JANAF Thermochemical Tables, 1975 Supplement

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The thermodynamic tabulations previously published in NSRDS–NBS–37 and the 1974 Supplement (J. Phys. Chem. Ref. Data **3**, 311 [1974]) are extended by 158 new and revised tables. The JANAF Thermochemical Tables cover the thermodynamic properties over a wide temperature range with single phase tables for the crystal, liquid, and ideal gas state. The properties given are heat capacity, entropy, Gibbs energy function, enthalpy, enthalpy of formation, Gibbs energy of formation, and the logarithm of the equilibrium constant for formation of each compound from the elements in their standard reference states. Each tabulation lists all pertinent input data and contains a critical evaluation of the literature upon which these values are based. Literature references are given.

Key words: Critically evaluated data; enthalpy; entropy; equilibrium constant of formation; free energy of formation; Gibbs energy function; heat capacity; heat of formation; thermochemical tables.

Contents

1. Introduction

Since the inception of the JANAF Thermochemical Tables project in late 1959, the tables have been collected together to form six publications [1–6]. The four early publications [3–6] are superceded by two more recent publications [1, 2]. NSRDS–NBS–37 [1] includes all work through June 30, 1970. Tables generated in the period June 30, 1970 to June 30, 1972 are included in the recently published 1974 Supplement [2]. Tables generated in the period June 30, 1972 to June 30, 1974 are combined in this article to provide 158 additional tables which are to be used in conjunction with the two more recent publications [1, 2].

An important aspect of this article is the inclusion of four new elements—V, Nb, Ta, and Cr. As of June 30, 1974, there are 1267 tabulations involving 35 elements and their compounds. The 35 elements include H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Fe, Co, Cu, Br, Sr, Zr, Nb, Mo, I, Cs, Ba, Ta, W, Hg, and Pb.

The JANAF Thermochemical Tables are prepared following the procedures outlined in NSRDS–NBS–37 [1]. In our analyses of equilibrium data we give tabulations for the 2nd and 3rd law results and often list values (in units of eu or gibbs/mol) for the "drift". This is discussed briefly on page 5 in NSRDS–NBS–37 [1] This drift actually refers to the difference, ΔS_{298} (3rd law) − ΔS_{298} (2nd law). ΔS_{298} (2nd law) is not calculated, however, via the usual second law method or the Σ-method. It is instead derived from the slope of the assumed linear temperature dependence of the deviations from the mean of the 3rd law heats of reaction. Our experience indicates that, this method agrees closely, but not exactly, with the Σ-method.

In the tabulations the Gibbs free energy function and the enthalpy are referenced to 298.15 K. Throughout the JANAF project we have striven for internal consistency. Internal and external reviews, however, do not always remove some minor discrepancies. In addition, changes in the nomenclature as adopted by Chemical Abstracts leave the tables with some outdated chemical names. Changes in the atomic weights and the temperature scale also cause minor internal inconsistencies. At present we are maintaining the nomenclature within the tables while gradually converting each new or revised table to the 1969 atomic weights and the IPTS–68 temperature scale. This is not an easy and unambiguous task, as the articles appearing in the literature do not always specify the standards used. Finally, the JANAF Tables are presented in terms of the thermochemical calorie. The symbols cal mol^{-1} deg^{-1} and gibbs/mol are identical and refer to units of defined calorie per degree-mole. These units can be converted to SI units of joules per degree-mole by multiplying the tabulated value by 4.184. Similarly, values in kilocalories per mole can be converted to kilojoules per mole by multiplying by the same factor. Vibrational frequencies are expressed in their wavenumber (cm^{-1}) equivalents.

Two indices are provided in this article. The index in section 4 lists the tables which appear in this article. The list is alphabetical by name. Where applicable, the appropriate cross reference for the currently accepted Chemical Abstracts name is also included. The index in section 5 is the complete index for the JANAF Thermochemical Tables. This complete index lists tables which are in NSRDS–NBS–37 [1], the 1974 Supplement [2], and tables which are in this article (the latter indicated

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by an "*"). It should be emphasized that the tables in this article may be new (in which case there is no corresponding entry in the previous two publications [1, 2]) or revised (in which case the table in this article supercedes the corresponding table in one of the previous two publications [1, 2]). The tables are arranged in this article in the same order as given in the complete index of section 5. The order is the same as that used by Chemical Abstracts in their formula index.

2. Acknowledgements

The JANAF Thermochemical Tables Project is currently sponsored solely by the Air Force Office of Scientific Research (Contract F44620-70-C-0104). The JANAF project has been monitored by Dr. Joseph F. Masi. His cooperation, direction, and encouragement is greatly appreciated. In Thermal Research of The Dow Chemical Company, Daniel R. Stull was the project director from 1959–1969; followed by Harold Prophet from 1969 until his untimely death in late 1972. Malcolm W. Chase is currently the project director with the principal contributors being Alan N. Syverud, Jerry L. Curnutt, and Richard A. McDonald. We thank the staff of Computation Research Laboratory of The Dow Chemical Company for their assistance in the production of these tables, with special thanks to Cheri Snow and Joan Weldon.

3. References

[1] JANAF Thermochemical Tables, 2nd Edition, NSRDS-NBS-37, Catalog Number C13.48:37, U.S. Government Printing Office, Washington, D.C., 1971.

[2] JANAF Thermochemical Tables, 1974 Supplement, J. Phys. Chem. Ref. Data **3**, 311 (1974).

[3] JANAF Thermochemical Tables, PB 168370, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1965.

[4] JANAF Thermochemical Tables, PB 168370-1, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1966.

[5] JANAF Thermochemical Tables, PB 168370-2, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1967.

[6] JANAF Thermochemical Tables, PB 168370-3, Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia, 1968.

4. List of Tables in 1975 Supplement

5. Complete List of JANAF Thermochemical Tables

Filing Order	Table Title
Al	Aluminum (ref. st.)
Al	Aluminum (c)
Al	Aluminum (ℓ)
Al	Aluminum, Monatomic (g)
Al^+	Aluminum Unipositive Ion (g)
$AlBO_2$	Aluminum Boron Dioxide (g)
AlBr	Aluminum Monobromide (g)
$AlBr_3$	Aluminum Tribromide (c)
$AlBr_3$	Aluminum Tribromide (ℓ)
$AlBr_3$	Aluminum Tribromide (g)
AlCl	Aluminum Monochloride (g)
$AlCl^+$	Aluminum Monochloride Unipositive Ion (g)
AlClF	Aluminum Chlorofluroide (g)
$AlClF_2$	Aluminum Chlorodifluoride (g)
AlClO	Aluminum Oxychloride (c)
AlClO	Aluminum Oxychloride (g)
$AlCl_2$	Aluminum Dichloride (g)
$AlCl_2^+$	Aluminum Dichloride Unipositive Ion (g)
$AlCl_2^-$	Aluminum Dichloride Uninegative Ion (g)
$AlCl_2F$	Aluminum Dichlorofluoride (g)
$AlCl_3$	Aluminum Trichloride (c)
$AlCl_3$	Aluminum Trichloride (ℓ)
$AlCl_3$	Aluminum Trichloride (g)
$AlCl_4K$	Potassium Tetrachloroaluminate (c)
$AlCl_4Na$	Sodium Tetrachloroaluminate (c)
$AlCl_6K_3$	Tripotassium Hexachloroaluminate (c)
$AlCl_6Na_3$	Trisodium Hexachloroaluminate (c)
AlF	Aluminum Monofluoride (g)
AlF^+	Aluminum Monofluoride Unipositive Ion (g)
AlFO	Aluminum Oxyfluoride (g)
AlF_2	Aluminum Difluoride (g)
AlF_2^+	Aluminum Difluoride Unipositive Ion (g)
AlF_2^-	Aluminum Difluoride Uninegative Ion (g)
AlF_3	Aluminum Trifluoride (c)
AlF_3	Aluminum Trifluoride (g)
AlF_4Li	Lithium Tetrafluoroaluminate (g)
AlF_4Na	Sodium Tetrafluoroaluminate (g)
AlF_6K_3	Tripotassium Hexafluoroaluminate (c)
AlF_6Li_3	Trilithium Hexafluoroaluminate (c)
AlF_6Li_3	Trilithium Hexafluoroaluminate (ℓ)
AlF_6Na_3	Cryolite (c)
AlF_6Na_3	Cryolite (ℓ)
AlH	Aluminum Monohydride (g)
AlH	Aluminum Monohydride (g)
AlHO	Aluminum Monohydroxide (g)
$AlHO^+$	Aluminum Monohydroxide Unipositive Ion (g)
$AlHO^-$	Aluminum Monohydroxide Uninegative Ion (g)
$AlHO_2$	Aluminum Dioxyhydride (g)
AlH_4Li	Lithium Aluminum Hydride (c)

Filing Order	Table Title
AlI	Aluminum Monoiodide (g)
AlI_3	Aluminum Triiodide (c)
AlI_3	Aluminum Triiodide (ℓ)
AlI_3	Aluminum Triiodide (g)
$AlLiO_2$	Lithium Aluminate (c)
$AlLiO_2$	Lithium Aluminate (ℓ)
AlN	Aluminum Nitride (c)
AlN	Aluminum Nitride (g)
$AlNaO_2$	Sodium Aluminate (c)
AlO	Aluminum Monoxide (g)
AlO^+	Aluminum Monoxide Unipositive Ion (g)
AlO_2	Aluminum Dioxide (g)
AlO_2	Aluminum Dioxide Uninegative Ion (g)
AlS	Aluminum Sulfide (g)
Al_2BeO_4	Beryllium Aluminate (c)
Al_2BeO_4	Beryllium Aluminate (ℓ)
Al_2Br_6	Aluminum Tribromide, Dimeric (g)
Al_2Cl_6	Aluminum Trichloride, Dimer (g)
$Al_2Cl_9K_3$	Potassium Nonachloroaluminate (c)
Al_2F_6	Aluminum Trifluoride, Dimer (g)
Al_2I_6	Aluminum Triiodide, Dimeric (g)
Al_2MgO_4	Magnesium Aluminate (c)
Al_2MgO_4	Magnesium Aluminate (ℓ)
Al_2O	Aluminum Suboxide (g)
Al_2O^+	Dialuminum Monoxide Unipositive Ion (g)
Al_2O_2	Aluminum Monoxide, Dimeric (g)
$Al_2O_2^+$	Dialuminum Dioxide Unipositive Ion (g)
Al_2O_3	Aluminum Oxide (c, alpha)
Al_2O_3	Aluminum Oxide (c, gamma)
Al_2O_3	Aluminum Oxide (ℓ)
Al_2O_5Si	Sillimanite (c)
Al_2O_5Si	Andalusite (c)
Al_2O_5Si	Kyanite (c)
Al_6BeO_{10}	Aluminum Beryllium Oxide (c)
Al_6BeO_{10}	Aluminum Beryllium Oxide (ℓ)
$Al_6O_{13}Si_2$	Mullite (c)
B	Boron (ref. st.)
B	Boron, Beta-Rhombohedral (c)
B	Boron (ℓ)
B	Boron, Monatomic (g)
B^+	Boron Unipositive Ion (g)
$BBeO_2$	Beryllium Boron Dioxide (g)
BBr	Boron Monobromide (g)
BBrCl	Boron Bromide Chloride (g)
$BBrCl_2$	Boron Bromide Dichloride (g)
$BBrCl_2$	Boron Bromide Dichloride (g)
$BBrF_2$	Boron Bromide Difluoride (g)
BBrO	Boron Oxide Bromide (g)
BBr_2	Boron Dibromide (g)
BBr_2Cl	Boron Dibromide Chloride (g)
BBr_2F	Boron Dibromide Fluoride (g)

