.000	88.479	67.229	29.750	-22.113	-11.983	1.871
1500	27.000	90.341	68.708	32.450	-21.179	-11.293	1.645
1600	27.000	92.084	70.115	35.150	-20.262	-10.662	1.456
1700	27.000	93.721	71.456	37.850	-19.653	-10.085	1.297
1800	27.000	95.264	72.736	40.550	-18.861	-9.544	1.159
1900	27.000	96.724	73.961	43.250	-21.757	-8.864	1.020
2000	27.000	98.109	75.134	45.950	-21.033	-8.207	.897

Sept. 30, 1966

IRON DIIODIDE (FeI_2) (LIQUID) GFW = 309.6558

$S^\circ_{298.15}$ = [46.720] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [16.969] kcal/mol

Tm = 860 ± 2° K ΔHm° = [10.7] kcal/mol

Tb =[1366] °K ΔHv° = [25.0] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) was obtained from $\Delta Hf^\circ_{298.15}$ (c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K. The value of Cp was calculated on an assumption that Cp = 9.0 gibbs/g-atom for $FeI_2(l)$. The entropy was obtained in a manner analogous to that of the heat of formation.

Vaporization Data.

Tb is the temperature at which the vapor pressure of $FeI_2(g)$ and $Fe_2I_4(g)$ over $FeI_2(l)$ equals one atmosphere. The value of ΔHv° is derived from the vapor composition and the heats of vaporization of $FeI_2(l)$ to monomer and dimer at Tb.

Iron Diiodide (FeI_2)

(Ideal Gas) GFW = 309.6558

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.864	21.365	21.365	INFINITE
100	12.887	68.365	96.158	-2.779	21.618	16.386	-35.811
200	14.172	77.789	84.851	-1.412	21.385	11.226	-12.268
298	14.545	83.530	83.530	.000	21.000	6.318	-4.631
300	14.549	83.620	83.530	.027	20.992	6.227	-4.537
400	14.698	87.828	84.103	1.490	16.657	1.512	-.826
500	14.772	91.117	85.189	2.964	5.933	-1.253	.548
600	14.819	93.815	86.408	4.444	5.786	-2.678	.976
700	14.861	96.102	87.634	5.928	5.582	-4.073	1.272
800	14.911	98.090	88.819	7.416	5.301	-5.435	1.485
900	14.972	99.849	89.949	8.910	4.915	-6.754	1.640
1000	15.046	101.430	91.019	10.411	4.354	-8.023	1.753
1100	15.131	102.868	92.032	11.920	3.581	-9.219	1.832
1200	15.222	104.189	92.991	13.438	3.027	-10.364	1.888
1300	15.317	105.411	93.900	14.964	2.821	-11.471	1.928
1400	15.411	106.550	94.763	16.501	2.607	-12.562	1.961
1500	15.502	107.616	95.585	18.047	2.387	-13.639	1.987
1600	15.588	108.619	96.368	19.601	2.158	-14.698	2.008
1700	15.667	109.567	97.117	21.164	1.630	-15.741	2.024
1800	15.738	110.464	97.834	22.734	1.292	-16.751	2.034
1900	15.801	111.317	98.521	24.311	-2.727	-17.560	2.020
2000	15.856	112.129	99.182	25.894	-3.120	-18.334	2.003
2100	15.902	112.903	99.817	27.482	-3.513	-19.080	1.986
2200	15.939	113.644	100.429	29.074	-3.908	-19.814	1.968
2300	15.970	114.353	101.019	30.670	-4.304	-20.528	1.951
2400	15.993	115.033	101.589	32.268	-4.703	-21.225	1.933
2500	16.010	115.687	102.139	33.868	-5.106	-21.906	1.915
2600	16.021	116.315	102.673	35.470	-5.512	-22.571	1.897
2700	16.027	116.920	103.189	37.072	-5.924	-23.220	1.880
2800	16.029	117.503	103.690	38.675	-6.340	-23.851	1.862
2900	16.026	118.065	104.176	40.278	-6.761	-24.469	1.844
3000	16.021	118.608	104.648	41.880	-7.189	-25.072	1.826
3100	16.012	119.133	105.107	43.482	-7.622	-25.658	1.809
3200	16.001	119.642	105.553	45.082	-91.487	-24.792	1.693
3300	15.987	120.134	105.988	46.682	-91.470	-22.708	1.504
3400	15.972	120.611	106.411	48.280	-91.464	-20.625	1.326
3500	15.956	121.074	106.823	49.876	-91.468	-18.542	1.158
3600	15.938	121.523	107.225	51.471	-91.484	-16.456	.999
3700	15.920	121.959	107.618	53.064	-91.510	-14.372	.849
3800	15.901	122.384	108.001	54.655	-91.548	-12.291	.707
3900	15.881	122.796	108.375	56.244	-91.598	-10.197	.571
4000	15.861	123.198	108.740	57.831	-91.660	-8.116	.443
4100	15.841	123.590	109.098	59.416	-91.733	-6.022	.321
4200	15.820	123.971	109.447	60.999	-91.820	-3.931	.205
4300	15.800	124.343	109.790	62.580	-91.919	-1.838	.093
4400	15.780	124.706	110.124	64.159	-92.031	.255	-.013
4500	15.760	125.060	110.452	65.736	-92.156	2.358	-.115
4600	15.740	125.407	110.774	67.311	-92.293	4.459	-.212
4700	15.721	125.745	111.089	68.884	-92.444	6.562	-.305
4800	15.701	126.076	111.398	70.455	-92.608	8.672	-.395
4900	15.682	126.399	111.700	72.025	-92.785	10.786	-.481
5000	15.664	126.716	111.998	73.592	-92.977	12.898	-.564
5100	15.646	127.026	112.289	75.157	-93.181	15.016	-.643
5200	15.628	127.330	112.576	76.721	-93.400	17.136	-.720
5300	15.611	127.627	112.857	78.283	-93.631	19.270	-.795
5400	15.594	127.919	113.133	79.843	-93.877	21.402	-.866
5500	15.577	128.205	113.404	81.402	-94.135	23.537	-.935
5600	15.561	128.485	113.671	82.959	-94.408	25.678	-1.002
5700	15.546	128.761	113.933	84.514	-94.694	27.822	-1.067
5800	15.530	129.031	114.191	86.068	-94.993	29.979	-1.130
5900	15.516	129.296	114.445	87.620	-95.305	32.135	-1.190
6000	15.501	129.557	114.695	89.171	-95.630	34.300	-1.249

Sept. 30, 1966

IRON DIIODIDE (FeI_2) (IDEAL GAS) GFW = 309.6558

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [83.5] gibbs/mol

ΔHf°_0 = [21.4 ± 3] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [21.0 ± 3] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[10]
[4200]	[10]
[6800]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
[140]	(1)
[32]	(2)
[280]	(1)

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I = [180]°

Rotational Constant: B_o =[0.01124] cm^{-1} σ = 2

Heat of Formation.

The chemical equilibria for the reactions: (A) $FeI_2(c) = FeI_2(g)$, (B) $FeI_2(l) = FeI_2(g)$, and (C) $Fe(c)+2I(g)=FeI_2(g)$, have been studied by several investigators. Based on the equilibrium pressures reported, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented in the table below. Using the third law $\Delta Hr^\circ_{298.15}$ values, the heats of formation for $FeI_2(g)$ were calculated. The adopted value for $\Delta Hf^\circ_{298.15}(FeI_2,g)$ is 21.0 ± 3 kcal/mol. The disagreement between the sets of second and third law $\Delta Hr^\circ_{298.15}$ values listed in the table may be due to the presence of dimer, $Fe_2I_4(g)$, which was not accounted for in deriving the partial pressure of $FeI_2(g)$. The data obtained from Schoonmaker et al. was adjusted for the presence of dimer.

Investigator	Reaction	Temperature, °K	Method	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$ kcal/mol
Schafer and Hones*[1]	(A)	790.15 - 850.15	Transpiration	41.81	46.58	+ 5.78	21.58
	(B)	874.15 - 959.15	Transpiration	43.56	35.58	- 8.75	18.6
Schoonmaker et al.[2]	(A)	714	Mass Spectrometric	-	46.78	-	21.78
Sime and Gregory*[3]	(A)	670.0 - 740.0	Torsion - Effusion	45.13	45.70	0.85	20.7
Zaugg and Gregory[4]	(C)	865.15 -1023.15	Transpiration	-32.53	-28.99	3.75	22.1

*The vapor pressure data used for evaluation were those adjusted by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 490 (1966).

1. H. Schäfer and W. J. Hones, Z. Anorg. Allgem. Chem. 288, 62 (1956).
2. R. C. Schoonmaker, A. H. Friedman and F. R. Porter, J. Chem. Phys. 31, 1586 (1959).
3. R. J. Sime and N. W. Gregory, J. Phys. Chem. 64, 86 (1960). The vapor pressure equation used for calculation is log P_{mm} = -(9760/T) + 11.82. In the original paper, the term A = 960 should be 9760.
4. W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 490 (1966).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The Fe-I bond distance was estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The vibrational frequencies were estimated so that the derived gibbs energy functions yielded second and third law $\Delta Hr^\circ_{298.15}$ values in reasonable agreements (see the above table). The electronic levels and quantum weights were estimated from those for $FeCl_2(g)$ reported by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The moment of inertia is 2.48844 x 10^{-37} g cm^2.

Wüstite ($Fe_{0.947}O$)

(Crystal) Mol. Wt. = 68.88651

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.262	-63.846	-63.846	INFINITE
100	5.577	2.938	23.548	-2.061	-64.100	-62.178	135.884
200	10.986	9.319	14.793	-1.095	-63.873	-60.299	65.888
298	11.500	13.764	13.764	.000	-63.640	-58.595	42.949
300	11.516	13.835	13.764	.021	-63.636	-58.564	42.662
400	12.041	17.224	14.223	1.201	-63.405	-56.908	31.092
500	12.392	19.950	15.104	2.423	-63.187	-55.309	24.174
600	12.674	22.235	16.107	3.676	-63.002	-53.752	19.578
700	12.923	24.207	17.127	4.956	-62.859	-52.222	16.304
800	13.155	25.948	18.123	6.260	-62.776	-50.710	13.853
900	13.377	27.510	19.080	7.587	-62.780	-49.201	11.947
1000	13.593	28.931	19.996	8.936	-62.941	-47.686	10.421
1100	13.805	30.237	20.868	10.305	-63.293	-46.140	9.167
1200	14.013	31.447	21.700	11.696	-63.427	-44.580	8.119
1300	14.220	32.577	22.493	13.108	-63.223	-43.017	7.232
1400	14.426	33.638	23.252	14.540	-63.017	-41.470	6.473
1500	14.630	34.640	23.978	15.993	-62.808	-39.938	5.819
1600	14.834	35.591	24.674	17.466	-62.596	-38.421	5.248
1700	15.006	36.496	25.343	18.959	-62.657	-36.911	4.745
1800	15.130	37.357	25.987	20.466	-62.533	-35.399	4.298
1900	15.224	38.178	26.607	21.984	-65.892	-33.721	3.879
2000	15.300	38.961	27.206	23.510	-65.815	-32.032	3.500
2100	15.353	39.709	27.783	25.043	-65.739	-30.343	3.158
2200	15.400	40.424	28.342	26.581	-65.665	-28.658	2.847
2300	15.440	41.109	28.882	28.123	-65.592	-26.978	2.563
2400	15.473	41.767	29.405	29.669	-65.523	-25.301	2.304
2500	15.500	42.399	29.912	31.217	-65.457	-23.625	2.065

June 30, 1965

WÜSTITE ($Fe_{0.947}O$) (CRYSTAL) MOL. WT. = 68.88651

$\Delta H_f^\circ{}_0 = -63.85 \pm 0.20$ kcal. mole^{-1}

$S^\circ_{298.15} = 13.764 \pm 0.10$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -63.64 \pm 0.20$ kcal. mole^{-1}

$T_m = 1650$°K.

$\Delta H_m^\circ = 7.49$ kcal. mole^{-1}

Heat of Formation.

The chemical equilibria in the Fe-C-O and Fe-H-O systems have been studied by many investigators. Using the reported equilibrium constants for the following two reactions (1) $Fe_{0.947}O(c) + CO(g) = 0.947Fe(c) + CO_2(g)$ and (2) $Fe_{0.947}O(c,l) + H_2(g) = 0.947Fe(c) + H_2O(g)$, the corresponding enthalpy changes (ΔH_r°) were evaluated by both the second and third law methods. Based on the third law values for ΔH_r°, the $\Delta H_f^\circ{}_{298.15}$ (Wüstite, c) values were also calculated. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	$\Delta H_r^\circ{}_{298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	$\Delta H_f^\circ{}_{298.15}$ kcal. mole^{-1}
Eastman[1]	(1)	873.2-1273.2	-3.80 ± 0.01	-4.01	-63.63
Eastman - Evans[2]	(1)	973.2-1273.2	-4.02 ± 0.01	-4.03	-63.61
Eastman[1]	(2)	873.2-1273.2	6.50 ± 0.12	5.90	-63.70
Eastman - Evans[2]	(2)	973.2-1273.2	5.81 ± 0.01	5.07	-62.86
Emmett - Schultz[3]	(2)	873.2-1273.2	5.95 ± 0.07	5.82	-63.62
Britzke et al.[4]	(2)	1123.2-1498.2	-2.25 ± 0.03	4.26	-62.06
Jominy - Murphy[5]	(2)	1360.0-1646.0	5.01 ± 0.61	6.01	-63.81
Chipman - Marshall[6]	(2)	1438.2-1633.2	5.03 ± 0.34	5.85	-62.83
Chipman - Marshall[6]	(2)	1653.2-1787.2	-2.61 ± 0.77	-0.02	-61.87
Jominy - Murphy[5]	(2)	1698.0-1700.0	———	0.87	-62.72
Britzke et al.[4]	(3)	1123.0-1473.0	-129.08 ± 0.18	-126.28	-63.14

[1] E. D. Eastman, J. Am. Chem. Soc. 44, 975 (1922).

[2] E. D. Eastman and R. M. Evans, J. Am. Chem. Soc. 46, 888 (1924). The K_p value at 1273.2°K. for reaction (1) is rejected by a statistical criterion.

[3] P. H. Emmett and J. F. Schultz, J. Am. Chem. Soc. 52, 4268 (1930).

[4] E. V. Britzke, A. F. Kapustinsky and T. I. Schaschkina, Z. anorg. allgem. Chem. 219, 287 (1934). The K_p value at 1123°K. for reaction (3) is rejected by a statistical criterion.

[5] W. E. Jominy and D. W. Murphy, Ind. Eng. Chem. 23, 384 (1931). The K_p values at 1590 and 1645°K. are rejected by a statistical criterion.

[6] J. Chipman and S. Marshall, J. Am. Chem. Soc. 62, 299 (1940).

Britzke et al. also determined the equilibrium pressures for the reaction (3) $1.894\ Fe(c) + O_2(g) = 2Fe_{0.947}O(c)$. The corresponding $\Delta H_f^\circ{}_{298.15}$ for Wüstite was evaluated based on the third law value for $\Delta H_r^\circ{}_{298.15}$. The adopted value of $\Delta H_f^\circ{}_{298.15}$ (Wüstite,c) is the weighted average of the $\Delta H_f^\circ{}_{298.15}$ listed in the above table.

Heat Capacity and Entropy.

The low temperature (54.37-298.16°K.) heat capacities (C_p) were measured by S. S. Todd and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3894 (1951). The high temperature (298-1650°K.) heat capacities were determined by J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 1650°K. were obtained by graphical extrapolation. The low temperature (70.7-279.8°K.)C_p's were also reported by R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929). $S^\circ_{298.15}$ was derived from the low temperature heat capacities, based on $S^\circ_{52} = 0.696$ cal. deg.$^{-1}$ mole^{-1}. S. S. Todd and K. R. Bonnickson, loc. cit. added 0.41 e.u., the amount calculated for completely random distribution of the vacant Fe spaces in the Wüstite lattice. However, the free energy functions derived from $S^\circ_{52} = 0.696$ e.u. give better agreement between second and third law values for ΔH_r° than those derived from $S^\circ_{52} = 1.11$ e.u. Therefore the value 0.41 e.u. was not added here.

Melting Data.

T_m and ΔH_m° were taken from J. P.Coughlin, E. G. King and K. R. Bonnickson, et al. T_m was reported as 1372°C. (1645°K.) by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946) and as 1369°C. (1642°K.) by J. Chipman and S. Marshall, loc. cit.

Iron Oxide (FeO)

(Crystal) Mol. Wt. = 71.8464

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	11.930	14.520	14.520	.000	-65.020	-60.097	44.050
300	11.950	14.594	14.520	.022	-65.015	-60.067	43.757
400	12.390	18.094	14.994	1.240	-64.779	-58.454	31.936
500	12.760	20.898	15.904	2.497	-64.562	-56.897	24.868
600	13.120	23.257	16.938	3.792	-64.375	-55.382	20.172
700	13.420	25.303	17.990	5.119	-64.226	-53.896	16.826
800	13.700	27.113	19.019	6.475	-64.137	-52.427	14.322
900	13.930	28.740	20.011	7.857	-64.138	-50.964	12.375
1000	14.190	30.222	20.959	9.263	-64.303	-49.495	10.817
1100	14.396	31.584	21.863	10.692	-64.668	-47.991	9.535
1200	14.600	32.845	22.727	12.142	-64.805	-46.474	8.464
1300	14.813	34.022	23.551	13.613	-64.586	-44.955	7.557
1400	15.000	35.127	24.339	15.104	-64.366	-43.453	6.783
1500	15.151	36.167	25.093	16.611	-64.147	-41.968	6.114
1600	15.300	37.150	25.816	18.134	-63.932	-40.496	5.531
1700	15.449	38.082	26.510	19.671	-64.010	-39.033	5.018
1800	15.590	38.969	27.178	21.223	-63.894	-37.566	4.561
1900	15.724	39.815	27.821	22.789	-67.452	-35.921	4.132
2000	15.850	40.625	28.441	24.368	-67.380	-34.266	3.744

June 30, 1965

IRON OXIDE (FeO) (CRYSTAL) MOL. WT. = 71.8464

$\Delta H_{f\ 0}^\circ$ = Unknown

$S^\circ_{298.15}$ = [14.52] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = [-65.02] kcal. mole^{-1}

T_m = [1650]°K.

ΔH_m° = [5.75] kcal. mole^{-1}

$\Delta H_{s\ 298.15}^\circ$ = [121.62] kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H_{f\ 298.15}^\circ$ for FeO(c) was derived based on an assumption that at 1650°K., ΔF_f° (FeO, c) = ΔF_f° (FeO, l). From the value $\Delta F_{f\ 1650}^\circ$ (FeO, c) = -39.77 kcal. mole^{-1}, $\Delta H_{f\ 1650}^\circ$ (FeO, c) was calculated to be -63.97 kcal. mole^{-1}, yielding $\Delta H_{f\ 298.15}^\circ$ (FeO, c) = -65.02 kcal. mole^{-1}.

Heat Capacity and Entropy.

The C_p values were estimated assuming C_p (FeO, c) = C_p (Wüstite, c) + 0.053 C_p (Fe, c). The C_p values obtained were plotted. The adopted C_p points were taken from the smoothed C_p curve. $S^\circ_{298.15}$ for FeO(c) was calculated as S° (FeO, c) = S° (Wüstite, c) + 0.053 S° (Fe, c) + ΔS° (mixing) where ΔS° is the entropy of mixing (0.41 cal. deg.$^{-1}$ mole^{-1}).

Melting Data.

T_m is assumed to be the same as that for Wüstite. The difference between $\Delta H_{f\ 1650}^\circ$ for FeO(l) and FeO(c) is ΔH_m°.

Heat of Sublimation.

$\Delta H_{s\ 298.15}^\circ$ is calculated as the difference between $\Delta H_{f\ 298.15}^\circ$ for FeO(g) and FeO(c).

Iron Oxide (FeO)

(Liquid) Mol. Wt. = 71.8464

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	11.500	18.029	18.029	.000	- 59.642	- 55.765	40.875
300	11.516	18.100	18.029	.021	- 59.638	- 55.741	40.606
400	12.041	21.489	18.488	1.201	- 59.440	- 54.473	29.761
500	12.392	24.215	19.370	2.423	- 59.259	- 53.252	23.275
600	12.674	26.500	20.373	3.676	- 59.113	- 52.065	18.964
700	12.923	28.473	21.392	4.956	- 59.011	- 50.899	15.891
800	13.155	30.214	22.388	6.260	- 58.974	- 49.745	13.589
900	13.377	31.776	23.346	7.587	- 59.030	- 48.588	11.798
1000	13.593	33.196	24.261	8.936	- 59.252	- 47.418	10.363
1100	16.300	34.502	25.133	10.306	- 59.676	- 46.210	9.181
1200	16.300	35.920	25.974	11.936	- 59.633	- 44.993	8.194
1300	16.300	37.225	26.790	13.566	- 59.255	- 43.788	7.361
1400	16.300	38.433	27.579	15.196	- 58.896	- 42.612	6.652
1500	16.300	39.558	28.341	16.826	- 58.554	- 41.462	6.041
1600	16.300	40.610	29.075	18.456	- 58.232	- 40.333	5.509
1700	16.300	41.598	29.783	20.086	- 58.218	- 39.218	5.042
1800	16.300	42.529	30.465	21.716	- 58.023	- 38.104	4.626
1900	16.300	43.411	31.124	23.346	- 61.518	- 36.819	4.235
2000	16.300	44.247	31.759	24.976	- 61.394	- 35.524	3.882
2100	16.300	45.042	32.373	26.606	- 61.276	- 34.231	3.562
2200	16.300	45.800	32.966	28.236	- 61.166	- 32.945	3.273
2300	16.300	46.525	33.540	29.866	- 61.062	- 31.667	3.009
2400	16.300	47.219	34.095	31.496	- 60.965	- 30.392	2.767
2500	16.300	47.884	34.634	33.126	- 60.875	- 29.118	2.545
2600	16.300	48.523	35.156	34.756	- 60.791	- 27.849	2.341
2700	16.300	49.139	35.662	36.386	- 60.714	- 26.586	2.152
2800	16.300	49.731	36.154	38.016	- 60.644	- 25.321	1.976
2900	16.300	50.303	36.632	39.646	- 60.580	- 24.060	1.813
3000	16.300	50.856	37.097	41.276	- 60.522	- 22.802	1.661
3100	16.300	51.390	37.550	42.906	- 60.471	- 21.543	1.519
3200	16.300	51.908	37.991	44.536	- 143.851	- 18.846	1.287
3300	16.300	52.409	38.420	46.166	- 143.349	- 14.948	.990
3400	16.300	52.896	38.839	47.796	- 142.857	- 11.065	.711
3500	16.300	53.369	39.247	49.426	- 142.374	- 7.199	.450
3600	16.300	53.828	39.646	51.056	- 141.902	- 3.340	.203
3700	16.300	54.274	40.035	52.686	- 141.439	.504	- .030
3800	16.300	54.709	40.415	54.316	- 140.987	4.331	- .249
3900	16.300	55.132	40.787	55.946	- 140.544	8.153	- .457
4000	16.300	55.545	41.151	57.576	- 140.112	11.956	- .653
4100	16.300	55.948	41.507	59.206	- 139.689	15.754	- .840
4200	16.300	56.340	41.856	60.836	- 139.278	19.541	- 1.017
4300	16.300	56.724	42.197	62.466	- 138.877	23.319	- 1.185
4400	16.300	57.099	42.531	64.096	- 138.486	27.081	- 1.345
4500	16.300	57.465	42.859	65.726	- 138.107	30.841	- 1.498
4600	16.300	57.823	43.181	67.356	- 137.737	34.597	- 1.644
4700	16.300	58.174	43.496	68.986	- 137.380	38.336	- 1.783
4800	16.300	58.517	43.805	70.616	- 137.033	42.074	- 1.916
4900	16.300	58.853	44.109	72.246	- 136.697	45.798	- 2.043
5000	16.300	59.182	44.407	73.876	- 136.373	49.520	- 2.164

June 30, 1965

IRON OXIDE (FeO) (LIQUID) MOL. WT. = 71.8464

$S^\circ_{298.15}$ = 18.029 cal. deg.$^{-1}$ mole^{-1}

T_m = [1650]°K.

T_d = [3687]°K.

$\Delta H^\circ_{f\ 298.15}$ = [-59.642] kcal. mole^{-1}

ΔH°_m = [5.75] kcal. mole^{-1}

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) was evaluated based on an assumption that the heat of melting of Wüstite, $\Delta H^\circ_{m\ 1650}$ = 7.49 kcal. mole^{-1}, represents the enthalpy change of the reaction $Fe_{0.947}O(c) = 0.947\ FeO(l) + \frac{0.053}{2} O_2(g)$. In other words, during melting the wüstite releases $O_2(g)$ and converts to FeO(l).

Heat Capacity and Entropy.

The enthalpy changes ($H^\circ_T - H^\circ_{298.15}$, 1650-1800°K.) of liquid iron oxide were determined by J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). The C_p (FeO, l) was derived as 16.3 cal. deg.$^{-1}$ mole^{-1}. This value was adopted as the heat capacity for FeO(l) up to 4000°K. A glass transition temperature was assumed at 1100°K. $S^\circ_{298.15}$ (FeO, l) was calculated based on an assumption that the entropy of melting of Wüstite represents also the entropy change of the reaction, $Fe_{0.947}O\ (c) = 0.947\ FeO\ (l) + \frac{0.053}{2} O_2\ (g)$. From the entropy of melting, $\Delta S^\circ_{m\ 1650}$ = 4.539 e.u., the value $S^\circ_{298.15}$ (FeO, l) = 18.029 e.u. was derived.

Melting Data.

The melting point (T_m) for Wüstite ($Fe_{0.947}O$, c) has been reported by many investigators. However, the composition of the liquid state of Wüstite was not identified. An assumption was made that during melting the reaction $Fe_{0.947}O\ (c) = 0.947\ FeO\ (l) + \frac{0.053}{2} O_2\ (g)$ occurs. Hence the related thermodynamic properties were derived.

Decomposition Temperature.

T_d is the temperature at which ΔF°_f equals zero.

Iron Oxide (FeO)

(Ideal Gas) GFW = 71.8464

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.112	60.000	60.000	INFINITE
100	6.957	50.035	64.204	- 1.417	60.246	57.458	- 125.575
200	7.108	54.885	58.467	- .716	60.176	54.681	- 59.753
298	7.506	57.794	57.794	.000	60.000	52.021	- 38.132
300	7.514	57.841	57.794	.014	59.996	51.971	- 37.861
400	7.903	60.058	58.094	.786	59.787	49.327	- 26.951
500	8.188	61.854	58.672	1.591	59.551	46.739	- 20.430
600	8.388	63.365	59.331	2.420	59.273	44.202	- 16.101
700	8.530	64.670	60.003	3.267	58.942	41.715	- 13.024
800	8.632	65.816	60.659	4.125	58.533	39.280	- 10.731
900	8.709	66.837	61.290	4.992	58.017	36.904	- 8.962
1000	8.768	67.758	61.892	5.866	57.321	34.593	- 7.560
1100	8.815	68.596	62.463	6.745	56.405	32.369	- 6.431
1200	8.854	69.365	63.007	7.629	55.702	30.209	- 5.502
1300	8.888	70.075	63.524	8.516	55.338	28.099	- 4.724
1400	8.918	70.734	64.015	9.407	54.957	26.020	- 4.062
1500	8.947	71.351	64.484	10.300	54.562	23.965	- 3.492
1600	8.975	71.929	64.932	11.196	54.150	21.939	- 2.997
1700	9.003	72.474	65.359	12.095	53.433	19.944	- 2.564
1800	9.032	72.989	65.769	12.996	52.899	17.991	- 2.184
1900	9.064	73.479	66.162	13.901	48.680	16.250	- 1.869
2000	9.097	73.944	66.540	14.809	48.082	14.558	- 1.591
2100	9.132	74.389	66.903	15.721	47.481	12.898	- 1.342
2200	9.169	74.815	67.253	16.636	46.876	11.264	- 1.119
2300	9.208	75.223	67.591	17.554	46.268	9.658	- .918
2400	9.249	75.616	67.917	18.477	45.658	8.079	- .736
2500	9.292	75.994	68.232	19.404	45.045	6.528	- .571
2600	9.336	76.359	68.538	20.336	44.431	4.999	- .420
2700	9.381	76.713	68.834	21.272	43.814	3.492	- .283
2800	9.428	77.055	69.122	22.212	43.195	2.011	- .157
2900	9.475	77.386	69.401	23.157	42.574	.553	- .042
3000	9.522	77.708	69.673	24.107	41.951	- .884	.064
3100	9.570	78.021	69.937	25.062	41.327	- 2.301	.162
3200	9.617	78.326	70.194	26.021	- 42.723	- 2.256	.154
3300	9.665	78.623	70.445	26.985	- 42.887	- .992	.066
3400	9.711	78.912	70.690	27.954	- 43.057	.281	- .018
3500	9.757	79.194	70.929	28.927	- 43.231	1.557	- .097
3600	9.802	79.469	71.162	29.905	- 43.411	2.844	- .173
3700	9.846	79.739	71.391	30.888	- 43.595	4.127	- .244
3800	9.889	80.002	71.614	31.875	- 43.786	5.418	- .312
3900	9.931	80.259	71.832	32.866	- 43.982	6.720	- .377
4000	9.972	80.511	72.046	33.861	- 44.185	8.019	- .438
4100	10.011	80.758	72.255	34.860	- 44.393	9.329	- .497
4200	10.048	81.000	72.461	35.863	- 44.609	10.638	- .554
4300	10.084	81.236	72.662	36.870	- 44.831	11.963	- .608
4400	10.119	81.469	72.860	37.880	- 45.060	13.279	- .660
4500	10.152	81.696	73.054	38.893	- 45.297	14.611	- .710
4600	10.183	81.920	73.244	39.910	- 45.541	15.947	- .758
4700	10.213	82.139	73.431	40.930	- 45.794	17.287	- .804
4800	10.242	82.355	73.614	41.953	- 46.054	18.631	- .848
4900	10.269	82.566	73.795	42.978	- 46.323	19.979	- .891
5000	10.294	82.774	73.972	44.006	- 46.600	21.332	- .932
5100	10.318	82.978	74.147	45.037	- 46.886	22.696	- .973
5200	10.341	83.179	74.319	46.070	- 47.181	24.064	- 1.011
5300	10.362	83.376	74.488	47.105	- 47.484	25.436	- 1.049
5400	10.382	83.570	74.654	48.142	- 47.798	26.812	- 1.085
5500	10.401	83.760	74.818	49.182	- 48.119	28.202	- 1.121
5600	10.418	83.948	74.979	50.223	- 48.451	29.588	- 1.155
5700	10.434	84.132	75.138	51.265	- 48.791	30.986	- 1.188
5800	10.449	84.314	75.295	52.309	- 49.142	32.392	- 1.221
5900	10.463	84.493	75.449	53.355	- 49.501	33.795	- 1.252
6000	10.476	84.669	75.602	54.402	- 49.869	35.214	- 1.283

June 30, 1965; Sept. 30, 1966

IRON OXIDE (FeO) (IDEAL GAS) GFW = 71.8464

Ground State Configuration [$^5\Delta$] ΔHf°_0 = 60 ± 5 kcal/mol

$S^\circ_{298.15}$ = [57.8] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 60 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1
0	[10]
[10000]	[10]
[16000]	[5]

ω_e = 880.0 cm^{-1} $\omega_e x_e$ = 5.0 cm^{-1} σ = 1

B_e = [0.4184] cm^{-1} α_e = [0.00293] cm^{-1} r_e = [1.8] Å

Heat of Formation.

The heat of formation for FeO(g) is not well established at the present time. The values of $\Delta Hf^\circ_{298.15}$ (FeO, g) derived from the following reactions: (1) FeO(g) = Fe(g) + O(g), (2) FeO(g) = Fe(g) + 1/2 O_2(g), and (3) FeO(l) = FeO(g), are not in agreement. There are three D° (Fe-O) values reported for reaction (1). The enthalpy change for reaction (2) was evaluated based on the partial pressure data (P_{FeO}/ P_{Fe}) = 0.2 at 1600°C, measured by Washburn[4], using a mass spectrometric method, U. S. Atomic Energy Commission, UCRL-10991, August 1963, and P_{O_2} = 1.66 x 10^{-6} atm reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). The enthalpy value for reaction (3) was calculated based on the reported value, ΔHv°_{2785} = 96.096 kcal/mol determined by Burtsev, Karasev and Samarin[5]. The results obtained are presented as follows. The value of $\Delta Hf^\circ_{298.15}$ for FeO(g) adopted is 60 ± 5 kcal/mol.

Investigator	Reaction	Method	$\Delta Hr^\circ_{298.15}$ kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
1. Herzberg (1950)	(1)	Spectroscopic	111.9	47.2
2. Gaydon (1953)	(1)	Spectroscopic	93.4 ± 23.1	65.7 ± 23.1
3. Lagerqvist and Huldt (1953)	(1)	Spectroscopic	99.0 ± 11.6	60.1 ± 11.6
4. Washburn et al. (1963)	(2)	Spectroscopic	99.3 ± 5	59.8 ± 5
5. Burtsev et al. (1964)	(3)	transpiration	111.8	52.2

1. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950.
2. A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.
3. A. Lagerqvist and L. Huldt, Z. Naturforsch. 8A, 493 (1953). D°_0 was derived from atomic spectra of Fe produced by acetylene-air flame method.
4. J.Washburn,UCRL 10991, August 1963,obtained from L. Brewer, private communication, October 18, 1966.
5. V. T. Burtsev, R. A. Karasev and A. M. Samarin, Fiz.-Khim. Osnovy Proizv. Stali, Akad. Nauk SSSR, Inst. Met., Tr. 6-01 [Shestoi] Konf., Moscow, 366 (1961); published in 1964.

Heat Capacity and Entropy.

Since the ground state configuration is due to Fe^{++} in a ligand field, it was assumed to be the same as that of $FeCl_2$(g) reported by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The electronic levels and quantum weights were estimated by comparison with those of $FeCl_2$(g). The values of ω_e and $\omega_e x_e$ were taken from G. Herzberg, loc. cit. The bond distance was calculated according to the method suggested by K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946), assuming FeO(g) as a polar molecule. The value of B_e was calculated by use of the relationship: B_e = (2.799076 x 10^{-39}) /I where I is the moment of inertia of FeO(g). The value of α_e was derived from ω_e, $\omega_e x_e$ and B_e by the method suggested by G. Herzberg, loc. cit. The principal moment of inertia is 6.6899 x 10^{-39} g cm^2.

Iron Sulfate ($FeSO_4$)

(Crystal) GFW = 151.9086

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.008	- 219.730	- 219.730	INFINITE
100	10.534	10.223	46.561	- 3.634	- 221.011	- 213.311	466.191
200	18.845	20.319	30.966	- 2.129	- 221.713	- 205.305	224.347
298	24.040	28.909	28.909	.000	- 222.000	- 197.176	144.534
300	24.140	29.058	28.910	.045	- 222.002	- 197.022	143.531
400	27.880	36.535	29.904	2.652	- 222.542	- 188.668	103.083
500	30.810	43.085	31.898	5.593	- 222.676	- 180.178	78.756
600	32.990	48.904	34.257	8.788	- 222.578	- 171.685	62.536
700	34.570	54.113	36.728	12.170	- 222.341	- 163.195	50.952
800	35.710	58.808	39.200	15.687	- 235.113	- 156.037	42.627
900	36.510	63.061	41.618	19.299	- 234.543	- 146.185	35.498
1000	37.160	66.943	43.960	22.983	- 234.111	- 136.392	29.808
1100	37.710	70.511	46.213	26.727	- 233.863	- 126.629	25.159
1200	38.200	73.813	48.377	30.523	- 233.370	- 116.906	21.292
1300	38.640	76.889	50.454	34.365	- 232.510	- 107.235	18.028
1400	39.040	79.767	52.446	38.250	- 231.639	- 97.631	15.241
1500	39.420	82.473	54.358	42.173	- 230.759	- 88.091	12.835
1600	39.780	85.029	56.196	46.133	- 229.870	- 78.608	10.737
1700	40.120	87.451	57.964	50.128	- 229.263	- 69.176	8.893
1800	40.460	89.754	59.667	54.157	- 228.453	- 59.782	7.259
1900	40.780	91.950	61.308	58.219	- 231.308	- 50.247	5.780
2000	41.100	94.050	62.893	62.313	- 230.521	- 40.743	4.452

June 30, 1966

IRON SULFATE ($FeSO_4$) (CRYSTAL) GFW = 151.9086

ΔHf°_0 = -219.7 ± 2 kcal/mol

$S^\circ_{298.15}$ = 28.91 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -222.0 ± 2 kcal/mol

Td = 944°K

Heat of Formation.

The enthalpy change for the reaction $FeSO_4(c) = FeSO_4\ (110\ H_2O)$ was determined to be -14.9 kcal/mol by R. de Forcrand, Comp. rend. 158, 20 (1914). Using $\Delta Hf^\circ_{298.85}$ = -235.85 kcal/mol for $FeSO_4\ (110\ H_2O)$, the heat of formation (298.15°K) for $FeSO_4(c)$ was calculated as -221 kcal/mol. The value of $\Delta Hf^\circ_{298.15}\ (FeSO_4,c)$ was estimated based on $\Delta Hf^\circ_{298.15}$ = 235.9 kcal/mol for $FeSO_4\ (200\ H_2O)$ which was derived from the enthalpy change for the reaction $FeCl_2(200\ H_2O) + H_2SO_4\ (200\ H_2O) = FeSO_4\ (200\ H_2O) + 2HCl\ (100\ H_2O)$ measured by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886. See the $Fe(OH)_2$ (c) table for details.

The decomposition pressures of $FeSO_4(c)$ at different temperatures were investigated by J. D'Ans and E. Greulich. Using their reported partial pressures for SO_3 (g) and $SO_2(g)$, the enthalpy change for the reaction $2\ FeSO_4\ (c) = Fe_2O_3\ (c) + SO_3(g) + SO_2(g)$ was evaluated by both the second and third law methods. The results obtained are presented in the following table.

Investigator	Temperature, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	Third Law Value	$\Delta Hf^\circ_{298.15}$ kcal/mol
1. J. D'Ans (1905)	753.15 - 908.15	83.2 ± 4.6	82.7 ± 1.1	- 222.7
2. E. Greulich (1927)	887.15 - 971.15	64.8 ± 8.8	80.1 ± 1.4	- 221.5
3. B. Neumann and G. Heintke (1937)	633.15 - 862.15	72.4 ± 5.4	75.3 ± 0.5	- 219.1

1. J. D'Ans, Dissertation, Darmstadt, 1905. Data quoted by B. Neumann and G. Heintke, loc. cit.
2. E. Greulich, Z. anorg. Chem. 168, 197 (1927). Only the last seven high temperature points were adopted for evaluation.
3. B. Neumann and G. Heintke, Z. Elektrochem. 43, 246 (1937), based on the last 18 high temperature points adopted.

The decomposition pressures assumed for the same reaction have been determined by B. Neumann and G. Heintke. From their data the partial pressures for $SO_3(g)$ and $SO_2(g)$ were evaluated. Using the derived $SO_3(g)$ and $SO_2(g)$ partial pressures, the corresponding enthalpy changes for the reaction were calculated by both the second and third law methods. The results obtained are also listed in the same table.

The value of $\Delta Hf^\circ_{298.15}$ for $FeSO_4(c)$ is selected as -222 ± 2 kcal/mol.

Heat Capacity and Entropy.

The low temperature heat capacities, 53.0-294.9°K, were determined by G. E. Moore and K. K. Kelley, J. Am. Chem. Soc., 64, 2949 (1942). Based on $S^\circ_{50.12}$ = 2.10 eu, the value of $S^\circ_{298.15}\ (FeSO_4,\ c)$ was reported to be 25.71 ± 0.2 eu. Using the free energy functions for $FeSO_4(c)$ based on this $S^\circ_{298.15}$ value, to evaluate the vapor pressure data for Reaction (1), the second and third law values of $\Delta Hf^\circ_{298.15}$ were derived as 72.36 ± 7.60 and 86.51 ± 1.26 kcal/mol, respectively. Since the report by Moore and Kelley, loc. cit., did not mention the magnetic entropy contribution, an attempt was made to add 3.20 (= Rln5) eu to $S^\circ_{298.15}\ (FeSO_4,\ c)$ and re-evaluate the decomposition pressure data. The results obtained were better than before (see the paragraph on "Heat of Formation," for details). Therefore the value, $S^\circ_{298.15}$ = 25.71 + 3.2 = 28.91 eu for $FeSO_4(c)$, was adopted. The heat capacities above 294.9°K were estimated by comparison with those for $MnSO_4(c)$. The high temperature heat capacities, 870.3-1082.3°K, were determined by J. C. Southard and C. H. Shomate, J. Am. Chem. Soc. 64, 1770 (1942). The two sets of data were joined smoothly at 298.15°K by use of Shomate-function plot.

Temperature of Decomposition.

Td is the temperature at which the vapor pressure of the gaseous decomposition products equals one atmosphere, which was obtained by graphical interpolation of the decomposition pressure data on $FeSO_4(c)$, reported by E. Greulich, loc. cit.

Iron Diiodide, Dimeric (Fe_2I_4)

(Ideal Gas) GFW = 619.3116

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-8.133	2.325	2.325	INFINITE
100	28.554	96.669	157.341	-6.067	2.727	-3.731	8.154
200	30.887	117.422	132.723	-3.060	2.534	-10.151	11.093
298	31.377	129.865	129.865	.000	2.000	-16.274	11.929
300	31.382	130.059	129.865	.058	1.988	-16.387	11.938
400	31.561	139.115	131.099	3.206	-6.460	-22.134	12.093
500	31.646	146.168	133.433	6.367	-27.695	-24.034	10.505
600	31.699	151.942	136.051	9.535	-27.781	-23.297	8.486
700	31.744	156.832	138.680	12.707	-27.985	-22.535	7.036
800	31.797	161.074	141.220	15.884	-28.346	-21.734	5.937
900	31.861	164.823	143.638	19.066	-28.924	-20.875	5.069
1000	31.939	168.184	145.927	22.256	-29.858	-19.936	4.357
1100	32.029	171.232	148.091	25.455	-31.223	-18.868	3.749
1200	32.129	174.023	150.138	28.663	-32.159	-17.715	3.226
1300	32.235	176.599	152.075	31.881	-32.405	-16.500	2.774
1400	32.343	178.992	153.914	35.110	-32.678	-15.265	2.383
1500	32.450	181.227	155.661	38.349	-32.971	-14.015	2.042
1600	32.554	183.325	157.325	41.600	-33.286	-12.738	1.740
1700	32.653	185.301	158.913	44.860	-34.208	-11.433	1.470
1800	32.744	187.170	160.431	48.130	-34.754	-10.076	1.223
1900	32.826	188.943	161.886	51.408	-42.668	-8.321	.957
2000	32.900	190.628	163.281	54.695	-43.333	-6.501	.710
2100	32.964	192.235	164.622	57.988	-44.002	-4.637	.483
2200	33.019	193.770	165.912	61.287	-44.677	-2.749	.273
2300	33.065	195.239	167.156	64.592	-45.356	-.831	.079
2400	33.102	196.647	168.355	67.900	-46.042	1.120	-.102
2500	33.131	197.999	169.514	71.212	-46.736	3.101	-.271
2600	33.152	199.299	170.635	74.526	-47.438	5.105	-.429
2700	33.167	200.550	171.720	77.842	-48.150	7.140	-.578
2800	33.175	201.756	172.771	81.159	-48.871	9.206	-.719
2900	33.178	202.921	173.791	84.477	-49.601	11.290	-.851
3000	33.176	204.045	174.781	87.794	-50.344	13.403	-.976
3100	33.169	205.133	175.742	91.112	-51.096	15.544	-1.096
3200	33.159	206.186	176.677	94.428	-218.710	20.592	-1.406
3300	33.146	207.206	177.587	97.743	-218.561	28.068	-1.859
3400	33.130	208.195	178.473	101.057	-218.431	35.539	-2.284
3500	33.112	209.156	179.336	104.369	-218.319	43.005	-2.685
3600	33.092	210.088	180.177	107.679	-218.231	50.473	-3.064
3700	33.071	210.994	180.998	110.988	-218.160	57.934	-3.422
3800	33.048	211.876	181.799	114.294	-218.112	65.390	-3.761
3900	33.024	212.734	182.581	117.597	-218.087	72.861	-4.083
4000	33.000	213.570	183.345	120.898	-218.084	80.308	-4.388
4100	32.975	214.385	184.093	124.197	-218.101	87.780	-4.679
4200	32.950	215.179	184.823	127.493	-218.145	95.238	-4.956
4300	32.925	215.954	185.538	130.787	-218.211	102.698	-5.220
4400	32.900	216.711	186.238	134.078	-218.302	110.154	-5.471
4500	32.874	217.450	186.924	137.367	-218.417	117.625	-5.713
4600	32.849	218.172	187.595	140.653	-218.555	125.107	-5.944
4700	32.825	218.878	188.253	143.937	-218.719	132.568	-6.164
4800	32.800	219.569	188.899	147.218	-218.908	140.051	-6.377
4900	32.776	220.245	189.531	150.497	-219.123	147.529	-6.580
5000	32.752	220.907	190.152	153.774	-219.364	155.011	-6.776
5100	32.729	221.555	190.762	157.048	-219.628	162.499	-6.964
5200	32.706	222.191	191.360	160.319	-219.923	169.989	-7.144
5300	32.684	222.813	191.948	163.589	-220.239	177.499	-7.319
5400	32.662	223.424	192.525	166.856	-220.584	185.010	-7.488
5500	32.641	224.023	193.092	170.121	-220.953	192.521	-7.650
5600	32.620	224.611	193.650	173.384	-221.350	200.034	-7.807
5700	32.600	225.188	194.198	176.645	-221.771	207.565	-7.958
5800	32.581	225.755	194.737	179.905	-222.217	215.108	-8.105
5900	32.562	226.312	195.268	183.162	-222.688	222.644	-8.247
6000	32.543	226.859	195.790	186.417	-223.185	230.205	-8.385

Sept. 30, 1966

IRON DIIODIDE, DIMERIC (Fe_2I_4) (IDEAL GAS) GFW = 619.3116

Point Group [D_{2h}]

ΔHf°_0 = 2.3 ± 5 kcal/mol

$S^\circ_{298.15}$ =[129.9]gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 2.0 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[5]
[4200]	[5]
[6800]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}		ω, cm^{-1}		ω, cm^{-1}	
[100]	(1)	[70]	(1)	[80]	(2)
[50]	(1)	[90]	(1)	[20]	(2)
[95]	(1)	[105]	(1)	[160]	(2)

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I_{bridge} = [135]° Fe - I_{bridge} - Fe = [90]°

I_{bridge} - Fe - I_{bridge} = [90]° σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [8.7771 x 10^{-110}]g^3cm^6

Heat of Formation.

The chemical equilibrium of the interaction of Fe(c) and I(g) has been studied by a transpiration method by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 490 (1966). Using the reported equilibrium constants in the temperature range from 591 to 751°K, the enthalpy change ($\Delta Hr^\circ_{298.15}$) of the reaction 2Fe(c) + 4 I (g) = Fe_2I_4(g) was evaluated by both the second and third law method to be -85.3 and -103.75 kcal/mol, respectively. The corresponding values of the heat of formation ($\Delta Hf^\circ_{298.15}$) for Fe_2I_4(g) were calculated as +16.9 and -1.6 kcal/mol.

Mass spectrometric and Knudsen effusion techniques have been used to study the vaporization of FeI_2(c) by R. C. Schoonmaker, A. H. Friedman and R. F. Porter, J. Chem. Phys. 31, 1586 (1959). Using the reported vapor pressure, P = 1.21 x 10^{-6} atm. at 714°K for Fe_2I_4(g), the enthalpy change ($\Delta Hr^\circ_{298.15}$) for the reaction 2 FeI_2(c) = Fe_2I_4(g) was evaluated by the third law method as 52.8 kcal/mol, yielding $\Delta Hf^\circ_{298.15}$ = 2.8 kcal/mol for Fe_2I_4(g).

The adopted value of $\Delta Hf^\circ_{298.15}$ for Fe_2I_4(g) is 2.0 ± 5 kcal/mol.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that assumed for Fe_2Br_4(g). The Fe-I bond distance was estimated from that in FeI_2(g) molecule. Four vibrational frequencies (ν_i), i.e. i = 2, 4, 5 and 6, were estimated by comparison with those for K_2I_2(g), calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The other frequency values were estimated from those for FeI_2(g). The electronic levels and quantum weights were estimated from those for FeI_2(g). The three principal moments of inertia are: I_A = 1.2442 x 10^{-37}, I_B = 7.7996 x 10^{-37} and I_C = 9.0439 x 10^{-37} g cm^2.

Hematite (Fe_2O_3)

(Crystal) Mol. Wt. = 159.6922

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.719	- 195.757	- 195.757	INFINITE
100	7.528	3.492	38.192	- 3.470	- 196.783	- 190.611	416.560
200	18.300	12.256	22.976	- 2.144	- 197.321	- 184.182	201.255
298	24.800	20.889	20.889	.000	- 197.300	- 177.719	130.265
300	24.900	21.043	20.889	.046	- 197.296	- 177.598	129.374
400	28.710	28.752	21.915	2.735	- 196.925	- 171.081	93.470
500	31.500	35.469	23.968	5.750	- 196.356	- 164.681	71.979
600	33.740	41.413	26.390	9.014	- 195.685	- 158.409	57.697
700	35.786	46.768	28.925	12.490	- 194.954	- 152.253	47.533
800	37.815	51.679	31.466	16.171	- 194.206	- 146.206	39.940
900	39.792	56.248	33.968	20.051	- 193.499	- 140.248	34.055
1000	36.000	60.440	36.415	24.025	- 193.079	- 134.363	29.364
1100	33.646	63.760	38.755	27.505	- 193.608	- 128.461	25.522
1200	33.822	66.695	40.963	30.879	- 193.832	- 122.540	22.316
1300	33.998	69.409	43.048	34.270	- 193.373	- 116.616	19.604
1400	34.174	71.935	45.022	37.678	- 192.938	- 110.728	17.285
1500	34.350	74.299	46.896	41.105	- 192.524	- 104.872	15.279
1600	34.552	76.522	48.679	44.550	- 192.132	- 99.040	13.528
1700	34.719	78.622	50.379	48.014	- 192.342	- 93.222	11.984
1800	34.842	80.611	52.004	51.492	- 192.179	- 87.396	10.611
1900	34.950	82.497	53.559	54.982	- 199.385	- 81.208	9.341
2000	35.083	84.293	55.051	58.484	- 199.346	- 74.994	8.195
2100	35.200	86.008	56.485	61.998	- 199.309	- 68.773	7.157
2200	35.300	87.648	57.865	65.523	- 199.280	- 62.559	6.214
2300	35.383	89.219	59.194	69.058	- 199.255	- 56.348	5.354
2400	35.450	90.726	60.477	72.599	- 199.241	- 50.133	4.565
2500	35.500	92.175	61.716	76.147	- 199.237	- 43.922	3.839

June 30, 1965

HEMATITE (Fe_2O_3) (CRYSTAL) MOL. WT. = 159.6922

$\Delta H_{f\ 0}^\circ = -195.8 \pm 0.3$ kcal. mole^{-1}

$S^\circ_{298.15} = 20.889$ cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15} = -197.3 \pm 0.3$ kcal. mole^{-1}

$T_d = 1735$°K.

Heat of Formation.

The chemical equilibria for the reaction $4Fe_3O_4(c) + O_2(g) = 6Fe_2O_3(c)$ have been studied by several investigators. From the reported data the corresponding values of $\Delta H^\circ_{r\ 298.15}$ and $\Delta H^\circ_{f\ 298.15}$ (Fe_2O_3, c) were evaluated. The results obtained are given as follows.

		$\Delta H^\circ_{r\ 298.15}$, kcal. mole^{-1}		$\Delta H^\circ_{f\ 298.15}$*
Investigator	Temperature, °K.	Second Law Value	Third Law Value	kcal. mole^{-1}
Tretyakov and Khomyakov[1]	1373-1728	-106.32 ± 0.19	-111.05	-197.11
Schmahl[2]	1583-1683	-123.95 ± 1.37	-112.94	-197.42
Smiltens[3]	1373-1673	-117.88 ± 0.38	-114.25	-197.64
Darken and Gurry[4]	1723	-110.29	——	-196.98

*Calculation based on the third law values for $\Delta H^\circ_{r\ 298.15}$.

[1] Y.D. Tretyakov and K. G. Khomyakov, Russ. J. Inorg. Chem. 7, 628 (1962).

[2] N. G. Schmahl, Z. Elektrochem. 47, 821 (1941).

[3] J. Smilten, J. Am. Chem. Soc. 79, 4877 (1957).

[4] L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). $\Delta H^\circ_{r\ 298.15}$ was calculated based on $\Delta H^\circ_{r\ 1723}$ = -54.5 kcal. mole^{-1}.

The value of $\Delta H^\circ_{f\ 298.15}$ adopted for $Fe_2O_3(c)$ is the weighted average of the $\Delta H^\circ_{f\ 298.15}$ values listed in the above table.

Heat Capacity and Entropy.

The low temperature (5.58-345.42°K.) heat capacities were determined by F. Gronvold and E. F. Westrum, Jr., J. Am. Chem. Soc. 81, 1780 (1959). The high temperature (298-1750°K.) C_p values were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). The two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1750°K. were obtained by graphical extrapolation. The heat capacities of $Fe_2O_3(c)$ have also been reported by G. G. Brown and C. C. Furnas, Trans. Am. Inst. Chem. Eng. 18, 309 (1926), 0-650°C, and G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926), 88-289°K. $S^\circ_{298.15}$ for $Fe_2O_3(c)$ was derived from the smoothed C_p data, based on $S^\circ_5 = 0.0003$ e.u. J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for hematite and found two anomalies, presumably of magnetic nature, at about 950 and 1050°K., respectively. Both appear to involve maxima in the heat-capacity curves rather than isothermal heats of transformation. The complex magnetic properties at low temperatures were discussed by F. Gronvold and E. F. Westrum, Jr., loc. cit. No heat capacity anomaly was observed at the magnetic transition about 250°K. The Curie points of the antiferromagnetic α-Fe_2O_3 were reported by A. Aharoni, E. H. Frei and M. Schieber, Phys. Rev. 127, 439 (1962) and J. Lielmezs and A. C. D. Chaklader, Phys. Rev. Letters, 13, 866 (1965).

Temperature of Decomposition.

T_d is the temperature at which $\Delta F^\circ_r = 0$ for the reaction $6Fe_2O_3(c) = 4Fe_3O_4(c) + O_2(g)$. In other words, $Fe_2O_3(c)$ decomposes into $Fe_3O_4(c)$ and $O_2(g)$ at 1735°K.

Diiron Trisulfate ($Fe_2(SO_4)_3$)

(Crystal) GFW = 399.8788

T, °K	gibbs/mol Cp°	S°	$-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	63.270	73.500	73.500	.000	- 617.350	- 540.882	396.477
300	63.540	73.892	73.501	.117	- 617.363	- 540.408	393.686
400	73.380	93.570	76.117	6.981	- 619.314	- 514.624	281.178
500	81.090	110.809	81.367	14.721	- 620.124	- 488.343	213.454
600	86.830	126.125	87.575	23.130	- 620.276	- 461.962	168.270
700	90.990	139.837	94.079	32.031	- 620.021	- 435.521	135.976
800	93.990	152.193	100.584	41.287	- 658.764	- 413.004	112.827
900	96.090	163.388	106.950	50.794	- 657.407	- 382.362	92.850
1000	97.810	173.604	113.112	60.492	- 656.308	- 351.860	76.899
1100	99.250	182.995	119.044	70.346	- 655.567	- 321.449	63.866
1200	100.540	191.687	124.740	80.337	- 654.322	- 291.136	53.023
1300	101.700	199.781	130.205	90.450	- 652.332	- 260.947	43.869
1400	102.750	207.357	135.448	100.672	- 650.313	- 230.919	36.048
1500	103.750	214.480	140.482	110.998	- 648.263	- 201.038	29.291
1600	104.700	221.207	145.319	121.421	- 646.184	- 171.287	23.397
1700	105.600	227.581	149.972	131.936	- 644.658	- 141.657	18.211
1800	106.490	233.642	154.453	142.541	- 642.719	- 112.124	13.614
1900	107.330	239.422	158.774	153.232	- 648.102	- 82.326	9.470
2000	108.180	244.949	162.946	164.007	- 646.192	- 52.610	5.749

June 30, 1966

DIIRON TRISULFATE ($Fe_2(SO_4)_3$) (CRYSTAL) GFW = 399.8788

$S°_{298.15}$ = [73.5 ± 2] gibbs/mol

Td = 1451°K

$\Delta Hf°_0$ = Unknown

$\Delta Hf°_{298.15}$ = -617.35 ± 0.40 kcal/mol

Heat of Formation.

The enthalpy change ($\Delta Hr°_{298.15}$) for the chemical reaction $Fe_2O_3(c) + 3H_2SO_4(14.855\ H_2O) = Fe_2(SO_4)_3(c) + 3H_2O(l)$ was measured to be 8.54 ± 0.18 kcal/mol by solution calorimetry by R. Barany and L. H. Adami, U. S. Bur. Mines RI 6687, 1965. Using $\Delta Hf°_{298.15}$ = -211.178 kcal/mol for $H_2SO_4(14.855\ H_2O)$ and -68.315 kcal/mol for $H_2O(l)$, obtained from "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, by D. D. Wagman and coworkers, National Bureau of Standards, 1965, and -197.3 kcal/mol for $Fe_2O_3(c)$, the heat of formation ($\Delta Hf°_{298.15}$) for $Fe_2(SO_4)_3(c)$ was evaluated as -617.35 ± 0.40 kcal/mol which was adopted here.

The equilibrium pressures for the decomposition of $Fe_2(SO_4)_3(c)$ have been determined by several investigators at different temperatures. The chemical reactions involved are: (1) $Fe_2(SO_4)_3(c) = Fe_2O_3(c) + 3SO_3(g)$ and (2) $SO_3(g) = SO_2(g) + 0.5\ O_2(g)$. However, the measured pressure of the chemical equilibrium is the total pressure of three partial pressures, namely, P_{SO_3}, P_{SO_2} and P_{O_2}. In order to calculate the enthalpy change of Reaction (1), the partial pressures of $SO_3(g)$ were evaluated from the total vapor pressure data at each temperature. Based on the derived values for P_{SO_3}, the $\Delta Hr°_{298.15}$ value for Reaction (1) was calculated by both the second and third law methods. The results obtained are presented in the following table. The $\Delta Hf°_{298.15}$ ($Fe_2(SO_4)_3$, c) values were derived, using the third law $\Delta Hr°_{298.15}$. These determinations were not given any weight.

Investigator	Temperature, °K	$\Delta Hr°_{298.15}$, kcal/mol Second Law Value	Third Law Value	Drift eu	$\Delta Hf°_{298.15}$ kcal/mol
1. Keppeler and D'Ans (1908)	753.15 - 1013.15	136.8 ± 0.5	139.9 ± 0.5	3.4 ± 0.6	-621.0
2. Wöhler, et al. (1908)	826.15 - 980.15	114.2 ± 6.2	133.1 ± 2.3	19.2 ± 6.9	-614.2
3. Bodenstein and Suzuki (1910)	903.65 - 997.15	140.7 ± 6.6	139.1 ± 1.3	- 1.2 ± 7.1	-620.2
4. Wöhler and Grünzweig (1913)	909.15 - 994.15	155.1 ± 1.3	135.5 ± 1.3	-20.4 ± 1.4	-616.6
5. Neumann and Heintke (1937)	793.15 - 973.15	136.4 ± 2.3	136.2 ± 1.2	- 1.2 ± 2.6	-617.3
6. Warner and Ingraham (1960)	903.15 - 997.15	133.9 ± 2.6	135.4 ± 0.5	1.7 ± 2.7	-616.5

1. G. Keppeler and J. D'Ans, Z. physik. Chem. 62, 89 (1908).
2. L. Wöhler, W. Plüddemann and P. Wöhler, Ber. Deut. Chem. Gesell. 41, 703 (1908).
3. M. Bodenstein and T. Suzuki, Z. Elektrochem. 16, 912 (1910).
4. L. Wöhler and M. Grünzweig, Ber. Deut. Chem. Gesell. 43, 1587 (1913).
5. B. Neumann and G. Heintke, Z. Elektrochem. 43, 246 (1937).
6. N. A. Warner and T. R. Ingraham, Can. J. Chem. 38, 2196 (1960).

The decomposition pressures of $Fe_2(SO_4)_3$ (c) have also been investigated by : M. Grünzweig, Ph. D. dissertation, Darmstadt, Germany, 1913, 793-994°K; R. F. Blanks, Ph. D. dissertation, University of Melbourne, Australia, 1961, 845 - 976° K; and T. R. Ingraham, Internal Rept. EMT-63-17, Department of Mines and Technical Surveys. Ottawa, Canada, 1963, 856-995°K. These data together with some of the data mentioned previously were critically reviewed by H. H. Kellogg, Trans. AIME, 230, 1622 (1964).

Heat Capacity and Entropy.

The heat capacities were estimated by comparison with those for $FeSO_4$ (c), assuming their average specific heats, gibbs/g, to be the same. The value of $S°_{298.15}$ was estimated so that the second and third law $\Delta Hr°_{298.15}$ values, derived from decomposition pressure data, are in reasonable agreement.

Temperature of Decomposition.

Td is the temperature at which the total pressure of the gaseous products equals one atmosphere, which was obtained by graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham, loc. cit.

Magnetite (Fe_3O_4)

(Crystal) Mol. Wt. = 231.5386

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. $mole^{-1}deg.^{-1}$			kcal. $mole^{-1}$			
0	.000	.000	INFINITE	- 5.873	- 266.398	- 266.398	INFINITE
100	13.464	6.599	60.756	- 5.416	- 267.676	- 259.592	567.310
200	27.950	22.076	37.732	- 3.131	- 268.017	- 251.358	274.658
298	35.190	34.720	34.720	.000	- 267.900	- 243.191	178.255
300	35.300	34.938	34.720	.065	- 267.894	- 243.038	177.044
400	40.900	45.878	36.174	3.881	- 267.378	- 234.820	128.294
500	45.980	55.555	39.100	8.228	- 266.518	- 226.772	99.117
600	50.800	64.364	42.586	13.067	- 265.379	- 218.926	79.740
700	55.620	72.557	46.289	18.388	- 263.981	- 211.290	65.965
800	60.440	80.299	50.060	24.191	- 262.378	- 203.874	55.693
900	48.000	87.696	53.834	30.476	- 260.649	- 196.661	47.754
1000	48.000	92.753	57.477	35.276	- 260.974	- 189.541	41.422
1100	48.000	97.328	60.895	40.076	- 261.977	- 182.336	36.225
1200	48.000	101.504	64.108	44.876	- 262.362	- 175.096	31.888
1300	48.000	105.347	67.134	49.676	- 261.745	- 167.849	28.217
1400	48.000	108.904	69.992	54.476	- 261.190	- 160.646	25.077
1500	48.000	112.215	72.698	59.276	- 260.691	- 153.483	22.361
1600	48.000	115.313	75.266	64.076	- 260.252	- 146.350	19.989
1700	48.000	118.223	77.708	68.876	- 260.741	- 139.227	17.898
1800	48.000	120.967	80.036	73.676	- 260.692	- 132.079	16.036
1900	48.000	123.562	82.259	78.476	- 271.713	- 124.380	14.306
2000	48.000	126.024	84.386	83.276	- 271.881	- 116.627	12.744
2100	48.000	128.366	86.425	88.076	- 272.071	- 108.853	11.328
2200	48.000	130.599	88.383	92.876	- 272.287	- 101.077	10.041
2300	48.000	132.733	90.265	97.676	- 272.523	- 93.296	8.865
2400	48.000	134.776	92.077	102.476	- 272.783	- 85.497	7.785
2500	48.000	136.735	93.825	107.276	- 273.067	- 77.685	6.791
2600	48.000	138.618	95.512	112.076	- 273.371	- 69.867	5.873
2700	48.000	140.429	97.142	116.876	- 273.699	- 62.033	5.021
2800	48.000	142.175	98.719	121.676	- 274.049	- 54.185	4.229
2900	48.000	143.859	100.247	126.476	- 274.421	- 46.325	3.491
3000	48.000	145.486	101.728	131.276	- 274.815	- 38.448	2.801

June 30, 1965

MAGNETITE (Fe_3O_4) (CRYSTAL) MOL. WT. = 231.5386

$\Delta H^\circ_{f\ 0}$ = -266.4 ± 0.2 kcal. $mole^{-1}$

$S^\circ_{298.15}$ = 34.72 cal. $deg.^{-1}$ $mole^{-1}$ $\Delta H^\circ_{f\ 298.15}$ = -267.9 ± 0.2 kcal. $mole^{-1}$

T_m = 1870 ± 2°K. ΔH°_m = 33.0 ± 2.0 kcal. $mole^{-1}$

Heat of Formation.

The equilibrium constants for the following four reactions, i.e. (1) $3Fe(c) + 4H_2O(g) = Fe_3O_4(c) + 4H_2(g)$; (2) $Fe_3O_4(c) + H_2(g) = 3FeO(c) + H_2O(g)$; (3) $Fe_3O_4(c) + CO(g) = 3FeO(c) + CO_2(g)$; and (4) $2Fe_3O_4(c) = 6FeO(c) + O_2(g)$, have been studied by several investigators. Using their reported equilibrium data, the corresponding enthalpy changes ($\Delta H^\circ_{r\ 298.15}$) were evaluated by both the second and third law methods. Based on the third law value for $\Delta H^\circ_{r\ 298.15}$, the respective $\Delta H^\circ_{f\ 298.15}$ values for $Fe_3O_4(c)$ were also derived. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	$\Delta H^\circ_{r\ 298.15}$, kcal. $mole^{-1}$ Second Law Value	Third Law Value	$\Delta H^\circ_{f\ 298.15}$, kcal. $mole^{-1}$
Fricke, et al.[1]	(1)	633.2- 823.2	-29.68 ± 1.30	-36.91	-268.10
Eastman[2]	(2)	873.2-1273.2	22.41 ± 0.09	19.29	-268.01
Eastman and Evans[3]	(2)	973.2-1273.2	21.56 ± 0.07	18.54	-267.26
Emmett and Shultz[4]	(2)	973.2-1073.2	———	19.18	-267.90
Eastman[2]	(3)	873.2-1273.2	11.87 ± 0.03	9.38	-267.93
Eastman and Evans[3]	(3)	973.2-1273.2	11.63 ± 0.03	9.38	-267.94
Salmon[5]	(4)	1473.2-1673.2	———	153.73	-267.79

[1] R. Fricke, K. Walter and W. Lohrer, Z. Elektrochem. 47, 487 (1941). The two $\Delta H^\circ_{f\ 298.15}$ values listed are the average values of three separate results derived from three sets of experimental data.

[2] E. D. Eastman, J. Am. Chem. Soc. 44, 975 (1922).

[3] E. D. Eastman and R. M. Evans, J. Am. Chem. Soc. 46, 888 (1924).

[4] P. H. Emmett and J. F. Schultz, J. Am. Chem. Soc. 52, 4268 (1930).

[5] O. N. Salmon, J. Phys. Chem. 65, 550 (1961).

The enthalpy change of the reaction $Fe_{0.947}O(c) + 0.8215\ Fe(c) + 0.6787\ O_2(g) = 0.5895\ Fe_3O_4(c)$ has been determined by G. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bur. Mines RI 4870 (1952). Bases on $\Delta H^\circ_{r\ 298.15}$ = -93.46 kcal. $mole^{-1}$ (average of two separate values derived from two experimental determinations) and $\Delta H^\circ_{f\ 298.15}$ (Wüstite, c) = -63.64 kcal. $mole^{-1}$, the value of $\Delta H^\circ_{f\ 298.15}$ (Fe_3O_4, c) was calculated as -266.5 kcal. $mole^{-1}$. The enthalpy change, $\Delta H^\circ_{r\ 298.15}$ = 4.33 kcal. $mole^{-1}$, for the reaction $3Fe(c) + 4CO_2(g) = Fe_3O_4(c) + 4CO(g)$ was reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). The corresponding $\Delta H^\circ_{f\ 298.15}$ (Fe_3O_4, c) was evaluated as -266.22 kcal. $mole^{-1}$. The adopted value of $\Delta H^\circ_{f\ 298.15}$ for $Fe_3O_4(c)$ is selected as -267.9 ± 0.2 kcal. $mole^{-1}$.

Heat Capacity and Entropy.

The low temperature (60.5-299.7°K.) heat capacities were reported by R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929). The high temperature (298-1800°K.) heat capacities were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). These two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1800°K. were obtained by graphical extrapolation. Heat capacities (90-295°K.) for $Fe_3O_4(c)$ were also reported by G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926). $S^\circ_{298.15}$ (Fe_3O_4, c) was derived from the smoothed C_p data mentioned previously, using $S^\circ_{44.7}$ = 0.969 e.u. J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for magnetite and found a magnetic anomaly around 880°K., corresponding to a maximum in heat capacity. A maximum heat capacity of 37.1 cal. $deg.^{-1}$ $mole^{-1}$ at 114.15°K. was also reported by R. W. Millar, loc. cit.

Melting Data.

T_m and ΔH°_m were obtained from L. S. Darken and R. W. Gurry, loc. cit.

Hydrogen, Monatomic (H)
(Ideal Gas) At. Wt. = 1.00797

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-1.481	51.631	51.631	INFINITE
100	4.968	21.965	31.809	-.984	51.748	50.771	-110.954
200	4.968	25.408	27.847	-.488	51.943	49.714	-54.322
298	4.968	27.392	27.392	.000	52.100	48.585	-35.612
300	4.968	27.423	27.392	.009	52.103	48.563	-35.377
400	4.968	28.852	27.587	.506	52.253	47.361	-25.876
500	4.968	29.961	27.955	1.003	52.400	46.121	-20.158
600	4.968	30.867	28.367	1.500	52.547	44.851	-16.336
700	4.968	31.632	28.780	1.996	52.692	43.558	-13.599
800	4.968	32.296	29.179	2.493	52.836	42.242	-11.539
900	4.968	32.881	29.559	2.990	52.977	40.910	-9.934
1000	4.968	33.404	29.917	3.487	53.115	39.562	-8.646
1100	4.968	33.878	30.256	3.984	53.249	38.200	-7.589
1200	4.968	34.310	30.576	4.481	53.379	36.826	-6.707
1300	4.968	34.708	30.879	4.977	53.503	35.441	-5.958
1400	4.968	35.076	31.166	5.474	53.623	34.048	-5.315
1500	4.968	35.419	31.438	5.971	53.737	32.645	-4.756
1600	4.968	35.739	31.697	6.468	53.845	31.236	-4.266
1700	4.968	36.041	31.944	6.965	53.948	29.819	-3.833
1800	4.968	36.325	32.179	7.461	54.046	28.396	-3.448
1900	4.968	36.593	32.405	7.958	54.140	26.970	-3.102
2000	4.968	36.848	32.621	8.455	54.230	25.538	-2.790
2100	4.968	37.090	32.828	8.952	54.314	24.102	-2.508
2200	4.968	37.322	33.027	9.449	54.395	22.659	-2.251
2300	4.968	37.542	33.218	9.945	54.472	21.217	-2.016
2400	4.968	37.754	33.403	10.442	54.546	19.769	-1.800
2500	4.968	37.957	33.581	10.939	54.615	18.316	-1.601
2600	4.968	38.152	33.753	11.436	54.682	16.864	-1.417
2700	4.968	38.339	33.919	11.933	54.745	15.409	-1.247
2800	4.968	38.520	34.081	12.430	54.806	13.949	-1.089
2900	4.968	38.694	34.237	12.926	54.863	12.491	-.941
3000	4.968	38.862	34.388	13.423	54.918	11.030	-.803
3100	4.968	39.025	34.535	13.920	54.971	9.565	-.674
3200	4.968	39.183	34.678	14.417	55.021	8.099	-.553
3300	4.968	39.336	34.817	14.914	55.068	6.632	-.439
3400	4.968	39.484	34.952	15.410	55.113	5.164	-.332
3500	4.968	39.628	35.083	15.907	55.156	3.695	-.231
3600	4.968	39.768	35.212	16.404	55.196	2.224	-.135
3700	4.968	39.904	35.337	16.901	55.233	.753	-.044
3800	4.968	40.037	35.459	17.398	55.269	-.722	.042
3900	4.968	40.166	35.578	17.895	55.302	-2.196	.123
4000	4.968	40.292	35.694	18.391	55.333	-3.671	.201
4100	4.968	40.414	35.808	18.888	55.362	-5.144	.274
4200	4.968	40.534	35.919	19.385	55.388	-6.621	.345
4300	4.968	40.651	36.027	19.882	55.412	-8.099	.412
4400	4.968	40.765	36.134	20.379	55.435	-9.575	.476
4500	4.968	40.877	36.238	20.875	55.454	-11.056	.537
4600	4.968	40.986	36.340	21.372	55.473	-12.531	.595
4700	4.968	41.093	36.440	21.869	55.489	-14.010	.651
4800	4.968	41.198	36.538	22.366	55.503	-15.492	.705
4900	4.968	41.300	36.634	22.863	55.515	-16.968	.757
5000	4.968	41.400	36.728	23.359	55.525	-18.447	.806
5100	4.968	41.499	36.821	23.856	55.534	-19.928	.854
5200	4.968	41.595	36.912	24.353	55.541	-21.406	.900
5300	4.968	41.690	37.001	24.850	55.545	-22.887	.944
5400	4.968	41.783	37.089	25.347	55.548	-24.369	.986
5500	4.968	41.874	37.175	25.844	55.550	-25.848	1.027
5600	4.968	41.963	37.260	26.340	55.549	-27.326	1.066
5700	4.968	42.051	37.343	26.837	55.547	-28.805	1.104
5800	4.968	42.138	37.425	27.334	55.543	-30.289	1.141
5900	4.968	42.223	37.506	27.831	55.537	-31.768	1.177
6000	4.968	42.306	37.585	28.328	55.530	-33.246	1.211

Dec. 31, 1960; Sept. 30, 1965

HYDROGEN, MONATOMIC (H) (IDEAL GAS) AT. WT. = 1.00797

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 27.392 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 51.631 ± 0.001 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 52.100 ± 0.001 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_1
0.000	2
82258.907	2
82258.942	2
82259.272	4
97492.198	2
97492.208	2
97492.306	4
97492.342	6

Heat of Formation.

The heat of formation was calculated from D_0° (H_2) = 36113.0 ± 0.3 cm.$^{-1}$, reported by G. Herzberg and A. Monfils, J. of Molecular Spectroscopy 5, 482 (1960). This value was measured more precisely than the value D_0° (H_2) = 36116 ± 6 cm.$^{-1}$ by H. Beutler, Z. Phys. Chem. B29, 315 (1935).

Heat Capacity and Entropy.

Electronic levels taken from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467 (1949).

Proton (H^+)

(Ideal Gas) GFW = 1.00742

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0							
100							
200							
298	4.968	26.012	26.012	.000	367.186	362.596	- 265.790
300	4.968	26.043	26.012	.009	367.198	362.567	- 264.130
400	4.968	27.472	26.207	.506	367.844	360.926	- 197.201
500	4.968	28.581	26.575	1.003	368.489	359.121	- 156.972
600	4.968	29.486	26.987	1.500	369.133	357.188	- 130.105
700	4.968	30.252	27.400	1.996	369.774	355.145	- 110.881
800	4.968	30.916	27.799	2.493	370.415	353.012	- 96.438
900	4.968	31.501	28.179	2.990	371.053	350.798	- 85.185
1000	4.968	32.024	28.537	3.487	371.688	348.514	- 76.168
1100	4.968	32.498	28.876	3.984	372.319	346.166	- 68.777
1200	4.968	32.930	29.196	4.480	372.945	343.762	- 62.608
1300	4.968	33.328	29.499	4.977	373.566	341.303	- 57.378
1400	4.968	33.696	29.786	5.474	374.183	338.799	- 52.889
1500	4.968	34.039	30.058	5.971	374.794	336.250	- 48.992
1600	4.968	34.359	30.317	6.467	375.398	333.660	- 45.576
1700	4.968	34.660	30.564	6.964	375.999	331.035	- 42.557
1800	4.968	34.944	30.799	7.461	376.593	328.371	- 39.870
1900	4.968	35.213	31.025	7.958	377.184	325.677	- 37.461
2000	4.968	35.468	31.240	8.455	377.770	322.950	- 35.290
2100	4.968	35.710	31.448	8.951	378.352	320.195	- 33.323
2200	4.968	35.941	31.647	9.448	378.930	317.412	- 31.532
2300	4.968	36.162	31.838	9.945	379.503	314.602	- 29.894
2400	4.968	36.373	32.023	10.442	380.073	311.771	- 28.391
2500	4.968	36.576	32.201	10.939	380.640	308.911	- 27.005
2600	4.968	36.771	32.373	11.435	381.203	306.031	- 25.724
2700	4.968	36.959	32.539	11.932	381.764	303.129	- 24.537
2800	4.968	37.139	32.700	12.429	382.321	300.207	- 23.432
2900	4.968	37.314	32.856	12.926	382.875	297.264	- 22.402
3000	4.968	37.482	33.008	13.423	383.427	294.301	- 21.440
3100	4.968	37.645	33.155	13.919	383.976	291.320	- 20.538
3200	4.968	37.803	33.298	14.416	384.523	288.325	- 19.692
3300	4.968	37.956	33.436	14.913	385.067	285.310	- 18.895
3400	4.968	38.104	33.572	15.410	385.609	282.279	- 18.145
3500	4.968	38.248	33.703	15.907	386.148	279.234	- 17.436
3600	4.968	38.388	33.831	16.403	386.685	276.171	- 16.766
3700	4.968	38.524	33.956	16.900	387.220	273.091	- 16.131
3800	4.968	38.656	34.078	17.397	387.752	270.004	- 15.529
3900	4.968	38.785	34.197	17.894	388.282	266.899	- 14.957
4000	4.968	38.911	34.314	18.390	388.809	263.777	- 14.412
4100	4.968	39.034	34.427	18.887	389.335	260.642	- 13.893
4200	4.968	39.154	34.538	19.384	389.858	257.499	- 13.399
4300	4.968	39.270	34.647	19.881	390.379	254.345	- 12.927
4400	4.968	39.385	34.753	20.378	390.899	251.172	- 12.476
4500	4.968	39.496	34.858	20.874	391.414	247.990	- 12.044
4600	4.968	39.606	34.960	21.371	391.930	244.796	- 11.630
4700	4.968	39.712	35.060	21.868	392.443	241.596	- 11.234
4800	4.968	39.817	35.158	22.365	392.954	238.377	- 10.854
4900	4.968	39.919	35.254	22.862	393.463	235.156	- 10.488
5000	4.968	40.020	35.348	23.358	393.969	231.917	- 10.137
5100	4.968	40.118	35.441	23.855	394.475	228.671	- 9.799
5200	4.968	40.215	35.532	24.352	394.978	225.414	- 9.474
5300	4.968	40.309	35.621	24.849	395.480	222.152	- 9.161
5400	4.968	40.402	35.708	25.346	395.980	218.874	- 8.858
5500	4.968	40.493	35.795	25.842	396.478	215.592	- 8.567
5600	4.968	40.583	35.879	26.339	396.974	212.291	- 8.285
5700	4.968	40.671	35.963	26.836	397.468	208.995	- 8.013
5800	4.968	40.757	36.045	27.333	397.961	205.683	- 7.750
5900	4.968	40.842	36.125	27.830	398.453	202.363	- 7.496
6000	4.968	40.926	36.204	28.326	398.942	199.034	- 7.250

June 30, 1966

PROTON (H^+) (IDEAL GAS) GFW = 1.00742

$\Delta Hf^\circ_0 = 365.236 \pm 0.01$ kcal/mol

$S^\circ_{298.15} = 26.012$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 367.186 \pm 0.01$ kcal/mol

Heat of Formation.

The heat of formation was calculated from the equation $H(g) \rightarrow H^+(g) + e^-$ with the JANAF auxiliary data for H(g), using an ionization potential = 13.598 eV (313.605 kcal/mol) for H(g) obtained from C. W. Beckett, National Bureau of Standards Report 8628, Jan. 1, 1965.

Heat Capacity and Entropy.

Calculated by assuming the proton to be an ideal monatomic gas. The enthalpy between 298° and 0°K is 1.481 kcal/mol as for all unexcited monatomic gases.

Hydrogen Uninegative Ion (H^-)

(Ideal Gas) At. Wt. = 1.00852

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	26.015	26.015	.000	33.200	31.583	- 23.150
300	4.968	26.045	26.015	.009	33.194	31.574	- 23.000
400	4.968	27.475	26.210	.506	32.847	31.085	- 16.983
500	4.968	28.583	26.578	1.003	32.497	30.685	- 13.412
600	4.968	29.489	26.990	1.500	32.147	30.356	- 11.057
700	4.968	30.255	27.403	1.996	31.796	30.086	- 9.393
800	4.968	30.918	27.802	2.493	31.443	29.865	- 8.158
900	4.968	31.503	28.181	2.990	31.087	29.689	- 7.209
1000	4.968	32.027	28.540	3.487	30.728	29.553	- 6.458
1100	4.968	32.500	28.879	3.984	30.365	29.453	- 5.851
1200	4.968	32.933	29.199	4.481	29.998	29.385	- 5.351
1300	4.968	33.330	29.502	4.977	29.626	29.351	- 4.934
1400	4.968	33.699	29.788	5.474	29.249	29.342	- 4.580
1500	4.968	34.041	30.061	5.971	28.866	29.364	- 4.278
1600	4.968	34.362	30.320	6.468	28.477	29.409	- 4.017
1700	4.968	34.663	30.566	6.965	28.083	29.480	- 3.790
1800	4.968	34.947	30.802	7.461	27.685	29.574	- 3.591
1900	4.968	35.216	31.027	7.958	27.282	29.688	- 3.415
2000	4.968	35.471	31.243	8.455	26.875	29.825	- 3.259
2100	4.968	35.713	31.450	8.952	26.462	29.984	- 3.120
2200	4.968	35.944	31.649	9.449	26.046	30.161	- 2.996
2300	4.968	36.165	31.841	9.945	25.627	30.359	- 2.885
2400	4.968	36.376	32.025	10.442	25.204	30.574	- 2.784
2500	4.968	36.579	32.204	10.939	24.776	30.805	- 2.693
2600	4.968	36.774	32.376	11.436	24.346	31.055	- 2.610
2700	4.968	36.962	32.542	11.933	23.912	31.318	- 2.535
2800	4.968	37.142	32.703	12.430	23.476	31.603	- 2.467
2900	4.968	37.317	32.859	12.926	23.037	31.900	- 2.404
3000	4.968	37.485	33.011	13.423	22.595	32.215	- 2.347
3100	4.968	37.648	33.158	13.920	22.151	32.542	- 2.294
3200	4.968	37.806	33.300	14.417	21.704	32.881	- 2.246
3300	4.968	37.959	33.439	14.914	21.254	33.238	- 2.201
3400	4.968	38.107	33.574	15.410	20.803	33.608	- 2.160
3500	4.968	38.251	33.706	15.907	20.349	33.992	- 2.122
3600	4.968	38.391	33.834	16.404	19.892	34.387	- 2.088
3700	4.968	38.527	33.959	16.901	19.432	34.800	- 2.055
3800	4.968	38.659	34.081	17.398	18.971	35.222	- 2.026
3900	4.968	38.788	34.200	17.895	18.507	35.655	- 1.998
4000	4.968	38.914	34.316	18.391	18.042	36.102	- 1.972
4100	4.968	39.037	34.430	18.888	17.574	36.559	- 1.949
4200	4.968	39.157	34.541	19.385	17.103	37.024	- 1.926
4300	4.968	39.274	34.650	19.882	16.630	37.502	- 1.906
4400	4.968	39.388	34.756	20.379	16.156	37.993	- 1.887
4500	4.968	39.499	34.860	20.875	15.679	38.499	- 1.870
4600	4.968	39.609	34.962	21.372	15.201	39.008	- 1.853
4700	4.968	39.715	35.062	21.869	14.720	39.536	- 1.838
4800	4.968	39.820	35.160	22.366	14.237	40.068	- 1.824
4900	4.968	39.922	35.257	22.863	13.752	40.612	- 1.811
5000	4.968	40.023	35.351	23.359	13.266	41.159	- 1.799
5100	4.968	40.121	35.444	23.856	12.778	41.728	- 1.788
5200	4.968	40.218	35.534	24.353	12.288	42.294	- 1.777
5300	4.968	40.312	35.624	24.850	11.795	42.883	- 1.768
5400	4.968	40.405	35.711	25.347	11.301	43.472	- 1.759
5500	4.968	40.496	35.798	25.844	10.806	44.072	- 1.751
5600	4.968	40.586	35.882	26.340	10.309	44.682	- 1.744
5700	4.968	40.674	35.966	26.837	9.810	45.295	- 1.737
5800	4.968	40.760	36.047	27.334	9.309	45.927	- 1.730
5900	4.968	40.845	36.128	27.831	8.806	46.563	- 1.725
6000	4.968	40.929	36.207	28.328	8.302	47.200	- 1.719

Sept. 30, 1965

HYDROGEN UNINEGATIVE ION (H^-) (IDEAL GAS) AT. WT. = 1.00852

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 26.015 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 34.2 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 33.2 ± 0.5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

$\mathcal{E}_1$cm.$^{-1}$	g_1
0	1

Heat of Formation.

The heat of formation was calculated from the equation: $H(g) + e^- \rightarrow H^-(g)$ with the JANAF auxiliary value for H(g) (this supplement); using an I.P. = 6.083096 X 10^3 cm^{-1} (.754 e.v. or 17.39 kcal/mole) for $H^-(g)$ obtained from C. L. Pekeris, Phys. Rev. 126, 1470 (1962). The I.P. value for $H^-(g)$ reported by C. W. Scherr and R. E. Knight, Rev. Mod. Phys. 35, 436 (1963) is in agreement with the value of Pekeris.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Helium. The electronic levels above 1 X 10^5 cm^{-1} were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.481 kcal/mole.

Mercury Monohydride (HgH)

(Ideal Gas) Mol. Wt. = 201.618

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	- 2.082	58.163	58.163	INFINITE
100	6.963	44.833	58.746	- 1.391	58.066	55.692	- 121.708
200	6.995	49.665	53.135	- .694	57.845	53.394	- 58.343
298	7.181	52.486	52.486	.000	57.000	51.421	- 37.691
300	7.186	52.530	52.486	.013	56.995	51.387	- 37.434
400	7.509	54.640	52.772	.748	56.721	49.560	- 27.077
500	7.845	56.353	53.322	1.515	56.487	47.798	- 20.891
600	8.140	57.810	53.951	2.315	56.288	46.078	- 16.783
700	8.386	59.084	54.595	3.142	42.089	45.962	- 14.349
800	8.588	60.217	55.228	3.991	42.088	46.515	- 12.707
900	8.757	61.238	55.840	4.858	42.103	47.069	- 11.429
1000	8.899	62.169	56.427	5.741	42.130	47.619	- 10.407
1100	9.022	63.023	56.989	6.637	42.166	48.166	- 9.569
1200	9.130	63.813	57.525	7.545	42.210	48.709	- 8.871
1300	9.227	64.547	58.037	8.463	42.259	49.249	- 8.279
1400	9.314	65.234	58.527	9.390	42.313	49.785	- 7.771
1500	9.395	65.880	58.996	10.326	42.369	50.318	- 7.331
1600	9.471	66.488	59.445	11.269	42.426	50.844	- 6.945
1700	9.541	67.065	59.877	12.220	42.486	51.370	- 6.604
1800	9.609	67.612	60.291	13.177	42.548	51.888	- 6.300
1900	9.673	68.133	60.690	14.141	42.613	52.407	- 6.028
2000	9.735	68.631	61.075	15.112	42.679	52.921	- 5.783
2100	9.796	69.108	61.446	16.088	42.747	53.431	- 5.560
2200	9.854	69.565	61.805	17.071	42.816	53.937	- 5.358
2300	9.911	70.004	62.152	18.059	42.888	54.441	- 5.173
2400	9.967	70.427	62.488	19.053	42.963	54.945	- 5.003
2500	10.022	70.835	62.814	20.053	43.038	55.439	- 4.846
2600	10.076	71.229	63.130	21.058	43.116	55.935	- 4.702
2700	10.130	71.610	63.437	22.068	43.195	56.427	- 4.567
2800	10.182	71.980	63.736	23.083	43.277	56.913	- 4.442
2900	10.235	72.338	64.026	24.104	43.363	57.403	- 4.326
3000	10.286	72.686	64.309	25.130	43.450	57.883	- 4.217
3100	10.338	73.024	64.585	26.162	43.541	58.362	- 4.114
3200	10.388	73.353	64.853	27.198	43.633	58.840	- 4.018
3300	10.439	73.673	65.116	28.239	43.728	59.314	- 3.928
3400	10.489	73.986	65.372	29.286	43.827	59.784	- 3.843
3500	10.539	74.290	65.623	30.337	43.927	60.253	- 3.762
3600	10.589	74.588	65.868	31.393	44.029	60.717	- 3.686
3700	10.638	74.879	66.107	32.455	44.134	61.179	- 3.614
3800	10.688	75.163	66.342	33.521	44.243	61.640	- 3.545
3900	10.737	75.441	66.572	34.592	44.353	62.096	- 3.480
4000	10.786	75.714	66.797	35.669	44.466	62.550	- 3.417
4100	10.835	75.981	67.018	36.750	44.582	62.998	- 3.358
4200	10.884	76.243	67.234	37.836	44.701	63.447	- 3.301
4300	10.932	76.499	67.447	38.926	44.822	63.892	- 3.247
4400	10.981	76.751	67.655	40.022	44.946	64.332	- 3.195
4500	11.029	76.998	67.860	41.123	45.073	64.772	- 3.146
4600	11.078	77.241	68.061	42.228	45.201	65.208	- 3.098
4700	11.126	77.480	68.259	43.338	45.333	65.646	- 3.052
4800	11.174	77.715	68.454	44.453	45.467	66.072	- 3.008
4900	11.222	77.946	68.645	45.573	45.604	66.502	- 2.966
5000	11.270	78.173	68.833	46.698	45.745	66.927	- 2.925
5100	11.318	78.397	69.019	47.827	45.886	67.352	- 2.886
5200	11.366	78.617	69.201	48.961	46.031	67.770	- 2.848
5300	11.414	78.834	69.381	50.100	46.178	68.187	- 2.812
5400	11.462	79.048	69.558	51.244	46.328	68.597	- 2.776
5500	11.510	79.258	69.732	52.393	46.480	69.008	- 2.742
5600	11.558	79.466	69.904	53.546	46.634	69.419	- 2.709
5700	11.605	79.671	70.074	54.704	46.791	69.826	- 2.677
5800	11.653	79.873	70.241	55.867	46.949	70.224	- 2.646
5900	11.701	80.073	70.406	57.035	47.109	70.623	- 2.616
6000	11.748	80.270	70.569	58.207	47.272	71.020	- 2.587

June 30, 1963

MERCURY MONOHYDRIDE (HgH) (IDEAL GAS) MOL. WT. = 201.618

Ground State Configuration $[^2\Sigma^+]$

$S^\circ_{298.15}$ = [52.486] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_0 = 58 \pm 4$ kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 57 \pm 4$ kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$	g_i
0	[2]

ω_e = 1387 cm.$^{-1}$

B_e = 5.549 cm.$^{-1}$

$\omega_e x_e$ = 83.01 cm.$^{-1}$

α_e = 0.312 cm.$^{-1}$

$\sigma = 1$

r_e = 1.74 Å

Heat of Formation.

The heat of formation was calculated from D_0, 8.671 kcal. mole^{-1}, taken from G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Company, Inc., New York (1950).

Heat Capacity and Entropy.

Molecular constants were taken from G. Herzberg, loc. cit.

Hydrogen Iodide (HI)

(Ideal Gas) Mol. Wt. = 127.918

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.069	6.820	6.820	INFINITE
100	6.959	41.746	55.541	- 1.379	6.766	4.539	- 9.920
200	6.961	46.570	49.988	- .683	6.571	2.379	- 2.599
298	6.969	49.351	49.351	.000	6.300	.376	- .276
300	6.969	49.394	49.351	.013	6.294	.340	- .247
400	7.010	51.403	49.625	.711	4.060	- 1.532	.837
500	7.107	52.977	50.143	1.417	- 1.346	- 2.413	1.055
600	7.253	54.285	50.727	2.134	- 1.427	- 2.620	.954
700	7.424	55.416	51.318	2.868	- 1.493	- 2.813	.878
800	7.600	56.419	51.894	3.620	- 1.545	- 2.997	.819
900	7.767	57.324	52.448	4.388	- 1.585	- 3.176	.771
1000	7.920	58.150	52.977	5.172	- 1.612	- 3.351	.732
1100	8.056	58.911	53.483	5.971	- 1.630	- 3.525	.700
1200	8.177	59.617	53.965	6.783	- 1.639	- 3.696	.673
1300	8.283	60.276	54.425	7.606	- 1.643	- 3.867	.650
1400	8.376	60.894	54.866	8.439	- 1.643	- 4.038	.630
1500	8.459	61.474	55.287	9.281	- 1.640	- 4.210	.613
1600	8.531	62.023	55.691	10.131	- 1.637	- 4.381	.598
1700	8.596	62.542	56.079	10.987	- 1.632	- 4.552	.585
1800	8.654	63.035	56.452	11.850	- 1.626	- 4.725	.574
1900	8.706	63.504	56.811	12.718	- 1.621	- 4.897	.563
2000	8.753	63.952	57.157	13.591	- 1.615	- 5.070	.554
2100	8.796	64.380	57.490	14.468	- 1.610	- 5.242	.546
2200	8.835	64.790	57.813	15.350	- 1.606	- 5.416	.538
2300	8.871	65.184	58.125	16.235	- 1.603	- 5.589	.531
2400	8.904	65.562	58.427	17.124	- 1.600	- 5.761	.525
2500	8.935	65.926	58.720	18.016	- 1.599	- 5.936	.519
2600	8.963	66.277	59.004	18.911	- 1.598	- 6.109	.513
2700	8.990	66.616	59.279	19.808	- 1.599	- 6.283	.509
2800	9.016	66.943	59.547	20.709	- 1.600	- 6.456	.504
2900	9.040	67.260	59.808	21.611	- 1.603	- 6.628	.499
3000	9.062	67.567	60.061	22.517	- 1.606	- 6.803	.496
3100	9.084	67.864	60.308	23.424	- 1.611	- 6.976	.492
3200	9.105	68.153	60.549	24.333	- 1.616	- 7.149	.488
3300	9.124	68.434	60.784	25.245	- 1.623	- 7.321	.485
3400	9.143	68.706	61.013	26.158	- 1.631	- 7.495	.482
3500	9.162	68.972	61.236	27.073	- 1.640	- 7.665	.479
3600	9.180	69.230	61.455	27.991	- 1.650	- 7.838	.476
3700	9.197	69.482	61.668	28.909	- 1.663	- 8.010	.473
3800	9.213	69.727	61.877	29.830	- 1.675	- 8.181	.471
3900	9.229	69.967	62.082	30.752	- 1.690	- 8.352	.468
4000	9.245	70.201	62.282	31.676	- 1.706	- 8.524	.466
4100	9.261	70.429	62.478	32.601	- 1.722	- 8.692	.463
4200	9.276	70.652	62.670	33.528	- 1.741	- 8.862	.461
4300	9.290	70.871	62.858	34.456	- 1.761	- 9.033	.459
4400	9.305	71.085	63.042	35.386	- 1.782	- 9.203	.457
4500	9.319	71.294	63.223	36.317	- 1.805	- 9.371	.455
4600	9.333	71.499	63.401	37.250	- 1.828	- 9.537	.453
4700	9.347	71.700	63.575	38.184	- 1.853	- 9.705	.451
4800	9.360	71.897	63.747	39.119	- 1.879	- 9.872	.449
4900	9.374	72.090	63.915	40.056	- 1.907	- 10.037	.448
5000	9.387	72.279	64.080	40.994	- 1.936	- 10.204	.446
5100	9.400	72.465	64.243	41.933	- 1.965	- 10.369	.444
5200	9.413	72.646	64.403	42.874	- 1.997	- 10.534	.443
5300	9.425	72.827	64.560	43.816	- 2.029	- 10.696	.441
5400	9.438	73.004	64.715	44.759	- 2.063	- 10.860	.439
5500	9.450	73.177	64.867	45.703	- 2.097	- 11.023	.438
5600	9.463	73.347	65.017	46.649	- 2.134	- 11.187	.437
5700	9.475	73.515	65.165	47.596	- 2.171	- 11.347	.435
5800	9.487	73.680	65.310	48.544	- 2.209	- 11.508	.434
5900	9.499	73.842	65.453	49.493	- 2.248	- 11.668	.432
6000	9.511	74.002	65.594	50.444	- 2.289	- 11.827	.431

September 30, 1961

HYDROGEN IODIDE (HI) (IDEAL GAS) MOL. WT. = 127.918

ΔH°_{f0} = 6.82 ± 0.05 kcal. mole^{-1}

Ground State = $^1\Sigma$

$\Delta H^\circ_{f\ 298}$ = 6.30 kcal. mole^{-1}

S°_{298} = 49.351

ω_e = 2309.06 cm.$^{-1}$

$\omega_e x_e$ = 39.73 cm.$^{-1}$

B_e = 6.512 cm.$^{-1}$

α_e = 0.1715 cm.$^{-1}$

σ = 1

Thermodynamic Functions.

Molecular constants are from M. Cowan and W. Gordy [Phys. Rev. 104, 551 (1956)] and D. R. J. Boyd and H. W. Thompson [Spectrochim. Acta 5, 308 (1952)]. The calculated functions are in reasonable agreement with the compilation of K. K. Kelley [U. S. Bur. Mines Bull. 584 (1960)].

Heat of Formation.

Using the calculated functions derived above and functions for $H_2(g)$ and $I_2(g)$ given in the JANAF tables, equilibrium data from the literature were used to calculate ΔH°_{298} for the reaction

$$H_2\ (g) + I_2\ (g) \rightarrow 2\ HI\ (g)$$

	ΔH°_{298}, kcal. mole^{-1}
Taylor and Crist[1] (667° to 764°K)	-2.375 ± .005
Bodenstein[2] (556° to 781°K)	-2.053 ± .133
Bright and Hagerty[3] (696° and 779°K)	-2.219 ± .070
Rittenberg and Urey[4] (671° and 741°K)	-2.156 ± .072

The data of Taylor and Crist are the most concordant and are given the most weight. Converting to the solid state of iodine, which has been adopted as a JANAF reference state gives the standard heat of formation of hydrogen iodide.

References

(1) A. H. Taylor and R. H. Crist, J. Am. Chem. Soc. 63, 1377 (1941).

(2) M. Bodenstein, Z. physikal. Chem. 29, 295 (1899).

(3) N. F. H. Bright and R. P. Hagerty, Trans. Faraday Soc. 43, 697 (1947).

(4) D. Rittenberg and H. C. Urey, J. Am. Chem. Soc. 56, 1885 (1934).

Potassium Hydride (KH)

(Crystal) Mol. Wt. = 40.108

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	9.060	12.000	12.000	.000	-13.819	-8.136	5.964
300	9.100	12.056	12.000	.017	-13.822	-8.101	5.901
400	10.550	14.906	12.379	1.011	-14.489	-6.069	3.316
500	11.600	17.378	13.137	2.120	-14.472	-3.964	1.732
600	12.410	19.568	14.029	3.323	-14.345	-1.872	.682
700	13.051	21.530	14.963	4.597	-14.138	.192	-.060
800	13.580	23.309	15.897	5.929	-13.871	2.220	-.607
900	13.996	24.933	16.812	7.309	-13.559	4.214	-1.023
1000	14.300	26.425	17.700	8.725	-13.223	6.170	-1.348
1100	14.571	27.801	18.556	10.169	-31.779	9.117	-1.811
1200	14.800	29.079	19.381	11.638	-31.174	12.809	-2.333
1300	14.986	30.271	20.173	13.127	-30.554	16.448	-2.765
1400	15.129	31.387	20.935	14.634	-29.921	20.041	-3.128
1500	15.230	32.435	21.667	16.152	-29.283	23.588	-3.437

March 31, 1963

POTASSIUM HYDRIDE (KH) (CRYSTAL) MOL. WT. = 40.108

$S^\circ_{298.15}$ = [12] cal. deg.$^{-1}$ mole^{-1}

T_d = [690]°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15} = -13.819 \pm 0.011$ kcal. mole^{-1}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ was taken from S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). The corresponding value reported by C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955) was -15.16 ± 0.6 kcal. mole^{-1}. In this paper the results of the previous investigations were also reviewed.

Heat Capacity and Entropy.

C_p and $S^\circ_{298.15}$ were estimated by comparison with those for NaH(c) and LiH(c).

Temperature of Decomposition.

T_d was assumed to be the temperature at which the value of ΔF°_f changes from negative to positive.

HK

Potassium Hydride (KH)

(Ideal Gas) Mol. Wt. = 40.108

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.102	30.003	30.003	INFINITE
100	6.964	39.575	51.669	- 1.409	29.902	28.015	- 61.223
200	7.071	44.421	47.970	- .710	29.680	26.205	- 28.634
298	7.418	47.304	47.304	.000	29.400	24.557	- 18.000
300	7.426	47.350	47.304	.014	29.394	24.527	- 17.867
400	7.818	49.541	47.600	.776	28.496	23.062	- 12.600
500	8.134	51.321	48.172	1.575	28.202	21.738	- 9.501
600	8.370	52.826	48.825	2.401	27.952	20.470	- 7.456
700	8.545	54.130	49.492	3.247	27.731	19.241	- 6.007
800	8.678	55.280	50.145	4.108	27.527	18.041	- 4.928
900	8.782	56.308	50.774	4.981	27.332	16.868	- 4.096
1000	8.867	57.238	51.374	5.864	27.135	15.715	- 3.434
1100	8.937	58.087	51.947	6.754	8.025	15.607	- 3.101
1200	8.996	58.867	52.491	7.651	8.058	16.295	- 2.968
1300	9.048	59.589	53.010	8.553	8.091	16.979	- 2.854
1400	9.095	60.261	53.504	9.460	8.124	17.663	- 2.757
1500	9.137	60.890	53.976	10.372	8.156	18.343	- 2.673
1600	9.175	61.481	54.426	11.288	8.186	19.021	- 2.598
1700	9.211	62.039	54.858	12.207	8.213	19.697	- 2.532
1800	9.245	62.566	55.272	13.130	8.240	20.372	- 2.473
1900	9.277	63.067	55.669	14.056	8.263	21.045	- 2.421
2000	9.308	63.543	56.051	14.985	8.285	21.718	- 2.373
2100	9.337	63.998	56.419	15.917	8.303	22.389	- 2.330
2200	9.366	64.433	56.773	16.853	8.317	23.060	- 2.291
2300	9.394	64.850	57.115	17.791	8.329	23.729	- 2.255
2400	9.421	65.251	57.446	18.731	8.336	24.399	- 2.222
2500	9.448	65.636	57.766	19.675	8.337	25.066	- 2.191
2600	9.474	66.007	58.076	20.621	8.335	25.738	- 2.163
2700	9.500	66.365	58.376	21.569	8.326	26.406	- 2.137
2800	9.525	66.711	58.668	22.521	8.310	27.075	- 2.113
2900	9.550	67.045	58.951	23.474	8.287	27.748	- 2.091
3000	9.575	67.370	59.226	24.431	8.258	28.417	- 2.070
3100	9.599	67.684	59.494	25.389	8.218	29.091	- 2.051
3200	9.624	67.989	59.755	26.351	8.170	29.766	- 2.033
3300	9.648	68.286	60.009	27.314	8.110	30.440	- 2.016
3400	9.672	68.574	60.256	28.280	8.037	31.116	- 2.000
3500	9.696	68.855	60.498	29.248	7.951	31.798	- 1.985
3600	9.719	69.128	60.734	30.219	7.849	32.482	- 1.972
3700	9.743	69.395	60.964	31.192	7.730	33.166	- 1.959
3800	9.767	69.655	61.190	32.168	7.591	33.855	- 1.947
3900	9.790	69.909	61.410	33.146	7.431	34.548	- 1.936
4000	9.813	70.157	61.626	34.126	7.247	35.247	- 1.926
4100	9.837	70.400	61.837	35.108	7.037	35.949	- 1.916
4200	9.860	70.637	62.043	36.093	6.796	36.658	- 1.907
4300	9.883	70.869	62.246	37.080	6.525	37.372	- 1.899
4400	9.906	71.097	62.445	38.070	6.217	38.091	- 1.892
4500	9.929	71.320	62.639	39.062	5.871	38.821	- 1.885
4600	9.952	71.536	62.830	40.056	5.483	39.557	- 1.879
4700	9.975	71.752	63.018	41.052	5.050	40.303	- 1.874
4800	9.998	71.963	63.202	42.051	4.571	41.060	- 1.869
4900	10.021	72.169	63.383	43.052	4.039	41.825	- 1.865
5000	10.044	72.372	63.561	44.055	3.455	42.599	- 1.862
5100	10.066	72.571	63.735	45.060	2.814	43.393	- 1.859
5200	10.089	72.767	63.907	46.068	2.115	44.193	- 1.857
5300	10.112	72.959	64.076	47.078	1.356	45.010	- 1.856
5400	10.135	73.146	64.242	48.090	.535	45.838	- 1.855
5500	10.157	73.334	64.406	49.105	- .348	46.684	- 1.855
5600	10.180	73.518	64.567	50.122	- 1.293	47.548	- 1.856
5700	10.203	73.698	64.726	51.141	- 2.299	48.429	- 1.857
5800	10.225	73.876	64.882	52.162	- 3.366	49.327	- 1.859
5900	10.248	74.051	65.036	53.186	- 4.492	50.248	- 1.861
6000	10.270	74.223	65.188	54.212	- 5.675	51.187	- 1.864

March 31, 1963

POTASSIUM HYDRIDE (KH) (IDEAL GAS) MOL. WT. = 40.108

Ground State Configuration $^1\Sigma^+$

$\Delta H_{f\ 0}^\circ = 30.0 \pm 3.5$ kcal. mole^{-1}

$S^\circ_{298.15} = 47.304$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 29.4 \pm 3.5$ kcal. mole^{-1}

$\omega_e = 985.0$ cm.$^{-1}$

$\omega_e x_e = 14.65$ cm.$^{-1}$

$\sigma = 1$

$B_e = 3.407$ cm.$^{-1}$

$\alpha_e = 0.0673$ cm.$^{-1}$

Heat of Formation.

$\Delta H_{f\ 298.15}^\circ$ was calculated from $D_0^\circ = 1.86 \pm 0.15$ e.v. reported by A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., 1953.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950.

HK

Potassium Hydroxide (KOH)

(Crystal) Mol. Wt. = 56.10937

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.926	- 100.694	- 100.694	INFINITE
100	8.164	5.705	31.303	- 2.560	- 101.477	- 97.901	213.963
200	12.978	12.857	20.368	- 1.502	- 101.681	- 94.220	102.959
298	15.746	18.949	18.949	.000	- 101.510	- 90.594	66.407
300	15.769	19.046	18.949	.029	- 101.507	- 90.526	65.948
400	17.400	23.798	19.586	1.685	- 101.868	- 86.786	47.418
500	19.020	27.853	20.843	3.505	- 101.505	- 83.055	36.303
600	18.800	34.200	22.685	6.909	- 99.555	- 79.632	29.006
700	18.800	37.098	24.543	8.789	- 99.131	- 76.345	23.836
800	18.800	39.609	26.272	10.669	- 98.715	- 73.120	19.975
900	18.800	41.823	27.880	12.549	- 98.310	- 69.944	16.985
1000	18.800	43.804	29.375	14.429	- 97.923	- 66.813	14.602
1100	18.800	45.596	30.769	16.309	- 116.463	- 62.697	12.457
1200	18.800	47.232	32.074	18.189	- 115.871	- 57.834	10.533
1300	18.800	48.736	33.299	20.069	- 115.288	- 53.022	8.914
1400	18.800	50.130	34.452	21.949	- 114.714	- 48.254	7.533
1500	18.800	51.427	35.541	23.829	- 114.150	- 43.525	6.342

Dec. 31, 1961; Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

POTASSIUM HYDROXIDE (KOH) (CRYSTAL) MOL. WT. = 56.10937

$S^\circ_{298.15}$ = 18.95 cal. deg.$^{-1}$ mole^{-1}
T_t = 522°K
T_m = 673°K.

$\Delta H^\circ_{f\ 0}$ = -100.7 ± 0.1 kcal. mole^{-1}
$\Delta H^\circ_{f\ 298.15}$ = -101.5 ± 0.1 kcal. mole^{-1}
ΔH°_t = 1.515 kcal. mole^{-1}
ΔH°_m = 2.240 kcal. mole^{-1}
$\Delta H^\circ_{s\ 298.15}$ (to monomer) = [46.1] kcal. mole^{-1}
$\Delta H^\circ_{s\ 298.15}$ (to dimer) = [45.6] kcal. mole^{-1}

Heat of Formation.

The standard enthalpy of formation, $\Delta H^\circ_{f\ 298}$ (KOH, c) = -101.5 ± 0.1 kcal. mole^{-1}, was calculated from the heat of solution of KOH(c), the heat of hydrolysis of potassium metal and the appropriate auxiliary data.

N. A. Peshetnikov[1] has measured the heat of solution KOH(c) → KOH(650 H_2O) as -13.665 ± 0.009 kcal. mole^{-1} at 298.15°K. in the solution calorimeter. Using the auxiliary heat of dilution reported by V. B. Parker[2], the selected heat of solution of KOH(c) at infinite dilution is -13.770 kcal. mole^{-1}. The heat of solution KOH(c) → KOH(25 H_2O) has also been measured as -13.80 ± 0.10 kcal. mole^{-1} in the solution calorimeter by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull[3]. Both results are in good agreement.

The heat of hydrolysis of potassium metal, $\Delta H^\circ_{r\ 298}$, has been measured in the solution calorimeter by the following investigators.

$K(c) + H_2O(l) \rightarrow KOH(nH_2O) + 1/2\ H_2(g)$ $\Delta H^\circ_{r\ 298}$

Source	Number of Moles of H_2O	$\Delta H^\circ_{r\ 298}$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}(KOH(\infty H_2O))$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}$(KOH, c) kcal. mole^{-1}
Gunn et al.[4]	1000	-46.877 ± 0.01	-115.281	-101.511
Messer et al.[5]	∞	-47.02 ± 0.15	-115.335	-101.565
Ketchen et al.[6]	∞	-46.894 ± 0.24	-115.209	-101.439

The values of $\Delta H^\circ_{f\ 298}(KOH(\infty H_2O))$ were calculated from the heats of reaction, $\Delta H^\circ_{r\ 298}$, using $\Delta H^\circ_{f\ 298}(H_2O,\ l)$ = -68.315 kcal. mole^{-1} [7]. Combination of the selected heat of solution of KOH(c) at infinite dilution with the heat of formation of KOH(∞H_2O) gives the heat of formation of KOH(c) in the last column of the table. A weighted average of these three measurements was taken for the selected heat of formation of KOH(c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini[8] and C. E. Messer et al.[5], and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of KOH(c) from 15° to 340°K. have been measured by W. E. Hatton et al.[3] who have also observed a sharp peak in the heat capacity curve in the temperature range from 210° to 230°K. These values of C_p were adopted in the calculation. W. D. Powers and G. C. Blalock[9] have measured the high temperature enthalpy changes of the solid KOH in the α and β phases by the drop method. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities in the α phase. Therefore, the selected heat capacities between 340° and 522°K. were estimated from a graphical extrapolation of the low temperature heat capacity curve, and the tabulated $H^\circ-H^\circ_{298}$ functions are in agreement with their enthalpy measurements within the experimental uncertainty. The heat capacities of KOH(c) in the β phase were obtained from Powers and Blalock[9].

The entropy (S°_{298} = 18.95 cal. deg.$^{-1}$ mole^{-1}) was taken from Hatton et al.[3], based on an extrapolation of S°_{15} = 0.054 cal. deg.$^{-1}$ mole^{-1}.

Transition and Melting Data.

Hatton et al.[3] have found a lambda transition at 227.4°K. in the heat capacity measurement. The adopted heat of α-β transition at 522°K. and heat of melting at 673°K. were obtained from Powers and Blalock[9]. P. S. Seward and K. E. Martin[10] found ΔH°_m = 1.83 kcal. mole^{-1} at 683°K. in phase diagram studies of the system $KOH-K_2CO_3$.

Heat of Sublimation.

See KOH(g) table for details.

References:

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5 C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955).
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9 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Hydroxides at High Temperatures," ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954.
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Potassium Hydroxide (KOH)

(Liquid) Mol. Wt. = 56.10937

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	19.860	23.518	23.518	.000	-98.433	-88.879	65.150
300	19.860	23.641	23.519	.037	-98.422	-88.820	64.705
400	19.860	29.355	24.298	2.023	-98.453	-85.594	46.767
500	19.860	33.786	25.769	4.009	-97.925	-82.441	36.035
600	19.860	37.407	27.416	5.995	-97.392	-79.393	28.919
700	19.860	40.469	29.068	7.981	-96.862	-76.436	23.864
800	19.860	43.121	30.662	9.967	-96.340	-73.555	20.094
900	19.860	45.460	32.179	11.953	-95.829	-70.736	17.177
1000	19.860	47.552	33.613	13.939	-95.337	-67.975	14.856
1100	19.860	49.445	34.968	15.925	-113.770	-64.238	12.763
1200	19.860	51.173	36.247	17.911	-113.072	-59.765	10.885
1300	19.860	52.763	37.458	19.897	-112.384	-55.352	9.306
1400	19.860	54.234	38.604	21.883	-111.704	-50.989	7.960
1500	19.860	55.605	39.692	23.869	-111.033	-46.676	6.801
1600	19.860	56.886	40.727	25.855	-110.372	-42.406	5.792
1700	19.860	58.090	41.714	27.841	-109.718	-38.179	4.908
1800	19.860	59.226	42.655	29.827	-109.073	-33.991	4.127
1900	19.860	60.299	43.556	31.813	-108.438	-29.836	3.432
2000	19.860	61.318	44.419	33.799	-107.809	-25.715	2.810
2100	19.860	62.287	45.247	35.785	-107.190	-21.625	2.251
2200	19.860	63.211	46.042	37.771	-106.581	-17.565	1.745
2300	19.860	64.094	46.808	39.757	-105.979	-13.534	1.286
2400	19.860	64.939	47.546	41.743	-105.388	-9.526	.867
2500	19.860	65.750	48.258	43.729	-104.808	-5.547	.485

Dec. 31, 1961; Mar. 31, 1962; Sep. 30, 1962; Mar. 31, 1966

POTASSIUM HYDROXIDE (KOH) (LIQUID) MOL. WT. = 56.10937

$S^\circ_{298.15}$ = 23.518 cal. deg.$^{-1}$ mole^{-1}

T_m = 673°K.

T_b(monomeric gas) = 1600°K.

ΔH°_f 298.15 = -98.433 kcal. mole^{-1}

ΔH°_m = 2.240 kcal. mole^{-1}

ΔH°_v (to monomer) = 32.0 kcal. mole^{-1}

Heat of Formation.

The heat of formation of KOH(l) at 298°K. was obtained from that of the crystal by adding ΔH°_m and the difference between $H^\circ_{673}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase, C_p = 19.86 cal. deg.$^{-1}$ mole^{-1}, was obtained from the enthalpy measurements in the drop calorimeter by W. D. Powers and G. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954. The constant C_p was extrapolated below the melting point and up to 2500°K.

The entropy, $S^\circ_{298.15}$ = 23.51 cal. deg.$^{-1}$ mole^{-1}, was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See KOH(c) table for details.

Vaporization Data.

The boiling point 1600°K. was calculated as the temperature at which the free energies of formation (ΔF°_f) for both KOH(l) and KOH(g) are equal. The difference in the heats of formation (ΔH°_f) of KOH(l) and KOH(g) at the boiling point is the heat of vaporization. If $K_2(OH)_2(g)$ is also considered as a minor component in the vapor mixture (approximately 2% of total vapor pressure at the boiling point) the calculated boiling point is unchanged as 1600°K. (see KOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 162 (1921), have studied the vapor pressures of liquid KOH and reported the boiling point as 1597°K.

Potassium Hydroxide (KOH)

(Ideal Gas) Mol. Wt. = 56.10937

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.566	-54.258	-54.258	INFINITE
100	8.143	48.787	66.467	-1.766	-54.610	-55.342	120.950
200	8.978	54.695	59.249	-.911	-55.014	-55.920	61.107
298	9.550	58.392	58.392	.000	-55.434	-56.277	41.252
300	9.559	58.451	58.393	.018	-55.442	-56.283	41.002
400	10.028	61.267	58.773	.998	-56.479	-56.385	30.807
500	10.420	63.549	59.507	2.021	-56.914	-56.311	24.614
600	10.743	65.478	60.346	3.079	-57.309	-56.152	20.454
700	11.012	67.155	61.201	4.167	-57.677	-55.930	17.462
800	11.247	68.641	62.040	5.281	-58.027	-55.658	15.205
900	11.459	69.978	62.849	6.416	-58.367	-55.340	13.438
1000	11.654	71.195	63.624	7.572	-58.705	-54.986	12.017
1100	11.834	72.315	64.364	8.746	-77.950	-53.574	10.644
1200	12.000	73.352	65.070	9.938	-78.046	-51.353	9.353
1300	12.153	74.318	65.744	11.146	-78.136	-49.125	8.259
1400	12.294	75.224	66.390	12.368	-78.219	-46.890	7.320
1500	12.422	76.077	67.007	13.604	-78.299	-44.649	6.505
1600	12.539	76.882	67.600	14.852	-78.375	-42.403	5.792
1700	12.645	77.646	68.168	16.112	-78.448	-40.154	5.162
1800	12.741	78.371	68.715	17.381	-78.520	-37.898	4.602
1900	12.827	79.062	69.242	18.659	-78.592	-35.640	4.099
2000	12.906	79.722	69.749	19.946	-78.663	-33.377	3.647
2100	12.978	80.354	70.239	21.240	-78.735	-31.111	3.238
2200	13.043	80.959	70.713	22.542	-78.811	-28.841	2.865
2300	13.101	81.540	71.171	23.849	-78.888	-26.569	2.525
2400	13.155	82.099	71.615	25.162	-78.970	-24.292	2.212
2500	13.204	82.637	72.045	26.480	-79.058	-22.015	1.925
2600	13.248	83.156	72.462	27.802	-79.150	-19.728	1.658
2700	13.289	83.656	72.868	29.129	-79.249	-17.441	1.412
2800	13.326	84.140	73.262	30.460	-79.357	-15.151	1.183
2900	13.361	84.609	73.645	31.794	-79.473	-12.854	.969
3000	13.392	85.062	74.018	33.132	-79.598	-10.556	.769
3100	13.421	85.502	74.382	34.473	-79.734	-8.252	.582
3200	13.448	85.928	74.736	35.816	-79.881	-5.942	.406
3300	13.472	86.342	75.081	37.162	-80.042	-3.630	.240
3400	13.495	86.745	75.418	38.511	-80.217	-1.315	.085
3500	13.516	87.137	75.748	39.861	-80.408	1.007	-.063
3600	13.536	87.518	76.069	41.214	-80.617	3.338	-.203
3700	13.554	87.889	76.384	42.568	-80.846	5.673	-.335
3800	13.571	88.250	76.691	43.925	-81.096	8.017	-.461
3900	13.587	88.603	76.992	45.283	-81.370	10.363	-.581
4000	13.602	88.947	77.287	46.642	-81.671	12.721	-.695
4100	13.616	89.283	77.575	48.003	-82.001	15.085	-.804
4200	13.628	89.612	77.858	49.365	-82.362	17.455	-.908
4300	13.641	89.932	78.135	50.729	-82.757	19.841	-1.008
4400	13.652	90.246	78.407	52.093	-83.192	22.228	-1.104
4500	13.663	90.553	78.673	53.459	-83.667	24.630	-1.196
4600	13.673	90.853	78.935	54.826	-84.185	27.045	-1.285
4700	13.682	91.148	79.192	56.193	-84.751	29.466	-1.370
4800	13.691	91.436	79.444	57.562	-85.366	31.905	-1.453
4900	13.699	91.718	79.691	58.932	-86.036	34.355	-1.532
5000	13.707	91.995	79.935	60.302	-86.761	36.814	-1.609
5100	13.715	92.266	80.174	61.673	-87.545	39.303	-1.684
5200	13.722	92.533	80.409	63.045	-88.389	41.791	-1.756
5300	13.729	92.794	80.640	64.417	-89.295	44.308	-1.827
5400	13.735	93.051	80.868	65.791	-90.265	46.830	-1.895
5500	13.741	93.303	81.091	67.164	-91.299	49.380	-1.962
5600	13.747	93.551	81.312	68.539	-92.398	51.945	-2.027
5700	13.752	93.794	81.529	69.914	-93.560	54.534	-2.091
5800	13.758	94.033	81.742	71.289	-94.786	57.145	-2.153
5900	13.762	94.269	81.952	72.665	-96.073	59.773	-2.214
6000	13.767	94.500	82.160	74.042	-97.419	62.430	-2.274

Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

POTASSIUM HYDROXIDE (KOH) (IDEAL GAS) MOL. WT. = 56.10937

Point Group C_s

$S^\circ_{298.15}$ = [58.4] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_{f\ 0}^\circ$ = -54.3 ± 5 kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = -55.4 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
408 (1)
[1300](1)
[3700](1)

Bond Distance: K-O = [2.21] Å O-H = [0.96] Å

Bond Angle: K-O-H = [110]°

$\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.22325] X 10^{-116} g.^{3} cm.^{6}

Heat of Formation.

R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 234 and 486 (1958), have investigated the potassium hydroxide vapor by the mass-spectrometric method and found that the KOH vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. Later, Schoonmaker and Porter, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container. Using the reported partial pressures of KOH(g) and $K_2(OH)_2(g)$ at 641° and 666°K. and JANAF free energy functions, the third law calculations give ΔH°_{298} = -45.4 ± 5 kcal. mole^{-1} for 2KOH(g) → $K_2(OH)_2(g)$, and $\Delta H^\circ_{s\ 298}$ = 45.41 ± 3.5 kcal. mole^{-1} for KOH(c) → KOH(g), and $\Delta H^\circ_{s\ 298}$ = 45.6 ± 5 kcal. mole^{-1} for 2KOH(c) → $K_2(OH)_2(g)$. The uncertainties given were derived by assuming K_p to be good to a factor of 5 as stated by the authors and including an extra factor of 2 as possible error in activity. To this was added an estimate of the uncertainty due to functions used. In order to have good agreement between the calculated total pressures of monomeric and dimeric KOH(g) and the observed vapor pressures measured by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), the heat of sublimation to monomeric gas was adjusted to $\Delta H^\circ_{s\ 298}$ (to monomer) = 46.08 kcal. mole^{-1}. (The heat of sublimation to dimeric gas was unchanged as $\Delta H^\circ_{s\ 298}$ (to dimer) = 45.64 kcal. mole^{-1}). The calculated boiling point is 1600°K. which is in good agreement with 1597 ± 10°K. reported by Wartenberg and Albrecht. The heats of formation were calculated from the selected heats of sublimation as $\Delta H^\circ_{f\ 298}$(KOH,g) = -55.4 and $\Delta H^\circ_{f\ 298}(K_2(OH)_2,g)$ = -157.4 kcal. mole^{-1}.

Heat Capacity and Entropy.

The bond distance K-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance K-F(g) (2.17146 Å) which has been accurately measured by R. K. Ritchie and H. Lew, Can. J. Phys. 42, 43 (1964). The bond distance O-H was estimated from that in $H_2O(g)$. The bent molecular configuration with the bond angle of 110° has been proposed by S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), but a linear model has also been suggested by R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959). The bent model has been adopted in the tabulation. The three principal moments of inertia are: I_A = [0.1256] X 10^{-39}, I_B = [9.8070] X 10^{-39} and I_C = [9.9326] X 10^{-39} g. cm.^{2}

The K-O stretching frequency (408 cm.$^{-1}$) was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta 12, 244 (1957) in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951), have calculated theoretically the bond distances of gaseous alkali oxides (Li-O = 1.52 Å, Na-O = 1.94 Å and K-O = 2.27 Å) which have been quoted by Bauer, Diner and Porter, loc. cit., and many other authors.

Lithium Hydride (LiH)

(Crystal) GFW = 7.94697

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-.903	-20.446	-20.446	INFINITE
100	1.525	.555	9.165	-.861	-20.903	-19.563	42.755
200	4.488	2.561	5.336	-.555	-21.338	-18.050	19.724
298	6.682	4.789	4.789	.000	-21.660	-16.362	11.994
300	6.712	4.830	4.789	.012	-21.665	-16.330	11.896
400	8.316	6.988	5.072	.766	-21.879	-14.515	7.931
500	9.736	8.998	5.659	1.669	-22.744	-12.583	5.500
600	11.085	10.893	6.374	2.711	-22.765	-10.546	3.842
700	12.399	12.700	7.150	3.885	-22.642	-8.518	2.660
800	13.695	14.441	7.953	5.190	-22.382	-6.517	1.780
900	14.980	16.128	8.768	6.624	-21.995	-4.556	1.106
1000	16.259	17.773	9.587	8.186	-21.482	-2.645	.578
1100	17.534	19.382	10.404	9.876	-20.843	-.791	.157
1200	18.805	20.962	11.218	11.693	-20.081	.999	-.182
1300	20.075	22.518	12.028	13.637	-19.195	2.720	-.457
1400	21.343	24.052	12.832	15.708	-18.186	4.370	-.682
1500	22.610	25.568	13.631	17.905	-17.055	5.942	-.866

Sept. 30, 1962; Sept. 30, 1967

LITHIUM HYDRIDE (LiH) (CRYSTAL) GFW = 7.94697

$\Delta Hf^\circ_0 = -20.45 \pm 0.03$ kcal/mol

$S^\circ_{298.15} = 4.789 \pm 0.03$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -21.66 \pm 0.03$ kcal/mol

Tm = 961.8°K

$\Delta Hm^\circ = 5.40 \pm 0.10$ kcal/mol

$\Delta Hs^\circ_{298.15} = 55.27$ kcal/mol

Heat of Formation

The heats of solution of Li(c) and LiH(c) in water have been measured by Guntz (1) and Moers (2) using an open Dewar flask calorimeter and by Messer (3) and Gunn (4) using closed bomb calorimetry. Based on the reported values of the enthalpy changes (ΔHr°) for the reaction (A) Li(c) + H_2O(ℓ) = LiOH(aq) + 1/2H_2(g), and (B) LiH(c) + H_2O(ℓ) = LiOH(aq) + H_2(g), the corresponding ΔHf°_{298} for LiH(c) are calculated. The results are presented in the table below.

The decomposition pressures of LiH(c) have been determined by Hurd (5), at temperatures 782 - 926°K. By use of the second and third law methods, the enthalpy changes for the decomposition reaction (C) LiH(c) = Li(ℓ) + 1/2H_2(g) are evaluated as 21.87 ± 0.3 and 22.34 kcal/mol, respectively. Based on the third law ΔHr°_{298} and ΔHf°_{298}(Li, ℓ) = 0.569 kcal/mol, we derive the value ΔHf°_{298}(LiH, c) = -21.77 ± 0.2 kcal/mol, which is in good agreement with the values obtained by calorimetric method. Gunts (1) measured the decomposition pressure at 953°K for the same reaction. The third law ΔHr°_{298} and ΔHf°_{298}(LiH, c) are evaluated as 21.86 and -21.29 kcal/mol, respectively.

Johnson (6) has determined the standard Gibbs energy of formation (ΔGf°) for LiH(c) from emf measurements over the temperature range 675 - 885°K. The cell utilized an Armco iron flag over which H_2 was passed as the cathode and a molten Li anode. LiCl, LiBr and LiI, each saturated with LiH were used as electrolytes. Using the reported emf values at different temperatures (47 data points) for reaction (C), we derive a ΔHf°_{298} = -21.81 kcal/mol for LiH(c).

The ΔHf°_{298}(LiH, c) value reported by Gunn (4) is adopted.

Investigator	ΔHr°_{298}, kcal/mol Reaction A	Reaction B	Reaction C	Drift eu	ΔHf°_{298} kcal/mol
1. Guntz (1896)	-53.2	-31.6	-	-	-21.6
	-	-	21.86	-	-21.29
2. Moers (1920)	-52.7±0.2	-31.1±0.1	-	-	-21.6±0.25
3. Messer (1955)	-53.10±0.11	-31.76±0.10	-	-	-21.34±0.15
4. Gunn (1958)	-53.14±0.02	-31.48±0.02	-	-	-21.66±0.03
5. Hurd (1935)	-	-	22.34	0.5±0.3	-21.77±0.2
6. Johnson (1966)	-	-	22.38	1.0±0.2	-21.81±0.15

Heat Capacity and Entropy

The low temperature heat capacities are obtained from the data of Kostyukov (7), 3.72 - 295.5°K. The cp data reported by Gunther (8) are consistently lower than the adopted ones in the temperature range 74.0 - 90.5°K but considerably higher at 292.7°K. The high temperature enthalpies have been determined by Fieldhouse (9), 413.2 - 914.3°K, and Vogt (14), 878.15 - 953.15°K. The derived high temperature heat capacities are joined smoothly with the low temperature values and extrapolated smoothly above 953.15°K.

S°_{298} is calculated based on the adopted low temperature heat capacities, using S°_7 = 0.0002 eu.

Melting Data

The value of Tm has been reported as 953 (1), 961 ± 1 (10, 12), 959.6 (11), and 961.8 ± 0.3 (13). The value reported by Messer (13) is adopted. The heat of melting (ΔHm°) has been determined as 5.095 ± 0.46 (13) and 5.237 ± 0.040 kcal/mol (14). The first ΔHm° value was evaluated cryogenically from the lowering of melting point in the systems LiH-Li_2O and LiH-CaH_2. The second value was derived from enthalpy data measured with copper block calorimeter. The adopted ΔHm° value is derived from the enthalpy data of Vogt (14) using the adopted heat capacities for LiH(c) and LiH(ℓ).

Heat of Sublimation

The value of ΔHs°_{298} is calculated as the difference between ΔHf°_{298} for LiH(g) and LiH(c).

References

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Lithium Hydride (LiH)

(Liquid) GFW = 7.94697

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	14.900	5.314	5.314	.000	-18.573	-13.432	9.846
300	14.900	5.406	5.314	.028	-18.563	-13.400	9.762
400	14.900	9.693	5.899	1.518	-18.041	-11.759	6.425
500	14.900	13.017	7.002	3.008	-18.318	-10.168	4.444
600	14.900	15.734	8.238	4.498	-17.891	-8.578	3.124
700	14.900	18.031	9.477	5.988	-17.452	-7.060	2.204
800	14.900	20.020	10.673	7.478	-17.007	-5.607	1.532
900	14.900	21.775	11.811	8.968	-16.564	-4.208	1.022
1000	14.900	23.345	12.888	10.458	-16.123	-2.859	.625
1100	14.900	24.765	13.904	11.948	-15.684	-1.553	.309
1200	14.900	26.062	14.864	13.438	-15.249	-.288	.052
1300	14.900	27.255	15.772	14.928	-14.817	.941	-.158
1400	14.900	28.359	16.632	16.418	-14.389	2.137	-.334
1500	14.900	29.387	17.448	17.908	-13.965	3.303	-.481
1600	14.900	30.348	18.225	19.398	-13.545	4.440	-.607
1700	14.900	31.252	18.965	20.888	-48.176	6.880	-.884
1800	14.900	32.103	19.671	22.378	-47.581	10.103	-1.227
1900	14.900	32.909	20.347	23.868	-46.991	13.292	-1.529
2000	14.900	33.673	20.994	25.358	-46.407	16.449	-1.797

Sept. 30, 1962; Sept. 30, 1967

LITHIUM HYDRIDE (LiH) (LIQUID) GFW = 7.94697

$S^\circ_{298.15}$ = 5.314 gibbs/mol

Tm = 961.8 ± 0.3°K

Td = 1223°K

$\Delta Hf^\circ_{298.15}$ = -18.573 kcal/mol

ΔHm° = 5.40 ± 0.10 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{961.8} - H^\circ_{298}$ for crystal and liquid.

The decomposition pressures of LiH(ℓ) at different temperatures have been investigated by Hill (1), Perlow (2), Johnson, and Gibb (4). Based on their reported equilibrium pressures, the enthalpy changes for the reaction $LiH(\ell) = Li(\ell) + 1/2H_2(g)$ are evaluated by the second and third law methods. The results are presented in the table below. It should be noted that the measured decomposition pressures are highly sensitive to composition and change extremely rapidly between 99 and 100 percent purity. Therefore we give no weight to the equilibrium data.

Investigator	Temperature, °K	No. of Points	ΔHr°_{298}, kcal/mol Second Law	Third Law	Drift eu	ΔHf°_{298}** kcal/mol
Hill (1938)	973.2	1	—	16.93	—	-16.36
Perlow (1941)	1043-1098	2	20.10	17.69	-2.2	-17.12
Johnson*	1050-1090	-	24.69	18.36	-5.9	-17.79
Gibb (1951)	1073-1173	2	5.66	15.2	+8.5	-14.63

*The vapor pressure values are calculated from an equation quoted by Gibb (3), but derived from the vapor pressures measured by W. C. Johnson, University of Chicago.

**Based on the third law ΔHr°_{298}.

Heat Capacity and Entropy

The enthalpies of LiH(ℓ) in the temperature range 975.15-1075.15°K have been measured by Vogt (5). Using the reported enthalpy values, the heat capacity of LiH(ℓ) is derived as 14.9 gibbs/mol. This Cp value is adopted and extrapolated above and below the measured range.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See LiH(c) table for details.

Decomposition Temperature

Td is calculated as the temperature at which LiH(ℓ) decomposes into Li(ℓ) and $H_2(g)$ where the partial pressure of $H_2(g)$ equals one atmosphere.

References

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2. M. R. J. Perlow, Ph. D. Thesis, University of Chicago, 1941.
3. T. R. P. Gibb, J. Electrochem. Soc. 93, 198 (1948).
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5. J. W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63-22167, June 1962.

Lithium Hydride (LiH)

(Ideal Gas) GFW = 7.94697

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.076	33.651	33.651	INFINITE
100	6.964	33.183	47.056	-1.387	33.841	31.918	-69.757
200	6.984	38.015	41.465	-.690	33.797	29.994	-32.776
298	7.106	40.821	40.821	.000	33.610	28.165	-20.645
300	7.109	40.865	40.821	.013	33.606	28.131	-20.493
400	7.364	42.943	41.102	.736	33.361	26.343	-14.393
500	7.655	44.617	41.643	1.487	32.344	24.694	-10.794
600	7.921	46.037	42.260	2.266	32.060	23.192	-8.448
700	8.145	47.276	42.890	3.070	31.813	21.734	-6.786
800	8.329	48.376	43.508	3.894	31.592	20.309	-5.548
900	8.478	49.366	44.105	4.735	31.386	18.911	-4.592
1000	8.601	50.265	44.677	5.589	31.191	17.535	-3.832
1100	8.703	51.090	45.223	6.454	31.005	16.179	-3.215
1200	8.790	51.851	45.744	7.329	30.825	14.839	-2.703
1300	8.864	52.558	46.241	8.212	30.650	13.513	-2.272
1400	8.929	53.217	46.716	9.101	30.477	12.202	-1.905
1500	8.987	53.835	47.170	9.997	30.307	10.903	-1.589
1600	9.038	54.417	47.605	10.898	30.138	9.615	-1.313
1700	9.085	54.966	48.022	11.805	-5.076	9.666	-1.243
1800	9.128	55.487	48.422	12.715	-5.061	10.534	-1.279
1900	9.168	55.981	48.807	13.630	-5.046	11.400	-1.311
2000	9.206	56.452	49.178	14.549	-5.033	12.265	-1.340
2100	9.241	56.902	49.535	15.471	-5.021	13.128	-1.366
2200	9.275	57.333	49.880	16.397	-5.011	13.993	-1.390
2300	9.307	57.746	50.213	17.326	-5.002	14.856	-1.412
2400	9.338	58.143	50.535	18.258	-4.996	15.720	-1.431
2500	9.367	58.525	50.847	19.194	-4.992	16.582	-1.450
2600	9.396	58.893	51.150	20.132	-4.990	17.445	-1.466
2700	9.424	59.248	51.443	21.073	-4.992	18.307	-1.482
2800	9.452	59.591	51.728	22.017	-4.995	19.170	-1.496
2900	9.479	59.923	52.005	22.963	-5.004	20.035	-1.510
3000	9.505	60.245	52.274	23.912	-5.015	20.898	-1.522
3100	9.531	60.557	52.536	24.864	-5.031	21.763	-1.534
3200	9.557	60.860	52.792	25.819	-5.050	22.627	-1.545
3300	9.583	61.154	53.041	26.776	-5.076	23.492	-1.556
3400	9.608	61.441	53.283	27.735	-5.106	24.359	-1.566
3500	9.634	61.720	53.521	28.697	-5.141	25.226	-1.575
3600	9.659	61.992	53.752	29.662	-5.183	26.094	-1.584
3700	9.685	62.257	53.978	30.629	-5.231	26.962	-1.593
3800	9.711	62.515	54.200	31.599	-5.286	27.836	-1.601
3900	9.736	62.768	54.416	32.571	-5.347	28.709	-1.609
4000	9.763	63.015	54.628	33.546	-5.416	29.581	-1.616
4100	9.789	63.256	54.836	34.524	-5.493	30.458	-1.624
4200	9.816	63.492	55.039	35.504	-5.578	31.335	-1.631
4300	9.843	63.723	55.238	36.487	-5.671	32.215	-1.637
4400	9.870	63.950	55.434	37.473	-5.771	33.098	-1.644
4500	9.899	64.172	55.625	38.461	-5.883	33.982	-1.650
4600	9.927	64.390	55.813	39.452	-6.003	34.870	-1.657
4700	9.956	64.604	55.998	40.446	-6.134	35.758	-1.663
4800	9.986	64.814	56.180	41.443	-6.276	36.650	-1.669
4900	10.016	65.020	56.358	42.444	-6.429	37.546	-1.675
5000	10.047	65.223	56.533	43.447	-6.593	38.446	-1.680
5100	10.079	65.422	56.706	44.453	-6.771	39.351	-1.686
5200	10.111	65.618	56.875	45.463	-6.963	40.256	-1.692
5300	10.144	65.811	57.042	46.475	-7.169	41.165	-1.697
5400	10.178	66.001	57.206	47.492	-7.390	42.078	-1.703
5500	10.213	66.188	57.368	48.511	-7.628	42.998	-1.709
5600	10.248	66.372	57.527	49.534	-7.882	43.916	-1.714
5700	10.284	66.554	57.684	50.561	-8.155	44.847	-1.720
5800	10.321	66.733	57.838	51.591	-8.448	45.779	-1.725
5900	10.358	66.910	57.990	52.625	-8.759	46.717	-1.730
6000	10.396	67.084	58.140	53.663	-9.092	47.660	-1.736

Dec. 31, 1960; Sept. 30, 1967

LITHIUM HYDRIDE (LiH) (IDEAL GAS) GFW = 7.94697

Ground State Configuration $^1\Sigma^+$

S°_{298} = 40.821 gibbs/mol

ΔHf°_0 = 33.65 ± 0.01 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 33.61 ± 0.01 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
26513.7	1
34912.0	2

ω_e = 1406.73 cm^{-1}

$\omega_e x_e$ = 23.24 cm^{-1}

σ = 1

B_e = 7.5247 cm^{-1}

α_e = 0.2137 cm^{-1}

r_e = 1.595 Å

Heat of Formation

R. Velasco, Can. J. Phys. 35, 1204 (1957), observed the absorption spectra of LiH(g) in the near ultraviolet with high dispersion and absorbing path lengths up to 16 meters. He found a new band system involving the ground state and a $^1\Pi$ excited state. Rotational and vibrational analyses of this system were carried out and the observed breaking off of the rotational structure of the bands was interpreted as due to predissociation by rotation. With this assumption very accurate dissociation limits of the $B^1\Pi$ state were obtained. From these dissociation limits the dissociation energy (D_0) of the ground state of LiH was found to be 2.4288 ± 0.0002 eV. Based on this D_0 value, we adopt ΔHf°_{298} = 33.61 kcal/mol for LiH(g).

W. Kemperer, J. Chem. Phys. 23, 2452 (1955), observed the infrared spectrum of LiH(g) in emission in the frequency region 1500 to 970 cm^{-1}, using a Perkin-Elmer double-pass monochromator with NaCl optics. Estimating the minimum LiH pressure as 10 mm and assuming the maximum possible Li pressure, he reported K = 0.005 (atm) at 1400°K for the reaction $2Li(g) + H_2(g) = 2LiH(g)$. We calculate the corresponding enthalpy change, ΔHr°_{1400}, to be -9.63 kcal/mol, employing ΔSr°_{1400} = -17.407 eu. Incorporating this ΔHr°_{1400} value with ΔHf°_{1400} = 35.601 kcal/mol for Li(g), we obtain $\Delta Hf^\circ_{298} \leqslant 33.92$ kcal/mol for LiH(g), which is in good agreement with the adopted value.

A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, derived the value $D_0(LiH)$ = 2.5 ± 0.2 eV from earlier spectroscopic data.

Heat Capacity and Entropy

The third electronic level and quantum weight are obtained from Velasco, loc. cit. All the other constants are taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., and corrected to the average isotopic species. The moment of inertia is 3.7193 x 10^{-40} g cm^2.

Lithium Hydroxide (LiOH)

(Crystal) Mol. Wt. = 23.94637

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.770	- 114.456	- 114.456	INFINITE
100	3.492	2.044	18.416	- 1.637	- 115.178	- 111.911	244.581
200	8.600	6.124	11.218	- 1.019	- 115.641	- 108.442	118.500
298	11.850	10.225	10.225	.000	- 115.840	- 104.858	76.863
300	11.900	10.299	10.225	.022	- 115.842	- 104.790	76.339
400	13.900	14.020	10.719	1.320	- 115.867	- 101.098	55.237
500	15.230	17.272	11.712	2.780	- 116.540	- 97.337	42.546
600	16.300	20.143	12.882	4.357	- 116.404	- 93.507	34.060
700	17.370	22.737	14.107	6.040	- 116.161	- 89.709	28.008
800	18.165	25.117	15.337	7.824	- 115.821	- 85.953	23.481
900	18.800	27.294	16.546	9.673	- 115.426	- 82.242	19.971
1000	19.336	29.303	17.723	11.580	- 114.981	- 78.578	17.173
1100	19.807	31.168	18.861	13.538	- 114.494	- 74.961	14.893
1200	20.234	32.910	19.960	15.540	- 113.971	- 71.390	13.002
1300	20.630	34.546	21.020	17.583	- 113.414	- 67.865	11.409
1400	21.004	36.088	22.042	19.665	- 112.826	- 64.382	10.050
1500	21.360	37.550	23.027	21.783	- 112.210	- 60.944	8.880
1600	21.704	38.939	23.979	23.937	- 111.565	- 57.546	7.860
1700	22.038	40.265	24.898	26.124	- 145.939	- 52.862	6.796
1800	22.364	41.534	25.787	28.344	- 145.059	- 47.412	5.757
1900	22.685	42.752	26.648	30.597	- 144.154	- 42.011	4.832
2000	23.000	43.923	27.483	32.881	- 143.225	- 36.659	4.006

Dec. 31, 1960; Mar. 31, 1966

LITHIUM HYDROXIDE (LiOH) (CRYSTAL) MOL. WT. = 23.94637

$S^\circ_{298.15}$ = 10.225 cal. deg.$^{-1}$ mole^{-1}

T_m = 744.3°K.

$\Delta H^\circ_{f\ 0}$ = -114.46 ± 0.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -115.84 ± 0.1 kcal. mole^{-1}

ΔH°_m = 5.010 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to monomer) = [57.0] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to dimer) = [50.2] kcal. mole^{-1}

Heat of Formation.

The standard enthalpy of formation, $\Delta H^\circ_{f\ 298}$ (LiOH, c) = -115.84 ± 0.1 kcal. mole^{-1}, was calculated from the heat of solution of lithium hydroxide (c), the heat of hydrolysis of lithium metal and the appropriate auxiliary data.

N. A. Peshetnikov[1] has measured the heat of solution LiOH(c) → LiOH(400 H_2O) as -5.479 ± 0.007 kcal. mole^{-1} at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker[2], the selected heat of solution of lithium hydroxide (c) at infinite dilution is -5.632 kcal. mole^{-1}.

The heat of hydrolysis of lithium metal, $\Delta H^\circ_{r\ 298}$, has been measured in the solution calorimeter by the following investigators.

$$Li(c) + H_2O(l) \rightarrow LiOH(nH_2O) + 1/2\ H_2(g) \qquad \Delta H^\circ_{r\ 298}$$

Source	Number of moles of H_2O	$\Delta H^\circ_{r\ 298}$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}(LiOH(\infty H_2O)$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}$(LiOH, c) kcal. mole^{-1}
Gunn et al.[3]	1000	-53.115 ± 0.019	-121.532	-115.900
Messer et al.[4]	∞	-53.075 ± 0.20	-121.390	-115.758

The values of $\Delta H^\circ_{f\ 298}(LiOH(\infty H_2O))$ were calculated from the heats of reaction $\Delta H^\circ_{r\ 298}$, using the $\Delta H^\circ_{f\ 298}(H_2O,\ l)$ = -68.315 kcal. mole^{-1}.[5] Combination of the selected heat of solution of LiOH(c) at infinite dilution with the heat of formation of LiOH(∞H_2O) gives the heat of formation of LiOH(c) in the last column of the table. A weighted average of these measurements was taken for the adopted heat of formation of lithium hydroxide (c).

The earlier calorimetric investigations have been reviewed by F. R. Bichowsky and F. D. Rossini[6], and C. E. Messer et al.[4], and these data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of lithium hydroxide (c) from 15.91° to 302.85°K. have been measured by T. W. Bauer, H. L. Johnston and E. C. Kerr[7]. The high temperature heat capacities which were determined from the enthalpy measurements in the temperature range from 418° to 878°K. by the drop method have been reported by C. H. Shomate and A. J. Cohen[8]. The low temperature and the high temperature heat capacities have been joined smoothly by the Shomate method[9]. The smooth values of heat capacity of LiOH(c) were adopted in the tabulation.

W. D. Powers and G. C. Blalock[10] have also measured the high temperature enthalpy changes of LiOH(c) by the drop method. Their results are in agreement with the tabulated H_T-H_{298} values within the experimental uncertainty.

The entropy (S°_{298} = 10.225 cal. deg.$^{-1}$ mole^{-1}) was obtained from Bauer et al.[7], based on an extrapolation of S°_{16} = 0.028 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The adopted heat of melting and the melting point were obtained from the enthalpy measurements by Shomate and Cohen[8]. Powers and Blalock[10] also found the heat of melting ΔH°_m = 5.029 kcal. mole^{-1} at 746°K. which is in good agreement with the adopted value.

Reference:

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5 D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, NBS Technical Note 270-1, Oct. 1965.
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8 C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. 77, 285 (1955).
9 C. H. Shomate, J. Phys. Chem. 58, 368 (1954).
10 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures" ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954.

Lithium Hydroxide (LiOH)

(Liquid) Mol. Wt. = 23.94637

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	20.740	11.574	11.574	.000	- 113.263	- 102.683	75.269
300	20.740	11.702	11.575	.038	- 113.249	- 102.618	74.757
400	20.740	17.669	12.388	2.112	- 112.498	- 99.189	54.194
500	20.740	22.297	13.924	4.186	- 112.557	- 95.866	41.903
600	20.740	26.078	15.644	6.260	- 111.924	- 92.587	33.725
700	20.740	29.275	17.369	8.334	- 111.290	- 89.415	27.916
800	20.740	32.045	19.034	10.408	- 110.660	- 86.334	23.585
900	20.740	34.488	20.618	12.482	- 110.040	- 83.330	20.235
1000	20.740	36.673	22.117	14.556	- 109.428	- 80.395	17.570
1100	20.740	38.650	23.531	16.630	- 108.825	- 77.521	15.402
1200	20.740	40.454	24.867	18.704	- 108.230	- 74.702	13.605
1300	20.740	42.114	26.131	20.778	- 107.642	- 71.932	12.093
1400	20.740	43.651	27.328	22.852	- 107.062	- 69.206	10.804
1500	20.740	45.082	28.465	24.926	- 106.490	- 66.522	9.692
1600	20.740	46.421	29.546	27.000	- 105.924	- 63.877	8.725
1700	20.740	47.678	30.576	29.074	- 140.412	- 59.937	7.705
1800	20.740	48.864	31.559	31.148	- 139.678	- 55.224	6.705
1900	20.740	49.985	32.499	33.222	- 138.951	- 50.551	5.815
2000	20.740	51.049	33.401	35.296	- 138.233	- 45.919	5.018
2100	20.740	52.061	34.265	37.370	- 137.522	- 41.321	4.300
2200	20.740	53.025	35.096	39.444	- 136.820	- 36.754	3.651
2300	20.740	53.947	35.896	41.518	- 136.124	- 32.222	3.062
2400	20.740	54.830	36.667	43.592	- 135.437	- 27.719	2.524
2500	20.740	55.677	37.410	45.666	- 134.759	- 23.247	2.032
2600	20.740	56.490	38.129	47.740	- 134.087	- 18.799	1.580
2700	20.740	57.273	38.823	49.814	- 133.424	- 14.378	1.164
2800	20.740	58.027	39.496	51.888	- 132.769	- 9.981	.779
2900	20.740	58.755	40.147	53.962	- 132.124	- 5.606	.422
3000	20.740	59.458	40.779	56.036	- 131.487	- 1.254	.091
3100	20.740	60.138	41.393	58.110	- 130.859	3.078	- .217
3200	20.740	60.797	41.989	60.184	- 130.240	7.385	- .504
3300	20.740	61.435	42.569	62.258	- 129.632	11.678	- .773
3400	20.740	62.054	43.133	64.332	- 129.033	15.952	- 1.025
3500	20.740	62.655	43.682	66.406	- 128.443	20.207	- 1.262

Dec. 31, 1960; Mar. 31, 1966

LITHIUM HYDROXIDE (LiOH) (LIQUID) MOL. WT. = 23.94637

$S^\circ_{298.15}$ = 11.574 cal. deg.$^{-1}$ mole^{-1}

T_m = 744.3°K.

T_b(monomeric gas) = 1803°K.

$\Delta H^\circ_{f\ 298.15}$ = -113.263 kcal. mole^{-1}

ΔH°_m = 5.010 kcal. mole^{-1}

ΔH°_v(to monomer) = 40.1 kcal. mole^{-1}

Heat of Formation.

The heat of formation of LiOH(l) at 298.15°K. was obtained from that of the crystal by adding ΔH°_m and the difference between $H_{744.3}-H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacity of the liquid phase, C_p = 20.74 cal. deg.$^{-1}$ mole^{-1}, was obtained from the enthalpy measurements in the drop calorimeter by C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. 77, 285 (1955).

W. D. Powers and G. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., have also determined the heat capacity of lithium hydroxide (l), C_p = 22.03 cal. deg.$^{-1}$ mole^{-1}, from the enthalpy measurements by the drop method.

The entropy ($S^\circ_{298.15}$ = 11.574 cal. deg.$^{-1}$, mole^{-1}) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiOH(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF°_f) for both LiOH(l) and LiOH(g) are equal. The difference in the heats of formation (ΔH°_f) of LiOH(l) and LiOH(g) at the boiling point is the heat of vaporization (ΔH°_v).

Lithium Hydroxide (LiOH)

(Ideal Gas) Mol. Wt. = 23.94637

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.400	- 58.089	- 58.089	INFINITE
100	7.949	43.240	59.292	- 1.605	- 58.149	- 59.001	128.947
200	8.041	48.764	52.803	- .808	- 58.433	- 59.762	65.305
298	8.474	52.044	52.044	.000	- 58.843	- 60.329	44.222
300	8.485	52.097	52.044	.016	- 58.851	- 60.339	43.957
400	9.107	54.622	52.384	.895	- 59.296	- 60.767	33.202
500	9.686	56.718	53.047	1.835	- 60.488	- 61.008	26.666
600	10.163	58.528	53.813	2.829	- 60.935	- 61.068	22.244
700	10.551	60.124	54.603	3.865	- 61.339	- 61.058	19.063
800	10.875	61.555	55.384	4.937	- 61.711	- 60.994	16.663
900	11.154	62.852	56.143	6.039	- 62.063	- 60.882	14.784
1000	11.400	64.041	56.874	7.166	- 62.398	- 60.733	13.273
1100	11.620	65.138	57.576	8.318	- 62.717	- 60.551	12.030
1200	11.818	66.157	58.249	9.490	- 63.024	- 60.340	10.989
1300	11.996	67.110	58.895	10.681	- 63.320	- 60.104	10.104
1400	12.157	68.005	59.514	11.888	- 63.606	- 59.846	9.342
1500	12.302	68.849	60.108	13.111	- 63.885	- 59.568	8.679
1600	12.432	69.647	60.680	14.348	- 64.156	- 59.271	8.096
1700	12.550	70.405	61.230	15.597	- 99.469	- 57.630	7.409
1800	12.656	71.125	61.760	16.858	- 99.548	- 55.165	6.698
1900	12.751	71.812	62.271	18.128	- 99.625	- 52.696	6.061
2000	12.837	72.468	62.764	19.408	- 99.701	- 50.225	5.488
2100	12.915	73.096	63.241	20.695	- 99.777	- 47.750	4.969
2200	12.985	73.699	63.703	21.990	- 99.854	- 45.271	4.497
2300	13.049	74.277	64.150	23.292	- 99.930	- 42.788	4.066
2400	13.106	74.834	64.584	24.600	- 100.010	- 40.301	3.670
2500	13.159	75.370	65.005	25.913	- 100.092	- 37.813	3.306
2600	13.207	75.887	65.413	27.231	- 100.176	- 35.320	2.969
2700	13.251	76.386	65.811	28.554	- 100.264	- 32.824	2.657
2800	13.291	76.869	66.197	29.881	- 100.356	- 30.325	2.367
2900	13.327	77.336	66.573	31.212	- 100.454	- 27.821	2.097
3000	13.361	77.788	66.939	32.547	- 100.556	- 25.313	1.844
3100	13.392	78.227	67.297	33.884	- 100.665	- 22.804	1.608
3200	13.420	78.653	67.645	35.225	- 100.779	- 20.293	1.386
3300	13.446	79.066	67.985	36.568	- 100.902	- 17.775	1.177
3400	13.471	79.468	68.316	37.914	- 101.031	- 15.254	.981
3500	13.493	79.859	68.641	39.262	- 101.167	- 12.731	.795
3600	13.514	80.239	68.958	40.613	- 101.312	- 10.200	.619
3700	13.533	80.610	69.268	41.965	- 101.466	- 7.669	.453
3800	13.552	80.971	69.571	43.319	- 101.629	- 5.128	.295
3900	13.568	81.323	69.868	44.675	- 101.801	- 2.586	.145
4000	13.584	81.667	70.158	46.033	- 101.983	- .043	.002
4100	13.599	82.002	70.443	47.392	- 102.175	2.512	- .134
4200	13.612	82.330	70.722	48.753	- 102.379	5.066	- .264
4300	13.625	82.651	70.996	50.115	- 102.592	7.625	- .388
4400	13.637	82.964	71.264	51.478	- 102.817	10.192	- .506
4500	13.649	83.271	71.528	52.842	- 103.055	12.761	- .620
4600	13.659	83.571	71.786	54.207	- 103.305	15.340	- .729
4700	13.669	83.864	72.040	55.574	- 103.569	17.924	- .833
4800	13.679	84.152	72.290	56.941	- 103.845	20.511	- .934
4900	13.688	84.434	72.535	58.310	- 104.137	23.104	- 1.030
5000	13.696	84.711	72.775	59.679	- 104.443	25.702	- 1.123
5100	13.704	84.982	73.012	61.049	- 104.766	28.314	- 1.213
5200	13.711	85.249	73.245	62.420	- 105.105	30.919	- 1.300
5300	13.719	85.510	73.474	63.791	- 105.462	33.541	- 1.383
5400	13.725	85.766	73.699	65.163	- 105.837	36.167	- 1.464
5500	13.732	86.018	73.921	66.536	- 106.232	38.803	- 1.542
5600	13.738	86.266	74.139	67.910	- 106.648	41.435	- 1.617
5700	13.744	86.509	74.354	69.284	- 107.085	44.087	- 1.690
5800	13.749	86.748	74.566	70.658	- 107.546	46.745	- 1.761
5900	13.754	86.983	74.774	72.033	- 108.030	49.409	- 1.830
6000	13.759	87.214	74.979	73.409	- 108.538	52.085	- 1.897

Dec. 31, 1960; Mar. 31, 1966

LITHIUM HYDROXIDE (LiOH) (IDEAL GAS) MOL. WT. = 23.94637

Point Group C_s

$S^\circ_{298.15}$ = [52.0] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -58.1 ± 4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -58.8 ± 4 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[1000](1)

[1300](1)

[3700](1)

Bond Distance: Li-O = [1.60] Å O-H = [0.96] Å

Bond Angle: Li-O-H = [110]°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [0.6156 X 10^{-117}] g.^{3} cm.^{6}

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have studied the equilibrium of $Li_2O(c) - H_2O(g)$ system by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K, the heat of reaction $Li_2O(c) + H_2O(g) \rightarrow 2LiOH(g)$ at 298.15°K. has been calculated by both the second and the third law methods as 86.1 and 83.2 kcal. mole^{-1}, respectively. (The third law drift is -2.2 ± 2.6 e.u.) The third law value was taken for the calculation of the heat of formation of LiOH(g) at 298.15°K.

Heat Capacity and Entropy.

Since the bond distance Li-F(g) (r_e = 1.56389 Å) was accurately measured from the microwave studies by L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallangh and V. E. Derr, J. Chem. Phys. 38, 1203 (1963), the bond distance Li-O in LiOH(g) was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Li-F(g). Also the bond distance Li-O(g) was estimated as 1.62 Å from the matrix-isolated infrared spectrum by D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963). These two are in good agreement. The bond distance O-H was estimated from that in $H_2O(g)$. The adopted bent molecular configuration with bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. 29, 991 (1958). The three principal moments of interia are I_A =[0.1237] X 10^{-39}, I_B =[2.1699] X 10^{-39} and I_C =[2.2936] X 10^{-39} g. cm.^{2}

The Li-O stretching frequency was estimated to be the same as that in $Li_2O(g)$ (ν = 987 cm.$^{-1}$, see $Li_2O(g)$ table). The bending and the O-H stretching frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

Magnesium Monohydride (MgH)

(Ideal Gas) GFW = 25.31997

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.075	40.533	40.533	INFINITE
100	6.961	38.524	52.371	-1.385	40.690	38.284	-83.670
200	6.974	43.352	46.792	-.688	40.523	35.811	-39.132
298	7.070	46.150	46.150	.000	40.400	33.622	-24.646
300	7.074	46.194	46.150	.013	40.396	33.580	-24.463
400	7.298	48.257	46.430	.731	40.152	31.344	-17.126
500	7.572	49.915	46.966	1.474	39.904	29.172	-12.751
600	7.834	51.319	47.577	2.245	39.656	27.047	-9.852
700	8.060	52.544	48.201	3.040	39.407	24.967	-7.795
800	8.248	53.633	48.813	3.856	39.145	22.921	-6.262
900	8.403	54.614	49.404	4.688	38.860	20.910	-5.078
1000	8.531	55.506	49.971	5.535	36.429	19.113	-4.177
1100	8.638	56.324	50.511	6.394	36.123	17.395	-3.456
1200	8.728	57.080	51.028	7.262	35.797	15.706	-2.861
1300	8.806	57.781	51.521	8.139	35.449	14.047	-2.362
1400	8.873	58.436	51.991	9.023	4.712	12.894	-2.013
1500	8.933	59.051	52.442	9.914	4.723	13.478	-1.964
1600	8.986	59.629	52.873	10.810	4.733	14.060	-1.920
1700	9.034	60.175	53.287	11.711	4.743	14.645	-1.883
1800	9.078	60.693	53.684	12.616	4.753	15.226	-1.849
1900	9.119	61.185	54.066	13.526	4.764	15.807	-1.818
2000	9.157	61.654	54.434	14.440	4.773	16.387	-1.791
2100	9.193	62.101	54.788	15.358	4.782	16.968	-1.766
2200	9.227	62.530	55.130	16.279	4.790	17.549	-1.743
2300	9.260	62.941	55.461	17.203	4.798	18.129	-1.723
2400	9.293	63.335	55.781	18.131	4.805	18.710	-1.704
2500	9.324	63.715	56.091	19.061	4.810	19.287	-1.686
2600	9.355	64.082	56.391	19.995	4.816	19.867	-1.670
2700	9.387	64.435	56.683	20.933	4.821	20.446	-1.655
2800	9.418	64.777	56.966	21.873	4.826	21.022	-1.641
2900	9.450	65.108	57.241	22.816	4.830	21.604	-1.628
3000	9.483	65.429	57.508	23.763	4.833	22.180	-1.616
3100	9.517	65.741	57.769	24.713	4.836	22.757	-1.604
3200	9.551	66.043	58.023	25.666	4.837	23.336	-1.594
3300	9.586	66.338	58.270	26.623	4.838	23.913	-1.584
3400	9.623	66.625	58.512	27.584	4.837	24.492	-1.574
3500	9.661	66.904	58.748	28.548	4.833	25.070	-1.565
3600	9.700	67.177	58.978	29.516	4.828	25.648	-1.557
3700	9.741	67.443	59.203	30.488	4.819	26.229	-1.549
3800	9.783	67.704	59.424	31.464	4.810	26.806	-1.542
3900	9.826	67.958	59.639	32.445	4.796	27.385	-1.535
4000	9.871	68.208	59.850	33.429	4.779	27.963	-1.528
4100	9.917	68.452	60.057	34.419	4.757	28.543	-1.522
4200	9.965	68.691	60.260	35.413	4.732	29.126	-1.516
4300	10.013	68.926	60.459	36.412	4.701	29.706	-1.510
4400	10.063	69.157	60.654	37.416	4.667	30.288	-1.504
4500	10.114	69.384	60.845	38.425	4.626	30.870	-1.499
4600	10.167	69.607	61.033	39.439	4.579	31.455	-1.494
4700	10.220	69.826	61.218	40.458	4.526	32.040	-1.490
4800	10.274	70.042	61.400	41.483	4.467	32.626	-1.485
4900	10.330	70.254	61.578	42.513	4.400	33.215	-1.481
5000	10.386	70.463	61.754	43.549	4.327	33.804	-1.478
5100	10.443	70.670	61.927	44.590	4.245	34.388	-1.474
5200	10.501	70.873	62.097	45.637	4.155	34.983	-1.470
5300	10.559	71.074	62.264	46.690	4.057	35.578	-1.467
5400	10.618	71.272	62.429	47.749	3.950	36.169	-1.464
5500	10.678	71.467	62.592	48.814	3.833	36.770	-1.461
5600	10.739	71.660	62.752	49.885	3.706	37.368	-1.458
5700	10.799	71.850	62.910	50.962	3.570	37.978	-1.456
5800	10.861	72.039	63.066	52.045	3.423	38.574	-1.454
5900	10.922	72.225	63.219	53.134	3.265	39.187	-1.452
6000	10.984	72.409	63.371	54.229	3.096	39.792	-1.449

Dec. 31, 1960; Dec. 31, 1966

MAGNESIUM MONOHYDRIDE (MgH) (IDEAL GAS) GFW = 25.31997

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 46.15 gibbs/mol

$\Delta Hf^\circ_0 = 40.5 \pm 11.5$ kcal/mol

$\Delta Hf^\circ_{298.15} = 40.4 \pm 11.5$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1	ϵ_1, cm^{-1}	g_1	ϵ_1, cm^{-1}	g_1
0	2	35400	2	42070	2
19221.2	2	[38730]	2	48000	4
19224.7	2	41120	4		

$\omega_e = 1495.7$ cm^{-1} $\omega_e x_e = 31.5$ cm^{-1} $\sigma = 1$

$B_e = 5.8181$ cm^{-1} $\alpha_e = 0.1668$ cm^{-1} $r_e = 1.73$ Å

Heat of Formation.

The heat of formation is calculated using $D^\circ_0 = 2.0 \pm 0.5$ e.v. derived from a graphical extrapolation of the ν(0-3) energy levels of the $X^2\Sigma^+$ state reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Edition, Chapman and Hall Ltd., London, 1953. G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Co., Inc., New York, 1950, reported $D^\circ_0 \leq 2.49$ e.v. assuming predissociation of the $C^2\pi$ state of MgH into Mg(^{3}P) and H(^{2}S).

Heat Capacity and Entropy.

The molecular constants and electronic levels are obtained from Herzberg, loc. cit., except for the electronic levels 35400 and 48000 obtained from M. A. Khan, Proc. Phys. Soc. (London) 80, 209 - 21 (1962).

Magnesium Monohydroxide (MgOH)

(Ideal Gas)   GFW = 41.31937

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.169	-50.923	-50.923	INFINITE
100	6.958	44.924	59.660	-1.474	-51.109	-52.085	113.831
200	7.320	49.812	53.644	-.767	-51.613	-52.995	57.910
298	8.360	52.916	52.916	.000	-52.000	-53.490	39.209
300	8.382	52.968	52.916	.015	-52.009	-53.499	38.974
400	9.485	55.535	53.259	.910	-52.430	-53.931	29.467
500	10.342	57.748	53.940	1.904	-52.793	-54.262	23.718
600	10.970	59.692	54.740	2.971	-53.123	-54.526	19.861
700	11.443	61.421	55.573	4.093	-53.434	-54.734	17.089
800	11.817	62.974	56.403	5.257	-53.747	-54.899	14.998
900	12.128	64.384	57.213	6.454	-54.074	-55.023	13.361
1000	12.394	65.676	57.995	7.681	-56.539	-54.929	12.005
1100	12.628	66.869	58.749	8.932	-56.872	-54.754	10.879
1200	12.835	67.976	59.472	10.205	-57.217	-54.545	9.934
1300	13.019	69.011	60.166	11.498	-57.577	-54.308	9.130
1400	13.183	69.982	60.833	12.809	-88.320	-53.563	8.362
1500	13.330	70.897	61.474	14.134	-88.310	-51.081	7.442
1600	13.462	71.761	62.090	15.474	-88.294	-48.601	6.639
1700	13.579	72.581	62.683	16.826	-88.274	-46.119	5.929
1800	13.685	73.360	63.255	18.190	-88.250	-43.640	5.299
1900	13.779	74.103	63.807	19.563	-88.224	-41.163	4.735
2000	13.864	74.812	64.339	20.945	-88.196	-38.688	4.228
2100	13.941	75.490	64.854	22.336	-88.167	-36.213	3.769
2200	14.010	76.140	65.353	23.733	-88.138	-33.738	3.352
2300	14.073	76.765	65.835	25.137	-88.109	-31.268	2.971
2400	14.129	77.365	66.303	26.548	-88.080	-28.796	2.622
2500	14.180	77.942	66.757	27.963	-88.054	-26.328	2.302
2600	14.227	78.500	67.198	29.383	-88.028	-23.858	2.005
2700	14.270	79.037	67.627	30.808	-88.004	-21.390	1.731
2800	14.309	79.557	68.044	32.237	-87.982	-18.926	1.477
2900	14.345	80.060	68.449	33.670	-87.962	-16.457	1.240
3000	14.378	80.547	68.845	35.106	-87.947	-13.994	1.019
3100	14.408	81.019	69.230	36.545	-87.933	-11.529	.813
3200	14.437	81.476	69.605	37.988	-87.924	-9.063	.619
3300	14.463	81.921	69.972	39.433	-87.918	-6.600	.437
3400	14.488	82.353	70.330	40.880	-87.918	-4.133	.266
3500	14.512	82.774	70.679	42.330	-87.922	-1.673	.104
3600	14.534	83.183	71.021	43.783	-87.932	.793	-.048
3700	14.555	83.581	71.355	45.237	-87.949	3.261	-.193
3800	14.575	83.970	71.682	46.694	-87.971	5.725	-.329
3900	14.595	84.349	72.002	48.152	-88.001	8.187	-.459
4000	14.614	84.718	72.315	49.613	-88.039	10.658	-.582
4100	14.633	85.079	72.622	51.075	-88.084	13.126	-.700
4200	14.652	85.432	72.923	52.539	-88.138	15.593	-.811
4300	14.670	85.777	73.218	54.005	-88.202	18.064	-.918
4400	14.688	86.115	73.507	55.473	-88.274	20.534	-1.020
4500	14.706	86.445	73.791	56.943	-88.356	23.010	-1.117
4600	14.725	86.768	74.070	58.415	-88.449	25.491	-1.211
4700	14.743	87.085	74.343	59.888	-88.553	27.968	-1.300
4800	14.762	87.396	74.612	61.363	-88.667	30.447	-1.386
4900	14.781	87.700	74.876	62.840	-88.793	32.930	-1.469
5000	14.800	87.999	75.135	64.319	-88.931	35.414	-1.548
5100	14.820	88.293	75.390	65.800	-89.082	37.898	-1.624
5200	14.840	88.580	75.641	67.283	-89.245	40.394	-1.698
5300	14.860	88.863	75.888	68.768	-89.421	42.894	-1.769
5400	14.881	89.141	76.131	70.256	-89.610	45.385	-1.837
5500	14.902	89.415	76.370	71.745	-89.813	47.885	-1.903
5600	14.924	89.683	76.605	73.236	-90.031	50.392	-1.967
5700	14.946	89.948	76.837	74.730	-90.262	52.902	-2.028
5800	14.969	90.208	77.065	76.225	-90.509	55.413	-2.088
5900	14.992	90.464	77.290	77.723	-90.772	57.935	-2.146
6000	15.015	90.716	77.512	79.224	-91.049	60.454	-2.202

Dec. 31, 1960; June 30, 1967

MAGNESIUM MONOHYDROXIDE (MgOH)   (IDEAL GAS)   GFW = 41.31937

Point Group [$C_{\infty v}$]

$S^\circ_{298.15}$ = [52.9] gibbs/mol

ΔHf°_0 = [-51 ± 20] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-52 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[2]
[27000]	[4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[3600] (1)
[1000] (2)
[800] (1)

Bond Distances: O-Mg = [1.80] Å   O-H = [0.97] Å

Bond Angle: Mg-O-H = [180°]   σ = 1

Rotational Constant: B_e = 0.47595 cm^{-1}

Heat of Formation

The heat of formation is based on the following estimates. The relation D°_0(M-X)/D°_0(X-M-X) = 0.46 ± 0.03 for several alkaline earth dihalides has been reported by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Assuming that this relation applies to hydroxides, we may estimate D°_0(Mg-OH) = 87 ± 12 kcal/mol. A value of D°_0(Mg-OH) = 105 ± 12 kcal/mol is obtained by comparison with D°_0(Be-OH) ≤ 111 ± 10, D°_0(Ca-OH) = 100 ± 10 and D°_0(Sr-OH) = 95 ± 10 kcal/mol. The value for BeOH is from the JANAF tables, while those for CaOH and SrOH are from flame studies of L. V. Gurvich, private communication, High Temperature Institute, Moscow, 1966. The average value of D°_0(Mg-OH) = 96 kcal/mol is used to calculate the heat of formation.

A value of D°_0(Mg-OH) = 56 ± 5 kcal/mol was derived from intensity measurements on the flame spectrum of magnesium by E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. 55, 720 (1959). This appears to be too small.

Heat Capacity and Entropy

The ground state is assumed to be $^2\Sigma$ by analogy with isoelectronic MgF. Ultraviolet emission spectra near 3800 Å were observed for MgOH and MgOD by D. Pesic and A. G. Gaydon, Proc. Phys. Soc. (London) 73, 244 (1959), and L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962). Vibrational and rotational analyses were not performed. Assuming that the observed spectra correspond to the transition $A^2\Pi \leftarrow X^2\Sigma$, we estimate the first excited state at 27000 cm^{-1}. The vibrational frequencies ν_1 and ν_3 are estimated from those of H_2O(g) and MgO(g). The ν_2 is tentatively estimated at 1000 cm^{-1}.

A linear structure is assumed by use of the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAB" molecules with less than 11 valence electrons (MgOH has 9 valence electrons). Confirmation of this prediction is scanty for molecules having "A" as the most electronegative element; however, recent microwave evidence [R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966)] for the linearity of KOH and CsOH confirms the prediction for these molecules having 8 valence electrons. The O-H bond distance is assumed to be the same as that of H_2O(g) and the Mg-O bond distance is estimated from that of MgO(g).

Magnesium Monohydroxide Unipositive Ion ($MgOH^+$)

(Ideal Gas) GFW = 41.31882

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	8.987	51.871	51.871	.000	143.000	140.335	-102.868
300	9.010	51.926	51.871	.017	143.002	140.318	-102.222
400	10.095	54.675	52.238	.975	143.140	139.404	-76.167
500	10.861	57.015	52.966	2.025	143.330	138.450	-60.516
600	11.398	59.046	53.814	3.139	143.545	137.452	-50.067
700	11.797	60.834	54.691	4.300	143.769	136.420	-42.592
800	12.115	62.431	55.561	5.496	143.985	135.354	-36.977
900	12.384	63.874	56.405	6.721	144.183	134.264	-32.604
1000	12.618	65.191	57.219	7.972	142.239	133.333	-29.140
1100	12.826	66.403	58.000	9.244	142.424	132.433	-26.312
1200	13.012	67.527	58.747	10.536	142.595	131.517	-23.953
1300	13.178	68.576	59.463	11.846	142.747	130.587	-21.954
1400	13.328	69.558	60.150	13.171	112.517	130.126	-20.314
1500	13.462	70.482	60.808	14.511	113.038	131.366	-19.140
1600	13.582	71.355	61.440	15.863	113.563	132.569	-18.108
1700	13.690	72.181	62.048	17.227	114.092	133.743	-17.194
1800	13.787	72.967	62.633	18.601	114.622	134.882	-16.377
1900	13.874	73.715	63.197	19.984	115.155	135.995	-15.643
2000	13.952	74.428	63.741	21.375	115.689	137.077	-14.979
2100	14.022	75.111	64.266	22.774	116.224	138.132	-14.376
2200	14.085	75.764	64.774	24.179	116.757	139.164	-13.825
2300	14.143	76.392	65.265	25.591	117.290	140.170	-13.319
2400	14.195	76.995	65.742	27.008	117.822	141.154	-12.854
2500	14.242	77.575	66.203	28.430	118.352	142.112	-12.423
2600	14.284	78.135	66.652	29.856	118.881	143.055	-12.025
2700	14.323	78.675	67.087	31.286	119.407	143.976	-11.654
2800	14.359	79.196	67.510	32.721	119.931	144.873	-11.308
2900	14.392	79.701	67.922	34.158	120.452	145.758	-10.985
3000	14.421	80.189	68.323	35.599	120.969	146.619	-10.681
3100	14.449	80.662	68.713	37.042	121.484	147.466	-10.396
3200	14.474	81.121	69.094	38.489	121.994	148.297	-10.128
3300	14.497	81.567	69.465	39.937	122.500	149.111	-9.875
3400	14.519	82.000	69.827	41.388	123.000	149.912	-9.636
3500	14.539	82.421	70.181	42.841	123.495	150.694	-9.410
3600	14.557	82.831	70.527	44.296	123.985	151.466	-9.195
3700	14.574	83.230	70.865	45.752	124.467	152.221	-8.991
3800	14.590	83.619	71.195	47.210	124.943	152.968	-8.798
3900	14.605	83.998	71.519	48.670	125.412	153.695	-8.613
4000	14.619	84.368	71.835	50.131	125.871	154.414	-8.437
4100	14.632	84.729	72.146	51.594	126.322	155.121	-8.269
4200	14.644	85.082	72.449	53.058	126.765	155.820	-8.108
4300	14.655	85.427	72.747	54.523	127.198	156.507	-7.955
4400	14.665	85.764	73.039	55.989	127.621	157.185	-7.807
4500	14.675	86.094	73.326	57.456	128.031	157.850	-7.666
4600	14.685	86.416	73.607	58.924	128.432	158.513	-7.531
4700	14.693	86.732	73.883	60.392	128.821	159.161	-7.401
4800	14.702	87.042	74.154	61.862	129.198	159.802	-7.276
4900	14.710	87.345	74.420	63.333	129.562	160.436	-7.156
5000	14.717	87.642	74.681	64.804	129.913	161.062	-7.040
5100	14.724	87.934	74.938	66.276	130.250	161.678	-6.928
5200	14.730	88.220	75.191	67.749	130.573	162.293	-6.821
5300	14.737	88.500	75.439	69.222	130.883	162.905	-6.718
5400	14.743	88.776	75.684	70.696	131.178	163.498	-6.617
5500	14.748	89.046	75.924	72.171	131.457	164.098	-6.521
5600	14.753	89.312	76.161	73.646	131.719	164.683	-6.427
5700	14.759	89.573	76.394	75.121	131.966	165.279	-6.337
5800	14.763	89.830	76.623	76.598	132.197	165.855	-6.250
5900	14.768	90.082	76.849	78.074	132.410	166.436	-6.165
6000	14.772	90.331	77.072	79.551	132.607	167.010	-6.083

June 30, 1968

MAGNESIUM MONOHYDROXIDE UNIPOSITIVE ION ($MgOH^+$) (IDEAL GAS) GFW = 41.31882

Point Group [$C_{\infty v}$]

ΔHf°_0 = [144 ± 40] kcal/mol

$S^\circ_{298.15}$ = [51.9 ± 2] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [143 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[600] (1)

[900] (2)

[3500] (1)

Bond Distance: Mg-O = [1.8] Å O-H = [0.96] Å

Bond Angle: Mg-O-H = [180°] σ = 1

Rotational Constant: B_0 = [0.4765] cm^{-1}

Heat of Formation

The gaseous molecules NaOH, MgOH and AlOH have 8, 9 and 10 valence electrons, respectively. Due to the similarity in molecular structure, we assume that the ionization potential (IP) of MgOH is approximately the average of IP(NaOH) and IP(AlOH). Adopting IP = 9 and 7.5 eV for NaOH (1) and AlOH (2), respectively, we obtain IP(MgOH) = 8.5 eV. Based on this value and ΔHf°_0(MgOH, g) = -52 ± 20 kcal/mol we derive ΔHf°_{298}($MgOH^+$, g) = 143 ± 40 kcal/mol which is tentatively adopted. The estimated value IP(MgOH) is close to IP(MgF) = 7.8 ± 0.3 eV (1), where MF and MgOH are isoelectronic molecules, and thus confirms the value within its uncertainty.

Heat Capacity and Entropy

Walsh (3) predicted that ABH molecules (H = hydrogen atom) containing 10 or less valence electrons will be linear in their ground state. Since $MgOH^+$ molecule has 8 valence electrons, we assume it to be linear. The vibrational frequencies are estimated by comparison with those for NaOH(g) and MgOH(g). The O-H bond distance is assumed to be the same as that in H_2O(g). The Mg-O bond distance is estimated (4). The moment of inertia is 5.874 x 10^{-39} g cm^2. The ground state quantum weight is assumed to be the same as that of NaOH(g). The enthalpy at 0°K is -2.24 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. See JANAF $AlOH^+$(g) table (Dec. 31, 1967) for details.
3. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
4. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

Imidogen (NH)

(Ideal Gas) Mol. Wt. = 15.01467

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.060	80.988	80.988	INFINITE
100	6.961	35.688	49.486	- 1.380	80.946	80.502	- 175.929
200	6.963	40.514	43.932	- .684	80.989	80.037	- 87.456
298	6.966	43.295	43.295	.000	81.000	79.567	- 58.321
300	6.966	43.338	43.295	.013	81.000	79.558	- 57.955
400	6.973	45.343	43.568	.710	81.001	79.077	- 43.204
500	6.994	46.901	44.085	1.408	80.998	78.596	- 34.353
600	7.041	48.179	44.664	2.110	80.994	78.117	- 28.453
700	7.119	49.270	45.746	2.817	80.987	77.638	- 24.238
800	7.223	50.228	45.810	3.534	80.979	77.159	- 21.078
900	7.343	51.085	46.349	4.262	80.972	76.682	- 18.620
1000	7.471	51.865	46.862	5.003	80.967	76.206	- 16.654
1100	7.601	52.583	47.350	5.757	80.963	75.730	- 15.046
1200	7.727	53.250	47.814	6.523	80.962	75.255	- 13.705
1300	7.847	53.874	48.257	7.302	80.963	74.778	- 12.571
1400	7.960	54.459	48.679	8.092	80.966	74.303	- 11.599
1500	8.064	55.012	49.083	8.894	80.970	73.827	- 10.756
1600	8.161	55.536	49.470	9.705	80.974	73.350	- 10.019
1700	8.250	56.033	49.842	10.526	80.980	72.874	- 9.368
1800	8.331	56.507	50.199	11.355	80.986	72.397	- 8.790
1900	8.406	56.959	50.543	12.192	80.994	71.921	- 8.272
2000	8.474	57.392	50.875	13.036	81.001	71.443	- 7.807
2100	8.538	57.807	51.195	13.886	81.009	70.964	- 7.385
2200	8.596	58.206	51.505	14.743	81.016	70.485	- 7.002
2300	8.650	58.589	51.804	15.605	81.025	70.007	- 6.652
2400	8.701	58.959	52.095	16.473	81.033	69.527	- 6.331
2500	8.747	59.315	52.377	17.345	81.041	69.046	- 6.036
2600	8.791	59.659	52.650	18.222	81.049	68.567	- 5.763
2700	8.832	59.991	52.916	19.103	81.057	68.088	- 5.511
2800	8.870	60.313	53.174	19.989	81.066	67.606	- 5.277
2900	8.907	60.625	53.426	20.878	81.075	67.127	- 5.059
3000	8.941	60.928	53.671	21.770	81.082	66.643	- 4.855
3100	8.973	61.221	53.910	22.666	81.091	66.163	- 4.664
3200	9.004	61.507	54.143	23.565	81.099	65.680	- 4.486
3300	9.034	61.784	54.370	24.466	81.106	65.200	- 4.318
3400	9.062	62.054	54.592	25.371	81.115	64.718	- 4.160
3500	9.089	62.317	54.809	26.279	81.122	64.236	- 4.011
3600	9.114	62.574	55.021	27.189	81.128	63.751	- 3.870
3700	9.139	62.824	55.229	28.102	81.135	63.269	- 3.737
3800	9.163	63.068	55.432	29.017	81.141	62.787	- 3.611
3900	9.186	63.306	55.631	29.934	81.146	62.305	- 3.491
4000	9.209	63.539	55.825	30.854	81.151	61.821	- 3.378
4100	9.230	63.767	56.016	31.776	81.155	61.336	- 3.269
4200	9.251	63.989	56.204	32.700	81.159	60.856	- 3.167
4300	9.272	64.207	56.387	33.626	81.163	60.372	- 3.068
4400	9.292	64.421	56.567	34.554	81.165	59.885	- 2.974
4500	9.311	64.630	56.744	35.484	81.167	59.400	- 2.885
4600	9.330	64.835	56.918	36.417	81.169	58.919	- 2.799
4700	9.349	65.035	57.088	37.351	81.170	58.438	- 2.717
4800	9.367	65.232	57.256	38.286	81.170	57.955	- 2.639
4900	9.385	65.426	57.421	39.224	81.170	57.467	- 2.563
5000	9.403	65.616	57.583	40.163	81.170	56.982	- 2.491
5100	9.420	65.802	57.742	41.104	81.168	56.500	- 2.421
5200	9.437	65.985	57.899	42.047	81.167	56.018	- 2.354
5300	9.454	66.165	58.053	42.992	81.165	55.534	- 2.290
5400	9.470	66.342	58.205	43.938	81.162	55.048	- 2.228
5500	9.486	66.516	58.355	44.886	81.158	54.566	- 2.168
5600	9.502	66.687	58.502	45.835	81.154	54.081	- 2.111
5700	9.518	66.855	58.647	46.786	81.150	53.602	- 2.055
5800	9.534	67.021	58.790	47.739	81.144	53.116	- 2.001
5900	9.549	67.184	58.931	48.693	81.139	52.633	- 1.950
6000	9.565	67.344	59.070	49.649	81.132	52.152	- 1.900

Dec. 31, 1960; Dec. 31, 1965

IMIDOGEN (NH) (IDEAL GAS) MOL. WT. = 15.01467

Ground State Configuration $^3\Sigma^-$

$S^\circ_{298.15}$ = 43.3 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 81.0 ± 2.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 81.0 ± 2.5 kcal. mole^{-1}

Electronic Level and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	3

ω_e = 3315 cm.$^{-1}$

B_e = 16.6684 cm.$^{-1}$

$\omega_e x_e$ = 94.7 cm.$^{-1}$

α_e = 0.646 cm.$^{-1}$

σ = 1

r_e = 1.038 Å

Heat of Formation.

The value, $\Delta H^\circ_{f\ 298}$ (NH, g) = 81.0 ± 2.5 kcal. mole^{-1}, was calculated from the selected dissociation energy, D_0 = 83 ± 2 kcal. mole^{-1}, based on the following investigations. J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Krause, J. Am. Chem. Soc. 80, 298 (1958) and R. I. Reed and W. Snedden, J. Chem. Soc. 4132 (1959) have determined the dissociation energy of NH(g) by electron impact as 83 ± 2 kcal. mole^{-1} and 85.3 ± 6 kcal. mole^{-1}, respectively. A. L. Companion and F. O. Ellison, J. Chem. Phys. 32, 1132 (1960), and P. C. H. Jordan and H. C. Lonquet-Higgins, Mol. Phys. 5, 121 (1962) have calculated theoretically the dissociation energy by a semi-empirical method and obtained 83.3 kcal. mole^{-1} and 81.2 kcal. mole^{-1}, respectively. These results are in good agreement. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, 1950, has estimated the dissociation energy D_0(NH, g) = 3.8 e.v. (87.6 kcal. mole^{-1}) based on the average of two earlier theoretical calculations by R. S. Mulliken, (D_0 = 4.2 e.v.), Rev. Mod. Phys. 4, 1 (1932) and G. King (D_0 = 3.4 e.v.), J. Chem. Phys. 6, 378 (1938). A. G. Gaydon, "Dissociation Energies", 2nd Ed., Champman & Hall Ltd., London, 1953, favored G. Glockler's estimation D_0 = 86.3 kcal. mole^{-1} which was based upon the comparison of force constants and D values of related hydrides (i.e. CH, OH and FH).

Heat Capacity & Entropy.

The rotational constants B_e and α_e were obtained from R. N. Dixon, Can. J. Phys. 37, 1171 (1959). The vibrational constants ω_e and $\omega_e x_e$ were calculated from Dixon's data: B_e = 16.6684 cm.$^{-1}$, D_e = 16.85 X 10^{-4} cm.$^{-1}$ and ω = 3125.6 cm.$^{-1}$ by the relation $D_e = 4\,B_e^3/\omega_e^2$ and $\omega = \omega_e - 2\,\omega_e x_e$.

D. E. Milligan and M. E. Jacox, J. Chem. Phys. 41, 2838 (1964) have observed from the spectrum of NH the vibrational fundamental ω = 3133 ± 2 cm.$^{-1}$ in Ar and N_2 matrices. K. Rosengren and G. C. Pimentel, J. Chem. Phys. 43, 507 (1965) also reported ω = 3122.2 ± 0.6 cm.$^{-1}$ in N_2 matrix and ω = 3131.6 ± 0.4 cm.$^{-1}$ in Ar matrix.

Nitroxyl Hydride (HNO)

(Ideal Gas) Mol. Wt. = 31.016

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.387	24.498	24.498	INFINITE
100	7.949	43.977	59.902	- 1.592	24.215	25.018	- 54.674
200	7.995	49.493	53.475	- .796	24.018	25.893	- 28.293
298	8.279	52.729	52.729	.000	23.800	26.859	- 19.688
300	8.287	52.781	52.730	.015	23.796	26.878	- 19.580
400	8.788	55.230	53.060	.868	23.598	27.937	- 15.263
500	9.342	57.251	53.702	1.775	23.438	29.041	- 12.693
600	9.869	59.001	54.442	2.735	23.315	30.174	- 10.990
700	10.345	60.559	55.207	3.747	23.222	31.325	- 9.779
800	10.766	61.968	55.965	4.803	23.155	32.486	- 8.874
900	11.134	63.258	56.705	5.898	23.107	33.656	- 8.172
1000	11.454	64.448	57.421	7.028	23.078	34.830	- 7.612
1100	11.731	65.553	58.110	8.187	23.061	36.006	- 7.153
1200	11.970	66.584	58.774	9.373	23.055	37.183	- 6.772
1300	12.177	67.551	59.412	10.580	23.056	38.361	- 6.449
1400	12.356	68.460	60.026	11.807	23.064	39.537	- 6.172
1500	12.511	69.318	60.618	13.051	23.074	40.714	- 5.932
1600	12.646	70.130	61.187	14.309	23.087	41.889	- 5.722
1700	12.764	70.900	61.736	15.579	23.101	43.065	- 5.536
1800	12.867	71.633	62.265	16.861	23.116	44.238	- 5.371
1900	12.958	72.331	62.777	18.152	23.130	45.412	- 5.223
2000	13.038	72.998	63.271	19.452	23.143	46.584	- 5.090
2100	13.108	73.635	63.750	20.760	23.155	47.756	- 4.970
2200	13.171	74.247	64.213	22.074	23.164	48.927	- 4.860
2300	13.227	74.834	64.662	23.394	23.172	50.097	- 4.760
2400	13.277	75.398	65.098	24.719	23.177	51.269	- 4.668
2500	13.322	75.940	65.521	26.049	23.178	52.437	- 4.584
2600	13.363	76.464	65.932	27.383	23.178	53.609	- 4.506
2700	13.399	76.969	66.331	28.721	23.174	54.780	- 4.434
2800	13.432	77.457	66.720	30.063	23.167	55.949	- 4.367
2900	13.463	77.929	67.098	31.408	23.158	57.123	- 4.305
3000	13.490	78.385	67.467	32.755	23.145	58.293	- 4.246
3100	13.515	78.828	67.826	34.106	23.130	59.464	- 4.192
3200	13.538	79.258	68.177	35.458	23.110	60.636	- 4.141
3300	13.559	79.675	68.519	36.813	23.088	61.810	- 4.093
3400	13.578	80.080	68.853	38.170	23.063	62.983	- 4.048
3500	13.596	80.473	69.180	39.529	23.034	64.157	- 4.006
3600	13.612	80.857	69.499	40.889	23.002	65.333	- 3.966
3700	13.628	81.230	69.811	42.251	22.966	66.510	- 3.928
3800	13.642	81.594	70.116	43.615	22.928	67.688	- 3.893
3900	13.655	81.948	70.415	44.980	22.887	68.866	- 3.859
4000	13.667	82.294	70.707	46.346	22.842	70.045	- 3.827
4100	13.678	82.632	70.994	47.713	22.794	71.226	- 3.796
4200	13.689	82.961	71.275	49.081	22.744	72.408	- 3.768
4300	13.699	83.283	71.551	50.451	22.691	73.592	- 3.740
4400	13.708	83.599	71.821	51.821	22.634	74.774	- 3.714
4500	13.717	83.907	72.086	53.192	22.574	75.959	- 3.689
4600	13.725	84.208	72.346	54.564	22.513	77.151	- 3.665
4700	13.732	84.503	72.602	55.937	22.448	78.338	- 3.643
4800	13.739	84.793	72.853	57.311	22.380	79.528	- 3.621
4900	13.746	85.076	73.100	58.685	22.310	80.716	- 3.600
5000	13.752	85.354	73.342	60.060	22.238	81.909	- 3.580
5100	13.758	85.626	73.580	61.435	22.162	83.104	- 3.561
5200	13.764	85.893	73.814	62.812	22.086	84.299	- 3.543
5300	13.770	86.156	74.045	64.188	22.006	85.499	- 3.525
5400	13.775	86.413	74.271	65.565	21.923	86.693	- 3.509
5500	13.779	86.666	74.494	66.943	21.839	87.898	- 3.493
5600	13.784	86.914	74.714	68.321	21.752	89.096	- 3.477
5700	13.788	87.158	74.930	69.700	21.663	90.301	- 3.462
5800	13.792	87.398	75.143	71.079	21.571	91.508	- 3.448
5900	13.796	87.634	75.353	72.458	21.478	92.712	- 3.434
6000	13.800	87.866	75.559	73.838	21.382	93.921	- 3.421

March 31, 1963

NITROXYL HYDRIDE (HNO) (IDEAL GAS) MOL. WT. = 31.016

Point Group C_s

$S^\circ_{298.15}$ = 52.729 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = 24.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 23.8 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	
2854.17	(1)
1570	(1)
1110	(1)

Bond Distance: H-N = 1.020 ± 0.02 Å N=O = 1.239 ± 0.005 Å

Bond Angle: H-N=O = 114° 25' ± 2°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = 5.939 X 10^{-118} g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ for HNO(g) was calculated from D(H-NO) = 48.6 kcal. mole^{-1} at 0°K. reported by M. J. Y. Clement and D. A. Ramsay, Can. J. Phys. 39, 205 (1961).

Heat Capacity and Entropy.

Vibrational frequencies were assigned by J. L. Bancroft, J. M. Hollas and D. A. Ramsay, Can. J. Phys. 40, 322 (1962) and H. Brown and G. Pimentel, J. Chem. Phys. 29, 883 (1958). Bond distances and bond angles were taken from J. L. Bancroft, J. M. Hollas, and D. A. Ramsay, loc. cit. The molecular constants given by F. W. Dalby, Can. J. Phys. 36, 1336 (1958) were: r(N=O) = 1.211$_6$ Å; r(N-H) = 1.0628 Å, and ∡ HNO = 108.5$_8$°. The three principal moments of inertia are: 1.262 X 10^{-40}, 2.1067 X 10^{-39}, and 2.2330 X 10^{-39} g. cm.^{2}

Nitrous Acid, Cis-(HNO_2)
(Ideal Gas) Mol. Wt. = 47.016

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.635	-16.852	-16.852	INFINITE
100	8.027	49.729	68.125	-1.840	-17.492	-15.187	33.190
200	9.238	55.595	60.527	-.986	-17.971	-12.693	13.870
298	10.840	59.586	59.586	.000	-18.340	-10.020	7.344
300	10.869	59.653	59.586	.020	-18.346	-9.968	7.261
400	12.275	62.979	60.030	1.180	-18.593	-7.135	3.898
500	13.412	65.845	60.913	2.466	-18.738	-4.252	1.858
600	14.318	68.374	61.950	3.854	-18.811	-1.347	.490
700	15.044	70.637	63.032	5.324	-18.835	1.567	-.489
800	15.637	72.686	64.113	6.859	-18.822	4.480	-1.224
900	16.131	74.557	65.171	8.448	-18.783	7.391	-1.795
1000	16.548	76.279	66.197	10.082	-18.721	10.296	-2.250
1100	16.905	77.873	67.187	11.755	-18.644	13.194	-2.621
1200	17.213	79.358	68.140	13.462	-18.553	16.085	-2.929
1300	17.480	80.746	69.057	15.197	-18.453	18.967	-3.189
1400	17.712	82.050	69.939	16.956	-18.345	21.841	-3.409
1500	17.915	83.279	70.787	18.738	-18.231	24.708	-3.600
1600	18.093	84.442	71.605	20.539	-18.115	27.567	-3.765
1700	18.250	85.543	72.393	22.356	-17.995	30.419	-3.910
1800	18.389	86.590	73.153	24.188	-17.874	33.263	-4.038
1900	18.511	87.588	73.886	26.033	-17.754	36.102	-4.152
2000	18.620	88.540	74.595	27.890	-17.634	38.932	-4.254
2100	18.717	89.451	75.281	29.757	-17.515	41.758	-4.346
2200	18.804	90.324	75.945	31.633	-17.400	44.577	-4.428
2300	18.882	91.162	76.589	33.517	-17.285	47.391	-4.503
2400	18.952	91.967	77.213	35.409	-17.174	50.203	-4.571
2500	19.015	92.742	77.819	37.308	-17.069	53.005	-4.633
2600	19.073	93.489	78.407	39.212	-16.965	55.808	-4.691
2700	19.125	94.209	78.979	41.122	-16.866	58.605	-4.743
2800	19.172	94.906	79.535	43.037	-16.771	61.397	-4.792
2900	19.215	95.579	80.077	44.956	-16.680	64.190	-4.837
3000	19.254	96.231	80.605	46.880	-16.594	66.976	-4.879
3100	19.290	96.863	81.119	48.807	-16.511	69.760	-4.918
3200	19.323	97.476	81.621	50.737	-16.433	72.541	-4.954
3300	19.353	98.071	82.110	52.671	-16.360	75.320	-4.988
3400	19.381	98.649	82.588	54.608	-16.291	78.097	-5.020
3500	19.407	99.212	83.055	56.547	-16.226	80.871	-5.050
3600	19.431	99.759	83.512	58.489	-16.165	83.646	-5.078
3700	19.453	100.291	83.958	60.433	-16.110	86.418	-5.104
3800	19.473	100.810	84.395	62.380	-16.057	89.190	-5.129
3900	19.493	101.316	84.822	64.328	-16.009	91.957	-5.153
4000	19.510	101.810	85.241	66.278	-15.966	94.723	-5.175
4100	19.527	102.292	85.651	68.230	-15.926	97.491	-5.197
4200	19.542	102.763	86.053	70.184	-15.890	100.257	-5.217
4300	19.557	103.223	86.447	72.139	-15.858	103.024	-5.236
4400	19.570	103.673	86.833	74.095	-15.830	105.785	-5.254
4500	19.583	104.113	87.212	76.053	-15.806	108.549	-5.272
4600	19.595	104.543	87.584	78.012	-15.784	111.318	-5.289
4700	19.606	104.965	87.950	79.972	-15.767	114.079	-5.304
4800	19.617	105.378	88.308	81.933	-15.752	116.842	-5.320
4900	19.627	105.782	88.661	83.895	-15.741	119.599	-5.334
5000	19.636	106.179	89.007	85.858	-15.732	122.361	-5.348
5100	19.645	106.568	89.348	87.822	-15.728	125.125	-5.362
5200	19.653	106.949	89.683	89.787	-15.725	127.885	-5.375
5300	19.661	107.324	90.012	91.753	-15.725	130.652	-5.387
5400	19.669	107.691	90.336	93.719	-15.729	133.407	-5.399
5500	19.676	108.052	90.655	95.687	-15.734	136.175	-5.411
5600	19.683	108.407	90.969	97.655	-15.743	138.932	-5.422
5700	19.689	108.755	91.278	99.623	-15.754	141.695	-5.433
5800	19.695	109.098	91.582	101.592	-15.768	144.461	-5.443
5900	19.701	109.435	91.882	103.562	-15.784	147.221	-5.453
6000	19.707	109.766	92.177	105.533	-15.803	149.985	-5.463

June 30, 1963

NITROUS ACID, CIS-(HNO_2) (IDEAL GAS) MOL. WT. = 47.016

Point Group C_s

$S^\circ_{298.15}$ = 59.586 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = -16.85 ± 0.32 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -18.34 ± 0.32 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
3462 (1)	855 (1)
1639 (1)	525 (1)
1330 (1)	638 (1)

Bond Distance: O=N = 1.20 Å N-O' = 1.46 Å O'-H = 0.98 Å

Bond Angle: O-N-O' = 114° N-O'-H = 103° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 5.50704 \times 10^{-116}$ g.^{3} cm.^{6}

Heat of Formation.

P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961) reported $\Delta H^\circ_{r\ 298.15} = -9.06 \pm 0.32$ kcal. mole^{-1} for the reaction: $NO(g) + NO_2(g) + H_2O(g) \rightleftarrows 2HNO_2(g)$, yielding $\Delta H^\circ_{f\ 298.15} = -18.57 \pm 0.20$ kcal. mole^{-1} for $HNO_2(g)$. L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys., 19, 1599 (1951) estimated the difference in energy of cis- and trans-$HNO_2(g)$ to be 506 ± 250 cal. mole^{-1}. Hence the value of $\Delta H^\circ_{f\ 298.15}$ for cis-$HNO_2(g)$ was calculated.

The heat of reaction and the equilibrium constants for the formation of $HNO_2(g)$ have been calculated by M. M. Karavaev and G. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962). The value of $\Delta H^\circ_{f\ 298.15}$ reported is -18.8 kcal. mole^{-1}. However, based on the heat of formation of liquid HNO_2, P. G. Ashmore and B. P. Levitt, Trans. Faraday Soc., 53, 945 (1957) give $\Delta H^\circ_f = -13.7$ kcal. mole^{-1}. The corresponding value reported by W. A. Rosser and H. Wise, J. Chem. Phys., 26, 571 (1957) is -20.0 kcal. mole^{-1}, based on the experimental data of L. G. Wayne and D. M. Yost, J. Chem. Phys. 19, 41 (1951), and the entropy of the equilibrium mixture of the trans- and cis-$HNO_2(g)$ calculated by L. H. Jones, R. M. Badger and G. E. Moore, loc. cit.

Heat Capacity and Entropy.

Vibrational frequencies, bond distances, and bond angles were obtained from L. D'or and P. Tarte, Bull. Soc. Roy. Sci., Lg. 478 (1951) and L. H. Jones, R. M. Badger and G. E. Moore, loc. cit. The three principal moments of inertia are: 1.0277×10^{-39}, 6.8242×10^{-39}, and 7.8520×10^{-39} g. cm.^{2}

Nitrous Acid, Trans-(HNO_2)

(Ideal Gas) Mol. Wt. = 47.016

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.651	-17.369	-17.369	INFINITE
100	8.027	49.616	68.177	-1.856	-18.008	-15.692	34.294
200	9.328	55.504	60.500	-.999	-18.484	-13.188	14.410
298	11.000	59.546	59.546	.000	-18.840	-10.508	7.702
300	11.029	59.614	59.546	.020	-18.846	-10.456	7.617
400	12.435	62.987	59.997	1.196	-19.076	-7.622	4.164
500	13.543	65.886	60.891	2.497	-19.207	-4.741	2.072
600	14.414	68.435	61.941	3.897	-19.269	-1.841	.671
700	15.110	70.712	63.034	5.374	-19.284	1.066	-.333
800	15.677	72.767	64.124	6.915	19.266	3.970	-1.085
900	16.149	74.642	65.190	8.507	-19.224	6.873	-1.669
1000	16.550	76.365	66.223	10.142	-19.161	9.770	-2.135
1100	16.895	77.959	67.218	11.815	-19.085	12.659	-2.515
1200	17.193	79.442	68.176	13.519	-18.996	15.542	-2.830
1300	17.454	80.829	69.096	15.252	-18.897	18.416	-3.096
1400	17.682	82.131	69.981	17.009	-18.792	21.282	-3.322
1500	17.882	83.357	70.832	18.788	-18.682	24.141	-3.517
1600	18.059	84.517	71.652	20.585	-18.569	26.992	-3.687
1700	18.215	85.617	72.441	22.399	-18.452	29.837	-3.836
1800	18.354	86.662	73.202	24.227	-18.335	32.673	-3.967
1900	18.477	87.658	73.937	26.069	-18.218	35.505	-4.084
2000	18.587	88.608	74.647	27.922	-18.101	38.328	-4.188
2100	18.685	89.518	75.334	29.786	-17.986	41.147	-4.282
2200	18.773	90.389	75.998	31.659	-17.874	43.960	-4.367
2300	18.852	91.225	76.642	33.540	-17.762	46.767	-4.444
2400	18.923	92.029	77.267	35.429	-17.655	49.573	-4.514
2500	18.987	92.803	77.873	37.324	-17.552	52.369	-4.578
2600	19.046	93.549	78.462	39.226	-17.451	55.166	-4.637
2700	19.099	94.268	79.034	41.133	-17.355	57.957	-4.691
2800	19.147	94.964	79.590	43.046	-17.262	60.743	-4.741
2900	19.191	95.637	80.132	44.963	-17.173	63.531	-4.788
3000	19.231	96.288	80.660	46.884	-17.090	66.311	-4.831
3100	19.268	96.919	81.174	48.809	-17.009	69.089	-4.871
3200	19.302	97.531	81.676	50.738	-16.933	71.864	-4.908
3300	19.334	98.126	82.165	52.669	-16.862	74.638	-4.943
3400	19.362	98.703	82.643	54.604	-16.794	77.410	-4.976
3500	19.389	99.265	83.110	56.542	-16.731	80.178	-5.006
3600	19.414	99.812	83.567	58.482	-16.673	82.948	-5.035
3700	19.436	100.344	84.013	60.424	-16.619	85.715	-5.063
3800	19.458	100.862	84.450	62.369	-16.568	88.481	-5.089
3900	19.477	101.368	84.877	64.316	-16.521	91.243	-5.113
4000	19.496	101.862	85.295	66.265	-16.479	94.005	-5.136
4100	19.513	102.343	85.705	68.215	-16.442	96.767	-5.158
4200	19.529	102.814	86.107	70.167	-16.407	99.528	-5.179
4300	19.544	103.273	86.501	72.121	-16.376	102.290	-5.199
4400	19.558	103.723	86.887	74.076	-16.349	105.046	-5.217
4500	19.571	104.162	87.266	76.032	-16.326	107.805	-5.235
4600	19.584	104.593	87.638	77.990	-16.305	110.569	-5.253
4700	19.595	105.014	88.004	79.949	-16.289	113.325	-5.269
4800	19.606	105.427	88.362	81.909	-16.276	116.084	-5.285
4900	19.617	105.831	88.715	83.870	-16.265	118.835	-5.300
5000	19.626	106.227	89.061	85.832	-16.258	121.592	-5.315
5100	19.636	106.616	89.401	87.795	-16.255	124.352	-5.329
5200	19.644	106.998	89.736	89.759	-16.253	127.106	-5.342
5300	19.652	107.372	90.065	91.724	-16.254	129.868	-5.355
5400	19.660	107.739	90.389	93.690	-16.258	132.619	-5.367
5500	19.668	108.100	90.708	95.656	-16.264	135.382	-5.379
5600	19.675	108.454	91.022	97.623	-16.275	138.134	-5.391
5700	19.681	108.803	91.331	99.591	-16.286	140.893	-5.402
5800	19.688	109.145	91.635	101.560	-16.301	143.654	-5.413
5900	19.694	109.482	91.934	103.529	-16.318	146.409	-5.423
6000	19.700	109.813	92.230	105.499	-16.337	149.168	-5.433

June 30, 1963

NITROUS ACID, TRANS-(HNO_2) (IDEAL GAS) MOL. WT. = 47.016

Point Group C_s

$S^\circ_{298.15}$ = 59.546 cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [1]

$\Delta H^\circ_{f\ 0}$ = -17.37 ± 0.32 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -18.84 ± 0.32 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
3590 (1)	794 (1)
1696 (1)	598 (1)
1260 (1)	543 (1)

Bond Distance: O=N = 1.20 Å N-O' = 1.46 Å O'-H = 0.98 Å

Bond Angle: O-N-O' = 118° N-O'-H = 105° σ = 1

Product of the Moments of Inertia: $I_AI_BI_C = 4.91847 \times 10^{-116}$ g.^{3} cm.^{6}

Heat of Formation.

P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961) reported $\Delta H^\circ_{r\ 298.15} = -9.06 \pm 0.32$ kcal. mole^{-1} for the reaction: $NO(g) + NO_2(g) + H_2O(g) \rightleftarrows 2HNO_2(g)$, yielding $\Delta H^\circ_{f\ 298.15} = -18.57 \pm 0.20$ kcal. mole^{-1} for $HNO_2(g)$. L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys., 19, 1599 (1951) estimated the difference in energy of cis- and trans- $HNO_2(g)$ to be 506 ± 250 cal. mole^{-1}. Hence the value of $\Delta H^\circ_{f\ 298.15}$ for trans-$HNO_2(g)$ was calculated.

The heat of reaction and the equilibrium constants for the formation of $HNO_2(g)$ have been calculated by M. M. Karavaev and G. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962). The value of $\Delta H^\circ_{f\ 298.15}$ reported is -18.8 kcal. mole^{-1}. However, based on the heat of formation of liquid HNO_2, P. G. Ashmore and B. P. Levitt, Trans. Faraday Soc., 53, 945 (1957) give $\Delta H^\circ_f = -13.7$ kcal. mole^{-1}. The corresponding value reported by W. A. Rosser and H. Wise, J. Chem. Phys., 26, 571 (1957) is -20.0 kcal. mole^{-1}, based on the experimental data of L. G. Wayne and D. M. Yost, J. Chem. Phys. 19, 41 (1951), and the entropy of the equilibrium mixture of the trans- and cis-$HNO_2(g)$ calculated by L. H. Jones, R. M. Badger and G. E. Moore, loc. cit.

Heat Capacity and Entropy.

Vibrational frequencies, bond distances, and bond angles were taken from L. H. Jones, R. M. Badger, and G. E. Moore, loc. cit. The values of vibrational frequencies were in good agreement to those reported by L. D'or and P. Tarte, Bull. Soc. Roy. Sci., Lg. 478 (1951). The three principal moments of inertia are: 7.860×10^{-40}, 7.5268×10^{-39}, and 8.3129×10^{-39} g. cm.^{2}

Nitric Acid (HNO_3)

(Ideal Gas) Mol. Wt. = 63.016

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.815	- 29.755	- 29.755	INFINITE
100	8.107	53.003	73.187	- 2.018	- 30.749	- 26.696	58.342
200	10.110	59.129	64.745	- 1.123	- 31.527	- 22.332	24.403
298	12.748	63.663	63.663	.000	- 32.100	- 17.690	12.966
300	12.795	63.742	63.663	.024	- 32.109	- 17.601	12.821
400	15.103	67.750	64.194	1.423	- 32.472	- 12.704	6.941
500	16.930	71.325	65.269	3.028	- 32.664	- 7.737	3.382
600	18.348	74.543	66.551	4.795	- 32.736	- 2.743	.999
700	19.451	77.458	67.904	6.687	- 32.725	2.256	- .704
800	20.325	80.114	69.267	8.678	- 32.656	7.248	- 1.980
900	21.031	82.550	70.610	10.747	- 32.544	12.230	- 2.970
1000	21.613	84.797	71.917	12.880	- 32.397	17.198	- 3.758
1100	22.098	86.880	73.184	15.066	- 32.227	22.149	- 4.400
1200	22.508	88.821	74.407	17.297	- 32.035	27.084	- 4.932
1300	22.858	90.637	75.587	19.566	- 31.829	32.002	- 5.380
1400	23.159	92.342	76.723	21.867	- 31.612	36.904	- 5.761
1500	23.419	93.949	77.819	24.196	- 31.386	41.791	- 6.089
1600	23.646	95.468	78.875	26.550	- 31.155	46.661	- 6.373
1700	23.843	96.908	79.893	28.924	- 30.919	51.519	- 6.623
1800	24.017	98.276	80.877	31.317	- 30.682	56.360	- 6.843
1900	24.170	99.578	81.827	33.727	- 30.444	61.191	- 7.038
2000	24.306	100.822	82.746	36.151	- 30.207	66.006	- 7.212
2100	24.426	102.010	83.635	38.588	- 29.971	70.811	- 7.369
2200	24.534	103.149	84.497	41.036	- 29.740	75.604	- 7.510
2300	24.630	104.242	85.332	43.494	- 29.510	80.387	- 7.638
2400	24.716	105.292	86.142	45.961	- 29.284	85.163	- 7.755
2500	24.793	106.303	86.928	48.437	- 29.066	89.923	- 7.861
2600	24.863	107.276	87.692	50.920	- 28.849	94.681	- 7.958
2700	24.927	108.216	88.435	53.409	- 28.640	99.428	- 8.048
2800	24.984	109.124	89.158	55.905	- 28.436	104.167	- 8.130
2900	25.037	110.001	89.861	58.406	- 28.236	108.902	- 8.207
3000	25.085	110.851	90.547	60.912	- 28.044	113.627	- 8.277
3100	25.129	111.674	91.215	63.423	- 27.856	118.346	- 8.343
3200	25.169	112.473	91.867	65.938	- 27.675	123.057	- 8.404
3300	25.206	113.248	92.503	68.457	- 27.500	127.765	- 8.461
3400	25.240	114.001	93.124	70.979	- 27.331	132.467	- 8.515
3500	25.271	114.733	93.731	73.504	- 27.167	137.163	- 8.564
3600	25.300	115.445	94.325	76.033	- 27.009	141.858	- 8.612
3700	25.327	116.139	94.905	78.564	- 26.857	146.547	- 8.656
3800	25.352	116.814	95.473	81.098	- 26.709	151.234	- 8.698
3900	25.375	117.473	96.028	83.635	- 26.567	155.912	- 8.737
4000	25.397	118.116	96.573	86.173	- 26.431	160.587	- 8.774
4100	25.417	118.743	97.106	88.714	- 26.301	165.263	- 8.809
4200	25.435	119.356	97.628	91.257	- 26.174	169.933	- 8.842
4300	25.453	119.955	98.140	93.801	- 26.052	174.605	- 8.874
4400	25.469	120.540	98.643	96.347	- 25.936	179.265	- 8.904
4500	25.485	121.113	99.136	98.895	- 25.824	183.927	- 8.932
4600	25.499	121.673	99.620	101.444	- 25.716	188.595	- 8.960
4700	25.513	122.221	100.095	103.995	- 25.613	193.250	- 8.986
4800	25.526	122.759	100.561	106.547	- 25.513	197.907	- 9.011
4900	25.538	123.285	101.020	109.100	- 25.417	202.553	- 9.034
5000	25.549	123.801	101.470	111.654	- 25.325	207.204	- 9.056
5100	25.560	124.307	101.913	114.209	- 25.238	211.858	- 9.078
5200	25.570	124.804	102.349	116.766	- 25.152	216.502	- 9.099
5300	25.580	125.291	102.777	119.323	- 25.070	221.156	- 9.119
5400	25.589	125.769	103.198	121.882	- 24.992	225.792	- 9.138
5500	25.597	126.239	103.613	124.441	- 24.916	230.443	- 9.157
5600	25.605	126.700	104.021	127.001	- 24.845	235.080	- 9.174
5700	25.613	127.153	104.423	129.562	- 24.776	239.721	- 9.191
5800	25.621	127.599	104.819	132.124	- 24.710	244.366	- 9.208
5900	25.628	128.037	105.209	134.686	- 24.646	249.001	- 9.223
6000	25.634	128.467	105.593	137.249	- 24.586	253.641	- 9.238

June 30, 1963

NITRIC ACID (HNO_3) (IDEAL GAS) MOL. WT. = 63.016

Point Group C_s

$\Delta H_{f\,0}^\circ = -29.76 \pm 0.10$ kcal. mole^{-1}

$S^\circ_{298.15} = 63.663$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\,298.15}^\circ = -32.10 \pm 0.10$ kcal. mole^{-1}

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
1320 (1)	765 (1)
886 (1)	3560 (1)
680 (1)	1335 (1)
1710 (1)	465 (1)
583 (1)	

Bond Distance: O=N = 1.206 ± 0.005 Å N-O' = 1.405 ± 0.005 Å O'-H = [0.96] Å

Bond Angle: O-N-O = 130° ± 20' N-O'-H = 102° ± 30' $\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 6.08612 \times 10^{-115}$ g.^{3} cm.^{6}

Heat of Formation.

$\Delta H_{f\,298.15}^\circ$ was taken from National Bureau of Standards Report 7437, January 1, 1962. Equilibria involving HNO_3 were measured by E. J. Jones, J. Am. Chem. Soc. 65, 2274 (1943), G. Feick, J. Am. Chem. Soc. 76, 5858 (1954) and H. E. Abel, H. Schmid and M. Stein-Wien, Z. Elektrochem. 36, 692 (1930), yielding $\Delta H_f^\circ = -32.06, -32.02$, and -32.09 kcal. mole^{-1}, respectively. G. Becker and W. A. Roth, Z. Elektrochem. 40, 836 (1934) and J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886, measured the heat of neutralization of HNO_3(aq.) with NH_3, combining these values with the data for NH_4NO_3 yields $\Delta H_f^\circ = -32.27$ and -32.07 kcal. M. Berthelot, "Sur la Force des Matieres Explosives," 3rd. ed., Paris, 1883, measured the heat of reaction of N_2O_4(g) and Cl_2(g), obtaining $\Delta H_f^\circ = -32.10$ kcal. mole^{-1}. The value of $\Delta H_{f\,298.15}^\circ$ reported by W. R. Forsythe and W. F. Giauque, J. Am. Chem. Soc. 64, 48 (1942) was -31.994 kcal. mole^{-1}. The value adopted is the weighed average of these six values.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and bond angles were taken from D. J. Millen and J. R. Morton, J. Chem. Soc., 1523 (1960). The basic parameters of HNO_3(g) reported by P. A. Akishin, L. V. Vilkov and V. Y. Rosolovskii, Zhur. Strukt. Khim. 1, 1 (1960) were: r(N=O) = 1.22 ± 0.01 Å; r(N-O) = 1.40 ± 0.01 Å; and ∡ O-N-O = 135° ± 2.5°. Forsythe and Giauque, loc. cit. have calculated the absolute entropy of pure nitric acid (g) from calorimetric data. The value obtained was $S^\circ_{298.1} = 63.62$ cal. deg.$^{-1}$ mole^{-1}. The entropy of nitric acid vapor at 298.1°K. has also been computed by H. Cohn, C. K. Ingold, and H. G. Poole, J. Chem. Soc. 4272 (1952) to be 63.70 cal. deg.$^{-1}$ mole^{-1}. The three principal moments of inertia are: 6.4299×10^{-39}, 7.0314×10^{-39}, and 1.3461×10^{-38} g. cm.^{2}

Sodium Hydride (NaH)

(Crystal) Mol. Wt. = 23.999

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH°_f (kcal. mole^{-1})	ΔF°_f (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-1.496	-12.433	-12.433	INFINITE
100	4.182	2.763	15.913	-1.315	-12.952	-11.439	25.000
200	6.748	6.483	10.303	-.764	-13.289	-9.789	10.696
298	8.698	9.564	9.564	.000	-13.490	-8.023	5.880
300	8.732	9.618	9.564	.016	-13.492	-7.988	5.819
400	10.150	12.343	9.926	.967	-14.233	-6.086	3.325
500	11.270	14.734	10.653	2.040	-14.250	-4.045	1.768
600	12.120	16.868	11.514	3.212	-14.149	-2.011	.733
700	12.840	18.792	12.419	4.461	-13.957	-.003	.001
800	13.400	20.545	13.327	5.775	-13.691	1.973	-.539
900	13.850	22.150	14.219	7.138	-13.374	3.913	-.950
1000	14.200	23.628	15.087	8.541	-13.020	5.815	-1.271
1100	14.500	24.996	15.927	9.977	-12.643	7.679	-1.526
1200	14.740	26.269	16.736	11.439	-35.488	9.967	-1.815
1300	14.920	27.456	17.515	12.923	-34.873	13.730	-2.308
1400	15.063	28.567	18.266	14.422	-34.248	17.445	-2.723
1500	15.160	29.610	18.987	15.934	-33.616	21.116	-3.076

March 31, 1963

SODIUM HYDRIDE (NaH) (CRYSTAL) MOL. WT. = 23.999

$\Delta H^\circ_{f\ 0} = -12.43 \pm 0.02$ kcal. mole^{-1}

$S^\circ_{298.15} = 9.564$ cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15} = -13.49 \pm 0.02$ kcal. mole^{-1}

$T_d = [700]$°K.

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was obtained from S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). The value of $\Delta H^\circ_{f\ 298.15}$ reported by C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955) was -13.60 ± 0.27 kcal. mole^{-1} which is in excellent agreement with the value given by S. R. Gunn and L. G. Green, loc. cit. The results of the previous investigations were also reviewed by C. E. Messer, et al., loc. cit.

Heat Capacity and Entropy.

C_p below 350°K were measured by E. F. Westrum, et al., University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. C_p above 350°K were estimated by comparison with those for LiH(c). C_p, 59.94 ~ 91.84°K., were also measured by E. V. Sayre and J. J. Beaver, J. Chem. Phys. 18, 584 (1950). S° at 100°, 200°, and 298.15° were taken from E. F. Westrum, et al., loc. cit., using S°_{10}(extrap.) = 0.008 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Decomposition.

T_d was estimated from the value of ΔF°_f in the table. The value of T_d given by D. M. Banus, J. J. McSharry and E. A. Sullivan, J. Am. Chem. Soc. 77, 2007 (1955) was 940°K. It was assumed that NaH would behave similarly to LiH and that decomposition pressures would be purity dependent, and this would produce apparently high T_d's.

Sodium Hydride (NaH)

(Ideal Gas) Mol. Wt. = 23.999

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.086	30.166	30.166	INFINITE
100	6.9[illegible]	37.330	51.286	-1.396	30.158	28.213	-61.657
200	7.011	42.165	45.654	-.698	29.967	26.331	-28.772
298	7.241	45.000	45.000	.000	29.700	24.602	-18.033
300	7.246	45.045	45.001	.013	29.695	24.571	-17.899
400	7.589	47.176	45.289	.755	28.745	22.959	-12.544
500	7.911	48.905	45.844	1.530	28.430	21.550	-9.419
600	8.172	50.372	46.480	2.335	28.164	20.199	-7.357
700	8.377	51.647	47.129	3.163	27.935	18.890	-5.897
800	8.537	52.777	47.766	4.009	27.733	17.612	-4.811
900	8.664	53.790	48.380	4.869	27.547	16.359	-3.972
1000	8.767	54.708	48.967	5.741	27.370	15.125	-3.305
1100	8.853	55.548	49.528	6.622	27.192	13.907	-2.763
1200	8.926	56.321	50.062	7.511	3.774	13.165	-2.398
1300	8.989	57.038	50.572	8.407	3.801	13.947	-2.345
1400	9.044	57.707	51.058	9.309	3.829	14.726	-2.299
1500	9.094	58.332	51.522	10.215	3.855	15.504	-2.259
1600	9.139	58.921	51.966	11.127	3.881	16.279	-2.224
1700	9.181	59.476	52.392	12.043	3.908	17.055	-2.192
1800	9.220	60.002	52.800	12.963	3.932	17.827	-2.164
1900	9.257	60.501	53.192	13.887	3.956	18.599	-2.139
2000	9.292	60.977	53.570	14.815	3.978	19.368	-2.118
2100	9.325	61.431	53.933	15.746	4.000	20.136	-2.095
2200	9.357	61.866	54.284	16.680	4.020	20.904	-2.077
2300	9.388	62.282	54.623	17.617	4.040	21.671	-2.059
2400	9.418	62.683	54.951	18.557	4.058	22.439	-2.043
2500	9.447	63.068	55.268	19.500	4.074	23.201	-2.028
2600	9.475	63.439	55.575	20.446	4.089	23.968	-2.015
2700	9.503	63.797	55.873	21.395	4.103	24.731	-2.002
2800	9.531	64.143	56.162	22.347	4.114	25.494	-1.990
2900	9.558	64.478	56.443	23.301	4.124	26.261	-1.979
3000	9.584	64.802	56.716	24.259	4.132	27.022	-1.968
3100	9.610	65.117	56.982	25.218	4.137	27.784	-1.959
3200	9.636	65.423	57.241	26.181	4.140	28.547	-1.950
3300	9.662	65.719	57.494	27.146	4.138	29.310	-1.941
3400	9.688	66.008	57.740	28.113	4.134	30.072	-1.933
3500	9.713	66.290	57.980	29.083	4.125	30.838	-1.926
3600	9.738	66.563	58.215	30.056	4.111	31.600	-1.918
3700	9.763	66.831	58.444	31.031	4.091	32.362	-1.911
3800	9.788	67.091	58.668	32.008	4.067	33.130	-1.905
3900	9.813	67.346	58.887	32.988	4.034	33.893	-1.899
4000	9.837	67.595	59.102	33.971	3.994	34.660	-1.894
4100	9.862	67.838	59.312	34.956	3.946	35.429	-1.888
4200	9.886	68.076	59.518	35.943	3.888	36.195	-1.883
4300	9.910	68.309	59.720	36.933	3.820	36.966	-1.879
4400	9.935	68.537	59.917	37.925	3.740	37.735	-1.874
4500	9.959	68.760	60.111	38.920	3.647	38.511	-1.870
4600	9.983	68.979	60.302	39.917	3.539	39.286	-1.866
4700	10.007	69.194	60.489	40.916	3.416	40.065	-1.863
4800	10.031	69.405	60.672	41.918	3.274	40.845	-1.860
4900	10.055	69.612	60.853	42.923	3.113	41.632	-1.857
5000	10.078	69.816	61.030	43.929	2.930	42.419	-1.854
5100	10.102	70.016	61.204	44.938	2.724	43.212	-1.852
5200	10.126	70.212	61.376	45.950	2.492	44.006	-1.849
5300	10.150	70.405	61.544	46.963	2.232	44.809	-1.848
5400	10.173	70.595	61.710	47.980	1.941	45.613	-1.846
5500	10.197	70.782	61.873	48.998	1.617	46.423	-1.845
5600	10.221	70.966	62.034	50.019	1.258	47.241	-1.844
5700	10.244	71.147	62.192	51.042	.863	48.067	-1.843
5800	10.268	71.325	62.348	52.068	.426	48.898	-1.842
5900	10.291	71.501	62.502	53.096	-.052	49.740	-1.842
6000	10.315	71.674	62.653	54.126	-.574	50.587	-1.843

Dec. 31, 1960; Mar. 31, 1963

SODIUM HYDRIDE (NaH) (IDEAL GAS) MOL. WT. = 23.999

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 45.0 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 30.2 ± 4.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 29.7 ± 4.6 kcal. mole^{-1}

ω_e = 1172.2 cm.$^{-1}$

B_e = 4.9012 cm.$^{-1}$

$\omega_e x_e$ = 19.72 cm.$^{-1}$

α_e = 0.1353 cm.$^{-1}$

σ = 1

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was calculated from D_0° = 2.05 ± 0.2 e.v. reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., 1953.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., 1950.

Sodium Hydroxide (NaOH)

(Crystal) Mol. Wt. = 39.99717

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.506	- 100.815	- 100.815	INFINITE
100	6.631	3.713	26.257	- 2.254	- 101.620	- 98.127	214.456
200	11.850	10.176	16.635	- 1.292	- 101.886	- 94.501	103.266
298	14.228	15.400	15.400	.000	- 101.900	- 90.867	66.607
300	14.260	15.488	15.400	.026	- 101.899	- 90.798	66.147
400	15.520	19.772	15.976	1.518	- 102.453	- 87.060	47.567
500	17.963	23.461	17.109	3.176	- 102.252	- 83.230	36.380
600	20.560	29.710	18.618	6.655	- 100.221	- 79.559	28.979
700	20.560	32.879	20.435	8.711	- 99.611	- 76.164	23.780
800	20.560	35.624	22.166	10.767	- 99.002	- 72.856	19.903
900	20.560	38.046	23.798	12.823	- 98.399	- 69.624	16.907
1000	20.560	40.212	25.333	14.879	- 97.805	- 66.458	14.524
1100	20.560	42.172	26.776	16.935	- 97.228	- 63.354	12.587
1200	20.560	43.961	28.135	18.991	- 119.903	- 59.842	10.899
1300	20.560	45.606	29.416	21.047	- 119.144	- 54.867	9.224
1400	20.560	47.130	30.628	23.103	- 118.394	- 49.951	7.798
1500	20.560	48.549	31.776	25.159	- 117.654	- 45.088	6.569
1600	20.560	49.875	32.866	27.215	- 116.922	- 40.274	5.501
1700	20.560	51.122	33.904	29.271	- 116.197	- 35.505	4.564
1800	20.560	52.297	34.893	31.327	- 115.481	- 30.779	3.737
1900	20.560	53.409	35.839	33.383	- 114.772	- 26.093	3.001
2000	20.560	54.463	36.744	35.439	- 114.072	- 21.444	2.343

Dec. 31, 1960; Mar. 31, 1966

SODIUM HYDROXIDE (NaOH) (CRYSTAL) MOL. WT. = 39.99717

$S^\circ_{298.15}$ = 15.400 cal. deg.$^{-1}$ mole^{-1}

T_t = 565.95°K.

T_m = 592.25°K.

$\Delta H^\circ_{f\ 0}$ = -100.82 ± 0.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -101.90 ± 0.1 kcal. mole^{-1}

ΔH°_t = 1.519 kcal. mole^{-1}

ΔH°_m = 1.519 kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to monomer) = [51.5] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$(to dimer) = [49.0] kcal. mole^{-1}

Heat of Formation.

The standard enthalpy of formation, $\Delta H^\circ_{f\ 298}$ (NaOH, c) = -101.90 ± 0.1 kcal. mole^{-1}, was calculated from the heat of solution of sodium hydroxide (c) and the heat of sodium metal hydrolysis and the appropriate auxiliary data.

N. A. Peshetnikov[1] has measured the heat of solution NaOH(c) → NaOH(400 H_2O) as -10.445 ± 0.015 kcal. mole^{-1} at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker[2], the selected heat of solution of sodium hydroxide (c) at infinite dilution is -10.555 kcal. mole^{-1}. Also L. E. Murch and W. F. Giauque[11] measured calorimetrically the heat of solution of solid samples of NaOH-nH_2O in the range from n = 0.1 to 1.0. When extrapolated to n = 0 and infinite dilution[2], this result yields the heat of solution of NaOH(c) at infinite dilution, $\Delta H^\circ_{s\ 298}$ = -10.636 kcal. mole^{-1}, which is in good agreement with the value selected.

The heat of sodium metal hydrolysis, $\Delta H^\circ_{r\ 298}$, has been measured in the solution calorimeter by the following investigators. $Na(c) + H_2O(l) \rightarrow NaOH(nH_2O) + 1/2\ H_2(g)$ $\Delta H^\circ_{r\ 298}$

Source	Number of Moles of H_2O	$\Delta H^\circ_{r\ 298}$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}(NaOH(\infty H_2O))$ kcal. mole^{-1}	$\Delta H^\circ_{f\ 298}$(NaOH, c) kcal. mole^{-1}
Gunn et al.[3]	1000	-44.047 ± 0.006	-112.446	-101.899
Messer et al.[4]	∞	-44.215 ± 0.20	-112.530	-101.975
Ketchen et al.[5]	∞	-44.054 ± 0.20	-112.369	-101.814

The values of $\Delta H^\circ_{f\ 298}(NaOH\cdot\infty H_2O)$ were calculated from the heats of reaction $\Delta H^\circ_{r\ 298}$, using the $\Delta H^\circ_{f\ 298}$ (H_2O, l) = -68.315 kcal. mole^{-1}.[6] Combination of the selected heat of solution of NaOH(c) at infinite dilution with the heat of formation of NaOH(∞H_2O) gives the heat of formation of NaOH(c) in the last column of the table. A weighted average of these three measurements has been taken for the selected heat of formation of sodium hydroxide (c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini[9], and C. E. Messer et al.[4], and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

L. E. Murch and W. F. Giauque[11] have measured low temperature heat capacities of NaOH·0.04014 H_2O and NaOH·0.97776 H_2O from 15° to 320°K. and calculated the values of C_p for the pure phase of NaOH(c). T. B. Douglas and J. L. Dever[9] have measured the enthalpy changes from 273° to 973°K. in the drop calorimeter and derived the heat capacities. The low temperature and the high temperature heat capacities were joined smoothly by Murch and Giauque, and the smooth values were adopted in the tabulation. Low temperature heat capacities from 60° to 300°K. have also been measured by J. C. R. Kelly and P. E. Snyder[7], whose data are in good agreement with those reported by Murch and Giauque. M. M. Popov and D. M. Ginzburg[10] have determined the heat capacities of NaOH(c) in the temperature range from 298° to 577°K. from the enthalpy measurements by drop calorimetry. The reported H_{500}-H_{298} = 3.112 kcal. mole^{-1} is in good agreement with the tabulated value.

Transition and Melting Data.

The adopted heat of transition and the transition temperature, and the adopted heat of melting and the melting point were obtained from Douglas and Dever.[8] Popov and Ginzburg[10] reported the heat of transition ΔH°_{tr} = 1.930 kcal. mole^{-1} at 576.8°K. and the heat of melting ΔH°_m = 1.629 kcal. mole^{-1} at 595.16°K.

Heat of Sublimation.

See NaOH(g) table for details.

Reference:

1 N. A. Peshetnikov, Zhur. Neorg. Khim. 6, 682 (1961).
2 V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, April, 1965.
3 S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters", UCRL-7992, Oct. 1964.
4 C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc. 77, 4524 (1955).
5 E. E. Ketchen and W. E. Wallace, J. Am. Chem. Soc. 76, 4736 (1954).
6 D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R.H. Schumm, NBS Tech. Note 270-1, Oct. 1965.
7 J. C. R. Kelly and P. E. Snyder, J. Am. Chem. Soc. 73, 4114 (1951), ibid, 73, 5933 (1951)
8 T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 53, 81 (1954).
9 F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances", Reinhold Publishing Corp., New York, 1936.
10 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956). G. M. Ginzburg, ibid. 26, 968 (1956).
11 L. E. Murch and W. F. Giauque, J. Phys. Chem. 66, 2052 (1962).

Sodium Hydroxide (NaOH)

(Liquid) Mol. Wt. = 39.99717

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	20.990	17.727	17.727	.000	-99.998	-89.659	65.722
300	20.988	17.857	17.727	.039	-99.984	-89.595	65.270
400	20.844	23.875	18.549	2.130	-99.939	-86.187	47.090
500	20.710	28.511	20.095	4.208	-99.317	-82.820	36.201
600	20.570	32.275	21.821	6.272	-98.702	-79.579	28.987
700	20.430	35.435	23.547	8.322	-98.098	-76.441	23.866
800	20.290	38.154	25.207	10.358	-97.509	-73.387	20.049
900	20.150	40.536	26.780	12.380	-96.940	-70.406	17.097
1000	20.010	42.651	28.264	14.388	-96.395	-67.487	14.749
1100	19.870	44.552	29.659	16.382	-95.879	-64.623	12.839
1200	19.730	46.275	30.973	18.362	-118.630	-61.346	11.173
1300	19.590	47.849	32.212	20.328	-117.962	-56.600	9.515
1400	19.450	49.295	33.381	22.280	-117.316	-51.903	8.102
1500	19.310	50.632	34.487	24.218	-116.693	-47.252	6.885
1600	19.170	51.874	35.536	26.142	-116.094	-42.643	5.825
1700	19.030	53.032	36.531	28.052	-115.514	-38.069	4.894
1800	18.910	54.116	37.478	29.949	-114.957	-33.530	4.071
1900	18.795	55.136	38.381	31.834	-114.419	-29.021	3.338
2000	18.690	56.097	39.243	33.708	-113.901	-24.541	2.682
2100	18.595	57.007	40.067	35.572	-113.398	-20.087	2.090
2200	18.515	57.870	40.857	37.428	-112.913	-15.654	1.555
2300	18.447	58.691	41.615	39.276	-112.440	-11.244	1.068
2400	18.393	59.475	42.343	41.118	-111.982	-6.851	.624
2500	18.346	60.225	43.043	42.955	-111.535	-2.484	.217
2600	18.310	60.944	43.718	44.787	-111.100	1.872	-.157
2700	18.287	61.634	44.369	46.617	-110.674	6.209	-.503
2800	18.265	62.299	44.997	48.445	-110.259	10.527	-.822
2900	18.250	62.940	45.605	50.270	-109.851	14.837	-1.118
3000	18.238	63.558	46.193	52.095	-109.453	19.130	-1.394

Dec. 31, 1960; Mar. 31, 1966

SODIUM HYDROXIDE (NaOH) (LIQUID) MOL. WT. = 39.99717

$S^\circ_{298.15}$ = 17.727 cal. deg.$^{-1}$ mole^{-1}

T_m = 592.25°K.

T_b(monomeric gas) = 1662.7°K.

ΔH°_f 298.15 = -99.998 kcal. mole^{-1}

ΔH°_m = 1.519 kcal. mole^{-1}

ΔH°_v(to monomer) = 37.9 kcal. mole^{-1}

Heat of Formation.

The heat of formation of NaOH(l) at 298°K. was obtained from that of the crystal by adding ΔH°_m and the difference between $H^\circ_{592.25} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacities in the temperature range from 592.3° to 1000°K. were obtained from the enthalpy measurements of sodium hydroxide (l) in the drop calorimeter by T. B. Douglas and J. L. Dever[1]. The heat capacities below the melting point and above 1000°K. were extrapolated from the selected heat capacity curve.

Douglas and Dever[1] have also compared their heat capacity values with those from W. D. Powers and G. C. Blalock[2] who have applied the same drop method to determine the heat capacities of NaOH(l). Both results are in reasonable agreement. M. M. Popov and G. M. Ginzburg[3] applying the same technique obtained different values of heat capacity. The smoothed enthalpy data reported by Ginzburg[4] are 200 to 500 cal. mole^{-1} smaller than the tabulated values at the temperature range from 700° to 1000°K.

The entropy (S°_{298} = 17.65 cal. deg.$^{-1}$ mole^{-1}) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See NaOH(c) table for details.

Vaporization Data.

The boiling point 1662.7°K. was calculated as the temperature at which the free energies of formation (ΔF°_f) for both NaOH(l) and NaOH(g) are equal. The difference in the heats of formation (ΔH°_f) of NaOH(l) and NaOH(g) at the boiling point is the heat of vaporization. If $Na_2(OH)_2(g)$ is also considered as a minor component in the vapor mixture (approximately 6% of total vapor pressure at the boiling point) the calculated boiling point is 1653°K. (see NaOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), have studied the vapor pressures of liquid NaOH and reported the boiling point as 1661°K.

Reference:

1 T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 53, 81 (1954).
2 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures", ORNL-1653, Oak Ridge Nat'l. Lab. Jan. 1954.
3 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956).
4 G. M. Ginzburg, ibid. 26, 968 (1956).

Sodium Hydroxide (NaOH)

(Ideal Gas) Mol. Wt. = 39.99717

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	-2.550	-49.359	-49.359	INFINITE
100	8.095	46.936	64.459	-1.752	-49.618	-50.447	110.252
200	8.889	52.790	57.306	-.903	-49.997	-51.135	55.878
298	9.486	56.456	56.456	.000	-50.400	-51.608	37.830
300	9.496	56.515	56.456	.018	-50.407	-51.615	37.602
400	9.986	59.316	56.835	.992	-51.479	-51.904	28.359
500	10.391	61.589	57.565	2.012	-51.916	-51.958	22.711
600	10.722	63.514	58.400	3.068	-52.308	-51.929	18.915
700	10.996	65.188	59.253	4.154	-52.668	-51.837	16.184
800	11.235	66.672	60.089	5.266	-53.003	-51.696	14.123
900	11.449	68.008	60.896	6.400	-53.322	-51.513	12.509
1000	11.646	69.224	61.669	7.555	-53.629	-51.294	11.210
1100	11.827	70.343	62.407	8.729	-53.934	-51.048	10.142
1200	11.995	71.379	63.112	9.920	-77.474	-50.314	9.163
1300	12.149	72.345	63.786	11.128	-77.564	-48.047	8.077
1400	12.290	73.251	64.430	12.350	-77.648	-45.774	7.146
1500	12.418	74.103	65.047	13.585	-77.728	-43.493	6.337
1600	12.535	74.909	65.638	14.833	-77.805	-41.210	5.629
1700	12.642	75.672	66.206	16.092	-77.876	-38.919	5.003
1800	12.738	76.397	66.752	17.361	-77.947	-36.625	4.447
1900	12.825	77.088	67.278	18.639	-78.016	-34.327	3.948
2000	12.904	77.748	67.785	19.926	-78.085	-32.027	3.500
2100	12.976	78.380	68.275	21.220	-78.153	-29.725	3.093
2200	13.041	78.985	68.748	22.521	-78.222	-27.416	2.724
2300	13.100	79.566	69.206	23.828	-78.290	-25.106	2.386
2400	13.154	80.124	69.649	25.140	-78.361	-22.788	2.075
2500	13.203	80.662	70.079	26.458	-78.434	-20.475	1.790
2600	13.247	81.181	70.496	27.781	-78.508	-18.153	1.526
2700	13.288	81.682	70.901	29.108	-78.586	-15.833	1.282
2800	13.325	82.166	71.295	30.438	-78.667	-13.508	1.054
2900	13.360	82.634	71.678	31.773	-78.751	-11.175	.842
3000	13.391	83.087	72.051	33.110	-78.840	-8.844	.644
3100	13.420	83.527	72.414	34.451	-78.932	-6.511	.459
3200	13.447	83.953	72.768	35.794	-79.029	-4.172	.285
3300	13.472	84.368	73.113	37.140	-79.133	-1.834	.121
3400	13.494	84.770	73.450	38.488	-79.242	.510	-.033
3500	13.516	85.162	73.779	39.839	-79.358	2.859	-.179
3600	13.535	85.543	74.101	41.191	-79.481	5.209	-.316
3700	13.554	85.914	74.415	42.546	-79.612	7.562	-.447
3800	13.571	86.275	74.722	43.902	-79.750	9.926	-.571
3900	13.586	86.628	75.023	45.260	-79.899	12.283	-.688
4000	13.601	86.972	75.317	46.619	-80.058	14.650	-.800
4100	13.615	87.308	75.606	47.980	-80.227	17.023	-.907
4200	13.628	87.637	75.888	49.342	-80.409	19.391	-1.009
4300	13.640	87.957	76.165	50.706	-80.603	21.775	-1.107
4400	13.651	88.271	76.437	52.070	-80.813	24.154	-1.200
4500	13.662	88.578	76.703	53.436	-81.038	26.544	-1.289
4600	13.672	88.878	76.965	54.803	-81.279	28.939	-1.375
4700	13.682	89.173	77.221	56.170	-81.539	31.334	-1.457
4800	13.691	89.461	77.473	57.539	-81.820	33.738	-1.536
4900	13.699	89.743	77.721	58.908	-82.122	36.152	-1.612
5000	13.707	90.020	77.964	60.279	-82.449	38.566	-1.686
5100	13.715	90.291	78.203	61.650	-82.802	40.996	-1.757
5200	13.722	90.558	78.438	63.022	-83.182	43.420	-1.825
5300	13.728	90.819	78.669	64.394	-83.593	45.865	-1.891
5400	13.735	91.076	78.897	65.767	-84.037	48.306	-1.955
5500	13.741	91.328	79.120	67.141	-84.516	50.762	-2.017
5600	13.747	91.576	79.341	68.515	-85.034	53.222	-2.077
5700	13.752	91.819	79.557	69.890	-85.590	55.699	-2.136
5800	13.757	92.058	79.771	71.266	-86.189	58.185	-2.192
5900	13.762	92.293	79.981	72.642	-86.832	60.683	-2.248
6000	13.767	92.525	80.188	74.018	-87.521	63.184	-2.301

Dec. 31, 1960; Mar. 31, 1966

SODIUM HYDROXIDE (NaOH) (IDEAL GAS) MOL. WT. = 39.99717

Point Group C_s

$S^\circ_{298.15}$ = [56.5] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -49.4 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -50.4 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
437 (1)
[1300](1)
[3700](1)

Bond Distance: Na-O = [1.97] Å O-H = [0.96] Å

Bond Angle: Na-O-H = [110°]

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.3062] X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 28, 454 (1958), have found in their mass-spectrometric studies that the NaOH(l) vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. They have also calculated by the slope method the heat of dimerization, $\Delta H^\circ_{d\ 660}$ = -54 ± 5 kcal. mole^{-1}, for 2NaOH(g) = $Na_2(OH)_2$(g) and the heat of sublimation, $\Delta H^\circ_{s\ 298}$ = 46.3 ± 3 kcal. mole^{-1}, for NaOH(c) = NaOH(g). **The second law values were determined using ion intensity ratios, however, a third law calculation using a single data point converted by the authors to absolute pressure (J. Phys. Chem. 62, 486 (1958)) yields $\Delta H^\circ_{d\ 298}$ = -51.8 kcal. mole^{-1},** $\Delta H^\circ_{s\ 298}$(to monomer) = 49.5 kcal. mole^{-1} and $\Delta H^\circ_{s\ 298}$ (to dimer) = 41.1 kcal. mole^{-1} which are in agreement within the limit of uncertainty. Later, Porter and Schoonmaker, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container, and the uncertainty in the heat of sublimation might be ±5 kcal. mole^{-1}, but the heat of dimerization should not be seriously affected because it was calculated from slopes of both species. In order to have good agreement between the calculated total pressures of monomer and dimer of sodium hydroxide (g) and the observed vapor pressures by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), the heat of dimerization and the heat of sublimation have been so chosen as $\Delta H^\circ_{d\ 298}$ = -54 kcal. mole^{-1} and $\Delta H^\circ_{s\ 298}$ (to monomer) = 51.5 kcal. mole^{-1}, respectively, which are still within the limit of Porter and Schoonmaker's data. The calculated boiling point is 1653°K. which is in good agreement with 1661 ± 20°K. reported by Wartenberg and Albrecht, loc. cit. The heats of formation were calculated from the selected heat of dimerization and heat of sublimation as $\Delta H^\circ_{f\ 298}$ (NaOH, g) = -50.4 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298}$($Na_2(OH)_2$, g) = -154.8 kcal. mole^{-1}.

Heat Capacity and Entropy.

The bent molecular configuration with the bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. 29, 991 (1958). The bond distance O-H was estimated from that in H_2O(g). The bond distance Na-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Na-F(g) (1.92595 Å) which has been accurately measured by R. K. Bauer and H. Lew, Can. J. Phys. 41, 1461 (1963). The Na-O stretching frequency was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta 12, 244 (1958), in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by compairson with H-OH, D-OH and T-OH which indicate rigid convergence to a constant as a heavier atom is attached. The three principal moments of inertia are I_A = [0.1252] X 10^{-39}, I_B = [6.449] X 10^{-39} and I_C = [6.5742] X 10^{-39} g. cm.^{2}

Hydroxyl (OH)

(Ideal Gas) Mol. Wt. = 17.0074

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.192	9.289	9.289	INFINITE
100	7.798	35.726	50.398	-1.467	9.278	9.001	-19.672
200	7.356	40.985	44.541	-.711	9.393	8.671	-9.475
298	7.167	43.880	43.880	.000	9.432	8.307	-6.089
300	7.165	43.925	43.881	.013	9.432	8.299	-6.046
400	7.087	45.974	44.160	.725	9.442	7.920	-4.327
500	7.055	47.551	44.687	1.432	9.434	7.540	-3.296
600	7.057	48.837	45.275	2.137	9.411	7.163	-2.609
700	7.090	49.927	45.863	2.845	9.379	6.791	-2.120
800	7.150	50.877	46.432	3.556	9.338	6.424	-1.755
900	7.233	51.724	46.974	4.275	9.294	6.062	-1.472
1000	7.332	52.491	47.488	5.003	9.250	5.706	-1.247
1100	7.439	53.195	47.975	5.742	9.206	5.353	-1.064
1200	7.549	53.847	48.437	6.491	9.164	5.005	-.912
1300	7.659	54.455	48.877	7.252	9.124	4.661	-.784
1400	7.766	55.027	49.296	8.023	9.086	4.318	-.674
1500	7.867	55.566	49.696	8.805	9.050	3.980	-.580
1600	7.963	56.077	50.079	9.596	9.014	3.642	-.497
1700	8.053	56.563	50.447	10.397	8.980	3.307	-.425
1800	8.137	57.025	50.799	11.207	8.947	2.975	-.361
1900	8.214	57.467	51.139	12.024	8.914	2.645	-.304
2000	8.286	57.891	51.466	12.849	8.881	2.313	-.253
2100	8.353	58.296	51.782	13.681	8.849	1.988	-.207
2200	8.415	58.686	52.087	14.520	8.815	1.662	-.165
2300	8.472	59.062	52.382	15.364	8.782	1.336	-.127
2400	8.526	59.424	52.668	16.214	8.748	1.014	-.092
2500	8.576	59.773	52.945	17.069	8.711	.690	-.060
2600	8.622	60.110	53.214	17.929	8.675	.372	-.031
2700	8.665	60.436	53.476	18.794	8.637	.054	-.004
2800	8.706	60.752	53.730	19.662	8.598	-.264	.021
2900	8.744	61.058	53.977	20.535	8.557	-.578	.044
3000	8.780	61.355	54.218	21.411	8.515	-.893	.065
3100	8.814	61.644	54.453	22.291	8.472	-1.208	.085
3200	8.846	61.924	54.682	23.174	8.427	-1.519	.104
3300	8.876	62.197	54.906	24.060	8.381	-1.829	.121
3400	8.905	62.462	55.124	24.949	8.333	-2.137	.137
3500	8.933	62.721	55.338	25.841	8.283	-2.446	.153
3600	8.959	62.973	55.546	26.735	8.232	-2.751	.167
3700	8.984	63.218	55.750	27.632	8.179	-3.052	.180
3800	9.008	63.458	55.950	28.532	8.125	-3.355	.193
3900	9.031	63.693	56.145	29.434	8.069	-3.660	.205
4000	9.053	63.922	56.337	30.338	8.011	-3.961	.216
4100	9.074	64.145	56.525	31.245	7.952	-4.256	.227
4200	9.095	64.364	56.709	32.153	7.892	-4.553	.237
4300	9.115	64.579	56.889	33.064	7.830	-4.851	.247
4400	9.134	64.788	57.066	33.976	7.766	-5.144	.255
4500	9.153	64.994	57.240	34.890	7.701	-5.439	.264
4600	9.171	65.195	57.411	35.807	7.635	-5.726	.272
4700	9.189	65.393	57.579	36.725	7.567	-6.018	.280
4800	9.206	65.586	57.744	37.644	7.499	-6.304	.287
4900	9.223	65.776	57.906	38.566	7.429	-6.592	.294
5000	9.239	65.963	58.065	39.489	7.358	-6.882	.301
5100	9.255	66.146	58.222	40.414	7.286	-7.162	.307
5200	9.271	66.326	58.376	41.340	7.213	-7.448	.313
5300	9.286	66.502	58.527	42.268	7.140	-7.722	.318
5400	9.301	66.676	58.677	43.197	7.065	-8.007	.324
5500	9.316	66.847	58.824	44.128	6.989	-8.284	.329
5600	9.330	67.015	58.968	45.060	6.912	-8.563	.334
5700	9.344	67.180	59.111	45.994	6.835	-8.837	.339
5800	9.358	67.343	59.252	46.929	6.757	-9.112	.343
5900	9.372	67.503	59.390	47.866	6.678	-9.385	.348
6000	9.386	67.661	59.527	48.803	6.598	-9.659	.352

Dec. 31, 1960; Mar. 31, 1966

HYDROXYL (OH) (IDEAL GAS) MOL. WT. = 17.0074

Ground State Configuration $^2\pi$

$S^\circ_{298.15}$ = 43.880 cal. deg.⁻¹ mole⁻¹

$\Delta H^\circ_{f\ 0}$ = 9.290 ± 0.3 kcal. mole⁻¹

$\Delta H^\circ_{f\ 298.15}$ = 9.432 ± 0.3 kcal. mole⁻¹

Electronic Levels and Multiplicities

ϵ_1, cm.⁻¹	g_1
0	2
139.7	2

ω_e = 3735.21 cm.⁻¹

B_e = 18.871 cm.⁻¹

$\omega_e x_e$ = 82.81 cm.⁻¹

α_e = 0.714 cm.⁻¹

$\sigma = 1$

r_e = 0.9706 Å

Heat of Formation.