Filing Order	Table Title
BBr_2H	Boron Dibromide Hydride (g)
BBr_3	Boron Tribromide (ℓ)
BBr_3	Boron Tribromide (g)
BCl	Boron Monochloride (g)
BCl^+	Boron Monochloride Unipositive Ion (g)
$BClF$	Boron Chloride Fluoride (g)
$BClF_2$	Boron Chloride Difluoride (g)
$BClO$	Boron Oxide Chloride (g)
BCl_2	Boron Dichloride (g)
BCl_2^+	Boron Dichloride Unipositive Ion (g)
BCl_2^-	Boron Dichloride Uninegative Ion (g)
BCl_2F	Boron Dichloride Fluoride (g)
BCl_2H	Boron Dichloride Hydride (g)
BCl_3	Boron Trichloride (g)
BF	Boron Monofluoride (g)
BFO	Boron Oxide Fluoride (g)
BF_2	Boron Difluoride (g)
BF_2^+	Boron Difluoride Unipositive Ion (g)
BF_2^-	Boron Difluoride Uninegative Ion (g)
BF_2H	Difluoroborane (g)
BF_2HO	Boron Hydroxide Difluoride (g)
BF_2O	Boron Oxide Difluoride (g)
BF_3	Boron Trifluoride (g)
BF_4K	Potassium Tetrafluoroborate (c)
BF_4K	Potassium Tetrafluoroborate (ℓ)
BF_4K	Potassium Tetrafluoroborate (g)
BH	Boron Monohydride (g)
BHO	Boron Oxide Hydride (g)
BHO^+	Boron Oxide Hydride Unipositive Ion (g)
BHO_2	Metaboric Acid (c)
BHO_2	Metaboric Acid (g)
BH_2	Boron Dihydride (g)
BH_2O_2	Boron Dihydroxide (g)
BH_3	Boron Trihydride (g)
BH_3O_3	Boric Acid (c)
BH_3O_3	Boric Acid (g)
BH_4K	Potassium Tetrahydroborate (c)
BH_4Li	Lithium Tetrahydroborate (c)
BH_4Na	Sodium Tetrahydroborate (c)
BI	Boron Iodide (g)
BI_2	Boron Diiodide (g)
BI_3	Boron Triiodide (g)
BKO_2	Potassium Metaborate (c)
BKO_2	Potassium Metaborate (ℓ)
BKO_2	Potassium Metaborate (g)
BKO_2	Potassium Metaborate (g)
$BLiO_2$	Lithium Metaborate (ℓ)
$BLiO_2$	Lithium Metaborate (g)
BN	Boron Nitride (c)
BN	Boron Nitride (g)
$BNaO_2$	Sodium Metaborate (c)

Filing Order	Table Title
$BNaO_2$	Sodium Metaborate (ℓ)
$BNaO_2$	Sodium Metaborate (g)
BO	Boron Monoxide (g)
BO_2	Boron Dioxide (g)
BO_2^-	Boron Dioxide Uninegative Ion (g)
BS	Boron Monosulfide (g)
BTi	Titanium Monoboride (c)
B_2	Boron, Diatomic (g)
B_2BeO_4	Beryllium Diborate (g)
$B_2Be_3O_6$	Triberyllium Diborate (c)
B_2Cl_4	Boron Dichloride, Dimeric (g)
B_2F_4	Boron Difluoride, Dimeric (g)
B_2F_4O	Diboron Tetrafluoromonoxide (g)
$B_2H_4O_4$	Boron Dihydroxide, Dimeric (c)
$B_2H_4O_4$	Boron Dihydroxide, Dimeric (g)
B_2H_6	Diborane (g)
B_2Mg	Magnesium Diboride (c)
B_2O	Diboron Monoxide (g)
B_2O_2	Boron Monoxide, Dimeric (g)
B_2O_3	Boron Oxide (c)
B_2O_3	Boron Oxide (ℓ)
B_2O_3	Boron Oxide (g)
B_2O_4Pb	Lead Diborate (c)
B_2Ti	Titanium Diboride (c)
B_2Ti	Titanium Diboride (ℓ)
B_2Zr	Zirconium Diboride (c)
B_2Zr	Zirconium Diboride (ℓ)
$B_3Cl_3O_3$	Boron Oxide Chloride, Trimeric (g)
$B_3FH_2O_3$	Monofluoroboroxin (g)
$B_3F_2HO_3$	Difluoroboroxin (g)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (c)
$B_3F_3O_3$	Boron Oxide Fluoride, Trimeric (g)
$B_3H_3O_3$	Boroxin (c)
$B_3H_3O_3$	Boroxin (g)
$B_3H_3O_6$	Metaboric Acid, Trimeric (g)
$B_3H_6N_3$	Borazine (g)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (c)
$B_4K_2O_7$	Dipotassium Tetraboron Heptaoxide (ℓ)
$B_4Li_2O_7$	Dilithium Tetraborate (c)
$B_4Li_2O_7$	Dilithium Tetraborate (ℓ)
B_4Mg	Magnesium Tetraboride (c)
$B_4Na_2O_7$	Disodium Tetraborate (c)
$B_4Na_2O_7$	Disodium Tetraborate (ℓ)
B_4O_7Pb	Lead Tetraborate (c)
B_5H_9	Pentaborane (ℓ)
B_5H_9	Pentaborane (g)
$B_6K_2O_{10}$	Dipotassium Hexaborate (c)
$B_6Li_2O_{10}$	Dilithium Hexaborate (c)
$B_6Na_2O_{10}$	Disodium Hexaborate (c)
$B_6Na_2O_{10}$	Disodium Hexaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (c)
$B_8K_2O_{13}$	Dipotassium Octaborate (ℓ)
$B_8Li_2O_{13}$	Dilithium Octaborate (c)
$B_{10}H_{14}$	Decaborane (c)

Filing Order	Table Title
$B_{10}H_{14}$	Decaborane (ℓ)
$B_{10}H_{14}$	Decaborane (g)
$B_{10}O_{17}Pb_2$	Dilead Decaborate (c)
Ba	Barium (ref. st.)
Ba	Barium (c)
Ba	Barium (ℓ)
Ba	Barium (g)
*BaCl	Barium Monochloride (g)
*$BaCl_2$	Barium Dichloride (c)
*$BaCl_2$	Barium Dichloride (ℓ)
*$BaCl_2$	Barium Dichloride (g)
*BaF	Barium Monofluoride (g)
*BaF^+	Barium Monofluoride Unipositive Ion (g)
*BaF_2	Barium Difluoride (c)
*BaF_2	Barium Difluoride (ℓ)
*BaF_2	Barium Difluoride (g)
*BaI	Barium Monoiodide (g)
*BaI_2	Barium Diiodide (c)
*BaI_2	Barium Diiodide (ℓ)
*BaI_2	Barium Diiodide (g)
*BaO	Barium Oxide (c)
*BaO	Barium Oxide (ℓ)
*BaO	Barium Oxide (g)
Be	Beryllium (ref. st.)
Be	Beryllium (c)
Be	Beryllium (ℓ)
Be	Beryllium (g)
Be^+	Beryllium Unipositive Ion (g)
BeBr	Beryllium Monobromide (g)
$BeBr_2$	Beryllium Dibromide (c)
$BeBr_2$	Beryllium Dibromide (ℓ)
$BeBr_2$	Beryllium Dibromide (g)
BeCl	Beryllium Monochloride (g)
$BeCl^+$	Beryllium Monochloride Unipositive Ion (g)
BeClF	Beryllium Chloride Fluoride (g)
$BeCl_2$	Beryllium Dichloride (c, α)
$BeCl_2$	Beryllium Dichloride (c, β)
$BeCl_2$	Beryllium Dichloride (ℓ)
$BeCl_2$	Beryllium Dichloride (g)
BeF	Beryllium Monofluoride (g)
BeF_2	Beryllium Difluoride (c)
BeF_2	Beryllium Difluoride (ℓ)
BeF_2	Beryllium Difluoride (g)
BeF_3Li	Lithium Trifluoroberyllate (c)
BeF_3Li	Lithium Trifluoroberyllate (ℓ)
BeF_3Li	Lithium Beryllium Fluoride (g)
BeF_4Li_2	Dilithium Tetrafluoroberyllate (c)
BeF_4Li_2	Dilithium Tetrafluoroberyllate (c)
BeH	Beryllium Monohydride (g)
BeH^+	Beryllium Monohydride Unipositive Ion (g)
BeHO	Beryllium Monohydroxide (g)
$BeHO^+$	Beryllium Monohydroxide Unipositive Ion (g)
BeH_2	Beryllium Dihydride (g)
BeH_2O_2	Beryllium Hydroxide (c, α)
BeH_2O_2	Beryllium Hydroxide (c, β)
BeH_2O_2	Beryllium Hydroxide (g)
BeI	Beryllium Monoiodide (g)
BeI_2	Beryllium Diiodide (c)
BeI_2	Beryllium Diiodide (ℓ)
BeI_2	Beryllium Diiodide (g)
BeN	Beryllium Nitride (g)
BeO	Beryllium Oxide (c, α)
BeO	Beryllium Oxide (c, β)
BeO	Beryllium Oxide (ℓ)
BeO	Beryllium Oxide (g)
BeO_4S	Beryllium Sulfate (c, α)
BeO_4S	Beryllium Sulfate (c, β)
BeO_4S	Beryllium Sulfate (c, γ)
BeO_4W	Beryllium Tungstate (c)
Be_2Cl_4	Beryllium Dichloride, Dimeric (g)
Be_2F_2O	Dilithium Oxide Difluoride (g)
Be_2O	Diberyllium Oxide (g)
Be_2O_2	Beryllium Oxide, Dimeric (g)
Be_2O_4Si	Beryllium Orthosilicate (c)
Be_3N_2	Beryllium Nitride (c, α)
Be_3N_2	Beryllium Nitride (ℓ)
Be_3O_3	Beryllium Oxide, Trimeric (g)
Be_4O_4	Beryllium Oxide, Tetrameric (g)
Be_5O_5	Beryllium Oxide, Pentameric (g)
Be_6O_6	Beryllium Oxide, Hexameric (g)
*Br	Bromine, Monatomic (g)
BrCl	Bromine Monochloride (g)
BrF	Bromine Monofluoride (g)
BrF_3	Bromine Trifluoride (g)
BrF_5	Bromine Pentafluoride (g)
BrH	Hydrogen Bromide (g)
BrH_4N	Ammonium Bromide (c)
BrHg	Mercurous Bromide (g)
BrI	Iodine Monobromide (g)
BrK	Potassium Bromide (c)
BrK	Potassium Bromide (ℓ)
BrK	Potassium Bromide (g)
BrLi	Lithium Bromide (c)
BrLi	Lithium Bromide (ℓ)
BrLi	Lithium Bromide (g)
BrMg	Magnesium Monobromide (g)
BrN	Nitrogen Bromide (g)
BrNO	Nitrosyl Bromide (g)
BrNa	Sodium Bromide (c)
BrNa	Sodium Bromide (ℓ)
BrNa	Sodium Bromide (g)
BrP	Phosphorus Monobromide (g)
*BrPb	Lead Monobromide (g)
BrTi	Titanium Monobromide (g)

Filing Order	Table Title
BrW	Tungsten Monobromide (g)
BrZr	Zirconium Monobromide (g)
Br_2	Bromine (ref. st.)
Br_2	Bromine (ℓ)
Br_2	Bromine, Diatomic (g)
*Br_2Ca	Calcium Dibromide (c)
*Br_2Ca	Calcium Dibromide (ℓ)
*Br_2Ca	Calcium Dibromide (g)
Br_2Fe	Iron Dibromide (c)
Br_2Fe	Iron Dibromide (ℓ)
Br_2Fe	Iron Dibromide (g)
Br_2Hg	Mercuric Bromide (c)
Br_2Hg	Mercuric Bromide (ℓ)
Br_2Hg	Mercuric Bromide (g)
Br_2Hg_2	Mercurous Bromide (c)
Br_2K_2	Potassium Bromide, Dimeric (g)
Br_2Li_2	Lithium Bromide, Dimeric (g)
*Br_2Mg	Magnesium Dibromide (c)
*Br_2Mg	Magnesium Dibromide (ℓ)
*Br_2Mg	Magnesium Dibromide (g)
*Br_2Mg^+	Magnesium Dibromide Unipositive Ion (g)
Br_2Na_2	Sodium Bromide, Dimeric (g)
*Br_2Pb	Lead Dibromide (c)
*Br_2Pb	Lead Dibromide (ℓ)
*Br_2Pb	Lead Dibromide (g)
*Br_2Sr	Strontium Dibromide (c)
*Br_2Sr	Strontium Dibromide (ℓ)
*Br_2Sr	Strontium Dibromide (g)
Br_2Ti	Titanium Dibromide (c)
Br_2Ti	Titanium Dibromide (g)
Br_2Zr	Zirconium Dibromide (c)
Br_2Zr	Zirconium Dibromide (ℓ)
Br_2Zr	Zirconium Dibromide (g)
Br_3OP	Phosphoryl Bromide (g)
Br_3P	Phosphorus Tribromide (g)
Br_3PS	Thiophosphoryl Bromide (g)
Br_3Ti	Titanium Tribromide (c)
Br_3Ti	Titanium Tribromide (g)
Br_3Zr	Zirconium Tribromide (c)
Br_3Zr	Zirconium Tribromide (g)
Br_4Fe_2	Iron Dibromide, Dimeric (g)
*Br_4Mg_2	Magnesium Dibromide, Dimeric (g)
*Br_4Pb	Lead Tetrabromide (g)
Br_4Ti	Titanium Tetrabromide (c)
Br_4Ti	Titanium Tetrabromide (ℓ)
Br_4Ti	Titanium Tetrabromide (g)
Br_4Zr	Zirconium Tetrabromide (c)
Br_4Zr	Zirconium Tetrabromide (g)
Br_5W	Tungsten Pentabromide (c)
Br_5W	Tungsten Pentabromide (ℓ)
Br_5W	Tungsten Pentabromide (g)
Br_6W	Tungsten Hexabromide (c)
Br_6W	Tungsten Hexabromide (g)
*$C_{0.98}Nb$	Niobium Carbide (c)

Filing Order	Table Title
C	Carbon (ref. st., Graphite)
C	Carbon, Monatomic (g)
C^-	Carbon Uninegative Ion (g)
CAl	Aluminum Carbide (g)
CB	Boron Carbide (g)
CB_4	Boron Carbide (c)
CB_4	Boron Carbide (ℓ)
CBe_2	Beryllium Carbide (c)
CBe_2	Beryllium Carbide (ℓ)
CBr	Carbon Monobromide (g)
$CBrF_3$	Bromotrifluoromethane (g)
CBrN	Cyanogen Bromide (g)
CBr_4	Carbon Tetrabromide (g)
CCl	Carbon Monochloride (g)
CClFO	Carbonyl Chlorofluoride (g)
$CClF_3$	Chlorotrifluoromethane (g)
CClN	Cyanogen Chloride (g)
CClO	Carbonyl Monochloride (g)
CCl_2	Carbon Dichloride (g)
CCl_2F_2	Dichlorodifluoromethane (g)
CCl_2O	Carbonyl Chloride (g)
CCl_3	Trichloromethyl (g)
CCl_3F	Trichlorofluoromethane (g)
CCl_4	Carbon Tetrachloride (g)
CCuN	Cuprous Cyanide (c)
CF	Carbon Monofluoride (g)
CF^+	Carbon Monofluoride Unipositive Ion (g)
CFN	Cyanogen Fluoride (g)
CFO	Carbonyl Monofluoride (g)
CF_2	Carbon Difluoride (g)
CF_2^+	Carbon Difluoride Unipositive Ion (g)
CF_2O	Carbonyl Fluoride (g)
CF_3	Trifluoromethyl (g)
CF_3^+	Trifluoromethyl Unipositive Ion (g)
CF_3I	Trifluoroiodomethane (g)
CF_4	Carbon Tetrafluoride (g)
CF_4O	Trifluoromethyl Hypofluorite (g)
CH	Methylidyne (g)
CH^+	Methylidyne Unipositive Ion (g)
CHCl	Monochloromethylene (g)
$CHClF_2$	Chlorodifluoromethane (g)
$CHCl_2F$	Dichlorofluoromethane (g)
$CHCl_3$	Chloroform (g)
CHF	Monofluoromethylene (g)
CHFO	Formyl Fluoride (g)
CHF_3	Trifluoromethane (g)
CHN	Hydrogen Cyanide (g)
CHNO	Hydrogen Isocyanate (g)
CHO	Formyl (g)
CHO^+	Formyl Unipositive Ion (g)
CHP	Methinophosphide (g)
*CH_2	Methylene (g)
CH_2ClF	Chlorofluoromethane (g)
CH_2Cl_2	Dichloromethane (g)

Filing Order	Table Title
CH_2F_2	Difluoromethane (g)
CH_2O	Formaldehyde (g)
CH	Methyl (g)
CH_3Cl	Methyl Chloride (g)
CH_3Cl_3Si	Trichloromethylsilane (g)
CH_3F	Fluoromethane (g)
CH_3F_3Si	Trifluoromethylsilane (g)
CH_4	Methane (g)
CIN	Cyanogen Iodide (g)
CKN	Potassium Cyanide (c)
CKN	Potassium Cyanide (ℓ)
CKN	Potassium Cyanide (g)
CK_2O_3	Potassium Carbonate (c)
CK_2O_3	Potassium Carbonate (ℓ)
CLi_2O_3	Lithium Carbonate (c)
CLi_2O_3	Lithium Carbonate (ℓ)
$CMgO_3$	Magnesium Carbonate (c)
CN	Cyano (g)
CN^+	Cyano Unipositive Ion (g)
CN^-	Cyano Uninegative Ion (g)
CNNa	Sodium Cyanide (c)
CNNa	Sodium Cyanide (ℓ)
CNNa	Sodium Cyanide (g)
CNO	NCO Radical (g)
CN_2	CNN Radical (g)
CN_2	NCN Radical (g)
CNa_2O_3	Sodium Carbonate (c)
CNa_2O_3	Sodium Carbonate (ℓ)
CO	Carbon Monoxide (g)
COS	Carbon Oxysulfide (g)
CO_2	Carbon Dioxide (g)
CO_2^-	Carbon Dioxide Uninegative Ion (g)
CP	Carbon Phosphide (g)
CS	Carbon Monosulfide (g)
CS_2	Carbon Disulfide (g)
CSi	Silicon Carbide (c, α)
CSi	Silicon Carbide (c, β)
CSi	Silicon Carbide (ℓ)
CSi	Silicon Carbide (g)
CSi_2	Disilicon Carbide (g)
*CTa	Tantalum Monocarbide (c)
*CTa	Tantalum Monocarbide (ℓ)
CTi	Titanium Carbide (c)
CTi	Titanium Carbide (ℓ)
CZr	Zirconium Carbide (c)
CZr	Zirconium Carbide (ℓ)
C_2	Carbon, Diatomic (g)
C_2^-	Dimeric Carbon Uninegative Ion (g)
C_2Be	Beryllium Carbide (g)
C_2Cl_2	Dichloroacetylene (g)
C_2Cl_4	Tetrachloroethylene (g)
C_2Cl_6	Hexachloroethane (g)
*C_2Cr_3	Trichromium Dicarbide (c)
C_2F_2	Difluoroacetylene (g)