P. Gray, Trans. Farad. Soc. 55, 408 (1959) has summarized the determinations of the heat of formation of OH and concludes that the short extrapolation by Barrow, Arkiv. Fysik, 11, 281 (1956) of the $B(^2\Sigma^+) \rightarrow A(^2\Sigma^+)$ system gives the most reliable result. The value of D_0 = 101.33 kcal. mole⁻¹ was adopted and leads to a heat of formation of 9.432 kcal. mole⁻¹. A recent determination of the dissociation energy from measurements of the concentration of the radicals in water oxygen mixtures by A. P. Purmal and A. V. Frost, Vestn. Mosk. Univ., Ser. II Khim. 16, 25 (1961) gives $\Delta E_D(OH)$ = 102.8 ± 0.8 kcal. mole⁻¹ in good agreement with the adopted value. Also V. A. Medvedev, V. V. Korobov and V. F. Baibuz, Zhur. Fiz. Khim. 33, 58 (1959) reported a heat of dissociation of 102.2 ± 1 kcal. mole⁻¹ from dissociation of water in a spherical bomb.

Heat Capacity and Entropy.

The molecular constants were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. This calculation gives values in excellent agreement with L. Haar, A. S. Friedman and C. W. Beckett, National Bureau of Standards Monograph No. 20, May 1961. The agreement with the higher order correction calculations of H. L. Johnston, J. Belzer and L. Savedoff, TR 316-5, Ohio State University, available as ATI 139 967, is good between 298 and 4000°K. This earlier work uses different constants and also a different value of the ground state splitting constant, but at 6000°K. the entropy difference is still less than 0.25%.

Hydroxyl Unipositive Ion (OH^+)

(Ideal Gas) Mol. Wt. = 17.0068

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	6.969	43.657	43.657	.000	314.800	312.254	- 228.888
300	6.969	43.700	43.657	.013	314.809	312.238	- 227.465
400	6.982	45.707	43.931	.710	315.301	311.306	- 170.090
500	7.020	47.268	44.448	1.410	315.783	310.252	- 135.611
600	7.095	48.554	45.028	2.115	316.257	309.101	- 112.590
700	7.204	49.655	45.612	2.830	316.728	307.871	- 96.122
800	7.337	50.626	46.179	3.557	317.200	306.573	- 83.752
900	7.480	51.498	46.723	4.298	317.675	305.217	- 74.117
1000	7.625	52.294	47.241	5.053	318.155	303.807	- 66.397
1100	7.765	53.027	47.734	5.823	318.639	302.349	- 60.071
1200	7.897	53.709	48.204	6.606	319.128	300.847	- 54.792
1300	8.019	54.345	48.652	7.402	319.619	299.304	- 50.317
1400	8.131	54.944	49.080	8.209	320.115	297.722	- 46.476
1500	8.233	55.508	49.490	9.028	320.612	296.106	- 43.143
1600	8.326	56.043	49.883	9.856	321.109	294.454	- 40.221
1700	8.410	56.550	50.260	10.692	321.608	292.775	- 37.639
1800	8.487	57.033	50.623	11.537	322.106	291.063	- 35.340
1900	8.557	57.494	50.973	12.390	322.605	289.326	- 33.280
2000	8.621	57.934	51.310	13.249	323.104	287.562	- 31.423
2100	8.680	58.356	51.636	14.114	323.601	285.772	- 29.741
2200	8.734	58.761	51.950	14.984	324.097	283.959	- 28.209
2300	8.785	59.151	52.255	15.860	324.591	282.121	- 26.808
2400	8.831	59.526	52.550	16.741	325.085	280.266	- 25.522
2500	8.875	59.887	52.837	17.626	325.575	278.387	- 24.337
2600	8.915	60.236	53.114	18.516	326.066	276.491	- 23.241
2700	8.954	60.573	53.384	19.409	326.554	274.576	- 22.225
2800	8.990	60.899	53.647	20.307	327.040	272.642	- 21.281
2900	9.024	61.216	53.903	21.207	327.524	270.690	- 20.400
3000	9.056	61.522	54.152	22.111	328.006	268.720	- 19.576
3100	9.087	61.819	54.394	23.019	328.488	266.738	- 18.805
3200	9.116	62.108	54.631	23.929	328.967	264.740	- 18.081
3300	9.144	62.389	54.862	24.842	329.445	262.725	- 17.400
3400	9.171	62.663	55.087	25.758	329.920	260.694	- 16.757
3500	9.197	62.929	55.307	26.676	330.394	258.652	- 16.151
3600	9.223	63.188	55.523	27.597	330.866	256.598	- 15.578
3700	9.247	63.441	55.733	28.521	331.336	254.526	- 15.034
3800	9.270	63.688	55.939	29.446	331.805	252.446	- 14.519
3900	9.293	63.929	56.141	30.375	332.273	250.351	- 14.029
4000	9.315	64.165	56.339	31.305	332.737	248.241	- 13.563
4100	9.337	64.395	56.532	32.238	333.201	246.123	- 13.120
4200	9.358	64.621	56.722	33.172	333.664	243.994	- 12.696
4300	9.379	64.841	56.909	34.109	334.125	241.856	- 12.292
4400	9.399	65.057	57.091	35.048	334.585	239.703	- 11.906
4500	9.419	65.268	57.271	35.989	335.042	237.541	- 11.537
4600	9.438	65.476	57.447	36.932	335.500	235.370	- 11.183
4700	9.457	65.679	57.620	37.877	335.956	233.188	- 10.843
4800	9.476	65.878	57.790	38.823	336.412	230.997	- 10.518
4900	9.494	66.074	57.957	39.772	336.866	228.794	- 10.205
5000	9.513	66.266	58.121	40.722	337.319	226.584	- 9.904
5100	9.530	66.454	58.283	41.674	337.771	224.367	- 9.615
5200	9.548	66.639	58.442	42.628	338.223	222.140	- 9.336
5300	9.566	66.821	58.598	43.584	338.674	219.906	- 9.068
5400	9.583	67.000	58.752	44.541	339.124	217.656	- 8.809
5500	9.600	67.176	58.904	45.500	339.574	215.406	- 8.559
5600	9.617	67.350	59.053	46.461	340.021	213.134	- 8.318
5700	9.634	67.520	59.200	47.424	340.470	210.872	- 8.085
5800	9.650	67.688	59.345	48.388	340.918	208.591	- 7.860
5900	9.667	67.853	59.488	49.354	341.365	206.305	- 7.642
6000	9.683	68.015	59.628	50.321	341.812	204.019	- 7.431

Mar. 31, 1966

HYDROXYL UNIPOSITIVE ION (OH^+) (IDEAL GAS) MOL. WT. = 17.0068

Ground State Configuration $^3\Sigma^-$

$S^\circ_{298.15}$ = 43.657 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 313.3 ± 2.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 314.8 ± 2.5 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1
0	3

ω_e = [2955] cm.$^{-1}$

$\omega_e x_e$ = [74]

σ = 1

B_e = 16.793 cm.$^{-1}$

α_e = 0.732 cm.$^{-1}$

r_e = 1.0289 Å

Heat of Formation.

The ionization potential of hydroxyl has been determined by M. M. Mann, A. Hustrulid and J. T. Tate, Phys. Rev. 58, 340 (1940) from electron impact data on water vapor, as 13.6 e.v. S. N. Foner and R. L. Hudson, J. Chem. Phys. 25, 602 (1956) have measured the appearance potential of OH^+ from OH as 13.18 ± 0.1 e.v. (303.96 kcal.). This value was the one adopted to obtain the heat of formation of $OH^+(g)$ from that of OH(g) at 0°K.

Heat Capacity and Entropy.

The molecular constants, with the exception of $\omega_e x_e$, were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. The value of $\omega_e x_e$ was estimated by analogy with OH(g) and other diatomic hydrides.

The value of H_T-H_{298} at 0°K. is -2.06 kcal. mole^{-1}.

Hydroxyl Uninegative Ion (OH^-)

(Ideal Gas) Mol. Wt. = 17.0079

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H_{298}^\circ$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0							
100							
200							
298	6.965	41.229	41.229	.000	-34.400	-33.248	24.371
300	6.965	41.272	41.229	.013	-34.409	-33.240	24.216
400	6.969	43.276	41.502	.710	-34.912	-32.776	17.908
500	6.978	44.832	42.018	1.407	-35.427	-32.182	14.067
600	7.002	46.106	42.596	2.106	-35.952	-31.484	11.468
700	7.047	47.188	43.177	2.808	-36.486	-30.696	9.584
800	7.116	48.133	43.739	3.516	-37.027	-29.833	8.150
900	7.204	48.977	44.275	4.232	-37.571	-28.902	7.018
1000	7.306	49.741	44.784	4.957	-38.115	-27.908	6.099
1100	7.415	50.442	45.267	5.693	-38.659	-26.862	5.337
1200	7.527	51.092	45.725	6.440	-39.200	-25.766	4.693
1300	7.638	51.699	46.162	7.199	-39.738	-24.623	4.140
1400	7.746	52.269	46.578	7.968	-40.275	-23.441	3.659
1500	7.848	52.807	46.975	8.748	-40.810	-22.219	3.237
1600	7.944	53.317	47.356	9.537	-41.345	-20.964	2.864
1700	8.034	53.801	47.721	10.336	-41.878	-19.672	2.529
1800	8.118	54.263	48.072	11.144	-42.409	-18.351	2.228
1900	8.196	54.704	48.409	11.960	-42.941	-17.001	1.956
2000	8.267	55.126	48.734	12.783	-43.472	-15.622	1.707
2100	8.334	55.531	49.049	13.613	-44.004	-14.215	1.479
2200	8.396	55.920	49.352	14.449	-44.536	-12.785	1.270
2300	8.453	56.294	49.646	15.292	-45.067	-11.327	1.076
2400	8.506	56.655	49.930	16.140	-45.601	-9.849	.897
2500	8.556	57.004	50.206	16.993	-46.136	-8.352	.730
2600	8.602	57.340	50.474	17.851	-46.671	-6.827	.574
2700	8.645	57.666	50.735	18.713	-47.208	-5.288	.428
2800	8.685	57.981	50.988	19.580	-47.747	-3.725	.291
2900	8.723	58.286	51.234	20.450	-48.285	-2.141	.161
3000	8.758	58.582	51.474	21.324	-48.827	-.539	.039
3100	8.792	58.870	51.708	22.202	-49.369	1.079	-.076
3200	8.823	59.150	51.936	23.082	-49.913	2.711	-.185
3300	8.853	59.422	52.159	23.966	-50.459	4.364	-.289
3400	8.881	59.686	52.377	24.853	-51.005	6.035	-.388
3500	8.908	59.944	52.589	25.742	-51.554	7.720	-.482
3600	8.934	60.196	52.797	26.635	-52.104	9.420	-.572
3700	8.958	60.441	53.000	27.529	-52.657	11.140	-.658
3800	8.982	60.680	53.199	28.426	-53.211	12.871	-.740
3900	9.004	60.913	53.394	29.326	-53.766	14.618	-.819
4000	9.026	61.142	53.585	30.227	-54.323	16.377	-.895
4100	9.047	61.365	53.772	31.131	-54.882	18.154	-.968
4200	9.067	61.583	53.955	32.036	-55.442	19.939	-1.038
4300	9.086	61.797	54.135	32.944	-56.004	21.740	-1.105
4400	9.105	62.006	54.312	33.854	-56.567	23.552	-1.170
4500	9.123	62.211	54.485	34.765	-57.132	25.380	-1.233
4600	9.141	62.411	54.655	35.678	-57.697	27.226	-1.294
4700	9.158	62.608	54.822	36.593	-58.265	29.077	-1.352
4800	9.174	62.801	54.987	37.510	-58.834	30.943	-1.409
4900	9.190	62.990	55.148	38.428	-59.404	32.817	-1.464
5000	9.206	63.176	55.307	39.348	-59.974	34.701	-1.517
5100	9.222	63.359	55.463	40.269	-60.546	36.603	-1.569
5200	9.237	63.538	55.616	41.192	-61.120	38.510	-1.619
5300	9.251	63.714	55.767	42.116	-61.694	40.437	-1.667
5400	9.266	63.887	55.916	43.042	-62.269	42.367	-1.715
5500	9.280	64.057	56.063	43.970	-62.845	44.312	-1.761
5600	9.294	64.224	56.207	44.898	-63.422	46.268	-1.806
5700	9.307	64.389	56.349	45.828	-64.000	48.225	-1.849
5800	9.321	64.551	56.489	46.760	-64.579	50.203	-1.892
5900	9.334	64.711	56.627	47.692	-65.159	52.184	-1.933
6000	9.347	64.868	56.763	48.626	-65.739	54.174	-1.973

Mar. 31, 1966

HYDROXYL UNINEGATIVE ION (OH^-) (IDEAL GAS) MOL. WT. = 17.0079

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 41.229 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = -32.9 ± 1.0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -34.4 ± 1.0 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1
0	1

ω_e = 3735 ± 560 cm.$^{-1}$

B_e = 18.87 cm.$^{-1}$

$\omega_e x_e$ = [74.7] cm.$^{-1}$

α_e = [0.65] cm.$^{-1}$

σ = 1

r_e = 1.834 Å

Heat of Formation.

L. M. Branscomb, Joint Institute for Laboratory Astrophysics Report No. 62, Feb. 1st, 1966 has deduced an electron affinity of OH of 1.83 ± 0.04 e.v. (42.2 ± 0.9 kcal.) from the photodetachment spectrum of $OH^-(g)$. The vibrational state was deduced to be the ground state since no other absorption sequences could be detected by a thorough search. F. M. Page, Faraday Soc. Discussions 19, 87 (1955) has reviewed the methods and results of earlier determinations of the electron affinity of OH(g) and concludes that it is 65 ± 1 kcal. However he does state that it is not generally known whether the flame systems chiefly investigated are in thermodynamic equilibrium. In a later paper F. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957) conclude that much higher concentrations of radicals are obtained in flames than predicted thermodynamically. However for certain systems at lower temperatures they estimate only a factor of 3 increase in concentration and thus calculate the electron affinity as 61 kcal. mole^{-1}. The value reported by Branscomb, loc. cit. is adopted here.

Heat Capacity and Entropy.

Branscomb loc. cit. has used his photodetachment spectra to obtain values of ω_e, B_e and r_e for $OH^-(g)$ which are remarkably similar to those for OH(g). The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other hydrides. The ground state configuration was assumed to be that of HF(g) with which it is isoelectronic.

The value of H_T-H_{298} at 0°K. is -2.057 kcal. mole^{-1}.

Hydroperoxyl (HO_2)

(Ideal Gas) Mol. Wt. = 33.008

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.390	5.697	5.697	INFINITE
100	7.949	45.618	61.574	-1.596	5.399	6.209	-13.568
200	8.003	51.135	55.132	-.799	5.214	7.085	-7.742
298	8.338	54.383	54.383	.000	5.000	8.049	-5.900
300	8.347	54.434	54.383	.015	4.996	8.067	-5.877
400	8.907	56.910	54.717	.877	4.800	9.122	-4.984
500	9.479	58.960	55.366	1.797	4.639	10.222	-4.468
600	9.980	60.734	56.116	2.771	4.508	11.351	-4.134
700	10.405	62.305	56.890	3.791	4.399	12.501	-3.903
800	10.769	63.719	57.657	4.850	4.307	13.663	-3.732
900	11.087	65.006	58.403	5.943	4.230	14.838	-3.603
1000	11.365	66.189	59.123	7.066	4.167	16.021	-3.501
1100	11.612	67.284	59.816	8.215	4.114	17.209	-3.419
1200	11.831	68.304	60.481	9.387	4.071	18.401	-3.351
1300	12.025	69.258	61.120	10.580	4.035	19.597	-3.294
1400	12.197	70.156	61.734	11.791	4.005	20.795	-3.246
1500	12.350	71.003	62.323	13.019	3.979	21.996	-3.205
1600	12.485	71.804	62.891	14.261	3.955	23.197	-3.168
1700	12.606	72.565	63.438	15.515	3.934	24.401	-3.137
1800	12.714	73.288	63.965	16.782	3.913	25.605	-3.109
1900	12.810	73.979	64.474	18.058	3.891	26.812	-3.084
2000	12.895	74.638	64.966	19.343	3.869	28.017	-3.061
2100	12.972	75.269	65.442	20.637	3.845	29.226	-3.041
2200	13.041	75.874	65.902	21.937	3.818	30.435	-3.023
2300	13.104	76.455	66.349	23.245	3.790	31.645	-3.007
2400	13.160	77.014	66.781	24.558	3.757	32.859	-2.992
2500	13.210	77.552	67.202	25.876	3.720	34.069	-2.978
2600	13.256	78.071	67.610	27.200	3.682	35.286	-2.966
2700	13.298	78.572	68.007	28.528	3.638	36.502	-2.954
2800	13.336	79.057	68.393	29.859	3.590	37.719	-2.944
2900	13.371	79.525	68.768	31.195	3.539	38.941	-2.935
3000	13.403	79.979	69.135	32.534	3.483	40.162	-2.926
3100	13.432	80.419	69.492	33.875	3.423	41.386	-2.918
3200	13.459	80.846	69.840	35.220	3.359	42.610	-2.910
3300	13.484	81.261	70.180	36.567	3.291	43.838	-2.903
3400	13.507	81.663	70.511	37.917	3.218	45.067	-2.897
3500	13.528	82.055	70.836	39.268	3.141	46.299	-2.891
3600	13.547	82.437	71.153	40.622	3.060	47.534	-2.886
3700	13.565	82.808	71.463	41.978	2.974	48.771	-2.881
3800	13.582	83.170	71.766	43.335	2.886	50.011	-2.876
3900	13.598	83.523	72.063	44.694	2.793	51.250	-2.872
4000	13.612	83.867	72.354	46.055	2.695	52.493	-2.868
4100	13.626	84.204	72.639	47.417	2.594	53.741	-2.864
4200	13.638	84.532	72.918	48.780	2.490	54.989	-2.861
4300	13.650	84.853	73.192	50.144	2.382	56.242	-2.858
4400	13.662	85.167	73.460	51.510	2.270	57.493	-2.856
4500	13.672	85.474	73.724	52.876	2.154	58.749	-2.853
4600	13.682	85.775	73.983	54.244	2.037	60.013	-2.851
4700	13.691	86.069	74.237	55.613	1.914	61.274	-2.849
4800	13.700	86.358	74.486	56.982	1.790	62.538	-2.847
4900	13.708	86.640	74.731	58.353	1.663	63.802	-2.846
5000	13.716	86.917	74.972	59.724	1.533	65.069	-2.844
5100	13.723	87.189	75.209	61.096	1.399	66.346	-2.843
5200	13.730	87.455	75.442	62.468	1.264	67.616	-2.842
5300	13.736	87.717	75.671	63.842	1.126	68.900	-2.841
5400	13.743	87.974	75.897	65.216	.985	70.174	-2.840
5500	13.748	88.226	76.119	66.590	.843	71.460	-2.839
5600	13.754	88.474	76.337	67.965	.697	72.742	-2.839
5700	13.759	88.717	76.552	69.341	.550	74.029	-2.838
5800	13.764	88.957	76.764	70.717	.400	75.323	-2.838
5900	13.769	89.192	76.973	72.094	.248	76.615	-2.838
6000	13.774	89.423	77.178	73.471	.094	77.911	-2.838

Mar. 31, 1964

HYDROPEROXYL (HO_2) (IDEAL GAS) MOL. WT. = 33.008

Point Group C_1

$S^\circ_{298.15}$ = 54.383 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = 6 ± 2 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 5 ± 2 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	g_i
1389.4	(1)
1101	(1)
3414	(1)

Bond length: H-O = [0.958] Å O-O = [1.30] Å

Bond angle: HOO = [120°]

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = [0.6424] X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

S. N. Foner and R. L. Hudson, J. Chem. Phys. 36, 2681 (1962) have determined the ionization potential of HO_2 and the appearance potential of HO_2^+ from H_2O_2. Using the ΔH_f° of $H_2O_2(g)$ determined by P. A. Giguere and I. D. Liu, J. Am. Chem. Soc. 77, 6477 (1955), they calculate $\Delta H^\circ_{f\ 0}$ HO_2 = 5.7 ± 2 kcal. mole^{-1}.

Heat Capacity and Entropy.

The point group must be C_1 as the two oxygen atoms have been shown to be non-equivalent, from the increased number of infra-red bands obtained when using O_2^{16} enriched with 28% of O_2^{18}, by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 38, 2027 (1963). They also reported the three frequencies given above in the infra-red spectrum of the matrix isolated HO_2 radical. The bond lengths were taken equal to those estimated by M. E. Boyd, J. Chem. Phys. 37, 1317 (1962), the angle was that recommended by Milligan and Jacox, loc. cit. Boyd's conclusion that the lowest energy configuration should be an isosceles triangle could not be accepted in view of the nonequivalence of the oxygen atoms. The electronic ground state was taken as 2A" as predicted by A. D. Walsh, J. Chem. Soc. London, 2288 (1953).

Phosphorus Monohydride (PH)

(Ideal Gas)   GFW = 31.98177

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.067	60.407	60.407	INFINITE
100	6.959	39.295	53.092	- 1.380	60.624	58.063	- 126.897
200	6.962	44.120	47.538	- .684	60.700	55.452	- 60.595
298	6.970	46.900	46.900	.000	60.600	52.894	- 38.772
300	6.970	46.944	46.901	.013	60.597	52.946	- 38.498
400	7.008	48.953	47.174	.711	60.416	50.289	- 27.476
500	7.100	50.525	47.693	1.416	60.200	47.781	- 20.885
600	7.242	51.832	48.277	2.133	59.966	45.318	- 16.507
700	7.411	52.961	48.867	2.866	59.715	42.896	- 13.393
800	7.586	53.962	49.442	3.616	39.029	35.201	- 9.616
900	7.756	54.865	49.996	4.383	39.004	34.725	- 8.432
1000	7.914	55.691	50.524	5.166	38.989	34.249	- 7.485
1100	8.057	56.452	51.029	5.965	38.984	33.776	- 6.711
1200	8.188	57.159	51.511	6.777	38.986	33.301	- 6.065
1300	8.308	57.819	51.971	7.602	38.995	32.828	- 5.519
1400	8.417	58.439	52.411	8.439	39.010	32.353	- 5.051
1500	8.519	59.023	52.832	9.285	39.027	31.878	- 4.645
1600	8.615	59.576	3.237	10.142	39.048	31.399	- 4.289
1700	8.706	60.101	53.625	11.008	39.073	30.922	- 3.975
1800	8.792	60.601	53.999	11.883	39.101	30.441	- 3.696
1900	8.874	61.078	54.359	12.767	39.133	29.961	- 3.446
2000	8.954	61.536	54.707	13.658	39.166	29.474	- 3.221
2100	9.030	61.974	55.042	14.557	39.204	28.991	- 3.017
2200	9.104	62.396	55.367	15.464	39.243	28.504	- 2.832
2300	9.175	62.802	55.682	16.378	39.287	28.015	- 2.662
2400	9.243	63.194	55.986	17.299	39.332	27.523	- 2.506
2500	9.308	63.573	56.282	18.226	39.381	27.030	- 2.363
2600	9.372	63.939	56.570	19.160	39.432	26.535	- 2.230
2700	9.432	64.294	56.849	20.101	39.486	26.037	- 2.108
2800	9.491	64.638	57.121	21.047	39.543	25.539	- 1.993
2900	9.547	64.972	57.386	21.999	39.603	25.039	- 1.887
3000	9.600	65.297	57.645	22.956	39.664	24.533	- 1.787
3100	9.651	65.612	57.897	23.919	39.729	24.030	- 1.694
3200	9.701	65.920	58.143	24.886	39.794	23.519	- 1.606
3300	9.748	66.219	58.383	25.859	39.863	23.012	- 1.524
3400	9.793	66.510	58.618	26.836	39.933	22.501	- 1.446
3500	9.836	66.795	58.847	27.817	40.005	21.987	- 1.373
3600	9.877	67.073	59.072	28.803	40.078	21.468	- 1.303
3700	9.917	67.344	59.292	29.793	40.152	20.951	- 1.238
3800	9.955	67.609	59.507	30.786	40.229	20.433	- 1.175
3900	9.992	67.868	59.718	31.784	40.305	19.912	- 1.116
4000	10.027	68.121	59.925	32.785	40.383	19.387	- 1.059
4100	10.062	68.369	60.128	33.789	40.462	18.862	- 1.005
4200	10.095	68.612	60.327	34.797	40.542	18.336	- .954
4300	10.127	68.850	60.523	35.808	40.622	17.802	- .905
4400	10.158	69.083	60.715	36.822	40.704	17.274	- .858
4500	10.188	69.312	60.903	37.839	40.785	16.737	- .813
4600	10.217	69.536	61.088	38.860	40.869	16.202	- .770
4700	10.246	69.756	61.270	39.883	40.952	15.666	- .728
4800	10.274	69.972	61.449	40.909	41.036	15.128	- .689
4900	10.302	70.184	61.626	41.938	41.121	14.590	- .651
5000	10.329	70.393	61.799	42.969	41.206	14.044	- .614
5100	10.356	70.597	61.969	44.004	41.291	13.504	- .579
5200	10.383	70.799	62.137	45.040	41.378	12.952	- .544
5300	10.409	70.997	62.303	46.080	41.465	12.407	- .512
5400	10.435	71.192	62.465	47.122	41.552	11.854	- .480
5500	10.461	71.383	62.626	48.167	41.640	11.310	- .449
5600	10.487	71.572	62.784	49.214	41.728	10.754	- .420
5700	10.513	71.758	62.940	50.264	41.817	10.202	- .391
5800	10.538	71.941	63.093	51.317	41.906	9.644	- .363
5900	10.564	72.121	63.245	52.372	41.997	9.090	- .337
6000	10.589	72.299	63.394	53.430	42.088	8.530	- .311

Dec. 31, 1960; Sept. 30, 1962; June 30, 1967

PHOSPHORUS MONOHYDRIDE (PH)   (IDEAL GAS)   GFW = 31.98177

Ground State Configuration $^3\Sigma^-$ ΔHf°_0 = 60.4 ± 8 kcal/mol

$S^\circ_{298.15}$ = 46.9 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 60.6 ± 8 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	3	29560	6
[7650]	2	[38110]	2
[15150]	1	[57490]	1

ω_e = 2380 cm^{-1} $\omega_e x_e$ = [55] cm^{-1} σ = 1

B_e = 8.412 cm^{-1} α_e = [0.28] cm^{-1} r_e = 1.43 Å

Heat of Formation

Jordan (1) estimated the dissociation energy (D_0) of PH(g) as 70.44 kcal/mol using a semiempirical theoretical method. The corresponding value for the heat of formation ($\Delta Hf^\circ_{298.15}$) is 60.6 ± 8 kcal/mol.

Heat Capacity and Entropy

Jordan (1) predicted five electronic levels ($X^3\Sigma$, $A^1\Delta$, $B^1\Sigma$, $D^1\Pi$, $E^1\Sigma$) based on the reported value (2) of 29560 cm^{-1} for the $C^3\Pi$ level (this level is designated $A^3\Pi$ by Herzberg (2)). Several qualitative spectroscopic investigations of PH(g) have been reported and are in general accord with the predictions of Jordan (1). Ishaq and Pearse (3) reported the values of the rotational constant B_e and the fundamental vibrational frequency ω_e. The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The value of the anharmonic vibrational term $\omega_e x_e$ is estimated from the relation $\omega_e x_e = \omega_e^2/(4D_0 + 2\omega_e)$.

References

1. P. C. Jordan, J. Chem. Phys. 41, 1442 (1964).
2. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
3. M. Ishaq and R. W. B. Pearse, Proc. Roy. Soc. (London) A173, 265 (1939), and R. W. B. Pearse, ibid., A129, 328 (1930).

Lead Monohydride (PbH)

(Ideal Gas) Mol. Wt. = 208.22

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.074	57.032	57.032	INFINITE
100	6.960	45.117	58.949	-1.383	56.920	54.508	-119.122
200	6.970	49.944	53.378	-.687	56.712	52.170	-57.006
298	7.045	52.737	52.737	.000	56.450	49.995	-36.646
300	7.048	52.780	52.737	.013	56.445	49.955	-36.391
400	7.244	54.833	53.015	.727	56.159	47.835	-26.135
500	7.501	56.476	53.548	1.464	55.874	45.786	-20.012
600	7.755	57.867	54.155	2.227	55.597	43.796	-15.952
700	7.980	59.079	54.774	3.014	54.163	42.041	-13.125
800	8.170	60.158	55.381	3.822	53.897	40.328	-11.016
900	8.328	61.129	55.966	4.647	53.652	38.647	-9.384
1000	8.461	62.014	56.527	5.487	53.427	36.992	-8.084
1100	8.574	62.826	57.064	6.338	53.216	35.358	-7.025
1200	8.672	63.576	57.575	7.201	53.021	33.744	-6.145
1300	8.761	64.274	58.064	8.072	52.834	32.145	-5.404
1400	8.843	64.926	58.531	8.953	52.653	30.560	-4.770
1500	8.921	65.539	58.978	9.841	52.474	28.990	-4.224
1600	8.997	66.117	59.407	10.737	52.294	27.429	-3.746
1700	9.072	66.665	59.818	11.640	52.115	25.882	-3.327
1800	9.146	67.185	60.213	12.551	51.933	24.342	-2.955
1900	9.220	67.682	60.593	13.470	51.751	22.814	-2.624
2000	9.294	68.157	60.959	14.395	51.566	21.296	-2.327
2100	9.368	68.612	61.313	15.328	8.929	21.340	-2.221
2200	9.441	69.049	61.655	16.269	8.833	21.932	-2.179
2300	9.513	69.471	61.985	17.217	8.721	22.530	-2.141
2400	9.583	69.877	62.306	18.171	8.590	23.135	-2.107
2500	9.652	70.270	62.616	19.133	8.439	23.741	-2.075
2600	9.720	70.650	62.918	20.102	8.272	24.358	-2.047
2700	9.785	71.018	63.211	21.077	8.088	24.980	-2.022
2800	9.848	71.375	63.497	22.059	7.885	25.608	-1.999
2900	9.908	71.721	63.774	23.047	7.668	26.247	-1.978
3000	9.966	72.058	64.045	24.040	7.435	26.891	-1.959
3100	10.021	72.386	64.309	25.040	7.191	27.543	-1.942
3200	10.074	72.705	64.566	26.044	6.932	28.203	-1.926
3300	10.124	73.016	64.817	27.054	6.665	28.873	-1.912
3400	10.171	73.319	65.063	28.069	6.388	29.550	-1.899
3500	10.215	73.614	65.303	29.088	6.103	30.235	-1.888
3600	10.257	73.902	65.538	30.112	5.812	30.930	-1.878
3700	10.296	74.184	65.768	31.140	5.515	31.632	-1.868
3800	10.333	74.459	65.993	32.171	5.217	32.343	-1.860
3900	10.368	74.728	66.213	33.206	4.914	33.060	-1.853
4000	10.400	74.991	66.430	34.245	4.610	33.783	-1.846
4100	10.430	75.248	66.642	35.286	4.306	34.517	-1.840
4200	10.459	75.500	66.850	36.331	4.002	35.259	-1.835
4300	10.485	75.746	67.054	37.378	3.698	36.004	-1.830
4400	10.510	75.987	67.254	38.428	3.398	36.761	-1.826
4500	10.533	76.224	67.451	39.480	3.099	37.520	-1.822
4600	10.555	76.456	67.644	40.534	2.803	38.291	-1.819
4700	10.575	76.683	67.834	41.591	2.510	39.063	-1.816
4800	10.594	76.906	68.020	42.649	2.221	39.848	-1.814
4900	10.612	77.124	68.204	43.709	1.936	40.632	-1.812
5000	10.629	77.339	68.385	44.772	1.655	41.423	-1.811
5100	10.644	77.549	68.562	45.835	1.377	42.223	-1.809
5200	10.659	77.756	68.737	46.900	1.104	43.027	-1.808
5300	10.673	77.959	68.909	47.967	.835	43.839	-1.808
5400	10.687	78.159	69.079	49.035	.569	44.651	-1.807
5500	10.699	78.355	69.245	50.104	.306	45.468	-1.807
5600	10.711	78.548	69.410	51.175	.048	46.292	-1.807
5700	10.723	78.738	69.572	52.247	-.207	47.118	-1.807
5800	10.734	78.924	69.731	53.319	-.459	47.954	-1.807
5900	10.744	79.108	69.889	54.393	-.709	48.789	-1.807
6000	10.754	79.289	70.044	55.468	-.955	49.627	-1.808

June 30, 1962

Lead Monohydride (PbH) (Ideal Gas)

Mol. Wt. = 208.22

$\Delta H_f^\circ{}_{298.15} = 56.5 \pm 4.6$ kcal. mole^{-1}

$S_{298.15}^\circ = 52.737$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi_{1/2}$

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_1
0	2
[8000]	2

$\omega_e = 1564.1$ cm.$^{-1}$ $\omega_e x_e = 29.75$ cm.$^{-1}$

$B_e = 4.971$ cm.$^{-1}$ $\alpha_e = 0.144$ cm.$^{-1}$

$\sigma = 1$

Heat of Formation. $\Delta H_f^\circ{}_{298.15}$ was calculated from the dissociation energy of PbH(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration and spectroscopic data were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). Electronic levels and multiplicity were estimated by comparison with those for PbF(g).

Sulfur Monohydride (SH)

(Ideal Gas) GFW = 33.07197

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.216	34.449	34.449	INFINITE
100	7.215	38.378	53.629	-1.525	34.596	32.274	-70.536
200	7.815	43.610	47.443	-.767	34.660	29.915	-32.689
298	7.755	46.729	46.729	.000	34.600	27.595	-20.228
300	7.752	46.777	46.730	.014	34.598	27.552	-20.072
400	7.579	48.983	47.031	.781	33.918	25.244	-13.793
500	7.479	50.662	47.596	1.533	33.383	23.137	-10.113
600	7.468	52.023	48.224	2.279	32.922	21.133	-7.698
700	7.524	53.178	48.851	3.029	32.521	19.224	-6.002
800	7.620	54.188	49.457	3.785	19.099	16.082	-4.393
900	7.735	55.092	50.033	4.553	19.073	15.707	-3.814
1000	7.855	55.914	50.581	5.333	19.053	15.334	-3.351
1100	7.973	56.668	51.100	6.124	19.038	14.961	-2.973
1200	8.084	57.366	51.594	6.927	19.030	14.593	-2.658
1300	8.187	58.017	52.063	7.741	19.027	14.224	-2.391
1400	8.280	58.628	52.511	8.564	19.026	13.854	-2.163
1500	8.366	59.202	52.938	9.396	19.027	13.483	-1.965
1600	8.443	59.744	53.346	10.237	19.031	13.115	-1.791
1700	8.512	60.236	53.738	11.085	19.036	12.745	-1.639
1800	8.576	60.747	54.114	11.939	19.042	12.373	-1.502
1900	8.634	61.212	54.475	12.800	19.050	12.004	-1.381
2000	8.686	61.656	54.823	13.666	19.057	11.633	-1.271
2100	8.734	62.081	55.159	14.537	19.064	11.261	-1.172
2200	8.779	62.488	55.483	15.412	19.072	10.891	-1.082
2300	8.820	62.880	55.796	16.292	19.079	10.516	-.999
2400	8.858	63.256	56.099	17.176	19.087	10.146	-.924
2500	8.893	63.618	56.393	18.064	19.094	9.773	-.854
2600	8.926	63.968	56.677	18.955	19.101	9.399	-.790
2700	8.957	64.305	56.954	19.849	19.107	9.026	-.731
2800	8.986	64.631	57.222	20.746	19.113	8.651	-.675
2900	9.014	64.947	57.483	21.646	19.119	8.279	-.624
3000	9.040	65.253	57.737	22.549	19.124	7.905	-.576
3100	9.065	65.550	57.984	23.454	19.130	7.530	-.531
3200	9.089	65.838	58.225	24.362	19.134	7.156	-.489
3300	9.112	66.118	58.460	25.272	19.138	6.781	-.449
3400	9.134	66.390	58.689	26.184	19.142	6.409	-.412
3500	9.155	66.656	58.913	27.098	19.144	6.029	-.376
3600	9.175	66.914	59.132	28.015	19.147	5.656	-.343
3700	9.195	67.165	59.346	28.934	19.147	5.285	-.312
3800	9.214	67.411	59.555	29.854	19.148	4.908	-.282
3900	9.233	67.650	59.759	30.776	19.148	4.535	-.254
4000	9.251	67.884	59.959	31.701	19.147	4.163	-.227
4100	9.269	68.113	60.155	32.627	19.146	3.785	-.202
4200	9.287	68.337	60.348	33.554	19.143	3.410	-.177
4300	9.304	68.555	60.536	34.484	19.141	3.037	-.154
4400	9.322	68.770	60.721	35.415	19.136	2.658	-.132
4500	9.338	68.979	60.902	36.348	19.131	2.288	-.111
4600	9.355	69.185	61.080	37.283	19.127	1.911	-.091
4700	9.372	69.386	61.254	38.219	19.121	1.538	-.072
4800	9.388	69.583	61.426	39.157	19.114	1.165	-.053
4900	9.404	69.777	61.594	40.097	19.107	.794	-.035
5000	9.421	69.967	61.760	41.038	19.099	.417	-.018
5100	9.437	70.154	61.923	41.981	19.091	.045	-.002
5200	9.453	70.338	62.083	42.926	19.082	-.332	.014
5300	9.469	70.518	62.240	43.872	19.073	-.704	.029
5400	9.485	70.695	62.395	44.819	19.063	-1.076	.044
5500	9.502	70.869	62.547	45.769	19.053	-1.448	.058
5600	9.518	71.040	62.698	46.720	19.041	-1.819	.071
5700	9.534	71.209	62.845	47.672	19.030	-2.194	.084
5800	9.550	71.375	62.991	48.627	19.018	-2.567	.097
5900	9.567	71.538	63.135	49.582	19.006	-2.939	.109
6000	9.583	71.699	63.276	50.540	18.994	-3.308	.120

Dec. 31, 1960; June 30, 1967

SULFUR MONOHYDRIDE (SH) (IDEAL GAS) GFW = 33.07197

Ground State Configuration $^2\Pi$ $\Delta Hf^\circ_0 = 34.4 \pm 4$ kcal/mol

$S^\circ_{298.15} = 46.73$ gibbs/mol $\Delta Hf^\circ_{298.15} = 34.6 \pm 4$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	59636	2
376.9	2	[63850]	4
30662.4	2	75000	18

$\omega_e = 2702$ cm^{-1} $\omega_e x_e = 60$ cm^{-1} $\sigma = 1$

$B_e = 9.611$ cm^{-1} $\alpha_e = [0.3]$ cm^{-1} $r_e = 1.3397$ Å

Heat of Formation

Mackle (1) estimated ΔHf°_{298} of SH(g) as 34.6 ± 4 kcal/mol, this value being an average of three independent determinations.

He obtained these three values by the following methods: (A) He calculated ΔHf°_{298} of SH(g) as 34.9 ± 4.5 kcal/mol from ΔHf°_{298} of thiobenzyl alcohol (g), ΔHf°_{298} of the benzyl radical (g) and the heat of dissociation (D°_0) of thiobenzyl alcohol reported by Sehon and Darwent (2). (B) A value of 35.2 ± 4.5 kcal/mol was calculated from ΔHf°_{298} of $C_2H_5{}^+(g)$, ΔHf°_{298} of $C_2H_5SH(g)$ and the appearance potential of $C_2H_5{}^+$ reported by Franklin and Lumpkin (3). (C) He calculated that ΔHf°_{298} of SH(g) is 33.7 ± 3 kcal/mol from ΔHf°_{298} of $H_2S(g)$ and the mass spectrographic data for the reactions $H_2S = SH^+ + H + e^-$ and $SH = SH^+ + e^-$ reported by Palmer and Lossing (4). The adopted value of 34.5 ± 4 kcal/mol compares with a value of 34.9 kcal/mol obtained from a linear Birge-Sponer extrapolation of the potential function.

Heat Capacity and Entropy

The high resolution spectra of SH(g) have been studied by Ramsay (5) and Johns and Ramsay (6) in the near UV and by Morrow (7) in the vacuum UV. The energy levels of the doublet ground state and of the first excited state ($^2\Sigma$) were reported by Ramsay (6). Six of the seven higher excited levels ($B^2\Sigma$, $D^2\Delta$, $E^2\Sigma$, $F^2\Delta$, $G^2\Delta$, $H^2\Delta$) were reported by Morrow (7), the last five of which are shown as an average of 75000 cm^{-1}. The remaining electronic level ($C^2\Delta$) is estimated by analogy with the electronic levels of SD(g) reported by Morrow (7).

Ramsay (5) reported the following rotational and vibrational constants: $B_0 = 9.461$ cm^{-1}, $\omega_e = 2702$ cm^{-1}, and $\omega_e x_e = 60$ cm^{-1}. The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + \alpha_e/2$. The bond distance is calculated from B_e.

References

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Silicon Monohydride (SiH)

(Ideal Gas) GFW = 29.09397

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.205	89.576	89.576	INFINITE
100	7.804	39.135	53.839	-1.470	89.867	87.265	-190.717
200	7.371	44.403	47.968	-.713	90.042	84.571	-92.415
298	7.191	47.306	47.306	.000	90.000	81.889	-60.026
300	7.190	47.350	47.306	.013	89.998	81.839	-59.619
400	7.180	49.414	47.587	.731	89.861	79.138	-43.239
500	7.285	51.026	48.120	1.453	89.690	76.477	-33.428
600	7.451	52.368	48.719	2.190	89.509	73.851	-26.900
700	7.636	53.531	49.325	2.944	89.327	71.256	-22.247
800	7.817	54.562	49.916	3.717	89.147	68.686	-18.764
900	7.983	55.493	50.485	4.507	88.969	66.141	-16.061
1000	8.129	56.348	51.029	5.313	88.792	63.613	-13.903
1100	8.257	57.122	51.548	6.132	88.613	61.104	-12.140
1200	8.369	57.846	52.043	6.964	88.433	58.611	-10.675
1300	8.465	58.520	52.515	7.805	88.247	56.133	-9.437
1400	8.550	59.150	52.967	8.656	88.056	53.670	-8.378
1500	8.624	59.743	53.399	9.515	87.857	51.222	-7.463
1600	8.690	60.301	53.813	10.381	87.649	48.785	-6.664
1700	8.748	60.830	54.211	11.253	75.439	46.469	-5.974
1800	8.801	61.331	54.592	12.130	75.268	44.770	-5.436
1900	8.848	61.809	54.960	13.013	75.098	43.080	-4.955
2000	8.891	62.264	55.314	13.900	74.927	41.400	-4.524
2100	8.931	62.698	55.655	14.791	74.756	39.728	-4.135
2200	8.967	63.115	55.985	15.686	74.585	38.063	-3.781
2300	9.001	63.514	56.303	16.584	74.414	36.407	-3.459
2400	9.033	63.898	56.612	17.486	74.242	34.759	-3.165
2500	9.063	64.267	56.911	18.391	74.070	33.116	-2.895
2600	9.092	64.623	57.201	19.298	73.897	31.482	-2.646
2700	9.119	64.967	57.482	20.209	73.724	29.853	-2.416
2800	9.146	65.299	57.755	21.122	73.551	28.232	-2.204
2900	9.172	65.620	58.021	22.038	73.378	26.618	-2.006
3000	9.198	65.932	58.279	22.957	73.205	25.006	-1.822
3100	9.224	66.234	58.531	23.878	73.032	23.402	-1.650
3200	9.249	66.527	58.776	24.801	72.858	21.806	-1.489
3300	9.275	66.812	59.016	25.728	72.685	20.214	-1.339
3400	9.301	67.089	59.249	26.656	72.512	18.625	-1.197
3500	9.328	67.359	59.477	27.588	72.339	17.042	-1.064
3600	9.355	67.622	59.700	28.522	-19.794	17.722	-1.076
3700	9.384	67.879	59.917	29.459	-19.868	18.766	-1.108
3800	9.413	68.130	60.130	30.399	-19.940	19.811	-1.139
3900	9.443	68.375	60.338	31.341	-20.013	20.857	-1.169
4000	9.474	68.614	60.542	32.287	-20.085	21.907	-1.197
4100	9.506	68.848	60.742	33.236	-20.157	22.955	-1.224
4200	9.540	69.078	60.938	34.189	-20.227	24.008	-1.249
4300	9.575	69.303	61.130	35.144	-20.296	25.061	-1.274
4400	9.611	69.523	61.318	36.104	-20.364	26.116	-1.297
4500	9.648	69.740	61.503	37.066	-20.431	27.177	-1.320
4600	9.687	69.952	61.684	38.033	-20.494	28.235	-1.341
4700	9.727	70.161	61.862	39.004	-20.558	29.296	-1.362
4800	9.768	70.366	62.037	39.979	-20.617	30.356	-1.382
4900	9.811	70.568	62.209	40.957	-20.675	31.420	-1.401
5000	9.854	70.767	62.378	41.941	-20.730	32.479	-1.420
5100	9.899	70.962	62.545	42.928	-20.783	33.549	-1.438
5200	9.946	71.155	62.709	43.921	-20.833	34.613	-1.455
5300	9.993	71.345	62.870	44.918	-20.879	35.682	-1.471
5400	10.042	71.532	63.028	45.919	-20.923	36.746	-1.487
5500	10.091	71.717	63.185	46.926	-20.964	37.814	-1.503
5600	10.141	71.899	63.339	47.937	-21.002	38.885	-1.518
5700	10.193	72.079	63.490	48.954	-21.036	39.957	-1.532
5800	10.245	72.257	63.640	49.976	-21.068	41.026	-1.546
5900	10.298	72.432	63.788	51.003	-21.097	42.094	-1.559
6000	10.351	72.606	63.933	52.036	-21.121	43.164	-1.572

Dec. 31, 1960; Dec. 31, 1969

SILICON MONOHYDRIDE (SiH) (IDEAL GAS) GFW = 29.09397

Ground State Configuration $^2\Pi$

ΔHf°_0 = 89.6 ± 2 kcal/mol

$S^\circ_{298.15}$ = 47.306 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 90 ± 2 kcal/mol

Electronic Levels and Degeneracies

State	ε_i, cm^{-1}	g_i
$X^2\Pi$	0	2
	142.83	2
$^4\Sigma^-$	[21510]	4
$A^2\Delta$	24193	4
$^2\Sigma^-$	[24730]	2
$B^2\Sigma^+$	30808	2
$C^2\Sigma^+$	30842	2
$D^2\Delta$	48510	4
$E^2\Sigma^+$	52399	2

ω_e = 2041.8 cm^{-1} $\omega_e x_e$ = 35.51 cm^{-1} σ = 1

B_e = 7.4996 cm^{-1} α_e = 0.219 cm^{-1} r_e = 1.5201 Å

Heat of Formation

Verma (1) has derived an upper limit to the dissociation energy of 24680 cm^{-1} (70.56 kcal) from predissociation in the $B^2\Sigma^+$ state. With JANAF values for Si(g) and H(g) this yields ΔHf°_0(SiH, g) ≥ 87.73 kcal/mol. We adopt a value of ΔHf°_{298}(SiH, g) = 90 ± 2 kcal/mol, assuming that the predissociation has a 2 kcal barrier similar to that in the predissociation of the $A^1\Pi$ state of AlH. Hildenbrand (5) has applied an ionic-covalent correction to the linear Birge-Sponer extrapolation of the ground state dissociation energy and obtains D°_0(SiH, g) = 70 kcal in excellent agreement with the predissociation value.

Heat Capacity and Entropy

The observed electronic levels and rotational and vibrational constants are from Herzberg et al. (2), Klynning and Lindgren (3), and Verma (1). The estimated levels are from the calculations of Jordan (4). The upper states are all assumed to have ground state molecular constants. This approximation introduces negligible error when the first state is as high as 21000 cm^{-1} and has the same multiplicity as the ground state.

References

1. R. D. Verma, Can. J. Phys. 43, 2136 (1965).
2. G. Herzberg, A. Lagerqvist, and B. J. McKenzie, Can. J. Phys. 47, 1891 (1969).
3. L. Klynning and B. Lindgren, Ark. Fysik 33, 73 (1966).
4. P. C. Jordan, J. Chem. Phys. 44, 3400 (1966).
5. D. L. Hildenbrand, Douglas Advanced Research Labs., Huntington Beach, Calif., private communication, Dec. 30, 1969.

Zirconium Hydride (ZrH)

(Ideal Gas) Mol. Wt. = 92.228

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.077	123.652	123.652	INFINITE
100	6.962	44.006	57.868	- 1.386	123.751	120.907	- 264.230
200	6.978	48.835	52.282	- .689	123.624	118.098	- 129.046
298	7.096	51.638	51.638	.000	123.400	115.432	- 84.610
300	7.099	51.682	51.638	.013	123.396	115.283	- 84.053
400	7.348	53.756	51.919	.735	123.135	112.750	- 61.601
500	7.632	55.426	52.459	1.484	122.864	110.186	- 48.160
600	7.891	56.841	53.074	2.260	122.586	107.676	- 39.219
700	8.108	58.075	53.702	3.061	122.311	105.213	- 32.847
800	8.284	59.169	54.319	3.880	122.040	102.789	- 28.079
900	8.427	60.153	54.913	4.716	121.774	100.399	- 24.379
1000	8.543	61.048	55.483	5.565	121.510	98.038	- 21.425
1100	8.639	61.866	56.026	6.424	121.236	95.704	- 19.014
1200	8.719	62.622	56.545	7.292	119.999	93.443	- 17.018
1300	8.787	63.322	57.039	8.168	119.729	91.240	- 15.338
1400	8.845	63.976	57.512	9.049	119.451	89.059	- 13.902
1500	8.896	64.588	57.963	9.936	119.167	86.898	- 12.660
1600	8.942	65.163	58.396	10.828	118.875	84.757	- 11.577
1700	8.982	65.707	58.810	11.725	118.575	82.634	- 10.623
1800	9.019	66.221	59.207	12.625	118.268	80.529	- 9.777
1900	9.053	66.710	59.589	13.528	117.952	78.441	- 9.022
2000	9.084	67.175	59.957	14.435	117.628	76.368	- 8.345
2100	9.113	67.619	60.312	15.345	117.296	74.313	- 7.734
2200	9.140	68.043	60.653	16.258	112.052	72.440	- 7.196
2300	9.166	68.450	60.984	17.173	111.698	70.647	- 6.713
2400	9.191	68.841	61.303	18.091	111.342	68.871	- 6.271
2500	9.214	69.216	61.612	19.011	110.985	67.108	- 5.866
2600	9.237	69.578	61.911	19.934	110.628	65.360	- 5.494
2700	9.258	69.927	62.202	20.858	110.269	63.626	- 5.150
2800	9.279	70.264	62.484	21.785	109.909	61.904	- 4.832
2900	9.300	70.590	62.758	22.714	109.549	60.199	- 4.537
3000	9.320	70.906	63.024	23.645	109.188	58.502	- 4.262
3100	9.339	71.212	63.283	24.578	108.827	56.816	- 4.005
3200	9.359	71.509	63.536	25.513	108.465	55.145	- 3.766
3300	9.377	71.797	63.782	26.450	108.102	53.486	- 3.542
3400	9.396	72.077	64.022	27.389	107.740	51.836	- 3.332
3500	9.414	72.350	64.256	28.329	107.376	50.197	- 3.134
3600	9.432	72.615	64.484	29.271	107.011	48.566	- 2.948
3700	9.449	72.874	64.708	30.215	106.646	46.949	- 2.773
3800	9.467	73.126	64.926	31.161	106.281	45.342	- 2.608
3900	9.484	73.372	65.139	32.109	105.914	43.744	- 2.451
4000	9.501	73.613	65.348	33.058	105.548	42.153	- 2.303
4100	9.518	73.847	65.552	34.009	105.180	40.573	- 2.163
4200	9.535	74.077	65.753	34.962	104.813	39.003	- 2.029
4300	9.552	74.301	65.949	35.916	104.444	37.440	- 1.903
4400	9.568	74.521	66.141	36.872	104.076	35.884	- 1.782
4500	9.585	74.736	66.330	37.830	103.707	34.337	- 1.668
4600	9.601	74.947	66.515	38.789	103.337	32.802	- 1.558
4700	9.617	75.154	66.697	39.750	102.967	31.274	- 1.454
4800	9.634	75.357	66.875	40.712	- 33.836	31.276	- 1.424
4900	9.650	75.555	67.050	41.677	- 34.261	32.634	- 1.455
5000	9.666	75.751	67.222	42.642	- 34.692	34.003	- 1.486
5100	9.682	75.942	67.391	43.610	- 35.127	35.383	- 1.516
5200	9.698	76.130	67.557	44.579	- 35.567	36.772	- 1.545
5300	9.714	76.315	67.721	45.549	- 36.012	38.163	- 1.574
5400	9.730	76.497	67.882	46.521	- 36.461	39.569	- 1.601
5500	9.745	76.676	68.040	47.495	- 36.913	40.978	- 1.628
5600	9.761	76.851	68.196	48.471	- 37.369	42.401	- 1.655
5700	9.777	77.024	68.349	49.447	- 37.827	43.827	- 1.680
5800	9.793	77.194	68.500	50.426	- 38.290	45.266	- 1.706
5900	9.808	77.362	68.649	51.406	- 38.753	46.712	- 1.730
6000	9.824	77.527	68.796	52.388	- 39.218	48.160	- 1.754

June 30, 1963

ZIRCONIUM HYDRIDE (ZrH) (IDEAL GAS) MOL. WT. = 92.228

Ground State Configuration [$^2\Pi$]

$S^\circ_{298.15}$ = [51.638] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [123.7] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [123.4] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1
0	[4]

ω_e = [1400] cm.$^{-1}$

B_e = [5.1] cm.$^{-1}$

$\omega_e x_e$ = [19] cm.$^{-1}$

α_e = [0.09] cm.$^{-1}$

σ = 1

r_e = [1.821] Å

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as 123.7 kcal. mole^{-1} by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. r_e was calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2}$ Å.

Hydrogen (H_2)

(Ideal Gas - Reference State) Mol. Wt. = 2.016

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.024	.000	.000	.000
100	5.393	24.387	37.035	-1.265	.000	.000	.000
200	6.518	28.520	31.831	-.662	.000	.000	.000
298	6.892	31.208	31.208	.000	.000	.000	.000
300	6.894	31.251	31.208	.013	.000	.000	.000
400	6.975	33.247	31.480	.707	.000	.000	.000
500	6.993	34.806	31.995	1.406	.000	.000	.000
600	7.009	36.082	32.573	2.106	.000	.000	.000
700	7.036	37.165	33.153	2.808	.000	.000	.000
800	7.087	38.107	33.715	3.514	.000	.000	.000
900	7.148	38.946	34.250	4.226	.000	.000	.000
1000	7.219	39.702	34.756	4.944	.000	.000	.000
1100	7.300	40.394	35.240	5.670	.000	.000	.000
1200	7.390	41.033	35.696	6.404	.000	.000	.000
1300	7.490	41.628	36.130	7.148	.000	.000	.000
1400	7.600	42.187	36.543	7.902	.000	.000	.000
1500	7.720	42.716	36.937	8.668	.000	.000	.000
1600	7.823	43.217	37.314	9.446	.000	.000	.000
1700	7.921	43.695	37.675	10.233	.000	.000	.000
1800	8.016	44.150	38.022	11.030	.000	.000	.000
1900	8.108	44.586	38.356	11.836	.000	.000	.000
2000	8.195	45.004	38.678	12.651	.000	.000	.000
2100	8.279	45.406	38.989	13.475	.000	.000	.000
2200	8.358	45.793	39.290	14.307	.000	.000	.000
2300	8.434	46.166	39.581	15.146	.000	.000	.000
2400	8.506	46.527	39.863	15.993	.000	.000	.000
2500	8.575	46.875	40.136	16.848	.000	.000	.000
2600	8.639	47.213	40.402	17.708	.000	.000	.000
2700	8.700	47.540	40.660	18.575	.000	.000	.000
2800	8.757	47.857	40.912	19.448	.000	.000	.000
2900	8.810	48.166	41.157	20.326	.000	.000	.000
3000	8.859	48.465	41.395	21.210	.000	.000	.000
3100	8.911	48.756	41.628	22.098	.000	.000	.000
3200	8.962	49.040	41.855	22.992	.000	.000	.000
3300	9.012	49.317	42.077	23.891	.000	.000	.000
3400	9.061	49.586	42.294	24.794	.000	.000	.000
3500	9.110	49.850	42.506	25.703	.000	.000	.000
3600	9.156	50.107	42.714	26.616	.000	.000	.000
3700	9.205	50.359	42.917	27.535	.000	.000	.000
3800	9.252	50.605	43.116	28.457	.000	.000	.000
3900	9.297	50.846	43.311	29.385	.000	.000	.000
4000	9.342	51.082	43.502	30.317	.000	.000	.000
4100	9.386	51.313	43.690	31.253	.000	.000	.000
4200	9.429	51.540	43.874	32.194	.000	.000	.000
4300	9.472	51.762	44.055	33.139	.000	.000	.000
4400	9.514	51.980	44.233	34.088	.000	.000	.000
4500	9.555	52.194	44.407	35.042	.000	.000	.000
4600	9.595	52.405	44.579	35.999	.000	.000	.000
4700	9.634	52.612	44.748	36.961	.000	.000	.000
4800	9.673	52.815	44.914	37.926	.000	.000	.000
4900	9.711	53.015	45.077	38.895	.000	.000	.000
5000	9.748	53.211	45.238	39.868	.000	.000	.000
5100	9.785	53.405	45.396	40.845	.000	.000	.000
5200	9.822	53.595	45.552	41.825	.000	.000	.000
5300	9.859	53.783	45.705	42.809	.000	.000	.000
5400	9.895	53.967	45.857	43.797	.000	.000	.000
5500	9.930	54.149	46.006	44.788	.000	.000	.000
5600	9.965	54.328	46.153	45.783	.000	.000	.000
5700	10.000	54.505	46.298	46.781	.000	.000	.000
5800	10.034	54.679	46.441	47.783	.000	.000	.000
5900	10.067	54.851	46.582	48.788	.000	.000	.000
6000	10.100	55.020	46.721	49.796	.000	.000	.000

March 31, 1961

Hydrogen (H_2) (Ideal Gas - Reference State) Mol. Wt. = 2.016

D_0° = 103.266 ± 0.15 kcal. mole^{-1}

Ground State Configuration $^1\Sigma_g^+$

$\Delta H_{f\,298.15}^\circ = 0$

$S^\circ_{298.15}$ = 31.21 ± 0.01 cal. deg.$^{-1}$ mole^{-1}

ω_e = 4405.3 cm.$^{-1}$

$\omega_e x_e$ = 125.325 cm.$^{-1}$

D_e = 0.04644 cm.$^{-1}$

$\sigma = 2$

B_e = 60.848 cm.$^{-1}$

α_e = 3.0664 cm.$^{-1}$

r_e = 0.7417 Å

Heat Capacities and Entropy

H. W. Woolley, R. B. Scott and F. G. Brickwedde, J. Research Nat. Bur. Standards 41, 379 (1948), calculated the thermodynamic functions by a method of direct summation for normal H_2 (75% ortho and 25% para) using spectroscopic constants derived from an analysis of U. V. band spectra. These constants are more preferable for use in a summation method than those obtained by G. Herzberg, Can. J. Res. A28, 144 (1950) from the measured quadrupole transitions in the ground state which accurately describe the lower vibrational levels only. In any case the difference in the functions resulting from the two sets of data are less than 0.2%.

Since the entropies of Woolley et al. contain a contribution from nuclear spin, a correction of -Rln4 was applied. However, the entropy due to the mixing of ortho and para hydrogen which is a consequence of nuclear spin is included in the total entropy since this results in correct equilibrium constants based upon third law calculations. Differences in the values of R and c_2 were found to have a negligible effect upon the functions.

Similar calculations with a different method of estimating the higher rotational levels by H. L. Johnston, L. G. Savedoff, and J. Belzer, Technical Report No. 2, Project R.F-316, Ohio State Univ. (1949), result in functions that are 0.5% lower above 5000°K.

For details concerning the dissociation energy see the monatomic hydrogen sheet.

Potassium Hydroxide, Dimeric ($K_2O_2H_2$)
(Ideal Gas) Mol. Wt. = 112.21874

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_P
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-4.415	-154.317	-154.317	INFINITE
100	13.560	60.001	94.314	-3.431	-155.633	-153.341	335.126
200	17.684	70.956	80.092	-1.827	-156.552	-150.679	164.654
298	19.465	78.366	78.366	.000	-157.387	-147.620	108.208
300	19.496	78.487	78.366	.036	-157.403	-147.559	107.497
400	21.073	84.315	79.150	2.066	-159.406	-143.932	78.641
500	22.452	89.170	80.682	4.244	-160.144	-139.975	61.183
600	23.578	93.366	82.454	6.548	-160.747	-135.881	49.495
700	24.488	97.072	84.283	8.952	-161.255	-131.695	41.117
800	25.239	100.392	86.092	11.440	-161.695	-127.444	34.816
900	25.879	103.403	87.851	13.997	-162.088	-123.137	29.902
1000	26.435	106.159	89.546	16.613	-162.459	-118.790	25.962
1100	26.925	108.702	91.173	19.281	-200.630	-112.358	22.323
1200	27.362	111.063	92.733	21.996	-200.491	-104.336	19.002
1300	27.751	113.269	94.229	24.752	-200.330	-96.333	16.195
1400	28.100	115.339	95.664	27.545	-200.149	-88.338	13.790
1500	28.412	117.288	97.041	30.371	-199.954	-80.356	11.708
1600	28.692	119.131	98.365	33.226	-199.748	-72.391	9.888
1700	28.943	120.878	99.638	36.108	-199.531	-64.439	8.284
1800	29.168	122.539	100.865	39.014	-199.307	-56.499	6.860
1900	29.370	124.122	102.047	41.941	-199.081	-48.573	5.587
2000	29.552	125.633	103.189	44.887	-198.850	-40.656	4.443
2100	29.716	127.079	104.293	47.851	-198.619	-32.751	3.408
2200	29.864	128.464	105.360	50.830	-198.394	-24.856	2.469
2300	29.998	129.795	106.394	53.823	-198.170	-16.976	1.613
2400	30.119	131.074	107.396	56.829	-197.953	-9.099	.829
2500	30.230	132.306	108.367	59.847	-197.748	-1.241	.108
2600	30.330	133.494	109.311	62.875	-197.548	6.622	-.557
2700	30.422	134.640	110.228	65.912	-197.364	14.467	-1.171
2800	30.505	135.748	111.120	68.959	-197.195	22.308	-1.741
2900	30.582	136.820	111.988	72.013	-197.041	30.151	-2.272
3000	30.652	137.858	112.833	75.075	-196.904	37.978	-2.767
3100	30.717	138.864	113.656	78.143	-196.789	45.808	-3.229
3200	30.776	139.840	114.459	81.218	-196.696	53.634	-3.663
3300	30.831	140.788	115.243	84.298	-196.629	61.451	-4.070
3400	30.881	141.709	116.008	87.384	-196.591	69.269	-4.453
3500	30.928	142.605	116.755	90.474	-196.584	77.088	-4.814
3600	30.972	143.477	117.485	93.569	-196.612	84.912	-5.155
3700	31.012	144.326	118.199	96.669	-196.679	92.731	-5.477
3800	31.050	145.154	118.898	99.772	-196.789	100.553	-5.783
3900	31.085	145.961	119.581	102.879	-196.946	108.377	-6.073
4000	31.117	146.748	120.251	105.989	-197.156	116.212	-6.350
4100	31.148	147.517	120.906	109.102	-197.424	124.049	-6.612
4200	31.176	148.268	121.549	112.218	-197.756	131.894	-6.863
4300	31.203	149.002	122.179	115.337	-198.154	139.749	-7.103
4400	31.228	149.719	122.797	118.459	-198.630	147.610	-7.332
4500	31.252	150.421	123.403	121.583	-199.187	155.489	-7.552
4600	31.274	151.108	123.998	124.709	-199.831	163.380	-7.762
4700	31.295	151.781	124.582	127.838	-200.570	171.284	-7.965
4800	31.314	152.440	125.155	130.968	-201.408	179.208	-8.160
4900	31.333	153.086	125.719	134.100	-202.354	187.142	-8.347
5000	31.350	153.719	126.272	137.234	-203.410	195.095	-8.528
5100	31.367	154.340	126.817	140.370	-204.584	203.090	-8.703
5200	31.382	154.950	127.352	143.508	-205.878	211.084	-8.872
5300	31.397	155.547	127.878	146.647	-207.296	219.126	-9.036
5400	31.411	156.134	128.396	149.787	-208.843	227.175	-9.194
5500	31.424	156.711	128.906	152.929	-210.517	235.264	-9.349
5600	31.437	157.277	129.407	156.072	-212.321	243.385	-9.499
5700	31.449	157.834	129.901	159.216	-214.251	251.536	-9.644
5800	31.460	158.381	130.387	162.362	-216.308	259.727	-9.787
5900	31.471	158.919	130.866	165.508	-218.487	267.957	-9.926
6000	31.482	159.448	131.338	168.656	-220.784	276.226	-10.062

June 30, 1962; Mar. 31, 1966

POTASSIUM HYDROXIDE, DIMERIC ($K_2O_2H_2$) (IDEAL GAS) MOL. WT. = 112.21874

Point Group C_{2h}

$S^\circ_{298.15}$ = [78.4] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = -154.3 ± 5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -157.4 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[273](1)	[3700](1)
[150](1)	[3700](1)
[235](1)	[1250](1)
[150](1)	[1250](1)
[255](1)	[1250](1)
[258](1)	[1250](1)

Bond Distance: K-O = [2.43] Å O-H = [0.96] Å

Bond Angle: K-O-K = [90°] K-O-H = [110°]

$\sigma = 2$

Products of the Moments of Inertia: $I_AI_BI_C$ = [3.7587] X 10^{-113} g.^{3} cm.^{6}

Heat of Formation.

See KOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for $Li_2(OH)_2(g)$ which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of $K_2(OH)_2$, but the bond angle O-K-O was modified to 90° (i.e. a square planar configuration for potassium and oxygen atoms). The bond angle K-O-H in $K_2(OH)_2(g)$ was assumed to be 110°. The bond distance K-O in $K_2(OH)_2(g)$ was estimated 10% longer than that in KOH(g). The bond distance O-H was estimated to be the same in $H_2O(g)$. The three principal moments of inertia are I_A = [17.5202] X 10^{-39}, I_B = [38.5534] X 10^{-39} and I_C = [55.6452] X 10^{-39} g. cm.^{2}

The first six selected vibrational frequencies were taken to be equal to those for $K_2F_2(g)$ (see $K_2F_2(g)$ table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.

Lithium Hydroxide, Dimeric ($Li_2O_2H_2$)

(Ideal Gas) Mol. Wt. = 47.89274

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.463	- 178.587	- 178.587	INFINITE
100	9.118	50.762	77.218	- 2.646	- 179.480	- 177.613	388.173
200	13.613	58.482	66.010	- 1.505	- 180.502	- 175.351	191.615
298	16.882	64.563	64.563	.000	- 181.433	- 172.621	126.534
300	16.935	64.668	64.563	.031	- 181.450	- 172.567	125.715
400	19.420	69.895	65.259	1.854	- 182.274	- 169.477	92.598
500	21.319	74.443	66.651	3.896	- 184.498	- 166.041	72.576
600	22.761	78.463	68.291	6.103	- 185.172	- 162.283	59.111
700	23.873	82.059	70.006	8.437	- 185.718	- 158.424	49.462
800	24.762	85.307	71.719	10.870	- 186.173	- 154.495	42.206
900	25.497	88.267	73.395	13.384	- 186.567	- 150.510	36.549
1000	26.123	90.986	75.020	15.966	- 186.910	- 146.484	32.014
1100	26.666	93.502	76.588	18.606	- 187.211	- 142.426	28.298
1200	27.143	95.843	78.096	21.297	- 187.478	- 138.344	25.196
1300	27.565	98.033	79.546	24.033	- 187.715	- 134.241	22.568
1400	27.939	100.090	80.941	26.809	- 187.927	- 130.119	20.312
1500	28.271	102.029	82.283	29.619	- 188.120	- 125.982	18.356
1600	28.568	103.863	83.575	32.462	- 188.294	- 121.834	16.642
1700	28.833	105.603	84.820	35.332	- 258.547	- 115.018	14.787
1800	29.069	107.258	86.021	38.227	- 258.332	- 106.579	12.940
1900	29.282	108.835	87.180	41.145	- 258.109	- 98.152	11.290
2000	29.472	110.342	88.301	44.083	- 257.882	- 89.742	9.807
2100	29.644	111.785	89.385	47.039	- 257.653	- 81.344	8.466
2200	29.798	113.167	90.435	50.011	- 257.425	- 72.951	7.247
2300	29.938	114.495	91.452	52.998	- 257.193	- 64.573	6.136
2400	30.064	115.772	92.439	55.998	- 256.968	- 56.201	5.118
2500	30.178	117.001	93.397	59.010	- 256.747	- 47.842	4.182
2600	30.283	118.187	94.328	62.033	- 256.528	- 39.490	3.319
2700	30.378	119.332	95.233	65.066	- 256.318	- 31.148	2.521
2800	30.464	120.438	96.114	68.109	- 256.113	- 22.812	1.781
2900	30.544	121.509	96.971	71.159	- 255.921	- 14.481	1.091
3000	30.616	122.545	97.806	74.217	- 255.736	- 6.157	.449
3100	30.683	123.550	98.621	77.282	- 255.564	2.161	- .152
3200	30.745	124.525	99.415	80.354	- 255.402	10.470	- .715
3300	30.801	125.472	100.190	83.431	- 255.256	18.776	- 1.243
3400	30.854	126.393	100.947	86.514	- 255.123	27.077	- 1.740
3500	30.902	127.288	101.687	89.602	- 255.004	35.373	- 2.209
3600	30.947	128.159	102.411	92.694	- 254.903	43.670	- 2.651
3700	30.989	129.007	103.118	95.791	- 254.819	51.963	- 3.069
3800	31.028	129.834	103.810	98.892	- 254.751	60.261	- 3.466
3900	31.064	130.641	104.488	101.996	- 254.703	68.545	- 3.841
4000	31.097	131.428	105.152	105.104	- 254.675	76.829	- 4.198
4100	31.129	132.196	105.802	108.216	- 254.666	85.121	- 4.537
4200	31.158	132.946	106.439	111.330	- 254.680	93.408	- 4.861
4300	31.186	133.680	107.064	114.447	- 254.714	101.696	- 5.169
4400	31.212	134.397	107.677	117.567	- 254.770	109.986	- 5.463
4500	31.236	135.099	108.279	120.690	- 254.852	118.274	- 5.744
4600	31.259	135.786	108.869	123.814	- 254.958	126.571	- 6.013
4700	31.280	136.458	109.449	126.941	- 255.091	134.863	- 6.271
4800	31.300	137.117	110.019	130.070	- 255.250	143.160	- 6.518
4900	31.319	137.762	110.579	133.201	- 255.439	151.462	- 6.756
5000	31.337	138.395	111.129	136.334	- 255.656	159.769	- 6.983
5100	31.354	139.016	111.669	139.469	- 255.907	168.086	- 7.203
5200	31.370	139.625	112.201	142.605	- 256.191	176.397	- 7.414
5300	31.386	140.223	112.724	145.743	- 256.510	184.720	- 7.617
5400	31.400	140.810	113.239	148.882	- 256.866	193.040	- 7.813
5500	31.414	141.386	113.745	152.023	- 257.261	201.384	- 8.002
5600	31.427	141.952	114.244	155.165	- 257.698	209.717	- 8.185
5700	31.439	142.508	114.735	158.308	- 258.177	218.075	- 8.361
5800	31.451	143.055	115.219	161.453	- 258.703	226.438	- 8.532
5900	31.462	143.593	115.695	164.598	- 259.275	234.803	- 8.698
6000	31.473	144.122	116.164	167.745	- 259.897	243.185	- 8.858

Dec. 31, 1960: Mar. 31, 1966

LITHIUM HYDROXIDE, DIMERIC ($Li_2O_2H_2$) (IDEAL GAS) MOL. WT. = 47.89274

Point Group C_{2h}
$S^\circ_{298.15}$ = [64.6] cal. deg.$^{-1}$ mole^{-1}
Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -178.6 ± 4 kcal. mole^{-1}
$\Delta H^\circ_{f\ 298.15}$ = -181.4 ± 4 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[465](1)	[3700](1)
[305](1)	[3700](1)
[407](1)	[1250](1)
[385](1)	[1250](1)
[640](1)	[1250](1)
[460](1)	[1250](1)

Bond Distance: Li-O = [1.76] Å O-H = [0.96] Å

Bond Angle: Li-O-Li = [90]° Li-O-H = [110]° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.56956] X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have studied the $Li_2O(c)$-$H_2O(g)$ equilibrium by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K. the heat of reaction $Li_2(OH)_2(g) \rightarrow 2LiOH(g)$ at 298° has been calculated by the second law and the third law methods as 63.2 and 63.7 kcal. mole^{-1}, respectively. (The third law drift is 0.5 ± 1.5 e.u.) Combination of the third law value ($\Delta H^\circ_{r\ 298}$ = 63.7 kcal. mole^{-1}) with the heat of formation of lithium hydroxide(g) ($\Delta H^\circ_{f\ 298}$ = -58.8 kcal. mole^{-1}) gives the heat of formation of dimeric lithium hydroxide (g) ($\Delta H^\circ_{f\ 298}$ = -181.4 kcal. mole^{-1}) which has been adopted in the tabulation.

J. B. Berkowitz-Mattuck and A. Buchler, J. Phys. Chem. 67, 1386 (1963), have also studied the $Li_2O(c)$-$H_2O(g)$ equilibrium by the transpiration method, and reported two equilibrium constants (K_{1095}° = 0.105 and K_{1145}° = 0.357) for the reaction $Li_2O(c) + H_2O(g) \rightarrow Li_2(OH)_2(g)$. Using the third law method, the heat of reaction has been calculated from the equilibrium constants as 12.7 kcal. mole^{-1} at 298.15°K. The heat of formation of $Li_2(OH)_2(g)$ can be derived as $\Delta H^\circ_{f\ 298}$ = -188.2 ± 3.5 kcal. mole^{-1} which is different from the adopted value of Berkowitz, Meschi and Chupka, loc. cit. Berkowitz-Mattuck and Buchler attempted to explain the difference by inferring that the solid-gas equilibrium was not properly established in the measurement of Berkowitz, Meschi and Chupka, however, the absence of drift in the third law analysis does not support this conclusion.

Heat Capacity and Entropy.

S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for $Li_2(OH)_2(g)$ which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of $Li_2(OH)_2(g)$, but the bond angle O-Li-O was modified to 90° (i.e. a square planar configuration for lithium and oxygen atoms). The bond angle Li-O-H in $Li_2(OH)_2(g)$ was assumed to be 110°. The bond distance Li-O in $Li_2(OH)_2(g)$ was estimated 10% longer than that in LiOH(g). The bond distance O-H was estimated to be the same in $H_2O(g)$. The three principal moments of inertia are: I_A = [9.445] X 10^{-39}, I_B = [3.7789] X 10^{-39} and I_C = [12.8035] X 10^{-39} g. cm.^{2}

The first six selected vibrational frequencies were taken to be equal to those for $Li_2F_2(g)$ (see $Li_2F_2(g)$ table) and the rest were O-H stretching and bending frequencies.

Magnesium Dihydride (MgH_2)

(Crystal) Mol. Wt. = 26.336

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.270	- 16.250	- 16.250	INFINITE
100	3.053	1.527	13.157	- 1.163	- 17.056	- 14.543	31.782
200	6.043	4.630	8.120	- .698	- 17.756	- 11.871	12.972
298	8.450	7.431	7.431	.000	- 18.200	- 8.781	6.436
300	8.487	7.483	7.431	.016	- 18.208	- 8.723	6.354
400	10.350	10.186	7.787	.960	- 18.572	- 5.503	3.006
500	11.950	12.673	8.519	2.077	- 18.796	- 2.206	.964
600	13.200	14.965	9.405	3.336	- 18.906	1.123	- .409
700	14.230	17.080	10.352	4.710	- 18.927	4.465	- 1.394
800	15.080	19.038	11.317	6.177	- 18.891	7.804	- 2.132
900	15.750	20.854	12.277	7.720	- 18.821	11.137	- 2.704
1000	16.250	22.541	13.220	9.321	- 20.857	14.643	- 3.200
1100	16.637	24.109	14.140	10.966	- 20.740	18.186	- 3.613
1200	16.910	25.569	15.032	12.644	- 20.623	21.719	- 3.955
1300	17.151	26.932	15.896	14.347	- 20.517	25.243	- 4.244
1400	17.350	28.211	16.730	16.073	- 50.789	29.240	- 4.564
1500	17.506	29.413	17.536	17.816	- 50.309	34.940	- 5.091
1600	17.620	30.547	18.314	19.573	- 49.827	40.605	- 5.546
1700	17.708	31.618	19.065	21.339	- 49.345	46.245	- 5.945
1800	17.800	32.632	19.791	23.114	- 48.864	51.853	- 6.295
1900	17.898	33.597	20.493	24.899	- 48.381	57.435	- 6.606
2000	18.000	34.518	21.171	26.694	- 47.898	62.992	- 6.883

Dec. 31, 1960; June 30, 1963; Sept. 30, 1963

MAGNESIUM DIHYDRIDE (MgH_2) (CRYSTAL) MOL. WT. = 26.336

$\Delta H_f^\circ{}_0$ = -16.3 ± 2.2 kcal. mole^{-1}

$S^\circ_{298.15}$ = 7.43 ± 0.20 cal. deg.$^{-1}$ mole^{-1} $\Delta H_f^\circ{}_{298.15}$ = -18.2 ± 2.2 kcal. mole^{-1}

T_d = [560]°K.

Heat of Formation.

The heat of hydrolysis of MgH_2(c) was measured by G. C. Sinke and D. R. Stull, Thermal Laboratory, The Dow Chemical Company, private communication, July, 1956. The value of $\Delta H_f^\circ{}_{298.15}$ was calculated to be -19.1 ± 2 kcal. mole^{-1}. From the decomposition pressure measurements for MgH_2(c) reported by F. H. Ellinger, et al., J. Am. Chem. Soc. 77, 2647 (1955) and J. F. Stampfer, Jr., C. E. Holley, Jr. and J. F. Suttle, J. Am. Chem. Soc. 82, 3504 (1960), the values of $\Delta H_f^\circ{}_{298.15}$ for MgH_2(c) were found to be -17.9 ± 1.0 and -17.7 kcal. mole^{-1}, respectively. The value used was the average of these three.

Heat Capacity and Entropy.

The low temperature heat capacities (25-300°K.) was measured by G. C. Sinke and D. L. Hildenbrand, Thermal Laboratory, The Dow Chemical Company, private communication, February 1958. Above 300°K. the C_p values were estimated by comparison with those for MgF_2(c). $S^\circ_{298.15}$ was obtained from G. C. Sinke and D. L. Hildenbrand, loc. cit., using S°_{25} (extrap.) = 0.037 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Decomposition.

T_d was estimated from the value of ΔF_f° in the table.

Magnesium Dihydroxide ($Mg(OH)_2$)

(Crystal) GFW = 58.32674

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.726	- 218.431	- 218.431	INFINITE
100	5.167	2.320	27.933	- 2.561	- 219.873	- 213.300	466.166
200	13.592	8.670	16.652	- 1.596	- 220.769	- 206.449	225.597
298	18.437	15.100	15.100	.000	- 221.000	- 199.257	146.059
300	18.500	15.214	15.100	.034	- 221.003	- 199.122	145.060
400	21.300	20.939	15.862	2.031	- 221.025	- 191.820	104.806
500	23.400	25.924	17.387	4.269	- 220.859	- 184.534	80.660
600	25.300	30.362	19.186	6.706	- 220.546	- 177.297	64.580
700	27.000	34.391	21.074	9.321	- 220.104	- 170.121	53.114
800	28.600	38.100	22.974	12.101	- 219.553	- 163.018	44.534
900	30.200	41.561	24.849	15.041	- 218.900	- 155.989	37.879
1000	31.800	44.826	26.685	18.141	- 220.264	- 148.857	32.533

Dec. 31, 1960; Dec. 31, 1966; Mar. 31, 1967

MAGNESIUM DIHYDROXIDE ($Mg(OH)_2$) (CRYSTAL) GFW = 58.32674

$\Delta Hf^\circ_0 = -218.43 \pm 0.5$ kcal/mol

$S^\circ_{298.15} = 15.10$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -221.0 \pm 0.5$ kcal/mol

$T_d = [541]$°K

Heat of Formation.

The adopted value is an average of -221.10 and -220.86 kcal/mol obtained from $\Delta Hr^\circ_{298} = 9.08$ and 8.84 kcal/mol for the dehydration reaction $Mg(OH)_2(c) = MgO(c) + H_2O(l)$. The two values correspond to naturally occurring brucite and to synthetic $Mg(OH)_2$ prepared from MgO by hydration at 177°C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells on the heats of solution of various samples of $Mg(OH)_2$ and MgO in aqueous HCl. These studies show that the heat of dehydration is quite dependent on the nature of the MgO sample; e.g., values for synthetic $Mg(OH)_2$ vary monotonically from 9.79 to 8.84 kcal/mol for MgO ignited at temperatures from 450 to 1425°C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. We have adopted the results at 1425°C, since they are reasonably consistent with the high temperature samples on which the JANAF heat of formation for MgO is based. The uncertainty is estimated as ± 0.5 kcal/mol.

Shomate and Huffman have confirmed the heat of solution of MgO (ignited at 1000°C) within about 0.3 kcal. Their value may be combined with the heat of solution for synthetic $Mg(OH)_2$, determined under similar conditions by Torgeson and Sahama, to obtain $\Delta Hr^\circ = 8.85$ kcal/mol for the dehydration reaction. At the other extreme, the heat of solution data of Giauque and Archibald lead to $\Delta Hr^\circ = 9.74$ kcal/mol; however, this value corresponds to MgO ignited at 350°C. The MgO sample was microcrystalline and had significant excess Cp°, as suggested by Giauque and Archibald and later confirmed by data of T. H. K. Barron et al., Proc. Roy. Soc. (London) A250, 70 (1959). Giauque and Archibald intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212°C). Thus, it is not surprising that third law analysis of their decomposition pressures yields essentially the same heat of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by W. S. Fyfe, Am. J. Sci. 256, 729 (1958); D. M. Roy and R. Roy, ibid. 255, 573 (1957); G. C. Kennedy, ibid. 254, 567 (1956); G. M. Zhabrova and B. M. Kadenatsi, J. Gen. Chem. USSR (Eng. Transl.) 24, 1129 (1954); and L. G. Berg and I. S. Rassonskaya, Dokl. Akad. Nauk SSSR 81, 855 (1951). These data do not significantly affect the heat of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	$Mg(OH)_2$ Sample	Temp. of MgO Formation, °C	Heat of Dehydration $\Delta Hr^\circ_{298.15}$ (kcal/mol)	$\Delta Hf^\circ_{298.15}$
1. Taylor & Wells (1938)	Brucite	1425	9.08	-221.10
	Synthetic	1425	8.84	-220.86
	Synthetic	1000	9.18	-221.20
	Synthetic	450	9.79	-221.81
2. Torgeson (1948) - Shomate (1943)	Synthetic	1000	8.85	-220.87
3. Giauque & Archibald (1937)	Synthetic*	350	9.74	-221.74
Kp data	Synthetic*	190, 212	20.13**	-221.62

*Prepared by reaction of KOH with $MgCl_2(aq)$ at 210°C, rather than by hydration of MgO.

**For $Mg(OH)_2(c) = MgO(c) + H_2O(g)$ rather than $Mg(OH)_2(c) = MgO(c) + H_2O(l)$.

References.

1. K. Taylor and L. S. Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
2. D. R. Torgeson and Th. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948); C. H. Shomate and E. H. Huffman, ibid. 65, 1625 (1943).
3. W. F. Giauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).

Heat Capacity and Entropy.

Low temperature heat capacities are from the data (22-321°K) of Giauque and Archibald, loc. cit., who used a synthetic, macrocrystalline sample prepared by reaction of KOH with aqueous $MgCl_2$ at 210°C. The entropy is derived from the heat capacities using $S^\circ_{20} = 0.027$ eu. Above 321°K the heat capacities are extrapolated graphically. Enthalpy data (393-667°K) reported by P. N. Lashchenko and D. I. Kompanskii, Zh. Prikl. Khim. 8, 628 (1935), were stated to be based on a calorimeter temperature close to room temperature. Within this uncertainty and the experimental scatter of about ± 5%, the enthalpy data are consistent with the selected values.

Temperature of Decomposition.

Td is calculated as the temperature at which $\Delta Gr^\circ = 0$ for $Mg(OH)_2(c) = MgO(c) + H_2O(g)$.

Magnesium Dihydroxide ($Mg(OH)_2$)

(Ideal Gas)   GFW = 58.32674

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.551	-134.556	-134.556	INFINITE
100	10.764	51.319	77.706	-2.639	-135.251	-133.577	291.932
200	13.455	59.653	66.758	-1.421	-135.894	-131.770	143.992
298	15.403	65.408	65.408	.000	-136.300	-129.556	94.967
300	15.435	65.503	65.408	.029	-136.308	-129.515	94.351
400	16.927	70.157	66.032	1.650	-136.706	-127.188	69.492
500	18.067	74.063	67.258	3.402	-137.026	-124.770	54.537
600	18.962	77.439	68.680	5.255	-137.297	-122.294	44.545
700	19.694	80.418	70.148	7.189	-137.536	-119.772	37.394
800	20.320	83.090	71.602	9.191	-137.763	-117.221	32.023
900	20.869	85.516	73.015	11.251	-137.990	-114.639	27.838
1000	21.356	87.740	74.378	13.362	-140.343	-111.850	24.445
1100	21.790	89.796	75.687	15.520	-140.552	-108.992	21.655
1200	22.176	91.709	76.944	17.719	-140.762	-106.113	19.326
1300	22.519	93.498	78.149	19.954	-140.981	-103.217	17.352
1400	22.824	95.178	79.306	22.221	-171.576	-99.824	15.583
1500	23.095	96.762	80.417	24.518	-171.413	-94.703	13.798
1600	23.336	98.261	81.486	26.839	-171.244	-89.599	12.239
1700	23.549	99.682	82.515	29.184	-171.065	-84.498	10.863
1800	23.739	101.034	83.507	31.548	-170.884	-79.413	9.642
1900	23.909	102.322	84.463	33.931	-170.698	-74.336	8.551
2000	24.060	103.552	85.387	36.330	-170.511	-69.269	7.569
2100	24.195	104.729	86.280	38.742	-170.325	-64.212	6.683
2200	24.317	105.858	87.145	41.168	-170.140	-59.163	5.877
2300	24.426	106.941	87.982	43.605	-169.955	-54.122	5.143
2400	24.525	107.983	88.794	46.053	-169.773	-49.089	4.470
2500	24.614	108.986	89.582	48.510	-169.597	-44.070	3.853
2600	24.694	109.953	90.347	50.975	-169.422	-39.047	3.282
2700	24.768	110.886	91.090	53.449	-169.252	-34.036	2.755
2800	24.834	111.788	91.813	55.929	-169.087	-29.034	2.266
2900	24.895	112.660	92.517	58.415	-168.927	-24.028	1.811
3000	24.951	113.505	93.203	60.908	-168.773	-19.037	1.387
3100	25.002	114.324	93.871	63.405	-168.624	-14.048	.990
3200	25.049	115.119	94.523	65.908	-168.482	-9.068	.619
3300	25.092	115.890	95.159	68.415	-168.347	-4.086	.271
3400	25.131	116.640	95.779	70.926	-168.220	.889	-.057
3500	25.168	117.369	96.386	73.441	-168.101	5.860	-.366
3600	25.202	118.079	96.979	75.960	-167.990	10.829	-.657
3700	25.234	118.770	97.558	78.481	-167.891	15.796	-.933
3800	25.263	119.443	98.125	81.006	-167.798	20.762	-1.194
3900	25.290	120.099	98.680	83.534	-167.716	25.720	-1.441
4000	25.315	120.740	99.224	86.064	-167.646	30.678	-1.676
4100	25.339	121.365	99.756	88.597	-167.587	35.638	-1.900
4200	25.361	121.976	100.278	91.132	-167.539	40.592	-2.112
4300	25.382	122.573	100.790	93.669	-167.504	45.548	-2.315
4400	25.401	123.157	101.292	96.208	-167.481	50.500	-2.508
4500	25.419	123.728	101.784	98.749	-167.472	55.454	-2.693
4600	25.436	124.287	102.267	101.292	-167.475	60.414	-2.870
4700	25.452	124.834	102.741	103.837	-167.493	65.368	-3.040
4800	25.467	125.370	103.207	106.383	-167.525	70.324	-3.202
4900	25.482	125.895	103.665	108.930	-167.572	75.277	-3.357
5000	25.495	126.410	104.115	111.479	-167.634	80.231	-3.507
5100	25.508	126.915	104.557	114.029	-167.713	85.191	-3.651
5200	25.520	127.411	104.992	116.580	-167.807	90.145	-3.789
5300	25.531	127.897	105.419	119.133	-167.916	95.118	-3.922
5400	25.542	128.374	105.840	121.687	-168.043	100.072	-4.050
5500	25.552	128.843	106.254	124.241	-168.187	105.042	-4.174
5600	25.562	129.304	106.661	126.797	-168.350	110.004	-4.293
5700	25.571	129.756	107.063	129.354	-168.529	114.983	-4.409
5800	25.580	130.201	107.458	131.911	-168.728	119.955	-4.520
5900	25.588	130.638	107.847	134.469	-168.946	124.939	-4.628
6000	25.596	131.068	108.230	137.029	-169.181	129.919	-4.732

June 30, 1967

MAGNESIUM DIHYDROXIDE [$Mg(OH)_2$]   (IDEAL GAS)   GFW = 58.32674

Point Group [C_{2h}]

ΔHf°_0 = [-134.6 ± 3] kcal/mol

$S^\circ_{298.15}$ = [65.4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-136.3 ± 3] kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[3200](1)	[600](1)	[1400](1)
[1200](1)	[240](1)	[360](1)
[700](1)	[3300](1)	[100](1)

Bond Distances: Mg-O = [1.80] Å   O-H = [0.97] Å

Bond Angles: Mg-O-H = [105°]   O-Mg-O = [180°]   σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [95.6929] x 10^{-117} g^3 cm^6

Heat of Formation

Vapor densities of magnesium-bearing species over magnesium oxide were determined, using the transpiration method, by C. A. Alexander, J. S. Ogden and A. Levy, J. Chem. Phys. 39, 3057 (1963). The MgO reacted with water vapor present in the carrier gas to form a gaseous product, presumably $Mg(OH)_2$. The authors eliminated MgOH (and other species requiring the formation of gaseous oxygen) as a likely product by holding constant the partial pressure of water but varying the ratio of oxygen and argon in the carrier gas. Experiments with different partial pressures of water indicated that each mole of water produced an equivalent number of moles of product in the vapor. This eliminates $[Mg(OH)_2]_2$ as a possible product, but not, for example, $(MgO)_2 \cdot H_2O$. Species of the latter type are quite unlikely with magnesium, so the reaction is considered to be $MgO(c) + H_2O(g) = Mg(OH)_2(g)$. Equilibrium data (1653-2020°K) given graphically by Alexander et al. yield ΔHr°_{298} = 67.6 ± 1.9 kcal/mol by second law analysis and ΔHr°_{298} = 65.2 kcal/mol with a drift of -1.5 ± 1 eu by third law analysis.

Heat Capacity and Entropy

The infrared spectra of $Mg(OH)_2(c)$ were observed in the region 365-3700 cm^{-1} by C. Cabannes-Ott, Ann. Chim. (Paris) 5, 905-60 (1960). The vibrational frequencies of the gas are estimated by comparison with those for $Mg(OH)_2(c)$, $H_2O(g)$, $H_2O_2(g)$, MgO(g) and $MgF_2(g)$, and are adjusted to give reasonable agreement between the second and third law heats of reaction. The bond distances are estimated by comparison with those of $MgF_2(g)$, MgO(g) and $H_2O(g)$. The O-Mg-O angle is assumed to be 180°, while the Mg-O-H angle is assumed to be the same as that in $H_2O(g)$. The three principal moments of inertia are $I_A = 2.713 \times 10^{-40}$, $I_B = 18.6455 \times 10^{-39}$ and $I_C = 18.9168 \times 10^{-39}$ g cm^2.

Molybdic Acid

(Ideal Gas) GFW = 161.9535

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	,000	,000	INFINITE	-5,326	-201,456	-201,456	INFINITE
100	16,279	62,711	104,590	-4,188	-202,582	-197,967	432,657
200	21,380	75,750	87,140	-2,278	-203,108	-193,136	211,049
298	24,893	84,970	84,970	,000	-203,400	-188,170	137,932
300	24,951	85,124	84,971	,046	-203,404	-188,076	137,013
400	27,582	92,684	85,983	2,680	-203,476	-182,950	99,959
500	29,440	99,050	87,977	5,537	-203,396	-177,825	77,727
600	30,781	104,542	90,291	8,551	-203,223	-172,726	62,915
700	31,789	109,367	92,678	11,682	-202,993	-167,660	52,346
800	32,578	113,665	95,038	14,902	-202,727	-162,633	44,429
900	33,216	117,540	97,326	18,192	-202,435	-157,636	38,279
1000	33,743	121,068	99,527	21,541	-202,124	-152,675	33,367
1100	34,188	124,305	101,634	24,938	-201,805	-147,746	29,354
1200	34,566	127,297	103,650	28,377	-201,482	-142,845	26,016
1300	34,892	130,077	105,577	31,850	-201,168	-137,972	23,195
1400	35,173	132,673	107,421	35,353	-200,865	-133,123	20,781
1500	35,418	135,108	109,186	38,883	-200,580	-128,292	18,692
1600	35,633	137,401	110,879	42,436	-200,317	-123,483	16,867
1700	35,821	139,567	112,503	46,009	-200,074	-118,687	15,258
1800	35,987	141,619	114,064	49,599	-199,862	-113,907	13,830
1900	36,133	143,569	115,566	53,206	-199,676	-109,136	12,553
2000	36,264	145,426	117,013	56,826	-199,522	-104,378	11,406
2100	36,380	147,198	118,409	60,458	-199,400	-99,623	10,368
2200	36,483	148,893	119,756	64,101	-199,317	-94,874	9,425
2300	36,576	150,517	121,058	67,754	-199,270	-90,129	8,564
2400	36,660	152,075	122,318	71,416	-199,269	-85,377	7,775
2500	36,735	153,573	123,539	75,086	-199,329	-80,640	7,050
2600	36,803	155,015	124,722	78,763	-199,453	-75,884	6,379
2700	36,865	156,405	125,870	82,446	-199,657	-71,130	5,758
2800	36,921	157,747	126,984	86,136	-199,947	-66,365	5,180
2900	36,972	159,044	128,068	89,830	-206,957	-61,564	4,640
3000	37,019	160,298	129,121	93,530	-207,047	-56,552	4,120
3100	37,062	161,512	130,147	97,234	-207,145	-51,533	3,633
3200	37,101	162,690	131,145	100,942	-207,255	-46,515	3,177
3300	37,137	163,832	132,119	104,654	-207,374	-41,489	2,748
3400	37,171	164,941	133,068	108,370	-207,503	-36,460	2,344
3500	37,201	166,019	133,994	112,088	-207,642	-31,431	1,963
3600	37,230	167,068	134,898	115,810	-207,789	-26,391	1,602
3700	37,256	168,088	135,781	119,534	-207,948	-21,349	1,261
3800	37,281	169,082	136,645	123,261	-208,113	-16,300	,937
3900	37,303	170,050	137,489	126,990	-208,288	-11,254	,631
4000	37,324	170,995	138,315	130,721	-208,473	-6,201	,339
4100	37,344	171,917	139,123	134,455	-208,665	-1,140	,061
4200	37,363	172,817	139,915	138,190	-208,865	3,923	-,204
4300	37,380	173,697	140,690	141,927	-209,073	8,995	-,457
4400	37,396	174,556	141,450	145,666	-209,289	14,064	-,699
4500	37,411	175,397	142,195	149,407	-209,512	19,143	-,930
4600	37,425	176,219	142,926	153,148	-209,742	24,233	-1,151
4700	37,439	177,024	143,643	156,892	-209,980	29,320	-1,363
4800	37,451	177,812	144,347	160,636	-210,223	34,417	-1,567
4900	37,463	178,585	145,037	164,382	-210,472	39,508	-1,762
5000	37,474	179,342	145,716	168,129	-351,741	46,940	-2,052
5100	37,485	180,084	146,383	171,877	-352,278	54,932	-2,354
5200	37,495	180,812	147,038	175,626	-352,847	62,909	-2,644
5300	37,504	181,526	147,682	179,376	-353,446	70,924	-2,925
5400	37,513	182,227	148,315	183,127	-354,078	78,924	-3,194
5500	37,522	182,916	148,938	186,878	-354,735	86,955	-3,455
5600	37,530	183,592	149,551	190,631	-355,421	94,988	-3,707
5700	37,538	184,256	150,154	194,384	-356,130	103,033	-3,950
5800	37,545	184,909	150,747	198,139	-356,859	111,107	-4,187
5900	37,552	185,551	151,332	201,893	-357,610	119,175	-4,415
6000	37,558	186,182	151,907	205,649	-358,377	127,268	-4,636

June 30, 1970

MOLYBDIC ACID (H_2MoO_4) (IDEAL GAS) GFW = 161.9535

Point Group [C_{2v}]

ΔHf°_0 = -201.5 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = [84.97 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -203.4 ± 1.0 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[2000] (1)	[100] (1)	[830] (1)
[1000] (1)	[150] (1)	[200] (1)
[700] (1)	[100] (1)	[950] (1)
[800] (1)	[3600] (1)	[200] (1)
[250] (1)	[600] (1)	[250] (1)

Bond Distance: Mo-O = [1.83] Å O-H = [0.958] Å

Bond Angle: O-Mo-O = [109.5°] H-O-Mo = [104.5°]

HO-Mo-OH plane perpendicular to O=M=O plane σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.5399×10^{-113}] g^3 cm^6

Heat of Formation

The enhanced volatility of metallic molybdenum and molybdenum trioxide in the presence of water vapor at high temperatures has been investigated by several workers (1, 2, 3) using transpiration techniques. Glemser and Haeseler (1) and Buiten (2) have shown that the major volatilization reaction of the oxide is:

$$\text{A.}\quad MoO_3(c) + H_2O(g) \rightleftarrows MoO_2(OH_2)(g).$$

For the reaction of metallic molybdenum with water vapor, Belton and Jordan (3) reported the existence of $MoO_2(OH)_2(g)$ according to the equilibrium:

$$\text{B.}\quad Mo(c) + 4H_2O(g) \rightleftarrows MoO_2(OH)_2(g) + 3H_2(g).$$

Second and third law analyses of these equilibrium data are summarized below.

Investigator	Reaction	Range, °K	No. of Points	ΔHr_{298}(kcal/mol) 2nd Law	ΔHr_{298}(kcal/mol) 3rd Law	Drift gibbs/mol	*ΔHf°($MoO_2(OH)_2$) kcal/mol
Glemser and Haeseler (1)	A	873-963	Equation	36.2	31.9±0.3	-4.2	-204.0 ± 0.5
Buiten (2)	A	673-773	Equation	30.0	32.2±0.3	3.6	-203.7 ± 0.5
Belton and Jordan (3)	B	1473-1773	Equation	30.1	28.6±0.1	-0.1	-202.6 ± 0.3

* Third law values

The adopted value, ΔHf°($MoO_2(OH)_2$, g) = -203.4 ± 1.0 kcal/mol, is an average of these three results.

Heat Capacity and Entropy

The assumed tetrahedral structure for $MoO_2(OH)_2$ is from Jordan (4). The O-H bond length and H-O-Mo bond angle are assumed to be the same as for $H_2O(g)$. The Mo-O bond length is from the compilation of Sutton (5) and assumed to be the same as for Ag_2MoO_4. Individual moments of inertia are $I_A = 23.782 \times 10^{-39}$, $I_B = 25.415 \times 10^{-39}$, and $I_C = 25.478 \times 10^{-39}$ g cm^2.

The vibrational frequencies are estimated by comparison with those for $H_2SO_4(g)$ (6, 7) and are adjusted to give S°($MoO_2(OH)_2$, g) = 137.4 gibbs/mol at 1600°K. This entropy value is derived from a second law analysis of the equilibrium data for reaction B reported by Belton and Jordan (3).

References

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Amidogen (NH_2)

(Ideal Gas) Mol. Wt. = 16.02264

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-2.373	40.757	40.757	INFINITE
100	7.949	37.792	53.574	-1.578	40.450	41.015	-89.635
200	7.954	43.303	47.219	-.783	40.291	41.633	-45.492
298	8.024	46.488	46.488	.000	40.070	42.337	-31.033
300	8.027	46.538	46.488	.015	40.065	42.351	-30.851
400	8.220	48.871	46.805	.826	39.834	43.148	-23.574
500	8.492	50.733	47.410	1.661	39.619	44.002	-19.232
600	8.804	52.308	48.099	2.526	39.427	44.897	-16.353
700	9.142	53.691	48.801	3.423	39.259	45.823	-14.306
800	9.491	54.934	49.491	4.355	39.113	46.770	-12.776
900	9.841	56.072	50.160	5.321	38.988	47.736	-11.591
1000	10.180	57.127	50.804	6.323	38.884	48.713	-10.646
1100	10.501	58.112	51.424	7.357	38.798	49.700	-9.874
1200	10.799	59.039	52.021	8.422	38.729	50.695	-9.232
1300	11.071	59.914	52.595	9.516	38.673	51.694	-8.690
1400	11.319	60.744	53.147	10.635	38.628	52.697	-8.226
1500	11.542	61.533	53.680	11.779	38.591	53.704	-7.824
1600	11.743	62.284	54.195	12.943	38.559	54.711	-7.473
1700	11.923	63.001	54.692	14.126	38.534	55.724	-7.163
1800	12.084	63.688	55.173	15.327	38.513	56.733	-6.888
1900	12.229	64.345	55.638	16.543	38.497	57.748	-6.642
2000	12.359	64.975	56.089	17.772	38.482	58.762	-6.421
2100	12.475	65.581	56.527	19.014	38.469	59.776	-6.221
2200	12.580	66.164	56.952	20.267	38.457	60.790	-6.039
2300	12.675	66.725	57.365	21.530	38.446	61.806	-5.873
2400	12.760	67.267	57.766	22.802	38.436	62.822	-5.720
2500	12.838	67.789	58.157	24.082	38.423	63.837	-5.580
2600	12.908	68.294	58.537	25.369	38.412	64.855	-5.451
2700	12.972	68.783	58.907	26.663	38.400	65.871	-5.332
2800	13.031	69.255	59.269	27.963	38.386	66.889	-5.221
2900	13.084	69.714	59.621	29.269	38.373	67.908	-5.117
3000	13.133	70.158	59.965	30.580	38.357	68.926	-5.021
3100	13.177	70.589	60.301	31.895	38.342	69.945	-4.931
3200	13.218	71.008	60.629	33.215	38.324	70.965	-4.846
3300	13.256	71.416	60.949	34.539	38.303	71.985	-4.767
3400	13.291	71.812	61.263	35.866	38.283	73.005	-4.693
3500	13.323	72.198	61.570	37.197	38.259	74.027	-4.622
3600	13.353	72.573	61.870	38.531	38.232	75.051	-4.556
3700	13.381	72.940	62.165	39.868	38.203	76.073	-4.493
3800	13.407	73.297	62.453	41.207	38.172	77.098	-4.434
3900	13.431	73.645	62.735	42.549	38.138	78.125	-4.378
4000	13.453	73.986	63.013	43.893	38.102	79.148	-4.324
4100	13.474	74.318	63.284	45.239	38.062	80.176	-4.274
4200	13.493	74.643	63.551	46.588	38.020	81.204	-4.225
4300	13.511	74.961	63.812	47.938	37.975	82.231	-4.179
4400	13.529	75.272	64.069	49.290	37.927	83.258	-4.135
4500	13.545	75.576	64.322	50.644	37.875	84.288	-4.093
4600	13.560	75.874	64.570	51.999	37.822	85.324	-4.054
4700	13.574	76.166	64.813	53.356	37.765	86.356	-4.015
4800	13.587	76.451	65.053	54.714	37.705	87.394	-3.979
4900	13.600	76.732	65.288	56.073	37.642	88.426	-3.944
5000	13.612	77.007	65.520	57.434	37.576	89.461	-3.910
5100	13.623	77.276	65.748	58.795	37.507	90.503	-3.878
5200	13.633	77.541	65.972	60.158	37.436	91.542	-3.847
5300	13.643	77.801	66.193	61.522	37.360	92.584	-3.818
5400	13.653	78.056	66.410	62.887	37.282	93.623	-3.789
5500	13.662	78.306	66.624	64.252	37.201	94.673	-3.762
5600	13.670	78.553	66.835	65.619	37.117	95.712	-3.735
5700	13.678	78.795	67.043	66.986	37.029	96.763	-3.710
5800	13.686	79.033	67.247	68.355	36.939	97.810	-3.685
5900	13.694	79.267	67.449	69.724	36.845	98.860	-3.662
6000	13.701	79.497	67.648	71.093	36.749	99.911	-3.639

Dec. 31, 1960; Dec. 31, 1965

AMIDOGEN (NH_2) (IDEAL GAS) MOL. WT. = 16.02264

Point Group C_{2v}

$S^\circ_{298.15}$ = 46.5 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 2

$\Delta H^\circ_{f\ 0}$ = 40.8 ± 3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 40.1 ± 3 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
3173 (1)
1499 (1)
3220 (1)

Bond Distance: N-H = 1.024 Å

Bond Angle: H-N-H = 103°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 8.5 \times 10^{-120}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation of amidogen at 298.15°K., ΔH_f° (NH_2, g) = 39.8 kcal. mole^{-1}, was obtained from the pyrolysis of N_2H_4 by J. A. Kerr, R. C. Sekhar and A. F. Trotman-Dickenson, J. Chem. Soc. 3217 (1963). They have reinvestigated the rate constants of the thermal decomposition $N_2H_4 \rightarrow 2NH_2$ at different temperatures using the same techniques as M. Szwarc, J. Chem. Phys. 17, 505 (1949), and revised the activation energy to 57.1 kcal. mole^{-1} for the reaction at 874°K. (instead of 60 kcal. mole^{-1} at 1000°K. reported by Szwarc). The activation energy was assumed to be the same as the dissociation energy of the N-N bond in hydrazine. Using all JANAF auxiliary data, one obtains D_0° (H_2N-NH_2) = 55.4 ± 3 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298}$ (NH_2, g) = 40.1 ± 3 kcal. mole^{-1}.

F. M. Page, Trans Faraday Soc. 57, 1254 (1961), has measured the electron affinity of NH_2 and has applied the results to calculate the dissociation energy, D_0 (H-NH_2) = 102 ± 3 kcal. mole^{-1}. This value leads to the heat of formation $\Delta H^\circ_{f\ 298}$ (NH_2, g) = 40.4 ± 3 kcal. mole^{-1} which is in good agreement with the value selected. E. R. Lippincott and M. O. Dayhoff, Spectrochim. Acta, 16, 807 (1960) calculated theoretically the dissociation energy D_0 (H_2N-NH_2) = 59 kcal. mole^{-1} which gives $\Delta H^\circ_{f\ 298}$ (NH_2, g) = 41.9 kcal. mole^{-1}.

Heat Capacity and Entropy.

The bond distance and angle were measured from the electronic absorption spectra of NH_2 by K. Dressler and D. A. Ramsay, Phil. Trans. Roy. Soc. London Ser. A 251, 553 (1959). The three principal moments of inertia are $I_A = 0.1189 \times 10^{-39}$ g. cm.^{2}, $I_B = 0.2149 \times 10^{-39}$ g. cm.^{2} and $I_C = 0.3338 \times 10^{-39}$ g. cm.^{2}

The selected vibrational frequencies were obtained from the infrared spectrum of NH_2 by matrix isolation by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965). K. N. Tanner and R. L. King, Nature 181, 963 (1958) have also determined the vibrational frequencies ω_1 = 3200 cm.$^{-1}$ and ω_3 = 3280 cm.$^{-1}$ by flash photolysis and calculated ω_2 = 1060 cm.$^{-1}$ The symmetric and the antisymmetric stretching frequencies are in good agreement. M. Tsuboi, Spectrochim. Acta 16, 505 (1960), has observed NH_2 bending frequencies, 1572 cm.$^{-1}$, 1619 cm.$^{-1}$ and 1623 cm.$^{-1}$, in $HCONH_2$(g), $C_6H_5NH_2$(g) and CH_3NH_2(g), respectively. In light of these observations and the adopted ω_2, Tanner and King's bending frequency seems to be in error.

Diimide, Cis-(N_2H_2)

(Ideal Gas) Mol. Wt. = 30.02934

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.416	52.580	52.580	INFINITE
100	7.950	43.355	59.564	-1.621	51.931	53.846	-117.674
200	8.095	48.889	52.998	-.822	51.424	55.948	-61.134
298	8.737	52.223	52.223	.000	50.900	58.281	-42.719
300	8.753	52.277	52.223	.016	50.890	58.326	-42.489
400	9.784	54.932	52.578	.941	50.424	60.878	-33.260
500	10.877	57.234	53.284	1.975	50.056	63.535	-27.770
600	11.882	59.307	54.118	3.114	49.783	66.259	-24.134
700	12.769	61.207	54.996	4.347	49.586	69.021	-21.548
800	13.548	62.964	55.884	5.664	49.454	71.807	-19.616
900	14.231	64.600	56.763	7.054	49.373	74.607	-18.116
1000	14.830	66.131	57.624	8.507	49.334	77.412	-16.918
1100	15.356	67.570	58.463	10.017	49.330	80.220	-15.938
1200	15.818	68.926	59.279	11.576	49.354	83.029	-15.121
1300	16.222	70.209	60.071	13.179	49.402	85.832	-14.429
1400	16.576	71.424	60.839	14.819	49.467	88.632	-13.835
1500	16.887	72.578	61.583	16.493	49.546	91.429	-13.321
1600	17.161	73.677	62.305	18.195	49.634	94.217	-12.869
1700	17.402	74.725	63.005	19.924	49.733	97.001	-12.470
1800	17.615	75.726	63.684	21.675	49.838	99.777	-12.114
1900	17.803	76.683	64.343	23.446	49.950	102.551	-11.796
2000	17.970	77.601	64.983	25.235	50.066	105.316	-11.508
2100	18.119	78.481	65.605	27.039	50.184	108.075	-11.247
2200	18.252	79.327	66.210	28.858	50.305	110.829	-11.009
2300	18.372	80.141	66.798	30.689	50.428	113.577	-10.792
2400	18.479	80.926	67.371	32.532	50.553	116.320	-10.592
2500	18.575	81.682	67.928	34.385	50.676	119.056	-10.407
2600	18.663	82.412	68.471	36.247	50.801	121.791	-10.237
2700	18.742	83.118	69.001	38.117	50.925	124.519	-10.079
2800	18.814	83.801	69.517	39.995	51.049	127.240	-9.931
2900	18.879	84.462	70.021	41.880	51.174	129.964	-9.794
3000	18.939	85.103	70.513	43.771	51.296	132.677	-9.665
3100	18.993	85.725	70.994	45.667	51.418	135.385	-9.544
3200	19.043	86.329	71.464	47.569	51.538	138.092	-9.431
3300	19.089	86.916	71.923	49.476	51.656	140.795	-9.324
3400	19.132	87.486	72.372	51.387	51.774	143.496	-9.223
3500	19.171	88.041	72.812	53.302	51.888	146.192	-9.128
3600	19.207	88.582	73.243	55.221	52.000	148.883	-9.038
3700	19.241	89.109	73.665	57.143	52.109	151.573	-8.953
3800	19.272	89.622	74.078	59.069	52.217	154.262	-8.872
3900	19.301	90.123	74.483	60.998	52.322	156.947	-8.795
4000	19.327	90.612	74.880	62.929	52.423	159.627	-8.721
4100	19.352	91.090	75.270	64.863	52.522	162.304	-8.651
4200	19.376	91.556	75.652	66.799	52.617	164.984	-8.585
4300	19.398	92.013	76.027	68.738	52.711	167.654	-8.521
4400	19.418	92.459	76.395	70.679	52.801	170.325	-8.460
4500	19.437	92.895	76.757	72.622	52.887	172.996	-8.401
4600	19.455	93.323	77.113	74.566	52.971	175.667	-8.346
4700	19.472	93.741	77.462	76.513	53.052	178.335	-8.292
4800	19.488	94.151	77.805	78.461	53.129	181.001	-8.241
4900	19.503	94.553	78.143	80.410	53.203	183.661	-8.191
5000	19.517	94.948	78.475	82.361	53.274	186.319	-8.144
5100	19.531	95.334	78.802	84.314	53.342	188.981	-8.098
5200	19.543	95.714	79.124	86.268	53.408	191.639	-8.054
5300	19.555	96.086	79.440	88.223	53.469	194.300	-8.012
5400	19.567	96.452	79.752	90.179	53.527	196.951	-7.971
5500	19.577	96.811	80.059	92.136	53.581	199.611	-7.931
5600	19.588	97.164	80.361	94.094	53.632	202.262	-7.893
5700	19.597	97.510	80.659	96.053	53.680	204.924	-7.857
5800	19.607	97.851	80.952	98.014	53.725	207.575	-7.821
5900	19.615	98.187	81.242	99.975	53.766	210.222	-7.787
6000	19.624	98.516	81.527	101.937	53.804	212.876	-7.754

Dec. 31, 1965

DIIMIDE, CIS-(N_2H_2) (IDEAL GAS) MOL. WT. = 30.02934

Point Group C_{2v}

$S^\circ_{298.15}$ = [52.2] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 52.6 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 50.9 ± 5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

Bond Distance: N-H = [1.014] Å N-N = [1.23] Å

Bond Angle: H-N-N = [100]°

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.3988] X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

The standard enthalpy of formation, $\Delta H^\circ_{f\ 298}$ (N_2H_2; g) = 50.9 kcal. mole^{-1}, was calculated from the appearance and ionization potentials of di-imide reported by S. N. Foner and R. L. Hudson, J. Chem. Phys. 29, 442 (1958), using the JANAF $\Delta H^\circ_{f\ 0}$ (N_2H_4; g) = 26.1 kcal. mole^{-1} in calculation. For example:

	$\Delta H^\circ_{r\ 0}$
$N_2H_4(g) \rightarrow N_2H_2^+ + H_2(g) + e$	11.0 ± 0.2 e.v.
$N_2H_2(g) \rightarrow N_2H_2^+ + e$	9.85 ± 0.1 e.v.
$N_2H_4(g) \rightarrow N_2H_2(g) + H_2$	1.15 ± 0.2 e.v. (26.5 ± 5 kcal. mole^{-1})

From the above heat of formation and that for NH(g) in the JANAF Tables 12-31-65, one can calculate a N-N bond energy of 109.4 ± 5 kcal. mole^{-1} at 0°K. This is in agreement with the N-N bond in molecules such as N_2F_2.

Heat Capacity and Entropy.

The bond distances and angle were obtained from a quantum-mechanical calculation by W. Wheland and P. S. K. Chen, J. Chem. Phys. 24, 67 (1956). The three principal moments of inertia are I_A = [0.3116] X 10^{-39}, I_B = [1.9686] X 10^{-39} and I_C = [2.2802] X 10^{-39} g. cm.^{2}

Since there are 12 valency electrons in N_2H_2, A. D. Walsh, J. Chem. Soc. 2288 (1953), has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. E. J. Blau and B. F. Hochheimer, J. Chem. Phys. 41, 1174 (1964), have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N_2H_4. The spectrum of the solid N_2H_2 at liquid nitrogen temperature agrees with the predicted non-linear planar structure, and the molecule N_2H_2 appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis N_2H_2(s) which have been adopted here for gaseous cis N_2H_2. Blau and Hochheimer also observed two gas phase bands (1277 - 1314 and 3050 - 3190 cm.$^{-1}$). K. Rosengren and G. C. Pimentel, J. Chem. Phys. 43, 507 (1965), have observed these bands in matrix isolation studies. They assigned ω_1 or ω_4 = 3074 cm.$^{-1}$ and ω_3 = 1279 cm.$^{-1}$ which are in satisfactory agreement with the selected frequencies.

Sodium Hydroxide, Dimeric ($Na_2O_2H_2$)

(Ideal Gas) Mol. Wt. = 79.99434

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.435	-151.754	-151.754	INFINITE
100	11.929	56.308	88.609	-3.230	-152.961	-150.863	329.711
200	16.732	66.319	75.110	-1.758	-153.946	-148.369	162.130
298	18.949	73.442	73.442	.000	-154.800	-145.448	106.616
300	18.985	73.559	73.442	.035	-154.815	-145.389	105.916
400	20.765	79.272	74.209	2.025	-156.918	-142.023	77.598
500	22.248	84.070	75.714	4.178	-157.677	-138.207	60.410
600	23.434	88.236	77.461	6.465	-158.287	-134.254	48.902
700	24.381	91.922	79.269	8.857	-158.787	-130.209	40.653
800	25.157	95.230	81.061	11.335	-159.203	-126.097	34.448
900	25.813	98.232	82.804	13.884	-159.560	-121.936	29.610
1000	26.381	100.981	84.486	16.495	-159.874	-117.737	25.731
1100	26.881	103.520	86.103	19.158	-160.168	-113.513	22.553
1200	27.324	105.878	87.654	21.869	-206.919	-108.344	19.732
1300	27.720	108.081	89.141	24.622	-206.761	-100.135	16.834
1400	28.073	110.148	90.569	27.412	-206.583	-91.940	14.352
1500	28.388	112.096	91.939	30.235	-206.391	-83.757	12.203
1600	28.671	113.937	93.257	33.088	-206.187	-75.588	10.325
1700	28.924	115.683	94.526	35.968	-205.968	-67.430	8.669
1800	29.151	117.343	95.748	38.872	-205.744	-59.289	7.199
1900	29.355	118.925	96.926	41.798	-205.513	-51.157	5.884
2000	29.538	120.435	98.064	44.742	-205.280	-43.042	4.703
2100	29.704	121.881	99.164	47.705	-205.040	-34.938	3.636
2200	29.853	123.266	100.228	50.683	-204.802	-26.842	2.667
2300	29.988	124.596	101.259	53.675	-204.561	-18.760	1.783
2400	30.110	125.875	102.258	56.680	-204.323	-10.682	.973
2500	30.221	127.106	103.228	59.696	-204.088	-2.625	.229
2600	30.322	128.294	104.169	62.724	-203.854	5.433	-.457
2700	30.414	129.440	105.084	65.761	-203.626	13.475	-1.091
2800	30.498	130.547	105.974	68.806	-203.405	21.511	-1.679
2900	30.575	131.619	106.840	71.860	-203.187	29.547	-2.227
3000	30.646	132.657	107.683	74.921	-202.979	37.564	-2.737
3100	30.711	133.663	108.505	77.989	-202.776	45.577	-3.213
3200	30.771	134.639	109.306	81.063	-202.584	53.586	-3.660
3300	30.826	135.586	110.088	84.143	-202.403	61.590	-4.079
3400	30.877	136.507	110.852	87.228	-202.232	69.585	-4.473
3500	30.924	137.403	111.598	90.318	-202.075	77.582	-4.844
3600	30.968	138.275	112.327	93.413	-201.931	85.568	-5.195
3700	31.008	139.124	113.040	96.512	-201.803	93.549	-5.526
3800	31.046	139.951	113.737	99.614	-201.690	101.539	-5.840
3900	31.081	140.758	114.420	102.721	-201.597	109.510	-6.137
4000	31.114	141.546	115.088	105.831	-201.523	117.485	-6.419
4100	31.145	142.314	115.743	108.943	-201.472	125.467	-6.688
4200	31.173	143.065	116.384	112.059	-201.444	133.435	-6.943
4300	31.200	143.799	117.013	115.178	-201.440	141.412	-7.187
4400	31.225	144.516	117.630	118.299	-201.467	149.381	-7.420
4500	31.249	145.218	118.236	121.423	-201.524	157.360	-7.642
4600	31.271	145.906	118.830	124.549	-201.614	165.333	-7.855
4700	31.292	146.578	119.413	127.677	-201.742	173.314	-8.059
4800	31.312	147.237	119.986	130.808	-201.909	181.294	-8.255
4900	31.331	147.883	120.548	133.940	-202.121	189.281	-8.442
5000	31.348	148.516	121.102	137.074	-202.381	197.269	-8.623
5100	31.365	149.137	121.645	140.209	-202.694	205.271	-8.796
5200	31.380	149.746	122.180	143.347	-203.060	213.267	-8.963
5300	31.395	150.344	122.706	146.485	-203.489	221.285	-9.125
5400	31.409	150.931	123.223	149.626	-203.983	229.296	-9.280
5500	31.423	151.508	123.732	152.767	-204.548	237.322	-9.430
5600	31.435	152.074	124.233	155.910	-205.188	245.360	-9.576
5700	31.447	152.631	124.726	159.054	-205.906	253.412	-9.716
5800	31.459	153.178	125.212	162.200	-206.709	261.478	-9.853
5900	31.470	153.715	125.691	165.346	-207.602	269.566	-9.985
6000	31.480	154.244	126.162	168.493	-208.586	277.660	-10.114

Mar. 31, 1966

SODIUM HYDROXIDE, DIMERIC ($Na_2O_2H_2$) (IDEAL GAS) MOL. WT. = 79.99434

Point Group C_{2h}

$S^\circ_{298.15}$ = [73.4] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -151.8 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -154.8 ± kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[350](1)	[3700](1)
[209](1)	[3700](1)
[270](1)	[1250](1)
[201](1)	[1250](1)
[294](1)	[1250](1)
[313](1)	[1250](1)

Bond Distance: Na-O = [2.17] Å O-H = [0.96] Å

Bond Angle: Na-O-Na = [90°] Na-O-H = [110]° σ = 2

Products of the Moments of Inertia: $I_AI_BI_C$ = [8.156754] X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

See NaOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. F. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for $Li_2(OH)_2(g)$ which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the angle O-Li-O = 100°. The last one was adopted for the molecular configuration of $Na_2(OH)_2$, but the bond angle O-Na-O was modified to 90° (i.e. a square planar configuration for sodium and oxygen atoms). The bond angle Na-O-H in $Na_2(OH)_2(g)$ was assumed to be 110°. The bond distance O-H was estimated to be the same in $H_2O(g)$. The three principal moments of inertia are I_A = [14.0831] X 10^{-39}, I_B = [18.1878] X 10^{-39} and I_C = [31.8449] X 10^{-39} g. cm.^{2}

The first six selected vibrational frequencies were taken to be equal to those for $Na_2F_2(g)$ (see $Na_2F_2(g)$ table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.

Water (H_2O)

(Ideal Gas) Mol. Wt. = 18.016

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.367	-57.103	-57.103	INFINITE
100	7.961	36.396	52.202	-1.581	-57.433	-56.557	123.600
200	7.969	41.916	45.837	-.784	-57.579	-55.635	60.792
298	8.025	45.106	45.106	.000	-57.798	-54.636	40.048
300	8.027	45.155	45.106	.015	-57.803	-54.617	39.786
400	8.186	47.484	45.422	.825	-58.042	-53.519	29.240
500	8.415	49.334	46.026	1.654	-58.277	-52.361	22.886
600	8.676	50.891	46.710	2.509	-58.500	-51.156	18.633
700	8.954	52.249	47.406	3.390	-58.710	-49.915	15.583
800	9.246	53.464	48.089	4.300	-58.905	-48.646	13.289
900	9.547	54.570	48.749	5.240	-59.084	-47.352	11.498
1000	9.851	55.592	49.382	6.209	-59.246	-46.040	10.062
1100	10.152	56.545	49.991	7.210	-59.391	-44.712	8.883
1200	10.444	57.441	50.575	8.240	-59.519	-43.371	7.899
1300	10.723	58.288	51.136	9.298	-59.634	-42.022	7.064
1400	10.987	59.092	51.675	10.384	-59.734	-40.663	6.347
1500	11.233	59.859	52.196	11.495	-59.824	-39.297	5.725
1600	11.462	60.591	52.698	12.630	-59.906	-37.927	5.180
1700	11.674	61.293	53.183	13.787	-59.977	-36.549	4.699
1800	11.869	61.965	53.652	14.964	-60.041	-35.170	4.270
1900	12.048	62.612	54.107	16.160	-60.099	-33.786	3.886
2000	12.214	63.234	54.548	17.373	-60.150	-32.401	3.540
2100	12.366	63.834	54.976	18.602	-60.198	-31.012	3.227
2200	12.505	64.412	55.392	19.846	-60.242	-29.621	2.942
2300	12.634	64.971	55.796	21.103	-60.282	-28.229	2.682
2400	12.753	65.511	56.190	22.372	-60.321	-26.832	2.443
2500	12.863	66.034	56.573	23.653	-60.359	-25.439	2.224
2600	12.965	66.541	56.947	24.945	-60.393	-24.040	2.021
2700	13.059	67.032	57.311	26.246	-60.428	-22.641	1.833
2800	13.146	67.508	57.667	27.556	-60.462	-21.242	1.658
2900	13.228	67.971	58.014	28.875	-60.496	-19.838	1.495
3000	13.304	68.421	58.354	30.201	-60.530	-18.438	1.343
3100	13.374	68.858	58.685	31.535	-60.562	-17.034	1.201
3200	13.441	69.284	59.010	32.876	-60.596	-15.630	1.067
3300	13.503	69.698	59.328	34.223	-60.631	-14.223	.942
3400	13.562	70.102	59.639	35.577	-60.666	-12.818	.824
3500	13.617	70.496	59.943	36.936	-60.703	-11.409	.712
3600	13.669	70.881	60.242	38.300	-60.741	-10.000	.607
3700	13.716	71.256	60.534	39.669	-60.782	-8.589	.507
3800	13.764	71.622	60.821	41.043	-60.822	-7.177	.413
3900	13.808	71.980	61.103	42.422	-60.865	-5.766	.323
4000	13.850	72.331	61.379	43.805	-60.910	-4.353	.238
4100	13.890	72.673	61.651	45.192	-60.957	-2.938	.157
4200	13.927	73.008	61.917	46.583	-61.006	-1.522	.079
4300	13.963	73.336	62.179	47.977	-61.056	-.105	.005
4400	13.997	73.658	62.436	49.375	-61.109	1.311	-.065
4500	14.030	73.973	62.689	50.777	-61.164	2.729	-.133
4600	14.061	74.281	62.938	52.181	-61.220	4.154	-.197
4700	14.091	74.584	63.182	53.589	-61.279	5.576	-.259
4800	14.120	74.881	63.423	55.000	-61.339	6.998	-.319
4900	14.148	75.172	63.660	56.413	-61.401	8.422	-.376
5000	14.174	75.459	63.893	57.829	-61.465	9.844	-.430
5100	14.201	75.740	64.122	59.248	-61.532	11.275	-.483
5200	14.228	76.016	64.348	60.669	-61.600	12.700	-.534
5300	14.254	76.287	64.571	62.093	-61.669	14.135	-.583
5400	14.279	76.553	64.791	63.520	-61.741	15.560	-.630
5500	14.303	76.816	65.007	64.949	-61.813	16.995	-.675
5600	14.328	77.074	65.220	66.381	-61.889	18.426	-.719
5700	14.351	77.327	65.430	67.815	-61.965	19.862	-.762
5800	14.375	77.577	65.637	69.251	-62.043	21.299	-.803
5900	14.396	77.823	65.842	70.690	-62.122	22.736	-.842
6000	14.422	78.065	66.044	72.131	-62.203	24.174	-.880

March 31, 1961

ΔH°_{f0} = -57.103 kcal. mole^{-1}

Point Group C_{2v}

ΔH°_f 298.15 = -57.7979 kcal. mole^{-1}

$S^\circ_{298.15}$ = 45.106 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
3657.05 (1)
1594.59 (1)
3755.79 (1)

Bond Length and Angle   O-H distance = 0.9584 Å   H-O-H angle = 104.45°   σ = 2

Product of Moments of Inertia $I_AI_BI_C$ = 5.7658 X 10^{-120} g.^{3} cm.^{6}

Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, H. H. Claassen and J. H. Shaw, J. Research Natl. Bur. Standards 49, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatt, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p, S, and H_T-H_0 at T = 298.15°K. was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards 35, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.

Hydrogen Peroxide (H_2O_2)

(Gas) Mol. Wt. = 34.016

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.594	-31.025	-31.025	INFINITE
100	8.013	44.558	62.538	-1.798	-31.682	-29.559	64.598
200	8.813	50.316	54.701	-.877	-32.060	-27.174	29.693
298	10.305	55.660	55.660	.000	-32.530	-25.208	18.477
300	10.330	55.724	55.660	.019	-32.537	-25.163	18.330
400	11.580	58.872	56.081	1.116	-32.844	-22.655	12.377
500	12.560	61.565	56.915	2.325	-33.065	-20.081	8.777
600	13.310	63.925	57.891	3.621	-33.225	-17.469	6.363
700	13.860	66.019	58.905	4.980	-33.345	-14.832	4.630
800	14.300	67.900	59.914	6.389	-33.440	-12.181	3.328
900	14.690	69.607	60.897	7.839	-33.516	-9.519	2.311
1000	15.020	71.173	61.848	9.325	-33.576	-6.850	1.497
1100	15.330	72.619	62.762	10.843	-33.622	-4.173	.829
1200	15.610	73.965	63.640	12.390	-33.658	-1.495	.272
1300	15.870	75.225	64.483	13.964	-33.684	1.186	-.199
1400	16.110	76.410	65.293	15.563	-33.703	3.870	-.604
1500	16.330	77.529	66.072	17.185	-33.718	6.554	-.955

December 31, 1960.

Hydrogen Peroxide (H_2O_2) (Gas)

Mol. Wt. = 34.016

$H_f^\circ{}_{298.15} = -32.53$ kcal. mole^{-1}

$S^\circ_{298.15} = 55.660$ cal. deg.$^{-1}$ mole^{-1}

Point Group C_2

C_p from P. A. Giguère and I. D. Lin, J. Am. Chem. Soc. 77, 6477 (1955). C_p below 298.15°K. estimated.

Sulfuric Acid (H_2SO_4)

(Liquid) GFW = 98.07754

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	33.200	37.501	37.501	.000	- 194.548	- 164.928	120.895
300	33.290	37.707	37.502	.062	- 194.535	- 164.745	120.016
400	36.700	47.790	38.853	3.575	- 194.237	- 154.912	84.640
500	38.650	56.206	41.506	7.350	- 193.561	- 145.155	63.447
600	40.000	63.380	44.569	11.287	- 192.691	- 135.553	49.375
700	40.830	69.611	47.711	15.330	- 191.706	- 126.082	39.364
800	41.447	75.105	50.799	19.445	- 203.718	- 118.048	32.249
900	41.900	80.015	53.777	23.614	- 202.327	- 107.422	26.086
1000	42.178	84.445	56.626	27.819	- 200.935	- 96.950	21.188
1100	42.307	88.471	59.341	32.044	- 199.557	- 86.620	17.210
1200	42.400	92.157	61.924	36.279	- 198.196	- 76.412	13.917
1300	42.467	95.553	64.382	40.523	- 196.855	- 66.317	11.149
1400	42.500	98.702	66.722	44.772	- 195.535	- 56.326	8.793
1500	42.500	101.634	68.953	49.022	- 194.241	- 46.429	6.765

Dec. 31, 1960; Dec. 31, 1966

SULFURIC ACID (H_2SO_4) (LIQUID) GFW = 98.07754

$S^\circ_{298.15}$ = 37.501 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -194.548 kcal/mol

Tm = 283.53°K

ΔHm° = 2.56 kcal/mol

Tb = [608.6]°K

ΔHv° = [13.39] kcal/mol

Heat of Formation.

The heat of combustion (ΔHc°) of rhombic sulfur (c) to H_2SO_4(aq), i.e. S(c, rhombic) + 3/2 O_2(g) + H_2O(l) = $H_2SO_4(nH_2O)$, has been determined by many investigators. Based on the reported ΔHc° data, values of $\Delta Hf^\circ_{298}(H_2SO_4,l)$ are derived using heats of solution and dilution for H_2SO_4(l), taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Technical Note 270-1, Natl. Bur. Std., 1965. The results obtained are presented in the table below. The value of $\Delta Hf^\circ_{298}(H_2SO_4,l)$ is adopted as -194.548 ± 0.10 kcal/mol, which is the same as that given by Technical Note 270-1, loc. cit.

Investigator	Product	ΔHc°, kcal/mol	ΔHf°_{298}, kcal/mol
1. McCullough et al. (1953)	$H_2SO_4(70H_2O)$	-143.58 ± 0.09	-194.400
2. Scott et al. (1956)	$H_2SO_4(75H_2O)$	-143.98 ± 0.22	-194.775
3. Good et al. (1960)	$H_2SO_4(115H_2O)$	-143.85 ± 0.06	-194.521
4. Mansson and Sunner (1963)	$H_2SO_4(115H_2O)$	-143.93 ± 0.07	-194.601

1. J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, J. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good and G. Waddington, J. Am. Chem. Soc. 75, 5075 (1953).
2. D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Messerly, I. A. Hossenlopp, F. R. Frow and G. Waddington, J. Am. Chem. Soc. 78, 5463 (1956).
3. W. D. Good, J. L. Lacina and J. P. McCullough, J. Am. Chem. Soc. 82, 5589 (1960).
4. M. Mansson and S. Sunner, Acta Chem. Scand. 17, 723 (1963).

Heat Capacity and Entropy.

The heat capacities, 283.46 to 300°K, were measured by W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Am. Chem. Soc. 82, 62 (1960). The Cp values above 300°C are obtained from graphical extrapolation. The value of S°_{298} was reported by Giauque, Hornung, Kunzler and Rubin, loc. cit., based on low temperature heat capacity measurements of H_2SO_4(c).

Melting Data.

Tm and ΔHm° are taken from T. R. Rubin and W. F. Giauque, J. Am. Chem. Soc. 74, 800 (1952). The value, Tm=283.53°K, has been reported by C. M. Gable, H. F. Betz and S. H. Maron, J. Am. Chem. Soc. 72, 1445 (1950), as well as J. E. Kunzler and W. F. Giauque, J. Am. Chem. Soc. 74, 797 (1952). The heat of melting (ΔHm°) has also been determined by the following investigators:

Hm° kcal/mol	Source
2.35	Pickering, Proc. Roy. Soc. (London) 49, 11 (1891).
2.25	Hantzsch, Z. Physik, Chem. 61, 262 (1907).
2.24	Knietsch, quoted by Hantsch, loc. cit.
2.55	Brönsted, Z. Physik, Chem. 68, 693 (1910).
2.56	Rubin and Giauque, J. Am. Chem. Soc. 74, 800 (1952).

Vaporization Data.

Tb is the temperature at which the Gibbs energy change (ΔGr°) for the reaction H_2SO_4(l) = H_2SO_4(g) approaches zero. The difference between ΔHf° for H_2SO_4(g) and H_2SO_4(l) at Tb is ΔHv°.

According to G. P. Luchinskii, Zh. Fiz. Khim. 30, 1207 (1956), the total vapor pressure over H_2SO_4(l) reaches one atmosphere at 553°K with a vapor composition of 76.6 mole percent SO_3, 22.6% H_2SO_4, and 0.8% H_2O. This composition implies that the real liquid phase enhances the vapor decomposition by reducing the partial pressure of water vapor.

Sulfuric Acid (H_2SO_4) (Ideal Gas) GFW = 98.07754

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.652	-173.425	-173.425	INFINITE
100	8.985	54.518	82.913	-2.840	-174.924	-169.361	370.138
200	14.549	62.396	70.748	-1.670	-176.142	-163.306	178.452
298	19.266	69.129	69.129	.000	-177.000	-156.810	114.945
300	19.343	69.248	69.129	.036	-177.013	-156.685	114.145
400	22.905	75.327	69.934	2.157	-178.107	-149.796	81.845
500	25.506	80.733	71.563	4.585	-178.778	-142.636	62.346
600	27.410	85.560	73.501	7.235	-179.195	-135.364	49.306
700	28.843	89.898	75.539	10.051	-179.437	-128.014	39.968
800	29.962	93.825	77.583	12.993	-192.622	-121.928	33.309
900	30.869	97.408	79.590	16.036	-192.357	-113.105	27.466
1000	31.625	100.701	81.539	19.162	-192.044	-104.315	22.798
1100	32.268	103.746	83.421	22.358	-191.695	-95.561	18.986
1200	32.821	106.578	85.234	25.613	-191.314	-86.836	15.815
1300	33.302	109.224	86.979	28.920	-190.910	-78.145	13.137
1400	33.722	111.708	88.657	32.271	-190.488	-69.487	10.847
1500	34.091	114.047	90.273	35.662	-190.053	-60.859	8.867
1600	34.416	116.258	91.828	39.088	-189.607	-52.262	7.139
1700	34.703	118.353	93.327	42.544	-189.151	-43.689	5.617
1800	34.957	120.344	94.774	46.027	-188.693	-35.147	4.267
1900	35.184	122.241	96.170	49.535	-188.231	-26.629	3.063
2000	35.386	124.050	97.519	53.063	-187.769	-18.137	1.982
2100	35.566	125.781	98.824	56.611	-187.307	-9.666	1.006
2200	35.728	127.440	100.087	60.176	-186.850	-1.219	.121
2300	35.874	129.031	101.311	63.756	-186.394	7.209	-.685
2400	36.005	130.561	102.498	67.350	-185.944	15.620	-1.422
2500	36.124	132.033	103.650	70.957	-185.501	24.004	-2.098
2600	36.231	133.452	104.769	74.575	-185.061	32.379	-2.722
2700	36.329	134.821	105.857	78.203	-184.630	40.733	-3.297
2800	36.418	136.144	106.915	81.840	-184.207	49.069	-3.830
2900	36.499	137.423	107.945	85.486	-183.790	57.400	-4.326
3000	36.573	138.662	108.949	89.140	-183.382	65.708	-4.787
3100	36.641	139.862	109.927	92.800	-182.979	74.005	-5.217
3200	36.704	141.027	110.881	96.468	-182.586	82.284	-5.620
3300	36.761	142.157	111.811	100.141	-182.200	90.555	-5.997
3400	36.815	143.255	112.720	103.820	-181.823	98.816	-6.352
3500	36.864	144.323	113.608	107.504	-181.454	107.061	-6.685
3600	36.909	145.362	114.476	111.192	-181.092	115.304	-7.000
3700	36.951	146.374	115.324	114.885	-180.741	123.533	-7.297
3800	36.990	147.360	116.154	118.583	-180.393	131.754	-7.578
3900	37.027	148.321	116.967	122.283	-180.056	139.959	-7.843
4000	37.061	149.259	117.762	125.988	-179.726	148.162	-8.095
4100	37.092	150.175	118.542	129.695	-179.404	156.354	-8.334
4200	37.122	151.069	119.306	133.406	-179.088	164.539	-8.562
4300	37.149	151.943	120.054	137.120	-178.779	172.720	-8.779
4400	37.175	152.797	120.789	140.836	-178.479	180.887	-8.985
4500	37.200	153.633	121.510	144.555	-178.185	189.051	-9.182
4600	37.223	154.451	122.217	148.276	-177.896	197.215	-9.370
4700	37.244	155.251	122.911	151.999	-177.616	205.368	-9.550
4800	37.264	156.036	123.593	155.725	-177.339	213.510	-9.721
4900	37.283	156.804	124.263	159.452	-177.069	221.649	-9.886
5000	37.301	157.558	124.922	163.181	-176.806	229.774	-10.043
5100	37.318	158.297	125.569	166.912	-176.549	237.913	-10.195
5200	37.335	159.021	126.205	170.645	-176.295	246.033	-10.340
5300	37.350	159.733	126.831	174.379	-176.046	254.160	-10.481
5400	37.364	160.431	127.447	178.115	-175.804	262.265	-10.614
5500	37.378	161.117	128.053	181.852	-175.564	270.381	-10.744
5600	37.391	161.790	128.649	185.590	-175.334	278.485	-10.868
5700	37.403	162.452	129.236	189.330	-175.105	286.584	-10.988
5800	37.415	163.103	129.815	193.071	-174.881	294.687	-11.104
5900	37.426	163.743	130.384	196.813	-174.661	302.773	-11.215
6000	37.437	164.372	130.946	200.556	-174.446	310.870	-11.323

Dec. 31, 1966

SULFURIC ACID (H_2SO_4) (IDEAL GAS) GFW = 98.07754

Point Group [C_{2v}]

$S°_{298.15}$ = [69.1] gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -173.4 ± 2 kcal/mol

$\Delta Hf°_{298.15}$ = -177.0 ± 2 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[3500] (1)	[380] (1)	883 (1)
1223 (1)	[450] (1)	[400] (1)
1138 (1)	[390] (1)	1450 (1)
834 (1)	3610 (1)	[450] (1)
550 (1)	1159 (1)	568 (1)

Bond Distance: S-O = [1.42]Å S-OH = [1.53]Å O-H = [0.97]Å

Bond Angle: O-S-O = [125]° HO-S-OH = [100]° S-O-H = [105]° σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.237×10^{-144}] g^3cm^6

Heat of Formation.

The vapor phase equilibria of the H_2SO_4, H_2O and SO_3 system have been studied by (1) B. Bodenstein and M. Katayama, Z. Elektrochem. 15, 244 (1909), Z. Physik. Chem. 69, 26 (1909); (2) G. P. Luchinskii, Zh. Fiz. Khim. 30, 1207 (1956), and (3) A. V. Suvorov, R. B. Dobrotin and S. M. Gadzhiev, Russ. J. Inorg. Chem. (English Transl.) 10, 710 (1965). The data of Bodenstein and Katayama and of Suvorov et al. were obtained from PVT studies, while those of Luchinskii were based on vapor pressure measurements. A translation of Luchinskii's paper is not yet available, so it is not known whether he obtained the vapor composition experimentally or by calculation. Using the reported equilibrium values for the reaction $H_2SO_4(g) = H_2O(g) + SO_3(g)$, we evaluate the corresponding enthalpy changes by both the second and third law methods. The results are presented in the table below. The value of $Hf°_{298}$ for $H_2SO_4(g)$ is adopted as -177 ± 2 kcal/mol.

	Investigator	Temp., °K	No. of Points	$\Delta Hr°_{298}$, kcal/mol Second Law	Third Law	Drift eu	$\Delta Hf°_{298}$ kcal/mol*
1.	Bodenstein & Katayama (1909)	596.2-756.2	53	-22.95 ± 0.66	-24.55	-2.3 ± 1.0	-176.94
2.	Luchinskii (1956)	333.2-473.2	8	-24.02 ± 0.22	-24.43	-1.2 ± 0.5	-176.82
3.	Suvorov (1965)	583.0-713.0	40	-27.14 ± 0.45	-24.90	+3.3 ± 0.6	-177.29

*Calculation based on the third law $\Delta Hr°_{298}$ value.

Heat Capacity and Entropy.

The molecular structure and bond angles (O-S-O, HO-S-OH) are estimated by comparison with those for $SF_2O_2(g)$ reported by D. R. Lide, D. E. Mann and R. M. Fristrom, J. Chem. Phys. 26, 734 (1957). The S-O and S-OH bond distances are assumed to be the same as those in $H_2SO_4(c)$, determined by R. Pascard, Compt. Rend. 240, 2162 (1955). The OH distance and S-O-H angle are taken from those for $H_2O(g)$. Electric deflection studies by A. Büchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 46, 605 (1967), indicate that $H_2SO_4(g)$ is polar, which is consistent with the assumed C_{2v} structure.

The infrared absorption spectrum in the range 4000 to 400 cm^{-1} of normal and deuterated $H_2SO_4(g)$ above $H_2SO_4(l)$ was observed by S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc. 88, 723 (1966). The authors assigned nine vibrational frequencies, which are adopted here. The three principal moments of inertia are: $I_A = 1.570 \times 10^{-38}$, $I_B = 1.586 \times 10^{-38}$, and $I_C = 1.702 \times 10^{-38}$ g cm^2.

Four of the six missing frequencies are obtained from P. A. Giguère and R. Savoie, J. Am. Chem. Soc. 85, 287 (1963), which were estimated by comparison with infrared frequencies for the crystal and Raman values for the liquid. The remaining two frequencies, ν_7 = 450 and ν_{14} = 450 cm^{-1}, are assigned arbitrarily so that the second and third law values for $\Delta Hr°_{298.15}$ derived from equilibrium data are in reasonable agreement.

Tungstic Acid (H_2WO_4)

(Crystal) GFW = 249.86354

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	26.920	34.600	34.600	.000	- 270.500	- 239.963	175.897
300	27.000	34.767	34.601	.050	- 270.500	- 239.774	174.675
400	31.000	43.082	35.707	2.950	- 270.305	- 229.552	125.422
500	35.000	50.431	37.929	6.251	- 269.766	- 219.419	95.908
600	38.200	57.116	40.579	9.922	- 268.916	- 209.425	76.283
700	40.800	63.219	43.384	13.885	- 267.832	- 199.591	62.315
800	42.200	68.768	46.216	18.041	- 266.611	- 189.929	51.886
900	43.600	73.826	49.007	22.338	- 265.296	- 180.419	43.812
1000	44.600	78.472	51.724	26.748	- 263.912	- 171.061	37.385

Dec. 31, 1962; June 30, 1963; Mar. 31, 1967

TUNGSTIC ACID (H_2WO_4) (CRYSTAL) GFW = 249.86354

$S^\circ_{298.15}$ = [34.6 ± 6] gibbs/mol

Td = [393]°K

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = -270.5 ± 0.4 kcal/mol

Heat of Formation

V. I. Spitsyn and N. N. Patsukova[1] have measured calorimetrically the heats of reaction (1) and (2) at 298°K as -13.80 ± 0.01 and -13.05 ± 0.02 kcal/mol, respectively. The reactions are given as follows:

(1) $WO_3(c) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + H_2O(l)$

(2) $H_2WO_4(c) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + 2\ H_2O(l)$

Combination of reactions(1) and (2) gives ΔHr°_{298} = -0.75 ± 0.04 kcal/mol for $WO_3(c) + H_2O(l) \rightarrow H_2WO_4(c)$, which leads to $\Delta Hf^\circ_{298}(H_2WO_4, c)$ = -270.5 ± 0.4 kcal/mol.

To obtain $WO_3(c)$ in a form soluble in the calorimetric solution, Spitsyn and Patsukova dehydrated $H_2WO_4(c)$ at the relatively low temperature of 250°C. The resulting $WO_3(c)$ was a very fine lemon-yellow powder which may have excess surface free energy compared with the JANAF standard state. The latter is WO_3 formed at high temperature in a calorimetric bomb. The actual heat of formation of tungstic acid should be less negative if this effect is significant.

The previously accepted value[2,3,4], -280.2 ± 0.4 kcal/mol, was based on the pressure-temperature-composition studies of G. F. Huttig and B. Kurre[5] for the WO_3-H_2O system. We suspect that the data do not correspond to equilibrium (see entropy section) for the reaction $H_2WO_4(c) = WO_3(c) + H_2O(g)$.

Heat Capacity and Entropy

Cp_{300} = 27.0 gibbs/mol is estimated using Kopp's rule. Since the decomposition temperature of $H_2WO_4(c)$ is approximately 400°K, which is relatively low for hydrogen and oxygen to reach their maximum Cp contribution, we estimate Cp_{400} = 31.0 gibbs/mol for $H_2WO_4(c)$.

The entropy, S°_{298} = 34.6 eu, is estimated so that the decomposition pressure of water is one atmosphere at 120°C. This value is quite uncertain as suggested by comparison with the following estimates. A lower limit may be obtained from $S^\circ_{283.5}$ = 26.8 eu for $H_2SO_4(c)$. Summation of the entropies for $WO_3(c)$ and $H_2O(c)$ [10.7 eu] yields 28.8 eu, an estimate which is somewhat larger than the lower limit. An upper limit may be obtained by assuming that the pressure of about 14 mm at 190°C corresponds to equilibrium for the reaction $H_2WO_4(c) = WO_3(c) + H_2O(g)$. This pressure, based on the plateau in the temperature-composition data of Huttig and Kurre[5], yields S°_{298} = 46.5 eu when combined with the adopted ΔHf°_{298} and JANAF auxiliary data. Since the estimate appears to be unreasonably large, we suggest that this region of the curve may correspond to the reaction $WO_3 \cdot 0.5\ H_2O(c) = WO_3(c) + 0.5\ H_2O(g)$. In contrast, the observed pressures[5] for samples having mole ratios (H_2O/WO_3) of 1.2 - 1.35 leads to S°_{298} = 34 eu, if the reaction is $WO_3 \cdot H_2O(c) = WO_3(c) + H_2O(g)$.

Temperature of Decomposition

Td is calculated as the temperature at which the Gibbs energy change of the reaction $H_2WO_4(c) \rightarrow WO_3(c) + H_2O(g)$ approaches zero.

Spitsyn and Patsukova[1] observed that some dehydration of stoichiometric $H_2WO_4(c)$ occurs at temperatures as low as 90°C. Thermal studies[6,7] on tungstic acid containing some excess water indicated the start of dehydration somewhere in the region of 60 - 120°C. These temperatures yield a lower limit for Td on the presumption that the experiments correspond to a partial pressure of water of less than one atmosphere.

References

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Tungstic Acid (H_2WO_4)

(Ideal Gas) GFW = 249.86354

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-5.034	-214.171	-214.171	INFINITE
100	14.502	63.357	102.816	-3.946	-215.386	-210.774	460.647
200	20.190	75.182	86.218	-2.207	-216.122	-205.555	224.948
298	24.504	84.103	84.103	.000	-216.500	-200.722	147.133
300	24.570	84.255	84.104	.045	-216.505	-200.625	146.155
400	27.446	91.746	85.106	2.656	-216.599	-195.312	106.713
500	29.394	98.093	87.085	5.504	-216.513	-189.997	83.048
600	30.811	103.583	89.387	8.518	-216.320	-184.710	67.281
700	31.903	108.418	91.767	11.655	-216.062	-179.460	56.030
800	32.772	112.737	94.123	14.891	-215.761	-174.255	47.604
900	33.477	116.639	96.412	18.204	-215.430	-169.084	41.059
1000	34.056	120.197	98.615	21.582	-215.078	-163.952	35.832
1100	34.534	123.466	100.728	25.012	-214.716	-158.859	31.562
1200	34.932	126.489	102.750	28.486	-214.347	-153.796	28.010
1300	35.266	129.298	104.685	31.996	-213.981	-148.765	25.010
1400	35.548	131.922	106.538	35.538	-213.618	-143.763	22.442
1500	35.787	134.383	108.313	39.105	-213.267	-138.783	20.221
1600	35.991	136.699	110.016	42.694	-212.929	-133.830	18.280
1700	36.166	138.887	111.650	46.302	-212.603	-128.895	16.571
1800	36.317	140.958	113.222	49.926	-212.296	-123.981	15.053
1900	36.449	142.925	114.734	53.565	-212.006	-119.081	13.697
2000	36.564	144.798	116.190	57.215	-211.736	-114.200	12.479
2100	36.665	146.585	117.596	60.877	-211.485	-109.329	11.378
2200	36.754	148.292	118.952	64.548	-211.259	-104.471	10.378
2300	36.832	149.928	120.264	68.227	-211.051	-99.623	9.466
2400	36.902	151.497	121.533	71.914	-210.867	-94.777	8.631
2500	36.965	153.005	122.762	75.607	-210.709	-89.951	7.864
2600	37.021	154.456	123.953	79.307	-210.569	-85.119	7.155
2700	37.072	155.854	125.109	83.012	-210.460	-80.296	6.500
2800	37.117	157.203	126.231	86.721	-210.389	-75.477	5.891
2900	37.158	158.506	127.322	90.435	-210.364	-70.657	5.325
3000	37.196	159.766	128.382	94.152	-210.393	-65.835	4.796
3100	37.230	160.986	129.414	97.874	-210.482	-61.019	4.302
3200	37.261	162.169	130.419	101.598	-210.644	-56.199	3.838
3300	37.289	163.316	131.399	105.326	-210.881	-51.369	3.402
3400	37.315	164.430	132.354	109.056	-211.205	-46.533	2.991
3500	37.339	165.512	133.286	112.789	-211.626	-41.684	2.603
3600	37.361	166.564	134.196	116.524	-212.171	-36.819	2.235
3700	37.382	167.588	135.085	120.261	-221.173	-31.892	1.884
3800	37.401	168.585	135.953	124.000	-221.176	-26.772	1.540
3900	37.418	169.557	136.802	127.741	-221.189	-21.661	1.214
4000	37.434	170.504	137.633	131.484	-221.212	-16.544	.904
4100	37.449	171.429	138.446	135.228	-221.244	-11.427	.609
4200	37.463	172.331	139.242	138.973	-221.284	-6.307	.328
4300	37.477	173.213	140.022	142.720	-221.332	-1.184	.060
4400	37.489	174.075	140.786	146.469	-221.388	3.927	-.195
4500	37.500	174.917	141.535	150.218	-221.453	9.051	-.440
4600	37.511	175.742	142.270	153.969	-221.523	14.181	-.674
4700	37.521	176.548	142.991	157.720	-221.604	19.309	-.898
4800	37.531	177.339	143.698	161.473	-221.688	24.432	-1.112
4900	37.540	178.112	144.393	165.227	-221.779	29.556	-1.318
5000	37.548	178.871	145.075	168.981	-221.878	34.682	-1.516
5100	37.556	179.615	145.745	172.736	-221.984	39.820	-1.706
5200	37.564	180.344	146.403	176.492	-222.094	44.947	-1.889
5300	37.571	181.060	147.050	180.249	-222.209	50.094	-2.066
5400	37.577	181.762	147.687	184.006	-222.332	55.223	-2.235
5500	37.584	182.451	148.312	187.764	-222.457	60.375	-2.399
5600	37.590	183.129	148.928	191.523	-222.591	65.507	-2.557
5700	37.595	183.794	149.534	195.282	-222.728	70.651	-2.709
5800	37.601	184.448	150.130	199.042	-222.870	75.807	-2.856
5900	37.606	185.091	150.717	202.802	-223.017	80.957	-2.999
6000	37.611	185.723	151.296	206.563	-417.072	88.194	-3.212

Dec. 31, 1962; June 30, 1963; Mar. 31, 1967

TUNGSTIC ACID (H_2WO_4) (IDEAL GAS) GFW = 249.86354

Point Group [C_{2v}]

$S°_{298.15}$ = [84] gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -214.1 ± 1.0 kcal/mol

$\Delta Hf°_{298.15}$ = -216.5 ± 1.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[2200]	[100]	[570]
[1000]	[225]	[120]
[620]	[100]	[1100]
[560]	[2500]	[300]
[500]	[630]	[540]

Bond Distance: W-O = [1.81] Å O-H = [0.97] Å

Bond Angle: O-W-O = [109.47]° W-O-H = [105]° σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.443×10^{-113}] g^3 cm^6

Heat of Formation.

The adopted heat of formation, $\Delta Hf°_{298}$ = -216.5 ± 1.0 kcal/mol, is derived from equilibrium data[1,2,3,4,5] obtained by the transpiration method. The data are in reasonable agreement and they are summarized below. Belton and McCarron[1] have concluded that $WO_3 \cdot H_2O$ is the species responsible for the increased volatilization of W(c) and WO_3(c) in the presence of water vapor. Based on their data for W(c) and the earlier data for WO_3(c), Belton and McCarron[1] ruled out the possibility of significant amounts of $(WO_3)_2 \cdot H_2O$ and $WO_3 \cdot 2\ H_2O$.

Investigator	Reaction*	Temp.(°K)	No. of Points	$\Delta Hr°_{298}$(kcal/mol) 2nd law	3rd law	Drift (eu)	$\Delta Hf°_{298}$** (kcal/mol)
Belton & McCarron[1]	A	1473-1773	Equation	14.70	14.63	-0.1±1.1	-216.56
Glemser & Ackermann[2]	B	673-1173	6	38.56	41.67	3.2±0.9	-217.59
Glemser & Haeseler[3]	B	1173-1373	Equation	38.27	42.27	1.6	-216.99
Glemser & Volz[4]	B	1373	1	-	43.44	-	-215.82
Meyer et al.[5]	B	1393-1518	Equation	26.14	43.51	11.9	-215.75

*Reaction A: $W(c) + 4H_2O(g) \rightarrow H_2WO_4(g) + 3H_2(g)$

B: $WO_3(c) + H_2O(g) \rightarrow H_2WO_4(g)$

**Based on the third law value

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Heat Capacity and Entropy.

The vibrational frequencies are estimated by comparison with those for H_2SO_4(g) reported by P. A. Giguere and R. Savoie, J. Am. Chem. Soc. 85, 287 (1963), and S. M. Chackalackal and F. E. Stafford, J. Am. Chem. Soc. 88, 723 (1966). These frequencies are also adjusted so that $S°_{1600}(H_2WO_4,g)$ is 136.7 eu as reported by Belton and McCarron, loc. cit. This entropy was derived from second law analysis of the equilibrium constants for reaction A.

The configuration of $WO_4^{=}$ group is assumed to be tetrahedral. The bond angle W-O-H is estimated to be the same as the angle of H_2O(g). The bond distances are assumed to be the same as those in WO_3(g) and H_2O(g). The three principal moments of inertia are $I_A = 2.328 \times 10^{-38}$, $I_B = 2.487 \times 10^{-38}$ and $I_C = 2.493 \times 10^{-38}$ g cm^2.

Phosphorus Hydride (PH_2)

(Ideal Gas) Mol. Wt. = 32.991

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 2.391	30.594	30.594	INFINITE
100	7.949	42.029	57.996	- 1.597	30.539	28.924	- 63.211
200	8.019	47.550	51.549	- .800	30.415	27.333	- 29.867
298	8.312	50.800	50.800	.000	30.100	25.884	- 18.972
300	8.319	50.851	50.800	.015	30.093	25.858	- 18.836
400	8.732	53.300	51.131	.867	29.718	24.502	- 13.386
500	9.185	55.297	51.770	1.763	29.344	23.240	- 10.158
600	9.656	57.013	52.504	2.705	28.985	22.053	- 8.032
700	10.121	58.536	53.259	3.694	28.639	20.926	- 6.533
800	10.557	59.917	54.006	4.728	7.884	14.536	- 3.971
900	10.951	61.183	54.734	5.804	7.812	15.373	- 3.733
1000	11.300	62.356	55.438	6.917	7.768	16.215	- 3.544
1100	11.604	63.447	56.118	8.063	7.747	17.060	- 3.389
1200	11.866	64.468	56.771	9.236	7.743	17.907	- 3.261
1300	12.092	65.427	57.401	10.435	7.754	18.754	- 3.153
1400	12.286	66.331	58.007	11.654	7.774	19.600	- 3.060
1500	12.454	67.184	58.590	12.891	7.799	20.445	- 2.979
1600	12.599	67.993	59.153	14.144	7.827	21.285	- 2.907
1700	12.724	68.760	59.696	15.410	7.858	22.127	- 2.845
1800	12.834	69.491	60.220	16.688	7.891	22.965	- 2.788
1900	12.930	70.187	60.726	17.976	7.924	23.802	- 2.738
2000	13.014	70.853	61.216	19.274	7.957	24.635	- 2.692
2100	13.088	71.489	61.690	20.579	7.988	25.469	- 2.651
2200	13.154	72.100	62.149	21.891	8.017	26.302	- 2.613
2300	13.213	72.686	62.595	23.209	8.045	27.131	- 2.578
2400	13.265	73.249	63.027	24.533	8.070	27.961	- 2.546
2500	13.311	73.792	63.447	25.862	8.093	28.789	- 2.517
2600	13.353	74.315	63.855	27.195	8.113	29.616	- 2.489
2700	13.391	74.819	64.252	28.533	8.131	30.442	- 2.464
2800	13.425	75.307	64.638	29.873	8.145	31.268	- 2.440
2900	13.456	75.779	65.014	31.218	8.159	32.096	- 2.419
3000	13.484	76.235	65.380	32.565	8.168	32.920	- 2.398
3100	13.510	76.678	65.738	33.914	8.175	33.745	- 2.379
3200	13.533	77.107	66.086	35.267	8.179	34.568	- 2.361
3300	13.555	77.524	66.427	36.621	8.180	35.395	- 2.344
3400	13.575	77.929	66.759	37.977	8.177	36.218	- 2.328
3500	13.593	78.323	67.084	39.336	8.172	37.045	- 2.313
3600	13.610	78.706	67.401	40.696	8.163	37.867	- 2.299
3700	13.625	79.079	67.712	42.058	8.150	38.693	- 2.285
3800	13.639	79.442	68.016	43.421	8.135	39.521	- 2.273
3900	13.653	79.797	68.313	44.786	8.115	40.348	- 2.261
4000	13.665	80.143	68.605	46.151	8.091	41.172	- 2.249
4100	13.676	80.480	68.890	47.519	8.066	42.000	- 2.239
4200	13.687	80.810	69.170	48.887	8.035	42.832	- 2.229
4300	13.697	81.132	69.445	50.256	8.001	43.656	- 2.219
4400	13.707	81.447	69.714	51.626	7.964	44.488	- 2.210
4500	13.715	81.755	69.978	52.997	7.922	45.316	- 2.201
4600	13.723	82.057	70.237	54.369	7.879	46.147	- 2.192
4700	13.731	82.352	70.492	55.742	7.831	46.982	- 2.185
4800	13.738	82.641	70.742	57.115	7.779	47.815	- 2.177
4900	13.745	82.925	70.988	58.490	7.726	48.652	- 2.170
5000	13.752	83.202	71.229	59.864	7.667	49.486	- 2.163
5100	13.758	83.475	71.467	61.240	7.605	50.324	- 2.156
5200	13.763	83.742	71.700	62.616	7.541	51.159	- 2.150
5300	13.769	84.004	71.930	63.993	7.473	52.002	- 2.144
5400	13.774	84.262	72.156	65.370	7.401	52.839	- 2.138
5500	13.779	84.514	72.378	66.747	7.326	53.684	- 2.133
5600	13.783	84.763	72.597	68.126	7.248	54.525	- 2.128
5700	13.788	85.007	72.813	69.504	7.166	55.373	- 2.123
5800	13.792	85.247	73.025	70.883	7.081	56.216	- 2.118
5900	13.796	85.482	73.234	72.262	6.993	57.065	- 2.114
6000	13.800	85.714	73.441	73.642	6.902	57.913	- 2.109

Dec. 31, 1960; Mar. 31, 1963

PHOSPHORUS HYDRIDE (PH_2) (IDEAL GAS) MOL. WT. = 32.991

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [50.8] cal. deg.$^{-1}$ mole^{-1}

Ground State Multiplicity = [2]

$\Delta H^\circ_{f\ 0}$ = [30.6 ± 23] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [30.1 ± 23] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[2327] (1)
[1020] (1)
[2322] (1)

Bond Distance: P-H = [1.419] Å

Bond Angle: H-P-H = [93.7]°

σ = 2

Product of Moments of Inertia: $I_A I_B I_C$ = [6.95 X 10^{-119}] g.^{3} cm.^{6}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was estimated by V. N. DiStefano, R. L. Potter, and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I.", American Cyanamid Company. The $\Delta H^\circ_{f\ 298.15}$ was estimated by taking 63% of the dissociation energy of PH_3 and using it as the dissociation energy of PH_2. D. Willes and C. Winkler, J. Phys. Chem. 61, 902 (1957) have estimated the $\Delta H^\circ_{f\ 298.15}$ for $PH_2(g)$ to be 30 kcal. mole^{-1}.

Heat Capacity and Entropy.

The vibrational spectra of PH_2 from the flash photolysis of PH_3 has been reported by D. A. Ramsey, Nature 178, 375 (1956) and in N. Y. Acad. Sci. 67, 485, (1957). Similarities between the spectra of NH_2 and PH_2 were found. For NH_2 and NH_3 bond angles and bond distances were reported to be about the same. By analogy then the bond angles and bond distances of PH_2 and PH_3 should be nearly the same. The moments of inertia for PH_2 were therefore calculated from the molecular constants for PH_3. The principal moments were found to be I_A = 3.587 X 10^{-40} g. cm.^{3}, I_B = 2.959 X 10^{-40} g. cm.^{3}, and I_C = 6.546 g. cm.^{3} X 10^{-40}.

DiStefano and Potter (loc. cit.) have assumed the ground state degeneracy to be 2, because of the unpaired electron. The vibrational frequencies reported by DiStefano and Potter (loc. cit.) have been used. They used a simple force field and the force constants of PH_3 to obtain the vibrational frequencies.

Hydrogen Sulfide (H_2S)

(Ideal Gas) Mol. Wt. = 34.07994

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.381	-4.184	-4.184	INFINITE
100	7.949	40.359	56.219	-1.586	-4.312	-5.613	12.266
200	7.978	45.872	49.827	-.791	-4.513	-6.859	7.495
298	8.172	49.151	49.151	.000	-4.880	-7.955	5.831
300	8.176	49.202	49.151	.015	-4.888	-7.974	5.809
400	8.504	51.597	49.476	.849	-5.847	-8.918	4.872
500	8.889	53.536	50.100	1.718	-6.615	-9.596	4.194
600	9.306	55.193	50.813	2.628	-7.262	-10.129	3.689
700	9.737	56.660	51.546	3.580	-7.812	-10.538	3.290
800	10.162	57.988	52.269	4.575	-21.348	-12.162	3.322
900	10.567	59.209	52.973	5.612	-21.461	-11.007	2.673
1000	10.943	60.342	53.654	6.687	-21.545	-9.841	2.151
1100	11.281	61.401	54.311	7.799	-21.602	-8.668	1.722
1200	11.584	62.396	54.944	8.943	-21.636	-7.490	1.364
1300	11.853	63.334	55.553	10.115	-21.653	-6.309	1.061
1400	12.092	64.221	56.141	11.312	-21.657	-5.129	.801
1500	12.303	65.063	56.708	12.532	-21.651	-3.949	.575
1600	12.491	65.863	57.255	13.772	-21.637	-2.770	.378
1700	12.658	66.625	57.784	15.030	-21.615	-1.589	.204
1800	12.808	67.353	58.296	16.303	-21.589	-.414	.050
1900	12.941	68.049	58.791	17.590	-21.558	.764	-.088
2000	13.063	68.716	59.271	18.891	-21.523	1.937	-.212
2100	13.171	69.356	59.736	20.203	-21.487	3.108	-.323
2200	13.270	69.971	60.187	21.525	-21.449	4.280	-.425
2300	13.360	70.563	60.625	22.856	-21.410	5.447	-.518
2400	13.444	71.133	61.051	24.197	-21.369	6.617	-.603
2500	13.520	71.684	61.466	25.545	-21.329	7.778	-.680
2600	13.590	72.215	61.869	26.900	-21.288	8.945	-.752
2700	13.655	72.729	62.262	28.263	-21.246	10.106	-.818
2800	13.715	73.227	62.645	29.631	-21.206	11.263	-.879
2900	13.771	73.709	63.018	31.005	-21.165	12.426	-.936
3000	13.824	74.177	63.382	32.385	-21.125	13.582	-.989
3100	13.874	74.631	63.738	33.770	-21.083	14.738	-1.039
3200	13.921	75.073	64.085	35.160	-21.044	15.890	-1.085
3300	13.965	75.502	64.425	36.554	-21.005	17.044	-1.129
3400	14.007	75.919	64.756	37.953	-20.966	18.198	-1.170
3500	14.047	76.326	65.081	39.356	-20.930	19.348	-1.208
3600	14.085	76.722	65.399	40.762	-20.894	20.499	-1.244
3700	14.122	77.108	65.710	42.173	-20.861	21.652	-1.279
3800	14.156	77.485	66.015	43.586	-20.828	22.800	-1.311
3900	14.190	77.854	66.314	45.004	-20.797	23.944	-1.342
4000	14.223	78.213	66.607	46.424	-20.768	25.096	-1.371
4100	14.254	78.565	66.895	47.848	-20.739	26.239	-1.399
4200	14.285	78.909	67.177	49.275	-20.713	27.386	-1.425
4300	14.314	79.245	67.453	50.705	-20.688	28.530	-1.450
4400	14.343	79.575	67.725	52.138	-20.665	29.671	-1.474
4500	14.371	79.897	67.992	53.574	-20.644	30.818	-1.497
4600	14.397	80.213	68.254	55.012	-20.624	31.963	-1.519
4700	14.423	80.523	68.512	56.453	-20.606	33.106	-1.539
4800	14.450	80.827	68.765	57.897	-20.589	34.246	-1.559
4900	14.475	81.125	69.015	59.343	-20.574	35.394	-1.579
5000	14.500	81.418	69.260	60.792	-20.561	36.529	-1.597
5100	14.523	81.705	69.501	62.243	-20.550	37.677	-1.614
5200	14.548	81.988	69.738	63.697	-20.539	38.813	-1.631
5300	14.571	82.265	69.972	65.153	-20.530	39.958	-1.648
5400	14.594	82.538	70.202	66.611	-20.524	41.095	-1.663
5500	14.616	82.806	70.429	68.071	-20.519	42.236	-1.678
5600	14.639	83.069	70.652	69.534	-20.516	43.380	-1.693
5700	14.661	83.328	70.873	70.999	-20.514	44.523	-1.707
5800	14.682	83.584	71.089	72.466	-20.514	45.658	-1.720
5900	14.705	83.835	71.303	73.936	-20.514	46.799	-1.733
6000	14.725	84.082	71.514	75.407	-20.517	47.943	-1.746

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

HYDROGEN SULFIDE (H_2S) (IDEAL GAS) MOL. WT. = 34.07994

Point Group C_{2v}

$\Delta H^\circ_{f\ 0} = -4.18 \pm 0.15$ kcal. mole^{-1}

$S^\circ_{298.15} = 49.15$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -4.88 \pm 0.15$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
2614.56 (1)
1182.68 (1)
2627.48 (1)

Bond Distance: S-H = 1.328 Å

Bond Angle: H-S-H = 92.2°

$\sigma = 2$

Moments of Inertia: $I_AI_BI_C = 4.69 \times 10^{-119}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation of hydrogen sulfide has been calorimetrically measured by H. Zeumer and W. A. Roth, Z. Elektrochem. 40, 777 (1934), and A. F. Kapustinskii and R. T. Kankovskii, Zhur. Fiz. Khim. 32, 2810 (1958), as $\Delta H^\circ_{f\ 293} = -4.80 \pm 0.15$ kcal. mole^{-1} and $\Delta H^\circ_{f\ 298} = -4.94 \pm 0.08$ kcal. mole^{-1}, respectively. A weighted average of these two values was taken for the standard enthalpy of formation of hydrogen sulfide.

Heat Capacity and Entropy.

The bond distance, angle and vibrational frequencies were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. 25, 1132 (1956).

J. S. Gordon, private communication, Feb. 7, 1961,has calculated C_p from 298 to 6000°K. by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes second order corrections for vibrational anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The correction constants were obtained from Allen and Plyler, loc. cit. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions, but at 298°K. and above Gordon's thermodynamic functions were adopted in this tabulation.

Titanium Dihydride (TiH_2)

(Crystal) Mol. Wt. = 49.916

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.182	- 32.508	- 32.508	INFINITE
100	3.030	1.012	12.312	- 1.070	- 33.289	- 30.816	67.345
200	5.430	4.551	7.716	- .633	- 33.913	- 28.108	30.714
298	7.191	7.101	7.101	.000	- 34.500	- 25.127	18.418
300	7.232	7.146	7.101	.013	- 34.511	- 25.069	18.262
400	9.400	9.524	7.411	.845	- 34.993	- 21.845	11.935
500	11.300	11.832	8.066	1.883	- 35.303	- 18.518	8.094
600	12.860	14.035	8.879	3.094	- 35.465	- 15.144	5.516
700	14.100	16.115	9.765	4.445	- 35.510	- 11.752	3.669
800	15.090	18.065	10.682	5.906	- 35.465	- 8.361	2.284
900	15.850	19.888	11.605	7.455	- 35.353	- 4.977	1.209
1000	16.380	21.588	12.519	9.068	- 35.198	- 1.611	.352
1100	16.744	23.166	13.416	10.725	- 35.021	1.738	- .345
1200	17.050	24.637	14.291	12.415	- 35.781	5.109	- .930
1300	17.298	26.012	15.140	14.133	- 35.585	8.509	- 1.430
1400	17.488	27.301	15.963	15.873	- 35.389	11.893	- 1.856
1500	17.620	28.512	16.760	17.629	- 35.199	15.265	- 2.224
1600	17.753	29.654	17.530	19.398	- 35.019	18.622	- 2.544
1700	17.858	30.734	18.276	21.178	- 34.847	21.970	- 2.824
1800	17.934	31.757	18.996	22.968	- 34.685	25.306	- 3.072
1900	17.981	32.728	19.694	24.764	- 34.536	28.636	- 3.294
2000	18.000	33.650	20.369	26.564	- 38.077	32.051	- 3.502

June 30, 1963

TITANIUM DIHYDRIDE (TiH_2) (CRYSTAL) MOL. WT. = 49.916

$\Delta H^\circ_{f\ 0}$ = [-32.5 ± 2.0] kcal. mole^{-1}

$S^\circ_{298.15}$ = 7.101 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-34.5 ± 2.0] kcal. mole^{-1}

Heat of Formation.

The heat of combustion of $TiH_{1.73}$(c), the stable species of titanium hydride, was reported to be -247.8 kcal. by A. Sieverts and A. Gotta, Z. anorg. allgem. Chem. 199, 384 (1931). From this data the value of $\Delta H^\circ_{f\ 298.15}$ for $TiH_{1.73}$(c) was calculated to be -29.40 kcal. mole^{-1}. The heat of dissociation of titanium hydride having compositions between the rough limits $TiH_{1.75}$-$TiH_{1.93}$ was given as 19.15 kcal. per mole of H_2 dissociated by T. R. P. Gibb, Jr., J. J. McSharry, and R. W. Bragdon, J. Am. Chem. Soc. 73, 1751 (1951). Assuming this value is applicable to compositions between the limits $TiH_{1.73}$-TiH_2, the difference in the heat of formation of titanium hydride between $TiH_{1.73}$ and TiH_2 was estimated to be -5.17 kcal. mole^{-1}. Thus the value of $\Delta H^\circ_{f\ 298.15}$ for TiH_2(c) was calculated.

Heat Capacity and Entropy.

The low temperature C_p for $TiH_{1.97}$(c), 24-363°K., were measured by B. Stalinski and Z. Bieganski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 8, No. 5, 243 (1960). This data were adopted for TiH_2(c) due to lack of the measured C_p values. A small but well marked λ-type anomaly with a maximal value of C_p at 288.5°K. in the C_p vs. T curve was observed. $S^\circ_{298.15}$ was reported by B. Stalinski and Z. Bieganski, loc. cit., based on S°_{25}(extrap.) = 0.065 cal. deg.$^{-1}$ mole^{-1}.

Ammonia (NH_3)

(Ideal Gas) Mol. Wt. = 17.03061

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.404	-9.302	-9.302	INFINITE
100	7.950	37.210	53.303	-1.609	-9.988	-8.146	17.801
200	8.064	42.740	46.794	-.811	-10.446	-6.139	6.708
298	8.515	46.033	46.033	.000	-10.970	-3.915	2.869
300	8.526	46.085	46.033	.016	-10.980	-3.871	2.820
400	9.241	48.633	46.375	.903	-11.482	-1.424	.778
500	10.036	50.780	47.047	1.867	-11.919	1.142	-.499
600	10.808	52.679	47.830	2.909	-12.282	3.790	-1.380
700	11.538	54.400	48.647	4.027	-12.582	6.494	-2.027
800	12.225	55.986	49.467	5.215	-12.824	9.235	-2.523
900	12.868	57.464	50.274	6.470	-13.016	12.005	-2.915
1000	13.467	58.851	51.063	7.787	-13.163	14.792	-3.233
1100	14.030	60.161	51.831	9.163	-13.271	17.594	-3.495
1200	14.550	61.404	52.578	10.592	-13.343	20.405	-3.716
1300	15.030	62.588	53.303	12.071	-13.385	23.218	-3.903
1400	15.460	63.718	54.007	13.596	-13.402	26.034	-4.064
1500	15.850	64.798	54.690	15.162	-13.399	28.853	-4.204
1600	16.205	65.833	55.355	16.765	-13.381	31.666	-4.325
1700	16.520	66.825	56.000	18.402	-13.347	34.483	-4.433
1800	16.762	67.776	56.628	20.066	-13.303	37.294	-4.528
1900	16.995	68.689	57.239	21.754	-13.250	40.104	-4.613
2000	17.220	69.566	57.834	23.465	-13.191	42.911	-4.689
2100	17.429	70.411	58.413	25.197	-13.125	45.715	-4.757
2200	17.630	71.227	58.977	26.950	-13.053	48.514	-4.819
2300	17.825	72.015	59.527	28.723	-12.973	51.310	-4.875
2400	18.014	72.777	60.063	30.515	-12.887	54.107	-4.927
2500	18.195	73.516	60.586	32.326	-12.797	56.893	-4.973
2600	18.370	74.234	61.097	34.154	-12.697	59.679	-5.016
2700	18.537	74.930	61.597	35.999	-12.592	62.461	-5.056
2800	18.698	75.607	62.085	37.861	-12.480	65.237	-5.092
2900	18.853	76.266	62.563	39.739	-12.360	68.015	-5.125
3000	19.000	76.908	63.030	41.631	-12.236	70.780	-5.156
3100	19.115	77.532	63.488	43.537	-12.105	73.546	-5.185
3200	19.228	78.141	63.937	45.454	-11.973	76.307	-5.211
3300	19.341	78.734	64.376	47.383	-11.838	79.067	-5.236
3400	19.452	79.314	64.807	49.322	-11.698	81.814	-5.259
3500	19.563	79.879	65.230	51.273	-11.557	84.565	-5.280
3600	19.672	80.432	65.644	53.235	-11.412	87.307	-5.300
3700	19.781	80.972	66.051	55.207	-11.265	90.051	-5.319
3800	19.888	81.501	66.451	57.191	-11.112	92.787	-5.336
3900	19.994	82.019	66.843	59.185	-10.958	95.520	-5.353
4000	20.100	82.527	67.229	61.190	-10.800	98.246	-5.368
4100	20.205	83.024	67.608	63.205	-10.639	100.972	-5.382
4200	20.308	83.512	67.981	65.231	-10.474	103.694	-5.396
4300	20.411	83.991	68.348	67.267	-10.306	106.409	-5.408
4400	20.512	84.462	68.709	69.313	-10.134	109.117	-5.420
4500	20.613	84.924	69.064	71.369	-9.961	111.823	-5.431
4600	20.712	85.378	69.414	73.435	-9.781	114.534	-5.441
4700	20.811	85.824	69.758	75.511	-9.600	117.236	-5.451
4800	20.908	86.264	70.098	77.597	-9.415	119.928	-5.460
4900	21.005	86.696	70.432	79.693	-9.226	122.621	-5.469
5000	21.100	87.121	70.761	81.798	-9.033	125.309	-5.477
5100	21.195	87.540	71.086	83.913	-8.838	127.995	-5.485
5200	21.288	87.952	71.407	86.037	-8.638	130.678	-5.492
5300	21.381	88.359	71.723	88.170	-8.436	133.355	-5.499
5400	21.472	88.759	72.035	90.313	-8.230	136.026	-5.505
5500	21.563	89.154	72.342	92.465	-8.021	138.697	-5.511
5600	21.652	89.543	72.646	94.625	-7.809	141.361	-5.517
5700	21.740	89.927	72.946	96.795	-7.592	144.028	-5.522
5800	21.828	90.306	73.242	98.974	-7.374	146.683	-5.527
5900	21.914	90.680	73.534	101.161	-7.152	149.337	-5.532
6000	22.000	91.049	73.823	103.356	-6.926	151.984	-5.536

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

AMMONIA (NH_3) (IDEAL GAS) MOL. WT. = 17.03061

Point Group C_{3v}

$S^\circ_{298.15}$ = 46.03 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -9.30 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -10.97 ± 0.1 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

Zero-order "Harmonic"		Observed Wave Numbers	
ω, cm.$^{-1}$	ω, cm.$^{-1}$	ν, cm.$^{-1}$	ν, cm.$^{-1}$
3506 (1)	3577 (2)	3336 (1)	3444 (2)
1022 (1)	1691 (2)	950 (1)	1627 (2)

Bond Length: N-H = 1.0124 Å Bond Angle: H-N-H = 106.67° σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = 3.4826 X 10^{-119} g.^{3} cm.^{6}

Heat of Formation.

A weighted average based on analysis using JANAF functions was selected. Haber, Tamaru and Oeholm, Z. Elektrochem. 21, 206 (1915) obtained ΔH_{298} = 11.10 for $NH_3 \rightarrow 0.5\ N_2 + 1.5\ H_2$ by flow calorimetry. Estimated uncertainty is 1% and the formation value was corrected by 0.025 kcal. for non-ideality of NH_3. Becker and Roth, ibid. 40, 836 (1934) measured ΔH_N [$NH_3(g) + H_2C_2O_4(aq)$], ΔH_C [hydrates of $H_2C_2O_4$ and $(NH_4)_2C_2O_4$], and the necessary ΔH_{Soln} leading to ΔH°_{298} = 182.9 ± 0.24 for $3H_2O(l) + N_2(g) \rightarrow 1.5\ O_2(g) + 2NH_3(g)$. Equilibrium data from Larson and Dodge, J. Am. Chem. Soc. 45, 2918 (1923) and Haber, Tamaru and Ponnaz, Z. Elektrochem. 21, 89 (1915) were analyzed as tabulated by Stephenson and McMahon, J. Am. Chem. Soc. 61, 437 (1939) from the non-ideality corrections of Gillespie and Beattie, Phys. Rev. 36, 743 (1930). Data (1000-3000 atm) from Winchester and Dodge, A.I.Ch.E. Journal 2, 431-6 (1956) were omitted because of uncertainty in non-ideality while data (1 atm) of Haber and Maschke, Z. Elektrochem. 21, 128 (1915) were assumed ideal. High-temperature calorimetry of the direct decomposition includes Haber and Tamaru, Z. Elektrochem. 21, 191 (1915) and Wittig and Schmatz, ibid. 63, 470 (1959).

Source	Method	$\Delta H^\circ_{f\ 298}$ (kcal. mole^{-1})	Drift (e.u.)
Haber, Tamaru, Oeholm (1915)	Flow calorimetry at 298°K	-11.07	
Becker, Roth (1934)	Indirect calorimetry at 294°K	-11.02±0.12	
Larson, Dodge (1923)	K_p° from K_p(10-1000 atm, 600-800°K)	-10.88(-10.82±0.03)*	-0.17±0.05
Haber, Tamaru, Ponnaz (1915)	K_p° from K_p(30 atm, 800-1200°K)	-10.89(-10.95±0.05)*	0.04±0.05
Haber, Maschke (1915)	K_p(1 atm, 900-1400°K)	-10.87(-10.60±0.1)*	-0.22±0.08
Haber, Tamaru (1915)	Flow calorimetry (739-932°K)	-10.97	
Wittig, Schmatz (1959)	Flow calorimetry at 823°K	-10.98	

*Third law values for equilibrium data are followed by second law values in parentheses.

Heat Capacity and Entropy.

The functions are an approximation of the non-rigid rotator anharmonic oscillator based on calculations of Harrison and Kobe, Chem. Eng. Progr. 49, No. 7, 349 (1953) and Yungman, Gurvich and Rtischeva, Trudy Gosudarst. Inst. Priklad. Khim. 49, 20 (1962). In these calculations anharmonicity of ν_2 associated with inversion doubling was treated by summation over the energy levels. Both calculations include rotational distortion corrections while Yungman, et al., also allow for anharmonicity and vibration-rotation interaction of the other fundamentals. JANAF functions agree with the results to within 0.02 e.u. in the range 298-1500°K.

Two sets of rigid rotator harmonic oscillator functions were also tested for consistency with the ammonia data (see below). These were obtained from molecular dimensions and either calculated zero order frequencies (ω) or observed wave numbers (ν) obtained by Benedict and Plyler, Can. J. Phys. 35, 1235 (1957) from high resolution infrared studies. Herzberg, "Infrared and Raman Spectra", pp. 503-4, 1945 states that ν should be used and the RRHOν functions give better, but not perfect, agreement with the observed C_p° for NH_3. Principal moments of inertia are I_A = 4.414 X 10^{-40} and $I_B = I_C$ = 2.809 X 10^{-40} g. cm.^{3} Electron diffraction studies by Bastiansen and Beagley, Acta Chem. Scand. 18, 2077 (1964) give slightly different constants (bond distance 1.019 Å and angle = 109.1°).

T °K	Heat Capacity, C_p° Observed	JANAF
253.15	8.271(a)	8.268
298.15	8.521(a)	8.515
423.15	9.422(a)	9.423
800.	12.07±0.2(f)	12.225

T °K	Entropy, S° Observed	JANAF
239.72	44.23(b,c)	44.21
298.15	—	46.03
—		—
800.	55.88(d,f) 56.02(e) 56.09(f)	55.99

(a) N. S. Osborne, H. F. Stimson, T. S. Sligh, Jr., and C. S. Cragoe, NBS Sci. Papers 20, 65 (1924-6) measured C_p of gaseous NH_3 (258 to 423°K and 0.5 to 20 atm) within an estimated maximum error of 0.3% (about 0.03 cal. deg.$^{-1}$ mole^{-1}) and obtained C_p° by use of a suitable equation of state.

(b) R. Overstreet and W. F. Giauque, J. Am. Chem. Soc. 59, 254 (1937) determined the entropy of the real gas at the normal boiling point as $S_{239.72}$ = 44.06 ± 0.10 cal. deg.$^{-1}$ mole^{-1}.

(c) $(S^\circ-S)_{239.72}$ = 0.17 cal. deg.$^{-1}$ mole^{-1} from the virial coefficient equation derived by Hirschfelder, McClure and Weeks, J. Chem. Phys. 10, 201 (1942) from the PVT data of Meyers and Jessup, Refrig. Eng. 11, 345 (1925).

(d) Combination of $\Delta H^\circ_{f\ 800}$ = -12.83 kcal. mole^{-1} from the calorimetric measurement of F. E. Wittig and W. Schmatz, Z. Elektrochem. 63, 470 (1959) with ΔG°_{800} = 9.315 kcal. mole^{-1} from equilibrium data (f).

(e) Σ second law analysis of the equilibrium data (f).

(f) K_p° values based on the equilibrium data of Haber, Tamaru and Ponnaz and of Larson and Dodge were analyzed by regression analysis to give ΔG°_{800} = 9.315 ± 0.004, ΔH°_{800} = -12.666 ± 0.017 and $\Delta C^\circ_{p\ 800}$ = -2.31 ± 0.20.

Hydronium Unipositive Ion (H_3O^+)
(Ideal Gas) GFW = 19.02276

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.400	45.924	45.924	.000	138.900	144.983	-106.275
300	8.411	45.976	45.924	.016	138.899	145.020	-105.647
400	9.101	48.485	46.261	.890	138.873	147.066	-80.353
500	9.873	50.599	46.922	1.838	138.905	149.112	-65.177
600	10.604	52.465	47.694	2.863	138.999	151.145	-55.055
700	11.271	54.150	48.497	3.957	139.147	153.159	-47.818
800	11.885	55.696	49.302	5.115	139.344	155.147	-42.384
900	12.459	57.129	50.093	6.333	139.584	157.109	-38.151
1000	13.002	58.470	50.864	7.606	139.863	159.041	-34.758
1100	13.514	59.734	51.614	8.932	140.178	160.944	-31.977
1200	13.994	60.931	52.341	10.308	140.526	162.818	-29.653
1300	14.442	62.069	53.046	11.730	140.899	164.659	-27.682
1400	14.857	63.154	53.729	13.195	141.299	166.473	-25.988
1500	15.239	64.193	54.392	14.700	141.716	168.257	-24.515
1600	15.590	65.187	55.036	16.242	142.149	170.011	-23.222
1700	15.910	66.142	55.662	17.817	142.600	171.742	-22.079
1800	16.202	67.060	56.270	19.423	143.062	173.440	-21.058
1900	16.468	67.943	56.861	21.057	143.536	175.117	-20.143
2000	16.710	68.794	57.436	22.716	144.020	176.766	-19.316
2100	16.930	69.615	57.997	24.398	144.510	178.390	-18.565
2200	17.131	70.407	58.543	26.101	145.007	179.992	-17.881
2300	17.313	71.173	59.076	27.823	145.508	181.569	-17.253
2400	17.480	71.913	59.595	29.563	146.014	183.131	-16.676
2500	17.632	72.630	60.102	31.319	146.520	184.661	-16.143
2600	17.772	73.324	60.598	33.089	147.031	186.181	-15.650
2700	17.899	73.997	61.081	34.873	147.542	187.678	-15.191
2800	18.016	74.651	61.555	36.669	148.054	189.150	-14.764
2900	18.124	75.285	62.017	38.476	148.566	190.613	-14.365
3000	18.223	75.901	62.470	40.293	149.078	192.050	-13.991
3100	18.314	76.500	62.913	42.120	149.592	193.474	-13.640
3200	18.398	77.083	63.346	43.956	150.102	194.883	-13.310
3300	18.476	77.650	63.771	45.800	150.612	196.277	-12.999
3400	18.548	78.203	64.188	47.651	151.119	197.650	-12.705
3500	18.615	78.741	64.596	49.509	151.623	199.015	-12.427
3600	18.677	79.266	64.996	51.374	152.127	200.363	-12.164
3700	18.735	79.779	65.389	53.244	152.625	201.692	-11.913
3800	18.789	80.279	65.774	55.120	153.122	203.016	-11.676
3900	18.839	80.768	66.152	57.002	153.615	204.321	-11.450
4000	18.886	81.246	66.524	58.888	154.103	205.611	-11.234
4100	18.930	81.712	66.888	60.779	154.589	206.895	-11.029
4200	18.971	82.169	67.247	62.674	155.071	208.168	-10.832
4300	19.009	82.616	67.599	64.573	155.550	209.425	-10.644
4400	19.045	83.053	67.945	66.476	156.025	210.673	-10.464
4500	19.079	83.482	68.286	68.382	156.493	211.902	-10.291
4600	19.111	83.901	68.621	70.291	156.961	213.138	-10.126
4700	19.141	84.313	68.950	72.204	157.423	214.351	-9.967
4800	19.170	84.716	69.275	74.120	157.882	215.557	-9.815
4900	19.197	85.112	69.594	76.038	158.337	216.753	-9.668
5000	19.222	85.500	69.908	77.959	158.787	217.937	-9.526
5100	19.246	85.881	70.217	79.882	159.234	219.118	-9.390
5200	19.269	86.255	70.522	81.808	159.678	220.286	-9.258
5300	19.290	86.622	70.823	83.736	160.117	221.454	-9.132
5400	19.310	86.983	71.118	85.666	160.552	222.598	-9.009
5500	19.330	87.337	71.410	87.598	160.984	223.750	-8.891
5600	19.348	87.686	71.698	89.532	161.409	224.877	-8.776
5700	19.366	88.028	71.981	91.468	161.833	226.017	-8.666
5800	19.382	88.365	72.261	93.405	162.251	227.136	-8.559
5900	19.398	88.697	72.537	95.344	162.667	228.248	-8.455
6000	19.413	89.023	72.809	97.285	163.079	229.358	-8.354

June 30, 1966

HYDRONIUM UNIPOSITIVE ION (H_3O^+) (IDEAL GAS) GFW = 19.02276

Point Group $[C_{3v}]$

$S^\circ_{298.15}$ = [45.92] gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = 139.1 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 138.9 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[3760](1)	[3870](2)
[1050](1)	[1550](2)

Bond Distance: H-O = [0.95] Å

Bond Angle: H-O-H = [109]°

σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.39] X 10^{-119} g^3 cm^6

Heat of Formation.

The proton affinity of water has been measured by the ion impact method as -169 kcal/mol by V. L. Tal'rose and E. L. Frankevitch, Doklady Akad. Nauk SSSR 111, 376 (1956), J. Am. Chem. Soc. 80, 2344 (1958). The selected heat of formation of hydronium ion, $\Delta Hf^\circ_0(H_3O^+, g)$ = 139.1 kcal/mol, was derived from the ΔHr°_0 = -169 kcal/mol for $H_2O(g) + H^+(g) \rightarrow H_3O^+(g)$, using the JANAF ΔHf°_0 (H_2O, g) = -57.1 and ΔHf°_0 (H^+, g) = 365.2 kcal/mol.

The values of 195 and 207 kcal/mol for the heat of formation of $H_3O^+(g)$ have also been reported by F. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, and R. R. Bernecker and F. A. Long, J. Phys. Chem. 65, 1565 (1961), respectively. These two values were based on the electron impact studies which may involve unaccounted excitations and excess energy in the fragments. Other literature values have been reviewed by D. M. Bishop, J. Chem. Phys. 43, 4453 (1965).

J. A. Green and T. M. Sugden, Ninth Symposium (International) on Combustion, Academic Press, New York, 1963, based on the studies of the positive ions in flames by mass spectrometry, prefer the value derived from the proton affinity of water obtained by Tal'rose and Frankevitch, rather than the electron impact data. From the approximate equilibrium constant calculations for the reaction $HCO^+(g) + H_2O(g) \rightleftarrows H_3O^+(g) + CO(g)$, D. G. Clifton, AD444078, G. M. Defense Research Laboratory, General Motors Corp., Santa Barbara, Calif., July 1964, has also found that the heat of formation of $H_3O^+(g)$ derived from the proton affinity of water, not from the electron impact data, leads to agreement with the experimental data given by Green and Sugden.

Heat Capacity and Entropy.

Since the molecule $H_3O^+(g)$ has the same number of valence electrons as $NH_3(g)$, a pyramidal molecular configuration (C_{3v}) is assumed for $H_3O^+(g)$ in the tabulation. D. G. Clifton, J. Chem. Phys. 41, 3656 (1964), has obtained a bond distance O-H of 0.95 Å from an application of covalent bond radii and the effect of electric charge, and a bond angle H-O-H of 109° by extrapolating a plot of bond length versus bond angle for $NH_3(g)$ and $PH_3(g)$ to 0.95 Å. Both values are adopted in the tabulation. The three principal moments of inertia are I_A = 0.4004 X 10^{-39}, I_B = I_C = 0.2445 X 10^{-39} g cm^2. D. M. Bishop, loc. cit., has calculated theoretically the bond distance H-O of 0.95 Å and the bond angle H-O-H of 114° 26' with a planar D_{3h} molecular configuration. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton.

Orthophosphoric Acid (H_3PO_4)

(Crystal) Mol. Wt. = 97.999

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 4.059	- 297.541	- 297.541	INFINITE
100	10.240	8.253	43.877	- 3.562	- 299.700	- 288.413	630.297
200	18.130	17.830	28.510	- 2.136	- 300.856	- 276.649	302.293
298	25.384	26.421	26.421	.000	- 301.530	- 264.604	193.951
300	25.480	26.578	26.421	.047	- 301.537	- 264.376	192.588
400	30.000	34.558	27.479	2.832	- 301.749	- 251.947	137.651
500	33.250	41.625	29.615	6.005	- 301.657	- 239.502	104.681
600	35.700	47.915	32.151	9.458	- 301.365	- 227.096	82.716
700	37.400	53.555	34.813	13.120	- 300.945	- 214.749	67.044
800	38.800	58.649	37.479	16.936	- 320.867	- 207.781	56.760
900	39.500	63.265	40.092	20.856	- 320.079	- 193.691	47.032
1000	40.000	67.453	42.622	24.831	- 319.274	- 179.690	39.269
1100	40.600	71.292	45.056	28.860	- 318.453	- 165.773	32.934
1200	41.000	74.842	47.393	32.940	- 317.613	- 151.929	27.669
1300	41.400	78.140	49.632	37.060	- 316.767	- 138.156	23.225
1400	41.700	81.219	51.780	41.215	- 315.916	- 124.449	19.426
1500	42.000	84.106	53.840	45.400	- 315.068	- 110.800	16.143

June 30, 1962

ORTHOPHOSPHORIC ACID (H_3PO_4) (CRYSTAL) MOL. WT. = 97.999

$\Delta H_f^\circ{}_{0} = -297.5 \pm 0.3$ kcal. mole^{-1}

$\Delta H_m^\circ = 3.100$ kcal. mole^{-1}

$T_m = 315.51$°K

$\Delta H_f^\circ{}_{298.15} = -301.5 \pm 0.3$ kcal. mole^{-1}

$S^\circ_{298.15} = 26.42$ cal. deg.$^{-1}$ mole^{-1}

Heat of Formation.

The heat of formation was determined by W. S. Holmes [private communication July 5, 1962, Albright and Wilson (MFG) Ltd., Oldbury, Birmingham, Great Britain (in press by Faraday Society)]. W. S. Holmes measured the enthalpy of combustion of white phosphorus (α form) in oxygen in a bomb calorimeter. The product, P_4O_{10}(hexagonal), was hydrolyzed in 10N perchloric acid to give H_3PO_4. Measurement of the enthalpy of solution of $H_3PO_4(c)$ then enabled the $\Delta H_f^\circ{}_{298.15}$ to be calculated according to the following cycle:

$$\begin{tikzcd}
4P_{(\alpha)} + 5O_2(g) \arrow[r, "\Delta H_r^*"] & P_4O_{10}(\text{hexagonal}) + 6H_2O(HClO_4) \arrow[r, "\Delta H_r^*"] & 4H_3PO_4(HClO_4) \\
6H_2O \arrow[r, "\Delta H_f\ \text{N.B.S. Cir 500}"] & 6H_2O(l) \arrow[u, "\Delta H_r^*"] & 4H_3PO_4(c) \arrow[u, "\Delta H_r^*"]
\end{tikzcd}$$

* All ΔH_r's were measured.

E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem., 65, 523 (1961), from partial molal heat contents of H_3PO_4 solutions found that a smooth extrapolation to 100% H_3PO_4 would give them a $\Delta H_f^\circ{}_{298.15}$ for H_3PO_4 (c) which was 755 cal. mole^{-1} greater than the $\Delta H_f^\circ{}_{298.15}$ reported in the National Bureau of Standards Circular 500. The Circular 500 (loc. cit.) heat of formation refers to the work of Thomsen, "Thermochemische Untersuchungen," Vol. 2, Barth, Leipzig (1882-1886). The heats of formation summarized:

$\Delta H_f^\circ{}_{298.15}$	Source
-305.7 ± 0.3 kcal. mole^{-1}	W. S. Holmes (loc. cit.)
-306.2 kcal. mole^{-1}	Circular 500 (loc. cit.)
-305.4 kcal. mole^{-1}	Egan and Luff (loc. cit.)

The selected $\Delta H_f^\circ{}_{298.15}$, -305.7 ± 0.3 kcal. mole^{-1}, was corrected by +4.17 kcal. mole^{-1}, which is the $\Delta H_f^\circ{}_{298.15}$ of white (α) phosphorus.

Heat Capacity and Entropy.

Third law entropy was calculated from the low temperature heat capacities measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Melting.

The heat of fusion, ΔH_m, was reported by E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem. 65, 523 (1961) from ΔH_m data measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957). The melting point T_m = 315.51°K was taken from the work of W. H. Ross and R. M. Jones, J. Am. Chem. Soc. 47, 2165 (1925).

Orthophosphoric Acid (H_3PO_4)

(Liquid) Mol. Wt. = 97.999

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	48.000	34.993	34.993	.000	- 298.810	- 264.440	193.830
300	48.000	35.289	34.993	.089	- 298.776	- 264.227	192.480
400	48.000	49.098	36.876	4.889	- 296.972	- 252.986	138.218
500	48.000	59.809	40.431	9.689	- 295.253	- 242.190	105.856
600	48.000	68.561	44.413	14.489	- 293.614	- 231.733	84.405
700	48.000	75.960	48.404	19.289	- 292.056	- 221.543	69.165
800	48.000	82.369	52.258	24.089	- 310.994	- 216.884	59.247
900	48.000	88.023	55.924	28.889	- 309.326	- 205.220	49.832
1000	48.000	93.080	59.391	33.689	- 307.696	- 193.739	42.340
1100	48.000	97.655	62.665	38.489	- 306.104	- 182.422	36.242
1200	48.000	101.832	65.758	43.289	- 304.544	- 171.247	31.187
1300	48.000	105.674	68.682	48.089	- 303.018	- 160.201	26.931
1400	48.000	109.231	71.453	52.889	- 301.522	- 149.271	23.301
1500	48.000	112.542	74.083	57.689	- 300.059	- 138.445	20.171
1600	48.000	115.640	76.585	62.489	- 298.627	- 127.721	17.445
1700	48.000	118.550	78.969	67.289	- 297.220	- 117.079	15.051
1800	48.000	121.294	81.244	72.089	- 295.841	- 106.524	12.933
1900	48.000	123.889	83.421	76.889	- 294.489	- 96.042	11.047
2000	48.000	126.351	85.507	81.689	- 293.162	- 85.636	9.357

June 30, 1962

Orthophosphoric Acid (H_3PO_4) (Liquid)

Mol. Wt. = 97.999

ΔH_f° 298.15 = -298.81 ± 0.5 kcal. mole^{-1}

$S^\circ_{298.15}$ = 35.0 cal. deg.$^{-1}$ mole^{-1}

T_m = 315.51°K

ΔH_m = 3.100 kcal. mole^{-1}

Heat of Formation. Calculated from ΔH_f° 298.15 for H_3PO_4(c) and ΔH_m° given by E. P. Egan, Jr., and B. B. Luff, J. Phys. Chem. 65, 523 (1961) using the ΔH_m data reported by E. P. Egan, Jr., and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Heat Capacity and Entropy. The heat capacity is estimated. The entropy at 298.15°K. is calculated using $S^\circ_{298.15}$ of H_3PO_4(c) and the ΔH_m at 298.15°K.

Melting Data. T_m reported by W. H. Ross and R. M. Jones, J. Am. Chem. Soc. 47, 2165 (1925). ΔH_m from E. P. Egan, Jr., and Z. T. Wakefield (loc. cit.).

Phosphine (PH_3)

(Ideal Gas) Mol. Wt. = 33.999

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.423	6.945	6.945	INFINITE
100	7.949	41.343	57.622	-1.628	6.511	6.184	-13.514
200	8.111	46.877	51.020	-.829	6.087	5.992	-6.547
298	8.868	50.238	50.238	.000	5.470	6.073	-4.452
300	8.887	50.293	50.238	.016	5.458	6.077	-4.427
400	9.987	52.997	50.600	.959	4.827	6.380	-3.486
500	11.110	55.347	51.319	2.014	4.262	6.835	-2.987
600	12.167	57.468	52.169	3.179	3.776	7.395	-2.694
700	13.130	59.417	53.067	4.445	3.356	8.033	-2.508
800	13.985	61.227	53.976	5.801	-17.430	3.416	-.933
900	14.729	62.918	54.876	7.238	-17.497	6.028	-1.464
1000	15.368	64.504	55.761	8.744	-17.507	8.641	-1.888
1100	15.915	65.995	56.624	10.308	-17.473	11.255	-2.236
1200	16.380	67.401	57.464	11.924	-17.401	13.864	-2.525
1300	16.776	68.728	58.280	13.582	-17.303	16.465	-2.768
1400	17.115	69.984	59.071	15.277	-17.184	19.059	-2.975
1500	17.405	71.175	59.839	17.004	-17.052	21.645	-3.154
1600	17.655	72.306	60.583	18.757	-16.913	24.217	-3.308
1700	17.871	73.383	61.305	20.533	-16.765	26.786	-3.443
1800	18.058	74.410	62.004	22.330	-16.612	29.342	-3.562
1900	18.222	75.391	62.683	24.144	-16.456	31.892	-3.668
2000	18.365	76.329	63.342	25.974	-16.299	34.431	-3.762
2100	18.491	77.228	63.982	27.817	-16.142	36.964	-3.847
2200	18.602	78.091	64.604	29.672	-15.986	39.490	-3.923
2300	18.701	78.920	65.209	31.537	-15.830	42.007	-3.991
2400	18.789	79.718	65.797	33.411	-15.678	44.520	-4.054
2500	18.868	80.487	66.369	35.294	-15.529	47.023	-4.111
2600	18.939	81.228	66.926	37.185	-15.381	49.523	-4.163
2700	19.002	81.944	67.469	39.082	-15.238	52.016	-4.210
2800	19.060	82.636	67.999	40.985	-15.097	54.503	-4.254
2900	19.112	83.306	68.515	42.894	-14.958	56.991	-4.295
3000	19.159	83.955	69.019	44.807	-14.825	59.466	-4.332
3100	19.202	84.584	69.511	46.725	-14.693	61.940	-4.367
3200	19.242	85.194	69.992	48.648	-14.566	64.410	-4.399
3300	19.278	85.787	70.461	50.574	-14.443	66.878	-4.429
3400	19.311	86.363	70.921	52.503	-14.324	69.338	-4.457
3500	19.341	86.923	71.370	54.436	-14.210	71.800	-4.483
3600	19.369	87.468	71.809	56.371	-14.100	74.253	-4.508
3700	19.395	87.999	72.240	58.309	-13.996	76.707	-4.531
3800	19.419	88.517	72.661	60.250	-13.894	79.159	-4.552
3900	19.441	89.021	73.074	62.193	-13.800	81.608	-4.573
4000	19.462	89.514	73.479	64.138	-13.710	84.050	-4.592
4100	19.481	89.995	73.876	66.086	-13.624	86.493	-4.610
4200	19.499	90.464	74.266	68.035	-13.544	88.938	-4.628
4300	19.516	90.923	74.648	69.985	-13.469	91.372	-4.644
4400	19.532	91.372	75.023	71.938	-13.398	93.811	-4.659
4500	19.546	91.811	75.391	73.892	-13.334	96.243	-4.674
4600	19.560	92.241	75.753	75.847	-13.272	98.679	-4.688
4700	19.573	92.662	76.108	77.804	-13.218	101.115	-4.702
4800	19.585	93.074	76.457	79.762	-13.167	103.546	-4.714
4900	19.596	93.478	76.800	81.721	-13.121	105.981	-4.727
5000	19.607	93.874	77.138	83.681	-13.080	108.407	-4.738
5100	19.617	94.262	77.470	85.642	-13.045	110.839	-4.750
5200	19.627	94.644	77.797	87.604	-13.013	113.264	-4.760
5300	19.636	95.017	78.118	89.567	-12.987	115.697	-4.771
5400	19.644	95.385	78.434	91.531	-12.966	118.119	-4.780
5500	19.652	95.745	78.746	93.496	-12.949	120.550	-4.790
5600	19.660	96.099	79.053	95.462	-12.938	122.973	-4.799
5700	19.667	96.447	79.355	97.428	-12.930	125.404	-4.808
5800	19.674	96.789	79.652	99.395	-12.928	127.827	-4.816
5900	19.681	97.126	79.946	101.363	-12.930	130.255	-4.825
6000	19.687	97.457	80.235	103.332	-12.936	132.680	-4.833

June 30, 1962

PHOSPHINE (PH_3) (IDEAL GAS) MOL. WT. = 33.999

$\Delta H^\circ_{f\ 0} = +7.0 \pm 0.4$ kcal mole⁻¹

$\Delta H^\circ_{f\ 298.15} = +5.5 \pm 0.4$ kcal/mole⁻¹

Point Group C_{3v}

$S^\circ_{298.15} = 50.24$ cal deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm⁻¹	ω, cm⁻¹
2332.9 (1)	2327.7 (2)
992 (1)	1122.4 (2)

P-H distance 1.42 Å

H-P-H angle = 93° 50'

$\sigma = 3$

$I_A = I_B = 6.29 \times 10^{-40}$ g cm^2

$I_C = 7.24 \times 10^{-40}$ g cm^2

Heat of Formation

The heat of formation was derived by S. R. Gunn and L. G. Green, J. Phys. Chem., 65, 779 (1961). In order to obtain the $\Delta H^\circ_{f\ 298.15}$ they measured the heat of explosive decomposition of phosphine gas. There is a good deal of uncertainty about the heat of formation of $PH_3(g)$, for instance:

$\Delta H^\circ_{f\ 298.15}$	Source
+3.6 kcal mole⁻¹	The heat of reaction between gaseous PH_3 and saturated bromine water. M. J. Ogier, Ann. Chim. Phys., 20, 5 (1880).
+6.3 kcal mole⁻¹	The heat of combustion of $PH_3(g)$ in $O_2(g)$ to form H_3PO_4. M. P. Lemoult, Compt. Rend., 145, 374 (1907).
-2.34 kcal mole⁻¹	Equilibrium data of W. N. Ipatiew, and A. W. Frost, Ber. dtsch. chem. Ges., 63B, 1104 (1930). Their data showed a wide variation in ΔH, as much as 11 kcal mole⁻¹.
+1.5 kcal mole⁻¹	National Bureau of Standards, Report No. 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," 1 January 1962 (page 80-91).

The heats of formation have been reviewed by T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth's Scientific Publications, London, (1958); and by F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of The Chemical Substances," Reinhold Publishing Corp., New York (1936).

The heat of formation selected was, +1.3 ± 0.4 kcal mole⁻¹, as reported by Gunn and Green (loc. cit.). The selected heat of formation was based on white (α) phosphorus and thus required an adjustment for the red (V) phosphorus reference state.

Heat Capacity and Entropy

The fundamental wave number and degeneracy assignments are from the infrared spectral data by V. N. McConaghie and H. H. Nielsen, J. Chem. Phys., 21, 1836, (1953). The molecular constants are those obtained from infrared data by H. H. Nielsen, J. Chem. Phys., 20, 759 (1952). Nielsen (loc. cit.) has reported the molecular constants after calculating the Coriolis coupling effect between the wave numbers 2 and 4, or (992 cm⁻¹) and (1122.4 cm⁻¹).

Ammonium Iodide (NH_4I)
(Crystal) Mol. Wt. = 144.95

INTERIM TABLE

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	19.540	27.000	27.000	.000	- 48.300	- 26.780	19.629
300	19.570	27.121	27.000	.036	- 48.308	- 26.646	19.411
400	21.271	32.980	27.788	2.077	- 50.590	- 19.301	10.545
500	22.980	37.910	29.331	4.290	- 55.888	- 10.972	4.796
600	24.680	42.251	31.130	6.673	- 55.710	- 2.003	.730
700	26.400	46.184	33.003	9.227	- 55.373	6.925	- 2.162
800	26.130	49.822	34.881	11.953	- 54.881	15.792	- 4.314
900	29.870	53.236	36.733	14.853	- 54.236	24.590	- 5.971
1000	31.570	56.472	38.546	17.926	- 53.439	33.306	- 7.279
1100	33.300	59.562	40.317	21.169	- 52.495	41.936	- 8.332
1200	35.000	62.533	42.045	24.585	- 51.403	50.475	- 9.192
1300	36.336	65.389	43.732	28.154	- 50.181	58.915	- 9.904
1400	37.308	68.120	45.377	31.840	- 48.870	67.259	- 10.499
1500	37.917	70.717	46.981	35.604	- 47.509	75.507	- 11.001
1600	38.161	73.174	48.542	39.411	- 46.133	83.661	- 11.427
1700	38.042	75.485	50.059	43.224	- 44.773	91.734	- 11.793
1800	37.558	77.648	51.533	47.007	- 43.467	99.724	- 12.108
1900	36.711	79.657	52.961	50.724	- 42.249	107.647	- 12.382
2000	35.500	81.511	54.343	54.337	- 41.154	115.506	- 12.621

March 31, 1962

Ammonium Iodide (NH_4I) (Crystal)

Mol. Wt. = 144.95

$\Delta H_f^\circ{}_{298.15} = -48.30$ kcal. mole^{-1}

$S^\circ_{298.15} = 27.0 \pm 1.5$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{s\ 798} = 40.280$ kcal. mole^{-1}

$T_t = 260$°K

$\Delta H_t = 0.70$ kcal. mole^{-1}

$T_m = 824$°K

$\Delta H_m = [5.0]$ kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$, T_t, and T_m. Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties". $S^\circ_{298.15}$ was taken from K. K. Kelley, U. S. Bureau of Mines Bulletin 584, (1960). Sublimation data from N. W. Luft, Ind. Chemist, 31, 502 (1955).

Heat Capacity. Data extrapolated from Simon, Simson, and Ruhemann Z. Phys. Chemie, 129, 339 (1927).

Hydrazine (N_2H_4)

(Liquid) Mol. Wt. = 32.04528

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100	20.850	5.028	49.091	-4.406	11.611	19.797	-43.263
200	22.250	19.910	31.166	-2.251	11.857	27.880	-30.464
298	23.623	29.050	29.050	-.000	12.100	35.694	-26.163
300	23.650	29.196	29.050	.044	12.105	35.840	-26.108
400	25.660	36.256	29.999	2.503	12.479	43.701	-23.876
500	27.860	42.218	31.861	5.179	13.054	51.444	-22.485
600	30.060	47.492	34.034	8.075	13.838	59.052	-21.509

Dec. 31, 1965

HYDRAZINE (N_2H_4) (LIQUID) MOL. WT. = 32.04528

$S_{298.15}$ = 29.05 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

T_m = 274.69°K.

T_b = 386.9°K.

$\Delta H^\circ_{f\ 298.15}$ = 12.10 ± 0.1 kcal. mole^{-1}

ΔH°_m = 3.025 kcal. mole^{-1}

ΔH°_v = 9.70 kcal. mole^{-1}

Heat of Formation.

A. M. Hughes, R. J. Corruccini and E. C. Gilbert, J. Am. Chem. Soc. 61, 2639 (1939), measured the heats of combustion of hydrazine and hydrazine monohydrate. The data, adjusted as suggested by L. G. Cole and E. C. Gilbert, J. Am. Chem. Soc. 73, 5423 (1951), are summarized below. Heats of solution determined by V. C. Bushnell, A. M. Hughes and E. C. Gilbert, J. Am. Chem. Soc. 59, 2142 (1937) interrelate $N_2H_4(l)$ and $N_2H_4 \cdot H_2O(l)$. An intermediate value was selected from the resulting heats of formation.

Source	Reaction	$\Delta H^\circ_{r\ 298}$	$\Delta H^\circ_{f\ 298}$
Hughes	$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$	-148.68 ± 0.06	12.05
Hughes	$N_2H_4 \cdot H_2O(l) + O_2(g) \rightarrow N_2(g) + 3H_2O(l)$	-147.00 ± 0.06	——
Bushnell	$N_2H_4(l) + H_2O(l) \rightarrow N_2H_4 \cdot H_2O(l)$	-1.80	12.17*

*From combination of second and third reactions.

Heat Capacity and Entropy.

Heat capacities (12-340°K) of hydrazine crystal and liquid were determined by D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. 71, 2293 (1949). Values beyond the experimental range for the liquid were extrapolated linearly. The entropy was obtained from the heat of melting and the smoothed heat capacities of the crystal using S°_{12} = 0.023 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

Taken from Scott et al., loc. cit.

Vaporization Data.

The normal boiling point and heat of vaporization are those calculated for the ideal gas from these tables. The boiling point found for the real gas (387.3°K) by W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934) is in good agreement. The selected heat of vaporization, ΔH°_{298} = 10.69 kcal. mole^{-1}, is based on the vapor pressure data of Scott et al., loc. cit., series III. Vapor pressure measurements of Hieber and Woerner, loc. cit., and E. T. Chang and N. A. Gokcen, AD-458288, Defense Documentation Center, January, 1964, are in satisfactory agreement as shown below.

Source	Temp. Range °K.	$\Delta H^\circ_{v\ 298}$(kcal. mole^{-1}) 2nd Law	3rd Law	3rd Law Drift e.u.
Scott, et al. (1949)	273-343	10.683 ± 0.003	10.696	0.05 ± 0.01
Chang, Gockcen (1964)	276-325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner (1934)	293-387	10.82 ± 0.03	10.71	-0.33 ± 0.07

The second law-third law consistency of Scott et al. reflects the use of these data in selection of the gas phase functions (see H_4N_2 gas).

Hydrazine (N_2H_4)
(Ideal Gas) Mol. Wt. = 32.04528

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.755	26.155	26.155	INFINITE
100	8.214	46.625	66.180	-1.956	24.751	28.778	-62.891
200	9.718	52.717	58.058	-1.068	23.730	33.192	-36.268
298	12.145	57.030	57.030	.000	22.790	38.042	-27.884
300	12.194	57.106	57.031	.023	22.774	38.136	-27.781
400	14.747	60.971	57.540	1.372	22.038	43.375	-23.698
500	16.861	64.498	58.584	2.957	21.522	48.772	-21.317
600	18.538	67.726	59.843	4.730	21.183	54.257	-19.762
700	19.910	70.690	61.184	6.654	20.975	59.787	-18.666
800	21.081	73.427	62.545	8.705	20.871	65.339	-17.849
900	22.111	75.970	63.897	10.866	20.849	70.901	-17.216
1000	23.030	78.348	65.225	13.124	20.897	76.460	-16.709
1100	23.854	80.583	66.520	15.469	21.002	82.011	-16.293
1200	24.592	82.690	67.781	17.892	21.156	87.553	-15.945
1300	25.252	84.685	69.005	20.384	21.349	93.077	-15.647
1400	25.842	86.579	70.193	22.940	21.576	98.585	-15.389
1500	26.367	88.380	71.346	25.551	21.826	104.080	-15.164
1600	26.836	90.097	72.465	28.211	22.094	109.552	-14.963
1700	27.254	91.737	73.551	30.916	22.382	115.012	-14.785
1800	27.626	93.305	74.605	33.660	22.683	120.450	-14.624
1900	27.960	94.808	75.629	36.440	22.998	125.875	-14.478
2000	28.258	96.250	76.624	39.251	23.321	131.281	-14.345
2100	28.525	97.635	77.592	42.091	23.651	136.671	-14.223
2200	28.766	98.968	78.533	44.955	23.985	142.044	-14.110
2300	28.982	100.251	79.450	47.843	24.326	147.404	-14.006
2400	29.177	101.489	80.343	50.751	24.669	152.750	-13.909
2500	29.354	102.684	81.213	53.678	25.011	158.073	-13.818
2600	29.515	103.838	82.061	56.621	25.357	163.394	-13.734
2700	29.660	104.955	82.888	59.580	25.703	168.695	-13.654
2800	29.793	106.036	83.696	62.553	26.049	173.981	-13.579
2900	29.915	107.084	84.484	65.539	26.397	179.264	-13.509
3000	30.026	108.100	85.254	68.536	26.741	184.526	-13.442
3100	30.128	109.086	86.007	71.543	27.086	189.777	-13.379
3200	30.221	110.044	86.744	74.561	27.428	195.021	-13.319
3300	30.307	110.975	87.464	77.587	27.766	200.257	-13.262
3400	30.387	111.881	88.169	80.622	28.105	205.476	-13.207
3500	30.460	112.763	88.859	83.664	28.437	210.689	-13.155
3600	30.528	113.622	89.535	86.714	28.767	215.891	-13.106
3700	30.591	114.459	90.197	89.770	29.091	221.088	-13.058
3800	30.650	115.276	90.846	92.832	29.413	226.272	-13.013
3900	30.704	116.073	91.483	95.900	29.729	231.448	-12.969
4000	30.755	116.851	92.108	98.973	30.040	236.616	-12.927
4100	30.802	117.611	92.720	102.051	30.347	241.775	-12.887
4200	30.847	118.354	93.322	105.133	30.647	246.930	-12.849
4300	30.888	119.080	93.913	108.220	30.944	252.076	-12.811
4400	30.927	119.790	94.493	111.311	31.235	257.214	-12.775
4500	30.963	120.486	95.063	114.405	31.518	262.341	-12.740
4600	30.998	121.167	95.623	117.503	31.799	267.476	-12.707
4700	31.030	121.834	96.173	120.605	32.073	272.595	-12.675
4800	31.060	122.487	96.715	123.709	32.341	277.712	-12.644
4900	31.089	123.128	97.247	126.817	32.605	282.818	-12.614
5000	31.116	123.756	97.771	129.927	32.862	287.922	-12.584
5100	31.141	124.373	98.287	133.040	33.113	293.019	-12.556
5200	31.165	124.978	98.794	136.155	33.360	298.113	-12.529
5300	31.188	125.572	99.294	139.273	33.600	303.205	-12.502
5400	31.210	126.155	99.786	142.393	33.834	308.283	-12.476
5500	31.230	126.728	100.271	145.514	34.061	313.368	-12.451
5600	31.249	127.291	100.748	148.638	34.283	318.439	-12.427
5700	31.268	127.844	101.219	151.764	34.500	323.519	-12.404
5800	31.285	128.388	101.682	154.892	34.710	328.584	-12.381
5900	31.302	128.923	102.140	158.021	34.914	333.649	-12.359
6000	31.318	129.449	102.590	161.152	35.113	338.707	-12.337

Dec. 31, 1960; Dec. 31, 1965

HYDRAZINE (N_2H_4) (IDEAL GAS) MOL. WT. = 32.04528

Point Group C_2

$S^\circ_{298.15}$ = 57.03 ± 0.4 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H_f^\circ{}_0$ = 26.16 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 22.79 ± 0.2 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
3350	875	3280
3261	780	1275
1312	377	[933]
1098	3330	966

Bond Distance: N-H = 1.022 Å N-N = 1.449 Å

Bond Angle: H-N-H = 109.47° H-N-N = 112.0° σ = 2

Torsional angle between two NH_2 groups ⩾ 90° from eclipsed position.

Product of the Moments of Inertia: $I_AI_BI_C$ = 7.307 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

This was obtained from the heat of formation of the liquid and the selected heat of vaporization, ΔH°_{298} = 10.69 kcal. mole^{-1}, derived from the vapor pressure data (Series III) of D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. 71, 2293 (1949). Other vapor pressure data from W. Hieber and A. Woerner, Z. Elektrochem. 40, 252 (1934) and E. T. Chang and N. A. Gokcen, AD-458288, Defense Documentation Center, January, 1964, are in satisfactory agreement (see N_2H_4 liquid table).

Heat Capacity and Entropy.

Functions were calculated from the constants given above using the rigid rotator harmonic oscillator method. The entropy was increased by R ln 2 because two rotameric forms are implied by use of the torsional frequency. Small but arbitrary adjustments were made in the assignment of the bending mode frequencies in order to reproduce the vapor pressure data of Scott et al., loc. cit., as closely as possible. Calculated values of S°_{298} = 57.03 and S°_{340} = 58.70 cal. deg.$^{-1}$ mole^{-1} may be compared with 56.99 and 58.69, respectively, derived from the data of Scott et al.. Internal rotation calculations would require a complex potential function in order to fit the data. The barrier to inversion (990 cm.$^{-1}$ ~ 2.8 kcal.) is slightly less than the barrier to internal rotation at the trans position (1110 cm.$^{-1}$ ~ 3.2 kcal.) according to analyses of the microwave data by T. Kasuya, Sci. Papers. Inst. Phys. Chem. Res. (Tokyo) 56, No. 1, 1-39 (1962) and T. Kasuya and T. Kojima, J. Phys. Soc. Japan 18, 364-8 (1963).

From matrix isolation and gas phase infrared studies, E. Catalano, R. H. Sanborn and J. W. Frazer, J. Chem. Phys. 38, 2265 (1963), have suggested possible uncertainties in the assignment of the bending mode frequencies in the region from 1630 to 740 cm.$^{-1}$ The question hinges on the uncertain existence of a gas phase fundamental at about 1600 cm.$^{-1}$ as observed by P. A. Giguere and I. D. Liu, J. Chem. Phys. 20, 136 (1952). No corresponding matrix band was found and the gas phase band appeared to be due to absorption on the cell windows. A vapor phase Raman frequency at 1564 cm.$^{-1}$ was observed, however, by Yu. I. Kotov and V. M. Tatevskii, Opt. i Spektroskopiya 15, 65 (1963). Catalano et al. suggest one assignment based on the uncertain fundamental and a tentative alternative assignment excluding it. The two assignments give entropies that are 0.26 cal. deg.$^{-1}$ mole^{-1} lower and 0.12 higher than the third law value. The lower calculated entropy is probably more reasonable, but the higher value could be more easily modified to agree with the third law value. Thus the alternative assignment was adopted with ν_{11} arbitrarily increased from ~810 to 933 cm.$^{-1}$

The structural constants are based primarily on the electron diffraction study of Y. Morino, T. Iijima and Y. Murata, Bull. Chem. Soc. Japan 33, 46 (1960). Related analyses of the infrared fine structure of the torsional frequency (377 cm.$^{-1}$), A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. Mizushima, Spectrochim. Acta 16, 1471 (1960), and of the microwave spectra, Kasuya and Kojima, loc. cit., are in close agreement. The microwave data give an H-N-H angle of 106° and a torsional angle of 90°2'. Principal moments of inertia of the adopted structure are I_A = 0.574 X 10^{-39}, I_B = 3.573 X 10^{-39} and I_C = 3.563 X 10^{-39} g. cm.^{2}

Silane (SiH_4)

(Ideal Gas) Mol. Wt. = 32.122

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.519	10.085	10.085	INFINITE
100	7.952	39.496	56.735	-1.724	9.298	10.317	-22.548
200	8.490	45.098	49.663	-.913	8.628	11.567	-12.639
298	10.236	48.789	48.789	.000	7.800	13.184	-9.664
300	10.274	48.852	48.789	.019	7.784	13.217	-9.628
400	12.303	52.088	49.216	1.149	7.017	15.147	-8.276
500	14.139	55.035	50.089	2.473	6.394	17.254	-7.541
600	15.751	57.759	51.143	3.969	5.917	19.473	-7.093
700	17.148	60.294	52.272	5.616	5.570	21.763	-6.794
800	18.344	62.664	53.424	7.392	5.332	24.093	-6.581
900	19.356	64.885	54.576	9.278	5.180	26.449	-6.422
1000	20.208	66.970	55.712	11.258	5.099	28.816	-6.297
1100	20.924	68.930	56.825	13.315	5.072	31.190	-6.196
1200	21.525	70.777	57.912	15.439	5.090	33.564	-6.113
1300	22.032	72.521	58.969	17.617	5.138	35.934	-6.041
1400	22.461	74.170	59.996	19.842	5.209	38.302	-5.979
1500	22.825	75.732	60.994	22.107	5.293	40.663	-5.924
1600	23.137	77.215	61.962	24.406	5.385	43.016	-5.875
1700	23.405	78.626	62.901	26.733	-6.620	45.476	-5.846
1800	23.637	79.971	63.812	29.086	-6.474	48.534	-5.893
1900	23.838	81.254	64.697	31.460	-6.325	51.586	-5.933
2000	24.014	82.482	65.555	33.852	-6.176	54.631	-5.970
2100	24.169	83.657	66.390	36.262	-6.027	57.668	-6.001
2200	24.305	84.785	67.200	38.686	-5.880	60.697	-6.029
2300	24.425	85.868	67.989	41.122	-5.735	63.721	-6.055
2400	24.532	86.910	68.755	43.570	-5.594	66.738	-6.077
2500	24.628	87.913	69.502	46.028	-5.459	69.746	-6.097
2600	24.713	88.881	70.229	48.495	-5.325	72.754	-6.115
2700	24.791	89.815	70.937	50.971	-5.196	75.753	-6.131
2800	24.860	90.716	71.627	53.453	-5.073	78.746	-6.146
2900	24.923	91.591	72.301	55.942	-4.953	81.743	-6.160
3000	24.980	92.437	72.958	58.438	-4.838	84.727	-6.172
3100	25.032	93.257	73.599	60.938	-4.727	87.709	-6.183
3200	25.079	94.052	74.226	63.444	-4.622	90.692	-6.194
3300	25.123	94.825	74.839	65.954	-4.523	93.672	-6.203
3400	25.163	95.575	75.438	68.468	-4.428	96.643	-6.212
3500	25.199	96.305	76.024	70.986	-4.341	99.615	-6.220
3600	25.233	97.016	76.597	73.508	-99.233	103.056	-6.256
3700	25.264	97.708	77.158	76.033	-99.097	108.674	-6.419
3800	25.293	98.382	77.708	78.561	-98.965	114.288	-6.573
3900	25.319	99.039	78.246	81.091	-98.843	119.897	-6.718
4000	25.344	99.680	78.774	83.625	-98.725	125.505	-6.857
4100	25.367	100.306	79.292	86.160	-98.614	131.107	-6.988
4200	25.389	100.918	79.799	88.698	-98.510	136.715	-7.114
4300	25.409	101.516	80.298	91.238	-98.412	142.308	-7.233
4400	25.427	102.100	80.786	93.780	-98.320	147.904	-7.346
4500	25.445	102.672	81.266	96.323	-98.238	153.494	-7.454
4600	25.461	103.231	81.738	98.869	-98.158	159.096	-7.558
4700	25.477	103.779	82.201	101.416	-98.087	164.687	-7.658
4800	25.491	104.315	82.656	103.964	-98.020	170.279	-7.753
4900	25.505	104.841	83.104	106.514	-97.960	175.866	-7.844
5000	25.518	105.356	83.544	109.065	-97.906	181.452	-7.931
5100	25.530	105.862	83.976	111.617	-97.859	187.043	-8.015
5200	25.541	106.358	84.402	114.171	-97.817	192.625	-8.095
5300	25.552	106.844	84.821	116.726	-97.782	198.216	-8.173
5400	25.562	107.322	85.233	119.281	-97.752	203.794	-8.248
5500	25.572	107.791	85.639	121.838	-97.728	209.380	-8.320
5600	25.581	108.252	86.039	124.396	-97.711	214.958	-8.389
5700	25.590	108.705	86.432	126.954	-97.700	220.549	-8.456
5800	25.598	109.150	86.820	129.514	-97.694	226.125	-8.520
5900	25.606	109.588	87.202	132.074	-97.695	231.715	-8.583
6000	25.613	110.018	87.579	134.635	-97.702	237.289	-8.643

December 31, 1960.

Silane (SiH_4) (Ideal Gas)

Mol. Wt. = 32.122

ΔH_f° 298.15 = 7.3 ± 0.3 kcal. mole^{-1}

$S^\circ_{298.15}$ = 48.789 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$
2183 (3)
910 (3)
978 (2)
2187 (1)

Si-H distance = 1.457 Å   H-Si-H angle = 109° 28' σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = 0.84659 X 10^{-117} g.^{3} cm.^{6}

Heat of Formation. ΔH_f° 298.15 was determined by S. Gunn and L. Greene, J. Phys. Chem. 65, 779 (1961). A value of 7.8 kcal. mole^{-1} was selected by J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from J. S. Gordon, op. cit.. G. Janz and Y. Mikawa, Bull. Chem. Soc. Japan, 34, 1495 (1961) reported slightly different values for the vibrational levels.

Mercury (Hg)

(Reference State) Mol. Wt. = 200.61

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.233	.000	.000	.000
100	5.797	8.895	27.145	- 1.825	.000	.000	.000
200	6.519	13.148	19.188	- 1.208	.000	.000	.000
298	6.687	18.171	18.171	.000	.000	.000	.000
300	6.684	18.212	18.171	.012	.000	.000	.000
400	6.552	20.115	18.431	.673	.000	.000	.000
500	6.495	21.570	18.919	1.325	.000	.000	.000
600	6.486	22.752	19.463	1.974	.000	.000	.000
700	4.968	46.034	22.250	16.649	.000	.000	.000
800	4.968	46.698	25.266	17.146	.000	.000	.000
900	4.968	47.283	27.680	17.642	.000	.000	.000
1000	4.968	47.806	29.667	18.139	.000	.000	.000
1100	4.968	48.280	31.338	18.636	.000	.000	.000
1200	4.968	48.712	32.768	19.133	.000	.000	.000
1300	4.968	49.110	34.010	19.630	.000	.000	.000
1400	4.968	49.478	35.102	20.126	.000	.000	.000
1500	4.968	49.821	36.072	20.623	.000	.000	.000
1600	4.968	50.141	36.941	21.120	.000	.000	.000
1700	4.968	50.443	37.727	21.617	.000	.000	.000
1800	4.968	50.726	38.441	22.114	.000	.000	.000
1900	4.968	50.995	39.095	22.610	.000	.000	.000
2000	4.968	51.250	39.696	23.107	.000	.000	.000
2100	4.968	51.492	40.252	23.604	.000	.000	.000
2200	4.968	51.723	40.769	24.101	.000	.000	.000
2300	4.968	51.944	41.250	24.598	.000	.000	.000
2400	4.968	52.156	41.700	25.094	.000	.000	.000
2500	4.968	52.358	42.122	25.591	.000	.000	.000
2600	4.968	52.553	42.519	26.088	.000	.000	.000
2700	4.968	52.741	42.895	26.585	.000	.000	.000
2800	4.968	52.921	43.249	27.082	.000	.000	.000
2900	4.968	53.096	43.586	27.578	.000	.000	.000
3000	4.968	53.264	43.906	28.075	.000	.000	.000
3100	4.968	53.427	44.210	28.572	.000	.000	.000
3200	4.968	53.585	44.501	29.069	.000	.000	.000
3300	4.968	53.738	44.778	29.566	.000	.000	.000
3400	4.968	53.886	45.044	30.062	.000	.000	.000
3500	4.968	54.030	45.299	30.559	.000	.000	.000
3600	4.969	54.170	45.543	31.056	.000	.000	.000
3700	4.969	54.306	45.778	31.553	.000	.000	.000
3800	4.969	54.439	46.005	32.050	.000	.000	.000
3900	4.969	54.568	46.222	32.547	.000	.000	.000
4000	4.970	54.694	46.433	33.044	.000	.000	.000
4100	4.970	54.816	46.636	33.541	.000	.000	.000
4200	4.971	54.936	46.832	34.038	.000	.000	.000
4300	4.972	55.053	47.022	34.535	.000	.000	.000
4400	4.973	55.167	47.206	35.032	.000	.000	.000
4500	4.975	55.279	47.384	35.529	.000	.000	.000
4600	4.976	55.388	47.557	36.027	.000	.000	.000
4700	4.978	55.496	47.724	36.525	.000	.000	.000
4800	4.981	55.600	47.887	37.023	.000	.000	.000
4900	4.984	55.703	48.046	37.521	.000	.000	.000
5000	4.987	55.804	48.200	38.019	.000	.000	.000
5100	4.991	55.903	48.350	38.518	.000	.000	.000
5200	4.996	56.000	48.496	39.018	.000	.000	.000
5300	5.001	56.095	48.639	39.518	.000	.000	.000
5400	5.007	56.188	48.778	40.018	.000	.000	.000
5500	5.014	56.280	48.913	40.519	.000	.000	.000
5600	5.022	56.371	49.046	41.021	.000	.000	.000
5700	5.031	56.460	49.175	41.523	.000	.000	.000
5800	5.041	56.547	49.301	42.027	.000	.000	.000
5900	5.052	56.633	49.425	42.532	.000	.000	.000
6000	5.064	56.718	49.546	43.037	.000	.000	.000

December 31, 1961

MERCURY (Hg) (REFERENCE STATE) MOL. WT. = 200.61

The reference state is chosen as follows:

0° to 234.29°K	Crystal
234.29° to 629.73°K	Liquid
629.73° to 6000°K	Ideal Gas

$S^\circ_{298.15}$ = 18.171 cal. deg.$^{-1}$ mole^{-1}

T_m = 234.29°K

T_b = 629.73°K

ΔH°_v $_{298.15}$ = 14.652 ± 0.015 kcal. mole^{-1}

ΔH_m = 0.5486 ± 0.0001 kcal. mole^{-1}

ΔH°_v $_{629.73}$ = 14.133 ± 0.020 kcal. mole^{-1}

Heat Capacity.

The heat capacities of P. L. Smith and N. M. Wolcott, Phil. Mag. 1 [8], 854 (1956), 1.2°-20.2°K, R. H. Busey and W. F. Giauque, J. Am. Chem. Soc. 75, 806 (1953), 15°-330°K, and T. B. Douglas, A. F. Ball, and D. C. Ginnings, J. Research Natl. Bur. Standards, 46, 334 (1951), 300°-770°K, have been smoothly joined. There is fair agreement between the selected values and those of G. L. Pickard and F. E. Simon, Proc. Phys. Soc. A61, 1 (1948), L. G. Carpenter and F. H. Oakley, Phil. Mag. 12, 511 (1931), L. G. Carpenter and L. G. Stoodley, Phil. Mag. 10, 249 (1930), E. Cohen, C. I. Kruisheer, and A. L. Moesveld, Z. phys. Chem. A96, 437 (1920), A. L. Dixon and W. H. Rodebush, J. Am. Chem. Soc. 49, 1162 (1927), F. Simon, Z. phys. Chem. 107, 282 (1923), Ann. Physik 68, 241 (1922), J. N. Brönsted, Z. Elektrochem. 18, 714 (1912), and F. Pollitzer, Z. Elektrochem. 17, 5 (1911).

Melting Data.

From Busey and Giauque, loc. cit.

Boiling Point and Heat of Vaporization.

Calculated from the vapor pressures determined by K. D. Carlson, R. J. Thorn, and P. W. Gilles, private communication, October 1961, F. M. Ernsberger and H. W. Pitman, Rev. Sci. Instrum. 26, 584 (1955), F. H. Spedding and J. L. Dye, J. Phys. Chem. 59, 581 (1955), and J. A. Beattie, B. E. Blaisdell, and J. Kaminsky, Proc. Am. Acad. Arts Sciences 71, 375 (1937). Earlier measurements are less accurate and have not been used. Gas imperfection has been allowed for by the method of Busey and Giauque, loc. cit.

Mercury (Hg)

(Liquid) Mol. Wt. = 200.61

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	6.687	18.171	18.171	.000	.000	.000	.000
300	6.684	18.212	18.171	.012	.000	.000	.000
400	6.552	20.115	18.431	.673	.000	.000	.000
500	6.495	21.570	18.919	1.325	.000	.000	.000
600	6.486	22.752	19.463	1.974	.000	.000	.000
700	6.523	23.754	20.006	2.624	-14.025	1.571	-.490
800	6.592	24.630	20.530	3.280	-13.866	3.788	-1.035
900	6.667	25.411	21.030	3.943	-13.699	5.986	-1.453
1000	6.742	26.117	21.504	4.613	-13.526	8.163	-1.784
1100	6.817	26.763	21.953	5.291	-13.345	10.324	-2.051
1200	6.892	27.359	22.379	5.977	-13.156	12.467	-2.270
1300	6.967	27.914	22.784	6.670	-12.960	14.594	-2.453
1400	7.042	28.433	23.169	7.370	-12.756	16.707	-2.608
1500	7.117	28.922	23.536	8.078	-12.545	18.804	-2.740
1600	7.192	29.383	23.887	8.793	-12.327	20.886	-2.853
1700	7.267	29.822	24.224	9.516	-12.101	22.956	-2.951
1800	7.342	30.239	24.546	10.247	-11.867	25.009	-3.036
1900	7.417	30.638	24.857	10.985	-11.625	27.053	-3.112
2000	7.492	31.020	25.155	11.730	-11.377	29.083	-3.178

December 31, 1961

MERCURY (Hg) (LIQUID) MOL. WT. = 200.61

$\Delta H^\circ_{f\ 298.15} = 0$

$S^\circ_{298.15} = 18.171$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 234.29°K$

$T_b = 629.73°K$

$\Delta H^\circ_{v\ 298.15} = 14.651 \pm 0.015$ kcal. mole^{-1}

$\Delta H_m = 0.5486 \pm 0.0001$ kcal. mole^{-1}

$\Delta H^\circ_{v\ 629.73} = 14.134 \pm 0.020$ kcal. mole^{-1}

See notes on reference state for sources of data.

Mercury, Monatomic (Hg)

(Ideal Gas) Mol. Wt. = 200.61

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-1.481	15.404	15.404	INFINITE
100	4.968	36.366	46.211	-.984	15.493	12.745	-27.854
200	4.968	39.810	42.248	-.488	15.372	10.040	-10.971
298	4.968	41.794	41.794	.000	14.652	7.609	-5.577
300	4.968	41.824	41.794	.009	14.649	7.565	-5.511
400	4.968	43.254	41.989	.506	14.485	5.230	-2.857
500	4.968	44.362	42.357	1.003	14.330	2.934	-1.282
600	4.966	45.266	42.769	1.500	14.178	.668	-.243
700	4.968	46.034	43.182	1.996	.000	.000	.000
800	4.968	46.697	43.581	2.493	.000	.000	.000
900	4.968	47.283	43.960	2.990	.000	.000	.000
1000	4.968	47.806	44.319	3.487	.000	.000	.000
1100	4.968	48.279	44.658	3.984	.000	.000	.000
1200	4.968	48.712	44.978	4.481	.000	.000	.000
1300	4.968	49.109	45.281	4.977	.000	.000	.000
1400	4.968	49.478	45.567	5.474	.000	.000	.000
1500	4.968	49.820	45.840	5.971	.000	.000	.000
1600	4.968	50.141	46.099	6.468	.000	.000	.000
1700	4.968	50.442	46.345	6.965	.000	.000	.000
1800	4.968	50.726	46.581	7.461	.000	.000	.000
1900	4.968	50.995	46.806	7.958	.000	.000	.000
2000	4.968	51.250	47.022	8.455	.000	.000	.000
2100	4.968	51.492	47.229	8.952	.000	.000	.000
2200	4.968	51.723	47.428	9.449	.000	.000	.000
2300	4.968	51.944	47.620	9.945	.000	.000	.000
2400	4.968	52.155	47.804	10.442	.000	.000	.000
2500	4.968	52.358	47.983	10.939	.000	.000	.000
2600	4.968	52.553	48.155	11.436	.000	.000	.000
2700	4.968	52.741	48.321	11.933	.000	.000	.000
2800	4.968	52.921	48.482	12.430	.000	.000	.000
2900	4.968	53.096	48.638	12.926	.000	.000	.000
3000	4.968	53.264	48.790	13.423	.000	.000	.000
3100	4.968	53.427	48.937	13.920	.000	.000	.000
3200	4.968	53.585	49.079	14.417	.000	.000	.000
3300	4.968	53.738	49.218	14.914	.000	.000	.000
3400	4.968	53.886	49.353	15.410	.000	.000	.000
3500	4.968	54.030	49.485	15.907	.000	.000	.000
3600	4.969	54.170	49.613	16.404	.000	.000	.000
3700	4.969	54.306	49.736	16.901	.000	.000	.000
3800	4.969	54.439	49.860	17.398	.000	.000	.000
3900	4.969	54.568	49.979	17.895	.000	.000	.000
4000	4.970	54.693	50.095	18.392	.000	.000	.000
4100	4.970	54.816	50.209	18.889	.000	.000	.000
4200	4.971	54.936	50.320	19.386	.000	.000	.000
4300	4.972	55.053	50.429	19.883	.000	.000	.000
4400	4.973	55.167	50.535	20.380	.000	.000	.000
4500	4.975	55.279	50.639	20.878	.000	.000	.000
4600	4.976	55.388	50.742	21.375	.000	.000	.000
4700	4.978	55.495	50.842	21.873	.000	.000	.000
4800	4.981	55.600	50.940	22.371	.000	.000	.000
4900	4.984	55.703	51.036	22.869	.000	.000	.000
5000	4.987	55.804	51.130	23.368	.000	.000	.000
5100	4.991	55.902	51.223	23.867	.000	.000	.000
5200	4.996	55.999	51.314	24.366	.000	.000	.000
5300	5.001	56.095	51.403	24.866	.000	.000	.000
5400	5.007	56.188	51.491	25.366	.000	.000	.000
5500	5.014	56.280	51.577	25.867	.000	.000	.000
5600	5.022	56.371	51.662	26.369	.000	.000	.000
5700	5.031	56.460	51.745	26.872	.000	.000	.000
5800	5.041	56.547	51.827	27.375	.000	.000	.000
5900	5.052	56.633	51.908	27.880	.000	.000	.000
6000	5.064	56.718	51.987	28.386	.000	.000	.000

December 31, 1961

MERCURY, MONATOMIC (Hg) (IDEAL GAS) MOL. WT. = 200.61

$\Delta H^\circ_{f0} = 15.404 \pm 0.015$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 14.652 \pm 0.015$ kcal. mole^{-1}

Ground State Configuration $^1S_0$

$S^\circ_{298.15} = 41.794$ cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0	1	68887	5	78573	12
37645	1	69626	4	79703	60
39412	3	71240	8	80603	8
44043	5	71384	20	81510	120
54069	3	73466	11	82622	132
62350	3	76812	21	83580	601
63928	1	77191	48		

Heat of Formation.

The same as the heat of vaporization; see notes on reference state.

Heat Capacity and Entropy.

The electronic levels and multiplicities are from C. E. Moore, Natl. Bur. Standards Circular 467, Vol. 3 (1958).

Hg

Mercury Monoiodide (HgI)

(Ideal Gas) Mol. Wt. = 327.52 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.531	33.179	33.179	INFINITE
100	8.544	57.402	75.019	-1.762	33.176	29.054	-63.495
200	8.929	63.477	67.893	-.883	32.848	25.052	-27.374
298	9.055	67.068	67.068	.000	31.900	21.459	-15.729
300	9.056	67.124	67.068	.017	31.893	21.395	-15.586
400	9.139	69.741	67.424	.927	29.556	18.026	-9.848
500	9.208	71.788	68.100	1.844	24.060	15.670	-6.849
600	9.272	73.473	68.859	2.768	23.886	14.007	-5.102
700	9.333	74.907	69.623	3.698	9.691	13.946	-4.354
800	9.393	76.157	70.363	4.635	9.680	14.555	-3.976
900	9.452	77.266	71.070	5.577	9.673	15.164	-3.682
1000	9.511	78.265	71.740	6.525	9.673	15.775	-3.447
1100	9.569	79.175	72.375	7.479	9.676	16.385	-3.255
1200	9.627	80.010	72.977	8.439	9.685	16.994	-3.095
1300	9.685	80.783	73.548	9.405	9.699	17.603	-2.959
1400	9.743	81.503	74.091	10.376	9.717	18.210	-2.843
1500	9.801	82.177	74.608	11.353	9.742	18.817	-2.741
1600	9.858	82.811	75.101	12.336	9.771	19.420	-2.653
1700	9.916	83.410	75.572	13.325	9.804	20.022	-2.574
1800	9.973	83.979	76.024	14.319	9.843	20.621	-2.504
1900	10.031	84.520	76.457	15.320	9.887	21.219	-2.441
2000	10.088	85.036	76.873	16.326	9.937	21.815	-2.384
2100	10.146	85.529	77.273	17.337	9.991	22.407	-2.332
2200	10.203	86.003	77.659	18.355	10.050	22.996	-2.284
2300	10.261	86.457	78.032	19.378	10.114	23.584	-2.241
2400	10.318	86.895	78.392	20.407	10.184	24.169	-2.201
2500	10.376	87.318	78.741	21.442	10.259	24.749	-2.163
2600	10.433	87.726	79.079	22.482	10.339	25.327	-2.129
2700	10.491	88.120	79.406	23.528	10.423	25.903	-2.097
2800	10.548	88.503	79.724	24.580	10.512	26.473	-2.066
2900	10.605	88.674	80.034	25.638	10.607	27.043	-2.038
3000	10.663	89.235	80.334	26.701	10.707	27.607	-2.011
3100	10.720	89.585	80.627	27.770	10.812	28.170	-1.986
3200	10.778	89.927	80.912	28.845	10.922	28.728	-1.962
3300	10.835	90.259	81.191	29.926	11.036	29.284	-1.939
3400	10.892	90.583	81.462	31.012	11.156	29.833	-1.918
3500	10.950	90.900	81.727	32.104	11.282	30.382	-1.897
3600	11.007	91.209	81.986	33.202	11.412	30.925	-1.877
3700	11.064	91.512	82.240	34.306	11.547	31.464	-1.858
3800	11.122	91.807	82.488	35.415	11.688	32.003	-1.840
3900	11.179	92.097	82.730	36.530	11.833	32.536	-1.823
4000	11.237	92.381	82.968	37.651	11.983	33.060	-1.806
4100	11.294	92.659	83.201	38.777	12.138	33.588	-1.790
4200	11.351	92.932	83.429	39.910	12.299	34.110	-1.775
4300	11.409	93.200	83.654	41.048	12.464	34.626	-1.760
4400	11.466	93.463	83.874	42.191	12.634	35.138	-1.745
4500	11.523	93.721	84.090	43.341	12.809	35.649	-1.731
4600	11.581	93.975	84.302	44.496	12.990	36.154	-1.718
4700	11.638	94.224	84.510	45.657	13.175	36.654	-1.704
4800	11.696	94.470	84.715	46.824	13.364	37.153	-1.692
4900	11.753	94.712	84.917	47.996	13.559	37.649	-1.679
5000	11.810	94.950	85.115	49.174	13.758	38.139	-1.667
5100	11.868	95.184	85.310	50.358	13.962	38.620	-1.655
5200	11.925	95.415	85.502	51.548	14.171	39.101	-1.643
5300	11.982	95.643	85.691	52.743	14.384	39.584	-1.632
5400	12.040	95.867	85.878	53.944	14.602	40.056	-1.621
5500	12.097	96.089	86.061	55.151	14.825	40.524	-1.610
5600	12.154	96.307	86.242	56.364	15.051	40.991	-1.600
5700	12.212	96.523	86.421	57.582	15.281	41.453	-1.589
5800	12.269	96.736	86.597	58.806	15.517	41.907	-1.579
5900	12.327	96.946	86.771	60.036	15.755	42.358	-1.569
6000	12.384	97.154	86.942	61.271	15.998	42.808	-1.559

December 31, 1961

MERCURY MONOIODIDE (HgI) (IDEAL GAS) MOL. WT. = 327.52

Ground State Configuration $^2\Sigma$

$\Delta H^\circ_{f\ 298.15} = 31.9 \pm 1.1$ kcal mole^{-1}

$S^\circ_{298.15} = 67.068$ cal deg^{-1} mole^{-1}

Electronic Level and Multiplicity

ϵ, cm^{-1}	g_i
0	2

$\omega_e = 125.0$ cm^{-1}

$\omega_e x_e = 1.00$ cm^{-1}

$\sigma = 1$

$B_e = [0.0351]$ cm^{-1}

$\alpha_e = [0.0003]$ cm^{-1}

$r_e = [2.49]$ Å

Heat of Formation

K. Wieland and A. Herczog, Helv. Chim. Acta, 32, 889 (1949) gave 8.3 ± 1.1 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants were taken from K. Wieland, Zeits, f. Electrochemie 64, 761 (1960). Rotational constants were estimated using equation III 123, p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides.

Mercury Diiodide (HgI_2)

(Crystal) Mol. Wt. = 454.43

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	kcal. mole^{-1} $H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	18.582	43.338	43.338	.000	-25.200	-24.427	17.905
300	18.600	43.453	43.338	.034	-25.202	-24.422	17.791
400	19.600	48.941	44.080	1.944	-29.125	-24.014	13.120
500	20.105	54.917	45.809	4.554	-38.690	-21.925	9.583
600	20.105	58.583	47.642	6.564	-38.226	-18.617	6.781
700	20.105	61.682	49.432	8.575	-51.789	-13.815	4.313
800	20.105	64.367	51.135	10.585	-51.177	-8.431	2.303
900	20.105	66.735	52.739	12.596	-50.566	-3.124	.759
1000	20.105	68.853	54.247	14.606	-49.958	2.114	-.462
1100	20.105	70.769	55.663	16.617	-49.351	7.292	-1.449
1200	20.105	72.518	56.996	18.627	-48.747	12.414	-2.261
1300	20.105	74.128	58.252	20.638	-48.142	17.487	-2.940
1400	20.105	75.618	59.440	22.648	-47.540	22.514	-3.514
1500	20.105	77.005	60.565	24.659	-46.939	27.496	-4.006

March 31, 1962

MERCURY DIIODIDE (HgI_2) (Crystal)

Mol. Wt. = 454.43

$\Delta H_f^\circ{}_{298.15} = -25.2 \pm 0.4$ kcal. mole^{-1}

$S^\circ_{298.15} = [43.338] \pm 1.5$ cal. deg.$^{-1}$ mole^{-1}

$T_t = 402°K$

$\Delta H_t = 0.601 \pm 0.04$ kcal. mole^{-1}

$T_m = 530°K$

$\Delta H_m = 4.533 \pm 0.05$ kcal. mole^{-1}

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties", (1952).