Filing Order	Table Title
C_2F_3N	Trifluoroacetonitrile (g)
C_2F_4	Tetrafluoroethylene (g)
C_2F_6	Hexafluoroethane (g)
C_2H	CCH Radical (g)
C_2HCL	Chloroacetylene (g)
C_2HF	Monofluorocetylene (g)
C_2H_2	Acetylene (g)
C_2H_4	Ethylene (g)
C_2H_4O	Ethylene Oxide (g)
$C_2K_2N_2$	Potassium Cyanide, Dimeric (g)
C_2Li_2	Lithium Carbide (c)
C_2Mg	Magnesium Carbide (c)
C_2N	CNC Radical (g)
C_2N_2	Cyanogen (g)
$C_2N_2Na_2$	Sodium Cyanide, Dimeric (g)
C_2O	CCO Radical (g)
C_2Si	Silicon Dicarbide (g)
C_3	Carbon, Trimeric (g)
C_3Al_4	Aluminum Carbide (c)
*C_3Cr_7	Heptachromium Tricarbide (c)
C_3Mg_2	Magnesium Carbide (c)
C_3O_2	Carbon Suboxide (g)
C_4	Carbon, Tetratomic (g)
$C_4H_{12}Si$	Tetramethylsilane (g)
C_4N_2	Carbon Subnitride (g)
C_5	Carbon, Pentatomic (g)
*C_6Cr_{23}	Chromium Carbide (c)
Ca	Calcium (ref. st.)
Ca	Calcium (α)
Ca	Calcium (β)
Ca	Calcium (ℓ)
Ca	Calcium (g)
Ca^+	Calcium Unipositive Ion (g)
CaCl	Calcium Monochloride (g)
$CaCl_2$	Calcium Chloride (c)
$CaCl_2$	Calcium Chloride (ℓ)
$CaCl_2$	Calcium Chloride (g)
CaF	Calcium Monofluoride (g)
CaF_2	Calcium Difluoride (c)
CaF_2	Calcium Difluoride (ℓ)
CaF_2	Calcium Difluoride (g)
CaHO	Calcium Monohydroxide (g)
$CaHO^+$	Calcium Monohydroxide Unipositive Ion (g)
CaH_2O_2	Calcium Hydroxide (c)
*CaI	Calcium Monoiodide (g)
*CaI_2	Calcium Diiodide (c)
*CaI_2	Calcium Diiodide (ℓ)
*CaI_2	Calcium Diiodide (g)
*CaO	Calcium Oxide (c)
*CaO	Calcium Oxide (ℓ)
CaS	Calcium Sulfide (c)
Cl	Chlorine, Monatomic (g)

Filing Order	Table Title
Cl^+	Chlorine Unipositive Ion (g)
Cl^-	Chlorine Uninegative Ion (g)
*$ClCo$	Cobalt Monochloride (g)
$ClCs$	Cesium Monochloride (c)
$ClCs$	Cesium Monochloride (ℓ)
$ClCs$	Cesium Monochloride (g)
$ClCu$	Copper Monochloride (c)
$ClCu$	Copper Monochloride (ℓ)
$ClCu$	Copper Monochloride (g)
ClF	Chlorine Monofluoride (g)
$ClFLi_2$	Lithium Chlorofluoride (g)
$ClFMg$	Magnesium Chloride Fluoride (g)
$ClFO_2S$	Sulfuryl Chloride Fluoride (g)
$ClFO_3$	Perchloryl Fluoride (g)
ClF_2OP	Phosphoryl Difluorochloride (g)
ClF_3	Chlorine Trifluoride (g)
ClF_3Si	Chlorotrifluorosilane (g)
ClF_5	Chlorine Pentafluoride (g)
$ClFe$	Iron Monochloride (g)
ClH	Hydrogen Chloride (g)
$ClHO$	Hydrogen Oxychloride (g)
ClH_3Si	Chlorosilane (g)
ClH_4N	Ammonium Chloride (c)
ClH_4NO_4	Ammonium Perchlorate (c)
$ClHg$	Mercurous Chloride (g)
ClI	Iodine Monochloride (c)
ClI	Iodine Monochloride (ℓ)
ClI	Iodine Monochloride (g)
ClK	Potassium Chloride (c)
ClK	Potassium Chloride (ℓ)
ClK	Potassium Chloride (g)
$ClKO_4$	Potassium Perchlorate (c)
$ClLi$	Lithium Chloride (c)
$ClLi$	Lithium Chloride (ℓ)
$ClLi$	Lithium Chloride (g)
$ClLiO$	Lithium Oxychloride (g)
$ClLiO_4$	Lithium Perchlorate (c)
$ClLiO_4$	Lithium Perchlorate (ℓ)
$ClMg$	Magnesium Monochloride (g)
$ClMg$	Magnesium Monochloride Unipositive Ion (g)
*$ClNO$	Nitrosyl Chloride (g)
$ClNO_2$	Nitryl Chloride (g)
$ClNa$	Sodium Chloride (c)
$ClNa$	Sodium Chloride (ℓ)
$ClNa$	Sodium Chloride (g)
$ClNaO_4$	Sodium Perchlorate (c)
ClO	Chlorine Monoxide (g)
$ClOTi$	Titanium Oxychloride (g)
ClO_2	Chlorine Dioxide (g)
ClP	Phosphorus Monochloride (g)
*$ClPb$	Lead Monochloride (g)
*$ClPb^+$	Lead Monochloride Unipositive Ion (g)
$ClSi$	Silicon Monochloride (g)

Filing Order	Table Title
*$ClSr$	Strontium Monochloride (g)
$ClTi$	Titanium Monochloride (g)
ClW	Tungsten Monochloride (g)
$ClZr$	Zirconium Monochloride (g)
Cl_2	Chlorine, Diatomic (ref. st., g)
*Cl_2Co	Cobalt Dichloride (c)
*Cl_2Co	Cobalt Dichloride (ℓ)
*Cl_2Co	Cobalt Dichloride (g)
Cl_2Cs_2	Cesium Monochloride, Dimeric (g)
Cl_2Cu	Copper Dichloride (c)
Cl_2FOP	Phosphoryl Fluorodichloride (g)
Cl_2Fe	Iron Dichloride (c)
Cl_2Fe	Iron Dichloride (ℓ)
Cl_2Fe	Iron Dichloride (g)
Cl_2H_2Si	Dichlorosilane (g)
Cl_2Hg	Mercuric Chloride (c)
Cl_2Hg	Mercuric Chloride (ℓ)
Cl_2Hg	Mercuric Chloride (g)
Cl_2Hg_2	Mercurous Chloride (c)
Cl_2K_2	Potassium Chloride, Dimeric (g)
Cl_2Li_2	Lithium Chloride, Dimeric (g)
Cl_2Mg	Magnesium Dichloride (c)
Cl_2Mg	Magnesium Dichloride (ℓ)
Cl_2Mg	Magnesium Dichloride (g)
Cl_2MoO_2	Molybdenum Dioxydichloride (g)
Cl_2Na_2	Sodium Chloride, Dimeric (g)
Cl_2O	Chlorine Monoxide (g)
Cl_2OTi	Titanium Oxydichloride (g)
Cl_2O_2S	Sulfuryl Chloride (g)
Cl_2O_2W	Tungsten Dioxydichloride (c)
Cl_2O_2W	Tungsten Dioxydichloride (g)
*Cl_2Pb	Lead Dichloride (c)
*Cl_2Pb	Lead Dichloride (ℓ)
*Cl_2Pb	Lead Dichloride (g)
*Cl_2Pb^+	Lead Dichloride Unipositive Ion (g)
Cl_2Si	Silicon Dichloride (g)
*Cl_2Sr	Strontium Dichloride (c)
*Cl_2Sr	Strontium Dichloride (ℓ)
*Cl_2Sr	Strontium Dichloride (g)
Cl_2Ti	Titanium Dichloride (c)
Cl_2Ti	Titanium Dichloride (g)
Cl_2W	Tungsten Dichloride (c)
Cl_2W	Tungsten Dichloride (g)
Cl_2Zr	Zirconium Dichloride (c)
Cl_2Zr	Zirconium Dichloride (ℓ)
Cl_2Zr	Zirconium Dichloride (g)
*Cl_3Co	Cobalt Trichloride (g)
Cl_3Cu_3	Copper Monochloride, Trimeric (g)
Cl_3FSi	Trichlorofluorosilane (g)
Cl_3Fe	Iron Trichloride (c)
Cl_3Fe	Iron Trichloride (ℓ)
Cl_3Fe	Iron Trichloride (g)
Cl_3HSi	Trichlorosilane (g)
Cl_3Li_3	Lithium Chloride, Trimeric (g)

Filing Order	Table Title
Cl_3OP	Phosphoryl Chloride (g)
Cl_3P	Phosphorus Trichloride (g)
Cl_3PS	Thiophosphoryl Chloride (g)
Cl_3Si	Silicon Trichloride (g)
Cl_3Ti	Titanium Trichloride (c)
Cl_3Ti	Titanium Trichloride (g)
Cl_3Zr	Zirconium Trichloride (c)
Cl_3Zr	Zirconium Trichloride (g)
*Cl_4Co_2	Cobalt Dichloride, Dimeric (g)
Cl_4Fe_2	Iron Dichloride, Dimeric (g)
Cl_4Mg_2	Magnesium Dichloride, Dimeric (g)
Cl_4Mo	Molybdenum Tetrachloride (c)
Cl_4Mo	Molybdenum Tetrachloride (ℓ)
Cl_4Mo	Molybdenum Tetrachloride (g)
Cl_4OW	Tungsten Oxytetrachloride (c)
Cl_4OW	Tungsten Oxytetrachloride (ℓ)
Cl_4OW	Tungsten Oxytetrachloride (g)
*Cl_4Pb	Lead Tetrachloride (g)
Cl_4Si	Silicon Tetrachloride (g)
Cl_4Ti	Titanium Tetrachloride (c)
Cl_4Ti	Titanium Tetrachloride (ℓ)
Cl_4Ti	Titanium Tetrachloride (g)
Cl_4W	Tungsten Tetrachloride (c)
Cl_4W	Tungsten Tetrachloride (g)
Cl_4Zr	Zirconium Tetrachloride (c)
Cl_4Zr	Zirconium Tetrachloride (g)
Cl_5Mo	Molybdenum Pentachloride (c)
Cl_5Mo	Molybdenum Pentachloride (ℓ)
Cl_5Mo	Molybdenum Pentachloride (g)
Cl_5P	Phosphorus Pentachloride (g)
Cl_5W	Tungsten Pentachloride (c)
Cl_5W	Tungsten Pentachloride (ℓ)
Cl_5W	Tungsten Pentachloride (g)
Cl_6Fe_2	Iron Trichloride, Dimeric (g)
Cl_6Mo	Molybdenum Hexachloride (c)
Cl_6Mo	Molybdenum Hexachloride (g)
Cl_6W	Tungsten Hexachloride (c, α)
Cl_6W	Tungsten Hexachloride (c, β)
Cl_6W	Tungsten Hexachloride (ℓ)
Cl_6W	Tungsten Hexachloride (g)
$Cl_{10}W_2$	Tungsten Pentachloride, Dimeric (g)
Co	Cobalt (ref. st.)
Co	Cobalt (c)
Co	Cobalt (ℓ)
Co	Cobalt (g)
Co^+	Cobalt Unipositive Ion (g)
CoF_2	Cobalt Difluoride (c)
CoF_2	Cobalt Difluoride (ℓ)
CoF_2	Cobalt Difluoride (g)
CoF_3	Cobalt Trifluoride (c)
CoO	Cobalt Monoxide (c)
CoO_4S	Cobalt Sulfate (c)
Co_3O_4	Tricobalt Tetraoxide (c)
*Cr	Chromium (ref. st.)

Filing Order	Table Title
*Cr	Chromium (c)
*Cr	Chromium (ℓ)
*Cr	Chromium (g)
*CrN	Chromium Mononitride (c)
*CrN	Chromium Mononitride (g)
*CrO	Chromium Monoxide (g)
*CrO_2	Chromium Dioxide (g)
*CrO_3	Chromium Trioxide (g)
*Cr_2N	Chromium Subnitride (c)
*Cr_2O_3	Dichromium Trioxide (c)
*Cr_2O_3	Dichromium Trioxide (ℓ)
Cs	Cesium (ref. st.)
Cs	Cesium (c)
Cs	Cesium (ℓ)
Cs	Cesium (g)
Cs^+	Cesium Unipositive Ion (g)
CsF	Cesium Monofluoride (c)
CsF	Cesium Monofluoride (ℓ)
CsF	Cesium Monofluoride (g)
CsHO	Cesium Hydroxide (c)
CsHO	Cesium Hydroxide (ℓ)
CsHO	Cesium Hydroxide (g)
$CsHO^+$	Cesium Hydroxide Unipositive Ion (g)
CsO	Cesium Monoxide (g)
Cs_2	Cesium, Dimeric (g)
Cs_2F_2	Cesium Monofluoride, Dimeric (g)
$Cs_2H_2O_2$	Cesium Hydroxide, Dimeric (g)
Cs_2O	Dicesium Monoxide (g)
Cu	Copper (ref. st.)
Cu	Coper (c)
Cu	Copper (ℓ)
Cu	Copper (g)
Cu^+	Copper Unipositive Ion (g)
CuF	Copper Monofluoride (c)
CuF	Copper Monofluoride (g)
CuF_2	Copper Difluoride (c)
CuF_2	Copper Difluoride (ℓ)
CuF_2	Copper Difluoride (g)
CuH_2O_2	Copper Dihydroxide (c)
CuO	Copper Monoxide (c)
CuO	Copper Monoxide (g)
CuO_4S	Copper Sulfate (c)
Cu_2	Copper, Diatomic (g)
Cu_2O	Dicopper Monoxide (c)
Cu_2O	Dicopper Monoxide (ℓ)
Cu_2O_5S	Copper Oxide Sulfate (c)
F	Fluorine, Monatomic (g)
F^-	Fluorine Uninegative Ion (g)
FFe	Iron Monofluoride (g)
FH	Hydrogen Fluoride (g)
*FHO	Hypofluorous Acid (g)
FHO_3S	Fluorosulfuric Acid (g)
FH_3Si	Fluorosilane (g)

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

Filing Order	Table Title
F_2OS	Thionyl Fluoride (g)
F_2OSi	Silicon Oxydifluoride (g)
F_2OTi	Titanium Oxydifluoride (g)
F_2O_2S	Sulfuryl Fluoride (g)
F_2P	Phosphorus Difluoride (g)
*F_2Pb	Lead Difluoride (c, α)
*F_2Pb	Lead Difluoride (c, β)
*F_2Pb	Lead Difluoride (ℓ)
*F_2Pb	Lead Difluoride (g)
F_2Si	Silicon Difluoride (g)
*F_2Sr	Strontium Difluoride (c)
*F_2Sr	Strontium Difluoride (ℓ)
*F_2Sr	Strontium Difluoride (g)
F_2Ti	Titanium Difluoride (g)
F_2Zr	Zirconium Difluoride (c)
F_2Zr	Zirconium Difluoride (ℓ)
F_2Zr	Zirconium Difluoride (g)
F_3Fe	Iron Trifluoride (c)
F_3Fe	Iron Trifluoride (g)
F_3HSi	Trifluorosilane (g)
F_3Li_3	Lithium Fluoride, Trimeric (g)
F_3N	Nitrogen Trifluoride (g)
F_3NO	Trifluoramine Oxide (g)
F_3OP	Phosphoryl Fluoride (g)
F_3P	Phosphorus Trifluoride (g)
F_3PS	Thiophosphoryl Fluoride (g)
F_3Si	Silicon Trifluoride (g)
F_3Ti	Titanium Trifluoride (c)
F_3Ti	Titanium Trifluoride (g)
F_3Zr	Zirconium Trifluoride (c)
F_3Zr	Zirconium Trifluoride (g)
F_4Mg_2	Magnesium Difluoride, Dimeric (g)
F_4MoO	Molybdenum Oxytetrafluoride (g)
F_4N_2	Tetrafluorohydrazine (g)
F_4OW	Tungsten Oxytetrafluoride (c)
F_4OW	Tungsten Oxytetrafluoride (ℓ)
F_4OW	Tungsten Oxytetrafluoride (g)
*F_4Pb	Lead Tetrafluoride (g)
F_4S	Sulfur Tetrafluoride (g)
F_4Si	Silicon Tetrafluoride (g)
F_4Ti	Titanium Tetrafluoride (c)
F_4Ti	Titanium Tetrafluoride (g)
F_4Zr	Zirconium Tetrafluoride (c)
F_4Zr	Zirconium Tetrafluoride (g)
F_5I	Iodine Pentafluoride (g)
F_5P	Phosphorus Pentafluoride (g)
F_6Mo	Molybdenum Hexafluoride (ℓ)
F_6Mo	Molybdenum Hexafluoride (g)
F_6S	Sulfur Hexafluoride (g)
F_6W	Tungsten Hexafluoride (ℓ)
F_6W	Tungsten Hexafluoride (g)
F_7I	Iodine Heptafluoride (g)
Fe	Iron (ref. st.)
Fe	Iron (c)

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

Filing Order	Table Title
HO_2	Hydroperoxyl (g)
HP	Phosphorus Monohydride (g)
HPb	Lead Monohydride (g)
HS	Sulfur Monohydride (g)
HSi	Silicon Monohydride (g)
HSi^+	Silicon Monohydride Unipositive Ion (g)
HZr	Zirconium Hydride (g)
H_2	Hydrogen, Diatomic (ref. st., g)
$H_2K_2O_2$	Potassium Hydroxide, Dimeric (g)
$H_2Li_2O_2$	Lithium Hydroxide, Dimeric (g)
H_2Mg	Magnesium Hydride (c)
H_2MgO_2	Magnesium Dihydroxide (c)
H_2MgO_2	Magnesium Dihydroxide (g)
H_2MoO_4	Molybdic Acid (g)
H_2N	Amidogen (g)
H_2N_2	Diimide (g)
$H_2Na_2O_2$	Sodium Hydroxide, Dimeric (g)
H_2O	Water (g)
H_2O_2	Hydrogen Peroxide (g)
H_2O_4S	Sulfuric Acid (ℓ)
H_2O_4S	Sulfuric Acid (g)
H_2O_4W	Tungstic Acid (c)
H_2O_4W	Tungstic Acid (g)
H_2P	Phophorus Hydride (g)
H_2S	Hydrogen Sulfide (g)
H_2Ti	Titanium Hydride (c)
H_3N	Ammonia (g)
H_3O^+	Hydronium Unipositive Ion (g)
H_3O_4P	Orthophosphoric Acid (c)
H_3O_4P	Orthophosphoric Acid (ℓ)
H_3P	Phosphine (g)
H_4IN	Ammonium Iodide (c)
H_4N_2	Hydrazine (ℓ)
H_4N_2	Hydrazine (g)
H_4Si	Silane (g)
Hg	Mercury (ref. st.)
Hg	Mercury (ℓ)
Hg	Mercury, Monatomic (g)
HgI	Mercurous Iodide (g)
HgI_2	Mercuric Iodide (c)
HgI_2	Mercuric Iodide (ℓ)
HgI_2	Mercuric Iodide (g)
HgO	Mercuric Oxide (c)
HgO	Mercury Monoxide (g)
Hg_2I_2	Mercurous Iodide (c)
Hg_2I_2	Mercurous Iodide (ℓ)
*I	Iodine, Monatomic (g)
IK	Potassium Iodide (c)
IK	Potassium Iodide (ℓ)
IK	Potassium Iodide (g)
ILi	Lithium Iodide (c)
ILi	Lithium Iodide (ℓ)

Filing Order	Table Title
ILi	Lithium Iodide (g)
INO	Nitrosyl Iodide (g)
INa	Sodium Iodide (c)
INa	Sodium Iodide (ℓ)
* IPb	Lead Monoiodide (g)
* ISr	Strontium Monoiodide (g)
ITi	Titanium Monoiodide (g)
IZr	Zirconium Monoiodide (g)
I_2	Iodine (ref. st.)
I_2	Iodine (ℓ)
I_2	Iodine, Diatomic (g)
I_2K_2	Potassium Iodide, Dimeric (g)
I_2Li_2	Lithium Iodide, Dimeric (g)
* I_2Pb	Lead Diiodide (c)
* I_2Pb	Lead Diiodide (ℓ)
* I_2Pb	Lead Diiodide (g)
* I_2Sr	Strontium Diiodide (c)
* I_2Sr	Strontium Diiodide (ℓ)
* I_2Sr	Strontium Diiodide (g)
I_2Ti	Titanium Diiodide (c)
I_2Ti	Titanium Diiodide (g)
I_2Zr	Zirconium Diiodide (c)
I_2Zr	Zirconium Diiodide (ℓ)
I_2Zr	Zirconium Diiodide (g)
I_3Ti	Titanium Triiodide (c)
I_3Ti	Titanium Triiodide (g)
I_3Zr	Zirconium Triiodide (c)
I_3Zr	Zirconium Triiodide (g)
* I_4Pb	Lead Tetraiodide (g)
I_4Ti	Titanium Tetraiodide (c)
I_4Ti	Titanium Tetraiodide (ℓ)
I_4Ti	Titanium Tetraiodide (g)
I_4Zr	Zirconium Tetraiodide (c)
I_4Zr	Zirconium Tetraiodide (g)
K	Potassium (ref. st.)
K	Potassium (ℓ)
K	Potassium, Monatomic (g)
K^+	Potassium Unipositive Ion (g)
KO	Potassium Monoxide (g)
KO^-	Potassium Monoxide Uninegative Ion (g)
KO_2	Potassium Superoxide (c)
K_2	Potassium, Diatomic (g)
K_2O	Potassium Oxide (c)
K_2O_2	Potassium Peroxide (c)
K_2O_3Si	Potassium Metasilicate (c)
K_2O_3Si	Potassium Metasilicate (ℓ)
K_2O_4S	Potassium Sulfate (c)
K_2O_4S	Potassium Sulfate (ℓ)
Li	Lithium (ref. st.)
Li	Lithium (c)
Li	Lithium (ℓ)
Li	Lithium, Monatomic (g)