Heat Capacity and Entropy. The heat capacity was calculated from the heat content data of M. Guinchant, Comp. Rend. 68, 145 (1907) and R. Ewald, Ann. d. Physik (4) 44, 1213 (1914). The entropy was estimated by adjusting its value to provide the best fit of the melting, sublimation and vaporization phenomena.

Transition. The heat and temperature of transition were taken from National Bureau of Standards Circular 500 (loc. cit.).

Melting. The heat of melting was taken from M. Guinchant (loc. cit.), the temperature of melting from National Bureau of Standards Circular 500 (loc. cit.).

Mercury Diiodide (HgI_2)

(Liquid) Mol. Wt. = 454.43

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	18.582	51.544	51.544	.000	- 20.862	- 22.536	16.519
300	18.600	51.659	51.544	.034	- 20.864	- 22.546	16.424
400	24.400	57.777	52.324	2.181	- 24.550	- 22.974	12.552
500	24.400	63.221	53.979	4.621	- 34.285	- 21.672	9.472
600	24.400	67.670	55.902	7.061	- 33.391	- 19.235	7.006
700	24.400	71.431	57.859	9.501	- 46.525	- 15.375	4.600
800	24.400	74.690	59.763	11.941	- 45.483	- 10.995	3.004
900	24.400	77.563	61.585	14.381	- 44.443	- 6.747	1.638
1000	24.400	80.134	63.313	16.821	- 43.405	- 2.614	.571
1100	24.400	82.460	64.950	19.261	- 42.369	1.415	- .281
1200	24.400	84.583	66.499	21.701	- 41.335	5.349	- .974
1300	24.400	86.536	67.966	24.141	- 40.301	9.198	- 1.546
1400	24.400	88.344	69.358	26.581	- 39.269	12.968	- 2.024
1500	24.400	90.028	70.680	29.021	- 38.239	16.662	- 2.427

March 31, 1962

MERCURY DIIODIDE (HgI_2) (Liquid)

Mol. Wt. = 454.43

ΔH_f° 298.15 = [-20.862] ± 0.45 kcal. mole^{-1}

$S^\circ_{298.15}$ = [51.544] ± 1.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 530°K

ΔH_m = 4.533 ± 0.05 kcal. mole^{-1}

T_b = 627°K

ΔH_v = 14.141 ± 0.25 kcal. mole^{-1}

Heat of Formation. Calculated from $\Delta H_f^\circ{}_{298}(c)$.

Heat Capacity and Entropy. Heat capacity measurements were obtained from the data of M. Guinchant, Comp. Rend. 68, 145 (1907) in the range 540-600°K and were assumed constant above and below this range. A glass type transition was assumed at 353°K below which the heat capacity was that of $HgI_2(c)$. The entropy was calculated from the entropy of the crystal and the measured entropy of fusion.

Fusion and Vaporization. T_m and T_b are taken from National Bur. of Standards (U.S.) Circular 500 (1952). ΔH_m is from the data of M. Guinchant (loc. cit.) and ΔH_v was obtained from the data of E. B. R. Prideaux, J. Chem. Soc. (London) 97, 2032 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Mercury Diiodide (HgI_2)

(Ideal Gas) Mol. Wt. = 454.43

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.885	-2.353	-2.353	INFINITE
100	13.023	65.034	93.049	-2.802	-2.407	-6.562	14.341
200	14.283	74.556	81.659	-1.421	-2.821	-10.563	11.542
298	14.608	80.331	80.331	.000	-3.855	-14.112	10.344
300	14.611	80.421	80.331	.027	-3.864	-14.175	10.326
400	14.736	84.644	80.906	1.495	-8.229	-17.400	9.506
500	14.796	87.940	81.995	2.972	-18.927	-18.673	8.162
600	14.828	90.640	83.218	4.454	-18.991	-18.618	6.781
700	14.848	92.928	84.446	5.937	-33.082	-16.979	5.301
800	14.861	94.911	85.633	7.423	-32.994	-14.684	4.011
900	14.870	96.662	86.763	8.910	-32.907	-12.400	3.011
1000	14.877	98.229	87.832	10.397	-32.822	-10.126	2.213
1100	14.882	99.648	88.843	11.885	-32.738	-7.861	1.562
1200	14.885	100.943	89.798	13.373	-32.656	-5.604	1.021
1300	14.888	102.134	90.702	14.862	-32.573	-3.352	.563
1400	14.890	103.238	91.558	16.351	-32.492	-1.106	.173
1500	14.892	104.265	92.372	17.840	-32.413	1.131	-.165
1600	14.894	105.226	93.145	19.329	-32.335	3.366	-.460
1700	14.895	106.129	93.883	20.819	-32.258	5.595	-.719
1800	14.896	106.981	94.587	22.308	-32.183	7.818	-.949
1900	14.897	107.786	95.261	23.798	-32.108	10.040	-1.155
2000	14.898	108.550	95.906	25.288	-32.035	12.255	-1.339
2100	14.898	109.277	96.526	26.777	-31.964	14.468	-1.506
2200	14.899	109.970	97.121	28.267	-31.894	16.676	-1.656
2300	14.899	110.632	97.694	29.757	-31.825	18.883	-1.794
2400	14.900	111.266	98.247	31.247	-31.756	21.089	-1.920
2500	14.900	111.875	98.780	32.737	-31.690	23.286	-2.036
2600	14.900	112.459	99.295	34.227	-31.625	25.484	-2.142
2700	14.901	113.021	99.793	35.717	-31.562	27.680	-2.240
2800	14.901	113.563	100.275	37.207	-31.500	29.873	-2.332
2900	14.901	114.086	100.742	38.697	-31.438	32.066	-2.416
3000	14.902	114.591	101.196	40.188	-31.378	34.251	-2.495
3100	14.902	115.080	101.636	41.678	-31.320	36.439	-2.569
3200	14.902	115.553	102.063	43.168	-31.263	38.624	-2.638
3300	14.902	116.012	102.479	44.658	-31.208	40.809	-2.703
3400	14.902	116.457	102.884	46.148	-31.153	42.989	-2.763
3500	14.902	116.889	103.278	47.638	-31.100	45.171	-2.820
3600	14.902	117.308	103.661	49.129	-31.048	47.348	-2.874
3700	14.903	117.717	104.036	50.619	-30.998	49.523	-2.925
3800	14.903	118.114	104.401	52.109	-30.949	51.701	-2.973
3900	14.903	118.501	104.758	53.599	-30.902	53.876	-3.019
4000	14.903	118.879	105.106	55.090	-30.855	56.047	-3.062
4100	14.903	119.246	105.446	56.580	-30.810	58.220	-3.103
4200	14.903	119.606	105.779	58.070	-30.767	60.392	-3.142
4300	14.903	119.956	106.105	59.561	-30.724	62.558	-3.179
4400	14.903	120.299	106.424	61.051	-30.684	64.726	-3.215
4500	14.903	120.634	106.736	62.541	-30.645	66.898	-3.249
4600	14.903	120.961	107.041	64.031	-30.608	69.064	-3.281
4700	14.903	121.282	107.341	65.522	-30.571	71.232	-3.312
4800	14.903	121.596	107.635	67.012	-30.537	73.395	-3.342
4900	14.903	121.903	107.923	68.503	-30.503	75.562	-3.370
5000	14.903	122.204	108.205	69.993	-30.472	77.728	-3.397
5100	14.903	122.499	108.483	71.483	-30.442	79.891	-3.423
5200	14.904	122.789	108.755	72.974	-30.415	82.052	-3.448
5300	14.904	123.072	109.023	74.464	-30.389	84.216	-3.473
5400	14.904	123.351	109.285	75.954	-30.365	86.378	-3.496
5500	14.904	123.625	109.544	77.445	-30.342	88.537	-3.518
5600	14.904	123.893	109.797	78.935	-30.323	90.699	-3.540
5700	14.904	124.157	110.047	80.425	-30.305	92.862	-3.560
5800	14.904	124.416	110.293	81.916	-30.289	95.020	-3.580
5900	14.904	124.671	110.534	83.406	-30.276	97.177	-3.599
6000	14.904	124.921	110.772	84.897	-30.264	99.340	-3.618

March 31, 1962

MERCURY DIIODIDE (HgI_2) (Ideal Gas)

Mol. Wt. = 454.43

$\Delta H_{f\ 298.15}^\circ = -3.855 \pm 0.5$ kcal. mole^{-1}

$S_{298.15}^\circ = 80.331$ cal. deg.$^{-1}$ mole^{-1}

Point Group = $D_{\infty h}$

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	
156	(1)
33	(2)
[233]	(1)

Hg-I distance = 2.58 Å

Moment of Inertia = 280.5×10^{-39} g. cm.^{2}

$\sigma = 2$

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties", 1952 was combined with the 3rd law heat of sublimation at 298°K derived from the data of K. Niwa and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III 2, 183 (1938); D. W. Magee, Univ. Microfilms No. 14474 Ann Arbor, Mich., and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The anti-symmetric stretching frequency was estimated by analogy with the bromide and chloride. The bond length was an average of the values given by H. Braune and S. Knoke, Naturwiss. 21, 349 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Farad. Soc. 33, 852 (1937) and P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).

Mercury Monoxide (HgO)

(Crystal) Mol. Wt. = 216.61

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.176	-20.605	-20.605	INFINITE
100	6.796	7.371	25.131	-1.776	-20.969	-18.741	40.955
200	9.123	12.872	17.717	-.969	-21.119	-16.441	17.964
298	10.531	16.795	16.795	.000	-21.699	-13.983	10.250
300	10.551	16.860	16.795	.020	-21.698	-13.935	10.151
400	11.550	20.037	17.222	1.126	-21.608	-11.358	6.206
500	12.340	22.703	18.058	2.323	-21.429	-8.815	3.853
600	12.935	25.008	19.029	3.587	-21.191	-6.315	2.300
700	13.400	27.038	20.031	4.905	-34.937	-2.286	.714
800	13.745	28.851	21.022	6.263	-34.475	2.347	-.641
900	14.012	30.486	21.984	7.652	-33.989	6.922	-1.681
1000	14.200	31.973	22.910	9.063	-33.489	11.440	-2.500

June 30, 1962

MERCURY MONOXIDE (HgO) (CRYSTAL) MOL. WT. = 216.61

$\Delta H_f^\circ{}_{298.15} = -21.699 \pm 0.024$ kcal. mole^{-1} $S^\circ_{298.15} = 16.795 \pm 0.03$ cal. deg.$^{-1}$ mole^{-1}

$T_{decomp} = 749°K.$

Heat of Formation.

Obtained from the entropy obtained by T. W. Bauer and H. L. Johnston, J. Am. Chem. Soc. 75, 2217 (1953) and the free energy of formation as determined from the numerous cell measurements described by Bauer and Johnston. The value adopted for $\Delta F_f^\circ{}_{298.15}$ was -42,707 ± 14 cal. mole^{-1}.

Heat Capacity and Entropy.

The heat capacity has been measured from 15° to 298°K. by Bauer and Johnston loc. cit. The extrapolation below 15°K was done assuming a T^3 law and gave $S_{15} = 0.264$ e.u. Above 298° the data was extrapolated smoothly and adjusted to give the observed decomposition vapor pressures of G. B. Taylor and G. A. Hulett, J. Phys. Chem. 17, 565 (1913).

Decomposition.

According to Taylor and Hulett, loc. cit., the vapor pressure reaches 1.89 atmospheres at 749°K. This corresponds to the decomposition to 2 Hg(g) + O_2(g), the equilibrium constant being unity at 1.89 atm.

Mercury Monoxide (HgO)

(Ideal Gas) GFW = 216.5894

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.153	11.117	11.117	INFINITE
100	6.969	49.187	63.768	-1.458	11.057	9.098	-19.884
200	7.340	54.103	57.837	-.747	10.804	7.235	-7.906
298	7.859	57.134	57.134	.000	10.000	5.688	-4.170
300	7.868	57.183	57.134	.015	9.996	5.662	-4.125
400	8.236	59.500	57.448	.821	9.786	4.250	-2.322
500	8.469	61.365	58.051	1.657	9.605	2.888	-1.262
600	8.620	62.923	58.736	2.512	9.433	1.560	-.568
700	8.724	64.261	59.432	3.380	-4.763	1.832	-.572
800	8.798	65.431	60.111	4.256	-4.783	2.775	-.758
900	8.854	66.470	60.760	5.139	-4.803	3.722	-.904
1000	8.898	67.405	61.379	6.026	-4.826	4.671	-1.021
1100	8.934	68.255	61.966	6.918	-4.851	5.622	-1.117
1200	8.964	69.034	62.523	7.813	-4.877	6.574	-1.197
1300	8.990	69.752	63.052	8.711	-4.905	7.530	-1.266
1400	9.012	70.419	63.555	9.611	-4.933	8.488	-1.325
1500	9.033	71.042	64.033	10.513	-4.963	9.448	-1.376
1600	9.052	71.625	64.490	11.417	-4.994	10.409	-1.422
1700	9.069	72.175	64.926	12.323	-5.026	11.373	-1.462
1800	9.086	72.694	65.343	13.231	-5.060	12.336	-1.498
1900	9.101	73.185	65.743	14.140	-5.094	13.306	-1.531
2000	9.116	73.652	66.127	15.051	-5.130	14.276	-1.560
2100	9.130	74.098	66.496	15.964	-5.167	15.245	-1.587
2200	9.144	74.523	66.851	16.877	-5.207	16.217	-1.611
2300	9.157	74.929	67.194	17.792	-5.247	17.193	-1.634
2400	9.170	75.319	67.524	18.709	-5.287	18.173	-1.655
2500	9.183	75.694	67.843	19.626	-5.331	19.147	-1.674
2600	9.195	76.054	68.152	20.545	-5.375	20.129	-1.692
2700	9.208	76.402	68.451	21.465	-5.421	21.110	-1.709
2800	9.220	76.737	68.741	22.387	-5.468	22.091	-1.724
2900	9.232	77.060	69.023	23.309	-5.515	23.082	-1.739
3000	9.244	77.374	69.296	24.233	-5.565	24.065	-1.753
3100	9.255	77.677	69.561	25.158	-5.615	25.054	-1.766
3200	9.267	77.971	69.820	26.084	-5.667	26.045	-1.779
3300	9.279	78.256	70.071	27.012	-5.720	27.037	-1.791
3400	9.290	78.533	70.316	27.940	-5.773	28.031	-1.802
3500	9.302	78.803	70.554	28.870	-5.827	29.024	-1.812
3600	9.313	79.065	70.787	29.800	-5.883	30.022	-1.823
3700	9.324	79.320	71.014	30.732	-5.939	31.020	-1.832
3800	9.335	79.569	71.236	31.665	-5.995	32.022	-1.842
3900	9.347	79.812	71.453	32.599	-6.052	33.020	-1.850
4000	9.358	80.049	71.665	33.534	-6.110	34.022	-1.859
4100	9.369	80.280	71.872	34.471	-6.168	35.024	-1.867
4200	9.380	80.506	72.075	35.408	-6.226	36.030	-1.875
4300	9.391	80.727	72.274	36.347	-6.285	37.038	-1.882
4400	9.402	80.943	72.468	37.286	-6.344	38.044	-1.890
4500	9.413	81.154	72.659	38.227	-6.402	39.057	-1.897
4600	9.424	81.361	72.846	39.169	-6.462	40.067	-1.904
4700	9.435	81.564	73.029	40.112	-6.522	41.082	-1.910
4800	9.446	81.763	73.209	41.056	-6.582	42.090	-1.916
4900	9.457	81.957	73.386	42.001	-6.641	43.109	-1.923
5000	9.468	82.149	73.559	42.947	-6.700	44.122	-1.929
5100	9.478	82.336	73.729	43.894	-6.761	45.145	-1.935
5200	9.489	82.520	73.897	44.843	-6.821	46.162	-1.940
5300	9.500	82.701	74.061	45.792	-6.881	47.181	-1.946
5400	9.511	82.879	74.223	46.743	-6.941	48.196	-1.951
5500	9.522	83.054	74.382	47.695	-7.001	49.217	-1.956
5600	9.533	83.225	74.538	48.647	-7.062	50.245	-1.961
5700	9.543	83.394	74.692	49.601	-7.122	51.268	-1.966
5800	9.554	83.560	74.844	50.556	-7.184	52.292	-1.970
5900	9.565	83.723	74.993	51.512	-7.246	53.317	-1.975
6000	9.576	83.884	75.140	52.469	-7.308	54.345	-1.980

June 30, 1967

MERCURY MONOXIDE (HgO) (IDEAL GAS) GFW = 216.5894

Ground State Configuration $^1\Sigma$

ΔHf°_0 = [11] kcal/mol

$S^\circ_{298.15}$ = [57] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = [680] cm^{-1}

$\omega_e x_e$ = [4.7] cm^{-1}

σ = 1

B_e = [0.336] cm^{-1}

α_e = [0.0027] cm^{-1}

r_e = [1.84] Å

Heat of Formation

The heat of formation (ΔHf°_{298}) of HgO(g) is estimated to be 10 ± 15 kcal/mol. This value is obtained from the heat of formation of PbO(g) and comparison of the heats of formation of analogous lead and mercury compounds using the method of Karapet'yants (1). The corresponding dissociation energy (D°_0) of HgO(g) is 64 ± 15 kcal/mol.

Heat Capacity and Entropy

The equilibrium internuclear separation (r_e) of HgO(g) is estimated from the corresponding quantity for PbO(g) and comparison of Hg-X and Pb-X bond distances for cases in which values of both distances are known. The rotational constant B_e is calculated from r_e. The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for multiple bonded molecules (2). The anharmonic vibrational term $\omega_e x_e$ is calculated from $\omega_e x_e = \omega_e^2/(4D_0 + 2\omega_e)$. The value of α_e is calculated from the Morse potential function. The ground state configuration is estimated from the building-up principle (3), the united atom theory (3), and from analogy with BeO.

References

1. M. Kh. Karapet'yants, Russ. J. Inorg. Chem. (English Transl.) 10, 837 (1965).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Mercury Monoiodide, Dimeric (Hg_2I_2)

(Crystal) Mol. Wt. = 655.04 **INTERIM TABLE**

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	25.300	57,670	57,670	.000	- 28,462	- 26.545	19,457
300	25.323	57.827	57.670	.047	- 28.463	- 26.532	19.328
400	26,390	65,266	58,678	2,635	- 32,369	- 25,742	14,064
500	27.170	71.243	60,612	5,315	- 42,516	- 23,129	10,109
600	27,740	76,249	62,812	8,062	- 41,964	- 19,304	7,031
700	28,180	80,560	65,047	10,859	- 69,416	- 12,432	3,881
800	28.540	84,347	67,228	13,696	- 68,474	- 4,354	1,190
900	28,830	87,726	69,321	16,565	- 67,501	3,603	- .875
1000	29,090	90,777	71,316	19,461	- 66,504	11,450	- 2,502
1100	29,323	93.561	73,214	22,382	- 65,484	19,196	- 3,814
1200	29.530	96,122	75,018	25,325	- 64,444	26,847	- 4,889
1300	29,693	98,491	76,733	28,285	- 63,387	34,413	- 5,785
1400	29,910	100,699	78,367	31,265	- 62,311	41,898	- 6,540
1500	30,180	102,772	79,926	34,269	- 61,214	49,302	- 7,183

March 31, 1962

MERCURY MONOIODIDE, DIMERIC (Hg_2I_2) (Crystal)

Mol. Wt. = 655.04

$\Delta H^\circ_{f\ 298.15} = -28.462 \pm 0.5$ kcal. mole^{-1}

$S^\circ_{298.15} = 57.670 \pm 2.0$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 563°K$

$\Delta H_m = [6.5] \pm 2.0$ kcal. mole^{-1}

Heat of Formation. The average value of the cell measurements of W. C. Vosburgh, J. Amer. Chem. Soc. 50, 2386 (1928); E. Cohen Zeits. f. physik, Chemie 94, 210 (1920); T. Yoshida, J. Chem. Soc. Japan 48, 435 (1927); L. W. Öholm, Acta. Soc. Scientarum Fennicae 41, 1 (1913) and the calorimetric values of R. Varet, Ann. Chim. Phys. (7) 8, 91 (1896) and W. Nernst, Zeits. f. physik. Chemie 2, 23 (1888) was adopted.

Heat Capacity and Entropy. The heat capacity at 298.15° was taken from National Bureau of Standards (U.S.) Circular 500 (1952) and was estimated above this by analogy with mercurous chloride. The entropy was obtained from the heat and free energy of formation obtained from the cell measurements listed under heat of formation.

Melting. P. Yvon, Comp. Rend. 76, 1607 (1873) gives 563°K for the melting point. The heat of melting was estimated by assuming the entropy of melting per atom to be the same as that for mercuric iodide.

Mercury Monoiodide, Dimeric (Hg_2I_2)

(Liquid) Mol. Wt. = 655.04 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	25.300	66.868	66.868	.000	- 23.021	- 23.846	17.479
300	25.323	67.025	66.868	.047	- 23.022	- 23.851	17.374
400	32.600	74.872	67.889	2.794	- 26.769	- 23.986	13.104
500	32.600	82.147	70.040	6.054	- 34.336	- 22.401	9.791
600	32.600	88.090	72.568	9.314	- 35.271	- 19.717	7.181
700	32.600	93.116	75.154	12.574	- 62.260	- 14.066	4.391
800	32.600	97.469	77.677	15.834	- 60.895	- 7.273	1.987
900	32.600	101.309	80.094	19.094	- 59.532	- .651	.158
1000	32.600	104.743	82.390	22.353	- 58.171	5.817	- 1.271
1100	32.600	107.850	84.565	25.613	- 56.812	12.150	- 2.414
1200	32.600	110.687	86.626	28.873	- 55.455	18.359	- 3.343
1300	32.600	113.296	88.578	32.133	- 54.098	24.456	- 4.111
1400	32.600	115.712	90.431	35.393	- 52.742	30.449	- 4.753
1500	32.600	117.961	92.192	38.653	- 51.389	36.343	- 5.295

March 31, 1962

MERCURY MONOIODIDE, DIMERIC (Hg_2I_2) (Liquid)

Mol. Wt. = 655.04

$\Delta H_f^\circ{}_{298.15} = [-23.021 \pm 2.5]$ kcal. mole^{-1}

$S^\circ_{298.15} = [66.868 \pm 6.0]$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 563°K$

$\Delta H_m = [6.5 \pm 2.0]$ kcal. mole^{-1}

$T_b = [630]°K$ (decomp.)

Heat of Formation. Calculated from ΔH_f° (crystal) and the estimated heat of melting and heat capacity.

Heat Capacity and Entropy. C_p was estimated as 1.33 times the heat capacity of mercuric iodide. The entropy was calculated from S° crystal, the estimated ΔH_m and the heat capacities of solid and liquid.

Melting and Vaporization. The melting point was given by P. Yvon, Comp. Rend. 76, 1607 (1873); the heat of melting was estimated from that of mercuric iodide, by assuming the entropies of melting per atom to be equal. Mercurous iodide decomposes to Hg(g) and $HgI_2(g)$ at the boiling point which was estimated from the free energy change of the reaction.

Iodine, Monatomic (I)

(Ideal Gas) Mol. Wt. = 126.91

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-1.481	25.633	25.633	INFINITE
100	4.968	37.756	47.601	-.984	25.765	22.718	-49.649
200	4.968	41.200	43.638	-.488	25.673	19.702	-21.529
298	4.968	43.184	43.184	.000	25.537	16.800	-12.314
300	4.968	43.214	43.184	.009	25.534	16.746	-12.199
400	4.968	44.644	43.379	.506	23.445	13.908	-7.599
500	4.968	45.752	43.747	1.003	18.180	12.023	-5.255
600	4.968	46.658	44.159	1.500	18.229	10.787	-3.929
700	4.968	47.424	44.572	1.996	18.276	9.543	-2.979
800	4.968	48.087	44.971	2.493	18.322	8.293	-2.265
900	4.969	48.673	45.350	2.990	18.367	7.036	-1.709
1000	4.970	49.196	45.709	3.487	18.412	5.775	-1.262
1100	4.973	49.670	46.048	3.984	18.455	4.509	-.896
1200	4.977	50.103	46.368	4.482	18.498	3.239	-.590
1300	4.984	50.502	46.671	4.980	18.542	1.966	-.331
1400	4.993	50.871	46.958	5.479	18.585	.690	-.108
1500	5.004	51.216	47.230	5.978	18.628	-.591	.086
1600	5.018	51.539	47.490	6.479	18.672	-1.873	.256
1700	5.034	51.844	47.737	6.982	18.717	-3.158	.406
1800	5.052	52.132	47.973	7.486	18.762	-4.447	.540
1900	5.072	52.406	48.199	7.993	18.809	-5.737	.660
2000	5.093	52.667	48.416	8.501	18.857	-7.031	.768
2100	5.115	52.916	48.625	9.011	18.907	-8.326	.866
2200	5.137	53.154	48.825	9.524	18.958	-9.624	.956
2300	5.160	53.383	49.018	10.039	19.011	-10.925	1.038
2400	5.182	53.603	49.205	10.556	19.066	-12.227	1.113
2500	5.204	53.815	49.385	11.075	19.121	-13.532	1.183
2600	5.226	54.020	49.559	11.597	19.179	-14.840	1.247
2700	5.247	54.217	49.728	12.120	19.238	-16.149	1.307
2800	5.267	54.408	49.892	12.646	19.298	-17.460	1.363
2900	5.286	54.594	50.051	13.174	19.360	-18.774	1.415
3000	5.304	54.773	50.205	13.703	19.422	-20.091	1.464
3100	5.321	54.947	50.356	14.234	19.486	-21.409	1.509
3200	5.336	55.116	50.502	14.767	19.551	-22.729	1.552
3300	5.351	55.281	50.644	15.302	19.616	-24.051	1.593
3400	5.364	55.441	50.783	15.837	19.682	-25.376	1.631
3500	5.376	55.596	50.918	16.374	19.749	-26.701	1.667
3600	5.387	55.748	51.050	16.912	19.816	-28.030	1.702
3700	5.397	55.896	51.179	17.452	19.884	-29.360	1.734
3800	5.406	56.040	51.305	17.992	19.952	-30.692	1.765
3900	5.414	56.180	51.428	18.533	20.020	-32.025	1.795
4000	5.421	56.318	51.549	19.075	20.089	-33.362	1.823
4100	5.427	56.452	51.667	19.617	20.157	-34.697	1.849
4200	5.432	56.582	51.782	20.160	20.225	-36.035	1.875
4300	5.436	56.710	51.895	20.703	20.293	-37.377	1.900
4400	5.439	56.835	52.006	21.247	20.360	-38.720	1.923
4500	5.442	56.957	52.115	21.791	20.427	-40.062	1.946
4600	5.444	57.077	52.222	22.335	20.494	-41.406	1.967
4700	5.446	57.194	52.326	22.880	20.560	-42.754	1.988
4800	5.446	57.309	52.429	23.425	20.626	-44.101	2.008
4900	5.447	57.421	52.529	23.969	20.691	-45.450	2.027
5000	5.447	57.531	52.628	24.514	20.755	-46.801	2.046
5100	5.446	57.639	52.726	25.059	20.820	-48.153	2.063
5200	5.445	57.745	52.821	25.603	20.882	-49.507	2.081
5300	5.444	57.849	52.915	26.148	20.945	-50.860	2.097
5400	5.442	57.950	53.007	26.692	21.006	-52.214	2.113
5500	5.440	58.050	53.098	27.236	21.066	-53.572	2.129
5600	5.438	58.148	53.187	27.780	21.126	-54.931	2.144
5700	5.436	58.244	53.275	28.324	21.185	-56.289	2.158
5800	5.433	58.339	53.362	28.867	21.243	-57.648	2.172
5900	5.431	58.432	53.447	29.410	21.300	-59.009	2.186
6000	5.428	58.523	53.531	29.953	21.356	-60.370	2.199

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IODINE, MONATOMIC (I) (IDEAL GAS) MOL. WT. = 126.91

ΔH°_{f0} = 25.633 ± .010 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298}$ = 25.537 kcal. mole^{-1}

Ground State = $^2P_{3/2}$

S°_{298} = 43.184 cal. mole^{-1} deg.$^{-1}$

Electronic Levels and Multiplicities

ω_1, cm.$^{-1}$	g_1	ω_1, cm.$^{-1}$	g_1	ω_1, cm.$^{-1}$	g_1
0	4	67082.12	4	68549.77	6
7603.15	2	65856.96	2	68588.00	6
54633.46	6	64990.01	4	68612.02	4
61819.81	4	65644.49	6	71850.	14
60896.27	2	65670.00	8	72750.	24
56092.88	4	66020.64	6	75300.	80
63186.76	2	66355.21	4	77110.	64
64906.34	6	67298.45	4	79210.	128
				81440.	218

Thermodynamic Functions.

Atomic constants were taken from C. E. Moore [U. S. Natl. Bur. Standards Circ. 467, Vol. III (1958)]. The higher levels were averaged. Calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards, 55, 147 (1955)].

Heat of Formation.

The dissociation energy of diatomic iodine is given as D_0° = 12452.5 ± 1.5 cm.$^{-1}$ by R. D. Verma [J. Chem. Phys. 32, 738 (1960)]. Converting to calories and combining with the heat of sublimation of iodine yields the heat of formation of the ideal monatomic gas. Evans, Munson, and Wagman [loc. cit.] list several investigations of the dissociation energy from equilibrium data. These are all less precise than the spectroscopic value and are not given any weight. The "best" average of the thermal data yields D_0° = 35.568 kcal. mole^{-1} (spectroscopic = 35.606 kcal. mole^{-1}).

Potassium Iodide (KI)

(Crystal) GFW = 166.0064

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.038	- 78.138	- 78.138	INFINITE
100	10.756	12.527	36.237	- 2.371	- 78.250	- 77.922	170.299
200	12.074	20.500	26.565	- 1.213	- 78.301	- 77.574	84.769
298	12.614	25.427	25.427	.000	- 78.370	- 77.205	56.592
300	12.621	25.505	25.427	.023	- 78.372	- 77.197	56.238
400	12.890	29.172	25.925	1.298	- 80.997	- 76.612	41.859
500	13.232	32.083	26.875	2.604	- 86.196	- 75.023	32.792
600	13.695	34.534	27.953	3.949	- 86.025	- 72.803	26.519
700	14.287	36.688	29.049	5.347	- 85.793	- 70.617	22.048
800	14.971	38.640	30.128	6.809	- 85.493	- 68.469	18.705
900	15.725	40.446	31.175	8.344	- 85.122	- 66.362	16.115
1000	16.500	42.144	32.188	9.956	- 84.684	- 64.301	14.053
1100	17.100	43.746	33.167	11.637	- 103.093	- 61.262	12.172
1200	17.480	45.251	34.112	13.369	- 102.314	- 57.493	10.471
1300	17.708	46.660	35.023	15.128	- 101.505	- 53.791	9.043
1400	17.830	47.977	35.902	16.905	- 100.681	- 50.151	7.829
1500	17.908	49.210	36.749	18.692	- 99.847	- 46.571	6.785
1600	17.960	50.368	37.564	20.486	- 99.008	- 43.046	5.880
1700	17.981	51.457	38.350	22.283	- 98.166	- 39.575	5.088
1800	17.995	52.485	39.107	24.082	- 97.324	- 36.152	4.389
1900	18.001	53.459	39.837	25.882	- 96.484	- 32.779	3.770
2000	18.000	54.382	40.541	27.682	- 95.644	- 29.447	3.218

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POTASSIUM IODIDE (KI) (CRYSTAL) GFW = 166.0064

$\Delta Hf_0^\circ = -78.14 \pm 0.1$ kcal/mol

$S^\circ_{298.15} = 25.427$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -78.37 \pm 0.1$ kcal/mol

Tm = 954°K

$\Delta Hm^\circ = 5.74$ kcal/mol

$\Delta Hs^\circ_{298.15}$(to monomer) = 48.37 kcal/mol

$\Delta Hs^\circ_{298.15}$(to dimer) = 55.84 kcal/mol

Heat of Formation

The heats of solution of KI(c) have been critically reviewed by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. Six pertinent results are quoted in the table below. Adopting the best value, $\Delta H^\circ_{\infty 298} = 4.86 \pm 0.03$ kcal/mol, reported by Parker, and $\Delta Hf^\circ_{298} = -60.32$ and -13.19 kcal/mol for $K^+(\infty H_2O)$ and $I^-(\infty H_2O)$, respectively, obtained from U.S. Natl. Bur. Std. Tech. Note 270-1, 1965, we obtain ΔHf°_{298}(KI, c) = −78.37 ± 0.1 kcal/mol, which is adopted.

ΔH°_∞, kcal/mol*	Temperature, °C	n**	Investigator
4.830 ± 0.05	19	200	J. Thomsen, Thermochemische Untersuchungen, J. Barth Verlag, Leipzig, 1882-86.
4.897 ± 0.04	25	18	J. Wüst and E. Lange, Z. Physik. Chem. 116, 161 (1925).
4.873	25	500	E. Lange and W. Martin, Z. Physik. Chem. A180, 233 (1937).
4.790 ± 0.10	20.5	600	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, Zhur. Obshch. Khim. 10, 2023 (1940).
5.020	24.5	18.5	M. Bobtelsky and R. D. Lairsch, J. Chem. Soc. 1950, 3612 (1950).
4.830 ± 0.07	25	75000	A. F. Kapustinskii and S. I. Drakin, Zhur. Fiz. Khim. 26, 581 (1952).

*Values are adjusted to 298.15°K and to infinite dilution.

**n is the number of moles of H_2O per mole of KI(c) in solution.

Heat Capacity and Entropy

The low temperature heat capacities are based on those measured by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 467 (1957), 2.86 - 268.0°K. The adopted values are in good agreement with the Cp values reported by W. W. Scales, Phys. Rev. 112, 49 (1958), 2 - 7°K. The data of K. Clusius, J. Goldmann, and A. Perlick, Z. Naturforsch. 4A, 424 (1949), 10.27 - 269.9°K, appear to be too low in the temperature range 70 - 270°K and are not used. Low temperature enthalpies, 83 - 273°K, have been measured by F. Koref, Ann. Physik 4, 49 (1911). The value of S°_{298} is derived based on the adopted low tempeature heat capacities, using $S^\circ_{2.86} = 0.0033$ eu.

The high temperature enthalpies were determined by S. M. Skuratov and S. A. Lapushkin, Russ. J. Gen. Chem. (English Transl.) 21, 2485 (1951), 623 - 923°K; A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1964, 854 - 954°K; and C. B. Cooper, J. Chem. Phys. 21, 777 (1953), 297 - 973°K. Heat Capacities are derived from the enthalpies by a curve fitting method which requires a smooth joint with the low temperature Cp. Enthalpy values used in the curve fit include smooth values calculated from the equation of Skuratov and the value $H^\circ_{954} - H^\circ_{298} = 9.2$ kcal/mol from Dworkin. Deviation of the input values from the selected enthalpies are all less than 0.3 percent, while the deviations of the data of Cooper range from +1.0 percent at 570°K to -1.6 percent at 974°K. Since the latter point is 20° above the melting point, there appears to be an error in Cooper's measurement of temperature. Cp above the melting point is obtained by graphical extrapolation.

Melting Data

Tm has been reported to be 953, 952 and 954°K by R. C. Ray and V. Dayal, Trans. Faraday Soc. 32, 741 (1936); T. E. Phipps and E. G. Partridge, J. Am. Chem. Soc. 51, 1331 (1929); and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 62, 604 (1958), respectively. The last value is adopted. The heat of melting was determined by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960), using drop calorimetry.

Heat of Sublimation

The difference between ΔHf°_{298} for KI(g) and KI(c) is ΔHs°_{298}(to monomer). The ΔHs°_{298}(to dimer) is calculated as the enthalpy change for the following reaction: $2KI(c) = K_2I_2(g)$.

Potassium Iodide (KI)

(Liquid) GFW = 166.0064

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.300	27.273	27.273	.000	- 74.771	- 74.156	54.358
300	17.300	27.380	27.273	.032	- 74.764	- 74.152	54.020
400	17.300	32.357	27.952	1.762	- 76.934	- 73.824	40.335
500	17.300	36.217	29.233	3.492	- 81.708	- 72.503	31.735
600	17.300	39.371	30.668	5.222	- 81.153	- 70.833	25.801
700	17.300	42.038	32.106	6.952	- 80.588	- 69.158	21.592
800	17.300	44.348	33.495	8.682	- 80.021	- 67.564	18.458
900	17.300	46.386	34.817	10.412	- 79.455	- 66.041	16.037
1000	17.300	48.208	36.066	12.142	- 78.898	- 64.580	14.114
1100	17.300	49.857	37.246	13.872	- 97.259	- 62.151	12.348
1200	17.300	51.363	38.361	15.602	- 96.480	- 58.994	10.744
1300	17.300	52.747	39.415	17.332	- 95.702	- 55.901	9.398
1400	17.300	54.029	40.414	19.062	- 94.925	- 52.868	8.253
1500	17.300	55.223	41.362	20.792	- 94.148	- 49.892	7.269
1600	17.300	56.339	42.263	22.522	- 93.372	- 46.964	6.415
1700	17.300	57.388	43.122	24.252	- 92.598	- 44.090	5.668
1800	17.300	58.377	43.943	25.982	- 91.825	- 41.258	5.009
1900	17.300	59.312	44.727	27.712	- 91.054	- 38.470	4.425
2000	17.300	60.200	45.479	29.442	- 90.284	- 35.723	3.904
2100	17.300	61.044	46.200	31.172	- 89.517	- 33.013	3.436
2200	17.300	61.849	46.893	32.902	- 88.753	- 30.341	3.014
2300	17.300	62.618	47.560	34.632	- 87.992	- 27.704	2.632
2400	17.300	63.354	48.203	36.362	- 87.235	- 25.098	2.285
2500	17.300	64.060	48.823	38.092	- 86.483	- 22.525	1.969

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POTASSIUM IODIDE (KI) (LIQUID) GFW = 166.0064

$S^\circ_{298.15}$ = 27.273 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -74.771 kcal/mol

Tm = 954°K

ΔHm° = 5.74 kcal/mol

Tb = 1618°K

ΔHv° = 45.62 kcal/mol

Heat of Formation

The heat of formation, ΔHf°_{298}, is obtained from ΔHf°_{298}(KI, c) by adding ΔHm° and the difference between $H^\circ_{954} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived as 17.3 gibbs/mol from the enthalpy measurements, 954 - 1014°K, by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1964. This Cp value is adopted in the temperature range 298 - 2500°K. S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

See KI(c) table for details.

Vaporization Data

The boiling point, Tb = 1618°K, is calculated as the temperature at which the sum of the partial pressures of KI(g) and K_2I_2(g) over KI(ℓ) equals one atmosphere. The value of ΔHv° is calculated as the heat required to produce one mole of vapor mixture, which contains 78 percent monomer (KI) and 22 percent dimer (K_2I_2) at Tb.

Tb was reported as 1603 and 1590°K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921), respectively.

Potassium Iodide (KI)

(Ideal Gas) GFW = 166.0064

T, °K	gibbs/mol Cp°	S°	−(G°−H°$_{298}$)/T	kcal/mol H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.448	-29.178	-29.178	INFINITE
100	8.104	52.335	69.459	-1.712	-29.221	-32.874	71.847
200	8.709	58.191	62.512	-.864	-29.582	-36.393	39.769
298	8.872	61.704	61.704	.000	-30.000	-39.651	29.065
300	8.874	61.759	61.704	.016	-30.009	-39.710	28.929
400	8.948	64.323	62.053	.908	-33.017	-42.693	23.326
500	8.993	66.325	62.715	1.805	-38.624	-44.573	19.483
600	9.027	67.968	63.457	2.706	-38.898	-45.736	16.659
700	9.055	69.362	64.204	3.610	-39.159	-46.855	14.629
800	9.081	70.572	64.926	4.517	-39.415	-47.937	13.096
900	9.104	71.643	65.614	5.426	-39.670	-48.987	11.896
1000	9.127	72.604	66.266	6.338	-39.932	-50.009	10.929
1100	9.148	73.475	66.882	7.252	-59.109	-49.980	9.930
1200	9.169	74.271	67.465	8.168	-59.144	-49.147	8.951
1300	9.190	75.006	68.017	9.086	-59.177	-48.313	8.122
1400	9.211	75.688	68.541	10.006	-59.210	-47.476	7.411
1500	9.231	76.324	69.039	10.928	-59.242	-46.636	6.795
1600	9.251	76.921	69.513	11.852	-59.272	-45.795	6.255
1700	9.272	77.482	69.966	12.778	-59.301	-44.953	5.779
1800	9.292	78.013	70.398	13.706	-59.330	-44.108	5.355
1900	9.312	78.516	70.812	14.636	-59.359	-43.262	4.976
2000	9.332	78.994	71.209	15.569	-59.387	-42.414	4.635
2100	9.351	79.449	71.591	16.503	-59.415	-41.562	4.325
2200	9.371	79.885	71.958	17.439	-59.446	-40.713	4.044
2300	9.391	80.302	72.312	18.377	-59.477	-39.861	3.788
2400	9.411	80.702	72.653	19.317	-59.509	-39.007	3.552
2500	9.431	81.087	72.983	20.259	-59.545	-38.154	3.335
2600	9.450	81.457	73.302	21.203	-59.583	-37.295	3.135
2700	9.470	81.814	73.610	22.149	-59.626	-36.439	2.950
2800	9.490	82.159	73.910	23.097	-59.675	-35.579	2.777
2900	9.510	82.492	74.200	24.047	-59.728	-34.715	2.616
3000	9.529	82.815	74.482	24.999	-59.787	-33.855	2.466
3100	9.549	83.128	74.756	25.953	-59.854	-32.988	2.326
3200	9.569	83.431	75.022	26.909	-59.930	-32.118	2.194
3300	9.588	83.726	75.281	27.867	-60.015	-31.250	2.070
3400	9.608	84.012	75.534	28.827	-60.111	-30.377	1.953
3500	9.628	84.291	75.780	29.788	-60.220	-29.500	1.842
3600	9.647	84.563	76.020	30.752	-60.343	-28.621	1.738
3700	9.667	84.827	76.255	31.718	-60.482	-27.739	1.638
3800	9.687	85.085	76.484	32.684	-60.639	-26.851	1.544
3900	9.706	85.337	76.708	33.655	-60.816	-25.960	1.455
4000	9.726	85.583	76.926	34.627	-61.016	-25.064	1.369
4100	9.746	85.824	77.140	35.600	-61.242	-24.163	1.288
4200	9.765	86.059	77.350	36.576	-61.496	-23.255	1.210
4300	9.785	86.289	77.555	37.554	-61.780	-22.343	1.136
4400	9.805	86.514	77.756	38.533	-62.100	-21.422	1.064
4500	9.824	86.734	77.953	39.514	-62.457	-20.487	.995
4600	9.844	86.950	78.147	40.498	-62.854	-19.552	.929
4700	9.864	87.162	78.336	41.483	-63.294	-18.607	.865
4800	9.883	87.370	78.522	42.471	-63.782	-17.649	.804
4900	9.903	87.574	78.705	43.460	-64.320	-16.682	.744
5000	9.922	87.775	78.884	44.451	-64.910	-15.710	.687
5100	9.942	87.971	79.061	45.444	-65.556	-14.719	.631
5200	9.962	88.164	79.234	46.440	-66.259	-13.711	.576
5300	9.981	88.354	79.404	47.437	-67.021	-12.694	.523
5400	10.001	88.541	79.572	48.436	-67.844	-11.663	.472
5500	10.021	88.725	79.736	49.437	-68.729	-10.618	.422
5600	10.040	88.906	79.898	50.440	-69.674	-9.555	.373
5700	10.060	89.083	80.058	51.445	-70.680	-8.467	.325
5800	10.080	89.259	80.215	52.452	-71.747	-7.372	.278
5900	10.099	89.431	80.370	53.461	-72.871	-6.248	.231
6000	10.119	89.601	80.522	54.472	-74.052	-5.106	.186

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Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 61.704 gibbs/mol

ΔHf°_0 = -29.2 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -30.0 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 186.287 ± 0.04 cm^{-1} $\omega_e x_e$ = 0.5725 ± 0.006 cm^{-1} σ = 1

B_e = 0.06072 cm^{-1} α_e = 0.000267 cm^{-1} r_e = 3.0478 Å

Heat of Formation

The heat of formation is derived from the sublimation and vaporization data analyzed below. Many investigators have determined the total pressures of KI(g) and K_2I_2(g) over KI(c) or KI(ℓ) by static methods or "apparent" pressures by Knudsen effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see K_2I_2(g) table] which are consistent with the dimer-monomer equilibrium data of Datz (9). Second and third law analyses of the monomer pressures show reasonable agreement. The selected value of ΔHf°_{298} = -30.0 ± 0.5 kcal/mol is also in good agreement with -30.23 ± 1.15 and -30.46 kcal/mol derived from D°_0 = 3.32 ± 0.05 and 3.33 eV reported by Gaydon (10) and Herzberg (11), respectively.

	Investigator	Reaction**	Temperature °K	No. of Points	ΔHr°_{298}, kcal/mol Second Law	 Third Law	Drift eu	ΔHf°_{298}* kcal/mol
1.	Wartenberg-Albrecht	(B)	1336.2-1606.2	9	47.79±0.38	44.76	-2.1±0.2	-30.01
2.	Ruff-Mugdan	(B)	1319.2-1590.2	12	49.38±1.03	44.59	-3.3±0.7	-30.18
3.	Fiock-Rodebush	(B)	1116.1-1275.7	8	45.43±0.03	44.75	-0.6±0.1	-30.02
4.	Greiner-Jellinek	(B)	1453.2	1	-	45.24	-	-29.53
5.	Niwa	(A)	803.2-873.2	8	46.11±0.35	48.30	2.6±0.4	-30.07
6.	Zimm-Mayer	(A)	618.4-892.9	10	48.66±0.25	48.47	-0.4±0.3	-29.90
7.	Cogin-Kimball	(A)	721.5-897.7	29	48.52±0.40	47.73	-1.1±0.5	-30.64
8.	Bridgers	(A)	697.5-891.7	25	48.48±0.22	47.72	-1.1±0.3	-30.65

*Based on the third law ΔHr°_{298} value.

**(A) KI(c) = KI(g); (B) KI(ℓ) = KI(g)

Heat Capacity and Entropy

The ground state configuration is obtained from Herzberg (11). The adopted values of ω_e, $\omega_e x_e$, B_e, α_e and r_e were determined using millimeter wave molecular beam spectroscopy by Rusk and Gordy (12), and corrected to the average isotopic species. Similar values were reported by Honig et al. (13) from microwave spectra, except ω_e which was given as 199.74 cm^{-1}. The value of ω_e was derived to be 200 and 173 cm^{-1} by Barrow and Caunt (14) and Rice and Klemperer (15). The moment of inertia is 4.5979 x 10^{-38} g cm^2.

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Lithium Iodide (LiI)

(Crystal) GFW = 133.8434

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.970	20.500	20.500	.000	-64.550	-64.451	47.244
300	11.995	20.574	20.500	.022	-64.551	-64.450	46.952
400	12.770	24.110	20.977	1.253	-66.527	-64.341	35.154
500	13.372	27.025	21.904	2.561	-72.399	-63.235	27.640
600	14.020	29.517	22.969	3.929	-72.192	-61.420	22.372
700	14.880	31.742	24.066	5.373	-71.898	-59.647	18.623
800	15.800	33.786	25.155	6.905	-71.508	-57.922	15.823
900	16.615	35.697	26.221	8.528	-71.028	-56.252	13.660
1000	17.200	37.480	27.259	10.221	-70.478	-54.639	11.941
1100	17.575	39.137	28.264	11.960	-69.880	-53.083	10.547
1200	17.820	40.678	29.236	13.731	-69.252	-51.586	9.395
1300	18.015	42.112	30.171	15.523	-68.600	-50.139	8.429
1400	18.135	43.452	31.073	17.330	-67.934	-48.744	7.609
1500	18.210	44.706	31.940	19.148	-67.255	-47.397	6.906
1600	18.210	45.881	32.775	20.969	-66.572	-46.094	6.296
1700	18.210	46.985	33.579	22.790	-100.936	-43.508	5.593
1800	18.210	48.026	34.353	24.611	-100.071	-40.153	4.875
1900	18.210	49.010	35.099	26.432	-99.206	-36.846	4.238
2000	18.210	49.944	35.818	28.253	-98.343	-33.588	3.670
2100	18.210	50.833	36.512	30.074	-97.482	-30.373	3.161
2200	18.210	51.680	37.182	31.895	-96.622	-27.197	2.702
2300	18.210	52.490	37.830	33.716	-95.763	-24.062	2.286
2400	18.210	53.265	38.457	35.537	-94.908	-20.963	1.909
2500	18.210	54.008	39.065	37.358	-94.054	-17.898	1.565

Sept. 30, 1961; June 30, 1966

ΔHf_0° = Unknown

$S^\circ_{298.15}$ = [20.5] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -64.55 ± 0.1 kcal/mol

Tm = 742°K

ΔHm° = 3.50 kcal/mol

Heat of Formation.

The heat of formation, ΔHf°_{298}(LiI, c) = -64.55 kcal/mol, was calculated from the heat of solution of lithium iodide (c) at infinite dilution and the ionic heats of formation of $Li^+(\infty H_2O)$ and $I^-(\infty H_2O)$.

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, Apr. 1, 1965, reviewed the literature heat of solution data and gave the "best" value, ΔH°_∞ = -15,130 ± 75 cal/mol for LiI(c) → $LiI(\infty H_2O)$ at 298.15°K. The ionic heat of formation, $\Delta Hf^\circ_{298}(Li^+\cdot\infty H_2O)$ = -66.49 kcal/mol, was calculated from ΔH°_{298} $(LiOH\cdot\infty H_2O)$ = -121.46 kcal/mol (see JANAF LiOH(c) Table, Mar. 31, 1966) with ΔHf°_{298} $(OH^-\cdot\infty H_2O)$ = -54.97 kcal/mol from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1965. The value ΔHf°_{298} $(I^-\cdot\infty H_2O)$ = -13.19 kcal/mol was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of $Li^+(\infty H_2O)$ and $I^-(\infty H_2O)$ gives the heat of formation of $LiI(\infty H_2O)$, ΔHf°_{298} = -79.68 kcal/mol.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method (642-802°K), yielding $(H_{742}-H_{298})$ = 6.0 kcal/mol for the crystal at the melting point. Heat capacities derived from his data were Cp_{692° = 14.8 and Cp_{772} = 15.1 cal/deg-mol for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(c), NaCl(c) and NaI(c).

The entropy, $S^\circ_{298.15}$ = 20.5 eu, was estimated by adding the entropy difference between NaI(c) and NaCl(c) to the entropy of lithium chloride (c) at 298.15°K. Comparisons with other alkali halides give results within ± 0.5 eu of this value.

K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960), 592 (1961), has estimated the heat capacities ($Cp = 12.30 + 2.44 \times 10^{-3}T$ gibbs/mol) and the entropy (S°_{298} = 17.50 eu).

Melting Data.

The selected heat of fusion (ΔH°_{823} = 3.50 kcal/mol) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Lithium Iodide (LiI)

(Liquid) GFW = 133.8434

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.100	23.568	23.568	.000	-61.749	-62.564	45.861
300	15.100	23.661	23.568	.028	-61.744	-62.570	45.582
400	15.100	28.005	24.161	1.538	-63.441	-62.813	34.319
500	15.100	31.375	25.279	3.048	-69.111	-62.121	27.153
600	15.100	34.128	26.531	4.558	-68.762	-60.756	22.130
700	15.100	36.456	27.787	6.068	-68.402	-59.451	18.561
800	15.100	38.472	29.000	7.578	-68.034	-58.197	15.899
900	15.100	40.250	30.153	9.088	-67.667	-56.989	13.839
1000	15.100	41.841	31.243	10.598	-67.300	-55.822	12.200
1100	15.100	43.281	32.273	12.108	-66.931	-54.693	10.866
1200	15.100	44.594	33.246	13.618	-66.564	-53.596	9.761
1300	15.100	45.803	34.166	15.128	-66.194	-52.531	8.831
1400	15.100	46.922	35.038	16.638	-65.825	-51.493	8.038
1500	15.100	47.964	35.865	18.148	-65.455	-50.484	7.355
1600	15.100	48.938	36.652	19.658	-65.083	-49.495	6.761
1700	15.100	49.854	37.402	21.168	-99.758	-47.206	6.069
1800	15.100	50.717	38.118	22.678	-99.203	-44.129	5.358
1900	15.100	51.533	38.803	24.188	-98.650	-41.083	4.726
2000	15.100	52.308	39.459	25.698	-98.098	-38.071	4.160
2100	15.100	53.045	40.088	27.208	-97.547	-35.084	3.651
2200	15.100	53.747	40.693	28.718	-96.999	-32.121	3.191
2300	15.100	54.418	41.276	30.228	-96.451	-29.184	2.773
2400	15.100	55.061	41.837	31.738	-95.906	-26.271	2.392
2500	15.100	55.677	42.378	33.248	-95.364	-23.380	2.044

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LITHIUM IODIDE (LiI) (LIQUID) GFW = 133.8434

$S°_{298.15}$ = [23.568] gibbs/mol

Tm = 742°K

Tb(to equilibrium mixture) = 1449°K

Tb(to monomer only) = [1497]°K

$\Delta Hf°_{298.15}$ = -61.749 kcal/mol

ΔHm° = 3.50 kcal/mol

ΔHv°(to equilibrium mixture) = 23.3 kcal/mol

ΔHv°(to monomer only) = [32.6] kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between $H°_{742}- H°_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity, Cp = 15.1 gibbs/mol, from enthalpy measurements, 742 - 802°K, by the drop method. The liquid heat capacity was assumed to be a constant, 15.1 gibbs/mol. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiI(c) table for detail.

Vaporization Data.

Tb (to monomer only) is determined as the temperature at which the Gibbs energy change (ΔGr°) for the reaction LiI(l) = LiI(g) approaches zero. The corresponding enthalpy change (ΔHr°) at boiling point is the heat of vaporization ΔHv°(to monomer only).

Tb (to equilibrium mixture) is the temperature at which the sum of the calculated partial vapor pressures of LiI(g) and $Li_2I_2(g)$ reaches one atmosphere (trimer and higher polymer have been neglected in calculation). This value is in good agreement with the boiling point of 1444°K from the least squares fit of the total vapor pressure data measured by O. Ruff and S. Mugdan, Z. anorg Chem. 117, 147 (1921). ΔHv°(to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 30.44 mole percent of dimer. For detailed information see LiI(g) and $Li_2I_2(g)$ tables.

Lithium Iodide (LiI)

(Ideal Gas) GFW = 133.8434

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.222	-21.290	-21.290	INFINITE
100	7.045	47.195	62.451	-1.526	-21.077	-24.892	54.401
200	7.742	52.280	56.219	-.788	-21.368	-28.606	31.260
298	8.263	55.478	55.478	.000	-21.750	-32.079	23.515
300	8.270	55.529	55.478	.015	-21.758	-32.144	23.417
400	8.556	57.951	55.806	.858	-24.122	-35.472	19.381
500	8.720	59.880	56.435	1.722	-30.437	-37.700	16.479
600	8.824	61.480	57.146	2.600	-30.721	-39.126	14.252
700	8.896	62.845	57.865	3.486	-30.984	-40.506	12.647
800	8.950	64.037	58.564	4.379	-31.234	-41.849	11.433
900	8.993	65.094	59.232	5.276	-31.480	-43.162	10.481
1000	9.029	66.043	59.866	6.177	-31.721	-44.446	9.714
1100	9.060	66.905	60.467	7.082	-31.958	-45.707	9.081
1200	9.087	67.695	61.037	7.989	-32.194	-46.948	8.550
1300	9.113	68.423	61.578	8.899	-32.424	-48.167	8.098
1400	9.136	69.099	62.091	9.811	-32.653	-49.369	7.707
1500	9.159	69.730	62.580	10.726	-32.877	-50.556	7.366
1600	9.180	70.322	63.045	11.643	-33.098	-51.726	7.065
1700	9.201	70.879	63.490	12.562	-68.364	-51.556	6.628
1800	9.221	71.406	63.915	13.483	-68.399	-50.565	6.139
1900	9.240	71.905	64.323	14.406	-68.432	-49.573	5.702
2000	9.260	72.379	64.714	15.331	-68.465	-48.580	5.309
2100	9.278	72.832	65.090	16.258	-68.498	-47.587	4.952
2200	9.297	73.264	65.451	17.187	-68.531	-46.590	4.628
2300	9.315	73.677	65.800	18.118	-68.562	-45.591	4.332
2400	9.334	74.074	66.137	19.050	-68.595	-44.591	4.061
2500	9.352	74.456	66.462	19.984	-68.628	-43.592	3.811
2600	9.370	74.823	66.776	20.920	-68.662	-42.591	3.580
2700	9.387	75.177	67.081	21.858	-68.698	-41.588	3.366
2800	9.405	75.518	67.376	22.798	-68.735	-40.580	3.167
2900	9.423	75.849	67.663	23.739	-68.776	-39.576	2.982
3000	9.440	76.168	67.941	24.682	-68.818	-38.566	2.809
3100	9.458	76.478	68.211	25.627	-68.864	-37.556	2.648
3200	9.475	76.779	68.474	26.574	-68.913	-36.548	2.496
3300	9.493	77.071	68.731	27.522	-68.966	-35.535	2.353
3400	9.510	77.354	68.980	28.473	-69.023	-34.519	2.219
3500	9.527	77.630	69.223	29.424	-69.085	-33.504	2.092
3600	9.545	77.899	69.461	30.378	-69.152	-32.488	1.972
3700	9.562	78.161	69.692	31.333	-69.224	-31.471	1.859
3800	9.579	78.416	69.918	32.290	-69.302	-30.445	1.751
3900	9.597	78.665	70.140	33.249	-69.386	-29.421	1.649
4000	9.614	78.908	70.356	34.210	-69.477	-28.397	1.552
4100	9.631	79.146	70.567	35.172	-69.575	-27.368	1.459
4200	9.648	79.378	70.774	36.136	-69.681	-26.337	1.370
4300	9.665	79.605	70.977	37.102	-69.794	-25.304	1.286
4400	9.682	79.828	71.176	38.069	-69.915	-24.269	1.205
4500	9.699	80.045	71.370	39.038	-70.046	-23.226	1.128
4600	9.717	80.259	71.561	40.009	-70.186	-22.187	1.054
4700	9.734	80.468	71.748	40.981	-70.335	-21.145	.983
4800	9.751	80.673	71.932	41.956	-70.496	-20.096	.915
4900	9.768	80.874	72.113	42.931	-70.669	-19.042	.849
5000	9.785	81.072	72.290	43.909	-70.852	-17.987	.786
5100	9.802	81.266	72.464	44.888	-71.050	-16.928	.725
5200	9.819	81.456	72.635	45.869	-71.262	-15.863	.667
5300	9.836	81.643	72.803	46.852	-71.488	-14.796	.610
5400	9.853	81.827	72.969	47.837	-71.729	-13.723	.555
5500	9.870	82.008	73.131	48.823	-71.989	-12.646	.503
5600	9.887	82.186	73.292	49.811	-72.265	-11.570	.452
5700	9.904	82.361	73.449	50.800	-72.561	-10.479	.402
5800	9.921	82.534	73.604	51.791	-72.877	-9.390	.354
5900	9.938	82.704	73.757	52.784	-73.213	-8.295	.307
6000	9.955	82.871	73.908	53.779	-73.572	-7.188	.262

Sept. 30, 1961; June 30, 1966

LITHIUM IODIDE (LiI) (IDEAL GAS) GFW = 133.8434 ILi

Ground State Configuration $^1\Sigma$

ΔHf°_0 = -21.3 ± 2 kcal/mol

$S^\circ_{298.15}$ = 55.478 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -21.75 ± 2 kcal/mol

Electronic Levels and Quantum Weights

ϵ, cm^{-1}	g_i
0	1

ω_e = 498.16 cm^{-1} $\omega_e x_e$ = 3.39 cm^{-1} σ = 1

B_e = 0.44837 cm^{-1} α_e = 0.00416 cm^{-1} r_e = 2.3919 Å

Heat of Formation.

The heat of formation (ΔHf°_{298} (LiI, g) = -21.75 ± 2 kcal/mol) was calculated from the selected heat of sublimation and the heat of formation for lithium iodide (c). The heat of sublimation has been determined mass-spectrometrically from the ion intensity measurement (2nd law method) by L. N. Gorokhov, Dokl. Akad. Nauk SSSR 142, 113 (1962), as ΔHs°(to monomer) = 42.9 ± 0.6 and ΔHs° (to dimer) = 43.2 ± 0.4 kcal/mol in the temperature range from 626-722°K. Gorokhov also reported the partial vapor pressure of monomeric lithium iodide ($P_{monomer}$ = 3 X 10^{-3} mm Hg) and the ratio of dimer to monomer ($P_{dimer}/P_{monomer}$ = 6) which have been used for third law calculation. Using the same technique, L. Friedman, J. Chem. Phys. 23, 477 (1955), reported the heats of sublimation as ΔHs°_{727} (to monomer) = 41.9 ± 0.5 and ΔHs°_{727} (to dimer) = 40.8 ± 0.5 kcal/mol in the temperature range from 630° to 730°K. J. Berkowitz, H. A. Tasman and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962) have also studied the lithium iodide vapor in the mass spectrometer and reported the second law and third law values of the heat of dimerization at 800°K as 37.9 and 40.4 kcal/mol, respectively. Using the JANAF thermodynamic functions, all the heats of sublimation and dimerization at different temperatures have been reduced to 298°K and summarized in the following table. The total vapor pressure over the liquid has been measured by a boiling point method in the temperature range 1223° to 1413°K by O. Ruff and S. Mugdan, Z. anorg. Chem. 117, 147 (1921). (Their data have been quoted by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).) In order to have good agreement between the calculated vapor pressure and the observed total vapor pressure, the heats of sublimation have been so chosen as ΔHs°_{298} (to monomer) = 42.8 kcal/mol and ΔHs°_{298} (to dimer) = 42.6 kcal/mol and the heat of dissociation of dimer, ΔHd°_{298} = 43.0 kcal/mol. The calculated boiling point (to equilibrium mixture) is 1449°K which agrees with 1443°K reported by Wartenberg and Schulz, and also 1462°K by Ruff and Mugdan.

Chemical Reaction	Investigator	ΔHr°_{298} kcal/mol 2nd law	3rd law
$LiI(c) \rightarrow LiI(g)$	Gorokhov	44.7	42.2
	Friedman	43.9	—
$2LiI(c) \rightarrow Li_2I_2(g)$	Gorokhov	46.0	41.3
	Friedman	44.1	—
$Li_2I_2(g) \rightarrow 2LiI(g)$	Berkowitz et al.	38.8	41.3
	Friedman	43.7	—
	Gorokov	43.2	43.1

Heat Capacity and Entropy.

The bond distance and the rotational constants (B_e and α_e), corrected to the isotopic abundance of 7.4% Li^6 and 92.6% Li^7, were obtained from the microwave studies by A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 96, 629 (1954). The vibrational constants (ω_e and $\omega_e x_e$) were determined from the infrared spectrum by W. Klemperer, W. G. Norris, A. Büchler and A. G. Emslie, J. Chem. Phys. 33, 1534 (1960).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

ILi

Nitrosyl Iodide (NOI)

(Ideal Gas) GFW = 156.9105

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.894	27.557	27.557	INFINITE
100	9.131	56.417	77.041	- 2.062	27.330	26.396	- 57.688
200	10.543	63.234	68.588	- 1.071	27.037	25.581	- 27.953
298	11.199	67.581	67.581	.000	26.800	24.917	- 18.265
300	11.208	67.650	67.581	.021	26.796	24.906	- 18.144
400	11.607	70.932	68.026	1.162	24.647	24.377	- 13.319
500	11.938	73.559	68.878	2.340	19.347	24.813	- 10.846
600	12.232	75.762	69.847	3.549	19.373	25.904	- 9.436
700	12.487	77.667	70.831	4.785	19.407	26.990	- 8.427
800	12.702	79.349	71.793	6.045	19.446	28.071	- 7.669
900	12.880	80.856	72.717	7.324	19.487	29.146	- 7.078
1000	13.026	82.220	73.600	8.620	19.529	30.218	- 6.604
1100	13.147	83.468	74.442	9.929	19.571	31.284	- 6.216
1200	13.246	84.616	75.242	11.249	19.612	32.348	- 5.891
1300	13.328	85.680	76.005	12.577	19.652	33.407	- 5.616
1400	13.397	86.670	76.732	13.914	19.690	34.464	- 5.380
1500	13.455	87.596	77.425	15.257	19.727	35.518	- 5.175
1600	13.504	88.466	78.089	16.605	19.761	36.571	- 4.995
1700	13.546	89.286	78.723	17.957	19.793	37.620	- 4.836
1800	13.582	90.062	79.332	19.314	19.822	38.666	- 4.695
1900	13.613	90.797	79.916	20.673	19.848	39.714	- 4.568
2000	13.640	91.496	80.478	22.036	19.872	40.757	- 4.454
2100	13.663	92.162	81.018	23.401	19.893	41.801	- 4.350
2200	13.684	92.798	81.540	24.768	19.910	42.844	- 4.256
2300	13.702	93.407	82.042	26.138	19.925	43.885	- 4.170
2400	13.718	93.990	82.528	27.509	19.937	44.929	- 4.091
2500	13.732	94.550	82.998	28.881	19.944	45.969	- 4.019
2600	13.745	95.089	83.453	30.255	19.950	47.010	- 3.952
2700	13.757	95.608	83.893	31.630	19.951	48.052	- 3.889
2800	13.767	96.109	84.321	33.006	19.950	49.091	- 3.832
2900	13.776	96.592	84.736	34.384	19.946	50.134	- 3.778
3000	13.785	97.059	85.139	35.762	19.938	51.174	- 3.728
3100	13.793	97.511	85.530	37.141	19.928	52.216	- 3.681
3200	13.800	97.949	85.912	38.520	19.915	53.257	- 3.637
3300	13.806	98.374	86.283	39.900	19.898	54.299	- 3.596
3400	13.812	98.786	86.645	41.281	19.879	55.343	- 3.557
3500	13.817	99.187	86.997	42.663	19.857	56.383	- 3.521
3600	13.822	99.576	87.341	44.045	19.832	57.429	- 3.486
3700	13.827	99.955	87.677	45.427	19.805	58.472	- 3.454
3800	13.831	100.324	88.005	46.810	19.776	59.518	- 3.423
3900	13.835	100.683	88.326	48.193	19.744	60.565	- 3.394
4000	13.839	101.033	88.639	49.577	19.709	61.611	- 3.366
4100	13.842	101.375	88.945	50.961	19.672	62.661	- 3.340
4200	13.845	101.709	89.245	52.346	19.633	63.708	- 3.315
4300	13.848	102.034	89.539	53.730	19.592	64.762	- 3.292
4400	13.851	102.353	89.827	55.115	19.548	65.808	- 3.269
4500	13.853	102.664	90.108	56.500	19.502	66.863	- 3.247
4600	13.856	102.969	90.385	57.886	19.455	67.916	- 3.227
4700	13.858	103.267	90.656	59.272	19.406	68.968	- 3.207
4800	13.860	103.558	90.921	60.657	19.354	70.028	- 3.188
4900	13.862	103.844	91.182	62.044	19.302	71.080	- 3.170
5000	13.864	104.124	91.438	63.430	19.246	72.139	- 3.153
5100	13.866	104.399	91.690	64.816	19.190	73.194	- 3.137
5200	13.868	104.668	91.937	66.203	19.132	74.254	- 3.121
5300	13.869	104.932	92.179	67.590	19.072	75.318	- 3.106
5400	13.871	105.192	92.418	68.977	19.010	76.375	- 3.091
5500	13.872	105.446	92.653	70.364	18.948	77.443	- 3.077
5600	13.873	105.696	92.883	71.751	18.882	78.503	- 3.064
5700	13.875	105.942	93.110	73.139	18.816	79.567	- 3.051
5800	13.876	106.183	93.334	74.526	18.749	80.638	- 3.039
5900	13.877	106.420	93.553	75.914	18.680	81.704	- 3.026
6000	13.878	106.653	93.770	77.302	18.609	82.776	- 3.015

Mar. 31, 1962; Dec. 31, 1966

NITROSYL IODIDE (NOI) (IDEAL GAS) GFW = 156.9105

Point Group C_s

ΔHf°_0 = [27.6 ± 5] kcal/mol

$S^\circ_{298.15}$ = [67.58] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [26.8 ± 5] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[1780] (1)
[440] (1)
[200] (1)

Bond Distance: O-N = [1.15] Å N-I = [2.3] Å

Bond Angle: O-N-I = [120]°

Product of the Moment of Inertia: $I_AI_BI_C$ = [7.742 x 10^{-115}] g^3 cm^6

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) for INO (g) is estimated by comparison with those for FNO(g), ClNO(g), BrNO(g), and the related cyanogen halides.

Heat Capacity and Entropy.

The molecular structure and bond angle are estimated by comparison with those for ClNO(g) and BrNO(g). The N-O bond distance is assumed to be the same as that in NO(g). The N-I bond distance (r_{N-I}) is calculated based on an assumption that $r_{ON-Cl} - r_{ON-I} = r_{I-Cl} - r_{I-I}$. The vibrational frequencies are estimated by comparison with those for FNO(g), ClNO(g) and BrNO(g). The three principal moments of inertia are: $I_A = 8.834 \times 10^{-40}$, $I_B = 2.916 \times 10^{-38}$ and $I_C = 3.005 \times 10^{-38}$ g cm^2.

Sodium Iodide (NaI)

(Crystal) Mol. Wt. = 149.901

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.933	- 68.615	- 68.615	INFINITE
100	10.285	10.899	34.199	- 2.330	- 68.697	- 68.488	149.674
200	11.915	18.667	24.667	- 1.200	- 68.743	- 68.261	74.589
298	12.482	23.542	23.542	.000	- 68.800	- 68.014	49.853
300	12.490	23.619	23.542	.023	- 68.801	- 68.009	49.542
400	12.860	27.265	24.037	1.291	- 71.463	- 67.614	36.941
500	13.150	30.167	24.982	2.592	- 76.664	- 66.158	28.916
600	13.440	32.591	26.054	3.922	- 76.504	- 64.071	23.337
700	13.710	34.683	27.141	5.280	- 76.302	- 62.016	19.361
800	13.980	36.531	28.201	6.664	- 76.063	- 59.990	16.388
900	14.246	38.193	29.221	8.076	- 75.793	- 57.997	14.083
1000	14.508	39.708	30.195	9.513	- 75.498	- 56.035	12.246
1100	14.766	41.103	31.124	10.977	- 75.184	- 54.105	10.749
1200	15.020	42.399	32.010	12.466	- 98.089	- 51.746	9.424
1300	15.275	43.611	32.856	13.981	- 97.526	- 47.906	8.053
1400	15.528	44.752	33.665	15.521	- 96.939	- 44.111	6.886
1500	15.778	45.832	34.441	17.087	- 96.327	- 40.360	5.880
1600	16.027	46.858	35.185	18.677	- 95.691	- 36.648	5.006
1700	16.273	47.837	35.901	20.292	- 95.030	- 32.977	4.239
1800	16.518	48.774	36.590	21.931	- 94.346	- 29.347	3.563
1900	16.760	49.674	37.255	23.595	- 93.638	- 25.755	2.962
2000	17.000	50.540	37.898	25.283	- 92.908	- 22.202	2.426

Sept. 30, 1963

SODIUM IODIDE (NaI) (CRYSTAL) MOL. WT. = 149.901

$S^\circ_{298.15}$ = 23.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 933°K.

$\Delta H_f^\circ{}_0$ = -68.6 ± 0.2 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -68.8 ± 0.2 kcal. mole^{-1}

ΔH_m = 5.64 kcal. mole^{-1}

Heat of Formation.

The heat of formation was obtained as follows:

		ΔH_{298}(kcal. mole^{-1})
(1)	$HI \cdot 100H_2O + NaOH \cdot 100H_2O \rightarrow NaI \cdot 201H_2O$ T. W. Richards, A. W. Rowe, J. Am. Chem. Soc. 44, 684 (1922).	-13.51 ± 0.02
(2)	$Na(c) + 1001H_2O(l) \rightarrow NaOH \cdot 1000H_2O + 1/2H_2(g)$ S. R. Gunn, L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958).	-44.069 ± 0.006
(3)	$NaOH \cdot 1000H_2O \rightarrow NaOH \cdot 100H_2O + 900H_2O(l)$ National Bureau of Standards Circular 500.	+0.031 ± 0.004
(4)	$1/2H_2(g) + 1/2I_2(s) \rightarrow HI(g)$ JANAF Tables.	+6.30 ± 0.05
(5)	$HI(g) + 100H_2O(l) \rightarrow HI \cdot 100H_2O$ W. A. Roth, Z. Elektrochem. 50, 107 (1944).	-19.30 ± 0.05
(6)	$NaI \cdot 201H_2O \rightarrow NaI(c) + 201H_2O(l)$ J. Wust, E. Lange, Z. physik. Chem. 116, 161 (1925). E. Lange, A. L. Robinson, Chem. Revs. 9, 89 (1931). Askew, Bullock, Smith, Tinkler, Gatty, Wolfenden, J. Chem. Soc., 1934, 1368.	+1.75 ± 0.06
	(1) + (2) + (3) + (4) + (5) + (6) gives $Na(c) + 1/2I_2(s) \rightarrow NaI(c)$	-68.80 ± 0.2

Heat Capacity and Entropy.

Smoothed heat capacities between 3° and 270°K. have been presented by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) 242A, 467 (1957). Above 270°K. the heat capacity was obtained by comparing with KI(c) on a reduced temperature plot of C_p/T versus T. The values so obtained were increased by 1.4% to bring them into line with the low temperature data.

Melting Data.

A. Dworkin and M. Bredig, J. Phys. Chem. 64, 269 (1960) have measured both T_m and ΔH_m.

Sodium Iodide (NaI)

(Liquid) Mol. Wt. = 149.901

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	12.482	28.862	28.862	.000	- 63.695	- 64.496	47.274
300	12.490	28.939	28.862	.023	- 63.696	- 64.500	46.986
400	12.860	32.585	29.357	1.291	- 66.358	- 64.637	35.314
500	13.150	35.487	30.302	2.592	- 71.559	- 63.713	27.848
600	15.500	37.910	31.374	3.922	- 71.399	- 62.158	22.640
700	15.500	40.300	32.483	5.472	- 71.005	- 60.650	18.935
800	15.500	42.370	33.592	7.022	- 70.600	- 59.198	16.171
900	15.500	44.195	34.671	8.572	- 70.192	- 57.797	14.034
1000	15.500	45.828	35.706	10.122	- 69.785	- 56.441	12.335
1100	15.500	47.306	36.695	11.672	- 69.384	- 55.128	10.952
1200	15.500	48.654	37.636	13.222	- 92.229	- 53.392	9.724
1300	15.500	49.895	38.532	14.772	- 91.630	- 50.179	8.436
1400	15.500	51.044	39.385	16.322	- 91.033	- 47.014	7.339
1500	15.500	52.113	40.198	17.872	- 90.437	- 43.891	6.395
1600	15.500	53.113	40.975	19.422	- 89.841	- 40.806	5.574
1700	15.500	54.053	41.717	20.972	- 89.245	- 37.759	4.854
1800	15.500	54.939	42.427	22.522	- 88.650	- 34.748	4.219
1900	15.500	55.777	43.107	24.072	- 88.057	- 31.769	3.654
2000	15.500	56.572	43.761	25.622	- 87.465	- 28.823	3.150
2100	15.500	57.328	44.389	27.172	- 86.872	- 25.906	2.696
2200	15.500	58.049	44.994	28.722	- 86.282	- 23.017	2.286
2300	15.500	58.738	45.577	30.272	- 85.692	- 20.155	1.915
2400	15.500	59.398	46.139	31.822	- 85.103	- 17.316	1.577
2500	15.500	60.031	46.682	33.372	- 84.516	- 14.506	1.268
2600	15.500	60.639	47.207	34.922	- 83.931	- 11.716	.985
2700	15.500	61.224	47.715	36.472	- 83.348	- 8.951	.724
2800	15.500	61.787	48.208	38.022	- 82.767	- 6.206	.484
2900	15.500	62.331	48.686	39.572	- 82.188	- 3.480	.262
3000	15.500	62.857	49.149	41.122	- 81.613	- .777	.057

Sept. 30, 1963

SODIUM IODIDE (NaI) (LIQUID) MOL. WT. = 149.901

$S^\circ_{298.15}$ = 28.862 cal. deg.$^{-1}$ mole^{-1}

ΔH_f° 298.15 = -63.695 kcal. mole^{-1}

T_m = 933°K.

ΔH_m = 5.64 kcal. mole^{-1}

T_b = 1577°K. (equilibrium mixture)

Heat of Formation.

ΔH_f° 298.15 was calculated from the heat of formation of the crystal plus the heat of melting and the difference between $H_{933}-H_{293}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p was estimated assuming each atom contributed 7.75 cal. deg.$^{-1}$ mole^{-1}. $S^\circ_{298.15}$ was calculated in a manner similar to ΔH_f° 298.15.

Melting Data.

See table for crystal.

Vaporization Data.

The boiling point is that given by K. K. Kelley, U. S. Bureau of Mines Bulletin 383, 1935 from examination of the high temperature vapor pressure.

Lead Monoiodide (PbI)

(Ideal Gas) Mol. Wt. = 334.12 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.470	26.451	26.451	INFINITE
100	8.262	57.411	74.642	-1.723	26.410	22.279	-48.688
200	8.752	63.334	67.663	-.866	26.076	18.273	-19.967
298	8.870	66.855	66.855	.000	25.700	14.522	-10.644
300	8.871	66.910	66.855	.016	25.692	14.453	-10.528
400	8.920	69.470	67.204	.906	23.344	10.836	-5.920
500	8.948	71.463	67.864	1.800	17.803	8.240	-3.602
600	8.966	73.096	68.604	2.696	17.561	6.350	-2.313
700	8.981	74.480	69.347	3.593	16.138	4.693	-1.465
800	8.993	75.680	70.065	4.492	15.866	3.077	-.840
900	9.005	76.740	70.749	5.392	15.600	1.494	-.363
1000	9.017	77.689	71.396	6.293	15.342	-.059	.013
1100	9.030	78.549	72.008	7.195	15.092	-1.588	.315
1200	9.045	79.335	72.586	8.099	14.850	-3.093	.563
1300	9.064	80.060	73.134	9.004	14.615	-4.578	.770
1400	9.086	80.733	73.653	9.912	14.382	-6.047	.944
1500	9.113	81.360	74.146	10.822	14.151	-7.497	1.092
1600	9.145	81.949	74.615	11.734	13.920	-8.932	1.220
1700	9.180	82.505	75.063	12.651	13.689	-10.353	1.331
1800	9.219	83.031	75.491	13.571	13.457	-11.762	1.428
1900	9.262	83.530	75.902	14.495	13.223	-13.157	1.513
2000	9.308	84.007	76.295	15.423	12.989	-14.539	1.589
2100	9.356	84.462	76.673	16.356	-29.697	-14.357	1.494
2200	9.405	84.898	77.037	17.294	-29.840	-13.624	1.353
2300	9.455	85.317	77.388	18.237	-30.000	-12.883	1.224
2400	9.505	85.721	77.727	19.185	-30.177	-12.134	1.105
2500	9.555	86.110	78.055	20.138	-30.372	-11.381	.995
2600	9.604	86.485	78.372	21.096	-30.584	-10.616	.892
2700	9.652	86.849	78.679	22.059	-30.813	-9.844	.797
2800	9.699	87.201	78.977	23.027	-31.058	-9.062	.707
2900	9.744	87.542	79.266	23.999	-31.318	-8.272	.623
3000	9.787	87.873	79.548	24.975	-31.593	-7.473	.544
3100	9.827	88.194	79.822	25.956	-31.880	-6.664	.470
3200	9.866	88.507	80.088	26.941	-32.179	-5.846	.399
3300	9.902	88.811	80.348	27.929	-32.488	-5.017	.332
3400	9.936	89.107	80.601	28.921	-32.805	-4.180	.269
3500	9.968	89.396	80.848	29.916	-33.130	-3.334	.208
3600	9.997	89.677	81.090	30.914	-33.461	-2.477	.150
3700	10.024	89.951	81.326	31.915	-33.796	-1.613	.095
3800	10.049	90.219	81.556	32.919	-34.133	-.737	.042
3900	10.072	90.480	81.782	33.925	-34.474	.147	-.008
4000	10.093	90.736	82.002	34.933	-34.816	1.034	-.056
4100	10.112	90.985	82.218	35.944	-35.157	1.937	-.103
4200	10.129	91.229	82.430	36.956	-35.498	2.848	-.148
4300	10.144	91.467	82.637	37.969	-35.838	3.761	-.191
4400	10.158	91.701	82.841	38.984	-36.176	4.688	-.233
4500	10.170	91.929	83.040	40.001	-36.510	5.620	-.273
4600	10.182	92.153	83.236	41.018	-36.842	6.562	-.312
4700	10.191	92.372	83.428	42.037	-37.169	7.504	-.349
4800	10.200	92.587	83.616	43.057	-37.494	8.463	-.385
4900	10.207	92.797	83.802	44.077	-37.814	9.422	-.420
5000	10.214	93.003	83.984	45.098	-38.130	10.388	-.454
5100	10.219	93.206	84.163	46.120	-38.442	11.361	-.487
5200	10.224	93.404	84.338	47.142	-38.750	12.342	-.519
5300	10.228	93.599	84.511	48.164	-39.054	13.330	-.550
5400	10.231	93.790	84.681	49.187	-39.354	14.322	-.580
5500	10.234	93.978	84.849	50.211	-39.650	15.315	-.609
5600	10.236	94.162	85.013	51.234	-39.942	16.317	-.637
5700	10.238	94.343	85.175	52.258	-40.231	17.322	-.664
5800	10.239	94.522	85.335	53.282	-40.517	18.339	-.691
5900	10.239	94.697	85.492	54.306	-40.800	19.353	-.717
6000	10.240	94.869	85.647	55.330	-41.080	20.374	-.742

June 30, 1962

Lead Monoiodide (PbI) (Ideal Gas)

Mol. Wt. = 334.12

ΔH_f° 298.15 = 25.7 ± 9.2 kcal. mole^{-1}

$S^\circ_{298.15}$ = 66.855 cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi_{1/2}$

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_i
0	2
[8000]	2

ω_e = 160.5 cm.$^{-1}$ $\omega_e x_e$ = 0.25 cm.$^{-1}$

B_e = [0.02940] cm.$^{-1}$ α_e = [0.00000] cm.$^{-1}$

σ = 1

Heat of Formation. ΔH_f° 298.15 was calculated from the dissociation energy of PbI(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950. B_e and α_e were estimated by comparison with the corresponding values for the other diatomic halide molecules. Electronic levels and multiplicities were estimated from those for PbF(g).

Titanium Monoiodide (TiI)

(Ideal Gas) GFW = 174.8044

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.423	65.806	65.806	INFINITE
100	7.786	54.962	72.003	-1.704	66.026	61.456	-134.312
200	8.647	60.668	65.048	-.876	65.808	56.957	-62.240
298	9.192	64.225	64.224	.000	65.500	52.673	-38.611
300	9.201	64.281	64.225	.017	65.494	52.594	-38.315
400	9.671	66.996	64.591	.962	63.235	48.412	-26.451
500	10.015	69.193	65.299	1.947	57.812	45.224	-19.768
600	10.239	71.040	66.106	2.961	57.712	42.715	-15.559
700	10.374	72.630	66.927	3.992	57.607	40.224	-12.559
800	10.451	74.021	67.729	5.033	57.488	37.749	-10.313
900	10.493	75.254	68.498	6.081	57.348	35.290	-8.570
1000	10.517	76.361	69.230	7.131	57.182	32.847	-7.179
1100	10.532	77.364	69.924	8.184	56.992	30.424	-6.045
1200	10.545	78.281	70.583	9.238	55.839	28.056	-5.110
1300	10.558	79.126	71.208	10.293	55.726	25.745	-4.328
1400	10.573	79.909	71.802	11.349	55.597	23.443	-3.660
1500	10.591	80.639	72.367	12.408	55.454	21.150	-3.082
1600	10.611	81.323	72.905	13.468	55.294	18.871	-2.578
1700	10.632	81.967	73.420	14.530	55.115	16.598	-2.134
1800	10.656	82.575	73.912	15.594	54.916	14.338	-1.741
1900	10.680	83.152	74.383	16.661	54.696	12.089	-1.391
2000	10.705	83.700	74.835	17.730	50.008	10.006	-1.093
2100	10.730	84.223	75.270	18.802	49.769	8.013	-.834
2200	10.755	84.723	75.688	19.876	49.532	6.029	-.599
2300	10.780	85.202	76.092	20.953	49.297	4.058	-.386
2400	10.804	85.661	76.481	22.032	49.063	2.097	-.191
2500	10.827	86.102	76.857	23.114	48.831	.144	-.013
2600	10.849	86.527	77.221	24.198	48.601	-1.800	.151
2700	10.870	86.937	77.573	25.283	48.372	-3.733	.302
2800	10.890	87.333	77.915	26.371	48.144	-5.659	.442
2900	10.908	87.715	78.246	27.461	47.918	-7.574	.571
3000	10.926	88.086	78.568	28.553	47.693	-9.485	.691
3100	10.943	88.444	78.881	29.647	47.469	-11.386	.803
3200	10.959	88.792	79.185	30.742	47.246	-13.284	.907
3300	10.974	89.129	79.481	31.838	47.024	-15.170	1.005
3400	10.989	89.457	79.770	32.936	46.802	-17.051	1.096
3500	11.002	89.776	80.051	34.036	46.582	-18.926	1.182
3600	11.015	90.086	80.326	35.137	-55.264	-20.533	1.246
3700	11.028	90.388	80.593	36.239	-55.455	-19.567	1.156
3800	11.040	90.682	80.855	37.342	-55.659	-18.596	1.070
3900	11.051	90.969	81.111	38.447	-55.875	-17.614	.987
4000	11.063	91.249	81.361	39.553	-56.104	-16.632	.909
4100	11.074	91.522	81.605	40.660	-56.345	-15.640	.834
4200	11.084	91.789	81.845	41.767	-56.599	-14.646	.762
4300	11.095	92.050	82.079	42.876	-56.863	-13.647	.694
4400	11.106	92.305	82.308	43.986	-57.139	-12.638	.628
4500	11.116	92.555	82.533	45.098	-57.424	-11.621	.564
4600	11.126	92.800	82.754	46.210	-57.720	-10.597	.503
4700	11.137	93.039	82.970	47.323	-58.025	-9.572	.445
4800	11.147	93.273	83.182	48.437	-58.339	-8.537	.389
4900	11.158	93.503	83.391	49.552	-58.663	-7.499	.334
5000	11.169	93.729	83.595	50.669	-58.994	-6.449	.282
5100	11.180	93.950	83.796	51.786	-59.332	-5.395	.231
5200	11.191	94.167	83.993	52.905	-59.678	-4.334	.182
5300	11.202	94.381	84.187	54.024	-60.031	-3.269	.135
5400	11.213	94.590	84.378	55.145	-60.390	-2.190	.089
5500	11.225	94.796	84.566	56.267	-60.754	-1.109	.044
5600	11.237	94.998	84.750	57.390	-61.124	-.027	.001
5700	11.249	95.197	84.932	58.514	-61.498	1.072	-.041
5800	11.261	95.393	85.110	59.640	-61.877	2.172	-.082
5900	11.274	95.586	85.286	60.766	-62.259	3.280	-.121
6000	11.287	95.775	85.460	61.894	-62.645	4.391	-.160

June 30, 1964; Sept. 30, 1964; June 30, 1968; Dec. 31, 1968

TITANIUM MONOIODIDE (TiI) (IDEAL GAS) GFW = 174.8044

Ground State Configuration $[^4\Sigma]$

$S^\circ_{298.15}$ = 64.22 ± 2.0 gibbs/mol

ΔHf°_0 = [65.8 ± 10.0] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [65.5 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

ω_e = [240] cm^{-1} $\omega_e x_e$ = [1.67] cm^{-1} σ = 1

B_e = [0.062] cm^{-1} α_e = [0.00043] cm^{-1} r_e = [2.8] Å

Heat of Formation

The heat of formation, ΔHf°_{298}, of TiI (g) is calculated from the dissociation energy, D°_0, which is estimated as 73 kcal/mol. This estimate is obtained from the relation $D(TiI_4) < D^\circ_0(TiI) < D(TiI_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e, and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+ (3). α_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Monoiodide (ZrI)

(Ideal Gas) Mol. Wt. = 218.13

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	- 2.411	141.783	141.783	INFINITE
100	7.864	56.651	73.535	- 1.688	141.929	137.330	- 300.120
200	8.603	62.385	66.670	- .857	141.649	132.831	- 145.144
298	8.823	65.868	65.868	.000	141.300	128.575	- 94.244
300	8.825	65.923	65.868	.016	141.293	128.497	- 93.605
400	8.924	68.477	66.216	.904	138.960	124.358	- 67.943
500	8.983	70.475	66.875	1.800	133.423	121.239	- 52.991
600	9.025	72.116	67.616	2.700	133.171	118.825	- 43.280
700	9.059	73.510	68.361	3.605	132.901	116.455	- 36.357
800	9.089	74.722	69.082	4.512	132.620	114.124	- 31.176
900	9.116	75.794	69.769	5.422	132.333	111.830	- 27.155
1000	9.142	76.756	70.421	6.335	132.040	109.568	- 23.945
1100	9.166	77.628	71.037	7.251	131.732	107.335	- 21.325
1200	9.190	78.427	71.620	8.168	130.457	105.179	- 19.155
1300	9.214	79.163	72.172	9.089	130.149	103.085	- 17.329
1400	9.237	79.847	72.696	10.011	129.833	101.014	- 15.768
1500	9.259	80.485	73.194	10.936	129.513	98.967	- 14.419
1600	9.282	81.083	73.669	11.863	129.188	96.944	- 13.241
1700	9.304	81.647	74.122	12.792	128.857	94.936	- 12.204
1800	9.327	82.179	74.555	13.724	128.521	92.952	- 11.285
1900	9.349	82.684	74.969	14.658	128.179	90.985	- 10.465
2000	9.371	83.164	75.367	15.594	127.831	89.034	- 9.729
2100	9.393	83.622	75.750	16.532	127.479	87.103	- 9.065
2200	9.415	84.059	76.117	17.472	122.218	85.355	- 8.479
2300	9.437	84.478	76.472	18.415	121.848	83.688	- 7.952
2400	9.459	84.880	76.814	19.360	121.481	82.038	- 7.470
2500	9.481	85.267	77.144	20.307	121.114	80.400	- 7.028
2600	9.503	85.639	77.464	21.256	120.749	78.779	- 6.622
2700	9.524	85.996	77.773	22.207	120.386	77.172	- 6.246
2800	9.546	86.345	78.073	23.161	120.024	75.578	- 5.899
2900	9.568	86.680	78.364	24.116	119.663	74.000	- 5.577
3000	9.590	87.005	78.647	25.074	119.304	72.429	- 5.276
3100	9.612	87.320	78.922	26.034	118.947	70.870	- 4.996
3200	9.633	87.626	79.189	26.997	118.591	69.324	- 4.734
3300	9.655	87.922	79.449	27.961	118.236	67.794	- 4.490
3400	9.677	88.211	79.703	28.928	117.884	66.270	- 4.260
3500	9.698	88.492	79.950	29.896	117.532	64.756	- 4.043
3600	9.720	88.765	80.191	30.867	117.182	63.252	- 3.840
3700	9.742	89.032	80.426	31.840	116.834	61.758	- 3.648
3800	9.764	89.292	80.656	32.816	116.487	60.276	- 3.466
3900	9.785	89.546	80.881	33.793	116.142	58.802	- 3.295
4000	9.807	89.794	81.101	34.773	115.798	57.334	- 3.132
4100	9.829	90.036	81.316	35.755	115.456	55.880	- 2.979
4200	9.850	90.273	81.526	36.738	115.114	54.433	- 2.832
4300	9.872	90.505	81.732	37.725	114.775	52.991	- 2.693
4400	9.894	90.733	81.934	38.713	114.437	51.552	- 2.560
4500	9.915	90.955	82.132	39.703	114.100	50.131	- 2.435
4600	9.937	91.173	82.326	40.696	113.765	48.715	- 2.314
4700	9.959	91.387	82.517	41.691	113.432	47.303	- 2.199
4800	9.980	91.597	82.704	42.688	- 23.333	47.424	- 2.159
4900	10.002	91.803	82.887	43.687	- 23.718	48.900	- 2.181
5000	10.024	92.005	83.068	44.688	- 24.107	50.388	- 2.202
5100	10.045	92.204	83.245	45.692	- 24.498	51.879	- 2.223
5200	10.067	92.399	83.419	46.697	- 24.894	53.384	- 2.244
5300	10.089	92.591	83.590	47.705	- 25.292	54.889	- 2.263
5400	10.110	92.780	83.759	48.715	- 25.692	56.410	- 2.283
5500	10.132	92.966	83.925	49.727	- 26.093	57.927	- 2.302
5600	10.154	93.149	84.088	50.741	- 26.498	59.460	- 2.320
5700	10.175	93.329	84.248	51.758	- 26.902	60.995	- 2.339
5800	10.197	93.506	84.406	52.776	- 27.309	62.545	- 2.357
5900	10.219	93.680	84.562	53.797	- 27.715	64.101	- 2.374
6000	10.240	93.852	84.715	54.820	- 28.122	65.658	- 2.391

Sept. 30, 1964

ZIRCONIUM MONOIODIDE (ZrI) (IDEAL GAS) MOL. WT. = 218.13

Ground State Configuration $^4\Sigma$

$S^\circ_{298.15}$ = [65.87] cal. deg.⁻¹ mole⁻¹

$\Delta H_f^\circ{}_0$ = [141.8 ± 10.0] kcal. mole⁻¹

$\Delta H_f^\circ{}_{298.15}$ = [141.3 ± 10.0] kcal. mole⁻¹

Electronic Levels and Multiplicities

ϵ_i cm.⁻¹	g_i
0	4

ω_e = [223] cm.⁻¹

$\omega_e x_e$ = [1.2] cm.⁻¹

σ = 1

B_e = [0.03789] cm.⁻¹

α_e = [0.00020] cm.⁻¹

r_e = [2.9] Å

Heat of Formation.

The dissociation energy was estimated from a correlation of the JANAF values for TiCl(g), TiI(g), and ZrCl(g). The resulting value, 29.7 kcal. mole⁻¹, was employed with auxiliary JANAF heats of formation for Zr(g) and I(g) in calculating $\Delta H_f^\circ{}_{298.15}$.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of TiI(g), TiCl(g), ZrCl(g), and the alkali halides. The ground state configuration was assumed to be analogous to the ground term of TiCl(g) as given by E. A. Shenyavskaya, et al., Optics and Spectroscopy, 12, 359 (1962). The interatomic distance was estimated from those of TiBr(g), TiI_4(g) and ZrI_4(g).

Iodine (I_2)
(Reference State) Mol. Wt. = 253.82

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.154	.000	.000	.000
100	10.911	14.581	38.830	-2.425	.000	.000	.000
200	12.325	22.696	28.930	-1.247	.000	.000	.000
298	13.011	27.758	27.758	.000	.000	.000	.000
300	13.028	27.839	27.758	.024	.000	.000	.000
400	19.281	41.602	28.612	5.196	.000	.000	.000
500	8.948	66.877	33.438	16.719	.000	.000	.000
600	8.980	68.511	39.152	17.616	.000	.000	.000
700	9.005	69.897	43.447	18.515	.000	.000	.000
800	9.025	71.101	46.830	19.416	.000	.000	.000
900	9.044	72.165	49.587	20.320	.000	.000	.000
1000	9.061	73.119	51.894	21.225	.000	.000	.000
1100	9.077	73.983	53.863	22.132	.000	.000	.000
1200	9.092	74.774	55.573	23.041	.000	.000	.000
1300	9.107	75.502	57.079	23.950	.000	.000	.000
1400	9.122	76.178	58.419	24.862	.000	.000	.000
1500	9.137	76.807	59.624	25.775	.000	.000	.000
1600	9.151	77.398	60.717	26.689	.000	.000	.000
1700	9.165	77.953	61.714	27.605	.000	.000	.000
1800	9.179	78.477	62.631	28.522	.000	.000	.000
1900	9.193	78.974	63.478	29.441	.000	.000	.000
2000	9.207	79.445	64.265	30.361	.000	.000	.000
2100	9.220	79.895	64.999	31.282	.000	.000	.000
2200	9.234	80.324	65.686	32.205	.000	.000	.000
2300	9.248	80.735	66.331	33.129	.000	.000	.000
2400	9.261	81.129	66.940	34.054	.000	.000	.000
2500	9.275	81.507	67.515	34.981	.000	.000	.000
2600	9.289	81.871	68.060	35.909	.000	.000	.000
2700	9.302	82.222	68.578	36.839	.000	.000	.000
2800	9.316	82.561	69.071	37.770	.000	.000	.000
2900	9.329	82.888	69.542	38.702	.000	.000	.000
3000	9.343	83.204	69.992	39.636	.000	.000	.000
3100	9.356	83.511	70.424	40.571	.000	.000	.000
3200	9.370	83.808	70.837	41.507	.000	.000	.000
3300	9.383	84.097	71.235	42.445	.000	.000	.000
3400	9.397	84.377	71.617	43.384	.000	.000	.000
3500	9.410	84.650	71.986	44.324	.000	.000	.000
3600	9.424	84.915	72.341	45.266	.000	.000	.000
3700	9.437	85.173	72.684	46.209	.000	.000	.000
3800	9.451	85.425	73.016	47.153	.000	.000	.000
3900	9.464	85.671	73.338	48.099	.000	.000	.000
4000	9.477	85.910	73.649	49.046	.000	.000	.000
4100	9.491	86.145	73.951	49.994	.000	.000	.000
4200	9.504	86.374	74.244	50.944	.000	.000	.000
4300	9.518	86.597	74.529	51.895	.000	.000	.000
4400	9.531	86.816	74.805	52.848	.000	.000	.000
4500	9.545	87.031	75.075	53.802	.000	.000	.000
4600	9.558	87.241	75.337	54.757	.000	.000	.000
4700	9.571	87.446	75.592	55.713	.000	.000	.000
4800	9.585	87.648	75.841	56.671	.000	.000	.000
4900	9.598	87.846	76.084	57.630	.000	.000	.000
5000	9.612	88.040	76.322	58.591	.000	.000	.000
5100	9.625	88.230	76.553	59.552	.000	.000	.000
5200	9.639	88.417	76.780	60.516	.000	.000	.000
5300	9.652	88.601	77.001	61.480	.000	.000	.000
5400	9.665	88.782	77.217	62.446	.000	.000	.000
5500	9.679	88.959	77.429	63.413	.000	.000	.000
5600	9.692	89.133	77.637	64.382	.000	.000	.000
5700	9.706	89.305	77.840	65.352	.000	.000	.000
5800	9.719	89.474	78.039	66.323	.000	.000	.000
5900	9.732	89.640	78.234	67.295	.000	.000	.000
6000	9.746	89.804	78.426	68.269	.000	.000	.000

September 30, 1961

IODINE (I_2) (REFERENCE STATE) MOL. WT. = 253.82

0°K to 386.75°K	Crystal
386.75°K to 458.39°K	Liquid
458.39°K to 6000°K	Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

The recent measurements of D. A. Shirley and W. F. Giauque [J. Am. Chem. Soc. 81, 4778 (1959)] over the temperature range 13° to 327°K are adopted, no weight being given to the earlier work of E. Lange [Z. physik. Chem. 110, 343 (1924)], which deviate by 1% or more. L. G. Carpenter and T. F. Harle [Phil. Mag. 23, 193 (1937)] measured the heat capacity of crystalline and liquid iodine by an adiabatic method. Their data are in poor agreement with Shirley and Giauque in the range 275° to 330°K and are given no weight. K. J. Frederick and J. H. Hildebrand [J. Am. Chem. Soc. 60, 1436 (1938)] measured the enthalpy of crystalline and liquid iodine relative to 298°K by the method of mixtures. For calibration they used a slug of copper. The enthalpy of copper which they used now appears to be too high [K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960)]. The results of Frederick and Hildebrand were corrected by a factor which varied linearly from zero at 300°K to 0.995 at 400°K and 0.990 at 500°K. These corrected enthalpies and the heat capacities of Shirley and Giauque above 298°K were used to derive the equations for crystalline iodine:

$$H_T - H_{298} = -12.1048\ T + 0.029506\ T^2 - 6.686 \times 10^5\ T^{-1} + 3228.65$$

$$C_p = -12.1048 \quad + 0.059012\ T + 6.686 \times 10^5\ T^{-2}$$

Heat Capacity of Liquid, Melting Point, and Heat of Melting.

For the liquid, the corrected results of Frederick and Hildebrand give:

$$H_T - H_{298} = 19.281\ T - 2516.5$$

$$C_p = 19.281$$

The melting point given by Frederick and Hildebrand is 113.6°C. The difference in the heat content equations at the melting point gives the heat of melting as 3708.7 cal. mole^{-1}.

Heat of Sublimation, Ideal Gas Functions.

See tables for ideal gases for details.

Iodine (I_2)

(Liquid) Mol. Wt. = 253.82

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	19.281	35.936	35.936	.000	3.232	.794	-.582
300	19.281	36.055	35.936	.036	3.244	.779	-.567
400	19.281	41.602	36.693	1.964	.000	.000	.000
500	19.281	45.905	38.121	3.892	-9.595	.891	-.389
600	19.281	49.420	39.720	5.820	-8.564	2.891	-1.053
700	19.281	52.392	41.323	7.748	-7.535	4.719	-1.473
800	19.281	54.967	42.871	9.676	-6.508	6.400	-1.748
900	19.281	57.238	44.344	11.604	-5.484	7.951	-1.931
1000	19.281	59.269	45.737	13.532	-4.461	9.389	-2.052

September 30, 1961

IODINE (I_2) (LIQUID) MOL. WT. = 253.82

T_m = 386.75°K

T_b = 458.39°K

$\Delta H_f^\circ{}_{298}$ = +3.232 kcal. mole^{-1}

S°_{298} = 35.936 cal. mole^{-1} deg.$^{-1}$

ΔH_m = 3708.7 cal. mole^{-1}

ΔH_v = 10025.5 cal. mole^{-1}

Heat of Formation.

Obtained as the heat of fusion calculated to 298.15°K by adding $H_{386.75}-H_{298.15}$ for solid and subtracting $H_{386.75}-H_{298.15}$ for liquid.

Heat Capacity.

The liquid heat capacity of 19.281 cal. mole^{-1} deg.$^{-1}$ derived from the data of Frederick and Hildebrand (see Reference State) was extrapolated back to 298.15°K and up to 1000°K.

Entropy.

The value at 400°K calculated for the reference state was back calculated to 298.15°K by means of the constant heat capacity of 19.281 cal. mole^{-1} deg.$^{-1}$

Vaporization.

See ideal gas tables for details.

Iodine, Diatomic (I_2)

(Ideal Gas) Mol. Wt. = 253.82

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.418	15.660	15.660	INFINITE
100	7.920	53.037	69.958	-1.692	15.657	11.811	-25.812
200	8.619	58.797	63.063	-.857	15.314	8.094	-8.844
298	8.814	62.281	62.281	.000	14.924	4.631	-3.394
300	8.817	62.336	62.281	.016	14.916	4.567	-3.327
400	8.901	64.885	62.628	.903	10.631	1.317	-.720
500	8.948	66.877	63.286	1.795	.000	.000	-.000
600	8.980	68.511	64.025	2.692	.000	.000	.000
700	9.005	69.897	64.767	3.591	.000	.000	.000
800	9.025	71.101	65.485	4.492	.000	.000	.000
900	9.044	72.165	66.170	5.396	.000	.000	.000
1000	9.061	73.119	66.818	6.301	.000	.000	.000
1100	9.077	73.983	67.430	7.208	.000	.000	.000
1200	9.092	74.774	68.010	8.117	.000	.000	.000
1300	9.107	75.502	68.559	9.027	.000	.000	.000
1400	9.122	76.178	69.079	9.938	.000	.000	.000
1500	9.137	76.807	69.573	10.851	.000	.000	.000
1600	9.151	77.398	70.044	11.765	.000	.000	.000
1700	9.165	77.953	70.493	12.681	.000	.000	.000
1800	9.179	78.477	70.922	13.598	.000	.000	.000
1900	9.193	78.974	71.333	14.517	.000	.000	.000
2000	9.207	79.446	71.727	15.437	.000	.000	.000
2100	9.220	79.895	72.105	16.358	.000	.000	.000
2200	9.234	80.324	72.469	17.281	.000	.000	.000
2300	9.248	80.735	72.820	18.205	.000	.000	.000
2400	9.261	81.129	73.158	19.131	.000	.000	.000
2500	9.275	81.507	73.484	20.057	.000	.000	.000
2600	9.289	81.871	73.800	20.986	.000	.000	.000
2700	9.302	82.222	74.105	21.915	.000	.000	.000
2800	9.316	82.561	74.401	22.846	.000	.000	.000
2900	9.329	82.888	74.688	23.778	.000	.000	.000
3000	9.343	83.204	74.967	24.712	.000	.000	.000
3100	9.356	83.511	75.238	25.647	.000	.000	.000
3200	9.370	83.806	75.501	26.583	.000	.000	.000
3300	9.383	84.097	75.757	27.521	.000	.000	.000
3400	9.397	84.377	76.006	28.460	.000	.000	.000
3500	9.410	84.650	76.250	29.400	.000	.000	.000
3600	9.424	84.915	76.487	30.342	.000	.000	.000
3700	9.437	85.173	76.718	31.285	.000	.000	.000
3800	9.451	85.425	76.944	32.229	.000	.000	.000
3900	9.464	85.671	77.164	33.175	.000	.000	.000
4000	9.477	85.910	77.380	34.122	.000	.000	.000
4100	9.491	86.145	77.591	35.070	.000	.000	.000
4200	9.504	86.374	77.797	36.020	.000	.000	.000
4300	9.518	86.597	77.999	36.971	.000	.000	.000
4400	9.531	86.816	78.197	37.924	.000	.000	.000
4500	9.545	87.031	78.391	38.877	.000	.000	.000
4600	9.558	87.241	78.581	39.833	.000	.000	.000
4700	9.571	87.446	78.768	40.789	.000	.000	.000
4800	9.585	87.648	78.951	41.747	.000	.000	.000
4900	9.598	87.846	79.130	42.706	.000	.000	.000
5000	9.612	88.040	79.306	43.667	.000	.000	.000
5100	9.625	88.230	79.480	44.628	.000	.000	.000
5200	9.639	88.417	79.650	45.592	.000	.000	.000
5300	9.652	88.601	79.817	46.556	.000	.000	.000
5400	9.665	88.782	79.981	47.522	.000	.000	.000
5500	9.679	88.959	80.143	48.489	.000	.000	.000
5600	9.692	89.134	80.302	49.458	.000	.000	.000
5700	9.706	89.305	80.456	50.428	.000	.000	.000
5800	9.719	89.474	80.612	51.399	.000	.000	.000
5900	9.732	89.640	80.764	52.371	.000	.000	.000
6000	9.746	89.804	80.913	53.345	.000	.000	.000

September 30, 1961

IODINE, DIATOMIC (I_2) (IDEAL GAS) MOL. WT. = 253.82

$\Delta H_{f0}^\circ = 15.66 \pm .01$ kcal. mole^{-1}

$\Delta H_{f\ 298}^\circ = 14.924$ kcal. mole^{-1}

Ground State = $^1\Sigma$

$S_{298}^\circ = 62.281$ cal. mole^{-1} deg.$^{-1}$

$\omega_e = 214.52$ cm.$^{-1}$

$\omega_e x_e = 0.6133$ cm.$^{-1}$

$D_e = 0.455 \times 10^{-8}$ cm.$^{-1}$

$B_e = 0.037364$ cm.$^{-1}$

$\alpha_e = 0.0001206$ cm.$^{-1}$

$\sigma = 2$

Thermodynamic Functions.

The molecular constants are from the work of D. H. Rank and W. M. Baldwin [J. Chem. Phys. 19, 1210 (1951)] with a revised value of $\omega_e = 214.52$ as given by R. D. Verma [J. Chem. Phys. 32, 738 (1960)]. The value of $\omega_e x_e$ has been adjusted to allow for the dropping of higher order corrections not used in the computer program. The calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 147 (1955)], who used very slightly different constants. L. Mathieson and A. L. G. Rees [J. Chem. Phys. 25, 753 (1956)] give further refinements to the spectroscopic data which are negligible for our purpose. Their ω_e is also slightly low since it is based on Rank and Baldwin.

Heat of Formation.

The heat of sublimation of iodine was calculated from published vapor pressure data as follows, using thermodynamic functions of condensed and gaseous phases described above.

	ΔH_0°, kcal. mole^{-1}
Baxter, Hickey, and Holmes[1] (273° to 328°K)	15.657 ± .004
Baxter and Grose[2] (323° to 368°K)	15.657 ± .002
Ramsay and Young[3] (solid) (331° to 386°K)	15.671 ± .018
Ramsay and Young[3] (liquid) (386° to 454°K)	15.676 ± .007
Haber and Kerschbaum[4] (225° to 263°K)	15.765 ± .012
Gillespie and Fraser[5] (303° to 333°K)	15.655 ± .005
Sklyarenko, Markin, and Belyaeva[6] (283° to 303°K)	15.813
Naumann[7] (as given by Haber and Kerschbaum) (232° to 292°K)	15.899 ± .034
Wiedemann[8] (393° to 453°K)	15.635 ± .008
Braune and Strassman[9] (305° to 358°K)	15.658 ± .012
Arctowski[10] (286° to 345°K)	15.623 ± .080
Wright[11] (352° to 372°K)	15.659 ± .003
Dewar[12] (273° to 303°K)	15.821 ± .103
Richter[13] (358° to 383°K)	15.639 ± .043

The uncertainties given are the average deviation from the mean. The data of Braune and Strassman are as recalculated by Gerry and Gillespie[14]. The data of Haber and Kerschbaum appear systematically too high. The results of Sklyarenko, et al., Naumann, Arctowski, Dewar, and Richter are scattered and are not given any weight. A weighted average of the remaining data yield $\Delta H_0^\circ = 15.66 \pm 0.01$ kcal. mole^{-1}, which calculates to ΔH_{298}° = 14.924 cal. mole^{-1}.

References to Vapor Pressure Data

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(2) G. P. Baxter and M. R. Grose, J. Am. Chem. Soc. 37, 1061 (1915).
(3) W. Ramsay and S. Young, J. Chem. Soc. 49, 453 (1886).
(4) F. Haber and F. Kerschbaum, Z. Elektrochem. 20, 296 (1914).
(5) L. J. Gillespie and C. H. D. Fraser, J. Am. Chem. Soc. 58, 2260 (1936).
(6) S. I. Sklyarenko, B. I. Markin, and L. B. Belyaeva, Zhur. Fiz. Khim. 32, 1916 (1958).
(7) R. Naumann, Dissertation, Berlin (1907).
(8) E. Wiedemann, Ber. deut. physikal. Ges. 3, 159 (1905).
(9) H. Braune and F. Strassman, Z. physik. Chem. 143A, 225 (1929).
(10) H. Arctowski, Z. anorg. Chem. 12, 427 (1896).
(11) R. Wright, J. Chem. Soc. 107, 1527 (1917).
(12) J. Dewar, Proc. Chem. Soc. 14, 241 (1899).
(13) V. Richter, Ber. 19, 1057 (1886).
(14) H. T. Gerry and L. J. Gillespie, Phys. Rev. 40, 269 (1932).

Potassium Iodide, Dimeric (K_2I_2)

(Ideal Gas) GFW = 332.0128

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-5.181	-99.541	-99.541	INFINITE
100	18.157	73.647	111.819	-3.817	-99.734	-103.939	227.158
200	19.408	86.752	96.351	-1.920	-100.255	-107.952	117.964
298	19.660	94.558	94.558	.000	-100.900	-111.599	81.805
300	19.662	94.680	94.559	.036	-100.914	-111.665	81.348
400	19.753	100.351	95.331	2.008	-106.742	-114.776	62.711
500	19.796	104.764	96.793	3.985	-117.774	-115.727	50.584
600	19.819	108.375	98.431	5.966	-118.142	-115.282	41.991
700	19.833	111.431	100.076	7.949	-118.490	-114.777	35.835
800	19.842	114.080	101.664	9.933	-118.831	-114.224	31.205
900	19.848	116.418	103.176	11.917	-119.175	-113.628	27.593
1000	19.853	118.509	104.607	13.902	-119.537	-112.993	24.695
1100	19.856	120.401	105.958	15.888	-157.732	-110.272	21.909
1200	19.858	122.129	107.235	17.873	-157.650	-105.960	19.298
1300	19.860	123.719	108.442	19.859	-157.567	-101.658	17.090
1400	19.862	125.191	109.587	21.846	-157.486	-97.358	15.198
1500	19.863	126.561	110.673	23.832	-157.407	-93.066	13.560
1600	19.864	127.843	111.707	25.818	-157.329	-88.777	12.126
1700	19.865	129.047	112.692	27.805	-157.254	-84.498	10.863
1800	19.866	130.183	113.632	29.791	-157.181	-80.220	9.740
1900	19.866	131.257	114.532	31.779	-157.113	-75.947	8.736
2000	19.867	132.276	115.394	33.764	-157.047	-71.677	7.832
2100	19.867	133.245	116.221	35.751	-156.985	-67.407	7.015
2200	19.868	134.169	117.016	37.738	-156.931	-63.143	6.273
2300	19.868	135.053	117.781	39.725	-156.882	-58.884	5.595
2400	19.868	135.898	118.518	41.711	-156.841	-54.622	4.974
2500	19.869	136.709	119.230	43.698	-156.811	-50.366	4.403
2600	19.869	137.489	119.917	45.685	-156.788	-46.106	3.876
2700	19.869	138.238	120.582	47.672	-156.779	-41.851	3.388
2800	19.869	138.961	121.226	49.659	-156.785	-37.595	2.934
2900	19.869	139.658	121.849	51.646	-156.804	-33.334	2.512
3000	19.870	140.332	122.454	53.633	-156.839	-29.081	2.119
3100	19.870	140.983	123.041	55.620	-156.895	-24.517	1.750
3200	19.870	141.614	123.612	57.607	-156.970	-20.554	1.404
3300	19.870	142.226	124.167	59.594	-157.069	-16.294	1.079
3400	19.870	142.819	124.707	61.581	-157.195	-12.029	.773
3500	19.870	143.395	125.233	63.568	-157.348	-7.755	.484
3600	19.870	143.955	125.745	65.555	-157.535	-3.477	.211
3700	19.870	144.499	126.244	67.542	-157.757	.803	-.047
3800	19.870	145.029	126.732	69.529	-158.020	5.091	-.293
3900	19.870	145.545	127.208	71.516	-158.327	9.389	-.526
4000	19.870	146.048	127.672	73.503	-158.683	13.693	-.748
4100	19.871	146.539	128.127	75.490	-159.094	18.010	-.960
4200	19.871	147.018	128.571	77.477	-159.567	22.335	-1.162
4300	19.871	147.485	129.005	79.464	-160.103	26.672	-1.356
4400	19.871	147.942	129.430	81.451	-160.715	31.020	-1.541
4500	19.871	148.388	129.847	83.438	-161.404	35.395	-1.719
4600	19.871	148.825	130.255	85.425	-162.178	39.772	-1.890
4700	19.871	149.253	130.654	87.412	-163.043	44.166	-2.054
4800	19.871	149.671	131.046	89.399	-164.006	48.591	-2.212
4900	19.871	150.081	131.430	91.387	-165.073	53.030	-2.365
5000	19.871	150.482	131.807	93.374	-166.249	57.491	-2.513
5100	19.871	150.876	132.177	95.361	-167.539	61.981	-2.656
5200	19.871	151.261	132.541	97.348	-168.950	66.495	-2.795
5300	19.871	151.640	132.898	99.335	-170.481	71.035	-2.929
5400	19.871	152.011	133.248	101.322	-172.138	75.609	-3.060
5500	19.871	152.376	133.593	103.309	-173.922	80.206	-3.187
5600	19.871	152.734	133.931	105.296	-175.832	84.843	-3.311
5700	19.871	153.086	134.264	107.283	-177.867	89.515	-3.432
5800	19.871	153.431	134.592	109.270	-180.027	94.226	-3.551
5900	19.871	153.771	134.914	111.258	-182.305	98.977	-3.666
6000	19.871	154.105	135.231	113.245	-184.702	103.772	-3.780

Dec. 31, 1961; June 30, 1967

POTASSIUM IODIDE, DIMERIC (K_2I_2) (IDEAL GAS) GFW = 332.0128

Point Group [D_{2h}]

ΔHf°_0 = -99.5 ± 1 kcal/mol

$S^\circ_{298.15}$ = [94.6] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -100.9 ± 1 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[90] (1)	[80] (1)
[60] (1)	[105] (1)
[110] (1)	[120] (1)

Bond Distance: K-I = [3.29] Å

Bond Angles: K-I-K = [75°] I-K-I = [105°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.041 x 10^{-111}] g^3 cm^6

Heat of Formation

The chemical equilibrium for the reaction $K_2I_2(g) = 2KI(g)$ has been studied by S. Datz, ORNL-2933, Oak Ridge, Tenn., 1960, and S. Datz, W. T. Smith, Jr. and E. H. Taylor, J. Chem. Phys. 34, 558 (1961). They measured the temperature dependence of the molecular weight of KI(g) which was determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. Based on the reported P-V-T measurements, the enthalpy change of the reaction at 298°K is evaluated by the second and third law methods. The results are given in the table below.

R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956), determined the molecular composition of KI vapor by measurement of the velocity distribution of the molecules in the beam produced as the vapor effused through a small slit in a source. The analysis was based on an assumption that the velocity distribution within the oven is Maxwellian and that the vapor effuses through the ideal slit of kinetic theory. The velocity distributions of potassium and thallium atomic beams were found to be in excellent agreement with the theoretical distributions, so the determination of the molecular composition of KI beams was tried. Using the derived equilibrium constants, we calculate the enthalpy change of the dissociation reaction by the second and third law methods. The results are presented in the following table.

The value of $\Delta Hf^\circ_{298}(K_2I_2,g)$ is adopted as -100.9± 1 kcal/mol.

			ΔHr°_{298}, kcal/mol			
Investigator	Temperature, °K	No. of Points	Second Law	Third Law	Drift eu	ΔHf°_{298} kcal/mol
Datz	1226-1385	10	40.09±0.82	40.66	0.4±0.6	-100.66
	1292-1408	6	41.37±1.91	41.01	-0.2±1.4	-101.01
Miller-Kusch	816-921	10	54.62±2.46	36.28	-21.4±2.8	-96.28

Heat Capacity

The molecular structure and bond distance and angles were estimated by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958). The vibrational frequencies are estimated by comparison with those calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), and adjusted to give good agreement between second and third law evaluations of the equilibrium data. The three principal moments of inertia are: $I_A = 5.194 \times 10^{-38}$, $I_B = 2.866 \times 10^{-37}$ and $I_C = 3.386 \times 10^{-37}$ g cm^2.

Lithium Iodide, Dimeric (Li_2I_2)

(Ideal Gas)   GFW = 267.6868

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-4.127	-85.263	-85.263	INFINITE
100	12.245	61.979	93.907	-3.193	-85.296	-89.684	196.004
200	16.580	72.031	80.618	-1.717	-85.878	-93.849	102.553
298	18.175	78.997	78.997	.000	-86.500	-97.630	71.565
300	18.193	79.109	78.997	.034	-86.512	-97.699	71.174
400	18.877	84.449	79.720	1.891	-91.069	-101.188	55.287
500	19.219	88.702	81.106	3.798	-103.521	-102.518	44.811
600	19.412	92.225	82.674	5.730	-103.912	-102.281	37.256
700	19.531	95.227	84.258	7.678	-104.263	-101.982	31.840
800	19.610	97.840	85.796	9.635	-104.591	-101.633	27.765
900	19.664	100.153	87.265	11.599	-104.913	-101.244	24.586
1000	19.703	102.227	88.659	13.568	-105.229	-100.819	22.034
1100	19.732	104.106	89.980	15.539	-105.541	-100.363	19.940
1200	19.754	105.824	91.229	17.514	-105.851	-99.880	18.191
1300	19.771	107.406	92.414	19.490	-106.156	-99.370	16.706
1400	19.785	108.872	93.538	21.468	-106.460	-98.836	15.429
1500	19.796	110.237	94.606	23.447	-106.760	-98.282	14.320
1600	19.805	111.515	95.623	25.427	-107.056	-97.704	13.346
1700	19.813	112.716	96.594	27.408	-177.445	-94.456	12.143
1800	19.819	113.849	97.521	29.390	-177.374	-89.574	10.876
1900	19.825	114.920	98.409	31.372	-177.305	-84.695	9.742
2000	19.829	115.937	99.260	33.354	-177.239	-79.827	8.723
2100	19.833	116.905	100.078	35.338	-177.174	-74.959	7.801
2200	19.836	117.828	100.864	37.321	-177.114	-70.093	6.963
2300	19.839	118.709	101.620	39.305	-177.054	-65.228	6.198
2400	19.842	119.554	102.350	41.289	-177.001	-60.368	5.497
2500	19.844	120.364	103.055	43.273	-176.952	-55.509	4.853
2600	19.846	121.142	103.735	45.258	-176.907	-50.654	4.258
2700	19.848	121.891	104.394	47.243	-176.870	-45.799	3.707
2800	19.850	122.613	105.032	49.227	-176.839	-40.943	3.196
2900	19.851	123.310	105.650	51.212	-176.818	-36.092	2.720
3000	19.853	123.983	106.250	53.198	-176.802	-31.239	2.276
3100	19.854	124.634	106.833	55.183	-176.800	-26.385	1.860
3200	19.855	125.264	107.399	57.168	-176.805	-21.534	1.471
3300	19.856	125.875	107.950	59.154	-176.823	-16.681	1.105
3400	19.857	126.468	108.486	61.140	-176.852	-11.827	.760
3500	19.858	127.044	109.008	63.125	-176.893	-6.975	.436
3600	19.858	127.603	109.516	65.111	-176.949	-2.118	.129
3700	19.859	128.147	110.013	67.097	-177.018	2.735	-.162
3800	19.860	128.677	110.497	69.083	-177.102	7.601	-.437
3900	19.860	129.193	110.970	71.069	-177.202	12.463	-.698
4000	19.861	129.695	111.432	73.055	-177.319	17.325	-.947
4100	19.862	130.186	111.883	75.041	-177.453	22.197	-1.183
4200	19.862	130.664	112.325	77.027	-177.607	27.068	-1.408
4300	19.862	131.132	112.757	79.014	-177.777	31.938	-1.623
4400	19.863	131.588	113.179	81.000	-177.968	36.822	-1.829
4500	19.863	132.035	113.593	82.986	-178.182	41.706	-2.026
4600	19.864	132.471	113.999	84.973	-178.416	46.597	-2.214
4700	19.864	132.899	114.397	86.959	-178.674	51.480	-2.394
4800	19.864	133.317	114.787	88.945	-178.958	56.382	-2.567
4900	19.865	133.726	115.169	90.932	-179.268	61.292	-2.734
5000	19.865	134.128	115.544	92.918	-179.605	66.205	-2.894
5100	19.865	134.521	115.912	94.905	-179.971	71.127	-3.048
5200	19.865	134.907	116.274	96.891	-180.371	76.052	-3.196
5300	19.866	135.285	116.629	98.878	-180.802	80.986	-3.340
5400	19.866	135.657	116.978	100.864	-181.268	85.930	-3.478
5500	19.866	136.021	117.321	102.851	-181.772	90.885	-3.611
5600	19.866	136.379	117.658	104.838	-182.314	95.838	-3.740
5700	19.866	136.731	117.990	106.824	-182.898	100.814	-3.865
5800	19.867	137.076	118.316	108.811	-183.526	105.801	-3.987
5900	19.867	137.416	118.637	110.798	-184.197	110.791	-4.104
6000	19.867	137.750	118.952	112.784	-184.919	115.801	-4.218

Sept. 30, 1961; June 30, 1966

LITHIUM IODIDE, DIMERIC (Li_2I_2)   (IDEAL GAS)   GFW = 267.6868

Point Group D_{2h} $\Delta Hf_0^\circ = -85.3 \pm 4$ kcal/mol

$S^\circ_{298.15} = [79.0]$ gibbs/mol $\Delta Hf^\circ_{298.15} = -86.5 \pm 4$ kcal/mol

Ground State Quantum Weight = 1

<u>Vibrational Frequencies and Degeneracies</u>

ω, cm⁻¹	ω, cm⁻¹
[166](1)	[310](1)
[160](1)	248 (1)
[383](1)	375 (1)

Bond Distance: Li-I = 2.54 Å   Li-Li = 2.71 Å

Bond Angle: I-Li-I = 116° ± 4° $\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C = 1.63429 \times 10^{-112}$ g^3 cm^6

Heat of Formation.

This was obtained from the heat of formation of the crystal and the heat of sublimation of the dimer, which derivation has been given in the LiI(g) table.

Heat Capacity and Entropy.

J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Akischin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances (r_{Li-Li} = 2.712 Å and r_{I-I} = 4.520 Å) calculated by Berkowitz are in good agreement with those from Akischin and Rambidi. The three principal moments of inertia are $I_A = 4.2152 \times 10^{-39}$, $I_B = 194.8074 \times 10^{-39}$ and $I_C = 199.0226 \times 10^{-39}$ g cm^2.

S. H. Bauer, T. Ino and R. F. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (501, 501, 148, 200, 294, 360 cm^{-1}) for $Li_2I_2(g)$ in the electron diffraction studies of the $Li_2Cl_2(g)$. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), have observed two fundamental vibrational frequencies (248 and 375 cm^{-1}) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.

Lead Diiodide (PbI_2)

(Crystal) Mol. Wt. = 461.03

INTERIM TABLE

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-4.688	-41.745	-41.745	INFINITE
100	16.680	22.396	58.086	-3.569	-41.778	-41.679	91.085
200	18.050	34.495	43.575	-1.816	-41.806	-41.571	45.425
298	18.918	41.869	41.869	.000	-41.855	-41.446	30.379
300	18.935	41.986	41.869	.035	-41.856	-41.443	30.190
400	19.610	47.534	42.621	1.965	-45.750	-41.163	22.489
500	20.290	51.984	44.063	3.961	-55.950	-39.055	17.070
600	20.820	55.729	45.703	6.016	-55.482	-35.719	13.010
700	21.290	58.974	47.372	8.121	-56.146	-32.274	10.076
800	21.760	61.848	49.006	10.274	-55.615	-28.898	7.894
900	22.230	64.438	50.579	12.473	-55.034	-25.594	6.215
1000	22.700	66.804	52.085	14.720	-54.398	-22.356	4.886
1100	23.170	68.990	53.523	17.013	-53.711	-19.185	3.812
1200	23.640	71.026	54.898	19.354	-52.970	-16.078	2.928
1300	24.110	72.937	56.213	21.741	-52.178	-13.035	2.191
1400	24.580	74.741	57.472	24.176	-51.340	-10.055	1.570
1500	25.050	76.453	58.681	26.657	-50.456	-7.137	1.040
1600	25.520	78.084	59.843	29.186	-49.528	-4.278	.584
1700	25.990	79.646	60.962	31.761	-48.558	-1.479	.190
1800	26.460	81.144	62.042	34.384	-47.546	1.260	-.153
1900	26.930	82.588	63.086	37.053	-46.494	3.943	-.453
2000	27.400	83.981	64.096	39.770	-45.400	6.568	-.718
2100	27.870	85.329	65.075	42.533	-86.716	10.693	-1.113
2200	28.340	86.636	66.026	45.344	-85.448	15.300	-1.520
2300	28.810	87.907	66.950	48.201	-84.156	19.851	-1.886
2400	29.280	89.143	67.849	51.106	-82.838	24.347	-2.217
2500	29.750	90.347	68.725	54.057	-81.499	28.783	-2.516

Lead Diiodide (PbI_2) (Crystal)

Mol. Wt. = 461.03

ΔH_f° 298.15 = -41.86 ± 0.06 kcal. mole^{-1}

$S^\circ_{298.15}$ = 41.869 cal. deg.$^{-1}$ mole^{-1}

ΔH_s° 298.15 = 41.70 ± 0.10 kcal. mole^{-1}

T_m = 680°K.

ΔH_m° = 3.87 kcal. mole^{-1}

Heat of Formation. Calculated from the data reported by H. Braune and F. Koref, Z. anorg. Chem. 87, 175 (1914) and R. H. Gerke, J. Am. Chem. Soc. 44, 1684 (1922).

Heat Capacity, Entropy, and Melting Data. C_p (10° to 298.15°K.) obtained from Edgar F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, private communication, May, 1961. Above 298.15°K., C_p given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation. T_m and ΔH_m° reported by M. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of K. Jellinek and A. Rudat, Z. physik. Chem., A143, 55 (1929) and B. Greiner and K. Jellinek, Z. physik. Chem., A165, 97 (1933).

Lead Diiodide (PbI_2)
(Liquid) Mol. Wt. = 461.03

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	16.920	42.786	42.786	.000	-40.637	-40.501	29.687
300	16.935	42.903	42.786	.035	-40.638	-40.500	29.503
400	19.610	48.450	43.538	1.965	-44.532	-40.312	22.024
500	32.400	54.084	45.035	4.525	-54.168	-38.323	16.750
600	32.400	59.991	47.051	7.765	-52.515	-35.310	12.861
700	32.400	64.986	49.265	11.005	-52.044	-32.381	10.109
800	32.400	69.312	51.507	14.245	-50.426	-29.681	8.108
900	32.400	73.129	53.701	17.485	-48.804	-27.186	6.601
1000	32.400	76.542	55.818	20.725	-47.175	-24.871	5.435
1100	32.400	79.630	57.844	23.965	-45.541	-22.720	4.514
1200	32.400	82.449	59.779	27.205	-43.901	-20.717	3.773
1300	32.400	85.043	61.624	30.445	-42.256	-18.851	3.169
1400	32.400	87.444	63.383	33.685	-40.613	-17.113	2.671
1500	32.400	89.679	65.063	36.925	-38.970	-15.491	2.257
1600	32.400	91.770	66.667	40.165	-37.331	-13.978	1.909
1700	32.400	93.735	68.202	43.405	-35.696	-12.569	1.616
1800	32.400	95.586	69.673	46.645	-34.067	-11.257	1.367
1900	32.400	97.338	71.083	49.885	-32.444	-10.034	1.154
2000	32.400	99.000	72.438	53.125	-30.827	-8.898	.972
2100	32.400	100.581	73.741	56.365	-71.666	-6.287	.654
2200	32.400	102.088	74.995	59.605	-69.969	-3.215	.319
2300	32.400	103.528	76.205	62.845	-68.294	-.217	.021
2400	32.400	104.907	77.372	66.085	-66.641	2.708	-.247
2500	32.400	106.230	78.500	69.325	-65.013	5.562	-.486
2600	32.400	107.501	79.591	72.565	-63.407	8.354	-.702
2700	32.400	108.723	80.648	75.805	-61.823	11.084	-.897
2800	32.400	109.902	81.671	79.045	-60.262	13.756	-1.074
2900	32.400	111.039	82.665	82.285	-58.720	16.373	-1.234
3000	32.400	112.137	83.629	85.525	-57.198	18.936	-1.379

March 31, 1962

Lead Diiodide (PbI_2) (Liquid)

Mol. Wt. = 461.03

ΔH_f° 298.15 = [-40.637] kcal. mole^{-1}

$S_{298.15}^\circ$ = [42.786] cal. deg.$^{-1}$ mole^{-1}

T_m = 680°K.

ΔH_m° = 3.87 kcal. mole^{-1}

T_b = 1135°K.

ΔH_v° = 26.99 ± 0.10 kcal. mole^{-1}

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). T_m and ΔH_m° reported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959). A glass transition temperature of 454°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v° calculated from ΔH_s° 298.15 and free energy functions for condensed and gaseous states.

Lead Diiodide (PbI_2)

(Ideal Gas) Mol. Wt. = 461.03 INTERIM TABLE

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-3.761	.881	.881	INFINITE
100	12.861	71.221	98.015	-2.679	.811	-3.973	8.683
200	13.608	80.441	87.167	-1.345	.364	-8.591	9.387
298	13.771	85.911	85.911	.000	-.156	-12.878	9.439
300	13.772	85.996	85.911	.025	-.167	-12.956	9.438
400	13.832	89.967	86.452	1.406	-4.610	-16.996	9.286
500	13.860	93.057	87.476	2.791	-15.421	-19.062	8.332
600	13.876	95.586	88.623	4.178	-15.621	-19.772	7.202
700	13.885	97.726	89.774	5.566	-17.002	-20.256	6.324
800	13.891	99.580	90.887	6.955	-17.235	-20.704	5.656
900	13.895	101.216	91.945	8.344	-17.464	-21.125	5.130
1000	13.898	102.681	92.947	9.734	-17.685	-21.519	4.703
1100	13.900	104.005	93.893	11.124	-17.901	-21.893	4.349
1200	13.902	105.215	94.787	12.514	-18.111	-22.245	4.051
1300	13.903	106.328	95.632	13.904	-18.316	-22.581	3.796
1400	13.904	107.358	96.434	15.294	-18.523	-22.902	3.575
1500	13.905	108.317	97.194	16.685	-18.729	-23.207	3.381
1600	13.906	109.215	97.918	18.075	-18.940	-23.498	3.209
1700	13.906	110.058	98.607	19.466	-19.154	-23.776	3.056
1800	13.907	110.853	99.266	20.857	-19.374	-24.043	2.919
1900	13.907	111.605	99.896	22.247	-19.601	-24.297	2.795
2000	13.908	112.318	100.499	23.638	-19.833	-24.539	2.681
2100	13.908	112.997	101.078	25.029	-62.521	-23.215	2.416
2200	13.908	113.644	101.635	26.420	-62.673	-21.341	2.120
2300	13.908	114.262	102.170	27.811	-62.847	-19.458	1.849
2400	13.909	114.854	102.687	29.201	-63.044	-17.566	1.599
2500	13.909	115.422	103.185	30.592	-63.265	-15.669	1.370
2600	13.909	115.967	103.666	31.983	-63.508	-13.760	1.157
2700	13.909	116.492	104.131	33.374	-63.773	-11.841	.958
2800	13.909	116.998	104.582	34.765	-64.061	-9.912	.774
2900	13.909	117.486	105.018	36.156	-64.368	-7.972	.601
3000	13.909	117.958	105.442	37.547	-64.695	-6.023	.439
3100	13.910	118.414	105.853	38.938	-65.039	-4.061	.286
3200	13.910	118.855	106.252	40.329	-65.400	-2.089	.143
3300	13.910	119.283	106.641	41.720	-65.775	-.103	.007
3400	13.910	119.698	107.019	43.111	-66.163	1.893	-.122
3500	13.910	120.102	107.387	44.502	-66.562	3.901	-.244
3600	13.910	120.494	107.746	45.893	-66.971	5.919	-.359
3700	13.910	120.875	108.095	47.284	-67.388	7.948	-.469
3800	13.910	121.246	108.437	48.675	-67.810	9.992	-.575
3900	13.910	121.607	108.770	50.066	-68.239	12.046	-.675
4000	13.910	121.959	109.095	51.457	-68.671	14.104	-.771
4100	13.910	122.303	109.413	52.848	-69.106	16.183	-.863
4200	13.910	122.638	109.724	54.239	-69.543	18.271	-.951
4300	13.910	122.965	110.028	55.630	-69.981	20.361	-1.035
4400	13.910	123.285	110.326	57.021	-70.419	22.470	-1.116
4500	13.910	123.598	110.617	58.412	-70.856	24.586	-1.194
4600	13.910	123.903	110.903	59.803	-71.292	26.714	-1.269
4700	13.910	124.202	111.182	61.194	-71.725	28.844	-1.341
4800	13.910	124.495	111.457	62.585	-72.157	30.994	-1.411
4900	13.910	124.782	111.726	63.976	-72.586	33.146	-1.478
5000	13.910	125.063	111.990	65.367	-73.013	35.306	-1.543
5100	13.910	125.339	112.249	66.758	-73.436	37.476	-1.606
5200	13.910	125.609	112.503	68.149	-73.857	39.655	-1.667
5300	13.911	125.874	112.753	69.540	-74.274	41.845	-1.725
5400	13.910	126.134	112.998	70.931	-74.689	44.043	-1.782
5500	13.911	126.389	113.239	72.322	-75.101	46.240	-1.837
5600	13.910	126.640	113.476	73.713	-75.510	48.449	-1.891
5700	13.910	126.886	113.710	75.104	-75.917	50.665	-1.942
5800	13.911	127.128	113.939	76.495	-76.321	52.893	-1.993
5900	13.911	127.366	114.164	77.886	-76.723	55.122	-2.042
6000	13.911	127.599	114.386	79.277	-77.123	57.360	-2.089

March 31, 1962

Lead Diiodide (PbI_2) (Ideal Gas)

Mol. Wt. = 461.03

ΔH_f° 298.15 = -0.16 ± 0.12 kcal. mole^{-1}

$S^\circ_{298.15}$ = [85.911] cal. deg.$^{-1}$ mole^{-1}

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$

[100] (1)
[40] (1)
[160] (1)

Pb-I distance = 2.79 ± 0.02 Å IPbI angle = 95° $\sigma = 2$

$I_A = 67.294 \times 10^{-39}$ g. cm.^{2} $I_B = 178.298 \times 10^{-39}$ g. cm.^{2}

$I_C = I_A + I_B = 245.592 \times 10^{-39}$

Heat of Formation. Calculated from ΔH_s° 298.15 and ΔH_f° 298.15 for $PbI_2(c)$.

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for $HgI_2(g)$.

Titanium Diiodide (TiI_2)

(Crystal) GFW = 301.7088

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	20.609	29.300	29.300	.000	-63.600	-61.876	45.356
300	20.612	29.428	29.300	.038	-63.597	-61.865	45.068
400	20.786	35.381	30.111	2.108	-67.317	-61.173	33.423
500	20.960	40.038	31.647	4.195	-77.399	-58.690	25.653
600	21.134	43.875	33.375	6.300	-76.857	-55.001	20.034
700	21.308	47.146	35.114	8.422	-76.320	-51.400	16.048
800	21.482	50.002	36.800	10.562	-75.791	-47.876	13.079
900	21.656	52.543	38.411	12.719	-75.274	-44.418	10.786
1000	21.830	54.833	39.940	14.893	-74.769	-41.016	8.964
1100	22.004	56.922	41.391	17.085	-74.273	-37.664	7.483
1200	22.178	58.844	42.766	19.294	-74.725	-34.320	6.251
1300	22.352	60.626	44.072	21.520	-74.122	-30.978	5.208
1400	22.526	62.289	45.315	23.764	-73.519	-27.682	4.321
1500	22.700	63.849	46.499	26.025	-72.916	-24.430	3.559
1600	22.874	65.320	47.630	28.304	-72.314	-21.214	2.898
1700	23.048	66.712	48.712	30.600	-71.717	-18.040	2.319
1800	23.222	68.034	49.749	32.914	-71.125	-14.900	1.809
1900	23.396	69.294	50.744	35.245	-70.540	-11.793	1.356
2000	23.570	70.499	51.702	37.593	-74.410	-8.563	.936

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM DIIODIDE (TiI_2) (CRYSTAL) GFW = 301.7088

ΔHf_0° = unknown

$S^\circ_{298.15}$ = [29.3 ± 3.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -63.6 ± 3.0 kcal/mol

Ts = [1358.2]°K

ΔHs° = [51.80] kcal/mol

Heat of Formation

The heat of formation of $TiI_2(c)$ is calculated from the heat of reaction for the process $2TiI_2(c) = Ti(c) + TiI_4(g)$, and the heat of formation of $TiI_4(c)$. Vapor pressure data for this reaction were reported by Herczog and Pidgeon (1) over the temperature range 750° to 902°K. Second and third law analyses of these data give values for ΔHr°_{298} of 60.5 ± 0.8 and 60.85 kcal/mol respectively, the third law drift being 0.4 ± 1.0 eu. The third law ΔHr°_{298} is used to obtain the adopted value of ΔHf°_{298}.

Heat Capacity and Entropy

The estimated heat capacity is that reported by Kelley (2). The value of $S^\circ_{298.15}$ is estimated from that of $TiCl_2(c)$ and the difference between ionic entropy contributions of Cl^- and I^-.

Heat of Sublimation

The heat of sublimation of $TiI_2(c)$ is taken as the difference in the heats of formation of $TiI_2(c)$ and $TiI_2(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta Gr^\circ = 0$ for the reaction $TiI_2(c) = TiI_2(g)$.

References

1. A. Herczog and L. M. Pidgeon, Can. J. Chem., 34, 1687 (1956).
2. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1961.

Titanium Diiodide (TiI_2)

(Ideal Gas) GFW = 301.7088

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.708	-4.102	-4.102	INFINITE
100	12.418	62.404	89.839	-2.743	-4.000	-8.586	18.764
200	14.027	71.635	78.648	-1.403	-4.296	-13.070	14.282
298	14.476	77.335	77.335	.000	-4.700	-17.297	12.679
300	14.481	77.425	77.335	.027	-4.708	-17.375	12.658
400	14.659	81.618	77.906	1.485	-9.040	-21.391	11.687
500	14.745	84.900	78.988	2.956	-19.738	-23.461	10.255
600	14.793	87.593	80.205	4.433	-19.824	-24.199	8.814
700	14.822	89.875	81.427	5.914	-19.928	-24.920	7.780
800	14.843	91.856	82.610	7.397	-20.056	-25.623	7.000
900	14.861	93.605	83.736	8.882	-20.211	-26.310	6.389
1000	14.880	95.172	84.803	10.369	-20.393	-26.979	5.896
1100	14.905	96.591	85.811	11.858	-20.600	-27.627	5.489
1200	14.939	97.889	86.764	13.350	-21.769	-28.218	5.139
1300	14.983	99.087	87.667	14.846	-21.896	-28.750	4.833
1400	15.037	100.199	88.522	16.347	-22.036	-29.272	4.570
1500	15.102	101.239	89.336	17.854	-22.187	-29.785	4.340
1600	15.177	102.216	90.111	19.368	-22.350	-30.284	4.137
1700	15.259	103.138	90.850	20.890	-22.527	-30.776	3.957
1800	15.348	104.013	91.557	22.420	-22.719	-31.256	3.795
1900	15.440	104.845	92.235	23.959	-22.926	-31.725	3.649
2000	15.535	105.640	92.885	25.508	-27.595	-32.030	3.500
2100	15.631	106.400	93.511	27.066	-27.808	-32.244	3.356
2200	15.725	107.129	94.114	28.634	-28.013	-32.453	3.224
2300	15.818	107.830	94.695	30.211	-28.210	-32.649	3.102
2400	15.907	108.505	95.256	31.798	-28.398	-32.837	2.990
2500	15.992	109.156	95.799	33.393	-28.580	-33.019	2.886
2600	16.074	109.785	96.325	34.996	-28.755	-33.194	2.790
2700	16.151	110.393	96.835	36.607	-28.924	-33.361	2.700
2800	16.223	110.982	97.330	38.226	-29.086	-33.521	2.616
2900	16.291	111.553	97.810	39.852	-29.242	-33.675	2.538
3000	16.355	112.106	98.278	41.484	-29.394	-33.827	2.464
3100	16.415	112.643	98.733	43.123	-29.540	-33.971	2.395
3200	16.471	113.165	99.175	44.767	-29.682	-34.115	2.330
3300	16.524	113.673	99.607	46.417	-29.820	-34.248	2.268
3400	16.574	114.167	100.028	48.072	-29.954	-34.381	2.210
3500	16.621	114.648	100.439	49.731	-30.085	-34.509	2.155
3600	16.666	115.117	100.840	51.396	-131.838	-34.371	2.087
3700	16.708	115.574	101.232	53.065	-131.934	-31.665	1.870
3800	16.749	116.020	101.616	54.737	-132.041	-28.955	1.665
3900	16.788	116.456	101.991	56.414	-132.158	-26.237	1.470
4000	16.826	116.881	102.358	58.095	-132.285	-23.522	1.285
4100	16.862	117.297	102.717	59.779	-132.423	-20.797	1.109
4200	16.897	117.704	103.069	61.467	-132.571	-18.074	.941
4300	16.931	118.102	103.414	63.159	-132.728	-15.351	.780
4400	16.964	118.492	103.752	64.853	-132.896	-12.620	.627
4500	16.996	118.873	104.084	66.551	-133.072	-9.880	.480
4600	17.026	119.247	104.410	68.252	-133.256	-7.137	.339
4700	17.056	119.614	104.729	69.957	-133.447	-4.397	.204
4800	17.085	119.973	105.043	71.664	-133.648	-1.648	.075
4900	17.113	120.326	105.351	73.374	-133.856	1.102	-.049
5000	17.140	120.672	105.654	75.086	-134.072	3.861	-.169
5100	17.166	121.011	105.952	76.802	-134.292	6.620	-.284
5200	17.191	121.345	106.245	78.520	-134.521	9.385	-.394
5300	17.215	121.672	106.533	80.240	-134.755	12.153	-.501
5400	17.237	121.994	106.816	81.962	-134.996	14.933	-.604
5500	17.259	122.311	107.095	83.687	-135.240	17.710	-.704
5600	17.279	122.622	107.370	85.414	-135.491	20.486	-.799
5700	17.298	122.928	107.640	87.143	-135.745	23.279	-.893
5800	17.315	123.229	107.906	88.874	-136.004	26.071	-.982
5900	17.332	123.525	108.168	90.606	-136.267	28.867	-1.069
6000	17.347	123.817	108.427	92.340	-136.534	31.666	-1.153

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM DIIODIDE (TiI_2) (IDEAL GAS) GFW = 301.7088

Point Group $[D_{\infty h}]$

$\Delta Hf_0^\circ = [-4.1 \pm 8.0]$ kcal/mol

$S^\circ_{298.15} = [77.3 \pm 4]$ gibbs/mol

$\Delta Hf^\circ_{298.15} = [-4.7 \pm 8.0]$ kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[134] (1)
[92] (2)
[290] (1)

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [180°]

σ = 2

Rotational Constant: $B_0 = [0.0091]$ cm^{-1}

Heat of Formation

The heat of formation of $TiI_2(g)$ is calculated from that of $TiI_2(c)$ and the heat of vaporization. Vapor pressure data over the temperature range 750°K to 902°K have been reported by Herczog and Pidgeon (1). Second and third law analyses of these data give values for ΔHv°_{298} of 51.9 and 58.9 kcal/mol, respectively. The third law drift for these data is 8.3 ± 1.1 eu, with one point rejected due to failure of a statistical test. The adopted value of ΔHf°_{298} is calculated from the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(g)$, $TiCl_4(g)$, $TiBr_2(g)$, $TiBr_4(g)$ and $TiI_4(g)$. The vibrational frequencies are estimated from a valence force field model. The force constant K is estimated as 1.0 millidynes/Å and the constant K_δ/ℓ^2 is assumed to be 0.05 millidynes/Å.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2$ are estimated by assuming they correspond to the inverted states of $NiCl_2(g)$ (2). The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (3, 4, 5, 6).

References

1. A. Herczog and L. M. Pidgeon, Can. J. Chem., 34, 1687 (1956).
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4. J. T. Houghen, G. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961).
5. G. E. Leroi, T. C. James, J. T. Hougen, and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
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Zirconium Diiodide (ZrI_2)

(Crystal) Mol. Wt. = 345.04 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	22.500	35.900	35.900	.000	- 62.000	- 61.652	45.190
300	22.550	36.039	35.900	.042	- 61.993	- 61.649	44.909
400	22.710	42.668	36.802	2.346	- 65.496	- 61.454	33.575
500	22.910	47.757	38.502	4.627	- 75.409	- 59.515	26.013
600	23.090	51.951	40.404	6.928	- 74.709	- 56.403	20.544
700	23.290	55.525	42.315	9.247	- 74.014	- 53.407	16.674
800	23.460	58.647	44.166	11.585	- 73.315	- 50.510	13.798
900	23.810	61.433	45.932	13.951	- 72.598	- 47.703	11.583
1000	23.860	63.947	47.610	16.337	- 71.871	- 44.974	9.829
1100	24.040	66.229	49.201	18.731	- 71.154	- 42.321	8.408
1200	24.240	68.329	50.708	21.145	- 71.387	- 39.683	7.227
1300	24.430	70.277	52.140	23.579	- 70.636	- 37.072	6.232
1400	24.620	72.095	53.501	26.031	- 69.878	- 34.519	5.388
1500	24.810	73.800	54.798	28.503	- 69.107	- 32.021	4.665
1600	24.990	75.407	56.036	30.993	- 68.326	- 29.570	4.039
1700	25.190	76.928	57.221	33.502	- 67.536	- 27.174	3.493
1800	25.390	78.373	58.356	36.031	- 66.733	- 24.822	3.014
1900	25.560	79.747	59.446	38.572	- 65.927	- 22.516	2.590
2000	26.420	81.077	60.494	41.165	- 65.078	- 20.255	2.213

Zirconium Diiodide (ZrI_2) (Crystal)

Mol. Wt. = 345.04

ΔH_f° 298.15 = [-62] kcal. mole^{-1}

$S^\circ_{298.15}$ = [35.9] cal. deg.$^{-1}$ mole^{-1}

T_m = [700]°K.

ΔH_m = [6] kcal. mole^{-1}

T_b = [1300]°K.

ΔH_v = [27] kcal. mole^{-1}

Heat of Formation. Estimated from a consideration of ΔH_f $ZrI_4(c)$ and of the disproportionation data given by R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley and Sons, Inc., New York, (1961).

Heat Capacity and Entropy. Heat capacity estimated by comparison to the other zirconium halides and titanium halides. Entropy estimated from additive constants.

Melting and Vaporization. ΔH_m was estimated. T_m, T_b, and ΔH_v from L. Brewer, National Nuclear Energy Series, Div. IV, 19B, paper 7, McGraw-Hill Book Co., Inc., New York, 1950.

Zirconium Diiodide (ZrI_2)

(Liquid) Mol. Wt. = 345.04

INTERIM TABLE

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	22.500	44.494	44.494	.000	- 55.985	- 58.199	42.659
300	22.550	44.633	44.494	.042	- 55.978	- 58.212	42.406
400	22.710	51.262	45.396	2.346	- 59.481	- 58.877	32.167
500	22.910	56.351	47.096	4.627	- 69.394	- 57.797	25.262
600	23.090	60.545	48.998	6.928	- 68.694	- 55.544	20.231
700	23.290	64.095	50.908	9.231	- 68.015	- 53.407	16.673
800	25.370	67.320	52.759	11.648	- 67.237	- 51.370	14.033
900	27.460	70.429	54.551	14.290	- 66.244	- 49.444	12.006
1000	29.540	73.429	56.289	17.140	- 65.053	- 47.638	10.411
1100	31.620	76.342	57.981	20.198	- 63.672	- 45.964	9.132
1200	33.700	79.183	59.630	23.464	- 63.053	- 44.374	8.081
1300	35.780	81.962	61.241	26.938	- 61.262	- 42.889	7.210
1400	37.870	84.690	62.819	30.620	- 59.274	- 41.549	6.486
1500	39.950	87.374	64.367	34.511	- 57.084	- 40.359	5.880
1600	42.030	90.019	65.887	38.610	- 54.694	- 39.317	5.370
1700	44.110	92.629	67.384	42.917	- 52.106	- 38.437	4.941
1800	46.190	95.209	68.858	47.432	- 49.317	- 37.711	4.579
1900	48.280	97.763	70.312	52.156	- 46.328	- 37.147	4.273
2000	50.360	100.292	71.748	57.088	- 43.140	- 36.748	4.015

June 30, 1962

Zirconium Diiodide (ZrI_2) (Liquid)

Mol. Wt. = 345.04

$\Delta H_f^\circ{}_{298.15}$ = [-56] kcal. mole^{-1}

$S^\circ_{298.15}$ = [44.5] cal. deg.$^{-1}$ mole^{-1}

T_m = [700]°K.

ΔH_m = [6] kcal. mole^{-1}

T_b = [1300]°K.

ΔH_v = [27] kcal. mole^{-1}

Heat of Formation. Based upon the ΔH_f ZrI_2(c) and the estimated functions of both crystal and liquid.

Heat Capacity and Entropy. Entropy based upon the estimated values for C_p(c), ΔH_m, and C_p(l).

Melting and Vaporization. ΔH_m was estimated. T_m, T_b, and ΔH_v from L. Brewer, National Nuclear Energy Series, Div. IV, 19B, paper 7, McGraw-Hill Book Co., Inc., 1950.

Zirconium Diiodide (ZrI_2)

(Ideal Gas) Mol. Wt. = 345.04 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 3.660	- 15.117	- 15.117	INFINITE
100	12,354	67,973	94,327	- 2.635	- 15.033	- 20.036	43,786
200	13.423	76,963	83,625	- 1,332	- 15.431	- 24,895	27,203
298	13.681	82,380	82,380	,000	- 15,928	- 29,438	21,577
300	13,683	82,465	82,380	,025	- 15,938	- 29,521	21,505
400	13,781	86,416	82,918	1,399	- 20,371	- 33,829	18,482
500	13.827	89.497	83.937	2.780	- 31.184	- 36.161	15.805
600	13,852	92,020	85,080	4.164	- 31,401	- 37,137	13.526
700	13,868	94,157	86,228	5.550	- 31,639	- 38,074	11.887
800	13,878	96.009	87,338	6.937	- 31,891	- 38,976	10,647
900	13,885	97,644	88,394	8,325	- 32,152	- 39,846	9,675
1000	13.890	99,107	89,393	9.714	- 32.422	- 40,685	8,891
1100	13,893	100.431	90,338	11,103	- 32,710	- 41.499	8,245
1200	13.896	101.640	91.230	12.493	- 33.967	- 42.237	7.692
1300	13,898	102,753	92,074	13,882	- 34.261	- 42,914	7,214
1400	13.900	103,783	92,874	15,272	- 34.565	- 43,569	6,801
1500	13.901	104,742	93,634	16,662	- 34,876	- 44,202	6,440
1600	13.903	105,639	94,356	18,053	- 35,194	- 44,810	6,121
1700	13.903	106,482	95,045	19,443	- 35,523	- 45,403	5,837
1800	13.904	107.277	95.703	20.833	- 35.859	- 45.974	5.582
1900	13,905	108,028	96,332	22,224	- 36,203	- 46,527	5,352
2000	13.906	108.742	96.935	23.614	- 36,557	- 47.064	5,143
2100	13,906	109,420	97,513	25,005	- 36,917	- 47,579	4,951
2200	13.906	110,067	98,069	26.396	- 42,189	- 47,914	4,760
2300	13,907	110,685	98,604	27,786	- 42,573	- 48,165	4,576
2400	13.907	111,277	99,120	29,177	- 42,957	- 48,398	4,407
2500	13.907	111,845	99,618	30,568	- 43,343	- 48,618	4,250
2600	13,908	112,390	100,099	31,958	- 43,731	- 48,822	4,104
2700	13,908	112,915	100,564	33,349	- 44,120	- 49,010	3,967
2800	13,908	113,421	101,014	34,740	- 44,510	- 49,183	3,839
2900	13,908	113.909	101,450	36,131	- 44,901	- 49,341	3,718
3000	13,908	114,381	101,873	37,522	- 45,294	- 49,490	3,605
3100	13.909	114.837	102,284	38,913	- 45.688	- 49,624	3.498
3200	13,909	115,278	102,683	40,303	- 46,084	- 49,745	3,397
3300	13,909	115,706	103,072	41,694	- 46,481	- 49,851	3,301
3400	13,909	116,121	103,449	43,085	- 46,879	- 49,947	3,210
3500	13,909	116,525	103,817	44,476	- 47,278	- 50,031	3,124
3600	13,909	116,916	104,176	45,867	- 47,679	- 50,107	3,042
3700	13,909	117,298	104,525	47,258	- 48,081	- 50,170	2,963
3800	13,909	117,669	104,866	48,649	- 48,484	- 50,219	2,888
3900	13,909	118,030	105,199	50.040	- 48,889	- 50.257	2.816
4000	13,910	118,382	105,524	51.431	- 49,295	- 50,291	2,748
4100	13,910	118.725	105,842	52,822	- 49,702	- 50,307	2,681
4200	13,910	119,061	106,153	54,213	- 50,111	- 50,316	2,618
4300	13,910	119,386	106,457	55,604	- 50,521	- 50,319	2,557
4400	13,910	119,708	106,754	56,995	- 50,933	- 50,312	2,499
4500	13.910	120,020	107.046	58.386	- 51.346	- 50.290	2.442
4600	13,910	120,326	107,331	59,776	- 51,761	- 50,261	2,388
4700	13,910	120,625	107,611	61,168	- 52,175	- 50,226	2,335
4800	13,910	120,916	107,885	62,558	- 189,026	- 48,654	2,215
4900	13,910	121,205	108,154	63,950	- 189,498	- 45,727	2,039
5000	13,910	121,486	108,418	65,341	- 189,978	- 42,788	1,870
5100	13,910	121,761	108,677	66,732	- 190,463	- 39,841	1,707
5200	13,910	122.031	108,931	68.123	- 190,954	- 36,881	1.550
5300	13,910	122,296	109,181	69,513	- 191,452	- 33,916	1,398
5400	13.910	122,556	109,426	70,905	- 191,954	- 30,933	1.252
5500	13,910	122,812	109,667	72,296	- 192,459	- 27,952	1.111
5600	13,910	123,062	109,904	73,687	- 192,971	- 24,956	,974
5700	13,910	123,308	110,137	75,078	- 193,486	- 21,953	,842
5800	13.910	123.550	110,366	76.469	- 194,006	- 18.936	.713
5900	13,910	123,788	110,592	77,860	- 194,528	- 15,913	,589
6000	13,910	124,022	110,813	79.251	- 195,054	- 12.882	.469

June 30, 1962

Zirconium Diiodide (ZrI_2) (Ideal Gas)

Mol. Wt. = 345.04

$\Delta H^\circ_{f\ 298.15}$ = [-16] kcal. mole^{-1}

$S^\circ_{298.15}$ = [82.4] cal. deg.$^{-1}$ mole^{-1}

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$

[60] (1)
[120] (1)
[210] (1)

rZr-I = [2.66 Å] ∢ I-Zr-I = 120° σ = 2

Product of Moments of Inertia $I_AI_BI_C = 1.0716 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation. Based upon the estimated value of the ΔH_f for the crystal and the appropriate crystal and gas functions.

Heat Capacity and Entropy. Molecular constants were all estimated by comparison to similar molecules of zirconium and titanium.

Titanium Triiodide (TiI_3)

(Crystal) GFW = 428.6132

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	27.909	46.000	46.000	.000	-77.000	-76.117	55.795
300	27.912	46.173	46.001	.052	-76.995	-76.111	55.447
400	28.086	54.226	47.097	2.852	-82.571	-75.645	41.331
500	28.260	60.512	49.174	5.669	-97.685	-72.494	31.687
600	28.434	65.680	51.507	8.504	-96.861	-67.535	24.600
700	28.608	70.076	53.854	11.356	-96.044	-62.712	19.579
800	28.782	73.908	56.126	14.225	-95.236	-58.004	15.846
900	28.956	77.308	58.294	17.112	-94.441	-53.398	12.967
1000	29.130	80.368	60.351	20.016	-93.658	-48.880	10.683
1100	29.304	83.152	62.299	22.938	-92.886	-44.439	8.829
1200	29.478	85.709	64.145	25.877	-93.062	-40.031	7.291
1300	29.652	88.076	65.896	28.834	-92.183	-35.647	5.993
1400	29.826	90.279	67.560	31.808	-91.306	-31.331	4.891
1500	30.000	92.343	69.144	34.799	-90.430	-27.080	3.945

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM TRIIODIDE (TiI_3) (CRYSTAL) GFW = 428.6132

ΔHf°_0 = unknown

$S^\circ_{298.15}$ = [46.0 ± 2.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-77 ±5] kcal/mol

Ts = [1000]°K

ΔHs° = [35.4] kcal/mol

Heat of Formation

The heat of formation of $TiI_3(c)$ is calculated from the free energy of formation at 623°K combined with the increment $\Delta Gf^\circ_{623} - \Delta Gf^\circ_{298.15}$ and the entropies, $S^\circ_{298.15}$, of $TiI_2(c)$, $TiI_3(c)$ and $TiI_4(g)$. The free energy of formation, ΔGf°_{623}, is estimated such that $\Delta Gr^\circ_{623} = 0$ for the process $2TiI_3(c) = TiI_2(c) + TiI_4(g)$. This assumption is based on the observations of Herczog and Pidgeon (1) and Fast (2).

Heat Capacity and Entropy

The heat capacities of $TiI_3(c)$ and the value of $S^\circ_{298.15}$ estimated by Kelley (3) have been adopted.

Heat of Sublimation

The heat of sublimation of $TiI_3(c)$ is taken as the difference in the heats of formation of $TiI_3(c)$ and $TiI_3(g)$ at the sublimation temperature. The sublimation temperature is estimated as the point at which $\Delta Gr^\circ = 0$ for the process $TiI_3(c) = TiI_3(g)$.

References

1. A. Herczog and L. M.Pidgeon, Can. J. Chem., 34, 1687 (1956).
2. J. P. Fast, Rec. Trav. Chim., 58, 174 (1939).
3. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1960; U. S. Bur. Mines Bull. 592, 1961.

Titanium Triiodide (TiI_3)

(Ideal Gas) GFW = 428.6132

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	,000	,000	INFINITE	-4,525	-34,542	-34,542	INFINITE
100	13,986	72,986	107,173	-3,419	-34,663	-39,578	86,497
200	17,598	83,901	93,015	-1,823	-35,292	-44,250	48,354
298	19,311	91,294	91,294	,000	-35,900	-48,521	35,567
300	19,332	91,414	91,294	,036	-35,911	-48,599	35,404
400	20,082	97,092	92,063	2,011	-42,312	-52,532	28,702
500	20,420	101,615	93,537	4,039	-58,215	-53,575	23,418
600	20,569	105,353	95,204	6,089	-58,176	-52,653	19,179
700	20,627	108,529	96,886	8,150	-58,150	-51,734	16,152
800	20,641	111,284	98,518	10,213	-58,148	-50,817	13,883
900	20,637	113,715	100,074	12,277	-58,176	-49,900	12,117
1000	20,625	115,889	101,549	14,840	-58,234	-48,978	10,704
1100	20,612	117,854	102,943	16,402	-58,322	-48,047	9,546
1200	20,599	119,647	104,261	18,463	-59,377	-47,071	8,573
1300	20,586	121,295	105,509	20,522	-59,395	-46,044	7,741
1400	20,574	122,820	106,692	22,580	-59,434	-45,016	7,027
1500	20,562	124,239	107,815	24,637	-59,492	-43,906	6,409
1600	20,551	125,566	108,883	26,692	-59,570	-42,946	5,866
1700	20,541	126,812	109,902	28,747	-59,672	-41,906	5,387
1800	20,530	127,986	110,874	30,801	-59,799	-40,858	4,961
1900	20,521	129,095	111,804	32,853	-59,952	-39,801	4,578
2000	20,512	130,148	112,695	34,905	-64,579	-38,585	4,216
2100	20,503	131,148	113,550	36,956	-64,759	-37,278	3,880
2200	20,495	132,102	114,372	39,005	-64,944	-35,967	3,573
2300	20,488	133,013	115,163	41,055	-65,131	-34,645	3,292
2400	20,481	133,885	115,925	43,103	-65,320	-33,314	3,034
2500	20,475	134,721	116,660	45,151	-65,513	-31,978	2,795
2600	20,469	135,523	117,370	47,198	-65,707	-30,633	2,575
2700	20,464	136,296	118,057	49,245	-65,906	-29,280	2,370
2800	20,459	137,040	118,722	51,291	-66,106	-27,918	2,179
2900	20,454	137,758	119,366	53,337	-66,308	-26,549	2,001
3000	20,449	138,451	119,991	55,382	-66,514	-25,178	1,834
3100	20,445	139,122	120,597	57,426	-66,722	-23,794	1,677
3200	20,441	139,771	121,186	59,471	-66,932	-22,409	1,530
3300	20,437	140,400	121,759	61,515	-67,145	-21,011	1,392
3400	20,432	141,010	122,316	63,558	-67,360	-19,611	1,261
3500	20,428	141,602	122,859	65,601	-67,577	-18,202	1,137
3600	20,424	142,177	123,387	67,644	-169,423	-16,527	1,003
3700	20,420	142,737	123,903	69,686	-169,618	-12,280	,725
3800	20,416	143,281	124,406	71,728	-169,827	-8,026	,462
3900	20,412	143,812	124,896	73,769	-170,052	-3,761	,211
4000	20,408	144,328	125,376	75,810	-170,293	,502	-,027
4100	20,403	144,832	125,844	77,851	-170,548	4,781	-,255
4200	20,399	145,324	126,302	79,891	-170,819	9,059	-,471
4300	20,395	145,804	126,750	81,930	-171,104	13,339	-,678
4400	20,390	146,273	127,189	83,970	-171,403	17,631	-,876
4500	20,385	146,731	127,618	86,008	-171,716	21,936	-1,065
4600	20,381	147,179	128,038	88,047	-172,040	26,247	-1,247
4700	20,376	147,617	128,450	90,085	-172,376	30,556	-1,421
4800	20,371	148,046	128,854	92,122	-172,726	34,880	-1,588
4900	20,367	148,466	129,250	94,159	-173,086	39,207	-1,749
5000	20,362	148,877	129,638	96,195	-173,458	43,545	-1,903
5100	20,357	149,281	130,019	98,231	-173,839	47,886	-2,052
5200	20,352	149,676	130,394	100,267	-174,232	52,237	-2,195
5300	20,347	150,063	130,761	102,302	-174,633	56,596	-2,334
5400	20,342	150,444	131,122	104,336	-175,045	60,969	-2,468
5500	20,337	150,817	131,477	106,370	-175,464	65,341	-2,596
5600	20,332	151,183	131,825	108,403	-175,893	69,714	-2,721
5700	20,327	151,543	132,168	110,436	-176,328	74,110	-2,842
5800	20,322	151,897	132,505	112,469	-176,771	78,507	-2,958
5900	20,317	152,244	132,837	114,501	-177,220	82,912	-3,071
6000	20,312	152,585	133,163	116,532	-177,676	87,324	-3,181

June 30, 1964; Dec. 31, 1968

TITANIUM TRIIODIDE (TiI_3) (IDEAL GAS) GFW = 428.6132

Point Group [C_{3v}]

ΔHf°_0 = [-34.5 ± 8.0] kcal/mol

$S^\circ_{298.15}$ = [91.3 ± 3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-35.9 ± 8.0] kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	4000	[2]
600	[2]	10000	[2]
1500	[2]		

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[341] (1)	[383] (2)
[123] (1)	[74] (2)

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [100°] σ = 3

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.3 x 10^{-110}] g^3 cm^6

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298.15}$, of $TiI_3(g)$ is estimated from the average Ti-I bond energy. The bond energy is estimated from the corresponding quantities for $TiBr_4(g)$, $TiBr_3(g)$ and $TiI_4(g)$.

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiI_4, $TiCl_4$ and $TiCl_3$. The pyramidal bond angle is estimated by assuming that $TiI_3(g)$ is similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 1.9 \times 10^{-37}$ g cm^2 and $I_C = 3.6 \times 10^{-37}$ g cm^2. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3} reported by C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Triiodide (ZrI_3)

(Crystal) Mol. Wt. = 471.950

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 5.822	- 94.774	- 94.774	INFINITE
100	19.925	24.059	69.939	- 4.588	- 94.846	- 94.727	207.016
200	23.501	39.242	51.132	- 2.378	- 94.926	- 94.575	103.342
298	24.813	48.897	48.897	.000	- 95.000	- 94.389	69.186
300	24.832	49.051	48.897	.046	- 95.001	- 94.384	68.756
400	25.300	56.267	49.878	2.556	- 100.884	- 93.962	51.336
500	25.400	61.923	51.742	5.091	- 116.305	- 90.775	39.676
600	25.500	66.564	53.837	7.636	- 115.809	- 85.717	31.221
700	25.550	70.499	55.944	10.189	- 115.330	- 80.740	25.207
800	25.600	73.914	57.981	12.746	- 114.862	- 75.830	20.715
900	25.650	76.932	59.922	15.309	- 114.400	- 70.979	17.235
1000	25.680	79.636	61.761	17.875	- 113.945	- 66.178	14.462
1100	25.700	82.085	63.499	20.444	- 113.507	- 61.424	12.203
1200	25.720	84.322	65.142	23.015	- 114.037	- 56.660	10.319
1300	25.740	86.381	66.698	25.588	- 113.602	- 51.896	8.724
1400	25.750	88.289	68.173	28.163	- 113.177	- 47.166	7.363
1500	25.760	90.066	69.574	30.738	- 112.759	- 42.467	6.187
1600	25.770	91.729	70.907	33.315	- 112.349	- 37.790	5.162
1700	25.780	93.291	72.178	35.892	- 111.948	- 33.144	4.261
1800	25.790	94.765	73.393	38.471	- 111.554	- 28.520	3.463
1900	25.800	96.160	74.554	41.050	- 111.169	- 23.917	2.751
2000	25.810	97.484	75.668	43.631	- 110.793	- 19.339	2.113

June 30, 1962; June 30, 1964

ZIRCONIUM TRIIODIDE (ZrI_3) (CRYSTAL) MOL. WT. = 471.950

$S^\circ_{298.15}$ = [48.90] cal. mole^{-1} deg.$^{-1}$

T_s = [970]°K.

Td = [1000]°K.

$\Delta H_f^\circ{}_0$ = [-95] kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = [-95] kcal. mole^{-1}

$\Delta H_s^\circ{}_{298.15}$ = [42] kcal. mole^{-1}

Heat of Formation.

E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956), studied the reaction $Zr(c) + 3ZrI_4(g) = 4ZrI_3(c)$ in the temperature range 473 to 973°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, at a number of temperatures, as a function of reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature the equilibrium constant was assumed to be 1, and $\Delta H_{r\ 298}$ accordingly calculated. These values and the heat of formation of $ZrI_4(g)$ [see ZrI_4 table] were used to compute a series of values for the heat of formation of $ZrI_3(c)$ at 298.15°K. The following table gives representative values at four temperatures.

T(°K.)	K_p	$\Delta H_{r\ 298}$	$\Delta H_f^\circ{}_{298.15}$ [$ZrI_3(c)$]
500	1	-66.0 kcal. mole^{-1}	-80.2 kcal. mole^{-1}
700	1	-90.3 kcal. mole^{-1}	-86.2 kcal. mole^{-1}
900	1	-113.5 kcal. mole^{-1}	-92.1 kcal. mole^{-1}
1100	1	-135.9 kcal. mole^{-1}	-97.7 kcal. mole^{-1}

If one assumes an initial pressure of from 5 to 10 atm. for ZrI_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrI_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate that the reaction proceeds to the extent of 88% at 973°K. From this it was assumed that at around 1000°K. the equilibrium constant attains a value of 1 giving -95 kcal. mole^{-1} for the heat of formation of ZrI_3 at 298.15°K.

Their data was subjected to a second law calculation but the results are of doubtful value in view of the uncertainty in the attainment of thermodynamic equilibrium at the lower temperatures. The limits of error assigned to the heat of formation are ±15 kcal. mole^{-1} corresponding to a temperature spread of ±500° in the above table.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $ZrBr_4(c)$ [see $ZrBr_4(c)$ table]. The values Θ_D = 60°K. and Θ_E = 115°K. were taken to be the same as those estimated for $ZrI_4(c)$. The internal contribution was obtained from the estimated ZrI_3 vibrational frequencies and the anharmonicity factor, "a", was taken to be 2.5 X 10^{-3}. The specific heat above 300°K. was obtained by graphical extrapolation.

For the above estimation, it was assumed that the crystalline lattice is made up of ZrI_3 molecules. However, E. Holze [see R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] came to the conclusion that crystalline ZrI_3 is composed of a chain lattice of $(Zr_2I_6)_n$ units. The results of an analysis for a crystalline lattice composed of Zr_2I_6 units would probably not differ significantly from that for a crystalline lattice composed of ZrI_3 units since both are approaching the classical harmonic heat capacity of 12R calories per formula weight of ZrI_3 at relatively low temperatures.

Until more quantitative information becomes available, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrI_3.

Temperature of Disproportionation.

As described in the "Heat of Formation" section, this was assumed to be 1000° ± 500°K.

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.

Zirconium Triiodide (ZrI_3)

(Ideal Gas) Mol. Wt. = 471.950

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.876	-51.828	-51.828	INFINITE
100	16.291	75.199	111.712	-3.651	-51.909	-56.905	124.359
200	18.704	87.442	96.799	-1.871	-52.419	-61.709	67.429
298	19.317	95.047	95.047	.000	-53.000	-66.148	48.486
300	19.324	95.166	95.047	.036	-53.011	-66.229	48.246
400	19.557	100.762	95.808	1.981	-59.459	-70.334	38.427
500	19.669	105.139	97.253	3.943	-75.452	-71.531	31.264
600	19.730	108.731	98.875	5.914	-75.531	-70.740	25.766
700	19.768	111.776	100.506	7.889	-75.630	-69.934	21.833
800	19.792	114.417	102.084	9.867	-75.741	-69.112	18.880
900	19.809	116.749	103.586	11.847	-75.862	-68.277	16.579
1000	19.821	118.837	105.009	13.828	-75.992	-67.426	14.735
1100	19.830	120.727	106.353	15.811	-76.140	-66.564	13.224
1200	19.837	122.452	107.624	17.794	-77.258	-65.638	11.954
1300	19.842	124.040	108.826	19.778	-77.412	-64.663	10.870
1400	19.846	125.511	109.966	21.763	-77.577	-63.677	9.940
1500	19.850	126.880	111.049	23.747	-77.750	-62.679	9.132
1600	19.852	128.161	112.079	25.733	-77.931	-61.664	8.423
1700	19.855	129.365	113.060	27.718	-78.123	-60.644	7.796
1800	19.857	130.500	113.998	29.703	-78.322	-59.610	7.237
1900	19.858	131.574	114.895	31.689	-78.530	-58.564	6.736
2000	19.860	132.592	115.755	33.675	-78.748	-57.512	6.284
2100	19.861	133.561	116.580	35.661	-78.974	-56.442	5.874
2200	19.862	134.485	117.373	37.647	-84.112	-55.200	5.483
2300	19.863	135.368	118.136	39.634	-84.362	-53.879	5.119
2400	19.864	136.213	118.872	41.620	-84.613	-52.547	4.785
2500	19.864	137.024	119.582	43.606	-84.867	-51.207	4.476
2600	19.865	137.803	120.268	45.593	-85.123	-49.856	4.191
2700	19.866	138.553	120.931	47.579	-85.381	-48.494	3.925
2800	19.866	139.276	121.574	49.566	-85.641	-47.122	3.678
2900	19.866	139.973	122.196	51.552	-85.903	-45.740	3.447
3000	19.867	140.646	122.800	53.539	-86.167	-44.354	3.231
3100	19.867	141.298	123.386	55.526	-86.433	-42.956	3.028
3200	19.868	141.928	123.956	57.513	-86.700	-41.550	2.838
3300	19.868	142.540	124.510	59.499	-86.970	-40.131	2.658
3400	19.868	143.133	125.049	61.486	-87.242	-38.708	2.488
3500	19.868	143.709	125.574	63.473	-87.515	-37.276	2.327
3600	19.869	144.269	126.085	65.460	-87.791	-35.840	2.176
3700	19.869	144.813	126.584	67.447	-88.069	-34.395	2.032
3800	19.869	145.343	127.071	69.434	-88.348	-32.938	1.894
3900	19.869	145.859	127.546	71.420	-88.630	-31.473	1.764
4000	19.869	146.362	128.010	73.407	-88.914	-30.010	1.640
4100	19.870	146.853	128.464	75.394	-89.199	-28.527	1.521
4200	19.870	147.331	128.907	77.381	-89.487	-27.043	1.407
4300	19.870	147.799	129.341	79.368	-89.776	-25.558	1.299
4400	19.870	148.256	129.766	81.355	-90.069	-24.063	1.195
4500	19.870	148.702	130.182	83.342	-90.363	-22.556	1.095
4600	19.870	149.139	130.589	85.329	-90.658	-21.044	1.000
4700	19.870	149.566	130.988	87.316	-90.955	-19.531	.908
4800	19.870	149.985	131.380	89.303	-227.688	-16.482	.750
4900	19.870	150.394	131.764	91.290	-228.045	-12.079	.539
5000	19.871	150.796	132.140	93.277	-228.409	-7.668	.335
5100	19.871	151.189	132.510	95.264	-228.778	-3.252	.139
5200	19.871	151.575	132.873	97.252	-229.155	1.175	-.049
5300	19.871	151.954	133.229	99.239	-229.538	5.606	-.231
5400	19.871	152.325	133.580	101.226	-229.927	10.053	-.407
5500	19.871	152.690	133.924	103.213	-230.321	14.494	-.576
5600	19.871	153.048	134.262	105.200	-230.721	18.948	-.739
5700	19.871	153.400	134.595	107.187	-231.125	23.408	-.897
5800	19.871	153.745	134.922	109.174	-231.534	27.882	-1.051
5900	19.871	154.085	135.244	111.161	-231.946	32.357	-1.199
6000	19.871	154.419	135.561	113.148	-232.363	36.840	-1.342

June 30, 1964

ZIRCONIUM TRIIODIDE (ZrI_3) (IDEAL GAS) MOL. WT. = 471.950

Point Group = [C_{3v}]

$S^\circ_{298.15}$ = [95.05] cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = [2]

$\Delta H^\circ_{f\ 0}$ = [-52] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-53] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[195] (1)
[88] (1)
[220] (2)
[65] (2)

Bond Distance: Zr-I = [2.59] Å

Bond Angle: I-Zr-I = [101]°

σ = [3]

Product of the Moments of Inertia: $I_AI_BI_C$ = [1.1545 X 10^{-110}] gm.^{3} cm.^{6}

Heat of Formation.

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole^{-1} greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium triiodide, the heat of formation from the gaseous atoms was -275 kcal. mole^{-1} and from the elements in their standard state, -53 kcal. mole^{-1}.

Heat Capacity and Entropy.

The measured internuclear distances for the triiodides of phosphorus, arsenic, and antimony were plotted as a function of the atomic weight of these elements and a smooth curve was drawn through the points. The bond distance in ZrI_3 was taken from this plot. The bond angle was assumed to be 101°. The individual moments of inertia are: $I_A = I_B = 1.8520 \times 10^{-37}$ gm. cm.^{2}, $I_C = 3.3661 \times 10^{-37}$ gm. cm.^{2}.

Force constants for ZrI_3 were estimated from those of the triiodides of phosphorus and arsenic. These were used in a valence force field calculation giving $\omega_1 = 195$, $\omega_2 = 88$, $\omega_3 = 181$, and $\omega_4 = 65$ cm.$^{-1}$ For the fluorides and chlorides of P, As, and Sb, ω_1 is greater than ω_3 but there appears to be a reversal as one goes to the bromides and iodides with ω_3 becoming greater than ω_1. An empirical correlation procedure for ZrI_3 gave $\omega_1 = 195$, $\omega_2 = 90$, $\omega_3 = 220$, and $\omega_4 = 65$ cm.$^{-1}$ in which $\omega_3 > \omega_1$. Since $\omega_3 > \omega_1$ for PI_3 and AsI_3, the correlation value for ω_3 was used to represent this frequency in ZrI_3.

Lead Tetraiodide (PbI_4)

(Ideal Gas) Mol. Wt. = 714.85 INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-6.603	.949	.949	INFINITE
100	22.757	84.703	133.594	-4.889	.782	-3.892	8.505
200	24.923	101.355	113.728	-2.475	.237	-8.361	9.136
298	25.410	111.416	111.416	.000	-.400	-12.450	9.126
300	25.415	111.573	111.416	.047	-.413	-12.524	9.123
400	25.596	118.913	112.416	2.599	-8.857	-16.181	8.840
500	25.681	124.634	114.308	5.163	-30.012	-16.003	6.995
600	25.727	129.321	116.431	7.734	-29.925	-13.210	4.812
700	25.756	133.289	118.563	10.308	-31.019	-10.240	3.197
800	25.774	136.730	120.624	12.885	-30.965	-7.273	1.987
900	25.787	139.766	122.585	15.463	-30.909	-4.316	1.048
1000	25.796	142.484	124.442	18.042	-30.846	-1.364	.298
1100	25.802	144.943	126.195	20.622	-30.779	1.580	-.314
1200	25.808	147.188	127.853	23.202	-30.708	4.520	-.823
1300	25.812	149.254	129.420	25.783	-30.631	7.453	-1.253
1400	25.815	151.167	130.906	28.365	-30.558	10.379	-1.620
1500	25.817	152.948	132.317	30.946	-30.487	13.300	-1.938
1600	25.819	154.614	133.659	33.528	-30.420	16.220	-2.215
1700	25.821	156.179	134.938	36.110	-30.359	19.132	-2.460
1800	25.823	157.655	136.160	38.692	-30.305	22.040	-2.676
1900	25.824	159.052	137.328	41.274	-30.259	24.947	-2.869
2000	25.825	160.376	138.448	43.857	-30.219	27.849	-3.043
2100	25.826	161.636	139.522	46.440	-72.636	32.306	-3.362
2200	25.827	162.838	140.555	49.022	-72.520	37.298	-3.705
2300	25.827	163.986	141.549	51.605	-72.426	42.289	-4.018
2400	25.828	165.085	142.507	54.187	-72.356	47.278	-4.305
2500	25.828	166.139	143.431	56.770	-72.312	52.258	-4.568
2600	25.829	167.152	144.324	59.353	-72.291	57.241	-4.811
2700	25.829	168.127	145.188	61.936	-72.294	62.223	-5.036
2800	25.830	169.066	146.024	64.519	-72.321	67.208	-5.246
2900	25.830	169.973	146.834	67.102	-72.368	72.192	-5.440
3000	25.830	170.849	147.620	69.685	-72.437	77.175	-5.622
3100	25.831	171.695	148.383	72.268	-72.524	82.165	-5.792
3200	25.831	172.515	149.124	74.851	-72.629	87.155	-5.952
3300	25.831	173.310	149.845	77.434	-72.750	92.153	-6.103
3400	25.831	174.081	150.547	80.017	-72.885	97.151	-6.245
3500	25.831	174.830	151.230	82.600	-73.032	102.156	-6.379
3600	25.832	175.558	151.896	85.184	-73.190	107.162	-6.505
3700	25.832	176.266	152.545	87.767	-73.358	112.172	-6.625
3800	25.832	176.955	153.178	90.350	-73.532	117.191	-6.740
3900	25.832	177.626	153.797	92.933	-73.715	122.215	-6.848
4000	25.832	178.280	154.400	95.516	-73.902	127.232	-6.951
4100	25.832	178.917	154.991	98.100	-74.092	132.271	-7.050
4200	25.832	179.540	155.568	100.683	-74.287	137.309	-7.145
4300	25.832	180.148	156.132	103.266	-74.484	142.340	-7.234
4400	25.833	180.742	156.685	105.849	-74.683	147.387	-7.320
4500	25.833	181.322	157.226	108.432	-74.882	152.440	-7.403
4600	25.833	181.890	157.756	111.016	-75.080	157.496	-7.482
4700	25.833	182.446	158.276	113.599	-75.277	162.545	-7.558
4800	25.833	182.989	158.785	116.182	-75.475	167.615	-7.631
4900	25.833	183.522	159.284	118.766	-75.670	172.681	-7.702
5000	25.833	184.044	159.774	121.348	-75.867	177.750	-7.769
5100	25.833	184.556	160.255	123.932	-76.058	182.821	-7.834
5200	25.833	185.057	160.727	126.515	-76.251	187.899	-7.897
5300	25.833	185.549	161.191	129.099	-76.439	192.985	-7.958
5400	25.833	186.032	161.647	131.682	-76.628	198.075	-8.016
5500	25.833	186.506	162.094	134.265	-76.815	203.157	-8.072
5600	25.833	186.971	162.534	136.849	-77.000	208.244	-8.127
5700	25.833	187.429	162.967	139.432	-77.185	213.340	-8.179
5800	25.833	187.878	163.393	142.015	-77.368	218.444	-8.231
5900	25.833	188.320	163.811	144.599	-77.549	223.541	-8.280
6000	25.834	188.754	164.224	147.182	-77.731	228.648	-8.328

June 30, 1962

Lead Tetraiodide (PbI_4) (Ideal Gas)

Mol. Wt. = 714.85

ΔH_f° 298.15 = [-0.4] kcal. mole^{-1}

$S^\circ_{298.15}$ = 111.4 cal. deg.$^{-1}$ mole^{-1}

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
137 (1)
37 (2)
168 (3)
48 (3)

Pb-I distance = 2.77 Å   I-Pb-I angle = 109° 28'

$I_AI_BI_C$ = 8.0044 X 10^{-110} g.^{3} cm.^{6} σ = 12

Heat of Formation. ΔH_f° 298.15 was estimated by comparison with the value of ΔH_f° 298.15 for PbI_2(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Titanium Tetraiodide (TiI_4)

(Crystal) GFW = 555.5176

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-6.965	-89.305	-89.305	INFINITE
100	24.061	28.695	84.359	-5.566	-89.498	-89.255	195.066
200	28.525	47.130	61.536	-2.881	-89.627	-88.961	97.212
298	30.026	58.831	58.831	.000	-89.800	-88.605	64.949
300	30.102	59.017	58.832	.056	-89.803	-88.597	64.543
400	35.400	74.583	60.393	5.676	-95.145	-88.041	48.103
500	35.400	82.482	64.050	9.216	-115.297	-84.372	36.879
600	35.400	88.937	67.676	12.756	-114.217	-78.291	28.517
700	35.400	94.394	71.113	16.296	-113.161	-72.387	22.600
800	35.400	99.121	74.325	19.836	-112.133	-66.631	18.203
900	35.400	103.290	77.317	23.376	-111.137	-61.004	14.814
1000	35.400	107.020	80.104	26.916	-110.171	-55.486	12.126
1100	35.400	110.394	82.706	30.456	-109.234	-50.062	9.946
1200	35.400	113.474	85.144	33.996	-109.264	-44.686	8.138
1300	35.400	116.308	87.434	37.536	-108.256	-39.345	6.614
1400	35.400	118.931	89.591	41.076	-107.269	-34.081	5.320
1500	35.400	121.373	91.629	44.616	-106.300	-28.890	4.209

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM TETRAIODIDE (TiI_4) (CRYSTAL) GFW = 555.5176

$\Delta Hf°_0$ = -89.3 ± 2.0 kcal/mol

$S°_{298.15}$ = 58.8 ± 1.6 gibbs/mol

$\Delta Hf°_{298.15}$ = -89.8 ± 2.0 kcal/mol

Tt = 379°K

ΔHt° = 2.37 ± 0.15 kcal/mol

Tm = 428°K

ΔHm° = 4.74 ± 0.15 kcal/mol

Heat of Formation

The heat of formation of TiI_4(c) was measured by Johnson et al. (1), based on the heats of hydrolysis of $TiBr_4$(c) and TiI_4(c) in sulfuric acid. These data result in a heat of reaction of -57.88 kcal/mol for the process $TiI_4(c) + 2Br_2(\ell) = TiBr_4(c) + 2I_2(c)$, when recalculated with revised values of $\Delta Hf°_{298}$ for HBr(aq) and HI(aq) (2). Combination of $\Delta Hr°_{298}$ with auxiliary JANAF data gives the adopted value of $\Delta Hf°_{298}$.

Heat Capacity and Entropy

King et al. (3) reported the heat capacity and enthalpy of TiI_4(c) over the temperature range 51° to 428°K. The value of $S°_{298}$ is calculated from these data based on $S°_{51}$ = 14.62 eu. The value of $H°_{51} - H°_0$ is calculated to be 0.356 kcal/mol from a Debye-Einstein extrapolation of the measured heat capacities.

Transition Data

A first order transition was observed by King et al. (2) at 379°K. They reported the measured value of 2.37 kcal/mol, noting that this value had an uncertainty of 0.15 kcal/mol due to hysteresis in the transition.

Melting Data

The melting temperature and heat of melting were reported by King et al. (2). The large uncertainty on ΔHm° is due to the uncertainty and close proximity of the transition at 379°K.

References

1. W. H. Johnson, A. A. Gilliland, and E. J. Prosen, J. Res. Natl. Bur. Std., 63A, 161 (1959).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Titanium Tetraiodide (TiI_4)

(Liquid) GFW = 555.5176

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	37.400	74.532	74.531	.000	- 83.250	- 86.736	63.579
300	37.400	74.763	74.532	.069	- 83.240	- 86.757	63.202
400	37.400	85.522	75.999	3.809	- 90.462	- 87.733	47.935
500	37.400	93.868	78.769	7.549	- 110.414	- 85.182	37.233
600	37.400	100.687	81.871	11.289	- 109.134	- 80.258	29.234
700	37.400	106.452	84.982	15.029	- 107.878	- 75.545	23.586
800	37.400	111.446	87.984	18.769	- 106.650	- 71.008	19.399
900	37.400	115.851	90.841	22.509	- 105.454	- 66.626	16.179
1000	37.400	119.791	93.542	26.249	- 104.288	- 62.374	13.632
1100	37.400	123.356	96.093	29.989	- 103.151	- 58.238	11.571
1200	37.400	126.610	98.503	33.729	- 102.981	- 54.166	9.865
1300	37.400	129.604	100.781	37.469	- 101.773	- 50.147	8.430
1400	37.400	102.376	102.940	41.209	- 100.586	- 46.220	7.215
1500	37.400	134.956	104.990	44.949	- 99.417	- 42.381	6.175

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM TETRAIODIDE (TiI_4) (LIQUID) GFW = 555.5176

$S^\circ_{298.15}$ = 74.532 gibbs/mol

Tm = 428°K

Tb = 652.6°K

ΔHf°_0 = unknown

$\Delta Hf^\circ_{298.15}$ = -83.25 kcal/mol

ΔHm° = 4.74 ± 0.15 kcal/mol

ΔHv° = 13.50 ± 0.5 kcal/mol

Heat of Formation

The heat of formation of $TiI_4(\ell)$ is calculated from the heat of melting, ΔHm°_{428}, the heat of formation of $TiI_4(c)$, and the values of $H^\circ_{428} - H^\circ_{298.15}$ for both crystal and liquid.

Heat Capacity and Entropy

King et al. (1) reported the enthalpy of $TiI_4(\ell)$ above the melting temperature. The heat capacity derived from these data is constant. The entropy, S°_{298}, of $TiI_4(\ell)$ is calculated from ΔSm°_{428} and the values of $S^\circ_{428} - S^\circ_{298.15}$ of both crystal and liquid.

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, Tb, is taken as the point at which Kp = 1 for the reaction $TiI_4(\ell) = TiI_4(g)$. The heat of vaporization is calculated as the difference between ΔHf° of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $TiI_4(g)$.

Reference

1. E. G. King, W. W. Weller, A. U. Christensen, and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Titanium Tetraiodide (TiI_4)

(Ideal Gas) GFW = 555.5176

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.169	-64.979	-64.979	INFINITE
100	20.496	78.168	124.839	-4.667	-65.069	-69.773	152.488
200	23.946	93.703	105.734	-2.406	-65.622	-74.271	81.159
298	24.917	103.479	103.479	.000	-66.270	-78.386	57.459
300	24.928	103.633	103.479	.046	-66.283	-78.461	57.159
400	25.309	110.864	104.462	2.560	-74.731	-82.139	44.879
500	25.493	116.533	106.330	5.102	-95.881	-81.982	35.834
600	25.595	121.191	108.430	7.657	-95.786	-79.213	28.853
700	25.658	125.142	110.543	10.219	-95.708	-76.457	23.871
800	25.698	128.571	112.586	12.787	-95.652	-73.710	20.137
900	25.727	131.599	114.534	15.359	-95.624	-70.970	17.234
1000	25.747	134.311	116.378	17.932	-95.625	-68.230	14.912
1100	25.762	136.766	118.122	20.508	-95.652	-65.490	13.012
1200	25.773	139.008	119.770	23.085	-96.645	-62.708	11.421
1300	25.782	141.071	121.331	25.662	-96.600	-59.881	10.067
1400	25.789	142.982	122.810	28.241	-96.574	-57.057	8.907
1500	25.795	144.761	124.215	30.820	-96.566	-54.238	7.902
1600	25.799	146.426	125.551	33.400	-96.577	-51.411	7.02
1700	25.803	147.990	126.826	35.980	-96.612	-48.589	6.247
1800	25.806	149.465	128.043	38.560	-96.671	-45.764	5.556
1900	25.809	150.861	129.207	41.141	-96.755	-42.933	4.938
2000	25.811	152.185	130.323	43.722	-101.312	-39.947	4.365
2100	25.813	153.444	131.395	46.303	-101.423	-36.873	3.837
2200	25.815	154.645	132.424	48.885	-101.537	-33.799	3.358
2300	25.817	155.792	133.416	51.466	-101.654	-30.716	2.919
2400	25.818	156.891	134.371	54.048	-101.772	-27.627	2.516
2500	25.819	157.945	135.293	56.630	-101.894	-24.537	2.145
2600	25.820	158.958	136.184	59.212	-102.018	-21.441	1.802
2700	25.821	159.932	137.046	61.794	-102.146	-18.339	1.484
2800	25.822	160.871	137.880	64.376	-102.276	-15.230	1.189
2900	25.823	161.778	138.688	66.959	-102.407	-12.117	.913
3000	25.823	162.653	139.473	69.541	-102.543	-9.006	.656
3100	25.824	163.500	140.234	72.123	-102.681	-5.882	.415
3200	25.825	164.320	140.974	74.706	-102.820	-2.762	.189
3300	25.825	165.114	141.694	77.288	-102.964	.371	-.025
3400	25.826	165.885	142.394	79.871	-103.109	3.504	-.225
3500	25.826	166.634	143.076	82.453	-103.257	6.644	-.415
3600	25.826	167.361	143.740	85.036	-205.034	10.046	-.610
3700	25.827	168.069	144.388	87.619	-205.159	16.019	-.946
3800	25.827	168.758	145.021	90.201	-205.300	21.998	-1.265
3900	25.827	169.429	145.638	92.784	-205.457	27.986	-1.568
4000	25.828	170.083	146.241	95.367	-205.629	33.968	-1.856
4100	25.828	170.720	146.830	97.950	-205.816	39.969	-2.131
4200	25.828	171.343	147.406	100.532	-206.020	45.965	-2.392
4300	25.828	171.951	147.970	103.115	-206.237	51.959	-2.641
4400	25.829	172.544	148.522	105.698	-206.469	57.965	-2.879
4500	25.829	173.125	149.062	108.281	-206.714	63.985	-3.108
4600	25.829	173.692	149.592	110.864	-206.971	70.007	-3.326
4700	25.829	174.248	150.110	113.447	-207.240	76.024	-3.535
4800	25.829	174.792	150.619	116.030	-207.523	82.057	-3.736
4900	25.830	175.324	151.118	118.613	-207.817	88.092	-3.929
5000	25.830	175.846	151.607	121.196	-208.123	94.136	-4.115
5100	25.830	176.358	152.087	123.779	-208.437	100.181	-4.293
5200	25.830	176.859	152.559	126.362	-208.765	106.234	-4.465
5300	25.830	177.351	153.022	128.945	-209.100	112.296	-4.631
5400	25.830	177.834	153.477	131.528	-209.446	118.371	-4.791
5500	25.830	178.308	153.924	134.111	-209.799	124.441	-4.945
5600	25.830	178.773	154.364	136.694	-210.163	130.510	-5.093
5700	25.830	179.231	154.796	139.277	-210.533	136.605	-5.238
5800	25.831	179.680	155.221	141.860	-210.911	142.698	-5.377
5900	25.831	180.121	155.640	144.443	-211.295	148.797	-5.512
6000	25.831	180.556	156.051	147.026	-211.687	154.904	-5.642

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM TETRAIODIDE (TiI_4) (IDEAL GAS) GFW = 555.5176

Point Group T_d

ΔHf°_0 = -65.0 ± 2 kcal/mol

$S^\circ_{298.15}$ = 103.48 ± 2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -66.27 ± 2 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[175] (1)	[260] (3)
[55] (2)	[69] (3)

Bond Distance: Ti-I = [2.5] Å

Bond Angle: I-Ti-I = [109°28']

σ = 12

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.33 x 10^{-110}] g^3cm^6

Heat of Formation

The heat of formation of $TiI_4(g)$ is calculated from that of $TiI_4(\ell)$ and the heat of vaporization of the liquid. Blocher and Campbell (1) reported vapor pressure data for $TiI_4(\ell)$ over the temperature range 473° to 655°K. Second and third law analyses of these data give values for ΔHv°_{298} of 17.2 ± 0.1 and 16.98 kcal/mol, respectively, the third law drift being -0.4 ± 0.2 eu. The adopted value of ΔHf°_{298} is based on the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiBr_4(c)$, $TiBr_4(g)$ and $TiI_4(c)$ (2). The tetrahedral model is assumed by analogy with $TiCl_4(g)$ and $TiBr_4(g)$. The principal moments of inertia are: $I_A = I_B = I_C = 3.51 \times 10^{-37}$ g cm^2.

The vibrational frequencies of $TiI_4(g)$ have been estimated by Ushanova et al. (3). The given estimates are based on their predictions and valence force field calculations.

References

1. J. M. Blocher, Jr. and I. E. Campbell, J. Am. Chem. Soc., 69, 2100 (1947).
2. O. Hasoel and H. Kringstand, Z. Phys. Chem. 1315, 274 (1932).
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Zirconium Tetraiodide (ZrI_4)

(Crystal) Mol. Wt. = 598.86

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 7.139	- 115.414	- 115.414	INFINITE
100	24.645	31.267	86.777	- 5.551	- 115.496	- 115.370	252.128
200	28.426	49.822	64.085	- 2.853	- 115.677	- 115.173	125.849
298	29.543	61.412	61.412	.000	- 115.900	- 114.882	84.207
300	29.556	61.595	61.413	.055	- 115.904	- 114.875	83.682
400	30.170	70.188	62.580	3.043	- 123.895	- 114.221	62.404
500	30.550	76.966	64.804	6.081	- 144.574	- 109.846	48.011
600	30.810	82.561	67.310	9.150	- 144.003	- 102.956	37.500
700	30.990	87.325	69.838	12.241	- 143.435	- 96.160	30.021
800	31.100	91.471	72.288	15.346	- 142.870	- 89.443	24.434
900	31.180	95.139	74.627	18.460	- 142.309	- 82.800	20.106
1000	31.220	98.426	76.846	21.580	- 141.753	- 76.216	16.656
1100	31.250	101.403	78.945	24.704	- 141.213	- 69.690	13.845
1200	31.260	104.123	80.931	27.830	- 141.643	- 63.163	11.503
1300	31.270	106.625	82.813	30.956	- 141.109	- 56.644	9.522
1400	31.280	108.943	84.598	34.084	- 140.587	- 50.167	7.831
1500	31.290	111.102	86.293	37.212	- 140.073	- 43.729	6.371

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TETRAIODIDE (ZrI_4) (CRYSTAL) MOL. WT. = 598.86

$\Delta H_f^\circ{}_0$ = [-115.4] ± 1.0 kcal. mole⁻¹

$S^\circ_{298.15}$ = [61.41] cal. mole⁻¹ deg.⁻¹

$\Delta H_f^\circ{}_{298.15}$ = -115.9 ± 0.8 kcal. mole⁻¹

T_s = 704°K.

$\Delta H_s^\circ{}_{298.15}$ = 31.0 ± 0.7 kcal. mole⁻¹

Heat of Formation.

A. G. Turnbull, J. Phys. Chem. 65, 1652 (1961), measured the heat of reaction for the following reactions:

(1) $ZrI_4(c) + 4NaOH(aq.) = ZrO_2(hyd.) + 4NaI(aq.) + 2H_2O$

(2) $ZrI_4(c) + 2H_2O = ZrOOH^+(aq.) + 4I^-(aq.) + 3H^+(aq.)$

Turnbull used the same procedure to calculate the heat of formation of zirconium tetraiodide as he did for zirconium tetrabromide [see $ZrBr_4$ table]. The heat of formation of the solid zirconium tetraiodide from reaction (1) was -115.6 ± 0.8 kcal. mole⁻¹ and from reaction (2) was -116.3 ± 0.8 kcal. mole⁻¹. An average of these was taken as the heat of formation of the tetraiodide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated in the same manner as for $ZrBr_4(c)$ [see $ZrBr_4(c)$ table]. The values, $\Theta_D^{3^\circ}$ = 60°K. and $\Theta_E^{3^\circ}$ = 115°K. were used in the analysis. The value, a = 1.5 X 10⁻³, was obtained from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. represents a graphical extrapolation.

Melting.

T_m = 772°K. was reported by O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.). Four values of "a" were used to compute the thermodynamic functions of the solid. That value of "a" was chosen which gave agreement between 2nd and 3rd law values for the heat of sublimation. The sublimation results for the four values of "a" are given in the following table.

"a"	$\Delta H_{s(298)}$ [3rd law]	$\Delta H_{s(298)}$ [2nd law]
3.0 X 10⁻³	29.98 kcal. mole⁻¹	31.65 kcal. mole⁻¹
2.5 X 10⁻³	30.39 kcal. mole⁻¹	31.34 kcal. mole⁻¹
2.0 X 10⁻³	30.76 kcal. mole⁻¹	31.17 kcal. mole⁻¹
1.5 X 10⁻³	31.02 kcal. mole⁻¹	31.04 kcal. mole⁻¹

A temperature dependent third law heat of sublimation at 298°K. was obtained for "a = 3.0 X 10⁻³"; this temperature trend decreased for smaller values of "a" and there was essentially no temperature dependnece for "a = 1.5 X 10⁻³". Various high temperature extrapolations were not used since, by experience with $ZrBr_4(c)$, they produced insignificant changes in the heat values. The heat of sublimation was taken to be 31.0 kcal. mole⁻¹ since the entire analysis was conducted to obtain 2nd and 3rd law agreement.

From experience with a number of other compounds, that were found to be amenable to the theoretical treatment used here, the value "a = 1.5 X 10⁻³" appears to be rather low, but no further analysis was deemed practical since all parameters for the gas and solid are estimated.

The sublimation point obtained from the free energy crossover of solid and gas was 703°K. The value reported by Rahlfs and Fischer (loc. cit.), was 704°K. The sublimation point was taken as 704°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Zirconium Tetraiodide (ZrI_4)

(Ideal Gas) Mol. Wt. = 598.86

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-6.330	-83.605	-83.605	INFINITE
100	21.258	80.985	128.418	-4.743	-83.688	-88.534	193.481
200	24.285	96.900	109.050	-2.430	-84.254	-93.166	101.802
298	25.090	106.775	106.775	.000	-84.900	-97.407	71.398
300	25.099	106.930	106.776	.046	-84.913	-97.484	71.014
400	25.411	114.200	107.765	2.574	-93.364	-101.294	55.342
500	25.560	119.888	109.641	5.123	-114.532	-101.265	44.261
600	25.643	124.556	111.750	7.684	-114.469	-98.620	35.920
700	25.693	128.513	113.869	10.251	-114.425	-95.981	29.965
800	25.726	131.946	115.919	12.822	-114.394	-93.348	25.500
900	25.749	134.978	117.871	15.396	-114.373	-90.719	22.029
1000	25.765	137.691	119.720	17.971	-114.362	-88.090	19.251
1100	25.777	140.148	121.467	20.549	-114.368	-85.464	16.979
1200	25.786	142.391	123.119	23.127	-115.346	-82.788	15.077
1300	25.793	144.455	124.681	25.706	-115.359	-80.074	13.461
1400	25.799	146.367	126.163	28.285	-115.386	-77.359	12.076
1500	25.803	148.147	127.570	30.865	-115.420	-74.643	10.875
1600	25.807	149.812	128.909	33.446	-115.462	-71.919	9.823
1700	25.810	151.377	130.185	36.027	-115.516	-69.198	8.896
1800	25.813	152.852	131.403	38.608	-115.578	-66.471	8.070
1900	25.815	154.248	132.569	41.189	-115.651	-63.741	7.331
2000	25.817	155.572	133.687	43.771	-115.733	-61.011	6.667
2100	25.819	156.832	134.759	46.353	-115.823	-58.270	6.064
2200	25.820	158.033	135.790	48.935	-120.827	-55.364	5.500
2300	25.821	159.181	136.782	51.517	-120.943	-52.384	4.977
2400	25.822	160.280	137.738	54.099	-121.061	-49.399	4.498
2500	25.823	161.334	138.661	56.681	-121.183	-46.412	4.057
2600	25.824	162.347	139.553	59.264	-121.306	-43.420	3.650
2700	25.825	163.321	140.415	61.846	-121.434	-40.421	3.272
2800	25.825	164.260	141.250	64.428	-121.564	-37.416	2.920
2900	25.826	165.167	142.059	67.011	-121.695	-34.407	2.593
3000	25.927	166.042	142.844	69.594	-121.830	-31.399	2.287
3100	25.827	166.889	143.606	72.176	-121.968	-28.382	2.001
3200	25.828	167.709	144.347	74.759	-122.107	-25.362	1.732
3300	25.828	168.504	145.067	77.342	-122.250	-22.332	1.479
3400	25.828	169.275	145.768	79.925	-122.395	-19.304	1.241
3500	25.829	170.024	146.450	82.508	-122.542	-16.267	1.016
3600	25.829	170.751	147.115	85.090	-122.694	-13.233	.803
3700	25.829	171.459	147.763	87.673	-122.847	-10.192	.602
3800	25.830	172.148	148.396	90.256	-123.002	-7.143	.411
3900	25.830	172.819	149.014	92.839	-123.161	-4.089	.229
4000	25.830	173.473	149.617	95.422	-123.322	-1.040	.057
4100	25.830	174.110	150.207	98.005	-123.485	2.027	-.108
4200	25.830	174.733	150.783	100.588	-123.652	5.091	-.265
4300	25.831	175.341	151.347	103.171	-123.821	8.152	-.414
4400	25.831	175.935	151.899	105.754	-123.994	11.220	-.557
4500	25.831	176.515	152.440	108.338	-124.168	14.301	-.695
4600	25.831	177.083	152.970	110.921	-124.345	17.382	-.826
4700	25.831	177.638	153.489	113.504	-124.524	20.460	-.951
4800	25.831	178.182	153.997	116.087	-261.140	25.074	-1.142
4900	25.831	178.715	154.496	118.670	-261.380	31.039	-1.384
5000	25.832	179.237	154.986	121.253	-261.629	37.008	-1.618
5100	25.832	179.748	155.467	123.836	-261.882	42.980	-1.842
5200	25.832	180.250	155.938	126.419	-262.146	48.961	-2.058
5300	25.832	180.742	156.402	129.003	-262.414	54.945	-2.266
5400	25.832	181.225	156.857	131.586	-262.690	60.945	-2.466
5500	25.832	181.699	157.304	134.169	-262.971	66.932	-2.660
5600	25.832	182.160	157.744	136.752	-263.260	72.930	-2.846
5700	25.832	182.621	158.177	139.335	-263.553	78.936	-3.026
5800	25.832	183.071	158.602	141.919	-263.851	84.951	-3.201
5900	25.832	183.512	159.020	144.502	-264.153	90.967	-3.369
6000	25.832	183.946	159.432	147.085	-264.461	96.989	-3.533

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TETRAIODIDE (ZrI_4) (IDEAL GAS) MOL. WT. = 598.86

Point Group = [T_d]

S°_{298} = [106.78] cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-83.6] ± 1.7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298}$ = -84.9 ± 1.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[146] (1)
[45] (2)
[237] (3)
[58] (3)

Bond Distance: Zr-I = [2.68] Å

σ = [12]

Bond Angle: I-Zr-I = [109° 28']

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.5718 X 10^{-110}] gm.^{3} cm.^{6}

Heat of Formation.

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy.

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Godnev, A. M. Aleksandrovskaya, and I. V. Regina, Optics and Spectroscopy 7, 172 (1959), estimated the interatomic distance and report 2.67 Å as the Zr-I distance. The I-Zr-I angle was taken as the tetrahedral angle. The three principal moments of inertia are: $I_A = I_B = I_C$ = 4.0355 X 10^{-37} gm. cm.^{2}.

The fundamental vibrational frequencies are estimated. The product of ω_1 and internuclear distance for the tetraiodides of Pb, Ti, Ge, and Sn was found to be approximately constant. Using the estimated Zr-I internuclear distance a value of 147 cm.$^{-1}$ was obtained for ω_1. Plots of ω_1 and ω_2 versus internuclear distance for these molecules were constructed and smooth curves drawn through the points. Values of ω_1 and ω_2 for ZrI_4 were read off from these plots; they were 146 cm.$^{-1}$ and 44 cm.$^{-1}$ respectively. Using ω_1 = 146 cm.$^{-1}$ and ω_2 = 45 cm.$^{-1}$, ω_3 = 237 cm.$^{-1}$ and ω_4 = 58 cm.$^{-1}$ were obtained from a valence force field calculation. Godnev, Aleksandrovskaya, and Regina (loc. cit.) estimated the vibrational frequencies and reported ω_1 = 152 cm.$^{-1}$, ω_2 = 44 cm.$^{-1}$, ω_3 = 211 cm.$^{-1}$ and ω_4 = 55 cm.$^{-1}$.

Potassium (K)

(Reference State) Mol. Wt. = 39.100

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.693	.000	.000	.000
100	5.887	8.509	21.296	-1.279	.000	.000	.000
200	6.454	12.785	16.078	-.659	.000	.000	.000
298	7.050	15.457	15.457	.000	.000	.000	.000
300	7.068	15.501	15.457	.013	.000	.000	.000
400	7.528	19.332	16.015	1.327	.000	.000	.000
500	7.336	20.990	16.851	2.070	.000	.000	.000
600	7.203	22.315	17.655	2.796	.000	.000	.000
700	7.128	23.419	18.401	3.512	.000	.000	.000
800	7.112	24.389	19.089	4.224	.000	.000	.000
900	7.155	25.208	19.723	4.936	.000	.000	.000
1000	7.256	25.967	20.310	5.657	.000	.000	.000
1100	4.966	44.782	21.788	25.294	.000	.000	.000
1200	4.968	45.215	23.722	25.791	.000	.000	.000
1300	4.969	45.612	25.391	26.288	.000	.000	.000
1400	4.970	45.981	26.849	26.785	.000	.000	.000
1500	4.972	46.324	28.136	27.282	.000	.000	.000
1600	4.975	46.645	29.283	27.779	.000	.000	.000
1700	4.980	46.946	30.313	28.277	.000	.000	.000
1800	4.988	47.231	31.245	28.775	.000	.000	.000
1900	4.999	47.501	32.094	29.275	.000	.000	.000
2000	5.013	47.758	32.870	29.775	.000	.000	.000
2100	5.033	48.003	33.585	30.277	.000	.000	.000
2200	5.057	48.238	34.246	30.782	.000	.000	.000
2300	5.087	48.463	34.859	31.289	.000	.000	.000
2400	5.122	48.680	35.431	31.799	.000	.000	.000
2500	5.164	48.890	35.965	32.314	.000	.000	.000
2600	5.213	49.094	36.466	32.832	.000	.000	.000
2700	5.270	49.291	36.937	33.356	.000	.000	.000
2800	5.334	49.484	37.382	33.887	.000	.000	.000
2900	5.407	49.673	37.802	34.424	.000	.000	.000
3000	5.489	49.857	38.201	34.968	.000	.000	.000
3100	5.582	50.039	38.580	35.522	.000	.000	.000
3200	5.685	50.218	38.941	36.085	.000	.000	.000
3300	5.802	50.394	39.285	36.659	.000	.000	.000
3400	5.932	50.569	39.615	37.246	.000	.000	.000
3500	6.079	50.743	39.930	37.846	.000	.000	.000
3600	6.242	50.917	40.233	38.462	.000	.000	.000
3700	6.426	51.090	40.524	39.095	.000	.000	.000
3800	6.630	51.264	40.804	39.748	.000	.000	.000
3900	6.858	51.439	41.075	40.422	.000	.000	.000
4000	7.111	51.616	41.336	41.120	.000	.000	.000
4100	7.392	51.795	41.589	41.845	.000	.000	.000
4200	7.701	51.977	41.834	42.600	.000	.000	.000
4300	8.041	52.162	42.072	43.386	.000	.000	.000
4400	8.412	52.351	42.304	44.209	.000	.000	.000
4500	8.815	52.545	42.529	45.070	.000	.000	.000
4600	9.250	52.743	42.749	45.973	.000	.000	.000
4700	9.717	52.947	42.964	46.921	.000	.000	.000
4800	10.215	53.157	43.174	47.917	.000	.000	.000
4900	10.741	53.373	43.380	48.965	.000	.000	.000
5000	11.294	53.595	43.582	50.066	.000	.000	.000
5100	11.871	53.825	43.781	51.224	.000	.000	.000
5200	12.467	54.061	43.976	52.441	.000	.000	.000
5300	13.079	54.304	44.169	53.718	.000	.000	.000
5400	13.701	54.554	44.359	55.057	.000	.000	.000
5500	14.327	54.811	44.546	56.459	.000	.000	.000
5600	14.953	55.075	44.732	57.923	.000	.000	.000
5700	15.572	55.345	44.916	59.449	.000	.000	.000
5800	16.178	55.621	45.098	61.037	.000	.000	.000
5900	16.765	55.903	45.279	62.684	.000	.000	.000
6000	17.326	56.190	45.458	64.389	.000	.000	.000

December 31, 1961

POTASSIUM (K) (REFERENCE STATE) MOL. WT. = 39.100

0°K. to 336.35°K.	Crystal
336.35°K. to 1043.7°K.	Liquid
1043.7°K. to 6000°K.	Ideal Monatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

Low temperature heat capacity measurements have been reported by L. M. Roberts [Proc. Phys. Soc. (London) 70B, 744-52 (1957)] (1.5°-20°K), by C. A. Krier, R. S. Craig, and W. E. Wallace [J. Phys. Chem. 61, 522 (1957)] (12°-320°K), by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas [Proc. Roy. Soc. (London), A233, 214 (1955)] (20°-330°K), by F. Simon and W. Zeidler [Z. physikal. Chem. 123, 383 (1926)] (15°-300°K), and by E. D. Eastman and W. H. Rodebush [J. Am. Chem. Soc. 40, 489 (1918)] (70°-290°K). A smooth curve was drawn through a large scale plot of the data, giving the most weight to the first three references. Above 300°K, the heat capacity data were adjusted to join smoothly with the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)].

Heat Capacity of Liquid and Heat of Melting.

The heat of melting and liquid heat capacity are from the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis (loc. cit.).

Heat of Sublimation, Ideal Gas Functions.

See tables for K(g) and $K_2(g)$ for details.

Potassium (K)

(Liquid) Mol. Wt. = 39.100

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	7.816	17.078	17.078	.000	.546	.063	- .046
300	7.810	17.126	17.078	.014	.547	.060	- .044
400	7.528	19.332	17.381	.781	.000	.000	.000
500	7.336	20.990	17.944	1.523	.000	.000	.000
600	7.203	22.315	18.566	2.250	.000	.000	.000
700	7.126	23.419	19.182	2.966	.000	.000	.000
800	7.112	24.369	19.772	3.677	.000	.000	.000
900	7.155	25.208	20.331	4.390	.000	.000	.000
1000	7.256	25.967	20.857	5.110	.000	.000	.000
1100	7.417	26.666	21.354	5.843	- 18.905	1.023	- .203
1200	7.620	27.320	21.824	6.595	- 18.650	2.824	- .514
1300	7.840	27.938	22.271	7.368	- 18.374	4.602	- .774
1400	8.060	28.527	22.697	8.163	- 18.076	6.359	- .993
1500	8.280	29.091	23.104	8.980	- 17.756	8.094	- 1.179
1600	8.500	29.632	23.495	9.819	- 17.414	9.806	- 1.339
1700	8.720	30.154	23.872	10.680	- 17.051	11.495	- 1.478
1800	8.940	30.659	24.235	11.563	- 16.666	13.164	- 1.598
1900	9.160	31.148	24.586	12.468	- 16.261	14.810	- 1.703
2000	9.380	31.623	24.926	13.395	- 15.834	16.435	- 1.796

December 31, 1961

POTASSIUM (K) (LIQUID) MOL. WT. = 39.100

$\Delta H_f^\circ{}_{298}$ = 0.546 kcal. mole^{-1}

T_m = 336.35°K.

T_b = 1037°K

ΔH_m = 0.558 kcal. mole^{-1}

ΔH_v = 18.38 kcal. per formula weight

Heat of Formation.

Back calculated from the heat of melting and the heat contents of solid and liquid at the melting point.

Heat of Melting and Heat Capacity.

The heat of melting, melting point, and liquid heat capacity were measured by T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)]. The heat capacity curve was extrapolated back to 298°K. and up to 2000°K. in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Potassium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1037°K. The vapor composition at this temperature is 94.5 mole % monatomic and 5.5 mole % diatomic gas. The heat of vaporization of 39.1 grams of liquid potassium to this equilibrium mixture is 18.38 kcal. See also tables for K(g) and $K_2(g)$.

Potassium, Monatomic (K)

(Ideal Gas) Mol. Wt. = 39.100

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-1.481	21.522	21.522	INFINITE
100	4.968	32.869	42.714	-.984	21.605	19.169	-41.891
200	4.968	36.313	38.751	-.488	21.481	16.776	-18.331
298	4.968	38.297	38.297	.000	21.310	14.500	-10.629
300	4.968	38.327	38.297	.009	21.306	14.458	-10.532
400	4.968	39.757	38.492	.506	20.489	12.319	-6.731
500	4.968	40.865	38.860	1.003	20.243	10.305	-4.504
600	4.968	41.771	39.272	1.500	20.014	8.340	-3.038
700	4.968	42.537	39.685	1.996	19.794	6.412	-2.002
800	4.968	43.200	40.084	2.493	19.579	4.514	-1.233
900	4.968	43.786	40.463	2.990	19.364	2.644	-.642
1000	4.968	44.309	40.822	3.487	19.140	.798	-.174
1100	4.966	44.782	41.161	3.984	.000	.000	.000
1200	4.968	45.215	41.481	4.481	.000	.000	.000
1300	4.969	45.612	41.784	4.977	.000	.000	.000
1400	4.970	45.981	42.070	5.474	.000	.000	.000
1500	4.972	46.324	42.343	5.971	.000	.000	.000
1600	4.975	46.645	42.602	6.469	.000	.000	.000
1700	4.980	46.946	42.848	6.966	.000	.000	.000
1800	4.988	47.231	43.084	7.465	.000	.000	.000
1900	4.999	47.501	43.310	7.964	.000	.000	.000
2000	5.013	47.758	43.526	8.465	.000	.000	.000
2100	5.033	48.003	43.733	8.967	.000	.000	.000
2200	5.057	48.238	43.932	9.471	.000	.000	.000
2300	5.087	48.463	44.125	9.978	.000	.000	.000
2400	5.122	48.680	44.310	10.489	.000	.000	.000
2500	5.164	48.890	44.489	11.003	.000	.000	.000
2600	5.213	49.094	44.662	11.522	.000	.000	.000
2700	5.270	49.291	44.830	12.046	.000	.000	.000
2800	5.334	49.484	44.993	12.576	.000	.000	.000
2900	5.407	49.673	45.151	13.113	.000	.000	.000
3000	5.489	49.857	45.305	13.658	.000	.000	.000
3100	5.582	50.039	45.454	14.211	.000	.000	.000
3200	5.685	50.218	45.601	14.775	.000	.000	.000
3300	5.802	50.394	45.743	15.349	.000	.000	.000
3400	5.932	50.569	45.883	15.935	.000	.000	.000
3500	6.079	50.743	46.019	16.536	.000	.000	.000
3600	6.242	50.917	46.153	17.152	.000	.000	.000
3700	6.426	51.090	46.284	17.785	.000	.000	.000
3800	6.630	51.264	46.412	18.438	.000	.000	.000
3900	6.858	51.440	46.539	19.112	.000	.000	.000
4000	7.111	51.616	46.664	19.810	.000	.000	.000
4100	7.392	51.795	46.787	20.535	.000	.000	.000
4200	7.701	51.977	46.908	21.289	.000	.000	.000
4300	8.041	52.162	47.028	22.076	.000	.000	.000
4400	8.412	52.351	47.147	22.899	.000	.000	.000
4500	8.815	52.545	47.265	23.760	.000	.000	.000
4600	9.250	52.743	47.382	24.663	.000	.000	.000
4700	9.717	52.947	47.498	25.611	.000	.000	.000
4800	10.215	53.157	47.614	26.607	.000	.000	.000
4900	10.741	53.373	47.729	27.655	.000	.000	.000
5000	11.294	53.595	47.844	28.756	.000	.000	.000
5100	11.871	53.825	47.959	29.915	.000	.000	.000
5200	12.467	54.061	48.074	31.131	.000	.000	.000
5300	13.079	54.304	48.189	32.409	.000	.000	.000
5400	13.701	54.555	48.305	33.747	.000	.000	.000
5500	14.327	54.812	48.421	35.149	.000	.000	.000
5600	14.953	55.075	48.537	36.613	.000	.000	.000
5700	15.572	55.346	48.654	38.139	.000	.000	.000
5800	16.178	55.622	48.772	39.727	.000	.000	.000
5900	16.765	55.903	48.891	41.374	.000	.000	.000
6000	17.326	56.190	49.010	43.079	.000	.000	.000

June 30, 1962

POTASSIUM, MONATOMIC (K) (IDEAL GAS) MOL. WT. = 39.100

ΔH°_{f0} = 21.522 kcal. mole^{-1}

Ground State = $^2S_{1/2}$

$\Delta H^\circ_{f\ 298.15}$ = 21.31 ± 0.20 kcal. mole^{-1}

$S^\circ_{298.15}$ = 38.297 cal. mole^{-1} deg.$^{-1}$

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.00	2	28999.27	2	33185.5	32
12985.17	2	29007.71	4	33578.5	32
13042.88	4	30185.44	10	33815.6	18
21026.58	2	30274.26	2	34059.8	24
21537.00	4	30614.08	32	34335.7	12
21534.70	6	31072.15	6	34472.3	6
24701.43	2	31072.90	12	34568.3	12
24720.17	4	31696.00	10	34662.3	12
27398.14	4	31765.37	2	34753.8	24
27397.10	6	31958.70	54	34858.4	54
27450.69	2	32229.20	6	34965.0	276
28127.85	14	32691.70	26		

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities from P. Risberg [Arkiv. Fysik 10, 583 (1956)] and C. E. Moore [Natl. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in excellent agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 83 (1955)].

Heat of Formation.

Evans, Munson, and Wagman (loc. cit.) have reviewed the vapor pressure data on potassium. Their calculations were revised slightly for the changes made in the functions for the condensed state. In addition, the recent data of M. M. Makansi, M. Madsen, W. A. Selke, and C. F. Bonilla, [J. Phys. Chem. 60, 138 (1956)] were considered in selecting the heat of sublimation of 21.31 ± 0.20 kcal. mole^{-1}. A review of the properties of potassium vapor using imperfect gas theory to establish the dimer dissociation energy has recently been published by R. J. Thorn and G. H. Winslow [J. Phys. Chem. 65, 1297 (1961)]. Although the imperfect gas treatment appears to be favored by the experimental data available, this could not be unequivocally established. Unpublished vapor pressure data cited by Thorn and Winslow are in agreement with the values selected here, assuming ideal gas behavior.

Potassium Unipositive Ion (K^+)

(Ideal Gas) At. Wt. = 39.100

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	36.919	36.919	.000	122.896	115.010	-84.301
300	4.968	36.950	36.919	.009	122.901	114.961	-83.745
400	4.968	38.379	37.114	.506	122.581	112.383	-61.400
500	4.968	39.488	37.482	1.003	122.832	109.804	-47.993
600	4.968	40.394	37.894	1.500	123.100	107.174	-39.036
700	4.968	41.159	38.307	1.996	123.376	104.498	-32.624
800	4.968	41.823	38.706	2.493	123.658	101.781	-27.804
900	4.968	42.408	39.086	2.990	123.940	99.031	-24.047
1000	4.968	42.931	39.445	3.487	124.213	96.248	-21.034
1100	4.968	43.405	39.783	3.984	105.570	94.463	-18.767
1200	4.968	43.837	40.104	4.481	106.067	93.433	-17.016
1300	4.968	44.235	40.406	4.977	106.562	92.357	-15.526
1400	4.968	44.603	40.693	5.474	107.059	91.248	-14.244
1500	4.968	44.946	40.965	5.971	107.556	90.100	-13.127
1600	4.968	45.267	41.224	6.468	108.053	88.920	-12.145
1700	4.968	45.568	41.471	6.965	108.549	87.708	-11.275
1800	4.968	45.852	41.706	7.461	109.043	86.468	-10.498
1900	4.968	46.120	41.932	7.958	109.537	85.202	-9.800
2000	4.968	46.375	42.148	8.455	110.031	83.909	-9.169
2100	4.968	46.618	42.355	8.952	110.523	82.589	-8.595
2200	4.968	46.849	42.554	9.449	111.012	81.248	-8.071
2300	4.968	47.070	42.745	9.945	111.497	79.882	-7.590
2400	4.968	47.281	42.930	10.442	111.981	78.499	-7.148
2500	4.968	47.484	43.108	10.939	112.460	77.093	-6.739
2600	4.968	47.679	43.280	11.436	112.936	75.670	-6.360
2700	4.968	47.866	43.447	11.933	113.406	74.229	-6.008
2800	4.968	48.047	43.608	12.430	113.869	72.767	-5.679
2900	4.968	48.221	43.764	12.926	114.324	71.294	-5.373
3000	4.968	48.390	43.915	13.423	114.774	69.798	-5.085
3100	4.968	48.552	44.062	13.920	115.214	68.296	-4.815
3200	4.968	48.710	44.205	14.417	115.645	66.778	-4.560
3300	4.968	48.863	44.344	14.914	116.065	65.241	-4.321
3400	4.968	49.011	44.479	15.410	116.470	63.696	-4.094
3500	4.968	49.155	44.610	15.907	116.864	62.138	-3.880
3600	4.968	49.295	44.739	16.404	117.242	60.571	-3.677
3700	4.968	49.431	44.864	16.901	117.603	58.988	-3.484
3800	4.968	49.564	44.986	17.398	117.944	57.398	-3.301
3900	4.968	49.693	45.105	17.895	118.264	55.801	-3.127
4000	4.968	49.819	45.221	18.391	118.558	54.194	-2.961
4100	4.968	49.941	45.335	18.888	118.827	52.583	-2.803
4200	4.968	50.061	45.446	19.385	119.066	50.967	-2.652
4300	4.968	50.178	45.554	19.882	119.274	49.343	-2.508
4400	4.968	50.292	45.661	20.379	119.445	47.716	-2.370
4500	4.968	50.404	45.765	20.875	119.576	46.082	-2.238
4600	4.968	50.513	45.867	21.372	119.667	44.448	-2.112
4700	4.968	50.620	45.967	21.869	119.713	42.812	-1.991
4800	4.968	50.725	46.065	22.366	119.711	41.173	-1.875
4900	4.968	50.827	46.161	22.863	119.657	39.542	-1.764
5000	4.968	50.927	46.256	23.359	119.548	37.908	-1.657
5100	4.968	51.026	46.348	23.856	119.384	36.275	-1.554
5200	4.968	51.122	46.439	24.353	119.161	34.651	-1.456
5300	4.968	51.217	46.528	24.850	118.878	33.023	-1.362
5400	4.968	51.310	46.616	25.347	118.533	31.404	-1.271
5500	4.968	51.401	46.702	25.844	118.125	29.795	-1.184
5600	4.968	51.490	46.787	26.340	117.653	28.193	-1.100
5700	4.968	51.578	46.870	26.837	117.121	26.605	-1.020
5800	4.968	51.665	46.952	27.334	116.527	25.015	-.943
5900	4.968	51.750	47.033	27.831	115.874	23.444	-.868
6000	4.968	51.833	47.112	28.328	115.163	21.893	-.797

Mar. 31, 1965

POTASSIUM UNIPOSITIVE ION (K^+) (IDEAL GAS) AT. WT. = 39.100

Ground State Configuration ^1S_o

$\Delta H^\circ_{f\ 0}$ = 121.627 kcal. mole^{-1}

$S^\circ_{298.15}$ = 36.919 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 122.896 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	1
167978	52
187837	36
217452	65

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic potassium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels", Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation K(ref. state) - e^-(ref. state) = K^+(monatomic gas), thus K^+ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore, loc. cit.

Potassium Monoxide (KO)

(Ideal Gas) GFW = 55.1014

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.310	17.420	17.420	INFINITE
100	7.309	48.130	64.207	-1.608	17.362	15.469	-33.808
200	8.205	53.502	57.639	-.827	17.174	13.552	-14.919
298	8.500	56.863	56.863	.000	17.000	11.960	-8.767
300	8.504	56.916	56.863	.016	16.996	11.929	-8.690
400	8.7[illegible]1	59.420	57.203	.887	16.198	10.381	-5.672
500	8.896	61.394	57.851	1.771	15.974	8.953	-3.913
600	8.966	63.022	58.581	2.665	15.764	7.569	-2.757
700	9.018	64.409	59.317	3.564	15.558	6.219	-1.942
800	9.060	65.616	60.030	4.468	15.351	4.898	-1.338
900	9.095	66.685	60.712	5.376	15.140	3.605	-.875
1000	9.128	67.645	61.358	6.287	14.916	2.335	-.510
1100	9.158	68.516	61.969	7.201	-4.226	2.112	-.420
1200	9.186	69.314	62.549	8.118	-4.230	2.689	-.490
1300	9.213	70.050	63.098	9.038	-4.235	3.265	-.549
1400	9.239	70.734	63.619	9.961	-4.242	3.843	-.600
1500	9.264	71.372	64.115	10.886	-4.249	4.421	-.644
1600	9.289	71.971	64.587	11.814	-4.257	4.999	-.683
1700	9.313	72.535	65.038	12.744	-4.266	5.577	-.717
1800	9.338	73.068	65.470	13.676	-4.276	6.156	-.748
1900	9.362	73.573	65.883	14.611	-4.288	6.736	-.775
2000	9.386	74.054	66.280	15.549	-4.301	7.317	-.800
2100	9.409	74.513	66.661	16.488	-4.316	7.899	-.822
2200	9.433	74.951	67.028	17.431	-4.334	8.481	-.842
2300	9.456	75.371	67.382	18.375	-4.355	9.063	-.861
2400	9.479	75.774	67.723	19.322	-4.379	9.647	-.878
2500	9.503	76.161	68.053	20.271	-4.409	10.231	-.894
2600	9.526	76.534	68.372	21.222	-4.442	10.820	-.909
2700	9.549	76.894	68.681	22.176	-4.481	11.405	-.923
2800	9.572	77.242	68.980	23.132	-4.527	11.994	-.936
2900	9.595	77.578	69.271	24.090	-4.580	12.587	-.949
3000	9.618	77.904	69.554	25.051	-4.640	13.179	-.960
3100	9.641	78.220	69.828	26.014	-4.709	13.775	-.971
3200	9.664	78.526	70.095	26.979	-4.788	14.373	-.982
3300	9.687	78.824	70.355	27.947	-4.878	14.971	-.991
3400	9.710	79.113	70.608	28.917	-4.980	15.573	-1.001
3500	9.733	79.395	70.855	29.889	-5.095	16.179	-1.010
3600	9.756	79.670	71.097	30.863	-5.226	16.791	-1.019
3700	9.779	79.937	71.332	31.840	-5.373	17.403	-1.028
3800	9.801	80.198	71.562	32.819	-5.539	18.021	-1.036
3900	9.824	80.453	71.787	33.800	-5.726	18.642	-1.045
4000	9.847	80.702	72.006	34.784	-5.937	19.270	-1.053
4100	9.870	80.946	72.221	35.770	-6.173	19.904	-1.061
4200	9.893	81.184	72.432	36.758	-6.439	20.543	-1.069
4300	9.916	81.417	72.638	37.748	-6.734	21.191	-1.077
4400	9.938	81.645	72.840	38.741	-7.065	21.842	-1.085
4500	9.961	81.869	73.038	39.736	-7.434	22.505	-1.093
4600	9.984	82.088	73.233	40.733	-7.844	23.175	-1.101
4700	10.007	82.303	73.424	41.733	-8.297	23.854	-1.109
4800	10.029	82.514	73.611	42.735	-8.797	24.545	-1.118
4900	10.052	82.721	73.795	43.739	-9.347	25.243	-1.126
5000	10.075	82.924	73.975	44.745	-9.949	25.953	-1.134
5100	10.098	83.124	74.153	45.754	-10.607	26.682	-1.143
5200	10.120	83.320	74.327	46.765	-11.322	27.417	-1.152
5300	10.143	83.513	74.498	47.778	-12.096	28.170	-1.162
5400	10.166	83.703	74.667	48.793	-12.930	28.934	-1.171
5500	10.189	83.890	74.833	49.811	-13.825	29.718	-1.181
5600	10.211	84.074	74.997	50.831	-14.781	30.518	-1.191
5700	10.234	84.254	75.157	51.853	-15.796	31.335	-1.201
5800	10.257	84.433	75.316	52.878	-16.872	32.172	-1.212
5900	10.280	84.608	75.472	53.905	-18.005	33.029	-1.223
6000	10.302	84.781	75.625	54.934	-19.195	33.908	-1.235

Dec. 31, 1962; Dec. 31, 1967

POTASSIUM MONOXIDE (KO) (IDEAL GAS) GFW = 55.1014

Ground State Configuration $[^2\Pi]$ $\Delta Hf°_0 = [17.4 \pm 10]$ kcal/mol

$S°_{298.15} = [56.9 \pm 0.5]$ gibbs/mol $\Delta Hf°_{298} = [17.0 \pm 10]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]

$\omega_e = [350]$ cm^{-1} $\omega_e x_e = [2.2]$ cm^{-1} $\sigma = 1$

$B_e = [0.3068]$ cm^{-1} $\alpha_e = [0.0027]$ cm^{-1} $r_e = [2.2]$ Å

Heat of Formation

Brewer and Margrave (1) suggested that the ΔHf° value for MO(g) from the gaseous ions can be taken as the mean of the corresponding ΔHf° values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal/mol. We obtain the values $\Delta Hr°_0 = -137.94$ and -117.7 kcal/mol for the reactions $K^+(g) + F^-(g) = KF(g)$ and $K^+(g) + Cl^-(g) = KCl(g)$, respectively. Assuming $\Delta Hr°_0 = -127.83$ kcal/mol for the reaction $K^+(g) + O^-(g) = KO(g)$, we calculate $\Delta Hf°_{298}(KO, g) = 19.0$ kcal/mol with the JANAF auxiliary values for the gaseous ions.

Based on the assumption that $D_0(KO) = 1/2[D_0(K_2) + D_0(O_2)]$, or $\Delta Hr°_0 = 64.9$ kcal/mol for the reaction $KO(g) = K(g) + O(g)$, we evaluate $\Delta Hf°_0(KO, g) = 15.6$ kcal/mol or $\Delta Hf°_{298}(KO, g) = 15.2$ kcal/mol.

According to Somayajulu (2), in a sequence of similar diatomic molecules, $k_e r_e/D_0$ = constant, where k_e = force constant, r_e = equilibrium bond distance and D_0 = dissociation energy. Using $r_e = 1.62$ Å, $D_0 = 77.9$ kcal/mol for LiO(g), $r_e = 2.2$ Å and $k_e(KO)/k_e(LiO) = 0.3015$, we calculate $D_0 = 55$ kcal/mol for KO(g), yielding $\Delta Hf°_{298}(KO, g) = 26.1$ kcal/mol. The value k_e is derived from the relation $k_e = 4\Pi^2\nu^2\mu$ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta Hf°_{298}(KO, g)$ is tentatively adopted as 17 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for the OH(g) molecule, which has the same number of valence electrons. The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiF(g) and KF(g). The bond distance is estimated from those for HO(g), HF(g) and KF(g). B_e and α_e are derived from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg (3).

References

1. L. Brewer and J. Margrave, J. Phys. Chem. 59, 421 (1955).
2. G. R. Somayajulu, J. Chem. Phys. 33, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Potassium Monoxide Uninegative Ion (KO$^-$)

(Ideal Gas) GFW = 55.10195

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°$_{298}$)/T (gibbs/mol)	H°−H°$_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	8.577	54.062	54.062	.000	-33.000	-35.718	26.182
300	8.582	54.115	54.062	.016	-33.013	-35.734	26.032
400	8.776	56.614	54.402	.885	-34.310	-36.425	19.902
500	8.885	58.585	55.048	1.768	-35.032	-36.871	16.116
600	8.956	60.211	55.777	2.660	-35.741	-37.171	13.540
700	9.009	61.596	56.512	3.559	-36.443	-37.353	11.662
800	9.051	62.802	57.224	4.462	-37.148	-37.435	10.227
900	9.087	63.870	57.904	5.369	-37.857	-37.429	9.089
1000	9.119	64.829	58.550	6.279	-38.578	-37.343	8.161
1100	9.149	65.700	59.161	7.193	-58.218	-36.161	7.185
1200	9.177	66.497	59.739	8.109	-58.720	-34.134	6.217
1300	9.203	67.232	60.288	9.028	-59.223	-32.064	5.390
1400	9.229	67.915	60.809	9.949	-59.727	-29.956	4.676
1500	9.254	68.553	61.304	10.874	-60.232	-27.811	4.052
1600	9.278	69.151	61.776	11.800	-60.738	-25.632	3.501
1700	9.302	69.714	62.226	12.729	-61.245	-23.425	3.011
1800	9.326	70.246	62.657	13.661	-61.752	-21.184	2.572
1900	9.349	70.751	63.070	14.594	-62.263	-18.918	2.176
2000	9.373	71.231	63.456	15.530	-62.774	-16.623	1.816
2100	9.396	71.689	63.847	16.469	-63.287	-14.301	1.488
2200	9.419	72.127	64.213	17.410	-63.804	-11.957	1.188
2300	9.441	72.546	64.567	18.353	-64.322	-9.589	.911
2400	9.464	72.948	64.908	19.298	-64.845	-7.198	.655
2500	9.487	73.335	65.237	20.245	-65.374	-4.787	.418
2600	9.510	73.708	65.556	21.195	-65.905	-2.350	.197
2700	9.532	74.067	65.864	22.147	-66.443	.101	-.008
2800	9.555	74.414	66.163	23.102	-66.988	2.577	-.201
2900	9.577	74.750	66.454	24.058	-67.538	5.073	-.382
3000	9.599	75.075	66.736	25.017	-68.097	7.585	-.553
3100	9.622	75.390	67.010	25.978	-68.665	10.120	-.713
3200	9.644	75.696	67.277	26.941	-69.243	12.569	-.865
3300	9.666	75.993	67.536	27.907	-69.832	15.235	-1.009
3400	9.689	76.282	67.789	28.875	-70.432	17.821	-1.145
3500	9.711	76.563	68.036	29.845	-71.046	20.425	-1.275
3600	9.733	76.837	68.277	30.817	-71.676	23.050	-1.399
3700	9.756	77.104	68.512	31.791	-72.323	25.691	-1.518
3800	9.778	77.364	68.741	32.768	-72.989	28.347	-1.630
3900	9.800	77.619	68.965	33.747	-73.675	31.021	-1.738
4000	9.822	77.867	69.185	34.728	-74.383	33.717	-1.842
4100	9.844	78.110	69.400	35.711	-75.120	36.430	-1.942
4200	9.867	78.347	69.610	36.697	-75.885	39.157	-2.038
4300	9.889	78.580	69.816	37.685	-76.680	41.907	-2.130
4400	9.911	78.807	70.018	38.675	-77.511	44.671	-2.219
4500	9.933	79.030	70.215	39.667	-78.379	47.463	-2.305
4600	9.955	79.249	70.409	40.661	-79.288	50.268	-2.388
4700	9.978	79.463	70.600	41.658	-80.241	53.095	-2.469
4800	10.000	79.674	70.787	42.657	-81.241	55.946	-2.547
4900	10.022	79.880	70.970	43.658	-82.291	58.810	-2.623
5000	10.044	80.083	71.150	44.661	-83.392	61.697	-2.697
5100	10.066	80.282	71.327	45.667	-84.550	64.619	-2.769
5200	10.088	80.477	71.502	46.675	-85.765	67.549	-2.839
5300	10.110	80.670	71.673	47.684	-87.039	70.513	-2.908
5400	10.133	80.859	71.841	48.697	-88.373	73.495	-2.974
5500	10.155	81.045	72.007	49.711	-89.769	76.504	-3.040
5600	10.177	81.228	72.170	50.728	-91.224	79.544	-3.104
5700	10.199	81.409	72.330	51.745	-92.740	82.600	-3.167
5800	10.221	81.586	72.498	52.767	-94.317	85.694	-3.229
5900	10.243	81.761	72.644	53.790	-95.951	88.814	-3.290
6000	10.265	81.933	72.797	54.816	-97.641	91.960	-3.350

Dec. 31, 1967

POTASSIUM MONOXIDE UNINEGATIVE ION (KO$^-$) (IDEAL GAS) GFW = 55.10195

Ground State Configuration [$^1\Sigma$]

ΔHf°_0 = [-33 ± 20] kcal/mol

$S^\circ_{298.15}$ = [54.1 ± 0.3] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-33 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[1]

ω_e = [360] cm^{-1}

B_e = [0.3068] cm^{-1}

$\omega_e x_e$ = [2.3] cm^{-1}

α_e = [0.0027] cm^{-1}

σ = 1

r_e = [2.2] Å

Heat of Formation

The electron affinity (E. A.) of KO$^-$(g) is unavailable, therefore the value of ΔHf°_{298}(KO$^-$, g) is estimated. Assuming that the enthalpy change (ΔHr°_0) of the reaction (1) KO$^-$(g) = K(g) + O$^-$(g) is approximately the average of the ΔHr°_0 value for the reaction (2) KO(g) = K(g) + O(g) and (3) KF(g) = K(g) + F(g), we obtain ΔHr°_0 = 1/2(63.5 + 117.3) = 90.4 kcal/mol for reaction (1). However, we compare the ΔHr°_0 values for the reactions (4) HO(g) = H(g) + O(g), (5) HO$^-$(g) = H(g) + O$^-$(g), and (6) HF(g) = H(g) + F(g), and find that ΔHr°_0 for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔHr°_0 values for reactions (4) and (6). Based on this fact we estimated ΔHr°_0 = 80 kcal/mol for reaction (1), yielding ΔHf°_{298}(KO$^-$, g) = -33 kcal/mol. The value of ΔHf°_{298}(KO$^-$, g) is tentatively adopted as -33 ± 20 kcal/mol. The electronic affinity of KO(g) is derived to be 2.2 ± 0.9 eV. The value of E. A. for HO(g) is determined as 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of KF(g) which is isoelectronic with KO$^-$(g). The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with those for KF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, 1950. The enthalpy at 0°K is -2.303 kcal/mol.

Potassium, Diatomic (K_2)

(Ideal Gas) Mol. Wt. = 78.200

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.566	31.194	31.194	INFINITE
100	8.723	49.923	67.650	-1.773	31.159	27.869	-60.904
200	8.969	56.066	60.492	-.885	30.807	24.708	-26.998
298	9.057	59.666	59.666	.000	30.374	21.802	-15.980
300	9.058	59.722	59.666	.017	30.365	21.749	-15.843
400	9.121	62.336	60.022	.926	28.646	19.177	-10.477
500	9.177	64.378	60.696	1.841	28.075	16.876	-7.376
600	9.230	66.056	61.454	2.761	27.543	14.688	-5.350
700	9.281	67.482	62.216	3.687	27.037	12.586	-3.929
800	9.332	68.725	62.953	4.617	26.543	10.554	-2.883
900	9.382	69.827	63.657	5.553	26.055	8.585	-2.085
1000	9.432	70.818	64.324	6.494	25.554	6.670	-1.458
1100	9.482	71.720	64.956	7.440	-12.774	6.854	-1.362
1200	9.532	72.547	65.555	8.390	-12.818	8.642	-1.574
1300	9.581	73.312	66.123	9.346	-12.856	10.430	-1.753
1400	9.631	74.024	66.662	10.307	-12.889	12.224	-1.908
1500	9.680	74.690	67.175	11.272	-12.918	14.019	-2.043
1600	9.730	75.316	67.664	12.243	-12.941	15.817	-2.160
1700	9.779	75.907	68.132	13.218	-12.962	17.612	-2.264
1800	9.828	76.468	68.580	14.198	-12.978	19.412	-2.357
1900	9.878	77.001	69.009	15.184	-12.992	21.211	-2.440
2000	9.927	77.508	69.421	16.174	-13.002	23.013	-2.515
2100	9.976	77.994	69.818	17.169	-13.011	24.814	-2.582
2200	10.026	78.459	70.200	18.169	-13.021	26.616	-2.644
2300	10.075	78.906	70.569	19.174	-13.030	28.416	-2.700
2400	10.124	79.336	70.926	20.184	-13.040	30.218	-2.752
2500	10.174	79.750	71.270	21.199	-13.055	32.020	-2.799
2600	10.223	80.150	71.604	22.219	-13.071	33.828	-2.843
2700	10.272	80.537	71.928	23.244	-13.094	35.628	-2.884
2800	10.322	80.911	72.242	24.273	-13.127	37.432	-2.922
2900	10.371	81.274	72.547	25.308	-13.166	39.242	-2.957
3000	10.420	81.627	72.844	26.348	-13.214	41.047	-2.990
3100	10.469	81.969	73.133	27.392	-13.278	42.859	-3.021
3200	10.519	82.302	73.414	28.442	-13.354	44.673	-3.051
3300	10.568	82.627	73.689	29.496	-13.448	46.484	-3.078
3400	10.617	82.943	73.956	30.555	-13.563	48.300	-3.105
3500	10.666	83.252	74.217	31.619	-13.699	50.122	-3.130
3600	10.716	83.553	74.473	32.688	-13.862	51.951	-3.154
3700	10.765	83.847	74.722	33.762	-14.054	53.779	-3.176
3800	10.814	84.135	74.966	34.841	-14.281	55.614	-3.198
3900	10.864	84.416	75.205	35.925	-14.545	57.456	-3.220
4000	10.913	84.692	75.438	37.014	-14.852	59.309	-3.240
4100	10.962	84.962	75.667	38.108	-15.208	61.167	-3.260
4200	11.011	85.227	75.892	39.207	-15.619	63.035	-3.280
4300	11.061	85.486	76.112	40.310	-16.088	64.914	-3.299
4400	11.110	85.741	76.328	41.419	-16.625	66.802	-3.318
4500	11.159	85.991	76.540	42.532	-17.234	68.709	-3.337
4600	11.208	86.237	76.748	43.651	-17.921	70.623	-3.355
4700	11.258	86.479	76.953	44.774	-18.694	72.557	-3.374
4800	11.307	86.716	77.153	45.902	-19.558	74.510	-3.392
4900	11.356	86.950	77.351	47.035	-20.521	76.479	-3.411
5000	11.406	87.180	77.545	48.173	-21.585	78.465	-3.430
5100	11.455	87.406	77.736	49.316	-22.758	80.485	-3.449
5200	11.504	87.629	77.925	50.464	-24.044	82.519	-3.468
5300	11.553	87.849	78.110	51.617	-25.445	84.579	-3.488
5400	11.603	88.065	78.292	52.775	-26.965	86.666	-3.507
5500	11.652	88.279	78.472	53.938	-28.606	88.782	-3.528
5600	11.701	88.489	78.649	55.105	-30.367	90.935	-3.549
5700	11.750	88.696	78.823	56.278	-32.246	93.117	-3.570
5800	11.800	88.901	78.995	57.455	-34.245	95.331	-3.592
5900	11.849	89.103	79.165	58.638	-36.356	97.589	-3.615
6000	11.898	89.303	79.332	59.825	-38.579	99.883	-3.638

December 31, 1961

POTASSIUM, DIATOMIC (K_2) (IDEAL GAS) MOL. WT. = 78.200

ΔH°_{f0} = 31.194 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298}$ = 30.374 ± 0.5 kcal. mole^{-1}

Ground State = $^1\Sigma$

S°_{298} = 59.666 cal. mole^{-1} deg.$^{-1}$

ω_e = 92.64 cm.$^{-1}$

$\omega_e x_e$ = 0.354 cm.$^{-1}$

D_0 = 8.3 X 10^{-8} cm.$^{-1}$

B_e = 0.05622 cm.$^{-1}$

α_e = 0.000219 cm.$^{-1}$

σ = 2

Thermodynamic Functions.

Spectroscopic data are the same as that selected by W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 83 (1955)]. The calculated functions are in excellent agreement with their results.

Heat of Formation.

The heat of dissociation selected by Evans, Munson, and Wagman (loc. cit.) was used with the previously adopted heat of sublimation of the monomer to derive the heat of formation.

Dipotassium Monoxide (K_2O)

(Crystal) Mol. Wt. = 94.20

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H_{298}^\circ$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	20.000	22.500	22.500	.000	- 86.800	- 76.986	56.430
300	20.050	22.624	22.500	.037	- 86.795	- 76.925	56.037
400	21.880	28.683	23.314	2.148	- 87.668	- 73.458	40.134
500	22.530	33.634	24.899	4.367	- 87.300	- 69.946	30.572
600	23.280	37.806	26.711	6.657	- 86.840	- 66.516	24.227
700	24.231	41.466	28.563	9.033	- 86.285	- 63.171	19.722
800	25.190	44.764	30.385	11.504	- 85.637	- 59.914	16.367
900	26.156	47.787	32.153	14.071	- 84.901	- 56.741	13.778
1000	27.130	50.593	33.858	16.735	- 84.092	- 53.656	11.726
1100	28.095	53.224	35.500	19.496	- 121.025	- 48.606	9.657
1200	29.061	55.710	37.082	22.354	- 119.585	- 42.084	7.664
1300	30.029	58.075	38.606	25.309	- 118.053	- 35.689	6.000
1400	30.999	60.335	40.078	28.360	- 116.427	- 29.412	4.591
1500	31.970	62.507	41.502	31.508	- 114.709	- 23.255	3.388
1600	32.94	64.602	42.880	34.754	- 112.895	- 17.216	2.352
1700	33.917	66.628	44.218	38.097	- 110.989	- 11.297	1.452
1800	34.89	68.594	45.518	41.538	- 108.989	- 5.489	.666
1900	35.871	70.507	46.783	45.076	- 106.899	.203	- .023
2000	36.850	72.372	48.016	48.712	- 104.713	5.786	- .632

June 30, 1963

K_2O

DIPOTASSIUM MONOXIDE (K_2O) (CRYSTAL) MOL. WT. = 94.20

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [22.5 ± 1.5] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -86.8 ± 0.5 kcal. mole^{-1}

T_d = 1154°K. (600 mm Hg)

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was reported by M. Rengade, Ann. Chim. et phys. [8] 14, 540 (1908), based on the measurements of the heats of solution of K(c) and K_2O(c) in H_2O. The same value of $\Delta H_f^\circ{}_{298.15}$ was also given by R. de Forcrand, Compt. rend. 158, 991 (1914).