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

Filing Order	Table Title
Mo^+	Molybdenum Unipositive Ion (g)
MoO	Molybdenum Monoxide (g)
MoO_2	Molybdenum Dioxide (c)
MoO_2	Molybdenum Dioxide (g)
MoO_3	Molybdenum Trioxide (c)
MoO_3	Molybdenum Trioxide (ℓ)
MoO_3	Molybdenum Trioxide (g)
*$N_{0.465}V$	Vanadium Subnitride (c)
N	Nitrogen, Monatomic (g)
NO	Nitric Oxide (g)
NO^+	Nitric Oxide Unipositive Ion (g)
NO_2	Nitrogen Dioxide (g)
NO_2^-	Nitrogen Dioxide Uninegative Ion (g)
NO_3	Nitrogen Trioxide (g)
NP	Phosphorous Nitride (g)
NS	Sulfur Nitride (g)
NSi	Silicon Nitride (g)
NSi_2	Disilicon Nitride (g)
NTi	Titanium Nitride (c)
NTi	Titanium Nitride (ℓ)
*NV	Vanadium Mononitride (c)
*NV	Vanadium Mononitride (g)
NZr	Zirconium Nitride (c)
NZr	Zirconium Nitride (ℓ)
NZr	Zirconium Nitride (g)
N_2	Nitrogen (ref. st., g)
N_2O	Dinitrogen Monoxide (g)
N_2O^+	Dinitrogen Monoxide Unipositive Ion (g)
N_2O_3	Dinitrogen Trioxide (g)
N_2O_4	Nitrogen Tetroxide (c)
N_2O_4	Dinitrogen Tetroxide (ℓ)
N_2O_4	Nitrogen Tetroxide (g)
N_2O_5	Dinitrogen Pentoxide (g)
N_3	Azide (g)
N_4Si_3	Silicon Nitride (c, α)
N_5P_3	Triphosphorus Pentanitride (c)
Na	Sodium (ref. st.)
Na	Sodium (c)
Na	Sodium (ℓ)
Na	Sodium Monatomic (g)
Na^+	Sodium Unipositive Ion (g)
NaO	Sodium Monoxide (g)
NaO^-	Sodium Monoxide Uninegative Ion (g)
NaO_2	Sodium Superoxide (c)
Na_2	Sodium Diatomic (g)
Na_2O	Disodium Monoxide (c)
Na_2O	Disodium Monoxide (ℓ)
Na_2O_2	Disodium Dioxide (c)
Na_2O_3Si	Sodium Metasilicate (c)
Na_2O_3Si	Sodium Metasilicate (ℓ)
Na_2O_4S	Sodium Sulfate (c, V)
Na_2O_4S	Sodium Sulfate (c, III)

Filing Order	Table Title
Na_2O_4S	Sodium Sulfate (c, I)
Na_2O_4S	Sodium Sulfate (c, δ)
Na_2O_4S	Sodium Sulfate (ℓ)
Na_2O_4W	Sodium Tungstate (c)
$Na_2O_5Si_2$	Sodium Disilicate (c)
$Na_2O_5Si_2$	Sodium Disilicate (ℓ)
Na_2S	Sodium Sulfide (c)
Na_2S	Sodium Sulfide (ℓ)
*Nb	Niobium (ref. st.)
*Nb	Niobium (c)
*Nb	Niobium (ℓ)
*Nb	Niobium, Monatomic (g)
*NbO	Niobium Monoxide (c)
*NbO	Niobium Monoxide (ℓ)
*NbO	Niobium Monoxide (g)
*NbO_2	Niobium Dioxide (c)
*NbO_2	Niobium Dioxide (ℓ)
*NbO_2	Niobium Dioxide (g)
*Nb_2O_5	Diniobium Pentoxide (c)
*Nb_2O_5	Diniobium Pentoxide (ℓ)
*O	Oxygen, Monatomic (g)
O^-	Oxygen Uninegative Ion (g)
OP	Phosphorus Monoxide (g)
OPb	Lead Monoxide (c, Red)
OPb	Lead Monoxide (c, Yellow)
OPb	Lead Monoxide (ℓ)
OPb	Lead Monoxide (g)
OS	Sulfur Monoxide (g)
OS_2	Disulfur Monoxide (g)
OSi	Silicon Monoxide (g)
*OSr	Strontium Oxide (c)
*OSr	Strontium Oxide (ℓ)
*OSr	Strontium Oxide (g)
*OTa	Tantalum Monoxide (g)
*OTi	Titanium Monoxide (c, α)
*OTi	Titanium Monoxide (c, β)
*OTi	Titanium Monoxide (ℓ)
*OTi	Titanium Monoxide (g)
*OV	Vanadium Monoxide (c)
*OV	Vanadium Monoxide (ℓ)
*OV	Vanadium Monoxide (g)
OW	Tungsten Monoxide (g)
OZr	Zirconium Monoxide (g)
O_2	Oxygen, Diatomic (ref. st., g)
O_2^-	Diatomic Oxygen Uninegative Ion (g)
O_2P	Phosphorus Dioxide (g)
O_2Pb	Lead Dioxide (c)
O_2S	Sulfur Dioxide (g)
O_2Si	Quartz (c)
O_2Si	Cristobalite (c, low)
O_2Si	Cristobalite (c, high)
O_2Si	Silicon Dioxide (ℓ)
O_2Si	Silicon Dioxide (g)

Filing Order	Table Title
*O_2Ta	Tantalum Dioxide (g)
*O_2Ti	Anatase (c)
*O_2Ti	Rutile (c)
*O_2Ti	Titanium Dioxide (ℓ)
*O_2Ti	Titanium Dioxide (g)
*O_2V	Vanadium Dioxide (g)
O_2W	Tungsten Dioxide (c)
O_2W	Tungsten Dioxide (g)
$O_{2.72}W$	Tungsten Oxide (c)
$O_{2.90}W$	Tungsten Oxide (c)
$O_{2.96}W$	Tungsten Oxide (c)
O_2Zr	Zirconium Dioxide (c)
O_2Zr	Zirconium Dioxide (ℓ)
O_2Zr	Zirconium Dioxide (g)
O_3	Ozone (g)
O_3PbSi	Lead Metasilicate (c)
O_3S	Sulfur Trioxide (g)
*O_3Ti_2	Dititanium Trioxide (c)
*O_3Ti_2	Dititanium Trioxide (ℓ)
*O_3V_2	Divanadium Trioxide (c)
*O_3V_2	Divanadium Trioxide (ℓ)
O_3W	Tungsten Trioxide (c)
O_3W	Tungsten Trioxide (ℓ)
O_3W	Tungsten Trioxide (g)
O_4Pb_2Si	Lead Orthosilicate (c)
O_4Pb_3	Lead Orthoplumbate (c)
O_4SiZr	Zirconium Orthoxilicate (c)
*O_4V_2	Divanadium Tetroxide (c)
*O_4V_2	Divanadium Tetroxide (ℓ)
*O_5Ta_2	Ditantalum Pentoxide (c)
*O_5Ta_2	Ditantalum Pentoxide (ℓ)
*O_5Ti_3	Trititanium Pentoxide (c, α)
*O_5Ti_3	Trititanium Pentoxide (c, β)
*O_5Ti_3	Trititanium Pentoxide (ℓ)
*O_5V_2	Divanadium Pentoxide (c)
*O_5V_2	Divanadium Pentoxide (ℓ)
O_6P_4	Phosphorus Trioxide, Dimeric (g)
O_6W_2	Tungsten Trioxide, Dimeric (g)
*O_7Ti_4	Tetratitanium Heptoxide (c)
*O_7Ti_4	Tetratitanium Heptoxide (ℓ)
O_8W_3	Tritungsten Octaoxide (g)
O_9W_3	Tungsten Trioxide, Trimeric (g)
$O_{10}P_4$	Phosphorus Pentoxide, Dimeric (c)
$O_{10}P_4$	Phosphorus Pentoxide, Dimeric (g)
$O_{12}W_4$	Tungsten Trioxide, Tetrameric (g)
P	Phosphorus (ref. st.)
P	Phosphorus (c, Red, V)
P	Phosphorus (c, White)
P	Phosphorus (ℓ)
P	Phosphorus (g)
PS	Phosphorus Sulfide (g)
P_2	Phosphorus, Diatomic (g)
P_4	Phosphorus, Tetratomic (g)
P_4S_3	Phosphorus Sulfide (c)
P_4S_3	Phosphorus Sulfide (ℓ)

Filing Order	Table Title
P_4S_3	Phosphorus Sulfide (g)
Pb	Lead (ref. st.)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
*PbS	Lead Sulfide (c)
*PbS	Lead Sulfide (ℓ)
*PbS	Lead Sulfide (g)
Pb_2	Lead, Diatomic (g)
S	Sulfur (ref. st.)
S	Sulfur (c)
S	Sulfur (ℓ)
S	Sulfur, Monatomic (g)
SSi	Silicon Monosulfide (g)
S_2	Sulfur, Diatomic (g)
S_2Si	Silicon Disulfide (c)
S_2Si	Silicon Disulfide (ℓ)
S_8	Sulfur Octatomic (g)
Si	Silicon (ref. st.)
Si	Silicon (c)
Si	Silicon (ℓ)
Si	Silicon, Monatomic (g)
Si^+	Silicon Unipositive Ion (g)
Si_2	Silicon, Diatomic (g)
Si_3	Silicon, Triatomic (g)
Sr	Strontium (ref. st.)
Sr	Strontium (c)
Sr	Strontium (ℓ)
Sr	Strontium (g)
*Ta	Tantalum (ref. st.)
*Ta	Tantalum (c)
*Ta	Tantalum (ℓ)
*Ta	Tantalum, Monatomic (g)
Ti	Titanium (ref. st.)
Ti	Titanium (c, α)
Ti	Titanium (c, β)
Ti	Titanium (ℓ)
Ti	Titanium, Monatomic (g)
Ti^+	Titanium Unipositive Ion (g)
*V	Vanadium (ref. st.)
*V	Vanadium (c)
*V	Vanadium (ℓ)
*V	Vanadium (g)
W	Tungsten (ref. st.)
W	Tungsten (c)
W	Tungsten (ℓ)
W	Tungsten, Monatomic (g)
W^+	Tungsten Unipositive Ion (g)
Zr	Zirconium (ref. st.)
Zr	Zirconium (c, α)

Filing Order	Table Title
Zr	Zirconium (c, β)
Zr	Zirconium (ℓ)
Zr	Zirconium (g)

Filing Order	Table Title
Zr^+	Zirconium Unipositive Ion (g)
e^-	Electron Gas (ref. st.)