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by comparison with those of the Na_2O(c).

Temperature of Decomposition.

T_d was taken from, "Data on Chemicals for Ceramic Use", National Research Council Bulletin 118 (1949).

Dipotassium Dioxide (K_2O_2)

(Crystal) Mol. Wt. = 110.20

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	23.940	27.000	27.000	.000	-118.500	-102.723	75.294
300	23.990	27.148	27.000	.044	-118.495	-102.624	74.758
400	25.600	34.322	27.967	2.542	-119.336	-97.163	53.085
500	27.600	40.263	29.847	5.208	-118.887	-91.667	40.066
600	28.850	45.417	32.022	8.037	-118.265	-86.279	31.425
700	30.581	49.995	34.268	11.009	-117.503	-81.005	25.290
800	32.200	54.186	36.499	14.149	-116.585	-75.854	20.721
900	33.706	58.067	38.683	17.445	-115.527	-70.824	17.198
1000	35.100	61.691	40.804	20.887	-114.354	-65.919	14.406
1100	36.548	65.104	42.860	24.469	-150.885	-59.089	11.739
1200	37.992	68.346	44.850	28.196	-149.000	-50.825	9.256
1300	39.432	71.444	46.777	32.067	-146.980	-42.726	7.183
1400	40.868	74.419	48.646	36.082	-144.823	-34.785	5.430
1500	42.300	77.287	50.460	40.241	-142.529	-27.004	3.934
1600	43.728	80.063	52.224	44.542	-140.099	-19.380	2.647
1700	45.152	82.757	53.941	48.986	-137.533	-11.916	1.532
1800	46.572	85.378	55.615	53.573	-134.831	-4.603	.559
1900	47.988	87.934	57.249	58.301	-131.998	2.554	-.294
2000	49.400	90.431	58.846	63.170	-129.029	9.561	-1.045

June 30, 1963; Sept. 30, 1963

DIPOTASSIUM DIOXIDE (K_2O_2) (CRYSTAL) MOL. WT. = 110.20

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [27.0 ± 1.5] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -118.5 ± 1.0 kcal. mole^{-1}

T_m = 763°K.

ΔH_m° = Unknown

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was reported by National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. The value was based on the measured decomposition pressure of K_2O_2(c) by M. Centnerzwer and M. Blumenthal, IX Congr. IUPAC, 3A, 201 (1935).

Heat Capacity and Entropy.

The heat capacities and $S^\circ_{298.15}$ were estimated by comparison with those for Na_2O_2(c), Na_2O(c), and K_2O(c).

Temperature of Melting.

T_m was reported by Centnerzwer and Blumenthal, loc. cit.

Lithium (Li)

(Reference State) At. Wt. = 6.940

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.105	.000	.000	.000
100	3.193	1.756	11.622	-.986	.000	.000	.000
200	5.156	4.742	7.474	-.546	.000	.000	.000
298	5.887	6.954	6.954	.000	.000	.000	.000
300	5.896	6.990	6.954	.011	.000	.000	.000
400	6.599	8.774	7.193	.632	.000	.000	.000
500	7.200	11.915	7.814	2.050	.000	.000	.000
600	7.060	13.216	8.610	2.763	.000	.000	.000
700	6.928	14.294	9.347	3.463	.000	.000	.000
800	6.916	15.218	10.024	4.155	.000	.000	.000
900	6.904	16.032	10.648	4.846	.000	.000	.000
1000	6.892	16.759	11.223	5.536	.000	.000	.000
1100	6.880	17.415	11.757	6.224	.000	.000	.000
1200	6.868	18.013	12.253	6.912	.000	.000	.000
1300	6.860	18.562	12.718	7.598	.000	.000	.000
1400	6.840	19.070	13.154	8.283	.000	.000	.000
1500	6.820	19.541	13.564	8.966	.000	.000	.000
1600	6.800	19.981	13.951	9.647	.000	.000	.000
1700	4.971	41.790	15.100	45.374	.000	.000	.000
1800	4.974	42.075	16.591	45.871	.000	.000	.000
1900	4.976	42.344	17.939	46.368	.000	.000	.000
2000	4.983	42.599	19.166	46.866	.000	.000	.000
2100	4.991	42.842	20.287	47.365	.000	.000	.000
2200	5.001	43.075	21.318	47.865	.000	.000	.000
2300	5.014	43.297	22.269	48.365	.000	.000	.000
2400	5.031	43.511	23.150	48.868	.000	.000	.000
2500	5.051	43.717	23.968	49.372	.000	.000	.000
2600	5.074	43.915	24.732	49.878	.000	.000	.000
2700	5.102	44.107	25.446	50.387	.000	.000	.000
2800	5.134	44.293	26.115	50.898	.000	.000	.000
2900	5.169	44.474	26.745	51.414	.000	.000	.000
3000	5.209	44.650	27.339	51.932	.000	.000	.000
3100	5.253	44.822	27.900	52.456	.000	.000	.000
3200	5.300	44.989	28.432	52.983	.000	.000	.000
3300	5.352	45.153	28.936	53.516	.000	.000	.000
3400	5.407	45.314	29.415	54.054	.000	.000	.000
3500	5.466	45.471	29.872	54.597	.000	.000	.000
3600	5.529	45.626	30.307	55.147	.000	.000	.000
3700	5.596	45.778	30.723	55.703	.000	.000	.000
3800	5.666	45.929	31.122	56.266	.000	.000	.000
3900	5.740	46.077	31.503	56.836	.000	.000	.000
4000	5.818	46.223	31.869	57.414	.000	.000	.000
4100	5.901	46.368	32.221	58.000	.000	.000	.000
4200	5.987	46.511	32.560	58.595	.000	.000	.000
4300	6.079	46.653	32.886	59.198	.000	.000	.000
4400	6.175	46.794	33.200	59.810	.000	.000	.000
4500	6.277	46.934	33.504	60.433	.000	.000	.000
4600	6.385	47.073	33.797	61.066	.000	.000	.000
4700	6.500	47.211	34.081	61.710	.000	.000	.000
4800	6.621	47.349	34.356	62.366	.000	.000	.000
4900	6.750	47.487	34.623	63.035	.000	.000	.000
5000	6.886	47.625	34.882	63.716	.000	.000	.000
5100	7.032	47.763	35.133	64.412	.000	.000	.000
5200	7.186	47.901	35.377	65.123	.000	.000	.000
5300	7.349	48.039	35.615	65.850	.000	.000	.000
5400	7.523	48.178	35.846	66.593	.000	.000	.000
5500	7.707	48.318	36.071	67.355	.000	.000	.000
5600	7.901	48.458	36.291	68.135	.000	.000	.000
5700	8.106	48.600	36.506	68.935	.000	.000	.000
5800	8.322	48.743	36.716	69.757	.000	.000	.000
5900	8.549	48.887	36.921	70.600	.000	.000	.000
6000	8.787	49.033	37.122	71.467	.000	.000	.000

June 30, 1962

LITHIUM (Li) (REFERENCE STATE) AT. WT. = 6.940

0° to 453.69°K	Crystal
453.69° to 1638°K	Liquid
1638° to 6000°K	Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

Lithium (Li)

(Crystal) At. Wt. = 6.940

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.105	.000	.000	INFINITE
100	3.193	1.758	11.618	-.986	.000	.000	.000
200	5.156	4.742	7.472	-.546	.000	.000	.000
298	5.887	6.954	6.954	.000	.000	.000	.000
300	5.896	6.990	6.954	.011	.000	.000	.000
400	6.599	8.774	7.193	.632	.000	.000	.000
500	7.222	10.328	7.667	1.330	.720	.074	-.032
600	7.261	11.650	8.224	2.055	-.708	.232	-.085
700	7.262	12.769	8.796	2.782	-.681	.386	-.120
800	7.262	13.739	9.354	3.508	-.647	.536	-.146
900	7.262	14.595	9.890	4.234	-.612	.682	-.166
1000	7.262	15.360	10.399	4.960	-.576	.824	-.180
1100	7.262	16.052	10.882	5.686	-.538	.962	-.191
1200	7.262	16.684	11.340	6.413	-.499	1.096	-.200
1300	7.262	17.265	11.774	7.139	-.459	1.227	-.206
1400	7.262	17.803	12.185	7.865	-.418	1.356	-.212
1500	7.262	18.304	12.577	8.591	-.375	1.481	-.216
1600	7.262	18.773	12.949	9.317	-.330	1.604	-.219
1700	7.262	19.213	13.305	10.044	-35.330	3.050	-.392
1800	7.262	19.628	13.645	10.770	-35.101	5.303	-.644
1900	7.262	20.021	13.970	11.496	-34.872	7.542	-.868
2000	7.262	20.393	14.282	12.222	-34.644	9.768	-1.067

LITHIUM (Li) (CRYSTAL) AT. WT. = 6.940

$\Delta H^\circ_{f\ 298.15} = 0$

$\Delta H^\circ_{s\ 298.15} = 50.41 \pm 0.90$ kcal. mole^{-1} (Diatomic gas)

$T_m = 453.69$°K

$\Delta H^\circ_{s\ 298.15} = 38.41 \pm 0.40$ kcal. mole^{-1} (Monatomic gas)

$S^\circ_{298.15} = 6.954$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_m = 0.7171 \pm 0.0037$ kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacities have been reported by the following authors for the temperature ranges indicated: L. M. Roberts, Proc. Phys. Soc. 70, 744 (1957), 1.5 to 20°K (Li 99.5% pure); F. Simon and R. C. Swain, Z. phys. Chem. B28, 189 (1935), 15° to 300°K; D. L. Martin, Proc. Roy. Soc. A254, 444 (1960), 22° to 300°K (Li 99.95% pure); T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955), 298° to 1200°K (Li 99.98% pure). Martin, in a series of determinations, found that C_p depended on the thermal history of the sample; a peak at roughly 107°K was ascribed to a martensitic transformation. There is excellent continuity between the results of Roberts and of Martin, while those of Martin and Douglas et al. differ by 1% at 300°K and have been smoothly joined. The values of Simon and Swain were not used as they were 5% lower than Martin's and did not show the peak at 107°K; also their values for Al_2O_3, reported at the same time, are lower than recent measurements. Heat capacities between 1200°K and the normal boiling point were obtained from the heat content equation given by Douglas et al. between 420° and 900°C.

Melting.

Douglas et al. (loc. cit.) report the triple point to be 180.54°C, which is here adopted as the melting point since the densities of solid and liquid lithium at 180°C are not available for calculating dT_m/dP. The same authors give the heat of melting as 432.3 ± 2.2 abs. joule g.$^{-1}$

Heat of Sublimation.

Lithium vapor contains an appreciable amount of dimer, whose heat of dissociation has been selected by W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bureau of Standards 55, 83 (1955), from spectroscopic and molecular beam measurements to be 25.76 ± 0.10 kcal. mole^{-1} at 0°K. This heat of dissociation, together with the thermodynamic functions calculated in this work, has been used to find the partial pressures of Li(g) and Li_2(g) from the measured total vapor pressures. H. Hartmann and R. Schneider, Z. anorg. allgem. Chem. 180, 275 (1929), report values from 1204° to 1353°K; while M. Mancherat, C. Rendus 208, 499 (1939), reports effusion measurements from 735° to 915°K. Mancherat's pressures are calculated on the assumption of monatomic vapor and have been recalculated to find the true total pressure. Effusion measurements by L. C. Lewis, Z. Physik 69, 786 (1931), and A. Bogros, C. Rendus 191, 560 (1930) and Ann. Phys. 17, 199 (1932), have been disregarded. Mancherat considers them to be inaccurate because of impurities in the lithium used, and Lewis used a doubtful calibration method. Heats of sublimation to monatomic vapor calculated from the vapor pressures of Hartmann and Schneider and of Mancherat agree to within 2% and the average value has been adopted. The heat of sublimation of the dimer was then calculated using this value.

Lithium (Li)

(Liquid) At. Wt. = 6.940

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	7.481	8.113	8.113	.000	.569	.223	-.164
300	7.477	8.159	8.113	.014	.572	.221	-.161
400	7.340	10.291	8.405	.755	.692	.085	-.046
500	7.200	11.914	8.951	1.482	.000	.000	.000
600	7.060	13.214	9.557	2.195	.000	.000	.001
700	6.978	14.292	10.158	2.894	.000	.000	.000
800	6.916	15.216	10.734	3.586	.000	.000	.000
900	6.904	16.030	11.278	4.277	.000	.000	.000
1000	6.892	16.757	11.791	4.966	.000	.000	.000
1100	6.880	17.413	12.272	5.655	.000	.000	.000
1200	6.866	18.011	12.726	6.342	.000	.000	.000
1300	6.860	18.561	13.154	7.029	.000	.000	.000
1400	6.840	19.068	13.559	7.714	.000	.000	.000
1500	6.820	19.540	13.942	8.397	.000	.000	.000
1600	6.800	19.979	14.306	9.078	.000	.000	.000
1700	6.780	20.391	14.652	9.757	-35.046	1.330	-.171
1800	6.770	20.778	14.981	10.434	-34.868	3.467	-.421
1900	6.770	21.144	15.296	11.111	-34.688	5.592	-.643
2000	6.770	21.491	15.597	11.788	-34.509	7.706	-.842
2100	6.770	21.822	15.886	12.465	-34.331	9.812	-1.021
2200	6.770	22.137	16.163	13.142	-34.154	11.911	-1.183
2300	6.770	22.437	16.429	13.819	-33.977	14.000	-1.330
2400	6.770	22.726	16.686	14.496	-33.803	16.082	-1.464
2500	6.770	23.002	16.933	15.173	-33.630	18.158	-1.587
2600	6.770	23.267	17.171	15.850	-33.459	20.225	-1.700
2700	6.770	23.523	17.402	16.527	-33.291	22.286	-1.804
2800	6.770	23.769	17.625	17.204	-33.125	24.342	-1.900
2900	6.770	24.007	17.841	17.881	-32.964	26.391	-1.989
3000	6.770	24.236	18.050	18.558	-32.805	28.436	-2.071
3100	6.770	24.458	18.253	19.235	-32.652	30.476	-2.148
3200	6.770	24.673	18.451	19.912	-32.502	32.509	-2.220
3300	6.770	24.881	18.642	20.589	-32.358	34.538	-2.287
3400	6.770	25.084	18.829	21.266	-32.219	36.564	-2.350
3500	6.770	25.280	19.010	21.943	-32.085	38.584	-2.409
3600	6.770	25.471	19.187	22.620	-31.958	40.602	-2.465
3700	6.770	25.656	19.360	23.297	-31.837	42.614	-2.517
3800	6.770	25.837	19.528	23.974	-31.723	44.628	-2.567
3900	6.770	26.012	19.692	24.651	-31.616	46.636	-2.613
4000	6.770	26.184	19.852	25.328	-31.517	48.640	-2.657

June 30, 1962

LITHIUM (Li) (LIQUID) AT. WT. = 6.940

ΔH_f° 298.15 = 0.569 kcal. mole^{-1}

$S^\circ_{298.15}$ = 8.113 cal. deg.$^{-1}$ mole^{-1}

T_m = 453.69°K

ΔH_m = 0.7171 ± 0.0035 kcal. mole^{-1}

T_b = 1620°K (Equilibrium mixture)

T_b (Monatomic gas) = 1638°K

ΔH_v 1638 = 35.16 kcal. mole^{-1}

Heat of Formation.

Obtained from the heat of fusion by adding $H_{453.69}-H_{298.15}$ for the solid and subtracting $H_{453.69}-H_{298.15}$ for the liquid.

Heat Capacity.

The data of T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955) were taken and extrapolated below T_m and above 1200°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Lithium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1620°K; the vapor pressure of the monatomic gas reaches 1 atm. at 1638°K and the heat of vaporization to monatomic gas is 35.16 kcal. mole^{-1}. See also Li(crystal).

Lithium, Monatomic (Li)

(Ideal Gas) At. Wt. = 6.940

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.481	38.034	38.034	INFINITE
100	4.968	27.716	37.560	- .984	38.412	35.816	- 78.272
200	4.968	31.160	33.598	- .488	38.468	33.185	- 36.261
298	4.966	33.143	33.143	.000	38.410	30.602	- 22.431
300	4.968	33.174	33.143	.009	38.408	30.553	- 22.257
400	4.966	34.603	33.338	.506	38.284	27.952	- 15.272
500	4.968	35.712	33.706	1.003	37.363	25.464	- 11.130
600	4.968	36.618	34.118	1.500	37.147	23.106	- 8.416
700	4.968	37.384	34.531	1.996	36.943	20.781	- 6.488
800	4.966	38.047	34.930	2.493	36.748	18.485	- 5.050
900	4.968	38.632	35.310	2.990	36.554	16.214	- 3.937
1000	4.968	39.156	35.669	3.487	36.361	13.964	- 3.052
1100	4.968	39.629	36.007	3.984	36.170	11.734	- 2.331
1200	4.968	40.061	36.328	4.481	35.979	9.521	- 1.734
1300	4.968	40.459	36.630	4.977	35.789	7.323	- 1.231
1400	4.968	40.827	36.917	5.474	35.601	5.141	- .803
1500	4.969	41.170	37.189	5.971	35.415	2.972	- .433
1600	4.970	41.491	37.448	6.468	35.231	.815	- .111
1700	4.971	41.792	37.695	6.965	.000	.000	.000
1800	4.974	42.076	37.931	7.462	.000	.000	.000
1900	4.976	42.345	38.156	7.960	.000	.000	.000
2000	4.983	42.601	38.372	8.458	.000	.000	.000
2100	4.991	42.844	38.579	8.957	.000	.000	.000
2200	5.001	43.076	38.778	9.456	.000	.000	.000
2300	5.014	43.299	38.970	9.957	.000	.000	.000
2400	5.031	43.513	39.155	10.459	.000	.000	.000
2500	5.051	43.719	39.333	10.963	.000	.000	.000
2600	5.074	43.917	39.506	11.469	.000	.000	.000
2700	5.102	44.109	39.673	11.978	.000	.000	.000
2800	5.134	44.295	39.835	12.490	.000	.000	.000
2900	5.169	44.476	39.991	13.005	.000	.000	.000
3000	5.209	44.652	40.144	13.524	.000	.000	.000
3100	5.253	44.823	40.292	14.047	.000	.000	.000
3200	5.300	44.991	40.436	14.575	.000	.000	.000
3300	5.352	45.155	40.577	15.107	.000	.000	.000
3400	5.407	45.315	40.714	15.645	.000	.000	.000
3500	5.466	45.473	40.848	16.189	.000	.000	.000
3600	5.529	45.628	40.978	16.738	.000	.000	.000
3700	5.596	45.780	41.106	17.295	.000	.000	.000
3800	5.666	45.930	41.231	17.858	.000	.000	.000
3900	5.740	46.078	41.353	18.428	.000	.000	.000
4000	5.818	46.225	41.473	19.006	.000	.000	.000
4100	5.901	46.369	41.591	19.592	.000	.000	.000
4200	5.987	46.513	41.706	20.186	.000	.000	.000
4300	6.079	46.655	41.820	20.789	.000	.000	.000
4400	6.175	46.795	41.931	21.402	.000	.000	.000
4500	6.277	46.935	42.041	22.025	.000	.000	.000
4600	6.385	47.074	42.149	22.658	.000	.000	.000
4700	6.500	47.213	42.255	23.302	.000	.000	.000
4800	6.621	47.351	42.360	23.958	.000	.000	.000
4900	6.750	47.489	42.463	24.626	.000	.000	.000
5000	6.886	47.627	42.565	25.308	.000	.000	.000
5100	7.032	47.764	42.666	26.004	.000	.000	.000
5200	7.186	47.902	42.765	26.715	.000	.000	.000
5300	7.349	48.041	42.863	27.441	.000	.000	.000
5400	7.523	48.180	42.960	28.185	.000	.000	.000
5500	7.707	48.320	43.057	28.946	.000	.000	.000
5600	7.901	48.460	43.152	29.727	.000	.000	.000
5700	8.106	48.602	43.246	30.527	.000	.000	.000
5800	8.322	48.745	43.340	31.348	.000	.000	.000
5900	8.549	48.889	43.433	32.192	.000	.000	.000
6000	8.787	49.034	43.525	33.058	.000	.000	.000

June 30, 1962

LITHIUM, MONATOMIC (Li) (IDEAL GAS) AT. WT. = 6.940

ΔH°_{f0} = 38.034 kcal. mole^{-1}

ΔH°_f 298.15 = 38.41 ± 0.40 kcal. mole^{-1}

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 33.143 cal. deg. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i
0	2	36596	30
14904	6	38300	2
27206	2	39623	50
30925	6	41756	70
31283	10	42736	52
35012	2	43319	162

Heat of Formation.

Same as the heat of sublimation to the monatomic gas; see notes on Li(crystal).

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 467," U. S. Government Printing Office, Washington (1949) p. 9. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Lithium Unipositive Ion (Li^+)

(Ideal Gas) At. Wt. = 6.940

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0							
100							
200							
298	4.968	31.766	31.766	.000	164.236	155.351	- 113.870
300	4.968	31.797	31.766	.009	164.243	155.295	- 113.127
400	4.968	33.226	31.961	.506	164.616	152.256	- 83.185
500	4.968	34.334	32.329	1.003	164.192	149.204	- 65.214
600	4.968	35.240	32.741	1.500	164.473	146.180	- 53.244
700	4.968	36.006	33.154	1.996	164.765	143.107	- 44.678
800	4.968	36.669	33.553	2.493	165.067	139.993	- 38.242
900	4.968	37.255	33.932	2.990	165.370	136.840	- 33.228
1000	4.968	37.778	34.291	3.487	165.674	133.654	- 29.209
1100	4.968	38.252	34.630	3.984	165.980	130.438	- 25.914
1200	4.968	38.684	34.950	4.481	166.286	127.193	- 23.164
1300	4.968	39.082	35.253	4.977	166.592	123.921	- 20.832
1400	4.968	39.450	35.540	5.474	166.901	120.628	- 18.830
1500	4.968	39.792	35.812	5.971	167.212	117.313	- 17.092
1600	4.968	40.113	36.071	6.468	167.525	113.976	- 15.568
1700	4.968	40.414	36.317	6.965	132.792	111.948	- 14.391
1800	4.968	40.698	36.553	7.461	133.287	110.708	- 13.441
1900	4.968	40.967	36.778	7.958	133.784	109.441	- 12.588
2000	4.968	41.222	36.994	8.455	134.280	108.146	- 11.817
2100	4.968	41.464	37.201	8.952	134.775	106.826	- 11.117
2200	4.968	41.695	37.400	9.449	135.269	105.485	- 10.478
2300	4.968	41.916	37.592	9.945	135.761	104.118	- 9.893
2400	4.968	42.128	37.777	10.442	136.252	102.732	- 9.355
2500	4.968	42.330	37.955	10.939	136.742	101.327	- 8.858
2600	4.968	42.525	38.127	11.436	137.230	99.899	- 8.397
2700	4.968	42.713	38.293	11.933	137.715	98.454	- 7.969
2800	4.968	42.893	38.454	12.430	138.198	96.993	- 7.570
2900	4.968	43.068	38.610	12.926	138.674	95.511	- 7.198
3000	4.968	43.236	38.762	13.423	139.150	94.015	- 6.849
3100	4.968	43.399	38.909	13.920	139.620	92.503	- 6.521
3200	4.968	43.557	39.052	14.417	140.087	90.976	- 6.213
3300	4.968	43.710	39.190	14.914	140.548	89.434	- 5.923
3400	4.968	43.858	39.325	15.410	141.002	87.881	- 5.649
3500	4.968	44.002	39.457	15.907	141.453	86.311	- 5.389
3600	4.968	44.142	39.585	16.404	141.897	84.729	- 5.144
3700	4.968	44.278	39.710	16.901	142.335	83.131	- 4.910
3800	4.968	44.411	39.832	17.398	142.766	81.529	- 4.689
3900	4.968	44.540	39.951	17.895	143.190	79.912	- 4.478
4000	4.968	44.665	40.068	18.391	143.604	78.284	- 4.277
4100	4.968	44.788	40.181	18.888	144.012	76.645	- 4.085
4200	4.968	44.908	40.292	19.385	144.411	74.998	- 3.902
4300	4.968	45.025	40.401	19.882	144.802	73.340	- 3.727
4400	4.968	45.139	40.507	20.379	145.184	71.677	- 3.560
4500	4.968	45.251	40.612	20.875	145.553	69.998	- 3.399
4600	4.968	45.360	40.714	21.372	145.914	68.317	- 3.246
4700	4.968	45.467	40.814	21.869	146.264	66.623	- 3.098
4800	4.968	45.571	40.912	22.366	146.602	64.925	- 2.956
4900	4.968	45.674	41.008	22.863	146.927	63.220	- 2.820
5000	4.968	45.774	41.102	23.359	147.238	61.513	- 2.689
5100	4.968	45.872	41.195	23.856	147.536	59.796	- 2.562
5200	4.968	45.969	41.286	24.353	147.819	58.072	- 2.441
5300	4.968	46.063	41.375	24.850	148.086	56.343	- 2.323
5400	4.968	46.156	41.462	25.347	148.337	54.609	- 2.210
5500	4.968	46.248	41.549	25.844	148.569	52.869	- 2.101
5600	4.968	46.337	41.633	26.340	148.781	51.123	- 1.995
5700	4.968	46.425	41.717	26.837	148.975	49.385	- 1.893
5800	4.968	46.511	41.799	27.334	149.147	47.635	- 1.795
5900	4.968	46.596	41.879	27.831	149.298	45.883	- 1.700
6000	4.968	46.680	41.959	28.328	149.425	44.131	- 1.607

Mar. 31, 1965

LITHIUM UNIPOSITIVE ION (Li^+) (IDEAL GAS) AT. WT. = 6.940

Ground State Configuration $^1S_0$

$S^\circ_{298.15}$ = 31.766 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 162.379 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 164.236 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_i
0	1
492008	16
561765	39
582517	61
595039	125
601915	85

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic lithium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation Li(ref. state) - e^-(ref. state) = Li^+(monatomic gas), thus Li^+ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

Lithium Nitride (LiN)

(Ideal Gas) GFW = 20.9457

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.151	79.990	79.990	INFINITE
100	6.971	41.807	56.368	-1.456	80.219	78.123	-170.738
200	7.326	46.719	50.446	-.745	80.142	76.046	-83.099
298	7.848	49.744	49.744	.000	80.000	74.065	-54.291
300	7.857	49.793	49.745	.015	79.997	74.028	-53.929
400	8.241	52.110	50.058	.821	79.834	72.063	-39.373
500	8.490	53.977	50.661	1.658	78.902	70.217	-30.692
600	8.655	55.541	51.348	2.516	78.690	68.501	-24.951
700	8.772	56.884	52.045	3.388	78.498	66.817	-20.861
800	8.858	58.062	52.725	4.269	78.316	65.160	-17.801
900	8.926	59.109	53.377	5.159	78.135	63.527	-15.427
1000	8.980	60.052	53.998	6.054	77.954	61.914	-13.531
1100	9.026	60.910	54.588	6.954	77.772	60.319	-11.984
1200	9.067	61.698	55.148	7.859	77.588	58.739	-10.698
1300	9.102	62.425	55.680	8.768	77.405	57.176	-9.612
1400	9.135	63.100	56.187	9.679	77.221	55.628	-8.684
1500	9.165	63.732	56.669	10.594	77.039	54.090	-7.881
1600	9.193	64.324	57.129	11.512	76.858	52.568	-7.180
1700	9.220	64.882	57.569	12.433	41.630	52.383	-6.734
1800	9.246	65.410	57.990	13.356	41.632	53.017	-6.437
1900	9.271	65.911	58.394	14.282	41.634	53.650	-6.171
2000	9.295	66.387	58.781	15.211	41.636	54.282	-5.932
2100	9.318	66.841	59.155	16.141	41.636	54.912	-5.715
2200	9.341	67.275	59.514	17.074	41.636	55.546	-5.518
2300	9.364	67.691	59.860	18.010	41.637	56.176	-5.338
2400	9.386	68.090	60.195	18.947	41.636	56.809	-5.173
2500	9.408	68.473	60.519	19.887	41.634	57.443	-5.022
2600	9.430	68.843	60.832	20.829	41.632	58.073	-4.881
2700	9.451	69.199	61.135	21.773	41.627	58.706	-4.752
2800	9.473	69.543	61.429	22.719	41.622	59.339	-4.632
2900	9.494	69.876	61.715	23.667	41.613	59.972	-4.520
3000	9.515	70.198	61.992	24.618	41.603	60.607	-4.415
3100	9.536	70.510	62.262	25.570	41.589	61.241	-4.317
3200	9.556	70.813	62.524	26.525	41.572	61.875	-4.226
3300	9.577	71.108	62.780	27.481	41.551	62.508	-4.140
3400	9.598	71.394	63.029	28.440	41.527	63.146	-4.059
3500	9.618	71.673	63.272	29.401	41.498	63.778	-3.982
3600	9.639	71.944	63.509	30.364	41.464	64.416	-3.911
3700	9.659	72.208	63.741	31.329	41.426	65.054	-3.843
3800	9.679	72.466	63.967	32.296	41.382	65.696	-3.778
3900	9.700	72.718	64.188	33.265	41.333	66.336	-3.717
4000	9.720	72.963	64.405	34.236	41.277	66.979	-3.660
4100	9.740	73.204	64.616	35.209	41.215	67.621	-3.605
4200	9.760	73.439	64.824	36.184	41.145	68.264	-3.552
4300	9.780	73.669	65.027	37.161	41.069	68.911	-3.502
4400	9.800	73.894	65.226	38.140	40.985	69.560	-3.455
4500	9.821	74.114	65.421	39.121	40.891	70.213	-3.410
4600	9.841	74.330	65.612	40.104	40.790	70.867	-3.367
4700	9.861	74.542	65.800	41.089	40.679	71.518	-3.326
4800	9.881	74.750	65.984	42.076	40.557	72.174	-3.286
4900	9.901	74.954	66.165	43.065	40.424	72.832	-3.248
5000	9.921	75.154	66.343	44.056	40.280	73.500	-3.213
5100	9.941	75.351	66.518	45.049	40.123	74.163	-3.178
5200	9.960	75.544	66.689	46.044	39.954	74.835	-3.145
5300	9.980	75.734	66.858	47.041	39.769	75.504	-3.113
5400	10.000	75.921	67.024	48.040	39.570	76.179	-3.083
5500	10.020	76.104	67.188	49.041	39.353	76.865	-3.054
5600	10.040	76.285	67.349	50.044	39.120	77.544	-3.026
5700	10.060	76.463	67.507	51.049	38.868	78.235	-3.000
5800	10.080	76.638	67.663	52.056	38.596	78.929	-2.974
5900	10.100	76.810	67.816	53.065	38.305	79.628	-2.950
6000	10.120	76.980	67.968	54.076	37.991	80.333	-2.926

Dec. 31, 1960; Sept. 30, 1966; Dec. 31, 1966

LITHIUM NITRIDE (LiN) (IDEAL GAS) GFW = 20.9457

Ground State Configuration [$^3\Sigma$]

ΔHf°_0 = 80 ± 40 kcal/mol

$S^\circ_{298.15}$ = [49.7] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 80 ± 40 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]

ω_e = [700] cm^{-1}

$\omega_e x_e$ = [7] cm^{-1}

σ = 1

B_e = [1.25] cm^{-1}

α_e = [0.0183] cm^{-1}

r_e = [1.71] Å

Heat of Formation.

The adopted $\Delta Hf^\circ_{298.15}$, 80 ± 40 kcal/mol, is calculated from the following estimates:

Method	D°_0 kcal/mol	$\Delta Hf^\circ_{298.15}$ kcal/mol
Estimate D°_0 from geometric mean for Li_2 and N_2	76	75
Estimate from D°_0 for series N_2(g), CN(g), BN(g) and BeN(g)	40 - 100	110 - 50
Estimate from D°_0 for series HN(g), HO(g), HF(g), LiF(g) and LiO(g)	20 - 60	130 - 90

J. L. Margrave and P. Sthapitanonda, J. Phys. Chem. 59, 1231 (1955), report estimated dissociation energies in the range 111-178 kcal/mol, based on approximate ionic binding energies calculated from ionic radii for N^- in the range 0.70 to 1.08 Å.

Heat Capacity and Entropy.

The molecular constants ω_e, r_e and $\omega_e x_e$ are estimated by comparison with those of CN, BN, CO, BO and LiO. The values of α_e and B_e are calculated from the above constants. The ground state configuration is assumed to be $^3\Sigma$ by analogy with NH and OH^+.

Lithium Nitroxide (LiON)

(Ideal Gas) GFW = 36.9451

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.701	43.478	43.478	INFINITE
100	8.359	48.373	67.350	-1.898	43.468	42.785	-93.507
200	9.640	54.567	59.550	-.997	43.233	42.189	-46.102
298	10.617	58.608	58.608	.000	43.000	41.728	-30.587
300	10.633	58.674	58.608	.020	42.996	41.719	-30.393
400	11.373	61.839	59.035	1.122	42.773	41.328	-22.581
500	11.932	64.440	59.863	2.288	41.804	41.069	-17.951
600	12.351	66.654	60.815	3.503	41.573	40.945	-14.914
700	12.663	68.583	61.790	4.755	41.371	40.855	-12.756
800	12.897	70.290	62.748	6.033	41.187	40.793	-11.144
900	13.075	71.819	63.672	7.332	41.009	40.756	-9.897
1000	13.212	73.204	64.557	8.647	40.833	40.738	-8.903
1100	13.319	74.469	65.402	9.974	40.658	40.736	-8.093
1200	13.404	75.632	66.207	11.310	40.482	40.750	-7.422
1300	13.473	76.707	66.973	12.654	40.306	40.780	-6.856
1400	13.529	77.708	67.705	14.004	40.129	40.823	-6.373
1500	13.575	78.643	68.403	15.360	39.951	40.878	-5.956
1600	13.613	79.520	69.071	16.719	39.773	40.947	-5.593
1700	13.645	80.347	69.710	18.082	4.546	42.353	-5.445
1800	13.672	81.127	70.323	19.448	4.546	44.579	-5.413
1900	13.696	81.867	70.911	20.816	4.544	46.805	-5.384
2000	13.716	82.570	71.477	22.187	4.537	49.027	-5.357
2100	13.733	83.240	72.021	23.559	4.527	51.250	-5.334
2200	13.749	83.879	72.546	24.934	4.513	53.477	-5.312
2300	13.762	84.490	73.052	26.309	4.496	55.703	-5.293
2400	13.774	85.076	73.541	27.686	4.473	57.930	-5.275
2500	13.784	85.639	74.013	29.064	4.445	60.157	-5.259
2600	13.793	86.180	74.471	30.443	4.414	62.385	-5.244
2700	13.802	86.700	74.914	31.822	4.376	64.617	-5.230
2800	13.809	87.203	75.344	33.203	4.333	66.846	-5.218
2900	13.816	87.687	75.762	34.584	4.284	69.083	-5.206
3000	13.822	88.156	76.167	35.966	4.229	71.318	-5.195
3100	13.828	88.609	76.561	37.349	4.166	73.556	-5.186
3200	13.833	89.048	76.944	38.732	4.097	75.794	-5.177
3300	13.837	89.474	77.318	40.115	4.019	78.035	-5.168
3400	13.841	89.887	77.681	41.499	3.935	80.282	-5.160
3500	13.845	90.288	78.036	42.883	3.843	82.526	-5.153
3600	13.849	90.678	78.382	44.268	3.742	84.778	-5.147
3700	13.852	91.058	78.719	45.653	3.633	87.027	-5.140
3800	13.855	91.427	79.049	47.038	3.514	89.288	-5.135
3900	13.858	91.787	79.371	48.424	3.388	91.546	-5.130
4000	13.860	92.138	79.686	49.810	3.251	93.805	-5.125
4100	13.863	92.480	79.994	51.196	3.104	96.074	-5.121
4200	13.865	92.814	80.295	52.582	2.947	98.342	-5.117
4300	13.867	93.141	80.590	53.969	2.781	100.614	-5.114
4400	13.869	93.460	80.879	55.356	2.603	102.890	-5.111
4500	13.871	93.771	81.162	56.743	2.413	105.175	-5.108
4600	13.872	94.076	81.439	58.130	2.212	107.462	-5.106
4700	13.874	94.374	81.711	59.517	1.998	109.750	-5.103
4800	13.875	94.667	81.978	60.905	1.771	112.042	-5.101
4900	13.877	94.953	82.240	62.292	1.530	114.338	-5.100
5000	13.878	95.233	82.497	63.680	1.276	116.649	-5.099
5100	13.879	95.508	82.749	65.068	1.005	118.958	-5.098
5200	13.880	95.777	82.997	66.456	.719	121.276	-5.097
5300	13.882	96.042	83.241	67.844	.416	123.593	-5.096
5400	13.883	96.301	83.481	69.232	.096	125.921	-5.096
5500	13.884	96.556	83.716	70.621	-.244	128.258	-5.096
5600	13.885	96.806	83.947	72.009	-.604	130.593	-5.097
5700	13.885	97.052	84.175	73.397	-.984	132.940	-5.097
5800	13.886	97.293	84.399	74.786	-1.387	135.299	-5.098
5900	13.887	97.531	84.620	76.175	-1.812	137.652	-5.099
6000	13.888	97.764	84.837	77.563	-2.262	140.025	-5.100

Sept. 30, 1966

LITHIUM NITROXIDE (LiON) (IDEAL GAS) GFW = 36.9451

Point Group C_s

$S^\circ_{298.15}$ = 58.61 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = [43.5 ± 10] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [43.0 ± 10] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
1350 (1)
330 (1)
650 (1)

Bond Distance: O-Li = 1.63 ± 0.07 Å

O-N = 1.30 ± 0.05 Å

Bond Angle: Li-O-N = 100 ± 10°

σ = 1

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.6523 x 10^{-116} g^3 cm^6

Heat of Formation

The heat of formation (ΔHf°_{298}) for LiON(g) has not been determined experimentally. The ΔHf°_{298} value adopted is calculated from the estimated Li-O and O-N bond energies. The value, D(Li-O) = 88 kcal/mol, is obtained by averaging the bonds in Li_2O(g). The value, D(O-N) = 69 kcal/mol, is calculated on the assumption that D(ClON-O) = D(N-OLi). The ΔHf°_{298} of LiOH(g), calculated similarly from bond energies (i.e. D(Li-O) = 88 kcal/mol and D(O-H) = 111 kcal/mol), is 10 kcal/mol more than the measured value. Therefore, we subtract 10 kcal/mol from the ΔHf°_{298} of LiON, 53 kcal/mol, estimated from the above bond energies, and arrive at 43 kcal/mol for the adopted value.

Heat Capacity and Entropy

The vibrational frequencies, bond distances and bond angle were obtained from W. L. S. Andrews and G. C. Pimentel, loc. cit. The three principal moments of inertia are: I_A = 1.2706 x 10^{-36}, I_B = 3.9776 x 10^{-39} and I_C = 5.2482 x 10^{-39} g cm^2.

Lithium Sodium Oxide (LiNaO)

(Ideal Gas) Mol. Wt. = 45.931

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.621	-23.938	-23.938	INFINITE
100	8.160	51.433	69.659	-1.823	-23.935	-26.257	57.382
200	9.195	57.391	62.176	-.957	-24.436	-28.398	31.030
298	10.296	61.270	61.270	.000	-25.000	-30.222	22.152
300	10.316	61.333	61.270	.019	-25.010	-30.254	22.039
400	11.257	64.436	61.686	1.100	-26.250	-31.862	17.408
500	11.939	67.026	62.502	2.262	-27.613	-33.117	14.475
600	12.415	69.247	63.446	3.481	-28.205	-34.161	12.443
700	12.748	71.188	64.416	4.740	-28.741	-35.113	10.962
800	12.986	72.906	65.372	6.027	-29.240	-35.988	9.831
900	13.160	74.446	66.296	7.335	-29.720	-36.802	8.936
1000	13.291	75.840	67.182	8.658	-30.191	-37.564	8.209
1100	13.391	77.112	68.028	9.992	-30.660	-38.280	7.605
1200	13.469	78.280	68.834	11.335	-54.369	-38.495	7.011
1300	13.531	79.361	69.603	12.685	-54.630	-37.161	6.247
1400	13.581	80.366	70.336	14.041	-54.888	-35.808	5.590
1500	13.622	81.304	71.036	15.401	-55.144	-34.436	5.017
1600	13.656	82.184	71.706	16.765	-55.396	-33.046	4.514
1700	13.684	83.013	72.347	18.132	-90.693	-30.313	3.897
1800	13.706	83.796	72.961	19.502	-90.762	-26.758	3.249
1900	13.728	84.538	73.551	20.874	-90.832	-23.199	2.668
2000	13.746	85.242	74.118	22.248	-90.904	-19.640	2.146
2100	13.761	85.913	74.664	23.623	-90.977	-16.077	1.673
2200	13.774	86.554	75.190	25.000	-91.054	-12.507	1.242
2300	13.785	87.166	75.698	26.378	-91.132	-8.937	.849
2400	13.795	87.753	76.188	27.757	-91.216	-5.359	.488
2500	13.804	88.316	76.662	29.137	-91.303	-1.782	.156
2600	13.812	88.858	77.121	30.517	-91.396	1.802	-.151
2700	13.819	89.379	77.565	31.899	-91.494	5.386	-.436
2800	13.826	89.882	77.996	33.281	-91.598	8.976	-.701
2900	13.831	90.367	78.414	34.664	-91.710	12.573	-.947
3000	13.837	90.836	78.820	36.048	-91.830	16.171	-1.178
3100	13.841	91.290	79.215	37.431	-91.958	19.773	-1.394
3200	13.845	91.730	79.600	38.816	-92.095	23.378	-1.597
3300	13.849	92.156	79.974	40.200	-92.243	26.989	-1.787
3400	13.853	92.569	80.338	41.586	-92.401	30.605	-1.967
3500	13.856	92.971	80.693	42.971	-92.571	34.226	-2.137
3600	13.859	93.361	81.040	44.357	-92.754	37.851	-2.298
3700	13.862	93.741	81.378	45.743	-92.950	41.478	-2.450
3800	13.864	94.111	81.708	47.129	-93.160	45.121	-2.595
3900	13.867	94.471	82.031	48.516	-93.387	48.759	-2.732
4000	13.869	94.822	82.346	49.902	-93.630	52.406	-2.863
4100	13.871	95.164	82.655	51.289	-93.892	56.064	-2.988
4200	13.873	95.499	82.957	52.677	-94.173	59.721	-3.107
4300	13.874	95.825	83.252	54.064	-94.473	63.392	-3.222
4400	13.876	96.144	83.542	55.452	-94.797	67.065	-3.331
4500	13.878	96.456	83.825	56.839	-95.146	70.751	-3.436
4600	13.879	96.761	84.103	58.227	-95.521	74.440	-3.537
4700	13.880	97.060	84.375	59.615	-95.924	78.136	-3.633
4800	13.882	97.352	84.643	61.003	-96.358	81.843	-3.726
4900	13.883	97.638	84.905	62.391	-96.827	85.561	-3.816
5000	13.884	97.918	85.163	63.780	-97.330	89.290	-3.903
5100	13.885	98.193	85.415	65.168	-97.873	93.031	-3.986
5200	13.886	98.463	85.664	66.557	-98.457	96.776	-4.067
5300	13.887	98.728	85.908	67.945	-99.087	100.537	-4.146
5400	13.888	98.987	86.148	69.334	-99.765	104.308	-4.221
5500	13.889	99.242	86.383	70.723	-100.496	108.095	-4.295
5600	13.889	99.492	86.615	72.112	-101.281	111.890	-4.367
5700	13.890	99.738	86.843	73.501	-102.124	115.707	-4.436
5800	13.891	99.980	87.068	74.890	-103.030	119.538	-4.504
5900	13.891	100.217	87.288	76.279	-104.001	123.384	-4.570
6000	13.892	100.451	87.506	77.668	-105.040	127.249	-4.635

June 30, 1961

Lithium Sodium Oxide (LiNaO) (Ideal Gas)

Mol. Wt. = 45.931

$\Delta H_f^\circ{}_{298.15}$ = [-25 ± 30] kcal. mole^{-1}

$S_{298.15}^\circ$ = [61.270] cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$

[400] (1)
[1000] (1)
[900] (1)

Li-O-Na angle = [105°], O-Li distance = [1.82] Å, ONa distance = [2.21] Å

Product of moments of inertia, $I_AI_BI_C$ = [3.179 X 10^{-115}] g.^{3} cm.^{6}

σ = 1

Heat of Formation. Estimated from bond energies derived from heats of formation used in JANAF tables.

Heat Capacity and Entropy. The molecular constants have been estimated by comparison of similar molecules.

Lithium Monoxide (LiO)

(Ideal Gas) Mol. Wt. = 22.940

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.138	20.105	20.105	INFINITE
100	6.966	42.517	56.050	-1.443	20.324	18.324	-40.045
200	7.252	47.407	51.088	-.736	20.251	16.341	-17.856
298	7.745	50.395	50.395	.000	20.100	14.453	-10.594
300	7.754	50.443	50.395	.014	20.097	14.418	-10.503
400	8.142	52.730	50.704	.810	19.916	12.552	-6.858
500	8.400	54.577	51.300	1.638	18.961	10.810	-4.725
600	8.573	56.125	51.979	2.488	18.720	9.204	-3.352
700	8.694	57.456	52.668	3.351	18.494	7.635	-2.384
800	8.782	58.623	53.341	4.225	18.277	6.098	-1.666
900	8.848	59.661	53.987	5.107	18.061	4.589	-1.114
1000	8.901	60.596	54.602	5.995	17.845	3.104	-.678
1100	8.945	61.447	55.186	6.887	17.630	1.640	-.326
1200	8.981	62.227	55.741	7.783	17.414	.195	-.036
1300	9.013	62.947	56.268	8.683	17.199	-1.231	.207
1400	9.042	63.616	56.769	9.586	16.985	-2.641	.412
1500	9.067	64.241	57.246	10.491	16.772	-4.035	.588
1600	9.091	64.827	57.702	11.399	16.561	-5.415	.740
1700	9.113	65.378	58.138	12.309	-18.697	-5.454	.701
1800	9.133	65.900	58.554	13.222	-18.726	-4.672	.567
1900	9.153	66.394	58.954	14.136	-18.757	-3.890	.447
2000	9.172	66.864	59.338	15.052	-18.788	-3.109	.340
2100	9.190	67.312	59.707	15.970	-18.822	-2.324	.242
2200	9.207	67.740	60.063	16.890	-18.858	-1.537	.153
2300	9.224	68.150	60.405	17.812	-18.894	-.750	.071
2400	9.241	68.543	60.736	18.735	-18.935	.041	-.004
2500	9.257	68.920	61.056	19.660	-18.978	.832	-.073
2600	9.273	69.283	61.366	20.586	-19.024	1.624	-.137
2700	9.289	69.634	61.665	21.514	-19.074	2.419	-.196
2800	9.305	69.972	61.956	22.444	-19.126	3.217	-.251
2900	9.320	70.299	62.238	23.375	-19.185	4.016	-.303
3000	9.335	70.615	62.512	24.308	-19.247	4.818	-.351
3100	9.350	70.921	62.778	25.242	-19.315	5.622	-.396
3200	9.365	71.218	63.038	26.178	-19.387	6.426	-.439
3300	9.380	71.507	63.290	27.116	-19.466	7.234	-.479
3400	9.395	71.787	63.536	28.054	-19.551	8.046	-.517
3500	9.410	72.060	63.775	28.995	-19.640	8.857	-.553
3600	9.424	72.325	64.009	29.936	-19.738	9.673	-.587
3700	9.439	72.583	64.237	30.879	-19.842	10.490	-.620
3800	9.453	72.835	64.460	31.824	-19.952	11.315	-.651
3900	9.468	73.081	64.678	32.770	-20.070	12.138	-.680
4000	9.482	73.321	64.891	33.718	-20.197	12.964	-.708
4100	9.497	73.555	65.100	34.667	-20.331	13.797	-.735
4200	9.511	73.784	65.304	35.617	-20.475	14.629	-.761
4300	9.525	74.008	65.504	36.569	-20.626	15.468	-.786
4400	9.540	74.227	65.699	37.522	-20.786	16.309	-.810
4500	9.554	74.442	65.891	38.477	-20.957	17.155	-.833
4600	9.568	74.652	66.080	39.433	-21.137	18.005	-.855
4700	9.582	74.858	66.264	40.390	-21.329	18.855	-.877
4800	9.596	75.060	66.445	41.349	-21.531	19.712	-.897
4900	9.610	75.258	66.623	42.310	-21.746	20.571	-.917
5000	9.624	75.452	66.798	43.271	-21.973	21.439	-.937
5100	9.639	75.643	66.969	44.234	-22.215	22.312	-.956
5200	9.653	75.830	67.138	45.499	-22.470	23.186	-.974
5300	9.667	76.014	67.304	46.165	-22.741	24.066	-.992
5400	9.681	76.195	67.467	47.132	-23.027	24.950	-1.010
5500	9.695	76.373	67.627	48.101	-23.330	25.844	-1.027
5600	9.709	76.547	67.785	49.071	-23.652	26.737	-1.043
5700	9.723	76.719	67.940	50.043	-23.993	27.641	-1.060
5800	9.737	76.889	68.093	51.016	-24.354	28.553	-1.076
5900	9.751	77.055	68.243	51.990	-24.736	29.466	-1.091
6000	9.765	77.219	68.392	52.966	-25.141	30.391	-1.107

Dec. 31, 1960; Mar. 31, 1964

LITHIUM MONOXIDE (LiO) (IDEAL GAS) MOL. WT. = 22.940

Ground State Configuration [$^2\Pi$]

$S^\circ_{298.15}$ =[50.395]cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 20.1 ± 5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 20.1 ± 5 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	4

ω_e = 745 cm.$^{-1}$

B_e = [1.333] cm.$^{-1}$

$\omega_e x_e$ = [4.835] cm.$^{-1}$

α_e = [0.01288] cm.$^{-1}$

σ =1

r_e = [1.62] Å

Heat of Formation.

D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963) calculated the heat of formation from their mass spectral data by two different methods.

For the first calculation (a) they combined the slope of the log IT vs 1/T curve for LiO^+ with the slopes for Li^+ and Li_2O^+ for the reaction $Li_2O\ (g) \rightarrow Li(g) + LiO(g)$. For the second calculation (b) they assumed a cross section $\sigma_{LiO}/\sigma_{Li_2O} = 1$ and from this they calculated a partial pressure for LiO(g) at 1500°K and an equilibrium constant for the reaction $Li_2O(g) \rightarrow Li(g) + LiO(g)$. They obtained (a) $\Delta H^\circ_{f\ 298}$ = 18.3 kcal. mole^{-1} and (b) $\Delta H^\circ_{f\ 298}$ = 16.3 kcal. mole^{-1}, and used the average value from the two methods for the heat of formation of LiO(g). The JANAF heat of formation, 20.1 ± 5 kcal. mole^{-1}, was obtained in the same way using their data and the present tables i.e. (a) $\Delta H^\circ_{f\ 298}$ = 22.0 kcal. mole^{-1} and (b) $\Delta H^\circ_{f\ 298}$ = 18.3 kcal. mole^{-1}.

Heat Capacity and Entropy.

The molecular constants, $\omega_e x_e$, Be, and α_e, were calculated from ω_e and r_e, reported by White et al. The ground state configuration, $^2\Pi$, was estimated by J. S. Gordon, Thiokol Chemical Corp., Reaction Motor Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960, by A Buchler and J. L. Stauffer, J. Chem. Phys. 39, 2299 (1963) and by White et al.

Lithium Monoxide Uninegative Ion (LiO^-)

(Ideal Gas) GFW = 22.93895

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	7.734	47.593	47.593	.000	-16.000	-19.324	14.165
300	7.742	47.641	47.593	.014	-16.012	-19.345	14.093
400	8.131	49.925	47.902	.809	-16.691	-20.354	11.121
500	8.390	51.769	48.496	1.636	-18.144	-21.112	9.228
600	8.564	53.315	49.174	2.484	-18.884	-21.636	7.881
700	8.685	54.645	49.863	3.347	-19.606	-22.037	6.880
800	8.773	55.810	50.535	4.220	-20.321	-22.337	6.102
900	8.840	56.848	51.180	5.101	-21.035	-22.546	5.475
1000	8.893	57.782	51.794	5.988	-21.749	-22.675	4.956
1100	8.936	58.632	52.378	6.879	-22.462	-22.733	4.517
1200	8.972	59.411	52.932	7.775	-23.175	-22.728	4.139
1300	9.004	60.130	53.458	8.674	-23.887	-22.661	3.810
1400	9.032	60.799	53.959	9.575	-24.599	-22.540	3.519
1500	9.057	61.423	54.436	10.480	-25.310	-22.368	3.259
1600	9.080	62.008	54.891	11.387	-26.020	-22.147	3.025
1700	9.101	62.559	55.326	12.296	-61.776	-20.555	2.643
1800	9.121	63.080	55.742	13.207	-62.302	-18.114	2.199
1900	9.141	63.573	56.142	14.120	-62.830	-15.645	1.800
2000	9.159	64.043	56.525	15.035	-63.360	-13.150	1.437
2100	9.176	64.490	56.894	15.952	-63.892	-10.626	1.106
2200	9.193	64.917	57.249	16.870	-64.427	-8.075	.802
2300	9.210	65.326	57.591	17.790	-64.961	-5.503	.523
2400	9.226	65.719	57.922	18.712	-65.500	-2.907	.265
2500	9.242	66.096	58.241	19.636	-66.041	-.288	.025
2600	9.257	66.458	58.550	20.561	-66.585	2.353	-.198
2700	9.272	66.808	58.850	21.487	-67.134	5.013	-.406
2800	9.287	67.145	59.140	22.415	-67.685	7.696	-.601
2900	9.302	67.472	59.422	23.345	-68.242	10.399	-.784
3000	9.317	67.787	59.695	24.275	-68.803	13.123	-.956
3100	9.331	68.093	59.961	25.208	-69.370	15.864	-1.118
3200	9.346	68.389	60.220	26.142	-69.941	18.618	-1.272
3300	9.360	68.677	60.472	27.077	-70.518	21.394	-1.417
3400	9.374	68.957	60.717	28.014	-71.101	24.189	-1.555
3500	9.389	69.229	60.957	28.952	-71.690	26.998	-1.686
3600	9.403	69.494	61.190	29.892	-72.286	29.828	-1.811
3700	9.417	69.751	61.418	30.832	-72.890	32.674	-1.930
3800	9.430	70.003	61.641	31.775	-73.500	35.537	-2.044
3900	9.444	70.248	61.858	32.719	-74.117	38.413	-2.153
4000	9.458	70.487	62.071	33.664	-74.742	41.306	-2.257
4100	9.472	70.721	62.279	34.610	-75.376	44.218	-2.357
4200	9.486	70.949	62.483	35.558	-76.018	47.138	-2.453
4300	9.499	71.173	62.682	36.507	-76.669	50.080	-2.545
4400	9.513	71.391	62.878	37.458	-77.329	53.034	-2.634
4500	9.527	71.605	63.069	38.410	-77.999	56.007	-2.720
4600	9.540	71.815	63.257	39.363	-78.679	58.992	-2.803
4700	9.554	72.020	63.442	40.318	-79.370	61.990	-2.883
4800	9.567	72.221	63.622	41.274	-80.072	65.007	-2.960
4900	9.581	72.419	63.800	42.231	-80.788	68.033	-3.034
5000	9.594	72.612	63.974	43.190	-81.513	71.079	-3.107
5100	9.608	72.802	64.145	44.150	-82.255	74.143	-3.177
5200	9.621	72.989	64.314	45.112	-83.010	77.212	-3.245
5300	9.635	73.172	64.479	46.075	-83.781	80.302	-3.311
5400	9.648	73.353	64.642	47.039	-84.567	83.404	-3.376
5500	9.662	73.530	64.802	48.004	-85.371	86.524	-3.438
5600	9.675	73.704	64.959	48.971	-86.192	89.656	-3.499
5700	9.689	73.875	65.114	49.939	-87.033	92.800	-3.558
5800	9.702	74.044	65.267	50.909	-87.895	95.968	-3.616
5900	9.715	74.210	65.417	51.880	-88.777	99.144	-3.673
6000	9.729	74.373	65.565	52.852	-89.683	102.336	-3.728

Dec. 31, 1967

LITHIUM MONOXIDE UNINEGATIVE ION (LiO^-) (IDEAL GAS) GFW = 22.93895

Ground State Configuration [$^1\Sigma$]

ΔHf_0° = [-16 ± 15] kcal/mol

$S_{298.15}^\circ$ = [47.6 ± 0.3] gibbs/mol

$\Delta Hf_{298.15}^\circ$ = [-16 ± 15] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[1]

ω_e = [750] cm^{-1}

B_e = [1.360] cm^{-1}

$\omega_e x_e$ = [4.5] cm^{-1}

α_e = [0.0121] cm^{-1}

σ = 1

r_e = [1.6] Å

Heat of Formation

Data on the electron affinity (E.A.) of LiO (g) are unavailable, therefore the value of $\Delta Hf_{298}^\circ(LiO^-, g)$ is estimated. We first assume that the enthalpy change (ΔHr_0°) of the reaction (1) $LiO^-(g) = Li(g) + O^-(g)$ is close to the average of the ΔHr_0° values for the reactions (2) $LiO(g) = Li(g) + O(g)$ and (3) $LiF(g) = Li(g) + F(g)$. The atom F(g) is isoelectronic with $O^-(g)$. In other words, the ΔHr_0° for reaction (1) is approximately 1/2(76.91 + 135.84) = 106.4 kcal/mol. Then we compare the ΔHr_0° values for the reactions (4) $HO(g) = H(g) + O(g)$, (5) $HO^-(g) = H(g) + O^-(g)$, and (6) $HF(g) = H(g) + F(g)$, and find that ΔHr_0° for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔHr_0° values for reactions (4) and (6). Based on this fact we estimate ΔHr_0° = 96.4 kcal/mol for reaction (1), yielding $\Delta Hf_{298}^\circ(LiO^-, g)$ = -15.5 kcal/mol.

Applying the difference in electron affinity between H(g) and Li(g) to OH(g) gives an approximate value, E. A. = 1.7 eV (39.2 kcal/mol) for LiO(g). The value of E. A. for H(g), Li(g) and OH(g) are taken from U. S. Bur. Std. Rept. 8628, Jan. 1, 1965. Based on ΔHr_0° = 39.2 kcal/mol for the reaction $LiO^-(g) = LiO(g) + e^-(g)$, we derive ΔHf_{298}° = -19.1 kcal/mol for $LiO^-(g)$, which is in reasonable agreement with the above estimated value.

The value of ΔHf_{298}° for $LiO^-(g)$ is tentatively adopted as -16 ± 15 kcal/mol. Using this ΔHf_{298}° value, we derive E. A. = 1.6 ± 0.7 eV for LiO(g). The electron affinity of OH(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of LiF(g) which is isoelectronic with $LiO^-(g)$. The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with the observed data for LiF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ by use of the method suggested by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.137 kcal/mol.

Lithium, Diatomic (Li_2)

(Ideal Gas) Mol. Wt. = 13.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.312	50.298	50.298	INFINITE
100	7.309	38.310	54.405	-1.610	50.762	47.283	-103.332
200	8.214	43.684	47.828	-.829	50.663	43.823	-47.885
298	8.622	47.050	47.050	.000	50.400	40.519	-29.700
300	8.627	47.104	47.051	.016	50.394	40.457	-29.471
400	8.826	49.616	47.392	.890	50.026	37.199	-20.323
500	8.942	51.599	48.042	1.778	48.078	34.194	-14.946
600	9.022	53.236	48.775	2.677	47.551	31.468	-11.462
700	9.084	54.632	49.514	3.582	47.056	28.826	-8.999
800	9.136	55.848	50.232	4.493	46.583	26.253	-7.172
900	9.182	56.927	50.917	5.409	46.117	23.740	-5.765
1000	9.224	57.897	51.567	6.330	45.658	21.279	-4.650
1100	9.264	58.778	52.183	7.254	45.206	18.863	-3.748
1200	9.301	59.585	52.767	8.182	44.758	16.487	-3.003
1300	9.338	60.331	53.320	9.114	44.318	14.149	-2.378
1400	9.374	61.025	53.846	10.050	43.884	11.845	-1.849
1500	9.409	61.673	54.347	10.989	43.457	9.571	-1.394
1600	9.444	62.281	54.824	11.932	43.038	7.327	-1.001
1700	9.478	62.855	55.279	12.878	-27.470	7.763	-.998
1800	9.512	63.397	55.716	13.827	-27.515	9.840	-1.195
1900	9.546	63.913	56.134	14.780	-27.556	11.918	-1.371
2000	9.579	64.403	56.535	15.736	-27.596	13.994	-1.529
2100	9.612	64.871	56.921	16.696	-27.634	16.073	-1.673
2200	9.646	65.319	57.292	17.659	-27.671	18.157	-1.804
2300	9.679	65.749	57.651	18.625	-27.705	20.239	-1.923
2400	9.712	66.161	57.997	19.595	-27.741	22.324	-2.033
2500	9.745	66.558	58.331	20.567	-27.777	24.413	-2.134
2600	9.778	66.941	58.655	21.543	-27.813	26.498	-2.227
2700	9.810	67.311	58.969	22.523	-27.851	28.588	-2.314
2800	9.843	67.668	59.273	23.506	-27.890	30.679	-2.395
2900	9.876	68.014	59.569	24.492	-27.937	32.772	-2.470
3000	9.909	68.350	59.856	25.481	-27.983	34.868	-2.540
3100	9.941	68.675	60.135	26.473	-28.039	36.965	-2.606
3200	9.974	68.991	60.407	27.469	-28.097	39.061	-2.668
3300	10.006	69.298	60.672	28.468	-28.164	41.161	-2.726
3400	10.039	69.598	60.930	29.470	-28.238	43.265	-2.781
3500	10.072	69.889	61.182	30.476	-28.318	45.367	-2.833
3600	10.104	70.173	61.428	31.485	-28.409	47.474	-2.882
3700	10.137	70.451	61.668	32.497	-28.509	49.580	-2.928
3800	10.169	70.721	61.902	33.512	-28.620	51.699	-2.973
3900	10.202	70.986	62.132	34.530	-28.742	53.814	-3.015
4000	10.234	71.245	62.357	35.552	-28.876	55.930	-3.056
4100	10.267	71.498	62.576	36.577	-29.023	58.054	-3.094
4200	10.299	71.746	62.792	37.606	-29.184	60.177	-3.131
4300	10.332	71.988	63.003	38.637	-29.359	62.307	-3.167
4400	10.364	72.226	63.210	39.672	-29.548	64.444	-3.201
4500	10.396	72.459	63.413	40.710	-29.756	66.582	-3.234
4600	10.429	72.688	63.612	41.751	-29.981	68.725	-3.265
4700	10.461	72.913	63.807	42.796	-30.224	70.868	-3.295
4800	10.494	73.134	63.999	43.843	-30.489	73.021	-3.325
4900	10.526	73.350	64.188	44.894	-30.776	75.181	-3.353
5000	10.559	73.563	64.373	45.949	-31.083	77.351	-3.381
5100	10.591	73.773	64.556	47.006	-31.418	79.524	-3.408
5200	10.623	73.979	64.735	48.067	-31.779	81.703	-3.434
5300	10.656	74.181	64.911	49.131	-32.169	83.884	-3.459
5400	10.688	74.381	65.085	50.198	-32.588	86.078	-3.484
5500	10.721	74.577	65.256	51.268	-33.042	88.282	-3.508
5600	10.753	74.771	65.424	52.342	-33.528	90.486	-3.531
5700	10.786	74.961	65.589	53.419	-34.051	92.710	-3.555
5800	10.818	75.149	65.753	54.499	-34.615	94.939	-3.577
5900	10.850	75.334	65.913	55.583	-35.217	97.177	-3.599
6000	10.883	75.517	66.072	56.669	-35.865	99.430	-3.622

June 0, 1960

LITHIUM, DIATOMIC (Li_2) (IDEAL GAS) MOL. WT. = 13.880

$\Delta H^\circ_{f0} = 50.298$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 50.4 \pm 0.9$ kcal. mole^{-1}

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15} = 47.050$ cal. deg. mole^{-1}

$\omega_e = 353.59$ cm.$^{-1}$

$\omega_e x_e = 2.625$ cm.$^{-1}$

$\sigma = 2$

$B_e = 0.6812$ cm.$^{-1}$

$\alpha_e = 0.00718$ cm.$^{-1}$

$r_e = 2.673$ Å

Heat of Formation.

Same as the heat of sublimation to the diatomic gas; see notes on Li (crystal).

Heat Capacity and Entropy.

The spectroscopic constants of Li_2^7 listed by G. Hertzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York (1950) have been corrected for the presence of 7.5% Li^6 in naturally occuring lithium, J. R. Stehn and E. F. Clancy, "Chart of the Nuclides", General Electric Co., Schenectady (1956).

Dilithium Monoxide (Li_2O)

(Crystal) Mol. Wt. = 29.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.732	- 141.585	- 141.585	INFINITE
100	2.497	.868	17.547	- 1.668	- 142.115	- 139.774	305.461
200	8.892	4.680	10.125	- 1.089	- 142.756	- 137.172	149.887
298	12.927	9.056	9.056	.000	- 143.100	- 134.348	98.475
300	12.997	9.136	9.056	.024	- 143.105	- 134.294	97.829
400	15.297	13.221	9.597	1.449	- 143.277	- 131.328	71.751
500	16.630	16.786	10.687	3.050	- 144.878	- 128.175	56.023
600	17.644	19.905	11.969	4.762	- 144.969	- 124.824	45.465
700	18.500	22.691	13.305	6.570	- 144.950	- 121.468	37.922
800	19.255	25.211	14.638	8.458	- 144.845	- 118.120	32.267
900	19.940	27.518	15.943	10.418	- 144.674	- 114.789	27.873
1000	20.605	29.654	17.209	12.446	- 144.440	- 111.480	24.363
1100	21.225	31.648	18.432	14.538	- 144.143	- 108.198	21.496
1200	21.800	33.519	19.612	16.689	- 143.792	- 104.946	19.112
1300	22.275	35.283	20.750	18.893	- 143.388	- 101.726	17.101
1400	22.675	36.949	21.848	21.141	- 142.942	- 98.536	15.381
1500	23.000	38.525	22.908	23.426	- 142.459	- 95.382	13.896
1600	23.260	40.018	23.931	25.739	- 141.947	- 92.658	12.601
1700	23.502	41.435	24.919	28.077	- 211.504	- 86.514	11.122
1800	23.770	42.786	25.875	30.440	- 210.579	- 79.185	9.614
1900	24.030	44.078	26.799	32.830	- 209.630	- 71.910	8.271
2000	24.240	45.316	27.694	35.244	- 208.663	- 64.689	7.069
2100	24.447	46.504	28.562	37.678	- 207.679	- 57.516	5.985
2200	24.652	47.646	29.403	40.133	- 206.680	- 50.387	5.005
2300	24.854	48.746	30.221	42.609	- 205.662	- 43.307	4.115
2400	25.053	49.808	31.015	45.104	- 204.634	- 36.269	3.303
2500	25.249	70.835	31.787	47.619	- 203.591	- 29.275	2.559
2600	25.443	51.829	32.539	50.154	- 202.534	- 22.325	1.877
2700	25.634	52.793	33.271	52.708	- 201.467	- 15.415	1.248
2800	25.822	53.728	33.985	55.280	- 200.388	- 8.543	.667
2900	26.007	54.638	34.682	57.872	- 199.303	- 1.710	.129
3000	26.190	55.522	35.362	60.482	- 198.205	5.087	- .371

Dec. 31, 1960; Mar. 31, 1964

DILITHIUM MONOXIDE (Li_2O) (CRYSTAL) MOL. WT. = 29.880

$S^\circ_{298.15}$ = 9.056 cal. deg.$^{-1}$ mole^{-1}

T_m = 1843°K.

$\Delta H^\circ_{f\ 0}$ = -141.6 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -143.1 ± 0.5 kcal. mole^{-1}

ΔH_m = [14] kcal. mole^{-1}

Heat of Formation.

The selected heat of formation was calculated as follows:

	Reaction	$\Delta H^\circ_{r\ 298.15}$ kcal. mole^{-1}	Ref.
(I)	$Li_2O(c) + H_2O(l) = 2LiOH(\infty H_2O)$	-31.74 ± 0.08	(a)
(II)	$Li(c) + 1/2\ O_2(g) = LiOH(\infty H_2O)$	-121.572 ± 0.019	(b)
(III)	$H_2(g) + 1/2\ O_2(g) = H_2O(l)$	-68.3174	(c)
(IV)	$2Li(c) + 1/2\ O_2(g) = Li_2O(c)$	-143.1 ± 0.5	(d)

(a) V. P. Kolesov, S. M. Skuratov, and I. D. Zaikin, Russian J. Inorganic Chemistry, 4, 558 (1959).

(b) S. R. Gunn and L. G. Green, J. Am. Chem. Soc., 80, 4782 (1958).

(c) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties" National Bureau of Standards Circular 500, 1952 (reprinted 1961).

(d) Reaction (IV) is the sum of -(I) + 2(II) - (III).

Kolesov, et al. (loc. cit) measured the enthalpy of the reaction of Li_2O with water at 20° in 5 experiments. The mean ΔH°_r was -31.41 ± 0.08 kcal. This was brought to 298°K by Kolesov using enthalpy data of (a) H. L. Johnston and T. W. Bauer, J. Am. Chem. Soc. 73, 1119 (1951), for Li_2O, (b) N. S. Osborne, J. F. Stimson, and D. C. Ginnings, J. Res. Natl. Bur. Stds. A, 23, 197 (1939) for H_2O, (c) F. T. Gucker and K. N. Schminke, J. Am. Chem. Soc., 55, 1013 (1933) for C_p of LiOH(aq) and (d) Rossini, et al., (loc. cit) for aqueous LiOH. In addition to the above, N. N. Beketov, Bull. Acad. Sci. Russ. 32, 186 (1888) and H. R. Forcrand, Compt Rend. 144, 1403 (1907) have reported experimental heats for Li_2O. Rossini et al. and Johnston and Bauer have reported heats of formation for Li_2O recalculated from older data. L. G. Fasolino, in a Natl. Research Corp. Quarterly Report, July 1 to Sept. 30, 1962, reported a $\Delta H^\circ_{f\ 298}$ of -141.1 ± 4.2 kcal. He measured the heat of combustion of Li(c) in $O_2(g)$ in a Parr bomb.

Heat Capacity and Entropy.

The low temperature C_p data of H. L. Johnston and T. W. Bauer, (loc. cit.) from [17° -298°K.] was joined graphically to the high temperature C_p data of C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. 77, 285 (1955) [425°-1045°K] and E. N. Rodigina, and K. A. Gomelskii, Russian J. Phys. Chem. 35, 898 (1961) [370°-1125°K]. The $S^\circ_{298.15}$ was reported by Johnston and Bauer using S°_{16} (extrap.) = 0.003 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The melting point of Li_2O is uncertain. The selected melting point, 1843°K., was measured by A. E. van Arkel, E. A. Flood, and N. F. H. Bright, Can. J. Chem. 31, 1009 (1953). L. Brewer and J. L. Margrave, J. Phys. Chem. 59, 421 (1955) reported the melting point 1700°K. They also stated that H. van Kooster and F. Jaeger, Proc. Roy. Acad. Sco., Amsterdam 16, 857 (1914) had reported 1700° (1973°K) as the melting point. The heat of melting, [14] kcal. mole^{-1}, was estimated by A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K", Argonne National Laboratory, University of Chicago, ANL-5750, 1957.

Heat of Sublimation.

$Li_2O(c)$ vaporizes to $Li_2O(g)$, LiO(g), $Li_2O_2(g)$, Li(g), and $O_2(g)$ [J. Berkowitz, W. A. Chupka, G. D. Blue and J. L. Margrave, J. Phys. Chem., 63, 644 (1959); D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963); D. L. Hildenbrand, W. F. Hall, and N. D. Potter, J. Chem. Phy. 39, 296 (1963); D. L. Hildenbrand, L. P. Theard, W. F. Hall, and N. D. Potter, Fifth Quarterly Technical Report, U-2289, Aeronutronic Division of Philco Corporation, 15 September 1963; L. P. Firsova and A. N. Nesmeyanov, Russian J. Phys. Chem., 34, 1232 (1960). The major species (0°-1700°K.) are reported to be $Li_2O(g)$, Li(g), and $O_2(g)$ with lesser amounts of LiO(g) and $Li_2O_2(g)$. Hildenbrand, et al., U-2298, have reported about equal amounts of Li_2O^+ and Li^+ (1300 to 1550°K.) and about 1/30th of this amount of LiO^+. White, et al., calculated ΔH_s from their mass spectra data. They made two different calculations: (a) for $Li_2O(c) \rightarrow Li_2O(g)$, and (b) for $Li_2O(g) \rightarrow 2Li(g) + 1/2\ O_2(g)$, and found: (a) 102.5 kcal. and (b) 99.0 kcal. They used a weighted average of (a) and (b) and obtained 101.6 kcal. at 0°K. The selected $\Delta H^\circ_{s\ 298}$ of 102.3 ± 3 kcal. was obtained in the same manner using their data and the present JANAF functions, i.e. (a) 104.2 kcal. and (b) 100.3 kcal. Knudson-effusion data of White et al., corrected for dissociation gave 3rd law heats at 298°K of 101.9 kcal. and a 2nd law heat of 94 kcal. Recalculation of Hildenbrand's dissociation pressure with JANAF values gives Li_2O pressures slightly different than those reported. The recalculated pressures give a 3rd law $\Delta H^\circ_{s\ 298}$ of 101.7 kcal. for both cells. The corresponding 2nd law values are 85 and 95.5 kcal. for cell 7 and 8. The 3rd law treatment of both sets of data show relatively large trends of ΔH_s with T which are probably too large to be only due to errors in the functions. (Continued on Lithium Oxide $Li_2O(g)$ table)

Dilithium Monoxide (Li_2O)

(Liquid) Mol. Wt. = 29.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	12.927	13.160	13.160	.000	- 132.129	- 124.601	91.330
300	12.997	13.240	13.160	.024	- 132.134	- 124.555	90.734
400	15.297	17.317	13.700	1.447	- 132.308	- 121.998	66.653
500	16.630	20.880	14.788	3.046	- 133.911	- 119.255	52.124
600	24.000	24.006	16.069	4.762	- 133.998	- 116.313	42.365
700	24.000	27.706	17.474	7.162	- 133.387	- 113.416	35.408
800	24.000	30.911	18.958	9.562	- 132.770	- 110.605	30.214
900	24.000	33.737	20.446	11.962	- 132.159	- 107.871	26.193
1000	24.000	36.266	21.904	14.362	- 131.552	- 105.205	22.991
1100	24.000	38.554	23.315	16.762	- 130.948	- 107.599	20.384
1200	24.000	40.642	24.673	19.162	- 130.348	- 100.050	18.221
1300	24.000	42.563	25.977	21.562	- 129.748	- 97.549	16.399
1400	24.000	44.341	27.226	23.962	- 129.150	- 95.094	14.844
1500	24.000	45.997	28.423	26.362	- 128.552	- 92.683	13.503
1600	24.000	47.546	29.570	28.762	- 127.952	- 90.310	12.335
1700	24.000	49.001	30.671	31.162	- 197.447	- 85.320	10.968
1800	24.000	50.373	31.727	33.562	- 196.486	- 78.749	9.561
1900	24.000	51.671	32.743	35.962	- 195.527	- 72.233	8.308
2000	24.000	52.902	33.721	38.362	- 194.573	- 65.771	7.187
2100	24.000	54.073	34.662	40.762	- 193.624	- 59.355	6.177
2200	24.000	55.189	35.570	43.162	- 192.680	- 52.982	5.763
2300	24.000	56.256	36.446	45.562	- 191.738	- 46.655	4.433
2400	24.000	57.277	37.293	47.962	- 190.805	- 40.367	3.676
2500	24.000	58.257	38.112	50.362	- 189.877	- 34.117	2.982
2600	24.000	59.198	38.905	52.762	- 188.955	- 27.907	2.346
2700	24.000	60.104	39.674	55.162	- 188.042	- 21.730	1.759
2800	24.000	60.977	40.419	57.562	- 187.135	- 15.586	1.217
2900	24.000	61.819	41.143	59.962	- 186.241	- 9.475	.714
3000	24.000	62.633	41.845	62.362	- 185.354	- 3.393	.247
3100	24.000	63.420	42.529	64.762	- 184.480	2.660	- .187
3200	24.000	64.182	43.194	67.162	- 183.615	8.680	- .593
3300	24.000	64.920	43.841	69.562	- 182.764	14.675	- .972
3400	24.000	65.637	44.471	71.962	- 181.926	20.649	- 1.327
3500	24.000	66.332	45.086	74.362	- 181.099	26.591	- 1.660
3600	24.000	67.009	45.686	76.762	- 180.288	32.515	- 1.974
3700	24.000	67.666	46.271	79.162	- 179.491	38.413	- 2.269
3800	24.000	68.306	46.842	81.562	- 178.709	44.299	- 2.548
3900	24.000	68.930	47.401	83.962	- 177.943	50.156	- 2.811
4000	24.000	69.537	47.947	86.362	- 177.195	55.992	- 3.059

Dec. 31, 1960; Mar. 31, 1964

DILITHIUM MONOXIDE (Li_2O) (LIQUID) MOL. WT. = 29.880

$S^\circ_{298.15}$ = 13.160 cal. deg.$^{-1}$ mole^{-1}

T_m = 1843°K.

T_b = [2836°K.]

ΔH_f° 298.15 = -132.129 kcal. mole^{-1}

ΔH_m° = [14] kcal. mole^{-1}

ΔH_v° = Unknown

Heat of Formation.

ΔH_f° (l) was obtained from ΔH_f° (c) by adding ΔH_m and the difference between $H_{1843}-H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated at 8 cal. deg.$^{-1}$ g. atom^{-1} from comparisons with similar compounds and from Kopp's rule. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See melting data given on the Li_2O crystal table.

Vaporization Data.

The vapor over Li_2O(c) at 1700°K. is composed of Li_2O(g), Li(g), O_2(g), LiO(g), and Li_2O_2(g). Thus a boiling point becomes almost meaningless. The value, 2836°K, listed above is the temperature at which the free energy of Li_2O(g) and the free energy of Li_2O(l) are equal. L. Brewer, Chem. Rev. 52, (1953) estimated a boiling point of 2600°K.

Dilithium Monoxide (Li_2O)

(Ideal Gas) Mol. Wt. = 29.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.984	-39.636	-39.636	INFINITE
100	9.825	42.987	64.643	-2.166	-39.413	-41.284	90.221
200	10.946	50.184	55.790	-1.121	-39.588	-43.105	47.101
298	11.893	54.732	54.732	.000	-39.900	-44.767	32.813
300	11.910	54.806	54.733	.022	-39.906	-44.797	32.633
400	12.713	58.348	55.210	1.255	-40.271	-46.373	25.336
500	13.287	61.250	56.137	2.557	-42.171	-47.700	20.849
600	13.682	63.710	57.199	3.907	-42.624	-48.762	17.761
700	13.957	65.841	58.285	5.289	-43.031	-49.754	15.533
800	14.152	67.718	59.349	6.695	-43.408	-50.689	13.847
900	14.295	69.393	60.374	8.118	-43.774	-51.577	12.524
1000	14.401	70.905	61.352	9.553	-44.133	-52.424	11.457
1100	14.483	72.282	62.284	10.997	-44.484	-53.236	10.576
1200	14.547	73.545	63.171	12.449	-44.832	-54.017	9.837
1300	14.597	74.711	64.014	13.906	-45.175	-54.769	9.207
1400	14.638	75.795	64.817	15.368	-45.515	-55.493	8.663
1500	14.671	76.806	65.583	16.834	-45.851	-56.195	8.187
1600	14.698	77.753	66.315	18.302	-46.184	-56.872	7.768
1700	14.721	78.645	67.014	19.773	-116.608	-54.875	7.054
1800	14.740	79.487	67.684	21.246	-116.573	-51.241	6.221
1900	14.757	80.285	68.326	22.721	-116.540	-47.612	5.476
2000	14.771	81.042	68.943	24.197	-116.509	-43.987	4.806
2100	14.783	81.763	69.537	25.675	-116.482	-40.363	4.200
2200	14.794	82.451	70.108	27.154	-116.459	-36.737	3.649
2300	14.803	83.109	70.659	28.634	-116.437	-33.115	3.147
2400	14.811	83.739	71.191	30.114	-116.424	-29.493	2.686
2500	14.818	84.344	71.705	31.596	-116.414	-25.871	2.261
2600	14.825	84.925	72.203	33.078	-116.410	-22.251	1.870
2700	14.830	85.485	72.684	34.561	-116.414	-18.630	1.508
2800	14.836	86.024	73.151	36.044	-116.424	-15.007	1.171
2900	14.840	86.545	73.604	37.528	-116.447	-11.384	.858
3000	14.844	87.048	74.044	39.012	-116.475	-7.759	.565
3100	14.848	87.535	74.471	40.497	-116.517	-4.133	.291
3200	14.852	88.006	74.887	41.982	-116.567	-.509	.035
3300	14.855	88.463	75.291	43.467	-116.630	3.118	-.206
3400	14.858	88.907	75.685	44.953	-116.706	6.751	-.434
3500	14.860	89.337	76.069	46.439	-116.793	10.380	-.648
3600	14.863	89.756	76.444	47.925	-116.896	14.016	-.851
3700	14.865	90.163	76.809	49.411	-117.013	17.651	-1.043
3800	14.867	90.560	77.166	50.898	-117.145	21.300	-1.225
3900	14.869	90.946	77.514	52.385	-117.292	24.943	-1.398
4000	14.871	91.322	77.855	53.872	-117.457	28.589	-1.562
4100	14.872	91.690	78.187	55.359	-117.639	32.246	-1.719
4200	14.874	92.048	78.513	56.846	-117.841	35.900	-1.868
4300	14.875	92.398	78.832	58.333	-118.059	39.566	-2.011
4400	14.876	92.740	79.144	59.821	-118.297	43.236	-2.147
4500	14.878	93.074	79.450	61.309	-118.558	46.910	-2.278
4600	14.879	93.401	79.750	62.797	-118.839	50.591	-2.403
4700	14.880	93.721	80.044	64.284	-119.145	54.272	-2.524
4800	14.881	94.035	80.332	65.772	-119.474	57.965	-2.639
4900	14.882	94.341	80.615	67.261	-119.830	61.663	-2.750
5000	14.883	94.642	80.892	68.749	-120.212	65.375	-2.857
5100	14.884	94.937	81.165	70.237	-120.624	69.094	-2.961
5200	14.884	95.226	81.432	71.726	-121.066	72.816	-3.060
5300	14.885	95.509	81.695	73.214	-121.541	76.547	-3.156
5400	14.886	95.788	81.954	74.703	-122.049	80.288	-3.249
5500	14.886	96.061	82.208	76.191	-122.595	84.044	-3.339
5600	14.887	96.329	82.458	77.680	-123.179	87.798	-3.426
5700	14.888	96.593	82.703	79.169	-123.802	91.575	-3.511
5800	14.888	96.851	82.945	80.657	-124.470	95.362	-3.593
5900	14.889	97.106	83.183	82.146	-125.180	99.156	-3.673
6000	14.889	97.356	83.417	83.635	-125.938	102.969	-3.750

Dec. 31, 1960; Mar. 31, 1964

DILITHIUM MONOXIDE (Li_2O) (IDEAL GAS) MOL. WT. = 29.880

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = 54.732 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H_f^\circ{}_0$ = -39.6 ± 2.5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -39.9 ± 2.5 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[760] (1)
[140] (2)
987 (1)

Bond Distance: Li-O = [1.59] Å

Bond Angle: Li-O-Li = 180°

$\sigma = 2$

Rotational Constant: B_0 = 0.48045 cm.$^{-1}$

Heat of Formation.

The heat of formation was calculated from the heat of formation of the crystal and the heat of sublimation.

Heat Capacity and Entropy.

D. White, K. S. Seshadri, and D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963) made an estimate of the bond distance Li-O = 1.59 Å based on an analysis of their vibrational spectra. They found that Li_2O was a linear molecule. A. Buchler and J. L Stauffer, J. Chem. Phys. 39, 2299 (1963) have shown from electric deflection experiments that Li_2O is very probably linear. They also report from the results of an effusion experiment evidence that the electron diffraction data and Li-O bond distance, 1.82 Å reported by P. A. Akishin and N. G. Rambidi, Dokl. Akad. Nauk. SSSR 118, 973 (1958) [English Translation, Proc. Acad. Sci. USSR, Phys. Chem. Sect. 118, 83 (1958)] are for Mo-O in Li_2MoO_4 rather than for Li-O in Li_2O. Buchler and Stauffer (loc. cit.) estimate an Li-O distance of 1.55 Å. White, et al., (loc. cit.) have estimated the vibrational frequencies ν_1 = [760] cm.$^{-1}$ and ν_2 = [140] cm.$^{-1}$ and assigned ν_3 = 987 cm.$^{-1}$ from their infrared matrix spectra. The principal moments of inertia calculated from the molecular constants are: $I_A = 0$, and $I_B = I_C$ = 5.8256 X 10^{-39} g. cm.^{2}.

Heat of Sublimation (continued from $Li_2O(c)$ table).

A sample of $LiAlO_2$ was melted 7 times in argon in an arc-image furnace, H. Prophet, "Melting Point of Lithium Aluminate", ARPA-1-150, Dow Chemical Co., Mar. 9, 1961. The sample decomposed on fusion and successive melting points approached that of Al_2O_3. The residue was found to be 95% Al_2O_3 and 5% $LiAl_5O_8$. The sample and residue were characterized by X-ray diffraction. A reasonable assumption from this is that ΔF_r (2000°K) = 0 for $2LiAlO_2(c) = Al_2O_3(c) + Li_2O(g)$. From this ΔF, a $\Delta H^\circ_{s\ 298}$ for Li_2O of 50 kcal. was calculated. A vapor pressure study of the molecular species over the decomposing $LiAlO_2$ might help resolve the discrepancies in lithium oxide ΔH_s° values.

Dilithium Dioxide (Li_2O_2)

(Crystal) Mol. Wt. = 45.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	16.880	13.500	13.500	.000	- 151.200	- 136.468	100.029
300	16.950	13.605	13.500	.031	- 151.204	- 136.377	99.346
400	19.760	18.911	14.205	1.883	- 151.305	- 131.414	71.798
500	21.700	23.536	15.618	3.959	- 152.796	- 126.288	55.198
600	23.290	27.638	17.286	6.211	- 152.725	- 120.990	44.068
700	24.720	31.336	19.033	8.612	- 152.502	- 115.718	36.127
800	26.070	34.726	20.786	11.152	- 152.144	- 110.487	30.182
900	27.350	37.871	22.512	13.824	- 151.668	- 105.307	25.571
1000	28.610	40.818	24.196	16.622	- 151.077	- 100.185	21.894
1100	29.850	43.603	25.835	19.545	- 150.369	- 95.130	18.900
1200	31.070	46.253	27.427	22.591	- 149.547	- 90.144	16.417
1300	32.261	48.787	28.973	25.758	- 148.609	- 85.232	14.328
1400	33.438	51.221	30.476	29.043	- 147.558	- 80.395	12.550
1500	34.600	53.568	31.938	32.445	- 146.393	- 75.638	11.020
1600	35.748	55.837	33.361	35.962	- 145.115	- 70.960	9.692
1700	36.883	58.039	34.748	39.594	- 213.819	- 63.712	8.190
1800	38.003	60.179	36.102	43.338	- 211.958	- 54.932	6.669
1900	39.108	62.263	37.424	47.194	- 209.991	- 46.260	5.321
2000	40.200	64.297	38.717	51.159	- 207.922	- 37.699	4.119

June 30, 1963; Sept. 30, 1963

DILITHIUM DIOXIDE (Li_2O_2) (CRYSTAL) MOL. WT. = 45.880

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15}$ = [13.5 ± 1.0] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -151.2 ± 2.0 kcal. mole^{-1}

T_d = 468°K.

Heat of Formation.

$\Delta H_f^\circ{}_{298.15}$ was reported by R. de Forcrand, Compt. rend. 130, 1465 (1900), based on the measured heats of the reactions of Li_2O_2(c) with HCl(aq.) and LiOH(aq.) with H_2O_2(aq.).

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by comparison with those of the Na_2O_2(c), respectively.

Temperature of Decomposition.

T_d was reported to be about 300°C. by N. M. Wiederhorn, N. F. Surprenant, and A. J. Leffler, "Research on New Methods of Separation of Air into O_2 and N_2 Components," C-63825, First-Quarterly Progress Report, September 1961, Arthur D. Little, Inc. The value adopted was reported by Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use", June, 1949, obtained from M. Centnerzwer and M. Blumenthal, Bull. intern. acad. polonaise, Classe. sci. math. nat., A 499 (1933).

Dilithium Dioxide (Li_2O_2)

(Ideal Gas) Mol. Wt. = 45.880

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-3.789	-57.504	-57.504	INFINITE
100	10.505	49.874	79.212	-2.934	-57.600	-58.083	126.935
200	15.284	58.806	66.892	-1.617	-57.843	-58.461	63.880
298	17.383	65.357	65.357	.000	-58.000	-58.729	43.048
300	17.409	65.465	65.358	.032	-58.003	-58.734	42.786
400	18.378	70.622	66.054	1.827	-58.161	-58.954	32.209
500	18.880	74.783	67.398	3.693	-59.862	-58.978	25.778
600	19.169	78.253	68.926	5.596	-60.140	-58.773	21.407
700	19.349	81.223	70.475	7.523	-60.391	-58.527	18.272
800	19.469	83.815	71.984	9.464	-60.632	-58.246	15.911
900	19.552	86.113	73.429	11.415	-60.877	-57.932	14.067
1000	19.611	88.176	74.802	13.374	-61.125	-57.591	12.586
1100	19.656	90.047	76.104	15.337	-61.377	-57.226	11.369
1200	19.690	91.759	77.339	17.305	-61.633	-56.838	10.351
1300	19.717	93.336	78.509	19.275	-61.892	-56.428	9.486
1400	19.738	94.798	79.621	21.248	-62.153	-55.998	8.741
1500	19.755	96.161	80.679	23.223	-62.415	-55.549	8.093
1600	19.770	97.436	81.687	25.199	-62.678	-55.082	7.523
1700	19.781	98.635	82.649	27.176	-133.037	-51.943	6.677
1800	19.791	99.766	83.569	29.155	-132.041	-47.173	5.727
1900	19.799	100.836	84.450	31.135	-132.850	-42.409	4.878
2000	19.806	101.852	85.295	33.115	-132.766	-37.654	4.114
2100	19.813	102.818	86.106	35.096	-132.688	-32.901	3.424
2200	19.818	103.740	86.887	37.077	-132.619	-28.150	2.796
2300	19.823	104.621	87.639	39.059	-132.553	-23.405	2.224
2400	19.827	105.465	88.364	41.042	-132.498	-18.659	1.699
2500	19.830	106.274	89.065	43.025	-132.451	-13.918	1.217
2600	19.833	107.052	89.742	45.008	-132.412	-9.178	.771
2700	19.836	107.801	90.397	46.991	-132.385	-4.439	.359
2800	19.839	108.522	91.031	48.975	-132.366	.300	-.023
2900	19.841	109.219	91.646	50.959	-132.362	5.039	-.380
3000	19.843	109.891	92.243	52.943	-132.367	9.779	-.712
3100	19.845	110.542	92.823	54.928	-132.387	14.519	-1.024
3200	19.847	111.172	93.387	56.912	-132.419	19.255	-1.315
3300	19.848	111.783	93.935	58.897	-132.466	23.995	-1.589
3400	19.850	112.375	94.469	60.882	-132.528	28.740	-1.847
3500	19.851	112.951	94.989	62.867	-132.603	33.480	-2.090
3600	19.852	113.510	95.495	64.852	-132.696	38.229	-2.321
3700	19.853	114.054	95.990	66.837	-132.805	42.976	-2.538
3800	19.854	114.583	96.472	68.823	-132.930	47.736	-2.745
3900	19.855	115.099	96.943	70.808	-133.073	52.489	-2.941
4000	19.856	115.602	97.403	72.794	-133.235	57.246	-3.128
4100	19.857	116.092	97.853	74.779	-133.417	62.014	-3.305
4200	19.858	116.571	98.293	76.765	-133.618	66.779	-3.475
4300	19.858	117.038	98.724	78.751	-133.838	71.557	-3.637
4400	19.859	117.494	99.145	80.737	-134.079	76.336	-3.791
4500	19.859	117.941	99.558	82.723	-134.344	81.122	-3.940
4600	19.860	118.377	99.962	84.709	-134.631	85.915	-4.082
4700	19.861	118.804	100.359	86.695	-134.943	90.707	-4.218
4800	19.861	119.222	100.747	88.681	-135.280	95.511	-4.349
4900	19.862	119.632	101.128	90.667	-135.645	100.320	-4.474
5000	19.862	120.033	101.503	92.653	-136.036	105.143	-4.596
5100	19.862	120.427	101.870	94.639	-136.459	109.976	-4.713
5200	19.863	120.812	102.230	96.626	-136.912	114.808	-4.825
5300	19.863	121.191	102.585	98.612	-137.399	119.653	-4.934
5400	19.863	121.562	102.933	100.598	-137.920	124.505	-5.039
5500	19.864	121.926	103.275	102.585	-138.478	129.375	-5.141
5600	19.864	122.284	103.611	104.571	-139.076	134.242	-5.239
5700	19.864	122.636	103.942	106.557	-139.714	139.131	-5.334
5800	19.865	122.981	104.267	108.544	-140.396	144.034	-5.427
5900	19.865	123.321	104.587	110.530	-141.122	148.941	-5.517
6000	19.865	123.655	104.902	112.517	-141.896	153.869	-5.604

Mar. 31, 1964

DILITHIUM DIOXIDE (Li_2O_2) (IDEAL GAS) MOL. WT. = 45.880

Point Group $[D_{2h}]$

$S^\circ_{298.15}$ = [65.357] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = [-57.5 ± 6] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-58.0 ± 6] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$
[400] (1)	[270] (1)
[250] (1)	330 (1)
[300] (1)	530 (1)

Bond Distance: Li-O = [1.90] Å

Bond Angle: O-Li-O = [116]°

σ = 4

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.66304 X 10^{-115}] g.^{3} cm.^{6}

Heat of Formation.

The heat of formation, -58 kcal., was calculated from an equilibrium constant for the reaction 1/2 $O_2(g) + Li_2O(g) \rightarrow Li_2O_2(g)$ and the current JANAF functions. The equilibrium constant, 0.39, was estimated by D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963), from their mass spectrometric data.

Heat Capacity and Entropy.

White, et al., (loc. cit.), from their spectral data have assigned two observed frequencies and estimated the remaining frequencies using the ionic model calculations of J. Berkowitz, J. Chem. Phys. 29, 1386 (1958); 32, 1519 (1960) as a guide. They proposed a planar rhombic structure of D_{2h} symmetry, similar to the alkali halide dimers, for the previously undetected Li_2O_2 molecule, and estimated the angle, 116°, and bond distance, 1.90 Å, from their matrix spectra. The principal moments calculated from these molecular constants are: I_A = 13.793 X 10^{-39}, I_B = 2.336 X 10^{-39}, and I_C = 16.129 X 10^{-39} g. cm.^{2}.

Lithium Metasilicate (Li_2SiO_3)

(Crystal) GFW = 89.9622

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.479	-391.627	-391.627	INFINITE
100	6.513	2.934	35.600	-3.267	-392.758	-386.399	844.474
200	17.217	10.946	21.191	-2.049	-393.746	-379.615	414.824
298	24.036	19.191	19.191	.000	-394.240	-372.558	273.092
300	24.142	19.340	19.191	.045	-394.245	-372.424	271.311
400	28.400	26.919	20.196	2.689	-394.417	-365.117	199.491
500	30.547	33.498	22.215	5.642	-395.941	-357.635	156.322
600	32.100	39.209	24.582	8.776	-395.933	-349.972	127.477
700	33.377	44.254	27.039	12.051	-395.810	-342.321	106.877
800	34.520	48.788	29.479	15.447	-395.595	-334.697	91.435
900	35.508	52.912	31.857	18.950	-395.307	-327.099	79.430
1000	36.401	56.700	34.154	22.546	-394.956	-319.539	69.835
1100	37.184	60.206	36.365	26.226	-394.545	-312.015	61.992
1200	37.900	63.473	38.499	29.980	-394.084	-304.534	55.463
1300	38.550	66.532	40.530	33.803	-393.574	-297.092	49.946
1400	39.183	69.412	42.491	37.690	-393.018	-289.690	45.223
1500	39.800	72.137	44.378	41.639	-392.416	-282.331	41.136
1600	40.400	74.725	46.194	45.649	-391.768	-275.012	37.565
1700	40.990	77.192	47.946	49.719	-473.164	-264.974	34.065
1800	41.560	79.551	49.636	53.846	-472.014	-252.756	30.689
1900	42.110	81.813	51.271	58.030	-470.816	-240.608	27.676
2000	42.540	83.986	52.853	62.268	-469.575	-228.525	24.972
2100	43.149	86.079	54.385	66.557	-468.291	-216.505	22.532
2200	43.540	88.098	55.872	70.897	-466.969	-204.546	20.320
2300	44.112	90.048	57.316	75.285	-465.605	-192.649	18.306
2400	44.565	91.935	58.719	79.719	-464.210	-180.809	16.465
2500	45.000	93.763	60.095	84.197	-462.782	-169.032	14.777

Sept. 30, 1961; March 31, 1964; June 30, 1967

LITHIUM METASILICATE (Li_2SiO_3) (CRYSTAL) GFW = 89.9622

$\Delta Hf^\circ_0 = -391.63 \pm 1.0$ kcal/mol

$S^\circ_{298.15} = 19.19 \pm 0.3$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -394.24 \pm 1.0$ kcal/mol

$Tm = 1474 \pm 1°K$

$\Delta Hm^\circ = 6.7 \pm 0.5$ kcal/mol

Heat of Formation

The heats of solution of LiCl(c), Li_2SO_4(c), SiO_2(quartz) and Li_2SiO_3(c) in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). The authors derived two values of ΔHsoln of Li_2O(c) from those of LiCl(c) and Li_2SO_4(c), presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate ΔHsoln of Li_2O(c) as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent ΔHf°_{298} values for LiCl(c), Li_2SO_4(c), HCl(aq), H_2SO_4(aq), and Li_2O(c). The corresponding enthalpy changes, ΔHr°_{298}, for the reaction $Li_2O(c) + SiO_2(quartz) = Li_2SiO_3(c)$ are derived as -33.08 and -34.17 kcal/mol. Adopting the weighted average $\Delta Hr^\circ_{298} = -33.44$ kcal/mol with $\Delta Hf^\circ_{298}(Li_2O,c) = -143.1$ kcal/mol and $\Delta Hf^\circ_{298}(SiO_2, quartz) = -217.7$ kcal/mol, we obtain $\Delta Hf^\circ_{298} = -394.24$ kcal/mol for Li_2SiO_3(c). This $\Delta Hf^\circ_{298}(Li_2SiO_3, c)$ value is independent of future changes in ΔHf°_{298} of Li_2O(c) but the values of ΔHsoln and ΔHr° are not independent.

The heats of solution of LiOH(c) and Li_2SiO_3(c) in 20 percent HF(aq) at 50°C were measured by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. The Li_2SiO_3 sample was prepared from lithium carbonate and silica by fusion under vacuum at 1500°K. Analysis gave 66.74 percent SiO_2 and 15.12 percent Li. The corresponding calculated values are 66.79 and 15.43. Also present were 0.5 percent K and 0.06 percent Na. Corrections were made for impurities in the heat of formation measurements. The results are given as follows:

	ΔHr°_{298}, kcal/mol
$2LiOH(c, 25°C) + 2HF(sol, 50°C) \rightarrow 2LiF(sol, 50°C) + 2H_2O(sol, 50°C)$	-38.728
$SiO_2(c, 25°C) + 6HF(sol, 50°C) \rightarrow H_2SiF_6(sol, 50°C) + 2H_2O(sol, 50°C)$	-32.810
$3H_2O(sol, 50°C) + 2LiF(sol, 50°C) + H_2SiF_6(sol, 50°C) \rightarrow Li_2SiO_3(c, 25°C) + 8HF(sol, 50°C)$	+58.850
$H_2O(sol, 50°C) \rightarrow H_2O(\ell, 25°C)$	-0.450
$2LiOH(c, 25°C) + SiO_2(c, 25°C) \rightarrow Li_2SiO_3(c, 25°C) + H_2O(\ell, 25°C)$	-13.14 ± 0.70

The ΔHr°_{298} for the second reaction was determined by D. R. Torgeson and T. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948). Based on the calculated enthalpy change for the overall reaction, $\Delta Hr^\circ_{298} = -13.14$ kcal/mol and $\Delta Hf^\circ_{298} = -115.84$, -217.7 and -68.32 kcal/mol for LiOH(c), SiO_2(low quartz), and $H_2O(\ell)$, respectively, we derived $\Delta Hf^\circ_{298}(Li_2SiO_3, c) = -394.21 \pm 1.0$ kcal/mol, which is in agreement with the adopted value.

C. Kroger and E. Fingas, Z. Anorg. Allgem. Chem. 213, 12 (1933), measured the equilibrium pressure of CO_2 over a mixture of Li_2CO_3(c), SiO_2(quartz), and Li_2SiO_3(c) from 585 to 781°K. The enthalpy change (ΔHr°_{298}) of the reaction $Li_2CO_3(c) + SiO_2(c) \rightarrow Li_2SiO_3(c) + CO_2(g)$ is evaluated by the second and third law methods to be 30.94 and 29.47 kcal/mol, respectively. Using $\Delta Hf^\circ_{298} = -290.64$, -217.7 and -94.05 kcal/mol for Li_2CO_3(c), SiO_2(c) and CO_2(g), respectively, and third law ΔHr°_{298}, we obtain $\Delta Hf^\circ_{298}(Li_2SiO_3, c) = -384.82 \pm 5$ kcal/mol, which is not used.

Heat Capacity and Entropy

The low temperature heat capacities, 25 - 340°K, were measured by Hatton et al., loc. cit., with an adiabatic vacuum calorimeter, using a nickel-plated copper sample container. During the filling and sealing of the calorimeter, the compound was handled in an anhydrous, CO_2-free atmosphere so as to avoid contamination. The purity of the sample is not well established. The high temperature heat capacities are estimated by summation of the Cp's of the constituent oxides, Li_2O and SiO_2, and a subsequent correction based upon a comparison of the heat capacities of Na_2SiO_3(c) and its constituent oxides. These estimated Cp values are plotted, and the resulting curve is joined smoothly with the low temperature Cp curve at 298°K. The entropy, S°_{298}, is derived using the measured low temperature heat capacities, based on $S^\circ_{25} = 0.023$ eu.

Melting Data

See $Li_2SiO_3(\ell)$ table for details.

Lithium Metasilicate (Li_2SiO_3)

(Liquid) GFW = 89.9622

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	24.036	22.958	22.958	- .000	- 388.441	- 367.882	269.665
300	24.142	23.107	22.959	.045	- 388.447	- 367.755	267.910
400	28.400	30.686	23.963	2.689	- 388.618	- 360.825	197.146
500	30.547	37.265	25.982	5.642	- 390.142	- 353.719	154.611
600	32.100	42.976	28.349	8.776	- 390.134	- 346.433	126.188
700	33.377	48.022	30.806	12.051	- 390.011	- 339.160	105.890
800	34.520	52.555	33.246	15.447	- 389.796	- 331.911	90.674
900	35.508	56.679	35.624	18.950	- 389.508	- 324.690	78.846
1000	40.000	60.467	37.921	22.546	- 389.157	- 317.506	69.391
1100	40.000	64.280	40.147	26.546	- 388.426	- 310.377	61.666
1200	40.000	67.760	42.305	30.546	- 387.719	- 303.314	55.241
1300	40.000	70.962	44.388	34.546	- 387.032	- 296.309	49.814
1400	40.000	73.926	46.393	38.546	- 386.363	- 289.355	45.170
1500	40.000	76.686	48.322	42.546	- 385.710	- 282.449	41.153
1600	40.000	79.267	50.176	46.546	- 385.073	- 275.583	37.643
1700	40.000	81.692	51.959	50.546	- 466.538	- 265.998	34.196
1800	40.000	83.979	53.675	54.546	- 465.515	- 254.228	30.868
1900	40.000	86.141	55.328	58.546	- 464.502	- 242.516	27.896
2000	40.000	88.193	56.920	62.546	- 463.498	- 230.862	25.227
2100	40.000	90.145	58.456	66.546	- 462.503	- 219.256	22.818
2200	40.000	92.005	59.939	70.546	- 461.521	- 207.694	20.632
2300	40.000	93.784	61.372	74.546	- 460.545	- 196.182	18.642
2400	40.000	95.486	62.758	78.546	- 459.584	- 184.705	16.820
2500	40.000	97.119	64.100	82.546	- 458.634	- 173.274	15.148
2600	40.000	98.688	65.401	86.546	- 457.694	- 161.879	13.607
2700	40.000	100.197	66.662	90.546	- 456.769	- 150.519	12.184
2800	40.000	101.652	67.886	94.546	- 455.856	- 139.191	10.864
2900	40.000	103.056	69.074	98.546	- 454.960	- 127.898	9.639
3000	40.000	104.412	70.230	102.546	- 454.075	- 116.634	8.497
3100	40.000	105.723	71.354	106.546	- 453.209	- 105.396	7.430
3200	40.000	106.993	72.448	110.546	- 452.356	- 94.192	6.433
3300	40.000	108.224	73.513	114.546	- 451.521	- 83.015	5.498
3400	40.000	109.418	74.552	118.546	- 450.703	- 71.856	4.619
3500	40.000	110.578	75.565	122.546	- 449.900	- 60.733	3.792
3600	40.000	111.704	76.553	126.546	- 541.078	- 47.362	2.875
3700	40.000	112.800	77.518	130.546	- 540.214	- 33.662	1.988
3800	40.000	113.867	78.460	134.546	- 539.369	- 19.975	1.149
3900	40.000	114.906	79.382	138.546	- 538.543	- 6.323	.354
4000	40.000	115.919	80.282	142.546	- 537.739	7.309	- .399

Sept. 30, 1961; March 31, 1964; June 30, 1967

LITHIUM METASILICATE (Li_2SiO_3) (LIQUID) GFW = 89.9622

$S^\circ_{298.15}$ = 22.958 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -388.441 kcal/mol

Tm = 1474 ± 1°K ΔHm° = 6.7 ± 0.5 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1474} - H^\circ_{298}$ for crystal and liquid.

Tschernobaeff, Rev. Met. 21, 729 (1905), measured the heat of reaction between SiO_2 and Li_2CO_3 in a bomb calorimeter, using carbon as the auxiliary combustible material. Based on the derived ΔHr°_{298} = 24.99 kcal/mol for the reaction $Li_2CO_3(c) + SiO_2(c) \rightarrow Li_2SiO_3(gl) + CO_2(g)$, the heat of formation for $Li_2SiO_3(gl)$ is evaluated as -389.30 kcal/mol, which is in fair agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $Na_2SiO_3(\ell)$, $Na_2O(\ell)$ and $Li_2O(\ell)$. A glass transition is assumed at 1000°K; i.e., the heat capacities below 1000°K are taken to be the same as those for $Li_2SiO_3(c)$.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been reported as 1474 ± 1 and 1461°K by F. C. Kracek, J. Phys. Chem. 34, 2641 (1930), and H. S. Van Klooster, Z. Anorg. Chem. 69, 135 (1911), respectively. The value reported by Kracek is adopted.

R. Schwarz and H. Sturm, Ber. 47, 1730 (1914), used a cooling-curve method to compare the heats of fusion of $Li_2SiO_3(c)$ and NaCl(c). From the reported ratio, $\varepsilon(Li_2SiO_3)/\varepsilon(NaCl) = 0.261/0.402$, where ε = heat of fusion in kcal/g, and heat of fusion of NaCl(c), the value ΔHm° = 6.7 kcal/mol is derived.

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.942	- 396.770	- 396.770	INFINITE
100	7.443	3.377	40.417	- 3.704	- 397.973	- 391.535	855.658
200	19.757	12.640	24.215	- 2.315	- 398.942	- 384.692	420.352
298	26.256	21.930	21.930	.000	- 399.300	- 377.591	276.768
300	26.470	22.093	21.931	.049	- 399.304	- 377.456	274.964
400	30.440	30.263	23.018	2.898	- 399.383	- 370.156	202.234
500	32.420	37.285	25.188	6.049	- 400.814	- 362.703	158.530
600	33.820	43.328	27.720	9.365	- 400.729	- 355.085	129.333
700	34.860	48.622	30.335	12.801	- 400.554	- 347.493	108.487
800	35.620	53.329	32.921	16.327	- 400.319	- 339.930	92.860
900	36.250	57.562	35.428	19.921	- 400.053	- 332.396	80.713
1000	36.780	61.409	37.836	23.573	- 399.762	- 324.893	71.002
1100	37.240	64.937	40.142	27.275	- 399.448	- 317.422	63.063
1200	37.600	68.194	42.346	31.018	- 400.069	- 309.944	56.446
1300	37.880	71.215	44.452	34.793	- 399.729	- 302.446	50.843
1400	38.120	74.032	46.465	38.594	- 399.384	- 294.976	46.046
1500	42.200	78.560	48.410	45.224	- 396.227	- 287.559	41.895
1600	43.000	81.309	50.381	49.484	- 395.455	- 280.337	38.290
1700	43.800	83.940	52.278	53.824	- 464.713	- 270.513	34.775
1800	44.600	86.466	54.108	58.244	- 463.452	- 259.122	31.460
1900	45.400	88.899	55.875	62.744	- 462.129	- 247.804	28.503
2000	46.200	91.248	57.586	67.324	- 464.420	- 236.470	25.839
2100	47.000	93.521	59.243	71.984	- 462.916	- 225.108	23.426
2200	47.800	95.726	60.852	76.724	- 461.344	- 213.820	21.240
2300	48.600	97.869	62.415	81.544	- 459.698	- 202.606	19.251
2400	49.400	99.954	63.936	86.444	- 457.987	- 191.464	17.434
2500	50.200	101.987	65.417	91.424	- 456.207	- 180.396	15.769
2600	51.000	103.971	66.862	96.484	- 454.357	- 169.403	14.239
2700	51.800	105.911	68.272	101.624	- 452.442	- 158.479	12.827
2800	52.600	107.809	69.651	106.844	- 450.458	- 147.626	11.522
2900	53.400	109.669	70.999	112.144	- 448.412	- 136.845	10.312
3000	54.200	111.493	72.318	117.524	- 446.298	- 126.136	9.189

June 30, 1961; Mar. 31, 1964

LITHIUM METATITANATE (Li$_2$TiO$_3$) (CRYSTAL) MOL. WT. = 109.780

$\Delta H^\circ_{f\ 0}$ = -396.8 kcal. mole^{-1}

$S^\circ_{298.15}$ = 21.930 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -399.3 kcal. mole^{-1}

T_{t_1} = 1485°K.

$\Delta H^\circ_{t_1}$ = 2.75 kcal. mole^{-1}

T_m = 1820°K.

ΔH_m = 26.33 kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was calculated from measurements of solution calorimetry by S. S. Todd and K. K. Kelley, "Heat and Free Energy Data for Tricalcium Dititanate, Sphene, Lithium Metatitanate and Zinc Titanium Spinel", U. S. Bureau Mines Report Invest. 5193 (1956), according to the following equation:

$TiO_2(c) + Li_2SO_4(c) + 13.312\ H_2O(l) = Li_2TiO_3(c) + H_2SO_4(12.312\ H_2O) \qquad \Delta H_{r\ 298.15} = 27.04$ kcal.

The $\Delta H_{f\ 298.15}$ $TiO_2(c)$ value for rutile was obtained from the JANAF Tables and the other $\Delta H_{f\ 298.15}$ values were obtained from "Selected Values of Chemical Thermodynamic Properties" NBS Circular 500 (1952).

Heat Capacity and Entropy.

The low temperature heat capacities were taken from E. G. King, J. Am. Chem. Soc. 77, 2150 (1955). These low temperature heat capacities were fit to the high temperature heat contents from A. U. Christensen, K. C. Conway, and K. K. Kelley, "High Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bur. Mines Rept. Invest. 5565 (1960).

The $S^\circ_{298.15}$ = 21.9 was obtained from E. G. King, loc. cit. based on the measured $S^\circ_{298.15}-S^\circ_{51}$ and the extrapolated $S^\circ_{51}-S^\circ_{0}$.

Transition Data.

A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit. reported that lithium metatitanate undergoes a transition from the α to the β form at 1,485°K. with an absorption of 2.750 kcal. mole^{-1}.

Melting Data.

The T_m and ΔH_m were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.

Lithium Metatitanate (Li_2TiO_3)

(Liquid) Mol. Wt. = 109.780

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	26.256	35.355	35.355	.000	- 374.374	- 356.667	261.432
300	26.470	35.518	35.356	.049	- 374.378	- 356.558	259.740
400	30.440	43.688	36.443	2.898	- 374.457	- 350.600	191.550
500	32.420	50.710	38.613	6.049	- 375.888	- 344.489	150.569
600	33.820	56.753	41.145	9.365	- 375.803	- 338.214	123.189
700	34.860	62.047	43.760	12.801	- 375.628	- 331.965	103.639
800	35.620	66.754	46.346	16.327	- 375.393	- 325.744	88.985
900	36.250	70.987	48.853	19.921	- 375.127	- 319.552	77.594
1000	36.780	74.834	51.261	23.573	- 374.836	- 313.392	68.488
1100	37.240	78.362	53.567	27.275	- 374.522	- 307.263	61.045
1200	37.600	81.619	55.771	31.018	- 375.143	- 301.128	54.840
1300	48.000	85.340	57.900	35.672	- 373.924	- 295.004	49.592
1400	48.000	88.898	59.989	40.472	- 372.580	- 288.983	45.110
1500	48.000	92.209	62.028	45.272	- 371.253	- 283.059	41.240
1600	48.000	95.307	64.012	50.072	- 369.041	- 277.220	37.865
1700	48.000	98.217	65.939	54.872	- 438.739	- 268.810	34.556
1800	48.000	100.961	67.809	59.672	- 437.098	- 258.858	31.428
1900	48.000	103.556	69.623	64.472	- 435.475	- 248.998	28.640
2000	48.000	106.018	71.382	69.272	- 437.546	- 239.136	26.130
2100	48.000	108.360	73.087	74.072	- 435.902	- 229.255	23.858
2200	48.000	110.593	74.742	78.872	- 434.270	- 219.452	21.800
2300	48.000	112.727	76.347	83.672	- 432.644	- 209.725	19.927
2400	48.000	114.769	77.906	88.472	- 431.033	- 200.067	18.218
2500	48.000	116.729	79.420	93.272	- 429.433	- 190.477	16.651
2600	48.000	118.611	80.891	98.072	- 427.843	- 180.953	15.210
2700	48.000	120.423	82.322	102.872	- 426.268	- 171.487	13.880
2800	48.000	122.169	83.714	107.672	- 424.704	- 162.078	12.650
2900	48.000	123.853	85.069	112.472	- 423.158	- 152.724	11.509
3000	48.000	125.480	86.389	117.272	- 421.624	- 143.424	10.448
3100	48.000	127.054	87.676	122.072	- 420.107	- 134.171	9.459
3200	48.000	128.578	88.930	126.872	- 418.604	- 124.979	8.535
3300	48.000	130.055	90.154	131.672	- 417.119	- 115.825	7.670
3400	48.000	131.488	91.349	136.472	- 415.652	- 106.716	6.859
3500	48.000	132.879	92.516	141.272	- 414.199	- 97.655	6.098
3600	48.000	134.232	93.656	146.072	- 515.228	- 87.185	5.293
3700	48.000	135.547	94.771	150.872	- 513.833	- 75.315	4.448
3800	48.000	136.827	95.861	155.672	- 512.470	- 63.471	3.650
3900	48.000	138.074	96.927	160.472	- 511.140	- 51.678	2.896
4000	48.000	139.289	97.971	165.272	- 509.844	- 39.920	2.181

June 30, 1961; Mar. 31, 1964

LITHIUM METATITANATE (Li_2TiO_3) (LIQUID) MOL. WT. = 109.780

$S^\circ_{298.15}$ = 35.355 cal. mole^{-1} deg.$^{-1}$

T_m = 1820°K.

ΔH_f° 298.15 = -374.374 kcal. mole^{-1}

ΔH_m = 26.33 kcal. mole^{-1}

Heat of Formation.

The ΔH_f° 298.15 was obtained from the heat of formation of the crystal by adding ΔH_m and the difference between $H_{1820}-H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacities were reported by A. U. Christensen, K. C. Conway, and K. K. Kelley, "High-Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bureau Mines Report Invest. 5565 (1960). The measured heat capacity is extrapolated to an assumed glass transition temperature of 1214°K., below which the heat capacity is taken to be equal to that of the crystal.

The $S^\circ_{298.15}$ was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The T_m and ΔH_m were obtained from A. U. Christensen, K. C. Conway and K. K. Kelley, loc. cit.

Lithium Disilicate ($Li_2Si_2O_5$)
(Crystal) GFW = 150.047

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	33.000	30.000	30.000	.000	- 612.070	- 577.559	423.436
300	33.200	30.205	30.001	.061	- 612.081	- 577.447	420.669
400	41.800	41.038	31.419	3.847	- 612.329	- 565.847	309.164
500	46.050	50.843	34.344	8.249	- 613.678	- 554.085	242.190
600	49.160	59.527	37.831	13.019	- 613.359	- 542.192	197.493
700	51.360	67.275	41.494	18.047	- 612.845	- 530.370	165.589
800	53.200	74.256	45.160	23.276	- 612.195	- 518.636	141.685
900	54.850	80.619	48.752	28.681	- 611.431	- 506.982	123.112
1000	56.250	86.472	52.235	34.237	- 610.571	- 495.421	108.274
1100	57.508	91.894	55.597	39.926	- 609.625	- 483.952	96.152
1200	58.600	96.946	58.835	45.733	- 608.604	- 472.574	86.067
1300	59.316	101.851	61.963	51.855	- 607.307	- 461.299	77.551
1400	60.040	106.273	64.972	57.822	- 606.199	- 450.107	70.265
1500	60.915	110.447	67.865	63.872	- 605.043	- 438.999	63.962
1600	61.500	114.401	70.651	69.999	- 603.840	- 427.965	58.457
1700	62.050	118.149	73.336	76.182	- 696.692	- 414.143	53.242
1800	62.400	121.706	75.925	82.406	- 694.985	- 397.567	48.271
1900	62.538	125.087	78.425	88.658	- 693.264	- 381.091	43.835
2000	62.800	128.304	80.839	94.931	- 691.538	- 364.708	39.853
2100	62.853	131.370	83.173	101.213	- 689.815	- 348.410	36.259
2200	62.900	134.295	85.430	107.501	- 688.109	- 332.194	33.000
2300	62.940	137.092	87.616	113.793	- 686.406	- 316.056	30.032
2400	62.973	139.771	89.734	120.089	- 684.721	- 299.984	27.317
2500	63.000	142.342	91.787	126.388	- 683.050	- 283.993	24.827

June 30, 1967

LITHIUM DISILICATE ($Li_2Si_2O_5$) (CRYSTAL) GFW = 150.047

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [30] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -612.07 ± 1.0 kcal/mol

Tt = 1209°K

ΔHt° = 0.225 kcal/mol

Tm = 1307 ± 1°K

ΔHm° = [12.86] kcal/mol

Heat of Formation

The heats of solution of LiCl(c), Li_2SO_4(c), SiO_2(quartz) and $Li_2Si_2O_5$(c) in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). The authors derived two values of ΔHsoln of Li_2O(c) from those of LiCl(c) and Li_2SO_4(c), presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate ΔHsoln of Li_2O(c) as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent ΔHf°_{298} values for LiCl(c), Li_2SO_4(c), HCl(aq), H_2SO_4(aq), and Li_2O(c). The corresponding enthalpy changes, ΔHr°_{298}, for the reaction Li_2O(c) + $2SiO_2$(quartz) = $Li_2Si_2O_5$(c) are derived as -33.21 and -34.30 kcal/mol. Adopting the weighted average ΔHr°_{298} = -33.57 kcal/mol with ΔHf°_{298}(Li_2O, c) = -143.1 kcal/mol and ΔHf°_{298}(SiO_2, quartz) = -217.7 kcal/mol, we obtain ΔHf°_{298} = -612.07 kcal/mol for $Li_2Si_2O_5$(c). This ΔHf°_{298}($Li_2Si_2O_5$, c) value is independent of future changes in ΔHf°_{298} of Li_2O(c) but the values of ΔHsoln and ΔHr° are not independent.

The heats of solution of LiOH(c) and $Li_2Si_2O_5$(c) in 20 per cent HF(aq) at 50°C were measured by W. E. Hatton, G. C. Sinke, D. L. Hildenbrand, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. By use of a reaction scheme similar to that described on the Li_2SiO_3(c) table, the enthalpy change at 298°K for the reaction 2LiOH(c) + $2SiO_2$(c) → $Li_2Si_2O_5$(c) + H_2O(ℓ) was calculated to be -13.44 kcal/mol. Incorporating this value with ΔHf°_{298} = -115.84, -217.7 and -68.315 kcal/mol for LiOH(c), SiO_2(c), and H_2O(ℓ), respectively, we obtain ΔHf°_{298}($Li_2Si_2O_5$,c) = -612.20 ± 2.0 kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy

Both heat capacities and S°_{298} are estimated by comparison with those for $Na_2Si_2O_5$(c), Na_2O(c) and Li_2O(c).

Transition Data

The transition temperature, Tt = 1209°K, is taken from F. C. Kracek, J. Am. Chem. Soc. 61, 2863 (1939). The author estimated a heat of transition of 1 to 2 cal/g based on the arrest in the cooling and heating curves. The value of ΔHt° is calculated assuming the heat of transition at 1209°K is 1.5 cal/g.

Melting Data

Incongruent melting of $Li_2Si_2O_5$(c) at 1033° has been reported by F. C. Kracek, J. Phys. Chem. 34, 2641 (1930); J. Am. Chem. Soc. 61, 2863 (1939). The liquidus temperature of 1034° at the composition 19.92 per cent Li_2O and 80.08 per cent SiO_2, reported by Kracek (1939), is adopted as Tm. The heat of melting is evaluated such that ΔHm°_{298} + ΔHt°_{298} = 11.43 kcal/mol, where the value 11.43 kcal/mol is the difference between ΔHf°_{298} for $Li_2Si_2O_5$(c) and $Li_2Si_2O_5$(ℓ). The latter were determined by solution calorimetry by Kracek (see Heat of Formation sections in $Li_2Si_2O_5$(c) and $Li_2Si_2O_5$(ℓ) tables).

Lithium Disilicate ($Li_2Si_2O_5$)

(Liquid) GFW = 150.047

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	33.000	38.297	38.297	.000	- 600.640	- 568.703	416.870
300	33.200	38.502	38.298	.061	- 600.651	- 568.506	414.156
400	41.500	49.335	39.716	3.847	- 600.899	- 557.736	304.733
500	46.050	59.140	42.641	8.249	- 602.248	- 546.804	239.008
600	49.160	67.824	46.128	13.018	- 601.929	- 535.740	195.143
700	51.360	75.572	49.791	18.047	- 601.415	- 524.748	163.834
800	60.000	82.555	53.458	23.278	- 600.763	- 513.844	140.376
900	60.000	89.621	57.091	29.278	- 599.404	- 503.057	122.159
1000	60.000	95.943	60.665	35.278	- 598.100	- 492.421	107.618
1100	60.000	101.662	64.137	41.278	- 596.843	- 481.916	95.748
1200	60.000	106.882	67.484	47.278	- 595.629	- 471.522	85.876
1300	60.000	111.685	70.702	53.278	- 594.454	- 461.229	77.540
1400	60.000	116.131	73.790	59.278	- 593.314	- 451.023	70.408
1500	60.000	120.271	76.753	65.278	- 592.207	- 440.898	64.239
1600	60.000	124.143	79.595	71.278	- 591.132	- 430.844	58.851
1700	60.000	127.781	82.323	77.278	- 684.167	- 417.992	53.736
1800	60.000	131.210	84.945	83.278	- 682.683	- 402.372	48.855
1900	60.000	134.454	87.466	89.278	- 681.215	- 386.839	44.497
2000	60.000	137.532	89.893	95.278	- 679.761	- 371.387	40.583
2100	60.000	140.459	92.232	101.278	- 678.321	- 356.003	37.050
2200	60.000	143.251	94.488	107.278	- 676.901	- 340.691	33.844
2300	60.000	145.918	96.667	113.278	- 675.491	- 325.442	30.924
2400	60.000	148.471	98.772	119.278	- 674.102	- 310.246	28.252
2500	60.000	150.921	100.810	125.278	- 672.730	- 295.120	25.799
2600	60.000	153.274	102.782	131.278	- 671.372	- 280.041	23.540
2700	60.000	155.538	104.695	137.278	- 670.035	- 265.017	21.452
2800	60.000	157.720	106.550	143.278	- 668.715	- 250.035	19.516
2900	60.000	159.826	108.351	149.278	- 667.417	- 235.105	17.718
3000	60.000	161.860	110.101	155.278	- 666.135	- 220.220	16.043

June 30, 1967

LITHIUM DISILICATE ($Li_2Si_2O_5$) (LIQUID) GFW = 150.047

$S°_{298.15}$ = [38.297] gibbs/mol

$\Delta Hf°_{298.15}$ = -600.640 ± 1.0 kcal/mol

Tm = 1307°K

ΔHm° = [12.86] kcal/mol

Heat of Formation

The heats of solution of LiCl(c), Li_2SO_4(c), SiO_2(quartz) and $Li_2Si_2O_5$(gl) in 20 percent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). Following the same procedure as described in $Li_2Si_2O_5$(c) table, we derived the enthalpy changes, $\Delta Hr°_{298}$, for the reaction Li_2O(c) + $2SiO_2$(quartz) = $Li_2Si_2O_5$(gl) as -21.78 and -22.87 kcal/mol. Adopting the weighted average $\Delta Hr°_{298}$ = -22.14 kcal/mol with $\Delta Hf°_{298}$(Li_2O, c) = -143.1 kcal/mol and $\Delta Hf°_{298}$(SiO_2, quartz) = -217.7 kcal/mol, we obtain $\Delta Hf°_{298}$ = -600.640 kcal/mol for $Li_2Si_2O_5$(gl). This $\Delta Hf°_{298}$($Li_2Si_2O_5$, gl) value is independent of future changes in $\Delta Hf°_{298}$ of Li_2O(c) but the values of ΔHsoln and ΔHr° are not independent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $Na_2Si_2O_5(\ell)$, $Na_2SiO_3(\ell)$ and $Li_2SiO_3(\ell)$. A glass transition temperature at 800°K is assumed, i.e. the heat capacities below 800°K are taken from those for $Li_2Si_2O_5$(c) and above 800°K are assumed to be constant.

The $S°_{298}$ value is obtained from $S°_{298}$(c) by adding ΔSm° and the difference between $S°_{1307} - S°_{298}$ for crystal and liquid.

Melting Data

See $Li_2Si_2O_5$(c) table for details.

Lithium Nitride (Li_3N)

(Crystal)   GFW = 34.8237

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.480	9.000	9.000	.000	-47.200	-36.840	27.005
300	18.530	9.114	9.000	.034	-47.205	-36.777	26.792
400	20.990	14.785	9.757	2.011	-47.440	-33.261	18.173
500	23.340	19.722	11.266	4.228	-49.829	-29.471	12.882
600	25.660	24.184	13.052	6.679	-49.872	-25.389	9.248
700	27.840	28.308	14.941	9.357	-49.658	-21.324	6.658
800	29.640	32.149	16.855	12.235	-49.228	-17.305	4.727
900	30.960	35.720	18.755	15.268	-48.647	-13.347	3.241
1000	31.900	39.033	20.619	18.414	-47.959	-9.461	2.068
1100	32.540	42.105	22.434	21.638	-47.193	-5.647	1.122
1200	32.970	44.956	24.194	24.914	-46.381	-1.908	.347
1300	33.250	47.606	25.894	28.226	-45.532	1.764	-.297
1400	33.450	50.078	27.534	31.561	-44.663	5.371	-.838
1500	33.600	52.391	29.115	34.914	-43.773	8.913	-1.299
1600	33.720	54.564	30.638	38.281	-42.868	12.398	-1.693
1700	33.800	56.611	32.107	41.657	-147.094	19.806	-2.546
1800	33.840	58.544	33.522	45.039	-145.628	29.586	-3.592
1900	33.880	60.374	34.888	48.425	-144.159	39.284	-4.519
2000	33.920	62.113	36.206	51.815	-142.692	48.898	-5.343
2100	33.960	63.769	37.479	55.209	-141.226	58.438	-6.082
2200	34.000	65.350	38.710	58.607	-139.761	67.913	-6.747

Dec. 31, 1960; Sept. 30, 1966

LITHIUM NITRIDE (Li_3N)   (CRYSTAL)   GFW = 34.8237

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [9 + 2] gibbs/mol $\Delta Hf^\circ_{298.15} = -47.2 \pm 1.0$ kcal/mol

Heat of Formation.

The adopted $\Delta Hf^\circ_{298.15} = -47.2 \pm 1.0$ kcal/mol was determined calorimetrically by Neumann et al[1]. by heating Li (c) at 600°C under 5 atm N_2 pressure for 1 minute. The $\Delta Hr^\circ_{291} = -131.1$ kcal/mol of reaction $Li_3N(c) + 3\ H_2O\ (l) = 3\ LiOH\ (aq) + NH_3\ (aq)$ was measured by Guntz[2]. Based on this ΔHr°_{291} the heat of formation was calculated to be -47.02 ± 2 kcal/mol which is in very good agreement with that of Neumann et al[1]. Unfortunately the author does not report the amount of water in LiOH (aq) and we assumed 300 H_2O as the best estimate. Heats of formation for $NH_3(aq)$ = [-19.17] kcal/mol and H_2O (l) = [-68.315] kcal/mol were taken from Wagman et al[3]. The ΔHf of $LiOH \cdot 300\ H_2$ (-121.30 kcal/mol) was derived from the heats of formation and solution of LiOH(c) (see JANAF table) and the heat of dilution selected by Parker[4].

References:1. B. Neumann, C. Kroger and H. Haebler, Z. anorg. allgem. Chem. 204, 81-96 (1932).
2. A. Guntz, Compt. rend 123, 995-8 (1896).
3. D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, Washington, 1965.
4. V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, Washington, D. C., 1965.

Heat Capacity and Entropy.

S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 35, 182 (1939), has measured enthalpies (273-578°K) and derived an equation for the specific heat of Li_3N. The adopted heat capacities were obtained from this equation. Above 773°K the heat capacities were graphically extrapolated. The entropy was estimated from the contribution 3.5 eu per Li given by W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, and a -1.5 eu contribution for N.

Magnesium (Mg)

(Reference State) At. Wt. = 24.32

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.196	.000	.000	.000
100	3.768	2.273	12.695	- 1.042	.000	.000	.000
200	5.440	5.533	7.933	- .480	.000	.000	.000
298	5.973	7.814	7.814	.000	.000	.000	.000
300	5.960	7.851	7.814	.011	.000	.000	.000
400	6.290	9.613	8.052	.625	.000	.000	.000
500	6.560	11.047	8.512	1.267	.000	.000	.000
600	6.802	12.264	9.038	1.936	.000	.000	.000
700	7.080	13.333	9.577	2.629	.000	.000	.000
800	7.420	14.300	10.108	3.354	.000	.000	.000
900	7.810	15.196	10.624	4.115	.000	.000	.000
1000	7.880	18.339	11.304	7.034	.000	.000	.000
1100	8.140	19.102	11.979	7.836	.000	.000	.000
1200	8.400	19.821	12.602	8.663	.000	.000	.000
1300	8.660	20.504	13.184	9.516	.000	.000	.000
1400	4.968	43.187	14.072	40.760	.000	.000	.000
1500	4.968	43.530	16.025	41.257	.000	.000	.000
1600	4.968	43.850	17.754	41.754	.000	.000	.000
1700	4.968	44.152	19.298	42.251	.000	.000	.000
1800	4.968	44.436	20.687	42.748	.000	.000	.000
1900	4.968	44.704	21.944	43.244	.000	.000	.000
2000	4.969	44.959	23.098	43.741	.000	.000	.000
2100	4.969	45.201	24.136	44.238	.000	.000	.000
2200	4.970	45.433	25.098	44.735	.000	.000	.000
2300	4.972	45.654	25.987	45.232	.000	.000	.000
2400	4.974	45.865	26.811	45.729	.000	.000	.000
2500	4.978	46.068	27.578	46.227	.000	.000	.000
2600	4.983	46.264	28.292	46.725	.000	.000	.000
2700	4.989	46.452	28.962	47.224	.000	.000	.000
2800	4.998	46.633	29.589	47.723	.000	.000	.000
2900	5.009	46.809	30.180	48.223	.000	.000	.000
3000	5.023	46.979	30.737	48.725	.000	.000	.000
3100	5.040	47.144	31.264	49.228	.000	.000	.000
3200	5.060	47.304	31.763	49.733	.000	.000	.000
3300	5.085	47.460	32.236	50.240	.000	.000	.000
3400	5.114	47.613	32.686	50.750	.000	.000	.000
3500	5.148	47.761	33.115	51.263	.000	.000	.000
3600	5.186	47.907	33.524	51.780	.000	.000	.000
3700	5.229	48.050	33.914	52.301	.000	.000	.000
3800	5.278	48.190	34.288	52.826	.000	.000	.000
3900	5.332	48.327	34.646	53.356	.000	.000	.000
4000	5.392	48.463	34.990	53.892	.000	.000	.000
4100	5.457	48.597	35.320	54.435	.000	.000	.000
4200	5.528	48.729	35.638	54.984	.000	.000	.000
4300	5.604	48.860	35.944	55.541	.000	.000	.000
4400	5.686	48.990	36.239	56.105	.000	.000	.000
4500	5.773	49.119	36.524	56.678	.000	.000	.000
4600	5.866	49.247	36.799	57.260	.000	.000	.000
4700	5.964	49.374	37.065	57.851	.000	.000	.000
4800	6.067	49.501	37.323	58.453	.000	.000	.000
4900	6.176	49.627	37.573	59.065	.000	.000	.000
5000	6.289	49.753	37.815	59.688	.000	.000	.000
5100	6.407	49.878	38.050	60.323	.000	.000	.000
5200	6.530	50.004	38.279	60.970	.000	.000	.000
5300	6.658	50.130	38.501	61.629	.000	.000	.000
5400	6.790	50.255	38.718	62.301	.000	.000	.000
5500	6.927	50.381	38.929	62.987	.000	.000	.000
5600	7.069	50.507	39.135	63.687	.000	.000	.000
5700	7.215	50.634	39.335	64.401	.000	.000	.000
5800	7.367	50.760	39.531	65.130	.000	.000	.000
5900	7.523	50.888	39.722	65.875	.000	.000	.000
6000	7.684	51.015	39.910	66.635	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM (Mg) (REFERENCE STATE) AT. WT. = 24.32

Crystal	Below 922°K
Liquid	922°K to 1378°K
Ideal gas, monatomic	above 1378°K

See crystal, liquid, and ideal monatomic gas for details.

Magnesium (Mg)

(Crystal) At. Wt. = 24.32

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	-(F°-H°₂₉₈)/T (cal. mole⁻¹deg.⁻¹)	H°-H°₂₉₈ (kcal. mole⁻¹)	ΔH°f (kcal. mole⁻¹)	ΔF°f (kcal. mole⁻¹)	Log Kp
0	.000	.000	INFINITE	-1.196	.000	.000	INFINITE
100	3.768	2.273	12.695	-1.042	.000	.000	.000
200	5.440	5.533	7.933	-.480	.000	.000	.000
298	5.953	7.814	7.814	.000	.000	.000	.000
300	5.960	7.851	7.814	.011	.000	.000	.000
400	6.290	9.613	8.052	.625	.000	.000	.000
500	6.560	11.047	8.512	1.267	.000	.000	.000
600	6.802	12.264	9.038	1.936	.000	.000	.000
700	7.080	13.333	9.577	2.629	.000	.000	.000
800	7.420	14.300	10.108	3.354	.000	.000	.000
900	7.810	15.197	10.624	4.115	.000	.000	.000
1000	8.190	16.039	11.124	4.915	-2.119	.181	-.040
1100	8.525	16.835	11.607	5.751	-2.085	.408	-.081
1200	8.860	17.592	12.075	6.620	-2.043	.633	-.115
1300	9.195	18.314	12.527	7.523	-1.993	.854	-.144
1400	9.530	19.008	12.965	8.459	-32.301	1.550	-.242
1500	9.865	19.677	13.391	9.429	-31.828	3.952	-.576
1600	10.200	20.324	13.804	10.432	-31.322	6.320	-.863
1700	10.535	20.952	14.206	11.469	-30.782	8.657	-1.113
1800	10.870	21.564	14.598	12.539	-30.209	10.961	-1.331
1900	11.205	22.161	14.980	13.643	-29.601	13.231	-1.522
2000	11.540	22.747	15.354	14.780	-28.961	15.469	-1.690

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM (Mg) (CRYSTAL) AT. WT. = 24.32

$\Delta H^\circ_{f\ 0} = 0$

$\Delta H^\circ_{s\ 298.15} = 35.28 \pm 0.01$ kcal. mole^{-1}

$T_m = 922 \pm 0.5$°K

$\Delta H^\circ_{f\ 298.15} = 0$

$S^\circ_{298.15} = 7.814$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_m = 2.14$ kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The following heat capacity measurements were considered in drawing a smooth curve of C_p with T: P. L. Smith (1.25-4.2°K) Phil. Mag. 46, 744 (1955); J. R. Clement and H. R. Jeffers (3-13°K) Phys. Rev. 105, 1435 (1957); K. Clusius and J. V. Vaughn (11.3-228.4°K) J. Am. Chem. Soc. 52, 4686, (1930); R. S. Craig, C. A. Krier, L. W. Coffer, E. A. Bates, and W. E. Wallace (12-320°K) J. Am. Chem. Soc. 76, 238 (1954); W. Mannchen and K. Bornkessel (190-300°K) Z. Metallkunde 51, 482-5 (1960); H. Seekamp (291-773°K) Z. anorg. Chem. 195, 345 (1931); and D. R. Stull and R. A. McDonald (700-900°K) J Am. Chem. Soc. 77, 5293 (1955). The following heat capacity measurements were noted but not used as the data were either not tabulated, or erratic, or inconsistent or would not have altered the C_p-T curve: D. L. Martin (0.4-1.5°K) Proc. Phys. Soc (London) 78, 1482-8 (1961); I. Estermann, S. A. Friedberg, and J. E. Goldman (1.8-4.2°K) Phys. Rev. 87, 582 (1952); E. P. Eastman and W. H. Rodebush (74.9-288.5°K) J. Am. Chem. Soc. 40 489 (1918); W. G. Saba, K. F. Sterrett, R. S. Craig, and W. E. Wallace (298-543°K) J. Am. Chem. Soc. 79, 3637 (1957); F. M. Jaeger and T. J. Poppema (273-873°K) Rec. Trav. chim. 55, 492 (1936); J. H. Awbery and E. Griffiths (323-898°K) Proc. Phys. Soc. 38, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young (373-873°K) J. Am. Chem. Soc. 46, 1178 (1926); and P. Schübel (323-773°K) Z. anorg. chem. 87, 81 (1914). $S^\circ_{298.15}$ was obtained by numerical integration using the low temperature C_p data cited above.

Melting.

Melting point is from J. L. Haughton and R. J. M. Payne (922 ± 0.5°K) J. Inst. Met. 54, 279 (1934). Also noted but not used were: R. Chadwick (923°K) J. Inst. Met. 39, 285-300 (1928); W. R. D. Jones (920.5°K) J. Inst. Met. 46, 395-419 (1931).

The heat of melting is from D. R. Stull and R. A. McDonald (loc. cit.)

Heat of Sublimation.

Is obtained by third law calculations from the vapor pressure data on the solid by F. F. Coleman and A. E. Egerton, Phil. Trans Roy. Soc. (London) A234, 177-204 (1935) and the value is confirmed by similar use of the vapor pressure data on the liquid by E. Scheil and F. Wolf, Z. Metallkunde 50, 229-33 (1959); A. Wejnarth, Tek. Tid. 72, 33-9, 44-8 (1942); A. Schneider and E. K. Stoll. Z. Elektrochem. 47, 519-26 (1941); E. Baur and R. Brunner, Helv. Chim. Acta, 17, 958-69 (1934); and H. Hartmann and R. Schneider, Z. anorg. Chem. 180, 275-83 (1929). Additional data noted but not used on the vapor pressure, as values were not tabulated or they were erratic, of the solid are by J. F. Smith and R. L. Smythe, Acta Metallurgica, 7, 261-7 (1959); A. Eucken, Metallwirtschaft, 15, 64-5 (1936); W. Leitgebel, Metallwirtschaft, 14, 269 (1935); and of the liquid by F. A. Vetter and O. Kubaschewski, Z. Elektrochem. 57, 243 (1953); W. Leitgebel, Z. anorg. Chem. 202, 312 (1931); C. Zwikker, Physica, 8, 246 (1928); O. Ruff and H. Hartmann, Z. anorg. Chem., 133, 29-45 (1924); and J. Johnston, Ind. Eng. Chem. 9, 876 (1917).

Magnesium (Mg)

(Liquid) At. Wt. = 24.32

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100							
200							
298	5.953	10.159	10.159	.000	2.158	1.459	-1.069
300	5.960	10.196	10.159	.011	2.158	1.455	-1.060
400	6.290	11.958	10.397	.625	2.158	1.219	-.666
500	6.560	13.392	10.857	1.267	2.158	.986	-.431
600	6.802	14.609	11.383	1.936	2.158	.750	-.273
700	7.080	15.679	11.922	2.630	2.159	.517	-.161
800	7.350	16.642	12.453	3.351	2.155	.282	-.077
900	7.610	17.523	12.968	4.099	2.142	.048	-.012
1000	7.880	18.338	13.465	4.874	.000	.000	.000
1100	8.140	19.102	13.943	5.675	.000	.000	.000
1200	8.400	19.821	14.403	6.502	.000	.000	.000
1300	8.660	20.504	14.846	7.355	.000	.000	.000
1400	8.920	21.155	15.274	8.234	-30.368	.477	-.074
1500	9.180	21.779	15.687	9.139	-29.960	2.666	-.388
1600	9.440	22.380	16.086	10.070	-29.526	4.826	-.659
1700	9.700	22.960	16.474	11.027	-29.066	6.960	-.895
1800	9.960	23.522	16.850	12.010	-28.580	9.065	-1.101
1900	10.220	24.067	17.215	13.019	-28.067	11.142	-1.282
2000	10.480	24.598	17.571	14.054	-27.529	13.192	-1.442
2100	10.740	25.116	17.918	15.115	-26.965	15.213	-1.583
2200	11.000	25.622	18.257	16.202	-26.375	17.210	-1.710
2300	11.260	26.116	18.588	17.315	-25.759	19.178	-1.822
2400	11.520	26.601	18.912	18.454	-25.117	21.117	-1.923
2500	11.780	27.076	19.229	19.619	-24.450	23.029	-2.013

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM (Mg) (LIQUID) AT. WT. = 24.32

$\Delta H^\circ_{f\ 298.15}$ = [2.158] kcal. mole^{-1}

T_m = 922 ± 0.5°K

T_b = 1378°K

$S^\circ_{298.15}$ = [10.159] cal. deg.$^{-1}$ mole^{-1}

ΔH°_m = 2,140 cal. mole^{-1}

ΔH_v = 30.5 kcal. mole^{-1}

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ (= $\Delta H_{m\ 298.15}$) obtained from $\Delta H_{m\ 922}$ by adding H_{922}-$H_{298.15}$ for solid and subtracting H_{922}-$H_{298.15}$ for liquid.

Heat Capacity and Entropy.

The heat capacity measurements of D. R. Stull and R. A. McDonald (950-1100°K) J. Am. Chem. Soc. 77, 5293 (1955) were used. Outside of the observed range C_p was extrapolated linearly with temperature. Below T_m the linear extrapolation was continued until the C_p curve for the solid is encountered at 710°K. At lower temperatures the C_p of the crystal is used. $S^\circ_{298.15}$ was calculated from that of the solid.

Melting.

See crystal for details.

Vaporization.

The normal boiling point was calculated by the third law and $\Delta H_{s\ 298.15}$. This compares with 1377°K computed from the general vapor pressure equation for liquid Mg given on p 221 of Gmelins Handbuch der anorganischen Chemie, System-Nummer 27 (1952), and experimentally determined values: 1376 ± 5°K by A. Schneider and U. Esch, Z. Elektrochem 45, 888 (1939); 1380°K by E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934); 1370°K by W. Leitgebel, Z. anorg. Chem. 202, 305 (1931); and 1393°K by Greenwood, Chem. News 104, 31 (1911).

The $\Delta H_{v\ 1378}$ is based on the liquid and ideal gas tables.

Magnesium, Monatomic (Mg)

(Ideal Gas) At. Wt. = 24.32

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.481	34.996	34.996	INFINITE
100	4.968	30.076	39.921	-.984	35.339	32.558	-71.153
200	4.968	33.520	35.958	-.488	35.273	29.676	-32.427
298	4.968	35.504	35.504	.000	35.281	27.025	-19.809
300	4.968	35.535	35.504	.009	35.279	26.974	-19.650
400	4.968	36.964	35.699	.506	35.162	24.222	-13.233
500	4.968	38.072	36.067	1.003	35.017	21.504	-9.399
600	4.968	38.978	36.479	1.500	34.845	18.816	-6.853
700	4.968	39.744	36.892	1.996	34.648	16.161	-5.045
800	4.968	40.407	37.291	2.493	34.420	13.534	-3.697
900	4.968	40.993	37.670	2.990	34.156	10.939	-2.656
1000	4.968	41.516	38.029	3.487	31.734	8.557	-1.870
1100	4.968	41.990	38.368	3.984	31.429	6.252	-1.242
1200	4.968	42.422	38.688	4.481	31.099	3.977	-.724
1300	4.968	42.820	38.991	4.977	30.742	1.732	-.291
1400	4.968	43.188	39.278	5.474	.000	.000	.000
1500	4.968	43.530	39.550	5.971	.000	.000	.000
1600	4.968	43.851	39.809	6.468	.000	.000	.000
1700	4.968	44.152	40.056	6.965	.000	.000	.000
1800	4.968	44.436	40.291	7.461	.000	.000	.000
1900	4.968	44.705	40.516	7.958	.000	.000	.000
2000	4.969	44.960	40.732	8.455	.000	.000	.000
2100	4.969	45.202	40.939	8.952	.000	.000	.000
2200	4.970	45.433	41.138	9.449	.000	.000	.000
2300	4.972	45.654	41.330	9.946	.000	.000	.000
2400	4.974	45.866	41.515	10.443	.000	.000	.000
2500	4.978	46.069	41.693	10.941	.000	.000	.000
2600	4.983	46.264	41.865	11.439	.000	.000	.000
2700	4.989	46.453	42.031	11.938	.000	.000	.000
2800	4.998	46.634	42.192	12.437	.000	.000	.000
2900	5.009	46.810	42.349	12.937	.000	.000	.000
3000	5.023	46.980	42.500	13.439	.000	.000	.000
3100	5.040	47.145	42.647	13.942	.000	.000	.000
3200	5.060	47.305	42.790	14.447	.000	.000	.000
3300	5.085	47.461	42.930	14.954	.000	.000	.000
3400	5.114	47.613	43.065	15.464	.000	.000	.000
3500	5.148	47.762	43.197	15.977	.000	.000	.000
3600	5.186	47.908	43.326	16.494	.000	.000	.000
3700	5.229	48.050	43.452	17.014	.000	.000	.000
3800	5.278	48.190	43.575	17.540	.000	.000	.000
3900	5.332	48.328	43.695	18.070	.000	.000	.000
4000	5.392	48.464	43.812	18.606	.000	.000	.000
4100	5.457	48.598	43.927	19.149	.000	.000	.000
4200	5.528	48.730	44.040	19.698	.000	.000	.000
4300	5.604	48.861	44.151	20.254	.000	.000	.000
4400	5.686	48.991	44.259	20.819	.000	.000	.000
4500	5.773	49.120	44.366	21.392	.000	.000	.000
4600	5.866	49.248	44.471	21.974	.000	.000	.000
4700	5.964	49.375	44.574	22.565	.000	.000	.000
4800	6.067	49.501	44.675	23.167	.000	.000	.000
4900	6.176	49.628	44.775	23.779	.000	.000	.000
5000	6.289	49.754	44.873	24.402	.000	.000	.000
5100	6.407	49.879	44.970	25.037	.000	.000	.000
5200	6.530	50.005	45.066	25.684	.000	.000	.000
5300	6.658	50.130	45.160	26.343	.000	.000	.000
5400	6.790	50.256	45.253	27.015	.000	.000	.000
5500	6.927	50.382	45.345	27.701	.000	.000	.000
5600	7.069	50.508	45.436	28.401	.000	.000	.000
5700	7.215	50.634	45.527	29.115	.000	.000	.000
5800	7.367	50.761	45.616	29.844	.000	.000	.000
5900	7.523	50.888	45.704	30.589	.000	.000	.000
6000	7.684	51.016	45.791	31.349	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM, MONATOMIC (Mg) (IDEAL GAS) AT. WT. = 24.32

$\Delta H^\circ_{f\ 0}$ = 35.0 ± 0.01 kcal. mole^{-1}

Ground State $^1S_0$

$\Delta H^\circ_{f\ 298.15}$ = 35.28 ± 0.01 kcal. mole^{-1}

$S^\circ_{298.15}$ = 35.504 cal. mole^{-1} deg.$^{-1}$

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1	ϵ_1, cm.$^{-1}$	g_1
0.00	1	46403.14	5	57020	9
21850.37	1	47850.0	9	57204	28
21870.43	3	47957.0	15	57854	12
21911.14	5	49346.6	3	58469	58
35051.36	3	51872.4	3	59315	51
41197.37	3	52556.4	1	59878	51
43503.0	1	53134.7	5	60397	102
				60887	154

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ $(=\Delta H_{s\ 298.15})$ is calculated as described on the table for crystal.

Heat Capacity and Entropy.

Thermodynamic functions were calculated using electronic levels and multiplicities from C. E. Moore [Natl. Bur. Standards Circ. 467, Vol. 1 (1949)]. Higher levels were averaged.

Magnesium Unipositive Ion (Mg$^+$)

(Ideal Gas) GFW = 24.31145

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	4.968	36.879	36.879	.000	211.559	201.406	-147.635
300	4.968	36.910	36.879	.009	211.565	201.343	-146.678
400	4.968	38.339	37.074	.506	211.946	197.876	-108.115
500	4.968	39.448	37.442	1.003	212.298	194.319	-84.937
600	4.968	40.353	37.854	1.500	212.623	190.691	-69.459
700	4.968	41.119	38.267	1.994	212.922	187.012	-58.388
800	4.968	41.782	38.666	2.493	213.191	183.292	-50.073
900	4.968	42.368	39.045	2.990	213.424	179.540	-43.598
1000	4.968	42.891	39.404	3.487	211.499	175.946	-38.453
1100	4.968	43.365	39.743	3.984	211.691	172.380	-34.249
1200	4.968	43.797	40.063	4.480	211.857	168.799	-30.743
1300	4.968	44.194	40.366	4.977	211.997	165.204	-27.773
1400	4.968	44.563	40.653	5.474	181.747	162.080	-25.302
1500	4.968	44.905	40.925	5.971	182.244	160.658	-23.408
1600	4.968	45.226	41.184	6.467	182.740	159.201	-21.746
1700	4.968	45.527	41.430	6.964	183.237	157.717	-20.276
1800	4.968	45.811	41.666	7.461	183.733	156.200	-18.965
1900	4.968	46.080	41.891	7.958	184.231	154.658	-17.790
2000	4.968	46.335	42.107	8.455	184.728	153.089	-16.729
2100	4.968	46.577	42.314	8.951	185.224	151.492	-15.766
2200	4.968	46.808	42.513	9.448	185.721	149.877	-14.889
2300	4.968	47.029	42.705	9.945	186.217	148.235	-14.086
2400	4.968	47.240	42.889	10.442	186.714	146.573	-13.347
2500	4.968	47.443	43.068	10.939	187.210	144.890	-12.666
2600	4.968	47.638	43.240	11.435	187.705	143.159	-12.036
2700	4.968	47.825	43.406	11.932	188.200	141.459	-11.451
2800	4.968	48.006	43.567	12.429	188.695	139.726	-10.906
2900	4.968	48.180	43.723	12.926	189.185	137.970	-10.398
3000	4.968	48.349	43.875	13.423	189.680	136.193	-9.922
3100	4.968	48.512	44.022	13.919	190.170	134.402	-9.475
3200	4.968	48.669	44.164	14.416	190.659	132.597	-9.056
3300	4.968	48.822	44.303	14.913	191.146	130.775	-8.661
3400	4.968	48.971	44.438	15.410	191.629	128.941	-8.288
3500	4.968	49.115	44.570	15.907	192.110	127.088	-7.936
3600	4.969	49.255	44.698	16.403	192.586	125.225	-7.602
3700	4.969	49.391	44.823	16.900	193.059	123.345	-7.286
3800	4.969	49.523	44.945	17.397	193.528	121.456	-6.985
3900	4.970	49.652	45.064	17.894	193.992	119.552	-6.699
4000	4.970	49.778	45.180	18.391	194.449	117.637	-6.427
4100	4.971	49.901	45.294	18.888	194.900	115.709	-6.168
4200	4.972	50.021	45.405	19.386	195.346	113.774	-5.920
4300	4.973	50.138	45.514	19.883	195.783	111.825	-5.684
4400	4.975	50.252	45.620	20.380	196.213	109.872	-5.457
4500	4.976	50.364	45.724	20.878	196.634	107.903	-5.240
4600	4.978	50.473	45.826	21.376	197.047	105.925	-5.033
4700	4.981	50.580	45.926	21.873	197.450	103.942	-4.833
4800	4.983	50.685	46.025	22.372	197.844	101.948	-4.642
4900	4.986	50.788	46.121	22.870	198.227	99.947	-4.458
5000	4.990	50.889	46.215	23.369	198.599	97.940	-4.281
5100	4.993	50.988	46.308	23.868	198.960	95.916	-4.110
5200	4.998	51.085	46.399	24.368	199.310	93.897	-3.946
5300	5.002	51.180	46.488	24.868	199.648	91.867	-3.788
5400	5.008	51.274	46.576	25.368	199.973	89.827	-3.635
5500	5.013	51.365	46.662	25.869	200.285	87.786	-3.488
5600	5.020	51.456	46.747	26.371	200.583	85.733	-3.346
5700	5.027	51.545	46.830	26.873	200.868	83.689	-3.209
5800	5.034	51.632	46.912	27.376	201.139	81.623	-3.076
5900	5.042	51.718	46.993	27.880	201.395	79.564	-2.947
6000	5.051	51.803	47.072	28.385	201.637	77.496	-2.823

Dec. 31, 1967

MAGNESIUM UNIPOSITIVE ION(Mg$^+$) (IDEAL GAS) GFW = 24.31145

Ground State Configuration $^1S_0$ ΔHf°_0 = 211.3 ± 0.1 kcal/mol

$S^\circ_{298.15}$ = 36.879 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 211.6 ± 0.1 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	2	106879.10	76
35730.45	6	112273.83	44
71209.84	12	114385.15	44
80641.13	6	115847.07	32
94271.23	32	117578.72	96

Heat of Formation

We derive the heat of formation at 0°K from the reaction Mg(g) - e$^-$(g) → Mg$^+$(g) using the JANAF auxiliary value for Mg(g) and an ionization potential of 176.278 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 467,Vol. I, 1949.

Heat Capacity and Entropy

We take the electronic levels and quantum weights from C. E. Moore, loc. cit. $H^\circ_0 - H^\circ_{298}$ = -1.481 kcal/mol at 0°K.

Monomagnesium Mononitride (MgN)

(Ideal Gas) Mol. Wt. = 38.328

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 2.148	69.084	69.084	INFINITE
100	6.968	45.789	60.321	- 1.453	69.282	66.836	- 146.064
200	7.311	50.696	54.412	- .743	69.079	64.345	- 70.309
298	7.823	53.713	53.713	.000	69.000	62.138	- 45.547
300	7.832	53.761	53.713	.014	68.997	62.096	- 45.235
400	8.208	56.070	54.025	.818	68.838	59.819	- 32.682
500	8.449	57.929	54.626	1.652	68.678	57.584	- 25.169
600	8.607	59.484	55.310	2.505	68.506	55.380	- 20.171
700	8.716	60.820	56.004	3.371	68.316	53.207	- 16.611
800	8.794	61.989	56.680	4.247	68.095	51.063	- 13.949
900	8.854	63.028	57.329	5.130	67.837	48.949	- 11.886
1000	8.901	63.964	57.946	6.017	65.419	47.048	- 10.282
1100	8.939	64.814	58.533	6.909	65.115	45.224	- 8.985
1200	8.971	65.593	59.089	7.805	64.783	43.429	- 7.909
1300	8.999	66.312	59.617	8.703	64.423	41.665	- 7.004
1400	9.023	66.980	60.120	9.605	33.670	40.408	- 6.308
1500	9.046	67.603	60.598	10.508	33.661	40.889	- 5.957
1600	9.066	68.188	61.054	11.414	33.652	41.371	- 5.651
1700	9.085	68.738	61.490	12.321	33.641	41.855	- 5.381
1800	9.103	69.258	61.908	13.230	33.629	42.338	- 5.140
1900	9.119	69.750	62.307	14.142	33.618	42.822	- 4.925
2000	9.136	70.219	62.691	15.054	33.604	43.307	- 4.732
2100	9.151	70.665	63.061	15.969	33.591	43.791	- 4.557
2200	9.166	71.091	63.416	16.885	33.577	44.279	- 4.398
2300	9.181	71.499	63.759	17.802	33.562	44.766	- 4.253
2400	9.195	71.890	64.089	18.721	33.549	45.252	- 4.121
2500	9.209	72.265	64.409	19.641	33.533	45.739	- 3.998
2600	9.223	72.627	64.718	20.562	33.518	46.229	- 3.886
2700	9.236	72.975	65.017	21.485	33.503	46.718	- 3.781
2800	9.249	73.311	65.308	22.410	33.488	47.206	- 3.684
2900	9.263	73.636	65.589	23.335	33.472	47.698	- 3.594
3000	9.276	73.950	65.863	24.262	33.455	48.189	- 3.510
3100	9.288	74.255	66.129	25.190	33.437	48.680	- 3.432
3200	9.301	74.550	66.387	26.120	33.417	49.171	- 3.358
3300	9.314	74.836	66.639	27.051	33.396	49.663	- 3.289
3400	9.326	75.114	66.884	27.983	33.373	50.160	- 3.224
3500	9.339	75.385	67.123	28.916	33.347	50.650	- 3.163
3600	9.351	75.648	67.356	29.850	33.318	51.147	- 3.105
3700	9.364	75.904	67.584	30.786	33.286	51.644	- 3.050
3800	9.376	76.154	67.806	31.723	33.250	52.140	- 2.999
3900	9.389	76.398	68.023	32.661	33.210	52.636	- 2.949
4000	9.401	76.636	68.236	33.601	33.164	53.135	- 2.903
4100	9.413	76.868	68.443	34.542	33.113	53.635	- 2.859
4200	9.425	77.095	68.647	35.484	33.056	54.135	- 2.817
4300	9.437	77.317	68.846	36.427	32.992	54.638	- 2.777
4400	9.449	77.534	69.041	37.371	32.921	55.142	- 2.739
4500	9.462	77.747	69.232	38.317	32.842	55.650	- 2.703
4600	9.474	77.955	69.419	39.263	32.755	56.159	- 2.668
4700	9.486	78.159	69.603	40.211	32.660	56.667	- 2.635
4800	9.498	78.358	69.783	41.160	32.554	57.181	- 2.603
4900	9.510	78.554	69.960	42.111	32.440	57.692	- 2.573
5000	9.522	78.747	70.134	43.062	32.315	58.212	- 2.544
5100	9.534	78.935	70.305	44.015	32.179	58.725	- 2.516
5200	9.546	79.121	70.473	44.969	32.032	59.251	- 2.490
5300	9.558	79.302	70.638	45.924	31.873	59.777	- 2.465
5400	9.569	79.481	70.800	46.881	31.702	60.302	- 2.440
5500	9.581	79.657	70.959	47.838	31.518	60.836	- 2.417
5600	9.593	79.830	71.116	48.797	31.320	61.369	- 2.395
5700	9.605	80.000	71.270	49.757	31.110	61.912	- 2.374
5800	9.617	80.167	71.422	50.718	30.885	62.450	- 2.353
5900	9.629	80.331	71.572	51.680	30.645	62.999	- 2.334
6000	9.641	80.493	71.719	52.644	30.390	63.545	- 2.315

Mar. 31, 1964

MONOMAGNESIUM MONONITRIDE (MgN) (IDEAL GAS) MOL. WT. = 38.328

Ground State Configuration $[^2\Pi]$

$S^\circ_{298.15}$ = [53.713] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [69 ± 6] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [69 ± 6] kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_1, cm.$^{-1}$	g_1
0	[4]

ω_e = [700] cm.$^{-1}$

B_e = [0.5542] cm.$^{-1}$

$\omega_e x_e$ = [4.8] cm.$^{-1}$

α_e = [0.0052]

σ = 1

r_e = [1.85] Å

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ for MgN was estimated from bond strengths using MgO and comparison with analogous pairs of compounds such as, PN and PO, and also the bond strengths of C-N and C-O in organic compounds.

Heat Capacity and Entropy.

The r_e value for MgN was estimated from MgO by comparison with similar pairs PO and PN, SiO and SiN, and AlO and AlN. Using Guggenheimer's Relation, Proc. Phys. Soc. (London) 58, 456 (1946), ω for MgO was found to lie between the single and multiple bonding cases. Magnesium nitride was assumed to be similar to MgO and ω_e = 700 cm.$^{-1}$ was obtained. It was assumed that the $x_e\mu^{1/2}$ value for MgN was equal to that for MgO thus giving $\omega_e x_e$ = 4.8 cm.$^{-1}$. B_e was calculated from r_e. The α_e value was calculated from B_e, ω_e and $\omega_e x_e$.

Magnesium Oxide (MgO)

(Crystal) Mol. Wt. = 40.3114

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.235	- 142.701	- 142.701	INFINITE
100	1.866	.608	12.465	- 1.186	- 143.163	- 140.920	307.966
200	6.370	3.369	7.177	- .762	- 143.640	- 138.584	151.431
298	8.882	6.440	6.440	.000	- 143.700	- 135.985	99.675
300	8.915	6.495	6.440	.016	- 143.701	- 135.937	99.025
400	10.169	9.251	6.807	.978	- 143.709	- 133.346	72.854
500	10.848	11.598	7.537	2.030	- 143.664	- 130.759	57.152
600	11.285	13.616	8.386	3.138	- 143.603	- 128.185	46.689
700	11.604	15.381	9.262	4.283	- 143.540	- 125.620	39.218
800	11.856	16.947	10.126	5.457	- 143.490	- 123.064	33.618
900	12.057	18.355	10.964	6.652	- 143.463	- 120.512	29.263
1000	12.232	19.635	11.768	7.867	- 145.580	- 117.780	25.740
1100	12.382	20.808	12.537	9.098	- 145.571	- 115.003	22.848
1200	12.507	21.891	13.272	10.343	- 145.577	- 112.224	20.438
1300	12.586	22.895	13.974	11.597	- 145.604	- 109.443	18.398
1400	12.664	23.831	14.645	12.860	- 176.018	- 106.181	16.575
1500	12.743	24.707	15.287	14.130	- 175.680	- 101.203	14.745
1600	12.821	25.532	15.902	15.409	- 175.337	- 96.251	13.147
1700	12.900	26.312	16.492	16.695	- 174.989	- 91.317	11.739
1800	12.978	27.052	17.058	17.988	- 174.637	- 86.407	10.491
1900	13.057	27.755	17.603	19.290	- 174.278	- 81.514	9.376
2000	13.136	28.427	18.127	20.600	- 173.916	- 76.642	8.375
2100	13.214	29.070	18.633	21.917	- 173.548	- 71.788	7.471
2200	13.293	29.686	19.122	23.243	- 173.175	- 66.948	6.650
2300	13.371	30.279	19.594	24.576	- 172.797	- 62.129	5.903
2400	13.450	30.850	20.051	25.917	- 172.414	- 57.327	5.220
2500	13.529	31.400	20.494	27.266	- 172.027	- 52.540	4.593
2600	13.607	31.933	20.924	28.623	- 171.634	- 47.768	4.015
2700	13.686	32.448	21.341	29.987	- 171.238	- 43.012	3.481
2800	13.764	32.947	21.747	31.360	- 170.836	- 38.271	2.987
2900	13.843	33.431	22.141	32.740	- 170.429	- 33.541	2.528
3000	13.921	33.902	22.526	34.128	- 170.020	- 28.829	2.100
3100	14.000	34.359	22.900	35.525	- 169.605	- 24.127	1.701
3200	14.079	34.805	23.265	36.928	- 169.187	- 19.443	1.328
3300	14.157	35.240	23.621	38.340	- 168.765	- 14.772	.978
3400	14.236	35.663	23.969	39.760	- 168.341	- 10.107	.650
3500	14.314	36.077	24.309	41.187	- 167.914	- 5.463	.341
3600	14.393	36.482	24.642	42.623	- 167.484	- .828	.050
3700	14.472	36.877	24.967	44.066	- 167.053	3.798	- .224
3800	14.550	37.264	25.286	45.517	- 166.619	8.410	- .484
3900	14.629	37.643	25.598	46.976	- 166.185	13.007	- .729
4000	14.707	38.014	25.904	48.443	- 165.750	17.598	- .961

Dec. 31, 1960; Dec. 31, 1965

MAGNESIUM OXIDE (MgO) (CRYSTAL) MOL. WT. = 40.311*

$S^\circ_{298.15}$ = 6.44 cal. deg.$^{-1}$ mole^{-1}

T_m = 3098 ± 20 °K.

T_s = 3466°K.

$\Delta H^\circ_{f\ 0}$ = -142.7 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -143.7 ± 0.3 kcal. mole^{-1}

ΔH_m = [18.5 ± 1.5] kcal. mole^{-1}

$\Delta H^\circ_{s\ 298}$ = 144.7 ± 20 kcal. mole^{-1}

Heat of Formation.

C. E. Holley and E. J. Huber, J. Am. Chem. Soc. 73, 5577 (1951) reported $\Delta H^\circ_{f\ 298}$ (MgO, c) = -143.7 kcal. mole^{-1} by combustion calorimetry. Heat of solution measurements by C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943) yielded $\Delta H^\circ_{f\ 298}$ (MgO, c) = -143.84 kcal. mole^{-1}, well within the adopted $\Delta H^\circ_{f\ 298}$ (MgO, c) = -143.7 ± 0.3 kcal. mole^{-1}.

Heat Capacity and Entropy.

Low temperature heat capacities have been reported by:

1. W. Lien and N. Phillips, J. Chem. Phys. 29, 1415 (1958), 1.5-4°K.
2. W. F. Giauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937), 20-301°K.
3. G. S. Parks and K. K. Kelley, J. Phys. Chem. 30, 47 (1926), 94-291°K.
4. T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) A250, 70 (1959), 10-270°K.
5. P. Gunther, Ann. Physik 51, 828 (1916), 21-84°K.

High temperature heat contents have been reported by:

6. A. C. Victor and T. B. Douglas, J. Res. N.B.S. 67A, 325 (1963), 373-1173°K.
7. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6295, (1963), 400-1800°K.

The samples of (1) and (2) were finely divided magnesia and the other samples were periclase. Periclase is taken to be the standard state. The high temperature heat content data of (6) and (7) were joined by a Shomate plot with the low temperature C_p data of (4). The heat capacity was extrapolated linearly above 1800°K to a value of 14 cal. mole^{-1} deg.$^{-1}$ at 3100°K. $S^\circ_{298.15}$ = 6.44 cal. deg.$^{-1}$ mole^{-1} is from (4).

Melting Data.

T_m(MgO, c) = 3098 ± 20°K by R. N. McNally, F. I. Peters, and P. H. Ribbe, J. Am. Ceram. Soc. 44, 491 (1961) was adopted. Their value is 41°K higher than the earlier measurements of C. W. Kanolt, J. Wash. Acad. Sci. 3, 315 (1913). K. K. Kelley, Bur. Mines Bull. 393 (1936) calculated ΔH_m (MgO, c) = 18.5 ± 1.5 kcal./mole from melting point measurements in the MgO - ZrO_2 system.

Sublimation Data.

T_s is the temperature at which the free energy change of the reaction MgO(c) = MgO(g) approaches zero. The difference between $\Delta H^\circ_{f\ 298.15}$ for MgO(c) and MgO(g) is $\Delta H^\circ_{s\ 298.15}$.

Magnesium Oxide (MgO)

(Liquid) Mol. Wt. = 40.3114

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	8.882	12.033	12.033	.000	- 126.137	- 120.090	88.024
300	8.915	12.088	12.033	.016	- 126.138	- 120.052	87.454
400	10.169	14.844	12.400	.978	- 126.146	- 118.021	64.480
500	10.848	17.191	13.130	2.030	- 126.101	- 115.993	50.698
600	11.285	19.209	13.979	3.138	- 126.040	- 113.978	41.514
700	11.604	20.974	14.855	4.283	- 125.977	- 111.972	34.957
800	11.856	22.540	15.719	5.457	- 125.927	- 109.975	30.042
900	12.057	23.948	16.557	6.652	- 125.900	- 107.982	26.220
1000	12.232	25.228	17.361	7.867	- 128.017	- 105.810	23.124
1100	12.382	26.401	18.130	9.098	- 128.008	- 103.592	20.581
1200	12.507	27.484	18.865	10.343	- 128.014	- 101.372	18.462
1300	12.586	28.488	19.567	11.597	- 128.041	- 99.150	16.668
1400	12.664	29.424	20.238	12.860	- 158.455	- 96.448	15.055
1500	12.743	30.300	20.880	14.130	- 158.117	- 92.030	13.408
1600	12.821	31.125	21.495	15.408	- 157.774	- 87.636	11.970
1700	12.900	31.905	22.085	16.695	- 157.426	- 83.263	10.704
1800	12.978	32.645	22.651	17.988	- 157.074	- 78.911	9.581
1900	13.057	33.348	23.196	19.290	- 156.715	- 74.577	8.578
2000	13.136	34.020	23.720	20.600	- 156.353	- 70.265	7.678
2100	14.500	34.684	24.226	21.962	- 155.940	- 65.970	6.865
2200	14.500	35.359	24.717	23.412	- 155.443	- 61.697	6.129
2300	14.500	36.003	25.194	24.862	- 154.948	- 57.446	5.458
2400	14.500	36.620	25.657	26.312	- 154.456	- 53.217	4.846
2500	14.500	37.212	26.108	27.762	- 153.968	- 49.011	4.284
2600	14.500	37.781	26.546	29.212	- 153.482	- 44.821	3.767
2700	14.500	38.328	26.972	30.662	- 153.000	- 40.651	3.290
2800	14.500	38.856	27.387	32.112	- 152.521	- 36.501	2.849
2900	14.500	39.364	27.791	33.562	- 152.045	- 32.362	2.439
3000	14.500	39.856	28.185	35.012	- 151.573	- 28.245	2.058
3100	14.500	40.331	28.570	36.462	- 151.105	- 24.140	1.702
3200	14.500	40.792	28.944	37.912	- 150.641	- 20.055	1.370
3300	14.500	41.238	29.310	39.362	- 150.181	- 15.981	1.058
3400	14.500	41.671	29.667	40.812	- 149.726	- 11.919	.766
3500	14.500	42.091	30.016	42.262	- 149.276	- 7.875	.492
3600	14.500	42.500	30.357	43.712	- 148.832	- 3.841	.233
3700	14.500	42.897	30.691	45.162	- 148.394	.183	- .011
3800	14.500	43.284	31.017	46.612	- 147.962	4.192	- .241
3900	14.500	43.660	31.337	48.062	- 147.536	8.189	- .459
4000	14.500	44.027	31.649	49.512	- 147.118	12.178	- .665
4100	14.500	44.385	31.956	50.962	- 146.708	16.156	- .861
4200	14.500	44.735	32.256	52.412	- 146.306	20.119	- 1.047
4300	14.500	45.076	32.550	53.862	- 145.913	24.079	- 1.224
4400	14.500	45.409	32.838	55.312	- 145.528	28.030	- 1.392
4500	14.500	45.735	33.121	56.762	- 145.154	31.971	- 1.553
4600	14.500	46.054	33.399	58.212	- 144.789	35.903	- 1.706
4700	14.500	46.366	33.672	59.662	- 144.435	39.826	- 1.852
4800	14.500	46.671	33.939	61.112	- 144.093	43.746	- 1.992
4900	14.500	46.970	34.202	62.562	- 143.761	47.652	- 2.125
5000	14.500	47.263	34.461	64.012	- 143.442	51.556	- 2.253

Dec. 31, 1965

MgO

MAGNESIUM OXIDE (MgO) (LIQUID) MOL. WT. = 40.3114

$S^\circ_{298.15}$ = [12.033] cal. deg.$^{-1}$ mole^{-1}

T_m = 3098°K.

T_B = [3533]°K.

ΔH_f° 298.15 = [-126.137] kcal. mole^{-1}

ΔH_m° = [18.5 ± 1.5] kcal. mole^{-1}

ΔH_v° = [113.4] kcal. mole^{-1}

Heat of Formation.

ΔH_f° 298.15(l) was calculated from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{T_m}-H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2066°K. C_p(l) below 2066°K. were assumed to be equal to those of MgO(c). At and above 2066°K. the heat capacities were assumed to be constant at 7.25 cal. deg.$^{-1}$ g. atom^{-1}. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgO(c) table for details.

Vaporization Data.

W. R. Mott, Tran. Am. Electrochem. Soc. 34, 255 (1918) estimated the boiling point at 3873°K. by comparing crater distances of arc image deposits with reference compounds. T_B = 3533°K. is the temperature at which the free energy change of the reaction MgO(l) = MgO(g) approaches zero. The difference between ΔH_f° 3533 for MgO(g) and MgO(l) is ΔH_v°.

MgO

Magnesium Oxide (MgO)
(Ideal Gas) Mol. Wt. = 40.3114

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.111	1.122	1.122	INFINITE
100	6.958	45.133	59.295	-1.416	1.307	-.903	1.974
200	7.104	49.983	53.562	-.716	1.105	-3.161	3.455
298	7.498	52.889	52.889	.000	1.000	-5.134	3.763
300	7.506	52.936	52.890	.014	.996	-5.172	3.768
400	7.897	55.151	53.189	.785	.798	-7.199	3.933
500	8.189	56.946	53.766	1.590	.595	-9.174	4.010
600	8.396	58.459	54.426	2.420	.379	-11.109	4.046
700	8.545	59.765	55.097	3.267	.144	-13.004	4.060
800	8.654	60.913	55.754	4.127	-.120	-14.866	4.061
900	8.737	61.937	56.385	4.997	-.418	-16.691	4.053
1000	8.802	62.861	56.987	5.874	-2.873	-18.299	3.999
1100	8.854	63.703	57.560	6.757	-3.212	-19.828	3.939
1200	8.897	64.475	58.105	7.645	-3.575	-21.323	3.883
1300	8.934	65.189	58.622	8.536	-3.965	-22.786	3.830
1400	8.966	65.852	59.115	9.431	-34.746	-23.739	3.706
1500	8.994	66.472	59.585	10.329	-34.781	-22.952	3.344
1600	9.019	67.053	60.034	11.230	-34.816	-22.163	3.027
1700	9.042	67.600	60.463	12.133	-34.850	-21.369	2.747
1800	9.063	68.118	60.874	13.038	-34.887	-20.576	2.498
1900	9.083	68.608	61.269	13.946	-34.923	-19.779	2.275
2000	9.101	69.075	61.647	14.855	-34.961	-18.983	2.074
2100	9.119	69.519	62.012	15.766	-34.999	-18.182	1.892
2200	9.135	69.944	62.363	16.679	-35.039	-17.380	1.726
2300	9.151	70.350	62.701	17.593	-35.080	-16.576	1.575
2400	9.167	70.740	63.028	18.509	-35.122	-15.771	1.436
2500	9.182	71.115	63.344	19.426	-35.167	-14.967	1.308
2600	9.196	71.475	63.650	20.345	-35.212	-14.155	1.190
2700	9.210	71.822	63.946	21.265	-35.260	-13.344	1.080
2800	9.224	72.157	64.233	22.187	-35.308	-12.532	.978
2900	9.238	72.481	64.512	23.110	-35.359	-11.716	.883
3000	9.251	72.795	64.783	24.035	-35.413	-10.902	.794
3100	9.265	73.098	65.047	24.961	-35.469	-10.081	.711
3200	9.278	73.393	65.303	25.888	-35.528	-9.265	.633
3300	9.291	73.678	65.552	26.816	-35.589	-8.442	.559
3400	9.303	73.956	65.795	27.746	-35.655	-7.617	.490
3500	9.316	74.226	66.032	28.677	-35.724	-6.795	.424
3600	9.329	74.488	66.264	29.609	-35.798	-5.963	.362
3700	9.341	74.744	66.489	30.543	-35.876	-5.133	.303
3800	9.353	74.993	66.710	31.477	-35.959	-4.300	.247
3900	9.366	75.237	66.926	32.413	-36.047	-3.473	.195
4000	9.378	75.474	67.136	33.350	-36.142	-2.634	.144
4100	9.390	75.706	67.342	34.289	-36.244	-1.796	.096
4200	9.402	75.932	67.544	35.228	-36.352	-.955	.050
4300	9.414	76.153	67.742	36.169	-36.468	-.108	.005
4400	9.426	76.370	67.936	37.111	-36.592	.738	-.037
4500	9.438	76.582	68.125	38.054	-36.724	1.589	-.077
4600	9.450	76.789	68.311	38.999	-36.865	2.446	-.116
4700	9.462	76.993	68.494	39.944	-37.016	3.299	-.153
4800	9.474	77.192	68.673	40.891	-37.176	4.161	-.189
4900	9.485	77.388	68.849	41.839	-37.347	5.019	-.224
5000	9.497	77.579	69.022	42.788	-37.528	5.889	-.257
5100	9.509	77.768	69.191	43.739	-37.721	6.753	-.289
5200	9.521	77.952	69.358	44.690	-37.926	7.631	-.321
5300	9.532	78.134	69.522	45.643	-38.142	8.511	-.351
5400	9.544	78.312	69.683	46.596	-38.371	9.390	-.380
5500	9.556	78.487	69.842	47.551	-38.612	10.280	-.408
5600	9.567	78.660	69.998	48.508	-38.868	11.165	-.436
5700	9.579	78.829	70.151	49.465	-39.137	12.067	-.463
5800	9.591	78.996	70.302	50.423	-39.420	12.963	-.488
5900	9.602	79.160	70.451	51.383	-39.718	13.872	-.514
6000	9.614	79.321	70.597	52.344	-40.031	14.782	-.538

Dec. 31, 1960; Dec. 31, 1965

MAGNESIUM OXIDE (MgO) (IDEAL GAS) MOL. WT. = 40.3114

Ground State Configuration $^3\Sigma$

$S^\circ_{298.15}$ = 52.889 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 1.0 ± 20 kcal mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 1.0 ± 20 kcal. mole^{-1}

Electronic Levels and Quantum Weights

ϵ_i, cm.$^{-1}$	g_i
0	3

ω_e = 902 cm.$^{-1}$

$\omega_e x_e$ = 13.0 cm.$^{-1}$

σ = 1

B_e = [0.625] cm.$^{-1}$

α_e = [0.0094] cm.$^{-1}$

r_e = [1.672] Å

Heat of Formation.

There is considerable discordance in the heat of formation results even though results were adjusted to a common $^3\Sigma$ ground state where necessary. A mean $\Delta H^\circ_{f\ 298}$ (MgO, g) = 1.0 ± 20 kcal. mole^{-1} was selected.

R. L. Altman, J. Phys. Chem. 67, 366 (1963) made a Knudsen effusion and oxygen transpiration study of the vaporization of MgO. The predominant vapor species over MgO(c) were shown to be Mg(g) and O_2(g). MgO transpiration results with oxygen at 1 atm yielded a 3rd law heat of sublimation $\Delta H^\circ_{s\ 298}$ (MgO, g) = 162.3 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298}$ (MgO, g) = 18.6 kcal. mole^{-1}.

J. Drowart, G. Exsteen and G. Verhaegen, Trans. Far. Soc. 60, 1920 (1964) used the Knudsen effusion-mass spectrometer technique to determine relative ion intensities and enthalpies for the reaction MgO(g) + O(g) → Mg(g) + O_2(g). After adjusting their values for a $^3\Sigma$ ground state we calculated $\Delta H^\circ_{f\ 298}$ (MgO, g) = 11.9 kcal. mole^{-1}. Similar calculations for their data on MgO(g) + WO_2(g) → Mg(g) + WO_3(g) yielded $\Delta H^\circ_{f\ 298}$ = 10.5 kcal. mole^{-1}. The agreement is fortuitous, however, since uncertainties in the JANAF values for WO_2(g) and WO_3(g) are on the order of 7 kcal. each.

R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 1347 (1955) mass spectrometrically determined an upper limit for the vapor pressure of MgO(g) over MgO(c) at 1950°K. Their results reduce to a lower limit of 148.6 kcal. mole^{-1} for $\Delta H^\circ_{s\ 298.15}$ (MgO, c) or a lower limit of 4.9 kcal. mole^{-1} for $\Delta H^\circ_{f\ 298}$ (MgO, g).

E. Bulewicz and T. Sugden, Trans. Far. Soc. 55, 720 (1959), using a flame photometric technique, reported D°_0 = 98 ± 2 kcal. mole^{-1} for MgO. $\Delta H^\circ_{f\ 298}$ (MgO, g) = -4.1 kcal. mole^{-1} was calculated.

I. Veits and L. Gurvich, Optika and Spektroskopiya 1, 22 (1956) used a flame technique to obtain D°_0 = 100 kcal. mole^{-1}. A 4 kcal. mole^{-1} adjustment for $^1\Sigma$ to $^3\Sigma$ yields $\Delta H^\circ_{f\ 298}$ (MgO, g) = -2.1 kcal. mole^{-1}.

The flame method data of L. Huldt and A. Lagerquist, Arkiv Fysik 2, 333 (1950) yielded a $^3\Sigma$ adjusted D°_0 = 115 kcal. mole^{-1}. $\Delta H^\circ_{f\ 298}$ (MgO, g) = -21.1 kcal. mole^{-1} was calculated.

L. Brewer and R. F. Porter, J. Chem. Phys. 22, 1876 (1954) have shown by vapor pressure measurements on MgO(c) that the solid vaporizes mainly into molecular species. They gave spectroscopic evidence that the $^1\Sigma$ electronic state of MgO(g) is not the principal vaporizing species. Using their vapor pressures for the reaction MgO(c) = MgO(g) and a $^3\Sigma$ ground state we calculated 2nd and 3rd law heat of sublimation at 298°K. of 120.0 and 129.1 kcal. mole^{-1}. The 3rd law value yields $\Delta H^\circ_{f\ 298}$ (MgO, g) = -14.6 kcal. mole^{-1}.

Heat Capacity and Entropy.

The fundamental frequency and anharmonicity correction were reported by L. Brewer and R. Porter, J. Chem. Phys. 22, 1876 (1954) and are based on a $^3\Sigma$ ground state. The rotational constants were estimated by H. L. Schick 35 al. AVCO Corp. RAD-SR-62-251, 15 Dec. 1962. Although the ground state and spectroscopic constants are in doubt, the free energies are probably within RT ln 3 of true values.

Magnesium Metasilicate ($MgSiO_3$)

(Crystal) GFW = 100.3962

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.895	-368.018	-368.018	INFINITE
100	5.715	2.657	29.737	-2.708	-369.090	-362.827	792.958
200	14.255	9.424	17.834	-1.682	-369.951	-356.306	389.353
298	19.581	16.197	16.197	.000	-370.200	-349.442	256.148
300	19.653	16.318	16.197	.036	-370.203	-349.314	254.475
400	22.513	22.404	17.008	2.158	-370.269	-342.337	187.044
500	24.262	27.627	18.622	4.502	-370.207	-335.357	146.584
600	25.573	32.170	20.510	6.996	-370.083	-328.400	119.619
700	26.678	36.197	22.468	9.610	-369.914	-321.464	100.365
800	27.672	39.825	24.415	12.328	-369.718	-314.558	85.933
900	28.603	43.139	26.314	15.142	-369.498	-307.675	74.714
1000	28.762	46.346	28.168	18.178	-371.245	-300.652	65.707
1100	28.762	49.087	29.947	21.054	-371.065	-293.604	58.334
1200	28.762	51.590	31.646	23.931	-370.932	-286.569	52.191
1300	29.262	54.218	33.282	27.218	-370.439	-279.556	46.998
1400	29.262	56.387	34.856	30.144	-400.718	-272.089	42.475
1500	29.262	58.406	36.359	33.070	-400.270	-262.916	38.307
1600	29.262	60.294	37.797	35.996	-399.841	-253.774	34.664
1700	29.262	62.068	39.173	38.923	-411.423	-244.551	31.439
1800	29.262	63.741	40.492	41.849	-410.977	-234.747	28.502
1900	29.262	65.323	41.757	44.775	-410.540	-224.969	25.877
2000	29.262	66.824	42.973	47.701	-410.110	-215.214	23.518
2100	29.262	68.252	44.143	50.627	-409.689	-205.480	21.385
2200	29.262	69.613	45.270	53.554	-409.277	-195.765	19.447
2300	29.262	70.914	46.357	56.480	-408.872	-186.069	17.681
2400	29.262	72.159	47.407	59.406	-408.476	-176.369	16.062
2500	29.262	73.354	48.421	62.332	-408.090	-166.731	14.576

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

MAGNESIUM METASILICATE ($MgSiO_3$) (CRYSTAL) GFW = 100.3962

ΔHf_0° = -368.02 ± 1.0 kcal/mol

$S_{298.15}^\circ$ = 16.197 ± 0.2 gibbs/mol

$\Delta Hf_{298.15}^\circ$ = -370.20 ± 1.0 kcal/mol

Tt_1 = 903 °K

ΔHt_1° = 0.16 kcal/mol

Tt_2 = 1258 °K

ΔHt_2° = 0.39 kcal/mol

Tm = 1850 ± 2 °K

ΔHm° = [18 ± 5] kcal/mol

Heat of Formation

Torgeson et al. (1) report a ΔHr_{298}° = -8.69 ± 0.15 kcal/mol for reaction (a). They used a hydrofluoric acid solution calorimeter and measured the heats of solution of each component. They appear to have made the water-absorption correction to the heat of solution of SiO_2(c) in the wrong direction. We reverse the correction so that the new ΔHsoln almost overlaps the range observed by King (11). We derive $\Delta Hf_{298}^\circ(MgSiO_3$, c) = -370.20 ± 1.0 kcal/mol using the ΔHf_{298}° of MgO(c) and SiO_2 (c, low quartz) from the JANAF tables.

Reesman et al. (2) calculated a ΔGr_{298}° = 23.72 kcal/mol for reaction (b) using aqueous solubility data. We use the ΔGf_{298}° of $H_2O(\ell)$ and OH^-(aq) from source 3, ΔGf_{298}° of H_4SiO_4(aq) from source 4 and ΔGf_{298}° of Mg^{++}(aq) from source 5 and we obtain a $\Delta Gf_{298}^\circ(MgSiO_3$, c) = -352.534 kcal/mol. We derive a $\Delta Hf_{298}^\circ(MgSiO_3$, c) = -373.293 kcal/mol using the above ΔGf_{298}° of $MgSiO_3$(c) and the entropies of Mg(c), Si(c) and O_2(g) from the JANAF tables.

We choose the heat of formation derived from the result of Torgeson et al. (1) which is considered to be better since it relates directly to the oxides. Also the $\Delta Gf_{1873}^\circ(MgSiO_2, \ell)$ thus calculated is in very good agreement with that derived from the activities of SiO_2 and MgO (in the SiO_2 - MgO system) measured by Rein et al. (6). The $\Delta Hf_{298}^\circ(MgSiO_3$, c) derived from the work of Reesman et al. is less accurate and involves uncertainties in the auxiliary data used to calculate the value.

Source	Method	Reaction	ΔHr_{298}° kcal/mol	ΔGr_{298}° kcal/mol	ΔHf_{298}° kcal/mol
Torgeson et al.	HF solution calorimeter	(a) $MgO(c)+SiO_2(c) = MgSiO_3(c)$	-8.7±0.15		-370.20
Reesman et al.	Aqueous solubility	(b) $MgSiO_3(c)+3H_2O(\ell) = Mg^{++}(aq) + H_4SiO_4(aq)+2OH^-(aq)$		23.72	-373.3

Source

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12. J. V. Smith, Acta Cryst. 12, 515 (1959).
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Heat Capacity and Entropy

Low temperature heat capacities are from the data (53 - 295°K) of Kelley (7). Wagner (8) measured the average heat capacities in the temperature range 580 - 1570°K. Using his data we derive the high temperature heat capacities which are joined smoothly with the low temperature values by a constrained fitting technique. The Cp values at 903 - 1258°K and above 1258°K are derived as 28.762 and 29.262 gibbs/mol, respectively, by assuming that the data of Wagner (8) pertain to the stable phase in these regions. The entropy is based on S_{50}° = 0.49 eu.

Transition Data

Tt_1 = 903°K is obtained from Boyd et al. (9). The authors determined the phase diagram boundary at high pressures and extrapolated to one atmosphere. Tt_2 = 1258°K is taken from Atlas (10). Below 903 °K the phase is known as clinoenstatite. Between 903° and 1258°K it is rhombic enstatite and above 1258°K it is protoenstatite. We calculate ΔHt_1° and ΔHt_2° from dT/dP (slopes of the inversion) = 2.6°/kbar and 84°/kbar reported by Boyd et al. (9, 13) and from the densities of clinoenstatite (3.210 gm/cc) and rhombic enstatite (3.208 gm/cc) reported by Stephenson et al. (11) and the density of protoenstatite (3.10 gm/cc) reported by Smith (12).

Melting Data

See liquid table.

Magnesium Metasilicate ($MgSiO_3$)

(Liquid) GFW = 100.3962

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	19.581	22.112	22.112	.000	- 357.281	- 338.287	247.971
300	19.653	22.233	22.112	.036	- 357.284	- 338.169	246.356
400	22.513	28.319	22.923	2.158	- 357.350	- 331.784	181.278
500	24.262	33.542	24.537	4.502	- 357.288	- 325.396	142.230
600	25.573	38.085	26.425	6.996	- 357.164	- 319.030	116.206
700	26.678	42.112	28.383	9.610	- 356.995	- 312.685	97.625
800	27.672	45.740	30.330	12.328	- 356.799	- 306.371	83.697
900	35.000	49.054	32.229	15.142	- 356.579	- 300.079	72.869
1000	35.000	52.741	34.099	18.642	- 357.862	- 293.664	64.180
1100	35.000	56.077	35.948	22.142	- 357.058	- 287.287	57.079
1200	35.000	59.123	37.754	25.642	- 356.302	- 280.978	51.173
1300	35.000	61.924	39.507	29.142	- 355.595	- 274.729	46.186
1400	35.000	64.518	41.202	32.642	- 385.300	- 268.055	41.845
1500	35.000	66.933	42.838	36.142	- 384.279	- 259.715	37.840
1600	35.000	69.192	44.415	39.642	- 383.276	- 251.445	34.346
1700	35.000	71.313	45.935	43.142	- 394.284	- 243.128	31.256
1800	35.000	73.314	47.401	46.642	- 393.265	- 234.266	28.444
1900	35.000	75.206	48.816	50.142	- 392.253	- 225.461	25.934
2000	35.000	77.002	50.180	53.642	- 391.250	- 216.709	23.681
2100	35.000	78.709	51.499	57.142	- 390.255	- 208.006	21.648
2200	35.000	80.337	52.773	60.642	- 389.270	- 199.351	19.804
2300	35.000	81.893	54.005	64.142	- 388.291	- 190.741	18.124
2400	35.000	83.383	55.198	67.642	- 387.321	- 182.170	16.589
2500	35.000	84.812	56.355	71.142	- 386.361	- 173.647	15.180
2600	35.000	86.184	57.476	74.642	- 385.407	- 165.154	13.882
2700	35.000	87.505	58.564	78.142	- 384.463	- 156.702	12.684
2800	35.000	88.778	59.620	81.642	- 383.526	- 148.283	11.574
2900	35.000	90.006	60.647	85.142	- 382.598	- 139.895	10.543
3000	35.000	91.193	61.645	88.642	- 381.680	- 131.543	9.583

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

MAGNESIUM METASILICATE ($MgSiO_3$) (LIQUID) GFW = 100.3962

$S^\circ_{298.15}$ = [22.112] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-357.281 ± 5] kcal/mol

Tt_1 = 903 °K

ΔHt°_1 = 0.16 kcal/mol

Tt_2 = 1258 °K

ΔHt°_2 = 0.39 kcal/mol

Tm = 1850 ± 2 °K

ΔHm° = [18 ± 5] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 900°K. Below 900°K the heat capacity is obtained from the heat capacity of the crystal. Above 900°K the heat capacity is assumed constant and estimated as 35 gibbs/mol or 7 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

See crystal table.

Melting Data

Tm is taken from N. L. Bowen and O. Andersen, Am. J. Sci. 37, 487 (1914). $MgSiO_3$(c) melts incongruently in the temperature range 1830 - 1850°K at atmospheric pressure. ΔHm° is estimated from the phase diagrams of the $MgSiO_3$ - TiO_2 system reported by I. D. MacGregor, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 135-9 (1965). The phase diagrams were determined at 10 and 20 kbars pressure where $MgSiO_3$(c) melts congruently.

Magnesium Metatitanate ($MgTiO_3$)

(Crystal) GFW = 120.2102

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.240	-373.630	-373.630	INFINITE
100	6.097	2.595	33.125	-3.053	-374.772	-368.398	805.132
200	16.222	10.167	19.672	-1.901	-375.684	-361.731	395.281
298	21.960	17.820	17.820	.000	-375.850	-354.734	260.027
300	22.037	17.956	17.820	.041	-375.851	-354.603	258.328
400	25.154	24.763	18.727	2.414	-375.776	-347.525	189.879
500	27.037	30.593	20.532	5.030	-375.544	-340.487	148.827
600	28.311	35.642	22.639	7.901	-375.241	-333.505	121.479
700	29.243	40.079	24.820	10.681	-374.907	-326.574	101.961
800	29.967	44.033	26.979	13.643	-374.577	-319.693	87.336
900	30.556	47.597	29.075	16.670	-374.268	-312.850	75.970
1000	31.056	50.843	31.092	19.751	-376.110	-305.859	66.845
1100	31.495	53.824	33.025	22.879	-375.832	-298.849	59.376
1200	31.891	56.582	34.875	26.049	-376.513	-291.825	53.149
1300	32.259	59.149	36.644	29.256	-376.158	-284.782	47.876
1400	32.606	61.553	38.338	32.500	-406.184	-277.289	43.287
1500	32.940	63.814	39.962	35.777	-405.455	-268.105	39.063
1600	33.266	65.950	41.520	39.087	-404.720	-258.973	35.374
1700	33.588	67.976	43.017	42.430	-403.980	-249.885	32.125
1800	33.910	69.905	44.458	45.805	-403.241	-240.842	29.242
1900	34.233	71.747	45.846	49.212	-402.499	-231.840	26.668
2000	34.559	73.511	47.186	52.652	-406.205	-222.725	24.338
2100	34.890	75.206	48.490	56.124	-405.437	-213.570	22.227
2200	35.228	76.836	49.732	59.630	-404.646	-204.451	20.310
2300	35.572	78.410	50.945	63.170	-403.827	-195.370	18.564
2400	35.925	79.931	52.121	66.745	-402.982	-186.322	16.967
2500	36.287	81.405	53.263	70.355	-402.112	-177.317	15.501
2600	36.659	82.836	54.373	74.002	-401.211	-169.342	14.150
2700	37.040	84.226	55.453	77.687	-400.282	-159.401	12.903
2800	37.432	85.580	56.505	81.411	-399.322	-150.498	11.747
2900	37.835	86.901	57.530	85.174	-398.331	-141.525	10.673
3000	38.250	88.190	58.531	88.978	-397.308	-132.790	9.674

June 30, 1961; June 30, 1967

MAGNESIUM METATITANATE ($MgTiO_3$) (CRYSTAL) GFW = 120.2102

ΔHf°_0 = -373.63 ± 1.5 kcal/mol

$S^\circ_{298.15}$ = 17.82 ± 0.1 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -375.85 ± 1.5 kcal/mol

Tm = 1953 ± 20°K

ΔHm° = [21.6] kcal/mol

Heat of Formation

The adopted heat of formation is calculated from $\Delta Hr^\circ_{298.15}$ = -6.35 ± 0.25 kcal/mol for the reaction MgO(c) + TiO_2(rutile) → $MgTiO_3$(c) measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. For the same reaction a value of $\Delta Hr^\circ_{298.15}$ = -5.5 ± 0.1 kcal/mol was obtained with a calorimetric bomb method by B. I. Ronfilov and N. N. Feodos'ev, Russ. J. Inorg. Chem. (English Transl.) 9, 1452 (1964). These authors used the oxidation of lampblack in order to initiate the formation of the titanate from the oxides. Unfortunately the desired heat of reaction was only 1.2 to 1.5 percent of the total measured heat, and consequently this result appears to be more uncertain than that measured by the solution calorimetric method.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52 - 296°K) of C. H. Shomate, J. Am. Chem. Soc. 67, 964 (1946). High temperature enthalpies have been measured (402 - 1720°K) by B. F. Naylor and O. A. Cook, J. Am. Chem. Soc. 68, 1003 (1946). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on S°_{52} = 0.45 eu.

Melting Data

See liquid table.

Magnesium Metatitanate ($MgTiO_3$)

(Liquid) Mol. Wt. = 120.2102

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	21.960	26.549	26.549	.000	-357.942	-339.429	248.807
300	22.037	26.685	26.549	.041	-357.943	-339.313	247.189
400	25.154	33.492	27.456	2.414	-357.865	-333.109	182.002
500	27.037	39.322	29.261	5.030	-357.636	-326.943	142.907
600	28.311	44.371	31.369	7.801	-357.333	-320.834	116.864
700	29.243	48.808	33.549	10.681	-356.999	-314.776	98.277
800	29.967	52.762	35.708	13.643	-356.669	-308.769	84.352
900	30.556	56.326	37.804	16.670	-356.360	-302.798	73.529
1000	31.056	59.572	39.821	19.751	-358.202	-296.680	64.839
1100	31.495	62.553	41.754	22.879	-357.924	-290.543	57.726
1200	31.891	65.311	43.604	26.049	-358.605	-284.392	51.795
1300	39.000	67.878	45.373	29.256	-358.250	-278.221	46.773
1400	39.000	70.768	47.085	33.156	-387.619	-271.524	42.402
1500	39.000	73.459	48.755	37.056	-386.268	-263.386	38.375
1600	39.000	75.976	50.378	40.956	-384.943	-255.238	34.864
1700	39.000	78.340	51.954	44.856	-383.646	-247.169	31.776
1800	39.000	80.570	53.483	48.756	-382.382	-239.190	29.040
1900	39.000	82.678	54.964	52.656	-381.147	-231.257	26.601
2000	39.000	84.679	56.400	55.556	-384.392	-223.248	24.395
2100	39.000	86.581	57.793	60.456	-383.197	-215.218	22.398
2200	39.000	88.396	59.143	64.356	-382.012	-207.248	20.588
2300	39.000	90.129	60.453	68.256	-380.833	-199.329	18.941
2400	39.000	91.789	61.724	72.156	-379.663	-191.462	17.435
2500	39.000	93.381	62.959	76.056	-378.503	-183.648	16.054
2600	39.000	94.911	64.159	79.956	-377.349	-175.875	14.784
2700	39.000	96.383	65.325	83.856	-376.205	-168.148	13.611
2800	39.000	97.801	66.460	87.756	-375.069	-160.464	12.525
2900	39.000	99.170	67.564	91.656	-373.940	-152.815	11.516
3000	39.000	100.492	68.640	95.556	-372.822	-145.210	10.579
3100	39.000	101.771	69.688	99.456	-371.710	-137.640	9.704
3200	39.000	103.009	70.710	103.356	-370.608	-130.112	8.886
3300	39.000	104.209	71.707	107.256	-369.514	-122.613	8.120
3400	39.000	105.373	72.680	111.156	-368.431	-115.143	7.401
3500	39.000	106.504	73.630	115.056	-367.355	-107.716	6.726
3600	39.000	107.602	74.559	118.956	-467.915	-100.043	6.073
3700	39.000	108.671	75.466	122.856	-466.831	-89.841	5.307
3800	39.000	109.711	76.354	126.756	-465.768	-79.667	4.582
3900	39.000	110.724	77.222	130.656	-464.728	-69.524	3.896
4000	39.000	111.711	78.072	134.556	-463.713	-59.401	3.246

June 30, 1967

MAGNESIUM METATITANATE ($MgTiO_3$) (LIQUID) GFW = 120.2102

$S°_{298.15}$ = [26.549] gibbs/mol

$\Delta Hf°_{298.15}$ = [-357.942 ± 1.5] kcal/mol

Tm = 1953 ± 20°K

ΔHm° = [21.6] kcal/mol

Heat of Formation

$\Delta Hf°_{298}$ is obtained from $\Delta Hf°_{298}$(c) by adding ΔHm° and the difference between $H°_{Tm} - H°_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300°K. The heat capacity below 1300°K is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 39 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting point at 1903°K. The ΔHm° is estimated from those of $Na_2O \cdot 2TiO_2$ and $Na_2O \cdot TiO_2$ observed by Naylor (3) and $CaO \cdot TiO_2 \cdot SiO_2$ observed by King (4).

Reference

1. F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProsse, J. Res. Natl. Bur. Std. 51, 87 (1953).
3. B. F. Naylor, J. Am. Chem. Soc. 67, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. 76, 4320 (1954).

Magnesium Sulfate ($MgSO_4$)

(Crystal) Mol. Wt. = 120.3736

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-3.678	-298.853	-298.853	INFINITE
100	8.679	4.775	38.312	-3.354	-300.273	-291.922	637.995
200	17.521	13.751	23.789	-2.008	-301.242	-283.268	309.540
298	23.000	21.844	21.844	.000	-301.574	-274.261	201.038
300	23.050	21.987	21.845	.043	-301.578	-274.092	199.675
400	26.290	29.085	22.790	2.518	-302.238	-264.885	144.726
500	28.540	35.199	24.675	5.262	-302.536	-255.506	111.682
600	30.500	40.581	26.886	8.217	-302.617	-246.090	89.638
700	32.100	45.404	29.193	11.348	-302.535	-236.648	73.885
800	33.580	49.788	31.497	14.633	-315.396	-228.519	62.428
900	34.950	53.823	33.757	18.060	-314.796	-217.693	52.863
1000	36.250	57.574	35.953	21.621	-316.249	-206.756	45.187
1100	37.450	61.086	38.080	25.306	-315.487	-195.848	38.911
1200	38.580	64.394	40.136	29.109	-314.651	-185.006	33.694
1300	39.520	67.520	42.124	33.016	-313.756	-174.237	29.292
1400	40.301	70.478	44.044	37.008	-343.183	-163.061	25.455
1500	40.963	73.282	45.901	41.072	-341.806	-150.244	21.891
1600	41.536	75.944	47.696	45.197	-340.380	-137.519	18.784
1700	42.040	78.478	49.433	49.376	-338.911	-124.884	16.055
1800	42.490	80.894	51.114	53.603	-337.409	-112.339	13.640
1900	42.896	83.202	52.742	57.873	-335.875	-99.874	11.488
2000	43.268	85.412	54.321	62.181	-334.315	-87.497	9.561
2100	43.611	87.531	55.852	66.525	-332.730	-75.194	7.826
2200	43.931	89.567	57.339	70.903	-331.125	-62.965	6.255
2300	44.232	91.527	58.783	75.311	-329.499	-50.815	4.829
2400	44.517	93.415	60.187	79.748	-327.856	-38.730	3.527
2500	44.788	95.238	61.553	84.214	-326.197	-26.722	2.336

Dec. 31, 1960; Mar. 31, 1966

MAGNESIUM SULFATE ($MgSO_4$) (CRYSTAL) MOL. WT. = 120.3736

$S^\circ_{298.15}$ = 21.844 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

T_m = 1400°K.

$\Delta H_f^\circ{}_0$ = -298.8 ± 5 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = -301.6 ± 5 kcal. mole^{-1}

ΔH_m° = 3.5 kcal. mole^{-1}

Heat of Formation.

The adopted $\Delta H_f^\circ{}_{298.15}$ = -301.6 ± 5 kcal. mole^{-1} was calculated from the $\Delta H_r^\circ{}_{298.15}$ = 63.3 ± 5 kcal. mole^{-1} for the reaction $MgO(c) + SO_3(g) = MgSO_4(c)$. The value of $\Delta H_r^\circ{}_{298.15}$ was calculated by the third law method using the equilibrium data obtained from a transpiration study by Knopf and Staude.[1] In addition Marchal[2] measured the total pressure of $SO_3(g)$, $SO_2(g)$ and $O_2(g)$ above $MgSO_4(c)$ and partial pressures were obtained by application of the SO_3-SO_2 equilibrium data. Another value of $\Delta H_f^\circ{}_{298.15}$ ($MgSO_4$, c) may be derived from the measured heat of solution of $MgSO_4(c)$ by Thomsen[3a] and the measured heats of mixing of $MgCl_2(200\ H_2O)$ with $H_2SO_4(200\ H_2O)$ and $MgSO_4(200\ H_2O)$ with $2HCl(100\ H_2O)$ by Thomsen[3b].

References	Reaction	T, °K range	Third Law drift, e.u.	ΔH_r° 298.15 kcal. mole^{-1}	ΔH_f° 298.15 kcal. mole^{-1}
1	$MgO(c) + SO_3(g) = MgSO_4(c)$	1144-1313	0.514	63.284	-301.574
2	$MgO(c) + SO_3(g) = MgSO_4(c)$	1223-1428	0.525	72.394	-310.867
3a	$MgSO_4(c) \rightarrow MgSO_4(200\ H_2O)$	298.15		-20.84	
3b	$MgCl_2(200\ H_2O) + H_2SO_4(200\ H_2O) \rightarrow MgSO_4(200\ H_2O) + 2HCl(100\ H_2O)$	298.15		- 3.52	-305.1*

*Combination of the reactions 3a and 3b with the following $\Delta H_f^\circ{}_{298.15}$: $H_2SO_4(200\ H_2O)$ = -212.387, $HCl(100\ H_2O)$ = -39.74 and $MgCl_2(200\ H_2O)$ = -189.5 kcal. mole^{-1}.

References

1 H. J. Knopf and H. Staude, Z. physik. Chem. (Leipzig) 204, 265-275 (1955).

2 G. Marchal, J. Chim. Phys. 22, 493 (1925).

3a and 3b J. Thomsen, "Thermochemische Untersuchungen," vols I-IV, Barth, Leipzig (1882-1886).

Heat Capacity and Entropy.

The low temperature heat capacities 53.3-295.4°K. were measured by G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. 64, 2949 (1942). The heat capacities in the temperature range 298-1400°K. were estimated from the equation $MgSO_4(c) = CaSO_4(c) + MgO(c) - CaO(c)$. $CaSO_4(c)$ and $CaO(c)$ C_p were calculated using the equations $C_p = 16.78 + 23.60 \times 10^{-3}T$ and $C_p = 11.67 + 1.08 \times 10^{-3}T - 1.56 \times 10^{5}T^{-2}$ respectively, K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). The heat capacity of $MgO(c)$ was calculated from the correlation of the low temperature heat capacities and high temperature heat content using the Shomate functions to back calculate the heat capacities. The values from the two sources join smoothly at 298°K. Above the melting point (1400°K.) the heat capacity was graphically extrapolated. The entropy was calculated at 50.12°K. using the Debye and Einstein function $D(\frac{242}{T}) + 2E(\frac{378}{T}) + 2E(\frac{866}{T}) + E(\frac{1683}{T})$ given by G. E. Moore and K. K. Kelley loc. cit. The value of $S^\circ_{50.12}$ = 1.08 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m and ΔH_m from K. K. Kelley, U. S. Bur. Mines Bull. 393 (1936).

Magnesium Sulfate ($MgSO_4$)

(Liquid) Mol. Wt. = 120.3736

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	23.000	24.464	24.464	- .000	- 297.864	- 271.332	198.892
300	23.050	24.606	24.464	.043	- 297.868	- 271.167	197.545
400	26.290	31.705	25.410	2.518	- 298.528	- 262.223	143.272
500	28.540	37.818	27.295	5.262	- 298.826	- 253.106	110.632
600	30.500	43.201	29.506	8.217	- 298.907	- 243.952	88.859
700	32.100	48.024	31.813	11.348	- 298.825	- 234.772	73.299
800	33.580	52.408	34.117	14.633	- 311.686	- 226.905	61.987
900	34.950	56.427	36.376	18.046	- 311.100	- 216.341	52.535
1000	38.000	60.248	38.573	21.676	- 312.484	- 205.665	44.948
1100	38.000	63.870	40.710	25.476	- 311.607	- 195.031	38.749
1200	38.000	67.176	42.780	29.276	- 310.774	- 184.468	33.596
1300	38.000	70.218	44.775	33.076	- 309.986	- 173.974	29.248
1400	38.000	73.034	46.694	36.876	- 339.605	- 163.061	25.455
1500	38.000	75.656	48.539	40.676	- 338.492	- 150.491	21.927
1600	38.000	78.108	50.311	44.476	- 337.391	- 137.993	18.849
1700	38.000	80.412	52.015	48.276	- 336.301	- 125.563	16.142
1800	38.000	82.584	53.653	52.076	- 335.226	- 113.198	13.744
1900	38.000	84.639	55.230	55.876	- 334.162	- 100.892	11.605
2000	38.000	86.588	56.750	59.676	- 333.110	- 88.644	9.687
2100	38.000	88.442	58.215	63.476	- 332.069	- 76.447	7.956
2200	38.000	90.210	59.630	67.276	- 331.042	- 64.297	6.387
2300	38.000	91.899	60.996	71.076	- 330.024	- 52.196	4.960
2400	38.000	93.516	62.318	74.876	- 329.018	- 40.135	3.655
2500	38.000	95.067	63.597	78.676	- 328.025	- 28.123	2.459

Dec. 31, 1960; Mar. 31, 1966

MAGNESIUM SULFATE ($MgSO_4$) (LIQUID) MOL. WT. = 120.3736

$S^\circ_{298.15}$ = 24.464 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

ΔH_f° 298.15 = -297.9 ± 5 kcal. mole^{-1}

T_m = 1400°K.

ΔH_m° = 3.5 kcal. mole^{-1}

Heat of Formation.

The ΔH_f° 298.15 was obtained from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1000°K. The heat capacity below 1000°K. was obtained from the heat capacity of the crystal. Above 1000°K. the heat capacity was assumed constant and estimated as 38.0 cal. deg.$^{-1}$ mole^{-1} by comparison with those for $MgCl_2(l)$, KCl(l) and $K_2SO_4(l)$. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $MgSO_4(c)$ table.

Magnesium Tungstate ($MgWO_4$)

(Crystal) GFW = 272.1596

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.115	-359.880	-359.880	INFINITE
100	9.135	5.055	42.817	-3.776	-361.239	-353.009	771.500
200	19.890	14.987	26.391	-2.281	-362.178	-344.469	376.418
298	26.070	24.184	24.184	.000	-362.300	-335.632	246.025
300	26.200	24.346	24.184	.048	-362.300	-335.467	244.388
400	29.500	32.367	25.256	2.845	-362.128	-326.543	178.415
500	31.450	39.171	27.376	5.898	-361.780	-317.683	138.859
600	32.750	45.023	29.841	9.109	-361.359	-308.903	112.518
700	33.860	50.156	32.384	12.440	-360.898	-300.195	93.725
800	34.930	54.747	34.898	15.880	-360.412	-291.559	79.650
900	35.950	58.920	37.338	19.424	-359.899	-282.982	68.717
1000	37.000	62.762	39.691	23.071	-361.479	-274.281	59.944
1100	38.100	66.340	41.953	26.826	-360.868	-265.594	52.769
1200	39.200	69.702	44.126	30.691	-360.201	-256.961	46.799
1300	40.300	72.884	46.217	34.666	-359.479	-248.386	41.757
1400	41.350	75.908	48.231	38.748	-389.066	-239.390	37.371
1500	42.450	78.799	50.173	42.939	-387.822	-228.741	33.328
1600	43.500	81.572	52.049	47.236	-386.495	-218.180	29.802
1700	44.600	84.242	53.865	51.641	-385.082	-207.700	26.702
1800	45.650	86.821	55.625	56.153	-383.587	-197.310	23.957
1900	46.750	89.319	57.333	60.771	-382.005	-187.005	21.510
2000	47.800	91.744	58.993	65.502	-380.339	-176.785	19.318

June 30, 1963; Mar. 31, 1967

MAGNESIUM TUNGSTATE ($MgWO_4$) (CRYSTAL) GFW = 272.1596

$S^\circ_{298.15}$ = 24.18 ± 0.2 gibbs/mol

Tm = Unknown

ΔHf°_0 = -359.9 ± 8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -362.3 ± 8 kcal/mol

ΔHm° = Unknown

Heat of Formation.

T. N. Rezukhina and V. A. Levitskii[1] measured the emf, E = 0.2433 - 0.0001264T, for the cell reaction $MgO(c) + W(c) + 3Fe_{0.95}O(c) \rightarrow MgWO_4(c) + 2.85\ Fe(c)$, in the temperature range 1220° - 1370°K. Incorporating the results with auxiliary thermal data, the authors obtained ΔGr° = -224,370 + 65.67T (cal/mol) for $MgO(c) + W(c) + 3/2O_2(g) \rightarrow MgWO_4(c)$. Third law analysis of the ΔGr° equation gives ΔHr°_{298} = -218.6 kcal/mol, from which the adopted $\Delta Hf^\circ_{298}(MgWO_4,c)$, -362.3 kcal/mol, is calculated. The second law analysis gives $\Delta Hf^\circ_{298}(MgWO_4,c)$ = -372.7 kcal/mol. The drift in the third law analysis is 8.0 eu.

T. N. Rezukhina, Ya. I. Gerasimov and Yu. P. Simanov[2] determined the Gibbs energy changes ΔGr° = 51,300 - 27.67T (cal/mol) for the reaction $MgWO_4(c) + 3H_2(g) \rightarrow MgO(c) + W(c) + 3H_2O(g)$ in the temperature range 1073°K - 1273°K by a circulation method. This leads to heats of formation of -366.1 kcal/mol by the third law method and -377.2 kcal/mol by the second law method. Both determinations were performed by Rezukhina and his co-workers, but they considered the data obtained by the emf method to be more reliable than that derived from heterogeneous equilibria.

Heat Capacity and Entropy.

Low temperature heat capacities, 52.92° - 296.09°K, were measured calorimetrically by E. G. King and W. W. Weller[3]. The heat capacities above 300°K are estimated by comparison with those of $CaWO_4(c)$[4], CaO(c)[5], and MgO(c)[6]. These two sets of data are joined smoothly at 298°K by a graphical method.

The entropy, S°_{298} = 21.184 eu, is taken from King and Weller[3], based on an extrapolation of S°_{51} = 1.27 eu. No spin-magnetic entropy is predicted below 51°K based on the diamagnetism observed by Ya. I. Gerasimov[7].

References.

1. T. N. Rezukhina and V. A. Levitskii, Russ. J. Phys. Chem. (English Transl.) 37, 1277 (1963).
2. T. N. Rezukhina, Ya. I. Gerasimov and Yu. P. Simanov, Vestnik Moskov. Univ. 4, No. 6, 103 (1949).
3. E. G. King and W. W. Weller, U. S. Bur. Mines Rept. Invest. 5791 (1961).
4. R. A. Yakovleva and T. N. Rezukhina, Russ. J. Phys. Chem. (English Transl.) 34, 390 (1960).
5. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).
6. JANAF MgO table (Dec. 31, 1965).
7. Ya. I. Gerasimov, Papers Presented to Section on Inorganic Chemistry, 16th Intern. Congress Pure and Applied Chem. Paris (1957), pp. 227-35, Butterworths Scientific Publications, London, 1958.

Magnesium Dititanate ($MgTi_2O_5$)

(Crystal) GFW = 200.109

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.363	- 596.425	- 596.425	INFINITE
100	11.025	5.310	55.240	- 4.993	- 598.213	- 587.774	1284.578
200	26.418	18.078	33.388	- 3.062	- 599.500	- 576.872	630.376
298	35.100	32.410	32.410	.000	- 599.750	- 566.189	415.028
300	35.214	32.627	32.411	.065	- 599.750	- 565.981	412.317
400	39.616	43.424	33.853	3.829	- 599.614	- 554.737	303.094
500	42.224	52.563	36.705	7.929	- 599.275	- 543.553	237.587
600	44.096	60.434	40.019	12.249	- 598.844	- 532.450	193.945
700	45.604	67.348	43.440	16.736	- 598.367	- 521.420	162.795
800	46.911	73.525	46.821	21.363	- 597.880	- 510.464	139.452
900	48.097	79.120	50.104	26.114	- 597.397	- 499.565	121.311
1000	49.204	84.245	53.265	30.980	- 599.046	- 488.538	106.770
1100	50.259	88.984	56.300	35.953	- 598.550	- 477.511	94.873
1200	51.276	93.401	59.209	41.030	- 599.924	- 466.454	84.953
1300	52.266	97.545	62.001	46.208	- 599.170	- 455.363	76.553
1400	53.236	101.454	64.680	51.483	- 628.757	- 443.852	69.288
1500	54.190	105.159	67.256	56.854	- 627.550	- 430.685	62.751
1600	55.132	108.687	69.736	62.320	- 626.299	- 417.602	57.042
1700	56.064	112.057	72.127	67.880	- 625.007	- 404.596	52.014
1800	56.988	115.288	74.436	73.533	- 623.684	- 391.670	47.555
1900	57.906	118.394	76.668	79.278	- 622.327	- 378.818	43.574
2000	58.819	121.387	78.830	85.114	- 629.834	- 365.732	39.965
2100	59.728	124.279	80.926	91.041	- 628.366	- 352.560	36.691
2200	60.633	127.078	82.960	97.059	- 626.825	- 339.463	33.723
2300	61.534	129.793	84.938	103.168	- 625.203	- 326.437	31.019
2400	62.433	132.431	86.862	109.366	- 623.507	- 313.480	28.546
2500	63.330	134.998	88.736	115.654	- 621.737	- 300.604	26.279
2600	64.224	137.499	90.564	122.032	- 619.887	- 287.792	24.191
2700	65.117	139.940	92.348	128.499	- 617.964	- 275.056	22.264
2800	66.008	142.324	94.090	135.055	- 615.964	- 262.393	20.481
2900	66.898	144.656	95.794	141.701	- 613.889	- 249.794	18.825
3000	67.787	146.939	97.461	149.435	- 611.739	- 237.278	17.286

June 30, 1961; June 30, 1967

MAGNESIUM DITITANATE ($MgTi_2O_5$) (CRYSTAL) GFW = 200.109

ΔHf°_0 = -596.43 ± 2.5 kcal/mol

$S^\circ_{298.15}$ = 32.41 ± 1.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -599.75 ± 2.5 kcal/mol

Tm = 1963 ± 20°K

ΔHm° = [35] kcal/mol

Heat of Formation

ΔHf°_{298} is calculated from ΔHr°_{298} = -4.45 ± 0.45 kcal/mol for the reaction MgO(c) + 2TiO$_2$(rutile) = $MgTi_2O_5$(c) measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. The uncertainty of ±2.5 kcal/mol assigned to the heat of formation is due primarily to TiO_2(rutile).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52 - 296°K) of S. S. Todd, J. Am. Chem. Soc. 74, 4669 (1952). High temperature enthalpies have been measured (397 - 1812°K) by R. L. Orr and J. P. Coughlin, J. Am. Chem. Soc. 74, 3186 (1952). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S^\circ_{51} - S^\circ_0$ = 1.11 eu.

Kelley et al., loc. cit., suggested that there may be a zero-point entropy due to randomness of the cations. The authors estimated S°_0 from the following alternative assumptions: (a) all the Mg and Ti ions are randomly distributed among the latice sites giving 3.79 eu and (b) all the Mg and one-half of the Ti ions are randomly distributed giving 2.75 eu. These assumptions were proposed in order to make $MgTi_2O_5$ stable relative to $MgTiO_3$ at high temperatures. Phase data of F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958, indicate that $MgTi_2O_5$ melts congruently at 1963±20°K and that there is a eutectic with $MgTiO_3$ at 1873±20°K. These data require that ΔGr°<0 for $MgTiO_3$(c) + TiO_2(rutile) → $MgTi_2O_5$(c) in this temperature range. To make $\Delta Gr^\circ_{1800}<0$ would require that $S^\circ_0 \geq 0.35$ eu. We adopt a compromise zero-point entropy of 2 eu between the upper (3.79 eu) and the lower (0.35 eu) limits.

Melting Data

See liquid table.

Magnesium Dititanate ($MgTi_2O_5$)
(Liquid) GFW = 200.109

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	35.100	47.270	47.270	.000	- 569.385	- 540.255	396.017
300	35.214	47.487	47.271	.065	- 569.385	- 540.074	393.443
400	39.516	58.284	48.713	3.829	- 569.249	- 530.316	289.751
500	42.224	67.423	51.565	7.929	- 568.910	- 520.618	227.562
600	44.396	75.294	54.879	12.240	- 568.479	- 511.001	186.132
700	45.604	82.208	58.300	16.736	- 568.002	- 501.457	156.562
800	46.911	88.385	61.691	21.363	- 567.515	- 491.987	134.405
900	48.397	93.980	64.964	26.114	- 567.032	- 482.574	117.185
1000	49.204	99.105	68.125	30.980	- 568.681	- 473.033	103.381
1100	50.259	103.844	71.160	35.953	- 569.185	- 463.492	92.087
1200	51.276	108.261	74.069	41.030	- 569.559	- 453.921	82.670
1300	62.400	112.405	76.861	46.208	- 569.805	- 444.316	74.696
1400	62.400	117.029	79.567	52.448	- 597.427	- 434.328	67.802
1500	62.400	121.334	82.209	58.688	- 595.351	- 422.749	61.595
1600	62.400	125.362	84.792	64.928	- 593.327	- 411.309	56.182
1700	62.400	129.145	87.281	71.168	- 591.355	- 399.994	51.423
1800	62.400	132.711	89.707	77.408	- 589.444	- 388.792	47.206
1900	62.400	136.085	92.050	83.648	- 587.592	- 377.696	43.445
2000	62.400	139.286	94.342	89.888	- 594.695	- 366.391	40.037
2100	62.400	142.330	96.555	96.128	- 592.914	- 355.016	36.947
2200	62.400	145.233	98.702	102.368	- 591.151	- 343.731	34.146
2300	62.400	148.007	100.786	108.608	- 589.398	- 332.524	31.597
2400	62.400	150.663	102.809	114.848	- 587.660	- 321.390	29.267
2500	62.400	153.210	104.775	121.088	- 585.938	- 310.336	27.130
2600	62.400	155.657	106.685	127.328	- 584.226	- 299.342	25.162
2700	62.400	158.012	108.543	133.568	- 582.530	- 288.417	23.346
2800	62.400	160.282	110.350	139.808	- 580.847	- 277.558	21.664
2900	62.400	162.471	112.110	146.048	- 579.177	- 266.745	20.102
3000	62.400	164.587	113.824	152.288	- 577.521	- 256.004	18.650
3100	62.400	166.633	115.495	158.528	- 575.877	- 245.310	17.294
3200	62.400	168.614	117.124	164.768	- 574.247	- 234.682	16.028
3300	62.400	170.534	118.714	171.008	- 572.629	- 224.094	14.841
3400	62.400	172.397	120.265	177.248	- 571.026	- 213.552	13.727
3500	62.400	174.206	121.781	183.488	- 569.434	- 203.070	12.680
3600	62.400	175.964	123.261	189.728	- 771.108	- 192.093	11.662
3700	62.400	177.673	124.709	195.968	- 769.488	- 176.031	10.398
3800	62.400	179.337	126.125	202.208	- 767.906	- 160.014	9.203
3900	62.400	180.958	127.510	208.448	- 766.362	- 144.041	8.072
4000	62.400	182.538	128.864	214.688	- 764.860	- 128.104	6.999

June 30, 1961; June 30, 1967

MAGNESIUM DITITANATE ($MgTi_2O_5$) (LIQUID) GFW = 200.109

$S^\circ_{298.15}$ = [47.27] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-569.385 ± 2] kcal/mol

Tm = 1963 ± 20°K

ΔHm° = [35] kcal/mol

Heat of Formation

The heat of formation is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300°K. Below 1300°K the heat capacity is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 62/4 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The congruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting at 1925°K. The ΔHm° is estimated from those of $Na_2O\cdot 2TiO_2$ and $Na_2O\cdot TiO_2$ observed by Naylor (3) and $CaO\cdot TiO_2\cdot SiO_2$ observed by King (4).

References

1. F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProsse, J. Res. Natl. Bur. Stds. 51, 87 (1953).
3. B. V. Naylor, J. Am. Chem. Soc. 67, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. 76, 4320 (1954).

Magnesium Sulfide (MgS)

(Solid) Mol. Wt. = 56.39

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	10.000	11.000	11.000	.000	-83.000	-81.672	59.864
300	10.000	11.062	11.000	.019	-83.003	-81.663	59.489
400	10.250	13.961	11.394	1.027	-83.703	-81.172	44.348
500	10.500	16.275	12.146	2.064	-84.241	-80.478	35.175
600	10.750	18.212	13.000	3.127	-84.696	-79.680	29.022
700	11.000	19.888	13.867	4.214	-85.100	-78.787	24.597
800	11.250	21.373	14.714	5.327	-98.536	-79.128	21.616
900	11.500	22.712	15.530	6.464	-98.598	-76.698	18.624
1000	11.750	23.937	16.310	7.627	-100.796	-74.083	16.190
1100	12.000	25.068	17.055	8.814	-100.853	-71.411	14.187
1200	12.250	26.123	17.768	10.027	-100.911	-68.730	12.517
1300	12.500	27.114	18.449	11.264	-100.972	-66.045	11.103
1400	12.750	28.049	19.101	12.527	-131.464	-62.892	9.817
1500	13.000	28.937	19.728	13.814	-131.122	-58.008	8.451
1600	13.250	29.784	20.330	15.127	-130.754	-53.145	7.259
1700	13.500	30.595	20.910	16.464	-130.362	-48.306	6.210
1800	13.750	31.374	21.470	17.827	-129.946	-43.492	5.280
1900	14.000	32.124	22.011	19.214	-129.506	-38.699	4.451
2000	14.250	32.848	22.535	20.627	-129.041	-33.932	3.708
2100	14.500	33.550	23.043	22.064	-128.553	-29.191	3.038
2200	14.750	34.230	23.536	23.527	-128.039	-24.470	2.431
2300	15.000	34.891	24.015	25.014	-127.502	-19.775	1.879
2400	15.250	35.535	24.482	26.527	-126.939	-15.101	1.375
2500	15.500	36.163	24.937	28.064	-126.353	-10.454	.914
2600	15.750	36.775	25.380	29.627	-125.742	-5.831	.490
2700	16.000	37.374	25.814	31.214	-125.107	-1.229	.099
2800	16.250	37.961	26.237	32.827	-124.449	3.343	-.261
2900	16.500	38.535	26.651	34.464	-123.767	7.898	-.595
3000	16.750	39.099	27.057	36.127	-123.061	12.428	-.905

December 31, 1960.

Magnesium Sulfide (MgS) (Solid)

Mol. Wt. = 56.39

ΔH_f° 298.15 = -83 kcal. mole^{-1}

$S^\circ_{298.15}$ = [11] cal. deg.$^{-1}$ mole^{-1}

ΔH_f° 298.15 from National Bureau of Standards Circular 500. Other data estimated.

Magnesium Sulfide (MgS)

(Ideal Gas) Mol. Wt. = 56.39

INTERIM TABLE

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.206	33.243	33.243	INFINITE
100	7.019	49.187	64.287	- 1.510	33.621	29.227	- 63.873
200	7.650	54.228	58.123	- .779	33.479	24.867	- 27.172
298	8.226	57.387	57.387	.000	33.200	20.698	- 15.171
300	8.231	57.438	57.387	.015	33.194	20.621	- 15.021
400	8.453	59.838	57.713	.850	32.320	16.500	- 9.015
500	8.611	61.742	58.335	1.704	31.599	12.628	- 5.519
600	8.705	63.321	59.038	2.570	30.947	8.897	- 3.241
700	8.764	64.668	59.748	3.444	30.330	5.296	- 1.653
800	8.804	65.841	60.438	4.322	16.659	.493	- .135
900	8.832	66.880	61.097	5.204	16.342	- 1.509	.366
1000	8.853	67.811	61.723	6.088	13.865	- 3.296	.720
1100	8.868	68.656	62.316	6.974	13.507	- 4.997	.993
1200	8.880	69.428	62.877	7.862	13.124	- 6.661	1.213
1300	8.889	70.139	63.408	8.750	12.714	- 8.293	1.394
1400	8.896	70.798	63.913	9.640	- 18.151	- 9.428	1.472
1500	8.902	71.412	64.393	10.529	- 18.207	- 8.805	1.283
1600	8.907	71.987	64.849	11.420	- 18.261	- 8.176	1.117
1700	8.911	72.527	65.285	12.311	- 18.315	- 7.544	.970
1800	8.914	73.036	65.702	13.202	- 18.371	- 6.909	.839
1900	8.917	73.518	66.101	14.094	- 18.426	- 6.269	.721
2000	8.920	73.976	66.483	14.986	- 18.482	- 5.628	.615
2100	8.922	74.411	66.850	15.878	- 18.539	- 4.986	.519
2200	8.924	74.826	67.204	16.770	- 18.596	- 4.338	.431
2300	8.925	75.223	67.544	17.662	- 18.654	- 3.690	.351
2400	8.927	75.603	67.872	18.555	- 18.711	- 3.036	.276
2500	8.928	75.967	68.188	19.448	- 18.769	- 2.382	.208
2600	8.929	76.317	68.494	20.341	- 18.828	- 1.727	.145
2700	8.930	76.654	68.790	21.234	- 18.887	- 1.066	.086
2800	8.931	76.979	69.077	22.127	- 18.949	- .408	.032
2900	8.932	77.293	69.355	23.020	- 19.011	.257	- .019
3000	8.932	77.595	69.624	23.913	- 19.075	.925	- .067
3100	8.933	77.888	69.886	24.806	- 19.141	1.591	- .112
3200	8.934	78.172	70.141	25.700	- 19.209	2.259	- .154
3300	8.934	78.447	70.388	26.593	- 19.279	2.930	- .194
3400	8.935	78.714	70.629	27.486	- 19.353	3.606	- .232
3500	8.935	78.973	70.864	28.380	- 19.430	4.280	- .267
3600	8.936	79.224	71.093	29.273	- 19.510	4.962	- .301
3700	8.936	79.469	71.316	30.167	- 19.596	5.641	- .333
3800	8.936	79.707	71.534	31.061	- 19.686	6.323	- .364
3900	8.937	79.940	71.746	31.954	- 19.782	7.009	- .393
4000	8.937	80.166	71.954	32.848	- 19.883	7.702	- .421
4100	8.937	80.387	72.157	33.742	- 19.991	8.391	- .447
4200	8.937	80.602	72.355	34.635	- 20.107	9.084	- .473
4300	8.938	80.812	72.550	35.529	- 20.229	9.780	- .497
4400	8.938	81.018	72.740	36.423	- 20.361	10.480	- .521
4500	8.938	81.219	72.926	37.317	- 20.501	11.185	- .543
4600	8.938	81.415	73.108	38.211	- 20.650	11.890	- .565
4700	8.938	81.607	73.287	39.104	- 20.809	12.598	- .586
4800	8.939	81.795	73.462	39.998	- 20.979	13.311	- .606
4900	8.939	81.980	73.634	40.892	- 21.159	14.029	- .626
5000	8.939	82.160	73.803	41.786	- 21.351	14.748	- .645
5100	8.939	82.337	73.969	42.680	- 21.555	15.469	- .663
5200	8.939	82.511	74.131	43.574	- 21.771	16.200	- .681
5300	8.939	82.681	74.291	44.468	- 22.000	16.933	- .698
5400	8.939	82.848	74.448	45.362	- 22.242	17.668	- .715
5500	8.940	83.012	74.602	46.256	- 22.499	18.409	- .731
5600	8.940	83.173	74.754	47.150	- 22.769	19.156	- .748
5700	8.940	83.332	74.903	48.044	- 23.054	19.909	- .763
5800	8.940	83.487	75.050	48.938	- 23.354	20.661	- .779
5900	8.940	83.640	75.194	49.832	- 23.670	21.424	- .794
6000	8.940	83.790	75.336	50.726	- 24.002	22.197	- .808

December 31, 1960.

Magnesium Sulfide (MgS) (Ideal Gas)

Mol. Wt. = 56.39

ΔH_f° 298.15 = 33.2 kcal. mole^{-1}

$S^\circ_{298.15}$ = 57.387 cal. deg.$^{-1}$ mole^{-1}

C_p, D_o, and other data from R. Altman, Rocketdyne Engineering, Canoga Park, Calif., "Thermodynamic Properties of Propellant Combustion Products", July, 1959. ΔH_f° 298.15 calculated from D_o.

Magnesium Orthosilicate (Mg_2SiO_4)

(Crystal) GFW = 140.7076

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 4.130	- 517.119	- 517.119	INFINITE
100	7.724	3.358	42.268	- 3.891	- 518.640	- 510.151	1114.933
200	20.589	12.945	25.110	- 2.433	- 519.979	- 501.310	547.806
298	28.367	22.739	22.739	.000	- 520.300	- 491.858	360.541
300	28.477	22.915	22.740	.053	- 520.304	- 491.682	358.190
400	32.877	31.769	23.917	3.141	- 520.373	- 482.124	263.420
500	35.539	39.411	26.270	6.570	- 520.234	- 472.571	206.561
600	37.388	46.062	29.026	10.221	- 519.999	- 463.063	168.670
700	38.793	51.935	31.888	14.033	- 519.714	- 453.593	141.618
800	39.929	57.192	34.728	17.971	- 519.422	- 444.171	121.342
900	40.891	61.952	37.493	22.013	- 519.142	- 434.780	105.579
1000	41.732	66.305	40.159	26.145	- 523.126	- 425.056	92.896
1100	42.488	70.318	42.721	30.357	- 522.831	- 415.268	82.506
1200	43.180	74.045	45.178	34.641	- 522.542	- 405.503	73.852
1300	43.824	77.527	47.534	38.991	- 522.267	- 395.760	66.533
1400	44.430	80.797	49.794	43.404	- 582.735	- 385.080	60.114
1500	45.007	83.882	51.965	47.876	- 581.674	- 370.997	54.054
1600	45.559	86.805	54.052	52.405	- 580.578	- 356.990	48.763
1700	46.091	89.583	56.061	56.987	- 591.442	- 342.942	44.088
1800	46.608	92.232	57.997	61.622	- 590.229	- 328.359	39.868
1900	47.110	94.765	59.866	66.308	- 588.975	- 313.846	36.100
2000	47.601	97.194	61.672	71.044	- 587.683	- 299.399	32.717
2100	48.082	99.528	63.420	75.828	- 586.353	- 285.018	29.662
2200	48.555	101.776	65.112	80.660	- 584.989	- 270.699	26.891
2300	49.020	103.945	66.754	85.539	- 583.586	- 256.445	24.368
2400	49.479	106.041	68.347	90.464	- 582.149	- 242.251	22.060
2500	49.932	108.070	69.896	95.434	- 580.681	- 228.125	19.943
2600	50.380	110.037	71.402	100.450	- 579.175	- 214.046	17.992
2700	50.824	111.946	72.869	105.510	- 577.639	- 200.034	16.192
2800	51.264	113.803	74.297	110.615	- 576.068	- 186.078	14.524
2900	51.701	115.609	75.691	115.763	- 574.466	- 172.173	12.975
3000	52.133	117.369	77.051	120.955	- 572.834	- 158.331	11.534

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

MAGNESIUM ORTHOSILICATE (Mg_2SiO_4) (CRYSTAL) GFW = 1400.7076

ΔHf°_0 = -517.12 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 22.739 ± 0.2 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -520.30 ± 1.0 kcal/mol

Tm = 2171 ± 11 °K

ΔHm° = [17 ± 5] kcal/mol

Heat of Formation

Torgeson et al. (1) have reported a ΔHr°_{298} = -15.1 ± 0.2 kcal/mol for reaction (a). They used an HF solution calorimeter and measured the heats of solution of each component. We derive $\Delta Hf^\circ_{298}(Mg_2SiO_4, c)$ = -520.30 ± 1.0 kcal/mol using the ΔHf°_{298} of MgO(c) and SiO_2 (c, low quartz) from JANAF tables.

Kapustinskii et al. (2) used the same method but measured only ΔHr°_{298} = 95.00 ± 0.47 kcal/mol for reaction (b). We calculate $\Delta Hf^\circ_{298}(Mg_2SiO_4, c)$ = -522.27 kcal/mol using the ΔHf°_{298} of H_2SiF_6(aq) from source 3 and the ΔHf°_{298} of $H_2O(\ell)$ and HF(aq) from source 4.

Reesman et al. (5) calculated a ΔGr°_{298} = 42.46 kcal/mol for reaction (c) using aqueous solubility data. We use the ΔGf°_{298} of $H_2O(\ell)$ and OH^-(aq) from source 4, ΔGf°_{298} of H_4SiO_4(aq) from source 3 and ΔGf°_{298} of Mg^{++}(aq) from source 6 and we obtain a $\Delta Gf^\circ_{298}(Mg_2SiO_4, c)$ = -498.764 kcal/mol. We derive a $\Delta Hf^\circ_{298}(Mg_2SiO_4, c)$ = -524.848 kcal/mol using the above ΔGf°_{298} of Mg_2SiO_4(c) and the entropies of Mg(c), Si(c) and O_2(g) from the JANAF tables.

The adopted value is from the work of Torgeson et al. (1) which is considered to be the most reliable since it relates directly to the oxides. The other reported values are less accurate and involve uncertainties in the auxiliary data used to derive the heat of formation.

Source	Method	Reaction	ΔHr°_{298} kcal/mol	ΔGf°_{298} kcal/mol	ΔHf°_{298} kcal/mol
Torgeson et al.	Hydrofluoric acid solution calorimeter	(a) $2MgO(c)+SiO_2(c) = Mg_2SiO_4(c)$	-15.10±0.2		-520.3
Kapustinskii et al.	Hydrofluoric acid solution calorimeter	(b) $Mg_2SiO_4(c)+10HF(4.44H_2O) = 2MgF_2(c) + H_2SiF_6(714HF+3220H_2O)+4H_2O(\ell)$	95.0±0.47		-522.27
Reesman et al.	Aqueous solubility	(c) $Mg_2SiO_4(c)+4H_2O(\ell) = 2Mg^{++}(aq) + H_4SiO_4(aq)+4OH^-(aq)$		42.46	-524.848

Source

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Heat Capacity and Entropy

Low temperature heat capacities are from the data (53-295°K) of Kelley (7). High temperature enthalpies have been measured (398-1808 °K) by Orr (8). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on S°_{50} = 0.60 eu.

Melting Data

Tm is obtained from Davis et al. (9). ΔHm° is estimated from MacGregor's (10) phase diagrams of the Mg_2SiO_4 - TiO_2 system. The phase diagrams were determined at 10 and 20 kbars pressure.

Magnesium Orthosilicate (Mg_2SiO_4)

(Liquid) GFW = 140.7076

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	28.367	29.407	29.407	.000	- 505.229	- 478.775	350.951
300	28.477	29.583	29.408	.053	- 505.233	- 478.611	348.668
400	32.877	38.437	30.585	3.141	- 505.302	- 469.721	256.643
500	35.539	46.079	32.938	6.570	- 505.163	- 460.834	201.430
600	37.388	52.730	35.694	10.221	- 504.928	- 451.993	164.638
700	38.793	58.603	38.556	14.033	- 504.643	- 443.190	138.370
800	39.929	63.860	41.396	17.971	- 504.351	- 434.435	118.682
900	40.891	68.620	44.161	22.013	- 504.071	- 425.710	103.377
1000	41.732	72.973	46.827	26.145	- 508.055	- 416.653	91.059
1100	42.488	76.986	49.389	30.357	- 507.760	- 407.531	80.969
1200	43.180	80.713	51.846	34.641	- 507.471	- 398.433	72.565
1300	43.824	84.195	54.202	38.991	- 507.196	- 389.357	65.457
1400	49.000	87.465	56.462	43.404	- 567.664	- 379.344	59.218
1500	49.000	90.846	58.643	48.304	- 566.175	- 365.944	53.318
1600	49.000	94.008	60.755	53.204	- 564.708	- 352.645	48.169
1700	49.000	96.979	62.800	58.104	- 575.254	- 339.327	43.623
1800	49.000	99.779	64.777	63.004	- 573.776	- 325.492	39.520
1900	49.000	102.429	66.690	67.904	- 572.308	- 311.739	35.858
2000	49.000	104.942	68.540	72.804	- 570.852	- 298.064	32.571
2100	49.000	107.333	70.331	77.704	- 569.406	- 284.461	29.604
2200	49.000	109.612	72.065	82.604	- 567.974	- 270.924	26.914
2300	49.000	111.790	73.745	87.504	- 566.550	- 257.454	24.464
2400	49.000	113.876	75.374	92.404	- 565.138	- 244.044	22.223
2500	49.000	115.876	76.954	97.304	- 563.740	- 230.700	20.168
2600	49.000	117.798	78.489	102.204	- 562.350	- 217.400	18.274
2700	49.000	119.647	79.979	107.104	- 560.974	- 204.161	16.526
2800	49.000	121.429	81.428	112.004	- 559.608	- 190.971	14.906
2900	49.000	123.149	82.837	116.904	- 558.254	- 177.825	13.401
3000	49.000	124.810	84.208	121.804	- 556.914	- 164.732	12.001
3100	49.000	126.417	85.544	126.704	- 555.584	- 151.680	10.693
3200	49.000	127.972	86.846	131.604	- 554.268	- 138.675	9.471
3300	49.000	129.480	88.115	136.504	- 552.964	- 125.710	8.325
3400	49.000	130.943	89.353	141.404	- 551.676	- 112.776	7.249
3500	49.000	132.363	90.562	146.304	- 550.400	- 99.895	6.238

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

MAGNESIUM ORTHOSILICATE (Mg_2SiO_4) (LIQUID) GFW = 140.7076

$S^\circ_{298.15}$ = [29.407] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-505.229 ± 5] kcal/mol

Tm = 2171 ± 11°K

ΔHm° = [17 ± 5] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400°K. Below 1400°K the heat capacity is obtained from the heat capacity of the crystal. Above 1400°K the heat capacity is assumed constant and estimated as 49 gibbs/mol or 7 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See crystal table.

Magnesium Orthotitanate (Mg_2TiO_4)

(Crystal) GFW = 160.5216

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.502	-514.108	-514.108	INFINITE
100	8.279	6.391	48.821	-4.243	-515.679	-507.389	1108.894
200	22.543	16.811	30.091	-2.656	-517.066	-498.714	544.969
298	30.730	27.510	27.510	.000	-517.300	-489.438	358.767
300	30.838	27.700	27.511	.057	-517.302	-489.265	356.429
400	34.963	37.198	28.777	3.368	-517.259	-479.919	262.216
500	37.383	45.277	31.291	6.993	-517.026	-470.606	205.702
600	39.122	52.253	34.216	10.822	-516.711	-461.354	168.048
700	40.531	58.393	37.240	14.807	-516.354	-452.154	141.169
800	41.756	63.887	40.234	18.922	-515.995	-443.010	121.025
900	42.868	68.870	43.143	23.154	-515.649	-433.906	105.367
1000	43.902	73.440	45.947	27.493	-519.566	-424.477	92.769
1100	44.880	77.671	48.641	31.933	-519.197	-414.989	82.451
1200	45.815	81.616	51.227	36.468	-519.764	-405.494	73.851
1300	46.715	85.319	53.708	41.095	-519.271	-395.991	66.572
1400	47.584	88.813	56.092	45.810	-579.501	-385.569	60.190
1500	48.426	92.125	58.385	50.610	-578.182	-371.762	54.166
1600	49.245	95.277	60.593	55.494	-576.809	-358.047	48.907
1700	50.040	98.286	62.722	60.459	-575.385	-344.415	44.278
1800	50.815	101.168	64.779	65.501	-573.920	-330.871	40.173
1900	51.569	103.936	66.767	70.621	-572.409	-317.410	36.510
2000	52.304	106.600	68.693	75.815	-575.307	-303.877	33.206
2100	53.019	109.169	70.559	81.081	-573.695	-290.344	30.216
2200	53.717	111.652	72.371	86.418	-572.026	-276.889	27.506
2300	54.396	114.055	74.131	91.824	-570.296	-263.513	25.039
2400	55.057	116.384	75.844	97.297	-568.511	-250.211	22.785
2500	55.700	118.644	77.511	102.835	-566.675	-236.990	20.718
2600	56.326	120.841	79.135	108.436	-564.784	-223.836	18.815
2700	56.934	122.978	80.720	114.099	-562.845	-210.759	17.060
2800	57.525	125.060	82.266	119.822	-560.856	-197.760	15.436
2900	58.099	127.088	83.777	125.604	-558.820	-184.919	13.928
3000	58.656	129.068	85.254	131.441	-556.743	-171.963	12.527

June 30, 1961; June 30, 1967

MAGNESIUM ORTHOTITANATE (Mg_2TiO_4) (CRYSTAL) GFW = 160.5216

$S^\circ_{298.15}$ = 27.51 ± 1.5 gibbs/mol

Tm = 2013 ± 20°K

ΔHf°_0 = -514.11 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -517.3 ± 1.5 kcal/mol

ΔHm° = [31] kcal/mol

Heat of Formation

The heat of formation is calculated from ΔHr°_{298} = -4.1 ± 0.25 kcal/mol for the reaction 2 MgO(c) + TiO_2(rutile) → Mg_2TiO_4(c) measured by Kelley (1), using a solution calorimetric method. The uncertainty of ± 1.5 kcal/mol assigned to the heat of formation is due primarily to TiO_2(rutile).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52 - 296°K) of Todd (2).

High temperature enthalpies have been measured (392 - 1817°K) by Orr (3). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values.

The entropy is based on S°_{51} = 0.66 + 2.75 = 3.41 eu, where the first term is a lattice contribution and the second term is a zero-point entropy of 2Rℓn2 corresponding to random distribution of Ti and Mg on the octahedral sites of the spinel lattice. The adopted value is S°_{298} = 27.51 ± 1.5 eu instead of 24.76 ± 0.15 eu as given by Todd.

Barth (4) showed from intensities of the X-ray diffraction lines that Mg_2TiO_4 is a spinel of the inverse (or variate) class. Thus, half of the Mg ions occupy the tetrahedral interstices in the oxygen lattice, while the remaining Mg ions and the Ti ions are (presumably) randomly located in the octahedral interstices. This conclusion was confirmed by Romeijn (5).

King and Kelley (6) suggested that the degree of structural randomness is not established and that it may vary with the sample of Mg_2TiO_4; thus, they recommended an intermediate value of Rℓn2 for the zero-point entropy. In a previous review, however, Kelley (1) used the theoretical value of 2Rℓn2 in order to make Mg_2TiO_4 stable relative to $MgTiO_3$ at high temperatures. We choose to adopt 2Rℓn2, although the evidence is not conclusive. Recent studies of solid state reactions by Bautsch and Werner (7) indicate that ΔGr° is negative for $MgTiO_3$(c) + MgO(c) → Mg_2TiO_4(c) at temperatures of 1673°K and above. Both Rℓn2 and 2Rℓ2 are consistent with this evidence.

Melting Data

See liquid table.

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Magnesium Orthotitanate (Mg_2TiO_4)
(Liquid) GFW = 160.5216

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
0							
100							
200							
298	30.730	41.208	41.208	.000	- 489.084	- 465.306	341.078
300	30.838	41.398	41.209	.057	- 489.086	- 465.158	338.867
400	34.963	50.996	42.475	3.368	- 489.043	- 457.182	249.793
500	37.383	58.975	44.989	6.993	- 488.810	- 449.239	196.362
600	39.122	65.951	47.914	10.822	- 488.495	- 441.356	160.764
700	40.531	72.091	50.938	14.807	- 488.138	- 433.526	135.353
800	41.756	77.585	53.932	18.922	- 487.779	- 425.752	116.310
900	42.868	82.568	56.841	23.154	- 487.433	- 418.018	101.509
1000	43.902	87.138	59.645	27.493	- 491.350	- 409.959	89.596
1100	44.880	91.369	62.339	31.933	- 490.981	- 401.841	79.838
1200	45.815	95.314	64.925	36.468	- 491.548	- 393.716	71.705
1300	46.715	99.017	67.406	41.095	- 491.055	- 385.583	64.822
1400	54.600	102.511	69.790	45.810	- 551.285	- 376.530	58.779
1500	54.600	106.278	72.098	51.270	- 549.306	- 364.116	53.052
1600	54.600	109.802	74.346	56.730	- 547.357	- 351.836	48.058
1700	54.600	113.112	76.530	62.190	- 545.438	- 339.672	43.668
1800	54.600	116.233	78.650	67.650	- 543.555	- 327.624	39.779
1900	54.600	119.185	80.706	73.110	- 541.704	- 315.678	36.311
2000	54.600	121.986	82.701	78.570	- 544.336	- 303.679	33.184
2100	54.600	124.650	84.635	84.030	- 542.530	- 291.689	30.357
2200	54.600	127.190	86.512	89.490	- 540.738	- 279.785	27.794
2300	54.600	129.617	88.334	94.950	- 538.954	- 267.964	25.462
2400	54.600	131.940	90.103	100.410	- 537.182	- 256.217	23.332
2500	54.600	134.169	91.821	105.870	- 535.424	- 244.552	21.379
2600	54.600	136.311	93.492	111.330	- 533.674	- 232.948	19.581
2700	54.600	138.371	95.116	116.790	- 531.938	- 221.414	17.922
2800	54.600	140.357	96.696	122.250	- 530.212	- 209.948	16.387
2900	54.600	142.273	98.235	127.710	- 528.498	- 198.533	14.962
3000	54.600	144.124	99.734	133.170	- 526.798	- 187.186	13.637
3100	54.600	145.914	101.195	138.630	- 525.108	- 175.890	12.400
3200	54.600	147.648	102.620	144.090	- 523.432	- 164.661	11.246
3300	54.600	149.328	104.010	149.550	- 521.768	- 153.475	10.164
3400	54.600	150.958	105.367	155.010	- 520.120	- 142.333	9.149
3500	54.600	152.541	106.692	160.470	- 518.484	- 131.255	8.196
3600	54.600	154.079	107.987	165.930	- 618.490	- 119.944	7.282
3700	54.600	155.575	109.253	171.390	- 616.858	- 106.118	6.268
3800	54.600	157.031	110.491	176.850	- 615.253	- 92.335	5.310
3900	54.600	158.449	111.703	182.310	- 613.677	- 78.601	4.405
4000	54.600	159.831	112.889	187.770	- 612.134	- 64.898	3.546

June 30, 1961; June 30, 1967

MAGNESIUM ORTHOTITANATE (Mg_2TiO_4) (LIQUID) GFW = 160.5216

$S°_{298.15}$ = [41.208] gibbs/mol $\Delta Hf°_{298.15}$ = [-489.084 ± 1.5] kcal/mol

Tm = 2013 ± 20°K $\Delta Hm°$ = [31] kcal/mol

Heat of Formation

$\Delta Hf°_{298}$ is obtained from $\Delta Hf°_{298}$(c) by adding ΔHm° and the difference between $H°_{Tm} - H°_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400°K. Below 1400°K the heat capacity is obtained from the heat capacity of the crystal. Above 1400°K the heat capacity is assumed constant and estimated as 54.6 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) suggested congruent melting at 2005°K. The ΔHm° is estimated from those of $Na_2O \cdot 2TiO_2$ and $Na_2O \cdot TiO_2$ observed by Naylor (3) and $CaO \cdot TiO_2 \cdot SiO_2$ observed by King (4).

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Dimagnesium Silicide (Mg_2Si)

(Crystal) Mol. Wt. = 76.73

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	16.220	19.500	19.500	.000	-18.600	-18.428	13.507
300	16.251	19.600	19.500	.030	-18.601	-18.426	13.423
400	17.630	24.477	20.156	1.729	-18.631	-18.362	10.032
500	18.470	28.512	21.435	3.538	-18.645	-18.296	7.997
600	19.080	31.934	22.907	5.416	-18.662	-18.223	6.637
700	19.600	34.916	24.414	7.351	-18.699	-18.146	5.665
800	20.050	37.563	25.895	9.334	-18.766	-18.063	4.934
900	20.480	39.949	27.326	11.360	-18.876	-17.968	4.363
1000	20.890	42.128	28.699	13.429	-23.272	-17.505	3.826
1100	21.290	44.138	30.013	15.538	-23.397	-16.923	3.362
1200	21.670	46.007	31.268	17.686	-23.541	-16.328	2.974
1300	22.050	47.756	32.470	19.872	-23.703	-15.721	2.643
1400	22.420	49.404	33.621	22.096	-84.741	-14.172	2.212
1500	22.780	50.963	34.726	24.356	-84.124	-9.153	1.334
1600	23.130	52.445	35.788	26.651	-83.474	-4.177	.571
1700	23.470	53.857	36.809	28.981	-94.894	.867	-.111
1800	23.800	55.208	37.794	31.345	-94.137	6.478	-.786
1900	24.120	56.503	38.745	33.741	-93.348	12.046	-1.386
2000	24.430	57.748	39.664	36.169	-92.527	17.574	-1.920
2100	24.730	58.948	40.554	38.627	-91.676	23.056	-2.399
2200	25.020	60.105	41.417	41.114	-90.796	28.497	-2.831
2300	25.300	61.223	42.254	43.630	-89.887	33.901	-3.221
2400	25.570	62.306	43.067	46.174	-88.950	39.263	-3.575
2500	25.830	63.355	43.857	48.744	-87.989	44.586	-3.898

December 31, 1960

DIMAGNESIUM SILICIDE (Mg_2Si) (Crystal)

Mol. Wt. = 76.73

$\Delta H_f^\circ{}_{298.15} = -18.6$ kcal. mole^{-1}

$S^\circ_{298.15} = [19.5]$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 1375$°K

$\Delta H_m = [15.33]$ kcal. mole^{-1}

Heat of Formation. $\Delta H_f^\circ{}_{298.15}$ was found in the National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy. C_p taken from Kubaschewski and Evans, "Metallurgical Thermochemistry," 3rd Edition, Pergamon Press Ltd., New York, (1958). $S^\circ_{298.15}$ was estimated.

Melting Data. T_m was taken from NBS Circular 500 (1952). ΔH_m was found in Wilson, Beahm, and Cooper, "Determination and Analysis of the Potentialities of Thermal Energy Storage Materials," Callery Chemical Co., Callery, Pa., June 30, 1961.

Dimagnesium Silicide (Mg_2Si)

(Liquid) Mol. Wt. = 76.73

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	
0							
100							
200							
298	22.500	29.561	29.561	.000	-.792	-3.619	2.653
300	22.500	29.700	29.561	.042	-.781	-3.637	2.649
400	22.500	36.173	30.444	2.292	-.260	-4.670	2.551
500	22.500	41.194	32.111	4.542	.167	-5.825	2.546
600	22.500	45.296	33.977	6.792	.522	-7.056	2.570
700	22.500	48.764	35.848	9.042	.800	-8.342	2.604
800	22.500	51.769	37.654	11.292	1.000	-9.663	2.640
900	22.500	54.419	39.373	13.542	1.114	-11.002	2.672
1000	22.500	56.790	40.998	15.792	-3.101	-11.996	2.622
1100	22.500	58.934	42.533	18.042	-3.085	-12.888	2.560
1200	22.500	60.892	43.982	20.292	-3.127	-13.776	2.509
1300	22.500	62.693	45.353	22.542	-3.225	-14.661	2.465
1400	22.500	64.360	46.652	24.792	-64.237	-14.606	2.280
1500	22.500	65.913	47.885	27.042	-63.630	-11.083	1.615
1600	22.500	67.365	49.057	29.292	-63.025	-7.601	1.038
1700	22.500	68.729	50.175	31.542	-74.525	-4.046	.520
1800	22.500	70.015	51.242	33.792	-73.882	.080	-.010
1900	22.500	71.231	52.262	36.042	-73.239	4.172	-.480
2000	22.500	72.385	53.240	38.292	-72.596	8.231	-.899
2100	22.500	73.483	54.178	40.542	-71.953	12.254	-1.275
2200	22.500	74.530	55.079	42.792	-71.310	16.248	-1.614
2300	22.500	75.530	55.947	45.042	-70.667	20.215	-1.921
2400	22.500	76.488	56.783	47.292	-70.024	24.153	-2.199
2500	22.500	77.406	57.589	49.542	-69.383	28.064	-2.453
2600	22.500	78.289	58.369	51.792	-68.742	31.946	-2.685
2700	22.500	79.138	59.122	54.042	-68.101	35.812	-2.899
2800	22.500	79.956	59.852	56.292	-67.464	39.644	-3.094
2900	22.500	80.745	60.559	58.542	-66.827	43.461	-3.275
3000	22.500	81.508	61.244	60.792	-66.192	47.255	-3.442
3100	22.500	82.246	61.910	63.042	-65.563	51.024	-3.597
3200	22.500	82.960	62.557	65.292	-64.936	54.774	-3.741
3300	22.500	83.653	63.186	67.542	-64.313	58.507	-3.875
3400	22.500	84.324	63.797	69.792	-63.696	62.218	-3.999
3500	22.500	84.977	64.393	72.042	-63.085	65.912	-4.116
3600	22.500	85.610	64.974	74.292	-157.455	70.067	-4.253
3700	22.500	86.227	65.540	76.542	-156.798	76.372	-4.511
3800	22.500	86.827	66.092	78.792	-156.152	82.663	-4.754
3900	22.500	87.411	66.632	81.042	-155.514	88.940	-4.984
4000	22.500	87.981	67.158	83.292	-154.888	95.203	-5.201

December 31, 1960.

DIMAGNESIUM SILICIDE (Mg_2Si) (Liquid)

Mol. Wt. = 76.73

ΔH_f° 298.15 = -3.749 kcal. mole^{-1}

$S_{298.15}^\circ$ = [30.2] cal. deg.$^{-1}$ mole^{-1}

T_m = 1375°K

ΔH_m = [15.33] kcal. mole^{-1}

Heat of Formation. ΔH_f° 298.15 was based on ΔH_f° 298.15 of the crystal and the heat of melting.

Heat Capacity and Entropy. C_p was estimated. A glass transition was assumed at 916°K. $S_{298.15}^\circ$ was calculated from the entropy of the crystal and the entropy of melting.

Trimagnesium Dinitride (Mg_3N_2)

(Solid) Mol. Wt. = 100.98

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	24.980	21.000	21.000	.000	- 110.200	- 95.820	70.234
300	25.000	21.155	21.000	.046	- 110.200	- 95.730	69.736
400	25.730	26.447	21.990	2.583	- 110.190	- 90.907	49.667
500	26.460	34.266	23.882	5.192	- 110.195	- 86.091	37.628
600	27.190	39.154	26.031	7.874	- 110.209	- 81.266	29.600
700	27.920	43.400	28.215	10.630	- 110.253	- 76.437	23.864
800	28.650	47.176	30.354	13.458	- 110.340	- 71.602	19.560
900	29.600	50.905	32.441	16.618	- 110.222	- 66.774	16.214
1000	29.600	54.024	34.446	19.578	- 116.797	- 61.404	13.419
1100	29.540	57.088	36.364	22.796	- 116.770	- 55.864	11.099
1200	29.540	59.658	38.200	25.750	- 117.097	- 50.311	9.163
1300	29.540	62.023	39.943	28.704	- 117.513	- 44.732	7.520
1400	29.540	64.212	41.599	31.658	- 209.304	- 37.723	5.888
1500	29.540	66.250	43.175	34.612	- 208.670	- 25.488	3.713
1600	29.540	68.156	44.678	37.566	- 208.043	- 13.300	1.817
1700	29.540	69.947	46.112	40.520	- 207.420	- 1.146	.147
1800	29.540	71.636	47.483	43.474	- 206.805	10.969	- 1.332
1900	29.540	73.233	48.797	46.428	- 206.195	23.054	- 2.652
2000	29.540	74.748	50.057	49.382	- 205.589	35.105	- 3.836
2100	29.540	76.189	51.267	52.336	- 204.988	47.121	- 4.904
2200	29.540	77.563	52.432	55.290	- 204.390	59.110	- 5.872
2300	29.540	78.876	53.553	58.244	- 203.795	71.075	- 6.753
2400	29.540	80.134	54.635	61.198	- 203.203	83.017	- 7.559
2500	29.540	81.339	55.679	64.152	- 202.617	94.927	- 8.298

December 31, 1960.

TRIMAGNESIUM DINITRIDE (Mg_3N_2) (Solid)

Mol. Wt. = 100.98

$\Delta H^\circ_{f\ 298.15} = -110.2 \pm 1$ kcal. mole^{-1}

$S^\circ_{298.15} = [21 \pm 2]$ cal. deg.$^{-1}$ mole^{-1}

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Magnesium Orthophosphate ($Mg_3P_2O_8$)

(Crystal) Mol. Wt. = 262.91

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	50.850	45.000	45.000	.000	- 895.100	- 839.836	615.586
300	51.000	45.315	45.001	.094	- 895.109	- 839.492	611.540
400	57.400	60.943	47.088	5.542	- 895.413	- 820.900	448.498
500	62.700	74.332	51.228	11.552	- 895.395	- 802.264	350.652
600	67.450	86.191	56.085	18.064	- 895.112	- 783.664	285.436
700	72.000	96.929	61.164	25.036	- 894.597	- 765.124	238.871
800	76.630	106.845	66.262	32.466	- 934.700	- 757.302	206.875
900	80.300	116.082	71.290	40.313	- 933.264	- 735.209	178.524
1000	84.020	124.735	76.207	48.528	- 937.992	- 712.742	155.762
1100	86.060	132.844	80.991	57.038	- 936.126	- 690.313	137.146
1200	87.400	140.395	85.631	65.717	- 934.206	- 668.053	121.663
1300	89.330	147.473	90.118	74.561	- 932.237	- 645.949	108.589
1400	90.320	154.135	94.455	83.551	-1021.325	- 622.565	97.182
1500	90.800	160.384	98.644	92.610	-1018.133	- 594.192	86.569
1600	91.000	166.252	102.688	101.702	-1014.934	- 566.038	77.314
1700	91.200	171.774	106.591	110.810	-1011.741	- 538.073	69.171
1800	91.200	176.987	110.359	119.930	-1008.564	- 510.304	61.956
1900	91.200	181.917	113.996	129.050	-1005.410	- 482.708	55.521
2000	91.200	186.595	117.510	138.170	-1002.281	- 455.286	49.749
2100	91.200	191.045	120.907	147.290	- 999.172	- 428.010	44.541
2200	91.200	195.288	124.192	156.410	- 996.093	- 400.880	39.822
2300	91.200	199.342	127.372	165.530	- 993.030	- 373.897	35.527
2400	91.200	203.223	130.452	174.650	- 989.993	- 347.043	31.601
2500	91.200	206.946	133.438	183.770	- 986.981	- 320.321	28.001
2600	91.200	210.523	136.334	192.890	- 983.989	- 293.707	24.687
2700	91.200	213.965	139.146	202.010	- 981.024	- 267.216	21.629
2800	91.200	217.281	141.878	211.130	- 978.079	- 240.835	18.797
2900	91.200	220.482	144.533	220.250	- 975.157	- 214.547	16.168
3000	91.200	223.573	147.117	229.370	- 972.263	- 188.370	13.722

Dec. 31, 1960; Mar. 31, 1963

MAGNESIUM ORTHOPHOSPHATE ($Mg_3P_2O_8$) (CRYSTAL) MOL. WT. = 262.91

$S^\circ_{298.15}$ = [45] cal. deg.$^{-1}$ mole^{-1}

T_m = 1621°K.

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = -895.1 ± 2.5 kcal. mole^{-1}

ΔH_m = [29 ± 10] kcal. mole^{-1}

Heat of Formation.

The selected $\Delta H^\circ_{f\ 298.15}$ is a weighted average of a revised calorimetric determination and a third law calculation using equilibrium data.

A calorimetric determination of the heat of formation reported by C. G. Stevens and E. T. Turkdogan, Trans. Faraday Soc. 50, 370 (1954) was revised three ways:

1. The heat of reaction for the reaction $3MgO(c) + P_2O_5$(orthorhombic) → $Mg_3P_2O_8(c)$ had been evaluated at 348°K. A small temperature correction to 298.15 was made with thermal data not available to Stevens and Turkdogan (loc. cit.) on MgO (W. F. Giauque, J. Am. Chem. Soc. 71, 3192 (1949)), P_2O_5 (JANAF Table, Dec. 31, 1962) and $Mg_3P_2O_8$ (this table).
2. A new $\Delta H^\circ_{f\ 298.15}$ for P_2O_5(hexagonal) as reported by W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962) was combined with the heat of reaction, -6.85 ± 1.0 kcal. mole^{-1}, for the reaction: P_2O_5(hexagonal) → P_2O_5(orthorhombic) as reported by W. L. Hill, G. T. Faust, and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943).
3. A correction of +8.35 kcal. mole^{-1} was made for the change in phosphorus reference state from white (α) → red (V). (The correction is +8.35 kcal./mole of $Mg_3P_2O_8$ or +4.173 kcal. mole^{-1} of P.)

This revised $\Delta H^\circ_{f\ 298.15}$, -897.60 ± 2.0 kcal. mole^{-1}, would appear to be more reliable than the original value reported by Stevens and Turkdogan (loc. cit.).

For the reaction

$$Mg_3P_2O_8(c) + 5H_2(g) \rightarrow 3MgO(c) + P_2(g) + 5H_2O(g)$$

the third law treatment of the equilibrium data of J. B. Bookey, J. Iron Steel Institute (London) 172, 66 (1952) and the JANAF Table free energy functions gave a $\Delta H^\circ_{f\ 298.15}$ = -893.11 kcal. mole^{-1}.

The quantity, -895.10 ± 2.50 kcal. mole^{-1}, is taken as the most probable value for the heat of formation of magnesium orthophosphate.

Heat Capacity and Entropy.

The entropy at 298.15 was estimated by considering the additive entropy constants of K. K. Kelley, private communication, June 1960, and E. L. Evans and O. Kubaschewski, "Metallurgical Thermochemistry, 1958. The heat capacity was estimated in a similar manner by considering the heat capacities of the constituent elements and related compounds such as Mg, O_2, MgO, P, P_2O_5, $Ca_2P_2O_7$, and $Ca_3P_2O_8$.

Melting Data.

The melting point, 1621°K, as reported by Stevens and Turkdogan (loc. cit.) was selected. There is disagreement on the melting point in the literature. From the work of H. Winter, Diss. Universitats zu Leipzig 1913, K. K. Kelley, U. S. Bureau of Mines Bulletin 393, (1936) has quoted a melting point of 1457°K and has calculated a "rather uncertain value" of 11.300 kcal./mole for the heat of fusion. J. B. Bookey (loc. cit.) has found a melting point of 1703°K. J. Berak, Roczniki Chim. 32, 17 (1958) gives 1630°K as the melting point.

Magnesium Orthophosphate ($Mg_3P_2O_8$)

(Liquid) Mol. Wt. = 262.91

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0							
100							
200							
298	50.850	54.764	54.764	.000	- 876.897	- 824.544	604.378
300	51.000	55.079	54.764	.094	- 876.906	- 824.218	600.414
400	57.969	70.758	56.855	5.561	- 877.191	- 806.604	440.687
500	62.700	84.243	61.017	11.613	- 877.131	- 788.955	344.835
600	67.450	96.098	65.894	18.123	- 876.850	- 771.346	280.949
700	72.000	106.840	70.987	25.097	- 876.333	- 753.797	235.335
800	76.630	116.767	76.096	32.536	- 916.427	- 746.967	204.052
900	80.300	126.014	81.135	40.391	- 914.983	- 725.866	176.256
1000	84.020	134.703	86.062	48.641	- 919.676	- 704.394	153.938
1100	103.550	143.074	90.858	57.438	- 917.523	- 682.963	135.686
1200	105.072	152.131	95.591	67.849	- 913.871	- 661.802	120.525
1300	109.100	160.684	100.271	78.536	- 910.059	- 640.945	107.748
1400	111.103	168.846	104.881	89.551	- 997.122	- 618.958	96.619
1500	112.500	176.562	109.405	100.737	- 991.803	- 592.129	86.269
1600	113.291	183.852	113.832	112.031	- 986.402	- 565.665	77.263
1700	113.600	190.730	118.155	123.377	- 980.971	- 539.528	69.358
1800	113.842	197.230	122.369	134.750	- 975.541	- 513.719	62.371
1900	114.044	203.391	126.473	146.144	- 970.113	- 488.210	56.154
2000	114.206	209.245	130.466	157.557	- 964.691	- 462.994	50.591
2100	114.327	214.820	134.351	168.984	- 959.275	- 438.040	45.585
2200	114.408	220.140	138.131	180.421	- 953.879	- 413.342	41.060
2300	114.448	225.227	141.808	191.864	- 948.493	- 388.896	36.952
2400	114.448	230.098	145.386	203.309	- 943.131	- 364.680	33.207
2500	114.408	234.769	148.868	214.753	- 937.795	- 340.693	29.782
2600	114.327	239.255	152.259	226.190	- 932.486	- 316.907	26.637
2700	114.206	243.567	155.561	237.617	- 927.214	- 293.334	23.743
2800	114.044	247.718	158.779	249.029	- 921.977	- 269.955	21.070
2900	113.842	251.717	161.915	260.424	- 916.780	- 246.751	18.595
3000	113.600	255.572	164.973	271.797	- 911.633	- 223.736	16.298
3100	113.600	259.297	167.956	283.157	- 906.518	- 200.887	14.162
3200	113.600	262.904	170.867	294.517	- 901.431	- 178.217	12.171
3300	113.600	266.399	173.709	305.877	- 896.364	- 155.696	10.311
3400	113.600	269.790	176.486	317.237	- 891.330	- 133.319	8.569
3500	113.600	273.083	179.199	328.597	- 886.315	- 111.109	6.938
3600	113.600	276.284	181.851	339.957	- 881.330	- 89.023	5.404
3700	113.600	279.396	184.446	351.317	- 876.373	- 67.080	3.962
3800	113.600	282.426	186.984	362.677	- 871.440	- 45.265	2.603
3900	113.600	285.376	189.469	374.037	- 866.536	- 23.603	1.323
4000	113.600	288.252	191.903	385.397	- 861.666	- 2.056	.112
4100	113.600	291.057	194.288	396.757	- 856.829	19.380	- 1.033
4200	113.600	293.795	196.624	408.117	- 852.020	40.690	- 2.117
4300	113.600	296.468	198.915	419.477	- 847.247	61.893	- 3.146
4400	113.600	299.080	201.162	430.837	- 842.507	82.982	- 4.122
4500	113.600	301.632	203.367	442.197	- 837.804	103.967	- 5.049
4600	113.600	304.129	205.530	453.557	- 833.134	124.852	- 5.932
4700	113.600	306.572	207.654	464.917	- 828.505	145.625	- 6.771
4800	113.600	308.964	209.740	476.277	- 823.915	166.311	- 7.572
4900	113.600	311.306	211.789	487.637	- 819.361	186.877	- 8.335
5000	113.600	313.601	213.802	498.997	- 814.850	207.368	- 9.064
5100	113.600	315.851	215.781	510.357	- 810.385	227.767	- 9.760
5200	113.600	318.057	217.727	521.717	- 805.958	248.068	- 10.425
5300	113.600	320.221	219.640	533.077	- 801.573	268.324	- 11.064
5400	113.600	322.344	221.522	544.437	- 797.235	288.440	- 11.673
5500	113.600	324.428	223.374	555.797	- 792.939	308.527	- 12.259
5600	113.600	326.475	225.197	567.157	- 788.699	328.499	- 12.820
5700	113.600	328.486	226.992	578.517	- 784.501	348.420	- 13.358
5800	113.600	330.462	228.759	589.877	- 780.352	368.259	- 13.876
5900	113.600	332.404	230.499	601.237	- 776.255	388.030	- 14.373
6000	113.600	334.313	232.213	612.597	- 772.209	407.728	- 14.851

Dec. 31, 1960; Mar. 31, 1963

MAGNESIUM ORTHOPHOSPHATE ($Mg_3P_2O_8$) (LIQUID) MOL. WT. = 262.91

$S^\circ_{298.15}$ = [54.8] cal. deg.$^{-1}$ mole^{-1}

T_m = 1621°K

T_b = Unknown

$\Delta H^\circ_{f\ 298.15}$ = [-877 ± 10] kcal. mole^{-1}

ΔH°_m = [29 ± 10] kcal. mole^{-1}

ΔH°_v = Unknown

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ was calculated from the estimated ΔH_m and the $\Delta H^\circ_{f\ 298.15}$ of the crystal.

Heat Capacity and Entropy.

The heat capacity was estimated as 13/11 of the corresponding heat capacity of $Ca_2P_2O_7$ as given in K. K. Kelley, U. S. Bur. Mines Bull. 5841 (1960).

Melting Data.

The heat of melting was estimated by taking 13/11 of the ΔH_m of $Ca_2P_2O_7$ as given in K. K. Kelley (loc. cit.)

Molybdenum (Mo)
(Reference State) GFW = 95.94

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.096	.000	.000	.000
100	3.232	1.679	11.469	-.979	.000	.000	.000
200	5.131	4.655	7.345	-.538	.000	.000	.000
298	5.729	6.837	6.837	.000	.000	.000	.000
300	5.737	6.873	6.838	.011	.000	.000	.000
400	6.050	8.569	7.067	.601	.000	.000	.000
500	6.246	9.942	7.509	1.217	.000	.000	.000
600	6.380	11.093	8.013	1.848	.000	.000	.000
700	6.476	12.084	8.525	2.491	.000	.000	.000
800	6.552	12.954	9.026	3.143	.000	.000	.000
900	6.622	13.730	9.506	3.801	.000	.000	.000
1000	6.698	14.431	9.964	4.467	.000	.000	.000
1100	6.794	15.074	10.400	5.141	.000	.000	.000
1200	6.927	15.670	10.814	5.827	.000	.000	.000
1300	7.090	16.231	11.210	6.528	.000	.000	.000
1400	7.274	16.763	11.587	7.246	.000	.000	.000
1500	7.473	17.272	11.950	7.983	.000	.000	.000
1600	7.684	17.761	12.298	8.741	.000	.000	.000
1700	7.906	18.233	12.633	9.520	.000	.000	.000
1800	8.140	18.692	12.957	10.323	.000	.000	.000
1900	8.377	19.138	13.270	11.148	.000	.000	.000
2000	8.630	19.574	13.575	11.999	.000	.000	.000
2100	8.897	20.001	13.871	12.875	.000	.000	.000
2200	9.190	20.422	14.159	13.779	.000	.000	.000
2300	9.520	20.837	14.440	14.714	.000	.000	.000
2400	9.920	21.251	14.715	15.684	.000	.000	.000
2500	10.463	21.666	14.985	16.703	.000	.000	.000
2600	11.090	22.089	15.250	17.780	.000	.000	.000
2700	11.816	22.520	15.511	18.924	.000	.000	.000
2800	12.618	22.964	15.770	20.145	.000	.000	.000
2900	10.000	25.713	16.032	28.075	.000	.000	.000
3000	10.000	26.052	16.360	29.075	.000	.000	.000
3100	10.000	26.380	16.678	30.075	.000	.000	.000
3200	10.000	26.697	16.986	31.075	.000	.000	.000
3300	10.000	27.005	17.285	32.075	.000	.000	.000
3400	10.000	27.304	17.576	33.075	.000	.000	.000
3500	10.000	27.593	17.858	34.075	.000	.000	.000
3600	10.000	27.875	18.132	35.075	.000	.000	.000
3700	10.000	28.149	18.399	36.075	.000	.000	.000
3800	10.000	28.416	18.659	37.075	.000	.000	.000
3900	10.000	28.676	18.913	38.075	.000	.000	.000
4000	10.000	28.929	19.160	39.075	.000	.000	.000
4100	10.000	29.176	19.401	40.075	.000	.000	.000
4200	10.000	29.417	19.637	41.075	.000	.000	.000
4300	10.000	29.652	19.867	42.075	.000	.000	.000
4400	10.000	29.882	20.092	43.075	.000	.000	.000
4500	10.000	30.107	20.312	44.075	.000	.000	.000
4600	10.000	30.326	20.527	45.075	.000	.000	.000
4700	10.000	30.541	20.738	46.075	.000	.000	.000
4800	10.000	30.752	20.945	47.075	.000	.000	.000
4900	10.000	30.958	21.147	48.075	.000	.000	.000
5000	12.592	59.829	21.812	190.088	.000	.000	.000
5100	12.879	60.082	22.560	191.362	.000	.000	.000
5200	13.150	60.334	23.284	192.664	.000	.000	.000
5300	13.405	60.587	23.985	193.991	.000	.000	.000
5400	13.642	60.840	24.665	195.344	.000	.000	.000
5500	13.861	61.092	25.325	196.719	.000	.000	.000
5600	14.061	61.344	25.966	198.115	.000	.000	.000
5700	14.242	61.594	26.589	199.531	.000	.000	.000
5800	14.403	61.844	27.195	200.963	.000	.000	.000
5900	14.546	62.091	27.784	202.411	.000	.000	.000
6000	14.669	62.337	28.358	203.872	.000	.000	.000

Dec. 31, 1966

MOLYBDENUM (Mo) (REFERENCE STATE) GFW = 95.94

0 - 2892°K	Crystal
2892 - 4919°K	Liquid
4919 - 6000°K	Ideal Monatomic gas

See crystal, liquid and monatomic gas tables for details.

Molybdenum (Mo)
(Crystal)

GFW = 95.94

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.096	.000	.000	.000
100	3.232	1.679	11.469	-.979	.000	.000	.000
200	5.131	4.655	7.345	-.538	.000	.000	.000
298	5.729	6.837	6.837	.000	.000	.000	.000
300	5.737	6.873	6.838	.011	.000	.000	.000
400	6.050	8.569	7.067	.601	.000	.000	.000
500	6.246	9.942	7.509	1.217	.000	.000	.000
600	6.380	11.093	8.013	1.848	.000	.000	.000
700	6.476	12.084	8.525	2.491	.000	.000	.000
800	6.552	12.954	9.026	3.143	.000	.000	.000
900	6.622	13.730	9.506	3.801	.000	.000	.000
1000	6.698	14.431	9.964	4.467	.000	.000	.000
1100	6.794	15.074	10.400	5.141	.000	.000	.000
1200	6.927	15.670	10.814	5.827	.000	.000	.000
1300	7.090	16.231	11.210	6.528	.000	.000	.000
1400	7.274	16.763	11.587	7.246	.000	.000	.000
1500	7.473	17.272	11.950	7.983	.000	.000	.000
1600	7.684	17.761	12.298	8.741	.000	.000	.000
1700	7.906	18.233	12.633	9.520	.000	.000	.000
1800	8.140	18.692	12.957	10.323	.000	.000	.000
1900	8.377	19.138	13.270	11.148	.000	.000	.000
2000	8.630	19.574	13.575	11.999	.000	.000	.000
2100	8.897	20.001	13.871	12.875	.000	.000	.000
2200	9.190	20.422	14.159	13.779	.000	.000	.000
2300	9.520	20.837	14.440	14.714	.000	.000	.000
2400	9.920	21.251	14.715	15.684	.000	.000	.000
2500	10.463	21.666	14.985	16.703	.000	.000	.000
2600	11.090	22.089	15.250	17.780	.000	.000	.000
2700	11.816	22.520	15.511	18.924	.000	.000	.000
2800	12.618	22.964	15.770	20.145	.000	.000	.000
2900	13.500	23.422	16.026	21.450	-6.625	.019	-.001
3000	14.480	23.897	16.280	22.850	-6.225	.240	-.017
3100	15.400	24.386	16.534	24.344	-5.731	.450	-.032
3200	16.320	24.890	16.787	25.930	-5.145	.637	-.044
3300	17.240	25.406	17.040	27.608	-4.467	.810	-.054
3400	18.160	25.934	17.294	29.378	-3.697	.961	-.062
3500	19.080	26.474	17.548	31.240	-2.835	1.081	-.068
3600	20.000	27.025	17.804	33.194	-1.881	1.179	-.072
3700	20.920	27.585	18.061	35.240	-.835	1.252	-.074
3800	21.840	28.155	18.319	37.378	.303	1.295	-.074
3900	22.760	28.734	18.579	39.608	1.533	1.307	-.073
4000	23.680	29.322	18.840	41.930	2.855	1.283	-.070

Dec. 31, 1966

MOLYBDENUM (Mo) (CRYSTAL) GFW = 95.94

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 6.837 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Tm = 2892 ± 10°K

ΔHm° = [6652 ± 600] kcal/mol

$\Delta Hs^\circ_{298.15}$ = 157.3 ± 0.5 kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Below 20°K several investigators [1,2,3,4,5,6] have determined the heat capacity, and an average of these determinations was used to obtain a Debye theta = 440 and an electronic gamma = 4.7 x 10^{-4} gibbs/mol-deg. From these the entropy at 20°K was calculated as 0.024 gibbs/mol and the enthalpy as 0.265 cal. Between 20°K and 271°K the data of Clusius and Franzosini[2] are the adopted heat capacities. The data of Simon and Zeidler[5] are as much as 2.5% high below 78°K and as much as 1% low above this.

Both the high temperature enthalpies and heat capacity have been measured by several investigators and there is generally good agreement in the 1000-2000°K range. A smooth curve was drawn through the high temperature enthalpy data of several investigators [7,8,9,10,11,12], which was also joined smoothly to the integrated low temperature data of Clusius and Franzosini. The heat capacity was obtained by fitting the smoothed enthalpy data with a polynomial and differentiating. The heat capacity obtained agreed satisfactorily with that reported in several investigations [13,14,15,16,17,18,19].

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Sublimation Data.

See Mo(g) for details.

Molybdenum (Mo)

(Liquid) GFW = 95.94

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	5.729	9.261	9.261	.000	7.076	6.353	- 4.657
300	5.737	9.296	9.261	.011	7.076	6.349	- 4.625
400	6.050	10.993	9.490	.601	7.076	6.106	- 3.336
500	6.246	12.366	9.932	1.217	7.076	5.864	- 2.563
600	6.380	13.517	10.436	1.848	7.076	5.622	- 2.048
700	6.476	14.508	10.949	2.491	7.076	5.379	- 1.679
800	6.552	15.377	11.449	3.143	7.076	5.137	- 1.403
900	6.622	16.153	11.930	3.801	7.076	4.896	- 1.189
1000	6.698	16.855	12.388	4.467	7.076	4.652	- 1.017
1100	6.794	17.497	12.823	5.141	7.076	4.411	- .876
1200	6.927	18.094	13.238	5.827	7.076	4.167	- .759
1300	7.090	18.655	13.633	6.528	7.076	3.925	- .660
1400	7.274	19.187	14.011	7.246	7.076	3.682	- .575
1500	7.473	19.695	14.373	7.983	7.076	3.442	- .501
1600	7.684	20.184	14.721	8.741	7.076	3.199	- .437
1700	7.906	20.657	15.056	9.520	7.076	2.956	- .380
1800	8.140	21.115	15.380	10.323	7.076	2.714	- .330
1900	8.377	21.562	15.694	11.148	7.076	2.471	- .284
2000	10.000	21.998	15.998	11.999	7.076	2.228	- .243
2100	10.000	22.486	16.296	12.999	7.200	1.981	- .206
2200	10.000	22.951	16.588	13.999	7.296	1.732	- .172
2300	10.000	23.395	16.874	14.999	7.361	1.477	- .140
2400	10.000	23.821	17.155	15.999	7.391	1.223	- .111
2500	10.000	24.229	17.430	16.999	7.372	.964	- .084
2600	10.000	24.621	17.699	17.999	7.295	.711	- .060
2700	10.000	24.999	17.962	18.999	7.151	.457	- .037
2800	10.000	25.362	18.220	19.999	6.930	.215	- .017
2900	10.000	25.713	18.472	20.999	.000	.000	.000
3000	10.000	26.052	18.719	21.999	.000	.000	.000
3100	10.000	26.380	18.961	22.999	.000	.000	.000
3200	10.000	26.698	19.198	23.999	.000	.000	.000
3300	10.000	27.005	19.430	24.999	.000	.000	.000
3400	10.000	27.304	19.657	25.999	.000	.000	.000
3500	10.000	27.594	19.880	26.999	.000	.000	.000
3600	10.000	27.876	20.098	27.999	.000	.000	.000
3700	10.000	28.150	20.312	28.999	.000	.000	.000
3800	10.000	28.416	20.522	29.999	.000	.000	.000
3900	10.000	28.676	20.728	30.999	.000	.000	.000
4000	10.000	28.929	20.929	31.999	.000	.000	.000
4100	10.000	29.176	21.128	32.999	.000	.000	.000
4200	10.000	29.417	21.322	33.999	.000	.000	.000
4300	10.000	29.652	21.513	34.999	.000	.000	.000
4400	10.000	29.882	21.701	35.999	.000	.000	.000
4500	10.000	30.107	21.885	36.999	.000	.000	.000
4600	10.000	30.327	22.066	37.999	.000	.000	.000
4700	10.000	30.542	22.244	38.999	.000	.000	.000
4800	10.000	30.752	22.419	39.999	.000	.000	.000
4900	10.000	30.959	22.591	40.999	.000	.000	.000
5000	10.000	31.161	22.761	41.999	- 141.013	2.327	- .102
5100	10.000	31.359	22.927	42.999	- 141.287	5.200	- .223
5200	10.000	31.553	23.091	43.999	- 141.589	8.072	- .339
5300	10.000	31.743	23.253	44.999	- 141.916	10.957	- .452
5400	10.000	31.930	23.412	45.999	- 142.269	13.845	- .560
5500	10.000	32.114	23.568	46.999	- 142.644	16.735	- .665
5600	10.000	32.294	23.723	47.999	- 143.040	19.640	- .766
5700	10.000	32.471	23.875	48.999	- 143.456	22.545	- .864
5800	10.000	32.645	24.024	49.999	- 143.888	25.466	- .960
5900	10.000	32.816	24.172	50.999	- 144.336	28.386	- 1.051
6000	10.000	32.984	24.317	51.999	- 144.797	31.321	- 1.141

Dec. 31, 1966

MOLYBDENUM (Mo) (LIQUID) GFW = 95.94

$S^\circ_{298.15}$ = [9.261] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [7.076] kcal/mol

Tm = 2892 ± 10°K

ΔHm° = [6652 ± 600] kcal/mol

Tb = [4919°K]

ΔHv° = [140.812] kcal/mol

Heat of Formation.

The ΔHf°_{298} was obtained from that of the crystal plus ΔHm° and the difference between $H_{2892} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated as 10 gibbs/mol in the real range in order to be comparable with the value in the crystal below the melting point. Below the melting point the heat capacity was assumed constant to a glass transition, assumed to be 2000°K, below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

The heat of melting was obtained from an entropy of melting of 2.3 eu, assumed by comparison with Fe, Cu, Co, Mg and Al. The melting point was reported by E. Rudy and S. Windisch, Aerojet-General Corporation, Report No. AFML-TR-65-2, Part 1, Vol. III, July 1965. A. G. Worthing, Phys. Rev. 25, 846 (1925), reports a melting point of 2895°K which, corrected to the 1948 International Temperature Scale, is 2882°K.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Molybdenum (Mo)
(Ideal Gas)

GFW = 95.94

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.481	156.915	156.915	INFINITE
100	4.968	38.033	47.877	-.984	157.295	153.659	-335.822
200	4.968	41.477	43.915	-.488	157.350	149.986	-163.897
298	4.968	43.460	43.460	.000	157.300	146.381	-107.300
300	4.968	43.491	43.460	.009	157.298	146.313	-106.589
400	4.968	44.920	43.655	.506	157.205	142.665	-77.948
500	4.968	46.029	44.023	1.003	157.086	139.042	-60.775
600	4.968	46.935	44.435	1.500	156.952	135.446	-49.336
700	4.968	47.700	44.848	1.996	156.805	131.874	-41.173
800	4.968	48.364	45.247	2.493	156.650	128.322	-35.056
900	4.968	48.949	45.627	2.990	156.489	124.792	-30.304
1000	4.968	49.472	45.986	3.487	156.320	121.279	-26.505
1100	4.969	49.946	46.324	3.984	156.143	117.783	-23.401
1200	4.970	50.378	46.645	4.480	155.953	114.304	-20.818
1300	4.972	50.776	46.947	4.978	155.750	110.841	-18.634
1400	4.977	51.145	47.234	5.475	155.529	107.394	-16.765
1500	4.985	51.488	47.506	5.973	155.290	103.966	-15.148
1600	4.998	51.810	47.765	6.472	155.031	100.553	-13.735
1700	5.016	52.114	48.012	6.973	154.753	97.155	-12.490
1800	5.043	52.401	48.248	7.476	154.453	93.776	-11.386
1900	5.079	52.675	48.474	7.982	154.134	90.413	-10.400
2000	5.125	52.937	48.691	8.492	153.793	87.067	-9.514
2100	5.183	53.188	48.899	9.007	153.432	83.739	-8.715
2200	5.254	53.431	49.099	9.529	153.050	80.430	-7.990
2300	5.340	53.666	49.293	10.058	152.644	77.138	-7.330
2400	5.440	53.895	49.480	10.597	152.213	73.868	-6.727
2500	5.556	54.120	49.661	11.147	151.744	70.609	-6.173
2600	5.689	54.340	49.837	11.709	151.229	67.376	-5.663
2700	5.838	54.558	50.008	12.285	150.661	64.159	-5.193
2800	6.005	54.773	50.174	12.877	150.032	60.967	-4.759
2900	6.189	54.987	50.336	13.487	142.712	57.817	-4.357
3000	6.391	55.200	50.495	14.116	142.341	54.897	-3.999
3100	6.610	55.413	50.650	14.766	141.991	51.988	-3.665
3200	6.847	55.627	50.802	15.438	141.663	49.087	-3.353
3300	7.099	55.841	50.952	16.135	141.360	46.202	-3.060
3400	7.368	56.057	51.099	16.859	141.084	43.323	-2.785
3500	7.652	56.275	51.243	17.610	140.835	40.448	-2.526
3600	7.949	56.494	51.386	18.389	140.614	37.586	-2.282
3700	8.259	56.716	51.527	19.200	140.425	34.727	-2.051
3800	8.580	56.941	51.667	20.042	140.267	31.872	-1.833
3900	8.910	57.168	51.805	20.916	140.141	29.022	-1.626
4000	9.248	57.398	51.942	21.824	140.049	26.173	-1.430
4100	9.591	57.630	52.078	22.766	139.991	23.329	-1.244
4200	9.938	57.866	52.213	23.742	139.967	20.481	-1.066
4300	10.287	58.104	52.347	24.753	139.978	17.635	-.896
4400	10.635	58.344	52.481	25.799	140.024	14.792	-.735
4500	10.980	58.587	52.614	26.880	140.105	11.945	-.580
4600	11.320	58.832	52.746	27.995	140.220	9.093	-.432
4700	11.653	59.079	52.878	29.144	140.369	6.240	-.290
4800	11.978	59.328	53.010	30.326	140.551	3.386	-.154
4900	12.291	59.578	53.141	31.539	140.764	.526	-.023
5000	12.592	59.829	53.273	32.783	.000	.000	.000
5100	12.879	60.082	53.404	34.057	.000	.000	.000
5200	13.150	60.334	53.535	35.359	.000	.000	.000
5300	13.405	60.587	53.665	36.686	.000	.000	.000
5400	13.642	60.840	53.796	38.039	.000	.000	.000
5500	13.861	61.092	53.926	39.414	.000	.000	.000
5600	14.061	61.344	54.056	40.810	.000	.000	.000
5700	14.242	61.594	54.186	42.226	.000	.000	.000
5800	14.403	61.844	54.316	43.658	.000	.000	.000
5900	14.546	62.091	54.446	45.106	.000	.000	.000
6000	14.669	62.337	54.575	46.567	.000	.000	.000

Dec. 31, 1966

MOLYBDENUM (Mo) (IDEAL GAS) GFW = 95.94

Ground State Configuration $^7S_3$

$\Delta Hf^\circ_0 = 156.9 \pm 0.5$ kcal/mol

$S^\circ_{298.15} = 43.46$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 157.3 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	7	21206.5	42	42864.0	138
10768.3	5	23571.2	21	44809.0	188
10966.0	1	24504.7	34	45765.0	119
11142.8	3	25990.1	152	46876.0	163
11454.4	5	27548.0	52	47794.5	194
11858.5	7	29551.1	133	48787.6	167
12346.3	9	31809.1	105	49856.1	211
16746.8	45	34546.4	109	50825.0	201
18321.8	15	37024.7	169	52783.0	330
20240.5	26	29620.1	168	54945.0	180
22639.0	8	40876.3	124	56851.0	58

Heat of Formation.

The heat of formation is simply the heat of sublimation at 298°K; this is obtained by second and third law analysis of several vapor pressure sets. A comparison of the results is tabulated below.

Reference	Method	Points	Range °K	ΔHs°_{298} kcal/mol 2nd law	ΔHs°_{298} kcal/mol 3rd law	Drift in 3rd law
1. Vozella	Langmuir	12	2140-2533°	156.4 ± 2.9	157.6 ± 0.9	0.2 ± 1.3 eu
2. Edwards	Langmuir	9	2150-2460°	146.7 ± 1.5	158.2 ± 1.2	5.0 ± 0.6 eu
3. Fries	Langmuir	12	2086-2489°	156.5 ± 1.6	156.7 ± 0.7	0.1 ± 0.7 eu
4. Jones	Langmuir	9*	2113-2496°	161.6 ± 3.8	156.0 ± 1.4	-2.6 ± 1.6 eu
5. Norris	Langmuir	Equn.	2000-2600°	131.1	148.6 ± 4.3	8.8 eu
6. Zwikker	Langmuir	Equn.	1200-2500°	159.1	158.2 ± 0.8	-0.8 eu
7. Babeliewsky	Mass Spec.		2220-2603°	149.6 ± 2.2		

* One point rejected due to failure of statistical test

The data of references 1 and 3 show no drift and thus indicate that the accommodation coefficient is essentially unity. A median value of the 3rd law heat is adopted as 157.3 ± 0.5 kcal/mol.

References:

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7. T.P.J.H. Babeliowsky, Physica 28, 1160 (1962).
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Heat Capacity and Entropy.

The electronic energy levels are those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467, Washington D. C. (1958). Several individual lines missing from given terms were estimated by analogy with the observed lines in the term. In addition, an estimate of the values of completely missing terms, arising out of low lying multiplets, was made as follows: The ^1D and ^1S; ^1D and ^1G; ^3D; ^3P and ^3F terms of the [Kr] $4d^45s^2$ multiplet were estimated at 25000, 30000, 34000 and 36000 cm^{-1}. The triplet P,D,F and G levels and the singlet S,D,F and G levels of the [Kr] $4d^6$ configuration were estimated at 30000 cm^{-1} and 40000 cm^{-1} respectively.

Higher configurations such as [Kr] $4d^45s(^6D)$ 5d which have many septuplet and quintuplet terms were thought to lie close to the ionization limit. However, upon calculating a table which contains an extra 100 levels at 35000 m^{-1} and 200 levels each at 40000 and 45000 cm^{-1}, the difference in free energy function at 6000°K is a negligible 0.008 gibbs/mol.

Molybdenum Unipositive Ion (Mo^+)
(Ideal Gas) GFW = 95.9395

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	4.968	43.154	43.154	.000	322.823	310.508	- 227.608
300	4.968	43.185	43.154	.009	322.830	310.431	- 226.149
400	4.968	44.614	43.349	.506	323.234	306.237	- 167.320
500	4.968	45.722	43.717	1.003	323.612	301.943	- 131.979
600	4.968	46.628	44.129	1.500	323.975	297.576	- 108.392
700	4.968	47.394	44.542	1.996	324.324	293.147	- 91.525
800	4.968	48.057	44.941	2.493	324.666	288.670	- 78.861
900	4.968	48.643	45.320	2.990	325.002	284.151	- 69.001
1000	4.968	49.166	45.679	3.487	325.330	279.594	- 61.105
1100	4.968	49.639	46.018	3.984	325.650	275.007	- 54.639
1200	4.969	50.072	46.338	4.480	325.957	270.388	- 49.244
1300	4.970	50.470	46.641	4.977	326.249	265.743	- 44.675
1400	4.972	50.838	46.928	5.474	326.525	261.080	- 40.756
1500	4.977	51.181	47.200	5.972	326.783	256.397	- 37.357
1600	4.986	51.503	47.459	6.470	327.020	251.695	- 34.380
1700	4.999	51.805	47.706	6.969	327.237	246.982	- 31.752
1800	5.020	52.091	47.942	7.470	327.431	242.255	- 29.414
1900	5.050	52.364	48.167	7.973	327.606	237.518	- 27.321
2000	5.091	52.624	48.384	8.480	327.759	232.771	- 25.436
2100	5.145	52.873	48.591	8.992	327.892	228.018	- 23.730
2200	5.214	53.114	48.792	9.510	328.003	223.261	- 22.179
2300	5.300	53.348	48.985	10.035	328.089	218.494	- 20.762
2400	5.405	53.575	49.171	10.570	328.151	213.734	- 19.463
2500	5.528	53.799	49.352	11.117	328.176	208.961	- 18.267
2600	5.672	54.018	49.527	11.677	328.156	204.196	- 17.164
2700	5.837	54.235	49.697	12.252	328.084	199.429	- 16.143
2800	6.022	54.451	49.863	12.845	327.953	194.664	- 15.194
2900	6.227	54.666	50.025	13.457	321.131	189.926	- 14.313
3000	6.452	54.880	50.183	14.091	321.262	185.401	- 13.506
3100	6.696	55.096	50.338	14.748	321.416	180.868	- 12.751
3200	6.956	55.313	50.491	15.431	321.596	176.332	- 12.043
3300	7.232	55.531	50.640	16.140	321.802	171.790	- 11.377
3400	7.522	55.751	50.787	16.877	322.035	167.244	- 10.750
3500	7.822	55.973	50.932	17.645	322.300	162.686	- 10.159
3600	8.132	56.198	51.075	18.442	322.594	158.121	- 9.599
3700	8.449	56.425	51.217	19.271	322.920	153.545	- 9.070
3800	8.769	56.655	51.357	20.132	323.278	148.965	- 8.567
3900	9.091	56.887	51.496	21.025	323.668	144.373	- 8.090
4000	9.411	57.121	51.633	21.950	324.089	139.769	- 7.637
4100	9.728	57.357	51.770	22.907	324.543	135.156	- 7.204
4200	10.039	57.595	51.906	23.896	325.029	130.535	- 6.792
4300	10.341	57.835	52.041	24.915	325.545	125.896	- 6.399
4400	10.632	58.076	52.175	25.963	326.090	121.248	- 6.022
4500	10.911	58.318	52.309	27.041	326.664	116.586	- 5.662
4600	11.176	58.561	52.442	28.145	327.265	111.907	- 5.317
4700	11.425	58.804	52.575	29.275	327.892	107.218	- 4.986
4800	11.658	59.047	52.708	30.430	328.544	102.517	- 4.668
4900	11.872	59.290	52.839	31.606	329.217	97.800	- 4.362
5000	12.067	59.532	52.971	32.804	188.597	95.102	- 4.157
5100	12.244	59.772	53.102	34.019	189.036	93.233	- 3.995
5200	12.401	60.012	53.232	35.252	189.464	91.345	- 3.839
5300	12.539	60.249	53.363	36.499	189.880	89.455	- 3.689
5400	12.658	60.485	53.492	37.759	190.285	87.555	- 3.544
5500	12.758	60.718	53.622	39.030	190.678	85.650	- 3.403
5600	12.839	60.948	53.750	40.310	191.057	83.738	- 3.268
5700	12.903	61.176	53.879	41.597	191.426	81.821	- 3.137
5800	12.950	61.401	54.006	42.890	191.784	79.896	- 3.011
5900	12.981	61.623	54.134	44.186	192.129	77.959	- 2.888
6000	12.996	61.841	54.260	45.485	192.464	76.028	- 2.769

Dec. 31, 1966

MOLYBDENUM UNIPOSITIVE ION (Mo^+) (IDEAL GAS) GFW = 95.9395

Ground State Configuration $^6S_{2\ 1/2}$

$S^\circ_{298.15}$ = 43.154 gibbs/mol

ΔHf°_0 = 320.957 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 322.823 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	6	22864.4	4	42560	32
11783.4	2	22980.5	12	43976	28
12034.1	4	23248.2	14	47797	54
12417.3	6	23904	28	49426	18
12900.3	8	24879	34	50454	30
13460.7	10	26544	64	52216	28
15199.3	6	27646	40	55208	20
15330.6	8	28975	36	60090	182
15427.7	10	30144	36	62260	44
15447.0	12	32124	2	63143	116
15691.2	6	34419	4	64560	104
15699.2	4	33350	70	65969	110
15890.1	2	35241	26	67971	72
16796.1	2	36547	14	69202	98
17174.1	4	37777	18	71319	52
17344.1	6	39645	10	73794	68
16946.8	8	41537	12	76227	106
22444.4	6			83557	82

Heat of Formation.

The heat of formation is obtained by adding the heat of ionization to the heat of formation of the gas at 0°K. The heat of ionization, 163.742 kcal/mol (7.10 eV), is obtained from C. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington, D. C. (1958).

Heat Capacity and Entropy.

The electronic energy levels are taken from C. E. Moore, loc. cit. The configuration [Kr] $4d^4 5s^2$ is completely missing in Mo^+, while in the isoelectronic Nb(g) this is a very low lying configuration. However, a comparison of Cr^+ with Mo^+, and V(g) with Nb(g) indicates that the similarities are much closer down a given group than across a row to an isoelectronic neighbor. Thus, by analogy with Cr^+, the missing configuration is expected to lie $>$ 50,000 cm^{-1} and thus be negligible.

The enthalpy at 0°K is calculated to be -1.481 kcal/mol.

Molybdenum Monoxide (MoO)
(Ideal Gas) GFW = 111.9394

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.102	92.531	92.531	INFINITE
100	6.956	49.156	63.226	-1.407	92.763	90.085	-196.880
200	7.059	53.995	57.537	-.708	92.672	87.426	-95.535
298	7.399	56.872	56.872	.000	92.500	84.887	-62.224
300	7.406	56.918	56.872	.014	92.496	84.840	-61.806
400	7.782	59.101	57.167	.774	92.311	82.316	-44.975
500	8.077	60.871	57.737	1.567	92.123	79.839	-34.898
600	8.291	62.364	58.387	2.386	91.933	77.400	-28.193
700	8.444	63.654	59.049	3.223	91.738	74.993	-23.414
800	8.556	64.789	59.697	4.074	91.538	72.614	-19.837
900	8.639	65.802	60.320	4.934	91.333	70.262	-17.062
1000	8.703	66.716	60.915	5.801	91.120	67.931	-14.846
1100	8.754	67.548	61.481	6.674	90.900	65.624	-13.038
1200	8.794	68.311	62.018	7.551	90.667	63.336	-11.535
1300	8.827	69.016	62.530	8.432	90.419	61.068	-10.266
1400	8.855	69.672	63.017	9.317	90.153	58.819	-9.182
1500	8.878	70.283	63.481	10.203	89.867	56.593	-8.246
1600	8.898	70.857	63.924	11.092	89.560	54.384	-7.428
1700	8.916	71.397	64.348	11.983	89.230	52.195	-6.710
1800	8.933	71.907	64.754	12.875	88.875	50.027	-6.074
1900	8.948	72.390	65.143	13.769	88.497	47.880	-5.507
2000	8.962	72.850	65.517	14.665	88.091	45.749	-4.999
2100	8.976	73.287	65.877	15.562	87.660	43.644	-4.542
2200	8.990	73.705	66.223	16.460	87.198	41.559	-4.129
2300	9.005	74.105	66.558	17.360	86.705	39.494	-3.753
2400	9.020	74.489	66.880	18.261	86.175	37.455	-3.411
2500	9.037	74.857	67.192	19.164	85.595	35.435	-3.098
2600	9.054	75.212	67.494	20.068	84.956	33.443	-2.811
2700	9.074	75.554	67.786	20.975	84.250	31.473	-2.548
2800	9.095	75.885	68.069	21.883	83.466	29.531	-2.305
2900	9.118	76.204	68.344	22.794	75.972	27.641	-2.083
3000	9.143	76.514	68.611	23.707	75.409	25.982	-1.893
3100	9.170	76.814	68.871	24.622	74.846	24.345	-1.716
3200	9.200	77.105	69.124	25.541	74.283	22.725	-1.552
3300	9.232	77.389	69.370	26.463	73.722	21.122	-1.399
3400	9.267	77.665	69.610	27.387	73.161	19.538	-1.256
3500	9.303	77.934	69.844	28.316	72.603	17.966	-1.122
3600	9.342	78.197	70.072	29.248	72.046	16.414	-.996
3700	9.384	78.453	70.295	30.184	71.491	14.878	-.879
3800	9.427	78.704	70.513	31.125	70.939	13.356	-.768
3900	9.472	78.950	70.727	32.070	70.390	11.846	-.664
4000	9.519	79.190	70.935	33.020	69.844	10.352	-.566
4100	9.568	79.426	71.139	33.974	69.301	8.871	-.473
4200	9.619	79.657	71.340	34.933	68.762	7.404	-.385
4300	9.670	79.884	71.536	35.898	68.226	5.949	-.302
4400	9.723	80.107	71.728	36.867	67.694	4.506	-.224
4500	9.777	80.326	71.917	37.842	67.167	3.078	-.149
4600	9.832	80.541	72.102	38.823	66.644	1.660	-.079
4700	9.887	80.753	72.284	39.809	66.125	.252	-.012
4800	9.943	80.962	72.462	40.800	65.611	-1.143	.052
4900	9.999	81.168	72.638	41.797	65.101	-2.533	.113
5000	10.055	81.370	72.810	42.800	-76.417	-1.574	.069
5100	10.111	81.570	72.980	43.808	-77.191	-.066	.003
5200	10.166	81.767	73.147	44.822	-77.988	1.447	-.061
5300	10.221	81.961	73.312	45.841	-78.805	2.987	-.123
5400	10.276	82.153	73.474	46.866	-79.644	4.534	-.184
5500	10.330	82.342	73.633	47.897	-80.499	6.101	-.242
5600	10.383	82.528	73.790	48.932	-81.371	7.688	-.300
5700	10.435	82.713	73.945	49.973	-82.258	9.278	-.356
5800	10.487	82.894	74.098	51.019	-83.157	10.905	-.411
5900	10.537	83.074	74.249	52.070	-84.067	12.528	-.464
6000	10.585	83.252	74.397	53.127	-84.985	14.174	-.516

June 30, 1967

MOLYBDENUM MONOXIDE (MoO) (IDEAL GAS) GFW = 111.9394

Ground State Configuration [$^3\Sigma$] ΔHf°_0 = 92.5 ± 15 kcal/mol

$S^\circ_{298.15}$ = [56.9 ± 2] gibbs/mol $\Delta Hf^\circ_{298.15}$ = 92.5 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
[0]	[3]
[14000]	[1]
[17000]	[2]
[19000]	[6]

ω_e = [955] cm^{-1} $\omega_e x_e$ = [3.61] cm^{-1} σ = 1

B_e = [0.37943] cm^{-1} α_e = [0.00188] cm^{-1} r_e = [1.80] Å

Heat of Formation

The heat of formation, ΔHf°_{298}(MoO,g) = 92.5 ± 15 kcal/mol, is derived from the heat of reaction, ΔHr°_{298} = 32.9 kcal/mol for Mo(c) + O(g) → MoO(g) with all JANAF auxiliary data. The value of ΔHr°_{298} is calculated by the third law method from the partial pressure data determined mass-spectrometrically in the temperature range from 2262 to 2466°K by G. DeMaria, et al. (1). The drift in the third law analysis is -14 ± 11 eu.

Heat Capacity and Entropy

The ground state configuration and the probable electronic levels are assumed to be similar to those for WO(g) (see JANAF WO(g) table of Sept. 30, 1966). T. M. Swaminathan and S. G. Krishnamurthy (2) observed ten band systems attributed to molybdenum oxide with lower state values of ω_e = 950 ± 10 cm^{-1}. T. V. Iorns and F. E. Stafford (3) also observed a band with a peak at 969 cm^{-1} in the vapor above MoO_3(c). It is surprising that the observed vibrational frequency of MoO(g) is lower than 1055 cm^{-1} observed for WO(g). The latter comes not only from electronic spectra of the gas but also from infrared observation in matrix isolation; the former comes only from tentative assignments of electronic spectra presumably arising from MoO(g). It is possible that the observed states could be low lying excited states. We tentatively assume the fundamental vibrational frequency to be 955 cm^{-1}. The bond distance is then calculated by Guggenheimer's relation (4) for multiple bond molecules from the estimated vibrational frequency. The anharmonicity correction x_e is estimated from the relation $x_e\mu^{1/2}$ = 0.014 given by R. F. Barrow and A. D. Caunt (5). The constant (0.014) is assumed to be the same as that for WO(g). The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from the estimated bond distance.

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Molybdenum Dioxide (MoO_2)

(Crystal) GFW = 127.9388

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 1.988	- 139.317	- 139.317	INFINITE
100	3.866	2.634	21.278	- 1.864	- 140.004	- 135.960	297.141
200	9.886	7.294	13.079	- 1.157	- 140.434	- 131.719	143.935
298	13.360	11.954	11.954	.000	- 140.500	- 127.415	93.398
300	13.407	12.037	11.954	.025	- 140.499	- 127.334	92.763
400	15.189	16.165	12.505	1.464	- 140.361	- 122.963	67.184
500	16.237	19.674	13.597	3.039	- 140.134	- 118.639	51.857
600	17.011	22.705	14.868	4.702	- 139.856	- 114.364	41.657
700	17.671	25.378	16.182	6.437	- 139.542	- 110.140	34.387
800	18.281	27.777	17.484	8.235	- 139.194	- 105.964	28.948
900	18.873	29.965	18.751	10.092	- 138.809	- 101.832	24.728
1000	19.464	31.984	19.975	12.009	- 138.385	- 97.746	21.362
1100	20.064	33.867	21.153	13.986	- 137.921	- 93.704	18.617
1200	20.677	35.639	22.287	16.022	- 137.419	- 89.707	16.338
1300	21.307	37.319	23.379	18.121	- 136.878	- 85.752	14.416
1400	21.958	38.921	24.433	20.285	- 136.296	- 81.841	12.776
1500	22.629	40.459	25.450	22.514	- 135.675	- 77.972	11.360
1600	23.324	41.942	26.435	24.811	- 135.013	- 74.147	10.128
1700	24.041	43.377	27.389	27.179	- 134.306	- 70.364	9.046
1800	24.782	44.772	28.316	29.620	- 133.557	- 66.524	8.059
1900	25.548	46.132	29.219	32.136	- 132.761	- 62.926	7.238
2000	26.338	47.463	30.098	34.731	- 131.917	- 59.275	6.477
2100	27.153	48.767	30.956	37.405	- 131.024	- 55.664	5.793
2200	27.993	50.050	31.794	40.162	- 130.083	- 52.097	5.175
2300	28.858	51.313	32.616	43.004	- 129.092	- 48.576	4.616
2400	29.749	52.560	33.421	45.934	- 128.054	- 45.093	4.106
2500	30.665	53.793	34.211	48.955	- 126.980	- 41.663	3.642
2600	31.607	55.014	34.988	52.068	- 125.876	- 38.269	3.217
2700	32.574	56.225	35.752	55.277	- 124.749	- 34.923	2.827
2800	33.566	57.427	36.505	58.584	- 123.606	- 31.615	2.468
2900	34.585	58.623	37.247	61.991	- 129.077	- 28.331	2.135
3000	35.629	59.813	37.979	65.502	- 127.519	- 24.883	1.813

June 30, 1967

$\Delta Hf^\circ_0 = -139.3 \pm 0.5$ kcal/mol

$S^\circ_{298.15} = 11.95 \pm 2$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -140.5 \pm 0.5$ kcal/mol

Td = Unknown

Heat of Formation

The adopted heat of formation, -140.5 kcal/mol, is a weighted average of values derived from calorimetric determinations, emf measurements and equilibrium studies. The results are given below.

Ignition of the bomb products from the calorimetric studies of Staskiewicz et al. indicated that oxidation was only about 70 per cent complete. The authors also digested the products with NH_4OH to remove the trioxide. The residue was the dioxide, as indicated by both oxidation and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah found 72 - 75 per cent conversion to trioxide by weighing the total combustion products; he performed no additional analysis.

Investigator	Method	Reaction	Temp. Range (°K)	No. of Points	ΔHr°_{298} (kcal/mol) 3rd Law	ΔHr°_{298} (kcal/mol) 2nd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
1. Staskiewicz et al.	Calorimetric	A	-	-	-37.12		-	-140.86±0.13**
2. Mah	Calorimetric	A	-	-	-37.52		-	-140.64±0.13**
3. Rapp	EMF	B	1023-1323	35	-13.18	-13.42	0.1±0.1	-140.46*
		C	1023-1273	22	-25.65	-25.63	0±0.1	-140.25*
4. Barbi	EMF	F	873-1073	Equation	-138.66	-140.3	1.7	-138.66*
5. Gleiser and Chipman	Equilibrium	D	1296-1341	9	-5.44	-0.3	-4.4±2.2	-140.71*
6. Gokcen	Equilibrium	E	949-1344	Equation	-24.58	-17.7	-6.0	-140.17*
7. Collins	Equilibrium	E	973-1173	Equation	-24.57	-22.2	-2.2	-140.17*
8. Tonosaki	Equilibrium	E	981-1096	Equation	-24.0	-18.5	-5.4	-139.61*

*Third law value used in the calculation.

**Auxiliary data for $MoO_3(c)$ are taken from corresponding measurements of the same authors. See JANAF $MoO_3(c)$ table for details.

Reaction:
- A. $MoO_2(c) + 1/2\ O_2(g) = MoO_3(c)$.
- B. $2Fe_xO(c) + Mo(c) = MoO_2(c) + 2xFe(c)$.
- C. $2NiO(c) + Mo(c) = MoO_2(c) + 2Ni(c)$.
- D. $Mo(c) + 2CO_2(g) = MoO_2(c) + 2CO(g)$.
- E. $Mo(c) + 2H_2O(g) = MoO_2(c) + 2H_2(g)$.
- F. $Mo(c) + O_2(g) = MoO_2(c)$ derived by the author from the cell reaction $2Fe_xO(c) + Mo(c) = MoO_2(c) + 2xFe(c)$ using ΔGf° data for $Fe_xO(c)$.

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Heat Capacity and Entropy

E. G. King, J. Am. Chem. Soc. 80, 1799 (1958), measured the low temperature heat capacities from 53.3° to 296°K. E. G. King, W. W. Weller and A.U . Christensen, U. S. Bur. Mines RI 5664, 1960, measured the high temperature enthalpy changes from 399° to 1801°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -1.3 to +0.7 percent, excluding the point at 1801°K. This point at the highest temperature deviates by +2.3 percent, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy $S^\circ_{298} = 11.054$ eu is obtained from the low temperature heat capacity data, based on $S^\circ_{51} = 0.31$ eu. B. N. Figgis and J. Lewis, "Progress in Inorg. Chem.," Vol. 6, page 123, Interscience Publishers, New York, 1964, indicated that MoO_2 is probably antiferromagnetic. Its small susceptibility is presumably due to Mo-Mo interactions. It is possible that at temperatures below 50°K entropy due to spin interactions of the d^2 electrons will appear, contributing up to 2.2 eu. The drifts in the equilibrium data do suggest that additional entropy may be appropriate; however, only the EMF data of Rapp appear to be sufficiently precise to influence the decision. These data suggest addition of 0.8±0.1 eu and 0.9±0.1 eu based on auxiliary data for Wüstite and NiO(c), respectively. We select the entropy of 11.954 eu from equilibrium data for NiO.

Molybdenum Dioxide (MoO_2)

(Ideal Gas) GFW = 127.9388

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.684	-2.613	-2.613	INFINITE
100	8.457	56.276	75.046	-1.877	-2.617	-3.937	8.605
200	9.487	62.475	67.359	-.977	-2.854	-5.174	5.654
298	10.422	66.436	66.436	.000	-3.100	-6.259	4.588
300	10.439	66.501	66.436	.019	-3.105	-6.279	4.574
400	11.298	69.626	66.856	1.108	-3.317	-7.304	3.990
500	11.947	72.221	67.677	2.272	-3.500	-8.279	3.619
600	12.410	74.442	68.624	3.491	-3.667	-9.218	3.358
700	12.739	76.381	69.596	4.749	-3.830	-10.130	3.163
800	12.976	78.099	70.554	6.036	-3.993	-11.020	3.011
900	13.150	79.637	71.479	7.342	-4.159	-11.887	2.887
1000	13.282	81.030	72.366	8.664	-4.330	-12.737	2.784
1100	13.383	82.301	73.212	9.998	-4.509	-13.569	2.696
1200	13.462	83.469	74.019	11.340	-4.701	-14.385	2.620
1300	13.525	84.549	74.788	12.690	-4.909	-15.183	2.553
1400	13.576	85.553	75.521	14.045	-5.136	-15.966	2.492
1500	13.619	86.491	76.222	15.404	-5.385	-16.730	2.437
1600	13.655	87.371	76.891	16.768	-5.656	-17.477	2.387
1700	13.687	88.200	77.532	18.135	-5.950	-18.207	2.341
1800	13.717	88.983	78.147	19.506	-6.271	-18.919	2.297
1900	13.745	89.726	78.737	20.879	-6.618	-19.612	2.256
2000	13.772	90.432	79.304	22.254	-6.994	-20.289	2.217
2100	13.800	91.104	79.850	23.633	-7.396	-20.943	2.180
2200	13.829	91.747	80.377	25.014	-7.831	-21.578	2.144
2300	13.859	92.362	80.884	26.399	-8.297	-22.194	2.109
2400	13.892	92.953	81.375	27.786	-8.802	-22.783	2.075
2500	13.927	93.521	81.850	29.177	-9.358	-23.359	2.042
2600	13.964	94.067	82.309	30.572	-9.972	-23.904	2.009
2700	14.004	94.595	82.754	31.970	-10.656	-24.429	1.977
2800	14.047	95.105	83.186	33.373	-11.417	-24.925	1.945
2900	14.091	95.599	83.606	34.780	-18.888	-25.373	1.912
3000	14.138	96.077	84.014	36.191	-19.430	-25.587	1.864
3100	14.187	96.542	84.410	37.607	-19.971	-25.783	1.818
3200	14.238	96.993	84.797	39.029	-20.511	-25.964	1.773
3300	14.291	97.432	85.173	40.455	-21.051	-26.126	1.730
3400	14.345	97.859	85.540	41.887	-21.590	-26.270	1.689
3500	14.400	98.276	85.898	43.324	-22.127	-26.404	1.649
3600	14.457	98.683	86.247	44.767	-22.662	-26.516	1.610
3700	14.513	99.079	86.539	46.216	-23.195	-26.616	1.572
3800	14.571	99.467	86.923	47.670	-23.726	-26.699	1.536
3900	14.628	99.846	87.249	49.130	-24.254	-26.771	1.500
4000	14.686	100.218	87.569	50.595	-24.781	-26.831	1.466
4100	14.743	100.581	87.882	52.067	-25.304	-26.874	1.433
4200	14.800	100.937	88.188	53.544	-25.824	-26.907	1.400
4300	14.857	101.286	88.489	55.027	-26.341	-26.925	1.368
4400	14.912	101.628	88.784	56.515	-26.856	-26.934	1.338
4500	14.967	101.964	89.073	58.009	-27.367	-26.929	1.308
4600	15.021	102.293	89.357	59.509	-27.874	-26.914	1.279
4700	15.074	102.617	89.635	61.013	-28.380	-26.889	1.250
4800	15.125	102.935	89.909	62.523	-28.881	-26.849	1.222
4900	15.175	103.247	90.178	64.038	-29.379	-26.806	1.196
5000	15.224	103.554	90.442	65.558	-170.887	-24.417	1.067
5100	15.272	103.856	90.703	67.083	-171.653	-21.474	.920
5200	15.317	104.153	90.958	68.613	-172.443	-18.529	.779
5300	15.362	104.445	91.210	70.147	-173.255	-15.555	.641
5400	15.404	104.733	91.458	71.685	-174.091	-12.576	.509
5500	15.445	105.016	91.702	73.228	-174.944	-9.575	.380
5600	15.485	105.295	91.942	74.774	-175.818	-6.561	.256
5700	15.522	105.569	92.179	76.324	-176.708	-3.536	.136
5800	15.558	105.839	92.412	77.878	-177.611	-.480	.018
5900	15.592	106.106	92.642	79.436	-178.527	2.577	-.095
6000	15.625	106.368	92.868	80.997	-179.454	5.659	-.206

June 30, 1968

MOLYBDENUM DIOXIDE (MoO_2) (IDEAL GAS) GFW = 127.9388

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [66.4 ± 3] gibbs/mol

Ground State Quantum Weight = [3]

ΔHf°_0 = -2.6 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -3.1 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[3]
[13000]	[6]
[25000]	[6]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
970 (1)
[300](1)
990 (1)

Bond Distance: Mo-O = [1.80] Å

Bond Angle: O-Mo-O = [110°] σ = [2]

Product of the Moments of Inertia: $I_A I_B I_C$ = [7.750 x 10^{-115}] g^3 cm^6

Heat of Formation

Burns et al. (1) have investigated mass-spectrometrically the vapor in equilibrium with powdered $MoO_2(c)$ and also reported the partial pressures of $MoO_2(g)$, $MoO_3(g)$, $(MoO_3)_2(g)$, and $(MoO_3)_3(g)$. Second and third analyses of their partial pressure data are given in the table below. The adopted value, $\Delta Hf^\circ_{298}(MoO_2, g)$ = -3.1 kcal/mol, is calculated from their 3rd law value of ΔHr°_{298} = 137.4 kcal/mol for $MoO_2(c) \rightarrow MoO_2(g)$, using all JANAF functions.

DeMaria et al. (2) have measured the partial pressures of gaseous oxides MoO, MoO_2, MoO_3 and O(g) in the Mo-Al_2O_3 system by mass spectrometry. Blackburn et al. (3) and Plante (4) have studied the vapor pressures above molybdenum dioxide(c) by the Knudsen effusion method. Second and third law analyses of these three sets of partial pressure data are reported in the following table.

	Investigator	Reaction	Temp. °K	No. of Points	ΔHr°_{298}, kcal/mol 2nd law	ΔHr°_{298}, kcal/mol 3rd law	Drift eu	$\Delta Hf^\circ_{298}(MoO_2, g)$ kcal/mol**
1.	Burns et al.	$MoO_2(c) \rightarrow MoO_2(g)$	1598-1777	11*	137.9±3.1	137.38	-0.1±1.8	-3.1
2.	DeMaria et al.	$Mo(c) + 2O(g) \rightarrow MoO_2(g)$	2262-2466	9	-61.8±32.1	-108.37	-19.9±13.6	10.7
3.	Blackburn et al.	$MoO_2(c) \rightarrow MoO_2(g)$	1818-2028	7	107.2±6.6	124.92	9.0±3.5	-15.6
4.	Plante	$MoO_2(c) \rightarrow MoO_2(g)$	1611-1802	6	149.6±13.0	140.92	-5.9±7.7	-0.4

*2 points rejected due to failure of statistical test

**based on the third law ΔHr°_{298} value

Heat Capacity and Entropy

The $MoO_2(g)$ is assumed to have a C_{2v} symmetry similar to that of TaO_2 reported by Weltner and McLeod (5). The bond angle O-Mo-O is estimated to be 110°. The bond distance Mo-O is estimated to be 1.80 Å, the same as that in MoO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectra of gaseous MoO_2Cl_2 and MoO_2Br_2, reported by Iorns and Stafford (6). The bending vibrational frequency (300 cm^{-1}) is estimated by comparison with other transition metal dioxides. The three principal moments of inertia are: I_A = 4.2470 x 10^{-39}, I_B = 11.5512 x 10^{-39} and I_C = 15.7982 x 10^{-39} g cm^2.

The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod (7) on WO_2. The ground state is assumed to be $^3A_1$ and the first excited level is assumed to lie close to the observed transitions at 7890Å and 7806Å in WO_2. Since both these states are presumed to be triplet, we have assigned a total degeneracy of 6. In addition, we expect from the electronic levels of $Mo^{+4}(g)$ (8) that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm^{-1}.

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Molybdenum Trioxide (MoO_3)
(Crystal) GFW = 143.9382

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 3.009	- 176.900	- 176.900	INFINITE
100	7.564	4.673	31.743	- 2.707	- 177.756	- 171.947	375.570
200	14.168	12.184	20.109	- 1.585	- 178.120	- 165.760	181.134
298	17.897	18.585	18.585	.000	- 178.100	- 159.687	117.054
300	17.951	18.696	18.585	.033	- 178.097	- 159.573	116.249
400	19.860	24.155	19.317	1.935	- 177.852	- 153.431	83.831
500	20.973	28.712	20.753	3.979	- 177.520	- 147.364	64.413
600	21.935	32.621	22.413	6.125	- 177.138	- 141.367	51.493
700	22.900	36.074	24.122	8.367	- 176.706	- 135.438	42.285
800	23.908	39.198	25.814	10.707	- 176.215	- 129.577	35.399
900	24.962	42.074	27.463	13.150	- 175.651	- 123.779	30.058
1000	26.061	44.760	29.060	15.700	- 175.007	- 118.048	25.799
1100	27.197	47.297	30.604	18.363	- 174.277	- 112.387	22.329
1200	28.365	49.714	32.096	21.141	- 173.457	- 106.798	19.450
1300	29.561	52.031	33.541	24.037	- 172.547	- 101.278	17.026
1400	30.779	54.266	34.942	27.054	- 171.545	- 95.833	14.960
1500	32.017	56.432	36.303	30.194	- 170.448	- 90.462	13.180

June 30, 1967

MOLYBDENUM TRIOXIDE (MoO_3) (CRYSTAL) GFW = 143.9382

ΔHf°_0 = -176.9 ± 0.1 kcal/mol

$S^\circ_{298.15}$ = 18.585 ± 0.15 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -178.1 ± 0.1 kcal/mol

Tm = 1074°K

ΔHm° = 11.60 kcal/mol

Heat of Formation

The adopted heat of formation, -178.1 kcal/mol, is the weighted average of two recent calorimetric determinations. The results are given below.

Staskiewicz et al. (2) found that oxidation was only about 80 per cent complete and tentatively attributed this to formation of MoO_2(c). The table for MoO_2(c) details the analytical methods applied to the combustion products and the heat of combustion of the dioxide which is necessary for reduction of the data of the trioxide. Combination of these investigations gives $\Delta Hf^\circ_{298}(MoO_3, c)$ = -177.98 kcal/mol. Subsequent discovery of oxides intermediate between MoO_2 and MoO_3 raises a possible uncertainty concerning the incomplete oxidation. Mah (1) also reported that completion of the combustion of Mo(c) sample ranged from 84 to 93 per cent, as determined only by weight gain of the total combustion products upon prolonged low temperature ignition. In contrast, the earlier workers reported almost complete combustion. Neumann et al. (3) found about 97 per cent completion using a wet analysis involving aqua regia. Moose and Parr (4) found that in several combustions, they obtained over 99 per cent completion, based on the weight of the oxide formed.

	Investigator	Year	Method	Reaction	ΔHf°_{298} (kcal/mol)
1.	Mah	1957	Calorimetric	$Mo(c) + 3/2O_2(g) \rightarrow MoO_3(c)$	-178.16
2.	Staskiewicz et al.	1955	Calorimetric	$Mo(c) + 3/2O_2(g) \rightarrow MoO_3(c)$	-177.98
3.	Neumann et al.	1934	Calorimetric	$Mo(c) + 3/2O_2(g) \rightarrow MoO_3(c)$	-180.4
4.	Moose and Parr	1924	Calorimetric	$Mo(c) + 3/2O_2(g) \rightarrow MoO_3(c)$	-175.6

Heat Capacity and Entropy

Smith et al. (5) measured low temperature heat capacities from 18.3 to 299.8°K. King et al. (6) measured high temperature enthalpy data from 399.3° to 1063.9°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -0.65 percent to +0.17 percent. Seltz et al. (7) have also measured low temperature heat capacities from 70° to 298.7°K which are not in agreement with the values adopted. (The discrepancy has been discussed by Smith.) Cosgrove and Snyder (8) have also measured high temperature enthalpy data from 273° to 1068°K by drop calorimetry. Their smooth values are about 2 percent higher than the values adopted in the tabulation.

The entropy, S°_{298} = 18.585 eu, is obtained from the low temperature heat capacity data of Smith (5), based on S°_{20} = 0.197 eu. This starting entropy was obtained by the authors from a T^2 extrapolation of the data. It is surprising that the entropy of MoO_3(c) is larger than that of WO_3(c) by about 0.4 eu. This may be due to the difference in the crystal structures, MoO_3 being orthorhombic and WO_3 monoclinic, and also to uncertainty in the entropy extrapolation below 50°K for WO_3(c).

Melting Data

The adopted melting point is obtained from King (6), and the heat of melting is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King. Cosgrove and Snyder (8) found the melting point 1068°K by the cooling curve method, and derived ΔHm° = 12.54 kcal/mol from their smooth enthalpy values at the melting point.

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Molybdenum Trioxide (MoO_3)

(Liquid) GFW = 143.9382

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	17.897	26.971	26.971	.000	- 168.555	- 152.642	111.890
300	17.951	27.082	26.971	.033	- 168.552	- 152.544	111.128
400	19.860	32.541	27.703	1.935	- 168.307	- 147.241	80.449
500	20.973	37.098	29.139	3.979	- 167.975	- 142.012	62.073
600	21.935	41.007	30.799	6.125	- 167.593	- 136.853	49.849
700	30.342	44.461	32.508	8.367	- 167.161	- 131.763	41.138
800	30.342	48.512	34.261	11.401	- 165.976	- 126.789	34.637
900	30.342	52.086	36.047	14.435	- 164.821	- 121.959	29.616
1000	30.342	55.283	37.813	17.469	- 163.693	- 117.257	25.627
1100	30.342	58.175	39.535	20.503	- 162.592	- 112.667	22.385
1200	30.342	60.815	41.200	23.538	- 161.515	- 108.177	19.702
1300	30.342	63.243	42.804	26.572	- 160.468	- 103.774	17.446
1400	30.342	65.492	44.345	29.606	- 159.447	- 99.453	15.525
1500	30.342	67.585	45.825	32.640	- 158.457	- 95.200	13.871
1600	30.342	69.544	47.247	35.674	- 157.496	- 91.016	12.432
1700	30.342	71.383	48.613	38.709	- 156.564	- 86.988	11.170
1800	30.342	73.117	49.927	41.743	- 155.666	- 82.816	10.055
1900	30.342	74.758	51.191	44.777	- 154.799	- 78.793	9.063
2000	30.342	76.314	52.409	47.811	- 153.966	- 74.816	8.176

June 30, 1967

MOLYBDENUM TRIOXIDE (MoO_3) (LIQUID) GFW = 143.9382

$S°_{298.15}$ = 26.971 gibbs/mol

$\Delta Hf°_{298.15}$ = -168.555 ± 0.1 kcal/mol

Tm = 1074°

ΔHm° = 11.60 kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between $H°_{1074} - H°_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity between the melting point and 1392.4°K is derived from the enthalpy data measured by E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664 (1960). The heat capacity is assumed constant above and below the measured range. At 700°K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. The entropy at 298°K is obtained in a manner analogous to that of the heat of formation.

L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. 75, 1227 (1953), also measured the enthalpy changes for $MoO_3(\ell)$ in the temperature range from 1068° to 1300°K. Their smooth values are +2.5 percent to +4.0 percent higher than our tabulated values. They have also found the melting point at 1068°K by the cooling curve method.

Melting Data

See JANAF MoO_3(c) table dated June 30, 1967.

Molybdenum Trioxide (MoO_3)

(Ideal Gas) GFW = 143.9382

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.225	-85.217	-85.217	INFINITE
100	9.299	54.186	78.191	-2.401	-85.550	-84.591	184.874
200	12.276	61.618	68.173	-1.311	-85.946	-83.473	91.215
298	14.347	66.924	66.924	.000	-86.200	-82.199	60.254
300	14.380	67.013	66.924	.027	-86.204	-82.175	59.864
400	15.917	71.373	67.508	1.546	-86.341	-80.808	44.151
500	16.972	75.046	68.658	3.194	-86.406	-79.416	34.713
600	17.688	78.208	69.992	4.929	-86.434	-78.014	28.417
700	18.182	80.974	71.368	6.724	-86.449	-76.610	23.919
800	18.532	83.426	72.725	8.561	-86.461	-75.205	20.545
900	18.787	85.624	74.038	10.427	-86.474	-73.796	17.920
1000	18.978	87.614	75.298	12.316	-86.491	-72.386	15.820
1100	19.123	89.430	76.501	14.221	-86.519	-70.975	14.101
1200	19.236	91.099	77.649	16.140	-86.558	-69.560	12.669
1300	19.326	92.642	78.744	18.068	-86.617	-68.142	11.456
1400	19.398	94.077	79.788	20.004	-86.694	-66.718	10.415
1500	19.457	95.417	80.786	21.947	-86.795	-65.287	9.512
1600	19.506	96.675	81.740	23.895	-86.920	-63.849	8.721
1700	19.546	97.858	82.654	25.848	-87.070	-62.402	8.022
1800	19.581	98.977	83.530	27.804	-87.250	-60.946	7.400
1900	19.610	100.036	84.371	29.764	-87.458	-59.479	6.842
2000	19.635	101.043	85.179	31.726	-87.696	-58.003	6.338
2100	19.656	102.001	85.958	33.691	-87.965	-56.512	5.881
2200	19.675	102.916	86.708	35.657	-88.271	-55.007	5.464
2300	19.692	103.791	87.432	37.626	-88.611	-53.489	5.083
2400	19.706	104.629	88.131	39.596	-88.994	-51.949	4.731
2500	19.719	105.434	88.807	41.567	-89.434	-50.402	4.406
2600	19.730	106.208	89.462	43.539	-89.937	-48.827	4.104
2700	19.740	106.952	90.096	45.513	-90.514	-47.237	3.824
2800	19.750	107.671	90.711	47.487	-91.175	-45.622	3.561
2900	19.758	108.364	91.308	49.463	-98.552	-43.961	3.313
3000	19.765	109.034	91.887	51.439	-99.005	-42.072	3.065
3100	19.772	109.682	92.451	53.416	-99.464	-40.165	2.832
3200	19.778	110.310	92.999	55.393	-99.929	-38.248	2.612
3300	19.784	110.918	93.533	57.371	-100.400	-36.314	2.405
3400	19.789	111.509	94.053	59.350	-100.878	-34.362	2.209
3500	19.793	112.083	94.560	61.329	-101.360	-32.404	2.023
3600	19.798	112.640	95.055	63.309	-101.847	-30.423	1.847
3700	19.801	113.183	95.537	65.289	-102.340	-28.432	1.679
3800	19.805	113.711	96.009	67.269	-102.838	-26.425	1.520
3900	19.808	114.226	96.469	69.250	-103.339	-24.411	1.368
4000	19.812	114.727	96.919	71.231	-103.846	-22.382	1.223
4100	19.814	115.216	97.360	73.212	-104.357	-20.337	1.084
4200	19.817	115.694	97.791	75.193	-104.871	-18.283	.951
4300	19.820	116.160	98.212	77.175	-105.389	-16.212	.824
4400	19.822	116.616	98.625	79.157	-105.912	-14.135	.702
4500	19.824	117.061	99.030	81.140	-106.437	-12.042	.585
4600	19.826	117.497	99.427	83.122	-106.965	-9.937	.472
4700	19.828	117.923	99.816	85.105	-107.497	-7.824	.364
4800	19.830	118.341	100.198	87.088	-108.031	-5.694	.259
4900	19.832	118.750	100.572	89.071	-108.567	-3.564	.159
5000	19.833	119.150	100.940	91.054	-250.119	.916	-.040
5100	19.835	119.543	101.301	93.037	-250.936	5.953	-.255
5200	19.836	119.928	101.655	95.021	-251.781	10.989	-.462
5300	19.837	120.306	102.003	97.005	-252.653	16.059	-.662
5400	19.839	120.677	102.346	98.988	-253.554	21.131	-.855
5500	19.840	121.041	102.682	100.972	-254.476	26.230	-1.042
5600	19.841	121.399	103.013	102.956	-255.424	31.340	-1.223
5700	19.842	121.750	103.339	104.941	-256.392	36.464	-1.398
5800	19.843	122.095	103.660	106.925	-257.377	41.622	-1.568
5900	19.844	122.434	103.975	108.909	-258.380	46.780	-1.733
6000	19.845	122.768	104.285	110.894	-259.397	51.967	-1.893

June 30, 1968

MOLYBDENUM TRIOXIDE (MoO_3) (IDEAL GAS) GFW = 143.9382

Point Group [D_{3h}]

$\Delta Hf°_0$ = -85.2 ± 5 kcal/mol

$S°_{298.15}$ = [66.9 ± 4] gibbs/mol

$\Delta Hf°_{298.15}$ = -86.2 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (1)	969 (2)
[350] (1)	[300](2)

Bond Distance: Mo-O = [1.80] Å

Bond Angle: O-Mo-O = [120°]

σ = [6]

Product of the Moments of Inertia: $I_AI_BI_C$ = [4.304×10^{-114}] $g^3\ cm^6$

Heat of Formation

Burns et al. (1) have determined the partial pressures of gaseous oxides MoO_2, MoO_3, $(MoO_3)_2$ and $(MoO_3)_3$ in equilibrium with powdered MoO_2(c) by mass spectrometry. Plante (2) and Blackburn et al. (3) have also investigated the vapor pressures above molybdenum dioxide (c) by the Knudsen effusion method. They all involve the disproportionation of MoO_2(c) to Mo(c) and MoO_3(g). DeMaria et al. (4) have reported the partial pressures of MoO(g), MoO_2(g), MoO_3(g) and O(g) in the Mo-Al_2O_3 system by mass spectrometry. Second and third law analyses of these partial pressure data are listed in the following table, using all JANAF functions.

				$\Delta Hr°_{298}$, kcal/mol			
Investigator	Reaction	Temp. °K	No. of Points	2nd law	3rd law	Drift eu	$\Delta Hf°_{298}(MoO_3, g)$ kcal/mol*
1. Burns et al.	$1.5MoO_2(c) \rightarrow MoO_3(g) + 0.5\ Mo(c)$	1481-1777	34	131.6±1.5	124.5	-4.2±0.9	-86.2
2. Plante	$1.5MoO_2(c) \rightarrow MoO_3(g) + 0.5Mo(c)$	1592-1918	119	134.6±1.4	120.3	-8.3±0.7	-90.4
3. Blackburn et al.	$1.5MoO_2(c) \rightarrow MoO_3(g) + 0.5Mo(c)$	1818-2028	7	108.7±6.4	117.2	4.2±3.4	-93.4
4. DeMaria et al.	$Mo(c) + 3\ O(g) \rightarrow MoO_3(g)$	2281-2416	5	-225.1±39.9	-255.1	-12.8±17.1	-76.4

*Based on the third law $\Delta Hr°_{298}$ value

The selected heat of formation is -86.2 kcal/mol, based on the third law value of $\Delta Hf°_{298}$ of Burns et al. The choice is made because there is serious doubt about the data of Blackburn as discussed by Burns et al. In addition the assumption made by Plante that the only vapor species of any importance is MoO_3 may be erroneous. The mass spectrometric work of Burns et al. is thus preferred.

Heat Capacity and Entropy

The MoO_3(g) is assumed to be a planar D_{3h} molecule with a bond angle O-Mo-O = 120°. The bond distance Mo-O is estimated to be 1.80 Å, the same as that of MoO(g). The three principal moments of inertia are $I_A = I_B = 12.9111 \times 10^{-39}$ and $I_C = 25.8222 \times 10^{-39}\ g\ cm^2$.

Iorns and Stafford (5) have observed two vibrational frequencies (969 and 715 cm^{-1}) in the infrared spectra of the vapor above MoO_3(c). They assigned the Mo-O stretching frequency at 969 cm^{-1} and the trimer ring vibration at 815 cm^{-1}, based on their infrared spectrum observations of gaseous molybdenum oxides and oxyhalides. Barraclough et al. (6) have also concluded that the presence of a metal-oxygen double bond can be correlated with a stretching frequency in the range 900-1100 cm^{-1}. For the MoO_3 molecule, they found the stretching frequency at 985 cm^{-1} in their spectrometric studies.

Based on the vibrational frequencies of MoO_4^{-2}(aq) reported by Nakamoto (7) and Siebert (8), and those of WO_3, WO_4^{2-}, SO_3 and SO_4^{2-}, we have estimated 800, 350 and 300 cm^{-1} for MoO_3(g).

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Nitrogen, Monatomic (N)

(Ideal Gas) At. Wt. = 14.008

T, °K.	C°_p (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH°_f (kcal. mole^{-1})	ΔF°_f (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 1.481	112.520	112.520	INFINITE
100	4.968	31.187	41.031	- .984	112.670	111.459	- 243.583
200	4.968	34.631	37.069	- .488	112.819	110.191	- 120.405
298	4.968	36.614	36.614	.000	112.965	108.870	- 79.800
300	4.968	36.645	36.614	.009	112.968	108.845	- 79.289
400	4.968	38.074	36.809	.506	113.116	107.448	- 58.704
500	4.968	39.183	37.177	1.003	113.261	106.014	- 46.336
600	4.968	40.089	37.589	1.500	113.402	104.551	- 38.081
700	4.968	40.855	38.002	1.996	113.535	103.066	- 32.177
800	4.968	41.518	38.401	2.493	113.660	101.562	- 27.744
900	4.968	42.103	38.781	2.990	113.778	100.042	- 24.292
1000	4.968	42.627	39.140	3.487	113.887	98.510	- 21.528
1100	4.968	43.100	39.479	3.984	113.990	96.967	- 19.265
1200	4.968	43.532	39.799	4.481	114.087	95.415	- 17.377
1300	4.968	43.930	40.101	4.977	114.178	93.856	- 15.778
1400	4.968	44.298	40.388	5.474	114.264	92.289	- 14.406
1500	4.968	44.641	40.660	5.971	114.346	90.716	- 13.217
1600	4.968	44.962	40.919	6.468	114.425	89.139	- 12.175
1700	4.968	45.263	41.166	6.965	114.501	87.556	- 11.256
1800	4.968	45.547	41.402	7.461	114.573	85.968	- 10.437
1900	4.969	45.815	41.627	7.958	114.644	84.378	- 9.705
2000	4.969	46.070	41.843	8.455	114.712	82.784	- 9.046
2100	4.970	46.313	42.050	8.952	114.778	81.185	- 8.449
2200	4.971	46.544	42.249	9.449	114.843	79.583	- 7.905
2300	4.972	46.765	42.440	9.946	114.906	77.979	- 7.409
2400	4.975	46.977	42.625	10.444	114.968	76.373	- 6.954
2500	4.978	47.180	42.803	10.941	115.028	74.763	- 6.535
2600	4.982	47.375	42.975	11.439	115.088	73.151	- 6.149
2700	4.987	47.563	43.142	11.938	115.148	71.537	- 5.790
2800	4.993	47.745	43.303	12.437	115.207	69.922	- 5.457
2900	5.001	47.920	43.459	12.936	115.265	68.303	- 5.147
3000	5.011	48.090	43.611	13.437	115.324	66.683	- 4.858
3100	5.022	48.254	43.758	13.939	115.383	65.060	- 4.587
3200	5.035	48.414	43.901	14.441	115.442	63.435	- 4.332
3300	5.050	48.569	44.040	14.946	115.503	61.810	- 4.093
3400	5.067	48.720	44.175	15.451	115.564	60.181	- 3.868
3500	5.086	48.867	44.307	15.959	115.626	58.551	- 3.656
3600	5.107	49.011	44.436	16.469	115.690	56.921	- 3.455
3700	5.130	49.151	44.562	16.980	115.755	55.287	- 3.265
3800	5.156	49.288	44.684	17.495	115.823	53.653	- 3.086
3900	5.183	49.422	44.804	18.012	115.892	52.015	- 2.915
4000	5.213	49.554	44.921	18.531	115.964	50.376	- 2.752
4100	5.245	49.683	45.036	19.054	116.038	48.735	- 2.598
4200	5.278	49.810	45.148	19.580	116.116	47.094	- 2.450
4300	5.314	49.934	45.258	20.110	116.196	45.449	- 2.310
4400	5.351	50.057	45.365	20.643	116.280	43.803	- 2.176
4500	5.390	50.178	45.471	21.180	116.367	42.154	- 2.047
4600	5.431	50.297	45.575	21.721	116.458	40.505	- 1.924
4700	5.473	50.414	45.676	22.266	116.552	38.853	- 1.807
4800	5.517	50.530	45.776	22.816	116.651	37.199	- 1.694
4900	5.562	50.644	45.874	23.370	116.753	35.542	- 1.585
5000	5.608	50.757	45.971	23.928	116.860	33.883	- 1.481
5100	5.655	50.868	46.066	24.491	116.971	32.222	- 1.381
5200	5.703	50.978	46.159	25.059	117.087	30.560	- 1.284
5300	5.751	51.087	46.251	25.632	117.207	28.894	- 1.191
5400	5.800	51.195	46.342	26.210	117.332	27.228	- 1.102
5500	5.850	51.302	46.431	26.792	117.461	25.557	- 1.016
5600	5.900	51.408	46.519	27.380	117.595	23.884	- .932
5700	5.950	51.513	46.606	27.972	117.734	22.211	- .852
5800	6.000	51.617	46.691	28.570	117.878	20.534	- .774
5900	6.050	51.720	46.775	29.172	118.026	18.853	- .698
6000	6.100	51.822	46.859	29.780	118.179	17.172	- .625

March 31, 1961

NITROGEN, MONATOMIC (N) (IDEAL GAS) AT. WT. = 14.008

$\Delta H^\circ_{f0} = 112.5 \pm 1$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 113.0 \pm 1$ kcal. mole^{-1}

Ground State Configuration $^4S^\circ_{3/2}$

$S^\circ_{298.15} = 36.61 \pm 0.01$ cal. deg. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i	g_i	ϵ_i	g_i	ϵ_i	g_i
0	4	94,883.1	8	104,654.9	2
19,223.9	6	95,476.5	2	104,665	4
19,223.1	4	95,494.9	4	104,684	6
28,840	5	95,533.2	6	104,718	8
83,285.5	2	96,751.7	4	104,767	10
83,319.3	4	96,788.2	4	104,810.9	6
83,366	6	96,864.2	6	104,882.7	8
86,131.4	2	97,770.1	2	105,845	76
86,223.2	4	97,805.8	4	110,091.1	90
88,109.5	6	99,663	9	111,849.3	84
88,153.4	4	103,618.1	2	113,144.5	80
93,582.3	2	103,668.1	4	114,288	102
94,772.2	2	103,736.8	6	115,214.5	112
94,794.8	4	104,142.2	2	115,808	116
94,832.1	6	104,227.4	4	116,200	98
88,173	2	104,615.4	4	116,450	96

Heat of Formation

The dissociation energy of N_2 has been the subject of considerable controversy and is presented by A. G. Gaydon, "Dissociation Energies", Chapman and Hall, London, 1953. L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem., 7, 259 (1956), discuss extensive and varied experiments which have now fixed the value of 9.76 e.v. as being highly probable. Additional support for this value is afforded by the recently observed predissociation in the x $^1\Sigma^-_g$ state by A. Loftus, Nature 186, 302 (1960).

Heat Capacities and Entropies

The electronic levels noted above are listed by C. E. Moore, Nat. Bur. Standards (U.S.) Circ. 467, Vol. I (1949), Vol. III (1958).

Nitric Oxide (NO)

(Ideal Gas) Mol. Wt. = 30.008

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.197	21.456	21.456	INFINITE
100	7.721	42.286	56.801	-1.451	21.503	21.256	-46.453
200	7.271	47.477	51.003	-.705	21.558	20.984	-22.929
298	7.133	50.347	50.347	.000	21.580	20.697	-15.171
300	7.132	50.392	50.348	.013	21.580	20.692	-15.073
400	7.157	52.444	50.627	.727	21.590	20.394	-11.142
500	7.287	54.053	51.157	1.448	21.594	20.095	-8.783
600	7.466	55.397	51.755	2.186	21.598	19.795	-7.210
700	7.655	56.562	52.360	2.942	21.601	19.494	-6.086
800	7.832	57.596	52.951	3.716	21.605	19.192	-5.243
900	7.988	58.528	53.520	4.507	21.610	18.890	-4.587
1000	8.123	59.377	54.064	5.313	21.615	18.588	-4.062
1100	8.238	60.157	54.583	6.131	21.620	18.285	-3.633
1200	8.336	60.878	55.078	6.960	21.624	17.981	-3.275
1300	8.419	61.548	55.550	7.798	21.628	17.678	-2.972
1400	8.491	62.175	56.001	8.644	21.631	17.373	-2.712
1500	8.552	62.763	56.432	9.496	21.633	17.069	-2.487
1600	8.605	63.317	56.845	10.354	21.635	16.765	-2.290
1700	8.651	63.840	57.242	11.217	21.635	16.461	-2.116
1800	8.692	64.335	57.622	12.084	21.633	16.156	-1.962
1900	8.727	64.806	57.988	12.955	21.630	15.853	-1.823
2000	8.759	65.255	58.340	13.829	21.626	15.548	-1.699
2100	8.788	65.683	58.680	14.706	21.619	15.244	-1.586
2200	8.813	66.092	59.007	15.587	21.611	14.941	-1.484
2300	8.837	66.484	59.324	16.469	21.601	14.637	-1.391
2400	8.858	66.861	59.630	17.354	21.589	14.336	-1.305
2500	8.877	67.223	59.927	18.241	21.574	14.033	-1.227
2600	8.895	67.571	60.214	19.129	21.558	13.732	-1.154
2700	8.912	67.908	60.493	20.020	21.540	13.432	-1.087
2800	8.927	68.232	60.763	20.911	21.520	13.132	-1.025
2900	8.941	68.545	61.026	21.805	21.498	12.834	-.967
3000	8.955	68.849	61.282	22.700	21.474	12.535	-.913
3100	8.968	69.143	61.531	23.596	21.449	12.237	-.863
3200	8.980	69.427	61.773	24.493	21.421	11.940	-.815
3300	8.991	69.704	62.010	25.392	21.392	11.644	-.771
3400	9.002	69.973	62.240	26.291	21.361	11.349	-.729
3500	9.012	70.234	62.464	27.192	21.329	11.054	-.690
3600	9.022	70.488	62.684	28.094	21.294	10.762	-.653
3700	9.032	70.735	62.898	28.997	21.259	10.470	-.618
3800	9.041	70.976	63.108	29.900	21.222	10.179	-.585
3900	9.050	71.211	63.312	30.805	21.185	9.889	-.554
4000	9.058	71.440	63.513	31.710	21.145	9.598	-.524
4100	9.066	71.664	63.709	32.616	21.104	9.311	-.496
4200	9.074	71.882	63.901	33.523	21.063	9.024	-.470
4300	9.082	72.096	64.089	34.431	21.021	8.739	-.444
4400	9.090	72.305	64.273	35.340	20.977	8.452	-.420
4500	9.097	72.509	64.454	36.249	20.932	8.169	-.397
4600	9.105	72.709	64.631	37.159	20.887	7.888	-.375
4700	9.112	72.905	64.805	38.070	20.841	7.605	-.354
4800	9.119	73.097	64.976	38.982	20.794	7.324	-.333
4900	9.125	73.285	65.144	39.894	20.747	7.040	-.314
5000	9.132	73.470	65.308	40.807	20.699	6.763	-.296
5100	9.139	73.651	65.470	41.720	20.650	6.484	-.278
5200	9.145	73.828	65.629	42.634	20.601	6.207	-.261
5300	9.152	74.002	65.786	43.549	20.551	5.932	-.245
5400	9.158	74.173	65.939	44.465	20.501	5.654	-.229
5500	9.164	74.342	66.091	45.381	20.451	5.383	-.214
5600	9.170	74.507	66.239	46.298	20.400	5.107	-.199
5700	9.176	74.669	66.386	47.215	20.348	4.835	-.185
5800	9.182	74.829	66.530	48.133	20.297	4.566	-.172
5900	9.188	74.986	66.672	49.051	20.245	4.292	-.159
6000	9.194	75.140	66.812	49.970	20.192	4.024	-.147

Dec. 31, 1960; June 30, 1963

NITRIC OXIDE (NO) (IDEAL GAS) MOL. WT. = 30.008

Ground State Configuration $^2\Pi$

$\Delta H_{f\ 0}^\circ = 21.46 \pm 0.04$ kcal. mole^{-1}

$S^\circ_{298.15} = 50.347$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 21.58 \pm 0.04$ kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1
0	2
121.1	2

$\omega_e = 1903.60$ cm.$^{-1}$

$\omega_e x_e = 13.97$ cm.$^{-1}$

$\sigma = 1$

$B_e = 1.7042$ cm.$^{-1}$

$\alpha_e = 0.0178$ cm.$^{-1}$

$r_e = 1.1508$ Å

Heat of Formation.

G. Herzberg, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, D. van Nostrand Co., Inc., New York, 1950, lists two D_0(NO) values, 5.296 and 6.487 e.v. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, Ltd., London, 1953, lists D_0(NO) = 6.49 ± 0.05 e.v. A Birge-Sponer extrapolation of the vibrational levels, up to v = 18, of the ground state leads to a D_0 of about 6.5 e.v. Gaydon's, loc. cit., analysis on the predissociation of NO also leads to the higher value for D_0(NO).

Y. Tanaka, J. Chem. Phys. 22, 2045 (1954), has observed and analyzed the emmission bands of NO in the vacuum ultraviolet region. Tanaka's, loc. cit., observation and interpretation of the abrupt cutoff (predissociation) of certain v' values in the β, γ, and δ bands and of the complete non appearance of ϵ and β' bands strongly favors a D_0(NO) = 6.48 e.v. $\Delta H^\circ_{f\ 298.15}$(NO)g was calculated on this basis to be 22.033 ± 1 kcal. mole^{-1}.

More recently M. A. Frisch, Diss. Absts. 23, 1940 (1961), Thesis, University of Wisconsin, Madison, Wisconsin, 1962, has calorimetrically determined the heat of reaction for:

$$NO(g) + CO(g) \rightarrow CO_2(g) + 1/2N_2(g)$$

at 298.15°K., from which the author derives a $\Delta H^\circ_{f\ 298.15}$ NO(g) = 21.58 ± 0.04 kcal. mole^{-1}. The auxiliary values used by Frisch to calculate the heat of formation of nitric oxide were based upon the 1961 atomic weight scale. Recalculating $\Delta H^\circ_{f\ 298.15}$ NO(g) using auxiliary functions based on the 1956 atomic weight scale had a negligible effect on the final result.

The calorimetrically determined heat of formation for nitric oxide, 21.58 ± 0.04 kcal. mole^{-1}, was selected as the best value.

Heat Capacity and Entropy.

The spectroscopic constants were taken from R. H. Gillette and E. H. Eyster, Phys. Revs. 56, 1113 (1939), who measured and analyzed the fundamental rotation-vibration band of nitric oxide using a grating spectrometer. The constants used in this calculation were adjusted to correspond to the naturally occurring isotopic mixture.

Nitric Oxide Unipositive Ion (NO^+)

(Ideal Gas) GFW = 30.00555

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.961	47.349	47.349	.000	236.660	235.184	-172.395
300	6.961	47.392	47.349	.013	236.669	235.175	-171.324
400	6.989	49.397	47.622	.710	237.159	234.603	-128.181
500	7.067	50.964	48.139	1.412	237.641	233.908	-102.241
600	7.191	52.263	48.721	2.125	238.117	233.117	-84.913
700	7.344	53.383	49.309	2.852	238.587	232.245	-72.510
800	7.505	54.374	49.881	3.594	239.056	231.307	-63.190
900	7.662	55.267	50.431	4.353	239.525	230.311	-55.927
1000	7.807	56.082	50.956	5.126	239.995	229.262	-50.105
1100	7.938	56.832	51.456	5.913	240.466	228.166	-45.332
1200	8.054	57.528	51.934	6.713	240.938	227.028	-41.347
1300	8.156	58.177	52.389	7.524	241.411	225.848	-37.968
1400	8.245	58.784	52.825	8.344	241.885	224.634	-35.067
1500	8.323	59.356	53.241	9.172	242.361	223.384	-32.547
1600	8.392	59.895	53.640	10.008	242.837	222.104	-30.338
1700	8.452	60.406	54.023	10.850	243.314	220.794	-28.385
1800	8.506	60.891	54.392	11.698	243.789	219.454	-26.645
1900	8.553	61.352	54.746	12.551	244.265	218.091	-25.086
2000	8.595	61.792	55.087	13.409	244.740	216.700	-23.680
2100	8.633	62.212	55.417	14.270	245.215	215.286	-22.405
2200	8.667	62.614	55.735	15.135	245.688	213.851	-21.244
2300	8.697	63.000	56.042	16.004	246.160	212.391	-20.182
2400	8.725	63.371	56.340	16.875	246.632	210.915	-19.206
2500	8.750	63.728	56.628	17.749	247.101	209.415	-18.307
2600	8.774	64.071	56.908	18.625	247.570	207.900	-17.476
2700	8.795	64.403	57.180	19.503	248.037	206.366	-16.704
2800	8.814	64.723	57.443	20.384	248.502	204.814	-15.986
2900	8.832	65.033	57.700	21.266	248.965	203.246	-15.317
3000	8.849	65.332	57.949	22.150	249.428	201.662	-14.691
3100	8.865	65.623	58.192	23.036	249.889	200.059	-14.104
3200	8.879	65.905	58.429	23.923	250.348	198.446	-13.553
3300	8.893	66.178	58.659	24.812	250.806	196.818	-13.035
3400	8.906	66.444	58.884	25.702	251.261	195.175	-12.546
3500	8.918	66.702	59.104	26.593	251.716	193.518	-12.084
3600	8.929	66.953	59.319	27.485	252.170	191.852	-11.647
3700	8.940	67.198	59.528	28.379	252.622	190.166	-11.233
3800	8.951	67.437	59.733	29.273	253.073	188.473	-10.840
3900	8.961	67.669	59.934	30.169	253.524	186.769	-10.466
4000	8.970	67.896	60.130	31.065	253.971	185.049	-10.111
4100	8.979	68.118	60.322	31.963	254.419	183.319	-9.772
4200	8.988	68.334	60.510	32.861	254.866	181.584	-9.449
4300	8.996	68.546	60.695	33.760	255.312	179.834	-9.140
4400	9.004	68.753	60.876	34.660	255.756	178.072	-8.845
4500	9.012	68.955	61.053	35.561	256.199	176.302	-8.562
4600	9.019	69.154	61.227	36.463	256.643	174.521	-8.292
4700	9.026	69.348	61.398	37.365	257.085	172.729	-8.032
4800	9.033	69.538	61.565	38.268	257.526	170.930	-7.783
4900	9.040	69.724	61.730	39.172	257.968	169.121	-7.543
5000	9.047	69.907	61.892	40.076	258.407	167.304	-7.313
5100	9.053	70.086	62.050	40.981	258.846	165.476	-7.091
5200	9.060	70.262	62.207	41.887	259.286	163.642	-6.878
5300	9.066	70.434	62.360	42.793	259.725	161.802	-6.672
5400	9.072	70.604	62.511	43.700	260.163	159.945	-6.473
5500	9.078	70.770	62.660	44.607	260.601	158.092	-6.282
5600	9.084	70.934	62.806	45.515	261.037	156.216	-6.097
5700	9.089	71.095	62.950	46.424	261.474	154.346	-5.918
5800	9.095	71.253	63.092	47.333	261.911	152.462	-5.745
5900	9.100	71.409	63.232	48.243	262.347	150.566	-5.577
6000	9.106	71.562	63.369	49.153	262.783	148.672	-5.415

June 30, 1966

NITRIC OXIDE UNIPOSITIVE ION (NO^+) (IDEAL GAS) GFW = 30.00555

Ground State $^1\Sigma^+$

ΔHf°_0 = 235.18 ± 0.2 kcal/mol

$S^\circ_{298.15}$ = 47.35 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 236.66 ± 0.2 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1

ω_e = 2377.1 cm^{-1}

$\omega_e x_e$ = 16.35 cm^{-1}

σ = 1

B_e = 2.002 cm^{-1}

α_e = 0.0202 cm^{-1}

r_e = 1.0619 Å

Heat of Formation.

K. Watanabe, J. Chem. Phys. 22, 1564 (1954), and W. C. Walker and G. L. Weissler, J. Chem. Phys. 23, 1962 (1955), have measured the ionization potential of NO(g) by photoionization, yielding I.P. = 9.25 ± 0.02 and 9.20 ± 0.03 eV, respectively. H. D. Hagstrum, J. Chem. Phys. 23, 1178 (1955), reported I.P. = 9.4 ± 0.2 eV by electron impact. K. P. Huber, Helv. Phys. Acta 34, 929 (1961), determined spectroscopcially the ionization potential for NO(g), I.P. = 9.267 ± 0.005 eV (213.72 ± 0.1 kcal/mol). The last value has been selected, and yields the heat of formation of NO^+(g), ΔHf°_0 (NO^+, g) = 235.18 kcal/mol, using ΔHf°_0 (NO, g) = 21.46 ± 0.04 kcal/mol.

Heat Capacity and Entropy.

The selected molecular constants were obtained from the ultraviolet spectra by E. Miescher, Can. J. Phys. 33, 355 (1955), Helv. Phys. Acta 29, 135 (1956).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by J. Hilsenrath and Carla G. Messina, NBS Report 8504, July 1, 1964, who have used slightly different molecular constants.

Nitrogen Dioxide (NO_2)

(Ideal Gas) Mol. Wt. = 46.008

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.435	8.586	8.586	INFINITE
100	7.953	48.387	64.785	-1.640	8.326	9.545	-20.859
200	8.218	53.954	58.130	-.835	8.099	10.853	-11.859
298	8.837	57.343	57.343	.000	7.910	12.247	-8.977
300	8.850	57.398	57.344	.016	7.907	12.274	-8.941
400	9.601	60.046	57.700	.939	7.770	13.751	-7.513
500	10.327	62.268	58.397	1.936	7.684	15.258	-6.669
600	10.955	64.208	59.207	3.001	7.638	16.778	-6.111
700	11.469	65.937	60.047	4.123	7.618	18.302	-5.714
800	11.881	67.496	60.882	5.291	7.617	19.828	-5.417
900	12.208	68.915	61.697	6.496	7.629	21.355	-5.185
1000	12.468	70.215	62.485	7.730	7.649	22.879	-5.000
1100	12.677	71.414	63.243	8.988	7.674	24.400	-4.848
1200	12.847	72.524	63.971	10.265	7.702	25.921	-4.721
1300	12.985	73.558	64.669	11.556	7.731	27.438	-4.612
1400	13.099	74.525	65.339	12.861	7.761	28.951	-4.519
1500	13.193	75.432	65.982	14.176	7.790	30.464	-4.438
1600	13.273	76.286	66.599	15.499	7.818	31.975	-4.367
1700	13.340	77.093	67.193	16.830	7.846	33.484	-4.304
1800	13.398	77.857	67.764	18.167	7.869	34.992	-4.248
1900	13.447	78.583	68.315	19.509	7.890	36.498	-4.198
2000	13.490	79.274	68.846	20.856	7.908	38.002	-4.152
2100	13.527	79.933	69.358	22.207	7.923	39.507	-4.111
2200	13.560	80.563	69.853	23.561	7.932	41.010	-4.074
2300	13.588	81.166	70.332	24.919	7.939	42.514	-4.040
2400	13.614	81.745	70.796	26.279	7.942	44.019	-4.008
2500	13.636	82.301	71.245	27.641	7.939	45.520	-3.979
2600	13.656	82.836	71.680	29.006	7.933	47.025	-3.953
2700	13.674	83.352	72.103	30.373	7.922	48.529	-3.928
2800	13.690	83.850	72.514	31.741	7.907	50.031	-3.905
2900	13.705	84.330	72.913	33.111	7.888	51.540	-3.884
3000	13.718	84.795	73.301	34.482	7.863	53.045	-3.864
3100	13.730	85.245	73.679	35.854	7.836	54.551	-3.846
3200	13.741	85.681	74.048	37.228	7.803	56.058	-3.828
3300	13.751	86.104	74.407	38.602	7.767	57.565	-3.812
3400	13.760	86.515	74.757	39.978	7.726	59.075	-3.797
3500	13.768	86.914	75.099	41.354	7.683	60.583	-3.783
3600	13.776	87.302	75.432	42.731	7.635	62.097	-3.770
3700	13.783	87.679	75.758	44.109	7.584	63.613	-3.757
3800	13.790	88.047	76.077	45.488	7.529	65.128	-3.746
3900	13.796	88.405	76.388	46.867	7.473	66.643	-3.734
4000	13.801	88.755	76.693	48.247	7.412	68.158	-3.724
4100	13.806	89.096	76.991	49.627	7.347	69.678	-3.714
4200	13.811	89.428	77.284	51.008	7.281	71.201	-3.705
4300	13.816	89.753	77.570	52.390	7.213	72.727	-3.696
4400	13.820	90.071	77.850	53.771	7.140	74.247	-3.688
4500	13.824	90.382	78.125	55.154	7.066	75.772	-3.680
4600	13.828	90.686	78.395	56.536	6.990	77.304	-3.673
4700	13.831	90.983	78.660	57.919	6.911	78.833	-3.666
4800	13.834	91.274	78.920	59.302	6.830	80.366	-3.659
4900	13.837	91.559	79.175	60.686	6.748	81.894	-3.652
5000	13.840	91.839	79.425	62.070	6.663	83.428	-3.646
5100	13.843	92.113	79.671	63.454	6.577	84.966	-3.641
5200	13.846	92.382	79.913	64.838	6.489	86.501	-3.635
5300	13.848	92.646	80.151	66.223	6.400	88.044	-3.630
5400	13.850	92.905	80.385	67.608	6.309	89.579	-3.625
5500	13.852	93.159	80.615	68.993	6.217	91.128	-3.621
5600	13.854	93.408	80.841	70.379	6.122	92.673	-3.617
5700	13.856	93.654	81.063	71.764	6.027	94.215	-3.612
5800	13.858	93.895	81.283	73.150	5.931	95.767	-3.608
5900	13.860	94.132	81.498	74.536	5.833	97.313	-3.605
6000	13.862	94.365	81.711	75.922	5.734	98.866	-3.601

Dec. 31, 1960; June 30, 1963; Sept. 30, 1964

NITROGEN DIOXIDE (NO_2) (IDEAL GAS) MOL. WT. = 46.008

Point Group C_{2v}

$\Delta H_{f\ 0}^\circ = 8.59 \pm 0.2$ kcal. mole^{-1}

$S_{298.15}^\circ = 57.34 \pm 0.03$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = 7.91 \pm 0.2$ kcal. mole^{-1}

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1357.8 (1)
756.8 (1)
1665.5 (1)

Bond Distance: N-O = 1.197Å

Bond Angle: O-N-O = 134° 15′

$\sigma = 2$

Product of the Moments of Inertia: $I_A I_B I_C = 15.3983 \times 10^{-117}$ g.^{3} cm.^{6}

Heat of Formation.

The equilibrium constants for $NO(g) + 1/2\ O_2 \rightarrow NO_2(g)$ of Bodenstein and Lindner, Zeits. fur physik. Chem. 100, 82 (1922) as given by W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) were subjected to 2nd and 3rd law analysis. Third law analysis gave $\Delta H_{298} = -13.67$ kcal. and 2nd law $\Delta H_{298}^\circ = -13.52 \pm 0.01$ kcal. The third law value had a very slight trend with temperature which was consistent with an entropy error of 0.25 cal. deg.$^{-1}$ mole^{-1}, the second law entropy was also consistent with an entropy error of 0.25 cal. deg.$^{-1}$ mole^{-1}. However the functions for all three gases are well established to about 0.03 cal. deg.$^{-1}$ mole^{-1} or better and so this must be interpreted as due to errors in the data. On this basis the 3rd law value of the heat was chosen and combined with JANAF auxiliary data to give $\Delta H_{f\ 298}^\circ$ = 7.91 ± 0.2 kcal. mole^{-1}, where the uncertainty includes that due to the possible error in the equilibrium constants.

Heat Capacity and Entropy.

G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl Jr., A. C. Kunkle, J. W. Bransford, J. Rastrup-Andersen and J. Rosenthal, J. Chem. Phys. 40, 3378 (1964) have given a complete review of the microwave spectrum of NO_2. They also give a corrected infra-red vibrational assignment, adopted here, which is in excellent agreement with calculations from the microwave data. They report $I_A = 0.34981 \times 10^{-39}$ g. cm.^{2} and $I_B = 6.45446 \times 10^{-39}$ g. cm.^{2} and $I_C = 6.81994 \times 10^{-39}$ g. cm.^{2} The bond length and angle were chosen to give the best fit of the moments of inertia.

Nitrogen Dioxide Uninegative Ion (NO_2^-)

(Ideal Gas) Mol. Wt. = 46.00605

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	9.016	56.517	56.517	.000	-85.850	-79.780	58.477
300	9.033	56.573	56.517	.017	-85.862	-79.742	58.089
400	9.951	59.298	56.882	.966	-86.469	-77.609	42.401
500	10.766	61.609	57.602	2.003	-87.011	-75.330	32.925
600	11.412	63.631	58.442	3.114	-87.509	-72.945	26.569
700	11.905	65.429	59.314	4.281	-87.980	-70.480	22.004
800	12.279	67.044	60.181	5.491	-88.436	-67.950	18.562
900	12.564	68.508	61.026	6.733	-88.884	-65.363	15.871
1000	12.785	69.844	61.842	8.001	-89.327	-62.725	13.708
1100	12.958	71.071	62.626	9.289	-89.770	-60.044	11.929
1200	13.095	72.204	63.378	10.592	-90.212	-57.322	10.439
1300	13.206	73.257	64.098	11.907	-90.656	-54.562	9.172
1400	13.296	74.239	64.787	13.232	-91.102	-51.770	8.081
1500	13.370	75.159	65.448	14.566	-91.551	-48.945	7.131
1600	13.432	76.024	66.083	15.906	-92.003	-46.089	6.295
1700	13.483	76.840	66.692	17.251	-92.458	-43.206	5.554
1800	13.528	77.612	67.277	18.602	-92.916	-40.295	4.892
1900	13.565	78.344	67.840	19.957	-93.380	-37.359	4.297
2000	13.598	79.041	68.383	21.315	-93.848	-34.400	3.759
2100	13.626	79.705	68.907	22.676	-94.320	-31.414	3.269
2200	13.650	80.339	69.412	24.040	-94.798	-28.408	2.822
2300	13.672	80.946	69.900	25.406	-95.278	-25.378	2.411
2400	13.691	81.529	70.373	26.774	-95.765	-22.330	2.033
2500	13.708	82.088	70.830	28.144	-96.257	-19.261	1.684
2600	13.723	82.626	71.274	29.516	-96.753	-16.170	1.359
2700	13.736	83.144	71.704	30.889	-97.255	-13.062	1.057
2800	13.748	83.644	72.121	32.263	-97.761	-9.935	.775
2900	13.759	84.126	72.527	33.638	-98.271	-6.786	.511
3000	13.769	84.593	72.922	35.015	-98.787	-3.622	.264
3100	13.778	85.045	73.305	36.392	-99.306	-.443	.031
3200	13.786	85.482	73.679	37.770	-99.831	2.753	-.188
3300	13.793	85.907	74.043	39.149	-100.360	5.964	-.395
3400	13.800	86.318	74.398	40.529	-100.893	9.198	-.591
3500	13.806	86.719	74.745	41.909	-101.429	12.438	-.777
3600	13.812	87.108	75.083	43.290	-101.971	15.701	-.953
3700	13.817	87.486	75.413	44.671	-102.515	18.982	-1.121
3800	13.822	87.855	75.735	46.053	-103.063	22.270	-1.281
3900	13.826	88.214	76.051	47.436	-103.614	25.574	-1.433
4000	13.830	88.564	76.359	48.819	-104.168	28.894	-1.579
4100	13.834	88.905	76.661	50.202	-104.726	32.232	-1.718
4200	13.838	89.239	76.956	51.585	-105.287	35.573	-1.851
4300	13.841	89.564	77.246	52.969	-105.850	38.940	-1.979
4400	13.844	89.883	77.530	54.354	-106.416	42.306	-2.101
4500	13.847	90.194	77.808	55.738	-106.984	45.696	-2.219
4600	13.850	90.498	78.080	57.123	-107.555	49.100	-2.333
4700	13.852	90.796	78.347	58.508	-108.129	52.510	-2.442
4800	13.855	91.088	78.610	59.893	-108.705	55.935	-2.547
4900	13.857	91.373	78.867	61.279	-109.282	59.366	-2.648
5000	13.859	91.653	79.120	62.665	-109.861	62.814	-2.745
5100	13.861	91.928	79.369	64.051	-110.443	66.275	-2.840
5200	13.863	92.197	79.613	65.437	-111.025	69.742	-2.931
5300	13.865	92.461	79.853	66.823	-111.610	73.230	-3.020
5400	13.866	92.720	80.089	68.210	-112.197	76.720	-3.105
5500	13.868	92.975	80.321	69.597	-112.784	80.225	-3.188
5600	13.870	93.225	80.549	70.984	-113.373	83.739	-3.268
5700	13.871	93.470	80.773	72.371	-113.963	87.261	-3.346
5800	13.872	93.711	80.994	73.758	-114.555	90.805	-3.421
5900	13.874	93.948	81.212	75.145	-115.148	94.349	-3.495
6000	13.875	94.182	81.426	76.533	-115.743	97.899	-3.566

Dec. 31, 1965

NITROGEN DIOXIDE UNINEGATIVE ION (NO_2^-) (IDEAL GAS) MOL. WT. = 46.00605

Point Group C_{2v}

$S^\circ_{298.15}$ = [56.5] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = -83.7 ± 12 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -85.9 ± 12 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$

[1320] (1)
[750] (1)
[1220] (1)

Bond Distance: N-O = [1.23] Å

Bond Angle: O-N-O = [116]°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [25.6905] X 10^{-117} g.^{3} cm.^{6}

Heat of Formation.

The heat of formation of $NO_2^-(g)$ was calculated from the electron affinity of $NO_2(g)$ and the JANAF value of $\Delta H^\circ_{f\ 0}$ for $NO_2(g)$, 4.0 ± 0.5 ev and 8.6 ± 0.2 kcal. mole^{-1}, respectively. The former was obtained from the National Bureau of Standards Report 8628, "Preliminary Report on the Thermodynamic Properties of Selected Light Element and Some Related Compounds", January 1965.

Heat Capacity and Entropy.

The bond distance N-O and the angle O-N-O of $NO_2^-(g)$ were estimated to be the same as those in $NaNO_2(c)$ which have been determined by G. B. Carpenter, Acta Cryst. 5, 132(1952). The three individual moments of inertia are I_A =[0.6872] X 10^{-39}g. cm.^{2}, I_B =[5.7804] X 10^{-39} g. cm.^{2} and I_C =[6.4676] X 10^{-39} g. cm.^{2}

The vibrational frequencies of $NO_2^-(g)$ were assumed to be the same as those for nitrite ion in solution which have been measured by D. Williams, J. Am. Chem. Soc. 61, 2987(1939). These measured frequencies in nitrite solution are comparable to those in $NO_2(g)$ (1357.8, 756.8 and 1665.5 cm.$^{-1}$), reported by G. R. Bird et al., J. Chem. Phys. 40, 3378 (1964).

Nitrogen Trioxide (NO_3)
(Ideal Gas) Mol. Wt. = 62.008

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.619	18.529	18.529	INFINITE
100	7.970	50.613	68.855	-1.824	17.912	20.985	-45.860
200	9.020	56.354	61.305	-.990	17.375	24.272	-26.522
298	11.218	60.352	60.352	.000	17.000	27.745	-20.337
300	11.260	60.422	60.353	.021	16.995	27.811	-20.260
400	13.368	63.961	60.821	1.256	16.815	31.449	-17.182
500	14.962	67.125	61.771	2.677	16.788	35.113	-15.347
600	16.105	69.960	62.904	4.233	16.856	38.774	-14.123
700	16.920	72.507	64.097	5.887	16.978	42.417	-13.243
800	17.511	74.807	65.294	7.610	17.133	46.040	-12.577
900	17.949	76.896	66.469	9.384	17.307	49.644	-12.055
1000	18.279	78.805	67.609	11.196	17.491	53.228	-11.632
1100	18.533	80.559	68.707	13.037	17.680	56.792	-11.283
1200	18.732	82.181	69.763	14.901	17.871	60.339	-10.989
1300	18.891	83.687	70.777	16.782	18.061	63.870	-10.737
1400	19.019	85.092	71.750	18.678	18.251	67.386	-10.519
1500	19.124	86.407	72.684	20.585	18.437	70.890	-10.328
1600	19.211	87.644	73.581	22.502	18.620	74.382	-10.160
1700	19.284	88.811	74.443	24.427	18.801	77.862	-10.009
1800	19.346	89.915	75.272	26.359	18.974	81.331	-9.874
1900	19.398	90.963	76.070	28.296	19.142	84.790	-9.753
2000	19.443	91.959	76.840	30.238	19.306	88.240	-9.642
2100	19.482	92.909	77.583	32.184	19.463	91.682	-9.541
2200	19.516	93.816	78.300	34.134	19.612	95.117	-9.449
2300	19.546	94.684	78.994	36.087	19.757	98.546	-9.364
2400	19.572	95.516	79.665	38.043	19.894	101.972	-9.285
2500	19.595	96.316	80.315	40.002	20.023	105.385	-9.212
2600	19.616	97.085	80.945	41.962	20.147	108.798	-9.145
2700	19.634	97.825	81.557	43.925	20.263	112.208	-9.082
2800	19.651	98.540	82.151	45.889	20.373	115.609	-9.023
2900	19.666	99.230	82.728	47.855	20.475	119.010	-8.968
3000	19.679	99.897	83.289	49.822	20.571	122.406	-8.917
3100	19.691	100.542	83.835	51.791	20.661	125.800	-8.868
3200	19.702	101.167	84.367	53.760	20.743	129.190	-8.823
3300	19.712	101.774	84.886	55.731	20.820	132.575	-8.780
3400	19.721	102.362	85.391	57.703	20.890	135.963	-8.739
3500	19.730	102.934	85.884	59.675	20.956	139.343	-8.701
3600	19.738	103.490	86.365	61.649	21.015	142.728	-8.664
3700	19.745	104.031	86.836	63.623	21.069	146.107	-8.630
3800	19.751	104.558	87.295	65.598	21.119	149.487	-8.597
3900	19.757	105.071	87.744	67.573	21.164	152.861	-8.566
4000	19.763	105.571	88.184	69.549	21.203	156.237	-8.536
4100	19.768	106.059	88.614	71.526	21.238	159.615	-8.508
4200	19.773	106.536	89.035	73.503	21.269	162.986	-8.481
4300	19.778	107.001	89.447	75.480	21.297	166.366	-8.455
4400	19.782	107.456	89.851	77.458	21.319	169.734	-8.430
4500	19.786	107.900	90.248	79.437	21.339	173.110	-8.407
4600	19.790	108.335	90.636	81.416	21.356	176.488	-8.385
4700	19.793	108.761	91.017	83.395	21.368	179.856	-8.363
4800	19.796	109.177	91.391	85.374	21.378	183.234	-8.342
4900	19.799	109.586	91.758	87.354	21.385	186.593	-8.322
5000	19.802	109.986	92.119	89.334	21.389	189.967	-8.303
5100	19.805	110.378	92.473	91.314	21.390	193.342	-8.285
5200	19.808	110.763	92.821	93.295	21.390	196.708	-8.267
5300	19.810	111.140	93.163	95.276	21.387	200.087	-8.250
5400	19.812	111.510	93.500	97.257	21.382	203.453	-8.234
5500	19.815	111.874	93.830	99.238	21.375	206.830	-8.218
5600	19.817	112.231	94.156	101.220	21.365	210.197	-8.203
5700	19.819	112.582	94.476	103.202	21.354	213.567	-8.188
5800	19.820	112.926	94.791	105.184	21.342	216.950	-8.174
5900	19.822	113.265	95.101	107.166	21.327	220.317	-8.161
6000	19.824	113.598	95.407	109.148	21.311	223.694	-8.148

Dec. 31, 1964

NITROGEN TRIOXIDE (NO_3) (IDEAL GAS) MOL. WT. = 62.008

Point Group [D_{3h}]

$\Delta H_f^\circ{}_0$ = 18.5 ± 5 kcal. mole^{-1}

$S^\circ_{298.15}$ = [60.4] cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15}$ = 17.0 ± 5 kcal. mole^{-1}

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
[1158] (2)
[940] (1)
[704] (2)
[765] (1)

Bond Distance: O-N = [1.27] Å

Bond Angle: O-N-O = [120°]

σ = [6]

Product of the Moments of Inertia: $I_AI_BI_C$ = [5.309 X 10^{-115}] g.^{3} cm.^{6}

Heat of Formation.

The heat of formation is based on equilibrium constants for the reaction $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ obtained from shock wave studies by Schott and Davidson, J. Am. Chem. Soc. 80, 1941 (1958). These equilibria give a second law value of $\Delta H_r^\circ{}_{495}$ = 21.5 ± 1.4 kcal., corresponding to $\Delta H_r^\circ{}_{298.15}$ = 22.2 kcal., and a third law value of $\Delta H_r^\circ{}_{298.15}$ = 22.2 kcal. The resulting heat of formation is 17.0 kcal. mole^{-1}.

Guillory and Johnston, J. Am. Chem. Soc. 85, 1695 (1963) report an equilibrium constant based on estimated Beer's law constants for NO_3 and attributed to the reaction $O_2 + NO \rightarrow NO_3$. This gives a third law heat of formation of 12 ± 2 kcal. mole^{-1}, which was not considered. A tentative value of 23 kcal. mole^{-1} (or greater) may be derived from the D_0 given by D. A. Ramsay, Proc. 10th Colloq. Spect. Intnl. (1962), Univ. Maryland, pp. 583-596, 1963.

Heat Capacity and Entropy.

The structure and frequencies are those estimated by I. C. Hisatsune, J. Phys. Chem. 65, 2249 (1961). A symmetry of D_{3h} was chosen on the basis of Walsh's correlation, J. Chem. Soc. 1953, 2301 (1953) and the bond distance was taken as 2% longer than in the nitrate ion. The planar mode frequencies were calculated from estimated Urey-Bradley force constants, while the out-of-plane wagging frequency (765 cm.$^{-1}$) was assumed the same as in $HNO_3(g)$.

There are several conflicting bits of information concerning NO_3 radicals. Chantry, Horsefield, Morton and Whiffen, Mol. Phys. 5,589 (1962) studied the electron resonance and optical absorption spectra of what appear to be NO_3 radicals trapped in crystals of urea nitrate. The authors suggest a planar structure without a threefold axis (thus C_s or C_{2v} symmetry), at least for the trapped radicals. Guillory and Johnston, loc. cit., report for gaseous NO_3 radicals an infrared frequency at 1840 cm.$^{-1}$ which they assign as the N-O stretch. The similarity of this frequency to those in N-O and X-N-O molecules led the authors to suggest an OONO structure (thus C_s symmetry) rather than the nitrate structure. The remaining frequencies for such a structure may be crudely estimated by analogy with those measured for $(NO)_2$ by Smith, Keller & Johnston, J. Chem. Phys. 19, 189 (1951). Based on such frequencies and reasonable bond distances, the room temperature entropy for the OONO structure would be 68-72 cal. deg.$^{-1}$ mole^{-1}. Such an entropy is quite inconsistent with the second law $\Delta S_r^\circ{}_{495}$ = 33.2 ± 3 cal. deg.$^{-1}$ mole^{-1} for $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ obtained from the shock wave studies of Schott and Davidson. The Hisatsune functions based on the nitrate structure were selected because they are consistent with the experimental entropy. The principal moments of inertia for this structure are I_A = 6.427 X 10^{-39}, I_B = 6.427 X 10^{-39} and I_C = 12.853 X 10^{-39} g. cm.^{2} A structure of C_{2v} symmetry would result if the nitrate structure were distorted to give one non-equivalent oxygen. Ramsay, loc. cit., suggests that such distortion can only be small, based on the high dispersion optical spectra of the gas phase.

Monophosphorus Mononitride (PN)

(Ideal Gas) Mol. Wt. = 44.983

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H_{298}^\circ)/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H_{298}^\circ$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.080	24.861	24.861	INFINITE
100	6.956	42.812	56.662	-1.385	25.122	22.896	-50.038
200	6.971	47.535	51.031	-.689	25.149	20.644	-22.558
298	7.096	50.437	50.437	.000	25.043	18.453	-13.526
300	7.100	50.491	50.437	.013	25.041	18.413	-13.413
400	7.355	52.556	50.718	.735	24.881	16.227	-8.865
500	7.636	54.229	51.256	1.485	24.708	14.082	-6.155
600	7.885	55.643	51.874	2.261	24.528	11.974	-4.361
700	8.088	56.874	52.502	3.060	24.330	9.896	-3.090
800	8.249	57.965	53.119	3.878	3.693	2.539	-.694
900	8.376	58.944	53.712	4.709	3.708	2.394	-.581
1000	8.476	59.832	54.281	5.552	3.725	2.246	-.491
1100	8.557	60.644	54.823	6.404	3.742	2.098	-.417
1200	8.623	61.392	55.339	7.263	3.758	1.947	-.355
1300	8.678	62.084	55.832	8.128	3.773	1.796	-.302
1400	8.723	62.729	56.302	8.998	3.788	1.643	-.257
1500	8.762	63.332	56.751	9.872	3.802	1.490	-.217
1600	8.794	63.899	57.180	10.750	3.815	1.335	-.182
1700	8.823	64.433	57.591	11.631	3.826	1.181	-.152
1800	8.848	64.938	57.985	12.515	3.837	1.024	-.124
1900	8.870	65.417	58.364	13.400	3.847	.869	-.100
2000	8.889	65.872	58.728	14.238	3.856	.710	-.078
2100	8.907	66.306	59.078	15.178	3.865	.553	-.058
2200	8.923	66.721	59.416	16.070	3.873	.396	-.039
2300	8.938	67.118	59.743	16.963	3.880	.236	-.022
2400	8.951	67.499	60.058	17.857	3.887	.077	-.007
2500	8.964	67.864	60.363	18.753	3.895	-.080	.007
2600	8.975	68.216	60.658	19.650	3.900	-.241	.020
2700	8.986	68.555	60.945	20.548	3.906	-.400	.032
2800	8.996	68.882	61.222	21.447	3.911	-.559	.044
2900	9.006	69.190	61.492	22.347	3.917	-.718	.054
3000	9.015	69.503	61.754	23.248	3.922	-.378	.064
3100	9.024	69.799	62.009	24.150	3.927	-1.038	.073
3200	9.032	70.083	62.257	25.053	3.931	-1.200	.082
3300	9.041	70.364	62.498	25.957	3.935	-1.359	.090
3400	9.048	70.624	62.733	26.861	3.939	-1.519	.098
3500	9.056	70.895	62.963	27.756	3.943	-1.680	.105
3600	9.063	71.151	63.187	28.672	3.946	-1.842	.112
3700	9.070	71.400	63.405	29.579	3.950	-2.003	.118
3800	9.077	71.642	63.619	30.486	3.953	-2.162	.124
3900	9.084	71.878	63.828	31.395	3.956	-2.322	.130
4000	9.090	72.106	64.032	32.303	3.959	-2.486	.136
4100	9.097	72.332	64.232	33.213	3.962	-2.647	.141
4200	9.103	72.552	64.427	34.123	3.964	-2.805	.146
4300	9.109	72.766	64.619	35.033	3.966	-2.969	.151
4400	9.116	72.975	64.806	35.945	3.969	-3.128	.155
4500	9.122	73.180	64.990	36.856	3.970	-3.290	.160
4600	9.127	73.381	65.170	37.769	3.973	-3.453	.164
4700	9.133	73.577	65.347	38.682	3.975	-3.614	.168
4800	9.139	73.769	65.520	39.595	3.975	-3.774	.172
4900	9.145	73.958	65.691	40.510	3.978	-3.936	.176
5000	9.150	74.143	65.858	41.424	3.979	-4.095	.179
5100	9.156	74.324	66.022	42.340	3.979	-4.260	.183
5200	9.161	74.502	66.184	43.256	3.981	-4.422	.186
5300	9.167	74.676	66.342	44.172	3.981	-4.583	.189
5400	9.172	74.848	66.498	45.089	3.982	-4.746	.192
5500	9.178	75.016	66.651	46.006	3.983	-4.903	.195
5600	9.183	75.182	66.802	46.925	3.983	-5.067	.198
5700	9.188	75.344	66.951	47.843	3.983	-5.226	.200
5800	9.194	75.504	67.097	48.762	3.983	-5.390	.203
5900	9.199	75.661	67.241	49.682	3.983	-5.553	.206
6000	9.204	75.815	67.382	50.602	3.982	-5.713	.208

Dec. 31, 1960; Sept. 30, 1962

MONOPHOSPHORUS MONONITRIDE (PN) (IDEAL GAS) MOL. WT. = 44.983

$\Delta H_{f\ 0}^\circ$ = 24.9 ± 1.2 kcal. mole^{-1}

$\Delta H_{f\ 298.15}^\circ$ = 25.0 ± 1.2 kcal. mole^{-1}

Ground State Configuration $^1\Sigma^+$

$S_{298.15}^\circ$ = 50.437 cal. deg.$^{-1}$ mole^{-1}

Electronic Level and Multiplicity

ϵ, cm.$^{-1}$	g_1
0	1

ω_e = 1337.24 cm.$^{-1}$

$\omega_e x_e$ = 6.983 cm.$^{-1}$

D_e = 1.09 X 10^{-6} cm.$^{-1}$

B_e = 0.7862 cm.$^{-1}$

α_e = 0.00557 cm.$^{-1}$

r_e = 1.4910 Å

σ = 1

Heat of Formation.

The selected $\Delta H_{f\ 298.15}^\circ$ was calculated from the D_0° = 165.8±1.2 kcal. mole^{-1} reported by R. L. Potter and V. N. DiStefano, J. Phys. Chem., 65, 849 (1961). A D_0° = 163.7±1.2 kcal. mole^{-1} was experimentally determined by E. O. Huffman, G. Tarbutton, K. L. Elmore, W. E. Cate, H. K. Walters, Jr., and G. V. Elmore, J. Am. Chem. Soc., 76, 6239 (1954). The D_0° reported by Huffman et. al was derived using a pressure-composition method i.e. measurement of equilibrium vapor pressure at 1173°K for the reaction [PN(g) → P_2(g) + N_2(g)]. Potter and DiStefano (loc. cit.) recalculated Huffman's results to obtain their D_0° value. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall (1953), lists a D_0° = 138.4 ± 19 kcal. mole^{-1}. The corresponding heats of formation are:

$\Delta H_{f\ 298.15}^\circ$	Source
25.0 ± 1.2 kcal. mole^{-1}	Potter and DiStefano (loc. cit.)
27.1 ± 1.2 kcal. mole^{-1}	Huffman et al. (loc. cit.).
53 ± 19 kcal. mole^{-1}	Gaydon (loc. cit.).

Heat Capacity and Entropy.

The molecular constants are taken from G. Herzburg, "Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., (1960) 2nd Ed.

Monosulfur Mononitride (SN)

(Ideal Gas) Mol. Wt. = 46.074

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 2.246	62.843	62.843	INFINITE
100	7.720	44.614	59.878	- 1.526	63.052	60.795	- 132.861
200	7.697	50.011	53.751	- .748	63.089	58.510	- 63.933
298	7.599	53.055	53.055	.000	63.000	56.278	- 41.251
300	7.600	53.102	53.056	.014	62.998	56.237	- 40.966
400	7.742	55.305	53.355	.780	62.316	54.025	- 29.517
500	7.951	57.055	53.926	1.565	61.811	52.012	- 22.733
600	8.146	58.522	54.573	2.370	61.403	50.092	- 18.245
700	8.306	59.790	55.229	3.193	61.062	48.259	- 15.066
800	8.433	60.908	55.871	4.030	47.703	45.182	- 12.343
900	8.534	61.907	56.487	4.878	47.734	44.866	- 10.894
1000	8.614	62.811	57.075	5.736	47.763	44.546	- 9.735
1100	8.678	63.635	57.634	6.600	47.790	44.221	- 8.786
1200	8.731	64.392	58.166	7.471	47.817	43.896	- 7.994
1300	8.775	65.093	58.673	8.346	47.842	43.570	- 7.324
1400	8.812	65.744	59.155	9.226	47.864	43.240	- 6.750
1500	8.843	66.354	59.615	10.108	47.884	42.907	- 6.251
1600	8.871	66.925	60.054	10.994	47.904	42.576	- 5.815
1700	8.895	67.464	60.474	11.882	47.921	42.242	- 5.430
1800	8.916	67.973	60.877	12.773	47.938	41.907	- 5.088
1900	8.935	68.455	61.263	13.666	47.954	41.573	- 4.782
2000	8.952	68.914	61.634	14.560	47.969	41.237	- 4.506
2100	8.968	69.351	61.991	15.456	47.982	40.898	- 4.256
2200	8.982	69.769	62.335	16.353	47.995	40.562	- 4.029
2300	8.996	70.168	62.667	17.252	48.007	40.223	- 3.822
2400	9.008	70.551	62.988	18.153	48.019	39.885	- 3.632
2500	9.020	70.919	63.298	19.054	48.030	39.545	- 3.457
2600	9.032	71.273	63.598	19.957	48.041	39.206	- 3.295
2700	9.042	71.614	63.888	20.860	48.051	38.865	- 3.146
2800	9.052	71.943	64.170	21.765	48.061	38.524	- 3.007
2900	9.062	72.261	64.444	22.671	48.071	38.184	- 2.877
3000	9.072	72.569	64.710	23.578	48.080	37.844	- 2.757
3100	9.081	72.866	64.968	24.485	48.090	37.502	- 2.644
3200	9.089	73.155	65.219	25.394	48.098	37.159	- 2.538
3300	9.098	73.435	65.464	26.303	48.107	36.818	- 2.438
3400	9.106	73.706	65.702	27.213	48.116	36.477	- 2.345
3500	9.114	73.970	65.935	28.124	48.123	36.131	- 2.256
3600	9.122	74.227	66.162	29.036	48.132	35.790	- 2.173
3700	9.130	74.477	66.383	29.949	48.140	35.448	- 2.094
3800	9.138	74.721	66.599	30.862	48.148	35.105	- 2.019
3900	9.145	74.958	66.811	31.776	48.156	34.760	- 1.948
4000	9.153	75.190	67.017	32.691	48.164	34.420	- 1.881
4100	9.160	75.416	67.219	33.607	48.172	34.074	- 1.816
4200	9.167	75.637	67.417	34.523	48.180	33.732	- 1.755
4300	9.174	75.853	67.611	35.440	48.187	33.386	- 1.697
4400	9.181	76.064	67.800	36.358	48.195	33.042	- 1.641
4500	9.188	76.270	67.986	37.277	48.202	32.699	- 1.588
4600	9.195	76.472	68.169	38.196	48.210	32.354	- 1.537
4700	9.202	76.670	68.347	39.116	48.219	32.009	- 1.488
4800	9.209	76.864	68.523	40.036	48.226	31.663	- 1.442
4900	9.216	77.054	68.695	40.957	48.234	31.321	- 1.397
5000	9.222	77.240	68.864	41.879	48.241	30.972	- 1.354
5100	9.229	77.423	69.030	42.802	48.249	30.628	- 1.312
5200	9.236	77.602	69.193	43.725	48.257	30.283	- 1.273
5300	9.242	77.778	69.354	44.649	48.265	29.935	- 1.234
5400	9.249	77.951	69.511	45.574	48.273	29.593	- 1.198
5500	9.255	78.120	69.666	46.499	48.281	29.245	- 1.162
5600	9.262	78.287	69.819	47.425	48.288	28.899	- 1.128
5700	9.268	78.451	69.969	48.351	48.296	28.552	- 1.095
5800	9.275	78.613	70.116	49.278	48.304	28.207	- 1.063
5900	9.281	78.771	70.262	50.206	48.313	27.856	- 1.032
6000	9.286	78.927	70.405	51.135	48.321	27.514	- 1.002

June 30, 1961

MONOSULFUR MONONITRIDE (SN) (IDEAL GAS) MOL. WT. = 46.074

D_0 = 115 ± 25 kcal. mole^{-1}

Ground State Configuration $^2\Pi_r$

ΔH_f° 298.15 = 63 ± 25 kcal. mole^{-1}

$S^\circ_{298.15}$ = 53.055 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_1, cm.$^{-1}$	g_1
0	2
223	2

ω_e = 1220.0 cm.$^{-1}$

B_e = [0.7762] cm.$^{-1}$

$\omega_e x_e$ = 7.75 cm.$^{-1}$

α_e = [0.0064] cm.$^{-1}$

σ = 1

r_e = 1.495(7) Å

Heat of Formation

The dissociation energy is listed by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London (1953).

Heat Capacity and Entropy

The spectroscopic constants other than B_e and α_e are from G. Herzberg "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, New York (1950). r_e is from "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London (1958), and has been used, together with the equation

$$\alpha_e = 6\,(\sqrt{\omega_e x_e B_e{}^3} - 6B_e{}^2)/\omega_e \text{ (Herzberg, op. cit., p. 108)}$$

to calculate B_e and α_e.

Silicon Nitride (SiN)

(Ideal Gas) GFW = 42.0927

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.087	88.718	88.718	INFINITE
100	6.956	44.138	58.060	-1.392	89.002	86.589	-189.239
200	6.995	48.965	52.444	-.696	89.070	84.134	-91.937
298	7.210	51.792	51.792	.000	89.000	81.722	-59.904
300	7.216	51.837	51.793	.013	88.998	81.677	-59.502
400	7.541	53.957	52.079	.751	88.880	79.254	-43.302
500	7.843	55.673	52.632	1.521	88.754	76.863	-33.597
600	8.086	57.125	53.263	2.318	88.627	74.496	-27.135
700	8.273	58.387	53.907	3.136	88.496	72.151	-22.526
800	8.421	59.501	54.538	3.971	88.360	69.825	-19.075
900	8.545	60.501	55.146	4.819	88.217	67.517	-16.395
1000	8.657	61.407	55.727	5.680	88.066	65.225	-14.255
1100	8.767	62.237	56.282	6.551	87.908	62.948	-12.507
1200	8.880	63.005	56.810	7.433	87.745	60.686	-11.052
1300	8.999	63.720	57.315	8.327	87.579	58.438	-9.824
1400	9.123	64.392	57.796	9.233	87.409	56.202	-8.773
1500	9.253	65.025	58.257	10.152	87.238	53.980	-7.865
1600	9.384	65.627	58.699	11.084	87.067	51.768	-7.071
1700	9.516	66.200	59.124	12.029	74.903	49.672	-6.386
1800	9.645	66.747	59.532	12.987	74.786	48.193	-5.851
1900	9.770	67.272	59.926	13.955	74.681	46.718	-5.374
2000	9.888	67.776	60.306	14.941	74.585	45.251	-4.945
2100	9.998	68.261	60.673	15.935	74.498	43.785	-4.557
2200	10.100	68.729	61.029	16.940	74.420	42.323	-4.204
2300	10.192	69.180	61.373	17.955	74.350	40.866	-3.883
2400	10.273	69.615	61.708	18.978	74.288	39.414	-3.589
2500	10.345	70.036	62.033	20.009	74.231	37.960	-3.318
2600	10.407	70.443	62.348	21.047	74.181	36.511	-3.069
2700	10.460	70.837	62.655	22.090	74.135	35.062	-2.838
2800	10.504	71.218	62.955	23.138	74.092	33.617	-2.624
2900	10.539	71.587	63.246	24.191	74.054	32.173	-2.425
3000	10.567	71.945	63.530	25.246	74.016	30.728	-2.239
3100	10.589	72.292	63.807	26.304	73.981	29.284	-2.065
3200	10.604	72.629	64.077	27.363	73.947	27.843	-1.902
3300	10.614	72.955	64.342	28.424	73.913	26.404	-1.749
3400	10.619	73.272	64.600	29.486	73.880	24.966	-1.605
3500	10.620	73.580	64.852	30.548	73.846	23.524	-1.469
3600	10.618	73.879	65.098	31.610	-18.151	24.346	-1.478
3700	10.612	74.170	65.340	32.672	-18.087	25.525	-1.508
3800	10.605	74.453	65.576	33.732	-18.025	26.703	-1.536
3900	10.595	74.728	65.807	34.792	-17.965	27.879	-1.562
4000	10.584	74.996	66.033	35.851	-17.907	29.055	-1.587
4100	10.571	75.257	66.255	36.909	-17.852	30.227	-1.611
4200	10.558	75.512	66.472	37.966	-17.797	31.397	-1.634
4300	10.544	75.760	66.686	39.021	-17.744	32.570	-1.655
4400	10.530	76.002	66.895	40.074	-17.695	33.739	-1.676
4500	10.516	76.239	67.100	41.127	-17.646	34.910	-1.695
4600	10.502	76.470	67.301	42.178	-17.598	36.077	-1.714
4700	10.488	76.696	67.498	43.227	-17.554	37.241	-1.732
4800	10.475	76.916	67.692	44.275	-17.511	38.409	-1.749
4900	10.462	77.132	67.883	45.322	-17.469	39.572	-1.765
5000	10.449	77.343	68.070	46.368	-17.429	40.736	-1.781
5100	10.438	77.550	68.254	47.412	-17.391	41.899	-1.796
5200	10.427	77.753	68.434	48.455	-17.353	43.060	-1.810
5300	10.417	77.951	68.612	49.497	-17.317	44.224	-1.824
5400	10.407	78.146	68.787	50.539	-17.283	45.381	-1.837
5500	10.399	78.337	68.959	51.579	-17.251	46.541	-1.849
5600	10.391	78.524	69.128	52.618	-17.219	47.704	-1.862
5700	10.384	78.708	69.294	53.657	-17.189	48.865	-1.874
5800	10.378	78.888	69.458	54.695	-17.161	50.026	-1.885
5900	10.373	79.066	69.620	55.733	-17.134	51.176	-1.896
6000	10.368	79.240	69.778	56.770	-17.108	52.336	-1.906

Dec. 31, 1960; Mar. 31, 1967

SILICON NITRIDE (SiN) (IDEAL GAS) GFW = 42.0927

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 51.792 gibbs/mol

ΔHf°_0 = 88.7 ± 15 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 89 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	2
[6000]	4
24299.4	2
[31000]	4

ω_e = 1150.8 cm^{-1}

$\omega_e x_e$ = 6.55 cm^{-1}

σ = 1

B_e = 0.7299 cm^{-1}

α_e = 0.00567

r_e = 1.5718 Å

Heat of Formation

A linear Birge-Sponer extrapolation of the ground state gives a dissociation energy of 142.9 kcal. The ground state can correlate with normal atoms Si(^3P) + N(^4S) or with Si(^3P) + N(^2D); in this latter case D°_0 would be 88 kcal. The uncertainty in the extrapolation is quite large, ± 30 kcal, since only 6 levels, of the estimated total of 87 levels, are observed.

A dissociation energy can also be calculated from the $B^2\Sigma^+$ state by a much shorter extrapolation. This extrapolation is done graphically since some curvature is evident in the first six levels. A value of $D^\circ_0(B^2\Sigma)$ = 50.4 kcal is obtained. This corresponds to $D^\circ_0(X^2\Sigma)$ = 119.9 kcal for normal products or $D^\circ_0(X^2\Sigma)$ = 65 kcal for excited nitrogen as a product. The uncertainty in this extrapolation is less than the ground state and is probably ± 20 kcal.

An estimate of D°_0(SiN) may be obtained by equating D_0(SiN)/D_0(SiO) = D_0(CN)/D_0(CO); this yields D_0(SiN) = 135 kcal.

A comparison of the isoelectronic molecules CP, BS and BeCl and the related molecules CN, BO, BeF indicates D_0(SiN) > 115 kcal.

A value of D_0(SiN) = 130 ± 15 kcal/mol is in agreement within the uncertainties of both ground state and B state extrapolations assuming normal atoms as products, and is in agreement with the other estimates. This value is adopted and yields ΔHf°_{298}(SiN,g) = 89 kcal/mol.

Heat Capacity and Entropy

The B-X transition has been reported by F. A. Jenkins and H. de Laszlo, Proc. Roy. Soc.(London) 122, 103 (1929). The rotational and vibrational constants are derived from their work and adjusted to normal isotopic abundance. The $A^2\Pi - C^2\Pi$ transition has been observed by M. D. Shetlar, Ph.D. Thesis, Univ. of California, Berkeley (1965). The height of the A state is estimated by correlation with CP(g). The level of the B state is taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd Edition, New York, 1950.

Disilicon Nitride (Si_2N)

(Ideal Gas) GFW = 70.1787

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.825	94.749	94.749	INFINITE
100	8.581	50.108	70.956	-2.085	95.015	92.096	-201.275
200	10.659	56.767	62.328	-1.112	95.077	89.138	-97.406
298	11.922	61.275	61.275	.000	95.000	86.236	-63.213
300	11.942	61.349	61.275	.022	94.998	86.182	-62.783
400	12.803	64.910	61.755	1.262	94.875	83.261	-45.492
500	13.374	67.833	62.687	2.573	94.747	80.374	-35.131
600	13.755	70.307	63.756	3.931	94.612	77.511	-28.233
700	14.017	72.449	64.848	5.320	94.468	74.672	-23.314
800	14.202	74.333	65.919	6.732	94.308	71.853	-19.629
900	14.336	76.014	66.949	8.159	94.131	69.059	-16.770
1000	14.435	77.530	67.932	9.598	93.935	66.283	-14.486
1100	14.512	78.909	68.868	11.045	93.719	63.528	-12.622
1200	14.571	80.175	69.759	12.499	93.482	60.793	-11.072
1300	14.618	81.343	70.605	13.959	93.226	58.079	-9.764
1400	14.656	82.428	71.411	15.423	92.950	55.385	-8.646
1500	14.687	83.440	72.180	16.890	92.652	52.713	-7.680
1600	14.712	84.389	72.914	18.360	92.334	50.061	-6.838
1700	14.733	85.281	73.615	19.832	68.009	47.641	-6.125
1800	14.751	86.124	74.287	21.306	67.759	46.451	-5.640
1900	14.767	86.922	74.931	22.782	67.508	45.273	-5.208
2000	14.780	87.680	75.550	24.260	67.257	44.111	-4.820
2100	14.791	88.401	76.145	25.739	67.004	42.959	-4.471
2200	14.801	89.089	76.718	27.218	66.751	41.819	-4.154
2300	14.810	89.747	77.270	28.698	66.497	40.692	-3.867
2400	14.817	90.378	77.803	30.180	66.243	39.576	-3.604
2500	14.824	90.983	78.318	31.662	65.987	38.469	-3.363
2600	14.830	91.564	78.817	33.145	65.732	37.375	-3.142
2700	14.836	92.124	79.299	34.628	65.475	36.287	-2.937
2800	14.841	92.664	79.767	36.112	65.219	35.213	-2.748
2900	14.846	93.185	80.221	37.596	64.962	34.145	-2.573
3000	14.851	93.688	80.661	39.081	64.705	33.086	-2.410
3100	14.856	94.175	81.089	40.566	64.447	32.035	-2.258
3200	14.860	94.647	81.506	42.052	64.189	30.997	-2.117
3300	14.865	95.104	81.911	43.538	63.930	29.965	-1.984
3400	14.869	95.548	82.305	45.025	63.672	28.939	-1.860
3500	14.874	95.979	82.690	46.512	63.413	27.918	-1.743
3600	14.879	96.398	83.065	48.000	-120.769	31.423	-1.908
3700	14.885	96.806	83.431	49.488	-120.829	35.651	-2.106
3800	14.890	97.203	83.788	50.977	-120.891	39.882	-2.294
3900	14.896	97.590	84.137	52.466	-120.953	44.110	-2.472
4000	14.903	97.967	84.478	53.956	-121.016	48.346	-2.641
4100	14.910	98.335	84.812	55.447	-121.081	52.576	-2.803
4200	14.918	98.695	85.138	56.938	-121.144	56.810	-2.956
4300	14.926	99.046	85.457	58.430	-121.206	61.050	-3.103
4400	14.934	99.389	85.770	59.923	-121.270	65.288	-3.243
4500	14.944	99.725	86.076	61.417	-121.331	69.536	-3.377
4600	14.953	100.053	86.377	62.912	-121.392	73.779	-3.505
4700	14.964	100.375	86.671	64.408	-121.454	78.021	-3.628
4800	14.975	100.690	86.960	65.905	-121.514	82.265	-3.746
4900	14.986	100.999	87.243	67.403	-121.573	86.510	-3.859
5000	14.999	101.302	87.521	68.902	-121.631	90.754	-3.967
5100	15.011	101.599	87.795	70.403	-121.689	95.008	-4.071
5200	15.025	101.891	88.063	71.904	-121.745	99.255	-4.172
5300	15.039	102.177	88.326	73.408	-121.799	103.507	-4.268
5400	15.053	102.458	88.586	74.912	-121.853	107.757	-4.361
5500	15.068	102.735	88.840	76.418	-121.907	112.005	-4.451
5600	15.084	103.006	89.091	77.926	-121.960	116.267	-4.538
5700	15.100	103.273	89.337	79.435	-122.011	120.527	-4.621
5800	15.116	103.536	89.580	80.946	-122.063	124.779	-4.702
5900	15.133	103.795	89.819	82.458	-122.114	129.025	-4.779
6000	15.151	104.049	90.054	83.973	-122.164	133.286	-4.855

Mar. 31, 1967

DISILICON NITRIDE (Si_2N) (IDEAL GAS) GFW = 70.1787

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [61.3 ± 2] gibbs/mol

ΔHf°_0 = 94.8 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 95 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[24000]	[4]
[28000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
[600]	(1)
[240]	(2)
[1000]	(1)

Bond Distance: Si-N = [170] Å

Bond Angle: Si-N-Si = [180°]

σ = 2

Rotational Constant: B_0 = [0.10384] cm^{-1}

Heat of Formation.

K. F. Zmbov and J. L. Margrave, Rice University, private communication, March 1967, have identified $Si_2N(g)$ in a mass spectrometer. They also determined partial pressures of $Si_2N(g)$ in equilibrium with Si(g) and $N_2(g)$. From four of these measurements, in the temperature range 1742° - 1846°K, we obtain a second law ΔHr°_{298} = 99.6 ± 6 kcal/mol for the reaction $Si_2N(g) = 2\,Si(g) + 0.5\,N_2(g)$; and a third law ΔHr°_{298} = 120.2 kcal/mol with a drift of -11.4 ± 3.4 eu. Considering the small temperature range and the uncertainties in the free energy functions, the data appear consistent. We adopt the 3rd law heat of reaction which yields $\Delta Hf^\circ_{298}(Si_2N,g))$ = 95 kcal/mol.

Heat Capacity and Entropy.

$Si_2N(g)$ is considered to be closely related to $C_2N(g)$, and its structure and electronic configuration are adopted by analogy to this species. The bond length was obtained by adding the difference between the bond distances of SiN(g) and CN(g) to the bond length in CNC(g). The vibrational frequencies were estimated by comparison with several molecules, CNC(g); $^1\Pi$ state of $C_3(g)$; NCN(g); and $Si_2C(g)$. It should be noted that there is a wide variation in observed frequencies for these molecules and ω_1 and ω_3 may be significantly different from the chosen values.

The electronic ground state is considered to be $^2\Pi_g$ with excited states of $^2\Delta_u$ and $^2\Sigma_u^-$ as in the case of CNC(g). The levels are obtained from those in CNC(g) by use of the shift between $C_3(g)$ and SiCSi(g).

Titanium Nitride (TiN)

(Crystal) GFW = 61.9067

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.311	-79.823	-79.823	INFINITE
100	2.572	1.057	13.395	-1.234	-80.226	-78.227	170.964
200	6.532	4.144	7.971	-.765	-80.564	-76.080	83.136
298	8.862	7.226	7.226	.000	-80.700	-73.847	54.132
300	8.900	7.281	7.227	.016	-80.701	-73.805	53.767
400	10.471	10.079	7.597	.993	-80.691	-71.504	39.068
500	11.247	12.509	8.343	2.083	-80.598	-69.217	30.255
600	11.645	14.597	9.215	3.229	-80.475	-66.953	24.387
700	11.898	16.412	10.117	4.407	-80.347	-64.710	20.203
800	12.098	18.014	11.006	5.606	-80.229	-62.484	17.070
900	12.281	19.449	11.866	6.825	-80.125	-60.271	14.636
1000	12.463	20.753	12.690	8.063	-80.039	-58.071	12.691
1100	12.648	21.949	13.478	9.318	-79.966	-55.877	11.102
1200	12.839	23.058	14.231	10.592	-80.845	-53.652	9.771
1300	13.035	24.093	14.950	11.886	-80.670	-51.393	8.640
1400	13.237	25.067	15.638	13.200	-80.496	-49.148	7.672
1500	13.443	25.987	16.298	14.534	-80.322	-46.915	6.836
1600	13.654	26.861	16.931	15.888	-80.148	-44.692	6.105
1700	13.867	27.695	17.540	17.264	-79.977	-42.483	5.462
1800	14.084	28.494	18.126	18.662	-79.809	-40.282	4.891
1900	14.304	29.261	18.692	20.081	-79.643	-38.090	4.381
2000	14.526	30.001	19.239	21.523	-83.928	-35.754	3.907
2100	14.749	30.715	19.769	22.987	-83.745	-33.349	3.471
2200	14.975	31.406	20.282	24.473	-83.542	-30.955	3.075
2300	15.202	32.077	20.780	25.982	-83.318	-28.569	2.715
2400	15.430	32.729	21.265	27.513	-83.072	-26.193	2.385
2500	15.659	33.363	21.736	29.068	-82.805	-23.829	2.083
2600	15.889	33.982	22.195	30.645	-82.516	-21.477	1.805
2700	16.120	34.586	22.643	32.245	-82.205	-19.134	1.549
2800	16.351	35.176	23.080	33.869	-81.872	-16.805	1.312
2900	16.584	35.754	23.507	35.516	-81.516	-14.484	1.092
3000	16.817	36.320	23.925	37.186	-81.139	-12.180	.887
3100	17.050	36.875	24.334	38.879	-80.738	-9.888	.697
3200	17.284	37.420	24.734	40.596	-80.316	-7.611	.520
3300	17.518	37.956	25.127	42.336	-79.871	-5.345	.354
3400	17.753	38.482	25.512	44.100	-79.402	-3.092	.199
3500	17.988	39.000	25.890	45.887	-78.911	-.857	.054
3600	18.223	39.510	26.261	47.697	-180.023	1.630	-.099
3700	18.458	40.013	26.626	49.531	-179.458	6.667	-.394
3800	18.694	40.508	26.985	51.389	-178.884	11.687	-.672
3900	18.930	40.997	27.338	53.270	-178.299	16.698	-.936
4000	19.167	41.479	27.685	55.175	-177.704	21.690	-1.185
4100	19.403	41.955	28.028	57.103	-177.099	26.668	-1.422
4200	19.639	42.426	28.365	59.055	-176.483	31.629	-1.646
4300	19.876	42.891	28.697	61.031	-175.855	36.576	-1.859
4400	20.113	43.350	29.025	63.031	-175.215	41.508	-2.062
4500	20.350	43.805	29.348	65.054	-174.564	46.427	-2.255

Dec. 30, 1960; June 30, 1968

TITANIUM NITRIDE (TiN) (CRYSTAL) GFW = 61.9067

$\Delta Hf°_0$ = -79.8 ± 1 kcal/mol

$S°_{298.15}$ = 7.23 ± 0.05 gibbs/mol

$\Delta Hf°_{298.15}$ = -80.7 ± 1 kcal/mol

Tm = 3220 ± 50°K

$\Delta Hm°$ = [16] kcal/mol

Heat of Formation

Humphrey (1) and Neumann et al. (2) determined the heat of combustion of titanium nitride by burning the material in an oxygen bomb calorimeter. For reaction (a) Humphrey obtained $\Delta Hr°_{298}$ = -145.05 ± 0.14 kcal/mol and Nuemann et al. $\Delta Hr°_{298}$ = -145.0 kcal/mol. From an examination of the combustion products Humphrey reported that the TiO_2 was >95 per cent rutile and <5 per cent anatase, but made no correction for the anatase. The adopted $\Delta Hf°_{298}$ = -80.7 kcal/mol is the average of three values, two from Humphrey (-80.75, -80.61), one as reported, and one corrected for anatase, and one from Neumann et al. (-80.8). The uncertainty in the adopted heat is due mainly to the uncertainty in the heat of formation of rutile. Hoch et al. (3) determined the vapor pressure of reaction (b), in the temperature range 1987-2241°K, using a Knudsen effusion method. Third law analysis of the data yields a $\Delta Hf°_{298}$ = -79.5 ± 9 kcal/mol. Linevsky (4) obtained the titanium partial pressures of reaction (c) (2088-2141°K) at fixed nitrogen pressures using atomic absorption spectroscopy. Third law analysis of the data gives a $\Delta Hf°_{298}$ = -81 ± 18 kcal/mol. These equilbrium measurements were not considered in deriving the heat of formation due to their large uncertainties in comparison to the calorimetric data.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52-296°K) of Shomate (5). Naylor (6) measured high temperature heat contents (388-1738°K). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 1738°K the heat capacity is graphically extrapolated. The entropy is based on $S°_{50} - S°_0$ = 0.138 eu.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	$\Delta Hr°_{298}$ kcal/mol 2nd Law	$\Delta Hr°_{298}$ kcal/mol 3rd Law	Drift eu	$\Delta Hf°_{298}$ kcal/mol
1	Calorimeter	(a) $TiN(c) + O_2(g) \rightarrow TiO_2(rutile) + 1/2N_2(g)$	298	-145.05±.14			-80.75
1	Calorimeter	(a) $TiN(c) + O_2(g) \rightarrow TiO_2(rutile) + 1/2N_2(g)$	298	-145.05±.14			-80.61*
2	Calorimeter	(a) $TiN(c) + O_2(g) \rightarrow TiO_2(rutile) + 1/2N_2(g)$	298	-145.0			-80.80
3	Equilibrium	(b) $TiN(c) \rightarrow Ti(g) + 1/2N_2(g)$	1987-2241	212±9	192.5	-9.3±4.3	-79.5
4	Equilibrium	(c) $TiN(c) \rightarrow Ti(g) + 1/2N_2(g)$	2088-2141	230±17	194.2	-17±8	-81.2

*Assumes that the product TiO_2 is 95 per cent rutile and 5 per cent anatase.

References

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3. M. Hoch, D. P. Dingledy and H. L. Johnston, J. Am. Chem. Soc. 77, 304-6 (1955).
4. M. J. Linevsky, General Electric Co., AFML-TR-64-420, February 1965.
5. C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946).
6. B. F. Naylor, J. Am. Chem. Soc. 68, 370 (1946).

Titanium Nitride (TiN)

(Liquid) GFW = 61.9067

T, °K	gibbs/mol Cp°	 S°	 −(G°−H°$_{298}$)/T	kcal/mol H°−H°$_{298}$	 ΔHf°	 ΔGf°	Log Kp
0							
100							
200							
298	8.862	12.603	12.603	.000	-63.531	-58.281	42.721
300	8.900	12.658	12.603	.016	-63.532	-58.249	42.434
400	10.471	15.456	12.974	.993	-63.522	-56.485	30.862
500	11.247	17.886	13.719	2.083	-63.429	-54.737	23.925
600	11.645	19.974	14.592	3.229	-63.306	-53.010	19.309
700	11.898	21.788	15.493	4.407	-63.178	-51.304	16.018
800	12.098	23.390	16.382	5.606	-63.060	-49.616	13.554
900	12.281	24.826	17.242	6.825	-62.956	-47.941	11.642
1000	12.463	26.129	18.067	8.063	-62.870	-46.279	10.114
1100	12.648	27.326	18.855	9.318	-62.797	-44.622	8.866
1200	12.839	28.434	19.607	10.592	-63.676	-42.935	7.819
1300	13.035	29.470	20.327	11.886	-63.501	-41.214	6.929
1400	13.237	30.443	21.015	13.200	-63.327	-39.507	6.167
1500	13.443	31.363	21.674	14.534	-63.153	-37.811	5.509
1600	13.654	32.238	22.307	15.886	-62.979	-36.126	4.935
1700	13.867	33.072	22.916	17.264	-62.808	-34.454	4.429
1800	14.084	33.871	23.503	18.662	-62.640	-32.791	3.981
1900	14.304	34.638	24.069	20.081	-62.474	-31.137	3.582
2000	14.526	35.377	24.616	21.523	-66.759	-29.338	3.206
2100	14.749	36.091	25.145	22.987	-66.576	-27.471	2.859
2200	15.000	36.783	25.659	24.473	-66.373	-25.614	2.545
2300	15.000	37.450	26.157	25.973	-66.158	-23.767	2.258
2400	15.000	38.088	26.641	27.473	-65.943	-21.927	1.997
2500	15.000	38.700	27.111	28.973	-65.731	-20.098	1.757
2600	15.000	39.289	27.568	30.473	-65.519	-18.277	1.536
2700	15.000	39.855	28.013	31.973	-65.309	-16.464	1.333
2800	15.000	40.400	28.446	33.473	-65.099	-14.659	1.144
2900	15.000	40.927	28.867	34.973	-64.890	-12.859	.969
3000	15.000	41.435	29.277	36.473	-64.683	-11.068	.806
3100	15.000	41.927	29.678	37.973	-64.476	-9.285	.655
3200	15.000	42.403	30.068	39.473	-64.270	-7.510	.513
3300	15.000	42.865	30.449	40.973	-64.065	-5.738	.380
3400	15.000	43.313	30.821	42.473	-63.860	-3.972	.255
3500	15.000	43.747	31.184	43.973	-63.656	-2.216	.138
3600	15.000	44.170	31.539	45.473	-165.079	-.200	.012
3700	15.000	44.581	31.886	46.973	-164.848	4.376	-.258
3800	15.000	44.981	32.225	48.473	-164.631	8.944	-.514
3900	15.000	45.371	32.557	49.973	-164.427	13.513	-.757
4000	15.000	45.750	32.882	51.473	-164.237	18.072	-.987
4100	15.000	46.121	33.201	52.973	-164.060	22.628	-1.206
4200	15.000	46.482	33.512	54.473	-163.896	27.178	-1.414
4300	15.000	46.835	33.818	55.973	-163.744	31.725	-1.612
4400	15.000	47.180	34.118	57.473	-163.604	36.268	-1.801
4500	15.000	47.517	34.412	58.973	-163.476	40.811	-1.982

Dec. 30, 1960; June 30, 1968

TITANIUM NITRIDE (TiN) (LIQUID) GFW = 61.9067

$S^\circ_{298.15}$ = [12.603] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-63.531 ± 1] kcal/mol

Tm = 3220 ± 50°K ΔHm° = [16] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°_{298}(c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K. Below 2200°K the heat capacity is obtained from the heat capacity of the crystal. Above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm is taken from C. Agte and K. Moers, Z. Anorg. Allgem. Chem. 198, 233-43 (1931). ΔHm° is derived from an estimated ΔSm = 2.5 gibbs/g-atom as suggested by O. Kubaschewski, E. Ll. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

Monozirconium Mononitride (ZrN)

(Crystal) Mol. Wt. = 105.228 **INTERIM TABLE**

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	- 1.575	- 86.522	- 86.522	INFINITE
100	3.716	1.944	16.347	- 1.440	- 86.942	- 84.894	185.526
200	7.592	5.826	10.115	- .858	- 87.234	- 82.711	90.377
298	9.670	9.288	9.288	.000	- 87.300	- 80.470	58.983
300	9.693	9.348	9.288	.018	- 87.300	- 80.428	58.589
400	10.697	12.285	9.682	1.041	- 87.260	- 78.142	42.693
500	11.252	14.740	10.455	2.142	- 87.181	- 75.871	33.162
600	11.630	16.826	11.347	3.287	- 87.096	- 73.616	26.813
700	11.925	18.642	12.262	4.466	- 87.007	- 71.377	22.284
800	12.175	20.251	13.162	5.671	- 86.911	- 69.151	18.890
900	12.400	21.698	14.032	6.900	- 86.807	- 66.936	16.254
1000	12.608	23.015	14.865	8.150	- 86.697	- 64.734	14.147
1100	12.806	24.226	15.662	9.421	- 86.590	- 62.544	12.426
1200	12.997	25.349	16.423	10.711	- 87.439	- 60.314	10.984
1300	13.182	26.396	17.150	12.020	- 87.309	- 58.060	9.760
1400	13.364	27.380	17.846	13.348	- 87.174	- 55.816	8.713
1500	13.544	28.308	18.513	14.693	- 87.032	- 53.580	7.806
1600	13.721	29.188	19.153	16.056	- 86.881	- 51.353	7.014
1700	13.896	30.025	19.768	17.437	- 86.725	- 49.139	6.317
1800	14.071	30.824	20.360	18.835	- 86.560	- 46.932	5.698
1900	14.244	31.590	20.931	20.251	- 86.387	- 44.734	5.145
2000	14.417	32.325	21.483	21.684	- 86.207	- 42.548	4.649
2100	14.573	33.032	22.016	23.134	- 86.018	- 40.370	4.201
2200	14.760	33.714	22.532	24.601	- 90.724	- 38.036	3.778
2300	14.931	34.374	23.033	26.086	- 90.524	- 35.645	3.387
2400	15.102	35.013	23.519	27.587	- 90.308	- 33.263	3.029
2500	15.272	35.633	23.991	29.106	- 90.077	- 30.891	2.700
2600	15.443	36.236	24.450	30.642	- 89.829	- 28.529	2.398
2700	15.612	36.822	24.898	32.194	- 89.566	- 26.176	2.119
2800	15.782	37.392	25.334	33.764	- 89.287	- 23.834	1.860
2900	15.952	37.949	25.759	35.351	- 88.991	- 21.499	1.620
3000	16.121	38.493	26.175	36.954	- 88.680	- 19.177	1.397
3100	16.290	39.024	26.581	38.575	- 88.352	- 16.869	1.189
3200	16.459	39.544	26.978	40.212	- 88.009	- 14.568	.995
3300	16.628	40.053	27.366	41.867	- 87.650	- 12.276	.813
3400	16.797	40.552	27.747	43.538	- 87.273	- 9.997	.643
3500	16.966	41.041	28.120	45.226	- 86.881	- 7.732	.483
3600	17.135	41.522	28.485	46.931	- 86.473	- 5.477	.333
3700	17.303	41.993	28.844	48.653	- 86.048	- 3.233	.191
3800	17.472	42.457	29.196	50.392	- 85.608	- .999	.057
3900	17.641	42.913	29.542	52.148	- 85.150	1.223	- .069
4000	17.809	43.362	29.882	53.920	- 84.676	3.430	- .187
4100	17.978	43.804	30.216	55.709	- 84.187	5.627	- .300
4200	18.146	44.239	30.545	57.516	- 83.680	7.813	- .407
4300	18.315	44.668	30.868	59.339	- 83.157	9.985	- .507
4400	18.483	45.091	31.187	61.179	- 82.618	12.143	- .603
4500	18.652	45.508	31.500	63.035	- 82.063	14.290	- .694
4600	18.820	45.920	31.809	64.909	- 81.491	16.427	- .780
4700	18.988	46.326	32.114	66.799	- 80.903	18.549	- .863
4800	19.157	46.728	32.414	68.707	- 216.731	22.184	- 1.010
4900	19.325	47.125	32.710	70.631	- 216.165	27.150	- 1.211
5000	19.493	47.517	33.003	72.572	- 215.588	32.113	- 1.404

June 30, 1961

NZr

MONOZIRCONIUM MONONITRIDE (ZrN) (Crystal)

Mol. Wt. = 105.228

ΔH_{f0}° = -86.5 ± 2 kcal. mole^{-1}

ΔH_f° 298.15 = -87.3 ± 2 kcal. mole^{-1}

T_m = [3225°K]

$S^\circ_{298.15}$ = 9.29 ± 0.05 cal. deg.$^{-1}$ mole^{-1}

ΔH_m = [16.1] kcal. mole^{-1}

Heat of Formation. The heat of reaction I, -174.25 ± 0.30 kcal. mole^{-1}, was measured by A. D. Mah and N. L. Gelbert. The ΔH_f° 298.15 of ZrN was obtained using -261.5 ± 0.2 kcal. mole^{-1} for ΔH_f° 298.15 of ZrO_2. For the same reaction B. Neumann, C. Kroger and H. Kunz, Z. anorg. Chem. 218, 379 (1934) obtain -176.0 kcal. mole^{-1} on a sample of unspecified purity. Vapor pressure measurements of M. Hoch, D. P. Dingledy and H. L. Johnston, J. Am. Chem. Soc. 77, 304 (1955) lead to -81 kcal. mole^{-1} for the ΔH_f° 298.15 of ZrN. However, this value is uncertain by 10% as evidenced by the work on ZrO_2 by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957).

$$\text{(I)}\quad ZrN(c) + O_2(g) = ZrO_2(c) + 1/2\ N_2(g)$$

Heat Capacity and Entropy. Low temperature measurements, 53-297°K, of S. S. Todd, J. Am. Chem. Soc. 72, 2914 (1950), were smoothly joined to those of J. P. Coughlin and E. G. King, J. Am. Chem. Soc. 72, 2262 (1950), 298-1073°K.

Melting. Estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

NZr

Monozirconium Mononitride (ZrN)

(Liquid) Mol. Wt. = 105.228

INTERIM TABLE

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0							
100							
200							
298	9.666	14.899	14.899	.000	-69.489	-64.332	47.155
300	9.693	14.959	14.899	.018	-69.489	-64.300	46.840
400	10.697	17.906	15.294	1.045	-69.445	-62.576	34.188
500	11.252	20.356	16.069	2.144	-69.369	-60.667	26.604
600	11.630	22.444	16.961	3.289	-69.283	-59.174	21.553
700	11.925	24.259	17.877	4.467	-69.194	-57.496	17.950
800	12.175	25.868	18.777	5.673	-69.098	-55.832	15.252
900	12.400	27.316	19.647	6.902	-68.994	-54.179	13.156
1000	12.608	28.633	20.481	8.152	-68.884	-52.539	11.482
1100	12.806	29.844	21.278	9.423	-68.777	-50.910	10.114
1200	12.997	30.966	22.039	10.713	-69.626	-49.243	8.968
1300	13.182	32.014	22.766	12.022	-69.496	-47.550	7.993
1400	13.364	32.998	23.462	13.350	-69.361	-45.868	7.160
1500	13.544	33.926	24.129	14.695	-69.219	-44.194	6.439
1600	13.721	34.806	24.769	16.058	-69.068	-42.528	5.809
1700	13.896	35.643	25.384	17.439	-68.912	-40.876	5.255
1800	14.071	36.442	25.977	18.837	-68.747	-39.231	4.763
1900	14.244	37.207	26.548	20.253	-68.574	-37.595	4.324
2000	14.417	37.942	27.099	21.686	-68.394	-35.970	3.930
2100	14.573	38.649	27.633	23.135	-68.206	-34.354	3.575
2200	14.000	39.315	28.149	24.566	-72.948	-32.581	3.237
2300	14.000	39.938	28.648	25.966	-72.832	-30.749	2.922
2400	14.000	40.533	29.131	27.366	-72.718	-28.921	2.633
2500	14.000	41.105	29.598	28.766	-72.605	-27.099	2.369
2600	14.000	41.654	30.051	30.166	-72.494	-25.281	2.125
2700	14.000	42.182	30.491	31.566	-72.383	-23.467	1.899
2800	14.000	42.691	30.918	32.966	-72.274	-21.658	1.690
2900	14.000	43.183	31.332	34.366	-72.165	-19.849	1.496
3000	14.000	43.657	31.735	35.766	-72.057	-18.048	1.315
3100	14.000	44.116	32.127	37.166	-71.950	-16.252	1.146
3200	14.000	44.561	32.509	38.566	-71.844	-14.457	.987
3300	14.000	44.992	32.881	39.966	-71.739	-12.663	.839
3400	14.000	45.410	33.243	41.366	-71.634	-10.873	.699
3500	14.000	45.815	33.596	42.766	-71.530	-9.090	.568
3600	14.000	46.210	33.941	44.166	-71.427	-7.309	.444
3700	14.000	46.593	34.278	45.566	-71.324	-5.529	.327
3800	14.000	46.967	34.607	46.966	-71.222	-3.750	.216
3900	14.000	47.330	34.929	48.366	-71.120	-1.975	.111
4000	14.000	47.685	35.243	49.766	-71.019	-.205	.011
4100	14.000	48.031	35.551	51.166	-70.919	1.565	-.083
4200	14.000	48.368	35.852	52.566	-70.819	3.333	-.173
4300	14.000	48.697	36.147	53.966	-70.719	5.098	-.259
4400	14.000	49.019	36.436	55.366	-70.620	6.857	-.341
4500	14.000	49.334	36.719	56.766	-70.521	8.617	-.418
4600	14.000	49.642	36.997	58.166	-70.423	10.376	-.493
4700	14.000	49.943	37.269	59.566	-70.325	12.132	-.564
4800	14.000	50.237	37.536	60.966	-206.661	15.410	-.702
4900	14.000	50.526	37.798	62.366	-206.619	20.031	-.893
5000	14.000	50.809	38.056	63.766	-206.582	24.659	-1.078
5100	14.000	51.086	38.308	65.166	-206.550	29.281	-1.255
5200	14.000	51.358	38.557	66.566	-206.523	33.910	-1.425
5300	14.000	51.625	38.801	67.966	-206.502	38.527	-1.589
5400	14.000	51.886	39.041	69.366	-206.484	43.154	-1.746
5500	14.000	52.143	39.277	70.766	-206.470	47.775	-1.898
5600	14.000	52.395	39.509	72.166	-206.460	52.400	-2.045
5700	14.000	52.643	39.737	73.566	-206.453	57.020	-2.186
5800	14.000	52.887	39.961	74.966	-206.450	61.646	-2.323
5900	14.000	53.126	40.183	76.366	-206.448	66.267	-2.455
6000	14.000	53.361	40.400	77.766	-206.449	70.887	-2.582

June 30, 1961

MONOZIRCONIUM MONONITRIDE (ZrN) (Liquid)

Mol. Wt. = 105.228

ΔH_f° 298.15 = [-69.5] cal. deg.$^{-1}$ mole^{-1}

T_m = [3225]°K

ΔH_m = [16.1] kcal. mole^{-1}

Heat of Formation. Calculated from the solid.

Entropy. Calculated from the solid.

Heat Capacity. The heat capacity function of the solid was assumed to approximate those of the liquid up to the estimated glass point of 2150°K. Above the glass point the heat capacity was estimated.

Monozirconium Mononitride (ZrN)

(Ideal Gas) Mol. Wt. = 105.228

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 2.118	169.418	169.418	INFINITE
100	6.959	47.993	62.224	- 1.423	169.770	166.877	- 364.691
200	7.141	52.851	56.458	- .721	170.121	163.849	- 179.037
298	7.567	55.780	55.780	.000	170.500	163.468	- 119.820
300	7.575	55.827	55.780	.014	170.497	163.425	- 119.049
400	7.965	58.062	56.082	.792	170.291	161.098	- 88.016
500	8.243	59.871	56.665	1.603	170.080	158.824	- 69.419
600	8.434	61.392	57.329	2.438	169.854	156.594	- 57.037
700	8.567	62.703	58.005	3.288	169.616	154.403	- 48.204
800	8.664	63.853	58.666	4.150	169.368	152.246	- 41.590
900	8.736	64.878	59.300	5.020	169.114	150.122	- 36.453
1000	8.791	65.802	59.905	5.897	168.849	148.026	- 32.350
1100	8.835	66.642	60.480	6.778	168.566	145.956	- 28.997
1200	8.871	67.412	61.026	7.663	167.313	143.962	- 26.218
1300	8.901	68.123	61.545	8.552	167.022	142.027	- 23.876
1400	8.926	68.784	62.039	9.443	166.721	140.115	- 21.872
1500	8.948	69.400	62.509	10.337	166.412	138.226	- 20.138
1600	8.968	69.978	62.958	11.233	166.095	136.359	- 18.625
1700	8.985	70.523	63.387	12.130	165.768	134.509	- 17.291
1800	9.001	71.037	63.798	13.030	165.434	132.680	- 16.109
1900	9.016	71.524	64.192	13.931	165.093	130.870	- 15.053
2000	9.029	71.986	64.570	14.833	164.742	129.077	- 14.104
2100	9.042	72.427	64.934	15.736	164.384	127.302	- 13.248
2200	9.054	72.848	65.284	16.641	159.116	125.710	- 12.488
2300	9.065	73.251	65.622	17.547	158.738	124.200	- 11.801
2400	9.076	73.637	65.948	18.454	158.359	122.707	- 11.173
2500	9.087	74.008	66.263	19.362	157.980	121.229	- 10.597
2600	9.097	74.364	66.568	20.271	157.600	119.766	- 10.067
2700	9.107	74.708	66.863	21.182	157.221	118.319	- 9.577
2800	9.116	75.039	67.149	22.093	156.842	116.884	- 9.123
2900	9.125	75.359	67.426	23.005	156.463	115.466	- 8.701
3000	9.135	75.669	67.696	23.918	156.083	114.059	- 8.309
3100	9.143	75.968	67.958	24.832	155.704	112.661	- 7.942
3200	9.152	76.259	68.213	25.746	155.325	111.279	- 7.600
3300	9.161	76.541	68.461	26.662	154.946	109.910	- 7.279
3400	9.170	76.814	68.703	27.579	154.567	108.553	- 6.977
3500	9.178	77.080	68.938	28.496	154.189	107.203	- 6.694
3600	9.186	77.339	69.168	29.414	153.810	105.864	- 6.427
3700	9.195	77.591	69.392	30.333	153.432	104.538	- 6.175
3800	9.203	77.836	69.611	31.253	153.054	103.223	- 5.936
3900	9.211	78.075	69.825	32.174	152.676	101.918	- 5.711
4000	9.219	78.308	70.034	33.095	152.299	100.620	- 5.497
4100	9.227	78.536	70.239	34.018	151.922	99.333	- 5.295
4200	9.235	78.759	70.439	34.941	151.545	98.056	- 5.102
4300	9.243	78.976	70.635	35.865	151.169	96.787	- 4.919
4400	9.251	79.188	70.827	36.789	150.792	95.524	- 4.744
4500	9.259	79.396	71.015	37.715	150.416	94.272	- 4.578
4600	9.266	79.600	71.200	38.641	150.041	93.031	- 4.420
4700	9.274	79.799	71.381	39.568	149.666	91.795	- 4.268
4800	9.282	79.995	71.558	40.496	12.858	92.093	- 4.193
4900	9.290	80.186	71.732	41.424	12.428	93.743	- 4.181
5000	9.297	80.374	71.903	42.354	11.994	95.410	- 4.170
5100	9.305	80.558	72.071	43.284	11.556	97.080	- 4.160
5200	9.312	80.739	72.236	44.215	11.114	98.766	- 4.151
5300	9.320	80.916	72.398	45.146	10.667	100.450	- 4.142
5400	9.328	81.091	72.558	46.079	10.217	102.152	- 4.134
5500	9.335	81.262	72.714	47.012	9.764	103.856	- 4.127
5600	9.343	81.430	72.868	47.946	9.308	105.574	- 4.120
5700	9.350	81.596	73.020	48.880	8.850	107.295	- 4.114
5800	9.358	81.758	73.169	49.816	8.389	109.029	- 4.108
5900	9.365	81.918	73.316	50.752	7.927	110.768	- 4.103
6000	9.373	82.076	73.461	51.689	7.462	112.512	- 4.098

June 30, 1963

MONOZIRCONIUM MONONITRIDE (ZrN) (IDEAL GAS) MOL. WT. = 105.228

Ground State Configuration [$^2\Sigma$]

$S^\circ_{298.15}$ = [55.78] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = [169.4] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [170.5] kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	[2]

ω_e = [840] cm.$^{-1}$

B_e = [0.4146] cm.$^{-1}$

$\omega_e x_e$ = [5] cm.$^{-1}$

α_e = [0.0025] cm.$^{-1}$

σ = 1

r_e = [1.83] Å

Heat of Formation.

$\Delta H^\circ_{f\ 0}$ was estimated as 170.7 kcal. mole^{-1} by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, January 10, 1963. $\Delta H^\circ_{f\ 298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. r_e was calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2}$ Å.

Nitrogen, Diatomic (N_2)

(Reference State - Ideal Gas) Mol. Wt. = 28.0134

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.072	.000	.000	.000
100	6.956	38.170	51.957	-1.379	.000	.000	.000
200	6.957	42.992	46.407	-.683	.000	.000	.000
298	6.961	45.770	45.770	.000	.000	.000	.000
300	6.961	45.813	45.770	.013	.000	.000	.000
400	6.990	47.818	46.043	.710	.000	.000	.000
500	7.069	49.386	46.561	1.413	.000	.000	.000
600	7.196	50.685	47.143	2.125	.000	.000	.000
700	7.350	51.806	47.731	2.853	.000	.000	.000
800	7.512	52.798	48.303	3.596	.000	.000	.000
900	7.670	53.692	48.853	4.355	.000	.000	.000
1000	7.815	54.507	49.378	5.129	.000	.000	.000
1100	7.945	55.258	49.879	5.917	.000	.000	.000
1200	8.061	55.955	50.357	6.718	.000	.000	.000
1300	8.162	56.604	50.813	7.529	.000	.000	.000
1400	8.252	57.212	51.248	8.350	.000	.000	.000
1500	8.330	57.784	51.665	9.179	.000	.000	.000
1600	8.398	58.324	52.065	10.015	.000	.000	.000
1700	8.458	58.835	52.448	10.858	.000	.000	.000
1800	8.512	59.320	52.816	11.707	.000	.000	.000
1900	8.559	59.782	53.171	12.560	.000	.000	.000
2000	8.601	60.222	53.513	13.418	.000	.000	.000
2100	8.638	60.642	53.842	14.280	.000	.000	.000
2200	8.672	61.045	54.160	15.146	.000	.000	.000
2300	8.703	61.431	54.468	16.015	.000	.000	.000
2400	8.731	61.802	54.766	16.886	.000	.000	.000
2500	8.756	62.159	55.055	17.761	.000	.000	.000
2600	8.779	62.503	55.335	18.638	.000	.000	.000
2700	8.800	62.835	55.606	19.517	.000	.000	.000
2800	8.820	63.155	55.870	20.398	.000	.000	.000
2900	8.838	63.465	56.127	21.280	.000	.000	.000
3000	8.855	63.765	56.376	22.165	.000	.000	.000
3100	8.871	64.055	56.619	23.051	.000	.000	.000
3200	8.886	64.337	56.856	23.939	.000	.000	.000
3300	8.900	64.611	57.087	24.829	.000	.000	.000
3400	8.914	64.877	57.312	25.719	.000	.000	.000
3500	8.927	65.135	57.532	26.611	.000	.000	.000
3600	8.939	65.387	57.747	27.505	.000	.000	.000
3700	8.950	65.632	57.957	28.399	.000	.000	.000
3800	8.962	65.871	58.162	29.295	.000	.000	.000
3900	8.972	66.104	58.362	30.191	.000	.000	.000
4000	8.983	66.331	58.559	31.089	.000	.000	.000
4100	8.993	66.553	58.751	31.988	.000	.000	.000
4200	9.002	66.770	58.940	32.888	.000	.000	.000
4300	9.012	66.982	59.124	33.788	.000	.000	.000
4400	9.021	67.189	59.305	34.690	.000	.000	.000
4500	9.030	67.392	59.482	35.593	.000	.000	.000
4600	9.039	67.591	59.657	36.496	.000	.000	.000
4700	9.048	67.785	59.827	37.400	.000	.000	.000
4800	9.057	67.976	59.995	38.306	.000	.000	.000
4900	9.066	68.162	60.160	39.212	.000	.000	.000
5000	9.074	68.346	60.322	40.119	.000	.000	.000
5100	9.083	68.525	60.481	41.027	.000	.000	.000
5200	9.091	68.702	60.637	41.935	.000	.000	.000
5300	9.100	68.875	60.791	42.845	.000	.000	.000
5400	9.109	69.045	60.942	43.755	.000	.000	.000
5500	9.118	69.213	61.091	44.667	.000	.000	.000
5600	9.127	69.377	61.238	45.579	.000	.000	.000
5700	9.136	69.539	61.382	46.492	.000	.000	.000
5800	9.145	69.698	61.524	47.406	.000	.000	.000
5900	9.155	69.854	61.664	48.321	.000	.000	.000
6000	9.165	70.008	61.802	49.237	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

NITROGEN, DIATOMIC (N_2) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 28.0134

Ground State Configuration $^1\Sigma_g^+$

$\Delta H^\circ_{f\ 0} = 0$

$S^\circ_{298.15} = 45.77 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 0$

$\omega_e = 2357.55$ cm.$^{-1}$

$\omega_e x_e = 14.059$ cm.$^{-1}$

$\sigma = 2$

$B_e = 1.99825$ cm.$^{-1}$

$\alpha_e = 0.01791 \pm 0.0001$ cm.$^{-1}$

$r_e = 1.08758 \pm 0.0001$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for $N_2(g)$ is zero at all temperatures by definition.

Heat Capacity and Entropy.

The functions adopted here are based on the direct summation calculations of L. Glatt, J. Belzer and H. L. Johnston, Ohio State Univ. Res. Found. Proj. 316, Report No. 9, 1953. They calculated the functions for $N^{14}N^{14}$ by a direct summation using spectroscopic data given by G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -Rln9 to remove the effects of nuclear spin included by Glatt, Belzer, and Johnston, and by 0.012 for the difference in spectroscopic constants. J. A. Goff and S. Gratch, Trans. Am. Soc. Mech. Engrs., 72, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatt, Belzer, and Johnston is within 0.1%.

B. P. Stoicheff, Can. J. Phys. 32, 630 (1954), determined the spectroscopic constants of $N^{14}N^{14}$ by combining his measured rotational spectra with the results of band spectra given in the literature. The constants listed above have been corrected to apply to the naturally occurring isotopic composition listed by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys., 30, 585 (1958).

Dinitrogen Monoxide (N_2O)

(Ideal Gas) Mol. Wt. = 44.016

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.290	20.430	20.430	INFINITE
100	7.015	43.988	59.924	-1.594	20.084	21.573	-47.145
200	8.033	49.108	53.353	-.849	19.786	23.185	-25.334
298	9.230	52.546	52.546	.000	19.610	24.896	-18.248
300	9.250	52.603	52.546	.017	19.608	24.928	-18.159
400	10.201	55.400	52.921	.992	19.530	26.716	-14.596
500	10.953	57.761	53.659	2.051	19.520	28.514	-12.463
600	11.565	59.813	54.517	3.178	19.558	30.311	-11.040
700	12.070	61.635	55.406	4.360	19.623	32.097	-10.021
800	12.486	63.275	56.289	5.589	19.710	33.873	-9.253
900	12.830	64.766	57.149	6.855	19.810	35.638	-8.654
1000	13.113	66.133	57.980	8.153	19.920	37.391	-8.171
1100	13.348	67.394	58.779	9.476	20.036	39.132	-7.774
1200	13.544	68.565	59.547	10.821	20.156	40.863	-7.442
1300	13.707	69.655	60.283	12.184	20.279	42.583	-7.158
1400	13.845	70.676	60.989	13.562	20.404	44.293	-6.914
1500	13.961	71.635	61.667	14.952	20.530	45.996	-6.701
1600	14.060	72.540	62.319	16.353	20.657	47.691	-6.514
1700	14.145	73.395	62.945	17.764	20.783	49.377	-6.347
1800	14.218	74.205	63.548	19.182	20.908	51.054	-6.198
1900	14.282	74.976	64.130	20.607	21.032	52.728	-6.065
2000	14.337	75.710	64.690	22.038	21.155	54.392	-5.943
2100	14.385	76.411	65.232	23.474	21.277	56.049	-5.833
2200	14.428	77.081	65.755	24.915	21.396	57.703	-5.732
2300	14.466	77.723	66.262	26.359	21.513	59.350	-5.639
2400	14.499	78.339	66.752	27.808	21.630	60.993	-5.554
2500	14.529	78.932	67.228	29.259	21.742	62.630	-5.475
2600	14.556	79.502	67.689	30.713	21.853	64.262	-5.401
2700	14.580	80.052	68.137	32.170	21.962	65.894	-5.333
2800	14.602	80.583	68.572	33.629	22.069	67.517	-5.270
2900	14.621	81.095	68.995	35.090	22.174	69.140	-5.210
3000	14.639	81.591	69.406	36.553	22.275	70.757	-5.154
3100	14.655	82.072	69.807	38.018	22.376	72.371	-5.102
3200	14.670	82.537	70.198	39.484	22.473	73.981	-5.052
3300	14.684	82.989	70.579	40.952	22.568	75.591	-5.006
3400	14.696	83.427	70.950	42.421	22.661	77.196	-4.962
3500	14.707	83.853	71.313	43.891	22.752	78.797	-4.920
3600	14.718	84.268	71.667	45.363	22.841	80.400	-4.881
3700	14.727	84.671	72.013	46.835	22.928	81.995	-4.843
3800	14.736	85.064	72.351	48.308	23.013	83.591	-4.807
3900	14.745	85.447	72.682	49.782	23.097	85.183	-4.773
4000	14.752	85.820	73.006	51.257	23.177	86.774	-4.741
4100	14.760	86.185	73.323	52.733	23.257	88.365	-4.710
4200	14.766	86.541	73.633	54.209	23.334	89.951	-4.680
4300	14.772	86.888	73.937	55.686	23.411	91.537	-4.652
4400	14.778	87.228	74.236	57.163	23.485	93.120	-4.625
4500	14.784	87.560	74.528	58.641	23.558	94.703	-4.599
4600	14.789	87.885	74.815	60.120	23.630	96.288	-4.574
4700	14.794	88.203	75.096	61.599	23.700	97.860	-4.550
4800	14.798	88.515	75.373	63.079	23.768	99.441	-4.527
4900	14.802	88.820	75.644	64.559	23.836	101.011	-4.505
5000	14.806	89.119	75.911	66.039	23.902	102.590	-4.484
5100	14.810	89.412	76.172	67.520	23.966	104.156	-4.463
5200	14.814	89.700	76.430	69.001	24.030	105.733	-4.444
5300	14.817	89.982	76.683	70.483	24.092	107.305	-4.425
5400	14.820	90.259	76.932	71.965	24.154	108.872	-4.406
5500	14.823	90.531	77.176	73.447	24.213	110.446	-4.388
5600	14.826	90.798	77.417	74.929	24.272	112.010	-4.371
5700	14.829	91.060	77.654	76.412	24.329	113.575	-4.354
5800	14.831	91.318	77.888	77.895	24.386	115.142	-4.338
5900	14.834	91.572	78.117	79.378	24.441	116.706	-4.323
5000	14.836	91.821	78.344	80.862	24.495	118.267	-4.308

Dec. 31, 1960; Dec. 31, 1964

DINITROGEN MONOXIDE (N_2O) (IDEAL GAS) MOL. WT. = 44.016

Point Group $C_{\infty v}$

$S^\circ_{298.15}$ = 52.55 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 20.43 ± 0.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 19.61 ± 0.1 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1276.5 (1)
589.2 (2)
2223.7 (1)

Bond Distance: N-N = 1.1282 Å N-O = 1.1842 Å

Bond Angle: N-N-O = 180°

B_e = 0.42109 cm.$^{-1}$

σ = 1

Heat of Formation.

An analysis of the heat of reaction data is summarized below. Carlton-Sutton, et al., studied the direct decomposition at pressures of 40 to 50 atmospheres and made P-V-T measurements in order to reduce the data. They obtained a similar but less certain heat of formation by combustion of N_2O in CO. Flame calorimetric measurements of the combustion by Awberry and Griffiths are in good agreement, but the bomb calorimetry of Fenning and Cotton gives a heat of formation about 0.2 kcal. larger. The selected heat of formation is a weighted average of these values.

Source	Method	Reaction	$\Delta H^\circ_{r\ 298.15}$ (kcal. mole^{-1})	$\Delta H^\circ_{f\ 298.15}$
1	Bomb Calorimetry	$N_2O(g) \rightarrow N_2(g) + 0.5\ O_2(g)$	-19.52 ± 0.10	19.52
1	Bomb Calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.10 ± 0.30	19.46*
2	Flame Calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.09 ± 0.22	19.45*
3	Bomb Calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.37 ± 0.12	19.73*
3	Bomb Calorimetry	$N_2O(g) + H_2(g) \rightarrow H_2O(l) + N_2(g)$	-88.03 ± 0.12	19.71*

*Based on $\Delta H^\circ_{f\ 298.15}$ = -68.32 (H_2O, l), - 94.054(CO_2, g), -26.417 (CO, g)

1) T. Carlton-Sutton, H. R. Ambler, G. W. Williams, Proc. Phys. Soc. (London) 48, 189 (1936).
2) J. H. Awberry, E. Griffiths, Proc. Roy. Soc. (London) A141, 17 (1933).
3) R. W. Fenning, F. T. Cotton, ibid., 1 (1933).

Heat Capacity and Entropy.

The functions are based on the rotational constants of Pliva, J. Mol. Spect. 12, 360 (1964), and the frequencies determined by Tidwell, Plyler and Benedict, J. Opt. Soc. Am. 50, 1243 (1960). The bond distances reported by Pliva were obtained from measurements of isotopic shifts in the infrared. They include higher-order corrections for vibration-rotation interaction and are in satisfactory agreement with the infrared and microwave studies of Douglas and Moller, J. Chem. Phys. 22, 275 (1954) and the electron diffraction data of Schomaker and Spurr, J. Am. Chem. Soc. 64, 1184 (1942).

Dinitrogen Trioxide (N_2O_3)

(Ideal Gas) Mol. Wt. = 76.016

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100	10.347	59.900	86.286	-2.639	20.591	24.641	-53.850
200	13.503	68.093	75.284	-1.438	20.069	28.917	-31.598
298	15.683	73.915	73.915	-.000	19.800	33.324	-24.426
300	15.718	74.012	73.915	.029	19.797	33.408	-24.337
400	17.385	78.771	74.553	1.687	19.691	37.965	-20.742
500	18.731	82.801	75.810	3.496	19.700	42.534	-18.591
600	19.821	86.316	77.274	5.425	19.785	47.095	-17.153
700	20.693	89.439	78.793	7.453	19.918	51.636	-16.121
800	21.386	92.249	80.302	9.558	20.083	56.155	-15.340
900	21.937	94.801	81.774	11.725	20.270	60.654	-14.728
1000	22.376	97.136	83.195	13.941	20.472	65.131	-14.234
1100	22.729	99.286	84.561	16.197	20.681	69.586	-13.825
1200	23.015	101.276	85.872	18.485	20.896	74.023	-13.481
1300	23.250	103.128	87.129	20.799	21.113	78.441	-13.187
1400	23.444	104.858	88.334	23.134	21.331	82.842	-12.932
1500	23.606	106.482	89.491	25.486	21.548	87.227	-12.708
1600	23.742	108.010	90.601	27.854	21.765	91.600	-12.511
1700	23.857	109.453	91.668	30.234	21.979	95.958	-12.336
1800	23.956	110.819	92.694	32.625	22.187	100.304	-12.178
1900	24.041	112.117	93.682	35.025	22.391	104.639	-12.036
2000	24.114	113.352	94.635	37.433	22.591	108.961	-11.906
2100	24.178	114.530	95.555	39.847	22.786	113.275	-11.788
2200	24.234	115.656	96.443	42.268	22.973	117.580	-11.680
2300	24.283	116.734	97.302	44.694	23.156	121.875	-11.580
2400	24.327	117.769	98.133	47.124	23.332	126.165	-11.488
2500	24.366	118.762	98.939	49.559	23.500	130.445	-11.403
2600	24.400	119.719	99.720	51.997	23.663	134.720	-11.324
2700	24.431	120.640	100.478	54.439	23.819	138.990	-11.250
2800	24.459	121.529	101.214	56.883	23.968	143.252	-11.181
2900	24.484	122.388	101.929	59.331	24.111	147.512	-11.116
3000	24.507	123.218	102.625	61.780	24.246	151.766	-11.056
3100	24.527	124.022	103.302	64.232	24.376	156.013	-10.998
3200	24.546	124.801	103.962	66.686	24.499	160.256	-10.944
3300	24.563	125.557	104.605	69.141	24.616	164.494	-10.893
3400	24.579	126.290	105.232	71.598	24.726	168.735	-10.846
3500	24.594	127.003	105.844	74.057	24.832	172.964	-10.800
3600	24.607	127.696	106.441	76.517	24.931	177.198	-10.757
3700	24.619	128.371	107.025	78.978	25.025	181.424	-10.716
3800	24.630	129.027	107.595	81.441	25.114	185.655	-10.677
3900	24.641	129.667	108.153	83.904	25.200	189.875	-10.640
4000	24.651	130.291	108.699	86.369	25.278	194.094	-10.604
4100	24.660	130.900	109.233	88.834	25.352	198.315	-10.571
4200	24.668	131.494	109.756	91.301	25.423	202.533	-10.538
4300	24.676	132.075	110.268	93.768	25.491	206.753	-10.508
4400	24.683	132.642	110.770	96.236	25.552	210.964	-10.478
4500	24.690	133.197	111.263	98.705	25.610	215.177	-10.450
4600	24.696	133.740	111.745	101.174	25.666	219.395	-10.423
4700	24.702	134.271	112.219	103.644	25.717	223.603	-10.397
4800	24.708	134.791	112.684	106.114	25.765	227.816	-10.372
4900	24.713	135.301	113.140	108.586	25.811	232.012	-10.348
5000	24.718	135.800	113.588	111.057	25.853	236.225	-10.325
5100	24.723	136.289	114.029	113.529	25.891	240.435	-10.303
5200	24.728	136.770	114.461	116.002	25.929	244.636	-10.281
5300	24.732	137.241	114.887	118.475	25.963	248.847	-10.261
5400	24.736	137.703	115.305	120.948	25.995	253.046	-10.241
5500	24.739	138.157	115.716	123.422	26.025	257.259	-10.222
5600	24.743	138.603	116.121	125.896	26.051	261.456	-10.203
5700	24.746	139.041	116.519	128.370	26.077	265.659	-10.185
5800	24.750	139.471	116.911	130.845	26.100	269.871	-10.169
5900	24.753	139.894	117.297	133.320	26.121	274.069	-10.152
6000	24.756	140.310	117.678	135.796	26.140	278.275	-10.136

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1964

DINITROGEN TRIOXIDE (N_2O_3) (IDEAL GAS) MOL. WT. = 76.016

Point Group C_s

$\Delta H_f^\circ{}_0$ = Unknown

$S^\circ_{298.15} = 73.91 \pm 0.5$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 19.80 \pm 0.2$ kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1863 (1)	783 (1)	313 (1)
1589 (1)	627 (1)	253 (1)
1297 (1)	407 (1)	[Rotation]

Bond Distance: N-N = 2.08 Å N-O (nitroso) = 1.12 Å N-O (nitro) = 1.18 Å

Bond Angle: O-N-N (nitroso) = 110° O-N-O = 134° $\sigma = 1$

Product of Moments of Inertia: $I_AI_BI_C = 4.6201 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

Equilibria for the reaction $N_2O_3(g) \rightarrow NO(g) + NO_2(g)$ have been studied by Beattie and Bell, J. Chem. Soc. 1957, 1681 (1957), Verhoek and Daniels, J. Am. Chem. Soc. 53, 1250 (1931) and Abel and Proisl, Z. Elektrochem. 35, 712 (1929). The results of Beattie and Bell are the most extensive, but they depend on the early analysis of Giauque and Kemp, J. Chem. Phys. 6, 40 (1938), for the simultaneous equilibrium $N_2O_4(g) \rightarrow 2NO_2(g)$. The JANAF analysis of the tetroxide dissociation has been used to recalculate the data of Beattie and Bell. Non-ideality of N_2O_4 and NO_2 was allowed for by use of the equations of state of Giauque and Kemp, while non-ideality of NO and N_2O_3 was removed by extrapolation of the equilibrium constants to zero pressure in a manner similar to that of Beattie and Bell. The data of Verhoek and Daniels and of Abel and Proisl have not been recalculated. Second and third law analyses of the results are summarized below. The heat of formation was obtained from $\Delta H_r^\circ{}_{298} = 9.70$ kcal. mole^{-1}.

Source	Temp. Range °K	T °K	Third Law ΔS_T°	Second Law ΔS_T°	Second Law ΔH_{298}°	Third Law ΔH_{298}°
			(cal. deg.$^{-1}$ mole-1)		(kcal. mole^{-1})	
Beattie - Bell[a]	278 - 318	298	——	33.25 ± 0.35	9.527 ±0.096	——
Beattie - Bell[b]	278 - 318	298	33.77	33.04 ± 0.31	9.476 ±0.093	9.695
Beattie - Bell[c]	278 - 318	298	33.77	33.56 ± 0.52	9.642 ±0.155	9.706
Verhoek - Daniels	298 - 318	308	33.78	38.8 ± 1.9	11.1 ±0.6	9.59
Abel - Proisl	281 - 308	294	33.77	32.9	9.60	9.86

a) Given by authors b) From author's K_p values c) From recalculated K_p values

Heat Capacity and Entropy.

The functions are similar to those calculated by I. C. Hisatsune, J. Phys. Chem 65, 2249 (1961), based on the analysis of Devlin and Hisatsune, Spectrochim. Acta 17, 218 (1961), of the Raman and infrared spectra in terms of Urey - Bradley force constants. Devlin and Hisatsune used observed isotopic shifts in the spectra along with force constants transferred from nitrogen oxides and oxyhalides in order to select the N-N bond distance and the O-N-N bond angle.

The unobserved mode was assumed to be free internal rotation around the N-N bond, leading to $S^\circ_{298} = 73.91$ cal. deg.$^{-1}$ mole^{-1} which is in good agreement with 74.13 ± 0.52 cal. deg.$^{-1}$ mole^{-1} obtained from the recalculated second law of Beattie and Bell. The principal moments of inertia are $I_A = 22.694 \times 10^{-39}$, $I_B = 29.577 \times 10^{-39}$, and $I_C = 6.883 \times 10^{-39}$ g. cm.^{2}, while the reduced moment for internal rotation was calculated as $I_r = 0.990 \times 10^{-39}$ g. cm.^{2}

Dinitrogen Tetroxide (N_2O_4)

(Crystal) Mol. Wt. = 92.016

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-5.112	-7.263	-7.263	INFINITE
100	14.508	13.415	56.802	-4.339	-8.601	2.174	-4.750
200	21.917	25.813	38.353	-2.508	-8.833	13.095	-14.309
298	29.183	35.920	35.920	-.000	-8.373	23.785	-17.434
300	29.320	36.101	35.921	.054	-8.358	23.984	-17.471
400	36.720	45.648	37.172	3.390	-7.141	34.600	-18.904
500	40.000	54.271	39.749	7.261	-5.435	44.844	-19.600

June 30, 1961; Sept. 30, 1964

DINITROGEN TETROXIDE (N_2O_4) (CRYSTAL) MOL. WT. = 92.016

$\Delta H_{f\ 0}^\circ = -7.263 \pm 0.4$ kcal. mole^{-1}

$S_{298.15}^\circ = 35.92$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_{f\ 298.15}^\circ = -8.373 \pm 0.4$ kcal. mole^{-1}

$T_m = 261.95 \pm 0.05$°K.

$\Delta H_m^\circ = 3.502 \pm 0.003$ kcal. mole^{-1}

Heat of Formation.

The heat of formation was back calculated from that of the liquid using the measured heat of melting and the enthalpy of the crystal and liquid.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) measured the low temperature heat capacity from 15-295°K. The entropy was obtained by integration of this data using $S_{15} = 0.34$ cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The temperature and heat of melting were also measured by Giauque and Kemp, loc. cit.

Dinitrogen Tetroxide (N_2O_4)

(Liquid) Mol. Wt. = 92.016

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 6.034	- 4.488	- 4.488	INFINITE
100	26.980	17.417	77.761	- 6.034	- 6.599	3.775	- 8.249
200	30.480	37.192	52.999	- 3.161	- 5.789	13.863	- 15.148
298	34.060	50.007	50.007	.000	- 4.676	23.282	- 17.065
300	34.140	50.218	50.008	.063	- 4.652	23.455	- 17.086
400	38.440	60.628	51.398	3.692	- 3.142	32.607	- 17.815
500	42.740	69.668	54.165	7.751	- 1.248	41.333	- 18.066

June 30, 1961; Sept. 30, 1964; Dec. 31, 1964

DINITROGEN TETROXIDE (N_2O_4) (LIQUID) MOL. WT. = 92.016

$\Delta H^\circ_{f\ 0} = -4.488 \pm 0.4$ kcal. mole^{-1}

$S^\circ_{298.15} = 50.007$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -4.676 \pm 0.4$ kcal. mole^{-1}

$T_m = 261.95 \pm 0.05$°K.

$\Delta H^\circ_m = 3.502 \pm 0.003$ kcal. mole^{-1}

$T_b = 294.25$°K. (to $N_2O_4 + NO_2$)

$\Delta H^\circ_v = 9.11 \pm 0.1$ kcal. mole^{-1} (to $N_2O_4 + NO_2$)

$T_b = [301.4$°K.$]$ (to N_2O_4)

$\Delta H^\circ_v = [6.79]$ kcal. mole^{-1} (to N_2O_4)

Heat of Formation.

The heat of formation was back calculated from that of the gas using the calorimetrically measured heat of vaporization to the equilibrium mixture, in conjunction with a dissociation constant $\alpha = 0.161$.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) measured the low temperature heat capacity from 15°-295°K., above 295°K. the heat capacity was smoothly extrapolated.

Melting and Vaporization Data.

Giauque and Kemp, loc. cit. measured the temperature and heat of melting and also the boiling point and the calorimetric value of the heat of vaporization to the equilibrium mixture. The heat of vaporization to a hypothetical pure N_2O_4 gas at 294.25°K. was calculated to be 6.91 kcal. mole^{-1}.

Dinitrogen Tetroxide (N_2O_4)

(Ideal Gas) Mol. Wt. = 92.016

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-3.919	4.473	4.473	INFINITE
100	11.057	57.138	86.759	-2.962	3.319	9.721	-21.244
200	15.107	66.037	74.310	-1.655	2.563	16.446	-17.971
298	18.465	72.724	72.724	.000	2.170	23.355	-17.119
300	18.520	72.838	72.724	.034	2.165	23.486	-17.109
400	21.157	78.542	73.484	2.023	2.035	30.619	-16.728
500	23.233	83.496	75.002	4.247	2.094	37.761	-16.505
600	24.860	87.881	76.790	6.655	2.280	44.880	-16.347
700	26.127	91.813	78.660	9.207	2.548	51.959	-16.222
800	27.113	95.369	80.530	11.871	2.873	58.994	-16.116
900	27.884	98.609	82.361	14.623	3.238	65.988	-16.023
1000	28.492	101.579	84.137	17.443	3.630	72.942	-15.941
1100	28.977	104.318	85.848	20.317	4.038	79.852	-15.864
1200	29.367	106.857	87.495	23.235	4.459	86.726	-15.794
1300	29.684	109.221	89.076	26.188	4.887	93.564	-15.729
1400	29.946	111.430	90.595	29.170	5.320	100.369	-15.667
1500	30.163	113.504	92.054	32.176	5.755	107.143	-15.610
1600	30.345	115.457	93.456	35.201	6.190	113.888	-15.556
1700	30.499	117.301	94.805	38.244	6.626	120.607	-15.504
1800	30.630	119.048	96.104	41.300	7.055	127.299	-15.455
1900	30.743	120.707	97.355	44.369	7.481	133.970	-15.409
2000	30.840	122.287	98.563	47.448	7.902	140.612	-15.365
2100	30.925	123.794	99.728	50.537	8.319	147.238	-15.323
2200	30.999	125.234	100.855	53.633	8.725	153.843	-15.282
2300	31.064	126.613	101.945	56.736	9.127	160.430	-15.244
2400	31.121	127.937	103.001	59.845	9.521	167.002	-15.207
2500	31.172	129.208	104.024	62.960	9.905	173.553	-15.171
2600	31.218	130.432	105.016	66.080	10.284	180.092	-15.137
2700	31.259	131.611	105.980	69.204	10.653	186.617	-15.105
2800	31.295	132.748	106.915	72.331	11.013	193.128	-15.074
2900	31.329	133.847	107.825	75.463	11.367	199.629	-15.044
3000	31.358	134.909	108.710	78.597	11.710	206.116	-15.015
3100	31.386	135.938	109.572	81.734	12.047	212.589	-14.987
3200	31.410	136.935	110.412	84.874	12.375	219.050	-14.960
3300	31.433	137.902	111.230	88.016	12.695	225.502	-14.934
3400	31.454	138.841	112.029	91.161	13.008	231.947	-14.909
3500	31.473	139.753	112.808	94.307	13.314	238.378	-14.884
3600	31.490	140.639	113.569	97.455	13.612	244.811	-14.861
3700	31.506	141.502	114.312	100.605	13.904	251.229	-14.839
3800	31.521	142.343	115.039	103.756	14.189	257.640	-14.817
3900	31.535	143.162	115.749	106.909	14.470	264.039	-14.796
4000	31.547	143.960	116.445	110.063	14.742	270.434	-14.775
4100	31.559	144.739	117.125	113.218	15.008	276.826	-14.755
4200	31.570	145.500	117.792	116.375	15.271	283.206	-14.736
4300	31.580	146.243	118.445	119.532	15.528	289.589	-14.718
4400	31.590	146.969	119.085	122.691	15.779	295.953	-14.699
4500	31.599	147.679	119.713	125.850	16.025	302.320	-14.682
4600	31.607	148.374	120.328	129.011	16.269	308.686	-14.665
4700	31.615	149.054	120.932	132.172	16.506	315.036	-14.648
4800	31.623	149.719	121.525	135.334	16.740	321.391	-14.633
4900	31.630	150.371	122.107	138.496	16.970	327.723	-14.616
5000	31.636	151.011	122.679	141.660	17.197	334.062	-14.601
5100	31.642	151.637	123.240	144.824	17.419	340.402	-14.586
5200	31.648	152.252	123.792	147.988	17.639	346.726	-14.572
5300	31.654	152.854	124.335	151.153	17.856	353.065	-14.558
5400	31.659	153.446	174.869	154.319	18.070	359.377	-14.544
5500	31.664	154.027	125.394	157.485	18.282	365.706	-14.531
5600	31.668	154.598	125.910	160.652	18.489	372.011	-14.518
5700	31.673	155.158	126.418	163.819	18.695	378.325	-14.505
5800	31.677	155.709	126.918	166.986	18.898	384.640	-14.493
5900	31.681	156.251	127.411	170.154	19.099	390.935	-14.480
6000	31.685	156.783	127.896	173.322	19.297	397.243	-14.469

Dec. 31, 1960; June 30, 1961; Sept. 30, 1964

DINITROGEN TETROXIDE (N_2O_4) (IDEAL GAS) MOL. WT. = 92.016

Point Group V_h

$S^\circ_{298.15}$ = 72.72 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = 4.47 ± 0.4 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 2.17 ± 0.4 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1373 (1)	1710 (1)	1748 (1)
823 (1)	480 (1)	385 (1)
260 (1)	430 (1)	1261 (1)
[50](1)	675 (1)	750 (1)

Bond Distance: N-N = 1.750Å N-O = 1.180Å

Bond Angle: O-N-O = 133.7°

$\sigma = 4$

Product of the Moments of Inertia: $I_AI_BI_C$ = 9.9304 X 10^{-114} g.^{3} cm.^{6}

Heat of Formation.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) calculated idealized equilibrium constants for the reaction $N_2O_4(g) = 2NO_2(g)$ from the work of Bodenstein and Boës$^{(1)}$, Zeits. fur physik. Chem. 100, 75 (1922), Verhoek and Daniels$^{(2)}$, J. Am. Chem. Soc. 53, 1250 (1931) and Wourtzel$^{(3)}$, Compt. Rend. 169, 1397 (1919). The second and third law analysis of these equilibrium constants has been repeated using more recent functions. The results are shown below.

Ref.	Third Law ΔH_{298}	Second Law ΔH_{298}
1.	13.644	13.634 ± 0.015*
2.	13.672	14.429 ± 0.126
3.	13.657	13.599 ± 0.019**

* Ten points rejected because of statistically significant scatter.

** One point rejected.

The second law value of Verhoek and Daniels was not considered significant due to the extremely small temperature range and the use of only three temperatures. The adopted value was 13.65 ± 0.03 kcal. which leads to 2.17 kcal. mole^{-1} for the heat of formation of $N_2O_4(g)$.

Heat Capacity and Entropy.

The structural parameters were taken from the electron diffraction measurements of D. W. Smith and K. Hedberg, J. Chem. Phys. 25, 1282 (1956). The vibrational frequencies are those chosen by I. C. Hitsatsune, J. P. Devlin and Y. Wade, J. Chem. Phys. 33, 714 (1960). The torsional frequency of 50 cm.$^{-1}$ was estimated in order to bring the entropy of the gas into agreement with that determined by Giauque and Kemp loc. cit. from low temperature heat capacities and heats of fusion and vaporization. The individual moments of inertia were I_A = 12.508 X 10^{-39} g. cm.^{2}, I_B = 22.609 X 10^{-39} g. cm.^{2}, and I_C = 35.117 X 10^{-39} g. cm.^{2}

Dinitrogen Pentoxide (N_2O_5)

(Ideal Gas) Nol. Wt. = 108.016

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200	18.691	74.506	84.772	-2.053	3.036	19.848	-21.688
298	23.017	82.801	82.801	.000	2.700	28.186	-20.660
300	23.089	82.944	82.801	.043	2.697	28.343	-20.647
400	26.494	90.077	83.751	2.530	2.710	36.898	-20.159
500	28.965	96.270	85.649	5.311	2.960	45.421	-19.852
600	30.684	101.713	87.882	8.298	3.348	53.879	-19.624
700	31.891	106.539	90.210	11.431	3.808	62.264	-19.439
800	32.744	110.856	92.525	14.664	4.303	70.579	-19.280
900	33.365	114.750	94.782	17.971	4.816	78.834	-19.143
1000	33.806	118.289	96.958	21.331	5.334	87.032	-19.020
1100	34.137	121.527	99.047	24.728	5.846	95.176	-18.909
1200	34.410	124.509	101.046	28.156	6.353	103.275	-18.808
1300	34.612	127.271	102.958	31.607	6.851	111.333	-18.716
1400	34.782	129.842	104.787	35.077	7.340	119.350	-18.631
1500	34.913	132.246	106.538	38.562	7.818	127.335	-18.552
1600	35.027	134.503	108.216	42.060	8.287	135.289	-18.479
1700	35.105	136.629	109.825	45.566	8.746	143.213	-18.410
1800	35.177	138.638	111.371	49.080	9.188	151.108	-18.346
1900	35.242	140.542	112.857	52.601	9.619	158.983	-18.286
2000	35.302	142.351	114.287	56.129	10.038	166.830	-18.229
2100	35.336	144.074	115.664	59.660	10.445	174.661	-18.176
2200	35.368	145.719	116.993	63.196	10.835	182.470	-18.126
2300	35.399	147.292	118.277	66.734	11.214	190.261	-18.078
2400	35.428	148.799	119.518	70.275	11.579	198.043	-18.033
2500	35.455	150.246	120.718	73.820	11.929	205.799	-17.990
2600	35.480	151.637	121.881	77.366	12.268	213.550	-17.950
2700	35.504	152.976	123.008	80.916	12.594	221.287	-17.911
2800	35.526	154.268	124.101	84.467	12.907	229.009	-17.874
2900	35.546	155.515	125.163	88.021	13.208	236.726	-17.839
3000	35.565	156.720	126.195	91.576	13.496	244.429	-17.806
3100	35.576	157.886	127.198	95.133	13.775	252.123	-17.774
3200	35.587	159.016	128.175	98.692	14.040	259.803	-17.743
3300	35.597	160.111	129.126	102.251	14.294	267.479	-17.714
3400	35.607	161.174	130.053	105.811	14.537	275.149	-17.686
3500	35.617	162.206	130.957	109.372	14.771	282.807	-17.658
3600	35.625	163.209	131.839	112.934	14.994	290.468	-17.633
3700	35.634	164.185	132.699	116.497	15.208	298.118	-17.608
3800	35.642	165.135	133.540	120.061	15.414	305.766	-17.585
3900	35.649	166.061	134.362	123.626	15.612	313.399	-17.562
4000	35.656	166.964	135.166	127.191	15.799	321.027	-17.539
4100	35.661	167.845	135.953	130.757	15.979	328.657	-17.518
4200	35.666	168.704	136.723	134.323	16.153	336.281	-17.498
4300	35.671	169.543	137.476	137.890	16.320	343.911	-17.479
4400	35.676	170.363	138.214	141.457	16.477	351.520	-17.459
4500	35.680	171.165	138.937	145.025	16.630	359.134	-17.441
4600	35.684	171.949	139.646	148.593	16.777	366.755	-17.424
4700	35.688	172.716	140.342	152.162	16.917	374.359	-17.407
4800	35.692	173.467	141.023	155.731	17.052	381.968	-17.391
4900	35.696	174.203	141.693	159.300	17.183	389.554	-17.374
5000	35.699	174.924	142.350	162.870	17.309	397.156	-17.359
5100	35.702	175.631	142.996	166.440	17.428	404.755	-17.344
5200	35.705	176.324	143.630	170.011	17.546	412.345	-17.330
5300	35.708	177.004	144.253	173.581	17.659	419.947	-17.316
5400	35.711	177.671	144.866	177.152	17.767	427.527	-17.302
5500	35.713	178.326	145.468	180.723	17.874	435.129	-17.290
5600	35.715	178.970	146.060	184.295	17.973	442.702	-17.276
5700	35.717	179.602	146.643	187.866	18.072	450.286	-17.264
5800	35.719	180.223	147.217	191.438	18.167	457.880	-17.253
5900	35.721	180.834	147.781	195.010	18.259	465.450	-17.241
6000	35.722	181.434	148.337	198.582	18.348	473.037	-17.230

Dec. 31, 1960; Dec. 31, 1964

DINITROGEN PENTOXIDE (N_2O_5) (IDEAL GAS) MOL. WT. = 108.016

Point Group C_{2v}

$S^\circ_{298.15}$ = 82.8 ± 1.0 cal. deg. mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = Unknown

$\Delta H^\circ_{f\ 298.15}$ = 2.7 ± 0.3 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
1728 (1)	614 (1)	[614](1)	[Rotation]	860 (1)
1338 (1)	353 (1)	[Rotation]	1728 (1)	743 (1)
743 (1)	[85](1)	577 (1)	1247 (1)	353 (1)

Bond Distance: O-N = 1.21 Å N-O' = 1.46 Å

Bond Angle: O-N-O = 134° N-O'-N = 95°

O-N-O planes perpendicular to N-O'-N plane

$\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 2.066 \times 10^{-113}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was obtained by recalculation of the calorimetric data of Ray and Ogg for the reaction of $N_2O_5(g)$ with NO. The stoichiometry of the reaction products, originally based on the results for $N_2O_4 \rightarrow 2\ NO_2$ from Giauque and Kemp, J. Chem. Phys. 6, 40 (1938), was based on the JANAF analysis of this simultaneous equilibrium. A correction of 0.29 kcal. was made in the heat of reaction because of the additional formation of N_2O_3 from NO and NO_2.

Confirmation of the heat of formation was obtained by combination of the heats of hydrolysis and sublimation of $N_2O_5(c)$. The results are summarized below. Second law values are given for the heats of sublimation, but third law analyses suggest that the value from Russ and Pokorny is more reliable. Most of the uncertainty in this path, however, arises from the heat of hydrolysis.

Source	Method	Reaction	$\Delta H^\circ_{r\ 298.15}$ (kcal. mole^{-1})	$\Delta H^\circ_{f\ 298.15}$
1	Calorimetric	$N_2O_5(g) + NO(g) \rightarrow$ $0.724\ NO_2(g) + 1.138\ N_2O_4(g)$	-16.05 ± 0.20	2.67
2	Calorimetric	$N_2O_5(c) + H_2O(l) \rightarrow 2\ HNO_3(aq)$	-20.2 ± 0.5	——
3	Vapor Pressure	$N_2O_5(c) \rightarrow N_2O_5(g)$	13.37 ± 0.06	2.79*
4	Vapor Pressure	$N_2O_5(c) \rightarrow N_2O_5(g)$	13.25 ± 0.12	2.67*

*Using reaction 2 and $\Delta H^\circ_{f\ 298.15} = -68.32(H_2O,\ l),\ -49.55(HNO_3,\ aq)$

1) J. D. Ray, R. A. Ogg, J. Phys. Chem. 61, 1087 (1957).
2) R. A. Ogg, J. Chem. Phys. 15, 337 (1947).
3) Russ and Pokorny, Monatsh. 34, 1027 (1913), dynamic vapor pressures.
4) F. Daniels, A. C. Bright, J. Am. Chem. Soc. 42, 1131 (1920).

Heat Capacity and Entropy.

Ray and Ogg, J. Chem. Phys. 26, 984 (1957) reported $S^\circ_{298.15}$ = 85 ± 0.5 cal. deg. mole^{-1} from combination of kinetic and thermochemical values. This entropy was recalculated as follows. The rate data of Ray and Ogg, loc. cit., and of Daniels and Johnston, J. Am. Chem. Soc. 43, 53 (1921) give for the reaction $N_2O_5(g) \rightarrow NO(g) + NO_2(g) + O_2(g)$ at 25°C the equilibrium constant $K = 5.15 \times 10^{-7}$ moles^2 liter^{-2} = 3.08×10^{-4} atm^2. The resulting value of $\Delta F^\circ_{r\ 298.15}$ = 4.79 kcal. mole^{-1} leads to $S^\circ_{298.15}$ = 82.8 cal. deg. mole^{-1} for $N_2O_5(g)$ when combined with the JANAF entropies and heats of formation of the components of the reaction.

The molecular structure is the nonplanar configuration derived from the electron diffraction study of Akishin, Vilkov and Rosolovskii, Zhur. Strukt. Khim. 1, 1 (1960). A planar model (also point group C_{2v}) was assumed by Hisatsune, Devlin and Wada, Spectrochim. Acta 18, 1641 (1962) in their approximate normal coordinate analysis of the infrared and Raman spectra. The frequency assignments of these authors are listed above in the order for the planar model, although the vibrations for the nonplanar form will separate differently into the species $5A_1$, $3A_2$, $3B_1$ and $4B_2$. Hisatsune, et al., estimated the N-O'-N deformation frequency (85 cm.$^{-1}$) from combination bands in the solid and gas phase spectra. The JANAF thermodynamic functions were obtained using these frequencies and assuming the two NO_2 groups to be hindered internal rotators. Barriers to internal rotation of 4.4 kcal. (corresponding to torsional vibrations of about 55 cm.$^{-1}$) were selected in order to give the observed entropy at room temperature. The principal moments of inertia for the nonplanar model were taken as $I_A = 30.60 \times 10^{-39}$, $I_B = 40.15 \times 10^{-39}$ and $I_C = 16.82 \times 10^{-39}$ g. cm.^{2}, while $I_r = 4.693 \times 10^{-39}$ g. cm.^{2} was used for the reduced moment of inertia of the O_2 tops.

Silicon Nitride, Alpha (α-Si_3N_4)
(Crystal) GFW = 140.2848

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	23.789	27.000	27.000	.000	- 178.000	- 154.734	113.423
300	23.850	27.147	27.000	.044	- 178.009	- 154.590	112.619
400	26.450	34.367	27.967	2.560	- 178.408	- 146.721	80.165
500	28.850	40.531	29.877	5.327	- 178.679	- 138.763	60.653
600	31.000	45.989	32.116	8.324	- 178.810	- 130.766	47.631
700	33.000	50.920	34.456	11.525	- 178.820	- 122.756	38.326
800	34.850	55.450	36.800	14.920	- 178.711	- 114.755	31.350
900	36.400	59.648	39.109	18.485	- 178.500	- 106.769	25.927
1000	37.800	63.556	41.360	22.196	- 178.209	- 98.815	21.596
1100	39.120	67.222	43.546	26.044	- 177.842	- 90.893	18.059
1200	40.270	70.677	45.665	30.014	- 177.409	- 83.008	15.118
1300	41.236	73.939	47.715	34.091	- 176.919	- 75.161	12.636
1400	42.046	77.026	49.700	38.256	- 176.391	- 67.354	10.514
1500	42.700	79.950	51.620	42.495	- 175.835	- 59.583	8.681
1600	43.152	82.720	53.478	46.788	- 175.269	- 51.850	7.082
1700	43.540	85.348	55.276	51.123	- 210.684	- 43.837	5.636
1800	43.846	87.846	57.017	55.493	- 209.962	- 34.043	4.133
1900	44.106	90.224	58.702	59.891	- 209.220	- 24.289	2.794
2000	44.320	92.492	60.335	64.313	- 208.464	- 14.572	1.592
2100	44.402	94.656	61.919	68.749	- 207.702	- 4.999	.510
2200	44.482	96.724	63.454	73.193	- 206.940	4.737	- .471
2300	44.558	98.703	64.944	77.645	- 206.176	14.341	- 1.363
2400	44.630	100.601	66.390	82.104	- 205.409	23.916	- 2.178
2500	44.700	102.424	67.795	86.571	- 204.642	33.453	- 2.924
2600	44.766	104.178	69.161	91.044	- 203.873	42.964	- 3.611
2700	44.830	105.869	70.490	95.524	- 203.101	52.441	- 4.245
2800	44.890	107.500	71.783	100.010	- 202.327	61.895	- 4.831
2900	44.946	109.077	73.042	104.502	- 201.549	71.318	- 5.375
3000	45.000	110.601	74.268	108.999	- 200.772	80.712	- 5.880

Dec. 31, 1960; Mar. 31, 1967

SILICON NITRIDE, ALPHA (α-Si_3N_4) (CRYSTAL) GFW = 140.2848

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [27 ± 4] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -178 ± 7 kcal/mol

Td = [2151]°K

Heat of Formation.

The equilibria (A) $Si_3N_4(c) = 3\ Si(l) + 2\ N_2(g)$ and (B) $Si_3N_4(c) = 3\ Si(c) + 2\ N_2(g)$ have been investigated by three groups. R. D. Pehlke and J. F. Elliott, Trans. Met. Soc. AIME 215, 781 (1959), made four series of measurements which mainly concerned reaction (A). W. B. Hincke and L. R. Brantley, J. Amer. Chem. Soc. 52, 48 (1930), made a single series of measurements which covered reactions (A) and (B). C. Matignon, Bull. Soc. Chim. France 13, 791 (1913), also gave a single equilibrium point for reaction (C) $3\ SiO_2(c) + 6\ C + 2\ N_2 = Si_3N_4(c) + 6\ CO(g)$. Below are shown 2nd and 3rd law analyses of the data. It should be noted that these analyses are based on the estimated heat capacities above 900°K, and on an estimated entropy. The uncertainty due to these estimates is estimated as ± 7 kcal in ΔHf°_{298}.

Reference	Points	Range °K	Reaction	ΔHr°_{298} kcal/mol 2nd law	ΔHr°_{298} kcal/mol 3rd law	Drift eu	*ΔHf°_{298} kcal/mol
Pehlke - 1	9	1699-1934	A	190.1±7.6	211.79	11.8±4.3	-177.04
Pehlke - 2	9	1691-1939	A	210.7±8.6	213.29	1.8±4.9	-178.53
Pehlke - 3	10	1692-1966	A	212.3±3.3	212.61	0.1±1.9	-177.85
Pehlke - 4	6	1690-1872	A	207.0±7.5	212.47	2.6±4.3	-177.71
Pehlke	30**	1690-1966	A	212.8±3.2	212.67	-0.2±1.8	-177.91
Hinke	4	1709-1802	A	196.0±18.5	213.43	10.3±10.4	-178.67
Pehlke	4	1659-1666	B		177.41		-177.41
Hinke	3	1606-1675	B		177.82	22.8±11.8	-177.82
Matignon	1	1700	C		318.9		-175.1

*Calculated from the third law ΔHr°_{298} values.

**Four points rejected due to failure of a statistical test; this set is a combination of the first four sets.

The adopted ΔHf°_{298}(α-Si_3N_4) = -178±7 kcal/mol.

L. A. McClaine and C. P. Coppel, A. D. Little, Inc., "Equilibrium Studies of Refractory Nitrides," Tech. Rept. AFML-TR-65-99, Part 11, Dec. 1966, have investigated the decomposition reaction (B). They conclude that at 1618°K the equilibrium pressure is roughly 0.15 mm. This corresponds to ΔHf°_{298} =-182.3 kcal, and was not given any weight in the adopted value.

Heat Capacity and Entropy.

The enthalpy of α-Si_3N_4 has been measured at three temperatures, in the range 373° - 858°K, by S. Sato, Bull. Chem. Soc. Japan 13, 41 (1938). The heat capacity is calculated from the data assuming that a limit of 45 gibbs/mol is attained by 3000°K. The entropy is obtained from the equilibrium data of Pehlke and Elliott, loc. cit.

Decomposition Data.

The temperature of decomposition is calculated as the point at which the decomposition pressure of nitrogen reaches 1 atm.

Triphosphorus Pentanitride (P_3N_5)

(Crystal) GFW = 162.9549

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	35.600	44.000	44.000	.000	-64.000	-38.128	27.949
300	35.800	44.221	44.001	.066	-63.993	-37.967	27.659
400	46.000	56.017	45.540	4.191	-63.210	-29.386	16.056
500	52.000	66.963	48.748	9.108	-61.764	-21.089	9.218
600	56.000	76.813	52.620	14.516	-59.938	-13.120	4.779
700	59.000	85.684	56.720	20.274	-57.899	-5.478	1.710
800	61.000	93.698	60.850	26.279	-117.001	-14.066	3.843
900	62.500	100.975	64.910	32.459	-114.027	-1.375	.334
1000	63.400	107.609	68.853	38.755	-110.982	10.976	-2.399
1100	64.027	113.682	72.657	45.128	-107.902	23.023	-4.574
1200	64.500	119.275	76.312	51.556	-104.806	34.787	-6.336
1300	64.820	124.451	79.818	58.023	-101.699	46.296	-7.783
1400	64.987	129.262	83.180	64.515	-98.594	57.563	-8.986
1500	65.000	133.747	86.403	71.015	-95.504	68.611	-9.997

Dec. 31, 1960; Sept. 30, 1962; Mar. 31, 1967

TRIPHOSPHORUS PENTANITRIDE (P_3N_5) (CRYSTAL) GFW = 162.9549

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [44 ± 6] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -64 ± 5 kcal/mol

Td = [730]°K

Heat of Formation.

The heat of formation is based on the work of A. Stock and F. Wrede, Chem. Ber. 40, 2923 (1907), who burned P_3N_5 in oxygen. They report a ΔHr°_{298} = -949.4 kcal for the reaction 2 $P_3N_5(c) + 7.5O_2(g) = 1.5\ P_4O_{10}(amorph) + 5N_2(g)$. In NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Washington, D.C. (1965), a value of -947.7 kcal is used for the above reaction and we adopt this value. Using the JANAF value for $P_4O_{10}(c)$ and correcting this to P_4O_{10}(amorph) by adding -13.8 kcal/mol, from Technical Note 270-1, we obtain ΔHf°_{298} P_4O_{10}(amorph) = -716.5 kcal/mol. Thus, we derive ΔHf°_{298} $P_3N_5(c)$ = -63.525 kcal/mol; however, because of the uncertainties in the heat of reaction and correction for amorphous P_4O_{10} we round the value to -64 ± 5 kcal/mol.

Heat Capacity and Entropy.

S. Sato, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 34, 584 (1938), gave an equation for the heat capacity in the range 273° - 578°K. Judging from his results for $Be_3N_2(c)$ in the same paper, we believe his values will be slightly high at the upper end of the range. Thus, taking 8.2 gibbs/g-atom as the limiting value, a curve was drawn through Sato's values at the low end and approaching the limit asymptotically. The entropy was estimated from that of $Si_3N_4(c)$ by assuming that the ratio Cp_{298}/S_{298} on a gram atom basis would be the same for $P_3N_5(c)$.

Temperature of Decomposition.

Td is calculated as the point at which the total pressure reaches 1 atm. This corresponds to log Kp = -0.76 for the reaction $P_3N_5(c) = 0.75P_4(g) + 2.5N_2(g)$. The temperature of decomposition has been reported by V. F. Postnikov and L. L. Kuzmin, J. Appl. Chem. (USSR) 8, 429 (1935) as 1073°K. This has been confirmed by H. Moreau and P. Rocquet, Compt. Rend. 198, 1691 (1934) and Bull. Soc. Chim. France, 3, 1801 (1936); and E. O. Huffman, G. Tarbutton, G. V. Elmore, A. J. Smith and M. G. Rountree, J. Am. Chem. Soc. 79, 1765 (1957). However, it was also noted that $P_3N_5(c)$ is not reformed on cooling the decomposition products; thus the decomposition is non-equilibrium. It is known that the decomposition of AlN, BN and Be_3N_2 is kinetically limited and the equilibrium pressure is not attained until the average energy is greater than the activation energy. It appears that this is also the case for P_3N_5 and a high activation energy is expected.

Sodium (Na)

(Reference State) At. Wt. = 22.991

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 1.541	.000	.000	.000
100	5.366	5.690	17.897	- 1.221	.000	.000	.000
200	6.211	9.725	12.894	- .634	.000	.000	.000
298	6.730	12.298	12.298	.000	.000	.000	.000
300	6.741	12.340	12.298	.012	.000	.000	.000
400	7.531	16.086	12.695	1.356	.000	.000	.000
500	7.302	17.741	13.546	2.097	.000	.000	.000
600	7.124	19.056	14.358	2.818	.000	.000	.000
700	6.996	20.143	15.109	3.524	.000	.000	.000
800	6.918	21.072	15.798	4.219	.000	.000	.000
900	6.892	21.885	16.430	4.909	.000	.000	.000
1000	6.918	22.612	17.012	5.599	.000	.000	.000
1100	6.993	23.274	17.552	6.295	.000	.000	.000
1200	4.968	43.631	18.435	30.235	.000	.000	.000
1300	4.968	44.029	20.389	30.732	.000	.000	.000
1400	4.968	44.397	22.091	31.229	.000	.000	.000
1500	4.968	44.740	23.589	31.726	.000	.000	.000
1600	4.968	45.061	24.921	32.223	.000	.000	.000
1700	4.969	45.362	26.115	32.719	.000	.000	.000
1800	4.970	45.646	27.192	33.216	.000	.000	.000
1900	4.971	45.915	28.171	33.713	.000	.000	.000
2000	4.973	46.170	29.064	34.211	.000	.000	.000
2100	4.975	46.412	29.885	34.708	.000	.000	.000
2200	4.979	46.644	30.641	35.206	.000	.000	.000
2300	4.985	46.865	31.342	35.704	.000	.000	.000
2400	4.992	47.078	31.993	36.203	.000	.000	.000
2500	5.001	47.281	32.601	36.702	.000	.000	.000
2600	5.013	47.478	33.169	37.203	.000	.000	.000
2700	5.027	47.667	33.702	37.705	.000	.000	.000
2800	5.044	47.850	34.205	38.209	.000	.000	.000
2900	5.065	48.028	34.678	38.714	.000	.000	.000
3000	5.089	48.200	35.126	39.222	.000	.000	.000
3100	5.116	48.367	35.550	39.732	.000	.000	.000
3200	5.148	48.530	35.954	40.245	.000	.000	.000
3300	5.184	48.689	36.337	40.762	.000	.000	.000
3400	5.225	48.844	36.703	41.282	.000	.000	.000
3500	5.272	48.997	37.052	41.807	.000	.000	.000
3600	5.324	49.146	37.386	42.337	.000	.000	.000
3700	5.383	49.292	37.705	42.872	.000	.000	.000
3800	5.449	49.437	38.012	43.413	.000	.000	.000
3900	5.522	49.579	38.307	43.962	.000	.000	.000
4000	5.604	49.720	38.591	44.518	.000	.000	.000
4100	5.696	49.860	38.864	45.083	.000	.000	.000
4200	5.799	49.998	39.127	45.658	.000	.000	.000
4300	5.913	50.136	39.382	46.243	.000	.000	.000
4400	6.041	50.273	39.628	46.841	.000	.000	.000
4500	6.182	50.411	39.866	47.452	.000	.000	.000
4600	6.339	50.548	40.096	48.078	.000	.000	.000
4700	6.513	50.686	40.320	48.720	.000	.000	.000
4800	6.705	50.825	40.538	49.381	.000	.000	.000
4900	6.915	50.966	40.749	50.062	.000	.000	.000
5000	7.147	51.108	40.955	50.765	.000	.000	.000
5100	7.399	51.252	41.155	51.492	.000	.000	.000
5200	7.674	51.398	41.351	52.245	.000	.000	.000
5300	7.972	51.547	41.542	53.027	.000	.000	.000
5400	8.294	51.699	41.728	53.840	.000	.000	.000
5500	8.639	51.854	41.911	54.687	.000	.000	.000
5600	9.009	52.013	42.090	55.569	.000	.000	.000
5700	9.402	52.176	42.266	56.489	.000	.000	.000
5800	9.818	52.343	42.438	57.450	.000	.000	.000
5900	10.256	52.515	42.607	58.454	.000	.000	.000
6000	10.716	52.691	42.774	59.502	.000	.000	.000

June 30, 1962

SODIUM (Na) (REFERENCE STATE) AT. WT. = 22.991

0° to 370.98°K	Crystal
370.98° to 1176.9°K	Liquid
1176.9° to 6000°K	Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

Sodium (Na)

(Crystal) At. Wt. = 22.991

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F°-H°_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H°-H°_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 1.541	.000	.000	INFINITE
100	5.366	5.690	17.897	- 1.221	.000	.000	.000
200	6.211	9.725	12.894	- .634	.000	.000	.000
298	6.730	12.296	12.296	.000	.000	.000	.000
300	6.741	12.338	12.296	.012	.000	.000	.000
400	7.765	14.416	12.572	.738	- .618	.000	.000
500	8.000	16.194	13.124	1.535	- .562	.211	- .092
600	8.000	17.653	13.761	2.335	- .483	.359	- .131
700	8.000	18.886	14.408	3.135	- .389	.491	- .153
800	8.000	19.954	15.036	3.935	- .284	.610	- .167
900	8.000	20.897	15.636	4.735	- .174	.715	- .174
1000	8.000	21.740	16.205	5.535	- .064	.808	- .177

SODIUM (Na) (CRYSTAL) AT. WT. = 22.991

ΔH_f° 298.15 = 0

ΔH_s° 298.15 = 32.87 kcal. mole^{-1} (Diatomic gas)

T_m = 370.98 ± 0.02°K.

ΔH_s° 298.15 = 25.755 kcal. mole^{-1} (Monatomic gas)

$S_{298.15}^\circ$ = 12.296 cal. deg.$^{-1}$ mole^{-1}

ΔH_m = 0.622 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

D. L. Martin, Proc. Roy. Soc. A254, 433 (1960) reports that the low temperature heat capacity of sodium depends on the thermal history of the sample and ascribes this to a martensitic transformation. The effect is most pronounced in the range 40-80°K., where the graph of C_p against T increases continuously for some samples and rises to a peak at 55°K. for others. Martin lists heat capacities obtained in several runs on "high purity" sodium at 21° to 300°K. and the higher values, those defining the peak at 55°K., have been selected here. The heat capacities reported by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. A233, 214 (1955), have not been used, since one of the authors in a later publication (Martin, loc. cit.) questions the accuracy of the measurements above 100°K, and at lower temperatures there is no rise to a peak at 55°K. In the range 1.5° to 20°K., L. M. Roberts, Proc. Phys. Soc. B70, 744 (1957) and D. H. Parkinson and J. E. Quarrington Proc. Phys. Soc. A68, 762 (1955) have measured the heat capacity of very high purity sodium. The values of Parkinson and Quarrington are somewhat higher than those of Roberts and have been given greater weight, since they show better continuity with Martin's results. The results of G. L. Pickard and F. E. Simon, Proc. Phys. Soc. 61, 1 (1948) have been rejected below 10°K, since they show a peak between 5° and 8°, a feature not verified by other workers; between 10° and 25°K they agree exactly with the results of Parkinson and Quarrington. J. Rayne, Phys. Rev. 95, 1428 (1954) states that the graph of C_p against T has a small peak at about 0.9°K. This peak has not been observed in the work of W. H. Lien and N. E. Phillips, Phys. Rev. 118, 958 (1960) from 0.15° to 1°K; R. E. Gaumer and C. V. Heer, Phys. Rev. 118, 955 (1960) from 0.4° to 2°K and D. L. Martin, Phys. Rev. 124, 438 (1961) from 0.4 to 1.5°K.

T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952) report heat capacities in the range 273° to 1173°K on a sample of not less than 99.9% purity. These values agree to within 1% with those of Martin in the range 273° to 300°K, and the two sets of dates have been smoothly joined.

Melting.

Douglas et al. (loc. cit.) have determined the triple point to be 97.82 ± 0.02°C., from which the melting point is calculated to be 97.83 ± 0.02°C., and have measured the heat of fusion.

Heat of Sublimation.

At the boiling point and higher temperatures sodium vapor contains an appreciable proportion of diatomic molecules. G. W. Thompson and E. Garelis "Sodium - its Manufacture, Properties and Uses," Ed. M. Sittig, Chapter 3, Reinhold Publishing Corporation, Inc., New York (1956), have made a careful analysis of the available vapor pressure data. Their results are consistent with the free energy functions calculated in the present work and have been adopted.