6. JANAF Thermochemical Tables, 1975 Supplement

Barium Monochloride (BaCl)

(Ideal Gas) GFW = 172.793

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.361	-33.612	-33.612	INFINITE
100	7.574	52.804	69.305	-1.650	-33.655	-35.863	78.379
200	8.421	58.365	62.579	-.843	-33.819	-38.008	41.533
298	8.708	61.790	61.790	.000	-34.000	-40.027	29.340
300	8.712	61.844	61.790	.016	-34.003	-40.064	29.186
400	8.837	64.370	62.134	.894	-34.262	-42.049	22.975
500	8.904	66.349	62.786	1.762	-34.713	-43.948	19.210
600	8.948	67.977	63.520	2.674	-35.360	-45.733	16.658
700	8.979	69.359	64.257	3.571	-35.815	-47.428	14.808
800	9.005	70.559	64.972	4.470	-36.393	-49.047	13.399
900	9.026	71.621	65.653	5.372	-36.869	-50.599	12.287
1000	9.045	72.573	66.298	6.275	-37.346	-52.100	11.386
1100	9.063	73.436	66.908	7.181	-39.823	-53.356	10.601
1200	9.081	74.225	67.486	8.083	-40.356	-54.562	9.937
1300	9.099	74.953	68.032	8.997	-40.864	-55.725	9.368
1400	9.119	75.628	68.551	9.908	-41.353	-56.851	8.875
1500	9.142	76.258	69.044	10.821	-41.827	-57.941	8.442
1600	9.169	76.849	69.514	11.735	-42.292	-59.000	8.059
1700	9.201	77.406	69.962	12.655	-42.750	-60.030	7.717
1800	9.238	77.933	70.390	13.577	-43.206	-61.033	7.410
1900	9.282	78.433	70.800	14.502	-43.667	-62.010	7.133
2000	9.332	78.911	71.194	15.433	-44.135	-62.964	6.880
2100	9.390	79.367	71.572	16.369	-44.615	-63.894	6.650
2200	9.454	79.806	71.937	17.311	-78.465	-63.575	6.316
2300	9.526	80.227	72.288	18.260	-78.766	-62.890	5.976
2400	9.604	80.634	72.627	19.217	-79.158	-62.191	5.663
2500	9.686	81.026	72.956	20.181	-79.580	-61.476	5.374
2600	9.777	81.410	73.273	21.154	-80.050	-60.742	5.106
2700	9.872	81.781	73.582	22.137	-80.567	-59.990	4.856
2800	9.970	82.141	73.881	23.129	-81.129	-59.218	4.622
2900	10.072	82.493	74.172	24.131	-81.729	-58.425	4.403
3000	10.177	82.836	74.455	25.143	-82.366	-57.610	4.197
3100	10.284	83.172	74.731	26.166	-83.034	-56.775	4.003
3200	10.391	83.500	75.000	27.200	-83.726	-55.917	3.819
3300	10.500	83.821	75.262	28.245	-84.437	-55.036	3.645
3400	10.609	84.136	75.519	29.300	-85.163	-54.135	3.480
3500	10.717	84.445	75.769	30.366	-85.898	-53.212	3.323
3600	10.824	84.749	76.014	31.444	-86.636	-52.266	3.173
3700	10.929	85.047	76.255	32.531	-87.377	-51.302	3.030
3800	11.033	85.340	76.490	33.629	-88.114	-50.318	2.894
3900	11.134	85.628	76.720	34.738	-88.844	-49.313	2.763
4000	11.233	85.911	76.947	35.856	-89.566	-48.290	2.638
4100	11.329	86.189	77.169	36.984	-90.275	-47.250	2.519
4200	11.421	86.463	77.387	38.122	-90.972	-46.193	2.404
4300	11.511	86.733	77.601	39.268	-91.655	-45.119	2.293
4400	11.597	86.999	77.812	40.424	-92.322	-44.026	2.187
4500	11.680	87.260	78.019	41.588	-92.975	-42.923	2.085
4600	11.759	87.518	78.222	42.759	-93.611	-41.803	1.986
4700	11.834	87.772	78.423	43.939	-94.230	-40.670	1.891
4800	11.906	88.022	78.620	45.126	-94.834	-39.525	1.800
4900	11.975	88.268	78.815	46.320	-95.423	-38.365	1.711
5000	12.040	88.510	79.006	47.521	-95.995	-37.196	1.626
5100	12.101	88.749	79.195	48.728	-96.553	-36.014	1.543
5200	12.159	88.985	79.381	49.941	-97.096	-34.821	1.463
5300	12.213	89.217	79.564	51.160	-97.626	-33.619	1.386
5400	12.264	89.446	79.745	52.384	-98.141	-32.406	1.312
5500	12.312	89.671	79.923	53.613	-98.645	-31.183	1.239
5600	12.357	89.894	80.100	54.846	-99.137	-29.954	1.169
5700	12.399	90.113	80.273	56.084	-99.618	-28.716	1.101
5800	12.438	90.329	80.445	57.326	-100.088	-27.465	1.035
5900	12.474	90.542	80.614	58.571	-100.548	-26.211	.971
6000	12.507	90.751	80.781	59.820	-100.998	-24.946	.909

Dec. 31, 1972

BARIUM MONOCHLORIDE (BaCl) (IDEAL GAS) GFW = 172.793 BaCl

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 61.79 ± 0.1 gibbs/mol

ΔHf°_0 = -33.6 ± 3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -34.0 ± 3 kcal/mol

Electronic Levels and Quantum Weights

	ϵ_i, cm^{-1}	g_i		ϵ_i, cm^{-1}	g_i
X $^2\Sigma^+$	0.0	2	D $^2\Sigma$	25471.5	2
A $^2\Pi$	10351.1	2	E $^2\Sigma$	27064.6	2
	10995.3	2	F $^2\Sigma$	29493.6	2
B $^2\Sigma^+$	11880.0	2	G $^2\Sigma$	32511.4	2
C $^2\Pi$	19062.9	2			
	19450.1	2			

ω_e = 277.9 cm^{-1} $\omega_e x_e$ = 0.88 cm^{-1} σ = 1

B_e = [0.08518 ± 0.003]cm^{-1} α_e = [0.00035]cm^{-1} r_e = [2.65 ± 0.05] Å

Heat of Formation

ΔHf° is based mainly on two sets of gas-phase equilibria measured mass spectrometrically by Hildenbrand (1) and, to a lesser extent, on the analogous data of Potter et al. (2). Analyses of the mass-spectrometric data (1-3) are summarized below. The results from Potter et al. (2) and Zmbov (3) are less negative by about 4 kcal/mol, suggesting the approximate uncertainty in ΔHf° From the adopted ΔHf° we derive D°_0 = 106.4 ± 3 kcal/mol. Independent methods yield D°_0 = 103 ± 5 (4), ≥110 (5), 106.8 ± 2 (6) and 105 ± 6 kcal/mol (6).

Electron-impact data (4) gave D°_0(ClBa-Cl) = 115.8 ± 3.3 kcal/mol and we use $\Delta H^\circ_{atom}(BaCl_2)$ = 219 ± 4 kcal/mol to derive D°_0 = 103 ± 5 kcal/mol. Chemiluminescence from crossed beams of Ba atoms with Cl_2 gave an approximate lower limit to D°_0 of 110 kcal/mol (5). Flame studies (6) gave D°_0 = 106.8 ± 2 kcal/mol and D°_0(ClBa-Cl) = 114 ± 4; we derive D°_0 = 105 ± 6 kcal/mol from the latter value using $\Delta H^\circ_{atom}(BaCl_2)$ = 219 kcal/mol. Ryabova (6) considered the flames to involve $BaCl_2$, BaOHCl, and BaOH as well as BaCl. Schofield and Sugden (7) inferred that the flames involved mainly $BaCl_2$ rather than BaCl as assumed in earlier flame studies. Gaydon (8) discounted the values derived from electronic spectra, but Hildenbrand (1) showed that ionicity corrections bring the Birge-Sponer extrapolation into reasonable agreement with D°_0.

Source	Reaction[b]	Range T, K	ΔHr°(298.15 K), kcal/mol 2nd Law	ΔHr°(298.15 K), kcal/mol 3rd Law	δS[a] gibbs/mol	ΔHf°(298.15 K) kcal/mol	D°_0
(1) Hildenbrand (1970)	A	1234-1380	3.3±3.6	6.76±0.8	-2.6±2.7	-34.82±2.2	107.2
(2) Potter (1970)	A	1507-1702	13.0±5.4	13.34±1.0	-0.2±3.3	-31.53±2.2	103.9
(3) Zmbov (1969)[c]	A	974-1052	21.8±9.4	5.89±1.3	5.9±9.3	-30.26±2.2	102.7
(1) Hildenbrand (1970)	B	1234-1380	10.3±5.1	13.21±1.1	-2.2±3.9	-34.29±2.6	106.7
(2) Potter (1970)	B	1507-1702	9.7±7.3	17.72±1.5	-5.0±4.5	-29.78±2.8	102.2

[a] δS = ΔSr°(2nd Law) - ΔSr°(3rd Law).

[b] Reactions: (A) Ba(g) + $BaCl_2$(g) = 2BaCl(g); (B) Ba(g) + AlCl(g) = BaCl(g) + Al(g).

[c] Data given in Table 2 (3) are assumed to be 10^3 x Kp instead of 10^4 x Kp.