Sodium (Na)

(Liquid) At. Wt. = 22.991

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	7.817	13.827	13.827	.000	.575	.119	-.087
300	7.812	13.875	13.827	.014	.577	.117	-.085
400	7.531	16.083	14.130	.781	.000	.000	.000
500	7.302	17.738	14.693	1.522	.000	.000	.000
600	7.124	19.053	15.314	2.243	.000	.000	.000
700	6.996	20.141	15.928	2.949	.000	.000	.000
800	6.918	21.069	16.514	3.644	.000	.000	.000
900	6.892	21.882	17.066	4.334	.000	.000	.000
1000	6.918	22.609	17.585	5.024	.000	.000	.000
1100	6.993	23.272	18.072	5.719	-.001	.000	.000
1200	7.120	23.885	18.531	6.425	-23.235	.460	-.084
1300	7.293	24.462	18.966	7.145	-23.012	2.426	-.408
1400	7.493	25.009	19.378	7.884	-22.770	4.373	-.683
1500	7.693	25.533	19.771	8.644	-22.507	6.303	-.918
1600	7.893	26.036	20.147	9.423	-22.225	8.215	-1.122
1700	8.093	26.521	20.508	10.222	-21.922	10.109	-1.299
1800	8.293	26.989	20.855	11.041	-21.600	11.983	-1.455
1900	8.493	27.443	21.190	11.881	-21.257	13.840	-1.592
2000	8.693	27.883	21.513	12.740	-20.896	15.677	-1.713

June 30, 1962

SODIUM (Na) (LIQUID) AT. WT. = 22.991

ΔH_f° 298.15 = 0.575 kcal. mole^{-1}

T_m = 370.98 ± 0.02°K

T_b = 1156°K (Equilibrium mixture)

ΔH_v 1176.9 = 23.285 kcal. mole^{-1}

$S^\circ_{298.15}$ = 13.827 cal. deg.$^{-1}$ mole^{-1}

ΔH_m = 0.622 kcal. mole^{-1}

T_b (Monatomic gas) = 1176.9°K

Heat of Formation.

Obtained from the heat of fusion by adding $H_{370.98}-H_{298.15}$ for the solid and subtracting $H_{370.98}-H_{298.15}$ for the liquid.

Heat Capacity.

The heat capacity data of T. B. Douglas, A. F. Ball, D. C. Ginnings and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952) were used and were extrapolated below T_m and above 1173°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1156°K. The vapor pressure of the monatomic gas reaches 1 atm. at 1176.9°K and the heat of vaporization to monatomic gas is 23.285 kcal. mole^{-1} [See Na(crystal)].

Sodium, Monatomic (Na)
(Ideal Gas) At. Wt. = 22.991

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.481	25.815	25.815	INFINITE
100	4.968	31.286	41.131	-.984	25.992	23.432	-51.208
200	4.968	34.730	37.168	-.488	25.901	20.900	-22.838
298	4.968	36.714	36.714	.000	25.755	18.475	-13.542
300	4.968	36.745	36.714	.009	25.752	18.431	-13.426
400	4.968	38.174	36.909	.506	24.905	16.070	-8.780
500	4.968	39.282	37.277	1.003	24.661	13.890	-6.071
600	4.968	40.188	37.689	1.500	24.437	11.757	-4.282
700	4.968	40.954	38.102	1.996	24.227	9.660	-3.016
800	4.968	41.617	38.501	2.493	24.029	7.593	-2.074
900	4.968	42.203	38.880	2.990	23.836	5.550	-1.348
1000	4.968	42.726	39.239	3.487	23.643	3.529	-.771
1100	4.968	43.200	39.578	3.984	23.444	1.526	-.303
1200	4.968	43.632	39.898	4.481	.000	.000	.000
1300	4.968	44.030	40.201	4.977	.000	.000	.000
1400	4.968	44.398	40.488	5.474	.000	.000	.000
1500	4.968	44.740	40.760	5.971	.000	.000	.000
1600	4.968	45.061	41.019	6.468	.000	.000	.000
1700	4.969	45.362	41.265	6.965	.000	.000	.000
1800	4.970	45.646	41.501	7.462	.000	.000	.000
1900	4.971	45.915	41.726	7.959	.000	.000	.000
2000	4.973	46.170	41.942	8.456	.000	.000	.000
2100	4.975	46.413	42.149	8.953	.000	.000	.000
2200	4.979	46.644	42.348	9.451	.000	.000	.000
2300	4.985	46.866	42.540	9.949	.000	.000	.000
2400	4.992	47.078	42.725	10.448	.000	.000	.000
2500	5.001	47.282	42.903	10.948	.000	.000	.000
2600	5.013	47.476	43.075	11.448	.000	.000	.000
2700	5.027	47.668	43.242	11.950	.000	.000	.000
2800	5.044	47.851	43.403	12.454	.000	.000	.000
2900	5.065	48.028	43.560	12.959	.000	.000	.000
3000	5.089	48.200	43.711	13.467	.000	.000	.000
3100	5.116	48.368	43.859	13.977	.000	.000	.000
3200	5.148	48.531	44.002	14.490	.000	.000	.000
3300	5.184	48.690	44.142	15.007	.000	.000	.000
3400	5.225	48.845	44.278	15.527	.000	.000	.000
3500	5.272	48.997	44.411	16.052	.000	.000	.000
3600	5.324	49.146	44.540	16.582	.000	.000	.000
3700	5.383	49.293	44.667	17.117	.000	.000	.000
3800	5.449	49.437	44.790	17.659	.000	.000	.000
3900	5.522	49.580	44.911	18.207	.000	.000	.000
4000	5.604	49.721	45.030	18.763	.000	.000	.000
4100	5.696	49.860	45.146	19.328	.000	.000	.000
4200	5.799	49.999	45.260	19.903	.000	.000	.000
4300	5.913	50.136	45.372	20.488	.000	.000	.000
4400	6.041	50.274	45.482	21.086	.000	.000	.000
4500	6.182	50.411	45.590	21.697	.000	.000	.000
4600	6.339	50.549	45.696	22.323	.000	.000	.000
4700	6.513	50.687	45.801	22.965	.000	.000	.000
4800	6.705	50.826	45.904	23.626	.000	.000	.000
4900	6.915	50.966	46.006	24.307	.000	.000	.000
5000	7.147	51.108	46.106	25.010	.000	.000	.000
5100	7.399	51.252	46.206	25.737	.000	.000	.000
5200	7.674	51.399	46.304	26.490	.000	.000	.000
5300	7.972	51.546	46.402	27.273	.000	.000	.000
5400	8.294	51.700	46.498	28.086	.000	.000	.000
5500	8.639	51.855	46.594	28.932	.000	.000	.000
5600	9.009	52.014	46.690	29.814	.000	.000	.000
5700	9.402	52.177	46.785	30.735	.000	.000	.000
5800	9.816	52.344	46.879	31.696	.000	.000	.000
5900	10.256	52.515	46.973	32.699	.000	.000	.000
6000	10.716	52.692	47.067	33.748	.000	.000	.000

June 30, 1962

SODIUM, MONATOMIC (Na) (IDEAL GAS) AT. WT. = 22.991

ΔH°_{f0} = 25.815 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 25.755 kcal. mole^{-1}

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 36.714 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_i cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i
0	2	34,549	10	38,012	2
16,956	2	34,589	14	38,399	46
16,973	4	35,042	6	38,541	2
25,740	2	36,373	2	39,230	34
29,173	10	37,037	10	40,700	94
30,267	2	37,058	14	40,736	100
30,273	4	37,060	18	41,330	258
33,201	2	37,297	6		

Heat of Formation.

Same as the heat of sublimation to the monatomic species; see notes on Na(crystal)

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 467," U. S. Government Printing Office, Washington (1949) p. 89-91. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Sodium Unipositive Ion (Na$^+$)

(Ideal Gas) At. Wt. = 22.991

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	35.336	35.336	.000	145.755	137.399	- 100.711
300	4.968	35.367	35.336	.009	145.761	137.347	- 100.053
400	4.968	36.796	35.531	.506	145.411	134.548	- 73.510
500	4.968	37.905	35.899	1.003	145.664	131.803	- 57.608
600	4.968	38.811	36.311	1.500	145.937	129.006	- 46.988
700	4.968	39.577	36.724	1.996	146.223	126.159	- 39.387
800	4.968	40.240	37.123	2.493	146.522	123.274	- 33.675
900	4.968	40.825	37.503	2.990	146.826	120.351	- 29.224
1000	4.968	41.349	37.862	3.487	147.130	117.392	- 25.655
1100	4.968	41.822	38.201	3.984	147.428	114.404	- 22.729
1200	4.968	42.254	38.521	4.481	124.482	111.847	- 20.369
1300	4.968	42.652	38.823	4.977	124.977	110.772	- 18.622
1400	4.968	43.020	39.110	5.474	125.474	109.661	- 17.118
1500	4.968	43.363	39.382	5.971	125.971	108.514	- 15.810
1600	4.968	43.684	39.641	6.468	126.468	107.333	- 14.660
1700	4.968	43.985	39.888	6.965	126.966	106.124	- 13.642
1800	4.968	44.269	40.124	7.461	127.461	104.882	- 12.734
1900	4.968	44.537	40.349	7.958	127.958	103.617	- 11.918
2000	4.968	44.792	40.565	8.455	128.454	102.322	- 11.181
2100	4.968	45.035	40.772	8.952	128.951	101.000	- 10.511
2200	4.968	45.266	40.971	9.449	129.447	99.659	- 9.900
2300	4.968	45.487	41.162	9.945	129.941	98.291	- 9.339
2400	4.968	45.698	41.347	10.442	130.436	96.908	- 8.824
2500	4.968	45.901	41.525	10.939	130.931	95.499	- 8.348
2600	4.968	46.096	41.697	11.436	131.424	94.072	- 7.907
2700	4.968	46.283	41.864	11.933	131.916	92.628	- 7.497
2800	4.968	46.464	42.025	12.430	132.406	91.162	- 7.115
2900	4.968	46.638	42.181	12.926	132.893	89.683	- 6.758
3000	4.968	46.807	42.332	13.423	133.379	88.181	- 6.424
3100	4.968	46.970	42.479	13.920	133.863	86.666	- 6.110
3200	4.968	47.127	42.622	14.417	134.344	85.141	- 5.815
3300	4.968	47.280	42.761	14.914	134.821	83.595	- 5.536
3400	4.968	47.428	42.896	15.410	135.293	82.036	- 5.273
3500	4.968	47.572	43.028	15.907	135.762	80.466	- 5.024
3600	4.968	47.712	43.156	16.404	136.226	78.878	- 4.788
3700	4.968	47.849	43.281	16.901	136.685	77.270	- 4.564
3800	4.968	47.981	43.403	17.398	137.138	75.665	- 4.352
3900	4.968	48.110	43.522	17.895	137.583	74.040	- 4.149
4000	4.968	48.236	43.638	18.391	138.019	72.403	- 3.956
4100	4.968	48.359	43.752	18.888	138.448	70.757	- 3.772
4200	4.968	48.478	43.863	19.385	138.867	69.105	- 3.596
4300	4.968	48.595	43.972	19.882	139.276	67.440	- 3.428
4400	4.968	48.709	44.078	20.379	139.672	65.765	- 3.266
4500	4.968	48.821	44.182	20.875	140.053	64.080	- 3.112
4600	4.968	48.930	44.284	21.372	140.421	62.387	- 2.964
4700	4.968	49.037	44.384	21.869	140.773	60.685	- 2.822
4800	4.968	49.142	44.482	22.366	141.106	58.973	- 2.685
4900	4.968	49.244	44.578	22.863	141.419	57.266	- 2.554
5000	4.968	49.345	44.673	23.359	141.708	55.543	- 2.428
5100	4.968	49.443	44.765	23.856	141.975	53.817	- 2.306
5200	4.968	49.539	44.856	24.353	142.216	52.090	- 2.189
5300	4.968	49.634	44.945	24.850	142.428	50.351	- 2.076
5400	4.968	49.727	45.033	25.347	142.609	48.611	- 1.967
5500	4.968	49.818	45.119	25.844	142.756	46.869	- 1.862
5600	4.968	49.908	45.204	26.340	142.866	45.118	- 1.761
5700	4.968	49.995	45.287	26.837	142.940	43.384	- 1.663
5800	4.968	50.082	45.369	27.334	142.973	41.630	- 1.569
5900	4.968	50.167	45.450	27.831	142.963	39.884	- 1.477
6000	4.968	50.250	45.529	28.328	142.909	38.143	- 1.389

Mar. 31, 1965

SODIUM UNIPOSITIVE ION (Na$^+$) (IDEAL GAS) AT. WT. = 22.991

Ground State Configuration $^1S_0$

$\Delta H^\circ_{f\ 0}$ = 144.334 kcal. mole^{-1}

$S^\circ_{298.15}$ = 35.336 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 145.755 kcal. mole^{-1}

Electronic Levels and Multiplicities

ϵ, cm.$^{-1}$	g_i
0	1
266192	12
298614	36
331860	72
358298	27

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic sodium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation Na(ref. state) - e$^-$(ref. state) = Na$^+$(monatomic gas), thus Na$^+$ involves the difference in enthalpies of the two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

Sodium Monoxide (NaO)

(Ideal Gas) GFW = 38.9892

T, °K	gibbs/mol			kcal/mol			
	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	-2.253	20.326	20.326	INFINITE
100	7.113	46.297	61.849	-1.555	20.356	18.365	-40.137
200	7.915	51.475	55.492	-.803	20.173	16.445	-17.970
298	8.400	54.737	54.737	.000	20.000	14.552	-10.740
300	8.407	54.789	54.737	.016	19.997	14.619	-10.650
400	8.656	57.245	55.071	.870	19.152	12.906	-7.052
500	8.798	59.194	55.707	1.743	18.919	11.373	-4.971
600	8.888	60.806	56.426	2.628	18.705	9.884	-3.600
700	8.952	62.181	57.153	3.520	18.502	8.429	-2.632
800	9.002	63.380	57.858	4.418	18.306	7.004	-1.913
900	9.042	64.443	58.531	5.320	18.111	5.603	-1.361
1000	9.077	65.397	59.171	6.226	17.914	4.224	-.923
1100	9.108	66.264	59.777	7.135	17.707	2.864	-.569
1200	9.137	67.058	60.351	8.048	-5.744	1.981	-.361
1300	9.163	67.790	60.896	8.963	-5.755	2.626	-.441
1400	9.188	68.470	61.413	9.880	-5.765	3.270	-.510
1500	9.213	69.105	61.905	10.800	-5.779	3.916	-.571
1600	9.236	69.700	62.373	11.723	-5.792	4.563	-.623
1700	9.259	70.261	62.821	12.647	-5.804	5.212	-.670
1800	9.281	70.791	63.249	13.575	-5.818	5.860	-.711
1900	9.304	71.293	63.659	14.504	-5.834	6.510	-.749
2000	9.325	71.771	64.053	15.435	-5.850	7.159	-.782
2100	9.347	72.226	64.432	16.369	-5.866	7.809	-.813
2200	9.368	72.662	64.796	17.305	-5.884	8.461	-.840
2300	9.389	73.078	65.147	18.242	-5.903	9.112	-.866
2400	9.410	73.478	65.486	19.182	-5.923	9.768	-.889
2500	9.431	73.863	65.813	20.124	-5.944	10.419	-.911
2600	9.452	74.233	66.130	21.069	-5.966	11.076	-.931
2700	9.473	74.590	66.437	22.015	-5.991	11.731	-.950
2800	9.493	74.935	66.734	22.963	-6.018	12.387	-.967
2900	9.514	75.269	67.023	23.913	-6.047	13.047	-.983
3000	9.534	75.592	67.303	24.866	-6.079	13.705	-.998
3100	9.555	75.905	67.575	25.820	-6.113	14.365	-1.013
3200	9.575	76.208	67.841	26.777	-6.151	15.026	-1.026
3300	9.595	76.503	68.099	27.735	-6.192	15.688	-1.039
3400	9.616	76.790	68.350	28.696	-6.237	16.351	-1.051
3500	9.636	77.069	68.595	29.658	-6.287	17.018	-1.063
3600	9.656	77.341	68.834	30.623	-6.341	17.685	-1.074
3700	9.676	77.606	69.068	31.590	-6.400	18.351	-1.084
3800	9.697	77.864	69.296	32.558	-6.465	19.024	-1.094
3900	9.717	78.116	69.519	33.529	-6.538	19.692	-1.103
4000	9.737	78.362	69.737	34.502	-6.617	20.366	-1.113
4100	9.757	78.603	69.950	35.476	-6.705	21.044	-1.122
4200	9.777	78.838	70.159	36.453	-6.801	21.719	-1.130
4300	9.798	79.069	70.364	37.432	-6.908	22.403	-1.139
4400	9.818	79.294	70.564	38.413	-7.026	23.082	-1.147
4500	9.838	79.515	70.760	39.395	-7.157	23.772	-1.155
4600	9.858	79.731	70.953	40.380	-7.302	24.459	-1.162
4700	9.878	79.944	71.142	41.367	-7.462	25.151	-1.170
4800	9.898	80.152	71.328	42.356	-7.640	25.846	-1.177
4900	9.918	80.356	71.510	43.347	-7.836	26.546	-1.184
5000	9.938	80.557	71.689	44.340	-8.054	27.250	-1.191
5100	9.958	80.754	71.865	45.334	-8.295	27.960	-1.198
5200	9.979	80.947	72.037	46.331	-8.560	28.671	-1.205
5300	9.999	81.138	72.207	47.330	-8.852	29.392	-1.212
5400	10.019	81.325	72.374	48.331	-9.175	30.115	-1.219
5500	10.039	81.509	72.539	49.334	-9.530	30.845	-1.226
5600	10.059	81.690	72.701	50.339	-9.919	31.582	-1.233
5700	10.079	81.868	72.860	51.346	-10.344	32.327	-1.239
5800	10.099	82.043	73.017	52.354	-10.809	33.081	-1.247
5900	10.119	82.216	73.171	53.365	-11.315	33.843	-1.254
6000	10.139	82.386	73.323	54.378	-11.863	34.613	-1.261

Dec. 31, 1960; Dec. 31, 1967

SODIUM MONOXIDE (NaO) (IDEAL GAS) GFW = 38.9892

Ground State Configuration [$^2\Pi$]

$S°_{298.15}$ = [54.7 ± 0.5] gibbs/mol

$\Delta Hf°_0$ = [20.3 ± 10] kcal/mol

$\Delta Hf°_{298.15}$ = [20.0 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]

ω_e = [440] cm^{-1}

B_e = [0.4467] cm^{-1}

$\omega_e x_e$ = [3.0] cm^{-1}

α_e = [0.0043] cm^{-1}

σ = 1

r_e = [2.0] Å

Heat of Formation

Bawn and Evans (1) have studied the reaction rate of sodium vapor with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite, using the diffusion flame method. On the evidence of reaction rate measurements they estimated the value, $\Delta Hr°_{298} < 0$, for the reaction Na(g) + NO_2(g) = NaO(g) + NO(g). Based on this result, we calculate $\Delta Hf°_{298}$(NaO, g) > 12 kcal/mol, using $\Delta Hf°_{298}$ = 25.8, 7.9 and 21.6 kcal/mol for Na(g), NO_2(g) and NO(g), respectively.

Assuming that D_0(NaO) = 1/2[$D_0(Na_2)$ + $D_0(O_2)$], or $\Delta Hr°_0$ = 68.1 kcal/mol for the reaction NaO(g) = Na(g) + O(g), we derive $\Delta Hf°_0$ = 16.7 and $\Delta Hf°_{298}$ = 16.4 kcal/mol, using $\Delta Hf°_0$ = 25.8 and 59.0 kcal/mol for Na(g) and O(g), respectively.

Somayajulu (2) found that in a sequence of similar diatomic molecules the force constant (k_e), dissociation energy (D_0) and equilibrium bond distance (r_e) are related by the expression $k_e r_e/D_0$ = constant. Using r_e = 1.62 Å, D_0 = 77.9 kcal/mol for LiO(g), r_e = 2.0 Å for NaO(g) and k_e(NaO)/k_e(LiO) = 0.4827, we evaluate D_0 = 65.4 kcal/mol for NaO(g), yielding $\Delta Hf°_{298}$(NaO, g) = 19.4 kcal/mol. The value k_e is calculated from the relation $k_e = 4\Pi^2 \nu^2 \mu$ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta Hf°_{298}$(NaO, g) is tentatively adopted as 20 ± 10 kcal/mol. The corresponding $D°_0$(NaO) is 65 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for OH(g) which has the same number of valence electrons as NaO(g). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiO(g), LiF(g) and NaF(g). The value of r_e is estimated from those for OH(g), HF(g) and NaF(g). B_e and α_e are derived from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg (3).

References

1. C. E. H. Bawn and A. G. Evans, Trans. Faraday Soc. 33, 1571 (1937).
2. G. R. Somayajulu, J. Chem. Phys. 33, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Sodium Monoxide Uninegative Ion (NaO^-)

(Ideal Gas) GFW = 38.98975

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.380	51.954	51.954	.000	-29.000	-32.031	23.479
300	8.387	52.006	51.954	.016	-29.012	-32.049	23.348
400	8.644	54.457	52.286	.868	-30.355	-32.907	17.979
500	8.791	56.403	52.922	1.741	-31.087	-33.459	14.625
600	8.895	58.015	53.640	2.625	-31.798	-33.865	12.336
700	8.952	59.390	54.366	3.517	-32.497	-34.155	10.664
800	9.003	60.589	55.070	4.415	-33.190	-34.345	9.383
900	9.045	61.652	55.744	5.317	-33.882	-34.448	8.365
1000	9.081	62.607	56.383	6.224	-34.576	-34.474	7.534
1100	9.114	63.474	56.989	7.133	-35.279	-34.432	6.841
1200	9.143	64.268	57.563	8.046	-59.227	-33.867	6.168
1300	9.171	65.001	58.107	8.962	-59.733	-31.731	5.334
1400	9.197	65.682	58.624	9.880	-60.240	-29.559	4.614
1500	9.222	66.317	59.116	10.801	-60.749	-27.350	3.985
1600	9.247	66.913	59.585	11.725	-61.258	-25.106	3.429
1700	9.270	67.474	60.033	12.651	-61.766	-22.830	2.935
1800	9.294	68.005	60.461	13.579	-62.275	-20.525	2.492
1900	9.316	68.508	60.871	14.509	-62.786	-18.192	2.093
2000	9.339	68.986	61.265	15.442	-63.298	-15.833	1.730
2100	9.361	69.442	61.644	16.377	-63.810	-13.446	1.399
2200	9.383	69.878	62.008	17.314	-64.324	-11.035	1.096
2300	9.405	70.296	62.360	18.254	-64.836	-8.602	.817
2400	9.427	70.697	62.699	19.195	-65.352	-6.145	.560
2500	9.449	71.082	63.026	20.139	-65.868	-3.670	.321
2600	9.470	71.453	63.343	21.085	-66.386	-1.170	.098
2700	9.492	71.811	63.650	22.033	-66.905	1.345	-.109
2800	9.513	72.156	63.948	22.983	-67.428	3.883	-.303
2900	9.534	72.491	64.237	23.936	-67.951	6.441	-.485
3000	9.556	72.814	64.517	24.890	-68.479	9.016	-.657
3100	9.577	73.128	64.790	25.847	-69.007	11.608	-.818
3200	9.598	73.432	65.055	26.806	-69.539	14.214	-.971
3300	9.619	73.728	65.314	27.767	-70.075	16.839	-1.115
3400	9.640	74.015	65.566	28.730	-70.613	19.480	-1.252
3500	9.661	74.295	65.811	29.695	-71.157	22.140	-1.382
3600	9.682	74.568	66.050	30.662	-71.706	24.813	-1.506
3700	9.703	74.833	66.284	31.631	-72.260	27.503	-1.625
3800	9.724	75.092	66.513	32.602	-72.819	30.209	-1.737
3900	9.745	75.345	66.736	33.576	-73.386	32.922	-1.845
4000	9.766	75.592	66.954	34.551	-73.958	35.658	-1.948
4100	9.787	75.834	67.168	35.529	-74.540	38.409	-2.047
4200	9.808	76.070	67.377	36.509	-75.131	41.165	-2.142
4300	9.829	76.301	67.582	37.491	-75.731	43.944	-2.233
4400	9.850	76.527	67.783	38.474	-76.344	46.730	-2.321
4500	9.870	76.748	67.979	39.460	-76.967	49.540	-2.406
4600	9.891	76.966	68.172	40.449	-77.605	52.356	-2.487
4700	9.912	77.179	68.362	41.439	-78.259	55.189	-2.566
4800	9.933	77.387	68.548	42.431	-78.931	58.036	-2.642
4900	9.954	77.592	68.730	43.425	-79.621	60.895	-2.716
5000	9.975	77.794	68.909	44.422	-80.331	63.769	-2.787
5100	9.995	77.991	69.085	45.420	-81.065	66.662	-2.857
5200	10.016	78.186	69.259	46.421	-81.823	69.561	-2.924
5300	10.037	78.377	69.429	47.423	-82.609	72.484	-2.989
5400	10.058	78.565	69.596	48.428	-83.425	75.416	-3.052
5500	10.079	78.749	69.761	49.435	-84.273	78.364	-3.114
5600	10.099	78.931	69.923	50.444	-85.154	81.331	-3.174
5700	10.120	79.110	70.083	51.455	-86.072	84.307	-3.233
5800	10.141	79.286	70.240	52.468	-87.029	87.309	-3.290
5900	10.162	79.460	70.395	53.483	-88.028	90.325	-3.346
6000	10.182	79.631	70.547	54.500	-89.069	93.354	-3.400

Dec. 31, 1967

SODIUM MONOXIDE UNINEGATIVE ION (NaO^-) (IDEAL GAS) GFW = 38.98975

Ground State Configuration [$^1\Sigma$]

$\Delta Hf°_0$ = [-29 ± 20] kcal/mol

$S°_{298.15}$ = [52.0 ± 0.5] gibbs/mol

$\Delta Hf°_{298.15}$ = [-29 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[1]

ω_e = [450] cm^{-1}

B_e = [0.4467] cm^{-1}

$\omega_e x_e$ = [3.2] cm^{-1}

α_e = [0.00495] cm^{-1}

σ = 1

r_e = [2.0] Å

Heat of Formation

The electron affinity (E. A.) of $NaO^-(g)$ is unavailable, therefore the value of $\Delta Hf°_{298}(NaO^-, g)$ is estimated. We first assume that the enthalpy change ($\Delta Hr°_0$) of the reaction (1) $NaO^-(g) = Na(g) + O^-(g)$ is close to the average of the $\Delta Hr°_0$ values for the reactions (2) $NaO(g) = Na(g) + O(g)$ and (3) $NaF(g) = Na(g) + F(g)$. The atom F(g) is isoelectronic with $O^-(g)$. In other words, the $\Delta Hr°_0$ for reaction (1) is approximately 1/2(64.8 + 113.9) = 89.3 kcal/mol. Then we compare the $\Delta Hr°_0$ values for the reactions (4) $HO(g) = H(g) + O(g)$, (5) $HO^-(g) = H(g) + O^-(g)$, and (6) $HF(g) = H(g) + F(g)$, and find that $\Delta Hr°_0$ for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of $\Delta Hr°_0$ values for reactions (4) and (6). Based on this fact we estimate $\Delta Hr°_0$ = 80 kcal/mol for reaction (1), yielding $\Delta Hf°_{298}(NaO^-, g)$ = -29 kcal/mol which is tentatively adopted. The uncertainty of this value may be ±20 kcal/mol. Based on this $\Delta Hf°_{298}$ value we calculate E. A. = 2.1 ± 0.9 eV for NaO(g). The corresponding value for HO(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of NaF(g) which is isoelectronic with $NaO^-(g)$. The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with the observed data for NaF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules." D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.248 kcal/mol.

Sodium Dioxide (NaO_2)

(Crystal) Mol. Wt. = 54.991

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-4.386	-63.070	-63.070	INFINITE
100	10.890	7.310	46.580	-3.927	-63.644	-59.654	130.367
200	31.700	18.700	28.365	-1.933	-62.917	-55.465	60.607
298	17.242	27.700	27.700	.000	-62.300	-52.282	38.322
300	17.260	27.807	27.700	.032	-62.293	-52.219	38.040
400	18.230	32.905	28.389	1.806	-62.574	-48.865	26.697
500	19.210	37.078	29.721	3.678	-62.174	-45.481	19.879
600	20.190	40.667	31.253	5.648	-61.680	-42.187	15.366
700	21.167	43.852	32.829	7.716	-61.096	-38.985	12.171
800	22.140	46.742	34.391	9.881	-60.424	-35.871	9.799
900	23.121	49.407	35.913	12.145	-59.664	-32.846	7.976
1000	24.100	51.894	37.388	14.506	-58.820	-29.910	6.536
1100	25.078	54.236	38.814	16.964	-57.897	-27.065	5.377
1200	26.055	56.460	40.193	19.521	-80.128	-23.848	4.343
1300	27.031	58.584	41.526	22.176	-78.827	-19.210	3.229
1400	28.006	60.623	42.818	24.927	-77.437	-14.676	2.291
1500	28.980	62.589	44.071	27.777	-75.955	-10.244	1.493
1600	29.957	64.490	45.288	30.724	-74.382	-5.914	.808
1700	30.935	66.336	46.472	33.768	-72.716	-1.684	.217
1800	31.913	68.132	47.626	36.911	-70.959	2.443	-.297
1900	32.891	69.883	48.751	40.151	-69.111	6.472	-.744
2000	33.870	71.595	49.851	43.489	-67.171	10.398	-1.136

June 30, 1963

SODIUM DIOXIDE (NaO_2) (CRYSTAL) MOL. WT. = 54.991

$S^\circ_{298.15}$ = 27.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 196.5°K.

T_{t_2} = 223.3°K.

T_m = 825° ± 10°K.

$\Delta H^\circ_{f\ 0}$ = -63.1 ± 0.7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -62.3 ± 0.7 kcal. mole^{-1}

$\Delta H^\circ_{t_1}$ = 350 cal. mole^{-1}

$\Delta H^\circ_{t_2}$ = 370 cal. mole^{-1}

ΔH°_m = Unknown

Heat of Formation.

$\Delta H^\circ_{f\ 298.15}$ was obtained from National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. P. W. Gilles and J. L. Margrave, J. Phys. Chem. 60, 1333 (1956) measured the heat of decomposition of $NaO_2(c)$ in H_2O, yielding $\Delta H^\circ_{f\ 298.15}$ = -62.1 ± 0.7 kcal. mole^{-1}. From the original experimental data by R. de Forcrand, Compt. rend., 127, 514 (1898); 158, 843, 991 (1914), the value of $\Delta H^\circ_{f\ 298.15}$ was recalculated to be -65.0 kcal. mole^{-1} by P. W. Gilles and J. L. Margrave. loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, 52.13° ~ 296.46°K., were measured by S. S. Todd, J. Am. Chem. Soc., 75, 1229 (1953). The heat capacities above 298.15°K. were estimated by comparison with those for $Na_2O(c)$. $S^\circ_{298.15}$ was given by S. S. Todd, loc. cit., using S°_{51}(extrap.) = 2.23 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_{t_1}, T_{t_2}, $\Delta H^\circ_{t_1}$ and $\Delta H^\circ_{t_2}$ were calculated from the data reported by S. S. Todd, loc. cit.

Temperature of Melting.

The melting temperature was obtained from J. L. Margrave, private communication, May 21, 1963.

Sodium, Diatomic (Na_2)
(Ideal Gas) Mol. Wt. = 45.982

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. $mole^{-1}deg.^{-1}$			kcal. $mole^{-1}$			
0	.000	.000	INFINITE	-2.485	33.467	33.467	INFINITE
100	8.302	45.484	62.844	-1.736	33.576	30.166	-65.924
200	8.816	51.443	55.810	-.873	33.265	26.866	-29.356
298	8.963	54.994	54.994	.000	32.870	23.807	-17.450
300	8.965	55.050	54.994	.017	32.863	23.752	-17.302
400	9.043	57.640	55.347	.917	31.075	20.888	-11.412
500	9.101	59.665	56.015	1.825	30.501	18.409	-8.046
600	9.150	61.328	56.766	2.737	29.971	16.041	-5.843
700	9.195	62.742	57.522	3.654	29.476	13.757	-4.295
800	9.237	63.973	58.253	4.576	29.008	11.545	-3.154
900	9.279	65.063	58.950	5.502	28.554	9.390	-2.280
1000	9.319	66.043	59.611	6.432	28.104	7.285	-1.592
1100	9.359	66.933	60.237	7.366	27.646	5.222	-1.038
1200	9.399	67.749	60.829	8.303	-19.297	4.119	-.750
1300	9.438	68.503	61.391	9.245	-19.349	6.073	-1.021
1400	9.477	69.204	61.924	10.191	-19.397	8.030	-1.253
1500	9.516	69.859	62.432	11.141	-19.441	9.990	-1.456
1600	9.555	70.474	62.915	12.094	-19.482	11.955	-1.633
1700	9.594	71.055	63.377	13.052	-19.516	13.922	-1.790
1800	9.633	71.604	63.819	14.013	-19.549	15.889	-1.929
1900	9.672	72.126	64.243	14.978	-19.578	17.860	-2.054
2000	9.711	72.623	64.649	15.948	-19.604	19.829	-2.167
2100	9.749	73.098	65.040	16.921	-19.625	21.799	-2.269
2200	9.788	73.552	65.417	17.897	-19.645	23.774	-2.362
2300	9.827	73.988	65.780	18.878	-19.660	25.746	-2.446
2400	9.865	74.407	66.131	19.863	-19.673	27.724	-2.524
2500	9.904	74.811	66.470	20.851	-19.683	29.695	-2.596
2600	9.942	75.200	66.799	21.844	-19.692	31.673	-2.662
2700	9.981	75.576	67.117	22.840	-19.700	33.646	-2.723
2800	10.020	75.940	67.425	23.840	-19.708	35.621	-2.780
2900	10.058	76.292	67.725	24.844	-19.714	37.602	-2.834
3000	10.097	76.634	68.016	25.851	-19.723	39.577	-2.883
3100	10.135	76.965	68.300	26.863	-19.731	41.552	-2.929
3200	10.174	77.288	68.576	27.878	-19.742	43.530	-2.973
3300	10.213	77.601	68.844	28.898	-19.756	45.507	-3.014
3400	10.251	77.907	69.106	29.921	-19.773	47.483	-3.052
3500	10.290	78.204	69.362	30.948	-19.796	49.467	-3.089
3600	10.328	78.495	69.612	31.979	-19.825	51.445	-3.123
3700	10.367	78.778	69.856	33.014	-19.860	53.420	-3.155
3800	10.405	79.055	70.094	34.052	-19.904	55.407	-3.186
3900	10.444	79.326	70.327	35.095	-19.959	57.385	-3.216
4000	10.482	79.591	70.556	36.141	-20.025	59.371	-3.244
4100	10.521	79.850	70.779	37.191	-20.105	61.361	-3.271
4200	10.559	80.104	70.998	38.245	-20.201	63.344	-3.296
4300	10.598	80.353	71.213	39.303	-20.313	65.338	-3.321
4400	10.636	80.597	71.424	40.365	-20.447	67.327	-3.344
4500	10.675	80.837	71.630	41.430	-20.604	69.330	-3.367
4600	10.713	81.072	71.833	42.500	-20.786	71.325	-3.389
4700	10.752	81.303	72.032	43.573	-20.997	73.329	-3.410
4800	10.790	81.529	72.227	44.650	-21.242	75.337	-3.430
4900	10.829	81.752	72.419	45.731	-21.523	77.358	-3.450
5000	10.868	81.971	72.608	46.816	-21.844	79.379	-3.469
5100	10.906	82.187	72.794	47.905	-22.209	81.407	-3.488
5200	10.945	82.399	72.977	48.997	-22.623	83.441	-3.507
5300	10.983	82.608	73.156	50.093	-23.091	85.485	-3.525
5400	11.022	82.814	73.333	51.194	-23.616	87.539	-3.543
5500	11.060	83.016	73.508	52.298	-24.206	89.598	-3.560
5600	11.099	83.216	73.679	53.406	-24.862	91.674	-3.578
5700	11.137	83.413	73.848	54.518	-25.590	93.764	-3.595
5800	11.176	83.607	74.015	55.633	-26.397	95.863	-3.612
5900	11.214	83.798	74.179	56.753	-27.285	97.983	-3.629
6000	11.253	83.987	74.341	57.876	-28.258	100.113	-3.646

June 30, 1962

SODIUM, DIATOMIC (Na_2) (IDEAL GAS) MOL. WT. = 45.982

ΔH°_{f0} = 33.467 kcal. $mole^{-1}$

$\Delta H^\circ_{f\ 298.15}$ = 32.87 kcal. $mole^{-1}$

Ground State Configuration = $^1\Sigma^+$

$S^\circ_{298.15}$ = 54.994 cal. $deg.^{-1}$ $mole^{-1}$

ω_e = 159.23 $cm.^{-1}$

$\omega_e x_e$ = 0.726 $cm.^{-1}$

σ = 2

B_e = 0.15471 $cm.^{-1}$

α_e = 0.00079 $cm.^{-1}$

r_e = 3.078(6) Å

Heat of Formation.

Same as the heat of sublimation for the diatomic gas; see notes on Na(crystal)

Heat Capacity and Entropy.

Spectroscopic data from G. Hertzberg, "Spectra of Diatomic Molecules," 2nd Edn., D. Van Nostrand Co., Inc., New York (1950).

Disodium Monoxide (Na_2O)

(Crystal) GFW = 61.979

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.964	-98.744	-98.744	INFINITE
100	7.828	3.979	30.827	-2.685	-99.452	-96.642	211.212
200	14.233	11.761	19.387	-1.525	-99.815	-93.655	102.341
298	16.516	17.935	17.935	.000	-99.900	-90.609	66.418
300	16.550	18.038	17.936	.031	-99.900	-90.550	65.966
400	18.111	23.017	18.604	1.765	-101.209	-87.329	47.714
500	19.478	27.212	19.917	3.648	-101.174	-83.858	36.654
600	20.485	30.856	21.443	5.648	-100.993	-80.410	29.289
700	21.236	34.073	23.022	7.735	-100.707	-77.003	24.041
800	21.819	36.948	24.586	9.889	-100.342	-73.640	20.118
900	22.291	39.546	26.106	12.095	-99.923	-70.327	17.078
1000	22.686	41.915	27.570	14.345	-99.467	-67.062	14.656
1100	23.029	44.504	29.004	17.051	-98.572	-63.879	12.692
1200	23.334	46.521	30.380	19.369	-144.558	-59.832	10.897
1300	23.611	50.693	31.795	24.567	-140.783	-52.938	8.900
1400	23.867	52.452	33.209	26.941	-139.835	-46.217	7.215
1500	24.108	54.107	34.547	29.339	-138.866	-39.564	5.764
1600	24.336	55.670	35.819	31.762	-137.876	-32.975	4.504
1700	24.554	57.152	37.031	34.206	-136.864	-26.448	3.400
1800	24.765	58.561	38.188	36.672	-135.837	-19.983	2.426
1900	24.969	59.906	39.296	39.159	-134.792	-13.574	1.561
2000	25.169	61.192	40.359	41.666	-133.731	-7.224	.789

June 30, 1962; June 30, 1968

DISODIUM MONOXIDE (Na_2O) (CRYSTAL) GFW = 61.979

$S^\circ_{298.15}$ = 17.935 gibbs/mol

$Tt(\gamma \rightarrow \beta)$ = 1023.2°K

$Tt(\beta \rightarrow \alpha)$ = 1243.2°K

Tm = 1405.2°K

ΔHf°_0 = -98.74 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -99.90 ± 1.0 kcal/mol

$\Delta Ht^\circ(\gamma \rightarrow \beta)$ = 0.42 kcal/mol

$\Delta Ht^\circ(\beta \rightarrow \alpha)$ = 2.85 kcal/mol

ΔHm° = 11.4 kcal/mol

Heat of Formation

The enthalpy change of the reaction $Na_2O(c) + H_2O(\ell) = 2NaOH(aq)$ has been determined by Matsui (1, 2), Roth (3, 4) and Rengade (5). Based on their reported ΔHr° values, the corresponding ΔHf°_{298} for $Na_2O(c)$ are calculated, using $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 kcal/mol obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965, and $\Delta Hf^\circ_{298}(NaOH, nH_2O)$ derived from JANAF $\Delta Hf^\circ_{298}(NaOH, c)$ and ΔHsoln and ΔHdil reported by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. The sample employed by Matsui was prepared by the method of Rengade (7) and contains $Na_2O_2(c)$ and Na(c) as impurities. The sample used by Roth also contains 3.96 per cent (by weight) $Na_2O_2(c)$. Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaction $2Na(c) + H_2O(\ell) = Na_2O(c) + H_2(g)$ was calculated by Rengade (5) from his measurements (5) incorporating with ΔHr = -85.2 kcal/mol for the reaction $2Na(c) + 2H_2O(\ell) = 2NaOH(aq) + H_2(g)$ determined by Joannis (8). The value ΔHf°_{298} = -94.9 kcal/mol is derived from the data of Forcrand (6) using $\Delta Hf^\circ_{298}(Na_2O_2, c)$ = -122.66 kcal/mol. The results are presented in the table below.

Brewer (11) determined the equilibrium constants, 918-1467°K, for the vaporization of $Na_2O(c)$, using an effusion method. The Na_2O vapor consists predominately of Na(g) and $O_2(g)$ molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na_2O. Based on the reported data, we derive the equilibrium constants for the reaction $Na_2O(c) = 2Na(g) + 1/2O_2(g)$ and evaluate the third law ΔHr°_{298} as 117.1 ± 10 kcal/mol. From this ΔHr°_{298} value, we obtain $\Delta Hf^\circ_{298}(Na_2O, c)$ = -65.6 ± 10 kcal/mol, employing ΔHf°_{298}= 25.76 kcal/mol for Na(g). The value -65.6 kcal/mol is not consistent with the other values described above. This may be caused by an invalid assumption used in the calculation.

The heat of formation at 298°K for $Na_2O(c)$ is tentatively selected as -99.90 ± 1.0 kcal/mol.

Investigator	Reaction	ΔHr°, kcal/mol	ΔHf°_{298}, kcal/mol
1. Matsui (1929)	$Na_2O(c)+H_2O(\ell) = 2NaOH(7890\ H_2O)$	-56.61 ± 0.16	-100.08
2. Matsui (1929)	$Na_2O(c)+H_2O(\ell) = 2NaOH(4600\ H_2O)$	-56.70 ± 0.07	-99.89
3. Roth (1947)	$Na_2O(c)+H_2O(\ell) = 2NaOH(825\ H_2O)$	-56.03 ± 0.13	-100.55
4. Roth (1948)	$Na_2O(c)+H_2O(\ell) = 2NaOH(825\ H_2O)$	-55.98 ± 0.13	-100.60
5. Rengade (1907)	$Na_2O(c)+H_2O(\ell) = 2NaOH(aq)$	-56.50	-100.09
	$2Na(c)+H_2O(\ell) = Na_2O(c)+H_2(g)$	-28.70	-97.02
6. Forcrand (1900)	$Na_2O(c)+1/2O_2(g) = Na_2O_2(c)$	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15-380°K, were obtained from Furukawa (9). We make the corrections in the reported Cp values for impurity $Na_2CO_3(c)$ 2.33 per cent (by weight), analyzed by Grimley (10). The effect on heat capacity due to the presence of Na_2O_2(0.91 per cent) impurity is insignificant. Using the smoothed low temperature Cp data the $S^\circ_{298.15}$ is calculated, based on S°_{15} = 0.0122 eu.

Grimley (10) measured the high temperature enthalpies, 380.1-1174.6°K, with a copper block drop-type calorimeter. The enthalpies for the γ phase, 380.1-980.4°K, are joined smoothly with the low temperature data and extrapolated to 1023.2°K (the $\gamma \rightarrow \beta$ transition temperature). The enthalpies above 1023.2°K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6°K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz (12) who used a very pure sample. The adopted ΔHt° = 0.42 and 2.85 kcal/mol, are averages of the derived values, 0.36 ~ 0.48 and 2.7 ~ 3.0 kcal/mol, respectively.

Melting Data

Tm and ΔHm° were obtained from Bouaziz (12). The adopted ΔHm° is an average of the reported 10.8-12.0 kcal/mol. Tm has been reported as 1193 and 1190 ± 10°K by Bunzel (13) and Brewer (11), respectively, which are not adopted.

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Disodium Monoxide (Na_2O)

(Liquid) GFW = 61.979

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	25.000	21.895	21.895	.000	-89.112	-81.001	59.376
300	25.000	22.050	21.895	.046	-89.096	-80.950	58.972
400	25.000	29.242	22.876	2.546	-89.640	-78.249	42.753
500	25.000	34.820	24.728	5.046	-88.987	-75.476	32.990
600	25.000	39.378	26.801	7.546	-88.307	-72.837	26.531
700	25.000	43.232	28.880	10.046	-87.608	-70.316	21.954
800	25.000	46.570	30.887	12.546	-86.897	-67.893	18.548
900	25.000	49.515	32.797	15.046	-86.184	-65.560	15.920
1000	25.000	52.149	34.603	17.546	-85.477	-63.306	13.836
1100	25.000	54.532	36.308	20.046	-84.789	-61.126	12.145
1200	25.000	56.707	37.918	22.546	-130.593	-58.089	10.579
1300	25.000	58.708	39.442	25.046	-129.515	-52.090	8.757
1400	25.000	60.561	40.885	27.546	-128.441	-46.176	7.208
1500	25.000	62.286	42.255	30.046	-127.371	-40.337	5.877
1600	25.000	63.899	43.558	32.546	-126.303	-34.569	4.722
1700	25.000	65.415	44.799	35.046	-125.236	-28.867	3.711
1800	25.000	66.844	45.985	37.546	-124.175	-23.229	2.820
1900	25.000	68.195	47.118	40.046	-123.116	-17.649	2.030
2000	25.000	69.478	48.204	42.546	-122.062	-12.127	1.325
2100	25.000	70.697	49.247	45.046	-121.009	-6.658	.693
2200	25.000	71.860	50.248	47.546	-119.961	-1.236	.123
2300	25.000	72.972	51.212	50.046	-118.915	4.135	-.393
2400	25.000	74.036	52.141	52.546	-117.874	9.466	-.862
2500	25.000	75.056	53.038	55.046	-116.836	14.746	-1.289
2600	25.000	76.037	53.903	57.546	-115.804	19.993	-1.681
2700	25.000	76.980	54.741	60.046	-114.777	25.194	-2.039
2800	25.000	77.889	55.551	62.546	-113.756	30.357	-2.369
2900	25.000	78.767	56.337	65.046	-112.740	35.491	-2.675
3000	25.000	79.614	57.099	67.546	-111.733	40.584	-2.957

June 30, 1962; June 30, 1968

DISODIUM MONOXIDE (Na_2O) (LIQUID) GFW = 61.979

$S^\circ_{298.15}$ = [21.895] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-89.112] kcal/mol

Tm = 1405.2°K ΔHm° = 11.4 kcal/mol

Td = 2223°K

Heat of Formation

The heat of formation is obtained from $\Delta Hf^\circ_{298.15}(c)$ by adding ΔHm° and the difference between $H^\circ_{1405.2} - H^\circ_{298}$ for $Na_2O(c)$ and $Na_2O(\ell)$.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $Na_2SiO_3(\ell)$ and $SiO_2(\ell)$. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the $Na_2O(c)$ table.

Decomposition Temperature

Td is the temperature at which the Gibbs energy change of the decomposition reaction $Na_2O(\ell) = 2Na(g) + 1/2O_2(g)$ approaches zero.

Disodium Dioxide (Na_2O_2)

(Crystal) GFW = 77.9784

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.754	-121.257	-121.257	INFINITE
100	9.725	4.991	39.081	-3.409	-122.246	-117.468	256.725
200	18.040	14.767	24.522	-1.951	-122.658	-112.478	122.910
298	21.335	22.658	22.658	.000	-122.660	-107.472	78.779
300	21.369	22.790	22.658	.040	-122.657	-107.376	78.224
400	23.356	29.223	23.522	2.280	-123.816	-102.200	55.839
500	24.801	34.596	25.214	4.691	-123.618	-96.814	42.317
600	25.919	39.219	27.172	7.228	-123.278	-91.483	33.323
700	26.848	43.286	29.189	9.868	-122.828	-86.220	26.919
800	27.150	48.662	31.215	13.957	-120.927	-81.052	22.142
900	27.150	51.860	33.335	16.672	-120.406	-76.098	18.479
1000	27.150	54.720	35.333	19.387	-119.898	-71.202	15.561
1100	27.150	57.308	37.215	22.102	-119.414	-66.359	13.184
1200	27.150	59.670	38.989	24.817	-165.427	-60.642	11.044
1300	27.150	61.843	40.665	27.532	-164.563	-51.944	8.733
1400	27.150	63.855	42.250	30.247	-163.706	-43.315	6.762
1500	27.150	65.729	43.754	32.962	-162.856	-34.745	5.062
1600	27.150	67.481	45.182	35.677	-162.012	-26.231	3.583
1700	27.150	69.127	46.543	38.392	-161.171	-17.768	2.284
1800	27.150	70.679	47.841	41.107	-160.339	-9.358	1.136
1900	27.150	72.147	49.082	43.822	-159.513	-.991	.114
2000	27.150	73.539	50.270	46.537	-158.694	7.328	-.801
2100	27.150	74.864	51.410	49.252	-157.878	15.608	-1.624
2200	27.150	76.127	52.505	51.967	-157.071	23.851	-2.369
2300	27.150	77.334	53.559	54.682	-156.268	32.055	-3.046
2400	27.150	78.489	54.574	57.397	-155.473	40.230	-3.663
2500	27.150	79.598	55.553	60.112	-154.684	48.363	-4.228

June 30, 1963; June 30, 1968

DISODIUM DIOXIDE (Na_2O_2) (CRYSTAL) GFW = 77.9784

ΔHf_0° = -121.26 ± 1.2 kcal/mol

$S^\circ_{298.15}$ = 22.66 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -122.66 ± 1.2 kcal/mol

Tt = 785 ± 1°K

ΔHt° = 1.37 kcal/mol

Tm = 948°K

ΔHm° = Unknown

Heat of Formation

The enthalpy change of the reaction $Na_2O_2(c) + H_2O(\ell) = 2NaOH(1200\ H_2O) + 1/2O_2(g)$ was measured at 18.5°C by Roth (1). He employed a sample with composition 96.81 per cent Na_2O_2 and 3.43 per cent Na_2O by weight. Using $\Delta H^\circ soln(Na_2O_2,\ c) = -56.02$ kcal/mol, Roth derived the value $\Delta H^\circ soln(Na_2O_2,\ c) = -34.85$kcal/mol. This value was later corrected to be -35.75 kcal/mol (2). From this data we calculate the heat of formation (298°K) of $Na_2O_2(c)$ as -121.0 kcal/mol. Forcrand obtained ΔHsoln = -36.65 kcal/mol for the same reaction, quoted by Roth (1), yielding $\Delta Hf^\circ_{298}(Na_2O_2,c\ ) = -120.0$ kcal/mol. The auxiliary data $\Delta Hf^\circ_{298}(H_2O,\ \ell) = -68.315$ kcal/mol is taken from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965; and $\Delta Hf^\circ_{298}(NaOH \cdot 1200\ H_2O) = -112.458$ kcal/mol is derived based on $\Delta Hf^\circ_{298}(NaOH,\ c) = -101.90$ kcal/mol from JANAF Table and $\Delta H^\circ_\infty = -10.637$ kcal/mol and $\Delta Hdil(1200\ H_2O \rightarrow \infty H_2O) = -0.079$ kcal/mol from V. B. Parker, U. S.Natl. Bur. Std. NSRDS-NBS 2, 1965.

Gilles (3) determined the enthalpy change of the reaction $Na_2O_2(c) + H_2O(\ell) = 2NaOH(3800\ H_2O) + 1/2O_2(g)$, using a purer sample ($Na_2O_2$ 99.2 per cent, Na_2O 0.8 per cent). Based on the reported value $\Delta Hr^\circ_{298} = -34.0 \pm 0.3$ kcal/mol and derived $\Delta Hf^\circ_{298}(NaOH \cdot 3800\ H_2O) = -112.487$ kcal/mol, we calculate $\Delta Hf^\circ_{298} = -122.66 \pm 1.2$ kcal/mol for $Na_2O_2(c)$.

Leffler (4) studied the oxygen pressure-melt composition for the liquid sodium-oxygen system between 780 and 980°C. These results,together with the thermodynamic data for Na_2O_2,were used to calculate the heats and free energies of formation of melt compositions betwen $NaO_{1.0}$ and $NaO_{0.5}$. However, there are no numerical results reported. Therefore this data is not used for evaluation.

The heat of formation at 298°K is adopted as -122.66 ± 1.2 kcal/mol.

Heat Capacity and Entropy

The low temperature heat capacities, 52.31-296.22°K, were measured by Todd (5). His sample contains (per cent) 94 $Na_2O_2(c)$, 3.6 $Na_2O(c)$ and 2.4 Na_2CO_3. Corrections in the reported results have been made for Na_2CO_3 content, but not for Na_2O content which was estimated to be small. The Cp values below 52.31°K are calculated using the equation $Cp = D(\frac{252}{T}) + 3E(\frac{399}{T})$,reported by Todd. S°_{298} is derived from the adopted Cp,based on $S^\circ_{50} = 1.012$ eu.

The high temperature enthalpies, 375.4-869.2°K, were determined by Chandrasekharaiah (6), using drop calorimetry. Corrections were made for the contributions from impurities (Na_2CO_3 1.5 and Na_2O 0.2 per cent). A discontinuity was observed in the enthalpies between 773 and 793°K, indicating some kind of transition (see Transition Data). The Cp for $Na_2O_2(\alpha)$ at temperatures 298-769.5°K are derived from the enthalpy measurements, 375.4-769.5°K, and joined smoothly with the low temperature data at 298°K,and extrapolated to 785°K(Tt). The Cp for $Na_2O_2(\beta)$ is derived from the enthalpy data, 794-869.2°K, as constant, 27.15 gibbs/mol, and extrapolated to 2500°K.

Vedeneev (7) measured the high temperature specific heat of $Na_2O_2(c)$ in the temperature interval 292-373°K using adiabatic calorimetry. The reported average value, 21.46 gibbs/mol, is in fair agreement with the adopted ones.

Transition Data

Tt was reported by Tallman (8),who measured the X-ray power diffraction pattern by a Geiger-counter diffractometer and found that at about 510°C the pattern changes entirely and a new set of peaks indicates a new phase. Separate thermal analysis measurements (8) confirm the transition temperature (α → β) is 512 ± 1°C or 785 ± 1°K, which is adopted here. Foppl (9) found a thermal anomaly at 485°C in both heating and cooling curves. ΔHt° is derived from the adopted enthalpy and Cp data on $Na_2O_2(\alpha)$ and $Na_2O_2(\beta)$.

Melting Data

Tm is obtained from Benzel (10). Tm = 733 and 783°K were reported by Blumenthal (11) and Rode (12), respectively, which are not adopted.

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Sodium Metasilicate (Na_2SiO_3)
(Crystal) GFW = 122.0738

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-4.520	-370.747	-370.747	INFINITE
100	11.546	6.111	47.083	-4.097	-372.069	-365.241	798.233
200	21.449	17.577	29.506	-2.386	-372.856	-358.059	391.268
298	26.740	27.210	27.210	.000	-373.190	-350.712	257.079
300	26.863	27.376	27.211	.050	-373.193	-350.572	255.392
400	30.540	35.640	28.312	2.931	-374.573	-342.912	187.358
500	33.154	42.750	30.506	6.122	-374.504	-334.998	146.428
600	35.161	48.979	33.076	9.542	-374.227	-327.121	119.154
700	36.794	54.525	35.751	13.142	-373.791	-319.304	99.691
800	38.181	59.531	38.416	16.892	-373.228	-311.558	85.114
900	39.398	64.100	41.019	20.772	-372.561	-303.886	73.794
1000	40.493	68.308	43.541	24.768	-371.810	-296.294	64.755
1100	41.498	72.215	45.972	28.868	-370.995	-288.785	57.376
1200	42.433	75.867	48.313	33.065	-416.595	-280.435	51.074
1300	43.315	79.298	50.565	37.352	-415.242	-269.142	45.247
1400	44.153	82.539	52.735	41.726	-413.823	-257.958	40.269
1500	44.957	85.613	54.825	46.182	-412.343	-246.875	35.970
1600	45.733	88.538	56.841	50.714	-410.805	-235.893	32.222
1700	46.785	91.345	58.789	55.345	-421.177	-224.903	28.913
1800	47.218	94.030	60.673	60.043	-419.457	-213.407	25.911
1900	47.934	96.602	62.496	64.801	-417.686	-202.006	23.236
2000	48.635	99.079	64.264	69.629	-415.853	-190.705	20.839
2100	49.325	101.468	65.979	74.527	-413.957	-179.494	18.680
2200	50.003	103.779	67.645	79.494	-412.004	-168.376	16.727
2300	50.673	106.016	69.265	84.528	-409.990	-157.348	14.951
2400	51.334	108.187	70.842	89.628	-407.921	-146.403	13.332
2500	51.988	110.296	72.378	94.794	-405.795	-135.557	11.850

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

SODIUM METASILICATE (Na_2SiO_3) (CRYSTAL) GFW = 122.0738

ΔHf°_0 = -370.75 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 27.21 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -373.19 ± 1.0 kcal/mol

Tm = 1362 ± 0.5°K

ΔHm° = 12.38 kcal/mol

Heat of Formation

The heats of solution of NaCl(c), Na_2SO_4(c), SiO_2(quartz),Na_2SiO_3(c), HCl(aq) and H_2SO_4(aq) in 20 percent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). The author derived two values of ΔHsoln of Na_2O(c) from those of NaCl(c), Na_2SO_4(c), HCl(aq) and H_2SO_4(aq) presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate ΔHsoln of Na_2O(c) in the calorimetric solution as -87.50 (chloride scheme, originally -87.66) and -88.74 kcal/mol (sulfate scheme, originally -89.19), using recent ΔHf°_{298} values for NaCl(c), Na_2SO_4(c), HCl(aq), H_2SO_4(aq), and Na_2O(c). The corresponding enthalpy changes, ΔHr°_{298}, for the reaction Na_2O(c) + SiO_2(quartz) = Na_2SiO_3(c) are derived as -55.20 and -56.38 kcal/mol. Adopting the weighted average ΔHr°_{298} = -55.59 kcal/mol with ΔHf°_{298}(Na_2O, c) = -99.9 kcal/mol and ΔHf°_{298}(SiO_2, quartz) = -217.7 kcal/mol, we obtain ΔHf°_{298} = -373.19 kcal/mol for Na_2SiO_3(c). This ΔHf°_{298}(Na_2SiO_3, c) value is independent of future changes in ΔHf°_{298} of Na_2O(c) but the values of ΔHsoln and ΔHr° are not independent. The adopted value of ΔHf°_{298}(Na_2O, c) is the average of -100.1 and -99.7 kcal/mol reported by W. A. Roth and H. L. Kaule, Z. Anorg. Chem. 253, 352 (1947); ibid. 255, 324 (1948), and M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929), respectively.

W. A. Roth and H. Troitzsch, Z. Anorg. Chem. 260, 337 (1949), have measured the heats of solution of SiO_2(quartz), Na_2SiO_3(c) and Na_2O(c) in 10.3 percent HF at 22°C to be -32.85, -67.96 and -88.9 kcal/mol, respectively. Using these results, we calculate the enthalpy change of the reaction Na_2O(c) + SiO_2(quartz) = Na_2SiO_3(c) as -53.79 kcal/mol and ΔHf°_{298}(Na_2SiO_3, c) = -371.39 kcal/mol.

By use of high temperature reaction calorimetry D. C. Kroger and W. Janetzko, Z. Anorg. Allgem Chem. 284, 83 (1956), have determined the enthalpy change of the reaction Na_2C_3(c) + $Na_2Si_2O_5$(gl) = 2Na_2SiO_3(c) + CO_2(g) as 17.99 kcal/mol. Based on ΔHf°_{298} = -270.26, -582.92 and -94.05 kcal/mol for Na_2CO_3(c), $Na_2Si_2O_5$(gl) and CO_2(g), respectively, we evaluate ΔHf°_{298} = =370.57 kcal/mol for Na_2SiO_3(c).

The heats of solution of Na_2CO_3(c), SiO_2(quartz) and Na_2SiO_3(c) in 39 percent HF at 26.5°C were measured to be -244.1, -564.5 and -673.6 cal/g, by C. Hummel and H. E. Schwiete, Glastech. Ber. 32, 327 (1959). From these results we calculate the enthalpy change to be 22.43 kcal/mol for the reaction Na_2CO_3(c) + SiO_2(quartz) = Na_2SiO_3(c) + CO_2(g), yielding ΔHf°_{298} (Na_2SiO_3,c) = -371.48 kcal/mol.

Many other older calorimetric measurements have been made in order to derive the heat of formation for Na_2SiO_2(c), but most of these are of questionable accuracy and in some cases the products of the reaction are uncertain. For further details the review by N. W. McCready, J. Phys. Colloid. Chem. 52, 1277 (1948).

Heat Capacity and Entropy

The low temperature heat capacities, 53.6 - 294.5°K, were measured by K. K. Kelley, J. Am. Chem. Soc. 61, 471 (1939), and high temperature enthalpies, 360.5 - 1747°K were determined by B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945). The high temperature heat capacities are derived from the measured enthalpy data and joined smoothly with the low temperature Cp values. The entropy at 298°K is calculated using the adopted low temperature heat capacities, based on S°_{50} = 1.195 eu.

Melting Data

See Na_2SiO_3(ℓ) table for details.

Sodium Metasilicate (Na_2SiO_3)

(Liquid) GFW = 122.0738

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	26.740	35.967	35.967	.000	-361.107	-341.240	250.136
300	26.863	36.132	35.967	.050	-361.110	-341.116	248.503
400	30.540	44.397	37.069	2.931	-362.490	-334.332	182.670
500	33.154	51.506	39.262	6.122	-362.421	-327.293	143.060
600	35.161	57.735	41.833	9.542	-362.144	-320.291	116.666
700	36.794	63.282	44.508	13.142	-361.708	-313.350	97.832
800	38.181	68.288	47.172	16.892	-361.145	-306.480	83.727
900	42.380	72.856	49.776	20.772	-360.478	-299.683	72.773
1000	42.380	77.322	52.311	25.010	-359.484	-292.982	64.031
1100	42.380	81.361	54.771	29.248	-358.532	-286.382	56.899
1200	42.380	85.048	57.143	33.486	-404.091	-278.948	50.803
1300	42.380	88.441	59.422	37.724	-402.787	-268.573	45.151
1400	42.380	91.581	61.608	41.962	-401.504	-258.297	40.322
1500	42.380	94.505	63.705	46.200	-400.242	-248.112	36.150
1600	42.380	97.240	65.716	50.438	-398.998	-238.009	32.511
1700	42.380	99.810	67.647	54.676	-409.763	-227.879	29.296
1800	42.380	102.232	69.502	58.914	-408.503	-217.216	26.374
1900	42.380	104.523	71.285	63.152	-407.251	-206.622	23.767
2000	42.380	106.697	73.002	67.390	-406.009	-196.097	21.428
2100	42.380	108.765	74.656	71.628	-404.773	-185.633	19.319
2200	42.380	110.736	76.252	75.866	-403.549	-175.226	17.407
2300	42.380	112.620	77.792	80.104	-402.331	-164.877	15.667
2400	42.380	114.424	79.281	84.342	-401.124	-154.574	14.076
2500	42.380	116.154	80.722	88.580	-399.926	-144.333	12.618

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

SODIUM METASILICATE (Na_2SiO_3) (LIQUID) GFW = 122.0738

$S^\circ_{298.15}$ = 35.967 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -361.107 kcal/mol

Tm = 1362 ± 0.5°K ΔHm = 12.38 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(\ell)$ is obtained from $\Delta Hf^\circ_{298}(c)$ by adding ΔHm° and the difference between $H^\circ_{1362} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity above 900°K is derived as constant from the high temperature enthalpy data, 1414 - 1747°K, measured by B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945). A glass transition temperature is assumed at 900°K; i.e. the heat capacities below 900°K are taken to be the same as those for $Na_2SiO_3(c)$.

The entropy is obtained in a manner analogous to that of the heat of formation. The low temperature heat capacities, 63.74 - 162.48°K, have been measured by V. V. Tarasov and Y. S. Savitskaya, Dokl. Akad. Nauk SSSR, 88, 1019 (1953); however, these are not adequate to be used to evaluate S°_{298}.

Melting Data

The adopted Tm = 1362°K, determined by F. C. Kracek, J. Phys. Chem. 34, 1583 (1930), is in good agreement with the value 1261°K reported by F. M. Jaeger, J. Wash. Acad. Sci. 1, 49 (1911), and later confirmed by G. W. Morey and N. L. Bowen, J. Phys. Chem. 28, 1167 (1924).

Other reported Tm values are 1280, 1291 and 1329°K by N. V. Kultascheff, Z. Anorg. Chem. 35, 186 (1903); R. C. Wallace, ibid., 63, 1 (1909); and H. S. van Klooster, ibid., 69, 135 (1910), respectively. These values are all lower than the adopted Tm value, probably because the sample compositions were not the exact composition of metasilicate.

The value of ΔHm° is evaluated from the adopted heat capacities for $Na_2SiO_3(c)$ and $Na_2SiO_3(\ell)$, and the enthalpy data reported by B. F. Naylor, loc. cit., assuming the final state of the calorimetric sample to be $Na_2SiO_3(c)$. From the phase diagrams of Na_2SiO_3 with other compounds, K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936, derived the values of ΔHm° of 9.8 - 10.5 kcal/mol.

Sodium Sulfate, V (Na_2SO_4)

(Crystal) GFW = 142.0412

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-5.550	-328.815	-328.815	INFINITE
100	15.941	10.329	59.049	-4.872	-330.329	-321.648	702.962
200	25.232	24.622	38.407	-2.757	-331.173	-312.596	341.589
298	30.549	35.764	35.764	.000	-331.550	-303.383	222.386
300	30.633	35.953	35.765	.057	-331.553	-303.208	220.886
400	34.678	45.345	37.018	3.331	-333.488	-293.615	160.424
500	37.999	53.450	39.511	6.969	-333.732	-283.610	123.966
600	40.670	60.622	42.443	10.907	-333.603	-273.592	99.656
700	42.790	67.056	45.508	15.084	-333.194	-263.596	82.298
800	44.490	72.885	48.571	19.451	-345.638	-254.963	69.653
900	45.830	78.205	51.573	23.969	-344.566	-243.690	59.176
1000	46.940	83.093	54.484	28.610	-343.400	-232.541	50.822
1100	47.820	87.610	57.293	33.349	-342.174	-221.520	44.012
1200	48.510	91.801	59.996	38.166	-387.377	-209.691	38.190
1300	49.100	95.708	62.594	43.048	-385.648	-194.952	32.774
1400	49.540	99.363	65.092	47.980	-383.885	-180.352	28.154
1500	50.000	102.797	67.492	52.957	-382.092	-165.878	24.168

Dec. 31, 1966

SODIUM SULFATE, V (Na_2SO_4) (CRYSTAL) GFW = 142.0412

$S^\circ_{298.15}$ = 35.76 ± 0.1 gibbs/mol

Tt(V→I) = 521.7°K

ΔHf°_0 = -328.82 ± 0.2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -331.55 ± 0.2 kcal/mol

$\Delta H^\circ_t(V \rightarrow I)$ = 2.584 kcal/mol

Heat of Formation.

F. L. E. Shibata, S. Oda and S. Furukawa, J. Sci. Hiroshima Univ. (Japan) Ser. A, 3, 227 (1933), measured the emf of the cell: Na-amalg. (0.2077%)$|Na_2SO_4$ (sat. soln.), $Hg_2SO_4|Hg$ at 33-37°C. Extrapolating their results to 25°C, we obtain the $\Delta Gr^\circ_{298.15}$ = -153.77 kcal/mol for the reaction $2Na(c) + Hg_2SO_4(c) = 2Hg(l) + Na_2SO_4(c)$, which yields $\Delta Gf^\circ_{298.15}$ = -303.36 and $\Delta Hf^\circ_{298.15}$ = -331.53 kcal/mol for $Na_2SO_4(c)$. The auxiliary value, $\Delta Gf^\circ_{298.15}$ = -149.59 kcal/mol, for $Hg_2SO_4(c)$ is obtained from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Tech. Note 270-1, Natl. Bur. Std., Washington, D.C., 1965.

The heat of formation for $Na_2SO_4(\infty H_2O)$ is evaluated as -332.10 kcal/mol, using $\Delta Hf^\circ_{298.15}$ = -57.39 and -217.32 kcal/mol for $Na^+(\infty H_2O)$ and $SO_4^=(\infty H_2O)$, respectively, from Tech. Note 270-1, loc. cit. J.P. Coughlin, J. Am. Chem. Soc. 77, 868 (1955), determined the enthalpy change, $\Delta Hr^\circ_{298.15}$ = -0.301 ± 0.035 kcal/mol for the reaction $Na_2SO_4(c,V) = Na_2SO_4(1050\ H_2O)$. Adopting $\Delta Hr^\circ_{298.15}$ = 0.244 kacl/mol for the reaction $Na_2SO_4(\infty H_2O) = Na_2SO_4\ (1050\ H_2O)$ from Natl. Bur. Std. Circ. 500, Washington, D.C., 1952, we derive the value, $\Delta Hr^\circ_{298.15}$ = 0.545 kcal/mol for the reaction $Na_2SO_4(\infty H_2O) = Na_2SO_4(c,V)$, yielding $\Delta Hf^\circ_{298.15}$ = -331.56 kcal/mol for $Na_2SO_4(c,V)$.

The heat of formation for $Na_2SO_4(c,V)$ is adopted as -331.55 ± 0.2 kcal/mol.

Heat Capacity and Entropy.

The low temperature heat capacities,13.74 - 313.44°K, have been measured by K. S. Pitzer and L. V. Coulter, J. Am. Chem. Soc. 60, 1310 (1938). The heat capacities in the temperature range 324.61 - 503.05°K were determined by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 6, 1321 (1961), using an adiabatic calorimeter. These two sets of data are joined smoothly and extrapolated graphically to 1500°K. The enthalpy values derived from the adopted Cp data are in fair agreement with those determined by J. P. Coughlin, J. Am. Chem. Soc. 77, 868 (1955). The corresponding Cp values, reported by M. M. Popov and G. L. Galchenko, J. Gen. Chem. USSR, 21, 2489 (1951), seem too high at the high temperature end. $S^\circ_{298.15}$ is derived using the low temperature Cp data reported by K. S. Pitzer and L. V. Coulter, loc. cit., based on S°_{14} = 0.057 eu.

Transition Data.

Polymorphism studies by F. C. Kracek, J. Phys. Chem. 33, 1281 (1929), and F. C. Kracek and R. E. Gibson, J. Phys. Chem. 33, 1304 (1929); ibid, 34, 188 (1930), indicate five distinct modifications, i.e. V, IV, III, II, I, of which only V and I are stable forms. Calorimetric studies of Shmidt and Sokolov, loc. cit., suggest another form, stable at high temperatures, which is labeled as δ.

The transition temperature and heat of transition are from the calorimetric data for thenardite reported by Shmidt and Sokolov, loc. cit.

Sodium Sulfate, III (Na_2SO_4)

(Crystal) GFW = 142.0412

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	31.790	36.653	36.653	.000	- 331.005	- 303.104	222.181
300	31.830	36.849	36.653	.059	- 331.006	- 302.929	220.684
400	35.769	46.503	37.944	3.424	- 332.850	- 293.440	160.328
500	41.735	55.087	40.524	7.282	- 332.874	- 283.571	123.949
600	47.130	63.208	43.635	11.744	- 332.221	- 273.761	99.717
700	50.651	70.755	46.977	16.645	- 331.088	- 264.080	82.450
800	52.950	77.679	50.389	21.833	- 342.711	- 255.871	69.901
900	54.480	84.010	53.778	27.209	- 340.781	- 245.130	59.526
1000	55.410	89.801	57.095	32.706	- 338.759	- 234.608	51.273
1100	56.000	95.113	60.313	38.279	- 336.699	- 224.298	44.564
1200	56.300	100.000	63.420	43.897	- 381.101	- 213.255	38.839

Dec. 31, 1966

SODIUM SULFATE, III (Na_2SO_4) (CRYSTAL) GFW = 142.0412

$S^\circ_{298.15}$ = 36.653 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −331.005 kcal/mol

Tt(III → I) = 521.7°K

ΔHt°(III → I) = 1.630 kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298.15}(Na_2SO_4$, III) value is obtained from $\Delta Hf^\circ_{298.15}(Na_2SO_4$, I) by subtracting ΔHt°(III → I) and the difference between $H^\circ_{521.7} - H^\circ_{298.15}$ for Na_2SO_4(III) and Na_2SO_4(I).

J. P. Coughlin, J. Am. Chem. Soc. <u>77</u>, 868 (1955), determined the heat of reaction of $Na_2SO_4(V) \rightarrow Na_2SO_4(III)$ as 0.735 ± 0.015 kcal/mol at 303.16°K by solution calorimetry. This value is in reasonable agreement with 0.55 kcal/mol obtained from the selected heat of formation.

Heat Capacity and Entropy.

The heat capacities in the temperature range 319.02 - 521.65°K were measured with an adiabatic calorimeter by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. <u>6</u>, 1321 (1961). The Cp values below 319°K and above 521°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data.

Na_2SO_4(III) is the meltable form obtained by cooling Na_2SO_4(I) in the absence of moisture. The temperature and heat of transition are taken from the calorimetric data of Shmidt and Sokolov, loc. cit. The value ΔHt°(III → I) = 1.630 + 0.005 kcal/mol is the average of three determinations.

J. P. Coughlin, loc. cit., reported the heat of transition (III → I) at 514°K to be 1.680 kcal/mol, obtained by drop calorimetry, which is in good agreement with the value adopted.

Sodium Sulfate, I (Na_2SO_4)

(Crystal) GFW = 142.0412

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	38.990	37.733	37.733	.000	- 330.096	- 302.517	221.751
300	39.000	37.975	37.734	.072	- 330.084	- 302.345	220.258
400	39.868	49.313	39.274	4.015	- 331.350	- 293.064	160.122
500	40.790	58.305	42.211	8.047	- 331.200	- 283.506	123.920
600	41.920	65.840	45.537	12.182	- 330.874	- 273.994	99.802
700	43.243	72.399	48.916	16.438	- 330.386	- 264.529	82.590
800	44.796	78.272	52.224	20.838	- 342.797	- 256.432	70.054
900	46.581	83.649	55.421	25.405	- 341.676	- 245.700	59.664
1000	48.190	88.640	58.496	30.143	- 340.413	- 235.101	51.381
1100	49.570	93.299	61.451	35.033	- 339.036	- 224.641	44.632
1200	50.640	97.659	64.289	40.045	- 384.044	- 213.389	38.863
1300	51.570	101.750	67.014	45.157	- 382.085	- 199.244	33.496
1400	52.300	105.600	69.634	50.351	- 380.060	- 185.258	28.920
1500	52.917	109.230	72.154	55.613	- 377.982	- 171.417	24.975
1600	53.390	112.661	74.580	60.930	- 375.861	- 157.712	21.542
1700	53.696	115.907	76.916	66.285	- 373.711	- 144.141	18.531
1800	53.900	118.983	79.169	71.666	- 371.552	- 130.701	15.869
1900	54.001	121.900	81.341	77.062	- 369.390	- 117.376	13.501
2000	54.000	124.671	83.439	82.463	- 367.236	- 104.174	11.384

Dec. 31, 1966

SODIUM SULFATE, I (Na_2SO_4) (CRYSTAL) GFW = 142.0412

$S^\circ_{298.15}$ = 37.733 gibbs/mol

$Tt(V \rightarrow I)$ = 521.7°K

$Tt(I \rightarrow \delta)$ = 980°K

Tm = 1157°K

$\Delta Hf^\circ_{298.15}$ = -330.096 kcal/mol

$\Delta Ht^\circ(V \rightarrow I)$ = 2.584 kcal/mol

$\Delta Ht^\circ(I \rightarrow \delta)$ = 0.08 kcal/mol

ΔHm° = 5.67 kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298.15}(Na_2SO_4,I)$ is obtained from $\Delta Hf^\circ_{298.15}(Na_2SO_4,V)$ by adding $\Delta Ht^\circ(V \rightarrow I)$ and the difference between $H^\circ_{521.7} - H^\circ_{298.15}$ for $Na_2SO_4(V)$ and $Na_2SO_4(I)$.

Heat Capacity and Entropy.

The heat capacities in the temperature range 538.65 - 917.65°K were measured with an adiabatic calorimeter by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 6, 1321 (1961). The Cp values below 538.65°K and above 917.65°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data.

The value $\Delta Ht^\circ(V \rightarrow I) = 2.584 \pm 0.015$ kcal/mol is the average of two determinations from the calorimetric studies of Shmidt and Sokolov, loc. cit. The transition temperature was derived from the heating curve obtained in measuring the heat of transition. It was taken to be the temperature at which the specimen began to show its lowest heating rate. The heat of transition was the difference between the quantity of heat actually dissipated and the sum of the heats calculated from the heat capacity curve of the apparatus and from the specific heat curves of (V) and (I) linearly extrapolated to the transition temperature.

The values of Tt and ΔHt° for $Na_2SO_4(I) \rightarrow Na_2SO_4(\delta)$ transition were reported by Shmidt and Sokolov, loc. cit. See $Na_2SO_4(\delta)$ table for details.

Melting Data.

See $Na_2SO_4(l)$ table for details.

Sodium Sulfate, Delta (δ - Na_2SO_4)

(Crystal) GFW = 142.0412

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	38.990	37.741	37.741	.000	-330.089	-302.512	221.747
300	39.000	37.982	37.741	.072	-330.077	-302.340	220.254
400	39.868	49.320	39.281	4.015	-331.343	-293.059	160.120
500	40.790	58.312	42.218	8.047	-331.193	-283.502	123.919
600	41.920	65.847	45.545	12.182	-330.867	-273.991	99.801
700	43.243	72.406	48.923	16.438	-330.379	-264.527	82.589
800	44.800	78.279	52.232	20.838	-342.790	-256.430	70.053
900	46.581	83.656	55.428	25.405	-341.669	-245.699	59.664
1000	48.254	88.733	58.505	30.228	-340.321	-235.102	51.382
1100	50.000	93.414	61.468	35.140	-338.922	-224.653	44.634
1200	51.710	97.840	64.317	40.228	-383.854	-213.416	38.868
1300	53.140	102.038	67.058	45.474	-381.761	-199.294	33.504
1400	54.140	106.015	69.700	50.841	-379.563	-185.343	28.933
1500	54.820	109.774	72.248	56.290	-377.298	-171.549	24.995
1600	55.310	113.329	74.705	61.798	-374.986	-157.906	21.569
1700	55.660	116.693	77.077	67.348	-372.641	-144.407	18.565
1800	55.810	119.879	79.367	72.922	-370.289	-131.051	15.912
1900	55.920	122.900	81.580	78.509	-367.936	-117.822	13.553
2000	56.000	125.770	83.718	84.105	-365.587	-104.723	11.444

Dec. 31, 1966

SODIUM SULFATE, δ (Na_2SO_4) (CRYSTAL) GFW = 142.0412

$S°_{298.15}$ = 37.741 gibbs/mol

Tt (I → δ) = 980°K

Tm = 1157°K

$\Delta Hf°_{298.15}$ = -330.089 kcal/mol

ΔHt° (I → δ) = 0.08 kcal/mol

ΔHm° = 5.50 kcal/mol

Heat of Formation

The heat of formation ($\Delta Ht°_{298.15}$) is obtained from $\Delta Hf°_{298.15}$ for Na_2SO_4 (I) by adding ΔHt° (I → δ) and the difference between $H°_{980}$ - $H°_{298.15}$ for Na_2SO_4(I) and Na_2SO_4 (δ).

Heat Capacity and Entropy

The heat capacities in the temperature range 930 - 1010°K were measured by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 6, 1321 (1961). The Cp values below 900°K are assumed to be the same as those for Na_2SO_4 (I). The heat capacities above 1010°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

A small anomalous region between 690 - 720°C (963.15 - 993.15°K) on the Cp curve for Na_2SO_4(c) was reported by N. E. Shmidt and V. A. Sokolov, loc. cit. By use of graphical integration of the area between the measured Cp curve and an arbitrary base line over the region 900 - 1100°K, a value of ΔHt° (I → δ) = 0.08 kcal/mol was obtained. Tt is assumed to be 980°K. This anomalous region was first observed by G. W. Wyrouboff, Z. Krist. 21, 284 (1893), and later confirmed by Y. P. Simanov and D. F. Kirkina, Zh. Neorg. Khim. 2, 699 (1957), as a transition from a hexagonal to an orthorhombic structure. This transition was not observed by the earlier investigators because their measurements did not extend to that temperature range.

Melting Data

The temperature and heat of melting of Na_2SO_4 (I) → Na_2SO_4 (l) were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ and liquid Na_2SO_4, we derive Hm°(δ → l) = 5.50 kcal/mol, using Coughlin's enthalpy data on Na_2SO_4 (l). The melting temperature is assumed to be the same as that reported by Coughlin.

Tm was reported to be 880°C (1153°K), 897°C (1170°K) and 888°C (1161°K) by Ruff and Plato, Ber. Deutsch. Chem. Ges. 36, 2357 (1903); K. Hüttner and G. Tammann, Z. Anorg. Chem. 43, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. 50, 355 (1906), respectively.

Sodium Sulfate (Na_2SO_4)

(Liquid) GFW = 142.0412

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
1							
200							
298	38.990	42.777	42.777	.000	- 324.241	- 298.165	218.561
300	39.000	43.018	42.777	.072	- 324.229	- 298.003	217.095
400	39.868	54.356	44.317	4.015	- 325.495	- 289.226	158.026
500	40.790	63.348	47.254	8.047	- 325.345	- 280.172	122.463
600	41.920	70.884	50.581	12.182	- 325.019	- 271.165	98.772
700	43.243	77.442	53.959	16.438	- 324.531	- 262.204	81.864
800	47.180	83.315	57.268	20.838	- 336.942	- 254.611	69.556
900	47.180	88.872	60.477	25.556	- 335.670	- 244.395	59.347
1000	47.180	93.843	63.569	30.274	- 334.427	- 234.318	51.210
1100	47.180	98.340	66.529	34.992	- 333.222	- 224.372	44.579
1200	47.180	102.445	69.353	39.710	- 378.524	- 213.612	38.904
1300	47.180	106.221	72.046	44.428	- 376.959	- 199.930	33.611
1400	47.180	109.718	74.613	49.146	- 375.410	- 186.374	29.094
1500	47.180	112.973	77.064	53.864	- 373.876	- 172.926	25.195
1600	47.180	116.018	79.404	58.582	- 372.354	- 159.577	21.797
1700	47.180	118.878	81.643	63.300	- 370.841	- 146.322	18.811
1800	47.180	121.575	83.787	68.018	- 369.345	- 133.160	16.168
1900	47.180	124.126	85.844	72.736	- 367.861	- 120.076	13.812
2000	47.180	126.546	87.819	77.454	- 366.390	- 107.078	11.701
2100	47.180	128.848	89.718	82.172	- 364.928	- 94.150	9.798
2200	47.180	131.042	91.547	86.890	- 363.482	- 81.286	8.075
2300	47.180	133.140	93.310	91.608	- 362.045	- 68.496	6.509
2400	47.180	135.148	95.012	96.326	- 360.622	- 55.757	5.077
2500	47.180	137.074	96.656	101.044	- 359.211	- 43.091	3.767
2600	47.180	138.924	98.246	105.762	- 357.813	- 30.468	2.561
2700	47.180	140.705	99.786	110.480	- 356.429	- 17.909	1.450
2800	47.180	142.420	101.278	115.198	- 355.060	- 5.396	.421
2900	47.180	144.076	102.726	119.916	- 353.703	7.074	- .533
3000	47.180	145.675	104.131	124.634	- 352.363	19.493	- 1.420

Dec. 31, 1966

Na_2O_4S

SODIUM SULFATE (Na_2SO_4) (LIQUID) GFW = 142.0412

$S^\circ_{298.15}$ = 42.777 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -324.241 kcal/mol

$Tm(\delta \rightarrow l)$ = 1157°K

$\Delta Hm^\circ(\delta \rightarrow l)$ = 5.50 kcal/mol

<u>Heat of Formation.</u>

The value of $\Delta Hf^\circ_{298.15}(l)$ is obtained from $\Delta Hf^\circ_{298.15}(I)$ by adding ΔHm° and the difference between $H^\circ_{1157} - H^\circ_{298.15}$ for $Na_2SO_4(\delta)$ and $Na_2SO_4(l)$.

<u>Heat Capacity and Entropy.</u>

The enthalpies for $Na_2SO_4(l)$ were measured by drop calorimetry in the temperature range 1157 - 1826°K by J. P. Coughlin, J. Am. Chem. Soc. <u>77</u>, 868 (1955); and in the temperature range 1173 - 1290°K by M. M. Popov and D. M. Ginzburg, J. Gen. Chem. USSR <u>26</u>, 1107 (1956). The constant heat capacity adopted here is derived from the enthalpy measurements reported by J. P. Coughlin, loc. cit. Below 800°K, the heat capacities are assumed to be the same as those of the δ phase. The entropy is calculated in a manner analogous to that of the heat of formation.

<u>Melting Data.</u>

The temperature and heat of melting of $Na_2SO_4(I) \rightarrow Na_2SO_4(l)$ were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase, and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ liquid Na_2SO_4, we derive $\Delta Hm^\circ(\delta \rightarrow l)$ = 5.50 kcal/mol, using Coughlin's enthalpy data on $Na_2SO_4(l)$. The melting temperature is assumed to be the same as that reported by Coughlin.

Tm was reported to be 880°C(1153°K), 897°C(1170°K) and 888°C(1161°K) by Ruff and Plato, Ber. Deutsch. Chem. Ges. <u>36</u>, 2357 (1903); K. Hüttner and G. Tammann, Z. Anorg. Chem. <u>43</u>, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. <u>50</u>, 355 (1906), respectively.

Sodium Tungstate (Na_2WO_4)

(Crystal) GFW = 293.8272

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 6.044	- 366.823	- 366.823	INFINITE
100	16.697	10.392	63.976	- 5.358	- 368.321	- 359.714	786.154
200	28.022	26.043	41.220	- 3.035	- 369.044	- 350.763	383.296
298	33.407	38.320	38.320	.000	- 369.200	- 341.743	250.505
300	33.490	38.527	38.321	.062	- 369.199	- 341.572	248.835
400	37.126	48.697	39.683	3.606	- 370.354	- 332.277	181.548
500	40.000	57.301	42.367	7.467	- 370.038	- 322.788	141.090
600	42.600	64.827	45.496	11.599	- 369.469	- 313.387	114.151
700	45.100	71.582	48.748	15.984	- 368.673	- 304.101	94.945
800	47.500	77.761	51.994	20.614	- 367.662	- 294.945	80.575
900	50.000	93.205	55.600	33.845	- 358.081	- 286.304	69.524
1000	52.400	98.597	59.633	38.964	- 356.650	- 278.402	60.845
1100	54.850	103.706	63.409	44.327	- 355.021	- 270.659	53.775
1200	57.300	108.584	66.972	49.934	- 399.665	- 262.153	47.745
1300	59.780	113.268	70.354	55.788	- 397.205	- 250.791	42.162
1400	62.250	117.789	73.582	61.890	- 394.522	- 239.631	37.408
1500	64.700	122.167	76.676	68.237	- 391.619	- 228.665	33.316

June 30, 1967

SODIUM TUNGSTATE (Na_2WO_4) (CRYSTAL) GFW = 293.8272

ΔHf_0° = -366.8 ± 2 kcal/mol

$S^\circ_{298.15}$ = 38.32 ± 0.5 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -369.2 ± 2 kcal/mol

Tt_1 = 862.0°K

ΔHt_1° = 0.983 kcal/mol

Tt_2 = 860.8°K

ΔHt_2° = 7.373 kcal/mol

Tm = 968.7°K

ΔHm° = 5.688 kcal/mol

Heat of Formation

The adopted heat of formation, ΔHf°_{298} (Na_2WO_4,c) = -369.2 kcal/mol, is calculated from $\Delta Hr^\circ_{303.15}$ = 19.44 ± 0.08 kcal/mol for the reaction H_2WO_4(c) + 2NaCl(c) = Na_2WO_4(c) + 2HCl(12.731 H_2O), using the JANAF value of ΔHf°_{298} (H_2WO_4,c) = -270.5 kcal/mol and ΔHf°_{298} (NaCl,c) = -98.26 kcal/mol, and auxiliary data for HCl(aq) (11). The value of $\Delta Hr^\circ_{303.15}$ was determined by solution calorimetry by M. F. Koehler, L. B. Pankratz and R. Barany (1).

J. M. Sherfey and A. Brenner (2) measured by electrochemical calorimetry the heat of reaction ΔHr°_{298} = -7 ± 1.5 kcal/mol for W(c) + 2NaOH(55.55H_2O) + $2H_2O(\ell)$ = Na_2WO_4 (∞H_2O) + $3H_2$(g). This value, combined with the heat of solution (1,3,9), ΔH°_{sol} = -1.7 ± 0.1 kcal/mol for Na_2WO_4(c) = Na_2WO_4 (∞H_2O), gives ΔHf°_{298} (Na_2WO_4,c) = -368.4 kcal/mol, which is in good agreement with the value adopted.

The previously accepted value (1,3), ΔHf°_{298} (Na_2WO_4,c) = -379 ± 0.5 kcal/mol, was based on the unreliable ΔHf°_{298} (H_2WO_4,c) = -280.2 ± 0.4 kcal/mol. (See JANAF H_2WO_4(c) table of March 31, 1967.) The other quoted value (4), ΔHf°_{298} (Na_2WO_4,c) = -395 kcal/mol, was obtained from W. G. Mixter's (5) measurement of the heat of reaction of tungsten powder with excess Na_2O_2. This value was probably in error because the complex tungstate and peroxytungstates were formed in the reaction.

Heat Capacity and Entropy

Low temperature heat capacities (52-299.87°K) were measured calorimetrically by E. G. King and W. W. Weller (6). The heat capacities above 300°K are estimated by extrapolation of the low temperature heat capacity curve to Cp_{860} = 49.0 gibbs/mol. The latter is obtained from an estimate of Cp equal to 7 gibbs/g-atom at the first transition temperature.

The entropy, S°_{298} = 38.32 ± 0.5 eu, is calculated from low temperature heat capacity data of King and Weller (6), based on an extrapolation of S°_{51} = 2.77 ± 0.5 eu.

Transition Data

Transition temperatures and heats were obtained from differential heating and cooling curves both at atmospheric and higher pressures by R. W. Goranson and F. C. Kracek (7). Existence of three phases is confirmed by the earlier birefringence studies of H. E. Boeke (8).

R. Riccardi and C. Sinistri (10) found only one transition at 864°K with ΔHt° = 8.23 kcal/mol by differential thermal analysis. This heat is apparently the sum of the two adopted heats of transition.

Melting Data

The adopted melting data were measured by the differential heating and cooling curve method by Goranson and Kracek (7). R. Riccardi and C. Sinistri (10) found the melting point at 971°K with ΔHm° = 7.52 kcal/mol by differential thermal analysis.

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Sodium Disilicate ($Na_2Si_2O_5$)

(Crystal) GFW = 182.1586

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 6.317	- 586.870	- 586.870	INFINITE
100	15.991	10.052	66.782	- 5.673	- 588.729	- 578.064	1263.357
200	29.656	25.807	42.412	- 3.321	- 589.853	- 566.900	619.479
298	37.520	39.210	39.210	.000	- 590.360	- 555.509	407.199
300	37.642	39.443	39.211	.070	- 590.365	- 555.292	404.530
400	43.834	51.149	40.765	4.154	- 591.760	- 543.474	296.940
500	48.577	61.467	43.894	8.786	- 591.525	- 531.418	232.283
600	52.002	70.643	47.602	13.825	- 590.952	- 519.447	189.208
700	54.455	78.854	51.491	19.154	- 590.150	- 507.591	158.477
800	56.205	86.246	55.381	24.692	- 589.197	- 495.864	135.464
900	57.439	92.942	59.189	30.378	- 588.150	- 484.256	117.593
1000	70.000	99.537	62.884	36.653	- 586.571	- 472.779	103.326
1100	70.000	106.208	66.524	43.653	- 584.330	- 461.514	91.694
1200	70.000	112.299	70.089	50.653	- 628.620	- 449.531	81.871
1300	70.000	117.902	73.554	57.653	- 626.067	- 434.710	73.081
1400	70.000	123.090	76.909	64.653	- 623.551	- 420.086	65.578
1500	70.000	127.919	80.151	71.653	- 621.072	- 405.638	59.101
1600	70.000	132.437	83.279	78.653	- 618.629	- 391.355	53.457
1700	70.000	136.681	86.297	85.653	- 640.202	- 377.011	48.468
1800	70.000	140.682	89.208	92.653	- 637.718	- 361.600	43.904
1900	70.000	144.466	92.018	99.653	- 635.250	- 346.328	39.837
2000	70.000	148.057	94.731	106.653	- 632.796	- 331.188	36.190

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

$S^\circ_{298.15}$ = 39.21 ± 1.0 gibbs/mol
Tt(B → Aβ) = 951°K
Tt(Aβ → Aα) = 980°K
Tm = 1147°K

ΔHf°_0 = -586.87 ± 1.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -590.36 ± 1.0 kcal/mol
ΔHt° = 0.1 kcal/mol
ΔHt° = 0.15 kcal/mol
ΔHm° = 8.5 kcal/mol

Heat of Formation

The heats of solution of NaCl(c), Na_2SO_4(c), SiO_2(quartz), $Na_2Si_2O_5$(c), HCl(aq) and H_2SO_4(aq), in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (1). The author derived two values of ΔHsoln of Na_2O(c) from those of NaCl(c), Na_2SO_4(c), HCl(aq) and H_2SO_4(aq), presumably employing auxiliary data from (2). We recalculate ΔHsoln of Na_2O(c) in the calorimetric solution as -87.50 (chlorine scheme,originally -87.66) and -88.74 kcal/mol (sulfate scheme, originally -89.19), using recent ΔHf°_{298} values (16, 17, 18) for NaCl(c), HCl(aq), H_2SO_4(aq), Na_2SO_4(c), and Na_2O(c). The corresponding enthalpy changes, ΔHr°_{298}, for the reaction Na_2O(c) + $2SiO_2$(quartz) = $Na_2Si_2O_5$(c) are derived as -54.65 and -55.89 kcal/mol. Adopting the weighted average ΔHr°_{298} = -55.06 kcal/mol with ΔHf°_{298}(Na_2O, c) = -99.9 kcal/mol and ΔHf°_{298}(SiO_2, quartz) = -217.7 kcal/mol, we obtain ΔHf°_{298} = -590.36 kcal/mol for $Na_2Si_2O_5$(c). This ΔHf°_{298}($Na_2Si_2O_5$, c) value is independent of future changes in ΔHf°_{298} of Na_2O(c), but the values of ΔHsoln and ΔHr° are not independent.

Stevens et al. (3) measured the heats of solution of $Na_2Si_2O_5$(c), Na_2O(c) and SiO_2(quartz) in HF(aq) at 25°C. Based on the reported results, the enthalpy change for the reaction Na_2O(c) + $2SiO_2$(quartz) = $Na_2Si_2O_5$(c) is calculated as -53.25 ± 0.32 kcal/mol, yielding ΔHf°_{298}($Na_2Si_2O_5$, c) = -588.55 kcal/mol.

Hummel (4) determined the heats of solution of $Na_2Si_2O_5$(c), SiO_2(quartz) and Na_2CO_3(c) in 39 percent HF at 26.5°C. From the data reported we derive the enthalpy change to be 20.88 kcal/mol for the reaction Na_2CO_3(c) + $2SiO_2$(quartz) = $Na_2Si_2O_5$(c) + CO_2(g). Employing ΔHf°_{298} = -270.26, -217.7 and -94.05 kcal/mol for Na_2CO_3(c), SiO_2(quartz) and CO_2(g), respectively, we obtain ΔHf°_{298} = -590.73 kcal/mol for $Na_2Si_2O_5$(c) which is in good agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, 54.3 - 294.7°K, have been measured by Kelley (5) and the high temperature enthalpies, 376.8 - 1100.2°K, by Naylor (6). The derived high temperature heat capacities are joined smoothly with the low temperature ones at 298°K. An approximate Cp of 70 gibbs/mol is derived from the enthalpies above 980°K; this value is extrapolated to 2000°K. The value of S°_{298} is calculated from the adopted low temperature heat capacities based on S°_{50} = 2.945 eu. The entropy extrapolation derives from the Debye-Einstein extrapolation of Kelley (5) which yields a Cp curve with an extra inflection in the region from 15 to 50°K. A more normal extrapolation would lead to a value of S°_{50} which is lower by 0.5 eu.

Transition Data

There are six slowly inverting polymorphous phases (1, 7-9), namely A, B, C, D, E and F, of which only the first two phases are stable. Two rapid transitions have been reported at 951 and 980°K (1, 10). Phase A, which has two subphases, Aα and Aβ, is stable above 951°K. The stable phase below 951°K is known as phase B, previously called β-$Na_2Si_2O_5$. The two values of ΔHt° are derived from the enthalpy data of Naylor (6) using the adopted Cp values. Three more rapid transitions have been reported at 822, 846 and 866°K (1, 10) in E, previously called γ-$Na_2Si_2O_5$. A recent examination of these transitions was reported by Willgallis and Range (10).

Melting Data

Tm is obtained from Morey (11). The selected value of ΔHm° is based on the following ΔHm° values derived from four different kinds of measurements.

Investigator	ΔHm°, kcal/mol* at 298°K	ΔHm°, kcal/mol* at 1147°K	Method**	Reference
Kelley (1936)	(7.51)	8.46	I	12
Kracek (1953)	5.25	(6.20)	II	1
Kröger-Janetzko (1956)	8.81	(9.76)	III	13
Kröger-Kreitlow (1956)	8.83	(9.78)	II	14
Schwiete-Ziegler (1958)	(7.50)	8.45	IV	15
Hummel-Schwiete (1959)	8.09	(9.04)	II	4

*The numbers in parentheses are derived from the measured ones at the other listed temperatures.

**I = phase diagram; II = solution calorimetry; III = high temperature reaction calorimetry; and IV = dynamic-differential calorimetric method.

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Sodium Disilicate ($Na_2Si_2O_5$)

(Liquid) GFW = 182.1586

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	37.520	45.101	45.101	.000	-582.811	-549.716	402.953
300	37.642	45.334	45.102	.070	-582.816	-549.510	400.318
400	43.834	57.040	46.656	4.154	-584.211	-538.281	294.103
500	48.577	67.358	49.785	8.786	-583.976	-526.815	230.270
600	52.002	76.527	53.493	13.820	-583.408	-515.432	187.746
700	58.750	84.972	57.390	19.308	-582.447	-504.172	157.409
800	65.050	93.296	61.360	25.548	-580.792	-493.098	134.708
900	66.020	101.053	65.347	32.135	-578.844	-482.249	117.106
1000	64.000	107.927	69.269	38.658	-577.017	-471.616	103.071
1100	62.430	113.935	73.062	44.960	-575.474	-461.157	91.623
1200	62.430	119.367	76.698	51.203	-620.521	-449.913	81.940
1300	62.430	124.364	80.175	57.446	-618.724	-435.768	73.259
1400	62.430	128.991	83.498	63.689	-616.965	-421.762	65.840
1500	62.430	133.298	86.677	69.932	-615.244	-407.878	59.428
1600	62.430	137.327	89.718	76.175	-613.557	-394.108	53.833
1700	62.430	141.112	92.631	82.418	-635.887	-380.230	48.882
1800	62.430	144.680	95.424	88.661	-634.161	-365.240	44.346
1900	62.430	148.056	98.106	94.904	-632.449	-350.347	40.299
2000	62.430	151.258	100.684	101.147	-630.752	-335.546	36.667
2100	62.430	154.304	103.166	107.390	-629.066	-320.828	33.389
2200	62.430	157.208	105.557	113.633	-627.399	-306.190	30.417
2300	62.430	159.983	107.863	119.876	-625.742	-291.630	27.711
2400	62.430	162.640	110.091	126.119	-624.102	-277.130	25.236
2500	62.430	165.189	112.244	132.362	-622.477	-262.716	22.967

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

SODIUM DISILICATE ($Na_2Si_2O_5$) (LIQUID) GFW = 182.1586

$S°_{298.15}$ = 45.101 gibbs/mol

$\Delta Hf°_{298.15}$ = -582.811 kcal/mol

Tm = 1147°K

ΔHm° = 8.5 kcal/mol

Heat of Formation

The $\Delta Hf°_{298}(\ell)$ is obtained from $\Delta Hf°_{298}(c)$ by adding ΔHm° and the difference between $H°_{1147} - H°_{298}$ for crystal and liquid.

The heats of solution of NaCl(c), Na_2SO_4(c), HCl(aq), H_2SO_4(aq), SiO_2(quartz) and $Na_2Si_2O_5$(gl) in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (1). Following the same procedure as described in the $Na_2Si_2O_5$(c) table, we derive the enthalpy changes, $\Delta Hr°_{298}$, for the reaction $Na_2O(c) + 2SiO_2(quartz) = Na_2Si_2O_5(gl)$ as -49.40 and -50.64 kcal/mol using the heats of solution of Na_2O(c) as -87.50 (chloride scheme) and -88.74 kcal/mol (sulfate scheme), respectively. Adopting the weighted average $\Delta Hr°_{298}$ = -49.81 kcal/mol with $\Delta Hf°_{298}(Na_2O, c)$ = -99.9 kcal/mol and $\Delta Hf°_{298}(SiO_2, quartz)$ = -217.7 kcal/mol, we obtain $\Delta Hf°_{298}$ = -585.113 kcal/mol for $Na_2Si_2O_5$(gl).

Using high temperature reaction calorimetry, Kröger (2) determined the enthalpy changes as 25.28 ± 0.22 and -18.58 ± 0.36 kcal/mol for the reactions $Na_2CO_3(c) + 2SiO_2(quartz) = Na_2Si_2O_5(gl) + CO_2(g)$ and $2NaOH(c) + 2SiO_2(quartz) = Na_2Si_2O_5(gl) + H_2O(\ell)$, respectively. From the given results, we calculate the corresponding values of $\Delta Hf°_{298}(Na_2Si_2O_5, gl)$ to be -586.32 and -589.46 kcal/mol, using $\Delta Hf°_{298}$ = -270.26, -217.70, -94.05, -101.90 and -68.32 kcal/mol for Na_2CO_3(c), SiO_2(quartz), CO_2(g), NaOH(c) and $H_2O(\ell)$, respectively. These two $\Delta Hf°_{298}[Na_2Si_2O_5, (\ell)]$ values, as well as the value -585.113 kcal/mol based on Kracek's data, are not adopted, because incorporating these $\Delta Hf°_{298}$(gl) values with the value of $\Delta Hf°_{298}$(c), gives values of the heat of melting at 298°K which are too low in comparison with the other values (see the $Na_2Si_2O_5$(c) table).

Hummel (3) measured the heats of solution of Na_2CO_3(c), SiO_2(quartz) and $Na_2Si_2O_5$(gl) in 39 percent hydrofluoric acid at 26.5°C, as -244.1, -564.5 and -673.7 cal/g, respectively. Based on these results, we derive the enthalpy change for the reaction $Na_2CO_3(c) + 2SiO_2(quartz) = Na_2Si_2O_5(gl) + CO_2(g)$ to be 29.01 kcal/mol, yielding $\Delta Hf°_{298}(Na_2Si_2O_5, gl)$ = -582.6 kcal/mol which is in good agreement with the adopted value.

Heat Capacity and Entropy

Using drop calorimetry, Naylor (4) has measured the enthalpies of $Na_2Si_2O_5$(gl), 445.5 - 1120.7°K, and $Na_2Si_2O_5(\ell)$, 1173.2 - 1744°K. Based on the liquid enthalpy data, we evaluate the heat capacity of $Na_2Si_2O_5(\ell)$ to be 62.43 gibbs/mol. The Cp values below 1147°K are derived from the enthalpies measured at 445.5 - 1120.7°K by Naylor (4). Below 600°K, Cp is identical with that of the crystal. The adopted curve rises rapidly to a maximum in the glass transition region, 650-950°K, then smoothly approaches the value of the real liquid near Tm. The heat capacity of $Na_2Si_2O_5(\ell)$ is assumed to be constant in the temperature range 1147 to 2500°K.

$S°_{298}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See $Na_2Si_2O_5$(c) table for details.

References

1. F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953).
2. C. Kröger and W. Janetzko, Z. Anorg. Allgem. Chem. 284, 84 (1956).
3. C. Hummel and H. E. Schwiete, Glastech. Ber. 32, 327 (1959).
4. B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945).

Disodium Sulfide (Na_2S)

(Solid) Mol. Wt. = 78.048 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	18.990	23.400	23.400	.000	- 89.000	- 86.368	63.307
300	19.000	23.517	23.400	.035	- 88.999	- 86.351	62.903
400	19.300	29.025	24.149	1.950	- 90.871	- 85.342	46.627
500	19.600	33.363	25.573	3.895	- 91.346	- 83.903	36.672
600	19.900	36.964	27.180	5.870	- 91.670	- 82.381	30.006
700	20.200	40.054	28.803	7.875	- 91.877	- 80.793	25.224
800	20.500	42.771	30.383	9.910	- 105.057	- 80.468	21.982
900	20.800	45.202	31.897	11.975	- 104.810	- 77.408	18.796
1000	21.100	47.409	33.339	14.070	- 104.536	- 74.377	16.254
1100	21.400	49.435	34.712	16.195	- 104.246	- 71.380	14.181
1200	21.700	51.309	36.018	18.350	- 150.415	- 67.489	12.291
1300	22.000	53.058	37.262	20.535	- 149.669	- 60.607	10.189
1400	22.300	54.700	38.449	22.750	- 148.895	- 53.787	8.396
1500	22.600	56.248	39.585	24.995	- 148.092	- 47.022	6.851
1600	22.900	57.716	40.673	27.270	- 147.259	- 40.309	5.506
1700	23.200	59.114	41.717	29.575	- 146.395	- 33.651	4.326
1800	23.500	60.448	42.721	31.910	- 145.504	- 27.045	3.284
1900	23.800	61.727	43.687	34.275	- 144.583	- 20.486	2.356
2000	24.100	62.955	44.620	36.670	- 143.635	- 13.982	1.528

December 31, 1960.

Na_2S

DISODIUM SULFIDE (Na_2S) (Solid)

Mol. Wt. = 78.048

$\Delta H_f^\circ{}_{298.15}$ = -89 kcal. mole^{-1}

$S^\circ_{298.15}$ = 23.4 cal. deg.$^{-1}$ mole^{-1}

T_m = 1223°K.

ΔH_m = 16 kcal. mole^{-1}

$\Delta H_f^\circ{}_{298.15}$, T_m, and ΔH_m from National Bureau of Standards Circular 500 (1952). $S^\circ_{298.15}$ calculated from $\Delta F_f^\circ{}_{298.15}$, as reported by N. A. Landiya, Zhur. Fiz. Khim. 24, 257 (1950). C_p estimated.

Na_2S

Disodium Sulfide (Na_2S)

(Liquid) Mol. Wt. = 78.048

INTERIM TABLE

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0							
100							
200							
298	17.618	24.136	24.136	.000	-87.870	-85.458	62.639
300	17.666	24.245	24.136	.033	-87.871	-85.441	62.241
400	19.445	29.603	24.855	1.899	-89.792	-84.494	46.163
500	20.341	34.048	26.262	3.893	-90.218	-83.117	36.329
600	20.848	37.806	27.881	5.955	-90.455	-81.672	29.747
700	21.162	41.045	29.536	8.056	-90.566	-80.176	25.031
800	21.368	43.885	31.155	10.183	-103.654	-79.956	21.842
900	21.511	46.410	32.713	12.328	-103.327	-77.012	18.700
1000	21.614	48.682	34.198	14.484	-102.992	-74.106	16.195
1100	21.690	50.746	35.610	16.650	-102.661	-71.238	14.153
1200	21.748	52.636	36.951	18.822	-148.813	-67.480	12.289
1300	21.794	54.379	38.226	20.999	-148.075	-60.730	10.209
1400	21.830	55.995	39.438	23.180	-147.335	-54.040	8.436
1500	21.860	57.502	40.592	25.365	-146.592	-47.404	6.906
1600	21.884	58.914	41.694	27.552	-145.847	-40.813	5.575
1700	21.904	60.241	42.746	29.741	-145.099	-34.271	4.406
1800	21.920	61.494	43.753	31.933	-144.351	-27.774	3.372
1900	21.934	62.679	44.718	34.125	-143.603	-21.315	2.452
2000	21.947	63.804	45.645	36.319	-142.856	-14.901	1.628
2100	21.956	64.876	46.535	38.515	-142.106	-8.524	.887
2200	21.965	65.897	47.392	40.711	-141.358	-2.178	.216
2300	21.973	66.874	48.218	42.908	-140.610	4.129	-.392
2400	21.980	67.809	49.015	45.105	-139.864	10.410	-.948
2500	21.987	68.706	49.785	47.304	-139.116	16.653	-1.456
2600	21.993	69.569	50.529	49.503	-138.373	22.871	-1.922
2700	21.998	70.399	51.250	51.702	-137.632	29.056	-2.352
2800	22.002	71.199	51.948	53.902	-136.895	35.213	-2.748
2900	22.006	71.971	52.625	56.103	-136.159	41.352	-3.116
3000	22.009	72.717	53.283	58.303	-135.431	47.461	-3.457

December 31, 1960.

DISODIUM SULFIDE (Na_2S) (Liquid)

Mol. Wt. = 78.048

ΔH_f° 298.15 = [-87.870] kcal. mole^{-1}

$S^\circ_{298.15}$ = [24.136] cal. deg.$^{-1}$ mole^{-1}

T_m = 1223°K.

ΔH_m = 16 kcal. mole^{-1}

T_m and ΔH_m from National Bureau of Standards Circular 500 (1952).

Other data estimated.

Oxygen, Monatomic (O)

(Ideal Gas) At. Wt. = 16.000

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- 1.608	58.989	58.989	INFINITE
100	5.666	32.466	43.266	- 1.080	59.160	57.989	- 126.730
200	5.434	36.340	38.953	- .523	59.377	56.733	- 61.992
298	5.237	38.468	38.468	.000	59.559	55.395	- 40.604
300	5.235	38.501	38.468	.010	59.562	55.369	- 40.334
400	5.135	39.991	38.672	.528	59.725	53.946	- 29.473
500	5.081	41.131	39.055	1.038	59.870	52.485	- 22.980
600	5.049	42.054	39.480	1.544	59.998	50.995	- 18.574
700	5.029	42.831	39.905	2.048	60.113	49.486	- 15.449
800	5.015	43.501	40.313	2.550	60.216	47.960	- 13.101
900	5.006	44.092	40.701	3.052	60.311	46.422	- 11.272
1000	4.999	44.619	41.067	3.552	60.397	44.875	- 9.807
1100	4.994	45.095	41.412	4.051	60.477	43.318	- 8.606
1200	4.990	45.529	41.737	4.551	60.553	41.755	- 7.604
1300	4.987	45.928	42.044	5.049	60.623	40.186	- 6.755
1400	4.984	46.298	42.335	5.548	60.689	38.611	- 6.027
1500	4.982	46.642	42.611	6.046	60.752	37.032	- 5.395
1600	4.981	46.963	42.873	6.544	60.812	35.448	- 4.842
1700	4.979	47.265	43.123	7.042	60.869	33.862	- 4.353
1800	4.979	47.550	43.361	7.540	60.922	32.271	- 3.918
1900	4.978	47.819	43.588	8.038	60.973	30.678	- 3.529
2000	4.978	48.074	43.806	8.536	61.020	29.082	- 3.178
2100	4.978	48.317	44.015	9.034	61.066	27.484	- 2.860
2200	4.979	48.549	44.216	9.532	61.108	25.884	- 2.571
2300	4.980	48.770	44.409	10.029	61.147	24.282	- 2.307
2400	4.981	48.982	44.596	10.527	61.184	22.679	- 2.065
2500	4.984	49.185	44.775	11.026	61.219	21.073	- 1.842
2600	4.986	49.381	44.948	11.524	61.251	19.467	- 1.636
2700	4.990	49.569	45.116	12.023	61.281	17.859	- 1.446
2800	4.994	49.751	45.278	12.522	61.309	16.251	- 1.268
2900	4.999	49.926	45.436	13.022	61.334	14.642	- 1.103
3000	5.004	50.096	45.588	13.522	61.358	13.031	- .949
3100	5.010	50.260	45.736	14.023	61.380	11.420	- .805
3200	5.017	50.419	45.880	14.524	61.401	9.807	- .670
3300	5.025	50.573	46.020	15.026	61.420	8.194	- .543
3400	5.033	50.724	46.156	15.529	61.437	6.581	- .423
3500	5.041	50.870	46.289	16.033	61.454	4.967	- .310
3600	5.050	51.012	46.418	16.537	61.469	3.354	- .204
3700	5.060	51.150	46.544	17.043	61.484	1.739	- .103
3800	5.070	51.285	46.667	17.549	61.498	.125	- .007
3900	5.081	51.417	46.787	18.057	61.511	- 1.492	.084
4000	5.091	51.546	46.904	18.565	61.524	- 3.107	.170
4100	5.103	51.672	47.019	19.075	61.536	- 4.723	.252
4200	5.114	51.795	47.131	19.586	61.549	- 6.339	.330
4300	5.126	51.915	47.241	20.098	61.561	- 7.955	.404
4400	5.138	52.033	47.349	20.611	61.572	- 9.573	.475
4500	5.150	52.149	47.454	21.126	61.584	- 11.189	.543
4600	5.162	52.262	47.558	21.641	61.596	- 12.805	.608
4700	5.174	52.373	47.659	22.158	61.608	- 14.423	.671
4800	5.186	52.482	47.758	22.676	61.620	- 16.041	.730
4900	5.198	52.589	47.856	23.195	61.633	- 17.661	.788
5000	5.210	52.695	47.951	23.715	61.646	- 19.279	.843
5100	5.222	52.798	48.045	24.237	61.659	- 20.896	.895
5200	5.234	52.899	48.138	24.760	61.673	- 22.517	.946
5300	5.246	52.999	48.229	25.284	61.687	- 24.134	.995
5400	5.258	53.097	48.318	25.809	61.702	- 25.755	1.042
5500	5.269	53.194	48.406	26.335	61.718	- 27.373	1.088
5600	5.280	53.289	48.492	26.863	61.733	- 28.995	1.132
5700	5.292	53.383	48.577	27.392	61.750	- 30.616	1.174
5800	5.302	53.475	48.661	27.921	61.767	- 32.234	1.215
5900	5.313	53.565	48.743	28.452	61.785	- 33.856	1.254
6000	5.323	53.655	48.824	28.984	61.803	- 35.476	1.292

June 30, 1962

OXYGEN, MONATOMIC (O) (IDEAL GAS) AT. WT. = 16.000

ΔH°_{f0} = 58.989 kcal. mole^{-1}

Ground State Configuration $^3P_2$

ΔH°_f 298.15 = 59.559 ± 0.03 kcal. mole^{-1}

$S^\circ_{298.15}$ = 38.47 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.0	5	73,767.8	5	95,476.0	5
158.5	3	76,794.7	3	96,226.0	3
226.5	1	86,628.0	15	97,420.0	30
15,867.7	5	88,630.0	9	97,488.0	15
33,792.4	1			105,000.0	400

Heat of Formation.

P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954), observed 21 bands in the transition $X^3\Sigma^-_g \longleftrightarrow B^3\Sigma^-_u$. The Birge-Sponer extrapolation to the dissociation products $^3P_2 + {}^1D_2$ was corrected to the zero levels, $^3P_2 + {}^3P_2$, to give the dissociation energy 41260 ± 15 cm.$^{-1}$ This is in agreement with the extrapolation of the band heads of the $X^3\Sigma^-_g \longleftrightarrow A^3\Sigma^+_u$ transition which goes to the normal products. The extrapolation of the B level is very small, the lowest $\Delta G_{1/2}$ is 34 cm.$^{-1}$

Heat Capacity and Entropy.

The electronic levels from C. E. Moore, Nat. Bur. Standards, Circ. 467, (1949), were averaged above 80,000 cm.$^{-1}$

Oxygen Uninegative Ion (O^-)
(Ideal Gas) Mol. Wt. = 15.99995

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	5.149	37.712	37.712	.000	24.300	21.849	- 16.015
300	5.147	37.743	37.712	.010	24.294	21.834	- 15.905
400	5.081	39.214	37.913	.521	23.953	21.064	- 11.508
500	5.045	40.344	38.290	1.027	23.596	20.383	- 8.909
600	5.024	41.261	38.711	1.530	23.225	19.776	- 7.203
700	5.010	42.035	39.132	2.032	22.842	19.231	- 6.004
800	5.001	42.703	39.538	2.532	22.446	18.742	- 5.120
900	4.994	43.292	39.923	3.032	22.042	18.302	- 4.444
1000	4.990	43.818	40.286	3.531	21.631	17.910	- 3.914
1100	4.986	44.293	40.629	4.030	21.213	17.557	- 3.488
1200	4.983	44.727	40.953	4.528	20.790	17.243	- 3.140
1300	4.981	45.125	41.259	5.027	20.364	16.966	- 2.852
1400	4.979	45.495	41.548	5.525	19.933	16.719	- 2.610
1500	4.978	45.838	41.823	6.022	19.498	16.506	- 2.405
1600	4.977	46.159	42.084	6.520	19.061	16.321	- 2.229
1700	4.976	46.461	42.333	7.018	18.620	16.163	- 2.078
1800	4.975	46.745	42.570	7.515	18.177	16.033	- 1.947
1900	4.974	47.014	42.797	8.013	17.730	15.924	- 1.832
2000	4.974	47.269	43.014	8.510	17.281	15.841	- 1.731
2100	4.973	47.512	43.223	9.008	16.829	15.781	- 1.642
2200	4.973	47.743	43.423	9.505	16.373	15.741	- 1.564
2300	4.972	47.965	43.616	10.002	15.916	15.722	- 1.494
2400	4.972	48.176	43.801	10.499	15.455	15.724	- 1.432
2500	4.972	48.379	43.980	10.997	14.992	15.744	- 1.376
2600	4.972	48.574	44.153	11.494	14.526	15.784	- 1.327
2700	4.971	48.762	44.321	11.991	14.057	15.839	- 1.282
2800	4.971	48.942	44.482	12.488	13.585	15.916	- 1.242
2900	4.971	49.117	44.639	12.985	13.113	16.007	- 1.206
3000	4.971	49.285	44.791	13.482	12.636	16.118	- 1.174
3100	4.971	49.448	44.939	13.979	12.158	16.242	- 1.145
3200	4.970	49.606	45.082	14.476	11.677	16.378	- 1.118
3300	4.970	49.759	45.222	14.973	11.194	16.532	- 1.095
3400	4.970	49.908	45.357	15.470	10.709	16.698	- 1.073
3500	4.970	50.052	45.490	15.967	10.222	16.881	- 1.054
3600	4.970	50.192	45.618	16.464	9.733	17.079	- 1.037
3700	4.970	50.328	45.744	16.961	9.242	17.293	- 1.021
3800	4.970	50.460	45.866	17.458	8.750	17.518	- 1.007
3900	4.970	50.589	45.986	17.955	8.256	17.754	- .995
4000	4.970	50.715	46.102	18.452	7.761	18.005	- .984
4100	4.970	50.838	46.216	18.949	7.263	18.268	- .974
4200	4.969	50.958	46.328	19.446	6.765	18.537	- .965
4300	4.969	51.075	46.437	19.943	6.265	18.825	- .957
4400	4.969	51.189	46.543	20.440	5.763	19.121	- .950
4500	4.969	51.301	46.648	20.937	5.261	19.432	- .944
4600	4.969	51.410	46.750	21.434	4.758	19.754	- .938
4700	4.969	51.517	46.851	21.931	4.253	20.085	- .934
4800	4.969	51.621	46.949	22.428	3.747	20.432	- .930
4900	4.969	51.724	47.045	22.925	3.241	20.778	- .927
5000	4.969	51.824	47.140	23.421	2.734	21.141	- .924
5100	4.969	51.923	47.233	23.918	2.225	21.516	- .922
5200	4.969	52.019	47.324	24.415	1.716	21.898	- .920
5300	4.969	52.114	47.413	24.912	1.207	22.293	- .919
5400	4.969	52.207	47.501	25.409	.696	22.693	- .918
5500	4.969	52.298	47.588	25.906	.185	23.107	- .918
5600	4.969	52.387	47.672	26.403	- .326	23.533	- .918
5700	4.969	52.475	47.756	26.900	- .838	23.957	- .919
5800	4.969	52.562	47.838	27.397	- 1.350	24.399	- .919
5900	4.969	52.647	47.919	27.894	- 1.863	24.846	- .920
6000	4.969	52.730	47.998	28.390	- 2.377	25.304	- .922

June 30, 1965

OXYGEN UNINEGATIVE ION (O^-) (IDEAL GAS) MOL. WT. = 15.99995

Ground State Configuration $^2P^\circ_{3/2}$

$S^\circ_{298.15}$ = 37.712 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 25.2 ± .5 kcal/mole

$\Delta H^\circ_{f\ 298.15}$ = 24.3 ± .5 kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_1$, cm.$^{-1}$	g_1
0.0	4
[160.0]	2

Heat of Formation.

The heat of formation was calculated from the equation: $O(g) + e^- \rightarrow O^-(g)$ with the JANAF auxiliary value for O(g); using the measured electron affinity = 1.465 e.v. (33.783 kcal/mole) obtained from L. M. Branscomb, D. S. Burch, S. J. Smith and S. Geltman, Phys. Rev. 111, 504 (1958). Other calculated values for the electron affinity are: 1.22 e.v. E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 1.16 e.v. E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. 133, A1274 (1964); and 1.47 e.v. B. Edlén, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were estimated by assuming that the extra electron would produce an electronic structure similar to the next higher atomic numbered element, in this case F(I). An analogy was then made between O^- and F(I) with O(I) and F(II), and O(II) and F(III) in order to estimate the height of the first level above the ground state. The data for F(I), O(I), F(II), O(II) and F(III) were obtained from C. E. Moore, "Atomic Energy Levels", Vol I, Circular of the National Bureau of Standards 467, June 15, 1949. It is possible that the entropy below 3000°K. could be in error by 0.5 e.v. due to the estimation of the low lying electronic level. The electronic levels above 1 X 10^5 cm.$^{-1}$ were omitted because their contribution is negligible below 6000°K. The $H^\circ-H^\circ_{298}$ value at 0°K. is -1.567 kcal/mole.

Phosphorus Monoxide (PO)

(Ideal Gas) Mol. Wt. = 46.975 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.245	-1.801	-1.801	INFINITE
100	7.722	44.781	60.037	-1.526	-1.519	-3.778	8.256
200	7.693	50.177	53.914	-.747	-1.407	-6.096	6.661
298	7.587	53.219	53.219	.000	-1.455	-8.391	6.151
300	7.588	53.266	53.219	.014	-1.456	-8.434	6.144
400	7.724	55.464	53.518	.778	-1.580	-10.742	5.869
500	7.931	57.210	54.088	1.561	-1.734	-13.016	5.689
600	8.126	58.673	54.733	2.364	-1.910	-15.257	5.557
700	8.287	59.938	55.388	3.185	-2.110	-17.465	5.453
800	8.415	61.054	56.028	4.020	-22.832	-25.029	6.837
900	8.516	62.051	56.643	4.867	-22.829	-25.305	6.145
1000	8.597	62.953	57.230	5.723	-22.827	-25.580	5.590
1100	8.662	63.775	57.788	6.586	-22.823	-25.853	5.136
1200	8.715	64.531	58.319	7.455	-22.822	-26.130	4.759
1300	8.759	65.230	58.824	8.329	-22.820	-26.406	4.439
1400	8.796	65.881	59.305	9.206	-22.820	-26.681	4.165
1500	8.827	66.469	59.764	10.088	-22.820	-26.957	3.927
1600	8.854	67.059	60.202	10.972	-22.822	-27.233	3.720
1700	8.878	67.597	60.621	11.858	-22.824	-27.509	3.536
1800	8.899	68.105	61.023	12.747	-22.829	-27.784	3.373
1900	8.917	68.587	61.409	13.638	-22.834	-28.060	3.227
2000	8.934	69.044	61.779	14.531	-22.841	-28.334	3.096
2100	8.949	69.481	62.136	15.425	-22.850	-28.609	2.977
2200	8.963	69.897	62.479	16.320	-22.861	-28.884	2.869
2300	8.976	70.296	62.810	17.217	-22.874	-29.156	2.770
2400	8.988	70.678	63.130	18.116	-22.887	-29.429	2.680
2500	8.999	71.045	63.439	19.015	-22.904	-29.700	2.596
2600	9.010	71.399	63.739	19.915	-22.923	-29.973	2.519
2700	9.020	71.739	64.029	20.817	-22.942	-30.243	2.448
2800	9.029	72.067	64.310	21.719	-22.964	-30.512	2.381
2900	9.038	72.384	64.583	22.623	-22.989	-30.783	2.320
3000	9.047	72.691	64.848	23.527	-23.015	-31.051	2.262
3100	9.056	72.987	65.106	24.432	-23.042	-31.318	2.208
3200	9.064	73.275	65.357	25.338	-23.072	-31.586	2.157
3300	9.071	73.554	65.601	26.245	-23.103	-31.850	2.109
3400	9.079	73.825	65.839	27.152	-23.136	-32.115	2.064
3500	9.086	74.088	66.071	28.061	-23.170	-32.378	2.022
3600	9.094	74.344	66.297	28.970	-23.206	-32.643	1.982
3700	9.101	74.594	66.518	29.879	-23.243	-32.904	1.943
3800	9.108	74.836	66.734	30.790	-23.281	-33.163	1.907
3900	9.115	75.073	66.945	31.701	-21.322	-33.425	1.873
4000	9.121	75.304	67.151	32.613	-23.363	-33.682	1.840
4100	9.128	75.529	67.352	33.525	-23.405	-33.941	1.809
4200	9.134	75.749	67.550	34.438	-23.448	-34.197	1.779
4300	9.141	75.964	67.743	35.352	-23.492	-34.452	1.751
4400	9.147	76.174	67.932	36.266	-23.538	-34.702	1.724
4500	9.153	76.380	68.118	37.181	-23.581	-34.958	1.698
4600	9.159	76.581	68.299	38.097	-23.624	-35.211	1.673
4700	9.165	76.778	68.478	39.013	-23.671	-35.461	1.649
4800	9.172	76.971	68.653	39.930	-23.720	-35.715	1.626
4900	9.178	77.161	68.824	40.848	-23.768	-35.963	1.604
5000	9.183	77.346	68.993	41.766	-23.818	-36.211	1.583
5100	9.189	77.528	69.159	42.684	-23.867	-36.459	1.562
5200	9.195	77.706	69.321	43.603	-23.918	-36.702	1.542
5300	9.201	77.882	69.481	44.523	-23.969	-36.952	1.524
5400	9.207	78.054	69.638	45.444	-24.020	-37.192	1.505
5500	9.213	78.223	69.793	46.365	-24.071	-37.440	1.488
5600	9.218	78.389	69.945	47.286	-24.123	-37.682	1.471
5700	9.224	78.552	70.094	48.208	-24.175	-37.923	1.454
5800	9.230	78.712	70.242	49.131	-24.227	-38.161	1.438
5900	9.235	78.870	70.386	50.054	-24.279	-38.399	1.422
6000	9.241	79.026	70.529	50.978	-24.331	-38.645	1.408

December 31, 1960.

Phosphorus Monoxide (PO) (Ideal Gas)

Mol. Wt. = 46.975

$\Delta H^\circ_{f\ 298.15} = -1.46 \pm 2$ kcal. mole^{-1}

$S^\circ_{298.15} = 53.22$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^2\Pi$

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i
0	2
222.6	2

$\omega_e = 1233.42$ cm.$^{-1}$

$\omega_e x_e = 6.57$ cm.$^{-1}$

$B_e = 0.734$ cm.$^{-1}$

$\alpha_e = 0.0055$ cm.$^{-1}$

$\sigma = 1$

$r_e = 1.473$ Å

Heat of formation based upon a dissociation energy of 49,000 cm.$^{-1}$, which is the value of two predissociations observed by K. Dressler, Helv. Phys. Acta 29, 563 (1955).

Heat Capacities and Entropies. Molecular and spectroscopic constants based upon measurements of K. Dressler, loc. cit., K. S. Rao, Can. J. Phys. 36, 1526 (1958), and those of N. L. Singh, Can. J. Phys. 37, 136 (1959).

Lead Monoxide, Red (PbO)

(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-2.177	-51.903	-51.903	INFINITE
100	6.422	5.919	24.279	-1.836	-52.341	-49.977	109.218
200	9.674	11.479	16.554	-1.015	-52.463	-47.541	51.948
298	10.943	15.592	15.592	.000	-52.407	-45.134	33.082
300	10.960	15.660	15.592	.020	-52.405	-45.089	32.846
400	11.760	18.928	16.032	1.158	-52.275	-42.668	23.312
500	12.420	21.626	16.889	2.368	-52.103	-40.286	17.608
600	12.970	23.940	17.876	3.639	-51.900	-37.941	13.819
700	13.400	25.974	18.890	4.958	-52.840	-35.441	11.065
800	13.800	27.789	19.891	6.318	-52.600	-32.972	9.007
900	14.200	29.438	20.862	7.718	-52.321	-30.535	7.415
1000	14.600	30.954	21.796	9.158	-52.000	-28.131	6.148
1100	15.000	32.365	22.693	10.638	-51.639	-25.761	5.118
1200	15.400	33.687	23.555	12.158	-51.234	-23.425	4.266
1300	15.800	34.935	24.383	13.718	-50.788	-21.126	3.551
1400	16.200	36.121	25.179	15.318	-50.305	-18.863	2.945
1500	16.600	37.252	25.947	16.958	-49.785	-16.634	2.423
1600	17.000	38.336	26.687	18.638	-49.230	-14.442	1.973
1700	17.400	39.379	27.404	20.358	-48.640	-12.285	1.579
1800	17.800	40.385	28.097	22.118	-48.019	-10.165	1.234
1900	18.200	41.358	28.769	23.918	-47.364	-8.081	.929
2000	18.600	42.302	29.423	25.758	-46.677	-6.031	.659
2100	19.000	43.219	30.058	27.638	-88.408	-2.463	.256
2200	19.400	44.112	30.676	29.558	-87.564	1.609	-.160
2300	19.800	44.983	31.280	31.518	-86.703	5.643	-.536
2400	20.200	45.834	31.868	33.518	-85.826	9.641	-.878
2500	20.600	46.667	32.444	35.558	-84.935	13.598	-1.189

March 31, 1962

Lead Monoxide, Red (PbO) (Crystal)

Mol. Wt. = 223.21

$\Delta H_f^\circ\ _{298.15} = -52.41 \pm 0.16$ kcal. mole^{-1}

$S^\circ_{298.15} = 15.6 \pm 0.2$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_s^\circ\ _{298.15} = 63.88 \pm 0.22$ kcal. mole^{-1}

$T_t = 762°K$

$\Delta H_t^\circ = 0.18 \pm 0.23$ kcal. mole^{-1}

Heat of Formation. Calculated from the cell reaction

$H_2(g) \mid Ba(OH)_2\ (0.766 \sim 0.2242M) \mid PbO(c) + Pb(c)$

reported by D. F. Smith and H. K. Woods, J. Am. Chem. Soc., 45, 2632 (1923), using $\Delta H_f^\circ\ _{298.15}$ for $H_2O(l)$, -68.317 kcal. mole^{-1}, given by Natl. Bur. Standards Circular 500 (1952). ΔH_f° values reported by other investigators were discussed by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. Heat capacity values (51° to 298.15°K) were obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, heat capacity given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used and joined smoothly to data of King at 298.15°K by graphical extrapolation. King obtained entropies below 51°K by empirical extrapolation of the heat capacity curve which fits the measured heat capacities within 1.3%.

Transition Data. Heat of transition recalculated from the data given by E. G. King, loc. cit.

Heat of Sublimation. Calculated from free-energy functions and vapor pressure reported by A. N. Nesmeyanov, L. P. Firsova and E. P. Isakova, Zhur. Fiz. Khim. 34, 1699 (1960) and R. Hörbe and O. Knacke, Z. Erzbergbau u. Metallhuttenw. 12, 321 (1959).

Lead Monoxide, Yellow (PbO)

(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.209	-51.594	-51.594	INFINITE
100	6.581	6.352	24.842	-1.849	-52.013	-49.692	108.596
200	9.720	11.990	17.080	-1.018	-52.125	-47.305	51.690
298	10.958	16.114	16.114	.000	-52.066	-44.949	32.947
300	10.970	16.182	16.114	.020	-52.064	-44.905	32.711
400	11.631	19.433	16.553	1.152	-51.940	-42.535	23.239
500	12.094	22.080	17.402	2.339	-51.791	-40.202	17.571
600	12.469	24.319	18.373	3.568	-51.630	-37.898	13.804
700	12.803	26.267	19.364	4.832	-52.625	-35.432	11.062
800	13.115	27.997	20.337	6.128	-52.449	-32.988	9.011
900	13.415	29.557	21.276	7.453	-52.245	-30.567	7.422
1000	13.706	30.986	22.177	8.809	-52.009	-28.170	6.156
1100	13.992	32.306	23.038	10.194	-51.742	-25.800	5.126
1200	14.275	33.535	23.862	11.607	-51.444	-23.453	4.271
1300	14.555	34.689	24.651	13.049	-51.117	-21.134	3.553
1400	14.833	35.778	25.408	14.518	-50.764	-18.842	2.941
1500	15.110	36.811	26.134	16.015	-50.387	-16.573	2.415
1600	15.386	37.794	26.832	17.540	-49.987	-14.332	1.958
1700	15.660	38.735	27.505	19.092	-49.565	-12.116	1.558
1800	15.935	39.638	28.154	20.672	-49.124	-9.927	1.205
1900	16.209	40.507	28.781	22.279	-48.662	-7.762	.893
2000	16.483	41.346	29.389	23.914	-48.181	-5.622	.614
2100	16.756	42.156	29.977	25.576	-90.129	-1.953	.203
2200	17.029	42.942	30.549	27.265	-89.516	2.230	-.222
2300	17.302	43.705	31.104	28.982	-88.898	6.387	-.607
2400	17.575	44.447	31.645	30.726	-88.277	10.518	-.958
2500	17.847	45.170	32.172	32.497	-87.655	14.619	-1.278
2600	18.119	45.876	32.685	34.295	-87.029	18.698	-1.572
2700	18.391	46.564	33.187	36.120	-86.399	22.753	-1.842
2800	18.663	47.238	33.676	37.973	-85.765	26.784	-2.091
2900	18.936	47.898	34.155	39.853	-85.125	30.794	-2.321
3000	19.208	48.544	34.624	41.760	-84.479	34.781	-2.534

March 31, 1962

Lead Monoxide, Yellow (PbO) (Crystal)

Mol. Wt. = 223.21

ΔH_f° 298.15 = -52.07 ± 0.28 kcal. mole^{-1}

$S^\circ_{298.15}$ = 16.1 ± 0.2 cal. deg.$^{-1}$ mole^{-1}

ΔH_s° 298.15 = 63.54 ± 0.32 kcal. mole^{-1}

T_m = 1170 ± 4°K.

ΔH_m° = 6.1 ± 0.1 kcal. mole^{-1}

Heat of Formation. Calculated from ΔH_f° 298.15 for PbO (c, red) and ΔH_t° 298.15 between PbO (c, red) and PbO (c, yellow).

Heat Capacity, Entropy, and Melting Data. C_p values (51° to 298.15°K.) obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, the heat capacity reported by E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961) was used and joined smoothly to data of King at 298.15°K. by graphical extrapolation. T_m and ΔH_m° given by E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, loc. cit.

Heat of Sublimation. Calculated from ΔH_t° 298.15 and ΔH_s° 298.15 for PbO (c, red).

Lead Monoxide (PbO)
(Liquid) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	10.950	20.546	20.546	.000	- 46.712	- 40.916	29.991
300	10.970	20.614	20.546	.020	- 46.710	- 40.880	29.780
400	11.629	23.866	20.985	1.152	- 46.586	- 38.954	21.283
500	12.094	26.513	21.834	2.340	- 46.437	- 37.064	16.200
600	12.469	28.752	22.805	3.568	- 46.276	- 35.204	12.822
700	12.802	30.700	23.797	4.832	- 47.271	- 33.181	10.359
800	15.535	32.492	24.771	6.177	- 47.046	- 31.181	8.518
900	15.535	34.322	25.732	7.730	- 46.614	- 29.223	7.096
1000	15.535	35.958	26.674	9.284	- 46.180	- 27.314	5.969
1100	15.535	37.439	27.587	10.837	- 45.745	- 25.449	5.056
1200	15.535	38.791	28.465	12.391	- 45.306	- 23.622	4.302
1300	15.535	40.034	29.308	13.944	- 44.867	- 21.833	3.670
1400	15.535	41.185	30.116	15.498	- 44.431	- 20.079	3.134
1500	15.535	42.257	30.890	17.051	- 43.997	- 18.353	2.674
1600	15.535	43.260	31.632	18.605	- 43.569	- 16.658	2.275
1700	15.535	44.202	32.344	20.158	- 43.145	- 14.988	1.927
1800	15.535	45.090	33.027	21.712	- 42.730	- 13.345	1.620
1900	15.535	45.930	33.685	23.265	- 42.322	- 11.725	1.349
2000	15.535	46.726	34.317	24.819	- 41.922	- 10.124	1.106
2100	15.535	47.484	34.926	26.372	- 83.979	- 6.991	.728
2200	15.535	48.207	35.513	27.926	- 83.501	- 3.337	.332
2300	15.535	48.898	36.080	29.479	- 83.047	.296	- .028
2400	15.535	49.559	36.628	31.033	- 82.616	3.912	- .356
2500	15.535	50.193	37.158	32.586	- 82.212	7.506	- .656
2600	15.535	50.802	37.671	34.140	- 81.830	11.088	- .932
2700	15.535	51.388	38.169	35.693	- 81.472	14.655	- 1.186
2800	15.535	51.953	38.651	37.247	- 81.138	18.209	- 1.421
2900	15.535	52.499	39.119	38.800	- 80.824	21.753	- 1.639
3000	15.535	53.025	39.574	40.354	- 80.531	25.286	- 1.842

March 31, 1962

Lead Monoxide (PbO) (Liquid)

Mol. Wt. = 223.21

ΔH_f° 298.15 = [-46.712] kcal. mole^{-1}

$S_{298.15}^\circ$ = [20.546] cal. deg.$^{-1}$ mole^{-1}

T_m = 1170 ± 4°K.

ΔH_m° = 6.1 ± 0.1 kcal. mole^{-1}

T_b = 1789°K.

ΔH_v° = 49.53 ± 0.22 kcal. mole^{-1}

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p, T_m, and ΔH_m° are obtained from E. N. Rodigina, K. Z. Gomel'skii and V. F. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961). The reported heat capacity is extrapolated to an assumed glass transition temperature of 780°K., below which the heat capacity is taken to be equal to that of the crystal, PbO (c, red).

Vaporization Phenomena. T_b and ΔH_v° calculated from ΔH_s° 298.15 for PbO (c, red) and functions for condensed and gaseous states.

Lead Monoxide (PbO)

(Ideal Gas) Mol. Wt. = 223.21 **INTERIM TABLE**

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.142	12.017	12.017	INFINITE
100	6.964	49.455	63.918	-1.446	11.933	9.944	-21.731
200	7.272	54.349	58.041	-.739	11.697	8.045	-8.791
298	7.769	57.346	57.346	.000	11.477	6.301	-4.619
300	7.778	57.395	57.347	.014	11.473	6.269	-4.567
400	8.155	59.687	57.657	.812	11.263	4.566	-2.495
500	8.400	61.535	58.254	1.641	11.053	2.915	-1.274
600	8.560	63.082	58.933	2.489	10.834	1.309	-.477
700	8.670	64.410	59.623	3.351	9.437	-.070	.022
800	8.748	65.573	60.295	4.222	9.188	-1.412	.386
900	8.806	66.607	60.940	5.100	8.945	-2.722	.661
1000	8.850	67.537	61.554	5.983	8.709	-4.005	.875
1100	8.886	68.383	62.137	6.870	8.477	-5.266	1.046
1200	8.915	69.157	62.690	7.760	8.252	-6.504	1.184
1300	8.940	69.872	63.216	8.653	8.030	-7.725	1.299
1400	8.962	70.535	63.715	9.548	7.809	-8.929	1.394
1500	8.980	71.154	64.191	10.445	7.586	-10.115	1.474
1600	8.997	71.734	64.644	11.344	7.360	-11.289	1.542
1700	9.013	72.280	65.077	12.245	7.130	-12.447	1.600
1800	9.027	72.796	65.492	13.147	6.894	-13.593	1.650
1900	9.040	73.284	65.889	14.050	6.651	-14.725	1.694
2000	9.052	73.748	66.271	14.954	6.403	-15.843	1.731
2100	9.064	74.190	66.638	15.860	-36.302	-15.396	1.602
2200	9.075	74.612	66.990	16.767	-36.471	-14.398	1.430
2300	9.086	75.016	67.331	17.675	-36.662	-13.391	1.272
2400	9.096	75.402	67.659	18.584	-36.876	-12.373	1.127
2500	9.106	75.774	67.976	19.494	-37.115	-11.350	.992
2600	9.116	76.131	68.283	20.406	-37.375	-10.313	.867
2700	9.126	76.476	68.580	21.318	-37.658	-9.267	.750
2800	9.135	76.808	68.868	22.231	-37.965	-8.210	.641
2900	9.144	77.128	69.147	23.145	-38.291	-7.140	.538
3000	9.153	77.438	69.419	24.060	-38.636	-6.059	.441
3100	9.162	77.739	69.682	24.975	-38.999	-4.968	.350
3200	9.171	78.030	69.939	25.892	-39.380	-3.865	.264
3300	9.180	78.312	70.188	26.809	-39.773	-2.749	.182
3400	9.188	78.586	70.431	27.728	-40.180	-1.620	.104
3500	9.197	78.853	70.668	28.647	-40.598	-.482	.030
3600	9.205	79.112	70.899	29.567	-41.025	.672	-.041
3700	9.214	79.364	71.124	30.488	-41.460	1.836	-.108
3800	9.222	79.610	71.344	31.410	-41.900	3.014	-.173
3900	9.230	79.850	71.559	32.333	-42.345	4.200	-.235
4000	9.238	80.084	71.770	33.256	-42.794	5.396	-.295
4100	9.247	80.312	71.975	34.180	-43.245	6.608	-.352
4200	9.255	80.535	72.176	35.105	-43.696	7.831	-.407
4300	9.263	80.753	72.373	36.031	-44.148	9.062	-.461
4400	9.271	80.966	72.566	36.958	-44.599	10.306	-.512
4500	9.279	81.174	72.755	37.885	-45.048	11.557	-.561
4600	9.287	81.378	72.940	38.814	-45.495	12.823	-.609
4700	9.295	81.578	73.122	39.743	-45.939	14.092	-.655
4800	9.303	81.774	73.300	40.673	-46.380	15.379	-.700
4900	9.311	81.966	73.475	41.603	-46.817	16.665	-.743
5000	9.319	82.154	73.647	42.535	-47.249	17.964	-.785
5100	9.327	82.338	73.815	43.467	-47.679	19.275	-.826
5200	9.335	82.520	73.981	44.400	-48.103	20.592	-.865
5300	9.343	82.697	74.144	45.334	-48.522	21.920	-.904
5400	9.351	82.872	74.304	46.269	-48.938	23.251	-.941
5500	9.359	83.044	74.461	47.205	-49.349	24.591	-.977
5600	9.367	83.213	74.616	48.141	-49.756	25.939	-1.012
5700	9.375	83.378	74.768	49.078	-50.159	27.291	-1.046
5800	9.382	83.542	74.918	50.016	-50.557	28.659	-1.080
5900	9.390	83.702	75.066	50.954	-50.953	30.025	-1.112
6000	9.398	83.860	75.211	51.894	-51.344	31.400	-1.144

Lead Monoxide (PbO) (Ideal Gas)

Mol. Wt. = 223.21

$\Delta H_f^\circ{}_{298.15} = 11.48 \pm 0.27$ kcal. mole^{-1}

$S^\circ_{298.15} = 57.346$ cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^1\Sigma^+$

<u>Electronic Level and Multiplicity</u>

ϵ cm.$^{-1}$	g_1
0	1

$\omega_e = 721.8$ cm.$^{-1}$

$B_e = 0.3072$ cm.$^{-1}$

$\sigma = 1$

$\omega_e x_e = 3.70$ cm.$^{-1}$

$\alpha_e = 0.0019$ cm.$^{-1}$

$r_e = 1.922$ Å

<u>Heat of Formation</u>. Calculated from $\Delta H_f^\circ{}_{298.15}$ for PbO (c, red) and $\Delta H_s^\circ{}_{298.15}$.

<u>Heat Capacity and Entropy</u>. The ground state configuration, molecular and spectroscopic constants are obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950), modified for the natural isotopic abundances reported by J. R. Stehn and E. F. Clancy, "Chart of the Nuclides", General Electric Co., N. Y. (1956).

Sulfur Monoxide (SO)

(Ideal Gas) Mol. Wt. = 48.0634

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.090	1.640	1.640	INFINITE
100	6.957	45.366	59.290	-1.392	1.818	-.346	.757
200	6.996	50.194	53.672	-.696	1.781	-2.510	2.742
298	7.212	53.021	53.021	.000	1.640	-4.588	3.363
300	7.217	53.066	53.021	.013	1.637	-4.626	3.370
400	7.543	55.186	53.308	.751	.920	-6.666	3.642
500	7.846	56.903	53.861	1.521	.387	-8.500	3.715
600	8.087	58.356	54.492	2.318	-.051	-10.235	3.728
700	8.272	59.617	55.136	3.137	-.421	-11.879	3.708
800	8.413	60.731	55.767	3.971	-13.811	-14.761	4.032
900	8.520	61.728	56.375	4.818	-13.809	-14.879	3.613
1000	8.605	62.631	56.956	5.674	-13.807	-14.998	3.278
1100	8.672	63.454	57.510	6.538	-13.806	-15.118	3.004
1200	8.726	64.211	58.037	7.408	-13.804	-15.237	2.775
1300	8.770	64.911	58.539	8.283	-13.802	-15.355	2.581
1400	8.808	65.563	59.018	9.162	-13.802	-15.476	2.416
1500	8.840	66.171	59.475	10.045	-13.803	-15.596	2.272
1600	8.867	66.743	59.911	10.930	-13.804	-15.715	2.146
1700	8.891	67.281	60.329	11.818	-13.807	-15.834	2.035
1800	8.912	67.790	60.730	12.708	-13.811	-15.954	1.937
1900	8.931	68.272	61.114	13.600	-13.816	-16.071	1.848
2000	8.948	68.731	61.484	14.494	-13.823	-16.191	1.769
2100	8.963	69.168	61.839	15.390	-13.832	-16.310	1.697
2200	8.978	69.585	62.182	16.287	-13.843	-16.426	1.632
2300	8.991	69.984	62.513	17.185	-13.856	-16.543	1.572
2400	9.003	70.367	62.832	18.085	-13.870	-16.659	1.517
2500	9.015	70.735	63.141	18.986	-13.886	-16.776	1.466
2600	9.026	71.089	63.440	19.888	-13.904	-16.891	1.420
2700	9.036	71.430	63.729	20.791	-13.924	-17.007	1.377
2800	9.046	71.759	64.010	21.695	-13.946	-17.123	1.336
2900	9.056	72.076	64.283	22.600	-13.970	-17.233	1.299
3000	9.065	72.383	64.548	23.506	-13.997	-17.343	1.263
3100	9.074	72.681	64.805	24.413	-14.023	-17.456	1.231
3200	9.082	72.969	65.056	25.321	-14.053	-17.567	1.200
3300	9.090	73.248	65.300	26.230	-14.084	-17.676	1.171
3400	9.098	73.520	65.538	27.139	-14.117	-17.784	1.143
3500	9.106	73.784	65.770	28.049	-14.152	-17.895	1.117
3600	9.114	74.040	65.996	28.960	-14.187	-17.997	1.093
3700	9.121	74.290	66.217	29.872	-14.225	-18.102	1.069
3800	9.129	74.534	66.432	30.785	-14.263	-18.209	1.047
3900	9.136	74.771	66.643	31.698	-14.303	-18.314	1.026
4000	9.143	75.002	66.849	32.612	-14.344	-18.412	1.006
4100	9.150	75.228	67.051	33.527	-14.385	-18.514	.987
4200	9.157	75.449	67.248	34.442	-14.429	-18.616	.969
4300	9.164	75.664	67.441	35.358	-14.473	-18.712	.951
4400	9.171	75.875	67.631	36.275	-14.518	-18.813	.934
4500	9.178	76.081	67.816	37.192	-14.564	-18.907	.918
4600	9.184	76.283	67.998	38.110	-14.611	-19.004	.903
4700	9.191	76.481	68.176	39.029	-14.658	-19.102	.888
4800	9.197	76.674	68.351	39.948	-14.706	-19.194	.874
4900	9.204	76.864	68.523	40.869	-14.754	-19.287	.860
5000	9.210	77.050	68.692	41.789	-14.804	-19.382	.847
5100	9.217	77.232	68.858	42.711	-14.854	-19.467	.834
5200	9.223	77.411	69.020	43.633	-14.904	-19.558	.822
5300	9.230	77.587	69.180	44.555	-14.954	-19.647	.810
5400	9.236	77.760	69.338	45.479	-15.005	-19.739	.799
5500	9.242	77.929	69.492	46.402	-15.056	-19.822	.788
5600	9.248	78.096	69.644	47.327	-15.109	-19.911	.777
5700	9.255	78.259	69.794	48.252	-15.160	-19.994	.767
5800	9.261	78.420	69.942	49.178	-15.212	-20.075	.756
5900	9.267	78.579	70.087	50.104	-15.264	-20.167	.747
6000	9.273	78.735	70.229	51.031	-15.316	-20.245	.737

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

OS

SULFUR MONOXIDE (SO) (IDEAL GAS) MOL. WT. = 48.0634

Ground State Configuration $^3\Sigma^-$

$S^\circ_{298.15}$ = 53.0 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 1.64 ± 0.3 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 1.64 ± 0.3 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	3

ω_e = 1148.19 cm.$^{-1}$

B_e = 0.7207 cm.$^{-1}$

$\omega_e x_e$ = 6.116 cm.$^{-1}$

α_e = 0.00562 cm.$^{-1}$

σ = 1

r_e = 1.481 Å

Heat of Formation.

The dissociation energy of sulfur monoxide has been reported by following investigators:

D_0 (SO) e.v.	(kcal. mole^{-1})	Investigator
5.053	(116.5)	E. V. Martin, Phys. Rev. 41, 167 (1932).
5.184	(119.5)	A. G. Gaydon, "Dissociation Energies", Chapman & Hall Ltd. London, 1953.
4.001	(92.3)	G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. 2nd Ed., 1950.
5.357	(123.5)	R. G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. A249, 498 (1959).
5.510	(127.1)	J. J. McGarvey, W. D. McGrath, Proc. Roy. Soc. A278, 490 (1964).

E. V. Martin, loc. cit., has measured the spectrum of SO(g) in the region 2400-4000 Å, and both Herzberg's and Gaydon's data were based on Martin's spectroscopic measurement. Because of the ambiguity of defining the state of excitation of the atomic products resulting from predissociation, the dissociation energy of SO was in question. Herzberg favored D_0 (SO) = 92.3 kcal. mole^{-1} but Gaydon D_0 (SO) = 119.5 kcal. mole^{-1}.

Norrish and Oldershaw, loc. cit., redetermined the absorption spectrum of SO by flash photolysis, and also corrected Martin's original vibrational numbering, and then obtained the dissociation energy, D_0(SO) = 123.5 kcal. mole^{-1}, based on the assumption of predissociation into $S(^1D)$ and $O(^3P)$. This value, D_0 = 123.5 kcal. mole^{-1}, has been selected as the dissociation energy for SO(g) and combination with JANAF values of ΔH_f° (S; g) and ΔH_f° (O; g) gives the heat of formation of sulfur monoxide, $\Delta H^\circ_{f\ 298}$ = 1.64 ± 0.3 kcal. mole^{-1}, which is adopted in this tabulation.

R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 60, 306 (1964), have confirmed the selected D_0 (SO) = 123.5 kcal. mole^{-1} in their mass spectrometric studies on the vaporization of CaS, SrS and BaS. J. J. McGarvey and W. D. McGrath, loc. cit., reported the dissociation energy to be 127.1 kcal. mole^{-1} based on their ultraviolet spectroscopic studies. This value appears to be the D_e from the minimum of the potential curve which corresponds to D_0 (SO) = 125 ± 1.5 kcal. mole^{-1}.

Besides the spectroscopic information , G. St. Pierre and J. Chipman, J. Am. Chem. Soc. 76, 4787 (1954), have reported $\Delta H^\circ_{r\ 298}$ = -19 kcal. mole^{-1} for the reaction 0.5 S_2(g) + 0.5 O_2(g) → SO(g) in the equilibrium study of lime-iron oxide slags with SO_2 or SO_2-CO mixtures. Using $\Delta H^\circ_{f\ 298}$ (S_2; g) = 30.8 kcal. mole^{-1}, the derived heat of formation, $\Delta H^\circ_{f\ 298}$ (SO; g) = -3.6 kcal. mole^{-1} was obtained. However, this value is doubtful because the reported $\Delta H^\circ_{r\ 298}$ = -19 kcal. mole^{-1} was dependent upon many assumptions and subsidiary data. E. W. Dewing and F. D. Richardson, Trans. Faraday Soc. 54, 679(1958) have measured the equilibrium constants for the reaction $S_2(g) + 2SO_2(g) \rightarrow 4SO(g)$ at 1250°C. and $SO_2(g) \rightarrow SO(g) + 1/2\ O_2(g)$ at 1500°C. Using the JANAF auxiliary data, the former yields $\Delta H^\circ_{f\ 298}$ (SO; g) = +0.13 kcal. mole^{-1} and the latter -0.17 kcal. mole^{-1}, respectively. The average of these two values is $\Delta H^\circ_{f\ 298}$ = 0 kcal. mole^{-1}. Although D. Meschi and R. Myers, J. Mol. Spectry. 3, 405 (1959) and U. Blukis and R. Myers, J. Phys. Chem. 69, 1154 (1965), have certainly concluded in their microwave spectroscopic studies that the S_2O species was one of the important products in the Sulfur - SO_2 equilibrium which was considered as unimportant by Dewing and Richardson, the value, $\Delta H^\circ_{f\ 298}$ (SO; g) = 0 kcal. mole^{-1}, derived from Dewing and Richardson is still very close to the selected value, $\Delta H^\circ_{f\ 298}$ (SO; g) = 1.64 kcal. mole^{-1}.

OS

Heat Capacity and Entropy.

The molecular constants ω_e, $\omega_e x_e$ and α_e were obtained from R. Norrish and G. Oldershaw, loc. cit., and the values of r_e and B_e were recently measured in the microwave spectrum by F. X. Powell and D. R. Lide, Jr., J. Chem. Phys. 41, 1413 (1964).

Disulfur Monoxide (S_2O)
(Ideal Gas) Mol. Wt. = 80.1274

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0	.000	.000	INFINITE	-2.660	-13.016	-13.016	INFINITE
100	8.195	53.775	72.381	-1.861	-12.902	-15.610	34.114
200	9.423	59.816	64.726	-.982	-13.149	-18.240	19.931
298	10.544	63.796	63.796	.000	-13.500	-20.665	15.147
300	10.562	63.861	63.796	.020	-13.507	-20.709	15.086
400	11.424	67.024	64.221	1.121	-14.959	-23.011	12.572
500	12.041	69.644	65.051	2.296	-16.025	-24.899	10.883
600	12.477	71.880	66.008	3.523	-16.890	-26.589	9.684
700	12.786	73.828	66.989	4.787	-17.615	-28.099	8.772
800	13.011	75.551	67.953	6.078	-44.373	-32.089	8.766
900	13.177	77.093	68.885	7.388	-44.346	-30.554	7.419
1000	13.303	78.488	69.776	8.712	-44.318	-29.022	6.342
1100	13.399	79.761	70.627	10.047	-44.288	-27.497	5.463
1200	13.475	80.930	71.438	11.391	-44.256	-25.970	4.730
1300	13.536	82.011	72.210	12.742	-44.224	-24.445	4.109
1400	13.585	83.016	72.946	14.098	-44.194	-22.926	3.579
1500	13.625	83.955	73.649	15.458	-44.165	-21.411	3.119
1600	13.658	84.835	74.321	16.822	-44.135	-19.892	2.717
1700	13.686	85.664	74.964	18.190	-44.107	-18.378	2.363
1800	13.709	86.447	75.581	19.559	-44.082	-16.866	2.048
1900	13.729	87.189	76.172	20.931	-44.057	-15.353	1.766
2000	13.747	87.893	76.741	22.305	-44.035	-13.843	1.513
2100	13.761	88.564	77.288	23.681	-44.016	-12.336	1.284
2200	13.774	89.205	77.815	25.057	-44.000	-10.826	1.075
2300	13.786	89.818	78.324	26.436	-43.985	-9.321	.886
2400	13.796	90.404	78.815	27.815	-43.973	-7.810	.711
2500	13.805	90.968	79.290	29.195	-43.963	-6.306	.551
2600	13.813	91.509	79.750	30.576	-43.956	-4.798	.403
2700	13.820	92.031	80.195	31.957	-43.952	-3.295	.267
2800	13.826	92.534	80.627	33.339	-43.951	-1.793	.140
2900	13.832	93.019	81.046	34.722	-43.952	-.284	.021
3000	13.837	93.488	81.453	36.106	-43.957	1.224	-.089
3100	13.841	93.942	81.848	37.490	-43.962	2.729	-.192
3200	13.846	94.381	82.233	38.874	-43.973	4.235	-.289
3300	13.849	94.807	82.608	40.259	-43.983	5.740	-.380
3400	13.853	95.221	82.973	41.644	-43.997	7.249	-.466
3500	13.856	95.622	83.328	43.029	-44.015	8.753	-.547
3600	13.859	96.013	83.675	44.415	-44.032	10.261	-.623
3700	13.862	96.392	84.014	45.801	-44.055	11.774	-.695
3800	13.864	96.762	84.344	47.187	-44.077	13.282	-.764
3900	13.867	97.122	84.667	48.574	-44.102	14.789	-.829
4000	13.869	97.473	84.983	49.961	-44.130	16.306	-.891
4100	13.871	97.816	85.292	51.348	-44.158	17.813	-.949
4200	13.873	98.150	85.594	52.735	-44.190	19.327	-1.006
4300	13.875	98.477	85.890	54.122	-44.222	20.837	-1.059
4400	13.876	98.796	86.180	55.510	-44.258	22.349	-1.110
4500	13.878	99.107	86.464	56.898	-44.295	23.871	-1.150
4600	13.879	99.413	86.742	58.285	-44.333	25.380	-1.206
4700	13.880	99.711	87.015	59.673	-44.372	26.897	-1.251
4800	13.882	100.003	87.282	61.061	-44.413	28.413	-1.294
4900	13.883	100.289	87.545	62.450	-44.455	29.937	-1.335
5000	13.884	100.570	87.802	63.838	-44.500	31.447	-1.374
5100	13.885	100.845	88.055	65.226	-44.547	32.971	-1.413
5200	13.886	101.115	88.304	66.615	-44.593	34.489	-1.449
5300	13.887	101.379	88.548	68.004	-44.640	36.013	-1.485
5400	13.888	101.639	88.788	69.392	-44.690	37.534	-1.519
5500	13.889	101.893	89.024	70.781	-44.739	39.061	-1.552
5600	13.889	102.144	89.256	72.170	-44.792	40.582	-1.584
5700	13.890	102.390	89.484	73.559	-44.845	42.102	-1.614
5800	13.891	102.631	89.709	74.948	-44.899	43.635	-1.644
5900	13.891	102.869	89.930	76.337	-44.953	45.152	-1.672
6000	13.892	103.102	90.148	77.726	-45.009	46.692	-1.701

Sept. 30, 1965

DISULFUR MONOXIDE (S_2O) (IDEAL GAS) MOL. WT. = 80.1274

Point Group C_s

$S^\circ_{298.15}$ = 63.8 cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\ 0}$ = [-13 ± 8] kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = [-13.5 ± 8] kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
679 (1)
388 (1)
1165 (1)

Bond Distance: S-S = 1.884 Å S-O = 1.465 Å

Bond Angle: S-S-O = 118°

σ = 1

Product of the Moment of Inertia: $I_AI_BI_C$ = 6.27441 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

There is no direct measurement of the standard enthalpy of formation for $S_2O(g)$. U. Blukis and R. Myers, J. Phys. Chem., 69, 1154 (1965), have discussed the discrepancy of the values of $\Delta H^\circ_{f\ 0}$ which vary from -1 to -35 kcal. mole^{-1}. R. Hagmann, Compt. Rend., 225, 1102 (1962), reported $\Delta H^\circ_{f\ 0}$ = -17 kcal. mole^{-1} from his ionization and appearance potential measurements by mass spectrometry. R. Steudel and P. W. Schenk, Z. Physik Chem., 43, 33 (1964), estimated the enthalpy of formation as -22.7 kcal. mole^{-1}. If the bond dissociation energies D_0(S-O) = 123.5 kcal. mole^{-1} and D_0(S-S) = 101 kcal. mole^{-1} were used to estimate the dissociation energy of S_2O (i.e. $D_0(S_2O)$ = 224.5 kcal. mole^{-1}), one will obtain $\Delta H^\circ_{f\ 0}$ = -35.3 kcal. mole^{-1}. A. V. Jones, J. Chem. Phys. 18, 1263 (1950), reported the predissociation energy, 91 kcal. mole^{-1}, for sulfur monoxide from the infrared and ultraviolet spectra. [D. Meschi and R. Myers, J. Mol. Spectro. 3, 405 (1959), have concluded from their experiment that the so called sulfur monoxide is S_2O.] Therefore, if SO(g) + S(g), were the dissociation products, the $\Delta H^\circ_{f\ 0}$ would be -25.4 kcal. mole^{-1}; and if $S_2(g)$ + O(g) were the products, the $\Delta H^\circ_{f\ 0}$ would be -1.2 kcal. mole^{-1}. (All JANAF auxiliary data used in calculation.)

E. Dewing and F. Richardson, Trans. Faraday Soc., 54, 679 (1958), have investigated the gas phase equilibria in the sulfur-oxygen vapor at 1250° and 1500°C respectively. U. Blukis and R. Myers (loc. cit.) recalculated their data based on the assumption that the S_2O (instead of SO) was the major product in the equilibrium, and obtained $\Delta H^\circ_{f\ 0}$ = -13 kcal. mole^{-1} for $S_2O(g)$ which is adopted in this table.

Heat Capacity and Entropy.

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by D. Meschi and R. Myers, loc. cit., and U. Blukis and R. Myers, loc. cit. The three principal moments of intertia are I_A = 2.0219 X 10^{-39}, I_B = 16.6342 X 10^{-39} and I_C = 18.6560 X 10^{-39} g. cm.^{2}

Silicon Monoxide (SiO)

(Ideal Gas) GFW = 44.0854

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.083	-24.276	-24.276	INFINITE
100	6.956	42.905	56.785	-1.388	-23.992	-26.122	57.089
200	6.980	47.730	51.189	-.692	-23.925	-28.292	30.916
298	7.146	50.542	50.542	.000	-24.000	-30.423	22.300
300	7.151	50.586	50.542	.013	-24.002	-30.463	22.192
400	7.441	52.682	50.826	.742	-24.136	-32.597	17.810
500	7.735	54.374	51.371	1.502	-24.286	-34.694	15.165
600	7.982	55.807	51.994	2.288	-24.445	-36.761	13.390
700	8.177	57.053	52.630	3.096	-24.611	-38.801	12.114
800	8.328	58.155	53.253	3.922	-24.784	-40.817	11.151
900	8.445	59.143	53.853	4.761	-24.964	-42.809	10.396
1000	8.538	60.038	54.428	5.610	-25.152	-44.782	9.787
1100	8.611	60.855	54.976	6.468	-25.349	-46.736	9.286
1200	8.671	61.607	55.497	7.332	-25.554	-48.672	8.864
1300	8.720	62.303	55.994	8.201	-25.768	-50.590	8.505
1400	8.761	62.951	56.468	9.075	-25.991	-52.491	8.194
1500	8.795	63.556	56.921	9.953	-24.224	-54.374	7.922
1600	8.825	64.125	57.354	10.834	-26.466	-56.244	7.683
1700	8.850	64.661	57.768	11.718	-38.711	-57.992	7.455
1800	8.873	65.167	58.165	12.604	-38.920	-59.118	7.178
1900	8.893	65.648	58.546	13.493	-39.129	-60.237	6.929
2000	8.911	66.104	58.913	14.383	-39.339	-61.341	6.703
2100	8.927	66.539	59.266	15.275	-39.549	-62.435	6.498
2200	8.942	66.955	59.606	16.168	-39.762	-63.522	6.310
2300	8.955	67.353	59.934	17.063	-39.975	-64.598	6.138
2400	8.968	67.734	60.251	17.959	-40.190	-65.661	5.979
2500	8.979	68.101	60.558	18.857	-40.406	-66.721	5.833
2600	8.990	68.453	60.855	19.755	-40.624	-67.768	5.696
2700	9.000	68.792	61.143	20.655	-40.843	-68.807	5.570
2800	9.010	69.120	61.422	21.555	-41.064	-69.839	5.451
2900	9.020	69.436	61.693	22.457	-41.287	-70.861	5.340
3000	9.029	69.742	61.956	23.359	-41.511	-71.878	5.236
3100	9.038	70.038	62.212	24.262	-41.736	-72.886	5.138
3200	9.047	70.326	62.461	25.167	-41.963	-73.889	5.046
3300	9.056	70.604	62.704	26.072	-42.191	-74.882	4.959
3400	9.065	70.875	62.940	26.978	-42.420	-75.871	4.877
3500	9.075	71.137	63.170	27.885	-42.650	-76.850	4.799
3600	9.084	71.393	63.395	28.793	-134.842	-75.566	4.588
3700	9.094	71.642	63.615	29.702	-134.975	-73.918	4.366
3800	9.105	71.885	63.829	30.612	-135.109	-72.266	4.156
3900	9.117	72.122	64.039	31.523	-135.244	-70.615	3.957
4000	9.129	72.353	64.244	32.435	-135.379	-68.955	3.768
4100	9.142	72.578	64.444	33.349	-135.516	-67.292	3.587
4200	9.156	72.799	64.641	34.263	-135.652	-65.630	3.415
4300	9.172	73.014	64.833	35.180	-135.788	-63.956	3.251
4400	9.188	73.225	65.021	36.098	-135.924	-62.286	3.094
4500	9.207	73.432	65.206	37.018	-136.059	-60.607	2.943
4600	9.226	73.635	65.387	37.939	-136.193	-58.931	2.800
4700	9.247	73.833	65.564	38.863	-136.327	-57.247	2.662
4800	9.270	74.028	65.739	39.789	-136.459	-55.564	2.530
4900	9.294	74.219	65.910	40.717	-136.589	-53.877	2.403
5000	9.320	74.407	66.078	41.648	-136.718	-52.190	2.281
5100	9.348	74.592	66.243	42.581	-136.845	-50.494	2.164
5200	9.378	74.774	66.405	43.517	-136.970	-48.804	2.051
5300	9.410	74.953	66.565	44.457	-137.091	-47.105	1.942
5400	9.444	75.129	66.722	45.399	-137.211	-45.408	1.838
5500	9.479	75.303	66.876	46.345	-137.327	-43.709	1.737
5600	9.517	75.474	67.028	47.295	-137.441	-42.003	1.639
5700	9.557	75.643	67.178	48.249	-137.552	-40.298	1.545
5800	9.599	75.809	67.325	49.207	-137.659	-38.587	1.454
5900	9.642	75.974	67.471	50.169	-137.763	-36.885	1.366
6000	9.688	76.136	67.614	51.135	-137.863	-35.170	1.281

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1967

SILICON MONOXIDE (SiO) (IDEAL GAS) GFW = 44.0854

Ground State Configuration $^1\Sigma^+$

ΔHf_0° = -24.3 ± 2 kcal/mol

$S^\circ_{298.15}$ = 50.54 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -24 ± 2 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	1
[30000]	6
42640	2

ω_e = 1241.44 $\omega_e x_e$ = 5.92 σ = 1

B_e = 0.7273 α_e = 0.00508 r_e = 1.509 Å

Heat of Formation

The adopted value is based on equilibrium data summarized below. The more reliable results from three different reactions lie in the range from about -23 to -26 kcal/mol. Extreme values, including -20 and -32 kcal/mol, can be discounted on experimental grounds. Margrave (1) recently reported ΔHr°_{298} = 82.8±1.5 kcal/mol for $0.5SiO_2(s)+0.5Si(s) = SiO(g)$, but details are not yet available. Assuming that this corresponds to reaction A below, we calculate ΔHf°_{298} = -25.4 kcal/mol. Reaction A involves the nominal composition SiO(s) which is treated as an intimate mixture of $0.5Si(c)+0.5SiO_2$(high cristobalite). X-ray studies (13, 14) suggest that the condensed "SiO" used in (4, 8) is probably a mixture of Si and amorphous or vitreous SiO_2. The adopted ΔHf° corresponds to D_0° = 190±3 kcal/mol. This may be compared with D_0'' = 179 kcal/mol obtained by linear Birge-Sponer extrapolation of the ground state vibrational constants and with D_0 = 185±7 kcal/mol obtained by Barrow (15) from D_0'(LBX) = 77.5 kcal/mol for the excited state at 52580 cm^{-1}. Barrow assumed D_0'/D_0'(LBX) = 0.456 based on related molecules.

Source	Reaction	Method	Range, T°K	No. of Points	ΔHr°_{298}, kcal/mol		Drift eu	ΔHf°_{298} kcal/mol
2. Ramstad (1961)	A	Carrier gas	1510-1758	6	80.2±2.3	85.08	3.0±1.4	-23.1
3. Bergman (1959)	A	ΔHs by explosion	---	-	-	87±2	-	-22
4. Gunther (1958)	A*	Knudsen wt. gain	1202-1520	18	97.0±0.7	86.76	-7.6±0.5	-21.5
5. Porter (1955)	A**	Knudsen mass spec.	1345-1463	2	105.1	87.35	-13	-20.9
6. Tombs (1952)	A	Carrier gas	1573-1920	7	66.4±1.1	84.75	11 ±1	-23.5
7. Schafer (1950)	A	Knudsen wt. loss	1336-1460	21	78.7±1.5	82.74	2.9±1.0	-25.5
8. Gel'd (1948)	A*	Knudsen wt. loss	1173-1428	11	77.2±1.8	85.87	6.8±1.4	-22.3
2. Ramstad (1961)	B***	Carrier gas	1698-1873	4	142.6±0.7	133.79	-4.9±0.4	-24.8
2. Bowles (1961)	B***	Carrier gas	1703-1898	-	135	132.3	-2	-26.3
6. Tombs (1952)	B***	Carrier gas	1501-1926	23	88 ± 3	127.3	22±2	-31.3
9. Grube (1949)	B***	Carrier gas	1473-1773	4	112±3	134.4	13±2	-24.2
10. Nesmeyanov (1960)	C**	Knudsen collection	1653-1739	24	-	-	-	-20.5
11. Yang (1958)	C	Knudsen wt. loss	1818-1960	15	199.3±3.4	194.5	-2±1.8	-21.9
5. Porter (1955)	C	Knudsen mass spec.	1800-1900	2	130	184.4	29	-32.0
12. Cochran (1962)	D	Knudsen effusion	?	-	-	11.5	-	-25.3

A. $0.5SiO_2$(high cristo.)$+0.5Si(c,\ell) = SiO(g)$

B. SiO_2(high cristo)$+H_2(g) = H_2O(g)+SiO(g)$

C. SiO_2(high cristo.) $= 0.5O_2(g)+SiO(g)$

D. $SiO_2(\ell)+Mg(g) = MgO(c)+SiO(g)$

*Starting material was "SiO" **Starting material was tridymite ***Starting material was quartz

Heat Capacity and Entropy

All constants for the ground state and the $A^1\Pi$ State at 42640 cm^{-1} are taken from the analysis of the A→X system reported by Lagerqvist (16). An intercombination transition has been observed and assigned as $^1\Sigma^- \leftarrow a^3\Pi_r$ by Verma (17). The value of the a-X excitation energy is unknown but is estimated here as 30000±5000 cm^{-1} by comparison with the a and A states of CO and AℓCl. Several additional excited states are known (15, 16) to lie near or above the A state, but they are omitted because their contribution to the thermal functions is negligible.

References

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Titanium Monoxide, Alpha (α-TiO)

(Crystal) GFW = 63.8994

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.476	-123.476	-123.476	INFINITE
100	3.051	5.259	19.036	-1.378	-123.859	-122.118	266.890
200	7.333	8.811	13.012	-.840	-124.128	-120.254	131.408
298	9.550	12.200	12.200	.000	-124.190	-118.338	86.744
300	9.574	12.259	12.200	.018	-124.190	-118.302	86.183
400	10.787	15.192	12.592	1.040	-124.141	-116.344	63.567
500	11.610	17.692	13.368	2.162	-124.030	-114.407	50.007
600	12.238	19.866	14.274	3.355	-123.881	-112.496	40.977
700	12.755	21.793	15.213	4.606	-123.705	-110.613	34.535
800	13.201	23.525	16.146	5.904	-123.516	-108.755	29.710
900	13.602	25.104	17.055	7.244	-123.319	-106.922	25.964
1000	13.970	26.556	17.933	8.623	-123.117	-105.110	22.972
1100	14.314	27.904	18.779	10.037	-122.912	-103.319	20.528
1200	14.640	29.163	19.592	11.485	-123.640	-101.509	18.487
1300	14.953	30.348	20.375	12.965	-123.303	-99.680	16.758
1400	15.255	31.467	21.127	14.475	-122.953	-97.876	15.279
1500	15.548	32.529	21.852	16.016	-122.593	-96.096	14.001
1600	15.835	33.542	22.552	17.585	-122.226	-94.341	12.886
1700	16.115	34.510	23.227	19.182	-121.852	-92.610	11.906
1800	16.391	35.439	23.880	20.808	-121.476	-90.901	11.037
1900	16.663	36.333	24.512	22.460	-121.098	-89.213	10.262
2000	16.931	37.194	25.124	24.140	-125.166	-87.390	9.550
2100	17.197	38.027	25.719	25.847	-124.762	-85.511	8.899
2200	17.460	38.833	26.297	27.579	-124.336	-83.653	8.310
2300	17.721	39.615	26.859	29.339	-123.884	-81.814	7.774
2400	17.980	40.375	27.406	31.124	-123.410	-79.994	7.284
2500	18.237	41.114	27.940	32.934	-122.914	-78.196	6.836

Dec. 31, 1960; Mar. 31, 1967

TITANIUM MONOXIDE, ALPHA (α-TiO) (CRYSTAL) GFW = 63.8994

$S°_{298.15}$ = [12.2] gibbs/mol

Tt = 1264°K

$\Delta Hf°_0 = -123.48 \pm 1$ kcal/mol

$\Delta Hf°_{298.15} = -124.19 \pm 1$ kcal/mol

$\Delta Ht° = 0.83$ kcal/mol

$\Delta Hs°_{298.15} = 128 \pm 10$ kcal/mol

Heat of Formation.

G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), determined the heat of combustion $\Delta Hr°_{298} = -101.61 \pm 0.12$ kcal/mol for the reaction $TiO(\alpha) + 1/2O_2(g) = TiO_2(rutile)$. Based on this result and on $\Delta Hf°_{298}(rutile) = -225.8 \pm 1$ kcal/mol, the adopted $\Delta Hf°_{298}$ for TiO(α) is calculated to be -124.19 ± 1 kcal/mol. A value of -125.4 ± 0.4 kcal/mol was reported by S. M. Ariya, M. P. Morozova and E. Vol'f, Russ. J. Inorg. Chem. (English Transl.) 2, 16 (1957), who measured the heats of combustion of various compositions in the Ti-O system. Ariya et al. used an estimated correction for the formation of TiO_{2-x}, while Humphrey obtained values of 0.2 - 0.4 kcal/mol by grinding the product and reburning it with white oil. Most of the assigned uncertainty arises from this problem of non-stoichiometry [see TiO_2(rutile) for further details].

Heat Capacity and Entropy.

The low temperature heat capacities, 52.6 - 296.3°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). The high temperature enthalpies, 357.0 - 1771°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by use of drop calorimetry. The high temperature Cp's, 357 - 1200.5°K, derived from the enthalpy data, are joined smoothly with the low temperature heat capacities at 298°K. The Cp values above 1200°K are obtained by extrapolation. The entropy is obtained from Cp° using $S°_{50} = 4.13$ eu; this extrapolation includes 0.23, 1.7 and 2.2 eu for contributions of the lattice, of vacancies and of spin magnetic effects, respectively.

P. W. Gilles, J. Chem. Phys. (in press), discussed the inconsistencies in the thermodynamic properties of TiO as derived from widely different measurements. These inconsistencies include(1) a difference of 10 kcal/mol in $D°_0$ values for TiO(g) obtained from vaporization of TiO and Ti_3O_5,(2) a difference of about 10 kcal/mol between the calorimetric data for TiO(β) and a recent re-assessment of the partial free energy of dissociation for the TiO system, and(3) emf. data which suggest that the entropy of TiO(β) should be increased relative to those of Ti and Ti_2O_3. In order to minimize these discrepancies, we tentatively increase the experimental value of $S°_{298}$ by addition of estimated contributions due to vacancies in the crystal lattice and to spin-magnetic effects of Ti^{++} ion.

P. Ehrlich, Z. Elektrochem. 45, 362 (1939) and Z. Anorg. Chem. 247, 53 (1941), concluded from the difference in pycnometric and X-ray densities of TiO(β) that about 15 percent of the Ti and O lattice sites are vacant. This was confirmed later by S. Anderson, B. Collen, U. Kuylenstierna and A. Magneli, Acta. Chem. Scand. 11, 1641 (1957), A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), and M. E. Straumanis and H. W. Li, Z. Anorg. Allgem. Chem. 305, 143 (1960). Andersson et al. noted that there may be a "close structural kinship" between the α and β forms, based on the similarity of their densities and the pronounced relationship between their powder diffraction patterns. The authors suggested that the (presumably) random vacancies in TiO(β) may occur in an ordered way in TiO(α). Recent electron diffraction studies by J. M. Cowley, Acta Cryst. (to be published), may provide an answer to this problem. Assuming the vacancies to be randomly arranged, we estimate the residual entropy of TiO(α) due to vacancies as $-2R(0.85 \ln 0.85 + 0.15 \ln 0.15) = 1.7$ eu, based on the method proposed by M. Hoch, A. S. Iyer and J. Nelken, J. Phys. Chem. Solids 23, 1463 (1962). An alternative possibility for increasing the entropy of TiO(β) is discussed in the Transition Data section of the table for TiO(β).

Metallic-type conductivity of TiO(α) at temperatures 80 - 1000°K was reported by A. D. Pearson, loc. cit., and F. J. Morin, Phys. Rev. Letters 3, 34 (1959). This led J. B. Goodenough, Phys. Rev. 117, 1442 (1960), to suggest the existence of strong cation-cation interactions and the possibility of a low temperature transformation of the martensitic or antiferromagnetic type. Goodenough noted that the isoelectric compound VN becomes superconducting below 8.2°K. We approximate the entropy contribution of these various possibilities at 50°K by a spin-magnetic term of $R\ln 3 = 2.2$ eu.

Transition Data.

See TiO(β) table.

Heat of Sublimation.

The difference between $\Delta Hf°_{298}$ for TiO(g) and TiO(α) is $\Delta Hs°_{298}$.

Titanium Monoxide, Beta (β - TiO)

(Crystal) GFW = 63.8994

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	9.550	12.372	12.372	.000	- 123.872	- 118.071	86.549
300	9.574	12.431	12.372	.018	- 123.872	- 118.035	85.989
400	10.787	15.364	12.764	1.040	- 123.823	- 116.095	63.431
500	11.610	17.864	13.540	2.162	- 123.712	- 114.175	49.906
600	12.238	20.038	14.446	3.355	- 123.563	- 112.281	40.898
700	12.755	21.965	15.385	4.606	- 123.387	- 110.415	34.473
800	13.201	23.697	16.318	5.904	- 123.198	- 108.575	29.661
900	15.290	25.276	17.227	7.244	- 123.001	- 106.758	25.924
1000	15.489	26.897	18.114	8.783	- 122.639	- 104.973	22.942
1100	15.688	28.383	18.981	10.342	- 122.289	- 103.223	20.509
1200	15.587	29.756	19.822	11.921	- 122.886	- 101.467	18.480
1300	16.086	31.036	20.636	13.520	- 122.430	- 99.701	16.761
1400	16.285	32.235	21.422	15.138	- 121.972	- 97.970	15.294
1500	16.484	33.365	22.181	16.777	- 121.514	- 96.271	14.027
1600	16.683	34.436	22.914	18.435	- 121.058	- 94.603	12.922
1700	16.882	35.453	23.622	20.113	- 120.603	- 92.964	11.951
1800	17.081	36.424	24.306	21.811	- 120.155	- 91.352	11.092
1900	17.280	37.353	24.969	23.529	- 119.711	- 89.764	10.325
2000	17.479	38.244	25.610	25.267	- 123.721	- 88.045	9.621
2100	17.678	39.102	26.232	27.025	- 123.266	- 86.272	8.978
2200	17.877	39.929	26.836	28.803	- 122.794	- 84.523	8.397
2300	18.076	40.728	27.423	30.601	- 122.304	- 82.794	7.867
2400	18.274	41.501	27.994	32.418	- 121.798	- 81.084	7.384
2500	18.473	42.251	28.549	34.255	- 121.275	- 79.400	6.941

Mar. 31, 1967

TITANIUM MONOXIDE, BETA (β-TiO) (CRYSTAL) GFW = 63.8994

$S^\circ_{298.15}$ = [12.372] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-123.872] kcal/mol

Tt = 1264°K ΔHt° = 0.83 kcal/mol

Tm = 2023°K ΔHm° = [13] kcal/mol

Heat of Formation.

The $\Delta Hf^\circ_{298}(\beta)$ is obtained from $\Delta Hf^\circ_{298}(\alpha)$ by adding ΔHt° and the difference between $H^\circ_{1264} - H^\circ_{298}$ for TiO(α) and TiO(β).

Heat Capacity and Entropy.

High temperature enthalpies, 1273 - 1771°K, have been measured with a drop calorimeter by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946). The adopted heat capacities are derived from these data, assuming the final state to be TiO(α). This problem is discussed in the Transition Data section. Cp values below 900°K are assumed to be the same as those for TiO(α). The heat capacities at temperatures 900 - 1273°K and above 1771°K are obtained by extrapolation.

The S°_{298} is derived in a manner analogous to that of the heat of formation.

Transition Data.

Tt and ΔHt° are derived from the enthalpy data of Naylor, loc. cit., assuming that TiO(α)is the final state of the drop experiment. The X-ray studies of C. C. Wang and N. J. Grant, J. Metals 8, 184 (1956), and A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), appear to contradict this assumption. These authors found that the α form of stoichiometric TiO was obtained at room temperature only by annealing the β phase for long periods below 1223°K. Samples quenched from temperatures of 1223°K or higher retained the NaCl structure of the β form. Since the drop calorimetric experiment is similar to quenching, it is possible that the final state was mostly the β form. If this is the case, then the derived values of ΔHt° and ΔSt° are probably much too small. This would be an alternative means for increasing the entropy of TiO(β). It is possible, however, that differences in particle size allowed Naylor's sample to drop to the α form, or that the β form was stabilized by impurities in the X-ray studies. Further experiments are desirable in order to resolve this question. Also related to the question is the fact that the structure of TiO(α) has not been reported, probably because the X-ray diffraction pattern is quite complex.

P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), reviewed the phase data and presented the most current phase diagram for the Ti-O system. This diagram suggests that stoichiometric TiO(α) starts to transform near 1210°K with formation of the two phases $TiO_{1+x}(\beta)$ and Ti_2O. Transformation to stoichiometric TiO(β) is complete near 1270°K, which is essentially the Tt chosen by Naylor. This behavior is consistent with Naylor's observation of "pre-transition effects" in the enthalpy between 1224 and 1264°K.

Melting Data.

See TiO(l) table for details.

Titanium Monoxide (TiO)

(Liquid) GFW = 63.8994

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.000	14.235	14.235	.000	- 112.801	- 107.556	78.841
300	16.000	14.333	14.235	.030	- 112.789	- 107.523	78.331
400	16.000	18.936	14.862	1.630	- 112.162	- 105.563	57.841
500	16.000	22.507	16.047	3.230	- 111.574	- 104.358	45.615
600	16.000	25.424	17.374	4.830	- 111.017	- 102.968	37.506
700	16.000	27.890	18.705	6.430	- 110.492	- 101.668	31.742
800	16.000	30.027	19.990	8.030	- 110.001	- 100.442	27.439
900	16.000	31.911	21.212	9.630	- 109.544	- 99.274	24.107
1000	16.000	33.597	22.367	11.230	- 109.122	- 98.156	21.452
1100	16.000	35.122	23.459	12.830	- 108.730	- 97.078	19.288
1200	16.000	36.514	24.490	14.430	- 109.306	- 95.997	17.483
1300	16.000	37.795	25.464	16.030	- 108.849	- 94.907	15.955
1400	16.000	38.981	26.388	17.630	- 108.410	- 93.852	14.651
1500	16.000	40.084	27.265	19.230	- 107.990	- 92.825	13.525
1600	16.000	41.117	28.099	20.830	- 107.592	- 91.827	12.543
1700	16.000	42.087	28.893	22.430	- 107.216	- 90.854	11.680
1800	16.000	43.002	29.652	24.030	- 106.865	- 89.903	10.916
1900	16.000	43.867	30.377	25.630	- 106.540	- 88.970	10.234
2000	16.000	44.687	31.073	27.230	- 110.688	- 87.898	9.605
2100	16.000	45.468	31.740	28.830	- 110.390	- 86.765	9.030
2200	16.000	46.212	32.381	30.430	- 110.096	- 85.648	8.508
2300	16.000	46.924	32.998	32.030	- 109.804	- 84.545	8.034
2400	16.000	47.605	33.592	33.630	- 109.515	- 83.451	7.599
2500	16.000	48.258	34.166	35.230	- 109.229	- 82.372	7.201
2600	16.000	48.885	34.720	36.830	- 108.945	- 81.302	6.834
2700	16.000	49.489	35.256	38.430	- 108.664	- 80.244	6.495
2800	16.000	50.071	35.775	40.030	- 108.386	- 79.197	6.182
2900	16.000	50.632	36.277	41.630	- 108.110	- 78.156	5.890
3000	16.000	51.175	36.765	43.230	- 107.836	- 77.130	5.619
3100	16.000	51.699	37.238	44.830	- 107.565	- 76.108	5.366
3200	16.000	52.207	37.698	46.430	- 107.296	- 75.101	5.129
3300	16.000	52.700	38.145	48.030	- 107.029	- 74.100	4.907
3400	16.000	53.177	38.581	49.630	- 106.764	- 73.103	4.699
3500	16.000	53.641	39.004	51.230	- 106.501	- 72.119	4.503
3600	16.000	54.092	39.417	52.830	- 207.866	- 70.877	4.303
3700	16.000	54.530	39.820	54.430	- 207.579	- 67.075	3.962
3800	16.000	54.957	40.212	56.030	- 207.307	- 63.285	3.640
3900	16.000	55.373	40.596	57.630	- 207.049	- 59.498	3.334
4000	16.000	55.778	40.970	59.230	- 206.806	- 55.718	3.044
4100	16.000	56.173	41.336	60.830	- 206.577	- 51.942	2.769
4200	16.000	56.558	41.694	62.430	- 206.362	- 48.173	2.507
4300	16.000	56.935	42.044	64.030	- 206.160	- 44.411	2.257
4400	16.000	57.303	42.387	65.630	- 205.970	- 40.654	2.019
4500	16.000	57.662	42.722	67.230	- 205.793	- 36.894	1.792

Dec. 31, 1960; Mar. 31, 1967

TITANIUM MONOXIDE (TiO) (LIQUID) GFW = 63.8994

$S^\circ_{298.15}$ = [14.235] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-112.801] kcal/mol

Tm = 2023°K ΔHm° = [13] kcal/mol

Tb = [3934] °K ΔHv° = [91.6] kcal/mol

Heat of Formation.

The value of ΔHf°_{298} for TiO(l) is obtained from that of TiO(β) by adding ΔHm° and the difference between $H^\circ_{2023} - H^\circ_{298}$ for TiO(β) and TiO(l).

Heat Capacity and Entropy.

The heat capacity for TiO(l) is estimated on the basis of 8 cal/g-atom. S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data.

Tm is taken from W. Dawihl and K. Schröter, Z. Anorg. Allgem. Chem. 233, 178 (1937). The heat of melting is estimated by comparison with that of VO(c) reported by C. E. Wicks and F. E. Block, U. S. Bur. Mines Bull. 605, 1963.

Tm has also been reported as 2023 and 2103°K by H. Nishimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20, 589 (1956), and R. DeVries, R. Roy, and E. Osborne, Trans. Brit. Ceram. Soc. 53, 525 (1954), respectively. According to the Ti-O phase diagram reported by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), TiO melts incongruently.

Vaporization Data.

Tb is calculated as the temperature at which the Gibbs energy change of the reaction TiO(l) = TiO(g) approaches zero. The difference between ΔHf° for TiO(g) and TiO(l) at Tb is ΔHv°.

Titanium Monoxide (TiO)

(Ideal Gas) GFW = 63.8994

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.290	3.649	3.649	INFINITE
100	7.801	47.655	62.774	-1.512	3.947	1.448	-3.164
200	7.551	52.929	56.692	-.752	3.900	-1.050	1.148
298	7.810	55.987	55.987	.000	3.750	-3.453	2.531
300	7.816	56.035	55.987	.014	3.747	-3.498	2.548
400	8.127	58.327	56.297	.812	3.571	-5.886	3.216
500	8.374	60.169	56.893	1.638	3.385	-8.230	3.597
600	8.558	61.713	57.571	2.485	3.189	-10.535	3.837
700	8.695	63.043	58.260	3.348	2.977	-12.806	3.998
800	8.797	64.211	58.932	4.223	2.743	-15.045	4.110
900	8.874	65.251	59.578	5.106	2.483	-17.252	4.189
1000	8.933	66.190	60.193	5.997	2.196	-19.431	4.247
1100	8.978	67.043	60.777	6.892	1.883	-21.577	4.287
1200	9.013	67.826	61.333	7.792	.607	-23.658	4.309
1300	9.041	68.549	61.860	8.695	.367	-25.671	4.316
1400	9.063	69.219	62.362	9.600	.112	-27.664	4.319
1500	9.081	69.845	62.840	10.507	-.162	-29.638	4.318
1600	9.096	70.432	63.297	11.416	-.454	-31.594	4.315
1700	9.109	70.984	63.733	12.326	-.768	-33.531	4.311
1800	9.121	71.505	64.150	13.238	-1.106	-35.449	4.304
1900	9.133	71.998	64.551	14.150	-1.468	-37.347	4.296
2000	9.145	72.467	64.935	15.064	-6.302	-39.072	4.270
2100	9.158	72.913	65.304	15.980	-6.689	-40.699	4.236
2200	9.172	73.340	65.660	16.896	-7.079	-42.312	4.203
2300	9.188	73.748	66.003	17.814	-7.469	-43.904	4.172
2400	9.206	74.139	66.334	18.734	-7.860	-45.478	4.141
2500	9.226	74.515	66.653	19.655	-8.253	-47.034	4.112
2600	9.248	74.878	66.963	20.579	-8.645	-48.584	4.084
2700	9.272	75.227	67.262	21.505	-9.038	-50.111	4.056
2800	9.299	75.565	67.553	22.433	-9.431	-51.626	4.030
2900	9.328	75.892	67.835	23.365	-9.824	-53.124	4.004
3000	9.359	76.208	68.109	24.299	-10.216	-54.609	3.978
3100	9.393	76.516	68.375	25.237	-10.607	-56.082	3.954
3200	9.430	76.815	68.634	26.178	-10.997	-57.547	3.930
3300	9.468	77.105	68.886	27.123	-11.385	-58.992	3.907
3400	9.508	77.389	69.132	28.071	-11.772	-60.431	3.884
3500	9.551	77.665	69.372	29.024	-12.156	-61.857	3.863
3600	9.594	77.934	69.606	29.982	-114.163	-63.006	3.825
3700	9.640	78.198	69.835	30.943	-114.515	-61.583	3.638
3800	9.686	78.456	70.058	31.910	-114.876	-60.150	3.459
3900	9.734	78.708	70.277	32.881	-115.247	-58.703	3.290
4000	9.782	78.955	70.491	33.856	-115.628	-57.249	3.128
4100	9.831	79.197	70.700	34.837	-116.019	-55.782	2.973
4200	9.881	79.435	70.905	35.823	-116.418	-54.313	2.826
4300	9.931	79.668	71.106	36.813	-116.825	-52.828	2.685
4400	9.981	79.897	71.304	37.809	-117.240	-51.337	2.550
4500	10.030	80.121	71.497	38.809	-117.662	-49.829	2.420
4600	10.080	80.342	71.687	39.815	-118.090	-48.313	2.295
4700	10.129	80.560	71.873	40.825	-118.525	-46.796	2.176
4800	10.178	80.773	72.057	41.841	-118.965	-45.261	2.061
4900	10.225	80.984	72.237	42.861	-119.410	-43.730	1.950
5000	10.272	81.191	72.414	43.886	-119.860	-42.177	1.844
5100	10.319	81.395	72.588	44.915	-120.314	-40.619	1.741
5200	10.364	81.596	72.759	45.949	-120.772	-39.054	1.641
5300	10.407	81.793	72.928	46.988	-121.233	-37.474	1.545
5400	10.450	81.988	73.094	48.031	-121.697	-35.889	1.452
5500	10.492	82.180	73.257	49.078	-122.163	-34.292	1.363
5600	10.532	82.370	73.418	50.129	-122.633	-32.699	1.276
5700	10.570	82.557	73.577	51.184	-123.102	-31.087	1.192
5800	10.608	82.741	73.733	52.243	-123.575	-29.467	1.110
5900	10.643	82.922	73.888	53.306	-124.048	-27.837	1.031
6000	10.678	83.102	74.040	54.372	-124.523	-26.210	.955

Dec. 31, 1960; Mar. 31, 1967

TITANIUM MONOXIDE (TiO) (IDEAL GAS) GFW = 63.8994

Ground State Configuration $3\Delta_r$

$S^\circ_{298.15}$ = 56.0 gibbs/mol

ΔHf°_0 = 3.65 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 3.75 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	2289.0	1	18502.0	2
66.7	2	11395.4	2	19434.6	2
141.3	2	14242.6	6	19499.4	2
581.0	2	16312.0	6	19565.2	2

ω_e = 1008.4 cm^{-1} $\omega_e x_e$ = 4.61 cm^{-1} σ = 1

B_e = 0.5355 cm^{-1} α_e = 0.0031 cm^{-1} r_e = 1.62 Å

Heat of Formation.

P. W. Gilles, J. Chem. Phys. (to be published), has discussed the difference of about 10 kcal/mol in the dissociation energies of TiO(g) obtained from vaporization of $Ti_3O_5(\beta)$ and TiO(β). By mass spectrometric and Knudsen effusion techniques, P. G. Wahlbeck and P. W. Gilles, J. Chem. Phys. 46, 2465 (1967), studied congruently vaporizing $Ti_3O_5(\beta)$ and derived D°_0(TiO, g) = 7.26 ± 0.10 eV. Values of 6.88, 6.93 and 6.8 eV were derived from incongruently vaporizing TiO(β) in earlier studies reported by G. D. Wheatley, Ph. D. Thesis, University of Kansas, 1954; W. O. Groves, M. Hoch, and H. L. Johnston, J. Phys. Chem. 59, 127 (1955); and J. Berkowitz, W. A. Chupka, and M. G. Inghram, J. Phys. Chem. 61, 1569 (1957). A spectroscopic value of 6.8 eV is obtained by Birge-Sponer extrapolation of the vibrational constants given on this table. Related discrepancies are listed in the Heat Capacity and Entropy section of the table for TiO(α).

G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, reported D°_0 = 6.9 eV.

In order to minimize these discrepancies, we tentatively increase the entropy of TiO(α) [see TiO(α) table for details] and re-evaluate the vapor pressure data by the second and third law methods. The results are given in the table below. Values derived from TiO(β) are uncertain due to excess oxygen in the condensed phase; e.g., the sample of Groves et al. contained an excess of about 3%. Our analysis assumes that the activity of TiO is unity in the actual condensed phase. The value of ΔHf°_{298}(TiO, g) adopted is 3.75 ± 5 kcal/mol.

Investigator	Reaction	Temperature, °K	No. of Points	ΔHr°_{298}, kcal/mol 2nd law	ΔHr°_{298}, kcal/mol 3rd law	Drift eu	ΔHf°_{298}* kcal/mol
Wahlbeck-Gilles	(A)	1837 - 2014	24	711.3 ± 7.7	715.72	2.2 ± 4.1	3.75
Groves et al.	(B)	1847 - 1968	8	157.7 ± 5.0	128.7	-15.1 + 2.6	4.83
Berkowitz et al.	(B)	2027, 2072	2	139.4**	129.4		5.53

(A) $Ti_3O_5(\beta) = TiO(g) + 2O(g)$. (B) $TiO(\beta) = TiO(g)$

*Calculation based on the third law ΔHr°_{298} value. The corresponding D°_0(TiO, g) values are 167.83, 166.75 and 166.05 kcal/mol.

**Average 2nd law value from ion intensities.

Heat Capacity and Entropy.

The electronic spectrum of TiO(g) consists of both singlet and triplet systems with near-degenerate low-lying states. The lowest-lying triplet was originally thought to be $^3\Pi$ by Herzberg, loc. cit., B. Rosen, "Selected Constants," Hermann & Co., Paris, 1951, and J. G. Phillips, J. Astrophys. 115, 567 (1952); ibid., 119, 274 (1954), but has been reidentified as $X^3\Delta_r$ by U. Uhler, Dissertation, University of Stockholm, Sweden, 1954, and W. Weltner, Jr. and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965). The values of the three lowest electronic levels and quantum weights are obtained from Herzberg. A $a^1\Delta$ state lying about 581 cm^{-1} above the ground state was reported by Phillips, loc. cit. A. V. Pettersson and B. Lindgren, Arkiv Fysik 22, 491 (1962); A. V. Pettersson, ibid., 16, 185 (1959), reported two electronic states, $d^1\Sigma$ and $b^1\Pi$, at 1708.0 and 10814.4 cm^{-1} above $^1\Delta$; thus, the values of 2289 and 11395.4 are derived. The next two electronic levels, $^3\Phi$ and $^3\Pi$, are obtained from Weltner et al., and the value $^1\Phi$ = 18502 cm^{-1} is obtained from Rosen. The last three levels and the values of $\omega_e x_e$, ω_e, B_e, α_e and r_e are taken from Herzberg, loc. cit. The moment of inertia is 5.226 x 10^{-39} g cm^2.

The rather thorough studies of the emission spectra of TiO(g) have been summarized by R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 3rd Ed., John Wiley & Sons, Inc., New York, 1963, and A. Gatterer, J. Junkes, E. W. Salpeter, and B. Rosen, "Molecular Spectra of Metallic Oxides," Vatican Press, Vatican City, 1957.

Tungsten Monoxide (WO)

(Ideal Gas) GFW = 199.8494

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.093	101.734	101.734	INFINITE
100	6.956	51.045	65.023	- 1.398	101.926	99.121	- 216.628
200	7.017	55.876	59.378	- .701	101.795	96.354	- 105.291
298	7.287	58.722	58.722	.000	101.600	93.725	- 68.702
300	7.294	58.767	58.722	.013	101.596	93.676	- 68.243
400	7.646	60.914	59.012	.781	101.399	91.065	- 49.756
500	7.947	62.654	59.572	1.541	101.212	88.503	- 38.685
600	8.176	64.124	60.211	2.348	101.031	85.979	- 31.318
700	8.346	65.398	60.863	3.174	100.847	83.485	- 26.065
800	8.472	66.521	61.502	4.015	100.656	81.017	- 22.133
900	8.567	67.524	62.116	4.867	100.459	78.575	- 19.081
1000	8.640	68.431	62.703	5.728	100.252	76.154	- 16.644
1100	8.698	69.257	63.262	6.595	100.036	73.754	- 14.654
1200	8.744	70.016	63.793	7.467	99.809	71.376	- 12.999
1300	8.781	70.717	64.299	8.343	99.571	69.016	- 11.603
1400	8.813	71.369	64.781	9.223	99.322	66.674	- 10.408
1500	8.839	71.978	65.241	10.106	99.061	64.352	- 9.376
1600	8.862	72.549	65.680	10.991	98.788	62.047	- 8.475
1700	8.881	73.087	66.100	11.878	98.503	59.760	- 7.683
1800	8.899	73.595	66.503	12.767	98.206	57.489	- 6.980
1900	8.915	74.077	66.889	13.658	97.896	55.235	- 6.353
2000	8.930	74.535	67.260	14.550	97.573	52.997	- 5.791
2100	8.945	74.971	67.616	15.444	97.238	50.777	- 5.284
2200	8.959	75.387	67.960	16.339	96.888	48.572	- 4.825
2300	8.974	75.786	68.292	17.236	96.527	46.383	- 4.407
2400	8.989	76.168	68.612	18.134	96.152	44.213	- 4.026
2500	9.005	76.535	68.922	19.033	95.763	42.056	- 3.677
2600	9.022	76.889	69.221	19.935	95.363	39.915	- 3.355
2700	9.040	77.230	69.512	20.838	94.944	37.790	- 3.059
2800	9.061	77.559	69.793	21.743	94.498	35.683	- 2.785
2900	9.082	77.877	70.067	22.650	94.017	33.589	- 2.531
3000	9.106	78.185	70.332	23.559	93.493	31.518	- 2.296
3100	9.132	78.484	70.590	24.471	92.918	29.459	- 2.077
3200	9.161	78.775	70.842	25.386	92.284	27.420	- 1.873
3300	9.191	79.057	71.086	26.304	91.584	25.404	- 1.682
3400	9.224	79.332	71.325	27.224	90.810	23.410	- 1.505
3500	9.259	79.600	71.557	28.148	89.950	21.440	- 1.339
3600	9.296	79.861	71.784	29.076	88.978	19.496	- 1.184
3700	9.336	80.116	72.006	30.008	79.563	17.628	- 1.041
3800	9.377	80.366	72.223	30.943	79.156	15.960	- .918
3900	9.420	80.610	72.435	31.883	78.752	14.302	- .801
4000	9.466	80.849	72.642	32.827	78.350	12.654	- .691
4100	9.513	81.083	72.845	33.776	77.951	11.019	- .587
4200	9.561	81.313	73.044	34.730	77.557	9.391	- .489
4300	9.611	81.539	73.239	35.689	77.165	7.772	- .395
4400	9.663	81.760	73.430	36.652	76.777	6.162	- .306
4500	9.715	81.978	73.618	37.621	76.394	4.560	- .221
4600	9.768	82.192	73.802	38.595	76.014	2.971	- .141
4700	9.822	82.403	73.983	39.575	75.639	1.386	- .064
4800	9.876	82.610	74.160	40.560	75.268	- .188	.009
4900	9.931	82.814	74.335	41.550	74.902	- 1.758	.078
5000	9.985	83.016	74.506	42.546	74.540	- 3.322	.145
5100	10.040	83.214	74.675	43.547	74.183	- 4.874	.209
5200	10.095	83.409	74.841	44.554	73.831	- 6.421	.270
5300	10.149	83.602	75.005	45.566	73.484	- 7.959	.328
5400	10.203	83.792	75.166	46.584	73.141	- 9.493	.384
5500	10.256	83.980	75.324	47.607	72.803	- 11.020	.438
5600	10.309	84.165	75.480	48.635	72.469	- 12.541	.489
5700	10.360	84.348	75.634	49.668	72.141	- 14.060	.539
5800	10.411	84.529	75.786	50.707	71.817	- 15.569	.587
5900	10.460	84.707	75.936	51.750	71.497	- 17.067	.632
6000	10.509	84.883	76.084	52.799	- 122.722	- 16.483	.600

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN MONOXIDE (WO) (IDEAL GAS) GFW = 199.8494

Ground State Configuration $[^3\Sigma^-]$

$S^\circ_{298.15}$ = [58.7] gibbs/mol

ΔHf°_0 = 101.7 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 101.6 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
[0]	[3]
[14160]	[1]
[17211]	[2]
[19189]	[6]

ω_e = 1055 cm^{-1} $\omega_e x_e$ = [3.85] cm^{-1} σ = 1

B_e = [0.3498] cm^{-1} α_e = [0.0016] cm^{-1} r_e = [1.81] Å

Heat of Formation

The heat of formation, $\Delta Hf^\circ_{298}(WO,g)$ = 101.6 kcal/mol, was derived from the heat of reaction, ΔHr°_{298} = -42.0 kcal/mol for $WO(g) \rightarrow W(c) + O(g)$ with all JANAF auxiliary data. The value of ΔHr°_{298} was calculated by the third law method from the partial pressure data, which were determined mass-spectrometrically in the temperature range 2188° to 2475°K, by G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960). The drift in the third law analysis was -20 ± 7 eu.

Heat Capacity and Entropy

The fundamental vibrational frequency, the ground state configuration, and the probable electronic levels for tungsten monoxide (g) were obtained from the infrared and ultraviolet spectroscopic investigations by matrix isolation by W. Weltner, Jr., and D. McLeod, Jr., J. Mol Spectry. 17, 276 (1965). The rotational constant B_e was calculated from an estimated bond distance, W-O = 1.81 Å. The value of x_e was calculated from the relation $x_e u_e^{1/2}$ = 0.014 which was given by R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) 219A, 120 (1953). The constant, 0.014, was estimated, based on those for ZrO(g) and VO(g). The value of α_e was calculated from the Morse potential function.

Zirconium Monoxide (ZrO)

(Ideal Gas) Mol. Wt. = 107.2194

T, °K.	C°_p	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.100	14.255	14.255	INFINITE
100	6.957	46.626	60.673	-1.405	14.381	12.132	-26.513
200	7.048	51.463	54.995	-.706	14.217	9.937	-10.858
298	7.373	54.332	54.332	.000	14.000	7.882	-5.777
300	7.380	54.378	54.332	.014	13.996	7.844	-5.714
400	7.754	56.553	54.627	.771	13.763	5.828	-3.184
500	8.066	58.318	55.194	1.562	13.518	3.873	-1.693
600	8.343	59.813	55.842	2.383	13.257	1.968	-.717
700	8.644	61.121	56.505	3.232	12.992	.108	-.034
800	9.010	62.299	57.157	4.114	12.737	-1.717	.469
900	9.450	63.385	57.789	5.036	12.507	-3.508	.852
1000	9.948	64.406	58.400	6.006	12.309	-5.276	1.153
1100	10.471	65.378	58.990	7.027	12.141	-7.026	1.396
1200	10.980	66.311	59.562	8.099	11.051	-8.714	1.587
1300	11.443	67.209	60.116	9.221	10.971	-10.359	1.741
1400	11.833	68.072	60.654	10.386	10.921	-11.999	1.873
1500	12.139	68.899	61.176	11.585	10.897	-13.634	1.986
1600	12.358	69.690	61.683	12.811	10.889	-15.268	2.085
1700	12.494	70.444	62.177	14.054	10.888	-16.904	2.173
1800	12.557	71.160	62.656	15.307	10.888	-18.538	2.251
1900	12.561	71.839	63.122	16.563	10.881	-20.172	2.320
2000	12.517	72.483	63.574	17.817	10.861	-21.809	2.383
2100	12.440	73.092	64.013	19.066	10.827	-23.441	2.439
2200	12.340	73.668	64.439	20.305	5.870	-24.906	2.474
2300	12.226	74.214	64.852	21.533	5.790	-26.303	2.499
2400	12.105	74.732	65.253	22.750	5.696	-27.696	2.522
2500	11.984	75.224	65.642	23.954	5.586	-29.086	2.543
2600	11.866	75.691	66.019	25.147	5.463	-30.469	2.561
2700	11.754	76.137	66.386	26.328	5.325	-31.849	2.578
2800	11.651	76.563	66.742	27.498	5.173	-33.225	2.593
2900	11.557	76.970	67.088	28.658	5.010	-34.590	2.607
3000	11.473	77.360	67.424	29.809	4.834	-35.952	2.619
3100	11.400	77.735	67.750	30.953	4.650	-37.311	2.630
3200	11.337	78.096	68.068	32.090	4.455	-38.662	2.640
3300	11.283	78.444	68.377	33.221	4.253	-40.005	2.649
3400	11.239	78.780	68.678	34.347	4.044	-41.341	2.657
3500	11.204	79.105	68.971	35.469	3.829	-42.674	2.665
3600	11.176	79.421	69.257	36.588	3.609	-44.003	2.671
3700	11.156	79.727	69.536	37.704	3.384	-45.322	2.677
3800	11.143	80.024	69.808	38.819	3.157	-46.633	2.682
3900	11.135	80.313	70.074	39.933	2.927	-47.939	2.686
4000	11.133	80.595	70.333	41.046	2.694	-49.242	2.690
4100	11.135	80.870	70.587	42.160	2.460	-50.537	2.694
4200	11.141	81.138	70.835	43.273	2.225	-51.825	2.697
4300	11.151	81.401	71.078	44.388	1.990	-53.111	2.699
4400	11.163	81.657	71.315	45.504	1.754	-54.390	2.701
4500	11.178	81.908	71.548	46.621	1.518	-55.663	2.703
4600	11.195	82.154	71.776	47.739	1.283	-56.930	2.705
4700	11.214	82.395	71.999	48.860	1.049	-58.192	2.706
4800	11.233	82.631	72.218	49.982	-135.617	-57.925	2.637
4900	11.254	82.863	72.433	51.106	-135.905	-56.309	2.511
5000	11.275	83.091	72.644	52.233	-136.196	-54.683	2.390
5100	11.297	83.314	72.851	53.361	-136.490	-53.046	2.273
5200	11.318	83.534	73.054	54.492	-136.787	-51.408	2.161
5300	11.340	83.750	73.254	55.625	-137.087	-49.767	2.052
5400	11.361	83.962	73.451	56.760	-137.390	-48.114	1.947
5500	11.382	84.170	73.644	57.897	-137.693	-46.456	1.846
5600	11.402	84.376	73.833	59.037	-138.000	-44.796	1.748
5700	11.421	84.578	74.020	60.178	-138.307	-43.134	1.654
5800	11.440	84.776	74.204	61.321	-138.616	-41.452	1.562
5900	11.457	84.972	74.385	62.466	-138.925	-39.776	1.473
6000	11.474	85.165	74.563	63.612	-139.235	-38.096	1.388

June 30, 1961; Sept. 30, 1961; Dec. 31, 1965

ZIRCONIUM MONOXIDE (ZrO) (IDEAL GAS) MOL. WT. = 107.2194

Ground State Configuration $^1\Sigma^+$

$S^\circ_{298.15}$ = 54.33 ± 2 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 14.26 ± 12 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 14.0 ± 12 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i cm.$^{-1}$	g_i
0	1	[18000]	2
[4000]	6	[22000]	6
[6000]	2	[25500]	2
15500	2	27300	1
[15700]	6	[28500]	6
[17500]	6		

ω_e = 978 cm.$^{-1}$

B_e = 0.4142 cm.$^{-1}$

$\omega_e x_e$ = 4 cm.$^{-1}$

α_e = 0.0023 cm.$^{-1}$

r_e = 1.711 Å

σ = 1

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = 14.0 ± 12 kcal. mole^{-1} was calculated from the $\Delta H^\circ_{r\ 298.15}$ = 290.342 ± 12.8 kcal. mole^{-1} for the reaction $Zr(c) + ZrO_2(c) = 2ZrO(g)$. The value of $\Delta H^\circ_{r\ 298.15}$ was obtained by the third law analysis from the mass spectrometric studies of W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957). They observed the variation of the ZrO^+ ion intensity over the system $Zr + ZrO_2$ and reported equilibrium constants for the reaction $Zr + ZrO_2 \rightarrow 2ZrO$ in the range 2124-2322°K. The third law drift is -58 ± 28 e.u.

Heat Capacity and Entropy.

The ground state of ZrO(g) was assumed to be $^1\Sigma^+$ as determined from the matrix isolation spectra of W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965). Previously this had been described as the lower state in the A band system reported by V. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955).

All molecular constants were obtained from Uhler and Akerlind,loc. cit.,except ω_e = 978 cm.$^{-1}$ and $\omega_e x_e$ = 4 cm.$^{-1}$ which were calculated from ω and α_e = 0.0023 cm.$^{-1}$ using the equations

$$\alpha_e = \frac{6\sqrt{\omega_e x_e \cdot B_e^{\,3}}}{\omega_e} - \frac{6\,B_e^{\,2}}{\omega_e} \quad \text{and} \quad \omega = \omega_e - 2\,\omega_e x_e = 969.76 \text{ cm.}^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeon,loc. cit.

Oxygen, Diatomic (O_2)

(Reference State - Ideal Gas)   Mol. Wt. = 31.9988

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.075	.000	.000	.000
100	6.958	41.395	55.205	-1.381	.000	.000	.000
200	6.961	46.218	49.643	-.685	.000	.000	.000
298	7.020	49.004	49.004	.000	.000	.000	.000
300	7.023	49.047	49.004	.013	.000	.000	.000
400	7.196	51.091	49.282	.724	.000	.000	.000
500	7.431	52.722	49.812	1.455	.000	.000	.000
600	7.670	54.098	50.414	2.210	.000	.000	.000
700	7.883	55.297	51.028	2.988	.000	.000	.000
800	8.063	56.361	51.629	3.786	.000	.000	.000
900	8.212	57.320	52.209	4.600	.000	.000	.000
1000	8.336	58.192	52.765	5.427	.000	.000	.000
1100	8.439	58.991	53.295	6.266	.000	.000	.000
1200	8.527	59.729	53.801	7.114	.000	.000	.000
1300	8.604	60.415	54.283	7.971	.000	.000	.000
1400	8.674	61.055	54.744	8.835	.000	.000	.000
1500	8.738	61.656	55.185	9.706	.000	.000	.000
1600	8.800	62.222	55.608	10.583	.000	.000	.000
1700	8.858	62.757	56.013	11.465	.000	.000	.000
1800	8.916	63.265	56.401	12.354	.000	.000	.000
1900	8.973	63.749	56.776	13.249	.000	.000	.000
2000	9.029	64.210	57.136	14.149	.000	.000	.000
2100	9.084	64.652	57.483	15.054	.000	.000	.000
2200	9.139	65.076	57.819	15.966	.000	.000	.000
2300	9.194	65.483	58.143	16.882	.000	.000	.000
2400	9.248	65.876	58.457	17.804	.000	.000	.000
2500	9.301	66.254	58.762	18.732	.000	.000	.000
2600	9.354	66.620	59.057	19.664	.000	.000	.000
2700	9.405	66.974	59.344	20.602	.000	.000	.000
2800	9.455	67.317	59.622	21.545	.000	.000	.000
2900	9.503	67.650	59.893	22.493	.000	.000	.000
3000	9.551	67.973	60.157	23.446	.000	.000	.000
3100	9.596	68.287	60.415	24.403	.000	.000	.000
3200	9.640	68.592	60.665	25.365	.000	.000	.000
3300	9.682	68.889	60.910	26.331	.000	.000	.000
3400	9.723	69.179	61.149	27.302	.000	.000	.000
3500	9.762	69.461	61.383	28.276	.000	.000	.000
3600	9.799	69.737	61.611	29.254	.000	.000	.000
3700	9.835	70.006	61.834	30.236	.000	.000	.000
3800	9.869	70.269	62.053	31.221	.000	.000	.000
3900	9.901	70.525	62.267	32.209	.000	.000	.000
4000	9.932	70.776	62.476	33.201	.000	.000	.000
4100	9.961	71.022	62.682	34.196	.000	.000	.000
4200	9.988	71.262	62.883	35.193	.000	.000	.000
4300	10.015	71.498	63.081	36.193	.000	.000	.000
4400	10.039	71.728	63.275	37.196	.000	.000	.000
4500	10.062	71.954	63.465	38.201	.000	.000	.000
4600	10.084	72.176	63.652	39.208	.000	.000	.000
4700	10.104	72.393	63.836	40.218	.000	.000	.000
4800	10.123	72.606	64.016	41.229	.000	.000	.000
4900	10.140	72.814	64.194	42.242	.000	.000	.000
5000	10.156	73.019	64.368	43.257	.000	.000	.000
5100	10.172	73.221	64.540	44.274	.000	.000	.000
5200	10.187	73.418	64.708	45.292	.000	.000	.000
5300	10.200	73.613	64.875	46.311	.000	.000	.000
5400	10.213	73.803	65.038	47.332	.000	.000	.000
5500	10.225	73.991	65.199	48.353	.000	.000	.000
5600	10.237	74.175	65.358	49.377	.000	.000	.000
5700	10.247	74.356	65.514	50.401	.000	.000	.000
5800	10.258	74.535	65.668	51.426	.000	.000	.000
5900	10.267	74.710	65.820	52.452	.000	.000	.000
6000	10.276	74.883	65.970	53.479	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

OXYGEN, DIATOMIC (O_2)   (REFERENCE STATE - IDEAL GAS)   MOL. WT. = 31.9988

Ground State Configuration $^3\Sigma_g^-$ $\Delta H^\circ_{f\ 0} = 0$

$S^\circ_{298.15} = 49.00 \pm 0.01$ cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15} = 0$

$\omega_e = 1580.246$ cm.$^{-1}$ $\omega_e x_e = 12.071$ cm.$^{-1}$ $\sigma = 2$

$B_e = 1.445$ cm.$^{-1}$ $\alpha_e = 0.0158$ cm.$^{-1}$ $r_e = 1.2074$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for O_2(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here are based on those of H. W. Woolley, J. Research, Nat. Bur. Standards 40, 163 (1948), who used a direct summation to 5000°K. The spectroscopic constants used were the same as those listed by G. Herzberg, Spectra of Diatomic Molecules", D. Van Nostrand Co., 1950. Raman measurements of rotation-vibration levels by A. Weber and E. A. McGinnis, J. Molec. Spect. 4, 195 (1960), support the constants selected by Herzberg which were changed on this table to apply to the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The entropies listed by Woolley were reduced by 0.0065 cal. deg.$^{-1}$ mole^{-1} which was added by Woolley to account for the contribution due to the presence of both odd and even rotational levels in O^{16}-O^{17} and O^{16}-O^{18} molecules. This correction is not necessary when isotope mixing entropy is neglected, cf. W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

Diatomic Oxygen Uninegative Ion (O_2^-)

(Ideal Gas) GFW = 31.99935

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	-(G°-H°298)/T (gibbs/mol)	H°-H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	7.202	49.913	49.913	.000	-11.390	-10.174	7.458
300	7.207	49.957	49.913	.013	-11.399	-10.166	7.406
400	7.529	52.074	50.199	.750	-11.870	-9.684	5.291
500	7.833	53.788	50.751	1.518	-12.330	-9.084	3.971
600	8.079	55.238	51.381	2.314	-12.786	-8.392	3.057
700	8.268	56.499	52.024	3.132	-13.242	-7.623	2.380
800	8.414	57.613	52.654	3.967	-13.702	-6.790	1.855
900	8.526	58.610	53.262	4.814	-14.166	-5.898	1.432
1000	8.615	59.514	53.842	5.671	-14.633	-4.954	1.083
1100	8.686	60.338	54.396	6.536	-15.104	-3.964	.788
1200	8.744	61.096	54.923	7.408	-15.577	-2.930	.534
1300	8.792	61.798	55.425	8.285	-16.053	-1.856	.312
1400	8.832	62.451	55.904	9.166	-16.533	-.747	.117
1500	8.867	63.062	56.361	10.051	-17.016	.397	-.058
1600	8.898	63.635	56.798	10.939	-17.502	1.575	-.215
1700	8.924	64.175	57.216	11.830	-17.990	2.783	-.358
1800	8.948	64.686	57.617	12.724	-18.481	4.019	-.488
1900	8.970	65.171	58.002	13.620	-18.977	5.280	-.607
2000	8.990	65.631	58.372	14.518	-19.476	6.570	-.718
2100	9.008	66.070	58.728	15.418	-19.978	7.887	-.821
2200	9.025	66.490	59.072	16.319	-20.486	9.223	-.916
2300	9.041	66.891	59.403	17.223	-20.994	10.587	-1.006
2400	9.055	67.276	59.723	18.128	-21.508	11.972	-1.090
2500	9.070	67.646	60.033	19.034	-22.027	13.375	-1.169
2600	9.083	68.002	60.332	19.941	-22.549	14.803	-1.244
2700	9.096	68.345	60.623	20.850	-23.075	16.248	-1.315
2800	9.108	68.676	60.905	21.761	-23.604	17.715	-1.383
2900	9.120	68.996	61.178	22.672	-24.137	19.201	-1.447
3000	9.132	69.305	61.444	23.585	-24.674	20.707	-1.508
3100	9.143	69.605	61.702	24.498	-25.215	22.228	-1.567
3200	9.154	69.896	61.954	25.413	-25.759	23.761	-1.623
3300	9.165	70.177	62.199	26.329	-26.306	25.319	-1.677
3400	9.176	70.451	62.438	27.246	-26.856	26.892	-1.729
3500	9.187	70.717	62.670	28.165	-27.408	28.480	-1.778
3600	9.197	70.976	62.897	29.084	-27.964	30.086	-1.826
3700	9.208	71.228	63.119	30.004	-28.523	31.709	-1.873
3800	9.219	71.474	63.336	30.925	-29.084	33.343	-1.918
3900	9.229	71.714	63.548	31.848	-29.646	34.988	-1.961
4000	9.240	71.948	63.755	32.771	-30.211	36.653	-2.003
4100	9.250	72.176	63.957	33.696	-30.778	38.335	-2.043
4200	9.261	72.399	64.156	34.621	-31.347	40.024	-2.083
4300	9.272	72.617	64.350	35.548	-31.917	41.733	-2.121
4400	9.283	72.830	64.540	36.476	-32.489	43.450	-2.158
4500	9.295	73.039	64.727	37.405	-33.061	45.185	-2.194
4600	9.306	73.243	64.910	38.335	-33.635	46.934	-2.230
4700	9.318	73.444	65.089	39.266	-34.211	48.687	-2.264
4800	9.330	73.640	65.265	40.198	-34.787	50.461	-2.298
4900	9.342	73.832	65.438	41.132	-35.363	52.239	-2.330
5000	9.355	74.021	65.608	42.067	-35.939	54.031	-2.362
5100	9.368	74.207	65.775	43.003	-36.517	55.839	-2.393
5200	9.381	74.389	65.939	43.940	-37.095	57.649	-2.423
5300	9.394	74.567	66.100	44.879	-37.672	59.488	-2.453
5400	9.408	74.743	66.258	45.819	-38.250	61.321	-2.482
5500	9.422	74.916	66.414	46.761	-38.826	63.171	-2.510
5600	9.436	75.086	66.567	47.703	-39.404	65.031	-2.538
5700	9.451	75.253	66.718	48.648	-39.980	66.895	-2.565
5800	9.465	75.417	66.867	49.594	-40.556	68.785	-2.592
5900	9.481	75.579	67.013	50.541	-41.132	70.673	-2.618
6000	9.496	75.739	67.157	51.490	-41.707	72.569	-2.643

Sept. 30, 1966; Dec. 31, 1966

DIATOMIC OXYGEN UNINEGATIVE ION (O_2^-) (IDEAL GAS) GFW = 31.99935

Ground State Configuration $[^2\Pi_g]$

$S^\circ_{298.15}$ = 49.91 ± 0.1 gibbs/mol

ΔHf°_0 = -9.92 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -11.39 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
29400	[4]

ω_e = 1170 cm^{-1}

$\omega_e x_e$ = 8.5 cm^{-1}

σ = 2

B_e = 1.247 cm^{-1}

α_e = [0.013] cm^{-1}

r_e = 1.30 Å

Heat of Formation.

The electron affinity of O_2(g) has been measured in the electron detachment experiments of J. L. Pack and A. V. Phelps, J. Chem. Phys. 44, 1870 (1966). The value reported is 0.43 ± 0.02eV (9.92 ± 0.46 kcal/mol) which is in good agreement with the value 0.46 ± 0.1eV selected by C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Report 8628, Jan. 1, 1965.

Heat Capacity and Entropy.

J. Rolfe, J. Chem. Phys. 40, 1664 (1964), has deduced from fluorescence emission spectra of O_2^-, in alkali halides, the vibrational constants and an exited electronic level. The $^2\Pi$ ground state is that predicted by molecular orbital theory and the first excited state should also be $^2\Pi$. By analogy with Cl_2^+, which is isoelectronic, the first excited level is estimated to lie in the 20000 - 30000 cm^{-1} region. Thus, the level observed by Rolfe is assumed to be the first excited $^2\Pi_u$ state. The bond length is taken from F. R. Gilmore, The Rand Corporation, Memorandum RM-4034-1-PR, AD 630997. B_e was calculated from the bond length,and α_e was estimated from the above quantities using the Morse potential function relation.

The enthalpy at 0°K is -2.086 kcal/mol.

Phosphorus Dioxide (PO_2)

(Ideal Gas) Mol. Wt. = 62.975 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.548	-70.611	-70.611	INFINITE
100	8.016	51.132	68.657	-1.752	-70.619	-71.431	156.105
200	8.802	56.890	61.476	-.917	-70.782	-72.190	78.882
298	9.897	60.607	60.607	.000	-71.000	-72.834	53.387
300	9.917	60.668	60.607	.018	-71.004	-72.846	53.065
400	10.913	63.663	61.009	1.062	-71.204	-73.429	40.118
500	11.659	66.183	61.798	2.192	-71.376	-73.964	32.328
600	12.189	68.358	62.714	3.386	-71.538	-74.468	27.123
700	12.566	70.267	63.660	4.625	-71.710	-74.942	23.397
800	12.837	71.964	64.594	5.896	-92.320	-80.703	22.046
900	13.038	73.488	65.499	7.190	-92.276	-79.253	19.244
1000	13.188	74.870	66.368	8.502	-92.230	-77.808	17.004
1100	13.304	76.132	67.199	9.827	-92.185	-76.369	15.172
1200	13.395	77.294	67.992	11.162	-92.141	-74.933	13.647
1300	13.467	78.369	68.750	12.505	-92.099	-73.500	12.356
1400	13.525	79.369	69.473	13.855	-92.058	-72.071	11.250
1500	13.573	80.304	70.164	15.210	-92.020	-70.644	10.292
1600	13.612	81.181	70.826	16.569	-91.985	-69.221	9.455
1700	13.645	82.008	71.459	17.932	-91.952	-67.798	8.716
1800	13.673	82.788	72.067	19.298	-91.923	-66.378	8.059
1900	13.697	83.528	72.651	20.666	-91.899	-64.959	7.472
2000	13.717	84.231	73.213	22.037	-91.878	-63.544	6.943
2100	13.735	84.901	73.753	23.410	-91.860	-62.126	6.465
2200	13.750	85.540	74.275	24.784	-91.849	-60.711	6.031
2300	13.763	86.152	74.778	26.160	-91.840	-59.297	5.634
2400	13.775	86.738	75.264	27.537	-91.837	-57.882	5.271
2500	13.786	87.300	75.734	28.915	-91.838	-56.467	4.936
2600	13.795	87.841	76.190	30.294	-91.844	-55.052	4.627
2700	13.803	88.362	76.631	31.674	-91.855	-53.637	4.341
2800	13.811	88.864	77.059	33.054	-91.871	-52.220	4.076
2900	13.818	89.349	77.474	34.436	-91.890	-50.803	3.828
3000	13.824	89.817	77.878	35.818	-91.915	-49.385	3.598
3100	13.829	90.271	78.271	37.201	-91.943	-47.966	3.381
3200	13.834	90.710	78.653	38.584	-91.977	-46.550	3.179
3300	13.839	91.136	79.024	39.967	-92.014	-45.130	2.989
3400	13.843	91.549	79.387	41.351	-92.057	-43.708	2.809
3500	13.847	91.950	79.740	42.736	-92.101	-42.286	2.640
3600	13.850	92.340	80.085	44.121	-92.150	-40.862	2.481
3700	13.853	92.720	80.421	45.506	-92.203	-39.437	2.329
3800	13.856	93.089	80.750	46.891	-92.259	-38.007	2.186
3900	13.859	93.449	81.071	48.277	-92.318	-36.580	2.050
4000	13.862	93.800	81.384	49.663	-92.381	-35.154	1.921
4100	13.864	94.143	81.691	51.049	-92.447	-33.720	1.797
4200	13.866	94.477	81.992	52.436	-92.515	-32.286	1.680
4300	13.868	94.803	82.286	53.823	-92.586	-30.851	1.568
4400	13.870	95.122	82.574	55.210	-92.660	-29.414	1.461
4500	13.872	95.434	82.856	56.597	-92.737	-27.976	1.359
4600	13.873	95.738	83.133	57.984	-92.815	-26.536	1.261
4700	13.875	96.037	83.405	59.371	-92.897	-25.093	1.167
4800	13.877	96.329	83.671	60.759	-92.980	-23.649	1.077
4900	13.878	96.615	83.932	62.147	-93.064	-22.206	.990
5000	13.879	96.895	84.189	63.534	-93.152	-20.759	.907
5100	13.880	97.170	84.440	64.922	-93.242	-19.308	.827
5200	13.882	97.440	84.688	66.311	-93.331	-17.863	.751
5300	13.883	97.704	84.931	67.699	-93.423	-16.405	.676
5400	13.884	97.964	85.170	69.087	-93.517	-14.957	.605
5500	13.885	98.219	85.405	70.476	-93.610	-13.495	.536
5600	13.886	98.469	85.636	71.864	-93.708	-12.042	.470
5700	13.886	98.715	85.863	73.253	-93.805	-10.583	.406
5800	13.887	98.956	86.087	74.641	-93.904	-9.119	.344
5900	13.888	99.193	86.307	76.030	-94.003	-7.659	.284
6000	13.889	99.427	86.524	77.419	-94.104	-6.191	.226

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Dioxide (PO_2) (Ideal Gas)

Mol. Wt. = 62.975

ΔH_f° 298.15 = [-71] kcal. mole^{-1}

$S^\circ_{298.15}$ = [60.6] cal. deg.$^{-1}$ mole^{-1}

Point Group = C_{2v}

Ground State Degeneracy = 2

<u>Vibrational Frequencies and Degeneracies</u>

ω, cm.$^{-1}$
[980] (1)
[515] (1)
[1044] (1)

Angle O-P-O = 134° 4'　　P-O distance = 1.485 Å

I_A = [10.81 X 10^{-39}] g. cm.^{2}　　I_B = [9.933 X 10^{-39}] g. cm.^{2}

I_C = [0.877 X 10^{-39}] g. cm.^{2}　　σ = 2

<u>Heat of Formation</u>. ΔH_f° 298.15 was calculated from an estimated heat of dissociation (270 ± 25 kcal. mole^{-1}) reported by L. Brewer and G. M. Rosenblatt, Chem. Reviews, <u>61</u>, 257 (1961).

<u>Heat Capacity and Entropy</u>. The molecular constants selected for this table were estimated by J. S. Gordon. The molecular constants for $PO_2(g)$ have been estimated by (1) J. S. Gordon, "Thermodynamic Data for Combustion Products," January 1960, Thiokol Chemical Corp., Reaction Motor Division, Denville, N. J.; (2) R. L. Potter, V. N. DiStefano and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I," American Cyanamid Company; and (3) C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia. The entropies at 3000° calculated from these three estimates differ by less than 0.8 cal. deg.$^{-1}$ mole^{-1}.

Lead Dioxide (PbO_2)

(Crystal) Mol. Wt. = 239.21 **INTERIM TABLE**

T, °K.	cal. mole⁻¹deg.⁻¹ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole⁻¹ $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.762	-63.590	-63.590	INFINITE
100	7.500	5.733	29.843	-2.411	-64.375	-59.916	130.940
200	12.720	12.723	19.583	-1.372	-64.619	-55.323	60.451
298	14.871	18.277	18.277	.000	-64.547	-50.769	37.213
300	14.890	18.369	18.277	.028	-64.544	-50.684	36.921
400	15.820	22.794	18.874	1.568	-64.367	-46.089	25.180
500	16.600	26.408	20.030	3.189	-64.150	-41.544	18.158
600	17.380	29.504	21.357	4.888	-63.896	-37.045	13.493
700	18.160	32.242	22.720	6.665	-64.767	-32.402	10.116
800	18.940	34.717	24.067	8.520	-64.431	-27.802	7.595
900	19.720	36.993	25.379	10.453	-64.026	-23.246	5.645
1000	20.500	39.111	26.647	12.464	-63.548	-18.739	4.095
1100	21.280	41.102	27.872	14.553	-62.997	-14.285	2.838
1200	22.060	42.987	29.053	16.720	-62.369	-9.883	1.800
1300	22.840	44.783	30.195	18.965	-61.667	-5.537	.931
1400	23.620	46.505	31.299	21.288	-60.893	-1.249	.195
1500	24.400	48.161	32.368	23.689	-60.047	2.983	-.435
1600	25.180	49.760	33.405	26.168	-59.132	7.155	-.977
1700	25.960	51.310	34.413	28.725	-58.146	11.270	-1.449
1800	26.740	52.816	35.394	31.360	-57.094	15.321	-1.860
1900	27.520	54.283	36.350	34.073	-55.974	19.314	-2.221

March 31, 1962

O_2Pb

Lead Dioxide (PbO_2) (Crystal)

Mol. Wt. = 239.21

$\Delta H_f^\circ{}_{298.15} = -64.55 \pm 0.16$ kcal. mole^{-1}

$S^\circ_{298.15} = 18.3 \pm 0.5$ cal. deg.$^{-1}$ mole^{-1}

Heat of Formation. Recalculated from $\Delta H^\circ_{290.15} = 12.14$ kcal. mole^{-1} for the reaction: $PbO(c) + 1/2O_2(g) = PbO_2(c)$ reported by M. Tscheltzow, Compt. rend., 100, 1458 (1885).

Heat Capacity and Entropy. C_p (69.9° to 297.2°K.) reported by R. W. Millar, J. Am. Chem. Soc. 51, 207 (1929). Above 298.15°K., the heat capacity value estimated by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

O_2Pb

Sulfur Dioxide (SO_2)

(Ideal Gas) Mol. Wt. = 64.066

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH_f° (kcal. mole⁻¹)	ΔF_f° (kcal. mole⁻¹)	Log K_p
0	.000	.000	INFINITE	-2.522	-70.341	-70.341	INFINITE
100	8.013	49.932	67.182	-1.725	-70.421	-70.966	155.088
200	8.693	55.670	60.135	-.893	-70.662	-71.425	78.046
298	9.530	59.298	59.298	.000	-70.947	-71.741	52.585
300	9.547	59.357	59.298	.018	-70.952	-71.746	52.264
400	10.395	62.222	59.683	1.016	-71.764	-71.947	39.308
500	11.132	64.623	60.437	2.093	-72.356	-71.923	31.436
600	11.723	66.707	61.312	3.237	-72.824	-71.790	26.148
700	12.180	68.550	62.217	4.433	-73.206	-71.562	22.342
800	12.532	70.200	63.114	5.669	-86.593	-72.574	19.825
900	12.806	71.693	63.985	6.937	-86.577	-70.822	17.197
1000	13.022	73.054	64.825	8.229	-86.553	-69.071	15.095
1100	13.194	74.303	65.631	9.540	-86.524	-67.326	13.376
1200	13.335	75.458	66.402	10.866	-86.490	-65.582	11.943
1300	13.451	76.530	67.141	12.206	-86.452	-63.840	10.732
1400	13.549	77.530	67.847	13.556	-86.413	-62.102	9.694
1500	13.632	78.468	68.524	14.915	-86.373	-60.369	8.795
1600	13.704	79.350	69.174	16.282	-86.331	-58.635	8.009
1700	13.767	80.183	69.797	17.656	-86.288	-56.905	7.315
1800	13.822	80.971	70.396	19.035	-86.248	-55.178	6.699
1900	13.872	81.720	70.973	20.420	-86.208	-53.452	6.148
2000	13.917	82.433	71.528	21.809	-86.170	-51.731	5.653
2100	13.958	83.113	72.064	23.203	-86.133	-50.010	5.204
2200	13.995	83.763	72.581	24.601	-86.099	-48.290	4.797
2300	14.030	84.386	73.080	26.002	-86.067	-46.573	4.425
2400	14.063	84.984	73.564	27.407	-86.037	-44.855	4.084
2500	14.093	85.558	74.032	28.815	-86.010	-43.141	3.771
2600	14.122	86.112	74.486	30.225	-85.986	-41.426	3.482
2700	14.149	86.645	74.927	31.639	-85.964	-39.713	3.214
2800	14.175	87.160	75.355	33.055	-85.946	-38.002	2.966
2900	14.200	87.658	75.770	34.474	-85.930	-36.288	2.735
3000	14.224	88.140	76.175	35.895	-85.918	-34.575	2.519
3100	14.247	88.607	76.568	37.319	-85.906	-32.864	2.317
3200	14.270	89.059	76.952	38.745	-85.899	-31.154	2.128
3300	14.291	89.499	77.325	40.173	-85.893	-29.446	1.950
3400	14.312	89.926	77.689	41.603	-85.891	-27.733	1.783
3500	14.333	90.341	78.045	43.035	-85.891	-26.026	1.625
3600	14.353	90.745	78.392	44.469	-85.892	-24.313	1.476
3700	14.373	91.138	78.731	45.906	-85.896	-22.602	1.335
3800	14.392	91.522	79.063	47.344	-85.901	-20.890	1.201
3900	14.411	91.896	79.387	48.784	-85.908	-19.183	1.075
4000	14.430	92.261	79.705	50.226	-85.917	-17.469	.954
4100	14.448	92.618	80.015	51.670	-85.927	-15.758	.840
4200	14.467	92.966	80.319	53.116	-85.938	-14.047	.731
4300	14.485	93.307	80.617	54.563	-85.951	-12.333	.627
4400	14.502	93.640	80.910	56.013	-85.965	-10.623	.528
4500	14.520	93.966	81.196	57.464	-85.980	-8.908	.433
4600	14.537	94.285	81.477	58.917	-85.995	-7.194	.342
4700	14.554	94.598	81.753	60.371	-86.012	-5.482	.255
4800	14.572	94.905	82.024	61.828	-86.028	-3.769	.172
4900	14.588	95.205	82.290	63.286	-86.045	-2.056	.092
5000	14.605	95.500	82.551	64.745	-86.064	-.345	.015
5100	14.622	95.790	82.808	66.207	-86.082	1.375	-.059
5200	14.639	96.074	83.060	67.670	-86.100	3.087	-.130
5300	14.655	96.353	83.308	69.134	-86.118	4.806	-.198
5400	14.672	96.627	83.553	70.601	-86.136	6.518	-.264
5500	14.688	96.896	83.793	72.069	-86.153	8.237	-.327
5600	14.704	97.161	84.029	73.538	-86.173	9.952	-.388
5700	14.720	97.421	84.262	75.010	-86.190	11.665	-.447
5800	14.736	97.677	84.491	76.482	-86.208	13.387	-.504
5900	14.753	97.930	84.717	77.957	-86.224	15.099	-.559
6000	14.769	98.178	84.939	79.433	-86.241	16.823	-.613

June 30, 1961

SULFUR DIOXIDE (SO_2) (IDEAL GAS) MOL. WT. = 64.066

$\Delta H^\circ_{f0} = -70.341 \pm 0.05$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -70.947 \pm 0.05$ kcal. mole^{-1}

Point Group C_{2v}

$S_{298.15} = 59.30 \pm 0.02$ cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
1151.38 (1)
517.69 (1)
1361.76 (1)

Bond Lengths and Angles S-O = 1.432 ± 0.003 A. OSO = 119.53 ± 0.4°

Moments of Inertia $I_A = 1.38046 \times 10^{-39}$ g. cm.^{2} $I_B = 8.13067 \times 10^{-39}$ g. cm.^{2} $\sigma = 2$

$I_C = 9.53376 \times 10^{-39}$ g. cm.^{2}

Heat of Formation

J. R. Eckman and F. D. Rossini, J. Research Nat. Bur. Standards 3, 597 (1929), measured the heat of combustion of rhombic sulfur to SO_2. Changes due to different atomic weights and electrical constants though negligible have been made.

Heat Capacities and Entropies

The functions were calculated by J. Gordon, private communication, Feb. 2, 1961, using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). Structural parameters are given by M. H. Sirvetz, J. Chem. Phys. 19, 938 (1951), obtained from microwave measurements. Frequencies were measured by R. D. Shelton, A. H. Nielsen, W. H. Fletcher, J. Chem. Phys. 21, 2178 (1953) and ibid., 22, 1791 (1954). A third law value of $S_{298.15} = 59.24$ cal. deg.$^{-1}$ mole^{-1} was obtained by W. F. Giauque and C. C. Stevenson, J. Am. Chem. Soc. 60, 1389 (1938).

Quartz (SiO_2)
(Crystal) GFW = 60.0848

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 1.653	- 216.509	- 216.509	INFINITE
100	3.749	2.317	17.327	- 1.501	- 217.115	- 213.116	465.764
200	7.801	6.235	10.800	- .913	- 217.504	- 208.950	228.330
298	10.657	9.910	9.910	.000	- 217.700	- 204.703	150.051
300	10.700	9.976	9.910	.020	- 217.702	- 204.623	149.067
400	12.770	13.354	10.357	1.199	- 217.741	- 200.253	109.413
500	14.255	16.372	11.264	2.554	- 217.661	- 195.888	85.622
600	15.396	19.075	12.344	4.038	- 217.500	- 191.547	69.771
700	16.436	21.526	13.483	5.630	- 217.271	- 187.239	58.459
800	17.615	23.794	14.632	7.330	- 216.969	- 182.969	49.985
900	16.240	26.006	15.778	9.204	- 216.521	- 178.748	43.406
1000	16.480	27.729	16.889	10.840	- 216.336	- 174.561	38.150
1100	16.720	29.311	17.947	12.500	- 216.150	- 170.393	33.854
1200	16.960	30.776	18.956	14.184	- 215.959	- 166.241	30.277
1300	17.200	32.143	19.918	15.892	- 215.763	- 162.106	27.253
1400	17.440	33.427	20.838	17.624	- 215.560	- 157.987	24.663
1500	17.680	34.638	21.718	19.380	- 215.350	- 153.881	22.420
1600	17.920	35.787	22.561	21.160	- 215.132	- 149.791	20.460
1700	18.160	36.880	23.372	22.964	- 226.898	- 145.607	18.719
1800	18.400	37.925	24.151	24.792	- 226.609	- 140.833	17.099
1900	18.640	38.926	24.903	26.644	- 226.302	- 136.076	15.652
2000	18.880	39.889	25.628	28.520	- 225.976	- 131.338	14.352

Dec. 31, 1960; Dec. 31, 1962; June 30, 1967

QUARTZ (SiO_2) (CRYSTAL) GFW = 60.0848 O_2Si

$S^\circ_{298.15}$ = 9.91 ± 0.03 gibbs/mol

Tt_1 = 847 ± 1.5°K(low quartz → high quartz)

Tt_2 = 1079 ± 250°K(high quartz → high cristobalite)

Tm = 1696 ± 50°K(high quartz → liquid)

ΔHf°_0 = −216.5 ± 0.4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −217.7 ± 0.4 kcal/mol

ΔHt°_1 = 0.174 ± 0.04 kcal/mol

ΔHt°_2 = 0.48 ± 0.15 kcal/mol

ΔHm° = 1.84 ± 0.2 kcal/mol

Heat of Formation

The heat of formation is based on data of Wise (1) for combustion of SiO_2(low quartz) and Si(c) in F_2 to form SiF_4(g). Good (2) burned a mixture of Si(c) and vinylidene fluoride polymer in oxygen in the presence of HF(aq) to form H_2SiF_6(aq HF). Combining this result with a previous heat of solution of quartz (3), the authors derived ΔHf°_{298} = −217.5 ± 0.5 kcal/mol. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of ΔHf°(HF), although the polymer-Si scheme depends on the heat of dilution of HF(aq). Wise (1) has reviewed other data which confirm the adopted value rather than the oxygen combustion value (4) of −209.9 kcal/mol. Pertinent equilibrium data are analyzed on the table for SiO_2(low cristobalite), while the calorimetric results are summarized below.

Source	Reaction	ΔHr°_{298}, kcal/mol	ΔHf°_{298}, kcal/mol
1. Wise (1963)	SiO_2(low quartz) + $2F_2$(g) → SiF_4(g) + O_2(g)	−168.26 ± 0.28	−217.72 ± 0.34
2. Good (1964)	See text.	-	−217.5
3. Humphrey (1952)	Si(c) + $2O_2$(g) → SiO_2(low quartz)	−209.9	−209.9

Heat Capacity and Entropy

Heat capacities below 300°K are based on data of Jones (5) and Westrum (6). Earlier data of Anderson (7) are in good agreement. The entropy is obtained from Cp° using S°_2 = 0.00001 eu. Cp° from 300° to 847°K is derived from adiabatic calorimetric data of Moser (8) and Sinel'nikov (9). The adopted Cp° is discontinuous at 847°K and ΔCp° = −2.17 gibbs/mol. Values above the transition temperature are based on data of Moser and on data up to 1473°K obtained with a thermal analysis method by Leonidov (10). Cp° is extrapolated linearly to higher temperatures.

From a review of data available before 1953, Kelley (11) selected almost identical enthalpies below 847°K but a value higher by 96 cal/mol at 900°K. The higher value, due to use of a larger ΔHt°_1, was presumably based on Roth (12), Wietzel (13) and White 14) whose enthalpy data were given the most weight by Kelley. Near 900°K these three sets of data deviate from the adopted function by −150±30, +130±40 and +15±35 cal/mol, respectively; however, a recent enthalpy datum (15) obtained by transposed temperature drop calorimetry deviates by +75 cal/mol at 968°K.

Transition Data

Tt_1 is taken as 847 ± 1.5°K based on thermal analysis of many specimens by Kieth and Tuttle (16). Wide variations in Tt_1 for some specimens were attributed by the authors to small amounts of impurities. The discontinuity in the volume curve (17) during inversion from trigonal low quartz to hexagonal high quartz suggests that the transition should be treated as first order. Thus, the heat of transition is derived as (1011-854+17) = 174 cal/mol, where 1011 ± 6 is ($H^\circ_{873.15} - H^\circ_{823.15}$) measured by Moser (8), 854 is the corresponding increment calculated from the JANAF Cp°, and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15°K. Some of the more recent data which confirm the adopted ΔHt°_1 are summarized below.

Source	Method		ΔHt°_1, kcal/mol
8. Moser (1936)	H and Cp from adiabatic calorimetry		0.174
9. Sinel'nikov (1953)	Integration of Cp from adiabatic calorimetry		0.143
10. Leonidov (1964)	Thermal analysis		0.198
17. Berger (1964)	ΔV with dT/dP = 0.026°K/atm		0.12
18. Berger (1965)	Microcalorimetric thermal analysis	Single crystal	0.156, 0.165, 0.178 ± 0.010
		Various crushed samples	0.124 to 0.193

Additional polymorphism of SiO_2 is discussed on the table for high cristobalite. Quartz has been superheated through the cristobalite region to some 300° above its metastable melting point. This melting point is calculated from the adopted tables as 1696 ± 50°K, which agrees well with the range 1673 - 1723°K indicated by the data of Mackenzie (19). The adopted tables predict the inversion of high quartz to high cristobalite at 1079 ± 250°K. Holmquist (20) tentatively placed this inversion at 1298 ± 25°K. ΔHt°_2 and ΔHm° are calculated from the differences in heats of formation of the appropriate phases at Tt_2 and Tm.

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Cristobalite, Low (SiO_2)

(Crystal) GFW = 60.0848

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.682	-215.938	-215.938	INFINITE
100	3.824	2.688	17.868	-1.518	-216.532	-212.570	464.571
200	7.886	6.663	11.268	-.921	-216.912	-208.443	227.776
298	10.744	10.372	10.372	.000	-217.100	-204.241	149.712
300	10.790	10.439	10.372	.020	-217.102	-204.161	148.731
400	12.702	13.826	10.821	1.202	-217.138	-199.839	109.187
500	14.023	16.808	11.726	2.541	-217.074	-195.519	85.461
600	15.050	19.461	12.799	3.998	-216.940	-191.220	69.652
700	15.700	21.833	13.923	5.537	-216.764	-186.946	58.367
800	16.150	23.960	15.047	7.130	-216.569	-182.702	49.912
900	16.500	25.882	16.146	8.763	-216.362	-178.478	43.340
1000	16.800	27.637	17.208	10.428	-216.148	-174.281	38.089

June 30, 1967

CRISTOBALITE, LOW (SiO_2) (CRYSTAL) GFW = 60.0848 O_2Si

ΔHf°_0 = -215.9 ± 0.5 kcal/mol

$S^\circ_{298.15}$ = 10.372 ± 0.03 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -217.1 ± 0.5 kcal/mol

Tt = 543 ± 3°K(low cristobalite → high cristobalite)

ΔHt° = 0.321 ± 0.06 kcal/mol

Heat of Formation

The heat of formation is calculated from that of quartz using ΔHr°_{970} = 0.45 ± 0.15 kcal/mol for high quartz → high cristobalite, as determined by Holm(1) from ΔHsoln in an oxide melt. This value reduces to ΔHr°_{298} = 0.60 kcal/mol for low quartz → low cristobalite. Kracek(2) obtained essentially the same value, ΔHr°_{298} = 0.63 kcal/mol, from ΔHsoln in HF(aq, 74.7°C), while Hummel(3) found ΔHr°_{298} = 1.80 kcal/mol from ΔHsoln in HF(aq, 26.5°C). The larger ΔHr° corresponds to a less negative ΔHf° (i.e., less stable) and suggests that the sample of Hummel has disorder approaching that of vitreous silica. Presumably, this disagreement arises from different methods of preparation of cristobalite from quartz. Holm heated for 24 hours at 1743°K, while Hummel heated for 4 hours at 1973°K. Hummel's sample was then ground and treated with dilute HF to remove amorphous surface layers created by grinding; particles smaller than 2.5 microns were used in order to obtain adequate rates of dissolution. Neither author gave X-ray or DTA evidence to confirm that the samples were the more stable, ordered form of cristobalite(15).

The calorimetric data are summarized below along with equilibrium data which confirm the adopted values of ΔHf° for cristobalite and quartz. Data from Matoba(5) and Rein(6) were reduced to the standard state of Si(ℓ) using activity coefficients from the curves of (10).

Source	Method	Reaction	Range T, °K	No. of Points	ΔHr°_T kcal/mol	ΔHr°_{298} kcal/mol	Drift eu	ΔHf°_{298} kcal/mol
1. Holm (1967)	ΔHsoln in oxide melt	A	970	3	0.45±0.15	0.6	-	-217.10
2. Hummel (1959)	ΔHsoln in HF(aq, 26.5°C)	A	299.65	8	1.80±0.2	1.80	-	-215.90
3. Kracek (1953)	ΔHsoln in HF(aq, 74.7°C)	A	298-348	-	-	0.63±0.05	-	-217.07
4. Humphrey (1952)	ΔHsoln in HF(aq, 73.7°C)	A	298-347	6	-	0.93±0.1	-	-216.77
5. Matoba (1959)	Keq + γ(Si)	B	1843-1953	3	104.5±0.6*	112.48*	0.8	-217.17
6. Rein (1963)	Keq + γ(Si)	C	1773-1798	5	-	175.42*	31±37	-217.38
	Keq + γ(Si)	D	1823-1873	6	-	228.5*	10±6	-212.3
7. Kay (1960)	Kp	E	1703-1829	14	145.9±1.3*	146.92*	-2.3±0.7	-217.94
8. Baird (1958)	Kp	E	1673-1853	5	145.5±3.5*	147.43*	-1.9±1.9	-218.45

*Values at T are from second law analysis while those at 298.15°K are from third law.

A. SiO_2(quartz, low or high) = SiO_2(cristobalite, low or high)

B. SiO_2(high cristobalite) + $2H_2(g)$ = Si(ℓ) + $2H_2O(g)$

C. SiO_2(high cristobalite) + 2C(graph) = Si(ℓ) + 2CO(g)

D. SiO_2(high cristobalite) + 2SiC(β) = 3Si(ℓ) + 2CO(g)

E. SiO_2(high cristobalite) + 3C(graph) = SiC(β) + 2CO(g)

Heat Capacity and Entropy

Cp° below 300°K is based on data of Westrum(11). Earlier data of Anderson(12) are in satisfactory agreement. The entropy is obtained from Cp° using S°_5 = 0.0007 eu. Cp° above 300°K is derived from enthalpy data of Mosesman(13) and White(14). The former deviate from the adopted functions by -0.7 to 0.5% and the latter by +0.4%. Although the functions above 300°K appear to be reliable, it would be desirable to have new data for a well-characterized sample (see Transition Data).

Transition Data

Low cristobalite is metastable with respect to quartz but persists up to Tt. Tt is taken as the temperature at the peak in the heating curve for well-ordered cristobalite; however, see (15, 16) for detailed discussions of temperatures about 25° lower which were found from cooling curves. ΔHt° is derived from enthalpy data(13, 14) for high cristobalite using the adopted enthalpy for the low form. The enthalpy data of Mosesman(13) gave a lower Tt which suggests that the sample was less well-ordered than desirable. ΔHt° is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	ΔHt°, kcal/mol
13. Mosesman (1941)	Enthalpy data	0.321
17. Berger (1965)	Microcalorimetric thermal analysis	0.318±0.018
18. Majumdar (1964)	ΔV and dT/DP	0.27
19. Sabatier (1957)	Differential thermal analysis	0.26±0.01

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Cristobalite, High (SiO_2)

(Crystal) GFW = 60.0848

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	6.353	11.963	11.963	.000	-216.417	-204.032	149.560
300	6.490	12.003	11.963	.012	-216.427	-203.956	148.581
400	11.332	14.632	12.289	.937	-216.720	-199.743	109.134
500	13.589	17.429	13.039	2.195	-216.737	-195.492	85.449
600	14.830	20.026	13.991	3.621	-216.634	-191.252	69.663
700	15.590	22.373	15.023	5.145	-216.473	-187.033	58.394
800	16.094	24.490	16.077	6.731	-216.285	-182.842	49.950
900	16.449	26.407	17.120	8.359	-216.083	-178.672	43.387
1000	16.712	28.154	18.137	10.017	-215.876	-174.526	38.143
1100	16.915	29.757	19.122	11.699	-215.668	-170.402	33.856
1200	17.076	31.236	20.070	13.399	-215.461	-166.296	30.287
1300	17.208	32.608	20.983	15.113	-215.259	-162.207	27.269
1400	17.320	33.888	21.859	16.840	-215.061	-158.134	24.686
1500	17.416	35.086	22.701	18.577	-214.870	-154.074	22.449
1600	17.500	36.213	23.511	20.323	-214.686	-150.027	20.493
1700	17.575	37.276	24.290	22.076	-226.503	-145.885	18.755
1800	17.642	38.282	25.039	23.837	-226.281	-141.148	17.138
1900	17.704	39.238	25.762	25.605	-226.058	-136.426	15.693
2000	17.762	40.147	26.458	27.378	-225.835	-131.713	14.393
2100	17.816	41.015	27.131	29.157	-225.611	-127.012	13.218
2200	17.866	41.845	27.781	30.941	-225.389	-122.323	12.152
2300	17.914	42.641	28.410	32.730	-225.166	-117.646	11.179
2400	17.960	43.404	29.019	34.524	-224.944	-112.972	10.288
2500	18.005	44.138	29.609	36.322	-224.724	-108.314	9.469
2600	18.047	44.845	30.182	38.125	-224.503	-103.661	8.713
2700	18.089	45.527	30.738	39.931	-224.285	-99.018	8.015
2800	18.129	46.186	31.278	41.742	-224.067	-94.382	7.367
2900	18.168	46.822	31.803	43.557	-223.850	-89.751	6.764
3000	18.207	47.439	32.314	45.376	-223.634	-85.133	6.202

June 30, 1967

CRISTOBALITE, HIGH (SiO_2) (CRYSTAL) GFW = 60.0848

$S^\circ_{298.15}$ = 11.963 gibbs/mol

Tt = 543 ± 3°K(low cristobalite → high cristobalite)

Tt = 1079 ± 250°K(high quartz → high cristobalite)

Tm = 1996 ± 5°K(high cristobalite → liquid)

$\Delta Hf^\circ_{298.15}$ = -216.417 kcal/mol

ΔHt° = 0.321 ± 0.06 kcal/mol

ΔHt° = 0.48 ± 0.15 kcal/mol

ΔHm° = 2.29 ± 0.5 kcal/mol

Heat of Formation

The heat of formation is calculated from that of low cristobalite by addition of ΔHt° = 0.321 kcal/mol and the difference between $H^\circ_{543} - H^\circ_{298}$ for low and high forms.

Heat Capacity and Entropy

Cp° is derived from enthalpies of Mosesman (1) and White (2), whose data deviate from the adopted functions by -0.6 to + 0.5% and +0.9 to 0.0%, respectively. White's deviations for cristobalite have a magnitude and trend similar to his deviations for quartz and vitreous silica. Data of Wietzel (3) for his sample prepared at 1600°C deviate by +3% at 673°K and +1.6% at 1973°K. Cp° below 543°K is smoothly extrapolated to give the proper trend in the Gibbs energy, but the heat capacity at 298°K is not realistic. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

Literature on the polymorphism of SiO_2 is voluminous but is summarized in detail in recent books by Sosman (4) and Eitel (5). The known phases of SiO_2 include quartz, tridymite(?), cristobalite, vitreous silica and the more recently discovered high pressure phases. Muan (6) concisely reviewed the still controversial question of whether tridymite is stabilized only by the presence of foreign ions or whether it is a stable phase of SiO_2 intermediate between quartz and cristobalite. Transitions among the different phases are generally sluggish because of large energy barriers to the structural change and small differences in Gibbs free energies. As a result, the phases often persist far into metastable regions. In contrast, transitions within a particular phase are rapid and reversible (i.e., the low → high inversions of quartz or cristobalite).

High cristobalite is the stable phase near Tm. It becomes metastable with respect to quartz at lower temperatures but persists down to the high → low inversion at 543°K (see table for low cristobalite). The high form is cubic and the low form tetragonal (12, 13).

The adopted tables give 1079±250°K as the temperature at which ΔGr° = 0 for high quartz → high cristobalite; ΔHt° = 0.48±0.15 kcal/mol is the corresponding enthalpy difference. The uncertainty in Tt is derived from that in ΔHt° which, in turn, is taken from ΔHr°_{970} = 0.45±0.15 kcal/mol obtained by Holm (7) from ΔHsoln measurements in an oxide melt. It is apparent that Tt is extremely sensitive to small changes in G or H. Holmquist (8) tentatively placed this inversion at 1298±25°K but did observe cristobalite formation at temperatures as low as 1171°K.

Melting Data

Melting point data were reviewed by Schneider (9) and adjusted to the 1948 International Temperature Scale. The adopted melting point for cristobalite is based on Greig (10). ΔHm° is calculated as the difference in ΔHf° for liquid and crystal at Tm. Mackenzie et al. (11) showed that cristobalite may be superheated by as much as 40° above Tm due to its slow rate of fusion.

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Silicon Dioxide (SiO_2)

(Liquid) GFW = 60.0848

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	1.098	INFINITE	- 1.672	- 214.568	- 214.568	INFINITE
100	3.861	3.820	18.870	- 1.505	- 215.159	- 211.310	461.817
200	7.824	7.792	12.337	- .909	- 215.540	- 207.297	226.524
298	10.560	11.455	11.455	.000	- 215.740	- 203.204	148.952
300	10.604	11.520	11.455	.020	- 215.742	- 203.126	147.977
400	12.552	14.856	11.897	1.184	- 215.796	- 198.909	108.679
500	13.882	17.808	12.790	2.509	- 215.746	- 194.690	85.099
600	14.829	20.427	13.849	3.947	- 215.631	- 190.490	69.386
700	15.529	22.768	14.959	5.467	- 215.474	- 186.311	58.169
800	16.063	24.878	16.069	7.047	- 215.292	- 182.159	49.763
900	16.481	26.795	17.156	8.675	- 215.090	- 178.028	43.231
1000	16.814	28.550	18.209	10.341	- 214.875	- 173.921	38.010
1100	17.083	30.165	19.223	12.036	- 214.654	- 169.837	33.743
1200	17.303	31.661	20.198	13.756	- 214.427	- 165.772	30.191
1300	17.485	33.054	21.134	15.495	- 214.200	- 161.728	27.189
1400	17.650	34.355	22.033	17.252	- 213.972	- 157.699	24.618
1500	17.800	35.576	22.895	19.022	- 213.748	- 153.687	22.392
1600	19.130	36.751	23.724	20.843	- 213.489	- 149.691	20.447
1700	20.490	37.968	24.527	22.850	- 225.052	- 145.611	18.720
1800	20.500	39.139	25.306	24.899	- 224.542	- 140.952	17.114
1900	20.500	40.247	26.064	26.949	- 224.037	- 136.321	15.681
2000	20.500	41.299	26.799	28.999	- 223.537	- 131.719	14.394
2100	20.500	42.299	27.514	31.049	- 223.042	- 127.139	13.232
2200	20.500	43.253	28.208	33.099	- 222.554	- 122.586	12.178
2300	20.500	44.164	28.882	35.149	- 222.070	- 118.052	11.218
2400	20.500	45.037	29.537	37.199	- 221.592	- 113.539	10.339
2500	20.500	45.873	30.174	39.249	- 221.120	- 109.047	9.533
2600	20.500	46.677	30.793	41.299	- 220.652	- 104.572	8.790
2700	20.500	47.451	31.396	43.349	- 220.190	- 100.118	8.104
2800	20.500	48.197	31.983	45.399	- 219.733	- 95.679	7.468
2900	20.500	48.916	32.554	47.449	- 219.281	- 91.254	6.877
3000	20.500	49.611	33.111	49.499	- 218.834	- 86.849	6.327
3100	20.500	50.283	33.654	51.549	- 218.391	- 82.456	5.813
3200	20.500	50.934	34.184	53.599	- 217.953	- 78.078	5.332
3300	20.500	51.565	34.701	55.649	- 217.519	- 73.715	4.882
3400	20.500	52.177	35.206	57.699	- 217.090	- 69.363	4.459
3500	20.500	52.771	35.700	59.749	- 216.664	- 65.026	4.060
3600	20.500	53.349	36.182	61.799	- 308.203	- 58.442	3.548
3700	20.500	53.910	36.654	63.849	- 307.686	- 51.509	3.042
3800	20.500	54.457	37.115	65.899	- 307.172	- 44.592	2.565
3900	20.500	54.989	37.567	67.949	- 306.662	- 37.690	2.112
4000	20.500	55.508	38.009	69.999	- 306.156	- 30.800	1.683
4100	20.500	56.015	38.442	72.049	- 305.654	- 23.926	1.275
4200	20.500	56.509	38.866	74.099	- 305.153	- 17.062	.888
4300	20.500	56.991	39.282	76.149	- 304.655	- 10.204	.519
4400	20.500	57.462	39.690	78.199	- 304.161	- 3.364	.167
4500	20.500	57.923	40.090	80.249	- 303.668	3.471	- .169

Dec. 31, 1960; Dec. 31, 1962; June 30, 1967

SILICON DIOXIDE (SiO_2) (LIQUID) GFW = 64.0848

$S^\circ_{298.15}$ = 11.455 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -215.74 kcal/mol

O_2Si

Tm = 1996 ± 5°K(high cristobalite → liquid)

ΔHm° = 2.29 ± 0.5 kcal/mol

Heat of Formation

The heat of formation is calculated from that of quartz using ΔHr°_{970} = 1.45 ± 0.15 kcal/mol for high quartz → $SiO_2(\ell)$, as determined by Holm (1) from ΔHsoln in an oxide melt. This value reduces to ΔHr°_{298} = 1.96 kcal/mol for low quartz → $SiO_2(\ell)$ and is consistent within ±0.3 kcal/mol with other calorimetric data summarized below. Earlier results were reviewed by Hummel (4).

Source	Method	Reaction	T, °K	ΔHr°_T kcal/mol	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
1. Holm (1967)	ΔHsoln in oxide melt	A	970	1.45±0.15	1.96	-215.74
2. Wise (1963)	ΔHc in fluorine	B	298	1.78±0.46	1.78	-215.92
3. Kracek (1953)	ΔHsoln in HF(aq, 74.7°C)	A	298-348	-	2.18±0.05	-215.52
4. Hummel (1959)	ΔHsoln in HF(aq, 26.5°C)	A	300	2.27±0.2	2.27	-215.43

A. SiO_2(quartz, low or high) → $SiO_2(\ell)$

B. $SiO_2(\ell) + 2F_2(g) \rightarrow SiF_4(g) + O_2(g)$

Heat Capacity and Entropy

Cp° below 300°K is based on data of Flubacher (5) and Westrum (6) for samples annealed at 1100 and 1070°C, respectively. Data of Turdakin (7) are higher by about 1 percent in the range 60-160°K and at 300°K but are in agreement elsewhere. The entropy is calculated from Cp° using $S^\circ_{2.34} - S^\circ_0$ = 0.0001 eu and S°_0 = 1.098 eu. Cp° data (6) for a different sample annealed at 1300°C yield an entropy larger by <0.04 eu. Earlier data were reviewed by Kelley (8). The residual entropy is calculated from $S^\circ_0 = S^\circ_{1996} - (S^\circ_{1996} - S^\circ_0)$ = 41.258 - 40.160 = 1.098 eu, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of ΔSm° = 1.147 eu and S°_{1996} = 40.111 eu for high cristobalite. We estimate the uncertainty as ±0.3 eu, primarily from the uncertainty in ΔHm°.

Cp° above 300°K is based on adiabatic calorimetric data of Moser (9) up to 900°K. Enthalpy data of White (10) and Fischer (11) are in excellent agreement. Cp° from 900 to 1500°K is derived from enthalpy data of Southard (12) and White (10). Maximum deviation of the data from the adopted values in this range is 0.5 percent. Enthalpy data of Egan (13) and Kelley (14) deviate from the adopted values by less than 1 percent in the range 1000-1500°K, although large positive deviations appear at lower temperatures.

In the region 1500-1700°K, the adopted Cp° shows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wietzel (15). This is presumed to be the glass transition region in which Cp° rises to that of the stable liquid. Cp° above 1700°K is estimated as 20.5 gibbs/mol or 6.83 gibbs/g-atom. This value is consistent with the enthalpy data (15) and with liquid heat capacities of Al_2O_3, $Na_2Si_2O_5$ and Na_2SiO_3.

Melting Data

The melting point of high cristobalite is 1996 ± 5°K, while the metastable melting point of high quartz is 1696 ± 50°K. ΔHm° is the difference between ΔHf° for liquid and high cristobalite at Tm. Values ranging from 1.8 to 3.6 kcal/mol have been derived from various interpretations of phase diagrams (1).

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Silicon Dioxide (SiO_2)
(Ideal Gas) GFW = 60.0848

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.529	-72.685	-72.685	INFINITE
100	7.510	44.948	63.180	-1.823	-72.737	-73.001	159.543
200	9.320	50.742	55.625	-.977	-72.868	-73.215	80.005
298	10.518	54.699	54.699	.000	-73.000	-73.357	53.772
300	10.537	54.765	54.700	.019	-73.003	-73.360	53.442
400	11.474	57.929	55.125	1.122	-73.118	-73.460	40.137
500	12.207	60.572	55.957	2.307	-73.208	-73.534	32.142
600	12.767	62.849	56.920	3.557	-73.281	-73.593	26.806
700	13.188	64.851	57.913	4.856	-73.345	-73.640	22.991
800	13.507	66.633	58.894	6.192	-73.407	-73.679	20.128
900	13.750	68.239	59.844	7.555	-73.470	-73.708	17.899
1000	13.938	69.698	60.758	8.940	-73.536	-73.730	16.114
1100	14.085	71.033	61.632	10.341	-73.609	-73.746	14.652
1200	14.203	72.264	62.468	11.756	-73.687	-73.755	13.433
1300	14.297	73.405	63.266	13.181	-73.774	-73.758	12.400
1400	14.374	74.467	64.028	14.615	-73.869	-73.753	11.513
1500	14.438	75.461	64.758	16.055	-73.975	-73.741	10.744
1600	14.491	76.395	65.456	17.502	-74.090	-73.722	10.070
1700	14.536	77.275	66.126	18.953	-86.209	-73.589	9.461
1800	14.573	78.107	66.768	20.409	-86.292	-72.844	8.845
1900	14.606	78.896	67.386	21.868	-86.378	-72.096	8.293
2000	14.634	79.645	67.980	23.330	-86.466	-71.340	7.796
2100	14.658	80.360	68.553	24.795	-86.556	-70.582	7.346
2200	14.679	81.042	69.105	26.261	-86.652	-69.819	6.936
2300	14.698	81.695	69.639	27.730	-86.749	-69.053	6.561
2400	14.714	82.321	70.154	29.201	-86.850	-68.279	6.218
2500	14.728	82.922	70.653	30.673	-86.956	-67.506	5.901
2600	14.741	83.500	71.136	32.146	-87.065	-66.725	5.609
2700	14.753	84.057	71.604	33.621	-87.178	-65.942	5.338
2800	14.763	84.593	72.059	35.097	-87.295	-65.150	5.085
2900	14.773	85.112	72.500	36.574	-87.416	-64.358	4.850
3000	14.781	85.613	72.929	38.052	-87.541	-63.562	4.631
3100	14.789	86.097	73.346	39.530	-87.670	-62.758	4.424
3200	14.796	86.567	73.752	41.009	-87.803	-61.953	4.231
3300	14.802	87.022	74.147	42.489	-87.939	-61.143	4.049
3400	14.808	87.464	74.532	43.970	-88.079	-60.329	3.878
3500	14.813	87.894	74.908	45.451	-88.222	-59.515	3.716
3600	14.818	88.311	75.274	46.932	-180.330	-56.432	3.426
3700	14.823	88.717	75.632	48.414	-180.381	-52.990	3.130
3800	14.827	89.112	75.982	49.897	-180.434	-49.543	2.849
3900	14.831	89.498	76.323	51.380	-180.491	-46.105	2.584
4000	14.834	89.873	76.657	52.863	-180.552	-42.656	2.331
4100	14.838	90.239	76.984	54.346	-180.617	-39.208	2.090
4200	14.841	90.597	77.304	55.830	-180.682	-35.761	1.861
4300	14.843	90.946	77.617	57.315	-180.749	-32.305	1.642
4400	14.846	91.288	77.924	58.799	-180.821	-28.858	1.433
4500	14.849	91.621	78.225	60.284	-180.893	-25.396	1.233
4600	14.851	91.948	78.520	61.769	-180.967	-21.941	1.042
4700	14.853	92.267	78.809	63.254	-181.045	-18.481	.859
4800	14.855	92.580	79.092	64.739	-181.123	-15.023	.684
4900	14.857	92.886	79.371	66.225	-181.202	-11.564	.516
5000	14.859	93.186	79.644	67.711	-181.283	-8.103	.354
5100	14.861	93.481	79.913	69.197	-181.366	-4.636	.199
5200	14.862	93.769	80.176	70.683	-181.450	-1.171	.049
5300	14.864	94.052	80.435	72.169	-181.534	2.302	-.095
5400	14.865	94.330	80.690	73.656	-181.620	5.765	-.233
5500	14.867	94.603	80.941	75.142	-181.707	9.237	-.367
5600	14.868	94.871	81.187	76.629	-181.796	12.709	-.496
5700	14.869	95.134	81.429	78.116	-181.885	16.184	-.621
5800	14.870	95.393	81.668	79.603	-181.976	19.661	-.741
5900	14.872	95.647	81.903	81.090	-182.068	23.134	-.857
6000	14.873	95.897	82.134	82.577	-182.161	26.615	-.969

Dec. 31, 1960; Dec. 31, 1962; Sept. 30, 1967

SILICON DIOXIDE (SiO_2) (IDEAL GAS) GFW = 60.0848

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [54.7] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -72.7 ± 8 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -73 ± 8 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[980] (1)
[370] (2)
[1430] (1)

Bond Distance: Si-O = [1.55] Å

Bond Angle: O-Si-O = [180°]

Rotational Constant: B_0 = [0.2193] cm^{-1}

Heat of Formation

The adopted value is based on the data summarized below. Margrave (1) has reported a value of ΔHs°_{298} = 140.9±1 kcal/mol but details are not yet available. Assuming that this corresponds to reaction A below, we calculate ΔHf°_{298} = -75.5 kcal/mol. Firsova(2) reported two values of the sublimation pressure which were derived from Knudsen effusion data using auxiliary data for SiO(g). Porter (4) derived two pressures from a mass spectrometric study and also obtained a 2nd Law value for ΔHs° from ion intensities. The resulting range for ΔHs°_{298}, 136 to 141 kcal/mol, is consistent with the lower limit of 130 kcal/mol obtained by Bergman (3) from a method involving explosion in a spherical bomb. An alternative analysis of the mass spectrometric data (4) using the gas phase reaction B suggests an even higher ΔHs° of 148 kcal/mol. The adopted ΔHf° corresponds to ΔHs°_{298} = 143.4±8 kcal/mol and to $\Delta Hatom^\circ_0$ = 297.3±8 kcal/mol.

Source	Reaction	Method	Range, T°K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}, kcal/mol
Margrave (1967)	A	-	-	-	140.9±1	-	-75.5
Firsova (1960)	A	Knudsen, calculation	1600-1800	-	137.0±2	-	-79.4
Bergman (1959)	A	Explosion	-	-	>130	-	>-86
Porter (1955)	A	Knudsen mass spec.	1800-1900	128	139.6±0.3	6	-76.8
	A	Ion intensities	1750-1980	136±8	-	-	-80
	B	Knudsen mass spec.	1800-1900	-2	-44.8±1.2	-23	-68.8

A. SiO_2(high cristobalite) = SiO_2(g)   B. SiO(g)+1/2O_2(g) = SiO_2(g)

Heat Capacity and Entropy

Point group, ground state quantum weight and the linear symmetrical configuration are estimated by analogy with the properties of CO_2. From the bond lengths in SiO, CO_2 and CO, the length in SiO_2 is estimated as 1.509 x 1.160/1.128. Bond lengths and atomization energies for these molecules are reasonably consistent with the existence of six-electron bonds in the monoxides and four-electron bonds in the dioxides (5). Vibrational frequencies are estimated from a valence bond calculation using force constants, $k = 9 \times 10^5$ and $k\delta/\ell^2 = 0.3 \times 10^5$ dyne/cm, which are obtained from those of SiO, CO_2 and CO. The moment of inertia is 12.76×10^{-39} g cm^2.

References

1. J. L. Margrave, 5th Meeting ICRPG Thermochemistry Working Group, Linden, New Jersey, March 1967.
2. L. P. Firsova and An. N. Nesmeyanov, Russ. J. Phys. Chem. (English Transl.) 34, 1279, 1232, 906 (1960).
3. G. A. Bergman and V. A. Medvedev, Sbornik Trudov Gosudarst. Inst. Priklad. Khim. 1959, 158 (1959).
4. R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 216 (1955).
5. J. W. Linnett, "The Electronic Structure of Molecules," pp. 43-55, Methuen and Co. Ltd., London, 1964.

Titanium Dioxide, Anatase (TiO_2)

(Crystal) GFW = 79.8988

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.062	- 221.835	- 221.835	INFINITE
100	4.585	2.302	21.322	- 1.902	- 222.503	- 218.397	477.306
200	10.009	7.293	13.048	- 1.151	- 222.906	- 214.107	233.965
298	13.257	11.931	11.931	.000	- 223.000	- 209.763	153.760
300	13.312	12.013	11.931	.025	- 222.999	- 209.681	152.752
400	15.244	16.144	12.481	1.465	- 222.888	- 205.253	112.145
500	16.153	19.654	13.575	3.040	- 222.690	- 200.867	87.799
600	16.658	22.647	14.843	4.682	- 222.469	- 196.524	71.584
700	16.973	25.239	16.148	6.364	- 222.251	- 192.217	60.013
800	17.186	27.520	17.429	8.073	- 222.050	- 187.941	51.343
900	17.341	29.554	18.666	9.799	- 221.874	- 183.688	44.605
1000	17.459	31.387	19.848	11.540	- 221.724	- 179.452	39.219
1100	17.553	33.056	20.974	13.290	- 221.602	- 175.231	34.815
1200	17.630	34.586	22.045	15.050	- 222.442	- 170.982	31.140
1300	17.696	36.000	23.065	16.816	- 222.247	- 166.702	28.025
1400	17.754	37.314	24.036	18.588	- 222.068	- 162.437	25.358
1500	17.806	38.541	24.963	20.366	- 221.906	- 158.184	23.047
1600	17.853	39.691	25.848	22.149	- 221.763	- 153.939	21.027
1700.	17.896	40.775	26.694	23.937	- 221.640	- 149.705	19.246
1800	17.936	41.799	27.505	25.729	- 221.542	- 145.476	17.663
1900	17.974	42.770	28.283	27.524	- 221.469	- 141.253	16.248
2000	18.011	43.693	29.031	29.323	- 225.868	- 136.880	14.958
2100	18.046	44.572	29.750	31.126	- 225.820	- 132.429	13.782
2200	18.079	45.412	30.443	32.932	- 225.776	- 127.983	12.714
2300	18.112	46.217	31.112	34.742	- 225.732	- 123.541	11.739
2400	18.144	46.988	31.757	36.555	- 225.691	- 119.095	10.845
2500	18.175	47.730	32.381	38.371	- 225.653	- 114.658	10.023

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE, ANATASE (TiO_2) (CRYSTAL) GFW = 79.8988

$S^\circ_{298.15}$ = 11.93 gibbs/mol

Tt = 918 °K

Tm = Unknown

ΔHf°_0 = -221.8 ± 1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -223.0 ± 1 kcal/mol

ΔHt° = [0.0] kcal/mol

ΔHm° = Unknown

$\Delta Hs^\circ_{298.15}$ = 161 kcal/mol

Heat of Formation.

The value of ΔHf°_{298} (anatase) is obtained from J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, August 1965, Rice University, Houston, Texas. The authors measured the heat of fluorination of anatase, according to the reaction TiO_2 (anatase) + $2F_2(g)$ = $TiF_4(c)$ + $O_2(g)$, but no experimental data were given.

F. W. Vahldiek, J. Less-Common Metals 11, 99 (1966), studied the irreversible anatase-rutile phase transition at pressures of 3.8 to 24 kbars and temperatures 20 to 1000°C. Isothermal phase-transition studies were also carried out at 1 bar pressure and 880-950°C. From the slope, dT/dP, the enthalpy differences between rutile and anatase were calculated to be -2.79 and -2.89 kcal/mol at 1183 and 1223°K, respectively. Using these data and ΔHf°_{298}(rutile) = -225.8 kcal/mol, the value of ΔHf°_{298}(anatase) is derived as -223.23 kcal/mol,which is in excellent agreement with the adopted value.

Heat Capacity and Entropy.

Low temperature heat capacities, 52-296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 69, 218 (1947). Enthalpy data were determined in the range 416-1305°K by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), and in the range 580 - 1000°K by J. Lietz, Hamburger Beitr. Angew. Mineral. Kristallphysik 1, 229 (1956). High temperature heat capacities are derived from the enthalpy data, subject to the constraint that there be a smooth joint at 298°K. The resulting enthalpies are higher by 1 to 3% than those measured by Lietz and lower by 1 to 4% than those measured by Naylor. Values above 1300°K are smoothly extrapolated. S°_{298} is calculated from the low temperature Cp° using S°_{50} = 0.45 eu.

In view of the discrepancies in the enthalpy data, a review of the anatase samples is pertinent. Those of Shomate and Lietz were prepared by precipitation of the hydrated oxide and conversion to the oxide at 550 - 565°C. Shomate's starting material was high purity Ti and the product analyzed as 99.3% TiO_2. Lietz' starting material was high purity $TiCl_4$. Naylor's sample, obtained from J. T. Baker Co., was dried at 1050°C; spectrographic analysis indicated 0.3% SiO_2 and 0.15% CaO. All three samples gave only the X-ray lines of anatase.

Transition Data.

Tm = 918°K and ΔHt° = 0.040 kcal/mol have been reported by J. Lietz, loc. cit. A. Schröder, Z. Kryst. 66, 493 (1928), suggested a transition temperature at 915°K on the basis of a peak in the thermal expansion curve. Lietz reported ΔHt° = 0.04 kcal/mol,but this value is not adopted since its magnitude is much less than the uncertainty in the selected enthalpies. Further study is desirable to confirm this transition.

Heat of Sublimation.

ΔHs°_{298} is calculated as the difference between ΔHf°_{298} for $TiO_2(g)$ and TiO_2(anatase).

Titanium Dioxide, Rutile (TiO_2)

(Crystal) GFW = 79.8988

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.065	- 224.638	- 224.638	INFINITE
100	4.430	2.438	21.438	- 1.900	- 225.301	- 221.208	483.450
200	10.053	7.375	13.149	- 1.155	- 225.710	- 216.927	237.047
298	13.153	12.031	12.031	.000	- 225.800	- 212.593	155.834
300	13.191	12.112	12.031	.024	- 225.800	- 212.511	154.814
400	14.621	16.126	12.569	1.423	- 225.730	- 208.089	113.694
500	15.429	19.481	13.625	2.928	- 225.602	- 203.692	89.034
600	15.991	22.346	14.846	4.500	- 225.451	- 199.325	72.604
700	16.438	24.845	16.099	6.122	- 225.293	- 194.983	60.876
800	16.824	27.066	17.334	7.785	- 225.138	- 190.665	52.087
900	17.173	29.068	18.528	9.485	- 224.988	- 186.364	45.255
1000	17.500	30.894	19.675	11.219	- 224.845	- 182.080	39.794
1100	17.813	32.577	20.772	12.985	- 224.707	- 177.810	35.328
1200	18.116	34.140	21.822	14.781	- 225.511	- 173.515	31.601
1300	18.412	35.601	22.826	16.608	- 225.255	- 169.191	28.444
1400	18.703	36.977	23.788	18.464	- 224.992	- 164.890	25.741
1500	18.990	38.277	24.711	20.348	- 224.724	- 160.606	23.400
1600	19.274	39.511	25.598	22.262	- 224.450	- 156.338	21.355
1700	19.556	40.688	26.451	24.203	- 224.174	- 152.091	19.553
1800	19.836	41.814	27.276	26.173	- 223.898	- 147.859	17.953
1900	20.115	42.894	28.068	28.170	- 223.623	- 143.642	16.523
2000	20.393	43.933	28.835	30.196	- 227.795	- 139.287	15.221
2100	20.670	44.934	29.578	32.249	- 227.497	- 134.866	14.036
2200	20.946	45.902	30.298	34.330	- 227.178	- 130.464	12.960
2300	21.221	46.840	30.997	36.438	- 226.836	- 126.078	11.980
2400	21.496	47.749	31.676	38.574	- 226.472	- 121.703	11.083
2500	21.771	48.632	32.337	40.737	- 226.087	- 117.347	10.258

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE, RUTILE (TiO_2) (CRYSTAL) GFW = 79.8988

$S^\circ_{298.15}$ = 12.03 gibbs/mol

Tm = 2143°K

ΔHf°_0 = -224.6 ± 1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -225.8 ± 1 kcal/mol

ΔHm° = [16] kcal/mol

$\Delta Hs^\circ_{298.15}$ = 163.8 kcal/mol

Heat of Formation.

The heat of formation for rutile has been determined from combustion calorimetry by many investigators. Several of the more consistent ΔHf°_{298} values are listed in the table below. Ariya et al.[3] reported that the composition of the rutile obtained from combustion of Ti(c) was between $TiO_{1.94}$ and $TiO_{1.95}$. Emf studies by R. N. Blumenthal and D. H. Whitmore, J. Electrochem. Soc. 110, 92 (1963), indicate that at 1200°K there is a two-phase region beginning at about $TiO_{1.99}$. If this region extends to 298°K, then the non-stoichiometric combustion products probably involve a mixture of two phases. Mah et al.[4] applied an approximate energy correction for incomplete combustion which corresponds to 0.7 - 1.5 kcal/mol in ΔHf°_{298}. Analogous corrections were applied by Ariya et al.[3] but were not mentioned by Neumann et al.[1] and Humphrey[2].

The ΔHf°_{298} value reported by Margrave and Kybett[5] was obtained by fluorine bomb calorimetry, according to the reaction $TiO_2(rutile) + 2F_2(g) = TiF_4(c) + O_2(g)$. No experimental data were given.

Comparison of the fluorine result with the oxygen results indicates that the magnitude of the corrections for the oxygen data is reasonable, probably within ± 1 kcal/mol, provided that the fluorine data refer to stoichiometric TiO_2. Corresponding ΔGf° corrections for TiO_{2-x} are of the same order of magnitude when estimated from the partial molar free energy values given by P. Kofstad, J. Phys. Chem. Solids 23, 1579 (1962), and J. B. Moser, R. N. Blumenthal and D. H. Whitmore, J. Am. Ceram. Soc. 48, 384 (1965).

The ΔHf°_{298} value determined by Mah et al.[4] is adopted.

ΔHf°_{298}, kcal/mol	Source
-225.3 ± 0.3	1. B. Neumann, C. Kröger and H. Kunz, Z. Anorg. Allgem. Chem. 218, 379 (1934).
-225.5 ± 0.2	2. G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951).
-224.9 ± 0.4	3. S. Ariya, M. Morozova, and E. Volf, Z. Neorg. Khim 2, 13 (1957).
-225.8 ± 0.1	4. A. Mah, K. K. Kelley, N. Gellert, E. G. King, and C. O'Brien, U. S. Bur Mines RI5316 (1957).
-225 ± 1	5. J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, Aug. 1965, Rice University, Houston, Texas.

Heat Capacity and Entropy.

The low temperature heat capacities, 10 - 297.7°K, have been measured by the following investigators: P. H. Keesom and N. Pearlman, Phys. Rev. 112, 800 (1958), 10 - 20°K; J. S. Dugdale, J. A. Morrison and D. Patterson, Proc. Roy. Soc. (London) A224, 228(1954), 20 - 50°K; H. Shomate, J. Am. Chem. Soc. 69, 218 (1947), 52.5 - 297.7°K; and H. J. McDonald and H. Seltz, J. Am. Chem. Soc. 61, 2405 (1939), 68.78 - 295.07°K. The first three sets of Cp data are joined smoothly and extrapolated to 298°K, yielding S°_{298} = 12.03 eu, based on S°_{10} = 0.0014 eu. The Cp values reported by McDonald and Seltz seem too high and are not used.

The high temperature enthalpies have been determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), 393.5 - 1746°K; J. S. Arthur, J. Appl. Phys. 21, 732 (1950), 293.2 - 1073.2°K; and J. Lietz, Hamburger Beitrage Angew. Mineral u. Kristall Phys. 1, 229 (1956), 577.7 - 1283.0°K. The Cp values are derived from the data of Lietz and join smoothly at 298°K with the low temperature data. Deviations from the selected values are -1.6 to+1.0% for Lietz, -6.1to + 4.0% for Arthur, and +8.6 to+0.8% for Naylor. The data point of Lietz at 947.95°K is omitted as a probable typographical error. The largest deviations in the case of Naylor and Arthur are near 400 and 500°K, respectively.

The mean specific enthalpies have also been measured by L. F. Nilson and O. Pettersson, Z. Physik, Chem. 1, 27 (1887), 373.2 - 717.2 °K.

The samples used by Keesom and Pearlman, Dugdale et al., Shomate, Arthur and Lietz were of high purity, according to chemical and spectroscopic analysis. However, the sample employed by Naylor was black-colored and chemical analysis gave 97.9% TiO_2. The main impurities were: 0.55% ZrO_2, 0.50% SiO_2, 0.27% V_2O_5, 0.15% CaO, 0.15% Fe_2O_3 and 0.12% Al_2O_3. The sample of McDonald and Seltz was obtained commercially. Therefore the results reported by Naylor and McDonald et al. are given the least weight.

Melting Data.

See TiO_2(l) table for details.

Heat of Sublimation.

The difference between ΔHf°_{298} for $TiO_2(g)$ and $TiO_2(rutile)$ is ΔHs°_{298}.

Titanium Dioxide (TiO_2)
(Liquid) GFW = 79.8988

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	13.153	18.934	18.934	.000	- 210.726	- 199.577	146.294
300	13.191	19.015	18.934	.024	- 210.726	- 199.507	145.341
400	14.621	23.029	19.472	1.423	- 210.656	- 195.776	106.967
500	15.429	26.384	20.528	2.928	- 210.528	- 192.070	83.954
600	15.991	29.249	21.749	4.500	- 210.377	- 188.393	68.622
700	16.438	31.748	23.002	6.122	- 210.219	- 184.741	57.679
800	16.824	33.969	24.237	7.785	- 210.064	- 181.113	49.478
900	17.173	35.971	25.431	9.485	- 209.914	- 177.503	43.104
1000	17.500	37.797	26.578	11.219	- 209.771	- 173.909	38.008
1100	17.813	39.480	27.675	12.985	- 209.633	- 170.329	33.841
1200	18.116	41.043	28.725	14.781	- 210.437	- 166.724	30.365
1300	18.412	42.504	29.729	16.608	- 210.181	- 163.091	27.418
1400	21.000	43.880	30.691	18.464	- 209.918	- 159.481	24.896
1500	21.000	45.328	31.619	20.564	- 209.434	- 155.893	22.714
1600	21.000	46.684	32.519	22.664	- 208.974	- 152.339	20.809
1700	21.000	47.957	33.390	24.764	- 208.539	- 148.813	19.131
1800	21.000	49.157	34.233	26.864	- 208.133	- 145.312	17.643
1900	21.000	50.293	35.049	28.964	- 207.755	- 141.833	16.315
2000	21.000	51.370	35.838	31.064	- 211.853	- 138.219	15.104
2100	21.000	52.394	36.602	33.164	- 211.508	- 134.543	14.002
2200	21.000	53.371	37.342	35.264	- 211.170	- 130.888	13.003
2300	21.000	54.305	38.060	37.364	- 210.836	- 127.247	12.091
2400	21.000	55.198	38.755	39.464	- 210.508	- 123.616	11.257
2500	21.000	56.056	39.430	41.564	- 210.186	- 120.006	10.491
2600	21.000	56.879	40.086	43.664	- 209.868	- 116.404	9.785
2700	21.000	57.672	40.722	45.764	- 209.556	- 112.815	9.132
2800	21.000	58.436	41.341	47.864	- 209.249	- 109.239	8.526
2900	21.000	59.173	41.944	49.964	- 208.947	- 105.670	7.963
3000	21.000	59.884	42.530	52.064	- 208.650	- 102.111	7.439
3100	21.000	60.573	43.101	54.164	- 208.357	- 98.565	6.949
3200	21.000	61.240	43.657	56.264	- 208.069	- 95.033	6.490
3300	21.000	61.886	44.200	58.364	- 207.785	- 91.503	6.060
3400	21.000	62.513	44.729	60.464	- 207.506	- 87.983	5.655
3500	21.000	63.122	45.246	62.564	- 207.230	- 84.475	5.275
3600	21.000	63.713	45.751	64.664	- 308.584	- 80.704	4.899
3700	21.000	64.289	46.244	66.764	- 308.288	- 74.382	4.394
3800	21.000	64.849	46.727	68.864	- 308.008	- 68.065	3.915
3900	21.000	65.394	47.198	70.964	- 307.744	- 61.752	3.460
4000	21.000	65.926	47.660	73.064	- 307.497	- 55.449	3.030
4100	21.000	66.444	48.112	75.164	- 307.266	- 49.147	2.620
4200	21.000	66.950	48.554	77.264	- 307.049	- 42.857	2.230
4300	21.000	67.445	48.988	79.364	- 306.847	- 36.571	1.859
4400	21.000	67.927	49.413	81.464	- 306.659	- 30.287	1.504
4500	21.000	68.399	49.830	83.564	- 306.484	- 24.006	1.166
4600	21.000	68.861	50.238	85.664	- 306.321	- 17.727	.842
4700	21.000	69.312	50.639	87.764	- 306.171	- 11.453	.533
4800	21.000	69.755	51.033	89.864	- 306.032	- 5.188	.236
4900	21.000	70.188	51.419	91.964	- 305.904	1.071	- .048
5000	21.000	70.612	51.799	94.064	- 305.786	7.339	- .321

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE (TiO_2) (LIQUID) GFW = 79.8988

$S°_{298.15}$ = [18.934] gibbs/mol $\Delta Hf°_{298.15}$ = [-210.726] kcal/mol

Tm = 2143°K $\Delta Hm°$ = [16] kcal/mol

Heat of Formation.

The $\Delta Hf°_{298}(l)$ is calculated from $\Delta Hf°_{298}$(rutile, c) by adding ΔHm° and the difference between $H°_{2143} - H°_{298.15}$ for TiO_2(rutile, c) and $TiO_2(l)$.

Heat Capacity and Entropy.

The heat capacity of $TiO_2(l)$ is estimated on the basis of 7.0 gibbs/g-atom. The value of $S°_{298}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting point of TiO_2(rutile) has been measured by many investigators. Eleven pertinent Tm values were reviewed and corrected, according to the International Temperature Scale of 1948, by S. J. Schneider, Natl. Bur. Std. Monograph 68, October 10, 1963. The adopted melting point is obtained from G. Brauer and W. Littke, J. Inorg. Nucl. Chem. 16, 67 (1960). These authors found that TiO_2 loses oxygen on heating and the solid residue consists of a non-stoichiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and on the oxygen pressure of the gaseous phase. Under oxygen pressures greater than or equal to 300 torr, the solid residue was $TiO_{2.000}$ within the sensitivity of chemical analysis; however, color of the residue was a more sensitive indicator of composition. At pressures of 600 torr or greater, the residue was bright yellow rather than blue-gray and the melting point was constant at the maximum value of 2143 ± 15°K. This value is adopted.

The heat of melting is calculated using an estimated entropy of melting, ΔSm° = 2.5 eu/g-atom.

Titanium Dioxide (TiO_2)

(Ideal Gas) GFW = 79.8988

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.597	-61.370	-61.370	INFINITE
100	7.760	46.055	64.906	-1.885	-61.486	-61.755	134.966
200	9.634	52.065	57.100	-1.007	-61.762	-61.918	67.661
298	10.838	56.146	56.146	.000	-62.000	-61.945	45.407
300	10.858	56.213	56.146	.020	-62.004	-61.945	45.127
400	11.920	59.474	56.584	1.156	-62.197	-61.895	33.818
500	12.548	62.194	57.442	2.374	-62.354	-61.801	27.013
600	13.079	64.531	58.433	3.659	-62.492	-61.677	22.466
700	13.464	66.578	59.453	4.987	-62.628	-61.531	19.211
800	13.746	68.395	60.460	6.348	-62.775	-61.365	16.764
900	13.957	70.027	61.434	7.734	-62.939	-61.179	14.856
1000	14.117	71.506	62.368	9.138	-63.126	-60.973	13.326
1100	14.241	72.858	63.261	10.556	-63.336	-60.748	12.069
1200	14.339	74.101	64.113	11.985	-64.507	-60.464	11.012
1300	14.417	75.252	64.926	13.423	-64.640	-60.122	10.107
1400	14.480	76.323	65.703	14.868	-64.788	-59.770	9.331
1500	14.532	77.324	66.444	16.319	-64.953	-59.406	8.655
1600	14.575	78.263	67.154	17.774	-65.138	-59.029	8.063
1700	14.611	79.147	67.834	19.234	-65.343	-58.640	7.539
1800	14.641	79.984	68.486	20.696	-65.575	-58.242	7.071
1900	14.667	80.776	69.112	22.162	-65.831	-57.827	6.652
2000	14.690	81.529	69.714	23.630	-70.561	-57.245	6.255
2100	14.709	82.246	70.294	25.099	-70.847	-56.571	5.887
2200	14.726	82.931	70.853	26.571	-71.137	-55.886	5.552
2300	14.741	83.586	71.392	28.045	-71.429	-55.187	5.244
2400	14.754	84.213	71.913	29.519	-71.727	-54.471	4.960
2500	14.765	84.816	72.418	30.995	-72.029	-53.749	4.699
2600	14.776	85.395	72.906	32.472	-72.334	-53.010	4.456
2700	14.785	85.953	73.379	33.950	-72.644	-52.261	4.230
2800	14.793	86.491	73.837	35.429	-72.958	-51.501	4.020
2900	14.800	87.010	74.283	36.909	-73.276	-50.726	3.823
3000	14.807	87.512	74.715	38.389	-73.599	-49.944	3.638
3100	14.813	87.997	75.136	39.870	-73.925	-49.146	3.465
3200	14.819	88.468	75.545	41.352	-74.255	-48.348	3.302
3300	14.824	88.924	75.944	42.834	-74.589	-47.532	3.148
3400	14.828	89.366	76.332	44.317	-74.927	-46.704	3.002
3500	14.832	89.796	76.711	45.800	-75.268	-45.872	2.864
3600	14.836	90.214	77.080	47.283	-177.239	-44.762	2.717
3700	14.840	90.621	77.441	48.767	-177.559	-41.081	2.427
3800	14.843	91.017	77.793	50.251	-177.895	-37.390	2.150
3900	14.846	91.402	78.137	51.736	-178.246	-33.685	1.888
4000	14.849	91.778	78.473	53.220	-178.615	-29.975	1.638
4100	14.852	92.145	78.802	54.705	-178.999	-26.253	1.399
4200	14.854	92.503	79.124	56.191	-179.396	-22.526	1.172
4300	14.856	92.852	79.439	57.676	-179.809	-18.782	.955
4400	14.858	93.194	79.748	59.162	-180.235	-15.037	.747
4500	14.860	93.528	80.050	60.648	-180.674	-11.276	.548
4600	14.862	93.854	80.347	62.134	-181.125	-7.495	.356
4700	14.864	94.174	80.638	63.620	-181.589	-3.722	.173
4800	14.866	94.487	80.923	65.107	-182.063	.068	-.003
4900	14.867	94.794	81.203	66.593	-182.549	3.857	-.172
5000	14.869	95.094	81.478	68.080	-183.044	7.671	-.335
5100	14.870	95.388	81.748	69.567	-183.549	11.496	-.493
5200	14.871	95.677	82.013	71.054	-184.063	15.321	-.644
5300	14.872	95.960	82.273	72.541	-184.585	19.163	-.790
5400	14.874	96.238	82.529	74.029	-185.115	23.012	-.931
5500	14.875	96.511	82.781	75.516	-185.651	26.875	-1.068
5600	14.876	96.779	83.029	77.004	-186.196	30.736	-1.200
5700	14.877	97.043	83.272	78.491	-186.746	34.614	-1.327
5800	14.878	97.301	83.512	79.979	-187.302	38.509	-1.451
5900	14.878	97.556	83.748	81.467	-187.863	42.402	-1.571
6000	14.879	97.806	83.980	82.955	-188.429	46.309	-1.687

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE (TiO_2) (IDEAL GAS) GFW = 79.8988

Point Group [$D_{\infty h}$]

$S°_{298.15}$ = [56] gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0 = 61.4 \pm 10$ kcal/mol

$\Delta Hf°_{298} = -62.0 \pm 10$ kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
940	(1)
[328]	(2)
[1214]	(1)

Bond Distance: Ti-O = [1.62] Å

Bond Angle: O-Ti-O = [180]°

Rotational Constant: B_0 = [0.2007] cm^{-1}

σ = 2

Heat of Formation.

P. W. Gilles, K. D. Carlson, H. F. Franzen, and P. G. Wahlbeck, J. Chem. Phys. 46, 2461 (1967), studied the vaporization behavior of the titanium-oxygen system and found that Ti_3O_5 is the final residue of both higher and lower titanium oxides; hence Ti_3O_5 is the congruently vaporizing phase. This conclusion was obtained by measurement of the change in composition of the solid residue accompanying vaporization as determined by x-ray diffraction, chemical analysis, and color of sample.

From mass spectrometric studies over $Ti_3O_5(\beta)$ near 2000°K, P. G. Wahlbeck and P. W. Gilles, J. Chem. Phys. 46, 2465 (1967), concluded that the partial pressure of TiO_2 is probably less than 1% of the pressure of TiO produced by the main vaporization, $Ti_3O_5(\beta) = 3\ TiO(g) + 2\ O(g)$. This yields $\Delta Gr°_{2000} \geq 228$ kcal for the reaction $Ti_3O_5(\beta) = 2\ TiO_2(g) + TiO(g)$ and $\Delta Hf°_{298}(TiO_2,g) \geq -62$ kcal/mol, which is the value adopted. The corresponding atomization energy is $D°_0 \leq 292$ kcal/mol.

Earlier vaporization studies over TiO_{2-x} gave apparent heats of formation which are more negative by 20-35 kcal; however, the results appear to be uncertain due to lack of sufficient auxiliary data for the oxygen-deficient condensed phase. Knudsen effusion-mass spectrometric studies of J. Berkowitz, W. A. Chupka and M. G. Inghram, J. Phys. Chem. 61, 1569 (1957), revealed the initial evolution of large amounts of $MoO_3(g)$, suggesting that the reduction of TiO_2 is enhanced by the Mo cell. In order to reduce the effect of the initial high rate of evaporation, W. O. Groves, M. Hoch and H. L. Johnston, J. Phys. Chem. 59, 127 (1955), conducted their Knudsen effusion-weight loss studies on $TiO_{1.94}$. Preferential loss of oxygen during the experiment, as indicated by a residue of $TiO_{1.85}$, was apparently ignored. Groves et al. estimated the activity of TiO_2(rutile) as 0.53; Berkowitz et al. assumed unit activity but did not indicate the composition of their condensed phase. These activities may be in serious error due to the presence of a series of distinct phases between $TiO_{1.8}$ and $TiO_{1.9}$ [cf. S. Andersson, Acta Chem. Scand. 14, 1161 (1960)] and to the possible existence of a two phase region near $TiO_{1.99}$ [cf. R. N. Blumenthal and D. H. Whitmore, J. Electrochem. Soc. 110, 92 (1963)]. Second and third law analyses of the data, using the authors' original assumptions, are summarized below. No weight is given to these results.

			$\Delta Hr°_{298}$ kcal/mol			$\Delta Hf°_{298}$*
Investigator	Temperature, °K	No. of Points	2nd law	3rd law	Drift eu	kcal/mol
Groves et al.	1849 - 2010	14	128.7 ± 7.5	130.1	1.1 ± 4.0	-95.7
Berkowitz et al.	1881	3	142.7 ± 5**	142.8	-	-83.0

*Calculation based on the third law $\Delta Hr°_{298}$.

**Obtained from the temperature variation experiments, reported in the original paper.

Heat Capacity and Entropy.

The molecular structure is assumed to be linear. The Ti-O bond distance is estimated as the same as that in TiO(g). The vibrational frequency 940 cm^{-1} was observed in matrix isolation by W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965). The other two frequencies are calculated, based on the valence bond method as suggested by Berkowitz, Chupka and Inghram, loc. cit. The moment of inertia is 1.3944×10^{-38} g cm^2.

Tungsten Dioxide (WO_2)

(Crystal) GFW = 215.8488

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.081	- 139.757	- 139.757	INFINITE
100	4.566	2.388	21.558	- 1.917	- 140.462	- 136.319	297.925
200	10.089	7.384	13.204	- 1.164	- 140.869	- 131.987	144.229
298	13.322	12.077	12.077	.000	- 140.940	- 127.603	93.535
300	13.360	12.159	12.077	.025	- 140.939	- 127.520	92.898
400	15.160	16.267	12.625	1.457	- 140.807	- 123.063	67.239
500	16.290	19.781	13.713	3.034	- 140.562	- 118.654	51.864
600	17.042	22.821	14.984	4.702	- 140.260	- 114.300	41.634
700	17.596	25.492	16.298	6.435	- 139.926	- 109.999	34.343
800	18.039	27.871	17.599	8.218	- 139.574	- 105.749	28.889
900	18.398	30.017	18.861	10.040	- 139.208	- 101.542	24.658
1000	18.684	31.971	20.076	11.895	- 138.834	- 97.376	21.281
1100	18.911	33.763	21.240	13.775	- 138.457	- 93.250	18.527
1200	19.113	35.417	22.353	15.676	- 138.079	- 89.156	16.237
1300	19.355	36.956	23.418	17.599	- 137.699	- 85.095	14.306
1400	19.830	38.406	24.437	19.556	- 137.303	- 81.063	12.655
1500	20.340	39.792	25.415	21.566	- 136.872	- 77.059	11.228
1600	21.040	41.128	26.356	23.636	- 136.398	- 73.088	9.983
1700	21.760	42.425	27.263	25.776	- 135.871	- 69.146	8.889
1800	22.430	43.688	28.140	27.986	- 135.292	- 65.238	7.921
1900	22.985	44.916	28.991	30.257	- 134.669	- 61.363	7.058
2000	23.470	46.108	29.817	32.580	- 134.011	- 57.523	6.286
2100	23.900	47.263	30.621	34.949	- 133.324	- 53.713	5.590
2200	24.320	48.385	31.403	37.360	- 132.614	- 49.942	4.961
2300	24.740	49.475	32.165	39.813	- 131.877	- 46.199	4.390
2400	25.150	50.537	32.909	42.307	- 131.117	- 42.489	3.869
2500	25.560	51.572	33.634	44.843	- 130.333	- 38.816	3.393
2600	25.960	52.582	34.344	47.419	- 129.526	- 35.169	2.956
2700	26.360	53.569	35.038	50.035	- 128.694	- 31.553	2.554
2800	26.760	54.535	35.717	52.691	- 127.856	- 27.972	2.183
2900	27.120	55.481	36.382	55.386	- 127.022	- 24.420	1.840
3000	27.510	56.406	37.034	58.117	- 126.200	- 20.894	1.522

June 30, 1962; Sept. 30, 1966

TUNGSTEN DIOXIDE (WO_2) (CRYSTAL) GFW = 215.8488

$S^\circ_{298.15}$ = 12.08 ± 0.07 gibbs/mol

Td = 1997°K

ΔHf°_0 = -139.76 ± 0.21 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -140.94 ± 0.21 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 159.24 kcal/mol

Heat of Formation.

The adopted heat of formation, − 140.94 ± 0.21 kcal/mol, was determined by combustion calorimetry by A. D. Mah, J. Am. Chem. Soc. 81, 1582 (1959). R. C. Griffis, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to WO_3(c) which yields ΔHf°_{298} (WO_2, c) = -139.8 ± 1.5 kcal/mol when recalculated with ΔHf°_{298}(WO_3,c) = -201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products.

Recent equilibrium data yield essentially the same average of the heat of formation by the third law method. The results are presented as follows.

Author	Reaction*	Temp. (°K)	No. of Points	ΔHr°_{298} (kcal/mol) 3rd law	2nd law	Drift (eu)	ΔHf°_{298} (kcal/mol)
1. St. Pierre (1962) et al.	A	1275 - 1497	10	2.672	0.036	1.9 ± 0.6	-140.62
	B	973 - 1467	6	11.994	12.076	0.2 ± 0.1	-139.58
2. Gerasimov (1962) et al.	C	923 - 1223	7	-70.281	-67.943	-2.2 ± 0.2	-140.56
3. Vasil'eva (1960) et al.	B	1075 - 1210	5	12.949	13.051	-0.1 ± 0.4	-141.49
4. Griffis (1959)	B	873 - 1273	30	12.550	10.295	2.1 ± 0.1	-140.70

*Reaction
A: 1/2 WO_2(c) + CO(g) = 1/2 W (c) + CO_2(g)
B: 1/2 WO_2(c) + H_2(g) = 1/2 W (c) + H_2O (g)
C: 1/2 W(c) + 1/2 O_2(g) = 1/2 WO_2(c)

Reference
1. G. R. St. Pierre, W. T. Ebihara, M. J. Pool and R. Speiser, Trans. AIME 224, 259 (1962).
2. Ya. I. Gerasimov, I. A. Vasil'eva, T. P. Chusova, V. W. Geiderikh, and M. A. Timofeeva, Zh. Fiz. Khim. 36, 358 (1962).
3. I. A. Vasil'eva, Ya. I. Gerasimov and Yu. P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960).
4. R. C. Griffis, J. Electrochem. Soc. 106, 418 (1959).

Heat Capacity and Entropy.

E. G. King, W. W. Weller, and A. U. Christensen, U. S. Bur. Mines RI 5664,(1960), have measured the low temperature heat capacities from 53° to 297°K and high temperature enthalpy changes from 396° to 1800°K by drop calorimetry. The low temperature and high temperature heat capacities were joined smoothly at 298.15°K. The entropy was obtained from the heat capacities based on S°_{51} = 0.52 eu. It is possible that at temperatures below 50°K the entropy due to the uncoupling of the d^2 electrons will appear, contributing an additional 2.2 eu.

Temperature of Decomposition.

Tungsten dioxide (c) has no melting point, since disproportionation occurs to yield W(c) and WO_3(l) before melting starts. The Td is calculated as the temperature at which ΔG equals zero for 3 WO_2(c) = 2 WO_3(l) + W(c).

Heat of Sublimation.

The heat of sublimation was calculated from the difference between the heats of formation of WO_2(g) and WO_2(c).

Tungsten Dioxide (WO_2)
(Ideal Gas) GFW = 215.8488

T, °K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.688	18.876	18.876	INFINITE
100	8.457	58.030	76.844	-1.881	18.833	17.399	-38.025
200	9.508	64.233	69.135	-.980	18.558	16.067	-17.557
298	10.471	68.209	68.209	.000	18.300	14.901	-10.923
300	10.489	68.274	68.209	.019	18.295	14.880	-10.840
400	11.355	71.415	68.631	1.113	18.089	13.774	-7.526
500	11.999	74.022	69.456	2.283	17.927	12.714	-5.557
600	12.454	76.252	70.407	3.507	17.785	11.686	-4.257
700	12.776	78.197	71.384	4.769	17.648	10.681	-3.335
800	13.006	79.919	72.345	6.059	17.507	9.693	-2.648
900	13.176	81.461	73.274	7.368	17.360	8.727	-2.119
1000	13.303	82.856	74.164	8.693	17.204	7.777	-1.700
1100	13.401	84.129	75.013	10.028	17.036	6.840	-1.359
1200	13.477	85.299	75.822	11.372	16.857	5.922	-1.078
1300	13.538	86.380	76.593	12.723	16.665	5.018	-.844
1400	13.587	87.385	77.328	14.079	16.460	4.129	-.645
1500	13.627	88.324	78.030	15.440	16.242	3.257	-.474
1600	13.660	89.204	78.701	16.805	16.011	2.399	-.328
1700	13.688	90.033	79.344	18.172	15.765	1.556	-.200
1800	13.711	90.816	79.960	19.542	15.504	.728	-.088
1900	13.731	91.558	80.551	20.914	15.228	-.086	.010
2000	13.748	92.263	81.119	22.288	14.937	-.885	.097
2100	13.763	92.934	81.666	23.664	14.631	-1.667	.174
2200	13.776	93.575	82.193	25.041	14.307	-2.440	.242
2300	13.787	94.187	82.701	26.419	13.969	-3.192	.303
2400	13.797	94.774	83.192	27.798	13.614	-3.928	.358
2500	13.806	95.338	83.666	29.178	13.242	-4.655	.407
2600	13.815	95.879	84.126	30.559	12.855	-5.360	.451
2700	13.822	96.401	84.571	31.941	12.446	-6.054	.490
2800	13.829	96.904	85.002	33.324	12.007	-6.731	.525
2900	13.836	97.389	85.421	34.707	11.527	-7.393	.557
3000	13.843	97.858	85.828	36.091	11.002	-8.033	.585
3100	13.850	98.312	86.223	37.476	10.421	-8.660	.611
3200	13.857	98.752	86.608	38.861	9.776	-9.267	.633
3300	13.864	99.179	86.983	40.247	9.062	-9.854	.653
3400	13.872	99.593	87.347	41.634	8.269	-10.414	.669
3500	13.880	99.995	87.703	43.021	7.385	-10.951	.684
3600	13.890	100.386	88.050	44.410	6.385	-11.460	.696
3700	13.900	100.767	88.389	45.799	-3.064	-11.896	.703
3800	13.910	101.138	88.719	47.190	-3.508	-12.127	.697
3900	13.922	101.499	89.042	48.581	-3.955	-12.347	.692
4000	13.935	101.852	89.358	49.974	-4.404	-12.560	.686
4100	13.950	102.196	89.667	51.369	-4.854	-12.755	.680
4200	13.965	102.532	89.969	52.764	-5.306	-12.941	.673
4300	13.982	102.861	90.265	54.162	-5.758	-13.116	.667
4400	14.000	103.183	90.555	55.561	-6.212	-13.287	.660
4500	14.020	103.498	90.839	56.962	-6.666	-13.443	.653
4600	14.041	103.806	91.118	58.365	-7.120	-13.583	.645
4700	14.064	104.108	91.391	59.770	-7.575	-13.718	.638
4800	14.088	104.405	91.659	61.178	-8.028	-13.846	.630
4900	14.113	104.695	91.922	62.588	-8.481	-13.964	.623
5000	14.140	104.981	92.181	64.000	-8.934	-14.074	.615
5100	14.168	105.261	92.434	65.416	-9.385	-14.169	.607
5200	14.198	105.536	92.684	66.834	-9.835	-14.260	.599
5300	14.228	105.807	92.929	68.255	-10.283	-14.337	.591
5400	14.260	106.073	93.170	69.680	-10.729	-14.412	.583
5500	14.294	106.335	93.407	71.107	-11.173	-14.473	.575
5600	14.328	106.593	93.640	72.539	-11.615	-14.533	.567
5700	14.363	106.847	93.869	73.973	-12.055	-14.586	.559
5800	14.400	107.097	94.095	75.411	-12.492	-14.620	.551
5900	14.437	107.344	94.318	76.853	-12.926	-14.655	.543
6000	14.475	107.587	94.537	78.299	-207.261	-12.597	.459

June 30, 1962; Sept. 30, 1966

TUNGSTEN DIOXIDE (WO_2) (IDEAL GAS) GFW = 215.8488

Point Group [C_{2v}]

$S°_{298.15}$ = [68.2] gibbs/mol

Ground State Quantum Weight = [3]

$\Delta Hf°_0$ = 18.9 ± 7 kcal/mol

$\Delta Hf°_{298.15}$ = 18.3 ± 7 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i cm^{-1}	g_i
0	[3]
[25,000]	[10]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
992	(1)
[300]	(1)
928	(1)

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [110°]

σ = [2]

Product of the Moments of Inertia: $I_AI_BI_C$ = [9.433 x 10^{-115}] g^3cm^6

Heat of Formation.

G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960), have reported the partial pressures of WO(g), WO_2(g), WO_3(g) and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188° to 2475°K. The adopted value, $\Delta Hf°_{298}$ (WO_2,g) = 18.3 ± 7 kcal/mol, was calculated from $\Delta Hr°_{298}$ = -100.9 kcal/mol for W(c) + 2 O(g) → WO_2(g), which was obtained from third law treatment of their partial pressure data, using all JANAF functions. The third law drift is 15.0 ± 5.2 eu. Partial pressures of WO_2(g), WO_3(g) and O(g) at 2242°K have also been reported by W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. 30, 827 (1959), in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives $\Delta Hr°_{298}$ = -105.9 kcal/mol, which yields $\Delta Hf°_{298}$ (WO_2,g) = 13.2 kcal/mol.

Heat Capacity and Entropy.

The WO_2(g) was assumed to have a C_{2v} symmetry with a bond angle O-W-O = 110°. The bond distance W-O was estimated to be the same as that in WO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectrum of WO_2 in a neon matrix by W. Weltner, Jr., and D. McLeod, Jr., J. Mol. Spectry. 17, 276 (1965). The bending vibrational frequency (300 cm^{-1}) was estimated by comparison with other dioxides. The electronic levels and quantum weights were estimated from W^{+4} ion by analogy with Mo^{+4} ion. The three principal moments of inertia are: I_A = 4.8776 x 10^{-39}, I_B = 1.1680 x 10^{-38} and I_C = 1.6558 x 10^{-38} g cm^2.

Zirconium Dioxide (ZrO_2)

(Crystal) Mol. Wt. = 123.2188

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	- 2.091	- 260.999	- 260.999	INFINITE
100	4.524	2.268	21.604	- 1.934	- 261.767	- 257.504	562.748
200	10.224	7.301	13.173	- 1.174	- 262.210	- 253.034	276.490
298	13.430	12.036	12.036	- .000	- 262.300	- 248.502	182.148
300	13.447	12.119	12.036	.025	- 262.299	- 248.416	180.962
400	15.260	16.268	12.590	1.471	- 262.199	- 243.802	133.201
500	16.196	19.782	13.686	3.048	- 262.024	- 239.221	104.558
600	16.787	22.791	14.959	4.699	- 261.832	- 234.678	85.477
700	17.214	25.412	16.269	6.400	- 261.634	- 230.168	71.858
800	17.555	27.733	17.560	8.139	- 261.431	- 225.687	61.652
900	17.845	29.818	18.808	9.909	- 261.220	- 221.231	53.720
1000	18.104	31.712	20.005	11.707	- 261.003	- 216.798	47.379
1100	18.342	33.449	21.149	13.529	- 260.790	- 212.390	42.196
1200	18.567	35.054	22.242	15.375	- 261.530	- 207.950	37.871
1300	18.781	36.549	23.286	17.242	- 261.294	- 203.496	34.209
1400	18.989	37.948	24.284	19.131	- 261.051	- 199.059	31.073
1500	17.800	40.206	25.253	22.430	- 259.411	- 194.661	28.361
1600	17.800	41.355	26.224	24.210	- 259.303	- 190.347	25.999
1700	17.800	42.434	27.146	25.990	- 259.208	- 186.040	23.916
1800	17.800	43.451	28.024	27.770	- 259.126	- 181.737	22.065
1900	17.800	44.414	28.861	29.550	- 259.057	- 177.441	20.409
2000	17.800	45.327	29.662	31.330	- 259.001	- 173.149	18.920
2100	17.800	46.195	30.429	33.110	- 258.956	- 168.856	17.572
2200	17.800	47.023	31.164	34.890	- 263.828	- 164.402	16.331
2300	17.800	47.814	31.871	36.670	- 263.814	- 159.882	15.192
2400	17.800	48.572	32.551	38.450	- 263.806	- 155.362	14.147
2500	17.800	49.299	33.207	40.230	- 263.804	- 150.847	13.186
2600	17.800	49.997	33.839	42.010	- 263.806	- 146.328	12.299
2700	17.800	50.669	34.450	43.790	- 263.814	- 141.810	11.478
2800	17.800	51.316	35.041	45.570	- 263.827	- 137.290	10.715
2900	17.800	51.941	35.613	47.350	- 263.845	- 132.768	10.005
3000	17.800	52.544	36.167	49.130	- 263.868	- 128.247	9.342
3100	17.800	53.128	36.705	50.910	- 263.895	- 123.729	8.722
3200	17.800	53.693	37.227	52.690	- 263.927	- 119.207	8.141
3300	17.800	54.240	37.735	54.470	- 263.963	- 114.681	7.595
3400	17.800	54.772	38.228	56.250	- 264.004	- 110.158	7.081
3500	17.800	55.288	38.708	58.030	- 264.048	- 105.635	6.596
3600	17.800	55.789	39.176	59.810	- 264.096	- 101.106	6.138
3700	17.800	56.277	39.631	61.590	- 264.148	- 96.579	5.704
3800	17.800	56.752	40.075	63.370	- 264.203	- 92.048	5.294
3900	17.800	57.214	40.509	65.150	- 264.261	- 87.517	4.904
4000	17.800	57.665	40.932	66.930	- 264.323	- 82.987	4.534

June 30, 1961; Dec. 31, 1965

ZICONIUM DIOXIDE (ZrO_2) (CRYSTAL) MOL. WT. = 123.2188

$\Delta H^\circ_{f\ 0}$ = -261.0 ± 0.4 kcal. mole^{-1}

$S^\circ_{298.15}$ = [12.036 ± 0.08] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -262.3 ± 0.4 kcal. mole^{-1}

T_t = 1478 ± 5°K.

ΔH°_t = 1.42 ± 0.1 kcal. mole^{-1}

T_m = 2950°K.

ΔH°_m = [20.8] kcal. mole^{-1}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = -262.3 ± 0.4 kcal. mole^{-1} is the average value of the $\Delta H^\circ_{f\ 298.15}$ = -261.5 ± 0.2 kcal. mole^{-1} and $\Delta H^\circ_{f\ 298.15}$ = -263.1 ± 0.5 kcal. mole^{-1} measured (by combustion calorimetry) by G. L. Humphrey, J. Am. Chem. Soc. 76, 978 (1954) and E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) respectively. Also the heat of formation was measured calorimetrically by B. Neumann, C. Kröger and H. Kunz, Z. anorg. Chem. 218, 379 (1934), by W. A. Roth, E. Börger, and H. Siemonsen, ibid., 239, 321 (1938) and by A. Sieverts, A. Gotta and S. Halberstadt, ibid., 187, 155 (1930) and was found -258.2, -258.8 and -256.1 kcal. mole^{-1} respectively. However more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.3-295°K., were measured by K. K. Kelley, Ind. Eng. Chem. 36, 377 (1944). The heat capacities in the temperature range 298-1478°K. were calculated by using the J. P. Coughlin and E. G. King equation $C_p = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^5\ T^{-2}$ obtained from their measured enthalpy data in the range 396.8 - 1841°K., J. Am. Chem. Soc. 72, 2262 (1950). The values from the two sources join smoothly at 298°K. Above the transition 1478°K. the heat capacity was taken as constant at 17.80 cal. mole^{-1} deg.$^{-1}$, Coughlin and King, loc. cit. The entropy was calculated at 54.30° using the Debye and Einstein function $D(\frac{345}{T}) + E(\frac{513}{T}) + E(\frac{861}{T})$ given by Kelley, loc. cit. The value of $S^\circ_{54.3}$ = 0.5507 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

T_t and ΔH°_t were taken from Coughlin and King loc. cit.

Melting Data.

The T_m and ΔH°_m were taken from Natl. Bur. Standards Circ. 500 Washington (1952).

Zirconium Dioxide (ZrO_2)

(Liquid) Mol. Wt. = 123.2188

T, °K.	C_p° (cal. mole⁻¹deg.⁻¹)	S° (cal. mole⁻¹deg.⁻¹)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole⁻¹deg.⁻¹)	$H^\circ-H^\circ_{298}$ (kcal. mole⁻¹)	ΔH°_f (kcal. mole⁻¹)	ΔF°_f (kcal. mole⁻¹)	Log K_p
0							
100							
200							
298	13.430	17.841	17.841	.000	- 244.550	- 232.483	170.406
300	13.447	17.924	17.841	.025	- 244.549	- 232.408	169.301
400	15.260	22.072	18.395	1.471	- 244.449	- 228.373	124.771
500	16.196	25.587	19.491	3.048	- 244.274	- 224.373	98.069
600	16.787	28.595	20.764	4.699	- 244.082	- 220.410	80.281
700	17.214	31.217	22.074	6.400	- 243.884	- 216.481	67.585
800	17.555	33.538	23.365	8.139	- 243.681	- 212.581	58.072
900	17.845	35.623	24.613	9.909	- 243.470	- 208.706	50.678
1000	18.104	37.517	25.810	11.707	- 243.253	- 204.853	44.769
1100	18.342	39.253	26.954	13.529	- 243.040	- 201.024	39.938
1200	18.567	40.859	28.047	15.375	- 243.780	- 197.166	35.907
1300	18.781	42.354	29.091	17.242	- 243.544	- 193.292	32.494
1400	18.989	43.753	30.088	19.131	- 243.301	- 189.436	29.571
1500	17.800	46.011	31.058	22.430	- 241.661	- 185.618	27.043
1600	17.800	47.160	32.029	24.210	- 241.553	- 181.885	24.843
1700	17.800	48.239	32.951	25.990	- 241.458	- 178.159	22.903
1800	17.800	49.256	33.829	27.770	- 241.376	- 174.436	21.178
1900	17.800	50.218	34.666	29.550	- 241.307	- 170.719	19.636
2000	21.000	51.132	35.467	31.330	- 241.251	- 167.009	18.249
2100	21.000	52.156	36.237	33.430	- 240.886	- 163.304	16.994
2200	21.000	53.133	36.983	35.530	- 245.438	- 159.454	15.839
2300	21.000	54.067	37.706	37.630	- 245.104	- 155.554	14.780
2400	21.000	54.960	38.406	39.730	- 244.776	- 151.664	13.810
2500	21.000	55.818	39.086	41.830	- 244.454	- 147.794	12.920
2600	21.000	56.641	39.745	43.930	- 244.136	- 143.932	12.098
2700	21.000	57.434	40.386	46.030	- 243.824	- 140.085	11.339
2800	21.000	58.197	41.008	48.130	- 243.517	- 136.247	10.634
2900	21.000	58.934	41.614	50.230	- 243.215	- 132.418	9.979
3000	21.000	59.646	42.203	52.330	- 242.918	- 128.603	9.368
3100	21.000	60.335	42.777	54.430	- 242.625	- 124.801	8.798
3200	21.000	61.002	43.336	56.530	- 242.337	- 121.006	8.264
3300	21.000	61.648	43.881	58.630	- 242.053	- 117.218	7.763
3400	21.000	62.275	44.413	60.730	- 241.774	- 113.438	7.291
3500	21.000	62.883	44.932	62.830	- 241.498	- 109.667	6.848
3600	21.000	63.475	45.439	64.930	- 241.226	- 105.906	6.429
3700	21.000	64.050	45.934	67.030	- 240.958	- 102.149	6.033
3800	21.000	64.610	46.418	69.130	- 240.693	- 98.399	5.659
3900	21.000	65.156	46.892	71.230	- 240.431	- 94.661	5.304
4000	21.000	65.688	47.355	73.330	- 240.173	- 90.929	4.968
4100	21.000	66.206	47.809	75.430	- 239.918	- 87.197	4.648
4200	21.000	66.712	48.253	77.530	- 239.665	- 83.476	4.344
4300	21.000	67.206	48.688	79.630	- 239.415	- 79.756	4.053
4400	21.000	67.689	49.114	81.730	- 239.168	- 76.052	3.777
4500	21.000	68.161	49.532	83.830	- 238.923	- 72.347	3.513
4600	21.000	68.623	49.942	85.930	- 238.680	- 68.646	3.261
4700	21.000	69.074	50.345	88.030	- 238.440	- 64.949	3.020
4800	21.000	69.516	50.739	90.130	- 374.634	- 59.735	2.720
4900	21.000	69.949	51.127	92.230	- 374.452	- 53.184	2.372
5000	21.000	70.374	51.508	94.330	- 374.277	- 46.632	2.038
5100	21.000	70.789	51.882	96.430	- 374.108	- 40.074	1.717
5200	21.000	71.197	52.249	98.530	- 373.945	- 33.527	1.409
5300	21.000	71.597	52.611	100.630	- 373.788	- 26.983	1.113
5400	21.000	71.990	52.966	102.730	- 373.636	- 20.444	.827
5500	21.000	72.375	53.315	104.830	- 373.487	- 13.903	.552
5600	21.000	72.754	53.659	106.930	- 373.345	- 7.369	.288
5700	21.000	73.125	53.997	109.030	- 373.205	- .836	.032
5800	21.000	73.490	54.330	111.130	- 373.070	5.704	- .215
5900	21.000	73.849	54.658	113.230	- 372.937	12.232	- .453
6000	21.000	74.202	54.981	115.330	- 372.807	18.759	- .683

June 30, 1961; Dec. 31, 1965

ZIRCONIUM DIOXIDE (ZrO_2) (LIQUID) MOL. WT. = 123.2188

$S^\circ_{298.15}$ =[17.841]cal. deg.

T_m = 2950°K.

T_b = 4548°K.

ΔH°_f 298.15 = [-244.55] kcal. mole^{-1}

ΔH°_m = [20.8] kcal. mole^{-1}

ΔH°_v = [149.2] kcal. mole^{-1}

Heat of Formation.

The ΔH°_f 298.15 (l) was obtained from ΔH°_f 298.15 (c) by adding ΔH°_m and the difference between $H^\circ_{T_m}-H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 2000°K. The heat capacity below 2000°K. was obtained from the heat capacity of the crystal. Above 2000°K. the heat capacity was assumed constant and estimated to be 21.0 cal. deg.$^{-1}$ mole^{-1} or 7 cal. deg.$^{-1}$ per g-atom as suggested by O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochemistry" Pergamon Press, New York (1958). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See ZrO_2(c) table.

Vaporization Data.

T_b was calculated as the temperature at which the free energy change of the reaction $ZrO_2(l) \rightarrow ZrO_2(g)$ approaches zero. The difference between $\Delta H^\circ_{f\ 4548}$ for ZrO_2(g) and ZrO_2(l) is ΔH°_v.

Zirconium Dioxide (ZrO_2)

(Ideal Gas) Mol. Wt. = 123.2188

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	-2.870	-67.878	-67.878	INFINITE
100	9.404	54.463	74.581	-2.012	-67.945	-68.902	150.578
200	10.115	61.199	66.379	-1.036	-68.172	-69.776	76.243
298	11.009	65.402	65.402	.000	-68.400	-70.513	51.685
300	11.026	65.470	65.402	.020	-68.404	-70.526	51.376
400	11.818	68.756	65.845	1.165	-68.605	-71.203	38.902
500	12.378	71.457	66.705	2.376	-68.796	-71.830	31.395
600	12.759	73.750	67.693	3.634	-68.997	-72.418	26.377
700	13.022	75.738	68.703	4.924	-69.210	-72.972	22.782
800	13.207	77.489	69.694	6.236	-69.434	-73.495	20.077
900	13.342	79.053	70.649	7.564	-69.665	-73.988	17.966
1000	13.442	80.464	71.561	8.903	-69.907	-74.454	16.271
1100	13.519	81.749	72.430	10.251	-70.168	-74.898	14.880
1200	13.578	82.928	73.256	11.606	-71.399	-75.267	13.707
1300	13.625	84.017	74.042	12.967	-71.669	-75.580	12.705
1400	13.663	85.028	74.791	14.331	-71.951	-75.871	11.843
1500	13.694	85.972	75.506	15.699	-72.242	-76.140	11.093
1600	13.720	86.856	76.188	17.070	-72.543	-76.388	10.434
1700	13.741	87.689	76.840	18.443	-72.855	-76.621	9.850
1800	13.759	88.475	77.465	19.818	-73.178	-76.832	9.328
1900	13.774	89.219	78.064	21.195	-73.512	-77.025	8.860
2000	13.787	89.926	78.640	22.573	-73.858	-77.204	8.436
2100	13.798	90.599	79.193	23.952	-74.214	-77.362	8.051
2200	13.808	91.241	79.726	25.332	-79.486	-77.338	7.682
2300	13.817	91.855	80.240	26.714	-79.870	-77.232	7.338
2400	13.824	92.443	80.737	28.096	-80.260	-77.107	7.021
2500	13.831	93.008	81.216	29.478	-80.656	-76.971	6.728
2600	13.837	93.550	81.680	30.862	-81.054	-76.813	6.456
2700	13.842	94.073	82.130	32.246	-81.458	-76.644	6.204
2800	13.847	94.576	82.565	33.630	-81.867	-76.457	5.967
2900	13.851	95.062	82.988	35.015	-82.280	-76.253	5.746
3000	13.855	95.532	83.398	36.401	-82.697	-76.040	5.539
3100	13.859	95.986	83.797	37.786	-83.119	-75.812	5.344
3200	13.862	96.426	84.185	39.172	-83.545	-75.570	5.161
3300	13.865	96.853	84.562	40.559	-83.974	-75.315	4.988
3400	13.868	97.267	84.930	41.945	-84.409	-75.045	4.824
3500	13.870	97.669	85.288	43.332	-84.846	-74.766	4.668
3600	13.872	98.060	85.638	44.719	-85.287	-74.472	4.521
3700	13.874	98.440	85.978	46.107	-85.731	-74.165	4.381
3800	13.876	98.810	86.311	47.494	-86.179	-73.844	4.247
3900	13.878	99.170	86.636	48.882	-86.629	-73.513	4.119
4000	13.879	99.522	86.954	50.270	-87.083	-73.175	3.998
4100	13.881	99.864	87.265	51.658	-87.540	-72.817	3.881
4200	13.882	100.199	87.569	53.046	-87.999	-72.455	3.770
4300	13.884	100.525	87.866	54.434	-88.461	-72.073	3.663
4400	13.885	100.845	88.158	55.823	-88.925	-71.695	3.561
4500	13.886	101.157	88.443	57.211	-89.392	-71.297	3.463
4600	13.887	101.462	88.723	58.600	-89.860	-70.885	3.368
4700	13.888	101.761	88.997	59.989	-90.331	-70.469	3.277
4800	13.889	102.053	89.266	61.378	-227.236	-68.515	3.119
4900	13.890	102.339	89.530	62.766	-227.766	-65.208	2.908
5000	13.891	102.620	89.789	64.155	-228.302	-61.887	2.705
5100	13.892	102.895	90.043	65.545	-228.843	-58.549	2.509
5200	13.892	103.165	90.293	66.934	-229.391	-55.207	2.320
5300	13.893	103.429	90.538	68.323	-229.945	-51.849	2.138
5400	13.894	103.689	90.779	69.712	-230.504	-48.486	1.962
5500	13.894	103.944	91.017	71.102	-231.065	-45.110	1.792
5600	13.895	104.194	91.250	72.491	-231.634	-41.721	1.628
5700	13.895	104.440	91.479	73.881	-232.204	-38.330	1.470
5800	13.896	104.682	91.704	75.270	-232.780	-34.919	1.316
5900	13.896	104.920	91.926	76.660	-233.357	-31.506	1.167
6000	13.897	105.153	92.145	78.050	-233.937	-28.077	1.023

June 30, 1961; Dec. 31, 1965

ZIRCONIUM DIOXIDE (ZrO_2) (IDEAL GAS) MOL. WT. = 123.2188

Point Group C_{2v}

$\Delta H^\circ_{f\ 0}$ = -67.9 ± 11 kcal. mole^{-1}

$S^\circ_{298.15}$ = 65.402 cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -68.4 ± 11 kcal. mole^{-1}

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
884 (1)
[137](1)
818 (1)

Bond Distance: O -Zr = 1.711 Å

Bond Angle: O-Zr-O = 109°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = 5.679636 X 10^{-115} g.^{3} cm.^{6}

Heat of Formation.

The $\Delta H^\circ_{f\ 298.15}$ = -68.4 ± 11 kcal. mole^{-1} was calculated from the $\Delta H^\circ_{r\ 298.15}$ = 193.867 ± 11.25 kcal. mole^{-1} for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$. The value of $\Delta H^\circ_{r\ 298.15}$ was obtained by the third law method using the determined vapor pressures (at the range 2331-2480°K) by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957). They observed the variation of the ZrO_2^+ ion intensity over ZrO_2 and reported equilibrium constants for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$ in the range 2331-2480°K. The third law drift is 80 ± 23 e.u.

Heat Capacity and Entropy.

The vibrational frequencies ν_1 = 884, ν_2 = [137], ν_3 = 818 and angle O -Zr-O = 109° were obtained from M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, Technical Report Nr. AFML TR-64-420 Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965). The bond distances (r_e) O-Zr = 1.711 Å was obtained from U. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955). The three principal moments of inertia are: I_A = 1.03083 X 10^{-38}, I_B = 3.8826 X 10^{-39}, I_C = 1.41909 X 10^{-38} g. cm.^{2}

Tungsten Oxide ($WO_{2.72}$)
(Crystal) GFW = 227.3684

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	16.320	16.354	16.354	.000	− 186.700	− 169.378	124.158
300	16.350	16.455	16.354	.030	− 186.698	− 169.271	123.314
400	18.380	21.446	17.021	1.770	− 186.515	− 163.485	89.324
500	19.820	25.713	18.343	3.685	− 186.195	− 157.763	68.958
600	20.790	29.417	19.887	5.718	− 185.800	− 152.113	55.407
700	21.465	32.677	21.486	7.833	− 185.363	− 146.531	45.749
800	21.950	35.576	23.069	10.005	− 184.910	− 141.017	38.524
900	22.340	38.185	24.606	12.221	− 184.443	− 135.557	32.918
1000	22.710	40.558	26.085	14.474	− 183.969	− 130.149	28.444
1100	23.050	42.739	27.501	16.762	− 183.486	− 124.792	24.794
1200	23.380	44.758	28.856	19.083	− 182.993	− 119.477	21.760
1300	23.730	46.643	30.152	21.438	− 182.489	− 114.204	19.199
1400	24.080	48.415	31.394	23.829	− 181.971	− 108.972	17.011
1500	24.380	50.087	32.585	26.252	− 181.440	− 103.776	15.120
1600	24.680	51.670	33.729	28.705	− 180.899	− 98.616	13.470
1700	24.980	53.175	34.829	31.188	− 180.346	− 93.489	12.019
1800	25.280	54.611	35.888	33.701	− 179.784	− 88.396	10.733
1900	25.580	55.986	36.910	36.244	− 179.212	− 83.334	9.586
2000	25.880	57.306	37.897	38.817	− 178.628	− 78.304	8.557
2100	26.180	58.576	38.852	41.420	− 178.032	− 73.302	7.629
2200	26.480	59.800	39.776	44.053	− 177.429	− 68.330	6.788
2300	26.780	60.984	40.673	46.716	− 176.811	− 63.385	6.023
2400	27.080	62.130	41.543	49.409	− 176.184	− 58.464	5.324
2500	27.380	63.242	42.389	52.132	− 175.547	− 53.576	4.684
2600	27.680	64.321	43.212	54.885	− 174.898	− 48.706	4.094
2700	27.980	65.372	44.013	57.668	− 174.244	− 43.867	3.551
2800	28.280	66.395	44.794	60.481	− 173.592	− 39.049	3.048
2900	28.580	67.392	45.556	63.324	− 172.953	− 34.255	2.582
3000	28.880	68.366	46.301	66.197	− 172.333	− 29.481	2.148

TUNGSTEN OXIDE ($WO_{2.72}$) (CRYSTAL) GFW = 227.3684

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [16.35] gibbs/mol

$\Delta Hf^\circ_{298.15} = -186.70 \pm 0.5$ kcal/mol

Heat of Formation.

The adopted heat of formation, -186.7 ± 0.5 kcal/mol, is derived from recent equilibrium data which are in excellent agreement; the results are summarized below. In addition R. C. Griffis, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to $WO_3(c)$ which yields $\Delta Hf^\circ_{298}(WO_{2.72}, c) = -185.4 \pm 1$ kcal/mol when recalculated with $\Delta Hf^\circ_{298}(WO_3,c) = -201.46$ kcal/mol. This result is less certain because of the incomplete characterization of the final products. The EMF data reported by Ya. I. Gerasimov, I. A. Vasil'eva, T. P. Chusova, V. A. Geiderikh, and M. A. Timofeeva, Zh. Fiz. Khim. 36, 358 (1962), give the value of -186.89 kcal/mol for the heat of formation at 298° K. R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600° K, they have derived indirectly from their measurements the heat of formation, -182.2 kcal/mol (corresponding to -187.2 kcal/mol at 298°K, using the JANAF functions).

Author	Reaction*	Temp. (°K)	No. of Points	ΔHr°_{298}(kcal/mol) 3rd law	ΔHr°_{298}(kcal/mol) 2nd law	Drift (eu)	$\Delta Hf^\circ_{298}(WO_{2.72},c)$ ** (kcal/mol)
1. Bousquet (1964) et al.	A	830 - 1048	5	4.095	2.951	1.2 ± 0.2	-186.65
2. St. Pierre (1962) et al.	B	1173 - 1423	-	-	-45.739	-	-186.68
3. Vasil'eva (1960) et al.	A	904 - 1066	4	4.279	2.676	1.6 ± 0.3	-186.83
4. Griffis (1959)	A	873 - 1173	24	4.314	4.314	-0.01 ± 0.06	-186.87

*Reaction A: $100/72\ WO_{2.72}(c) + H_2(g) = 100/72\ WO_2(c) + H_2O\ (g)$

B: $WO_2\ (c) + 0.72\ O_2(g) = WO_{2.72}(c)$

** Based on the 3rd law value wherever possible.

1. J. Bousquet and G. Perachon, Compt. rend. 258, 3869 (1964)
2. G. R. St. Pierre, W. T. Ebihara, M. J. Pool, and R. Speiser, Trans. AIME 224, 259 (1962)
3. I. A. Vasil'eva, Ya. I. Gerasimov and Yu. P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960)
4. R. C. Griffis, J. Electrochem. Soc. 106, 418 (1959).

Heat Capacity and Entropy.

The monoclinic unit cell of $WO_{2.72}$ corresponds to $W_{18}O_{49}$, as shown by the X-ray diffraction studies of A. Magneli, G. Anderson, B. Blomberg and L. Kihlborg, Anal. Chem. 24, 1998 (1952). The tabulated heat capacities of $WO_{2.72}(c)$ were estimated from those of $WO_2(c)$ and $WO_3(c)$, because all three have similar monoclinic structures as identified by Magneli et al.

The entropy ($S^\circ_{298} = 16.35$ eu) was calculated from $\Delta S^\circ_{298} = 7.96 \pm 0.09$ eu for reaction A, using all JANAF values. The value of ΔS°_{298} was derived from the second law analysis of Griffis' data, loc. cit.

Tungsten Oxide ($WO_{2.90}$)

(Crystal) GFW = 230.2483

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	17.060	17.536	17.536	.000	− 196.000	− 177.716	130.269
300	17.100	17.642	17.536	.032	− 195.998	− 177.603	129.383
400	19.200	22.857	18.233	1.850	− 195.800	− 171.496	93.701
500	20.700	27.313	19.614	3.849	− 195.462	− 165.457	72.321
600	21.730	31.184	21.227	5.974	− 195.043	− 159.494	58.096
700	22.450	34.590	22.898	8.185	− 194.581	− 153.605	47.957
800	22.940	37.622	24.552	10.455	− 194.100	− 147.786	40.373
900	23.340	40.347	26.159	12.770	− 193.608	− 142.025	34.488
1000	23.720	42.827	27.703	15.124	− 193.107	− 136.319	29.792
1100	24.035	45.099	29.183	17.507	− 192.604	− 130.667	25.961
1200	24.350	47.203	30.598	19.926	− 192.090	− 125.057	22.776
1300	24.690	49.165	31.951	22.378	− 191.567	− 119.491	20.088
1400	24.990	51.006	33.247	24.862	− 191.032	− 113.968	17.791
1500	25.260	52.740	34.490	27.375	− 190.491	− 108.482	15.806
1600	25.530	54.379	35.682	29.914	− 189.942	− 103.033	14.074
1700	25.830	55.935	36.828	32.482	− 189.384	− 97.617	12.549
1800	26.130	57.420	37.931	35.080	− 188.817	− 92.236	11.199
1900	26.430	58.841	38.994	37.708	− 188.240	− 86.886	9.994
2000	26.730	60.204	40.021	40.366	− 187.652	− 81.567	8.913
2100	27.030	61.516	41.014	43.054	− 187.053	− 76.277	7.938
2200	27.330	62.780	41.974	45.772	− 186.446	− 71.018	7.055
2300	27.630	64.002	42.906	48.520	− 185.826	− 65.786	6.251
2400	27.930	65.184	43.809	51.298	− 185.197	− 60.577	5.516
2500	28.230	66.330	44.687	54.106	− 184.559	− 55.401	4.843
2600	28.530	67.443	45.541	56.944	− 183.908	− 50.245	4.223
2700	28.830	68.525	46.373	59.812	− 183.253	− 45.115	3.652
2800	29.130	69.579	47.183	62.710	− 182.602	− 40.010	3.123
2900	29.430	70.607	47.973	65.638	− 181.963	− 34.932	2.633
3000	29.730	71.610	48.744	68.596	− 181.343	− 29.871	2.176

Sept. 30, 1966

TUNGSTEN OXIDE ($WO_{2.90}$) (CRYSTAL) GFW = 230.2483

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [17.54] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = −196.0 ± 3 kcal/mol

Heat of Formation.

The adopted heat of formation, −196.0 ± 3 kcal/mol, is a weighted average of those derived from equilibrium data; in addition the following results have been reported.

R. C. Griffis, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to WO_3(c), which yields −195.6 kcal/mol when recalculated with ΔHf°_{298} (WO_3, c) = −201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products. R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600°K, they have derived indirectly two values of ΔHf° ($WO_{2.90}$,c) −190.9 and −188.0 kcal/mol (corresponding to −196.1 and −193.3 kcal/mol, respectively, at 298.15°K, using all JANAF functions).

Author	Reaction*	Temperature (°K)	No. of Points	ΔHr°_{298}(kcal/mol) 3rd law	ΔHr°_{298}(kcal/mol) 2nd law	Drift (eu)	ΔHf°_{298} ($WO_{2.90}$,c)** (kcal/mol)
1. Bousquet (1963) et al.	A	773-898	5	0.270	2.168	−2.3 ± 0.07	−195.4
3. Vasil'eva (1960) et al.	A	897-993	4	0.240	2.178	−2.1 ± 0.01	−195.4
4. Griffis (1959)	A	873-1073	18	0.284	1.504	−1.3 ± 0.02	−195.4
1. Bousquet (1964) et al.	B	844-934	5	0.754	2.657	−2.1 ± 0.09	−197.9
3. Vasil'eva (1960) et al.	B	915-1021	5	0.834	1.585	−0.76 ± 0.1	−197.9
4. Griffis (1959)	B	873-1073	18	0.589	3.388	−2.88 ± 0.02	−197.7
1. Bousquet (1964) et al.	C	737-798	5	5.013	6.762	−2.3 ± 0.9	−198.0
2. St. Pierre (1962) et al.	D	1023-1273	-	-	−7.97	-	−193.5
2. St. Pierre (1962) et al.	E	1173-1322	-	-	−13.67	-	−200.4

* Reaction
A: $WO_3(c) + 0.1\ H_2(g) = WO_{2.90}(c) + 0.1\ H_2O\ (g)$
B: $WO_{2.90}(c) + 0.18\ H_2(g) = WO_{2.72}(c) + 0.18\ H_2O\ (g)$
C: $WO_{2.90}(c) + 0.9\ H_2\ (g) = WO_2(c) + 0.9\ H_2O(g)$
D: $WO_{2.90}(c) + 0.05\ O_2(g) = WO_3(c)$
E: $WO_{2.72}(c) + 0.09\ O_2(g) = WO_{2.90}(c)$

** Based on the third law value wherever possible and ΔHf°_{298} ($WO_{2.72}$,c) = −186.7 kcal/mol.

1. J. Bousquet and G. Perachon, Compt. rend. 258, 3869 (1964); 256, 694 (1963)
2. G. R. St. Pierre, W. T. Ebihara, M. J. Pool and R. Speiser, Trans. AIME 224, 259 (1962)
3. I. A. Vasil'eva, Ya. I. Perasimov and Yu P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960)
4. R. C. Griffis, J. Electrochem. Soc. 106, 418 (1959)

Heat Capacity and Entropy.

The monoclinic unit cell of $WO_{2.90}$ corresponds to $W_{20}O_{58}$, as shown by the X-ray diffraction studies of A. Magneli, G. Anderson, B. Blomberg and L. Kihlborg, Anal. Chem. 24, 1998 (1952). The tabulated heat capacities and the entropy (S°_{298} = 17.536 eu) were estimated from those of WO_2(c) and WO_3(c), because all three have the similar monoclinic structure as identified by Magneli et al.

Tungsten Oxide ($WO_{2.96}$)
(Crystal) GFW = 231.2082

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.300	17.900	17.900	.000	- 199.560	- 180.946	132.637
300	17.360	18.007	17.900	.032	- 199.558	- 180.831	131.735
400	19.480	23.298	18.607	1.876	- 199.355	- 174.615	95.405
500	21.000	27.819	20.009	3.905	- 199.009	- 168.467	73.637
600	22.050	31.746	21.645	6.061	- 198.582	- 162.397	59.153
700	22.780	35.202	23.340	8.304	- 198.111	- 156.402	48.831
800	23.280	38.278	25.018	10.608	- 197.621	- 150.480	41.109
900	23.750	41.046	26.648	12.958	- 197.118	- 144.616	35.118
1000	24.070	43.562	28.215	15.347	- 196.607	- 138.808	30.336
1100	24.430	45.874	29.717	17.772	- 196.087	- 133.055	26.436
1200	24.740	48.013	31.154	20.231	- 195.559	- 127.347	23.193
1300	25.060	50.006	32.528	22.721	- 195.023	- 121.684	20.457
1400	25.360	51.874	33.844	25.242	- 194.478	- 116.064	18.118
1500	25.620	53.633	35.105	27.791	- 193.926	- 110.482	16.097
1600	25.880	55.294	36.315	30.366	- 193.368	- 104.936	14.334
1700	26.180	56.872	37.479	32.969	- 192.801	- 99.426	12.782
1800	26.480	58.377	38.598	35.602	- 192.226	- 93.951	11.407
1900	26.780	59.817	39.677	38.265	- 191.640	- 88.507	10.181
2000	27.080	61.198	40.719	40.958	- 191.044	- 83.095	9.080
2100	27.380	62.527	41.726	43.681	- 190.438	- 77.712	8.088
2200	27.680	63.807	42.701	46.434	- 189.824	- 72.360	7.188
2300	27.980	65.044	43.646	49.217	- 189.196	- 67.034	6.370
2400	28.280	66.241	44.562	52.030	- 188.560	- 61.733	5.622
2500	28.580	67.402	45.453	54.873	- 187.914	- 56.467	4.936
2600	28.880	68.529	46.319	57.746	- 187.257	- 51.220	4.305
2700	29.180	69.624	47.162	60.649	- 186.595	- 45.999	3.723
2800	29.480	70.691	47.983	63.582	- 185.936	- 40.804	3.185
2900	29.780	71.731	48.784	66.545	- 185.292	- 35.634	2.685
3000	30.080	72.745	49.566	69.538	- 184.665	- 30.480	2.220

Sept. 30, 1966

TUNGSTEN OXIDE ($WO_{2.96}$) (CRYSTAL) GFW = 231.2082

ΔHf°_0 = Unknown

$S^\circ_{298.15}$ = [17.90] gibbs/mol $\Delta Hf^\circ_{298.15}$ = -199.56 ± 3 kcal/mol

Heat of Formation.

The adopted value, $\Delta Hf^\circ_{298}(WO_{2.96}, c)$ = -199.56 kcal/mol, was obtained by third law treatment of ΔGf° = 191,600 + 54.0 T (cal/mol) in the temperature range from 1300 - 1550°K, using all JANAF functions. The equation for ΔGf° was reported by R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), based on studies by mass spectroscopy and X-ray diffraction. In this study ΔGf° was obtained by comparison of the gibbs energies of sublimation (to gaseous W_2O_6, W_3O_8, W_3O_9 and W_4O_{12}) over the two systems W-$WO_2(c)$ and $WO_{2.96}(c)$; thus $WO_{2.96}(c)$ was related to $WO_2(c)$ through the gaseous species.

J. E. Battles, Ph. D. Thesis, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, (1964), has reported partial pressures of $W_3O_9(g)$ and $W_4O_{12}(g)$ in equilibrium with WO_3 - $WO_{2.90}(c)$. In light of Ackermann and Rauh's observation, the condensed phase was presumed to have the composition of $WO_{2.96}(c)$. The pressure data are in reasonable agreement with the studies of Ackermann and Rauh as summarized below. Values of ΔHf°_{298} for $WO_{2.96}(c)$ derived from the data of Battles are based on the same author's data for $W_3O_9(g)$, and $W_4O_{12}(g)$ in order to relate $WO_{2.96}$ to WO_2 directly.

Investigator	Reaction	Temperature (°K)	ΔHr°_{298} (kcal/mol) 3rd law	ΔHr°_{298} (kcal/mol) 2nd law	Drift (eu)	$\Delta Hf^\circ_{298}(WO_{2.96}, c)$* (kcal/mol)
1. Ackermann & Rauh	A	1300-1550	60.82	56.32	3.2 ± 0.6	-199.57
2. Ackermann & Rauh	B	1300-1550	41.37	38.35	2.09± 0.09	-199.58
3. Battles	B	1274-1418	40.82	43.28	-1.85± 0.05	-199.72
4. Ackermann & Rauh	C	1300-1550	35.81	33.58	1.55± 0.09	-199.60
5. Battles	C	1333-1418	35.37	38.74	-2.46± 0.1	-199.95

Reaction: A: $WO_{2.96}(c) = 0.44\ W_2O_6(g) + 0.04\ W_3O_8(g)$

B: $WO_{2.96}(c) = 0.29333\ W_3O_9(g) + 0.04\ W_3O_8(g)$

C: $WO_{2.96}(c) = 0.22\ W_4O_{12}(g) + 0.04\ W_3O_8(g)$

* Third law value adopted in calculation.

Heat Capacity and Entropy.

The tabulated heat capacities and the entropy at 298.15°K were estimated from those of $WO_2(c)$ and $WO_3(c)$.

Ackermann and Rauh, loc. cit., have found that the composition $WO_{2.96}$ probably represents the azeotropic composition of the WO_{3-x} solid solution and is the only single phase which evaporates congruently below 1550°K.

Ozone (O_3)

(Ideal Gas) Mol. Wt. = 48.000

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.474	34.739	34.739	INFINITE
100	7.957	47.964	47.981	-.002	36.141	37.573	-82.112
200	8.379	53.564	57.909	-.869	34.254	37.411	-40.879
298	9.378	57.080	57.080	.000	34.100	38.997	-28.585
300	9.400	57.138	57.080	.017	34.098	39.028	-28.430
400	10.455	59.992	57.462	1.012	34.026	40.684	-22.227
500	11.296	62.419	58.217	2.101	34.019	42.351	-18.511
600	11.916	64.536	59.097	3.263	34.048	44.015	-16.032
700	12.369	66.409	60.011	4.479	34.097	45.672	-14.259
800	12.704	68.083	60.917	5.733	34.154	47.321	-12.927
900	12.956	69.595	61.799	7.017	34.217	48.963	-11.889
1000	13.151	70.971	62.648	8.323	34.282	50.599	-11.058
1100	13.303	72.232	63.463	9.646	34.347	52.227	-10.376
1200	13.426	73.395	64.243	10.982	34.411	53.850	-9.807
1300	13.526	74.473	64.989	12.330	34.474	55.468	-9.324
1400	13.611	75.479	65.702	13.687	34.535	57.080	-8.910
1500	13.682	76.420	66.386	15.052	34.593	58.688	-8.550
1600	13.743	77.305	67.041	16.423	34.649	60.293	-8.235
1700	13.796	78.140	67.670	17.800	34.703	61.895	-7.957
1800	13.843	78.930	68.273	19.182	34.751	63.492	-7.709
1900	13.885	79.680	68.854	20.569	34.795	65.088	-7.486
2000	13.922	80.393	69.413	21.959	34.835	66.680	-7.286
2100	13.957	81.073	69.953	23.353	34.872	68.272	-7.105
2200	13.988	81.723	70.473	24.750	34.901	69.861	-6.940
2300	14.017	82.345	70.976	26.150	34.927	71.449	-6.789
2400	14.045	82.943	71.462	27.554	34.948	73.039	-6.651
2500	14.070	83.516	71.933	28.959	34.961	74.623	-6.523
2600	14.094	84.069	72.389	30.368	34.972	76.211	-6.406
2700	14.117	84.601	72.831	31.778	34.975	77.797	-6.297
2800	14.139	85.115	73.261	33.191	34.973	79.383	-6.196
2900	14.160	85.611	73.678	34.606	34.966	80.971	-6.102
3000	14.180	86.092	74.084	36.023	34.954	82.557	-6.014
3100	14.199	86.557	74.479	37.442	34.937	84.145	-5.932
3200	14.216	87.008	74.864	38.863	34.915	85.731	-5.855
3300	14.236	87.446	75.238	40.285	34.889	87.318	-5.783
3400	14.254	87.871	75.604	41.710	34.857	88.908	-5.715
3500	14.272	88.285	75.960	43.136	34.822	90.496	-5.651
3600	14.288	88.687	76.308	44.564	34.783	92.090	-5.590
3700	14.305	89.079	76.648	45.994	34.740	93.682	-5.533
3800	14.321	89.460	76.980	47.425	34.694	95.278	-5.479
3900	14.337	89.833	77.305	48.858	34.645	96.869	-5.428
4000	14.353	90.196	77.623	50.293	34.591	98.464	-5.380
4100	14.369	90.550	77.934	51.729	34.535	100.064	-5.334
4200	14.384	90.897	78.238	53.166	34.477	101.661	-5.290
4300	14.399	91.235	78.536	54.605	34.416	103.266	-5.248
4400	14.414	91.567	78.829	56.046	34.352	104.864	-5.208
4500	14.429	91.891	79.116	57.488	34.287	106.468	-5.171
4600	14.444	92.208	79.397	58.932	34.220	108.078	-5.135
4700	14.458	92.519	79.673	60.377	34.150	109.682	-5.100
4800	14.473	92.823	79.943	61.824	34.080	111.291	-5.067
4900	14.487	93.122	80.209	63.272	34.009	112.894	-5.035
5000	14.501	93.415	80.471	64.721	33.935	114.504	-5.005
5100	14.515	93.702	80.727	66.172	33.861	116.121	-4.976
5200	14.529	93.984	80.979	67.624	33.786	117.730	-4.948
5300	14.543	94.261	81.227	69.078	33.711	119.352	-4.921
5400	14.557	94.533	81.471	70.533	33.635	120.962	-4.895
5500	14.571	94.800	81.711	71.989	33.559	122.585	-4.871
5600	14.585	95.063	81.947	73.447	33.481	124.200	-4.847
5700	14.598	95.321	82.180	74.906	33.404	125.818	-4.824
5800	14.612	95.575	82.408	76.366	33.327	127.447	-4.802
5900	14.625	95.825	82.634	77.828	33.250	129.067	-4.781
6000	14.639	96.071	82.856	79.292	33.173	130.695	-4.760

June 30, 1961

OZONE (O_3) (IDEAL GAS) MOL. WT. = 48.000

ΔH°_{f0} = 34.8 ± 0.4 kcal. mole^{-1}

Point Group C_{2v}

$\Delta H^\circ_{f\ 298.15}$ = 34.2 ± 0.4 kcal. mole^{-1}

$S^\circ_{298.15}$ = 57.080 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$
1110 (1)
705 (1)
1043 (1)

Ground state multiplicity = 1

No α_1 available $\sigma = 2$

Rotational constants: A_{000} = 3.55381 cm.$^{-1}$ B_{000} = 0.44530 cm.$^{-1}$ C_{000} = 0.39477 cm.$^{-1}$

X_{11} = -3.8 cm.$^{-1}$ X_{33} = -4.0 cm.$^{-1}$ X_{23} = -3.5 cm.$^{-1}$

X_{22} = -3.5 cm.$^{-1}$ X_{12} = -2.0 cm.$^{-1}$ X_{31} = -9.0 cm.$^{-1}$

Heat of Formation

P. Günther, E. Wassmuth, and L. A. Schryver, Z. phys. Chem. 158, 297 (1932), measured ΔE for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in a calorimeter calibrated my means of the reaction $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$, and found the ratio of the ΔE values for these reactions to be 0.5077 ± 0.0024. The temperature of the experiments is not reported and is assumed to have been 18°C. From the above ratio, $\Delta H^\circ_{f\ 298.15}$ is calculated to be 33.89 ± 0.36 cal. mole^{-1}. A. Kailan and S. Jahn, Z. anorg. Chem. 68, 243 (1910), measured ΔH at an unspecified temperature for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in an electrically calibrated calorimeter. If the temperature of the experiments is assumed to have been 18°C and the modern joule-calorie conversion factor is used, $\Delta H^\circ_{f\ 298.15}$ is found to be 34.3 ± 0.6 kcal. mole^{-1}. Variability in the O_3 content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.2 ± 0.4 kcal. mole^{-1}.

Heat Capacity and Entropy

J. S. Gordon, private communication, April, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from L. Pierce, J. Chem. Phys. 24, 139 (1956). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Lead Metasilicate ($PbSiO_3$)

(Crystal) Mol. Wt. = 283.2742

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 3.876	- 272.011	- 272.011	INFINITE
100	10.680	8.883	42.363	- 3.348	- 273.039	- 266.727	582.904
200	17.343	18.523	28.116	- 1.919	- 273.514	- 260.197	284.316
298	21.520	26.273	26.273	.000	- 273.660	- 253.620	185.900
300	21.590	26.406	26.274	.040	- 273.661	- 253.496	184.663
400	24.580	33.046	27.159	2.355	- 273.572	- 246.782	134.829
500	26.760	38.776	28.922	4.927	- 273.320	- 240.112	104.948
600	28.380	43.806	30.992	7.688	- 272.954	- 233.503	85.049
700	29.500	48.269	33.148	10.585	- 273.684	- 226.770	70.797
800	30.250	52.260	35.292	13.574	- 273.215	- 220.101	60.126
900	30.780	55.855	37.380	16.627	- 272.711	- 213.491	51.840
1000	31.150	59.118	39.393	19.724	- 272.185	- 206.938	45.224
1100	31.440	62.101	41.324	22.854	- 271.645	- 200.441	39.822
1200	31.690	64.847	43.171	26.011	- 271.089	- 193.991	35.329
1300	31.890	67.392	44.938	29.190	- 270.523	- 187.589	31.535
1400	32.080	69.762	46.627	32.389	- 269.952	- 181.232	28.290
1500	32.270	71.982	48.244	35.607	- 269.373	- 174.914	25.484
1600	32.420	74.070	49.794	38.841	- 268.792	- 168.635	23.033
1700	32.550	76.039	51.280	42.090	- 280.312	- 162.283	20.862
1800	32.690	77.904	52.708	45.352	- 279.690	- 155.361	18.863
1900	32.780	79.674	54.081	48.626	- 279.070	- 148.472	17.077
2000	32.850	81.357	55.403	51.907	- 278.454	- 141.614	15.474

June 30, 1965

LEAD METASILICATE ($PbSiO_3$) (CRYSTAL) MOL. WT. = 283.2742

$\Delta H_f^\circ{}_0 = -272.01 \pm 1$ kcal. mole^{-1}

$S^\circ_{298.15} = 26.273 \pm 0.3$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = -273.66 \pm 1$ kcal. mole^{-1}

$T_m = 1037$°K.

Heat of Formation.

The heat of the reaction $PbO_{(red)} + SiO_2 \rightarrow PbSiO_3(c)$ was reported by K. K. Kelley, U. S. Bureau of Mines, Report Investigation 5901 (1962). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for PbO(c) (March 31, 1962) and for SiO_2(c) (Dec. 31, 1962). The above $\Delta H_r^\circ{}_{298.15} = -3.75 \pm 0.12$ kcal. mole^{-1}.

Heat Capacity and Entropy.

In the low temperature region (53.25-298.15°K.) the C_p values are those determined by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). Above 298.15 C_p values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25°K. using the Debye and Einstein functions $D(\frac{140}{T}) + E(\frac{213}{T}) + 2E(\frac{596}{T}) + E(\frac{1440}{T})$ given by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). The $S^\circ_{53.25} = 3.662$ cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

Sulfur Trioxide (SO_3)

(Ideal Gas)   Mol. Wt. = 80.0622

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-2.796	-93.220	-93.220	INFINITE
100	8.145	50.733	70.715	-1.998	-93.656	-92.205	201.504
200	10.119	56.920	62.390	-1.094	-94.165	-90.555	98.949
298	12.108	61.344	61.344	.000	-94.590	-88.689	65.007
300	12.142	61.419	61.345	.022	-94.597	-88.652	64.580
400	13.784	65.146	61.842	1.322	-95.463	-86.597	47.312
500	15.082	68.367	62.832	2.768	-96.052	-84.310	36.850
600	16.075	71.209	63.996	4.328	-96.481	-81.919	29.837
700	16.824	73.746	65.211	5.975	-96.801	-79.441	24.801
800	17.391	76.031	66.423	7.687	-110.111	-78.213	21.366
900	17.823	78.105	67.607	9.448	-110.009	-74.230	18.025
1000	18.157	80.001	68.753	11.248	-109.891	-70.260	15.354
1100	18.419	81.745	69.856	13.077	-109.763	-66.306	13.173
1200	18.628	83.357	70.915	14.930	-109.626	-62.360	11.357
1300	18.796	84.855	71.930	16.802	-109.485	-58.426	9.822
1400	18.933	86.253	72.904	18.688	-109.341	-54.504	8.508
1500	19.046	87.563	73.838	20.587	-109.197	-50.593	7.371
1600	19.140	88.795	74.735	22.497	-109.051	-46.689	6.377
1700	19.219	89.958	75.596	24.415	-108.905	-42.796	5.502
1800	19.286	91.058	76.425	26.340	-108.763	-38.911	4.724
1900	19.344	92.103	77.223	28.272	-108.624	-35.034	4.030
2000	19.393	93.096	77.992	30.209	-108.488	-31.166	3.405
2100	19.436	94.044	78.734	32.150	-108.356	-27.304	2.841
2200	19.474	94.949	79.451	34.096	-108.230	-23.447	2.329
2300	19.507	95.815	80.143	36.045	-108.108	-19.596	1.862
2400	19.536	96.646	80.814	37.997	-107.992	-15.748	1.434
2500	19.562	97.444	81.463	39.952	-107.882	-11.910	1.041
2600	19.585	98.212	82.093	41.909	-107.777	-8.072	.678
2700	19.605	98.951	82.703	43.869	-107.678	-4.239	.343
2800	19.623	99.664	83.296	45.830	-107.586	-.409	.032
2900	19.640	100.353	83.873	47.793	-107.500	3.419	-.258
3000	19.655	101.019	84.433	49.758	-107.421	7.244	-.528
3100	19.669	101.664	84.979	51.724	-107.345	11.064	-.780
3200	19.681	102.289	85.510	53.692	-107.278	14.879	-1.016
3300	19.692	102.895	86.028	55.660	-107.214	18.693	-1.238
3400	19.702	103.483	86.532	57.630	-107.158	22.510	-1.447
3500	19.712	104.054	87.025	59.601	-107.106	26.319	-1.643
3600	19.721	104.609	87.506	61.573	-107.058	30.136	-1.829
3700	19.729	105.150	87.975	63.545	-107.018	33.945	-2.005
3800	19.736	105.676	88.434	65.518	-106.980	37.756	-2.171
3900	19.743	106.189	88.883	67.492	-106.947	41.559	-2.329
4000	19.749	106.689	89.322	69.467	-106.920	45.368	-2.479
4100	19.755	107.176	89.751	71.442	-106.896	49.179	-2.621
4200	19.761	107.652	90.172	73.418	-106.876	52.985	-2.757
4300	19.766	108.117	90.584	75.394	-106.859	56.794	-2.886
4400	19.770	108.572	90.988	77.371	-106.848	60.594	-3.010
4500	19.775	109.016	91.383	79.348	-106.839	64.404	-3.128
4600	19.779	109.451	91.771	81.326	-106.833	68.211	-3.241
4700	19.783	109.876	92.152	83.304	-106.831	72.016	-3.349
4800	19.787	110.293	92.526	85.283	-106.831	75.819	-3.452
4900	19.790	110.701	92.892	87.261	-106.834	79.621	-3.551
5000	19.793	111.101	93.253	89.241	-106.840	83.423	-3.646
5100	19.796	111.493	93.606	91.220	-106.849	87.234	-3.738
5200	19.799	111.877	93.954	93.200	-106.859	91.037	-3.826
5300	19.802	112.254	94.296	95.180	-106.871	94.850	-3.911
5400	19.805	112.625	94.632	97.160	-106.886	98.646	-3.992
5500	19.807	112.988	94.962	99.141	-106.901	102.460	-4.071
5600	19.809	113.345	95.287	101.122	-106.921	106.263	-4.147
5700	19.812	113.695	95.607	103.103	-106.941	110.070	-4.220
5800	19.814	114.040	95.922	105.084	-106.962	113.882	-4.291
5900	19.816	114.379	96.232	107.065	-106.985	117.682	-4.359
6000	19.817	114.712	96.537	109.047	-107.009	121.498	-4.425

Dec. 31, 1960; Sept. 30, 1965

SULFUR TRIOXIDE (SO_3)   (IDEAL GAS)   MOL. WT. = 80.0622

Point Group D_{3h}

$S^\circ_{298.15}$ = 61.344 cal. mole^{-1} deg.$^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_{f\,0}$ = -93.22 ± 0.17 kcal. mole^{-1}

$\Delta H^\circ_{f\,298.15}$ = -94.59 ± 0.17 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$
1068 (1)
495 (1)
1391 (2)
529 (2)

Bond Distance: S-O = 1.43 Å

Bond Angle: O-S-O = 120°

σ = 6

Product of the Moments of Inertia: $I_AI_BI_C = 1.0813 \times 10^{-114}$ g.^{3} cm.^{6}

Heat of Formation.

The heat of formation was calculated from the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$ for which three sets of equilibrium constants are available. A summary of the second and third law treatment of the data is given below.

Ref.	Temp. Range	Points	2nd law ΔH°_{298} kcal. mole^{-1}	3rd law ΔH°_{298} kcal. mole^{-1}	Drift cal. mole^{-1} deg.$^{-1}$
1	933- 945°K	5	-27.67 ± 2.7	-23.608	3.7 ± 2.9
2	801-1170°K	8	-23.45 ± 0.1	-23.661	-0.8 ± 0.1
3	850-1001°K	11	-22.74 ± 0.6	-23.614	-1.5 ± 0.6
4	801-1170°K	23*	-23.40 ± 0.2	-23.638	-0.9 ± 0.2

References

1. G. B. Taylor and S. Lehner, Z. Physik. Chem. B30. (1931).
2. M. Bodenstein and W. Pohl, Z. Electrochem. 11, 373 (1905).
3. A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochem. URSS 4, 791 (1936).
4. Combination of above references, with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors Ref. 2. Although there is a definite trend in all the data it cannot be considered definitive enough for use in the modification of the SO_3 functions.

Heat Capacity and Entropy.

The bond length and angles were taken from the electron diffraction data of K. J. Palmer, J. Am. Chem. Soc. 60, 2360 (1938). The vibrational frequencies were taken from the infrared studies of R. W. Lovejoy, J. H. Colwell, D. F. Eggers and G. D. Halsey, J. Chem. Phys. 36, 612 (1962), which are in excellent accord with those of R. Bent and W. R. Ladner, Spectrochim. Acta 19, 931 (1963) using different techniques. These values differ from the assignment used by W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. 12, 408 (1944) in their analysis of the thermodynamic properties of SO_3.

The individual moments of inertia were $I_A = I_B = 8.148 \times 10^{-39}$ g. cm.^{2} and $I_C = 16.296 \times 10^{-39}$ g. cm.^{2}

Dititanium Trioxide (Ti_2O_3)

(Crystal) GFW = 143.7982

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.431	-361.505	-361.505	INFINITE
100	6.308	2.717	35.077	-3.236	-362.619	-356.287	778.665
200	17.254	10.671	20.796	-2.025	-363.368	-349.609	382.034
298	23.266	18.829	18.829	.000	-363.490	-342.820	251.294
300	23.352	18.973	18.829	.043	-363.488	-342.692	249.651
400	28.718	26.427	19.810	2.647	-363.187	-335.792	183.468
500	31.250	33.735	21.859	5.938	-362.284	-329.032	143.820
600	32.630	39.562	24.335	9.136	-361.551	-322.451	117.452
700	33.510	44.661	26.882	12.445	-360.781	-315.994	98.658
800	34.130	49.178	29.392	15.829	-360.014	-309.650	84.592
900	34.590	53.226	31.820	19.265	-359.271	-303.399	73.675
1000	34.960	56.890	34.146	22.743	-358.561	-297.229	64.959
1100	35.270	60.237	36.368	26.255	-357.886	-291.127	57.842
1200	35.530	63.317	38.487	29.796	-359.121	-285.011	51.908
1300	35.770	66.170	40.508	33.361	-358.270	-278.870	46.882
1400	35.980	68.829	42.437	36.948	-357.436	-272.796	42.585
1500	36.180	71.318	44.281	40.557	-356.624	-266.777	38.869
1600	36.360	73.659	46.044	44.184	-355.839	-260.812	35.625
1700	36.540	75.869	47.734	47.829	-355.083	-254.898	32.769
1800	36.710	77.962	49.356	51.491	-354.364	-249.025	30.236
1900	36.870	79.951	50.914	55.170	-353.681	-243.192	27.973
2000	37.030	81.847	52.414	58.865	-361.932	-237.088	25.908
2100	37.181	83.657	53.859	62.576	-361.279	-230.859	24.026
2200	37.330	85.390	55.253	66.301	-360.622	-224.666	22.318
2300	37.475	87.053	56.600	70.042	-359.955	-218.502	20.762
2400	37.620	88.651	57.902	73.796	-359.284	-212.363	19.338
2500	37.766	90.189	59.163	77.566	-358.606	-206.256	18.031
2600	37.910	91.673	60.385	81.350	-357.920	-200.176	16.826
2700	38.050	93.107	61.571	85.148	-357.229	-194.122	15.713
2800	38.190	94.493	62.722	88.960	-356.532	-188.094	14.681
2900	38.330	95.836	63.841	92.786	-355.828	-182.086	13.722
3000	38.470	97.137	64.929	96.626	-355.117	-176.106	12.829

Dec. 31, 1960; March 31, 1967; June 30, 1967

DITITANIUM TRIOXIDE (Ti_2O_3) (CRYSTAL) GFW = 143.7982

$S^\circ_{298.15}$ = 18.83 gibbs/mol

Tt = 473°K

Tm = 2112°K

ΔHf°_0 = -361.50 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -363.49 ± 2 kcal/mol

ΔHt° = 0.215 kcal/mol

ΔHm° = [26.4] kcal/mol

Heat of Formation

G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), determined the enthalpy change ΔHr°_{298} = -88.11 ± 0.1 kcal/mol for the reaction Ti_2O_3(c) + 1/2O_2(g) = 2TiO_2(rutile) using bomb calorimetry. Based on this result and ΔHf°_{298}(rutile) = -225.8 kcal/mol, the adopted value of ΔHf°_{298} for Ti_2O_3(c) is calculated to be -363.49 ± 2 kcal/mol. A value of ΔHf°_{298}(Ti_2O_3, c) = -362.8 ± 0.6 kcal/mol was reported by S. M. Ariya, M. P. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (English Transl.) 2, 16 (1957), who measured the heat of combustion of various compositions in the Ti-O system. Ariya et al. used an estimated correction for the formation of TiO_{2-x}, while Humphrey obtained values of 0.1 - 1.3 kcal/mol by grinding the product and reburning it with white oil. Most of the assigned uncertainty arises from this problem. [See TiO_2(rutile) for further details.]

Heat Capacity and Entropy

The low temperature heat capacities, 53 - 296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). The data indicate a small anomaly in Cp near 240°K. High temperature enthalpies, 375 - 1750°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by drop calorimetry. The heat capacities, 298 - 473°K, derived by Naylor, loc. cit., are joined smoothly with the low temperature Cp at 298°K. Cp values above 473°K are calculated from the heat capacity equation for the β phase derived by Naylor.

S. Nomura, T. Kawakubo, and T. Yanagi, J. Phys. Soc. Japan, 16, 706 (1961), measured the specific heat in the range 70 - 250°C with a conduction-type calorimeter. A broad anomaly in the specific heat was observed from 160 to 200°C. Below this region the Cp° values are unreasonably small, but near 200°C the data are closer to the adopted values.

The S°_{298} is calculated from the adopted low temperature Cp based on S°_{50} = 0.442 eu. A. D. Pearson, J. Phys. Chem. Solids, 5, 316 (1958), studied the crystal structure of Ti_2O_3 by X-ray method and found that the agreement between calculated and observed density values is good; in other words, there are no significant vacant sites in Ti_2O_3 crystal lattice. This was later confirmed by S. C. Abrahams, Phys. Rev. 130, 2230 (1963). Therefore we do not add vacancy entropy to S°_{298}. Because of the magnetic transition (α→β) at 473°K, we have assumed that no spin-magnetic entropy is likely below 50°K. See Transition Data for more information.

Transition Data

Tt and ΔHt° were obtained from B. F. Naylor, loc. cit. S. Nomura, T. Kawakubo and T. Yanagi, J. Phys. Soc. Japan 16, 706 (1961), derived the much smaller ΔHt° = 0.036 kcal/mol from their observations with a conduction-type calorimeter. These authors suggested that the discrepancy may be due to non-stoichiometry or to impurities in the sample studied by Naylor.

Single-crystal neutron diffraction studied by S. C. Abrahams, Phys. Rev. 130, 2230 (1963), indicate that Ti_2O_3 undergoes an antiferromagnetic ordering of small magnetic moment, associated with the Ti^{3+} cations, below a Néel temperature of about 660°K. The temperature of this transition has been reported variously as about 450 to 600°K based on other properties. A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), found no change in the Ti_2O_3 corundum-type structure, but noted a rapid change in the lattice parameters between 430 and 473°K. Observations of corresponding changes in magnetic susceptibility, resistivity and thermoelectric power have been summarized by the same authors and by J. B. Goodenough, Phys. Rev. 117, 1442 (1960). Goodenough attempted to interpret the earlier observations in terms of strong cation-cation interactions.

The magnetic nature of the transition suggests that any spin-magnetic entropy in Ti_2O_3 would be included in ΔHt° and in the observed Cp° values for α and β phases. Magnetic contributions are thus unlikely below 50°K.

Melting Data

See Ti_2O_3(ℓ) table for details.

Dititanium Trioxide (Ti_2O_3)

(Liquid) GFW = 143.7982

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	37.500	22.952	22.952	.000	- 342.087	- 322.646	236.506
300	37.500	23.184	22.953	.069	- 342.059	- 322.526	234.960
400	37.500	33.972	24.424	3.819	- 340.612	- 316.235	172.782
500	37.500	42.340	27.201	7.569	- 339.250	- 310.301	135.632
600	37.500	49.177	30.311	11.319	- 337.965	- 304.633	110.963
700	37.500	54.958	33.430	15.069	- 336.754	- 299.175	93.407
800	37.500	59.965	36.441	18.819	- 335.621	- 293.886	80.286
900	37.500	64.382	39.305	22.569	- 334.564	- 288.732	70.114
1000	37.500	68.333	42.014	26.319	- 333.582	- 283.693	62.001
1100	37.500	71.907	44.571	30.069	- 332.669	- 278.747	55.382
1200	37.500	75.170	46.987	33.819	- 333.695	- 273.908	49.867
1300	37.500	78.172	49.272	37.569	- 332.658	- 268.861	45.200
1400	37.500	80.951	51.437	41.319	- 331.662	- 263.992	41.211
1500	37.500	83.538	53.492	45.069	- 330.709	- 259.192	37.764
1600	37.500	85.958	55.446	48.819	- 329.800	- 254.451	34.756
1700	37.500	88.232	57.308	52.569	- 328.939	- 249.771	32.110
1800	37.500	90.375	59.086	56.319	- 328.133	- 245.137	29.764
1900	37.500	92.402	60.787	60.069	- 327.379	- 240.546	27.669
2000	37.500	94.326	62.416	63.819	- 335.575	- 235.689	25.755
2100	37.500	96.156	63.980	67.569	- 334.883	- 230.710	24.010
2200	37.500	97.900	65.482	71.319	- 334.201	- 225.767	22.428
2300	37.500	99.567	66.928	75.069	- 333.525	- 220.853	20.986
2400	37.500	101.163	68.322	78.819	- 332.858	- 215.966	19.666
2500	37.500	102.694	69.666	82.569	- 332.200	- 211.112	18.455
2600	37.500	104.165	70.965	86.319	- 331.548	- 206.282	17.340
2700	37.500	105.580	72.221	90.069	- 330.905	- 201.475	16.308
2800	37.500	106.944	73.437	93.819	- 330.269	- 196.694	15.353
2900	37.500	108.260	74.615	97.569	- 329.641	- 191.929	14.464
3000	37.500	109.531	75.758	101.319	- 329.021	- 187.191	13.637

Dec. 31, 1960; March 31, 1967; June 30, 1967

DITITANIUM TRIOXIDE (Ti_2O_3) (LIQUID) GFW = 143.7982

$S^\circ_{298.15}$ = [22.952] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-342.087] kacl/mol

Tm = 2112 ± 10°K ΔHm° = [26.4] kcal/mol

Heat of Formation

The heat of formation , ΔHf°_{298}, for $Ti_2O_3(\ell)$ is obtained from that of the crystal by adding ΔHm° and the difference between $H^\circ_{2112} - H^\circ_{298}$ for $Ti_2O_3(c)$ and $Ti_2O_3(\ell)$.

Heat Capacity and Entropy

The heat capacity of $Ti_2O_3(\ell)$ is estimated on the basis of 7.5 gibbs/g-atom. The S°_{298} is derived in a manner analogous to that of the heat of formation.

Melting Data

The adopted Tm was determined by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 18) (1966). ΔHm° is estimated based on the assumption that at Tm the entropy of melting is 2.5 eu/g-atom. Other Tm values reported are listed as follows:

Tm, °K	Source
2073	T. H. Schofield and A. E. Bacon, J. Inst. Metals 84, 47 (1956).
2093	G. Brauer and W. Littke, J. Inorg. Nucl. Chem. 16, 67 (1960).
2103	H. Nishimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20, 524 (1956).
2173	E. Junker, Z. Anorg. Allgem. Chem. 228, 97 (1936).
2193	R. C. DeVries and R. Roy, Bull. Am. Ceram. Soc. 33, 370 (1954).

Tungsten Trioxide (WO_3)

(Crystal) GFW = 231.8482

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.951	- 200.110	- 200.110	INFINITE
100	7.277	4.508	31.096	- 2.659	- 201.014	- 195.026	426.229
200	13.909	11.826	19.649	- 1.565	- 201.444	- 188.832	206.345
298	17.481	18.143	18.143	.000	- 201.460	- 182.626	133.869
300	17.520	18.252	18.144	.032	- 201.458	- 182.510	132.958
400	19.649	23.599	18.858	1.896	- 201.250	- 176.221	96.283
500	21.186	28.158	20.274	3.942	- 200.901	- 170.001	74.307
600	22.255	32.122	21.925	6.118	- 200.469	- 163.861	59.686
700	22.978	35.610	23.636	8.382	- 199.993	- 157.796	49.266
800	23.480	38.713	25.331	10.706	- 199.499	- 151.803	41.471
900	23.882	41.502	26.975	13.074	- 198.994	- 145.870	35.422
1000	24.300	44.040	28.556	15.483	- 198.479	- 139.994	30.596
1100	23.653	46.663	30.086	18.235	- 197.650	- 134.188	26.661
1200	24.044	48.738	31.555	20.620	- 197.212	- 128.437	23.392
1300	24.435	50.678	32.952	23.044	- 196.759	- 122.724	20.632
1400	24.827	52.503	34.284	25.507	- 196.289	- 117.047	18.272
1500	25.218	54.230	35.557	28.009	- 195.802	- 111.404	16.232
1600	25.609	55.870	36.775	30.551	- 195.295	- 105.794	14.451
1700	26.001	57.434	37.945	33.131	- 194.768	- 100.215	12.884
1800	26.400	58.931	39.069	35.751	- 194.224	- 94.668	11.494
1900	26.800	60.369	40.153	38.411	- 193.659	- 89.153	10.255
2000	27.200	61.754	41.199	41.111	- 193.074	- 83.668	9.143
2100	27.600	63.091	42.209	43.851	- 192.469	- 78.212	8.140
2200	28.000	64.384	43.188	46.631	- 191.846	- 72.788	7.231
2300	28.400	65.638	44.137	49.451	- 191.200	- 67.392	6.404
2400	28.800	66.855	45.058	52.311	- 190.535	- 62.020	5.648
2500	29.200	68.039	45.954	55.211	- 189.851	- 56.683	4.955
2600	29.600	69.192	46.826	58.151	- 189.145	- 51.368	4.318
2700	30.000	70.316	47.675	61.131	- 188.425	- 46.081	3.730
2800	30.400	71.414	48.503	64.151	- 187.698	- 40.820	3.186
2900	30.800	72.488	49.312	67.211	- 186.975	- 35.589	2.682
3000	31.200	73.539	50.102	70.311	- 186.261	- 30.379	2.213

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN TRIOXIDE (WO_3) (CRYSTAL) GFW = 231.8482

ΔHf°_0 = -200.11 ± 0.2 kcal/mol

$S^\circ_{298.15}$ = 18.14 ± 0.3 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -201.46 ± 0.2 kcal/mol

Tt = 1050°K

ΔHt° = 0.355 kcal/mol

Tm = 1745°K

ΔHm° = 17.55 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to monomer) = 131.46 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to dimer) = 62.36 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to trimer) = 40.26 kcal/mol

$\Delta Hs^\circ_{298.15}$ (to tetramer) = 33.91 kcal/mol

Heat of Formation.

The selected heat of formation, ΔHf°_{298} (WO_3, c) = -201.46 ±0.2 kcal/mol, was determined by A. D. Mah, J. Am. Chem. Soc. 81, 1582 (1959), using bomb calorimetry. G. Huff, E. Squitieri and P. E. Snyder, J. Am. Chem. Soc. 70, 3380 (1948), have reviewed the literature heat of formation data and also measured calorimetrically the heat of formation, -201.84 ± 0.1 kcal/mol, which is in good agreement with the value selected. Other combustion values were reported as ΔHf°_{298} = -199 ± 1 kcal/mol by R. C. Griffis, J. Electrochem. Soc. 105, 398 (1958); and ΔHf°_{298} = -205.3 kcal/mol by I. A. Vasil'eva, V. I. Gerasimov, and Y. P. Simanov, Zh. Fiz. Khim. 31, 682 (1957). R. C. Griffis, J. Electrochem. Soc. 106, 418 (1959), also derived the heat of formation, -202.8 ± 1.4 kcal/mol from equilibrium data.

Heat Capacity and Entropy.

The low temperature (53-296.7°K) heat capacities and high temperature (399.6 - 1835.8°K) enthalpy changes have been measured by E. G. King, W. W. Weller, and A. U. Christensen, U.S. Bur. Mines R.I. 5664 (1960); and these data have been used to derive the tabulated heat capacities. Low temperature and high temperature values were joined smoothly at 298.15°K. The entropy was calculated from the heat capacities based on S°_{51} = 1.31 eu.

King et al. were apparently unaware of the transition near 593°K which was reported by J. A. Perri, E. Banks, and B. Post, J. Appl. Phys. 28, 1272 (1957), and they did not take sufficient points in that region to fix the precise enthalpy curve. We have adopted only one curve through the region because of the insufficiency of the data and also because the heat effects appear to be small or gradual.

Transition and Melting Data.

The heat of transition, the transition point, the heat of melting and the melting point were derived from the high temperature enthalpy data of King et al., loc. cit.

The melting point, 1746 ± 1°K, has also been quoted by S. J. Schneider, NBS Monograph 68, "Compilation of the Melting Points of the Metal Oxides," October 10, 1963.

In the high temperature X-ray diffractometric studies, Perri et al., loc. cit., indicate that WO_3 undergoes a phase transition from monoclinic to orthorhombic at approximately 593°K and from orthorhombic to tetragonal at 993°K.

Heat of Sublimation.

The values of ΔHs° at 298.15°K are calculated as the heat of sublimation of one mole of crystal to one mole of monomer, 1/2 mole of dimer, 1/3 mole of trimer and 1/4 mole of tetramer, respectively.

Tungsten Trioxide (WO_3)
(Liquid) GFW = 231.8484

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.481	24.738	24.738	.000	- 188.555	- 171.687	125.850
300	17.520	24.846	24.738	.032	- 188.553	- 171.583	124.998
400	19.649	30.194	25.453	1.896	- 188.345	- 165.954	90.673
500	21.186	34.753	26.868	3.942	- 187.996	- 160.394	70.108
600	22.255	38.716	28.520	6.118	- 187.564	- 154.912	56.427
700	22.978	42.205	30.231	8.382	- 187.088	- 149.507	46.678
800	23.480	45.308	31.925	10.706	- 186.594	- 144.174	39.387
900	23.882	48.097	33.570	13.074	- 186.089	- 138.901	33.730
1000	31.500	50.634	35.151	15.483	- 185.574	- 133.683	29.216
1100	31.500	53.636	36.697	18.633	- 184.347	- 128.556	25.542
1200	31.500	56.377	38.225	21.783	- 183.144	- 123.536	22.499
1300	31.500	58.899	39.719	24.933	- 181.965	- 118.617	19.941
1400	31.500	61.233	41.174	28.083	- 180.808	- 113.788	17.763
1500	31.500	63.406	42.584	31.233	- 179.673	- 109.039	15.887
1600	31.500	65.439	43.950	34.383	- 178.557	- 104.367	14.256
1700	31.500	67.349	45.271	37.533	- 177.461	- 99.764	12.826
1800	31.500	69.149	46.548	40.683	- 176.387	- 95.224	11.562
1900	31.500	70.852	47.782	43.833	- 175.332	- 90.744	10.438
2000	31.500	72.468	48.977	46.983	- 174.297	- 86.319	9.433
2100	31.500	74.005	50.132	50.133	- 173.282	- 81.945	8.528
2200	31.500	75.470	51.251	53.283	- 172.289	- 77.621	7.711
2300	31.500	76.871	52.335	56.433	- 171.313	- 73.341	6.969
2400	31.500	78.211	53.385	59.583	- 170.358	- 69.097	6.292
2500	31.500	79.497	54.404	62.733	- 169.424	- 64.901	5.674
2600	31.500	80.733	55.393	65.883	- 168.508	- 60.738	5.105
2700	31.500	81.921	56.354	69.033	- 167.618	- 56.607	4.582
2800	31.500	83.067	57.287	72.183	- 166.761	- 52.512	4.099
2900	31.500	84.172	58.196	75.333	- 165.948	- 48.446	3.651
3000	31.500	85.240	59.079	78.483	- 165.184	- 44.405	3.235

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN TRIOXIDE (WO_3) **(LIQUID)** **GFW = 231.8484**

$S^\circ_{298.15}$ = 24.738 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -188.555 kcal/mol

Tm = 1745°K

ΔHm° = 17.55 kcal/mol

Tb (to equilibrium vapor) = 2110°K

ΔHv° (to equilibrium vapor) = 18.3 kcal/mol

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of melting and the difference between $H_{1745} - H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity between the melting point and 1836°K was determined from the enthalpy measurement by E. G. King, W. W. Weller, and A. U. Christensen, U. S. Bur. Mines RI 5664 (1960). The heat capacity was assumed constant above and below the measured range. At 1000°K, a glass transition was assumed, below which the heat capacity was assumed to be that of the crystal. The entropy at 298.15°K was obtained in a manner analogous to that of the heat of formation.

Melting and Vaporization Data.

The heat and temperature of melting were obtained from E. G. King et al., loc. cit.

Tb (to equilibrium vapor) is the temperature at which the total pressure reaches one atm based on the calculated partial pressures of $WO_3(g)$, $W_2O_6(g)$, $W_3O_8(g)$, $W_3O_9(g)$, and $W_4O_{12}(g)$. ΔHv° (to equilibrium vapor) at the boiling point is calculated as the heat of vaporization of one mole of the liquid to vapor containing 23.7 mole percent of $W_2O_6(g)$, 0.57 mole percent of $W_3O_8(g)$, 58.2 mole percent of $W_3O_9(g)$, and 17.53 mole percent of $W_4O_{12}(g)$.

Tungsten Trioxide (WO_3)

(Ideal Gas) GFW = 231.8484

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.248	-68.947	-68.947	INFINITE
100	9.189	55.587	79.865	-2.428	-69.323	-68.443	149.582
200	12.474	63.033	69.705	-1.334	-69.754	-67.383	73.632
298	14.580	68.434	68.434	.000	-70.000	-66.160	48.497
300	14.613	68.524	68.434	.027	-70.003	-66.137	48.181
400	16.071	72.941	69.026	1.566	-70.120	-64.828	35.420
500	17.065	76.641	70.189	3.226	-70.158	-63.499	27.755
600	17.746	79.816	71.535	4.968	-70.159	-62.167	22.644
700	18.219	82.589	72.920	6.768	-70.147	-60.835	18.993
800	18.557	85.045	74.285	8.608	-70.137	-59.507	16.257
900	18.805	87.246	75.605	10.477	-70.131	-58.178	14.127
1000	18.990	89.237	76.871	12.367	-70.136	-56.848	12.424
1100	19.133	91.054	78.079	14.273	-70.152	-55.520	11.031
1200	19.244	92.724	79.230	16.192	-70.180	-54.188	9.869
1300	19.332	94.268	80.329	18.121	-70.222	-52.854	8.886
1400	19.403	95.703	81.376	20.058	-70.279	-51.516	8.042
1500	19.461	97.044	82.376	22.001	-70.350	-50.173	7.310
1600	19.509	98.301	83.333	23.950	-70.436	-48.825	6.669
1700	19.549	99.485	84.249	25.903	-70.537	-47.470	6.103
1800	19.583	100.604	85.126	27.859	-70.656	-46.112	5.599
1900	19.612	101.663	85.969	29.819	-70.791	-44.743	5.147
2000	19.637	102.670	86.779	31.782	-70.944	-43.370	4.739
2100	19.658	103.629	87.559	33.746	-71.114	-41.987	4.370
2200	19.677	104.543	88.310	35.713	-71.304	-40.596	4.033
2300	19.693	105.419	89.035	37.682	-71.509	-39.198	3.725
2400	19.707	106.257	89.735	39.652	-71.734	-37.784	3.441
2500	19.720	107.062	90.413	41.623	-71.979	-36.369	3.179
2600	19.731	107.835	91.068	43.596	-72.240	-34.936	2.937
2700	19.741	108.580	91.703	45.569	-72.527	-33.496	2.711
2800	19.750	109.298	92.318	47.544	-72.846	-32.043	2.501
2900	19.758	109.992	92.916	49.519	-73.207	-30.583	2.305
3000	19.766	110.662	93.496	51.495	-73.617	-29.104	2.120
3100	19.772	111.310	94.061	53.472	-74.084	-27.614	1.947
3200	19.779	111.938	94.609	55.450	-74.618	-26.109	1.783
3300	19.784	112.546	95.144	57.428	-75.222	-24.582	1.628
3400	19.789	113.137	95.664	59.407	-75.909	-23.038	1.481
3500	19.794	113.711	96.172	61.386	-76.688	-21.474	1.341
3600	19.798	114.268	96.667	63.365	-77.587	-19.880	1.207
3700	19.802	114.811	97.150	65.345	-86.936	-18.219	1.076
3800	19.805	115.339	97.622	67.326	-87.283	-16.354	.941
3900	19.809	115.853	98.083	69.306	-87.634	-14.484	.812
4000	19.812	116.355	98.533	71.288	-87.991	-12.607	.689
4100	19.815	116.844	98.974	73.269	-88.352	-10.715	.571
4200	19.817	117.322	99.405	75.250	-88.716	-8.819	.459
4300	19.820	117.788	99.827	77.232	-89.084	-6.907	.351
4400	19.822	118.244	100.241	79.214	-89.457	-4.999	.248
4500	19.824	118.689	100.646	81.197	-89.832	-3.072	.149
4600	19.826	119.125	101.043	83.179	-90.210	-1.135	.054
4700	19.828	119.551	101.432	85.162	-90.592	.807	-.038
4800	19.830	119.969	101.814	87.145	-90.976	2.754	-.125
4900	19.832	120.378	102.188	89.128	-91.362	4.703	-.210
5000	19.833	120.778	102.556	91.111	-91.751	6.671	-.292
5100	19.835	121.171	102.917	93.095	-92.143	8.645	-.370
5200	19.836	121.556	103.272	95.078	-92.537	10.621	-.446
5300	19.838	121.934	103.621	97.062	-92.932	12.615	-.520
5400	19.839	122.305	103.963	99.046	-93.329	14.603	-.591
5500	19.840	122.669	104.300	101.030	-93.727	16.611	-.660
5600	19.841	123.027	104.631	103.014	-94.129	18.613	-.726
5700	19.842	123.378	104.957	104.998	-94.531	20.627	-.791
5800	19.843	123.723	105.278	106.982	-94.934	22.658	-.854
5900	19.844	124.062	105.593	108.967	-95.338	24.691	-.915
6000	19.845	124.396	105.904	110.951	-289.649	28.810	-1.049

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN TRIOXIDE (WO_3) (IDEAL GAS) GFW = 231.8484

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [68.4] gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -68.9 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -70 ± 7 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[564] (1)	1040 (2)
[347] (1)	[320](2)

Bond Distance: W-O = [1.81] A°

Bond Angle: O-W-O = [120°]

σ = [6]

Product of the Moments of Inertia: $I_A I_B I_C$ = [4.450×10^{-114}] $g^3 cm^6$

Heat of Formation.

The gibbs energy of formation of gaseous tungsten trioxide, ΔGf° (WO_3, g) = -75,700 + 15.54 T cal/mol, over the temperature range 1920° - 2020°K has been reported by R. J. Ackermann and R. J. Thorn, J. Phys. Chem. 64, 350 (1960), using the reaction 3 MgO (c) + W(c) → 3 Mg(g) + WO_3(g). Third law calculation gives ΔHf°_{298} (WO_3, g) = -71.3 kcal/mol, using JANAF functions. The second law value of ΔHf°_{298} is -74.8 kcal/mol.

G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960), have reported the partial pressures of WO(g), WO_2(g), WO_3(g) and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188° to 2475°K. Third law treatment of their partial pressure data gives ΔHr°_{298} = -245.2 kcal/mol for W(c) + 3 O(g) → WO_3(g) which yields ΔHf°_{298}(WO_3,g) = -66.5 kcal/mol. The third law drift is 21 ± 7 eu. Partial pressures of WO_2(g), WO_3(g), and O(g) at 2242°K have also been reported by W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. 30, 827 (1959), in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives ΔHr°_{298}(WO_3,g) = -73.0 kcal/mol.

The value, -70 ± 7 kcal/mol, is selected for the heat of formation at 298°K.

Heat Capacity and Entropy.

The WO_3(g) was assumed to be a planar D_{3h} molecule with a bond angle ∡ OWO = 120°. The bond distance W-O was estimated to be the same as that in WO(g). W. Weltner, Jr., and D. McLeod, Jr., J. Mol. Spectry. 17, 276 (1965), have observed the vibrational frequency of 1040 cm^{-1} in the infrared spectrum by matrix isolation, and also estimated the frequencies 347 and 564 cm^{-1} based on the stretching force constant of WO(g). The estimation of 320 cm^{-1}(2) was obtained from DeMaria et al., loc. cit. These frequencies have been adopted in the tabulation. The three principal moments of inertia are $I_A = I_B = 1.3055 \times 10^{-38}$ and $I_C = 2.611 \times 10^{-38}$ g cm^2.

Lead Orthosilicate (Pb_2SiO_4)

(Crystal) Mol. Wt. = 506.4636

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 6.198	- 327.311	- 327.311	INFINITE
100	17.636	17.210	69.708	- 5.250	- 328.699	- 320.263	699.901
200	27.239	32.672	47.489	- 2.963	- 329.259	- 311.554	340.434
298	32.740	44.654	44.654	.000	- 329.320	- 302.839	221.976
300	32.800	44.857	44.655	.061	- 329.318	- 302.675	220.488
400	36.330	54.794	45.986	3.523	- 329.090	- 293.822	160.529
500	39.140	63.212	48.610	7.301	- 328.670	- 285.051	124.590
600	41.430	70.561	51.669	11.335	- 328.099	- 276.377	100.665
700	43.050	77.077	54.842	15.564	- 329.756	- 267.428	83.491
800	44.020	82.893	57.992	19.921	- 329.039	- 258.574	70.636
900	44.640	88.114	61.054	24.354	- 328.276	- 249.809	60.659
1000	45.200	92.848	64.000	28.848	- 327.473	- 241.132	52.697
1100	45.600	97.175	66.822	33.389	- 326.640	- 232.540	46.199
1200	45.900	101.155	69.520	37.963	- 325.782	- 224.021	40.798
1300	46.300	104.845	72.097	42.573	- 324.900	- 215.577	36.240
1400	46.680	108.291	74.560	47.222	- 323.995	- 207.204	32.344
1500	47.000	111.522	76.918	51.907	- 323.069	- 198.890	28.977
1600	47.300	114.565	79.177	56.622	- 322.133	- 190.642	26.039
1700	47.570	117.441	81.344	61.365	- 333.288	- 182.343	23.441
1800	47.830	120.167	83.426	66.135	- 332.297	- 173.495	21.064
1900	48.110	122.761	85.428	70.932	- 331.299	- 164.703	18.944
2000	48.400	125.236	87.357	75.758	- 330.292	- 155.960	17.042

LEAD ORTHOSILICATE (Pb_2SiO_4) (CRYSTAL) MOL. WT. = 506.4636

$\Delta H^\circ_{f\ 0} = -327.3 \pm 3.5$ kcal. mole^{-1}

$S^\circ_{298.15} = 44.654 \pm 0.5$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -329.3 \pm 3.5$ kcal. mole^{-1}

$T_m = 1016$°K.

Heat of Formation.

The heat of the reaction $2PbO(c) + SiO_2(c) \rightarrow Pb_2SiO_4(c)$ was reported by O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York (1958). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for PbO(c) (March 31, 1962) and for $SiO_2(c)$ (Dec. 31, 1962). The above $\Delta H^\circ_{r\ 298.15} = -7.00 \pm 3.5$ kcal. mole^{-1}.

Heat Capacity and Entropy.

In the low temperature region (53.07-298.15°K.) the C_p values are those determined by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). Above 298.15 C_p values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.07°K. using the Debye and Einstein functions $D(\frac{78.5}{T}) + 2E(\frac{164}{T}) + 3E(\frac{547}{T}) + E(\frac{1379}{T})$ given by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). The $S^\circ_{53.07} = 8.248$ cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

Trilead Tetroxide (Pb_3O_4)
(Crystal) Mol. Wt. = 685.63

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	-7.144	-173.373	-173.373	INFINITE
100	20.800	19.087	78.517	-5.943	-174.867	-165.830	362.405
200	31.100	37.071	53.516	-3.289	-175.382	-156.520	171.029
298	35.136	50.394	50.394	.000	-175.311	-147.265	107.943
300	35.150	50.611	50.395	.065	-175.308	-147.092	107.151
400	35.920	60.829	51.783	3.618	-175.133	-137.712	75.239
500	36.697	68.927	54.429	7.249	-174.983	-128.377	56.111
600	37.480	75.687	57.424	10.958	-174.854	-119.066	43.368
700	38.260	81.523	60.459	14.745	-178.233	-109.205	34.094
800	39.040	86.683	63.421	18.610	-178.127	-99.353	27.141
900	39.820	91.326	66.267	22.553	-177.954	-89.515	21.736
1000	40.600	95.562	68.988	26.574	-177.705	-79.699	17.417
1100	41.380	99.466	71.584	30.673	-177.381	-69.916	13.890
1200	42.160	103.102	74.061	34.850	-176.973	-60.161	10.956
1300	42.940	106.508	76.427	39.105	-176.490	-50.446	8.480
1400	43.720	109.718	78.691	43.438	-175.940	-40.773	6.365
1500	44.500	112.761	80.862	47.849	-175.323	-31.135	4.536
1600	45.280	115.658	82.947	52.338	-174.649	-21.545	2.943
1700	46.060	118.427	84.953	56.905	-173.913	-11.996	1.542
1800	46.840	121.082	86.887	61.550	-173.128	-2.498	.303
1900	47.620	123.635	88.754	66.273	-172.289	6.957	-.800
2000	48.400	126.097	90.560	71.074	-171.397	16.368	-1.789

March 31, 1962

TRILEAD TETROXIDE (Pb_3O_4) (Crystal)

Mol. Wt. = 685.63

ΔH_f° 298.15 = -175.31 ± 0.48 kcal. mole^{-1}

$S^\circ_{298.15}$ = 50.4 ± 1.6 cal. deg.$^{-1}$ mole^{-1}

Heat of Formation. Calculated from $\Delta F^\circ_{298.15}$ = -147.27 kcal. mole^{-1} for the reaction: $3Pb(c) + 2O_2(g) = Pb_3O_4(c)$ given by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. C_p (71.5° to 292.6°K.) reported by R. W. Millar, loc. cit. Above 298.15°K., heat capacity values were estimated by comparison with C_p values for the other lead oxides. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

Zirconium Orthosilicate ($ZrSiO_4$)

(Crystal)   Mol. Wt. = 183.3036

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0	.000	.000	INFINITE	- 3.562	- 481.062	- 481.062	INFINITE
100	7.417	3.363	36.589	- 3.323	- 482.525	- 474.128	1036.156
200	17.519	11.889	22.058	- 2.034	- 483.400	- 465.337	508.473
298	23.580	20.083	20.083	- .000	- 483.736	- 456.386	334.524
300	23.690	20.229	20.083	.044	- 483.738	- 456.216	332.337
400	27.400	27.576	21.060	2.607	- 483.740	- 447.036	244.238
500	30.100	33.996	23.019	5.489	- 483.541	- 437.879	191.387
600	31.950	39.657	25.330	8.596	- 483.221	- 428.775	156.174
700	33.180	44.679	27.742	11.855	- 482.833	- 419.731	131.040
800	34.100	49.173	30.145	15.222	- 482.402	- 410.748	112.206
900	34.720	53.226	32.488	18.664	- 481.947	- 401.815	97.569
1000	35.200	56.910	34.749	22.161	- 481.483	- 392.935	85.872
1100	35.550	60.283	36.919	25.700	- 481.024	- 384.105	76.311
1200	35.780	63.387	38.997	29.267	- 481.529	- 375.266	68.342
1300	35.890	66.255	40.985	32.851	- 481.075	- 366.429	61.599
1400	35.950	68.917	42.886	36.443	- 480.639	- 357.628	55.826
1500	36.000	71.399	44.705	40.041	- 480.220	- 348.856	50.826
1600	36.000	73.723	46.447	43.641	- 479.820	- 340.109	46.455
1700	36.000	75.905	48.116	47.241	- 491.543	- 331.280	42.587
1800	36.000	77.963	49.718	50.841	- 491.143	- 321.865	39.078
1900	36.000	79.909	51.256	54.441	- 490.762	- 312.472	35.941
2000	36.000	81.756	52.735	58.041	- 490.399	- 303.101	33.120
2100	36.000	83.512	54.159	61.641	- 490.052	- 293.742	30.569
2200	36.000	85.187	55.532	65.241	- 494.629	- 284.238	28.235
2300	36.000	86.787	56.856	68.841	- 494.324	- 274.683	26.100
2400	36.000	88.320	58.136	72.441	- 494.031	- 265.138	24.143
2500	36.000	89.789	59.373	76.041	- 493.750	- 255.607	22.344
2600	36.000	91.201	60.570	79.641	- 493.477	- 246.087	20.684
2700	36.000	92.560	61.730	83.241	- 493.216	- 236.578	19.149
2800	36.000	93.869	62.854	86.841	- 492.965	- 227.077	17.723
2900	36.000	95.132	63.946	90.441	- 492.724	- 217.581	16.397
3000	36.000	96.353	65.006	94.041	- 492.493	- 208.099	15.159

Sept. 30, 1961; June 30, 1965

ZIRCONIUM ORTHOSILICATE ($ZrSiO_4$)   (CRYSTAL)   MOL. WT. = 183.3036

$S^\circ_{298.15}$ = 20.083 ± 0.3 cal. deg.$^{-1}$ mole^{-1}

T_d = 1811°K.

$\Delta H^\circ_{f\ 0}$ = -481.1 ± 0.7 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -483.7 ± 0.7 kcal. mole^{-1}

Heat of Formation.

The ΔH°_f 298.15 was calculated from the ΔH°_r 298.15 of its constituent oxides $ZrO_2(c) + SiO_2(c) = ZrSiO_4(c)$ and from the ΔH°_f 298.15 of $ZrO_2(c)$ (June 30, 1961) and $SiO_2(c)$ (Dec. 31, 1962) in JANAF tables. The ΔH°_r 298.15 = -4.736 kcal. mole^{-1} was based on the free energy of formation of its constituent oxides at the decomposition temperature 1811°K.

Heat Capacity and Entropy.

At low temperatures C_p were used from K. K. Kelley, J. Am. Chem. Soc. 63, 2750 (1941). From 298-940°K. C_p was calculated by using the J. P. Coughlin and E. G. King equation $C_p = 31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^5T^{-2}$, J. Am. Chem. Soc., 72, 2262 (1950), which joined smoothly with the low temperature data. Above 940°K. the data was estimated by extending the curve smoothly. The entropy was calculated at 52.7°K. using the Debye and Einstein functions $D(\frac{321}{T}) + 2E(\frac{407}{T}) + 2E(\frac{796}{T}) + E(\frac{1624}{T})$ given by K. K. Kelley, J. Am. Chem. Soc., 63, 2750 (1941). $S^\circ_{52.7}$ = 0.65404 cal. deg.$^{-1}$ mole^{-1}.

Temperature of Decomposition.

T_d is the temperature at which $\Delta F^\circ_r = 0$ for the reaction $ZrSiO_4(c) \rightarrow ZrO_2(c) + SiO_2(c)$. T_d = 1811°K. was taken from C. E. Curtis and H. G. Sowman, J. Am. Soc., 36, 190 (1953).

Trititanium Pentoxide, Alpha (α-Ti_3O_5)

(Crystal) GFW = 223.697

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 5.523	- 584.630	- 584.630	INFINITE
100	11.022	5.045	56.695	- 5.165	- 586.409	- 575.974	1258.789
200	27.355	18.095	34.033	- 3.188	- 587.545	- 565.014	517.418
298	36.990	30.935	30.935	.000	- 587.750	- 553.895	406.016
300	37.150	31.164	30.936	.069	- 587.747	- 553.685	403.359
400	43.700	42.851	32.484	4.147	- 587.300	- 542.383	296.344
500	46.400	52.939	35.594	8.673	- 586.540	- 531.240	232.205
600	48.000	61.546	39.220	13.396	- 585.702	- 520.259	189.504
700	49.250	69.043	42.956	18.261	- 584.840	- 509.420	159.048
800	50.200	75.683	46.640	23.234	- 583.992	- 498.706	136.240
900	51.000	81.644	50.204	28.296	- 583.173	- 488.093	118.525
1000	51.600	87.048	53.622	33.426	- 582.403	- 477.570	104.373
1100	52.200	91.995	56.889	38.617	- 581.676	- 467.119	92.808
1200	52.700	96.558	60.007	43.862	- 583.807	- 456.622	83.162
1300	53.200	100.797	62.983	49.158	- 582.796	- 446.066	74.991
1400	53.600	104.754	65.827	54.498	- 581.803	- 435.588	67.998
1500	54.000	108.466	68.547	59.878	- 580.835	- 425.177	61.948

Dec. 31, 1960; Mar. 31, 1967

TRITITANIUM PENTOXIDE, ALPHA (α- Ti_3O_5) (CRYSTAL) GFW = 223.697

$S^\circ_{298.15}$ = 30.935 gibbs/mol

Tt = 450°K

ΔHf°_0 = -584.63 ± 0.7 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -587.75 ± 3.0 kcal/mol

ΔHt° = [2.81] kcal/mol

Heat of Formation

The enthalpy change, ΔHr°_{298} = -89.65 ± 0.05 kcal/mol, for the reaction $Ti_3O_5(c) + 1/2\ O_2(g) = 3\ TiO_2$(rutile) has been measured by G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), using combustion bomb calorimetry. Based on the reported ΔHr°_{298} and ΔHf°_{298}(rutile) = -225.8 kcal/mol, the value of ΔHf°_{298} for $Ti_3O_5(\alpha)$ is derived as -587.75 ± 0.7 kcal/mol. A value of -587.0 ± 1.0 kcal/mol was obtained by S. M. Ariya, M. P. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (English transl.) 2, 16 (1957), from a similar calorimetric study on Ti-O compounds of various compositions. The latter authors observed that their combustion product had a composition of about $TiO_{1.95}$, so they applied an approximate correction to their data. Presumably, the rutile in Humphrey's combustion was also deficient in oxygen, but we have not attempted to make a correction (see TiO_2 (rutile) table for further details).

Heat Capacity and Entropy

Low temperature heat capacities, 53.1 - 296.6°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). High temperature enthalpies, 360.5 - 1340°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by use of drop calorimetry. The heat capacities, 298 - 450°K, derived by Naylor are too high to join smoothly at 298°K with the low temperature data, hence they are not used. The Cp values above 296.6°K are obtained by graphical extrapolation of the adopted low temperature Cp.

The samples used by both Shomate and Naylor were prepared by reduction of titanium dioxide with carbon at 1350°C. Analysis of the product gave 99.1% Ti_3O_5, 0.2% TiC and 0.7% SiO_2. X-ray lines from the sample were weak and fuzzy but no data were given. Thus comparison with subsequent studies is not possible. According to Naylor, the enthalpy measurements showed a transition at about 450°K. When Ti_3O_5 was heated above this temperature, it did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10 percent. The change in the enthalpy curve seemed to depend upon both the temperature and time of heating above Tt. Regrinding was the only method found for returning the sample to its original state. Possible explanations are presented in the Transition Data.

S°_{298} is calculated from S°_{50} = 0.88 eu using the low temperature Cp reported by Shomate, loc. cit. It is pertinent to ask if there should be entropy contributions due to vacancies in the crystal lattice or to spin-magnetic effects below 50°K. S. Asbrink and A. Magneli, Acta Cryst. 12, 575 (1959), showed that the X-ray crystallographic density is greater than the experimental density by less than 1%, thus the entropy due to the presence of vacancies is considered to be negligible. We also assume that any spin-magnetic entropy is related to the $\alpha \rightarrow \beta$ transition, by analogy with the $\alpha \rightarrow \beta$ transition of Ti_2O_3. Consistent with this assumption is the observation that the entropy of β-Ti_3O_5 is already larger than the sum of entropies for β-Ti_2O_3 and TiO_2.

Transition Data

See $Ti_3O_5(\beta)$ table.

Trititanium Pentoxide, Beta (β-Ti_3O_5)

(Crystal) GFW = 223.697

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	44.165	35.913	35.913	.000	-585.354	-552.983	405.347
300	44.180	36.186	35.914	.082	-585.338	-552.783	402.702
400	44.984	49.006	37.656	4.540	-584.511	-542.056	296.165
500	45.789	59.130	40.973	9.079	-583.738	-531.533	232.333
600	46.593	67.550	44.720	13.698	-583.004	-521.164	189.834
700	47.397	74.792	48.511	18.397	-582.308	-510.912	59.514
800	48.201	81.174	52.202	23.177	-581.653	-500.760	136.801
900	49.005	86.897	55.745	28.037	-581.036	-490.683	119.154
1000	49.809	92.102	59.124	32.978	-580.454	-480.675	105.051
1100	50.614	96.887	62.343	37.999	-579.898	-470.722	93.524
1200	51.418	101.326	65.408	43.101	-582.172	-460.709	83.906
1300	52.222	105.473	68.333	48.283	-581.275	-450.624	75.757
1400	53.026	109.373	71.126	53.545	-580.359	-440.611	68.782
1500	53.830	113.059	73.800	58.888	-579.429	-430.660	62.747
1600	54.634	116.558	76.364	64.311	-578.487	-420.769	57.474
1700	55.439	119.895	78.827	69.815	-577.538	-410.944	52.830
1800	56.243	123.086	81.198	75.399	-576.591	-401.171	48.709
1900	57.047	126.149	83.484	81.063	-575.645	-391.452	45.027
2000	57.851	129.095	85.691	86.808	-588.044	-381.322	41.669
2100	58.655	131.937	87.826	92.634	-587.031	-371.006	38.611
2200	59.459	134.684	89.894	98.539	-585.956	-360.748	35.837
2300	60.264	137.345	91.899	104.526	-584.809	-350.537	33.309
2400	61.068	139.927	93.847	110.592	-583.598	-340.372	30.995
2500	61.872	142.436	95.741	116.739	-582.321	-330.268	28.872

Mar. 31, 1967

TRITITANIUM PENTOXIDE, BETA (β-Ti_3O_5) (CRYSTAL) GFW = 223.697

$S^\circ_{298.15}$ = [35.913] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-585.354] kcal/mol

Tt = 450°K

ΔHt° = [2.81] kcal/mol

Tm = 2047 ± 10°K

ΔHm° = [33] kcal/mol

Heat of Formation

The value of $\Delta Hf^\circ_{298}(\beta)$ is obtained from $\Delta Hf^\circ_{298}(\alpha)$ by adding ΔHt° and the difference between $H^\circ_{450} - H^\circ_{298}$ for $Ti_3O_5(\alpha)$ and $Ti_3O_5(\beta)$.

Heat Capacity and Entropy

The heat capacities are derived from the enthalpy data, 452 - 1340°K, measured by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946). The Cp values beyond the experimental range are obtained by linear extrapolation.

The S°_{298} is calculated in a manner analogous to that of the heat of formation. For a discussion pertaining to the entropy uncertainty, see the Transition Data.

Transition Data

Tt and ΔHt° are based on the β-phase enthalpy data of Naylor, loc. cit., and on the selected enthalpies of the α-phase. ΔHt° is thus subject to an unknown error since the β-phase enthalpies correspond to a somewhat different state than do the α-phase values (see α-Ti_3O_5). The enthalpy data also show unusual scatter in the range 452-530°K. Because of these uncertainties, the more recent X-ray studies are summarized below.

S. Asbrink and A. Magneli, Acta Cryst. 12, 575 (1959), found that monoclinic α-Ti_3O_5 transforms to a β form of the anosovite type (slightly deformed pseudo-brookite) at about 393°K, i. e., over 50° lower than Naylor's value. P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), confirmed that the transition occurs between 373 and 473°K but did not measure the temperature accurately. In both studies only the α form was observed on cooling the samples to room temperature. Asbrink and Magneli noted the following in X-ray studies at elevated temperatures. In a wide region around 393°K, the powder reflections of the unstable phase disappeared, while the general characteristics of the stable one formed within considerably less than one hour. Complete development of some reflections of the stable phase took several hours, while some lines appeared with anomalous intensities at temperatures approaching the transformation point, thus "forewarning" the change of structure. Small contents of Fe or Mg stabilized the β form at room temperature.

These observations suggest that the transformation may be considered as a "pernt" which occurs over a range of temperatures. The anomalous enthalpy data observed by Naylor may arise from slow completion of the transition and from stabilization of part of the sample in the β form due to impurities. The latter suggestion is consistent with Naylor's observation that regrinding returned the sample to its normal α form. Correction of the enthalpy data based on these assumptions does not appear practical. Pending new data for a well-characterized sample, we must rely on the results of Naylor.

Melting Data.

P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), found that Ti_3O_5 melts incongruently at 2047 ± 10°K which is adopted. ΔHm° is estimated assuming that at Tm the entropy of melting is 2 eu/g-atom. Melting points of 2173 and 1983°K were reported by R. DeVries and R. Roy, Bull. Am. Ceram. Soc. 33, 370 (1954), and G. Brauer and W. Littke, J. Inorg. Nucl. Chem. 16, 67 (1960), respectively.

Trititanium Pentoxide (Ti_3O_5)

(Liquid) GFW = 223.697

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	56.000	38.679	38.679	.000	-560.754	-529.208	387.920
300	56.000	39.025	38.680	.104	-560.716	-529.012	385.385
400	56.000	55.135	40.876	5.704	-558.747	-518.744	283.428
500	56.000	67.631	45.024	11.304	-556.913	-508.959	222.466
600	56.000	77.841	49.669	16.904	-555.198	-499.532	181.954
700	56.000	86.474	54.326	22.504	-553.601	-490.383	153.104
800	56.000	93.951	58.822	28.104	-552.126	-481.455	131.527
900	56.000	100.547	63.099	33.704	-550.769	-472.702	114.788
1000	56.000	106.447	67.144	39.304	-549.529	-464.095	101.428
1100	56.000	111.785	70.963	44.904	-548.393	-455.606	90.520
1200	56.000	116.657	74.571	50.504	-550.169	-447.103	81.429
1300	56.000	121.140	77.983	56.104	-548.854	-438.570	73.730
1400	56.000	125.290	81.216	61.704	-547.601	-430.135	67.147
1500	56.000	129.154	84.284	67.304	-546.413	-421.787	61.454
1600	56.000	132.768	87.203	72.904	-545.295	-413.513	56.483
1700	56.000	136.163	89.984	78.504	-544.249	-405.310	52.106
1800	56.000	139.364	92.639	84.104	-543.286	-397.167	48.223
1900	56.000	142.391	95.179	89.704	-542.405	-389.072	44.753
2000	56.000	145.264	97.612	95.304	-554.949	-380.565	41.586
2100	56.000	147.996	99.947	100.904	-554.161	-371.860	38.700
2200	56.000	150.601	102.190	106.504	-553.391	-363.201	36.081
2300	56.000	153.090	104.350	112.104	-552.631	-354.573	33.692
2400	56.000	155.474	106.431	117.704	-551.886	-345.974	31.505
2500	56.000	157.760	108.438	123.304	-551.156	-337.414	29.497
2600	56.000	159.956	110.378	128.904	-550.436	-328.877	27.645
2700	56.000	162.070	112.253	134.504	-549.731	-320.369	25.932
2800	56.000	164.106	114.069	140.104	-549.039	-311.886	24.344
2900	56.000	166.071	115.829	145.704	-548.359	-303.419	22.866
3000	56.000	167.970	117.535	151.304	-547.691	-294.988	21.490
3100	56.000	169.806	119.192	156.904	-547.034	-286.570	20.203
3200	56.000	171.584	120.802	162.504	-546.389	-278.191	19.000
3300	56.000	173.307	122.367	168.104	-545.754	-269.815	17.869
3400	56.000	174.979	123.890	173.704	-545.131	-261.461	16.807
3500	56.000	176.602	125.373	179.304	-544.516	-253.133	15.806
3600	56.000	178.180	126.818	184.904	-848.789	-244.024	14.814
3700	56.000	179.714	128.227	190.504	-848.110	-227.236	13.422
3800	56.000	181.208	129.601	196.104	-847.478	-210.471	12.105
3900	56.000	182.662	130.943	201.704	-846.892	-193.710	10.855
4000	56.000	184.080	132.254	207.304	-846.355	-176.971	9.669

Mar. 31, 1967

TRITITANIUM PENTOXIDE (Ti_3O_5) (LIQUID) GFW = 223.697

$S°_{298.15}$ = [38.679] gibbs/mol

$\Delta Hf°_{298.15}$ = [-560.754] kcal/mol

Tm = 2047 ± 10°K

ΔHm° = [33] kcal/mol

Heat of Formation

The $\Delta Hf°_{298.15}(l)$ is obtained from $\Delta Hf°_{298.15}(\beta)$ by adding ΔHm° and the difference between $H°_{2047} - H°_{298}$ for $Ti_3O_5(\beta)$ and $Ti_3O_5(l)$.

Heat Capacity and Entropy

The heat capacity is estimated on the basis of 7.0 gibbs/g-atom. $S°_{298}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See $Ti_3O_5(\beta)$ table for details.

Diphosphorus Trioxide, Dimeric

(Ideal Gas) Mol. Wt. = 219.90 **INTERIM TABLE**

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 5.534	- 508.401	- 508.401	INFINITE
100	11.239	59.176	105.919	- 4.674	- 510.044	- 502.908	1099.051
200	24.210	70.884	85.432	- 2.910	- 511.592	- 495.133	541.031
298	34.402	82.584	82.584	.000	- 512.540	- 486.831	356.840
300	34.556	82.798	82.585	.064	- 512.551	- 486.671	354.523
400	41.168	93.719	84.029	3.876	- 513.004	- 477.965	261.135
500	45.319	103.386	86.954	8.216	- 513.141	- 469.185	205.071
600	47.996	111.902	90.417	12.891	- 513.135	- 460.395	167.691
700	49.789	119.444	94.036	17.786	- 513.106	- 451.608	140.992
800	51.036	126.179	97.640	22.831	- 594.787	- 464.067	126.771
900	51.931	132.244	101.154	27.981	- 593.823	- 447.782	108.731
1000	52.594	137.752	104.543	33.209	- 592.832	- 431.608	94.323
1100	53.096	142.789	107.794	38.495	- 591.827	- 415.537	82.556
1200	53.485	147.427	110.906	43.825	- 590.813	- 399.557	72.766
1300	53.793	151.720	113.882	49.189	- 589.796	- 383.656	64.495
1400	54.040	155.716	116.729	54.581	- 588.776	- 367.838	57.419
1500	54.241	159.451	119.454	59.996	- 587.758	- 352.090	51.297
1600	54.406	162.958	122.065	65.428	- 586.745	- 336.415	45.950
1700	54.544	166.260	124.568	70.876	- 585.735	- 320.796	41.239
1800	54.661	169.381	126.972	76.336	- 584.734	- 305.241	37.060
1900	54.760	172.339	129.283	81.807	- 583.744	- 289.738	33.326
2000	54.845	175.150	131.506	87.288	- 582.763	- 274.300	29.973
2100	54.918	177.828	133.649	92.776	- 581.790	- 258.894	26.942
2200	54.981	180.384	135.716	98.271	- 580.835	- 243.540	24.192
2300	55.037	182.830	137.711	103.772	- 579.886	- 228.236	21.686
2400	55.086	185.173	139.640	109.278	- 578.954	- 212.966	19.392
2500	55.129	187.423	141.507	114.789	- 578.031	- 197.732	17.285
2600	55.168	189.586	143.315	120.304	- 577.124	- 182.542	15.343
2700	55.202	191.668	145.067	125.822	- 576.232	- 167.382	13.548
2800	55.233	193.676	146.768	131.344	- 575.351	- 152.252	11.883
2900	55.260	195.615	148.419	136.869	- 574.482	- 137.154	10.336
3000	55.285	197.489	150.024	142.396	- 573.630	- 122.088	8.894
3100	55.308	199.302	151.584	147.926	- 572.787	- 107.047	7.546
3200	55.328	201.058	153.103	153.458	- 571.961	- 92.046	6.286
3300	55.347	202.761	154.582	158.991	- 571.142	- 77.060	5.103
3400	55.364	204.414	156.023	164.527	- 570.343	- 62.100	3.992
3500	55.380	206.019	157.429	170.064	- 569.548	- 47.165	2.945
3600	55.394	207.579	158.801	175.603	- 568.767	- 32.252	1.958
3700	55.407	209.097	160.139	181.143	- 567.997	- 17.359	1.025
3800	55.419	210.575	161.447	186.684	- 567.235	- 2.478	.143
3900	55.431	212.014	162.726	192.227	- 566.484	12.371	- .693
4000	55.441	213.418	163.975	197.770	- 565.745	27.191	- 1.486
4100	55.451	214.787	165.198	203.315	- 565.013	42.012	- 2.239
4200	55.460	216.123	166.395	208.861	- 564.290	56.816	- 2.956
4300	55.468	217.429	167.566	214.407	- 563.576	71.592	- 3.639
4400	55.476	218.704	168.714	219.954	- 562.870	86.360	- 4.289
4500	55.484	219.951	169.839	225.502	- 562.173	101.106	- 4.910
4600	55.490	221.170	170.942	231.051	- 561.477	115.835	- 5.503
4700	55.497	222.364	172.023	236.600	- 560.794	130.555	- 6.070
4800	55.503	223.532	173.084	242.150	- 560.117	145.262	- 6.614
4900	55.508	224.677	174.125	247.701	- 559.441	159.945	- 7.134
5000	55.514	225.798	175.148	253.252	- 558.775	174.620	- 7.632
5100	55.519	226.897	176.152	258.803	- 558.119	189.284	- 8.111
5200	55.524	227.976	177.138	264.356	- 557.460	203.916	- 8.570
5300	55.528	229.033	178.107	269.908	- 556.809	218.570	- 9.012
5400	55.532	230.071	179.060	275.461	- 556.163	233.176	- 9.437
5500	55.536	231.090	179.997	281.015	- 555.516	247.807	- 9.846
5600	55.540	232.091	180.918	286.568	- 554.883	262.393	- 10.240
5700	55.544	233.074	181.824	292.123	- 554.248	276.983	- 10.620
5800	55.547	234.040	182.716	297.677	- 553.617	291.565	- 10.986
5900	55.550	234.990	183.594	303.232	- 552.988	306.125	- 11.339
6000	55.553	235.923	184.459	308.787	- 552.366	320.693	- 11.681

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1962

DIPHOSPHORUS TRIOXIDE, DIMERIC (P_4O_6) (Ideal Gas)

Mol. Wt. = 219.90

ΔH_f° 298.15 = -512.5 ± 8 kcal. mole^{-1}

$S^\circ_{298.15}$ = 82.6 cal. deg.$^{-1}$ mole^{-1}

Point Group = T_d

Vibrational Frequencies and Degeneracies

ω cm.$^{-1}$	ω cm.$^{-1}$
613 (1)	465 (2)
613 (1)	643 (3)
302 (3)	919 (3)
370 (3)	1029 (2)
407 (3)	636 (3)

Bond Lengths and Angles: P-O distance = 1.65 ± 0.02 Å

P-O-P angle = 127.5 ± 1.0° O-P-O angle = 99° ± 1° σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = 4.832 X 10^{-112} g.^{3} cm.^{6}

Heat of Formation. ΔH_f° 298.15 for liquid P_4O_6 was measured by W. E. Koerner and F. Daniels, J. Chem. Phys. 20, 113 (1952). The measurement was made by burning samples of red phosphorus in nitric oxide in a flow calorimeter. Calculation of the heat of formation of the gas was made using ΔH_v° 298.15 = 11.46 kcal. mole^{-1} as reported by T. D. Farr, Tenn. Valley Authority, Chem. Engr. Report No. 8 (1950).

Heat Capacity and Entropy. The vibrational levels are from the Raman data of H. Gerding, H. van Brederode and H. C. J. de Decker, Rec. Trav. Chim. 61, 549 (1942), and infra-red spectra data of T. A. Sidorov and N. N. Sobolev, Optics and Spect. 2, 710 (1957). Bond lengths and angles are from electron diffraction data by G. C. Hampson and A. J. Stosick, J. Am. Chem. Soc. 60, 1814 (1938).

Tungsten Trioxide, Dimeric $(WO_3)_2$

(Ideal Gas) GFW = 463.6964

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 7.162	- 276.759	- 276.759	INFINITE
100	19.445	67.918	127.934	- 6.002	- 277.993	- 271.907	594.251
200	31.427	85.631	102.516	- 3.377	- 278.416	- 265.586	290.219
298	36.726	99.298	99.298	.000	- 278.200	- 259.319	190.086
300	36.793	99.526	99.299	.068	- 278.193	- 259.203	188.829
400	39.407	110.510	100.779	3.892	- 277.680	- 252.946	138.203
500	40.814	119.469	103.649	7.910	- 277.057	- 246.833	107.891
600	41.642	126.990	106.930	12.036	- 276.418	- 240.849	87.729
700	42.165	133.451	110.268	16.228	- 275.802	- 234.968	73.360
800	42.515	139.106	113.527	20.463	- 275.227	- 229.179	62.609
900	42.759	144.128	116.653	24.728	- 274.688	- 223.453	54.262
1000	42.937	148.643	119.630	29.013	- 274.192	- 217.785	47.597
1100	43.069	152.742	122.457	33.314	- 273.736	- 212.170	42.154
1200	43.171	156.494	125.139	37.626	- 273.318	- 206.590	37.625
1300	43.251	159.953	127.686	41.947	- 272.940	- 201.045	33.799
1400	43.314	163.160	130.106	46.276	- 272.597	- 195.529	30.523
1500	43.366	166.151	132.411	50.610	- 272.292	- 190.034	27.688
1600	43.408	168.951	134.608	54.948	- 272.023	- 184.559	25.210
1700	43.443	171.583	136.706	59.291	- 271.788	- 179.097	23.025
1800	43.472	174.067	138.714	63.637	- 271.593	- 173.652	21.084
1900	43.497	176.418	140.637	67.985	- 271.436	- 168.214	19.349
2000	43.519	178.650	142.482	72.336	- 271.315	- 162.787	17.789
2100	43.537	180.774	144.255	76.689	- 271.231	- 157.361	16.377
2200	43.553	182.800	145.962	81.043	- 271.191	- 151.946	15.094
2300	43.567	184.736	147.606	85.399	- 271.183	- 146.525	13.923
2400	43.579	186.590	149.192	89.757	- 271.215	- 141.097	12.849
2500	43.590	188.370	150.724	94.115	- 271.289	- 135.684	11.861
2600	43.600	190.079	152.205	98.475	- 271.397	- 130.251	10.949
2700	43.608	191.725	153.638	102.835	- 271.557	- 124.820	10.103
2800	43.616	193.311	155.027	107.196	- 271.783	- 119.379	9.318
2900	43.623	194.842	156.373	111.558	- 272.095	- 113.935	8.586
3000	43.629	196.321	157.680	115.921	- 272.503	- 108.469	7.902
3100	43.634	197.751	158.950	120.284	- 273.029	- 102.994	7.261
3200	43.640	199.137	160.184	124.648	- 273.687	- 97.505	6.659
3300	43.644	200.480	161.385	129.012	- 274.489	- 91.989	6.092
3400	43.648	201.783	162.554	133.376	- 275.456	- 86.443	5.556
3500	43.652	203.048	163.693	137.742	- 276.606	- 80.869	5.050
3600	43.656	204.278	164.804	142.107	- 277.997	- 75.256	4.569
3700	43.659	205.474	165.887	146.473	- 296.289	- 69.509	4.106
3800	43.662	206.638	166.944	150.839	- 296.578	- 63.368	3.645
3900	43.665	207.773	167.976	155.205	- 296.876	- 57.236	3.207
4000	43.668	208.878	168.985	159.572	- 297.185	- 51.089	2.791
4100	43.670	209.956	169.971	163.939	- 297.503	- 44.927	2.395
4200	43.672	211.009	170.936	168.306	- 297.827	- 38.767	2.017
4300	43.674	212.036	171.880	172.673	- 298.160	- 32.583	1.656
4400	43.676	213.040	172.804	177.041	- 298.501	- 26.414	1.312
4500	43.678	214.022	173.709	181.408	- 298.849	- 20.227	.982
4600	43.680	214.982	174.596	185.776	- 299.202	- 14.020	.666
4700	43.681	215.921	175.465	190.144	- 299.564	- 7.816	.363
4800	43.683	216.841	176.318	194.513	- 299.928	- 1.604	.073
4900	43.684	217.742	177.154	198.881	- 300.299	4.598	- .205
5000	43.686	218.624	177.975	203.249	- 300.676	10.829	- .473
5100	43.687	219.489	178.780	207.618	- 301.058	17.070	- .731
5200	43.688	220.338	179.571	211.987	- 301.443	23.297	- .979
5300	43.689	221.170	180.348	216.356	- 301.831	29.562	- 1.219
5400	43.690	221.987	181.112	220.725	- 302.225	35.804	- 1.449
5500	43.691	222.788	181.862	225.094	- 302.619	42.082	- 1.672
5600	43.692	223.576	182.600	229.463	- 303.022	48.339	- 1.886
5700	43.693	224.349	183.326	233.832	- 303.425	54.609	- 2.094
5800	43.694	225.109	184.040	238.201	- 303.831	60.908	- 2.295
5900	43.695	225.856	184.742	242.571	- 304.239	67.201	- 2.489
6000	43.695	226.590	185.433	246.940	- 692.459	77.671	- 2.829

Sept. 30, 1966

TUNGSTEN TRIOXIDE, DIMERIC $((WO_3)_2)$ (IDEAL GAS) GFW = 463.6964

Point Group $[D_{2h}]$

$S°_{298.15}$ = [99.3] gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -276.8 kcal/mol

$\Delta Hf°_{298.15}$ = -278.2 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[600] (4)
[300] (8)
[172] (6)

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O =[109.47°] , $W\text{-}O_{bridge}\text{-}W$ = [70.53°] σ = [4]

Product of the Moments of Inertia: $I_AI_BI_C$=[5.917 x 10^{-112}] g^3 cm^6

Heat of Formation.

The adopted value, $\Delta Hf°_{298}$ (W_2O_6, g) = -278.2 kcal/mol, was reduced from $\Delta Hf°_{1450}$ = -272.5 kcal/mol, reported by R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963). They have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion, and X-ray diffraction, and also have determined ΔGf° (W_2O_6,g) = - 272,500 + 54.98T (cal/mol) from partial pressure measurements over the W-WO_2(c) system.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, 1964, has also studied the same system in the temperature range from 1418 to 1527° K. Third law calculation of the partial pressure data gives $\Delta Hr°_{298}$ = 144.0 kcal/mol for 3 WO_2(c) = W_2O_6(g) + W(c) which yields $\Delta Hf°_{298}$ (W_2O_6,g) = -278.8 kcal/mol, using all JANAF functions. This value is in good agreement with the value adopted.

J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965), have obtained $\Delta Hr°_{1800}$ = -127 kcal/mol for 2 WO_3(g) = W_2O_6(g) by mass spectrometric study of the vapor over WO_3 dissolved in CaO-Al_2O_3-SiO_2. The value of ΔHr° was determined by the second law method from ion intensities and leads to $\Delta Hf°_{298}$ (W_2O_6,g) = -275 kcal/mol, using all JANAF functions (dated Sept. 30, 1966). The absolute pressure values reported by Norman and Staley appear to be quite inconsistent with the JANAF functions, since they lead to $\Delta Hf°_{298}$ (W_2O_6,g) = -246 kcal/mol by the third law method.

		Temperature	$\Delta Hr°_{298}$ (kcal/mol)		Drift	$\Delta Hf°_{298}$(W_2O_6,g)
Investigator	Chemical Reaction	(°K)	2nd law	3rd law	(eu)	(kcal/mol)
Ackermann & Rauh	3 WO_2(c) = W_2O_6(g) + W(c)	1300-1600	144.54	144.63	0.01	-278.2*
Battles	3 WO_2(c) = W_2O_6(g) + W(c)	1418-1527	142.66	143.97	0.85 ± 0.40	-278.8*
Norman & Staley	2 WO_3(g) = W_2O_6(g)	1700-1900	-135	-106		-275 **

* Third law value adopted in calculation.

** Second law value adopted in calculation.

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 600 cm^{-1}(4), 300 cm^{-1}(8), and 172 cm^{-1}(6) in order to give the entropy at 1450°K, $S°_{1450}$ = 164.66 eu, corresponding to $\Delta Sf°_{1450}$ = 54.98 eu which was reported by Ackermann and Rauh. The adopted value, $S°_{298}$ (W_2O_6,g) = 99.3 eu, was reduced from the entropy at 1450°K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta S°_{1470}$ = 63.5 eu for 3 WO_2(c) = W_2O_6(g) + W(c). This yields $S°_{298}$ (W_2O_6,g) = 97.9 eu.

The molecular configuration for W_2O_6(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and two of these tetrahedra share a common oxygen edge to form a planar four-member ring. The bond distance W-O was estimated as 1.81 Å and the bond angle O-W-O = 109.47° and $W\text{-}O_{bridge}\text{-}W$ = 70.53°. The three principal moments of inertia are: I_A = 3.481 x 10^{-38}, I_B = 1.363 x 10^{-37} and I_C = 1.247 x 10^{-37} g cm^2.

Tritungsten Octaoxide (W_3O_8)

(Ideal Gas) GFW = 679.5452

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-9.552	-406.385	-406.385	INFINITE
100	26.940	75.456	156.609	-8.115	-408.192	-398.491	870.901
200	42.309	99.703	122.349	-4.529	-408.830	-388.459	424.488
298	49.301	118.036	118.036	.000	-408.700	-378.468	277.425
300	49.398	118.341	118.037	.091	-408.694	-378.282	275.578
400	53.445	133.157	120.029	5.251	-408.145	-368.220	201.186
500	55.875	145.366	123.912	10.727	-407.396	-358.322	156.623
600	57.403	155.699	128.371	16.397	-406.579	-348.583	126.971
700	58.409	164.628	132.927	22.190	-405.761	-338.980	105.834
800	59.101	172.475	137.390	28.068	-404.974	-329.500	90.015
900	59.594	179.466	141.684	34.004	-404.220	-320.108	77.733
1000	59.956	185.765	145.783	39.982	-403.512	-310.798	67.925
1100	60.230	191.493	149.682	45.992	-402.850	-301.564	59.915
1200	60.442	196.743	153.388	52.026	-402.233	-292.380	53.250
1300	60.608	201.588	156.912	58.079	-401.666	-283.249	47.618
1400	60.741	206.084	160.265	64.147	-401.145	-274.162	42.799
1500	60.850	210.279	163.461	70.227	-400.673	-265.106	38.626
1600	60.939	214.209	166.511	76.316	-400.249	-256.082	34.979
1700	61.013	217.906	169.427	82.414	-399.872	-247.083	31.765
1800	61.076	221.395	172.218	88.518	-399.550	-238.106	28.910
1900	61.129	224.699	174.894	94.629	-399.278	-229.145	26.358
2000	61.175	227.835	177.463	100.744	-399.058	-220.196	24.062
2100	61.214	230.821	179.934	106.864	-398.889	-211.254	21.986
2200	61.248	233.670	182.312	112.987	-398.781	-202.332	20.100
2300	61.278	236.393	184.605	119.113	-398.719	-193.403	18.377
2400	61.304	239.001	186.817	125.242	-398.714	-184.466	16.798
2500	61.327	241.504	188.955	131.374	-398.766	-175.549	15.346
2600	61.348	243.910	191.023	137.508	-398.868	-166.613	14.005
2700	61.366	246.226	193.024	143.643	-399.044	-157.677	12.763
2800	61.383	248.458	194.965	149.781	-399.315	-148.729	11.609
2900	61.397	250.612	196.847	155.920	-399.713	-139.778	10.534
3000	61.411	252.694	198.674	162.060	-400.253	-130.799	9.529
3100	61.423	254.708	200.449	168.202	-400.966	-121.811	8.588
3200	61.434	256.658	202.175	174.345	-401.875	-112.797	7.704
3300	61.444	258.548	203.855	180.489	-402.997	-103.747	6.871
3400	61.453	260.383	205.491	186.633	-404.364	-94.658	6.085
3500	61.461	262.164	207.085	192.779	-406.005	-85.527	5.341
3600	61.469	263.896	208.639	198.926	-408.003	-76.343	4.635
3700	61.476	265.580	210.155	205.073	-435.352	-66.958	3.955
3800	61.483	267.220	211.635	211.221	-435.694	-56.990	3.278
3900	61.489	268.817	213.081	217.369	-436.048	-47.026	2.635
4000	61.494	270.374	214.494	223.519	-436.416	-37.052	2.024
4100	61.499	271.892	215.875	229.668	-436.797	-27.055	1.442
4200	61.504	273.374	217.227	235.818	-437.185	-17.059	.888
4300	61.509	274.821	218.550	241.969	-437.584	-7.038	.358
4400	61.513	276.236	219.845	248.120	-437.995	2.960	-.147
4500	61.517	277.618	221.113	254.272	-438.413	12.991	-.631
4600	61.520	278.970	222.356	260.424	-438.839	23.042	-1.095
4700	61.524	280.293	223.575	266.576	-439.277	33.087	-1.539
4800	61.527	281.589	224.770	272.728	-439.719	43.142	-1.964
4900	61.530	282.857	225.943	278.881	-440.168	53.189	-2.372
5000	61.533	284.100	227.093	285.034	-440.625	63.265	-2.765
5100	61.536	285.319	228.223	291.188	-441.089	73.353	-3.143
5200	61.538	286.514	229.333	297.341	-441.558	83.429	-3.506
5300	61.541	287.686	230.423	303.495	-442.030	93.551	-3.858
5400	61.543	288.836	231.494	309.650	-442.509	103.647	-4.195
5500	61.545	289.966	232.547	315.804	-442.989	113.776	-4.521
5600	61.547	291.075	233.582	321.959	-443.480	123.889	-4.835
5700	61.549	292.164	234.600	328.113	-443.972	134.014	-5.138
5800	61.551	293.234	235.602	334.268	-444.467	144.181	-5.433
5900	61.552	294.287	236.588	340.424	-444.965	154.333	-5.717
6000	61.554	295.321	237.558	346.579	-1027.180	170.750	-6.220

Sept. 30, 1966

TRITUNGSTEN OCTAOXIDE (W_3O_8) (IDEAL GAS) GFW = 679.5452

Point Group [D_{2d}]

ΔHf°_0 = -406.4 kcal/mol

$S^\circ_{298.15}$ = [118.0] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -408.7 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (6)	[199] (3)
[350] (4)	[150] (6)
[242] (8)	

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°]

σ = [4]

Product of the Moments of Inertia : $I_AI_BI_C$ = [7.65 x 10^{-111}] g^3 cm^6

Heat of Formation.

R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and X-ray diffraction, and also have determined the $\Delta Gf^\circ(W_3O_8, g)$ = -400,900 + 9054 T (cal/mol) from partial pressure measurements over W-WO_2 (c). The adopted value, ΔHf°_{298} (W_3O_8, g) = -408.7 kcal/mol, was reduced from ΔHf°_{1450} (W_3O_8, g) = -400.9 kcal/mol, using JANAF functions.

Investigator	Chemical Reaction	Temperature (°K)	ΔHr°_{298} (kcal/mol) 2nd law	ΔHr°_{298} (kcal/mol) 3rd law	Drift (eu)	$\Delta Hf^\circ_{298}(W_3O_8,g)$ (kcal/mol)
Ackermann & Rauh	4 $WO_2(c) = W_3O_8(g)+W(c)$	1300-1600°	155.05	155.09	-0.04	-408.7

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(6), 350 cm^{-1}(4), 242 cm^{-1} (8), 199 cm^{-1}(3) and 150 cm^{-1} (6) in order to give the entropy at 1450°K, S°_{1450} = 208.18 eu, corresponding to ΔSf°_{1450} = -90.54 eu, which was reported by Ackermann and Rauh.

The molecular configuration for $W_3O_8(g)$ was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, the three tetrahedra are connected by two common edges, and also the three tungsten atoms are in the same axis. The bond distance W-O was estimated as 1.81 A° and the bond angle ∡OWO = 109.47°. The three principal moments of inertia are: $I_A = I_B = 4.060 \times 10^{-37}$ and $I_C = 4.641 \times 10^{-38}$ g cm^2.

Tungsten Trioxide, Trimeric $(WO_3)_3$
(Ideal Gas) GFW = 695.5446

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 9.956	- 480.652	- 480.652	INFINITE
100	26.614	76.163	161.514	- 8.535	- 482.822	- 471.121	1029.634
200	44.668	100.980	125.233	- 4.851	- 483.709	- 458.972	501.541
298	53.284	120.599	120.599	.000	- 483.600	- 446.827	327.533
300	53.401	120.929	120.600	.099	- 483.593	- 446.600	325.348
400	58.219	137.015	122.760	5.702	- 482.956	- 434.356	237.321
500	61.048	150.337	126.982	11.677	- 482.073	- 422.305	184.589
600	62.806	161.634	131.840	17.876	- 481.105	- 410.440	149.503
700	63.956	171.408	136.811	24.218	- 480.127	- 398.738	124.492
800	64.742	180.003	141.683	30.656	- 479.179	- 387.184	105.774
900	65.301	187.662	146.374	37.159	- 478.265	- 375.735	91.241
1000	65.711	194.565	150.854	43.711	- 477.397	- 364.387	79.637
1100	66.020	200.843	155.117	50.298	- 476.577	- 353.131	70.161
1200	66.259	206.598	159.171	56.913	- 475.803	- 341.939	62.276
1300	66.446	211.909	163.026	63.548	- 475.082	- 330.813	55.615
1400	66.597	216.839	166.696	70.201	- 474.409	- 319.745	49.914
1500	66.719	221.438	170.194	76.867	- 473.786	- 308.716	44.980
1600	66.819	225.747	173.533	83.544	- 473.213	- 297.730	40.668
1700	66.903	229.801	176.725	90.230	- 472.689	- 286.778	36.868
1800	66.973	233.627	179.781	96.924	- 472.221	- 275.857	33.494
1900	67.033	237.250	182.711	103.624	- 471.807	- 264.959	30.477
2000	67.084	240.689	185.524	110.330	- 471.447	- 254.083	27.765
2100	67.128	243.963	188.230	117.041	- 471.139	- 243.218	25.312
2200	67.166	247.087	190.835	123.755	- 470.896	- 232.380	23.085
2300	67.200	250.074	193.346	130.474	- 470.699	- 221.544	21.051
2400	67.229	252.934	195.770	137.195	- 470.563	- 210.703	19.187
2500	67.255	255.679	198.111	143.919	- 470.487	- 199.889	17.474
2600	67.278	258.317	200.377	150.646	- 470.462	- 189.059	15.892
2700	67.299	260.857	202.570	157.375	- 470.513	- 178.235	14.427
2800	67.317	263.305	204.696	164.106	- 470.663	- 167.404	13.067
2900	67.334	265.667	206.758	170.838	- 470.941	- 156.572	11.800
3000	67.349	267.950	208.759	177.573	- 471.363	- 145.718	10.616
3100	67.363	270.159	210.705	184.308	- 471.961	- 134.860	9.508
3200	67.375	272.298	212.596	191.045	- 472.757	- 123.980	8.467
3300	67.386	274.371	214.437	197.783	- 473.768	- 113.067	7.488
3400	67.396	276.383	216.229	204.522	- 475.026	- 102.115	6.564
3500	67.406	278.337	217.976	211.262	- 476.560	- 91.131	5.690
3600	67.414	280.236	219.679	218.003	- 478.453	- 80.089	4.862
3700	67.422	282.083	221.341	224.745	- 505.698	- 68.854	4.067
3800	67.430	283.881	222.963	231.488	- 505.938	- 57.034	3.280
3900	67.436	285.633	224.548	238.231	- 506.190	- 45.228	2.535
4000	67.443	287.340	226.096	244.975	- 506.460	- 33.408	1.825
4100	67.448	289.006	227.611	251.720	- 506.743	- 21.574	1.150
4200	67.454	290.631	229.092	258.465	- 507.035	- 9.738	.507
4300	67.459	292.218	230.541	265.210	- 507.339	2.121	- .108
4400	67.464	293.769	231.961	271.956	- 507.657	13.955	- .693
4500	67.468	295.285	233.351	278.703	- 507.982	25.817	- 1.254
4600	67.472	296.768	234.714	285.450	- 508.317	37.698	- 1.791
4700	67.476	298.219	236.050	292.197	- 508.665	49.571	- 2.305
4800	67.480	299.640	237.360	298.945	- 509.016	61.454	- 2.798
4900	67.483	301.031	238.645	305.693	- 509.377	73.322	- 3.270
5000	67.486	302.395	239.906	312.442	- 509.746	85.217	- 3.725
5100	67.489	303.731	241.145	319.191	- 510.123	97.131	- 4.162
5200	67.492	305.042	242.361	325.940	- 510.505	109.023	- 4.582
5300	67.495	306.327	243.556	332.689	- 510.892	120.966	- 4.988
5400	67.497	307.589	244.730	339.439	- 511.286	132.871	- 5.378
5500	67.500	308.828	245.884	346.188	- 511.681	144.818	- 5.755
5600	67.502	310.044	247.019	352.938	- 512.089	156.744	- 6.117
5700	67.504	311.239	248.135	359.689	- 512.497	168.676	- 6.467
5800	67.506	312.413	249.233	366.439	- 512.909	180.652	- 6.807
5900	67.508	313.567	250.314	373.190	- 513.325	192.616	- 7.135
6000	67.510	314.701	251.378	379.941	-1095.458	210.841	- 7.680

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN TRIOXIDE, TRIMERIC $((WO_3)_3)$ (IDEAL GAS) GFW = 695.5446

Point Group $[D_{3h}]$

ΔHf_0° = -480.7 kcal/mol

$S^\circ_{298.15}$ = [120.6] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -483.6 ± 10 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (6)	[200] (6)
[396] (3)	[150] (6)
[330] (9)	

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°], W-O_{bridge}-W = [130.53°]

σ = [6]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.865 x 10^{-110}] g^3cm^6

Heat of Formation.

The adopted value, ΔHf°_{298} (W_3O_9,g) = -483.6 kcal/mol, was reduced from $\Delta Hf^\circ_{1450}(W_3O_9,g)$ = -474.1 kcal/mol of R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600 °K by mass spectrometry, mass effusion, and X-ray diffraction, and determined ΔGf° (W_3O_9,g) = -474,100 + 110.26T (cal/mol) from partial pressure measurements over W-WO_2(c). They reviewed the previous determinations [1, 2, 3, 4] of the thermodynamic properties of sublimation of WO_3, and also pointed out that it was not possible to make quantitative observations on stoichiometric WO_3 in vacuo, since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches $WO_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of W_3O_9(g) over W-WO_2(c) in the temperature range from 1389° to 1527°K. Third law calculation of the partial pressure data gives ΔHr°_{298} = 148.2 kcal/mol for 4.5 WO_2(c) = W_3O_9(g) + 1.5 W (c), which yields ΔHf°_{298} (W_3O_9,g) = -486.0 kcal/mol, using all JANAF functions.

J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965), have obtained ΔHr°_{1800} = -240 kcal/mol for 3 WO_3(g) = W_3O_9(g) by mass spectrometric study of the vapor over WO_3 dissolved in CaO-Al_2O_3-SiO_2. The value of $\Delta H\overset{\circ}{r}$ was determined by the second law method from ion intensities and leads to ΔHf°_{298} (W_3O_9,g) = -463.4 kcal/mol, using all JANAF functions (dated September 30, 1966). The absolute pressure values reported by Norman and Staley also appear to be quite inconsistent with the JANAF functions, since they lead to -443 kcal/mol by the third law method.

Reference 1. K. Ueno, J. Chem. Soc. Japan 62, 990 (1941).
2. J. Berkowitz, W. A. Chupka, and M. G. Inghram, J. Chem. Phys. 27, 85 (1957).
3. P. E. Blackburn, J. Hoch, and H. L. Johnston, J. Phys. Chem. 62, 769 (1958); P. E. Blackburn, WADC TR 59 - 575, part 1, Mar. 1960; and part 2, Dec. 1960.
4. G. Meyer, J. F. Oosterom, and J. L. DeRoo, Rec. Trav. Chim. 78, 412 (1959).

Investigator	Chemical Reaction	Temperature (°K)	ΔHr°_{298}(kcal/mol) 2nd law	ΔHr°_{298}(kcal/mol) 3rd law	Drift (eu)	$\Delta Hf^\circ_{298}(W_3O_9,g)$ (kcal/mol)
Ackermann & Rauh	4.5 WO_2(c) = W_3O_9(g) + 1.5 W(c)	1300-1600	150.61	150.64	-0.05	-483.6 *
Battles	4.5 WO_2(c) = W_3O_9(g) + 1.5 W(c)	1389-1527	148.20	148.20	-1.91 ± 0.24	-486.0 *
Norman & Staley	3 WO_3(g) = W_3O_9(g)	1700-1900	-253.4	-233		-463.4 **

* Third law value adopted in calculation

** Second law value adopted in calculation

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1} (6), 396 cm^{-1}(3), 330 cm^{-1}(9), 200 cm^{-1}(6), and 150 cm^{-1}(6) in order to give the entropy at 1450°K, S°_{1450} = 219.14 eu, corresponding to ΔSf°_{1450} = 110.26 eu, reported by Ackermann and Rauh. The adopted value, S°_{298} $(W_3O_9,$ g) = 120.6 eu, was reduced from the entropy at 1450°K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives ΔS°_{1455} = 71.7 eu for 4.5 WO_2(c) = W_3O_9(g) + 1.5 W (c). This yields $S^\circ_{298}(W_3O_9,g)$ = 122.4 eu.

The molecular configuration for W_3O_9(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedron shares two oxygen atoms to form a planar six-member ring. The bond distance W-O is estimated as 1.81 Å and the bond angles O-W-O = 109.47° and W-O_{bridge}-W = 130.53°. The three principal moments of inertia are: $I_A = I_B$ = 2.805 x 10^{-37} and I_C = 4.913 x 10^{-37} g cm^2.

Diphosphorus Pentoxide, Dimeric $((P_2O_5)_2)$
(Crystal) Mol. Wt. = 283.8892

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	- 8.117	- 696.994	- 696.994	INFINITE
100	18.550	18.530	89.940	- 7.141	- 699.947	- 680.441	1487.032
200	36.940	37.260	58.920	- 4.332	- 701.810	- 660.134	721.326
298	50.600	54.680	54.680	.000	- 702.700	- 639.450	468.707
300	50.830	54.994	54.681	.094	- 702.707	- 639.058	465.531
400	62.200	71.218	56.816	5.761	- 702.727	- 617.815	337.542
500	71.700	86.135	61.708	12.463	- 701.964	- 596.660	260.787
600	80.300	99.982	66.530	20.071	- 700.535	- 575.725	209.698
700	88.000	112.950	72.245	28.493	- 698.535	- 555.074	173.294
800	94.800	125.153	78.103	37.640	- 777.710	- 555.992	151.883
900	100.800	136.675	83.977	47.428	- 773.736	- 528.506	128.333
1000	105.800	147.560	89.796	57.763	- 769.292	- 501.492	109.596
1100	110.200	157.858	95.520	68.572	- 764.442	- 474.948	94.359
1200	113.600	167.598	101.124	79.768	- 759.258	- 448.857	81.744
1300	116.200	176.797	106.595	91.263	- 753.824	- 423.206	71.144
1400	118.300	185.487	111.923	102.991	- 748.196	- 397.983	62.125
1500	120.000	193.710	117.103	114.909	- 742.417	- 373.168	54.368

Dec. 31, 1962; Dec. 31, 1965

DIPHOSPHORUS PENTOXIDE, DIMERIC $((P_2O_5)_2)$ (CRYSTAL) MOL. WT. = 283.8892

$\Delta H^\circ_{f\ 0} = -697.0 \pm 2.1$ kcal. mole^{-1}

$S^\circ_{298.15} = 54.68 \pm 0.10$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 298.15} = -702.7 \pm 2.1$ kcal. mole^{-1}

$T_s = 631$°K.

$\Delta H^\circ_{s\ 298.15} = 25.34 \pm 0.08$ kcal. mole^{-1}

Heat of Formation.

The heat of formation ($\Delta H^\circ_{f\ 298.15}$) of P_4O_{10}(c) has been reported by many investigators. The most recent value, $\Delta H^\circ_{r\ 298.15} = -719.4 \pm 2.0$ kcal. mole^{-1} for the reaction $P_4(\alpha$, white, c) + $5O_2$(g) = P_4O_{10}(hex., c), was determined by E. P. Egan, Jr. and B. B. Luff, "Heats of Formation of Phosphorus Oxides", June 1, 1963 to Nov. 30, 1963, Tennessee Valley Authority, Office of Agriculture and Chemical Development, Fundamental Research Branch, Wilson Dam, Alabama. This $\Delta H^\circ_{r\ 298.15}$ value was derived from energy of combustion, $\Delta E_c = -716.397$ kcal. mole^{-1}, which is an average value of many measurements using three different sample forms, i.e. uncoated phosphorus, lucite-coated phosphorus and cellulose acetate-coated phosphorus. The adopted $\Delta H^\circ_{f\ 298.15}$ (P_4O_{10}, c) value was recalculated based on the P(red, V, c) as reference state.

The heat of combustion of white phosphorus was determined as -713.2 ± 1.0 kcal. mole^{-1} by W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962), yielding $\Delta H^\circ_{f\ 298.15}$ (P_4O_{10}, c) = -696.5 ± 1.3 kcal. mole^{-1}, based on P(red, V, c) as reference state. The heat of formation of P_2O_5 from red phosphorus was reported to be -355 ± 2 kcal. mole^{-1} by W. E. Koerner and F. Daniels, J. Chem. Phys. 20, 113 (1952). The product, P_2O_5, was considered to be a mixture of two forms, i.e. crystalline and amorphous. The other $\Delta H^\circ_{f\ 298.15}$ (P_4O_{10}, c) values reported by early investigators were reviewed by Egan and Luff, loc. cit.

Heat Capacity and Entropy.

The heat capacities (12-324°K.) and $S^\circ_{298.15}$ adopted were taken from R. J. L. Andon, J. F. Counsell, H. McKerrell and J. F. Martin, Trans. Faraday Soc. 59, 2702 (1963). The C_p values above 324°K. were obtained by graphical extrapolation. The $S^\circ_{298.15}$ value was calculated based on $S^\circ_{10} = 0.36$ e.u.

Low temperature (15-310°K.) and high temperature (298.15-623.15°K.) heat capacities were also measured by Thermal Laboratory, The Dow hemical Company, private communication, June 18, 1962, and M. Frandsen, J. Res. Natl. Bur. Std. 10, 35 (1933), respectively. The low temperature data were not adopted becuase they are less satisfactory than the data of Andon et al. The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data.

The value of $\Delta H^\circ_{s\ 298.15}$ was derived from the vapor pressure data by both the second and third law analyses. See the P_4O_{10}(g) table for details. T_s is the temperature at which the free energy change of the reaction P_4O_{10}(hex. c) = P_4O_{10}(g) approaches zero. Sublimation temperature for P_4O_{10}(c) was derived to be 632°K., 636°K. (average of three determinations) and 623.7°K. (average of two determinations) by M. Frandsen, loc. cit. from the vapor pressure data reported by J. M. Hoeflake and M. F. Scheffer, Rec. trav. chim. 45, 191 (1926); A. Smits, Z. physik. Chem. A149, 337 (1930); and A. Smits and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924), respectively.

Diphosphorus Pentoxide, Dimeric ($(P_2O_5)_2$)

(Ideal Gas) Mol. Wt. = 283.8892

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 7.398	- 670.975	- 670.975	INFINITE
100	16.835	64.368	127.811	- 6.344	- 673.850	- 658.929	1440.018
200	32.689	81.035	100.277	- 3.848	- 676.026	- 643.105	702.719
298	45.126	96.525	96.525	.000	- 677.400	- 626.627	459.308
300	45.325	96.805	96.526	.084	- 677.417	- 626.311	456.245
400	54.377	111.161	98.422	5.096	- 678.092	- 609.157	332.812
500	60.662	124.013	102.279	10.867	- 678.260	- 591.896	258.705
600	65.043	135.484	106.875	17.165	- 678.141	- 574.633	209.300
700	68.149	145.757	111.709	23.833	- 677.895	- 557.400	174.020
800	70.399	155.011	116.553	30.766	- 759.284	- 561.452	153.374
900	72.067	163.404	121.300	37.894	- 757.970	- 536.797	130.346
1000	73.329	171.066	125.899	45.166	- 756.589	- 512.295	111.957
1100	74.304	178.102	130.329	52.550	- 755.164	- 487.938	96.940
1200	75.069	184.602	134.585	60.020	- 753.706	- 463.710	84.449
1300	75.681	190.635	138.667	67.559	- 752.228	- 439.599	73.900
1400	76.175	196.263	142.582	75.152	- 750.735	- 415.608	64.876
1500	76.581	201.532	146.338	82.791	- 749.235	- 391.719	57.071
1600	76.918	206.486	149.944	90.466	- 747.733	- 367.937	50.255
1700	77.200	211.158	153.409	98.173	- 746.228	- 344.241	44.253
1800	77.439	215.577	156.741	105.905	- 744.733	- 320.639	38.929
1900	77.642	219.770	159.949	113.659	- 743.250	- 297.116	34.175
2000	77.817	223.757	163.041	121.433	- 741.776	- 273.686	29.906
2100	77.969	227.557	166.023	129.222	- 740.312	- 250.309	26.049
2200	78.101	231.188	168.903	137.026	- 738.872	- 227.012	22.550
2300	78.216	234.662	171.687	144.842	- 737.440	- 203.783	19.363
2400	78.318	237.993	174.381	152.668	- 736.032	- 180.607	16.446
2500	78.408	241.192	176.990	160.505	- 734.639	- 157.494	13.767
2600	78.489	244.269	179.519	168.350	- 733.266	- 134.437	11.300
2700	78.560	247.232	181.972	176.202	- 731.916	- 111.429	9.019
2800	78.625	250.091	184.354	184.062	- 730.583	- 88.471	6.905
2900	78.682	252.851	186.669	191.927	- 729.270	- 65.556	4.940
3000	78.735	255.519	188.920	199.798	- 727.980	- 42.690	3.110
3100	78.782	258.101	191.110	207.674	- 726.705	- 19.862	1.400
3200	78.825	260.603	193.243	215.554	- 725.455	2.907	- .199
3300	78.864	263.030	195.321	223.439	- 724.216	25.646	- 1.698
3400	78.900	265.384	197.347	231.327	- 723.007	48.354	- 3.108
3500	78.933	267.672	199.324	239.219	- 721.805	71.018	- 4.434
3600	78.963	269.896	201.254	247.113	- 720.625	93.656	- 5.685
3700	78.991	272.060	203.138	255.011	- 719.461	116.258	- 6.867
3800	79.017	274.167	204.980	262.912	- 718.309	138.841	- 7.985
3900	79.041	276.220	206.780	270.815	- 717.174	161.375	- 9.043
4000	79.063	278.221	208.541	278.720	- 716.057	183.875	- 10.046
4100	79.083	280.174	210.265	286.627	- 714.953	206.366	- 11.000
4200	79.102	282.080	211.952	294.536	- 713.861	228.829	- 11.907
4300	79.120	283.941	213.605	302.447	- 712.782	251.266	- 12.770
4400	79.137	285.760	215.224	310.360	- 711.716	273.673	- 13.593
4500	79.152	287.539	216.811	318.275	- 710.662	296.055	- 14.378
4600	79.167	289.279	218.368	326.191	- 709.613	318.418	- 15.128
4700	79.180	290.981	219.895	334.108	- 708.582	340.759	- 15.845
4800	79.193	292.649	221.393	342.027	- 707.558	363.077	- 16.531
4900	79.205	294.282	222.864	349.947	- 706.539	385.357	- 17.187
5000	79.216	295.882	224.308	357.868	- 705.533	407.632	- 17.817
5100	79.227	297.451	225.727	365.790	- 704.540	429.894	- 18.421
5200	79.237	298.989	227.121	373.713	- 703.547	452.106	- 19.001
5300	79.246	300.499	228.492	381.637	- 702.562	474.345	- 19.559
5400	79.255	301.980	229.839	389.562	- 701.586	496.518	- 20.094
5500	79.263	303.434	231.164	397.488	- 700.609	518.725	- 20.611
5600	79.271	304.863	232.467	405.415	- 699.650	540.862	- 21.107
5700	79.279	306.266	233.750	413.342	- 698.691	563.004	- 21.586
5800	79.286	307.645	235.012	421.271	- 697.735	585.143	- 22.048
5900	79.293	309.000	236.254	429.200	- 696.784	607.245	- 22.493
6000	79.300	310.333	237.478	437.129	- 695.842	629.354	- 22.923

Dec. 31, 1962; Dec. 31, 1965

DIPHOSPHORUS PENTOXIDE, DIMERIC ($(P_2O_5)_2$) (IDEAL GAS) MOL. WT. = 283.8892

Point Group T_d

$S^\circ_{298.15}$ = [96.5] cal. deg.$^{-1}$ mole^{-1}

Ground State Quantum Weight = [1]

$\Delta H^\circ_{f\ 0}$ = -671.0 ± 2.1 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = -677.4 ± 2.1 kcal. mole^{-1}

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
424 (1)	650 (2)	[750](3)	764 (3)
721 (1)	952 (2)	257 (3)	1015 (3)
1417 (1)	[170](3)	329 (3)	1390 (3)
278 (2)	[470](3)	573 (3)	

Bond Distance: P-O$_{apical}$ = 1.40 ± 0.03 Å P-O = 1.60 ± 0.01 Å P-P = 2.83 ± 0.03 Å

Bond Angle: O$_{apical}$-P-O = 117 ± 1° O-P-O = 101 ± 1° P-O-P = 124°30' ± 1° σ = 12

Product of the Moments of Inertia: $I_AI_BI_C$ = 2.93798 X 10^{-111} g.^{3} cm.^{6}

Heat of Formation.

The value of $\Delta H^\circ_{f\ 298.15}$ (P_4O_{10}, g) was calculated from the heats of formation and sublimation for P_4O_{10} (hex., c). The heat of sublimation ($\Delta H^\circ_{s\ 298.15}$) was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K	$\Delta H^\circ_{s\ 298.15}$, kcal. mole^{-1} Second Law Value	Third Law Value	Drift, e.u.
Hoeflake and Scheffer[1]	260 -401	25.42±0.07	25.33	-0.39±0.13
Southard and Nelson[2]	216.2-300.4	25.59±0.06	25.35	-0.18±0.14
	283.6-389.3	25.45±0.07	25.35	-0.10±0.07

1. J. M. A. Hoeflake and F. E. C. Scheffer, Rec. trav. chim. 45, 191 (1926).
2. J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. 59, 911 (1937).

The value of $\Delta H^\circ_{s\ 298.15}$ adopted was 25.34 ± 0.08 kcal. mole^{-1}. There are many vapor pressure measurements reported but only the above two over P_4O_{10}(hex., c).

It has been shown that P_4O_{10} has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P_4O_{10} follows the same order. The metastable liquid, according to data of Hoeflake and Scheffer, loc. cit., is from hexagonal form. The stable liquid is from tetragonal form. W. L. Hill, G. T. Faust and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943) reported that molecules of P_4O_{10} having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P_4O_{10} over different condensed phases have been measured by many investigators and reviewed by T. D. Farr, "Phosphorus, Properties of the Elements and Some of Its Compounds", Tennessee Valley Authority, Wilson Dam, Alabama, 1950. The complexity of the solid state of P_4O_{10} has also been discussed by A. Smits and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924); A. Smits, Z. physik. Chem. A149, 337 (1930); A. Smits, J. A. A. Ketelaar and J. L. Meyering, ibid., B41, 87 (1938); and A. Smits, ibid., B46, 43 (1940).

Heat Capacity and Entropy.

The molecular structure and constants were obtained from P. A. Akishin, N. G. Rambidi and E. Z. Zasorin, Kristallografiya, 4, 360 (1959). The molecular structure of P_4O_{10}(g) has also been studied by the electron diffraction method by L. R. Maxwell, S. B. Hendricks and L. S. Deming, J. Chem. Phys. 5, 626 (1937), and G. C. Hampson and A. J. Stosick, J. Am. Chem. Soc. 60, 1814 (1938). The model of the P_4O_{10} molecule was later confirmed by the X-ray method reported by H. C. J. Decker and C. H. MacGillavry, Rec. trav. chim. 60, 153 (1941); and spectroscopic studies reported by H. Gerding and H. C. J. DeDecker, Rec. trav. chim. 64, 191 (1945), and T. A. Sidorov and N. N. Sobolev, Opt. Spectr. (USSR) 2, 717 (1957). All vibrational frequencies were obtained from E. P. Egan, Jr., private communication, Feb. 23, 1960, except nine frequencies, i.e. 170 (3), 470 (3) and 750 (3) cm.$^{-1}$ which were estimated in order To make the second and third law values of $\Delta H^\circ_{s\ 298.15}$ agree. The three principal moments of inertia are: $I_A = I_B = I_C$ = 1.4322 X 10^{-37} g. cm.^{2} The heat capacities (549-1098°C. or 822-1371°K.) of P_4O_{10}(g) have been determined by M. Frandsen, J. Res. Natl. Bur. Std. 10, 35 (1933). His results are in fair agreement with the calculated ones.

Tungsten Trioxide, Tetrameric $(WO_3)_4$
(Ideal Gas) GFW = 927.3928

T, °K	gibbs/mol Cp°	S°	$-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-13.719	-666.713	-666.713	INFINITE
100	37.142	81.799	202.183	-12.038	-669.820	-652.244	1425.479
200	63.224	117.169	151.101	-6.786	-670.664	-634.187	693.007
298	73.894	144.635	144.635	.000	-670.200	-616.350	451.797
300	74.038	145.093	144.637	.137	-670.185	-616.018	448.769
400	79.917	167.276	147.621	7.862	-669.082	-598.118	326.796
500	83.380	185.513	153.431	16.041	-667.693	-580.533	253.751
600	85.538	200.920	160.095	24.495	-666.213	-563.239	205.159
700	86.952	214.219	166.899	33.124	-664.736	-546.190	170.528
800	87.921	225.897	173.559	41.871	-663.309	-529.363	144.615
900	88.611	236.295	179.962	50.699	-661.933	-512.698	124.500
1000	89.118	245.658	186.072	59.587	-660.623	-496.181	108.440
1100	89.500	254.171	191.881	68.518	-659.382	-479.805	95.329
1200	89.794	261.972	197.402	77.484	-658.204	-463.528	84.420
1300	90.026	269.168	202.649	86.475	-657.099	-447.349	75.206
1400	90.212	275.847	207.642	95.488	-656.058	-431.259	67.323
1500	90.363	282.076	212.399	104.517	-655.087	-415.231	60.499
1600	90.487	287.912	216.938	113.559	-654.183	-399.271	54.538
1700	90.591	293.401	221.276	122.613	-653.345	-383.363	49.285
1800	90.678	298.582	225.428	131.677	-652.583	-367.506	44.621
1900	90.752	303.487	229.409	140.749	-651.893	-351.688	40.453
2000	90.815	308.143	233.230	149.827	-651.275	-335.905	36.706
2100	90.870	312.576	236.904	158.911	-650.729	-320.147	33.318
2200	90.917	316.804	240.440	168.001	-650.267	-304.427	30.242
2300	90.959	320.846	243.849	177.095	-649.869	-288.714	27.434
2400	90.995	324.718	247.138	186.192	-649.552	-273.006	24.861
2500	91.028	328.434	250.316	195.294	-649.314	-257.339	22.497
2600	91.056	332.004	253.390	204.398	-649.146	-241.653	20.313
2700	91.082	335.441	256.366	213.505	-649.079	-225.981	18.292
2800	91.105	338.754	259.249	222.614	-649.144	-210.306	16.415
2900	91.125	341.952	262.046	231.726	-649.380	-194.637	14.668
3000	91.144	345.041	264.761	240.839	-649.809	-178.938	13.036
3100	91.160	348.030	267.400	249.954	-650.472	-163.239	11.508
3200	91.176	350.924	269.965	259.071	-651.399	-147.514	10.075
3300	91.190	353.730	272.461	268.189	-652.613	-131.754	8.726
3400	91.202	356.453	274.891	277.309	-654.155	-115.945	7.453
3500	91.214	359.097	277.260	286.430	-656.066	-100.095	6.250
3600	91.225	361.666	279.569	295.552	-658.456	-84.170	5.110
3700	91.234	364.166	281.822	304.675	-694.649	-67.995	4.016
3800	91.244	366.599	284.021	313.799	-694.835	-51.043	2.936
3900	91.252	368.969	286.169	322.923	-695.039	-34.110	1.911
4000	91.260	371.280	288.268	332.049	-695.265	-17.169	.938
4100	91.267	373.533	290.320	341.175	-695.509	-.202	.011
4200	91.274	375.733	292.327	350.302	-695.764	16.754	-.872
4300	91.280	377.880	294.292	359.430	-696.036	33.743	-1.715
4400	91.286	379.979	296.216	368.558	-696.326	50.693	-2.518
4500	91.291	382.031	298.100	377.687	-696.627	67.676	-3.287
4600	91.296	384.037	299.947	386.816	-696.940	84.688	-4.024
4700	91.301	386.001	301.757	395.946	-697.270	101.679	-4.728
4800	91.305	387.923	303.532	405.077	-697.605	118.687	-5.404
4900	91.310	389.806	305.273	414.207	-697.953	135.665	-6.051
5000	91.314	391.650	306.983	423.338	-698.312	152.688	-6.674
5100	91.317	393.459	308.660	432.470	-698.682	169.720	-7.273
5200	91.321	395.232	310.308	441.602	-699.058	186.731	-7.848
5300	91.324	396.971	311.927	450.734	-699.440	203.802	-8.404
5400	91.327	398.678	313.518	459.867	-699.833	220.824	-8.937
5500	91.330	400.354	315.082	469.000	-700.226	237.898	-9.453
5600	91.333	402.000	316.619	478.133	-700.637	254.936	-9.949
5700	91.336	403.616	318.131	487.266	-701.048	271.988	-10.429
5800	91.338	405.205	319.619	496.400	-701.464	289.089	-10.893
5900	91.341	406.766	321.083	505.534	-701.886	306.176	-11.341
6000	91.343	408.302	322.524	514.668	-1477.930	331.598	-12.078

Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN TRIOXIDE, TETRAMERIC $((WO_3)_4)$ (IDEAL GAS) GFW = 927.3928

Point Group $[D_{4h}]$

$S°_{298.15}$ = [144.6] gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -666.7 kcal/mol

$\Delta Hf°_{298.15}$ = -670.2 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (8)	[240] (8)
[300] (8)	[200] (18)

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O= [109.47°], $W-O_{bridge}-W$ = [160.53°] σ = [8]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.854 x 10^{-109}] g^3cm^6

Heat of Formation.

The adopted value, $\Delta Hf°_{298}$ (W_4O_{12}, g) = -670.2 kcal/mol, was reduced from $\Delta Hf°_{1450}$ (W_4O_{12}, g) =-655.6 kcal/mol of R. J. Ackermann and E. G. Rauh, J. Phys, Chem. 67, 2596 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and x-ray diffraction, and determined ΔGf° (W_4O_{12}, g) = -655,600 + 160.29 T (cal/mol) from partial pressure measurements over the $W-WO_2(c)$. They reviewed the previous determinations [1,2,3,4] of the thermodynamic properties of sublimation of WO_3, and also pointed out that it was not possible to make quantitative observations on stoichiometric WO_3 in vacuo,since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches $WO_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of $W_4O_{12}(g)$ over $W-WO_2(c)$ in the temperature range from 1449 to 1527°K. Third law calculation of the partial pressure data gives $\Delta Hr°_{298}$ = 172.0 kcal/mol for 6 $WO_2(c) = W_4O_{12}(g) + 2 W(c)$, which yields $\Delta Hf°_{298}$ (W_4O_{12}, g) = -673.6 kcal/mol, using all JANAF functions.

References 1. K. Ueno, J. Chem. Soc. Japan 62, 990 (1941).
2. J. Berkowitz, W. A. Chupka, and M. G. Inghram,J. Chem. Phys. 27, 85(1957).
3. P. E. Blackburn, M. Hoch, and H. L. Johnston, J. Phys. Chem. 62, 769 (1958).
P. E. Blackburn, WADC TR 59-575, part 1, Mar. 1960; and part 2, Dec. 1960.
4. G. Meyer, J. F. Oosterom, and J. L. DeRoo, Rec. Trav. Chim. 78, 412 (1959).

Investigator	Chemical Reaction	Temperature (°K)	$\Delta Hr°_{298}$(kcal/mol) 2nd law	 3rd law	Drift (eu)	$\Delta Hf°_{298}(W_4O_2, g)$* (kcal/mol)
Ackermann & Rauh	6 $WO_2(c) = W_4O_{12}(g) + 2W(c)$	1300 - 1600°	175.41	175.55	0.01	-670.2
Battles	6 $WO_2(c) = W_4O_{12}(g) + 2W(c)$	1449 - 1527°	176.16	172.01	-2.90 ± 0.39	-673.6

* Third law value adopted in calculation.

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(8), 300 cm^{-1} (8), 240 cm^{-1} (8), and 200 cm^{-1} (18) in order to give the entropy at 1450°K, $S°_{1450}$ = 278.9 eu, corresponding to $\Delta Sf°_{1450}$ = -160.29 eu, reported by Ackermann and Rauh. The adopted value, $S°_{298}$ (W_4O_{12}, g) = 144.6 eu, was reduced from the entropy at 1450°K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta S°_{1487}$ = 82.3 eu for 6 $WO_2(c) = W_4O_{12}(g) + 2W(c)$. This yields $S°_{298}$ (W_4O_{12}, g) = 147.4 eu.

The molecular configuration for $W_4O_{12}(g)$ is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedron shares two oxygen atoms to form a planar eight-member ring. The bond distance W-O is estimated as 1.81 Å and the bond angles O-W-O = 109.47° and $W-O_{bridge}-W$ = 160.53°. The three principal moments of inertia are: $I_A = I_B$ = 5.935 x 10^{-37} g cm^2, and I_C = 1.094 x 10^{-36} g cm^2.

Phosphorus (P)

(Reference State) At. Wt. = 30.975

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	.000	.000	INFINITE	- .862	.000	.000	.000
100	2.085	1.494	9.208	- .771	.000	.000	.000
200	4.074	3.619	5.885	- .453	.000	.000	.000
298	5.064	5.450	5.450	.000	.000	.000	.000
300	5.079	5.481	5.450	.009	.000	.000	.000
400	5.540	7.011	5.655	.542	.000	.000	.000
500	5.852	8.283	6.057	1.113	.000	.000	.000
600	6.165	9.377	6.521	1.714	.000	.000	.000
700	6.500	10.352	7.000	2.347	.000	.000	.000
800	4.345	30.124	.837	23.430	.000	.000	.000
900	4.376	30.638	4.120	23.866	.000	.000	.000
1000	4.400	31.100	6.795	24.305	.000	.000	.000
1100	4.419	31.520	9.024	24.746	.000	.000	.000
1200	4.434	31.905	10.915	25.189	.000	.000	.000
1300	4.447	32.261	12.543	25.633	.000	.000	.000
1400	4.457	32.591	13.964	26.078	.000	.000	.000
1500	4.467	32.899	15.216	26.524	.000	.000	.000
1600	4.475	33.187	16.330	26.971	.000	.000	.000
1700	4.482	33.459	17.330	27.419	.000	.000	.000
1800	4.488	33.715	18.233	27.867	.000	.000	.000
1900	4.494	33.958	19.054	28.316	.000	.000	.000
2000	4.499	34.188	19.805	28.766	.000	.000	.000
2100	4.504	34.408	20.496	29.216	.000	.000	.000
2200	4.509	34.618	21.133	29.667	.000	.000	.000
2300	4.513	34.818	21.723	30.118	.000	.000	.000
2400	4.518	35.010	22.273	30.570	.000	.000	.000
2500	4.522	35.195	22.786	31.021	.000	.000	.000
2600	4.526	35.372	23.267	31.474	.000	.000	.000
2700	4.529	35.543	23.718	31.927	.000	.000	.000
2800	4.533	35.708	24.144	32.380	.000	.000	.000
2900	4.537	35.867	24.545	32.833	.000	.000	.000
3000	4.540	36.021	24.925	33.287	.000	.000	.000
3100	4.544	36.170	25.286	33.741	.000	.000	.000
3200	4.547	36.314	25.628	34.196	.000	.000	.000
3300	4.550	36.454	25.954	34.650	.000	.000	.000
3400	4.553	36.590	26.265	35.106	.000	.000	.000
3500	4.557	36.722	26.562	35.561	.000	.000	.000
3600	4.560	36.850	26.846	36.017	.000	.000	.000
3700	4.563	36.975	27.118	36.473	.000	.000	.000
3800	4.566	37.097	27.379	36.929	.000	.000	.000
3900	4.569	37.215	27.629	37.386	.000	.000	.000
4000	4.572	37.331	27.871	37.843	.000	.000	.000
4100	4.575	37.444	28.103	38.300	.000	.000	.000
4200	4.578	37.555	28.326	38.758	.000	.000	.000
4300	4.581	37.662	28.542	39.216	.000	.000	.000
4400	4.584	37.768	28.751	39.674	.000	.000	.000
4500	4.587	37.871	28.952	40.133	.000	.000	.000
4600	4.589	37.971	29.147	40.591	.000	.000	.000
4700	4.592	38.070	29.336	41.050	.000	.000	.000
4800	4.595	38.167	29.519	41.510	.000	.000	.000
4900	4.598	38.262	29.697	41.969	.000	.000	.000
5000	4.601	38.355	29.869	42.429	.000	.000	.000
5100	4.604	38.446	30.036	42.890	.000	.000	.000
5200	4.607	38.535	30.199	43.350	.000	.000	.000
5300	4.609	38.623	30.357	43.811	.000	.000	.000
5400	4.612	38.709	30.511	44.272	.000	.000	.000
5500	4.615	38.794	30.660	44.733	.000	.000	.000
5600	4.618	38.877	30.806	45.195	.000	.000	.000
5700	4.621	38.959	30.949	45.657	.000	.000	.000
5800	4.623	39.039	31.088	46.119	.000	.000	.000
5900	4.626	39.118	31.223	46.581	.000	.000	.000
6000	4.629	39.196	31.355	47.044	.000	.000	.000

June 30, 1961

PHOSPHORUS (P) (REFERENCE STATE) AT. WT. = 30.975

The selected reference states are:

0 to 704°K. Solid Phosphorus (Red,V)

704 to 6000°K. Ideal Diatomic Gas

For details see Phosphorus (Red,V) and P_2 (Ideal Gas).

P

Phosphorus, Red, V, (P)
(Crystal) At. Wt. = 30.975

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-.862	.000	.000	INFINITE
100	2.085	1.494	9.204	-.771	.000	.000	.000
200	4.074	3.619	5.884	-.453	.000	.000	.000
298	5.069	5.450	5.450	.000	.000	.000	.000
300	5.079	5.481	5.450	.009	.000	.000	.000
400	5.540	7.009	5.655	.542	.000	.000	.000
500	5.852	8.282	6.057	1.112	.000	.000	.000
600	6.165	9.376	6.521	1.713	.000	.000	.000
700	6.500	10.351	7.000	2.346	.000	.000	.000
800	6.840	11.241	7.475	3.013	-20.417	-5.311	1.451
900	7.180	12.067	7.940	3.714	-20.152	-3.438	.835
1000	7.520	12.841	8.392	4.449	-19.856	-1.597	.349
1100	7.860	13.573	8.830	5.218	-19.528	.213	-.042
1200	8.200	14.272	9.254	6.021	-19.168	1.992	-.363
1300	8.540	14.942	9.666	6.858	-18.775	3.740	-.629
1400	8.880	15.587	10.066	7.729	-18.349	5.457	-.852
1500	9.220	16.211	10.455	8.634	-17.890	7.142	-1.041
1600	9.560	16.817	10.834	9.573	-17.398	8.794	-1.201
1700	9.900	17.407	11.203	10.546	-16.873	10.416	-1.339
1800	10.240	17.982	11.564	11.553	-16.314	12.005	-1.458
1900	10.580	18.545	11.917	12.594	-15.722	13.563	-1.560
2000	10.920	19.096	12.262	13.669	-15.097	15.086	-1.648

June 30, 1961

PHOSPHORUS, RED, V, (P) (CRYSTAL) AT. WT. = 30.975

ΔH_{f0}° = 0 kcal. mole^{-1}

ΔH_s 298.15 = 7.69 ± 0.1 kcal. mole^{-1}

T_m = 870°K

ΔH_f° 298.15 = 0 kcal. mole^{-1}

$S^\circ_{298.15}$ = 5.45 ± 0.02 cal. deg.$^{-1}$ mole^{-1}

ΔH_m = 4.5 ± 0.2 kcal. mole^{-1}

Heat of Formation

Zero by definition below 704°K. See P_2(g) sheet for details above 704°K.

Heat Capacity and Extrapolation

The only reliable low temperature measurements, 15 to 305°K, are reported by R. L. Potter, Dissertation, Massachusetts Institute of Technology (1946). A value at 10°K was obtained by graphical extrapolation and a T^3 function was assumed from 0 to 10°K. High temperature heat capacities were obtained from a smooth curve joining the measurements of O. Kubashewski and G. Schrag, Z. Elektrochem. 46, 675 (1940), in the range 573 to 773°K and that of V. Regnault, Ann. chim. phys. 9, 322 (1843) at 331°K with those of Potter. Measurements of A. Wigand, Ann. Physik, 22, 64 (1907), are too high. The uncertainty in the high temperature heat capacity is about 2%.

Melting

The values of ΔH_m and T_m were calculated from the functions of the solid and liquid. This may be compared with a reported triple point of 862.7°K by A. Smits and S. C. Bokhorst, Verslag. Akad. Wetenschap. 23, 930 (1914).

Heat of Sublimation

Vapor pressure measurements on the triclinic allotrope, T. V. A. designation V, are reported by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950). These data lead to a sublimation point of 704°K and ΔH_s 298.15 of 30.77 ± 0.4 kcal. mole^{-1} of P_4. A. Smits and S. C. Bokhorst, Z. phys. Chem. 91, 248 (1916), measured the vapor pressure of a sample whose preparation indicates that it was probably P, V. These results lead to ΔH_s 298.15 = 30.6 ± 1 kcal. An unpublished value of 30.84 kcal. mole^{-1} of P_4 by C. C. Stephenson is quoted by J. S. Kane, Thesis Univ. of California (1955).

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), show that the vapor density measurements of A. Stock, G. E. Gibson and E. Stamm, Ber. 45, 3527 (1912) are best explained by a vapor essentially composed of only P_4(g) below 800°K. This conclusion is supported by recent mass spectrometer measurements of J. S. Kane and J. H. Reynolds, J. Chem. Phys. 25, 342 (1956).

Phosphorus, White (P)
(Crystal) At. Wt. = 30.975

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0	.000	.000	INFINITE	-1.281	3.754	3.754	INFINITE
100	3.281	4.277	14.967	-1.069	3.875	3.597	-7.860
200	5.041	7.678	10.318	-.528	4.098	3.286	-3.591
298	5.698	9.818	9.818	.000	4.173	2.871	-2.104
300	5.705	9.853	9.818	.011	4.175	2.863	-2.085
400	6.050	11.543	10.046	.599	4.230	2.417	-1.320
500	6.330	12.925	10.488	1.218	4.278	1.958	-.856
600	6.330	14.079	10.993	1.851	4.310	1.489	-.542
700	6.330	15.054	11.505	2.484	4.310	1.019	-.318
800	6.330	15.900	12.003	3.117	-16.140	-4.760	1.300
900	6.330	16.645	12.478	3.750	-15.943	-3.349	.813
1000	6.330	17.312	12.929	4.383	-15.749	-1.961	.429
1100	6.330	17.916	13.355	5.016	-15.557	-.592	.118
1200	6.330	18.466	13.759	5.649	-15.367	.760	-.138
1300	6.330	18.973	14.140	6.282	-15.178	2.097	-.352
1400	6.330	19.442	14.503	6.915	-14.990	3.419	-.534
1500	6.330	19.879	14.847	7.548	-14.803	4.728	-.689

June 30, 1961

PHOSPHORUS, WHITE (P) (CRYSTAL) AT. WT. = 30.975

$\Delta H_f^\circ = 3.75 \pm 0.2$ kcal. mole^{-1}

ΔH_s $_{298.15} = 3.52 \pm 0.05$ kcal. mole^{-1}

$T_t = 195.4 \pm 0.1$°K (white $\beta \rightarrow$ white α)

$T_m = 317.30 \pm 0.05$°K

ΔH_f° $_{298.15} = 4.17 \pm 0.2$ kcal. mole^{-1}

$S^\circ_{298.15} = 9.82 \pm 0.02$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_t = 124.62 \pm 0.2$ cal. mole^{-1}

$\Delta H_m = 157.43 \pm 0.5$ cal. mole^{-1}

Heat Capacity and Extrapolation

Low temperature measurements, 15-315°K, were made by R. T. Maples, Dissertation, Massachusetts Institute of Technology (1949). A Debye θ temperature of 124 was used to extrapolate to 0°K. F. E. Young and J. H. Hildenbrand, J. Am. Chem. Soc. 64, 839 (1942), obtained heat capacities from enthalpy measurements that are 4% higher than those from the low temperature calorimeter which are preferred because of the proximity to the melting point.

Transition

Observed by Maples.

Melting

The selected heat of fusion is that observed by Maples. Young and Hildenbrand obtain 125 cal. mole^{-1} for the same quantity. Maples' value is consistent with vapor pressures and other thermochemical data; see P(liq) and P_4(g) sheets.

Heat of Sublimation

The vapor pressure measurements of F. S. Dainton and H. M. Kimberly, Trans. Faraday Soc. 46, 912 (1950), are the most precise and lead to ΔH_s $_{298.15} = 14.08 \pm 0.2$ kcal. mole^{-1} of P_4. Measurements of A. Jolibois, Compt. rend. 149, 287 (1908), A. Smits and S. C. Bokhorst, Z. Phys. Chem. 91, 248 (1916), and M. Centzwer, Z. phys. Chem. 85, 99 (1913) lead to values that agree within the assigned uncertainty.

Heat of Formation

The heat of formation is obtained from the heats of sublimation represented by reaction I and II at 298.15°K. See P, V sheet for details.

(I) $4P_\alpha(c) = P_4(g)$ 14.08 kcal.

(II) $4P_V(c) = P_4(g)$ 30.771 kcal.

Of the calorimetric determinations only those of H. Giran, Ann Chim. Phys. 30, 203 (1903) result in a reliable value for the heat of formation, 4.4 ± 0.4 kcal. mole^{-1}. A comprehensive review is given by H. J. Rodewald, Helv. Chim. Acta 43, 878 (1960).

Phosphorus (P)

(Liquid) At. Wt. = 30.975

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	6.292	10.249	10.249	.000	4.322	2.891	-2.119
300	6.292	10.288	10.249	.012	4.325	2.883	-2.100
400	6.292	12.098	10.496	.641	4.421	2.386	-1.304
500	6.292	13.502	10.962	1.270	4.479	1.870	-.817
600	6.292	14.649	11.484	1.899	4.507	1.344	-.489
700	6.292	15.619	12.007	2.528	4.503	.816	-.255
800	6.292	16.459	12.512	3.158	-15.950	-5.019	1.371
900	6.292	17.200	12.993	3.787	-15.757	-3.663	.890
1000	6.292	17.863	13.447	4.416	-15.567	-2.330	.509
1100	6.292	18.463	13.876	5.045	-15.379	-1.016	.202
1200	6.292	19.010	14.282	5.674	-15.193	.281	-.051
1300	6.292	19.514	14.665	6.304	-15.007	1.564	-.263
1400	6.292	19.980	15.028	6.933	-14.823	2.832	-.442
1500	6.292	20.414	15.373	7.562	-14.640	4.087	-.595
1600	6.292	20.821	15.701	8.191	-14.458	5.329	-.728
1700	6.292	21.202	16.014	8.820	-14.277	6.560	-.843
1800	6.292	21.562	16.312	9.450	-14.095	7.781	-.945
1900	6.292	21.902	16.597	10.079	-13.915	8.992	-1.034
2000	6.292	22.225	16.871	10.708	-13.736	10.191	-1.114
2100	6.292	22.532	17.133	11.337	-13.557	11.384	-1.185
2200	6.292	22.824	17.385	11.966	-13.379	12.568	-1.248
2300	6.292	23.104	17.628	12.596	-13.200	13.742	-1.306
2400	6.292	23.372	17.861	13.225	-13.023	14.909	-1.358
2500	6.292	23.629	18.087	13.854	-12.845	16.071	-1.405
2600	6.292	23.875	18.305	14.483	-12.669	17.223	-1.448
2700	6.292	24.113	18.516	15.112	-12.493	18.369	-1.487
2800	6.292	24.342	18.720	15.742	-12.316	19.509	-1.523
2900	6.292	24.562	18.917	16.371	-12.140	20.643	-1.556
3000	6.292	24.776	19.109	17.000	-11.965	21.771	-1.586

June 30, 1961

PHOSPHORUS (P) (LIQUID) AT. WT. = 30.975

$\Delta H_{f0}^\circ = 5.2 \pm 0.3$ kcal. mole^{-1}

$T_m = 317.30 \pm 0.05$°K, $P_\alpha \rightarrow P(liq)$

$T_m = 870$°K , $P_V \rightarrow P(liq)$

$T_b = 550 \pm 3$°K

$T_c = 993.8$°K

$\Delta H_f^\circ{}_{298.15} = 4.32 \pm 0.2$ kcal. mole^{-1}

$S^\circ_{298.15} = 10.25 \pm 0.03$ cal. deg.$^{-1}$ mole^{-1}

ΔH_m, $P_\alpha \rightarrow P(liq) = 157.43 \pm 0.5$ cal. mole^{-1}

ΔH_m, $P_V \rightarrow P(liq) = 4.5 \pm 0.2$ kcal. mole^{-1}

$\Delta H_{V\ 298.15} = 3.37 \pm 0.03$ kcal. mole^{-1}

$P_c = [93.3]$ atm.

Heat of Formation

Derived from the ΔH_m by the following cycle:

(I)	$P_{317.30} = P(liq)$	0.157 kcal.
(II)	$P_{\alpha\ 298.15} = P_{\alpha\ 317.30}$	0.113
(III)	$P(liq)_{317.30} = P(liq)_{298.15}$	-0.121
(IV)	$P_{V\ 298.15} = P_{\alpha\ 298.15}$	4.08

The $\Delta H_f^{\circ\prime}{}_{289.15}$ obtained from vapor pressure measurements on P_V and on the liquid is 4.32 kcal. mole^{-1} in agreement with that derived from the melting point.

Heat Capacity

F. E. Young and J. H. Hildenbrand, J. Am. Chem. Soc. 64, 839 (1942), obtained an equation from enthalpy measurements which decreased with temperature. However, a better fit to the thermochemical data realts if a constant heat capacity is assumed.

Entropy

Derived from low temperature measurements on P, White. See P, White sheet for details.

Vaporization Phenomena

D. MacRae and C. C. Van Voorhis, J. Am. Chem. Soc. 43, 547 (1921), determinations of the vapor pressure, 44 to 150°C, are the most precise and lead to a $\Delta H_{v\ 298.15}$ of 13.504 ± 0.1 kcal. mole^{-1} of P_4. A vapor pressure equation derived by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950) to fit the measurements reported in the literature leads to a value of 13.6 ± 0.1 kcal. mole^{-1} of P_4. The boiling point is calculated from the functions of P(liq) and $P_4(g)$, and may be compared with the values of 552.7 and 553.7 resulting from Farr's equation and observations of A Smits and S. C. Bokhorst, Proc. Akad. Wetenschop. 18, 106 (1915) respectively.

Critical Phenomena

T_c determined and P_c estimated by W. Marckwald and R. Helmholtz, Z. anorg. Chem. 124, 81 (1922).

Phosphorus (P)

(Ideal Gas) Mol. Wt. = 30.975

T, °K.	C_p° (cal. mole^{-1}deg.$^{-1}$)	S° (cal. mole^{-1}deg.$^{-1}$)	$-(F^\circ-H^\circ_{298})/T$ (cal. mole^{-1}deg.$^{-1}$)	$H^\circ-H^\circ_{298}$ (kcal. mole^{-1})	ΔH_f° (kcal. mole^{-1})	ΔF_f° (kcal. mole^{-1})	Log K_p
0	.000	.000	INFINITE	- 1.481	79.176	79.176	INFINITE
100	4.968	33.552	43.397	- .984	79.582	76.376	- 166.911
200	4.968	36.996	39.434	- .488	79.760	73.085	- 79.860
298	4.968	38.980	38.980	.000	79.795	69.798	- 51.161
300	4.948	39.011	38.980	.009	79.795	69.736	- 50.800
400	4.968	40.440	39.175	.506	79.759	66.388	- 36.271
500	4.968	41.548	39.543	1.003	79.685	63.052	- 27.559
600	4.968	42.454	39.955	1.500	79.581	59.734	- 21.757
700	4.968	43.220	40.368	1.996	79.444	56.437	- 17.620
800	4.968	43.883	40.767	2.493	58.858	47.851	- 13.072
900	4.968	44.469	41.146	2.990	58.919	46.472	- 11.284
1000	4.968	44.992	41.505	3.487	58.977	45.085	- 9.853
1100	4.969	45.466	41.844	3.984	59.033	43.693	- 8.681
1200	4.969	45.898	42.164	4.481	59.087	42.295	- 7.703
1300	4.971	46.296	42.467	4.978	59.140	40.894	- 6.875
1400	4.974	46.664	42.754	5.475	59.192	39.489	- 6.164
1500	4.979	47.008	43.026	5.972	59.243	38.081	- 5.548
1600	4.987	47.329	43.285	6.471	59.295	36.667	- 5.008
1700	4.999	47.632	43.532	6.970	59.346	35.252	- 4.532
1800	5.015	47.918	43.768	7.471	59.399	33.833	- 4.108
1900	5.036	48.190	43.993	7.973	59.452	32.412	- 3.728
2000	5.062	48.449	44.210	8.478	59.507	30.986	- 3.386
2100	5.094	48.696	44.417	8.986	59.565	29.559	- 3.076
2200	5.132	48.934	44.617	9.497	59.625	28.130	- 2.794
2300	5.175	49.163	44.810	10.012	59.689	26.695	- 2.537
2400	5.225	49.384	44.996	10.532	59.757	25.259	- 2.300
2500	5.279	49.599	45.176	11.057	59.831	23.822	- 2.082
2600	5.339	49.807	45.350	11.588	59.909	22.378	- 1.881
2700	5.403	50.010	45.519	12.125	59.993	20.933	- 1.694
2800	5.471	50.207	45.683	12.669	60.084	19.486	- 1.521
2900	5.542	50.401	45.842	13.220	60.182	18.034	- 1.359
3000	5.617	50.590	45.997	13.777	60.285	16.579	- 1.208
3100	5.693	50.775	46.148	14.343	60.397	15.121	- 1.066
3200	5.772	50.957	46.296	14.916	60.515	13.657	- .933
3300	5.851	51.136	46.440	15.497	60.642	12.192	- .807
3400	5.931	51.312	46.581	16.086	60.775	10.721	- .689
3500	6.011	51.485	46.718	16.683	60.917	9.247	- .577
3600	6.090	51.655	46.853	17.289	61.067	7.767	- .472
3700	6.168	51.823	46.985	17.901	61.223	6.285	- .371
3800	6.245	51.989	47.115	18.522	61.388	4.799	- .276
3900	6.320	52.152	47.242	19.150	61.559	3.309	- .185
4000	6.393	52.313	47.366	19.786	61.738	1.811	- .099
4100	6.464	52.472	47.489	20.429	61.924	.311	- .017
4200	6.532	52.628	47.609	21.079	62.116	- 1.192	.062
4300	6.597	52.783	47.728	21.735	62.314	- 2.705	.137
4400	6.659	52.935	47.845	22.398	62.519	- 4.216	.209
4500	6.718	53.085	47.959	23.067	62.729	- 5.736	.279
4600	6.773	53.234	48.072	23.742	62.946	- 7.263	.345
4700	6.825	53.380	48.184	24.421	63.166	- 8.790	.409
4800	6.874	53.524	48.294	25.106	63.391	- 10.323	.470
4900	6.919	53.666	48.402	25.796	63.622	- 11.859	.529
5000	6.961	53.806	48.508	26.490	63.856	- 13.401	.586
5100	6.999	53.945	48.614	27.188	64.093	- 14.950	.641
5200	7.034	54.081	48.718	27.890	64.335	- 16.504	.694
5300	7.065	54.215	48.820	28.595	64.579	- 18.060	.745
5400	7.094	54.348	48.921	29.303	64.826	- 19.623	.794
5500	7.119	54.476	49.021	30.013	65.075	- 21.186	.842
5600	7.141	54.606	49.120	30.726	65.326	- 22.758	.888
5700	7.160	54.733	49.217	31.442	65.580	- 24.332	.933
5800	7.177	54.858	49.313	32.158	65.834	- 25.914	.976
5900	7.191	54.981	49.408	32.877	66.091	- 27.498	1.019
6000	7.202	55.101	49.502	33.597	66.348	- 29.085	1.059

June 30, 1962

PHOSPHORUS (P) (IDEAL GAS) MOL. WT. = 30.975

$\Delta H_f^\circ{}_0$ = 79.18 ± 0.05 kcal. mole^{-1}

Ground State Configuration $^4S_{3/2}$

$\Delta H_f^\circ{}_{298.15}$ = 79.8 ± 0.05 kcal. mole^{-1}

$S^\circ_{298.15}$ = 38.98 cal. mole^{-1} deg.$^{-1}$

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0	4	59,643	12
11,370	10	65,984	58
18,740	6	69,696	102
56,190	12	75,380	160
58,075	6	78,762	162
		80,835	202

Heat of Formation.

The $\Delta H_f^\circ{}_{298.15}$ was derived by the following cycle:

(1) 4 $P_{red(V)}$[298.15°] = P_4(g)[298.15°]	ΔH_r = 30.77 kcal. mole^{-1} of P_4	See $P_{red(V)}$ sheet under Heat of Sublimation.
(2) P_4(g)[298.15°] = 2P_2(g)[298.15°]	ΔH_r = 54.59 kcal. mole^{-1} of P_4	See P_2(g) sheet under Heat of Formation.
(3) 2P_2(g)[298.15°] = 2P_2(g)[0°]	ΔH_r = 2(-2.128) kcal. mole^{-1} of P_4	See P_2(g) table.
(4) 2P_2(g)[0°] = 4P(g)[0°]	ΔH_r = 2(116.075) kcal. mole^{-1}of P_4	A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, 1953.
(5) 4 P(g)[0°] = 4 P(g)[298.15°]	ΔH_r = 4(1.481) kcal. mole^{-1} of P_4	See P(g) table.

D_0° for reaction (4) was given by A. G. Gaydon (loc. cit.). He reported a predissociation limit at 51,958 ± 9 cm.$^{-1}$ He considered the dissociation to be $P_2 \rightarrow P(^4S) + P(^2D)$. From the predissociation limit and the energy level of the excited $P(^2D)$ state [11,360.8 cm.$^{-1}$] Gaydon (loc. cit.) obtained a D_0° = 5.033 e.v. or 116.075 kcal. mole^{-1}. As a check, a graphical Birge-Sponer extrapolation by Gaydon (loc. cit.) [$X^1\Sigma_g^+(\nu, 4\text{-}32)$] agrees with a D_0° = 5.0 e.v.

The vapor equilibrium data of G. Preuner and I. Brockmoller, Z. physik Chem. 81, 129 (1913) gave a ΔH_r for reaction (4) which was much lower than the spectroscopic value i.e. $31.5_{(1073°K)}$ vs. $116_{(0°)}$ kcal. mole^{-1} of P_2. D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941) reported that the vapor equilibrium measurements of G. Preuner and I. Brockmoller (loc. cit.) were doubtful while the measurements of A. Stock, G. E. Gibson, and E. Stamm Ber 45, 3527 (1913) were correct. Stock et al. (loc. cit.) have shown that the reaction $P_2(g) \rightarrow 2P(g)$ is extremely slight even at 1473°K which is the highest temperature of the vapor equilibrium studies.

Heat Capacity and Entropy.

The thermodynamic functions were calculated from the electronic levels which were evaluated by averaging the spectroscopic values of W. C. Martin, J. Opt. Soc. Am. 49, 1071, (1959).

Monophosphorus Monosulfide (PS)

(Ideal Gas) GFW = 63.0378

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.297	36.918	36.918	INFINITE
100	7.362	47.280	63.209	-1.593	37.367	33.085	-72.307
200	8.114	52.654	56.720	-.813	37.436	28.753	-31.420
298	8.423	55.958	55.958	.000	37.300	24.516	-17.971
300	8.427	56.010	55.958	.016	37.297	24.437	-17.803
400	8.606	58.461	56.291	.868	36.517	20.207	-11.040
500	8.718	60.395	56.925	1.735	35.875	16.203	-7.082
600	8.793	61.991	57.640	2.610	35.292	12.324	-4.489
700	8.845	63.351	58.361	3.492	34.741	8.563	-2.673
800	8.883	64.534	59.061	4.379	.720	-1.718	.469
900	8.913	65.582	59.728	5.269	.736	-2.023	.491
1000	8.937	66.523	60.361	6.161	.748	-2.331	.509
1100	8.956	67.376	60.961	7.056	.759	-2.641	.525
1200	8.973	68.156	61.528	7.953	.769	-2.950	.537
1300	8.988	68.874	62.066	8.851	.778	-3.258	.548
1400	9.001	69.541	62.577	9.750	.785	-3.569	.557
1500	9.013	70.162	63.062	10.651	.792	-3.881	.565
1600	9.025	70.744	63.524	11.553	.799	-4.192	.573
1700	9.035	71.292	63.965	12.456	.805	-4.504	.579
1800	9.045	71.809	64.387	13.360	.811	-4.819	.585
1900	9.055	72.298	64.790	14.265	.817	-5.128	.590
2000	9.064	72.763	65.177	15.171	.822	-5.444	.595
2100	9.073	73.205	65.549	16.077	.826	-5.757	.599
2200	9.082	73.627	65.907	16.985	.831	-6.068	.603
2300	9.091	74.031	66.251	17.894	.836	-6.384	.607
2400	9.100	74.418	66.584	18.803	.840	-6.698	.610
2500	9.109	74.790	66.904	19.714	.847	-7.011	.613
2600	9.118	75.147	67.215	20.625	.851	-7.326	.616
2700	9.128	75.492	67.515	21.537	.856	-7.643	.619
2800	9.137	75.824	67.806	22.451	.862	-7.959	.621
2900	9.148	76.145	68.088	23.365	.868	-8.273	.623
3000	9.158	76.455	68.362	24.280	.873	-8.586	.625
3100	9.170	76.755	68.628	25.197	.881	-8.900	.627
3200	9.182	77.047	68.886	26.114	.886	-9.219	.630
3300	9.195	77.330	69.138	27.033	.895	-9.536	.632
3400	9.208	77.604	69.383	27.953	.902	-9.849	.633
3500	9.223	77.871	69.621	28.875	.911	-10.167	.635
3600	9.238	78.131	69.854	29.798	.921	-10.484	.636
3700	9.254	78.385	70.081	30.722	.930	-10.802	.638
3800	9.271	78.632	70.303	31.649	.943	-11.119	.639
3900	9.289	78.873	70.520	32.577	.955	-11.436	.641
4000	9.309	79.108	70.732	33.507	.969	-11.751	.642
4100	9.329	79.338	70.939	34.438	.984	-12.070	.643
4200	9.350	79.563	71.141	35.372	1.000	-12.385	.644
4300	9.372	79.784	71.340	36.308	1.018	-12.711	.646
4400	9.395	79.999	71.534	37.247	1.038	-13.025	.647
4500	9.418	80.211	71.725	38.187	1.058	-13.346	.648
4600	9.443	80.418	71.911	39.130	1.082	-13.670	.649
4700	9.469	80.621	72.095	40.076	1.108	-13.988	.650
4800	9.495	80.821	72.274	41.024	1.134	-14.312	.652
4900	9.522	81.017	72.451	41.975	1.164	-14.629	.652
5000	9.550	81.210	72.624	42.929	1.195	-14.955	.654
5100	9.578	81.399	72.794	43.885	1.227	-15.277	.655
5200	9.607	81.585	72.961	44.844	1.263	-15.600	.656
5300	9.637	81.769	73.126	45.806	1.301	-15.929	.657
5400	9.667	81.949	73.288	46.772	1.342	-16.252	.658
5500	9.698	82.127	73.447	47.740	1.385	-16.579	.659
5600	9.729	82.302	73.603	48.711	1.429	-16.905	.660
5700	9.760	82.474	73.757	49.686	1.477	-17.231	.661
5800	9.792	82.644	73.909	50.663	1.527	-17.561	.662
5900	9.823	82.812	74.059	51.644	1.581	-17.895	.663
6000	9.856	82.977	74.206	52.628	1.636	-18.218	.664

Dec. 31, 1960; June 30, 1961; June 30, 1967

MONOPHOSPHORUS MONOSULFIDE (PS) (IDEAL GAS) GFW = 63.0378

Ground State Configuration $^2\Pi$

$S^\circ_{298.15}$ = 56 ± 0.2 gibbs/mol

ΔHf°_0 = 36.9 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 37.3 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1} g	g_i
0	2
324	2
[20000]	2
22000	4
34594	2

ω_e = 743.5 ± 3.8 cm^{-1} $\omega_e x_e$ = 3.8 ± 0.9 cm^{-1} σ = 1

B_e = [0.29] cm^{-1} α_e = [0.0016] cm^{-1} r_e = [1.92] Å

Heat of Formation

The dissociation energy (D°_0) of PS(g) is estimated to be 140 ± 25 kcal/mol by comparison with the corresponding quantity for PO(g) and from a linear Birge-Sponer extrapolation of the third excited ($C^2\Sigma$) electronic state potential function. It is assumed that the $C^2\Sigma$ state dissociates to S(g) in its ground (^3P) state and P(g) in its first excited (^2D) state. The fundamental vibrational frequency in the $C^2\Sigma$ state (ω_e') is 531.8 ± 2.5 cm^{-1} and the corresponding anharmonic term ($\omega_e x_e'$) is 2.6 ± 0.5 cm^{-1}. These constants are calculated from a reanalysis of the spectral data of Dressler (1). The corresponding heat of formation of PS(g) is 37.3 ± 25 kcal/mol. The excited state ($C^2\Sigma$) data are used to calculate D°_0 instead of the ground state($X^2\Pi$) data because the vibrational constants of the upper level are known more accurately and because the extrapolation is 50 kcal/mol smaller for this level.

Heat Capacity and Entropy

The spectra of PS(g) have been studied by Dressler (1) in the near UV and visible regions. He reported the above electronic levels which correspond to the doublet pi ground state and two of the excited levels ($B^2\Pi$, $C^2\Sigma$). The level of the first excited electronic state ($A^2\Sigma$) is estimated by analogy with NO(g).

Dressler (1) estimated the value of the rotational constant B_e. The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The fundamental vibrational frequency ω_e and the anharmonic vibrational term $\omega_e x_e$ are calculated from a reanalysis of the spectral data reported by Dressler (1).

References

1. K. Dressler, Helv. Phys. Acta 28, 563 (1955).

Phosphorus, Diatomic (P_2)
(Ideal Gas) Mol. Wt. = 61.950

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.128	42.276	42.276	INFINITE
100	6.960	44.279	58.608	-1.433	42.789	38.660	-84.487
200	7.195	49.151	52.795	-.729	42.857	34.475	-37.670
298	7.657	52.110	52.110	.000	42.680	30.393	-22.278
300	7.665	52.157	52.110	.014	42.676	30.318	-22.085
400	8.050	54.418	52.415	.801	42.397	26.239	-14.335
500	8.311	56.244	53.004	1.620	42.074	22.235	-9.718
600	8.485	57.776	53.675	2.460	41.712	18.299	-6.665
700	8.604	59.093	54.357	3.315	41.301	14.429	-4.505
800	8.690	60.248	55.023	4.180	.000	.000	.000
900	8.752	61.275	55.662	5.052	.000	.000	.000
1000	8.800	62.200	56.270	5.930	.000	.000	.000
1100	8.838	63.041	56.848	6.812	.000	.000	.000
1200	8.868	63.811	57.397	7.697	.000	.000	.000
1300	8.893	64.522	57.918	8.585	.000	.000	.000
1400	8.914	65.182	58.413	9.476	.000	.000	.000
1500	8.933	65.797	58.885	10.368	.000	.000	.000
1600	8.949	66.374	59.335	11.262	.000	.000	.000
1700	8.963	66.917	59.766	12.158	.000	.000	.000
1800	8.976	67.430	60.177	13.055	.000	.000	.000
1900	8.987	67.916	60.572	13.953	.000	.000	.000
2000	8.998	68.377	60.951	14.852	.000	.000	.000
2100	9.008	68.816	61.315	15.752	.000	.000	.000
2200	9.018	69.235	61.665	16.654	.000	.000	.000
2300	9.026	69.636	62.003	17.556	.000	.000	.000
2400	9.035	70.021	62.329	18.459	.000	.000	.000
2500	9.043	70.390	62.645	19.363	.000	.000	.000
2600	9.051	70.745	62.949	20.268	.000	.000	.000
2700	9.058	71.086	63.244	21.173	.000	.000	.000
2800	9.066	71.416	63.530	22.079	.000	.000	.000
2900	9.073	71.734	63.808	22.986	.000	.000	.000
3000	9.080	72.042	64.077	23.894	.000	.000	.000
3100	9.087	72.340	64.339	24.802	.000	.000	.000
3200	9.093	72.628	64.593	25.711	.000	.000	.000
3300	9.100	72.908	64.841	26.621	.000	.000	.000
3400	9.106	73.180	65.083	27.531	.000	.000	.000
3500	9.113	73.444	65.318	28.442	.000	.000	.000
3600	9.119	73.701	65.547	29.354	.000	.000	.000
3700	9.125	73.951	65.771	30.266	.000	.000	.000
3800	9.131	74.194	65.989	31.179	.000	.000	.000
3900	9.137	74.431	66.203	32.092	.000	.000	.000
4000	9.143	74.663	66.411	33.006	.000	.000	.000
4100	9.149	74.889	66.615	33.921	.000	.000	.000
4200	9.155	75.109	66.815	34.836	.000	.000	.000
4300	9.161	75.325	67.010	35.752	.000	.000	.000
4400	9.167	75.535	67.202	36.668	.000	.000	.000
4500	9.173	75.741	67.389	37.585	.000	.000	.000
4600	9.178	75.943	67.573	38.503	.000	.000	.000
4700	9.184	76.141	67.753	39.421	.000	.000	.000
4800	9.190	76.334	67.930	40.340	.000	.000	.000
4900	9.196	76.524	68.103	41.259	.000	.000	.000
5000	9.201	76.709	68.274	42.179	.000	.000	.000
5100	9.207	76.892	68.441	43.099	.000	.000	.000
5200	9.213	77.070	68.605	44.020	.000	.000	.000
5300	9.218	77.246	68.766	44.942	.000	.000	.000
5400	9.224	77.418	68.925	45.864	.000	.000	.000
5500	9.229	77.588	69.081	46.786	.000	.000	.000
5600	9.235	77.754	69.234	47.710	.000	.000	.000
5700	9.241	77.918	69.385	48.633	.000	.000	.000
5800	9.246	78.078	69.534	49.558	.000	.000	.000
5900	9.252	78.236	69.680	50.483	.000	.000	.000
6000	9.257	78.392	69.824	51.408	.000	.000	.000

June 30, 1961

PHOSPHORUS, DIATOMIC (P_2) (IDEAL GAS) MOL. WT. = 61.950

D_0° = 116 ± 1 kcal. mole^{-1}

Ground State Configuration $^1\Sigma^+$

ΔH_f° 298.15 = 42.68 ± 0.5 kcal. mole^{-1}

S°_{298} = 52.11 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

ω_e = 780.43 cm.$^{-1}$

B_e = 0.30327 cm.$^{-1}$

$\omega_e x_e$ = 2.804 cm.$^{-1}$

α_e = 0.00142 cm.$^{-1}$

D_e = 0.21 X 10^{-6} cm.$^{-1}$

r_e = 1.8943 Å

Heat of Formation

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), have shown that the vapor density measurements of A Stock, G. E. Gibson and E. Stamm, Ber. 45, 3527 (1912), best fit a vapor composed of P_2 and P_4 molecular specie. From these data T. D. Farr, Tennessee Valley Authority, Chemical Engineering Report No. 8, calculated the equilibrium constants which lead to a ΔH_r for I. From which ΔH_f° of P_2 is obtained based upon a ΔH_f° 298.15 of 30.77 kcal. mole^{-1} of $P_4(g)$.

(I) $P_4(g)_{298.15} = P_2(g)_{298.15}$ ΔH_r = 54.59 ± 0.1 kcal. mole^{-1}

Heat Capacity and Entropy

Molecular and spectroscopic constants are those listed by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co. Inc., New York, 1945. More recent measurements of K. Dressler, Helv. Phys. Acta 28, 563 (1955) are in agreement with the values selected by Herzberg.

The dissociation energy is given by A. G. Gaydon, "Dissociation Energies", Chapman and Hall, Ltd., London, 1953.

Phosphorus, Tetratomic (P_4)
(Ideal Gas) Mol. Wt. = 123.90

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			Log K_p
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	
0	.000	.000	INFINITE	-3.378	30.841	30.841	INFINITE
100	8.899	53.486	79.150	-2.566	31.289	26.538	-57.995
200	13.294	61.010	68.285	-1.455	31.128	21.821	-23.844
298	16.051	66.893	66.893	.000	30.771	17.327	-12.700
300	16.088	66.992	66.893	.030	30.765	17.244	-12.562
400	17.510	71.837	67.544	1.717	30.320	12.803	-6.995
500	18.281	75.835	68.814	3.510	29.829	8.478	-3.706
600	18.735	79.212	70.273	5.363	29.278	4.256	-1.550
700	19.022	82.123	71.763	7.252	28.635	.135	-.042
800	19.214	84.676	73.221	9.164	-53.785	-25.129	6.865
900	19.346	86.947	74.622	11.093	-53.600	-21.556	5.234
1000	19.445	88.991	75.958	13.033	-53.416	-18.007	3.935
1100	19.518	90.848	77.229	14.981	-53.232	-14.477	2.876
1200	19.574	92.549	78.436	16.936	-53.049	-10.964	1.997
1300	19.617	94.117	79.582	18.895	-52.866	-7.461	1.254
1400	19.652	95.572	80.673	20.859	-52.682	-3.974	.620
1500	19.680	96.929	81.712	22.826	-52.499	-.499	.073
1600	19.703	98.200	82.703	24.795	-52.318	2.958	-.404
1700	19.722	99.395	83.651	26.766	-52.139	6.410	-.824
1800	19.738	100.523	84.557	28.739	-51.958	9.849	-1.196
1900	19.752	101.591	85.426	30.714	-51.779	13.279	-1.527
2000	19.764	102.604	86.259	32.689	-51.604	16.692	-1.824
2100	19.774	103.569	87.061	34.666	-51.427	20.106	-2.092
2200	19.783	104.489	87.832	36.644	-51.253	23.510	-2.335
2300	19.790	105.368	88.576	38.623	-51.078	26.900	-2.556
2400	19.797	106.211	89.293	40.602	-50.907	30.284	-2.758
2500	19.803	107.019	89.986	42.582	-50.731	33.672	-2.943
2600	19.808	107.796	90.656	44.563	-50.562	37.038	-3.113
2700	19.813	108.543	91.305	46.544	-50.393	40.404	-3.270
2800	19.817	109.264	91.934	48.525	-50.224	43.767	-3.416
2900	19.821	109.959	92.543	50.507	-50.054	47.121	-3.551
3000	19.824	110.631	93.135	52.489	-49.888	50.470	-3.677
3100	19.827	111.282	93.710	54.472	-49.721	53.814	-3.794
3200	19.830	111.911	94.269	56.455	-49.558	57.146	-3.903
3300	19.832	112.521	94.813	58.438	-49.391	60.482	-4.005
3400	19.835	113.113	95.342	60.421	-49.232	63.807	-4.101
3500	19.837	113.688	95.858	62.405	-49.068	67.131	-4.192
3600	19.839	114.247	96.361	64.389	-48.908	70.442	-4.276
3700	19.841	114.791	96.852	66.373	-48.748	73.756	-4.356
3800	19.842	115.320	97.331	68.357	-48.588	77.070	-4.432
3900	19.844	115.835	97.799	70.341	-48.432	80.380	-4.504
4000	19.845	116.338	98.256	72.326	-48.275	83.669	-4.571
4100	19.847	116.828	98.703	74.310	-48.119	86.969	-4.636
4200	19.848	117.306	99.141	76.295	-47.966	90.272	-4.697
4300	19.849	117.773	99.569	78.280	-47.813	93.549	-4.754
4400	19.850	118.229	99.988	80.265	-47.660	96.847	-4.810
4500	19.851	118.676	100.398	82.250	-47.511	100.127	-4.863
4600	19.852	119.112	100.800	84.235	-47.358	103.394	-4.912
4700	19.853	119.539	101.194	86.220	-47.209	106.675	-4.960
4800	19.854	119.957	101.581	88.205	-47.064	109.950	-5.006
4900	19.854	120.366	101.960	90.191	-46.914	113.227	-5.050
5000	19.855	120.767	102.332	92.176	-46.769	116.495	-5.092
5100	19.856	121.160	102.697	94.162	-46.627	119.753	-5.132
5200	19.856	121.546	103.056	96.147	-46.482	123.007	-5.170
5300	19.857	121.924	103.409	98.133	-46.340	126.269	-5.207
5400	19.858	122.295	103.755	100.119	-46.198	129.521	-5.242
5500	19.858	122.660	104.095	102.105	-46.056	132.782	-5.276
5600	19.859	123.018	104.430	104.091	-45.918	136.027	-5.308
5700	19.859	123.369	104.759	106.076	-45.781	139.280	-5.340
5800	19.860	123.715	105.083	108.062	-45.643	142.518	-5.370
5900	19.860	124.054	105.402	110.048	-45.505	145.761	-5.399
6000	19.860	124.388	105.715	112.034	-45.371	149.006	-5.427

June 30, 1961

PHOSPHORUS, TETRATOMIC (P_4) (IDEAL GAS) MOL. WT. = 123.90

ΔH°_{f0} = 30.84 ± 0.5 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 30.77 ± 0.5 kcal. mole^{-1}

Point Group T_d

$S^\circ_{298.15}$ = 66.89 ± 0.1 cal. deg.$^{-1}$ mole^{-1}

Vibrational Levels and Multiplicities

ω, cm.$^{-1}$	
606	(1)
363	(2)
464.5	(3)

Bond Lengths and Angles P-P = 2.21 ± 0.2 Å ∢P-P-P = 109°.28'

Moments of Inertia $I_A = I_B = I_C = 25.1 \times 10^{-39}$ g. cm.^{2} σ = 12

Heat of Formation

Taken as the heat of sublimation of P (Red,V).

Heat Capacity and Entropy

The frequency and multiplicities are those assigned by H. S. Gutowsky and G. S. Hoffman, J. Am. Chem. Soc. 72, 5751 (1950). Molecular parameters of the gas were determined from electron diffraction measurements by L. R. Maxwell, S. B. Hendricks and V. M. Moseley, J. Chem. Phys. 3, 699 (1935). C. D. Thomas and N. S. Gingrich, J. Chem. Phys. 6, 659 (1938) obtained a P-P distance of 2.25 Å from x-ray studies on the liquid. On the basis of the selected values for P, White (see sheet) a third law entropy of 66.89 cal. deg.$^{-1}$ mole^{-1} is derived for P_4(g) at 298.15°K.

Tetraphosphorus Trisulfide (P_4S_3)

(Solid) Mol. Wt. = 220.098

INTERIM TABLE

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	35.000	48.000	48.000	.000	-37.000	-37.986	27.843
300	35.000	48.217	48.001	.065	-37.001	-37.991	27.675
400	35.000	58.285	49.374	3.565	-38.930	-38.218	20.880
500	35.000	66.095	51.966	7.065	-40.528	-37.858	16.547
600	35.000	72.477	54.869	10.565	-42.003	-37.185	13.544
700	35.000	77.872	57.779	14.065	-43.435	-36.198	11.301
800	35.000	82.546	60.590	17.565	-166.042	-60.411	16.503
900	35.000	86.668	63.263	21.065	-165.604	-47.235	11.470
1000	35.000	90.356	65.791	24.565	-165.183	-34.103	7.453
1100	35.000	93.691	68.178	28.065	-164.776	-21.016	4.175
1200	35.000	96.737	70.433	31.565	-164.380	-7.964	1.450
1300	35.000	99.538	72.565	35.065	-163.991	5.056	-.850
1400	35.000	102.132	74.586	38.565	-163.612	18.046	-2.817
1500	35.000	104.547	76.504	42.065	-163.240	31.006	-4.517
1600	35.000	106.806	78.328	45.565	-162.876	43.947	-6.003
1700	35.000	108.926	80.066	49.065	-162.511	56.861	-7.310
1800	35.000	110.928	81.725	52.565	-162.157	69.756	-8.469
1900	35.000	112.820	83.313	56.065	-161.803	82.629	-9.504
2000	35.000	114.616	84.833	59.565	-161.456	95.485	-10.434

December 31, 1960.

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (Solid)

Mol. Wt. = 220.098

ΔH_f° 298.15 = [-37] kcal. mole^{-1}

$S^\circ_{298.15}$ = [48] cal. deg.$^{-1}$ mole^{-1}

T_m = 440°K.

ΔH_m = [2.2] kcal. mole^{-1}

ΔH_f° 298.15 estimated from vapor density reported by D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth- and Sixth- Group Nonmetallic Elements", Prentice-Hall, New York (1944). T_m from Yost and Russell, loc. cit. Other data estimated.

Tetraphosphorus Trisulfide (P_4S_3

(Liquid) Mol. Wt. = 220.098 **INTERIM TABLE**

T, °K.	cal. mole^{-1}deg.$^{-1}$ C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	kcal. mole^{-1} $H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	44.000	49.510	49.510	.000	-36.077	-37.513	27.497
300	44.000	49.782	49.511	.081	-36.062	-37.521	27.332
400	44.000	62.440	51.237	4.481	-37.091	-38.040	20.783
500	44.000	72.259	54.496	8.881	-37.789	-38.200	16.696
600	44.000	80.281	58.145	13.281	-38.364	-38.228	13.924
700	44.000	87.063	61.804	17.681	-38.896	-38.092	11.892
800	44.000	92.939	65.337	22.081	-160.603	-63.286	17.288
900	44.000	98.121	68.697	26.481	-159.265	-51.204	12.433
1000	44.000	102.757	71.876	30.881	-157.944	-39.265	8.581
1100	44.000	106.951	74.877	35.281	-156.637	-27.461	5.456
1200	44.000	110.779	77.711	39.681	-155.341	-15.775	2.873
1300	44.000	114.301	80.392	44.081	-154.052	-4.195	.705
1400	44.000	117.562	82.932	48.481	-152.773	7.284	-1.137
1500	44.000	120.597	85.343	52.881	-151.501	18.669	-2.720
1600	44.000	123.437	87.636	57.281	-150.237	29.976	-4.094
1700	44.000	126.105	89.821	61.681	-148.972	41.200	-5.296
1800	44.000	128.620	91.908	66.081	-147.718	52.352	-6.356
1900	44.000	130.998	93.903	70.481	-146.464	63.430	-7.296
2000	44.000	133.255	95.815	74.881	-145.217	74.445	-8.135
2100	44.000	135.402	97.649	79.281	-143.973	85.398	-8.887
2200	44.000	137.449	99.412	83.681	-142.733	96.289	-9.565
2300	44.000	139.405	101.109	88.081	-141.496	107.128	-10.179
2400	44.000	141.277	102.743	92.481	-140.259	117.913	-10.737
2500	44.000	143.074	104.321	96.881	-139.026	128.651	-11.246
2600	44.000	144.799	105.845	101.281	-137.800	139.326	-11.711
2700	44.000	146.460	107.319	105.681	-136.570	149.963	-12.138
2800	44.000	148.060	108.745	110.081	-135.347	160.552	-12.531
2900	44.000	149.604	110.128	114.481	-134.128	171.098	-12.894
3000	44.000	151.096	111.468	118.881	-132.912	181.607	-13.229

December 31, 1960.

P_4S_3

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (Liquid)

Mol. Wt. = 220.098

ΔH_f° 298.15 = [-36.077] kcal. mole^{-1}

$S^\circ_{298.15}$ = [49.510] cal. deg.$^{-1}$ mole^{-1}

T_m = 440°K.

ΔH_m = [2.2] kcal. mole^{-1}

T_b = 680°K.

ΔH_v 680 = [14.3] kcal. mole^{-1}

T_m and T_b from D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth- and Sixth- Group Nonmetallic Elements", Prentice-Hall, New York (1944). Other data estimated.

P_4S_3

Tetraphosphorus Trisulfide (P_4S_3
(Ideal Gas) Mol. Wt. = 220.098 INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	37.000	76.280	76.280	.000	-19.408	-28.826	21.129
300	37.000	76.509	76.281	.068	-19.406	-28.883	21.040
400	37.000	87.153	77.732	3.768	-21.135	-31.969	17.466
500	37.000	95.409	80.473	7.468	-22.533	-34.519	15.088
600	37.000	102.155	83.541	11.168	-23.808	-36.797	13.402
700	37.000	107.859	86.618	14.868	-25.040	-38.793	12.111
800	37.000	112.800	89.589	18.568	-147.447	-66.018	18.034
900	37.000	117.158	92.415	22.268	-146.809	-55.880	13.569
1000	37.000	121.056	95.087	25.968	-146.188	-45.807	10.011
1100	37.000	124.582	97.611	29.668	-145.581	-35.800	7.112
1200	37.000	127.802	99.995	33.368	-144.985	-25.846	4.707
1300	37.000	130.763	102.249	37.068	-144.396	-15.940	2.680
1400	37.000	133.505	104.385	40.768	-143.817	-6.081	.949
1500	37.000	136.058	106.412	44.468	-143.245	3.734	-.544
1600	37.000	138.446	108.341	48.168	-142.681	13.518	-1.846
1700	37.000	140.689	110.178	51.868	-142.116	23.262	-2.990
1800	37.000	142.804	111.933	55.568	-141.562	32.976	-4.004
1900	37.000	144.804	113.610	59.268	-141.008	42.655	-4.906
2000	37.000	146.702	115.218	62.968	-140.461	52.307	-5.716
2100	37.000	148.507	116.761	66.668	-139.917	61.933	-6.445
2200	37.000	150.229	118.243	70.368	-139.377	71.529	-7.105
2300	37.000	151.873	119.670	74.068	-138.840	81.106	-7.706
2400	37.000	153.448	121.044	77.768	-138.303	90.660	-8.255
2500	37.000	154.958	122.371	81.468	-137.770	100.194	-8.759
2600	37.000	156.410	123.652	85.168	-137.244	109.695	-9.220
2700	37.000	157.806	124.892	88.868	-136.714	119.185	-9.647
2800	37.000	159.152	126.091	92.568	-136.191	128.652	-10.041
2900	37.000	160.450	127.254	96.268	-135.672	138.100	-10.407
3000	37.000	161.704	128.381	99.968	-135.156	147.537	-10.748
3100	37.000	162.917	129.476	103.668	-134.637	156.951	-11.065
3200	37.000	164.092	130.540	107.368	-134.128	166.342	-11.360
3300	37.000	165.231	131.574	111.068	-133.612	175.725	-11.637
3400	37.000	166.335	132.580	114.768	-133.107	185.095	-11.897
3500	37.000	167.408	133.560	118.468	-132.601	194.440	-12.141
3600	37.000	168.450	134.514	122.168	-132.096	203.773	-12.370
3700	37.000	169.464	135.445	125.868	-131.597	213.100	-12.587
3800	37.000	170.451	136.354	129.568	-131.095	222.414	-12.791
3900	37.000	171.412	137.240	133.268	-130.600	231.696	-12.983
4000	37.000	172.348	138.106	136.968	-130.105	240.994	-13.167
4100	37.000	173.262	138.953	140.668	-129.614	250.260	-13.339
4200	37.000	174.154	139.780	144.368	-129.122	259.519	-13.504
4300	37.000	175.024	140.590	148.068	-128.634	268.767	-13.660
4400	37.000	175.875	141.382	151.768	-128.149	278.016	-13.809
4500	37.000	176.706	142.158	155.468	-127.656	287.239	-13.950
4600	37.000	177.519	142.918	159.168	-127.159	296.449	-14.084
4700	37.000	178.315	143.662	162.868	-126.678	305.656	-14.212
4800	37.000	179.094	144.392	166.568	-126.204	314.829	-14.334
4900	37.000	179.857	145.108	170.268	-125.726	324.030	-14.452
5000	37.000	180.605	145.811	173.968	-125.255	333.198	-14.563
5100	37.000	181.337	146.500	177.668	-124.784	342.365	-14.671
5200	37.000	182.056	147.177	181.368	-124.317	351.532	-14.774
5300	37.000	182.760	147.842	185.068	-123.850	360.658	-14.871
5400	37.000	183.452	148.495	188.768	-123.386	369.818	-14.967
5500	37.000	184.131	149.137	192.468	-122.922	378.931	-15.057
5600	37.000	184.798	149.768	196.168	-122.465	388.050	-15.144
5700	37.000	185.453	150.388	199.868	-122.008	397.162	-15.227
5800	37.000	186.096	150.998	203.568	-121.551	406.284	-15.308
5900	37.000	186.729	151.598	207.268	-121.094	415.373	-15.386
6000	37.000	187.350	152.189	210.968	-120.644	424.454	-15.460

December 31, 1960.

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (Ideal Gas)

Mol. Wt. = 220.098

$\Delta H_f^\circ{}_{298.15}$ = [-19.408] kcal. mole^{-1}

$S^\circ_{298.15}$ = [76.280] cal. deg.$^{-1}$ mole^{-1}

C_p = [37] cal. deg.$^{-1}$ mole^{-1}

All data estimated.

Lead (Pb)

(Reference State) At. Wt. = 207.21

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	$\log K_p$
0	.000	.000	INFINITE	- 1.644	.000	.000	.000
100	5.838	8.803	21.013	- 1.221	.000	.000	.000
200	6.183	12.972	16.062	- .618	.000	.000	.000
298	6.414	15.484	15.484	.000	.000	.000	.000
300	6.418	15.524	15.484	.012	.000	.000	.000
400	6.626	17.399	15.738	.664	.000	.000	.000
500	6.823	18.898	16.225	1.337	.000	.000	.000
600	7.028	20.157	16.776	2.027	.000	.000	.000
700	7.250	23.180	17.613	3.897	.000	.000	.000
800	7.174	24.143	18.371	4.618	.000	.000	.000
900	7.098	24.984	19.060	5.332	.000	.000	.000
1000	7.026	25.728	19.690	6.038	.000	.000	.000
1100	6.953	26.394	20.270	6.737	.000	.000	.000
1200	6.880	26.996	20.806	7.428	.000	.000	.000
1300	6.848	27.545	21.303	8.114	.000	.000	.000
1400	6.841	28.052	21.767	8.799	.000	.000	.000
1500	6.853	28.525	22.202	9.483	.000	.000	.000
1600	6.880	28.968	22.612	10.170	.000	.000	.000
1700	6.914	29.386	22.998	10.859	.000	.000	.000
1800	6.957	29.782	23.364	11.553	.000	.000	.000
1900	7.002	30.159	23.712	12.251	.000	.000	.000
2000	7.050	30.520	24.043	12.954	.000	.000	.000
2100	6.094	51.819	25.099	56.112	.000	.000	.000
2200	6.301	52.107	26.320	56.732	.000	.000	.000
2300	6.516	52.392	27.447	57.373	.000	.000	.000
2400	6.734	52.674	28.493	58.035	.000	.000	.000
2500	6.951	52.953	29.465	58.720	.000	.000	.000
2600	7.165	53.230	30.374	59.426	.000	.000	.000
2700	7.372	53.504	31.226	60.152	.000	.000	.000
2800	7.569	53.776	32.026	60.900	.000	.000	.000
2900	7.754	54.045	32.781	61.666	.000	.000	.000
3000	7.926	54.311	33.494	62.450	.000	.000	.000
3100	8.082	54.573	34.170	63.250	.000	.000	.000
3200	8.221	54.832	34.812	64.066	.000	.000	.000
3300	8.345	55.087	35.422	64.894	.000	.000	.000
3400	8.451	55.338	36.004	65.734	.000	.000	.000
3500	8.542	55.584	36.560	66.584	.000	.000	.000
3600	8.616	55.826	37.092	67.442	.000	.000	.000
3700	8.675	56.063	37.601	68.307	.000	.000	.000
3800	8.720	56.295	38.090	69.176	.000	.000	.000
3900	8.752	56.522	38.560	70.050	.000	.000	.000
4000	8.772	56.743	39.012	70.926	.000	.000	.000
4100	8.781	56.960	39.447	71.804	.000	.000	.000
4200	8.780	57.172	39.866	72.682	.000	.000	.000
4300	8.770	57.378	40.271	73.560	.000	.000	.000
4400	8.753	57.580	40.662	74.436	.000	.000	.000
4500	8.730	57.776	41.041	75.310	.000	.000	.000
4600	8.701	57.968	41.406	76.182	.000	.000	.000
4700	8.667	58.154	41.761	77.050	.000	.000	.000
4800	8.630	58.337	42.104	77.915	.000	.000	.000
4900	8.590	58.514	42.437	78.776	.000	.000	.000
5000	8.549	58.687	42.761	79.633	.000	.000	.000
5100	8.506	58.856	43.075	80.486	.000	.000	.000
5200	8.462	59.021	43.380	81.334	.000	.000	.000
5300	8.419	59.182	43.676	82.178	.000	.000	.000
5400	8.377	59.339	43.965	83.018	.000	.000	.000
5500	8.335	59.492	44.246	83.854	.000	.000	.000
5600	8.296	59.642	44.519	84.685	.000	.000	.000
5700	8.258	59.788	44.786	85.513	.000	.000	.000
5800	8.223	59.932	45.046	86.337	.000	.000	.000
5900	8.191	60.072	45.299	87.158	.000	.000	.000
6000	8.163	60.209	45.547	87.975	.000	.000	.000

March 31, 1962

LEAD (Pb) **(REFERENCE STATE)** **AT. WT. = 207.21**

0° to 600.58°K	Crystal
600.58° to 2026°K	Liquid
2026° to 6000°K	Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

Lead (Pb)

(Crystal) At. Wt. = 207.21

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.644	.000	.000	INFINITE
100	5.838	8.803	21.013	-1.221	.000	.000	.000
200	6.183	12.972	16.062	-.618	.000	.000	.000
298	6.414	15.484	15.484	.000	.000	.000	.000
300	6.416	15.524	15.484	.012	.000	.000	.000
400	6.626	17.399	15.738	.664	.000	.000	.000
500	6.821	18.898	16.225	1.337	.000	.000	.000
600	7.028	20.157	16.778	2.027	.000	.000	.000
700	7.256	21.257	17.341	2.741	-1.156	.190	-.059
800	7.491	22.242	17.893	3.479	-1.139	.382	-.104
900	7.723	23.137	18.427	4.239	-1.093	.569	-.138
1000	7.956	23.963	18.940	5.023	-1.015	.750	-.164
1100	8.189	24.732	19.432	5.831	-.906	.921	-.183
1200	8.422	25.455	19.904	6.661	-.767	1.083	-.197
1300	8.654	26.138	20.357	7.515	-.599	1.230	-.207
1400	8.887	26.788	20.794	8.392	-.407	1.363	-.213
1500	9.120	27.409	21.214	9.292	-.191	1.483	-.216

March 31, 1962

LEAD (Pb) (CRYSTAL) AT. WT. = 207.21

$\Delta H_{f0}^\circ = 0$

ΔH_s° 298.15 = 46.75 ± 0.13 kcal. mole^{-1}

T_m = 600.58 ± 0.00°K

ΔH_f° 298.15 = 0

$S_{298.15}^\circ$ = 15.484 cal. deg.$^{-1}$ mole^{-1}

ΔH_m° = 1.141 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacity measurements have been reported by M. Horowitz, A. A. Silvidi, S. F. Malaker and J. G. Daunt, (1° to 4°, 14° to 21°, and 64° to 77°K.), Phys. Rev. 88, 1182 (1952); P. F. Meads, W. R. Forsythe and W. F. Giauque, (15° to 300°K.), J. Am. Chem. Soc. 63, 1902 (1941); T. B. Douglas and J. L. Dever, (298.16° to 1200°K.), J. Am. Chem. Soc. 76, 4824 (1954), and many others whose work is listed by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

Heat capacities from 15° to 300° and 1° to 4°K. (in superconducting state) were taken from Meads, Forsythe, and Giauque, and Horowitz, Silvidi, Malaker, and Daunt, respectively. The missing data below the melting point were obtained by graphical extrapolation and joined smoothly to data of Douglas and Dever on approaching the melting point.

Melting.

The melting point of pure Pb(c) was found by E. H. McLaren and E. G. Mardock, Can. J. Phys. 38, 577 (1960) to be 327.426 ± 0.002°C. ΔH_m given by Douglas and Dever, loc. cit.

Heat of Sublimation.

ΔH_s° 298.15 was derived from third law analysis of the vapor pressure data of W. H. Rodebush and A. L. Dixon, J. Am. Chem. Soc. 47, 1036 (1925) and Phys. Rev. 26, 851 (1925); A. C. G. Egerton, Proc. Roy. Soc. (London) A103, 469 (1923); P. Harteck, Z. physik. Chem. 134, 1 (1928); A. T. Aldsed and J. N. Pratt, Trans. Faraday Soc. 57, 611 (1961); E. Baur and R. Brunner, Helv. Chim. Acta. 17, 958 (1934), and J. Fischer, Z. anorg. Chem. 219, 1, 367 (1934), which are in good agreement. Most weight was given to the results of Rodebush and Dixon. Older vapor pressure data of lower accuracy have not been used.

Lead (Pb)

(Liquid) At. Wt. = 207.21

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	6.414	17.141	17.141	.000	1.025	.531	- .389
300	6.418	17.181	17.141	.012	1.025	.528	- .385
400	7.470	19.056	17.395	.664	1.025	.362	- .198
500	7.396	20.715	17.900	1.407	1.095	.187	- .082
600	7.322	22.056	18.484	2.143	1.141	.002	- .001
700	7.250	23.179	19.077	2.871	.000	.000	.000
800	7.174	24.142	19.651	3.592	.000	.000	.000
900	7.098	24.982	20.198	4.306	.000	.000	.000
1000	7.026	25.726	20.714	5.012	.000	.000	.000
1100	6.953	26.393	21.201	5.711	.000	.000	.000
1200	6.880	26.994	21.659	6.403	.000	.000	.000
1300	6.848	27.544	22.091	7.089	.000	.000	.000
1400	6.841	28.051	22.498	7.773	.000	.000	.000
1500	6.853	28.523	22.885	8.458	.000	.000	.000
1600	6.880	28.966	23.251	9.144	.000	.000	.000
1700	6.914	29.384	23.599	9.834	.000	.000	.000
1800	6.957	29.780	23.932	10.527	.000	.000	.000
1900	7.002	30.158	24.250	11.225	.000	.000	.000
2000	7.050	30.518	24.554	11.928	.000	.000	.000
2100	7.100	30.863	24.847	12.635	- 42.452	1.555	- .162
2200	7.151	31.195	25.128	13.348	- 42.359	3.648	- .362
2300	7.202	31.514	25.398	14.066	- 42.282	5.737	- .545
2400	7.253	31.821	25.660	14.788	- 42.222	7.824	- .712
2500	7.303	32.119	25.912	15.516	- 42.179	9.907	- .866
2600	7.352	32.406	26.156	16.249	- 42.152	11.991	- 1.008
2700	7.400	32.684	26.393	16.986	- 42.141	14.073	- 1.139
2800	7.450	32.954	26.623	17.729	- 42.146	16.155	- 1.261
2900	7.499	33.217	26.845	18.476	- 42.165	18.238	- 1.374
3000	7.548	33.472	27.062	19.229	- 42.196	20.322	- 1.480

LEAD (Pb) (LIQUID) AT. WT. = 207.21

ΔH_f° 298.15 = [1.025] kcal. mole^{-1}

T_m = 600.58 ± 0.00°K

T_b = 2026°K

$S^\circ_{298.15}$ = [17.141] cal. deg.$^{-1}$ mole^{-1}

ΔH_m° = 1.141 kcal. mole^{-1}

ΔH_v° = 42.53 ± 0.13 kcal. mole^{-1}

Heat of Formation.

Obtained from ΔH_m°.

Heat Capacity and Extrapolation.

Heat capacity from T_m to 1200°K taken from T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954). C_p values below T_m and above 1200°K were extrapolated, a glass transition being assumed at 400°K.

Entropy.

Calculated from that of crystal.

Vaporization Phenomena.

T_b and ΔH_v° calculated from ΔH_s° 298.15 and functions for condensed and gaseous states.

From the vapor pressure, the free energy functions of Pb(g) and Pb_2(g), and the dissociation energy of Pb_2 (g), it appears that below the boiling point the amount of Pb_2(g) in the vapor is negligible.

Lead (Pb)

(Ideal Gas) At. Wt. = 207.21

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1,481	46,910	46,910	INFINITE
100	4,968	36,463	46,307	-,984	46,984	44,218	-96,633
200	4,968	39,907	42,345	-,468	46,877	41,490	-45,337
298	4,968	41,890	41,890	,000	46,747	38,874	-28,494
300	4,968	41,921	41,890	,009	46.744	38,825	-28,283
400	4,968	43.350	42.085	.506	46.589	36.209	-19,782
500	4,968	44,459	42,453	1,003	46,413	33,632	-14,700
600	4,968	45,365	42,865	1,500	46.220	31,095	-11,326
700	4,968	46.130	43,278	1,996	44,846	28,781	-8,985
800	4,969	46,794	43,677	2,493	44,622	26.502	-7,240
900	4,972	47,379	44,057	2,990	44,405	24,250	-5,888
1000	4,978	47,903	44,416	3.488	44.197	22.021	-4.813
1100	4.992	48.379	44.755	3,986	43.996	19.813	-3.936
1200	5.017	48,814	45.075	4,487	43.806	17.624	-3.210
1300	5,056	49,217	45,378	4.990	43,623	15,450	-2,597
1400	5.113	49.594	45,666	5,499	43,447	13,288	-2,074
1500	5.191	49,949	45,940	6.014	43,278	11,142	-1.623
1600	5,290	50,287	46,201	6,537	43,114	9,004	-1.230
1700	5.411	50.611	46,451	7,072	42.960	6.877	-,884
1800	5,554	50,924	46,691	7.620	42.814	4.758	-.578
1900	5.716	51,229	46,922	8.184	42.680	2,647	-.304
2000	5,899	51,527	47,145	8,764	42,557	.544	-,059
2100	6,094	51,819	47,360	9.364	.000	.000	,000
2200	6,301	52,108	47,569	9,984	.000	.000	,000
2300	6,516	52,392	47,773	10,625	.000	.000	,000
2400	6,734	52.674	47,971	11.287	.000	.000	,000
2500	6.951	52,954	48,165	11,971	.000	.000	,000
2600	7,165	53.230	48,355	12,677	.000	.000	.000
2700	7,372	53.505	48,540	13.404	.000	.000	,000
2800	7,569	53.776	48,722	14,151	.000	.000	,000
2900	7,754	54,045	48,901	14,917	.000	.000	,000
3000	7,926	54,311	49,077	15,702	.000	.000	,000
3100	8,082	54,574	49,250	16.502	.000	.000	,000
3200	8.221	54,832	49,421	17.317	.000	.000	.000
3300	8.345	55,087	49,589	18,146	.000	.000	,000
3400	8,451	55,338	49,754	18,986	.000	.000	,000
3500	8,542	55,584	49,917	19,835	.000	.000	,000
3600	8,616	55.826	50,078	20,693	.000	.000	,000
3700	8,675	56,063	50,236	21,558	.000	.000	,000
3800	8.720	56,295	50,393	22.428	.000	.000	.000
3900	8,752	56,522	50,547	23,302	.000	.000	,000
4000	8,772	56,744	50,699	24.178	.000	.000	,000
4100	8,781	56,961	50,849	25,056	.000	.000	,000
4200	8,780	57,172	50,997	25,934	.000	.000	,000
4300	8,770	57,379	51,143	26,812	.000	.000	,000
4400	8.753	57.580	51.287	27.688	.000	.000	.000
4500	8,730	57,776	51,429	28,562	.000	.000	,000
4600	8,701	57,968	51,569	29,434	.000	.000	,000
4700	8,667	58,155	51,708	30,302	.000	.000	,000
4800	8,630	58,337	51,844	31,167	.000	.000	,000
4900	8,590	58,514	51,978	32,028	.000	.000	,000
5000	8,549	58,688	52,111	32,885	.000	.000	,000
5100	8.506	58.856	52.241	33.738	.000	.000	.000
5200	8,462	59,021	52,370	34,586	.000	.000	.000
5300	8.419	59.182	52,497	35.430	.000	.000	.000
5400	8,377	59,339	52,622	36,270	.000	.000	,000
5500	8,335	59,492	52,746	37,105	.000	.000	,000
5600	8,296	59,642	52,868	37,937	.000	.000	,000
5700	8.256	59.789	52,988	38.765	.000	.000	.000
5800	8,223	59,932	53,106	39,589	.000	.000	,000
5900	8.191	60.072	53,223	40.409	.000	.000	.000
6000	8,163	60,210	53,338	41,227	.000	.000	,000

March 31, 1962

LEAD (Pb) (IDEAL GAS) AT. WT. = 207.21

ΔH°_{f0} = 46.91 ± 0.13 kcal. mole^{-1}

ΔH°_f 298.15 = 46.75 ± 0.13 kcal. mole^{-1}

Ground State Configuration $^3P_0$

$S^\circ_{298.15}$ = 41.890 cal. deg.$^{-1}$ mole^{-1}

Electronic Levels and Multiplicities

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.00	1	46,152.76	15
7,819.35	3	48,760.32	12
10,650.47	5	51,741.79	12
21,457.90	5	52,505.53	48
29,466.81	1	53,493.33	4
34,959.90	1	54,895.15	4
35,287.24	3	55,343.74	60
42,918.68	3	56,716.24	52
44,400.92	1	57,520.36	68
44,675.00	3	58,403.73	139
44,809.41	5	59,321.54	51
45,443.26	5		

Heat of Formation.

The same as ΔH°_s 298.15

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467, Vol. III (1958).

Lead, Diatomic (Pb_2)
(Ideal Gas) Mol. Wt. = 414.42

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.391	80.397	80.397	INFINITE
100	7.712	58.087	74.840	-1.675	80.267	76.219	-166.568
200	8.545	63.744	68.016	-.854	79.882	72.322	-79.026
298	8.825	67.216	67.216	.000	79.500	68.693	-50.351
300	8.828	67.270	67.216	.016	79.492	68.626	-49.991
400	8.964	69.830	67.564	.907	79.079	65.066	-35.548
500	9.050	71.840	68.225	1.807	78.633	61.611	-26.929
600	9.115	73.496	68.970	2.716	78.162	58.252	-21.217
700	9.169	74.905	69.720	3.630	75.336	55.354	-17.282
800	9.219	76.133	70.446	4.549	74.813	52.536	-14.351
900	9.265	77.222	71.140	5.474	74.310	49.781	-12.088
1000	9.309	78.200	71.798	6.402	73.826	47.082	-10.289
1100	9.351	79.089	72.421	7.335	73.361	44.430	-8.827
1200	9.393	79.905	73.011	8.273	72.917	41.821	-7.616
1300	9.434	80.658	73.571	9.214	72.486	39.247	-6.598
1400	9.475	81.359	74.102	10.159	72.061	36.705	-5.730
1500	9.515	82.014	74.608	11.109	71.643	34.197	-4.982
1600	9.555	82.629	75.090	12.063	71.223	31.713	-4.332
1700	9.595	83.210	75.551	13.020	70.802	29.258	-3.761
1800	9.635	83.759	75.992	13.982	70.376	26.824	-3.257
1900	9.674	84.281	76.415	14.947	69.945	24.415	-2.808
2000	9.714	84.779	76.820	15.916	69.508	22.031	-2.407
2100	9.753	85.254	77.211	16.890	-15.834	22.773	-2.370
2200	9.793	85.708	77.587	17.867	-16.097	24.616	-2.445
2300	9.832	86.144	77.949	18.848	-16.398	26.473	-2.515
2400	9.871	86.564	78.300	19.834	-16.736	28.346	-2.581
2500	9.910	86.967	78.638	20.823	-17.117	30.229	-2.642
2600	9.949	87.357	78.966	21.816	-17.536	32.132	-2.701
2700	9.988	87.733	79.284	22.812	-17.992	34.051	-2.756
2800	10.027	88.097	79.592	23.813	-18.487	35.987	-2.809
2900	10.066	88.450	79.892	24.818	-19.014	37.943	-2.859
3000	10.105	88.792	80.183	25.827	-19.573	39.918	-2.908
3100	10.144	89.123	80.466	26.839	-20.161	41.909	-2.954
3200	10.183	89.446	80.741	27.855	-20.777	43.920	-2.999
3300	10.222	89.760	81.010	28.876	-21.412	45.953	-3.043
3400	10.261	90.066	81.272	29.900	-22.068	48.006	-3.086
3500	10.300	90.364	81.527	30.928	-22.740	50.074	-3.127
3600	10.339	90.655	81.777	31.960	-23.424	52.167	-3.167
3700	10.378	90.938	82.021	32.996	-24.118	54.276	-3.206
3800	10.417	91.216	82.259	34.036	-24.816	56.406	-3.244
3900	10.456	91.487	82.492	35.079	-25.521	58.552	-3.281
4000	10.495	91.752	82.720	36.127	-26.225	60.711	-3.317
4100	10.534	92.012	82.944	37.178	-26.930	62.894	-3.352
4200	10.573	92.266	83.163	38.234	-27.630	65.097	-3.387
4300	10.612	92.515	83.377	39.293	-28.327	67.308	-3.421
4400	10.651	92.760	83.588	40.356	-29.016	69.546	-3.454
4500	10.690	92.999	83.794	41.423	-29.697	71.790	-3.486
4600	10.728	93.235	83.997	42.494	-30.370	74.055	-3.518
4700	10.767	93.466	84.196	43.569	-31.031	76.326	-3.549
4800	10.806	93.693	84.391	44.647	-31.683	78.626	-3.580
4900	10.845	93.916	84.584	45.730	-32.322	80.926	-3.609
5000	10.884	94.136	84.772	46.816	-32.950	83.242	-3.638
5100	10.923	94.352	84.958	47.907	-33.565	85.572	-3.667
5200	10.962	94.564	85.141	49.001	-34.167	87.918	-3.695
5300	11.001	94.773	85.321	50.099	-34.757	90.274	-3.722
5400	11.040	94.979	85.498	51.201	-35.335	92.638	-3.749
5500	11.078	95.182	85.672	52.307	-35.901	95.009	-3.775
5600	11.117	95.382	85.843	53.417	-36.453	97.397	-3.801
5700	11.156	95.579	86.013	54.530	-36.996	99.786	-3.826
5800	11.195	95.774	86.179	55.648	-37.526	102.198	-3.851
5900	11.234	95.965	86.343	56.769	-38.047	104.608	-3.875
6000	11.273	96.154	86.505	57.895	-38.555	107.026	-3.898

Mar. 31, 1962; June 30, 1963; Sept. 30, 1963.

LEAD, DIATOMIC (Pb_2) (IDEAL GAS) MOL. WT. = 414.42

Ground State Configuration $[{}^3\Sigma_g^-]$

$S^\circ_{298.15}$ = [67.216] cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0}$ = 80.4 ± 4.6 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 79.5 ± 4.6 kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i
0	[3]

ω_e = 256.5 cm.$^{-1}$

B_e = [0.01727] cm.$^{-1}$

$\omega_e x_e$ = 2.96 cm.$^{-1}$

α_e = [0.00020] cm.$^{-1}$

σ = 2

r_e = [3.08] Å

Heat of Formation.

Heat of formation was calculated from the dissociation energy of Pb_2(g) reported by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Heat Capacity and Entropy.

The values of ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950. Those for B_e and α_e were estimated according to the method suggested by G. Herzberg, loc..cit. The bond distance (r_e) was calculated from the moment of inertia, I = 1630 X 10^{-40} g. cm.^{2}, estimated by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961. The ground state configuration was assumed to be ${}^3\Sigma$ by comparison to that for Si_2(g) reported by A. E. Douglas, Can. J. Phys. 33, 801 (1955).

Sulfur (S)

(Reference State) At. Wt. = 32.064

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-1.053	.000	.000	.000
100	3.060	2.965	11.855	-.889	.000	.000	.000
200	4.639	5.622	8.104	-.496	.000	.000	.000
298	5.401	7.631	7.631	.000	.000	.000	.000
300	5.412	7.665	7.632	.010	.000	.000	.000
400	7.734	10.674	7.901	1.109	.000	.000	.000
500	9.081	12.768	8.673	2.047	.000	.000	.000
600	8.200	14.333	9.492	2.904	.000	.000	.000
700	7.799	15.601	10.309	3.704	.000	.000	.000
800	4.368	31.363	9.452	17.529	.000	.000	.000
900	4.396	31.879	11.916	17.967	.000	.000	.000
1000	4.418	32.344	13.936	18.408	.000	.000	.000
1100	4.435	32.765	15.628	18.851	.000	.000	.000
1200	4.450	33.152	17.073	19.295	.000	.000	.000
1300	4.461	33.509	18.324	19.740	.000	.000	.000
1400	4.471	33.840	19.420	20.187	.000	.000	.000
1500	4.480	34.148	20.392	20.635	.000	.000	.000
1600	4.488	34.438	21.261	21.083	.000	.000	.000
1700	4.495	34.710	22.044	21.532	.000	.000	.000
1800	4.501	34.967	22.755	21.982	.000	.000	.000
1900	4.507	35.211	23.404	22.432	.000	.000	.000
2000	4.513	35.442	24.000	22.883	.000	.000	.000
2100	4.518	35.662	24.550	23.335	.000	.000	.000
2200	4.523	35.873	25.060	23.787	.000	.000	.000
2300	4.528	36.074	25.535	24.240	.000	.000	.000
2400	4.532	36.267	25.978	24.693	.000	.000	.000
2500	4.537	36.452	26.393	25.146	.000	.000	.000
2600	4.541	36.630	26.784	25.600	.000	.000	.000
2700	4.545	36.801	27.151	26.054	.000	.000	.000
2800	4.549	36.966	27.499	26.509	.000	.000	.000
2900	4.553	37.126	27.828	26.964	.000	.000	.000
3000	4.557	37.281	28.141	27.420	.000	.000	.000
3100	4.561	37.430	28.438	27.875	.000	.000	.000
3200	4.565	37.575	28.721	28.332	.000	.000	.000
3300	4.568	37.715	28.992	28.788	.000	.000	.000
3400	4.572	37.852	29.250	29.245	.000	.000	.000
3500	4.575	37.984	29.498	29.703	.000	.000	.000
3600	4.579	38.113	29.735	30.160	.000	.000	.000
3700	4.583	38.239	29.964	30.619	.000	.000	.000
3800	4.586	38.361	30.183	31.077	.000	.000	.000
3900	4.590	38.480	30.394	31.536	.000	.000	.000
4000	4.593	38.597	30.598	31.995	.000	.000	.000
4100	4.596	38.710	30.794	32.454	.000	.000	.000
4200	4.600	38.821	30.984	32.914	.000	.000	.000
4300	4.603	38.929	31.168	33.374	.000	.000	.000
4400	4.607	39.035	31.345	33.835	.000	.000	.000
4500	4.610	39.139	31.517	34.296	.000	.000	.000
4600	4.613	39.240	31.684	34.757	.000	.000	.000
4700	4.617	39.339	31.846	35.218	.000	.000	.000
4800	4.620	39.436	32.003	35.680	.000	.000	.000
4900	4.624	39.532	32.156	36.142	.000	.000	.000
5000	4.627	39.625	32.304	36.605	.000	.000	.000
5100	4.630	39.717	32.449	37.068	.000	.000	.000
5200	4.633	39.807	32.589	37.531	.000	.000	.000
5300	4.637	39.895	32.726	37.994	.000	.000	.000
5400	4.640	39.982	32.860	38.458	.000	.000	.000
5500	4.643	40.067	32.990	38.922	.000	.000	.000
560C	4.647	40.151	33.117	39.387	.000	.000	.000
5700	4.650	40.233	33.241	39.852	.000	.000	.000
5800	4.653	40.314	33.363	40.317	.000	.000	.000
5900	4.656	40.393	33.481	40.782	.000	.000	.000
6000	4.660	40.472	33.597	41.248	.000	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

SULFUR (S) (REFERENCE STATE) AT. WT. = 32.064

0°	to 368.54°K,	Crystal, Rhombic
368.54°	to 388.36°K,	Crystal, Monoclinic
388.36°	to 717.75°K,	Liquid
717.75°	to 6000°K.	Ideal Gas, Diatomic

See crystal, liquid and diatomic gas for details.

Sulfur (S)

(Crystal) At. Wt. = 32.064

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.053	.000	.000	.000
100	3.060	2.965	11.855	- .889	.000	.000	.000
200	4.639	5.622	8.104	- .469	.000	.000	.000
298	5.401	7.631	7.631	.000	.000	.000	.000
300	5.412	7.665	7.632	.010	.000	.000	.000
400	6.133	9.571	7.871	.680	- .429	.012	- .007
500	6.819	11.013	8.356	1.327	- .720	.158	- .069
600	7.504	12.317	8.911	2.044	- .860	.349	- .127
700	8.190	13.525	9.485	2.828	- .876	.577	- .180
800	8.876	14.664	10.062	3.682	- 13.847	- .488	.133
900	9.561	15.749	10.634	4.603	- 13.364	1.154	- .280
1000	10.247	16.792	11.198	5.594	- 12.814	2.738	- .598
1100	10.933	17.860	11.752	6.653	- 12.198	4.263	- .847
1200	11.619	18.781	12.297	7.780	- 11.515	5.731	- 1.044
1300	12.304	19.738	12.833	8.977	- 10.763	7.139	- 1.200
1400	12.990	20.675	13.360	10.241	- 9.946	8.485	- 1.325
1500	13.676	21.595	13.878	11.575	- 9.060	9.770	- 1.423
1600	14.361	22.499	14.389	12.976	- 8.107	10.996	- 1.502
1700	15.047	23.390	14.892	14.447	- 7.085	12.158	- 1.563
1800	15.733	24.270	15.389	15.986	- 5.996	13.259	- 1.610
1900	16.418	25.139	15.879	17.593	- 4.839	14.298	- 1.645
2000	17.104	25.998	16.364	19.270	- 3.613	15.274	- 1.669

Dec. 31, 1960; Dec. 31, 1965

SULFUR (S) (CRYSTAL) AT. WT. = 32.064

$S^\circ_{298.15}$ = 7.63 ± 0.5 cal. deg.$^{-1}$ mole^{-1}

T_{t_1} = 368.54°K.

T_{t_2} = 374°K.

T_m = 388.36°K.

$\Delta H^\circ_{f\ 0}$ = 0 kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15}$ = 0 kcal. mole^{-1}

ΔH_{t_1} = 96.01 ± 0.5 cal. mole^{-1}

ΔH_{t_2} = 0.38 ± 0.2 cal. mole^{-1}

ΔH_m = 410.52 ± 0.5 cal. mole^{-1}

$\Delta H^\circ_{s\ 298.15}$ = 66.68 ± 0.3 kcal. mole^{-1}

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

E. D. Eastman and W. C. McGavock, J. Am. Chem. Soc. 59, 145 (1937), have measured the low temperature heat capacities of sulfur from 15° to 375°K. E. D. West, J. Am. Chem. Soc. 81, 29 (1959), has measured the high temperature heat capacities from 298° to 678°K. These two sets of data were joined smoothly at 298.15 K.by a graphical method.

The values of entropy at 110°C and above in E. D. West's paper (table VIII) have been lowered by 0.5841 Joule. deg.$^{-1}$ mole^{-1} because of a calculational error which was pointed out by J. P. McCullough and D. W. Scott, private communication, Sept. 27, 1960.

The entropy of rhombic sulfur at 298.15°K.was taken from E. D. Eastman and W. C. McGavock, loc. cit., based on an extrapolation of S°_{15} = 0.12 cal. deg.$^{-1}$ mole^{-1}.

Transition Data.

The enthalpies of transition at 368.54°K.and 374°K.were obtained from E. D. West, loc. cit. The first transition at 368.54°K.was the known rhombic-monoclinic transition, but the second one near 374°K.was a previously unreported transition.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Heat of Sublimation.

The heat of sublimation of sulfur (c) is the heat of formation of monatomic sulfur (g). See S(g) table for details. Since S_8 and lower polymers are major vapor species at room temperature, the heat of sublimation to the equilibrium gas is much smaller. See S_8(g) table for details.

Sulfur (S)

(Liquid)   At. Wt. = 32.064

T, °K.	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	7.579	8.444	8.444	.000	.336	.093	-.068
300	7.579	8.491	8.444	.014	.340	.092	-.067
400	7.734	10.674	8.741	.773	.000	.000	.000
500	9.081	12.768	9.346	1.711	.000	.000	.000
600	8.200	14.333	10.053	2.568	.000	.000	.000
700	7.799	15.601	10.790	3.368	-.000	-.000	.000
800	7.694	16.634	11.457	4.142	-13.051	-1.269	.347
900	7.694	17.540	12.084	4.910	-12.721	.185	-.045
1000	7.694	18.350	12.671	5.680	-12.393	1.601	-.350
1100	7.694	19.084	13.221	6.449	-12.066	2.983	-.593
1200	7.694	19.753	13.738	7.218	-11.741	4.338	-.790
1300	7.694	20.369	14.224	7.988	-11.416	5.666	-.952
1400	7.694	20.939	14.684	8.757	-11.094	6.967	-1.088
1500	7.694	21.470	15.119	9.527	-10.773	8.245	-1.201
1600	7.694	21.966	15.531	10.296	-10.451	9.503	-1.298
1700	7.694	22.433	15.924	11.065	-10.131	10.740	-1.381
1800	7.694	22.873	16.298	11.835	-9.811	11.959	-1.452
1900	7.694	23.289	16.655	12.604	-9.492	13.161	-1.514
2000	7.694	23.683	16.996	13.374	-9.174	14.344	-1.567

Dec. 31, 1960; Dec. 31, 1965

SULFUR (S)   (LIQUID)   AT. WT. = 32.064

$S^\circ_{298.15}$ = 8.44 ± 0.5 cal. deg.$^{-1}$ mole^{-1}

T_m = 388.36°K.

T_b = 717.75°K.

ΔH°_f 298.15 = 0.34 ± 0.01 kcal. mole^{-1}

ΔH°_m = 410.52 ± 0.5 cal. mole^{-1}

ΔH°_v = [2.30] kcal. mole^{-1}

Heat of Formation.

The ΔH°_f 298.15 (S, l) was obtained from that of the crystal by adding ΔH°_m and the difference between $H_{388.36}$-$H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was obtained from E. D. West, J. Am. Chem. Soc. 81, 29 (1959). No simple equation fits the curve of C_p against T which shows a peak.

The value of $S^\circ_{298.15}$ (S, l) was obtained in a manner analogous to that of the heat of formation. The heat capacity of sulfur (liquid) below the melting point was assumed to be constant as 7.579 cal. deg.$^{-1}$ mole^{-1}; and above the boiling point, it was assumed as 7.694 cal. deg.$^{-1}$ mole^{-1}.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Vaporization Data.

According to the international practical temperature scale, the boiling point is 717.75°K. The heat of vaporization to the equilibrium vapor mixture was estimated by D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956. The equilibrium vapor involves monomeric and several polymeric species; S_2 and S predominate above 1000°K. while S_8, S_6 and possible S_4 and S_3 are favored at lower temperatures.

Sulfur, Monatomic (S)

(Ideal Gas) At. Wt. = 32.064

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	- 1.591	66.142	66.142	INFINITE
100	5.103	34.127	45.046	- 1.092	66.477	63.361	- 138.468
200	5.589	37.831	40.604	- .555	66.621	60.180	- 65.758
298	5.659	40.086	40.086	.000	66.680	57.004	- 41.783
300	5.658	40.121	40.086	.010	66.680	56.944	- 41.481
400	5.554	41.736	40.307	.572	66.143	53.718	- 29.349
500	5.436	42.962	40.720	1.121	65.754	50.657	- 22.141
600	5.340	43.944	41.178	1.659	65.435	47.669	- 17.363
700	5.266	44.762	41.634	2.190	65.166	44.753	- 13.972
800	5.211	45.461	42.069	2.713	51.864	40.586	- 11.087
900	5.169	46.072	42.481	3.232	51.945	39.172	- 9.512
1000	5.137	46.615	42.868	3.747	52.019	37.748	- 8.250
1100	5.112	47.103	43.231	4.260	52.089	36.317	- 7.215
1200	5.093	47.547	43.572	4.770	52.155	34.881	- 6.352
1300	5.079	47.954	43.894	5.279	52.219	33.440	- 5.622
1400	5.070	48.331	44.198	5.786	52.279	31.992	- 4.994
1500	5.064	48.680	44.485	6.293	52.338	30.540	- 4.449
1600	5.062	49.007	44.758	6.799	52.396	29.085	- 3.973
1700	5.063	49.314	45.017	7.305	52.453	27.626	- 3.551
1800	5.068	49.603	45.263	7.812	52.510	26.165	- 3.177
1900	5.075	49.877	45.499	8.319	52.567	24.701	- 2.841
2000	5.085	50.138	45.725	8.827	52.624	23.232	- 2.539
2100	5.097	50.386	45.941	9.336	52.681	21.761	- 2.265
2200	5.112	50.624	46.148	9.846	52.739	20.287	- 2.015
2300	5.127	50.851	46.348	10.358	52.798	18.811	- 1.787
2400	5.144	51.070	46.540	10.872	52.859	17.332	- 1.578
2500	5.162	51.280	46.725	11.387	52.921	15.851	- 1.386
2600	5.181	51.483	46.905	11.904	52.984	14.367	- 1.208
2700	5.200	51.679	47.078	12.423	53.049	12.879	- 1.042
2800	5.219	51.869	47.246	12.944	53.115	11.387	- .889
2900	5.239	52.052	47.408	13.467	53.183	9.898	- .746
3000	5.258	52.230	47.566	13.992	53.252	8.405	- .612
3100	5.277	52.403	47.719	14.519	53.324	6.908	- .487
3200	5.295	52.571	47.868	15.048	53.396	5.408	- .369
3300	5.313	52.734	48.013	15.578	53.470	3.907	- .259
3400	5.331	52.893	48.154	16.110	53.545	2.406	- .155
3500	5.347	53.047	48.292	16.644	53.621	.901	- .056
3600	5.363	53.198	48.426	17.180	53.700	- .606	.037
3700	5.378	53.345	48.557	17.717	53.778	- 2.115	.125
3800	5.392	53.489	48.685	18.255	53.858	- 3.628	.209
3900	5.406	53.629	48.810	18.795	53.939	- 5.142	.288
4000	5.419	53.766	48.932	19.336	54.021	- 6.655	.364
4100	5.430	53.900	49.052	19.879	54.105	- 8.174	.436
4200	5.441	54.031	49.169	20.422	54.188	- 9.694	.504
4300	5.451	54.159	49.283	20.967	54.273	- 11.216	.570
4400	5.461	54.285	49.396	21.513	54.358	- 12.742	.633
4500	5.470	54.408	49.506	22.059	54.443	- 14.267	.693
4600	5.477	54.528	49.613	22.607	54.530	- 15.795	.750
4700	5.485	54.646	49.719	23.155	54.617	- 17.326	.806
4800	5.491	54.761	49.823	23.703	54.703	- 18.857	.859
4900	5.497	54.875	49.925	24.253	54.791	- 20.390	.909
5000	5.502	54.986	50.025	24.803	54.878	- 21.927	.958
5100	5.507	55.095	50.124	25.353	54.965	- 23.462	1.005
5200	5.511	55.202	50.220	25.904	55.053	- 25.001	1.051
5300	5.515	55.307	50.315	26.456	55.142	- 26.542	1.094
5400	5.518	55.410	50.409	27.007	55.229	- 28.082	1.136
5500	5.521	55.511	50.500	27.559	55.317	- 29.625	1.177
5600	5.523	55.611	50.591	28.111	55.404	- 31.172	1.216
5700	5.525	55.708	50.680	28.664	55.492	- 32.716	1.254
5800	5.526	55.805	50.767	29.216	55.579	- 34.269	1.291
5900	5.528	55.899	50.853	29.769	55.667	- 35.818	1.327
6000	5.529	55.992	50.938	30.322	55.754	- 37.366	1.361

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

SULFUR, MONATOMIC (S) (IDEAL GAS) AT. WT. = 32.064

Ground State Configuration $^3P_2$

$S^\circ_{298.15} = 40.1 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H^\circ_{f\ 0} = 66.14 \pm 0.5$ kcal. mole^{-1}

$\Delta H^\circ_{f\ 298.15} = 66.68 \pm 0.5$ kcal. mole^{-1}

Electronic Levels and Quantum Weight

ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i	ϵ_i, cm.$^{-1}$	g_i
0.0	5	67,878.03	9	73,921.14	7
396.8	3	67,890.45	7	74,269.2	5
573.6	1	67,888.25	5	74,270.28	3
9,239.0	5	67,885.97	3	74,272.32	1
22,181.4	1	67,884.67	1	75,342.02	40
52,623.88	5	69,238.7	5	76,706.70	73
55,331.15	3	70,165.9	3	77,986.31	39
63,446.36	3	70,166.8	5	78,338.35	54
63,457.33	5	70,170.7	7	79,014.3	83
63,475.26	7	[70,706.0]	5	79,782.1	52
64,891.71	1	71.352.5	3	80,158.61	24
64,889.23	3	72,025.5	5	80,634.	89
64,892.89	5	72,382.5	3	81,089.9	29
67,816.87	3	72,572.4	1	81,405.23	84
67,825.72	5	73,911.53	3	81,864.6	101
67,843.38	7	73,915.16	5	82,353.3	25

Heat of Formation.

L. Brewer, J. Chem. Phys. 31, 1143 (1959), has reviewed the three possible values of D_0° (S_2), i.e. 4.4 e.V., 3.6 e.V. and 3.3 e.V., which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. The value of 4.4 e.V. (101.5 kcal. mole^{-1}) was shown to be the most probable one. Since this review, further support for his value have been given by the following investigators. J. R. Marquart, Dissertation Abstract 24, 5027 (1964), has found that the value of D_0° (S_2) to be consistent with the value of 4.4 e.V. in mass spectrometric studies. R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. 60, 306 (1964), have found D_0° (S_2) = 97 ± 5 kcal. mole^{-1} in their mass-spectrometric studies of the vaporization of CaS, BaS, SnS and PbS, but they reported a revised value, i.e. D_0° (S_2) = 101 ± 1 kcal. mole^{-1}, which was given in the note in proof. A. N. Singh and D. K. Rai, J. Chem. Phys. 43, 2151 (1965), have selected the best value of D_0° (S_2) = 4.4 e.V. in theoretical comparisons of the potential-energy curve. As pointed out by L. Brewer, loc. cit., and A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 2nd. Ed., London, 1953, the old vapor pressure measurements which are not consistent with D_0 (S_2) = 4.4 e.V. (101.5 kcal. mole^{-1}) are probably not reliable.

The value D_0 (S_2, g) = 4.4 e.V. (101.5 kcal. mole^{-1}) was selected as the dissociation energy of diatomic sulfur, and combination of this value with heat of formation of diatomic sulfur gives the heat of formation of monatomic sulfur, $\Delta H^\circ_{f\ 298}$ (S, g) = 66.68 kcal. mole^{-1}.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weight were obtained from C. E. Moore, "Atomic Energy Levels", Vol. 1, National Bureau of Standards Circular 467, June, 1949.

Silicon Monosulfide (SiS)

(Ideal Gas) Mol. Wt. = 60.156

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-2.135	16.600	16.600	INFINITE
100	6.962	45.567	59.960	-1.439	17.068	12.899	-28.189
200	7.231	50.449	54.117	-.733	17.106	8.691	-9.496
298	7.711	53.427	53.427	.000	16.926	4.593	-3.366
300	7.720	53.474	53.427	.014	16.921	4.516	-3.290
400	8.100	55.751	53.735	.806	16.105	.443	-.242
500	8.352	57.587	54.327	1.630	15.442	-3.396	1.484
600	8.518	59.126	55.002	2.474	14.856	-7.107	2.589
700	8.632	60.448	55.688	3.332	14.324	-10.701	3.341
800	8.712	61.606	56.357	4.199	.764	-15.509	4.237
900	8.771	62.636	56.998	5.074	.587	-17.532	4.257
1000	8.817	63.562	57.609	5.953	.400	-19.535	4.269
1100	8.852	64.405	58.189	6.837	.209	-21.521	4.276
1200	8.881	65.176	58.740	7.723	.013	-23.487	4.277
1300	8.905	65.888	59.263	8.613	-.184	-25.437	4.276
1400	8.925	66.549	59.760	9.504	-.386	-27.372	4.273
1500	8.943	67.165	60.233	10.398	-.589	-29.295	4.268
1600	8.958	67.743	60.685	11.293	-.793	-31.199	4.261
1700	8.972	68.286	61.116	12.189	-13.104	-32.985	4.240
1800	8.984	68.799	61.529	13.087	-13.269	-34.151	4.146
1900	8.996	69.285	61.924	13.986	-13.433	-35.306	4.061
2000	9.006	69.747	62.304	14.886	-13.597	-36.453	3.983
2100	9.016	70.187	62.669	15.787	-13.761	-37.593	3.912
2200	9.026	70.606	63.020	16.689	-13.924	-38.723	3.847
2300	9.035	71.008	63.359	17.592	-14.087	-39.846	3.786
2400	9.043	71.392	63.686	18.496	-14.249	-40.964	3.730
2500	9.051	71.762	64.001	19.401	-14.410	-42.072	3.678
2600	9.059	72.117	64.307	20.307	-14.571	-43.176	3.629
2700	9.067	72.459	64.602	21.213	-14.732	-44.275	3.584
2800	9.074	72.789	64.889	22.120	-14.893	-45.368	3.541
2900	9.081	73.107	65.167	23.028	-15.053	-46.453	3.501
3000	9.088	73.415	65.437	23.936	-15.214	-47.531	3.462
3100	9.095	73.713	65.699	24.845	-15.373	-48.606	3.427
3200	9.102	74.002	65.954	25.755	-15.533	-49.675	3.392
3300	9.108	74.283	66.202	26.666	-15.691	-50.739	3.360
3400	9.115	74.555	66.444	27.577	-15.850	-51.797	3.329
3500	9.122	74.819	66.679	28.489	-16.009	-52.857	3.300
3600	9.128	75.076	66.909	29.401	-111.142	-53.434	3.244
3700	9.134	75.326	67.133	30.314	-111.239	-51.828	3.061
3800	9.141	75.570	67.352	31.228	-111.335	-50.223	2.888
3900	9.147	75.807	67.566	32.142	-111.432	-48.615	2.724
4000	9.153	76.039	67.775	33.057	-111.528	-46.999	2.568
4100	9.159	76.265	67.979	33.973	-111.623	-45.388	2.419
4200	9.165	76.486	68.179	34.889	-111.719	-43.766	2.277
4300	9.171	76.702	68.375	35.806	-111.814	-42.152	2.142
4400	9.177	76.912	68.566	36.723	-111.910	-40.530	2.013
4500	9.183	77.119	68.754	37.641	-112.006	-38.906	1.889
4600	9.189	77.321	68.938	38.560	-112.100	-37.279	1.771
4700	9.195	77.518	69.119	39.479	-112.193	-35.655	1.658
4800	9.201	77.712	69.296	40.399	-112.287	-34.023	1.549
4900	9.207	77.902	69.469	41.319	-112.381	-32.392	1.445
5000	9.213	78.088	69.640	42.240	-112.474	-30.758	1.344
5100	9.219	78.270	69.807	43.162	-112.566	-29.121	1.248
5200	9.225	78.449	69.972	44.084	-112.659	-27.485	1.155
5300	9.230	78.625	70.133	45.007	-112.750	-25.847	1.066
5400	9.236	78.798	70.292	45.930	-112.841	-24.204	.980
5500	9.242	78.967	70.448	46.854	-112.932	-22.563	.897
5600	9.248	79.134	70.602	47.779	-113.023	-20.919	.816
5700	9.254	79.298	70.753	48.704	-113.114	-19.273	.739
5800	9.259	79.459	70.902	49.629	-113.204	-17.629	.664
5900	9.265	79.617	71.048	50.556	-113.293	-15.978	.592
6000	9.271	79.773	71.192	51.482	-113.385	-14.329	.522

December 31, 1960.

Silicon Monosulfide (SiS) (Ideal Gas)

Mol. Wt. = 60.156

$\Delta H^\circ_{f\ 298.15}$ = 16.926 kcal. mole^{-1}

$S^\circ_{298.15}$ = 53.427 cal. deg.$^{-1}$ mole^{-1}

Ground State Configuration $^1\Sigma^+$

Electronic Level and Multiplicity

ϵ cm.$^{-1}$	g_i
0	1

ω_e = 749.5 cm.$^{-1}$ $\omega_e x_e$ = 2.56 cm.$^{-1}$

B_e = 0.30363 cm.$^{-1}$ α_e = 0.00149 cm.$^{-1}$

σ = 1 r_e = 1.9288 Å

Heat of Formation. $\Delta H^\circ_{f\ 298.15}$ was found in J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from J. S. Gordon, op. cit.

Sulfur, Diatomic (S_2)

(Ideal Gas) Mol. Wt. = 64.128

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. $mole^{-1}deg.^{-1}$			kcal. $mole^{-1}$			
0	.000	.000	INFINITE	- 2.141	30.805	30.805	INFINITE
100	6.964	46.623	61.075	- 1.445	31.173	27.104	- 59.232
200	7.265	51.515	55.204	- .738	31.094	23.040	- 25.176
298	7.759	54.510	54.510	.000	30.840	19.138	- 14.028
300	7.768	54.558	54.510	.014	30.834	19.066	- 13.889
400	8.144	56.848	54.819	.811	29.433	15.233	- 8.323
500	8.389	58.693	55.416	1.639	28.385	11.806	- 5.160
600	8.549	60.238	56.094	2.486	27.518	8.575	- 3.123
700	8.658	61.564	56.783	3.347	26.779	5.525	- 1.725
800	8.735	62.726	57.455	4.217	.000	.000	.000
900	8.792	63.758	58.099	5.093	.000	.000	.000
1000	8.836	64.687	58.712	5.975	.000	.000	.000
1100	8.870	65.531	59.294	6.860	.000	.000	.000
1200	8.899	66.304	59.846	7.749	.000	.000	.000
1300	8.922	67.017	60.371	8.640	.000	.000	.000
1400	8.942	67.679	60.870	9.533	.000	.000	.000
1500	8.960	68.296	61.344	10.428	.000	.000	.000
1600	8.976	68.875	61.797	11.325	.000	.000	.000
1700	8.990	69.420	62.230	12.223	.000	.000	.000
1800	9.002	69.934	62.643	13.123	.000	.000	.000
1900	9.014	70.421	63.040	14.024	.000	.000	.000
2000	9.025	70.884	63.421	14.926	.000	.000	.000
2100	9.036	71.324	63.787	15.829	.000	.000	.000
2200	9.046	71.745	64.139	16.733	.000	.000	.000
2300	9.055	72.147	64.479	17.638	.000	.000	.000
2400	9.064	72.533	64.806	18.544	.000	.000	.000
2500	9.073	72.903	65.123	19.451	.000	.000	.000
2600	9.081	73.259	65.429	20.358	.000	.000	.000
2700	9.090	73.602	65.725	21.267	.000	.000	.000
2800	9.098	73.932	66.012	22.176	.000	.000	.000
2900	9.106	74.252	66.291	23.086	.000	.000	.000
3000	9.113	74.561	66.562	23.997	.000	.000	.000
3100	9.121	74.860	66.824	24.909	.000	.000	.000
3200	9.129	75.149	67.080	25.822	.000	.000	.000
3300	9.136	75.430	67.329	26.735	.000	.000	.000
3400	9.143	75.703	67.571	27.649	.000	.000	.000
3500	9.150	75.968	67.807	28.563	.000	.000	.000
3600	9.158	76.226	68.038	29.479	.000	.000	.000
3700	9.165	76.477	68.262	30.395	.000	.000	.000
3800	9.172	76.722	68.482	31.312	.000	.000	.000
3900	9.179	76.960	68.696	32.229	.000	.000	.000
4000	9.186	77.193	68.906	33.148	.000	.000	.000
4100	9.192	77.419	69.111	34.066	.000	.000	.000
4200	9.199	77.641	69.311	34.986	.000	.000	.000
4300	9.206	77.858	69.507	35.906	.000	.000	.000
4400	9.213	78.069	69.699	36.827	.000	.000	.000
4500	9.220	78.276	69.888	37.749	.000	.000	.000
4600	9.226	78.479	70.072	38.671	.000	.000	.000
4700	9.233	78.678	70.253	39.594	.000	.000	.000
4800	9.240	78.872	70.431	40.518	.000	.000	.000
4900	9.247	79.063	70.605	41.442	.000	.000	.000
5000	9.253	79.250	70.776	42.367	.000	.000	.000
5100	9.260	79.433	70.944	43.293	.000	.000	.000
5200	9.266	79.613	71.109	44.219	.000	.000	.000
5300	9.273	79.789	71.271	45.146	.000	.000	.000
5400	9.280	79.963	71.431	46.074	.000	.000	.000
5500	9.286	80.133	71.587	47.002	.000	.000	.000
5600	9.293	80.300	71.741	47.931	.000	.000	.000
5700	9.299	80.465	71.893	48.861	.000	.000	.000
5800	9.306	80.627	72.042	49.791	.000	.000	.000
5900	9.312	80.786	72.189	50.722	.000	.000	.000
6000	9.319	80.942	72.334	51.653	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1965

SULFUR, DIATOMIC (S_2) (IDEAL GAS) MOL. WT. = 64.128

Ground State Configuration $^3\Sigma_g^-$

$S^\circ_{298.15}$ = 54.51 cal. $deg.^{-1}$ $mole^{-1}$

$\Delta H^\circ_{f\ 0}$ = 30.80 ± 0.2 kcal. $mole^{-1}$

$\Delta H^\circ_{f\ 298.15}$ = 30.84 ± 0.2 kcal. $mole^{-1}$

Electronic Levels and Quantum Weight

ϵ, $cm.^{-1}$	g_1
0	3

ω_e = 724.66 $cm.^{-1}$

B_e = 0.2948 $cm.^{-1}$

$\omega_e x_e$ = 2.852 $cm.^{-1}$

α_e = 0.0016 $cm.^{-1}$

σ = 2

r_e = 1.889 Å

Heat of Formation.

The standard enthalpy of formation of gaseous diatomic sulfur, $\Delta H^\circ_{f\ 298}$ = 30.84 kcal. $mole^{-1}$, was calculated from $\Delta H^\circ_{r\ 298}$ = -20.30 kcal. $mole^{-1}$ for the reaction $H_2(g) + 0.5\ S_2(g) \rightarrow H_2S(g)$ with JANAF value $\Delta H^\circ_{f\ 298}(H_2S, g)$ = -4.88 ± 0.15 kcal. $mole^{-1}$. The $\Delta H^\circ_{r\ 298}$ was obtained by the second and third law analyses of equilibrium constants which have been determined by G. Preuner and W. Schupp (ref. 1) and M. Randall and F. R. Bichowsky (ref. 2). The results obtained are presented as follows:

Ref.	Temp. Range	Points	2nd law $\Delta H^\circ_{r\ 298}$ kcal. $mole^{-1}$	3rd law $\Delta H^\circ_{r\ 298}$ kcal. mole	Drift cal. $mole^{-1}$ $deg.^{-1}$
1	1023-1405°K	5	-19.92 ± 0.13	-20.295	-0.282 ± 0.097
2	1362-1667°K	4	-20.74 ± 0.40	-20.307	+0.281 ± 0.269
3	1023-1667°K	9	-20.13 ± 0.12	-20.300	-0.066 ± 0.093

References

1. G. Preuner and W. Schupp, Z. physik Chem. 68, 157 (1910).
2. M. Randall and F. R. Bichowsky, J. Am. Chem. Soc. 40, 368 (1918).
3. Combination of above references.

The third law value of the combination set was selected to calculate the heat of formation of diatomic sulfur.

The dissociation energy of gaseous diatomic sulfur, D°_0 (S_2) = 101.5 kcal. $mole^{-1}$, was chosen. For discussions see JANAF monatomic sulfur (g) and sulfur monoxide (g) tables.

Heat Capacity and Entropy.

The molecular constants which were taken from G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, have been modified for the natural isotopic abundances reported by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

Silicon Disulfide (SiS_2)
(Solid) Mol. Wt. = 92.222

INTERIM TABLE

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0							
100							
200							
298	14.990	16.000	16.000	.000	-43.000	-41.899	30.711
300	15.000	16.093	16.000	.028	-43.001	-41.892	30.517
400	15.700	20.496	16.596	1.560	-44.176	-41.467	22.656
500	16.400	24.075	17.745	3.165	-44.996	-40.693	17.786
600	17.100	27.127	19.060	4.840	-45.608	-39.772	14.486
700	17.800	29.815	20.408	6.585	-46.053	-38.714	12.087
800	18.500	32.238	21.738	8.400	-72.490	-40.179	10.976
900	19.200	34.457	23.029	10.285	-72.095	-36.162	8.781
1000	19.900	36.517	24.276	12.240	-71.647	-32.192	7.035
1100	20.600	38.446	25.478	14.265	-71.140	-28.274	5.617
1200	21.300	40.268	26.635	16.360	-70.571	-24.400	4.444
1300	22.000	42.001	27.751	18.525	-69.938	-20.576	3.459
1400	22.700	43.657	28.828	20.760	-69.243	-16.805	2.623
1500	23.400	45.247	29.870	23.065	-68.483	-13.089	1.907
1600	24.100	46.780	30.879	25.440	-67.655	-9.419	1.287
1700	24.800	48.262	31.859	27.885	-78.866	-5.699	.733
1800	25.500	49.699	32.810	30.400	-77.864	-1.425	.173
1900	26.200	51.096	33.736	32.985	-76.792	2.794	-.321

December 31, 1960.

Silicon Disulfide (SiS_2) (Crystal)

Mol. Wt. = 92.222

$\Delta H_f^\circ{}_{298.15} = -50.7$ kcal. mole^{-1}

$S^\circ_{298.15} = [16.0]$ cal. deg.$^{-1}$ mole^{-1}

$T_m = 1363$°K.

$\Delta H_m = [5.0]$ kcal. mole^{-1}

Heat of Formation. $\Delta H_f^\circ{}_{298.15}$ was calculated from the measured ΔH_R's of the following reactions:

$$SiS_2(c) + HF(aq) \rightarrow H_2SiF_6(l) + 2H_2S(g)$$
$$\Delta H_{R1} = 72.8 \pm 2.2 \text{ kcal. mole}^{-1}$$

$$SiO_2(c) + HF(aq) \rightarrow H_2SiF_6(l) + 2H_2O(l)$$
$$\Delta H_{R2} = -33.00 \pm .02 \text{ kcal. mole}^{-1}$$

ΔH_{R1} was taken from R. Rocquet, M. T. Ancey-Maret, Bull. Soc. Chim. France 1954, 1039 (1954); ΔH_{R2} was from D. Torgeson and Th. G. Samaha, J. Am. Chem. Soc. 70, 2156 (1948). $\Delta H_f^\circ{}_{298.15}$ of SiS_2 was recalculated using the corrected value for $\Delta H_f^\circ{}_{298.15}$ of SiO_2.

Heat Capacity and Entropy. C_p and $S^\circ_{298.15}$ values are estimated.

Melting Data. T_m was from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties", 1952. ΔH_m was estimated.

Silicon Disulfide (SiS_2)

(Liquid) Mol. Wt. = 92.222 **INTERIM TABLE**

	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	11.040	21,621	21,621	,000	- 37,303	- 37,878	27,764
300	11.070	21.690	21.622	.020	- 37,312	- 37,881	27,595
400	12.700	25.097	22.075	1.209	- 38,830	- 37,962	20,740
500	14.300	28.109	22.986	2.561	- 39,903	- 37,617	16,442
600	15.600	30,835	24,071	4.059	- 40,692	- 37,081	13,506
700	16.900	33.339	25.218	5.685	- 41,256	- 36,384	11,359
800	18.100	35,675	26,381	7.435	- 67,758	- 38,196	10,434
900	19.200	37,871	27,537	9.301	- 67,382	- 34,521	8,383
1000	20.200	39,947	28,675	11,272	- 66,918	- 30,894	6,752
1100	21.200	41.920	29,790	13,343	- 66,365	- 27,320	5,428
1200	22.150	43.805	30,880	15,510	- 65,724	- 23,797	4,334
1300	23.000	45.613	31,944	17,770	- 64,996	- 20,330	3,418
1400	23.600	47.341	32,983	20,102	- 64,204	- 16,924	2,642
1500	24.000	48,986	33,995	22,485	- 63,366	- 13,580	1,979
1600	24,000	50,537	34,981	24,889	- 62,509	- 10,285	1,405
1700	24,000	51,992	35,939	27,289	- 73,765	- 6,939	,892
1800	24,000	53,364	36,870	29,689	- 72,878	- 3,035	,369
1900	24.000	54.661	37.772	32.089	- 71.991	.822	- .095
2000	24,000	55,892	38,648	34,489	- 71,106	4,632	- ,506

December 31, 1960.

Silicon Disulfide (SiS_2) (Liquid)

Mol. Wt. = 92.222

ΔH_f° 298.15 = [45.0] kcal. mole^{-1}

$S_{298.15}^\circ$ = [21.621] cal. deg.$^{-1}$ mole^{-1}

T_m = 1363°K.

ΔH_m = [5.0] kcal. mole^{-1}

Heat of Formation. ΔH_f° 298.15 was calculated from the ΔH_f° 298.15 of the crystal and the heat of melting.

Heat Capacity and Entropy. C_p and $S_{298.15}^\circ$ were estimated.

Melting Data. T_m was from National Bureau of Standards Circ. 500, 1952. ΔH_m was estimated.

Sulfur, Octatomic (S_8)

(Ideal Gas) Mol. Wt. = 256.528

T, °K.	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0	.000	.000	INFINITE	-7.487	25.137	25.137	INFINITE
100	20.831	70.614	132.035	-6.142	25.170	20.481	-44.758
200	32.066	88.909	106.096	-3.437	24.731	15.944	-17.422
298	37.296	102.823	102.823	.000	24.200	11.745	-8.609
300	37.361	103.054	102.824	.069	24.189	11.669	-8.500
400	39.841	114.183	104.324	3.944	19.272	7.755	-4.237
500	41.137	123.227	107.229	7.999	15.823	5.281	-2.308
600	41.887	130.799	110.544	12.153	13.121	3.440	-1.253
700	42.355	137.293	113.912	16.367	10.935	2.195	-.685
800	42.665	142.971	117.197	20.619	-95.413	-9.066	2.477
900	42.882	148.009	120.346	24.897	-94.639	1.681	-.408
1000	43.038	152.536	123.342	29.193	-93.871	12.346	-2.698
1100	43.154	156.643	126.186	33.503	-93.105	22.919	-4.553
1200	43.244	160.402	128.883	37.823	-92.337	33.440	-6.090
1300	43.313	163.866	131.442	42.151	-91.569	43.898	-7.380
1400	43.369	167.078	133.875	46.485	-90.811	54.288	-8.474
1500	43.414	170.072	136.189	50.824	-90.056	64.612	-9.414
1600	43.450	172.875	138.395	55.168	-89.296	74.910	-10.232
1700	43.481	175.510	140.502	59.514	-88.542	85.147	-10.946
1800	43.507	177.996	142.516	63.864	-87.792	95.339	-11.575
1900	43.528	180.349	144.446	68.216	-87.040	105.503	-12.135
2000	43.547	182.582	146.298	72.569	-86.295	115.613	-12.633
2100	43.563	184.707	148.077	76.925	-85.555	125.681	-13.079
2200	43.577	186.734	149.788	81.282	-84.814	135.735	-13.483
2300	43.589	188.672	151.437	85.640	-84.080	145.737	-13.848
2400	43.599	190.527	153.027	90.000	-83.344	155.717	-14.179
2500	43.609	192.307	154.563	94.360	-82.608	165.665	-14.482
2600	43.617	194.018	156.048	98.721	-81.879	175.580	-14.758
2700	43.625	195.664	157.485	103.083	-81.149	185.461	-15.011
2800	43.631	197.250	158.877	107.446	-80.426	195.311	-15.244
2900	43.637	198.782	160.227	111.810	-79.702	205.154	-15.460
3000	43.643	200.261	161.537	116.174	-78.986	214.974	-15.660
3100	43.648	201.692	162.809	120.538	-78.262	224.756	-15.845
3200	43.652	203.078	164.046	124.903	-77.553	234.517	-16.016
3300	43.656	204.421	165.249	129.269	-76.835	244.250	-16.175
3400	43.660	205.725	166.420	133.634	-76.126	253.985	-16.325
3500	43.663	206.990	167.562	138.000	-75.424	263.662	-16.463
3600	43.666	208.220	168.674	142.367	-74.713	273.348	-16.594
3700	43.669	209.417	169.759	146.734	-74.018	283.014	-16.716
3800	43.672	210.581	170.818	151.101	-73.315	292.650	-16.830
3900	43.674	211.716	171.852	155.468	-72.620	302.264	-16.938
4000	43.676	212.822	172.863	159.836	-71.924	311.893	-17.040
4100	43.678	213.900	173.851	164.203	-71.229	321.469	-17.135
4200	43.680	214.953	174.817	168.571	-70.541	331.044	-17.225
4300	43.682	215.981	175.762	172.939	-69.853	340.589	-17.310
4400	43.684	216.985	176.688	177.308	-69.172	350.127	-17.390
4500	43.685	217.966	177.594	181.676	-68.492	359.663	-17.467
4600	43.687	218.927	178.482	186.045	-67.811	369.158	-17.538
4700	43.688	219.866	179.353	190.413	-67.131	378.645	-17.606
4800	43.690	220.786	180.206	194.782	-66.458	388.112	-17.670
4900	43.691	221.687	181.044	199.151	-65.785	397.604	-17.733
5000	43.692	222.570	181.865	203.521	-65.119	407.033	-17.791
5100	43.693	223.435	182.672	207.890	-64.454	416.482	-17.847
5200	43.694	224.283	183.464	212.259	-63.789	425.910	-17.900
5300	43.695	225.116	184.242	216.629	-63.123	435.312	-17.950
5400	43.696	225.932	185.007	220.998	-62.466	444.722	-17.998
5500	43.697	226.734	185.758	225.368	-61.808	454.102	-18.043
5600	43.698	227.521	186.497	229.737	-61.159	463.486	-18.087
5700	43.698	228.295	187.223	234.107	-60.509	472.835	-18.129
5800	43.699	229.055	187.938	238.477	-59.859	482.193	-18.169
5900	43.700	229.802	188.641	242.847	-59.209	491.510	-18.206
6000	43.700	230.536	189.334	247.217	-58.567	500.871	-18.243

Dec. 31, 1960; June 30, 1964

SULFUR, OCTATOMIC (S_8) (IDEAL GAS) MOL. WT. = 256.528

Point group D_{4d}

$\Delta H_f^\circ{}_0 = 25.14 \pm 0.15$ kcal. mole^{-1}

$S_{298.15}^\circ = 102.823$ cal. deg.$^{-1}$ mole^{-1}

$\Delta H_f^\circ{}_{298.15} = 24.20 \pm 0.15$ kcal. mole^{-1}

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.$^{-1}$	ω, cm.$^{-1}$	ω, cm.$^{-1}$
475 (1)	475 (2)	243 (1)
218 (1)	152 (2)	437 (2)
471 (2)	56 (2)	248 (2)
191 (2)	411 (1)	

Bond Distance: S-S = 2.059 ± 0.002 Å

Bond Angle: S-S-S = 107.9 ± 0.6°

$\sigma = 8$

Product of the Moments of Inertia: $I_AI_BI_C = 3.90326 \times 10^{-111}$ g.^{3} cm.^{6}

Heat of Formation.

The vapor pressure of S(c) has been measured by many investigators. Using the seven more recent vapor pressure date, the respective heat of sublimation ($\Delta H_s^\circ{}_{298.15}$) was calculated by both the third and second law methods. The values obtained are tabulated as follows:

Investigator	Temperature Range, °K.	$\Delta H_s^\circ{}_{298.15}$, kcal. mole^{-1} Third Law Value	Second Law Value
West-Menzies [1]	376.6 - 448.8	24.29	21.29
Neumann [2]	332.6 - 362.1	24.35	26.47
Fouretier [3]	304.1 - 351.6	24.36	24.10
Taillade [4]	303.6 - 352.5	24.29	24.87
Bradley [5]	288.3 - 305.7	24.29	23.80
Magee [6]	331.9 - 368.0	24.11	24.44
	332.7 - 367.4	24.12	23.88
Briske [7]	273.2 - 313.2	24.28	24.00

1 W. A. West and A. W. Menzies, J. Phys. Chem. 33, 1880 (1929).
2 K. Neumann, Z. physik. Chem. A171, 416 (1934).
3 G. Fouretier, Compt. rend. 218, 194 (1944).
4 M. Taillade, Compt. rend. 218, 836 (1944).
5 R. S. Bradley, Proc. Roy. Soc. (London) A 205, 553 (1951).
6 D. W. Magee, Ph. D. Thesis, The Ohio State University, 1955.
7 C. Briske, N. H. Hartshorne and D. R. Stranks, J. Chem. Soc. (London), 1200 (1960).

Due to the presence of S_6(g) in S_8(g), the measured total pressures were corrected to give the partial pressures of S_8(g) for the first five sets of vapor pressure data, according to D. W. Scott, U. S. Bureau of Mines, Bartlesville, Oklahoma, private communication, May 22, 1964. However, the magnitude of the correction is only 0.1 - 0.2 kcal. mole^{-1}. The adopted value is the weighted average of both the third and second law values.

Heat Capacity and Entropy.

The vibrational frequencies were taken from D. W. Scott, J. P. McCullough and F. H. Kruse, "Vibrational Assignment and Force Constants of S_8 (condensed States) from a Normal-Coordinate Treatment", Prepublication Report 64, U. S. Bureau of Mines, May 20, 1963. Four of the eighteen frequencies, i.e. 86(2) and 218(2) cm.$^{-1}$, were changed to 56(2) and 248(2) cm.$^{-1}$, respective, suggested by D. W. Scott, loc. cit., private communication, April 23, 1964. The molecular structure and bond distance and angle were reported by J. Donohur, A. Caron and E. Goldish, J. Am. Chem. Soc. 83, 3748 (1961). The three principle moments of inertia are: $I_A = I_B = 1.28594 \times 10^{-37}$ and $I_C = 2.36042 \times 10^{-37}$ g. cm.^{2}.

Silicon (Si)

(Reference State) GFW = 28.086

	gibbs/mol			kcal/mol			
T, °K	$C_p°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	-.769	.000	.000	.000
100	1.737	.916	7.966	-.705	.000	.000	.000
200	3.737	2.788	4.908	-.424	.000	.000	.000
298	4.780	4.498	4.498	.000	.000	.000	.000
300	4.792	4.528	4.498	.009	.000	.000	.000
400	5.292	5.983	4.693	.516	.000	.000	.000
500	5.576	7.197	5.076	1.060	.000	.000	.000
600	5.773	8.231	5.518	1.628	.000	.000	.000
700	5.928	9.133	5.971	2.213	.000	.000	.000
800	6.061	9.933	6.417	2.813	.000	.000	.000
900	6.184	10.655	6.849	3.425	.000	.000	.000
1000	6.295	11.312	7.263	4.049	.000	.000	.000
1100	6.400	11.917	7.659	4.684	.000	.000	.000
1200	6.500	12.478	8.037	5.329	.000	.000	.000
1300	6.600	13.002	8.399	5.984	.000	.000	.000
1400	6.700	13.495	8.746	6.649	.000	.000	.000
1500	6.800	13.961	9.078	7.324	.000	.000	.000
1600	6.900	14.403	9.397	8.009	.000	.000	.000
1700	6.500	21.941	9.767	20.697	.000	.000	.000
1800	6.500	22.313	10.454	21.347	.000	.000	.000
1900	6.500	22.664	11.087	21.997	.000	.000	.000
2000	6.500	22.998	11.674	22.647	.000	.000	.000
2100	6.500	23.315	12.221	23.297	.000	.000	.000
2200	6.500	23.617	12.732	23.947	.000	.000	.000
2300	6.500	23.906	13.212	24.597	.000	.000	.000
2400	6.500	24.183	13.663	25.247	.000	.000	.000
2500	6.500	24.448	14.089	25.897	.000	.000	.000
2600	6.500	24.703	14.493	26.547	.000	.000	.000
2700	6.500	24.948	14.876	27.197	.000	.000	.000
2800	6.500	25.185	15.240	27.847	.000	.000	.000
2900	6.500	25.413	15.586	28.497	.000	.000	.000
3000	6.500	25.633	15.918	29.147	.000	.000	.000
3100	6.500	25.846	16.235	29.797	.000	.000	.000
3200	6.500	26.053	16.538	30.447	.000	.000	.000
3300	6.500	26.253	16.830	31.097	.000	.000	.000
3400	6.500	26.447	17.110	31.747	.000	.000	.000
3500	6.500	26.635	17.379	32.397	.000	.000	.000
3600	5.508	52.990	18.265	125.008	.000	.000	.000
3700	5.513	53.141	19.206	125.559	.000	.000	.000
3800	5.516	53.288	20.101	126.110	.000	.000	.000
3900	5.519	53.431	20.954	126.662	.000	.000	.000
4000	5.521	53.571	21.767	127.214	.000	.000	.000
4100	5.523	53.707	22.545	127.767	.000	.000	.000
4200	5.524	53.840	23.288	128.319	.000	.000	.000
4300	5.524	53.970	24.000	128.871	.000	.000	.000
4400	5.524	54.097	24.683	129.424	.000	.000	.000
4500	5.524	54.222	25.338	129.976	.000	.000	.000
4600	5.523	54.343	25.967	130.528	.000	.000	.000
4700	5.522	54.462	26.572	131.081	.000	.000	.000
4800	5.521	54.578	27.155	131.633	.000	.000	.000
4900	5.520	54.692	27.715	132.185	.000	.000	.000
5000	5.519	54.803	28.256	132.737	.000	.000	.000
5100	5.519	54.913	28.778	133.289	.000	.000	.000
5200	5.518	55.020	29.281	133.841	.000	.000	.000
5300	5.518	55.125	29.768	134.392	.000	.000	.000
5400	5.519	55.228	30.238	134.944	.000	.000	.000
5500	5.520	55.329	30.694	135.496	.000	.000	.000
5600	5.521	55.429	31.134	136.048	.000	.000	.000
5700	5.524	55.527	31.562	136.600	.000	.000	.000
5800	5.527	55.623	31.976	137.153	.000	.000	.000
5900	5.531	55.717	32.377	137.706	.000	.000	.000
6000	5.536	55.810	32.767	138.259	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

SILICON (Si) (REFERENCE STATE) GFW = 28.086

0 to 1685°K Crystal

1685 to 3513.8°K Liquid

3513.8 to 6000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Silicon (Si)

(Crystal) GFW = 28.086

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- .769	.000	.000	INFINITE
100	1.737	.916	7.066	- .705	.000	.000	.000
200	3.737	2.788	4.908	- .424	.000	.000	.000
298	4.780	4.498	4.498	.000	.000	.000	.000
300	4.792	4.528	4.498	.009	.000	.000	.000
400	5.292	5.983	4.693	.516	.000	.000	.000
500	5.576	7.197	5.076	1.060	.000	.000	.000
600	5.773	8.231	5.518	1.628	.000	.000	.000
700	5.928	9.133	5.971	2.213	.000	.000	.000
800	6.061	9.933	6.417	2.813	.000	.000	.000
900	6.184	10.655	6.849	3.425	.000	.000	.000
1000	6.295	11.312	7.263	4.049	.000	.000	.000
1100	6.400	11.917	7.659	4.684	.000	.000	.000
1200	6.500	12.478	8.037	5.329	.000	.000	.000
1300	6.600	13.002	8.399	5.984	.000	.000	.000
1400	6.700	13.495	8.746	6.649	.000	.000	.000
1500	6.800	13.961	9.078	7.324	.000	.000	.000
1600	6.900	14.403	9.397	8.009	.000	.000	.000
1700	7.000	14.824	9.704	8.704	- 11.993	.106	- .014
1800	7.100	15.227	10.000	9.409	- 11.938	.817	- .099
1900	7.200	15.614	10.285	10.124	- 11.873	1.522	- .175
2000	7.300	15.985	10.561	10.849	- 11.798	2.228	- .243
2100	7.400	16.344	10.828	11.584	- 11.713	2.926	- .305
2200	7.500	16.691	11.086	12.329	- 11.618	3.619	- .360
2300	7.600	17.026	11.337	13.084	- 11.513	4.311	- .410
2400	7.700	17.352	11.581	13.849	- 11.398	4.996	- .455
2500	7.800	17.668	11.818	14.624	- 11.273	5.677	- .496

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966

SILICON (Si) (CRYSTAL) GFW = 28.086

$\Delta Hf^\circ_0 = 0$ kcal/mol

$S^\circ_{298.15} = 4.498 \pm 0.01$ gibbs/mol

$\Delta Hf^\circ_{298.15} = 0$ kcal/mol

$T_m = 1685 \pm 3$ °K

$\Delta Hm^\circ = 12.0 \pm 0.1$ kcal/mol

$\Delta Hs^\circ_{298.15} = 107.7 \pm 1$ kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities are based on the precise data (8-300°K) of Flubacher, Leadbetter and Morrison. The entropy is obtained from the heat capacity using $S^\circ_8 = 0.0003$ eu. The selected values are consistent with recent data of Keesom and Seidel (1.2 - 4.2°K) and Kalishevich et al. (60-300°K). Earlier data have been reviewed by R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965.

High temperature studies are summarized below, along with the pertinent low temperature studies. The selected heat capacities above 300°K are obtained from a Shomate plot of the adopted low temperature heat capacities and the enthalpies reported or derived from the work of Dennison (1963), Kantor et al. (1960), Olette (1956), Serebrennikov and Gel'd (1952), and Magnus (1923). Discrepancies are apparent in the enthalpy data, particularly in the range of 370 to 1100°K, where only the recent study of Dennison made use of a high purity sample. Enthalpies from Dennison join most smoothly with the low temperature Cp° but deviate increasingly at higher temperatures, being 1-2% lower than the other measurements above 1000°K. The selected functions agree with Dennison below 600°K, with Magnus from 600 to 1200°K, and with Kantor et al. above 1200°K. The resulting heat capacities are slightly different from those selected by Hultgren et al., loc. cit.; the latter are 0.07 gibbs/mol higher at 800°K and 0.21 gibbs/mol lower at the melting point.

Investigators	Method	Quantity Reported	T Range, °K	Sample
1. Flubacher et al. (1959)	Calorimetry	Cp°	7.7 - 300	Single crystal, 3mm pieces, Resistance (300°K) = 100 ohm cm, Carrier Concentration ⩽ 10^{15} cm^{-3}
2. Keesom et al. (1959)	Calorimetry	Specific Heat	1.2 - 4.2	
3. Kalishevich et al. (1965)	Calorimetry	Cp°	60 - 300	99.999%
4. Gerlich et al. (1965)	Temperature Modulation	Cp°	300 - 900	Resistance (300°K) = 0.027 ohm cm, Carrier Concentration = 10^{19} cm^{-3}
5. Dennison (1963)	Drop Calorimetry	Specific Heat	273 - 1373	Resistance (300°K) = 107 ohm cm
6. Kantor et al. (1960)	Drop Calorimetry	Enthalpy Equation	1148 - 1685	"Highly purified"
7. Olette (1956)	Drop Calorimetry	Specific Enthalpy	1467 - 1685	99.99%
8. Serebrennikov et al.	Drop Calorimetry	Specific Enthalpy	302 - 1556	99.3%
9. Magnus (1923)	Drop Calorimetry	Specific Enthalpy	372 - 1175	99.2%

Reference:
1. P. Flubacher, A. J. Leadbetter and J. A. Morrison, Phil. Mag. 4, 273 (1959).
2. P. H. Keesom and G. Seidel, Phys. Rev. 113, 33 (1959).
3. G. I. Kalishevich, P. V. Gel'd. and R. P. Krentsis, Russ. J. Phys. Chem. 39, 1602 (1965).
4. D. Gerlich, B. Abeles and R. E. Miller, J. Appl. Phys. 36, 76 (1965).
5. D. H. Dennison quoted by H. R. Shanks et al., Phys. Rev. 130, 1743 (1963).
6. P. B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960).
7. M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956, 18-26 (Pub. 1958).
8. N. N. Serebrennikov and P. V. Gel'd, Doklad. Akad. Nauk SSSR 87, 1021 (1952).
9. A. Magnus, Ann. Physik 70, 303 (1923).

Melting Data.

See the Si(l) table for details.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Si(g) and Si(c).

Silicon (Si)
(Liquid) GFW = 28.086

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.500	10.626	10.626	.000	11.585	9.758	-7.153
300	6.500	10.666	10.626	.012	11.588	9.747	-7.100
400	6.500	12.536	10.881	.662	11.731	9.110	-4.977
500	6.500	13.987	11.363	1.312	11.837	8.442	-3.690
600	6.500	15.172	11.902	1.962	11.919	7.754	-2.825
700	6.500	16.174	12.442	2.612	11.984	7.055	-2.203
800	6.500	17.042	12.964	3.262	12.034	6.347	-1.734
900	6.500	17.807	13.460	3.912	12.072	5.635	-1.368
1000	6.500	18.492	13.930	4.562	12.098	4.915	-1.075
1100	6.500	19.112	14.373	5.212	12.113	4.199	-.834
1200	6.500	19.677	14.792	5.862	12.118	3.479	-.634
1300	6.500	20.197	15.188	6.512	12.113	2.760	-.464
1400	6.500	20.679	15.563	7.162	12.098	2.040	-.319
1500	6.500	21.128	15.920	7.812	12.073	1.323	-.193
1600	6.500	21.547	16.258	8.462	12.038	.608	-.083
1700	6.500	21.941	16.581	9.112	.000	.000	.000
1800	6.500	22.313	16.889	9.762	.000	.000	.000
1900	6.500	22.664	17.184	10.412	.000	.000	.000
2000	6.500	22.997	17.466	11.062	.000	.000	.000
2100	6.500	23.315	17.737	11.712	.000	.000	.000
2200	6.500	23.617	17.998	12.362	.000	.000	.000
2300	6.500	23.906	18.249	13.012	.000	.000	.000
2400	6.500	24.183	18.490	13.662	.000	.000	.000
2500	6.500	24.448	18.723	14.312	.000	.000	.000
2600	6.500	24.703	18.948	14.962	.000	.000	.000
2700	6.500	24.948	19.166	15.612	.000	.000	.000
2800	6.500	25.185	19.377	16.262	.000	.000	.000
2900	6.500	25.413	19.581	16.912	.000	.000	.000
3000	6.500	25.633	19.779	17.562	.000	.000	.000
3100	6.500	25.846	19.971	18.212	.000	.000	.000
3200	6.500	26.053	20.158	18.862	.000	.000	.000
3300	6.500	26.253	20.340	19.512	.000	.000	.000
3400	6.500	26.447	20.517	20.162	.000	.000	.000
3500	6.500	26.635	20.689	20.812	.000	.000	.000
3600	6.500	26.818	20.856	21.462	-91.961	2.255	-.137
3700	6.500	26.996	21.020	22.112	-91.862	4.875	-.288
3800	6.500	27.170	21.180	22.762	-91.763	7.485	-.431
3900	6.500	27.338	21.335	23.412	-91.665	10.098	-.566
4000	6.500	27.503	21.487	24.062	-91.567	12.705	-.694
4100	6.500	27.663	21.636	24.712	-91.470	15.310	-.816
4200	6.500	27.820	21.782	25.362	-91.372	17.912	-.932
4300	6.500	27.973	21.924	26.012	-91.274	20.513	-1.043
4400	6.500	28.122	22.063	26.662	-91.177	23.113	-1.148
4500	6.500	28.269	22.199	27.312	-91.079	25.710	-1.249

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

SILICON (Si) (LIQUID) GFW = 28.086

$S^\circ_{298.15}$ = 10.626 gibbs/mol

Tm = 1685 ± 3°K

Tb = [3513.8] °K (to monomer only)

Tb = [3492] °K (to equilibrium mixture)

$\Delta Hf^\circ_{298.15}$ = 11.585 kcal/mol

ΔHm° = 12.0 ± 0.1 kcal/mol

ΔHv° = [92.047] kcal/mol

ΔHv° = [85.8] kcal/mol

Heat of Formation.

The heat of formation is obtained from that of the crystal by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

Enthalpy data for high purity samples in quartz or vitreous silica capsules have been reported for the range 1698-1915°K by P.B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960), and for the range 1686-1825°K by M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956, 18-26 (Pub. 1958). Due to the limited temperature range and the experimental uncertainty, the data do not appear to justify more than a constant heat capacity. A value of 6.5 gibbs/mol is selected, intermediate between the values of 6.75 and 6.15 obtained from the separate experiments. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

Modern determinations of the melting point range from 1683 ± 1 to 1690 ± 4 °K, the former from the specific volume study of L. D. Lucas and G. Urbain, Compt. Rend. 255, 2414 (1962), and the latter from the enthalpy study of Kantor et al. The selected value of Tm = 1685°K is taken from R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, who have reviewed the melting data. The heat of melting is calculated from the selected enthalpy of the crystal and the liquid enthalpy measurements of Kantor et al. and Olette, who reported comparable values of ΔHm° = 11.95 ± 0.18 and 12.095 ± 0.1 kcal/mol, respectively.

Vaporization Data.

Tb is calculated as the temperature for which the ΔGr° = 0 for Si(l) = Si(g). ΔHv° is calculated as the difference between ΔHf°(g) and ΔHf°(l) at Tb. The normal boiling for the equilibrium vapor is calculated as the temperature at which Si, Si_2 and Si_3 attain a total pressure of one atm. ΔHv° at this temperature is calculated as the enthalpy of vaporization of one GFW of liquid to vapor containing 92.1, 7.0 and 0.9 mole percent of monomer, dimer and trimer, respectively. Tetramer and higher polymers, which are ignored in the equilibrium calculation, are probably negligible at this temperature.

Silicon, Monatomic (Si)

(Ideal Gas) GFW = 28.086

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.805	106.664	106.664	INFINITE
100	6.697	33.646	45.140	-1.149	107.256	103.983	-227.254
200	5.687	37.931	40.617	-.537	107.587	100.558	-109.885
298	5.318	40.121	40.121	.000	107.700	97.079	-71.161
300	5.314	40.154	40.121	.010	107.701	97.013	-70.674
400	5.166	41.660	40.328	.533	107.717	93.446	-51.057
500	5.095	42.804	40.713	1.045	107.685	89.882	-39.287
600	5.056	43.729	41.141	1.553	107.625	86.326	-31.444
700	5.033	44.506	41.568	2.057	107.544	82.783	-25.846
800	5.019	45.178	41.978	2.560	107.447	79.251	-21.650
900	5.012	45.768	42.367	3.061	107.336	75.734	-18.391
1000	5.011	46.296	42.734	3.562	107.213	72.229	-15.786
1100	5.016	46.774	43.080	4.064	107.080	68.737	-13.657
1200	5.027	47.211	43.406	4.566	106.937	65.257	-11.885
1300	5.043	47.614	43.715	5.069	106.785	61.790	-10.388
1400	5.063	47.988	44.007	5.574	106.625	58.335	-9.107
1500	5.087	48.338	44.284	6.082	106.458	54.892	-7.998
1600	5.113	48.668	44.548	6.592	106.283	51.459	-7.029
1700	5.142	48.978	44.799	7.105	94.108	48.145	-6.189
1800	5.171	49.273	45.040	7.620	93.973	45.445	-5.518
1900	5.202	49.553	45.270	8.139	93.842	42.753	-4.918
2000	5.232	49.821	45.491	8.660	93.713	40.067	-4.378
2100	5.261	50.077	45.703	9.185	93.588	37.388	-3.891
2200	5.289	50.322	45.908	9.713	93.466	34.715	-3.449
2300	5.316	50.558	46.105	10.243	93.346	32.046	-3.045
2400	5.341	50.785	46.295	10.776	93.229	29.384	-2.676
2500	5.364	51.003	46.479	11.311	93.114	26.726	-2.336
2600	5.386	51.214	46.657	11.848	93.001	24.073	-2.024
2700	5.406	51.418	46.830	12.388	92.891	21.422	-1.734
2800	5.423	51.615	46.997	12.930	92.783	18.779	-1.466
2900	5.439	51.805	47.160	13.473	92.676	16.139	-1.216
3000	5.454	51.990	47.318	14.017	92.570	13.499	-.983
3100	5.466	52.169	47.471	14.563	92.466	10.865	-.766
3200	5.478	52.343	47.621	15.111	92.364	8.236	-.562
3300	5.487	52.511	47.766	15.659	92.262	5.610	-.372
3400	5.495	52.675	47.908	16.208	92.161	2.986	-.192
3500	5.502	52.835	48.047	16.758	92.061	.361	-.023
3600	5.508	52.990	48.182	17.308	.000	.000	.000
3700	5.513	53.141	48.314	17.859	.000	.000	.000
3800	5.516	53.288	48.443	18.411	.000	.000	.000
3900	5.519	53.431	48.569	18.963	.000	.000	.000
4000	5.521	53.571	48.692	19.515	.000	.000	.000
4100	5.523	53.707	48.813	20.067	.000	.000	.000
4200	5.524	53.840	48.931	20.619	.000	.000	.000
4300	5.524	53.970	49.047	21.172	.000	.000	.000
4400	5.524	54.097	49.160	21.724	.000	.000	.000
4500	5.524	54.222	49.271	22.276	.000	.000	.000
4600	5.523	54.343	49.380	22.829	.000	.000	.000
4700	5.522	54.462	49.487	23.381	.000	.000	.000
4800	5.521	54.578	49.592	23.933	.000	.000	.000
4900	5.520	54.692	49.695	24.485	.000	.000	.000
5000	5.519	54.803	49.796	25.037	.000	.000	.000
5100	5.519	54.913	49.895	25.589	.000	.000	.000
5200	5.518	55.020	49.993	26.141	.000	.000	.000
5300	5.518	55.125	50.089	26.693	.000	.000	.000
5400	5.519	55.228	50.183	27.245	.000	.000	.000
5500	5.520	55.329	50.275	27.797	.000	.000	.000
5600	5.521	55.429	50.367	28.349	.000	.000	.000
5700	5.524	55.527	50.456	28.901	.000	.000	.000
5800	5.527	55.623	50.544	29.453	.000	.000	.000
5900	5.531	55.717	50.631	30.006	.000	.000	.000
6000	5.536	55.810	50.717	30.560	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

Ground State Configuration $^3P_0$

$S^\circ_{298.15}$ = 40.121 gibbs/mol

ΔHf°_0 = 106.66 ± 1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 107.7 ± 1 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	45,303	15	50,533	9	56,699	9	58,782	28	61,489	75
77.12	3	47,284	3	51,612	1	56,780	3	58,802	3	62,720	117
223.16	5	47,352	5	53,362	7	57,094	15	58,893	7	62,727	69
6,298.86	5	48,161	15	53,387	3	57,402	9	59,077	15	63,405	18
15,394.37	1	49,128	9	54,226	15	57,489	21	59,108	56	63,653	81
33,326	5	49,400	3	54,425	9	57,542	3	59,674	21	63,707	45
39,860	9	49,966	21	54,871	3	57,798	5	60,706	36	64,456	75
40,992	3	50,189	5	56,503	5	58,311	1	61,278	72	[65,300]	[200]

Heat of Formation.

The heat of formation is the heat of sublimation, $\Delta Hs^\circ_{298.15}$ = 107.7 kcal/mol, selected from third law analyses of the vapor pressure data reviewed below. Langmuir, Knudsen and transport studies are all in satisfactory agreement throughout the range of 1400 - 2000°K. In addition, O. C. Trulson and P. O. Schissel, Condensation Evaporation Solids Proc. Symp., Dayton, Ohio 1962, 313-17 (Pub. 1964), have experimentally verified that the vaporization coefficient is about 0.8 at 1300°K. This was accomplished by mass spectrometric determination of the Langmuir and Knudsen rates of sublimation from a single crystal sample in a cell designed to give Knudsen effusion from one end and free evaporation from the other end.

The recent studies confirm the mass spectrometric data of R. E. Honig, J. Chem. Phys. 22, 1610 (1954), and substantiate the author's postulate that vapor pressures obtained in early boiling point experiments are too large due to reaction or decomposition of the alumina and silicon carbide containers. In their review of the earlier experiments, R. Hultgren, R. L Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, calculated apparent heats of sublimation of less than 90 kcal/mol from the data. Neither these values nor the value of 92 kcal/mol, obtained from the Knudsen data (1485 - 1593°K) of A. V. Tseplyaeva, Yu. A. Priselkov and V. V. Karelin, Vestnik Moskov. Univ., Ser. 2 Khim. 15, No. 5, 36 (1960), were considered in the JANAF selection. It is not clear why Tseplyaeva et al. obtain pressures larger by a factor of 200 from their molybdenum cell.

Source	Method	Container or Support	T Range (°K)	No. of Points	ΔHs°_{298} (kcal/mol) 2nd Law	3rd Law	Drift eu
1. Gulbransen (1966)	Langmuir	Quartz fiber	1373-1623	10	104.9 ± 4.1	107.15	1.0 ± 2.8
2. Nannichi (1963)	Langmuir	Tantalum	1399-1527	4	95.3 ± 6.0	107.99	8.6 ± 4.1
3. Batdorf (1959)	Langmuir	Tantalum	1473-1600	12	108.8 ± 5.7	109.02	0.5 ± 3.7
4. Davis (1961)	Knudsen	SiC-lined graphite	1848-2003*	11	112.6 ± 12	108.50	-2.2 ± 6.2
5. Grieveson (1959)	Knudsen	SiC-lined graphite	1640-1684	3	97.5 ± 0.2	107.72	6.1 ± 0.1
Grieveson (1959)	Knudsen	SiC-lined graphite	1701-1900*	9	109.7 ± 0.1	107.74	-1.1 ± 0.04
Grieveson (1959)	Transport	SiC-lined graphite and $MoSi_2$	1853*	14	-	107.73	-
6. Drowart (1960)	Mass Spec.	SiC-lined graphite	1703-2160*	12	108 ± 1.0	107.00	-0.5 ± 0.5

*Data for liquid phase.

1. E. A. Gulbransen, K. F. Andrew and F. A. Brassart, J. Electrochem. Soc. 113, 834 (1966).
2. Y. Nannichi, Japan J. Appl. Phys. 2, 586 (1963), data given graphically.
3. R. L. Batdorf and F. M. Smits, J. Appl. Phys. 30, 259 (1959), data given graphically.
4. S. G. Davis, D. F. Anthrop and A. W. Searcy, J. Chem. Phys. 34, 659 (1961).
5. P. Grieveson and C. B. Alcock, Special Ceramics, Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208 (Pub. 1960). Points above 1900°K are omitted.
6. J. Drowart and G. De Maria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, London, 1960.

Heat Capacity and Entropy.

Electronic levels and quantum weights are from L. J. Radziemski and K. L. Andrew, J. Opt. Soc. Am. 55, 474 (1965), and V. Kaufman, L. J. Radziemski and K. L. Andrew, ibid. 56, 911 (1966). An additional level with quantum weight of 200 is estimated above the observed levels and below the dissociation limit; however, the effect of this level on the entropy at 6000°K is negligible. Levels above 39000 cm^{-1} are averaged.

Silicon, Diatomic (Si_2)

(Ideal Gas) GFW = 56.172

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-2.214	140.324	140.324	INFINITE
100	7.029	46.655	61.829	-1.517	140.893	136.410	-298.124
200	7.692	51.715	55.632	-.783	141.065	131.837	-144.064
298	8.234	54.895	54.895	.000	141.000	127.315	-93.325
300	8.242	54.946	54.895	.015	140.997	127.230	-92.687
400	8.658	57.375	55.224	.861	140.829	122.665	-67.021
500	9.079	59.352	55.857	1.747	140.627	118.148	-51.643
600	9.499	61.045	56.584	2.676	140.420	113.671	-41.404
700	9.867	62.537	57.330	3.645	140.219	109.230	-34.103
800	10.151	63.875	58.066	4.647	140.021	104.814	-28.634
900	10.343	65.082	58.779	5.672	139.822	100.428	-24.387
1000	10.453	66.178	59.465	6.713	139.615	96.061	-20.994
1100	10.502	67.177	60.122	7.761	139.393	91.716	-18.222
1200	10.507	68.091	60.748	8.812	139.154	87.392	-15.916
1300	10.485	68.932	61.346	9.861	138.893	83.087	-13.968
1400	10.447	69.707	61.916	10.908	138.610	78.806	-12.302
1500	10.401	70.427	62.460	11.951	138.303	74.545	-10.861
1600	10.354	71.096	62.979	12.989	137.970	70.306	-9.603
1700	10.309	71.723	63.475	14.022	113.628	66.298	-8.523
1800	10.268	72.311	63.950	15.050	113.356	63.523	-7.713
1900	10.232	72.865	64.404	16.075	113.081	60.761	-6.989
2000	10.200	73.389	64.841	17.097	112.803	58.017	-6.340
2100	10.174	73.886	65.260	18.116	112.522	55.284	-5.753
2200	10.153	74.359	65.663	19.132	112.238	52.563	-5.222
2300	10.135	74.810	66.050	20.146	111.952	49.857	-4.737
2400	10.122	75.241	66.425	21.159	111.665	47.165	-4.295
2500	10.112	75.654	66.785	22.171	111.377	44.482	-3.889
2600	10.106	76.050	67.134	23.182	111.088	41.813	-3.515
2700	10.101	76.432	67.472	24.192	110.798	39.151	-3.169
2800	10.099	76.799	67.798	25.202	110.508	36.507	-2.849
2900	10.099	77.153	68.115	26.212	110.218	33.870	-2.552
3000	10.100	77.496	68.422	27.222	109.928	31.239	-2.276
3100	10.103	77.827	68.720	28.232	109.638	28.619	-2.018
3200	10.107	78.148	69.009	29.242	109.348	26.014	-1.777
3300	10.111	78.459	69.291	30.253	109.059	23.414	-1.551
3400	10.117	78.761	69.565	31.265	108.771	20.923	-1.338
3500	10.124	79.054	69.832	32.277	108.483	18.239	-1.139
3600	10.131	79.339	70.092	33.289	-75.727	20.181	-1.225
3700	10.139	79.617	70.346	34.303	-75.815	22.945	-1.349
3800	10.147	79.887	70.594	35.317	-75.903	25.515	-1.467
3900	10.156	80.151	70.835	36.332	-75.992	28.181	-1.579
4000	10.165	80.408	71.071	37.349	-76.080	30.956	-1.686
4100	10.175	80.660	71.302	38.365	-76.169	33.523	-1.787
4200	10.185	80.905	71.528	39.383	-76.255	36.200	-1.884
4300	10.195	81.145	71.749	40.402	-76.340	38.879	-1.976
4400	10.206	81.379	71.965	41.422	-76.426	41.560	-2.064
4500	10.218	81.609	72.177	42.444	-76.508	44.249	-2.149
4600	10.229	81.833	72.384	43.466	-76.590	46.934	-2.230
4700	10.241	82.053	72.588	44.489	-76.673	49.621	-2.307
4800	10.254	82.269	72.787	45.514	-76.752	52.306	-2.382
4900	10.266	82.481	72.983	46.540	-76.830	54.995	-2.453
5000	10.279	82.688	73.175	47.567	-76.907	57.683	-2.521
5100	10.293	82.892	73.363	48.596	-76.982	60.381	-2.588
5200	10.306	83.092	73.548	49.626	-77.056	63.074	-2.651
5300	10.320	83.288	73.730	50.657	-77.127	65.772	-2.712
5400	10.335	83.481	73.909	51.690	-77.198	68.467	-2.771
5500	10.349	83.671	74.085	52.724	-77.268	71.161	-2.828
5600	10.364	83.858	74.258	53.760	-77.336	73.864	-2.883
5700	10.379	84.041	74.428	54.797	-77.403	76.571	-2.936
5800	10.395	84.222	74.595	55.836	-77.470	79.269	-2.987
5900	10.410	84.400	74.760	56.876	-77.536	81.965	-3.036
6000	10.426	84.575	74.922	57.918	-77.600	84.670	-3.084

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

SILICON, DIATOMIC (Si_2) (IDEAL GAS) GFW = 56.172

Ground State Configuration $^3\Sigma_g^-$

$S°_{298.15}$ = 54.895 gibbs/mol

$\Delta Hf°_0$ = 140.3 ± 3 kcal/mol

$\Delta Hf°_{298.15}$ = 141 ± 3 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$^3\Sigma_g^-$	0	3	$[^1\Delta_g]$	[10000]	[2]	$^3\Pi_g$	[30000]	6
$^3\Pi_u$	[2000]	6	$[^1\Sigma_g^+]$	[13000]	[1]	$^3\Sigma_u^-$	30769	3
$[^1\Sigma_g^+]$	[6000]	[1]	$[^3\Sigma_u^+]$	[20000]	[3]	$[^1\Pi_g]$	[40000]	[2]
$[^1\Pi_u]$	[8000]	[2]	$^3\Sigma_u^-$	24583	3	$[^1\Sigma_u^+]$	[45000]	[1]
						$^3\Sigma_u^-$	46762	3

ω_e = 510.98 cm^{-1} $\omega_e x_e$ = 2.02 cm^{-1} σ = 2

B_e = 0.2390 cm^{-1} α_e = 0.0013 cm^{-1} r_e = 2.246 Å

Heat of Formation.

The selected value is based on the spectroscopic and equilibrium data summarized below. Verma and Warsop[1] concluded from analysis of the absorption spectra that $D_0°$ = 70 ± 4 kcal/mol. Predissociation of the H state suggested the upper limit $D_0° \leq 74.0$, while linear Birge-Sponer extrapolations of the H and K states gave 78.4 and 68.9 kcal/mol for the ground state. By assuming that the true extrapolation would not reduce the linear extrapolation for the H state by more than half, i.e. from 26 to 13 kcal, the authors arrived at the lower limit of $D_0° \geq 65.5$ for the ground state.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite[2], SiC-silicon[3] and boron-carbon-silicon[4]. Third law analysis of the partial pressures of Si_2 and Si over the three systems yields $D_0°$ values of 73.3, 74.3 and 70.4 kcal/mol, which are in good agreement with the spectroscopic values. The selected value, $\Delta Hf°_{298}$ = 141 ± 3 kcal/mol, corresponds to $D_0°$ = 73.0 kcal/mol.

Source	Method	Range, T°K	No. of Points	$\Delta Hr°_{298}$ (kcal/mol)*		Drift (eu)	$\Delta Hf°_{298}$ (kcal/mol)
				2nd law	3rd law		
Verma (1963)	Prediss. of H state		-	≤75.4		-	≥140.0
	LBX of K state		-	70.3			145.1
	Extrap. of H state		-	≥66.9			≤148.5
Drowart (1958)	Mass Spec.	2149-2316	7	95.3±7.1	74.68	-9±3	140.7
Drowart (1960)	Mass Spec.	1703-2160	9	81.0±1.1	75.71	-2.7±0.6	139.7
Verhaegen (1964)	Mass Spec.	2166-2344	4	68 ± 16	71.76	2±7	143.6

*For the reaction $Si_2(g) = 2\ Si(g)$

Heat Capacity and Entropy.

Vibrational and rotational constants are those obtained by Verma and Warsop[1] through combination of their data for the H-X system with those of Douglas[5]. Observation of the same H-X system in matrix isolation by Weltner and McLeod[6] confirms that the lower state is the ground state. Comparison with the isoelectronic molecules C_2, BN, BeO and MgO (7,8,9,10) suggests that there are several possible low-lying excited states in Si_2. Tentative estimates for these levels are given above, based on this comparison and on the observed states (1,5). These estimates are relatively uncertain and probably yield an upper limit for the entropy at temperatures where Si_2 is significant. A probable lower limit may be obtained by increasing the two $^3\Pi$ states by 8000 cm^{-1} and omitting the other estimated levels. This would reduce the entropy by 1.7 eu at 2000°K, corresponding to a change of 3.4 kcal/mol in ΔHr° values based on equilibrium data.

References.

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2. J. Drowart, G. DeMaria and M. G. Inghram, J. Chem. Phys. 29, 1015 (1958).
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Silicon, Triatomic (Si_3)

(Ideal Gas) GFW = 84.258

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.088	151.219	151.219	INFINITE
100	9.357	51.599	74.779	- 2.318	151.797	146.912	- 321.076
200	11.927	58.983	65.172	- 1.238	152.034	141.910	- 155.072
298	13.158	64.002	64.002	.000	152.000	136.941	- 100.380
300	13.174	64.084	64.002	.024	151.997	136.847	- 99.693
400	13.811	67.971	64.528	1.377	151.829	131.820	- 72.023
500	14.162	71.094	65.539	2.777	151.597	126.846	- 55.444
600	14.371	73.696	66.688	4.205	151.321	121.919	- 44.409
700	14.504	75.922	67.852	5.649	151.010	117.044	- 36.543
800	14.594	77.865	68.985	7.104	150.665	112.212	- 30.655
900	14.656	79.587	70.069	8.567	150.292	107.432	- 26.088
1000	14.702	81.134	71.099	10.035	149.888	102.690	- 22.443
1100	14.738	82.537	72.076	11.507	149.455	97.990	- 19.469
1200	14.766	83.821	73.002	12.982	148.995	93.331	- 16.998
1300	14.790	85.004	73.881	14.460	148.508	88.711	- 14.914
1400	14.814	86.101	74.715	15.940	147.993	84.131	- 13.133
1500	14.838	87.123	75.508	17.423	147.451	79.591	- 11.596
1600	14.863	88.082	76.264	18.908	146.881	75.084	- 10.256
1700	14.893	88.984	76.986	20.396	110.305	70.931	- 9.119
1800	14.926	89.836	77.677	21.886	109.845	68.631	- 8.333
1900	14.964	90.644	78.338	23.381	109.390	66.351	- 7.632
2000	15.007	91.413	78.973	24.879	108.938	64.100	- 7.005
2100	15.055	92.146	79.583	26.382	108.49.	61.869	- 6.439
2200	15.107	92.847	80.170	27.890	108.049	59.658	- 5.926
2300	15.164	93.520	80.736	29.404	107.613	57.468	- 5.461
2400	15.224	94.167	81.282	30.923	107.182	55.299	- 5.036
2500	15.288	94.790	81.810	32.449	106.758	53.143	- 4.646
2600	15.354	95.390	82.321	33.981	106.340	51.009	- 4.288
2700	15.423	95.971	82.816	35.520	105.929	48.886	- 3.957
2800	15.493	96.533	83.296	37.066	105.525	46.786	- 3.652
2900	15.564	97.078	83.762	38.618	105.127	44.694	- 3.368
3000	15.636	97.607	84.214	40.178	104.737	42.613	- 3.104
3100	15.707	98.121	84.655	41.746	104.355	40.547	- 2.859
3200	15.777	98.621	85.083	43.320	103.979	38.500	- 2.629
3300	15.847	99.107	85.501	44.901	103.610	36.462	- 2.415
3400	15.915	99.581	85.908	46.489	103.248	34.432	- 2.213
3500	15.981	100.044	86.305	48.084	102.893	32.406	- 2.024
3600	16.046	100.495	86.693	49.685	- 173.339	37.171	- 2.257
3700	16.108	100.935	87.072	51.293	- 173.384	43.022	- 2.541
3800	16.168	101.366	87.443	52.907	- 173.423	48.869	- 2.811
3900	16.225	101.786	87.805	54.526	- 173.460	54.718	- 3.066
4000	16.279	102.198	88.160	56.152	- 173.490	60.570	- 3.309
4100	16.331	102.600	88.507	57.782	- 173.519	66.417	- 3.540
4200	16.380	102.995	88.847	59.418	- 173.539	72.266	- 3.760
4300	16.426	103.381	89.181	61.058	- 173.555	78.120	- 3.970
4400	16.469	103.759	89.508	62.703	- 173.569	83.972	- 4.171
4500	16.509	104.129	89.829	64.352	- 173.576	89.840	- 4.363
4600	16.547	104.493	90.144	66.005	- 173.579	95.686	- 4.546
4700	16.582	104.849	90.453	67.661	- 173.582	101.542	- 4.722
4800	16.614	105.198	90.756	69.321	- 173.578	107.395	- 4.890
4900	16.643	105.541	91.055	70.984	- 173.571	113.250	- 5.051
5000	16.670	105.878	91.348	72.649	- 173.562	119.093	- 5.206
5100	16.694	104.208	91.636	74.319	- 173.549	124.959	- 5.355
5200	16.716	106.532	91.919	75.989	- 173.535	130.811	- 5.498
5300	16.735	106.851	92.198	77.661	- 173.515	136.662	- 5.635
5400	16.752	107.164	92.472	79.335	- 173.497	142.511	- 5.768
5500	16.767	107.471	92.742	81.011	- 173.477	148.361	- 5.895
5600	16.780	107.774	93.008	82.688	- 173.456	154.217	- 6.019
5700	16.791	108.071	93.270	84.367	- 173.433	160.074	- 6.138
5800	16.800	108.363	93.527	86.046	- 173.413	165.922	- 6.252
5900	16.807	108.650	93.781	87.727	- 173.391	171.765	- 6.363
6000	16.813	108.933	94.031	89.408	- 173.369	177.613	- 6.470

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

SILICON, TRIATOMIC (Si_3) (IDEAL GAS) GFW = 84.258

Point Group [$D_{\infty h}$]

$S^\circ_{298.15}$ = [64.0] gibbs/mol

ΔHf°_0 = 151.2 ± 10 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 152 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	3
[10000]	[6]
[18000]	[2]
21460	3

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[360] (1)
[200] (2)
[630] (1)

Bond Distance: Si-Si = [2.25] Å

Bond Angle: Si-Si-Si = [180°]

σ = [2]

Rotational Constant: B_0 = [0.05928] cm^{-1}

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the systems SiC-graphite[1] and SiC-silicon[2]. Third law analysis of the partial pressures of Si_3 and Si yields the values 154.0 and 149.9 kcal/mol. Both drifts suggest that the entropy may be lower than the tabulated values. It is unlikely that the entropy is in error by more than 5 eu so that most of the drift is inherent in the data. The adopted value of ΔHf°_{298} = 152 ± 10 kcal/mol includes allowance for an error of up to 5 eu.

Source	Method	Range, T°K	No. of Points	ΔHr°_{298} (kcal/mol)* 2nd Law	3rd Law	Drift (eu)	ΔHf°_{298} (kcal/mol)
Drowart (1958)	Mass Spec.	2230-2316	2	209	169.1	-18	154.0
Drowart (1960)	" "	1703-1890	4	204±3	173.2	-17±2	149.9

*For reaction $Si_3(g) = 3\ Si(g)$

Heat Capacity and Entropy.

Weltner and McLeod[3] observed an absorption band near 4660 Å in matrix isolation studies. Their tentative assignment of this band as the $^3\Sigma^-_u \leftarrow {}^3\Sigma^-_g$ transition of Si_3 is adopted here. A $^1\Pi_u$ state is assumed at 18000 cm^{-1}, which is 7000 and 2000 cm^{-1} below the analogous levels[3] for C_3 and C_2Si. Also a $^3\Pi_u$ level is assumed at 10000 cm^{-1}, presumably arising from the same molecular orbital configuration as the $^1\Pi_u$ state. The molecule is assumed to be linear with a bond distance equal to that in Si_2. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 2.16 \times 10^5$ and $k\delta/l^2 = 0.11 \times 10^5$ dyn/cm. The stretching force constant is obtained from Si_2, while the bending force constant is based on C_2Si and the $^1\Pi_u$ excited state[3] of C_3. The moment of inertia is 47.22×10^{-39} g cm^2.

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Titanium (Ti)
(Reference State) GFW = 47.90

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.152	.000	.000	.000
100	3.412	1.969	12.152	- 1.018	.000	.000	.000
200	5.333	5.069	7.870	- .560	.000	.000	.000
298	5.987	7.325	7.325	.000	.000	.000	.000
300	5.996	7.362	7.325	.011	.000	.000	.000
400	6.341	9.139	7.565	.629	.000	.000	.000
500	6.559	10.578	8.028	1.275	.000	.000	.000
600	6.755	11.791	8.557	1.941	.000	.000	.000
700	6.976	12.848	9.096	2.627	.000	.000	.000
800	7.229	13.796	9.625	3.337	.000	.000	.000
900	7.499	14.663	10.137	4.073	.000	.000	.000
1000	7.767	15.467	10.631	4.837	.000	.000	.000
1100	8.025	16.220	11.105	5.626	.000	.000	.000
1200	7.068	17.741	11.592	7.378	.000	.000	.000
1300	7.210	18.312	12.087	8.092	.000	.000	.000
1400	7.367	18.852	12.551	8.821	.000	.000	.000
1500	7.540	19.366	12.989	9.566	.000	.000	.000
1600	7.730	19.859	13.403	10.329	.000	.000	.000
1700	7.940	20.333	13.797	11.112	.000	.000	.000
1800	8.160	20.793	14.173	11.917	.000	.000	.000
1900	8.390	21.240	14.533	12.744	.000	.000	.000
2000	8.500	23.977	14.956	18.042	.000	.000	.000
2100	8.500	24.392	15.396	18.892	.000	.000	.000
2200	8.500	24.787	15.814	19.742	.000	.000	.000
2300	8.500	25.165	16.212	20.592	.000	.000	.000
2400	8.500	25.527	16.593	21.442	.000	.000	.000
2500	8.500	25.874	16.957	22.292	.000	.000	.000
2600	8.500	26.207	17.307	23.142	.000	.000	.000
2700	8.500	26.528	17.642	23.992	.000	.000	.000
2800	8.500	26.837	17.965	24.842	.000	.000	.000
2900	8.500	27.136	18.276	25.692	.000	.000	.000
3000	8.500	27.424	18.576	26.542	.000	.000	.000
3100	8.500	27.703	18.866	27.392	.000	.000	.000
3200	8.500	27.972	19.147	28.242	.000	.000	.000
3300	8.500	28.234	19.418	29.092	.000	.000	.000
3400	8.500	28.488	19.681	29.942	.000	.000	.000
3500	8.500	28.734	19.936	30.792	.000	.000	.000
3600	8.146	57.276	20.257	133.268	.000	.000	.000
3700	8.283	57.501	21.260	134.090	.000	.000	.000
3800	8.417	57.723	22.217	134.925	.000	.000	.000
3900	8.548	57.944	23.130	135.773	.000	.000	.000
4000	8.676	58.162	24.003	136.634	.000	.000	.000
4100	8.799	58.378	24.839	137.508	.000	.000	.000
4200	8.919	58.591	25.640	138.394	.000	.000	.000
4300	9.035	58.802	26.409	139.292	.000	.000	.000
4400	9.146	59.011	27.147	140.201	.000	.000	.000
4500	9.252	59.218	27.858	141.121	.000	.000	.000
4600	9.354	59.423	28.542	142.051	.000	.000	.000
4700	9.451	59.625	29.201	142.991	.000	.000	.000
4800	9.544	59.825	29.837	143.941	.000	.000	.000
4900	9.631	60.022	30.451	144.900	.000	.000	.000
5000	9.713	60.218	31.044	145.867	.000	.000	.000
5100	9.791	60.411	31.618	146.842	.000	.000	.000
5200	9.864	60.602	32.174	147.825	.000	.000	.000
5300	9.933	60.790	32.712	148.815	.000	.000	.000
5400	9.996	60.977	33.234	149.812	.000	.000	.000
5500	10.056	61.161	33.740	150.814	.000	.000	.000
5600	10.111	61.342	34.231	151.823	.000	.000	.000
5700	10.161	61.522	34.708	152.836	.000	.000	.000
5800	10.208	61.699	35.172	153.855	.000	.000	.000
5900	10.251	61.874	35.623	154.878	.000	.000	.000
6000	10.289	62.046	36.062	155.905	.000	.000	.000

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TITANIUM (Ti) **(REFERENCE STATE)** **GFW = 47.90**

0	to	1155°K	Crystal alpha
1155	to	1933°K	Crystal beta
1933	to	3591°K	Liquid
3591	to	6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

Titanium, Alpha (Ti)
(Crystal) GFW = 47.90

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 1.152	.000	.000	.000
100	3.412	1.969	12.152	- 1.018	.000	.000	.000
200	5.333	5.069	7.870	- .560	.000	.000	.000
298	5.987	7.325	7.325	.000	.000	.000	.000
300	5.996	7.362	7.325	.011	.000	.000	.000
400	6.341	9.139	7.565	.629	.000	.000	.000
500	6.559	10.578	8.028	1.275	.000	.000	.000
600	6.755	11.791	8.557	1.941	.000	.000	.000
700	6.976	12.848	9.096	2.627	.000	.000	.000
800	7.229	13.796	9.625	3.337	.000	.000	.000
900	7.499	14.663	10.137	4.073	.000	.000	.000
1000	7.767	15.467	10.631	4.837	.000	.000	.000
1100	8.025	16.220	11.105	5.626	.000	.000	.000
1200	8.296	16.929	11.561	6.442	- .936	.038	- .007
1300	8.556	17.603	12.000	7.285	- .807	.114	- .019
1400	8.816	18.247	12.423	8.153	- .668	.179	- .028
1500	9.076	18.864	12.832	9.048	- .518	.235	- .034
1600	9.336	19.458	13.228	9.968	- .361	.281	- .038
1700	9.596	20.032	13.611	10.915	- .197	.315	- .040
1800	9.856	20.588	13.984	11.887	- .030	.339	- .041
1900	10.116	21.128	14.346	12.886	.142	.355	- .041
2000	10.376	21.653	14.698	13.910	- 4.132	.516	- .056

Dec. 31, 1960; Sept. 30, 1966

TITANIUM, ALPHA (Ti) (CRYSTAL) GFW = 47.90

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 7.325 ± 0.02 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

Tt = 1155 ± 3 °K

ΔHt° = 0.99 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 113.0 ± 1.0 kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature heat capacities, 1.1 - 305.51°K, have been measured by many investigators. Their measured temperature range, specimen purity and value of $S^\circ_{298.15}$ reported are listed in the following table. The Cp values, below 298°K, adopted were mainly derived from the data obtained from references 3, 5 and 6, which are in good agreement with other sets of Cp data.

Investigator	Temperature, °K	Purity, %	$S^\circ_{298.15}$, eu
1. K. K. Kelley (1944)	53.5 - 295.1	98.75	7.24 ± 0.07
2. Estermann et al. (1952)	1.8 - 4.2	99	-
3. Kothen and Johnston (1953)	15.44 - 305.51	99.96	7.33 ± 0.02
4. Aven et al. (1956)	3.95 - 15.76	99.95	-
5. Wolcott (1957)	1.17 - 20.95	99.98	-
6. Clusius and Franzosini (1958)	13.72 - 271.92	99.88	-
7. Burk et al. (1958)	22.5 - 200.0	99	-
8. Kneip et al. (1963)	1.1 - 4.5	99.86	-
9. Hake and Cape (1964)	1.2 - 4.5	99.92	-

1. K. K. Kelley, Ind. Eng. Chem. 36, 865 (1944). $S^\circ_{50.12}$ = 0.401 eu.
2. I. Estermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. 87, 582 (1952).
3. C. W. Kothen and H. L. Johnston, J. Am. Chem. Soc. 75, 3101 (1953). S°_{15} = 0.013 eu.
4. M. H. Aven, R. S. Craig, T. R. Waite and W. E. Wallace, Phys. Rev. 102, 1263 (1956).
5. N. M. Wolcott, Phil. Mag. 2, 1246 (1957).
6. K. Clusius and P. Franzosini, Z. Physik. Chem. 16, 194 (1958).
7. D. L. Burk, I. Estermann and S. A. Friedberg, Z. Physik. Chem. 16, 183 (1958).
8. G. D. Kneip, Jr., J. O. Betterton, Jr. and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).
9. R. P. Hake and J. A. Cape, Phys. Rev. 135, A1151 (1964).

The high temperature heat capacities, 320-1856°K, have also been determined by many investigators. The values above Tt are not in good agreement. The measured temperature range, method used, and kind of data reported by these investigators are presented in the table below.

Investigator	Temperature, °K	Method	Property Measured
1. Jaeger et al. (1936)	492.9 - 1475.6	drop calorimetry	$H^\circ_T - H^\circ_{295.15}$
2. Kothen (1952)	1067.0 - 1856.0	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
3. Scott (1957)	333.2 - 1233.2	adiabatic calorimetry	Cp
4. Backhurst (1958)	873.2 - 1353.2	adiabatic calorimetry	Cp
5. Golutvin (1959)	388.0 - 1401.9	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
6. Holland (1963)	599.0 - 1345.0	resistance measurement	Cp
7. Kohlhaas et al. (1965)	320.0 - 1800.0	adiabatic calorimetry	Cp

1. F. M. Jaeger, E. Rosenbohm and R. Fonteyne, Rec. trav. chim, 55, 615 (1936).
2. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952. Sample purity 99.96%.
3. J. L. Scott, ORNL -2328, Oak Ridge National Laboratory, July 1957.
4. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1958).
5. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).
6. L. R. Holland, J. Appl. Phys. 34, 2350 (1963).
7. R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). Sample purity 99.8%.

The adopted Cp values, 298.15 - 1155°K, were mainly derived from the Cp data reported by reference 7. The low temperature and high temperature Cp data were joined smoothly at 298°K. The Cp values above 1155°K were estimated by graphical extrapolation. $S^\circ_{298.15}$ was derived from the adopted Cp, based on S°_{13} = 0.015 eu.

Transition Data.

See the Ti (β , c) table for details.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Ti(g) and Ti (α ,c).

Titanium, Beta (Ti)

(Crystal) GFW = 47.90

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.205	8.691	8.691	.000	1.433	1.026	- .752
300	6.206	8.729	8.691	.011	1.433	1.023	- .746
400	6.280	10.525	8.935	.636	1.440	.885	- .484
500	6.358	11.934	9.399	1.268	1.426	.748	- .327
600	6.439	13.101	9.922	1.907	1.399	.613	- .223
700	6.525	14.100	10.449	2.556	1.362	.485	- .151
800	6.618	14.977	10.961	3.213	1.309	.364	- .099
900	6.718	15.762	11.452	3.879	1.239	.250	- .061
1000	6.825	16.475	11.919	4.556	1.152	.144	- .032
1100	6.940	17.131	12.363	5.245	1.052	.050	- .010
1200	7.068	17.741	12.786	5.945	.000	.000	.000
1300	7.210	18.312	13.190	6.659	.000	.000	.000
1400	7.367	18.852	13.575	7.387	.000	.000	.000
1500	7.540	19.366	13.944	8.133	.000	.000	.000
1600	7.730	19.858	14.298	8.896	.000	.000	.000
1700	7.940	20.333	14.639	9.679	.000	.000	.000
1800	8.160	20.793	14.969	10.484	.000	.000	.000
1900	8.390	21.240	15.287	11.311	.000	.000	.000
2000	8.630	21.677	15.596	12.162	- 4.447	.153	- .017
2100	8.860	22.103	15.895	13.037	- 4.422	.385	- .040
2200	9.090	22.521	16.187	13.934	- 4.375	.611	- .061
2300	9.312	22.930	16.471	14.855	- 4.304	.836	- .079
2400	9.530	23.331	16.749	15.797	- 4.212	1.058	- .096
2500	9.750	23.724	17.020	16.761	- 4.098	1.277	- .112

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TITANIUM, BETA (Ti) (CRYSTAL) GFW = 47.90

$S^\circ_{298.15}$ = 8.691 gibbs/mol

Tt = 1155 ± 3 °K

Tm = 1933 ± 10 °K

ΔHf°_0 = Unknown

$\Delta Hf^\circ_{298.15}$ = 1.433 kcal/mol

ΔHt° = 0.99 kcal/mol

ΔHm° = [4.45] kcal/mol

$\Delta Hs^\circ_{298.15}$ = [111.57] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) was obtained from $\Delta Hf^\circ_{298.15}$ (α , c) by adding ΔHt° and the difference $H^\circ_{Tt} - H^\circ_{298.15}$ for Ti (α, c) and Ti (β, c).

Heat Capacity and Entropy.

The heat capacities, 1155 - 1856°K, have been determined by many investigators. See the Ti (α , c) table for details. The selected Cp values were evaluated based on the data reported by C. W. Kothen, Ph. D. dissertation, The Ohio State University, 1952, and R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). The heat capacities below 1155°K and above 1800°K were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

Titanium has two crystal forms, i.e. the hexagonal close-packed low-temperature form and the body-centered cubic high-temperature form. The α→β transition temperature has been determined and reported over a range of temperatures, 1154-1167°K, by many investigators. The value of Tt is affected by the impurities in the specimen or adsorbed by the specimen during the measurement and the method used for the determination. The following table indicates the values of Tt reported by different investigators. Also included are the heats of transition (ΔHt°), purity of specimen and property measured. The value of Tt adopted is 1155 ± 3°K, and the value of ΔHt° is selected as 0.99 kcal/mol.

Investigator	Tt, °K	ΔHt°, kcal/mol	Purity, %	Method or Property Measured
1. Fast (1939)	1158 ± 10	-	Iodide	electrical resistance
2. Greiner and Ellis (1949)	1158 ± 2	-	99.9	electrical resistance
3. McQuillan (1950)	1155.7 ± 1	-	99.93	hydrogen solubility
4. Duwez (1951)	1155 ± 4	-	Iodide	cooling curve
5. Worner (1951)	1158 ± 2	-	99.93	thermoelectric power
6. Kothen (1952)	1154	0.943	99.96	dropping calorimetry
7. Edwards et al. (1953)	1157 ± 3.5	-	99.88	cooling curve
8. Schofield (1956)	1158	0.814	-	rate of heating
9. Scott (1957)	1156 ± 2	0.978 ± 0.025	Iodide	adiabatic calorimetry
10. Backhurst (1958)	-	0.880	Commercial	adiabatic calorimetry
11. Golutvin (1959)	1155	0.820 ± 0.020	Iodide	dropping calorimetry
12. Kohlhaas, et al. (1965)	1167	0.992	99.8	adiabatic calorimetry

1. J. D. Fast, Rec. trav. chim. 58, 973 (1939).
2. E. S. Greiner and W. C. Ellis, Trans. Am. Inst. Min. Met. Eng. 180, 657 (1949).
3. A. D. McQuillan, J. Inst. Metals, 78, 249 (1950).
4. P. Duwez, J. Metals, 3, 765 (1951).
5. H. W. Worner, Australian J. Sci. Res. 4, 62 (1951).
6. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952.
7. J. W. Edwards, H.L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).
8. T. H. Schofield, J. Inst. Metals, 85, 68 (1956).
9. J. L. Scott, ORNL - 2328, Oak Ridge National Laboratory, July 1957.
10. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1958).
11. Y. M. Golutvin, Russ J. Phys, Chem. 33, 164 (1959).
12. R. Kohlhaas, M. Braun and D. Vollmer, Z. Naturforsch. 20A, 1077 (1965).

Melting Data.

See the Ti(l) table for details.

Heat of Sublimation.

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Ti(g) and Ti(β, c).

Titanium (Ti)
(Liquid) GFW = 47.90

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	6.205	10.695	10.695	.000	5.433	4.428	- 3.246
300	6.206	10.733	10.695	.011	5.433	4.422	- 3.222
400	6.280	12.529	10.939	.636	5.440	4.084	- 2.231
500	6.358	13.938	11.403	1.268	5.426	3.746	- 1.637
600	6.439	15.105	11.926	1.907	5.399	3.411	- 1.242
700	6.525	16.104	12.453	2.556	5.362	3.082	- .962
800	6.618	16.981	12.965	3.213	5.309	2.761	- .754
900	6.718	17.766	13.456	3.879	5.239	2.447	- .594
1000	6.825	18.479	13.923	4.556	5.152	2.140	- .468
1100	6.940	19.135	14.367	5.245	5.052	1.845	- .367
1200	7.068	19.745	14.790	5.945	4.000	1.595	- .291
1300	8.500	20.316	15.194	6.659	4.000	1.395	- .234
1400	8.500	20.946	15.582	7.509	4.121	1.189	- .186
1500	8.500	21.532	15.960	8.359	4.226	.977	- .142
1600	8.500	22.081	16.325	9.209	4.313	.758	- .103
1700	8.500	22.596	16.679	10.059	4.380	.533	- .068
1800	8.500	23.082	17.021	10.909	4.425	.305	- .037
1900	8.500	23.541	17.353	11.759	4.448	.076	- .009
2000	8.500	23.977	17.673	12.609	.000	.000	.000
2100	8.500	24.392	17.983	13.459	.000	.000	.000
2200	8.500	24.788	18.284	14.309	.000	.000	.000
2300	8.500	25.165	18.575	15.159	.000	.000	.000
2400	8.500	25.527	18.857	16.009	.000	.000	.000
2500	8.500	25.874	19.131	16.859	.000	.000	.000
2600	8.500	26.208	19.396	17.709	.000	.000	.000
2700	8.500	26.528	19.655	18.559	.000	.000	.000
2800	8.500	26.837	19.906	19.409	.000	.000	.000
2900	8.500	27.136	20.150	20.259	.000	.000	.000
3000	8.500	27.424	20.388	21.109	.000	.000	.000
3100	8.500	27.703	20.619	21.959	.000	.000	.000
3200	8.500	27.973	20.845	22.809	.000	.000	.000
3300	8.500	28.234	21.065	23.659	.000	.000	.000
3400	8.500	28.488	21.279	24.509	.000	.000	.000
3500	8.500	28.734	21.489	25.359	.000	.000	.000
3600	8.500	28.974	21.693	26.209	- 101.615	.258	- .016
3700	8.500	29.207	21.893	27.059	- 101.585	3.088	- .182
3800	8.500	29.433	22.089	27.909	- 101.569	5.918	- .340
3900	8.500	29.654	22.280	28.759	- 101.566	8.745	- .490
4000	8.500	29.869	22.467	29.609	- 101.576	11.576	- .632
4100	8.500	30.079	22.650	30.459	- 101.599	14.402	- .768
4200	8.500	30.284	22.829	31.309	- 101.634	17.230	- .897
4300	8.500	30.484	23.005	32.159	- 101.680	20.061	- 1.020
4400	8.500	30.679	23.177	33.009	- 101.738	22.896	- 1.137
4500	8.500	30.870	23.346	33.859	- 101.807	25.732	- 1.250

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TITANIUM (Ti) (LIQUID) GFW = 47.90

$S^\circ_{298.15}$ = [10.695] gibbs/mol

Tm = 1933 ± 10°K

Tb = [3591]°K

$\Delta Hf^\circ_{298.15}$ = [5.433] kcal/mol

ΔHm° = [4.45] kcal/mol

ΔHv° = [101.83] kcal/mol

Heat of Formation.

The heat of formation ($\Delta Hf^\circ_{298.15}$) was obtained from $\Delta Hf^\circ_{298.15}$ (β, c) by adding ΔHm° and the difference between $H^\circ_{Tm} - H^\circ_{298.15}$ for Ti (β , c) and Ti(l).

Heat Capacity and Entropy.

A glass transition temperature at 1300°K was assumed. The heat capacities below 1300°K were obtained from those for Ti (β, c). The Cp value above 1300°K was estimated by comparison with those for the other transition elements and assumed to be constant in the temperature range 1300 - 4500°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

Because of the highly reactive nature of Ti(c), the accurate determination of the melting point is difficult. The results reported by different investigators show wide discrepancies. The Tm value adopted was determined by Schofield and Bacon (1953) and later confirmed by Westrum and Feick (1963). The other values of Tm reported are presented in the table below. The heat of melting was calculated based on an estimated entropy of melting, ΔSm°_{1933} = 2.3 eu.

Tm, °K	Investigator
2068 ± 15	G. K. Burgess and R. G. Waltenberg, Z. anorg. Chem. 82, 361 (1913).
1993	J. D. Fast, Rec. trav. chim. 58, 973 (1939).
1993 ± 25	M. Hansen, H. D. Kessler and D. J. McPherson, Trans. Am. Soc. Metals, 44, 518 (1952).
1973 ± 15	H. K. Adenstedt, J. R. Pequignot and J. M. Raymer, Trans. Am. Soc. Metals, 44, 990 (1952).
1953 ± 10	D. J. Maykuth, H. R. Ogden and R. I. Jaffee, Trans. Am. Inst. Min. Met. Eng. 197, 231 (1953).
1933 ± 10	T. H. Schofield and A. E. Bacon, J. Inst. Metals, 82, 167 (1953).
1945 ± 4	R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 25, 248 (1954).
1941 ± 10	D. K. Deardorff and E. T. Hayes, J. Metals, 8, 509 (1956).
1933	E. F. Westrum, Jr. and G. Feick, ASD-TDR-62-204, Part II, University of Michigan, Ann Arbor, Michigan, May 1963.

Vaporization Data.

Tb is the temperature at which the gibbs energy change (ΔGr°) for the reaction Ti(l) = Ti(g) approaches zero. The difference between ΔHf° (Ti,g) and ΔHf° (Ti,l) at Tb is ΔHv°.

Titanium (Ti)

(Ideal Gas) GFW = 47.90

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.802	112.350	112.350	INFINITE
100	6.447	36.123	48.584	-1.246	112.772	109.357	-238.998
200	6.330	40.635	43.615	-.596	112.964	105.851	-115.668
298	5.839	43.066	43.066	.000	113.000	102.344	-75.020
300	5.831	43.102	43.066	.011	113.000	102.278	-74.509
400	5.522	44.733	43.291	.577	112.948	98.710	-53.933
500	5.344	45.945	43.706	1.120	112.845	95.161	-41.595
600	5.237	46.909	44.162	1.648	112.707	91.636	-33.379
700	5.170	47.711	44.613	2.168	112.541	88.137	-27.518
800	5.128	48.398	45.044	2.683	112.346	84.664	-23.129
900	5.104	49.001	45.451	3.194	112.121	81.217	-19.722
1000	5.096	49.538	45.833	3.704	111.867	77.796	-17.002
1100	5.106	50.024	46.193	4.214	111.588	74.404	-14.783
1200	5.132	50.469	46.531	4.726	110.348	71.074	-12.944
1300	5.176	50.881	46.850	5.241	110.149	67.810	-11.400
1400	5.237	51.267	47.152	5.762	109.941	64.560	-10.078
1500	5.313	51.631	47.438	6.289	109.723	61.326	-8.935
1600	5.403	51.977	47.711	6.825	109.496	58.107	-7.937
1700	5.504	52.307	47.972	7.370	109.259	54.902	-7.058
1800	5.616	52.625	48.222	7.926	109.009	51.711	-6.279
1900	5.737	52.932	48.461	8.494	108.750	48.535	-5.583
2000	5.864	53.229	48.692	9.074	104.032	45.528	-4.975
2100	5.996	53.518	48.915	9.666	103.774	42.610	-4.434
2200	6.132	53.801	49.131	10.273	103.531	39.700	-3.944
2300	6.271	54.076	49.340	10.893	103.301	36.806	-3.497
2400	6.413	54.346	49.543	11.527	103.085	33.920	-3.089
2500	6.557	54.611	49.740	12.176	102.884	31.041	-2.714
2600	6.701	54.871	49.933	12.839	102.697	28.170	-2.368
2700	6.847	55.126	50.120	13.516	102.524	25.309	-2.049
2800	6.993	55.378	50.304	14.208	102.366	22.451	-1.752
2900	7.140	55.626	50.483	14.915	102.223	19.602	-1.477
3000	7.286	55.871	50.659	15.636	102.094	16.753	-1.220
3100	7.432	56.112	50.831	16.372	101.980	13.912	-.981
3200	7.578	56.350	50.999	17.122	101.880	11.071	-.756
3300	7.722	56.585	51.165	17.887	101.795	8.237	-.546
3400	7.866	56.818	51.328	18.667	101.725	5.403	-.347
3500	8.007	57.048	51.488	19.461	101.669	2.570	-.160
3600	8.146	57.276	51.646	20.268	.000	.000	.000
3700	8.283	57.501	51.801	21.090	.000	.000	.000
3800	8.417	57.723	51.954	21.925	.000	.000	.000
3900	8.548	57.944	52.105	22.773	.000	.000	.000
4000	8.676	58.162	52.253	23.634	.000	.000	.000
4100	8.799	58.378	52.400	24.508	.000	.000	.000
4200	8.919	58.591	52.545	25.394	.000	.000	.000
4300	9.035	58.802	52.688	26.292	.000	.000	.000
4400	9.146	59.011	52.829	27.201	.000	.000	.000
4500	9.252	59.218	52.969	28.121	.000	.000	.000
4600	9.354	59.423	53.107	29.051	.000	.000	.000
4700	9.451	59.625	53.244	29.991	.000	.000	.000
4800	9.544	59.825	53.379	30.941	.000	.000	.000
4900	9.631	60.022	53.512	31.900	.000	.000	.000
5000	9.713	60.218	53.644	32.867	.000	.000	.000
5100	9.791	60.411	53.775	33.842	.000	.000	.000
5200	9.864	60.602	53.905	34.825	.000	.000	.000
5300	9.933	60.790	54.033	35.815	.000	.000	.000
5400	9.996	60.977	54.160	36.812	.000	.000	.000
5500	10.056	61.161	54.285	37.814	.000	.000	.000
5600	10.111	61.342	54.410	38.823	.000	.000	.000
5700	10.161	61.522	54.533	39.836	.000	.000	.000
5800	10.208	61.699	54.655	40.855	.000	.000	.000
5900	10.251	61.874	54.776	41.878	.000	.000	.000
6000	10.289	62.046	54.895	42.905	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1966; June 30, 1967

TITANIUM (Ti) (IDEAL GAS) GFW = 47.90

Ground State Configuration $^3F_2$

$S^\circ_{298.15}$ = 43.066 gibbs/mol

ΔHf°_0 = 112.4 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 113.0 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	5	11639.82	7	17467.00	15	35943.00	147
170.13	7	11776.82	9	18101.00	9	37685.00	105
386.87	9	[12000.00]	[1]	18392.00	76	38939.00	161
6556.86	3	12118.46	9	19789.00	44	40121.00	80
6598.83	5	13981.75	3	21381.00	38	41471.00	190
6661.00	7	14028.47	5	22270.00	12	42106.00	216
6742.79	9	14105.68	7	25405.00	87	43734.00	145
6843.00	11	15108.15	7	27178.00	123	44732.00	127
7255.29	5	15156.80	9	28745.00	65	46284.00	213
8436.63	1	15220.40	11	30144.00	89	48513.00	330
8492.44	3	16008.00	21	31849.00	76		
8602.35	5	16371.00	24	33751.00	54		
11531.81	5	17046.00	35	34698.00	28		

Heat of Formation

The vapor pressure of Ti(β), 1510-1822°K, has been measured in three separate investigations. Based on the reported vapor pressures, the enthalpies of sublimation ($\Delta Hs^\circ_{298.15}$) are evaluated by both the second and third law methods. The results obtained are presented in the following table. The adopted value of $\Delta Hf^\circ_{298.15}$ for Ti(g) is 113.0 ± 1.0 kcal/mol.

Reference	Temperature, °K	$\Delta Hr^\circ_{298.15}$, kcal/mol Second Law Value	$\Delta Hr^\circ_{298.15}$, kcal/mol Third Law Value	Drift eu	$\Delta Hf^\circ_{298.15}$* kcal/mol
1	1510 - 1822	112.23 ± 1.91	110.26 ± 0.81	-1.3 ± 1.2	111.69
2	1658 - 1808	112.41 ± 6.30	110.71 ± 1.10	-1.1 ± 3.7	112.14
3	1587 - 1764	112.26 ± 1.12	111.79 ± 0.18	-0.2 ± 0.6	113.22

*Calculation based on the third law ΔHr°_{298} and $\Delta Hf^\circ_{298}(\beta)$ = 1.43 kcal/mol.

1. J. M. Blocher, Jr., and I. E. Campbell, J. Am. Chem. Soc. 71, 4040 (1949).
2. L. G. Carpenter and W. N. Mair, Proc. Phys. Soc. 64, 57 (1951). The preliminary results were reported by L. G. Carpenter and F. R. Reavell, Nature, 163, 527 (1949).
3. J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from C. E. Moore, National Bureau of Standards Circular 467 (1949). However, above the level ε_i = 15877.17 cm^{-1}, the values of ε_i and g_i listed in the above table are average values calculated from those given by Moore. The $^1S_0$ level of the ground multiplet which has not been observed is estimated to lie at 12000 cm^{-1} by comparison with the corresponding levels for Ti^{++} ion, Zr and Zr^{++} ion reported by C. E. Moore, loc. cit.

Titanium Unipositive Ion (Ti^+)

(Ideal Gas) GFW = 47.89945

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.257	43.854	43.854	.000	271.840	259.462	-190.190
300	6.257	43.893	43.854	.012	271.850	259.385	-188.961
400	6.245	45.692	44.100	.637	272.354	255.153	-139.409
500	6.177	47.079	44.562	1.258	272.826	250.797	-109.623
600	6.060	48.196	45.078	1.871	273.270	246.349	-89.733
700	5.931	49.120	45.591	2.470	273.679	241.928	-75.502
800	5.812	49.904	46.083	3.057	274.053	237.253	-64.814
900	5.712	50.583	46.546	3.633	274.390	232.633	-56.491
1000	5.633	51.180	46.990	4.200	274.690	227.976	-49.824
1100	5.573	51.714	47.387	4.760	274.958	223.293	-44.364
1200	5.529	52.197	47.768	5.315	274.258	218.624	-39.817
1300	5.499	52.639	48.126	5.867	274.592	213.972	-35.972
1400	5.481	53.045	48.463	6.416	274.909	209.297	-32.673
1500	5.474	53.423	48.781	6.963	275.208	204.600	-29.810
1600	5.475	53.776	49.082	7.511	275.490	199.884	-27.303
1700	5.484	54.109	49.368	8.059	275.752	195.150	-25.088
1800	5.499	54.422	49.640	8.608	275.992	190.401	-23.118
1900	5.521	54.720	49.900	9.159	276.213	185.641	-21.354
2000	5.547	55.004	50.148	9.712	271.965	181.023	-19.781
2100	5.578	55.276	50.356	10.268	272.168	176.470	-18.365
2200	5.613	55.536	50.614	10.828	272.375	171.909	-17.077
2300	5.650	55.786	50.834	11.391	272.584	167.335	-15.901
2400	5.690	56.027	51.045	11.958	272.798	162.757	-14.821
2500	5.731	56.261	51.249	12.529	273.016	158.167	-13.827
2600	5.773	56.486	51.446	13.104	273.238	153.568	-12.909
2700	5.817	56.705	51.637	13.684	273.465	148.963	-12.058
2800	5.860	56.917	51.822	14.267	273.695	144.346	-11.267
2900	5.904	57.124	52.001	14.856	273.930	139.725	-10.530
3000	5.946	57.324	52.175	15.448	274.169	135.091	-9.841
3100	5.988	57.520	52.344	16.045	274.413	130.452	-9.197
3200	6.029	57.711	52.509	16.646	274.661	125.804	-8.592
3300	6.069	57.897	52.669	17.251	274.913	121.149	-8.023
3400	6.107	58.079	52.826	17.859	275.167	116.487	-7.488
3500	6.144	58.256	52.979	18.472	275.427	111.815	-6.982
3600	6.179	58.430	53.128	19.088	174.064	107.400	-6.520
3700	6.212	58.600	53.273	19.708	174.359	105.540	-6.234
3800	6.243	58.766	53.416	20.330	174.643	103.675	-5.963
3900	6.273	58.928	53.555	20.956	174.918	101.909	-5.705
4000	6.300	59.087	53.691	21.585	175.182	99.929	-5.460
4100	6.326	59.243	53.825	22.216	175.436	98.044	-5.226
4200	6.351	59.396	53.955	22.850	175.681	96.154	-5.003
4300	6.373	59.546	54.084	23.486	175.916	94.256	-4.791
4400	6.394	59.692	54.210	24.125	176.143	92.356	-4.587
4500	6.414	59.836	54.333	24.765	176.359	90.449	-4.393
4600	6.432	59.978	54.454	25.407	176.568	88.540	-4.207
4700	6.448	60.116	54.573	26.051	176.769	86.623	-4.028
4800	6.463	60.252	54.690	26.697	176.962	84.701	-3.857
4900	6.477	60.385	54.805	27.344	177.147	82.776	-3.692
5000	6.490	60.516	54.918	27.992	177.324	80.853	-3.534
5100	6.502	60.645	55.029	28.642	177.496	78.918	-3.382
5200	6.513	60.771	55.138	29.293	177.661	76.987	-3.236
5300	6.523	60.896	55.246	29.945	177.820	75.045	-3.095
5400	6.533	61.018	55.351	30.597	177.972	73.107	-2.959
5500	6.541	61.138	55.455	31.251	178.121	71.165	-2.828
5600	6.549	61.255	55.558	31.906	178.263	69.211	-2.701
5700	6.557	61.371	55.659	32.561	178.402	67.272	-2.579
5800	6.563	61.486	55.758	33.217	178.536	65.317	-2.461
5900	6.570	61.598	55.856	33.874	178.667	63.364	-2.347
6000	6.576	61.708	55.953	34.531	178.794	61.409	-2.237

Dec. 31, 1967

TITANIUM UNIPOSITIVE ION (Ti^+) (IDEAL GAS) GFW = 47.89945

Ground State Configuration $^4F_{3/2}$

ΔHf°_0 = 269.62 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 43.854 ± 0.01 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 271.84 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	4	9508.611	14	46339.691	42
93.94	6	9970.051	16	52658.791	26
225.47	8	12722.863	32	56744.104	36
393.22	10	15593.028	24	62717.485	42
907.96	4	22558.664	26	65139.311	54
983.80	6	30448.862	64	65650.954	46
1087.21	8	32094.291	44	67896.381	58
1215.58	10	36951.357	36	69610.661	48
4782.319	14	40329.191	38		
8945.376	28	43558.293	40		

Heat of Formation

The heat of formation is calculated from the reaction $Ti(g) = Ti^+(g) + e^-(g)$ with the JANAF auxiliary value for Ti(g) and an ionization potential = 6.82 eV or 157.276 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. I, 1949. The electronic levels above 4700 cm^{-1} are averaged. The $H^\circ - H^\circ_{298}$ value at 0°K is -1.888 kcal/mol.

Tungsten (W)

(Reference State) GFW = 183.85

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-1.189	.000	.000	.000
100	3.832	2.297	12.624	-1.033	.000	.000	.000
200	5.375	5.562	8.327	-.553	.000	.000	.000
298	5.807	7.806	7.806	.000	.000	.000	.000
300	5.811	7.842	7.806	.011	.000	.000	.000
400	5.958	9.535	8.036	.600	.000	.000	.000
500	6.061	10.875	8.474	1.201	.000	.000	.000
600	6.164	11.989	8.970	1.812	.000	.000	.000
700	6.269	12.947	9.471	2.433	.000	.000	.000
800	6.374	13.791	9.959	3.066	.000	.000	.000
900	6.480	14.548	10.428	3.708	.000	.000	.000
1000	6.588	15.237	10.875	4.362	.000	.000	.000
1100	6.696	15.869	11.301	5.026	.000	.000	.000
1200	6.805	16.457	11.706	5.701	.000	.000	.000
1300	6.914	17.006	12.093	6.387	.000	.000	.000
1400	7.025	17.522	12.462	7.084	.000	.000	.000
1500	7.137	18.011	12.816	7.792	.000	.000	.000
1600	7.250	18.475	13.155	8.511	.000	.000	.000
1700	7.363	18.918	13.481	9.242	.000	.000	.000
1800	7.477	19.342	13.795	9.984	.000	.000	.000
1900	7.592	19.749	14.098	10.737	.000	.000	.000
2000	7.709	20.142	14.391	11.502	.000	.000	.000
2100	7.826	20.521	14.673	12.279	.000	.000	.000
2200	7.944	20.887	14.948	13.068	.000	.000	.000
2300	8.063	21.243	15.214	13.868	.000	.000	.000
2400	8.182	21.589	15.472	14.680	.000	.000	.000
2500	8.302	21.925	15.724	15.504	.000	.000	.000
2600	8.424	22.253	15.968	16.340	.000	.000	.000
2700	8.650	22.575	16.207	17.193	.000	.000	.000
2800	8.950	22.895	16.440	18.072	.000	.000	.000
2900	9.350	23.215	16.668	18.987	.000	.000	.000
3000	9.800	23.540	16.892	19.943	.000	.000	.000
3100	10.380	23.870	17.112	20.952	.000	.000	.000
3200	11.000	24.209	17.328	22.020	.000	.000	.000
3300	11.700	24.558	17.542	23.154	.000	.000	.000
3400	12.500	24.919	17.754	24.363	.000	.000	.000
3500	13.500	25.295	17.964	25.660	.000	.000	.000
3600	14.750	25.692	18.173	27.071	.000	.000	.000
3700	8.500	28.374	18.394	36.927	.000	.000	.000
3800	8.500	28.601	18.660	37.777	.000	.000	.000
3900	8.500	28.822	18.917	38.627	.000	.000	.000
4000	8.500	29.037	19.168	39.477	.000	.000	.000
4100	8.500	29.247	19.411	40.327	.000	.000	.000
4200	8.500	29.452	19.648	41.177	.000	.000	.000
4300	8.500	29.652	19.878	42.027	.000	.000	.000
4400	8.500	29.847	20.102	42.877	.000	.000	.000
4500	8.500	30.038	20.321	43.727	.000	.000	.000
4600	8.500	30.225	20.534	44.577	.000	.000	.000
4700	8.500	30.408	20.742	45.427	.000	.000	.000
4800	8.500	30.587	20.946	46.277	.000	.000	.000
4900	8.500	30.762	21.144	47.127	.000	.000	.000
5000	8.500	30.934	21.338	47.977	.000	.000	.000
5100	8.500	31.102	21.528	48.827	.000	.000	.000
5200	8.500	31.267	21.714	49.677	.000	.000	.000
5300	8.500	31.429	21.896	50.527	.000	.000	.000
5400	8.500	31.588	22.074	51.377	.000	.000	.000
5500	8.500	31.744	22.248	52.227	.000	.000	.000
5600	8.500	31.897	22.419	53.077	.000	.000	.000
5700	8.500	32.047	22.587	53.927	.000	.000	.000
5800	8.500	32.195	22.751	54.777	.000	.000	.000
5900	8.500	32.341	22.912	55.627	.000	.000	.000
6000	9.755	65.148	23.418	250.381	.000	.000	.000

Dec. 31, 1961; June 30, 1966

TUNGSTEN (W) (REFERENCE STATE) GFW = 183.85

0	to	3680°K	Crystal
3680	to	5936°K	Liquid
5936		6000°K	Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

Tungsten (W)

(Crystal) GFW = 183.85

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.189	.000	.000	.000
100	3.832	2.297	12.624	-1.033	.000	.000	.000
200	5.375	5.562	8.327	-.553	.000	.000	.000
298	5.807	7.806	7.806	.000	.000	.000	.000
300	5.811	7.842	7.806	.011	.000	.000	.000
400	5.958	9.535	8.036	.600	.000	.000	.000
500	6.061	10.875	8.474	1.201	.000	.000	.000
600	6.164	11.989	8.970	1.812	.000	.000	.000
700	6.269	12.947	9.471	2.433	.000	.000	.000
800	6.374	13.791	9.959	3.066	.000	.000	.000
900	6.480	14.548	10.428	3.708	.000	.000	.000
1000	6.588	15.237	10.875	4.362	.000	.000	.000
1100	6.696	15.869	11.301	5.026	.000	.000	.000
1200	6.805	16.457	11.706	5.701	.000	.000	.000
1300	6.914	17.006	12.093	6.387	.000	.000	.000
1400	7.025	17.522	12.462	7.084	.000	.000	.000
1500	7.137	18.011	12.816	7.792	.000	.000	.000
1600	7.250	18.475	13.155	8.511	.000	.000	.000
1700	7.363	18.918	13.481	9.242	.000	.000	.000
1800	7.477	19.342	13.795	9.984	.000	.000	.000
1900	7.592	19.749	14.098	10.737	.000	.000	.000
2000	7.709	20.142	14.391	11.502	.000	.000	.000
2100	7.826	20.521	14.673	12.279	.000	.000	.000
2200	7.944	20.887	14.948	13.068	.000	.000	.000
2300	8.063	21.243	15.214	13.868	.000	.000	.000
2400	8.182	21.589	15.472	14.680	.000	.000	.000
2500	8.302	21.925	15.724	15.504	.000	.000	.000
2600	8.424	22.253	15.968	16.340	.000	.000	.000
2700	8.650	22.575	16.207	17.193	.000	.000	.000
2800	8.950	22.895	16.440	18.072	.000	.000	.000
2900	9.350	23.215	16.668	18.987	.000	.000	.000
3000	9.800	23.540	16.892	19.943	.000	.000	.000
3100	10.380	23.870	17.112	20.952	.000	.000	.000
3200	11.000	24.209	17.328	22.020	.000	.000	.000
3300	11.700	24.558	17.542	23.154	.000	.000	.000
3400	12.500	24.919	17.754	24.363	.000	.000	.000
3500	13.500	25.295	17.964	25.660	.000	.000	.000
3600	14.750	25.693	18.173	27.073	.000	.000	.000
3700	16.063	26.115	18.382	28.613	-8.314	.045	-.003
3800	17.375	26.561	18.591	30.285	-7.492	.260	-.015
3900	18.688	27.029	18.801	32.088	-6.539	.454	-.025
4000	20.000	27.519	19.013	34.023	-5.454	.618	-.034
4100	21.313	28.029	19.227	36.088	-4.239	.755	-.040
4200	22.625	28.558	19.443	38.285	-2.892	.863	-.045
4300	23.938	29.106	19.661	40.613	-1.414	.934	-.047
4400	25.250	29.671	19.882	43.073	.196	.970	-.048
4500	26.563	30.253	20.106	45.663	1.936	.969	-.047
4600	27.875	30.852	20.333	48.385	3.808	.924	-.044
4700	29.188	31.465	20.563	51.238	5.811	.843	-.039
4800	30.500	32.093	20.797	54.223	7.946	.717	-.033

Dec. 31, 1961; June 30, 1966

TUNGSTEN (W) (CRYSTAL) GFW = 183.85

$S^\circ_{298.15}$ = 7.806 gibbs/mol

Tm = 3680 ± 20°K

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

ΔHm° = [8.46 ± 2.5] kcal/mol

$\Delta Hs^\circ_{298.15}$ = 203.4 ± 1.5 kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

There have been several investigations of the low temperature heat capacity of tungsten: F. Lange, Z. physik. Chem. 110, 343 (1924), covered the range 26-91°K. M. Horowitz and J. G. Daunt, Phys. Rev. 91, 1099 (1953), reported values in the range 1-77°K, while T. R. Waite, R. S. Craig, and W. E. Wallace, Phys. Rev. 104, 1240 (1956), worked from 4-15° and W. DeSorbo, J. Phys. Chem. 62, 965 (1958), from 15-90°K. C. Zwikker and G. Schmidt, Z. Physik. 52, 668 (1928), covered the range from 90 to 2521°K. K. Clusius and P. Franzozini, Z. Naturforsch. 14A, 99 (1959), made a thorough study of the heat capacity in the range 12-274°K, and their measurements were adopted leading to S°_{298} = 7.806 eu based on $S_{12.5^\circ}$ = 0.0088 eu. This value is in disagreement with the quoted value of 7.83 eu but agrees exactly with a separate integration by V. A. Kirillin, A. E. Sheindlin, V. Ya. Chekhovskoi and V. A. Petrov, Zhur. Fiz. Khim. 37, 2249 (1963). In the intermediate temperature range the adiabatic heat capacity measurements of H. L. Bronson, H. M. Chisholm and S. M. Dockerty, Can. J. Res. 8, 282 (1933), from 253 to 773°K joined well with the low temperature measurements and were adopted. The high temperature enthalpies have been measured by several investigators from which were selected the values of F. M. Jaeger and E. Rosenbohm, Rec. trav. chim. 51, 1 (1932), from 273-1800°K; A. Magnus and H. Holzmann, Ann. Physik Ser 5, 3, 585 (1929), who covered the range 373 to 1173°K; M. Hoch and H. L. Johnston, J. Phys. Chem. 65, 855 (1961) who made measurements between 1382 and 2900°K; Kirillin et al., loc. cit., who have made several determinations over the range 600 to 3100°K, and have also analysed the above data and have presented smooth functions from 0 to 3500°K. The present table agrees with that of Kirillin et al. up to 2700°K. Above this temperature the values of Cp adopted follow those reported by I. I. Novikov and P. G. Strelkov, Vestnik. Akad. Nauk SSSR 34, 26(1964), measured by an electric modulation method, up to the melting point. These values rise rapidly above 2700°K and are not inconsistent with the individual measurements of Kirillin et al. at their highest temperatures.

Melting Data.

I. Langmuir, Phys. Rev. 6, 138 (1915), determined the melting point as 3540°K from intrinsic brilliance measurements; this was later corrected to 3655 ± 30°K by H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. 30, 201 (1927). M. Pirani and H. Alterthum, Z. Elektrochem. 29, 5 (1923), from pyrometer measurements on a black body hole found 3660 ± 60°K. Using the same technique C. F. Zalabak, NASA Tech. Note D-761 (1961), reports 3680°K on a low carbon specimen; he reports a decrease of the melting point with increasing carbon content. E. Rudy and S. Windisch, Aerojet-General Tech. Rept. No. AFML- TR-65-2 Part 1, Vol. III July 1965, report a melting point of 3696 ± 20°K. The value adopted was 3680 ± 20°K. The heat of melting was obtained by assuming an entropy of melting of 2.3 eu obtained from a comparison of several high melting metals (Fe, Cu, Co, Mg, Al).

Sublimation Data.

See W(g) for details.

Tungsten (W)

(Liquid) GFW = 183.85

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.807	10.923	10.923	.000	11.223	10.294	- 7.545
300	5.810	10.959	10.923	.011	11.223	10.288	- 7.495
400	5.958	12.652	11.153	.600	11.223	9.976	- 5.450
500	6.061	13.992	11.591	1.200	11.222	9.664	- 4.224
600	6.164	15.106	12.087	1.812	11.223	9.353	- 3.407
700	6.269	16.064	12.588	2.433	11.223	9.041	- 2.823
800	6.374	16.908	13.077	3.066	11.223	8.729	- 2.385
900	6.480	17.665	13.545	3.708	11.223	8.418	- 2.044
1000	6.588	18.354	13.992	4.362	11.223	8.106	- 1.771
1100	6.696	18.987	14.418	5.026	11.223	7.793	- 1.548
1200	6.805	19.574	14.823	5.701	11.223	7.482	- 1.363
1300	6.914	20.123	15.210	6.387	11.223	7.171	- 1.206
1400	7.025	20.639	15.580	7.084	11.223	6.859	- 1.071
1500	7.137	21.128	15.933	7.792	11.223	6.547	- .954
1600	7.250	21.592	16.273	8.511	11.223	6.236	- .852
1700	7.363	22.035	16.599	9.242	11.223	5.924	- .762
1800	7.477	22.459	16.912	9.984	11.223	5.612	- .681
1900	7.593	22.866	17.215	10.737	11.223	5.301	- .610
2000	7.709	23.259	17.508	11.502	11.223	4.989	- .545
2100	7.826	23.638	17.791	12.279	11.223	4.677	- .487
2200	7.944	24.005	18.065	13.068	11.223	4.363	- .433
2300	8.062	24.360	18.331	13.868	11.223	4.054	- .385
2400	8.182	24.706	18.589	14.680	11.223	3.742	- .341
2500	8.500	25.042	18.841	15.504	11.223	3.431	- .300
2600	8.500	25.376	19.086	16.354	11.237	3.118	- .262
2700	8.500	25.697	19.325	17.204	11.234	2.805	- .227
2800	8.500	26.006	19.558	18.054	11.205	2.495	- .195
2900	8.500	26.304	19.785	18.904	11.140	2.182	- .164
3000	8.500	26.592	20.007	19.754	11.034	1.878	- .137
3100	8.500	26.871	20.224	20.604	10.875	1.572	- .111
3200	8.500	27.141	20.436	21.454	10.657	1.275	- .087
3300	8.500	27.402	20.643	22.304	10.373	.988	- .065
3400	8.500	27.656	20.846	23.154	10.014	.709	- .046
3500	8.500	27.902	21.044	24.004	9.567	.443	- .028
3600	8.500	28.142	21.238	24.854	9.006	.186	- .011
3700	8.500	28.375	21.428	25.704	.000	.000	.000
3800	8.500	28.601	21.613	26.554	.000	.000	.000
3900	8.500	28.822	21.795	27.404	.000	.000	.000
4000	8.500	29.037	21.974	28.254	.000	.000	.000
4100	8.500	29.247	22.149	29.104	.000	.000	.000
4200	8.500	29.452	22.320	29.954	.000	.000	.000
4300	8.500	29.652	22.488	30.804	.000	.000	.000
4400	8.500	29.848	22.653	31.654	.000	.000	.000
4500	8.500	30.039	22.815	32.504	.000	.000	.000
4600	8.500	30.225	22.974	33.354	.000	.000	.000
4700	8.500	30.408	23.131	34.204	.000	.000	.000
4800	8.500	30.587	23.284	35.054	.000	.000	.000
4900	8.500	30.762	23.435	35.904	.000	.000	.000
5000	8.500	30.934	23.583	36.754	.000	.000	.000
5100	8.500	31.102	23.729	37.604	.000	.000	.000
5200	8.500	31.268	23.872	38.454	.000	.000	.000
5300	8.500	31.429	24.013	39.304	.000	.000	.000
5400	8.500	31.588	24.152	40.154	.000	.000	.000
5500	8.500	31.744	24.289	41.004	.000	.000	.000
5600	8.500	31.897	24.423	41.854	.000	.000	.000
5700	8.500	32.048	24.556	42.704	.000	.000	.000
5800	8.500	32.196	24.686	43.554	.000	.000	.000
5900	8.500	32.341	24.815	44.404	.000	.000	.000
6000	8.500	32.484	24.941	45.254	- 193.904	2.080	- .076

Dec. 31, 1961; June 30, 1966

TUNGSTEN (W) (LIQUID) GFW = 183.85

$S^\circ_{298.15}$ = 10.923 gibbs/mol

Tm° = 3680 ± 20°K

Tb° = [5936]°K

$\Delta Hf^\circ_{298.15}$ = 11.223 kcal/mol

ΔHm° = [8.46 ± 2.5] kcal/mol

ΔHv° = [192.824] kcal/mol

<u>Heat of Formation</u>.

The heat of formation at 298°K was calculated from that of the crystal by adding ΔHm° and the difference between $H_{3680}-H_{298}$ for (c) and (l).

<u>Heat Capacity and Entropy</u>.

The heat capacity was estimated as 8.5 gibbs/g-atom by analogy with other monatomic metals. The entropy at 298°K was calculated in a manner analogous to that of the heat of formation. At 2500°K a glass transition was assumed, below which the heat capacity was that of the crystal.

<u>Melting Data</u>.

See crystal table for details.

<u>Vaporization Data</u>.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Tungsten (W)

(Ideal Gas) GFW = 183.85

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.486	203.103	203.103	INFINITE
100	4.968	36.105	45.995	- .989	203.444	200.063	- 437.238
200	4.973	39.549	42.009	- .492	203.461	196.664	- 214.904
298	5.092	41.549	41.549	.000	203.400	193.340	- 141.722
300	5.097	41.581	41.549	.009	203.398	193.277	- 140.802
400	5.536	43.099	41.754	.538	203.338	189.913	- 103.763
500	6.296	44.411	42.156	1.127	203.326	186.558	- 81.545
600	7.251	45.641	42.635	1.804	203.392	183.201	- 66.731
700	8.217	46.833	43.150	2.578	203.545	179.825	- 56.144
800	9.026	47.985	43.683	3.442	203.776	176.421	- 48.196
900	9.577	49.083	44.222	4.374	204.066	172.985	- 42.006
1000	9.855	50.109	44.760	5.348	204.386	169.514	- 37.047
1100	9.904	51.052	45.290	6.338	204.712	166.011	- 32.983
1200	9.787	51.910	45.807	7.324	205.023	162.479	- 29.591
1300	9.569	52.685	46.306	8.292	205.305	158.922	- 26.717
1400	9.297	53.384	46.787	9.236	205.552	155.345	- 24.250
1500	9.007	54.016	47.249	10.151	205.759	151.751	- 22.110
1600	8.721	54.588	47.690	11.037	205.926	148.145	- 20.236
1700	8.451	55.108	48.111	11.896	206.054	144.531	- 18.581
1800	8.205	55.584	48.513	12.728	206.144	140.909	- 17.109
1900	7.987	56.022	48.897	13.537	206.200	137.282	- 15.791
2000	7.796	56.427	49.264	14.326	206.224	133.654	- 14.605
2100	7.634	56.803	49.614	15.098	206.219	130.026	- 13.532
2200	7.499	57.155	49.949	15.854	206.186	126.397	- 12.556
2300	7.389	57.486	50.269	16.598	206.130	122.771	- 11.666
2400	7.304	57.798	50.576	17.333	206.053	119.151	- 10.850
2500	7.240	58.095	50.871	18.060	205.956	115.531	- 10.100
2600	7.197	58.378	51.155	18.781	205.841	111.916	- 9.407
2700	7.174	58.649	51.427	19.500	205.707	108.307	- 8.767
2800	7.167	58.910	51.690	20.217	205.545	104.703	- 8.172
2900	7.176	59.162	51.943	20.934	205.347	101.101	- 7.619
3000	7.200	59.405	52.188	21.652	205.109	97.514	- 7.104
3100	7.236	59.642	52.425	22.374	204.822	93.929	- 6.622
3200	7.284	59.872	52.654	23.100	204.480	90.359	- 6.171
3300	7.342	60.097	52.876	23.831	204.077	86.799	- 5.748
3400	7.409	60.318	53.092	24.569	203.606	83.249	- 5.351
3500	7.484	60.533	53.301	25.313	203.053	79.720	- 4.978
3600	7.565	60.745	53.505	26.066	202.395	76.204	- 4.626
3700	7.652	60.954	53.703	26.827	193.300	72.754	- 4.297
3800	7.744	61.159	53.897	27.596	193.219	69.499	- 3.997
3900	7.839	61.361	54.086	28.375	193.148	66.246	- 3.712
4000	7.937	61.561	54.270	29.164	193.087	62.991	- 3.442
4100	8.038	61.758	54.450	29.963	193.036	59.741	- 3.184
4200	8.140	61.953	54.627	30.772	192.995	56.491	- 2.940
4300	8.242	62.146	54.799	31.591	192.964	53.240	- 2.706
4400	8.345	62.337	54.968	32.420	192.943	49.987	- 2.483
4500	8.448	62.525	55.134	33.260	192.933	46.741	- 2.270
4600	8.550	62.712	55.297	34.110	192.933	43.493	- 2.066
4700	8.651	62.897	55.457	34.970	192.943	40.245	- 1.871
4800	8.750	63.080	55.614	35.840	192.963	36.996	- 1.684
4900	8.847	63.262	55.768	36.720	192.993	33.743	- 1.505
5000	8.943	63.441	55.920	37.609	193.032	30.497	- 1.333
5100	9.036	63.619	56.069	38.508	193.081	27.245	- 1.168
5200	9.127	63.796	56.216	39.416	193.139	23.989	- 1.008
5300	9.215	63.971	56.360	40.334	193.207	20.734	- .855
5400	9.301	64.144	56.503	41.259	193.282	17.480	- .707
5500	9.383	64.315	56.643	42.194	193.367	14.226	- .565
5600	9.463	64.485	56.782	43.136	193.459	10.966	- .428
5700	9.541	64.653	56.919	44.086	193.559	7.705	- .295
5800	9.615	64.820	57.053	45.044	193.667	4.442	- .167
5900	9.686	64.985	57.186	46.009	193.782	1.182	- .044
6000	[illegible].755	65.148	57.318	46.981	.000	.000	.000

Dec. 31, 1961; June 30, 1966

TUNGSTEN (W) (IDEAL GAS) GFW = 183.85

Ground State Configuration $^5D_0$

$S^\circ_{298.15}$ = 41.549 gibbs/mol

ΔHf°_0 = 203.1 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 203.4 ± 1.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	1	17701.14	7	20983.06	5
1670.3	3	17107.02	9	20427.81	3
3325.53	5	15459.99	7	20174.28	1
4830.00	7	14976.21	5	26035.67	35
6219.33	9	18082.80	3	26585.14	68
2951.29	7	18116.84	5	28413.86	60
9528.07	1	18974.47	7	30061.53	47
13307.06	3	19256.23	9	33420.02	44
19253.58	5	19535.04	11	34874.19	45
12161.95	9	19648.56	13	38611.26	277
15069.94	11	18280.48	5	43092.16	307
17008.50	13	19389.43	1	45985.57	309
13348.54	7	20756.53	8	48987.49	305
16431.28	9	23905.35	16	52348.75	321
19826.04	11	28159.77	24	55770.38	367
13777.70	5	19827.67	7	59180.98	183

Heat of Formation.

ΔHf°_{298} is the heat of sublimation of the crystal at 298°K; this has been obtained by 2nd and 3rd law analysis of the vapor pressure data of three investigators. The results are summarized below:

			$\Delta Hs^\circ_{298.15}$ kcal/mol		
Ref.	Range°K**	Points	2nd law	3rd law	3rd law drift eu
1	2511-3053	12*	200.9 ± 3.6	201.57 ± 1.6	0.1 ± 1.4
2	2383-3123	14	214.8 ± 1.4	202.17 ± 2.5	-4.7 ± 0.5
3	2574-3183	10	202.4 ± 2.7	203.35 ± 1.2	0.4 ± 1.0

*1 point rejected due to failure of a statistical test.

**All temperatures are taken from Ref. 3, in which the earlier measurements have been corrected.

References:

1. H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. 30, 201 (1927).
2. C. Zwikker, Physica 5, 249 (1925).
3. R. Szwarc, E. R. Plante, and J. J. Diamond, J. Res. Natl. Bur. Std. 69A, 417 (1965).

The values are remarkably good, since even at the highest temperature the pressures are less than 10^{-6} atm; all workers used the Langmuir technique. Since the data of Refs. 1 and 3 do not drift, it may be assumed that the accommodation coefficient is unity or close to unity. The drift in the second set cannot be eliminated by assuming a non-unity accomodation coefficient, nor does there appear to be a constant pressure error. Most probably the drift is due to slight errors in temperature. For example, if the readings were 24° high at the low end and 10° low at the high end, the drift would be eliminated; errors of this magnitude are quite possible. The value adopted for $\Delta Hs^\circ_{298.15}$ is 203.4 ± 1.5 kcal/mol.

Heat Capacity and Entropy.

The electronic energy levels were taken from those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467 (1958). Levels above 25000 cm^{-1} were averaged.

Tungsten Unipositive Ion (W^+)
(Ideal Gas) GFW = 183.8495

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	5.108	42.931	42.931	.000	388.918	376.958	- 276.318
300	5.113	42.963	42.931	.009	388.925	376.883	- 274.559
400	5.471	44.478	43.136	.537	389.361	372.805	- 203.691
500	5.934	45.748	43.534	1.107	389.827	368.612	- 161.120
600	6.380	46.870	43.998	1.723	390.329	364.323	- 132.704
700	6.762	47.884	44.482	2.381	390.862	359.946	- 112.380
800	7.078	48.808	44.966	3.073	391.418	355.491	- 97.116
900	7.338	49.657	45.441	3.795	391.995	350.967	- 85.226
1000	7.553	50.442	45.902	4.540	392.583	346.377	- 75.701
1100	7.731	51.170	46.348	5.304	393.180	341.728	- 67.895
1200	7.877	51.849	46.779	6.085	393.783	337.025	- 61.381
1300	7.993	52.485	47.193	6.878	394.386	332.269	- 55.859
1400	8.081	53.080	47.593	7.682	394.990	327.468	- 51.120
1500	8.146	53.640	47.978	8.494	395.591	322.625	- 47.006
1600	8.189	54.167	48.348	9.311	396.186	317.741	- 43.401
1700	8.213	54.665	48.705	10.131	396.772	312.819	- 40.216
1800	8.223	55.134	49.049	10.953	397.348	307.865	- 37.380
1900	8.222	55.579	49.382	11.775	397.914	302.878	- 34.839
2000	8.214	56.001	49.702	12.597	398.468	297.862	- 32.549
2100	8.202	56.401	50.012	13.418	399.009	292.818	- 30.474
2200	8.190	56.782	50.311	14.238	399.537	287.748	- 28.585
2300	8.179	57.146	50.600	15.056	400.051	282.654	- 26.858
2400	8.173	57.494	50.880	15.874	400.554	277.542	- 25.274
2500	8.172	57.828	51.151	16.691	401.044	272.404	- 23.814
2600	8.179	58.148	51.414	17.508	401.522	267.250	- 22.464
2700	8.194	58.457	51.670	18.327	401.985	262.079	- 21.214
2800	8.218	58.756	51.917	19.147	402.423	256.888	- 20.051
2900	8.251	59.045	52.158	19.971	402.828	251.680	- 18.967
3000	8.292	59.325	52.392	20.798	403.196	246.464	- 17.955
3100	8.342	59.598	52.620	21.629	403.515	241.230	- 17.007
3200	8.399	59.863	52.843	22.466	403.781	235.996	- 16.118
3300	8.464	60.123	53.059	23.309	403.987	230.747	- 15.282
3400	8.534	60.377	53.271	24.159	404.124	225.495	- 14.495
3500	8.609	60.625	53.477	25.016	404.181	220.242	- 13.753
3600	8.688	60.869	53.679	25.881	404.132	214.985	- 13.051
3700	8.770	61.108	53.877	26.754	395.646	209.777	- 12.391
3800	8.853	61.343	54.070	27.635	396.174	204.749	- 11.776
3900	8.937	61.574	54.260	28.525	396.711	199.706	- 11.191
4000	9.020	61.801	54.445	29.423	397.255	194.647	- 10.635
4100	9.101	62.025	54.628	30.329	397.808	189.573	- 10.105
4200	9.180	62.245	54.806	31.243	398.369	184.492	- 9.600
4300	9.256	62.462	54.982	32.165	398.938	179.393	- 9.118
4400	9.327	62.676	55.154	33.094	399.514	174.278	- 8.656
4500	9.394	62.886	55.324	34.030	400.096	169.151	- 8.215
4600	9.455	63.093	55.490	34.972	400.685	164.015	- 7.793
4700	9.511	63.297	55.654	35.921	401.281	158.864	- 7.387
4800	9.561	63.498	55.816	36.875	401.882	153.698	- 6.998
4900	9.604	63.695	55.974	37.833	402.487	148.525	- 6.624
5000	9.641	63.890	56.131	38.795	403.095	143.335	- 6.265
5100	9.672	64.081	56.285	39.761	403.708	138.130	- 5.919
5200	9.696	64.269	56.437	40.729	404.323	132.920	- 5.586
5300	9.713	64.454	56.586	41.700	404.941	127.692	- 5.265
5400	9.724	64.636	56.734	42.672	405.560	122.454	- 4.956
5500	9.730	64.814	56.879	43.644	406.179	117.209	- 4.657
5600	9.729	64.990	57.022	44.617	406.798	111.942	- 4.369
5700	9.723	65.162	57.163	45.590	407.418	106.675	- 4.090
5800	9.711	65.331	57.303	46.562	408.037	101.391	- 3.821
5900	9.695	65.497	57.440	47.532	408.654	96.102	- 3.560
6000	9.674	65.659	57.576	48.501	215.366	92.888	- 3.383

Dec. 31, 1966

TUNGSTEN UNIPOSITIVE ION (W^+) (IDEAL GAS) GFW = 183.8495

Ground State Configuration $^6D_{1/2}$ ΔHf°_0 = 387.139 kcal/mol

$S^\circ_{298.15}$ = 42.931 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 388.918 kcal/mol

Electronic Levels and Quantum Weights

ϵ_1, cm^{-1}	g_1	ϵ_1, cm^{-1}	g_1	ϵ_1, cm^{-1}	g_1
0	2	16553	10	26929	12
1518.8	4	17437	12	36165	2
3172.5	6	18001	10	39441	12
4716.3	8	18991	10	42256	18
6147.2	10	19071	10	44709	30
7420.4	6	19277	6	45522	6
8711.3	4	19404	6	46373	26
11301.1	6	19443	20	47397	14
13412.0	8	19637	10	48543	30
14857.2	10	[20000]	[30]	49176	26
8832.7	2	20040	8	50605	20
10592.5	4	20628	28	51443	38
13434.1	6	[21000]	[20]	52486	36
13173.4	2	[22000]	[20]	53323	34
14634.4	4	22187	40	54406	66
14967.8	6	23166	36	55342	20
15147.0	8	23921	36	56554	56
16234.8	6	25081	8	59910	194
16589.7	8	26189	18	63660	16

Heat of Formation.

The heat of formation is obtained by adding the heat of ionization at 0°K to the ΔHf°_0 W(g). The heat of ionization, 184.036 kcal (7.98 eV), is obtained from C. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington D. C. (1958).

Heat Capacity and Entropy.

The electronic energy levels are obtained from C. E. Moore, loc. cit. In the low lying configuration [Xe] $4f^1 5d^5$ the ^2F, ^2G, ^2F, ^2H and ^2S multiplets have not been observed. The total degeneracy of these levels (70) is split among three estimated levels of 20000, 21000, and 22000 cm^{-1}, obtained by analogy with Mo^+. A realistic uncertainty in these levels would produce a maximum uncertainty of 0.03 gibbs/mol in the free energy function and 0.09 gibbs/mol in the entropy at 6000°K.

The enthalpy at 0°K is -1.487 kcal/mol.

Zirconium (Zr)

(Reference State) GFW = 91.22

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.321	.000	.000	.000
100	4.466	3.352	14.443	-1.109	.000	.000	.000
200	5.754	6.946	9.862	-.583	.000	.000	.000
298	6.068	9.314	9.314	.000	.000	.000	.000
300	6.097	9.352	9.314	.011	.000	.000	.000
400	6.367	11.143	9.556	.634	.000	.000	.000
500	6.642	12.593	10.023	1.285	.000	.000	.000
600	6.919	13.828	10.557	1.963	.000	.000	.000
700	7.197	14.916	11.103	2.669	.000	.000	.000
800	7.475	15.895	11.642	3.402	.000	.000	.000
900	7.753	16.791	12.165	4.164	.000	.000	.000
1000	8.032	17.623	12.670	4.953	.000	.000	.000
1100	8.311	18.401	13.156	5.770	.000	.000	.000
1200	6.886	19.888	13.667	7.466	.000	.000	.000
1300	6.997	20.444	14.167	8.160	.000	.000	.000
1400	7.108	20.966	14.634	8.865	.000	.000	.000
1500	7.219	21.461	15.073	9.581	.000	.000	.000
1600	7.330	21.930	15.487	10.309	.000	.000	.000
1700	7.441	22.378	15.879	11.047	.000	.000	.000
1800	7.552	22.806	16.252	11.797	.000	.000	.000
1900	7.663	23.218	16.608	12.558	.000	.000	.000
2000	7.774	23.613	16.949	13.330	.000	.000	.000
2100	7.885	23.995	17.275	14.113	.000	.000	.000
2200	8.000	26.719	17.669	19.910	.000	.000	.000
2300	8.000	27.075	18.071	20.710	.000	.000	.000
2400	8.000	27.415	18.453	21.510	.000	.000	.000
2500	8.000	27.742	18.818	22.310	.000	.000	.000
2600	8.000	28.056	19.167	23.110	.000	.000	.000
2700	8.000	28.358	19.502	23.910	.000	.000	.000
2800	8.000	28.649	19.824	24.710	.000	.000	.000
2900	8.000	28.929	20.133	25.510	.000	.000	.000
3000	8.000	29.201	20.430	26.310	.000	.000	.000
3100	8.000	29.463	20.718	27.110	.000	.000	.000
3200	8.000	29.717	20.995	27.910	.000	.000	.000
3300	8.000	29.963	21.263	28.710	.000	.000	.000
3400	8.000	30.202	21.522	29.510	.000	.000	.000
3500	8.000	30.434	21.774	30.310	.000	.000	.000
3600	8.000	30.659	22.017	31.110	.000	.000	.000
3700	8.000	30.878	22.254	31.910	.000	.000	.000
3800	8.000	31.092	22.484	32.710	.000	.000	.000
3900	8.000	31.299	22.707	33.510	.000	.000	.000
4000	8.000	31.502	22.924	34.310	.000	.000	.000
4100	8.000	31.700	23.136	35.110	.000	.000	.000
4200	8.000	31.892	23.342	35.910	.000	.000	.000
4300	8.000	32.081	23.543	36.710	.000	.000	.000
4400	8.000	32.264	23.739	37.510	.000	.000	.000
4500	8.000	32.444	23.931	38.310	.000	.000	.000
4600	8.000	32.620	24.118	39.110	.000	.000	.000
4700	8.000	32.792	24.301	39.910	.000	.000	.000
4800	9.020	62.511	24.622	181.867	.000	.000	.000
4900	9.073	62.697	25.397	182.771	.000	.000	.000
5000	9.122	62.881	26.145	183.681	.000	.000	.000
5100	9.169	63.062	26.867	184.596	.000	.000	.000
5200	9.212	63.240	27.564	185.515	.000	.000	.000
5300	9.252	63.416	28.239	186.438	.000	.000	.000
5400	9.288	63.590	28.892	187.365	.000	.000	.000
5500	9.322	63.760	29.525	188.296	.000	.000	.000
5600	9.352	63.929	30.138	189.229	.000	.000	.000
5700	9.379	64.094	30.732	190.166	.000	.000	.000
5800	9.403	64.258	31.308	191.105	.000	.000	.000
5900	9.424	64.419	31.868	192.046	.000	.000	.000
6000	9.442	64.577	32.412	192.990	.000	.000	.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

ZIRCONIUM (Zr) (REFERENCE STATE) GFW = 91.22

0	to	1135°K	Crystal alpha
1135.	to	2125°K	Crystal beta
2125	to	4776.9°K	Liquid
4776.9	to	6000°K	Ideal Monatomic gas

See crystal, liquid and monatomic gas for details.

Zirconium, Alpha (Zr)

(Crystal) GFW = 91.22

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.321	.000	.000	.000
100	4.466	3.352	14.443	-1.109	.000	.000	.000
200	5.754	6.946	9.862	-.583	.000	.000	.000
298	6.068	9.314	9.314	.000	.000	.000	.000
300	6.097	9.352	9.314	.011	.000	.000	.000
400	6.367	11.143	9.556	.634	.000	.000	.000
500	6.542	12.593	10.023	1.285	.000	.000	.000
600	6.919	13.828	10.557	1.963	.000	.000	.000
700	7.197	14.916	11.103	2.669	.000	.000	.000
800	7.475	15.895	11.642	3.402	.000	.000	.000
900	7.753	16.791	12.165	4.164	.000	.000	.000
1000	8.032	17.623	12.670	4.953	.000	.000	.000
1100	8.311	18.401	13.156	5.770	.000	.000	.000
1200	8.589	19.136	13.624	6.615	-.851	.051	-.009
1300	8.868	19.835	14.075	7.488	-.672	.120	-.020
1400	9.145	20.502	14.510	8.389	-.476	.173	-.027
1500	9.425	21.143	14.931	9.317	-.264	.214	-.031

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

ZIRCONIUM, ALPHA (Zr) (CRYSTAL) GFW = 91.22

ΔHf°_0 = 0 kcal/mol

$S^\circ_{298.15}$ = 9.314 ± 0.10 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

T_t = 1135 ± 5°K

ΔHt° = 0.96 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 148.3 ± 3.5 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 1.1 - 298.2°K, have been measured by Todd (1), Skinner (2), Eastermann (3), Wolcott (4), Burk (5), and Kneip (6). Values of $Cp_{298.15}$ were reported as 6.19 and 6.01 gibbs/mol by Todd (1) and Skinner (2), respectively. The difference (beginning at 150°K) is probably caused by different amounts of impurities (e.g. O_2, H_2, N_2) in the samples. Neither sample was analyzed for hydrogen and oxygen content. Small amounts of either of these impurities would cause important changes in Cp. Remeasurement of Cp using a high purity sample is desirable to resolve the difference. Tentatively, we adopt smooth Cp values which are intermediate between those of Todd and Skinner in the temperature range 200 - 298°K. The curve at lower temperatures is based on references 1, 2, 4, 5 and 6. $S^\circ_{298.15}$ is derived from the adopted Cp based on $S^\circ_{1.16}$ = 0.0008 eu.

Enthalpies have been measured using drop calorimetry by Jaeger (7), Coughlin (8), Skinner (9), Redmond (10), Adenstedt (11) and Douglas (13). Cp above 298°K has been measured by Scott (12) and Vollmer (15) using adiabatic calorimetry and by Klein (14) using pulse heating. The data lead to differences in Cp which are even greater than those noted at 298°K. Observed Cp's are lower than the adopted curve by roughly 3 to 6 per cent, but the observed enthalpies are generally higher by 0 to 10 per cent. Impurities are partly to blame but there also may be a systematic difference between the methods. The purest and best-characterized samples are those of Douglas (13) and Vollmer (15). Even the high-purity sample of Douglas gives H values which are abnormally high at 573°K, suggesting the presence of thermal effects of solid solution and precipitation due to a small amount of hydrogen in the sample (12).

The adopted Cp is based mainly on Douglas (13), but references (7, 9, 15) were also given some weight. Deviations of (13) from the adopted values range from +3.3 per cent at 573°K to +0.3 at 1123°K. Other deviations (each in order of increasing T) are 3 to 0 per cent (7), 1.3 to -1.7 per cent (9), -4 to -6 per cent (15), 5.4 to 1.7 per cent (8) and -1 to 9.5 per cent (10) in terms of enthalpy. Cp is extrapolated linearly above 1133°K.

Transition Data

See Zr(β) table for details.

Heat of Sublimation

$\Delta Hs^\circ_{298.15}$ is calculated as the difference between $\Delta Hf^\circ_{298.15}$ for Zr(g) and Zr(α).

References

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Zirconium, Beta (Zr)

(Crystal) GFW = 91.22

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.887	11.152	11.152	.000	1.706	1.159	-.849
300	5.889	11.188	11.152	.011	1.706	1.155	-.841
400	5.999	12.897	11.384	.605	1.677	.975	-.533
500	6.110	14.248	11.826	1.211	1.632	.804	-.351
600	6.221	15.372	12.326	1.827	1.570	.644	-.235
700	6.332	16.339	12.832	2.455	1.492	.496	-.155
800	6.443	17.192	13.325	3.094	1.397	.360	-.098
900	6.554	17.957	13.798	3.744	1.285	.236	-.057
1000	6.665	18.653	14.249	4.404	1.157	.127	-.028
1100	6.776	19.294	14.679	5.077	1.012	.030	-.006
1200	6.886	19.888	15.098	5.760	.000	.000	.000
1300	6.997	20.444	15.479	6.454	.000	.000	.000
1400	7.108	20.966	15.853	7.159	.000	.000	.000
1500	7.219	21.461	16.210	7.875	.000	.000	.000
1600	7.330	21.930	16.553	8.603	.000	.000	.000
1700	7.441	22.378	16.883	9.341	.000	.000	.000
1800	7.552	22.806	17.200	10.091	.000	.000	.000
1900	7.663	23.217	17.506	10.852	.000	.000	.000
2000	7.774	23.613	17.801	11.624	.000	.000	.000
2100	7.885	23.995	18.087	12.407	.000	.000	.000
2200	7.995	24.365	18.364	13.201	-5.004	.176	-.018
2300	8.106	24.722	18.633	14.006	-4.998	.412	-.039
2400	8.217	25.070	18.894	14.822	-4.982	.645	-.059
2500	8.328	25.407	19.148	15.649	-4.955	.881	-.077
2600	8.439	25.736	19.395	16.487	-4.917	1.115	-.094
2700	8.550	26.057	19.636	17.337	-4.867	1.346	-.109
2800	8.661	26.370	19.871	18.197	-4.807	1.575	-.123
2900	8.772	26.676	20.100	19.069	-4.735	1.800	-.136
3000	8.883	26.975	20.324	19.952	-4.652	2.023	-.147

Dec. 31, 1967

ZIRCONIUM, BETA (Zr) (CRYSTAL) GFW = 91.22

$S^\circ_{298.15}$ = 11.152 gibbs/mol $\Delta Hf^\circ_{298.15}$ = 1.706 kcal/mol

T_t = 1135 ± 10°K ΔHt° = 0.96 kcal/mol

Tm = 2125 ± 2 °K ΔHm° = 5.0 ± 0.3 kcal/mol

Heat of Formation

The heat of formation is obtained from $\Delta Hf^\circ_{298}(\alpha)$ by adding ΔHt° and the difference between $H^\circ_{Tt} - H^\circ_{298}$ for Zr(α) and Zr(β).

Heat Capacity and Entropy

The enthalpies and Cp of Zr(β), at temperatures 1135 - 2118.2 °K, have been measured by many investigators (see Zr(α) table for details). The selected Cp values are based on the data reported by Douglas (1) and Skinner (2). Deviations from the adopted enthalpies are -1.4 to 0.8 per cent (1), -0.4 to 0.3 (2), and 0.2 to 3.0 per cent (7). Deviations of the measured Cp from the adopted values are -5 to -3 per cent (14) and about -6 per cent (10). The heat capacities below 1143.2 and above 1798°K are estimated by linear extrapolation.

The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

Zirconium has two crystal forms, i.e. the hexagonal-close-packed α-form and the cubic-body-centered β-form (3, 4, 5). The value and range of Tt for α → β depends strongly on the kind and amount of impurities (5, 15). For example, nitrogen and oxygen increase Tt while hydrogen decreases it. The adopted value is Tt = 1135 ± 10°K, although recent measurements using purer samples indicate a somewhat higher value. These are summarized below along with the data for ΔHt°. The value ΔHt° = 0.96 kcal/mol is derived from the adopted enthalpy and Cp data on Zr(α) and Zr(β).

	Investigator	Tt, °K	ΔHt°, kcal/mol	Purity, Percent	Method or Property Measured
3.	Vogel (1931)	1135±5	-	unavailable	cooling and dilatometric curves
7.	Coughlin (1950)	1135*	0.920	97.85	drop calorimetry
6.	Komar (1957)	1135*	-	unavailable	Electron miscroscope
8.	Hertzricken (1962)	1135	0.712 ± 0.060	unavailable	differential calorimetry
1.	Douglas (1958)	1136*	0.894	99.91	drop calorimetry
9.	Duwez (1951)	1138±10	-	unavailable	cooling curve
10.	Klein (1962)	1138±?	-	unavailable	resistivity
15.	Kneip (1956)	1142±4	-	∿ 99.95	unavailable
2.	Skinner (1951)	1143±5	1.042	99.05	drop calorimetry
12.	Scott (1957)	1143±2	0.993±0.025	unavailable	adiabatic calorimetry
13.	Rudy (1965)	1145±15	-	99.81	differential thermal analysis
11.	Jaeger (1934)	<1150	-	unavailable	drop calorimetry
14.	Vollmer (1967)	1155±?	0.950	99.8	adiabatic calorimetry

* Adopted by the original authors.

Melting Data

See the Zr(ℓ) table for details.

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Zirconium (Zr)

(Liquid) GFW = 91.22

T, °K	gibbs/mol Cp°	 S°	 −(G°−H°298)/T	kcal/mol H°−H°298	 ΔHf°	 ΔGf°	Log Kp
0							
100							
200							
298	5.887	13.289	13.289	.000	6.351	5.166	- 3.787
300	5.889	13.325	13.289	.011	6.351	5.159	- 3.758
400	5.999	15.034	13.521	.605	6.322	4.766	- 2.604
500	6.110	16.385	13.963	1.211	6.277	4.381	- 1.915
600	6.221	17.509	14.463	1.827	6.215	4.007	- 1.460
700	6.332	18.476	14.969	2.455	6.137	3.645	- 1.138
800	6.443	19.329	15.462	3.094	6.043	3.295	- .900
900	6.554	20.094	15.935	3.744	5.931	2.958	- .718
1000	6.665	20.790	16.386	4.405	5.803	2.635	- .576
1100	6.776	21.431	16.816	5.077	5.658	2.325	- .462
1200	6.887	22.025	17.225	5.760	4.645	2.080	- .379
1300	6.997	22.581	17.616	6.454	4.645	1.867	- .314
1400	8.000	23.103	17.990	7.159	4.645	1.653	- .258
1500	8.000	23.655	18.349	7.959	4.729	1.437	- .209
1600	8.000	24.172	18.697	8.759	4.801	1.215	- .166
1700	8.000	24.657	19.034	9.559	4.863	.989	- .127
1800	8.000	25.114	19.359	10.359	4.913	.759	- .092
1900	8.000	25.546	19.673	11.159	4.952	.527	- .061
2000	8.000	25.957	19.977	11.959	4.980	.293	- .032
2100	8.000	26.347	20.271	12.759	4.997	.058	- .006
2200	8.000	26.719	20.556	13.559	.000	.000	.000
2300	8.000	27.075	20.832	14.359	.000	.000	.000
2400	8.000	27.415	21.099	15.159	.000	.000	.000
2500	8.000	27.742	21.358	15.959	.000	.000	.000
2600	8.000	28.056	21.610	16.759	.000	.000	.000
2700	8.000	28.358	21.854	17.559	.000	.000	.000
2800	8.000	28.649	22.092	18.359	.000	.000	.000
2900	8.000	28.929	22.323	19.159	.000	.000	.000
3000	8.000	29.201	22.547	19.959	.000	.000	.000
3100	8.000	29.463	22.766	20.759	.000	.000	.000
3200	8.000	29.717	22.980	21.559	.000	.000	.000
3300	8.000	29.963	23.187	22.359	.000	.000	.000
3400	8.000	30.202	23.390	23.159	.000	.000	.000
3500	8.000	30.434	23.588	23.959	.000	.000	.000
3600	8.000	30.659	23.782	24.759	.000	.000	.000
3700	8.000	30.878	23.970	25.559	.000	.000	.000
3800	8.000	31.092	24.155	26.359	.000	.000	.000
3900	8.000	31.299	24.336	27.159	.000	.000	.000
4000	8.000	31.502	24.512	27.959	.000	.000	.000
4100	8.000	31.700	24.685	28.759	.000	.000	.000
4200	8.000	31.892	24.854	29.559	.000	.000	.000
4300	8.000	32.081	25.020	30.359	.000	.000	.000
4400	8.000	32.264	25.183	31.159	.000	.000	.000
4500	8.000	32.444	25.342	31.959	.000	.000	.000
4600	8.000	32.620	25.499	32.759	.000	.000	.000
4700	8.000	32.792	25.652	33.559	.000	.000	.000
4800	8.000	32.961	25.802	34.359	- 141.157	.683	- .031
4900	8.000	33.126	25.950	35.159	- 141.261	3.640	- .162
5000	8.000	33.287	26.095	35.959	- 141.371	6.598	- .288
5100	8.000	33.446	26.238	36.759	- 141.486	9.558	- .410
5200	8.000	33.601	26.378	37.559	- 141.605	12.521	- .526
5300	8.000	33.753	26.516	38.359	- 141.728	15.486	- .639
5400	8.000	33.903	26.651	39.159	- 141.855	18.453	- .747
5500	8.000	34.050	26.784	39.959	- 141.986	21.422	- .851

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

ZIRCONIUM (Zr) (LIQUID) GFW = 91.22

$S^\circ_{298.15}$ = [13.289] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [6.351] kcal/mol

Tm = 2125 ± 5 °K ΔHm° = 5.0 ± 0.4 kcal/mol

Tb = [4776.9] °K ΔHv° = 141.13 kcal/mol

Heat of Formation

The heat of formation is obtained from $\Delta Hf^\circ_{298}(\beta)$ by adding ΔHm° and the difference between $H^\circ_{2125} - H^\circ_{298}$ for Zr(β) and Zr(ℓ).

Heat Capacity and Entropy

A glass transition temperature at 1400°K is assumed. The heat capacities below 1400°K are taken from those for Zr(β). The Cp value above 1400°K is estimated by comparison with that of Zr(β) at Tm and assumed to be constant in the temperature range 1400 - 5500°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point of Zr(β) has been determined by many investigators. The results reported show wide discrepancies, probably caused by the differences in purity of the samples used for determination. The Tm value adopted is obtained from Oriani and Jones. The other values of Tm reported are presented in the table below.

The adopted heat of melting was determined calorimetrically by V. P. Elyntin, M. A. Maurakh and G. M. Sverdlov, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 10, No. 2, 87 (1967). Zirconium samples from two different sources were melted in an Arc-crucible furnace. The crucible contained an insert of graphite which had a thick lining (presumably of zirconium carbide) in order to minimize carbonization of Zr(ℓ). The molten Zr was poured through an opening in the bottom of the crucible into a calorimeter containing molten Mg as the calorimetric fluid. The method of calculating the value of ΔHm° was described in detail by V. P. Elytin, M. A. Maurakh, V. Y. Mishuk, and G. M. Sverdlov, Izv. Vyssihikh Uchebn. Zavendenii, Tsvetn. Met. 10, 60 (1967). The authors estimated the uncertainty as about 7 percent in ΔHm°.

Tm, °K	Reference
2113±25	H. K. Adenstedt, Trans. Am. Soc. Metals 44, 949 (1952).
2118	J. L. Scott, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-2328, 1957.
2125±2	R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 25, 248 (1954).
2128	D. K. Deardorff and E. T. Hayes, Trans. AIME 206, 509 (1956).
2130	J. H. deBoer, Ind. Eng. Chem. 19, 1256 (1927); J. H. deBoer, and J. D. Fast, Z. Anorg. Allgem. Chem. 187, 193 (1930); and F. M. Jaeger and W. A. Veenstra, Rec. Trav. Chim. 53, 917 (1934).
2133±15	R. V. Sara, J. Am. Ceram. Soc. 48, 243 (1965).
2141±10	R. A. Oriani and T. S. Jones, Rev. Sci. Inst. 25, 248 (1954). This value is not adopted.
2149±4	E. Rudy and S. Windisch, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. VIII, January 1966.
2150±20	E. Rudy, D. P. Harmon, and C. E. Brukl, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. II, May 1965.

Vaporization Data

Tb is the temperature at which the Gibbs energy change (ΔGr°) for the reaction Zr(ℓ) = Zr(g) approaches zero. The difference between ΔHf°(Zr, g) and ΔHf°(Zr, ℓ) at Tb is ΔHv°.

Zirconium (Zr)

(Ideal Gas) GFW = 91.22

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.629	147.992	147.992	INFINITE
100	5.019	37.221	48.536	-1.132	148.277	144.891	-316.658
200	5.743	40.892	43.880	-.598	148.285	141.496	-154.620
298	6.367	43.315	43.315	.000	148.300	138.163	-101.276
300	6.375	43.354	43.315	.012	148.301	138.100	-100.606
400	6.612	45.229	43.569	.664	148.330	134.695	-73.594
500	6.594	46.706	44.054	1.326	148.341	131.284	-57.384
600	6.464	47.897	44.599	1.979	148.316	127.875	-46.578
700	6.315	48.882	45.142	2.618	148.249	124.472	-38.862
800	6.198	49.717	45.663	3.243	148.141	121.083	-33.078
900	6.133	50.443	46.155	3.859	147.995	117.709	-28.584
1000	6.121	51.088	46.617	4.472	147.819	114.353	-24.992
1100	6.155	51.673	47.050	5.085	147.615	111.016	-22.057
1200	6.225	52.211	47.458	5.704	146.538	107.750	-19.624
1300	6.320	52.713	47.843	6.331	146.471	104.521	-17.572
1400	6.428	53.185	48.208	6.968	146.403	101.297	-15.813
1500	6.542	53.633	48.555	7.617	146.336	98.077	-14.290
1600	6.655	54.059	48.886	8.276	146.267	94.862	-12.958
1700	6.763	54.465	49.202	8.947	146.200	91.652	-11.783
1800	6.865	54.855	49.505	9.629	146.132	88.444	-10.739
1900	6.959	55.229	49.797	10.320	146.062	85.241	-9.805
2000	7.046	55.588	50.077	11.021	145.991	82.042	-8.965
2100	7.127	55.934	50.348	11.729	145.916	78.846	-8.206
2200	7.202	56.267	50.610	12.446	140.836	75.831	-7.533
2300	7.273	56.588	50.863	13.169	140.759	72.878	-6.925
2400	7.341	56.899	51.108	13.900	140.690	69.928	-6.368
2500	7.408	57.201	51.345	14.638	140.628	66.981	-5.855
2600	7.475	57.492	51.576	15.382	140.572	64.037	-5.383
2700	7.542	57.776	51.801	16.133	140.523	61.094	-4.945
2800	7.609	58.051	52.019	16.890	140.480	58.153	-4.539
2900	7.678	58.319	52.232	17.654	140.444	55.213	-4.161
3000	7.749	58.581	52.439	18.426	140.416	52.275	-3.808
3100	7.821	58.836	52.641	19.204	140.394	49.337	-3.478
3200	7.894	59.086	52.839	19.990	140.380	46.400	-3.169
3300	7.969	59.330	53.032	20.783	140.373	43.463	-2.878
3400	8.045	59.569	53.220	21.584	140.374	40.527	-2.605
3500	8.121	59.803	53.405	22.392	140.382	37.590	-2.347
3600	8.198	60.033	53.586	23.208	140.398	34.653	-2.104
3700	8.274	60.259	53.763	24.032	140.422	31.715	-1.873
3800	8.351	60.480	53.937	24.863	140.453	28.776	-1.655
3900	8.426	60.698	54.108	25.702	140.492	25.837	-1.448
4000	8.500	60.912	54.275	26.548	140.538	22.897	-1.251
4100	8.573	61.123	54.440	27.402	140.592	19.955	-1.064
4200	8.644	61.331	54.601	28.263	140.653	17.012	-.885
4300	8.713	61.535	54.760	29.131	140.721	14.067	-.715
4400	8.780	61.736	54.916	30.005	140.795	11.121	-.552
4500	8.844	61.934	55.070	30.887	140.877	8.173	-.397
4600	8.906	62.129	55.222	31.774	140.964	5.223	-.248
4700	8.965	62.321	55.371	32.668	141.058	2.271	-.106
4800	9.020	62.511	55.517	33.567	.000	.000	.000
4900	9.073	62.697	55.662	34.472	.000	.000	.000
5000	9.122	62.881	55.805	35.381	.000	.000	.000
5100	9.169	63.062	55.945	36.296	.000	.000	.000
5200	9.212	63.240	56.084	37.215	.000	.000	.000
5300	9.252	63.416	56.220	38.138	.000	.000	.000
5400	9.288	63.590	56.355	39.065	.000	.000	.000
5500	9.322	63.760	56.488	39.996	.000	.000	.000
5600	9.352	63.929	56.620	40.929	.000	.000	.000
5700	9.379	64.094	56.749	41.866	.000	.000	.000
5800	9.403	64.258	56.877	42.805	.000	.000	.000
5900	9.424	64.419	57.004	43.747	.000	.000	.000
6000	9.442	64.577	57.129	44.690	.000	.000	.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

ZIRCONIUM (Zr) (IDEAL GAS) GFW = 91.22

Ground State Configuration $^3F_2$

ΔHf°_0 = 148.0 ± 3.5 kcal/mol

$S^\circ_{298.15}$ = 43.32 ± 0.10 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 148.3 ± 3.5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	5	8057.30	9	14348.78	5	16316.96	11
570.41	7	10885.36	3	14697.03	7	16978.29	13
1240.84	9	11016.65	5	14783.54	5	17631.20	110
4186.11	5	11258.38	7	14791.28	9	22124.13	146
4196.85	1	11640.72	5	14988.51	11	26202.88	196
4376.28	3	11956.33	7	15119.66	13	28636.78	125
4870.53	3	12342.37	9	15146.48	5	31603.58	130
5023.41	5	12503.44	7	15201.26	7	34729.28	139
5101.68	5	12760.66	9	15457.40	7	36284.48	156
5249.07	7	12772.78	11	15699.86	9	38650.05	181
5540.54	9	13141.76	1	15720.36	9	41296.57	188
5888.93	11	14123.01	3	15932.10	9	45443.61	144

Heat of Formation

Vapor pressures of Zr(β) and Zr(ℓ) were measured, using the Langmuir free-vaporization method, by Skinner (1) and Koch (3), respectively. Based on the reported results, the corresponding enthalpies of sublimation and vaporization are evaluated by the second and third law methods. See the table below for details. The values of evaporation rate and vapor pressure given by Koch in Table 2 on page 9 are too big by a factor of 10 due to typographical errors. The samples employed by Koch were prepared from iodide-process zirconium of 99.9 percent purity by tungsten-electrode melting in an inert atmosphere. The measured weight losses were in general more than one hundred times greater than those reported by Skinner. The value of ΔHf°_{298}(Zr, g) adopted is 148.3 ± 3.5 kcal/mol, which is derived using the data of Koch.

Trulson (2) used a mass spectrometer with a high temperature Knudsen effusion source to obtain the vapor pressure for Zr(β) and Zr(ℓ). Based on the reported vapor pressures the values of heat of sublimation of Zr(β) are evaluated by the second and third law methods. The results are presented in the table below. Because of the uncertainties in obtaining absolute pressures from ion intensities, these results are not adopted.

Zwikker (4) determined the vapor pressures of Zr(β) by the Langmuir method. However, the zirconium sample was reported to be covered by an oxide layer during the measurement. Therefore, the pressures obtained are probably not the vapor pressures of pure zirconium and are not used for evaluation.

Investigator	Temperature, °K	No. of Points	ΔHr°_{298}, kcal/mol Second Law	Third Law	Drift eu	ΔHf°_{298}* kcal/mol
1. Skinner (1951)	1951 - 2047	12	138.6±2.1	144.2	2.8±1.0	145.9
2. Trulson (1965)	1968 - 2274	22	141.3±1.5	142.1	0.4±0.7	143.8
3. Koch (1968)	2229 - 2795	16	142.7±4.3	141.9	-0.3±1.7	148.3

*Calculation based on the third law ΔHr°_{298}, $\Delta Hf^\circ_{298}(\beta)$ = 1.706 and $\Delta Hf^\circ_{298}(\ell)$ = 6.351 kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore (5). Above the level ε_i = 15932.10 cm^{-1}, the values of ε_i and g_i listed in the above table are average values calculated from those given by Moore. The entropy contributed by the the unobserved electronic is estimated to be less than 0.1 eu at 6000°K.

References

1. G. B. Skinner, Ph. D. Thesis, The Ohio State University, 1951; and G. B. Skinner, J. W. Edwards and H. L. Johnston, J. Am. Chem. Soc. 73, 174 (1951).
2.. O. C. Trulson and H. W. Goldstein, J. Phys. Chem. 69, 2531 (1965).
3. R. K. Koch and W. E. Anable, U. S. Bur. Mines RI 7063, 1968.
4. C. Zwikker, Versl. Kon. Ak. van Wetenschappen, Amsterdam 35, 336 (1926); Proc. Roy. Ac. Amsterdam 29, 792 (1926); Physica 8, 240 (1928); and J. H. DeBoer and J. D. Fact, Z. Anorg. Allgem. Chem. 187, 193 (1930).
5. C. E. Moore, Matl. Bur. Std. Circ. 467, Vol. II, 1952.

Zirconium Unipositive Ion (Zr^+)

(Ideal Gas) GFW = 91.21945

T, °K	gibbs/mol Cp°	 S°	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 ΔHf°	 ΔGf°	Log Kp
0							
100							
200							
298	6.759	43.864	43.864	.000	306.200	294.412	-215.810
300	6.760	43.906	43.864	.013	306.211	294.339	-214.425
400	6.754	45.853	44.130	.689	306.761	290.298	-158.611
500	6.657	47.351	44.630	1.360	307.278	286.121	-125.063
600	6.558	48.555	45.187	2.021	307.758	281.844	-102.662
700	6.497	49.561	45.742	2.673	308.200	277.488	-86.636
800	6.478	50.427	46.275	3.322	308.613	273.073	-74.600
900	6.492	51.190	46.779	3.970	308.996	268.607	-65.227
1000	6.524	51.876	47.255	4.621	309.355	264.100	-57.719
1100	6.565	52.500	47.704	5.275	309.689	259.559	-51.570
1200	6.607	53.073	48.128	5.934	309.149	255.040	-46.449
1300	6.648	53.603	48.529	6.596	309.613	250.511	-42.115
1400	6.685	54.097	48.909	7.263	310.072	245.948	-38.394
1500	6.718	54.560	49.271	7.933	310.523	241.352	-35.165
1600	6.746	54.994	49.615	8.606	310.965	236.726	-32.335
1700	6.770	55.404	49.943	9.282	311.400	232.073	-29.835
1800	6.790	55.791	50.258	9.960	311.824	227.394	-27.609
1900	6.806	56.159	50.559	10.640	312.240	222.693	-25.615
2000	6.819	56.508	50.847	11.321	312.646	217.969	-23.818
2100	6.829	56.841	51.125	12.004	313.043	213.224	-22.190
2200	6.836	57.159	51.392	12.687	308.426	208.639	-20.726
2300	6.841	57.463	51.650	13.371	308.806	204.094	-19.393
2400	6.844	57.754	51.898	14.055	309.187	199.534	-18.170
2500	6.845	58.034	52.138	14.740	309.569	194.957	-17.043
2600	6.845	58.302	52.370	15.424	309.950	190.365	-16.002
2700	6.843	58.560	52.594	16.109	310.332	185.760	-15.036
2800	6.840	58.809	52.812	16.793	310.713	181.138	-14.138
2900	6.836	59.049	53.023	17.477	311.093	176.504	-13.302
3000	6.831	59.281	53.228	18.160	311.473	171.855	-12.520
3100	6.824	59.505	53.426	18.843	311.853	167.195	-11.787
3200	6.817	59.721	53.620	19.525	312.232	162.525	-11.100
3300	6.810	59.931	53.808	20.206	312.610	157.840	-10.453
3400	6.801	60.134	53.991	20.887	312.987	153.145	-9.844
3500	6.793	60.331	54.169	21.566	313.363	148.438	-9.269
3600	6.783	60.522	54.343	22.245	313.739	143.721	-8.725
3700	6.774	60.708	54.513	22.923	314.114	138.990	-8.210
3800	6.764	60.889	54.678	23.600	314.488	134.254	-7.721
3900	6.754	61.064	54.840	24.276	314.861	129.507	-7.257
4000	6.744	61.235	54.997	24.951	315.232	124.747	-6.816
4100	6.734	61.401	55.152	25.625	315.603	119.980	-6.395
4200	6.724	61.564	55.302	26.298	315.973	115.207	-5.995
4300	6.714	61.722	55.450	26.969	316.341	110.422	-5.612
4400	6.705	61.876	55.594	27.640	316.709	105.630	-5.247
4500	6.695	62.027	55.735	28.310	317.075	100.827	-4.897
4600	6.686	62.174	55.874	28.979	317.441	96.018	-4.562
4700	6.677	62.317	56.009	29.648	317.807	91.200	-4.241
4800	6.669	62.458	56.142	30.315	177.014	87.056	-3.964
4900	6.661	62.595	56.272	30.981	177.273	85.182	-3.799
5000	6.653	62.730	56.400	31.647	177.525	83.301	-3.641
5100	6.646	62.861	56.526	32.312	177.772	81.411	-3.489
5200	6.640	62.990	56.649	32.976	178.014	79.522	-3.342
5300	6.634	63.117	56.770	33.640	178.252	77.623	-3.201
5400	6.628	63.241	56.888	34.303	178.485	75.722	-3.065
5500	6.623	63.362	57.005	34.966	178.714	73.817	-2.933
5600	6.619	63.482	57.119	35.628	178.939	71.906	-2.806
5700	6.615	63.599	57.232	36.290	179.161	69.997	-2.684
5800	6.612	63.714	57.343	36.951	179.380	68.077	-2.565
5900	6.610	63.827	57.452	37.612	179.597	66.156	-2.451
6000	6.608	63.938	57.559	38.273	179.811	64.234	-2.340

Dec. 31, 1967

ZIRCONIUM UNIPOSITIVE ION (Zr^+) (IDEAL GAS) GFW = 91.21945

Ground State Configuration $^4F_{3/2}$

$S°_{298.15}$ = 43.864 ± 0. 01 gibbs/mol

$\Delta Hf°_0$ = 305.7 ± 4 kcal/mol

$\Delta Hf°_{298.15}$ = 306.2 ± 4 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	4	15611.151	30	43469.453	36
314.67	6	24311.416	46	49607.744	30
763.44	8	30405.276	54	58906.836	30
1322.91	10	31980.999	40	65207.022	42
3003.126	18	34607.328	36	71059.874	42
4080.140	20	37180.173	38	76599.790	60
6466.284	26	38077.586	40	78870.977	56
8624.116	36	40045.807	26	85380.553	58
12983.250	40	41556.750	50		

Heat of Formation

The heat of formation is calculated from the reaction $Zr(g) - e^-(g) = Zr+(g)$ with the JANAF auxiliary value for Zr(g); and an ionization potential = 6.84 eV or 157.737 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. II, 1952 and Vol. III, 1958. The electronic levels above 2500 cm^{-1} are averaged. The $H° - H°_{298}$ value at 0°K is -1.786 kcal/mol.

Electron Gas (e^-)

(Reference State) At. Wt. = 0.00054876

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			
0							
100							
200							
298	4.968	4.989	4.989	.000	.000	.000	.000
300	4.968	5.019	4.989	.009	.000	.000	.000
400	4.968	6.449	5.184	.506	.000	.000	.000
500	4.968	7.557	5.552	1.003	.000	.000	.000
600	4.968	8.463	5.964	1.500	.000	.000	.000
700	4.968	9.229	6.377	1.996	.000	.000	.000
800	4.968	9.892	6.776	2.493	.000	.000	.000
900	4.968	10.477	7.155	2.990	.000	.000	.000
1000	4.968	11.001	7.514	3.487	.000	.000	.000
1100	4.968	11.474	7.853	3.984	.000	.000	.000
1200	4.968	11.906	8.173	4.480	.000	.000	.000
1300	4.968	12.304	8.475	4.977	.000	.000	.000
1400	4.968	12.672	8.762	5.474	.000	.000	.000
1500	4.968	13.015	9.034	5.971	.000	.000	.000
1600	4.968	13.336	9.293	6.467	.000	.000	.000
1700	4.968	13.637	9.540	6.964	.000	.000	.000
1800	4.968	13.921	9.776	7.461	.000	.000	.000
1900	4.968	14.189	10.001	7.958	.000	.000	.000
2000	4.968	14.444	10.217	8.455	.000	.000	.000
2100	4.968	14.686	10.424	8.951	.000	.000	.000
2200	4.968	14.918	10.623	9.448	.000	.000	.000
2300	4.968	15.138	10.814	9.945	.000	.000	.000
2400	4.968	15.350	10.999	10.442	.000	.000	.000
2500	4.968	15.553	11.177	10.939	.000	.000	.000
2600	4.968	15.748	11.349	11.435	.000	.000	.000
2700	4.968	15.935	11.516	11.932	.000	.000	.000
2800	4.968	16.116	11.677	12.429	.000	.000	.000
2900	4.968	16.290	11.833	12.926	.000	.000	.000
3000	4.968	16.458	11.984	13.423	.000	.000	.000
3100	4.968	16.621	12.131	13.919	.000	.000	.000
3200	4.968	16.779	12.274	14.416	.000	.000	.000
3300	4.968	16.932	12.413	14.913	.000	.000	.000
3400	4.968	17.080	12.548	15.410	.000	.000	.000
3500	4.968	17.224	12.679	15.907	.000	.000	.000
3600	4.968	17.364	12.808	16.403	.000	.000	.000
3700	4.968	17.500	12.933	16.900	.000	.000	.000
3800	4.968	17.633	13.055	17.397	.000	.000	.000
3900	4.968	17.762	13.174	17.894	.000	.000	.000
4000	4.968	17.888	13.290	18.390	.000	.000	.000
4100	4.968	18.010	13.404	18.887	.000	.000	.000
4200	4.968	18.130	13.515	19.384	.000	.000	.000
4300	4.968	18.247	13.623	19.881	.000	.000	.000
4400	4.968	18.361	13.730	20.378	.000	.000	.000
4500	4.968	18.473	13.834	20.874	.000	.000	.000
4600	4.968	18.582	13.936	21.371	.000	.000	.000
4700	4.968	18.689	14.036	21.868	.000	.000	.000
4800	4.968	18.793	14.134	22.365	.000	.000	.000
4900	4.968	18.896	14.230	22.862	.000	.000	.000
5000	4.968	18.996	14.324	23.358	.000	.000	.000
5100	4.968	19.095	14.417	23.855	.000	.000	.000
5200	4.968	19.191	14.508	24.352	.000	.000	.000
5300	4.968	19.286	14.597	24.849	.000	.000	.000
5400	4.968	19.379	14.685	25.346	.000	.000	.000
5500	4.968	19.470	14.771	25.842	.000	.000	.000
5600	4.968	19.559	14.856	26.339	.000	.000	.000
5700	4.968	19.647	14.939	26.836	.000	.000	.000
5800	4.968	19.734	15.021	27.333	.000	.000	.000
5900	4.968	19.818	15.102	27.830	.000	.000	.000
6000	4.968	19.902	15.181	28.326	.000	.000	.000

Mar. 31, 1965

ELECTRON GAS (e^-) (REFERENCE STATE) AT. WT. = 0.00054876

0 to 6000°K. IDEAL GAS

$S^\circ_{298.15}$ = 4.988 cal. deg.$^{-1}$ mole^{-1} $\Delta H^\circ_{f\ 298.15} = 0$

Electronic Levels and Multiplicities

ϵ_1 cm.$^{-1}$,	g_1
0	2

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Calculated by assuming to be an ideal monatomic gas of mass 0.00054876 with two equivalent spin states. The enthalpy between 298 and 0°K. is 1.481 kcal. mole^{-1} as for all unexcited monatomic gases.

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1. PUBLICATION OR REPORT NO. NSRDS-NBS 37

2. Gov't Accession No.

3. Recipient's Accession No.

4. TITLE AND SUBTITLE

JANAF Thermochemical Tables, Second Edition

5. Publication Date

6. Performing Organization Code

7. AUTHOR(S)
D. R. Stull, H. Prophet, et al.

8. Performing Organization

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.
F04611-67-C-0009
F04611-70-0028

12. Sponsoring Organization Name and Address

The Thermal Research Laboratory
Dow Chemical Company
Midland, Michigan

13. Type of Report & Period Covered
NA

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

Superseding PB168-370 and Addenda 1, 2, and 3

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

This monograph is the second edition of the JANAF Thermochemical Tables. It contains thermodynamic properties for some 1099 chemical species. The following properties are tabulated as functions of temperatures: C°_p, S°, $(F^\circ-H^\circ_{298})/T$, $H^\circ-H^\circ_{298}$, ΔH°_f and Log Kp.

17. KEY WORDS (Alphabetical order, separated by semicolons) Evaluated Data; Thermal Functions; Thermodynamic Properties of Materials; Thermodynamics.

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UNCLASSIFIED

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UNCLASSIFIED

21. NO. OF PAGES
1141

22. Price
$9.75

USCOMM-DC 66244-P71

☆ U. S. GOVERNMENT PRINTING OFFICE : 1971 O - 428-649