Heat Capacity and Entropy

Electronic levels and vibrational constants are taken from the review of Rosen (9). The level at 10351.1 cm^{-1} is T_o rather than T_e. Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX_2(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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BaCl

Barium Dichloride ($BaCl_2$)

(Crystal) GFW = 208.246

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.993	-205.347	-205.347	INFINITE
100	13.614	11.794	44.736	-3.294	-205.750	-201.600	440.596
200	16.978	22.569	31.172	-1.721	-205.511	-197.525	215.845
298	17.959	29.557	29.557	.000	-205.200	-193.672	141.966
300	17.972	29.668	29.557	.033	-205.194	-193.600	141.038
400	18.482	34.914	30.269	1.858	-204.921	-189.781	103.692
500	18.847	39.079	31.629	3.725	-204.819	-186.012	81.306
600	19.222	42.547	33.167	5.628	-204.890	-182.241	66.381
700	19.654	45.542	34.726	7.571	-204.737	-178.481	55.724
800	20.148	48.198	36.247	9.561	-204.667	-174.734	47.735
900	20.704	50.602	37.710	11.603	-204.448	-171.003	41.525
1000	21.384	52.817	39.112	13.706	-204.173	-167.303	36.564
1100	22.354	54.898	40.453	15.889	-205.821	-163.436	32.472
1200	29.600	60.287	41.746	22.248	-201.352	-159.606	29.068
1300	29.600	62.656	43.265	25.208	-200.260	-156.171	26.255
1400	29.600	64.845	44.729	28.168	-199.152	-152.822	23.857
1500	29.600	66.892	46.139	31.128	-198.032	-149.552	21.790
1600	29.600	68.802	47.497	34.088	-196.906	-146.357	19.991
1700	29.600	70.596	48.803	37.048	-195.777	-143.230	18.414
1800	29.600	72.286	50.061	40.008	-194.651	-140.173	17.019
1900	29.600	73.889	51.274	42.968	-193.533	-137.175	15.779
2000	29.600	75.407	52.443	45.928	-192.430	-134.239	14.669

Dec. 31, 1972

BARIUM DICHLORIDE ($BaCl_2$) (CRYSTAL) GFW = 208.246 $BaCl_2$

$S^\circ_{298.15}$ = 29.557 ± 0.03 gibbs/mol

Tt = 1198 ± 1 K

Tm = 1235 ± 1 K

ΔHf°_0 = -205.35 ± 3 (or ±0.6) kcal/mol

$\Delta Hf^\circ_{298.15}$ = -205.2 ± 3 (or ±0.6) kcal/mol

ΔHt° = 4.04 ± 0.05 kcal/mol

ΔHm° = 3.822 ± 0.08 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 86.0 ± 1.5 kcal/mol

Heat of Formation

ΔHf° is from NBS Technical Note 270-6 (1) and its selection was discussed in detail by Parker (2). The adopted value was derived by Ehrlich et al. (3) from their measurements of ΔH_{soln} of Ba(c) and $BaCl_2$(c) in HCl (550 H_2O). Earlier solution data for Ba (4) and $BaCl_2$ (5, 6) are in good agreement (2), but a recent study by Vorob'ev et al. (7) of Ba in HCl (240 and 400 H_2O) yields ΔHf° = -201.8 kcal/mol. The deviation (+3.4 kcal/mol) from the adopted value is confirmed by direct measurements (7) of ΔHf° and ΔH_{soln} of BaH_2(c), yielding -202.1 kcal/mol for $BaCl_2$(c). All authors reported difficulties in obtaining or maintaining Ba and BaH_2 free of impurities; this provides conceivable reasons for bias in either of the opposing results. We assign an uncertainty of ±3 kcal/mol to include the possibility that Vorob'ev et al. (7) are correct but add an alternative of ±0.6 kcal/mol if their data are biased.

Parker (2) rejected ΔHf° = -219.3 kcal/mol obtained by Siemonsen (8) by direct chlorination and ΔHf° = -212.0 kcal/mol which would result from BaO(c) based on Mah's direct combustion (9). Parker noted that these more negative values are incompatible with data for BaO_2, $Ba(OH)_2$ and $BaCO_3$. They are also incompatible with calorimetric data for BaH_2 noted above and equilibrium data as discussed on the tables for $BaCl_2$(ℓ and g).

Heat Capacity and Entropy

Cp° is based on adiabatic calorimetry (6-346 K) of Goodman and Westrum (10). S° is calculated from Cp° using S°(6 K) = 0.012 gibbs/mol. Cp° above 300 K is from constrained fitting of enthalpy data (340-1197 K for α-phase and 1201-1231 K for β-phase) measured in an ice calorimeter by Gardner and Taylor (11). The sample studied at high temperatures was a portion of that used at low temperatures. Deviations of the H data (11) from the adopted values are <0.1% for most points but show a maximum of -0.3% for two points near 400 K.

Other enthalpy studies include those of Dworkin and Bredig (12), Janz et al. (13) and Gant (14). Deviations from the adopted values are about +2% for the smooth values (~1100-1230 K) of (12), +1.8 to +2.9% for the equations (892-1235 K) of (13), and -1.7 to +6.7% for the data (406-1230 K) of (14). Popov and Gal'chenko (15) used a continuous heating method to obtain Cp° values which deviate by +4 to +9% (443-973 K).

Transition Data

Tt = 1198 K is from the enthalpy study of Gardner and Taylor (11). Other enthalpy studies gave 1193 (12) and 1198 K (13), while thermal analysis gave 1199 (16) and 1197 K (17). ΔHt° is calculated from our adopted fits of the enthalpy data (11). Published values include 4.04 (11), 4.10 (12) and 4.15 ± 0.16 (13).

Melting Data - see $BaCl_2$(ℓ).

Heat of Sublimation - see $BaCl_2$(g).

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$BaCl_2$

Barium Dichloride ($BaCl_2$)

(Liquid) GFW = 208.246

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.959	34.302	34.302	.000	-198.964	-188.851	138.432
300	17.972	34.413	34.302	.033	-198.958	-188.788	137.532
400	18.482	39.659	35.014	1.858	-198.685	-185.443	101.322
500	18.847	43.823	36.373	3.725	-198.584	-182.148	79.617
600	19.222	47.292	37.912	5.628	-198.655	-178.852	65.147
700	19.654	50.287	39.471	7.571	-198.501	-175.567	54.814
800	20.148	52.943	40.992	9.561	-198.432	-172.294	47.069
900	26.000	56.005	42.493	12.161	-197.655	-169.072	41.056
1000	26.000	58.744	43.984	14.761	-196.883	-165.939	36.266
1100	26.000	61.223	45.440	17.361	-198.114	-162.686	32.323
1200	26.000	63.485	46.851	19.961	-197.404	-159.496	29.048
1300	26.000	65.566	48.211	22.561	-196.672	-156.367	26.288
1400	26.000	67.493	49.521	25.161	-195.924	-153.294	23.930
1500	26.000	69.287	50.779	27.761	-195.164	-150.276	21.895
1600	26.000	70.965	51.989	30.361	-194.398	-147.309	20.121
1700	26.000	72.541	53.152	32.961	-193.629	-144.368	18.562
1800	26.000	74.027	54.271	35.561	-192.863	-141.514	17.182
1900	26.000	75.433	55.348	38.161	-192.105	-138.680	15.952
2000	26.000	76.766	56.386	40.761	-191.362	-135.889	14.849
2100	26.000	78.035	57.387	43.361	-190.635	-133.134	13.855
2200	26.000	79.244	58.353	45.961	-223.286	-129.186	12.833
2300	26.000	80.400	59.287	48.561	-222.416	-124.927	11.871
2400	26.000	81.507	60.190	51.161	-221.605	-120.706	10.992
2500	26.000	82.566	61.064	53.761	-220.853	-116.518	10.186
2600	26.000	83.588	61.910	56.361	-220.159	-112.358	9.445
2700	26.000	84.569	62.732	58.961	-219.522	-108.225	8.760
2800	26.000	85.515	63.528	61.561	-218.942	-104.113	8.126
2900	26.000	86.427	64.302	64.161	-218.411	-100.022	7.538
3000	26.000	87.308	65.055	66.761	-217.928	-95.949	6.990

Dec. 31, 1972

BARIUM DICHLORIDE ($BaCl_2$) (LIQUID) GFW = 208.246 $BaCl_2$

$S^\circ_{298.15}$ = 34.302 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -198.964 kcal/mol

Tm = 1235 ± 1 K

ΔHm° = 3.822 ± 0.08 kcal/mol

Tb = 2301.8 K

ΔHv° = 58.90 kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference in ($H^\circ_{1235} - H^\circ_{298.15}$) between crystal and liquid. Independent values of ΔHf° for liquid (and crystal) may be derived from equilibrium data (1, 2) for Ca(ℓ) + $BaCl_2$(ℓ) → Ba(ℓ) + $CaCl_2$(ℓ). Our third-law analysis is summarized below; it shows that the data of Feschotte-Ostertag (1) are consistent with the adopted ΔHf°(c) = -205.2 kcal/mol from Ehrlich et al. (cf. $BaCl_2$, c), while the data of Peterson and Hinkebein (2) are more consistent with the alternative ΔHf°(c) = -201.8 kcal/mol from Vorob'ev et al. Both are incompatible with ΔHf°(c) = -219.3 from direct chlorination and ΔHf°(c) = -212.0 derived from Mah's ΔHc value for ΔHf° of BaO(c).

Source	Remarks	Range T, K	δS[a] gibbs/mol	3rd Law ΔHr°(298.15 K)	ΔHf°(ℓ)	ΔHf°(c)
				kcal/mol		
(1) Feschotte-Ostertag	Direct measurement	1273		13.24±1.6	-198.3±2	-204.5±2
(1) Feschotte-Ostertag	Indirect via $SrCl_2$	1273		14.12±1.8	-199.1±2	-205.4±2
(2) Peterson	Direct measurement	1173-1223	-2.5±8.1	11.47±0.6	-196.5±1	-202.7±1

[a] δS = ΔSr° (2nd law) - ΔSr° (3rd law).

Heat Capacity and Entropy

The constant Cp° of 26.0 gibbs/mol is based on enthalpy data (1238-1347 K) measured in an ice calorimeter by Gardner and Taylor (3). Deviations of the data from the adopted fit are all less than 0.05%. Smoothed enthalpies of Dworkin and Bredig (4) deviate by +1.2% and those of Janz et al. (5) by +2.7 to 2.1%. Enthalpy data of Gant (6) deviate by +1.5%. Cp° is taken equal to that of the crystal from 298 to 800 K, the assumed glass transition. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Tm is from the enthalpy study of Gardner and Taylor (3). Some other reported values include 1233 (4) and 1235 K (5, 6) from enthalpy studies and 1234 (7) and 1235 K (8) from thermal analysis. ΔHm° is obtained from the difference in the adopted enthalpy fits for liquid and β-phases. Published values include 3.82 (3), 3.90 (4) and 4.13 ± 0.12 (5) kcal/mol.

Vaporization Data

Tb is calculated as the temperature at which ΔGr° = 0 for $BaCl_2$(ℓ) → $BaCl_2$(g). ΔHv° is calculated as the corresponding ΔHr°.

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Barium Dichloride ($BaCl_2$)

(Ideal Gas) GFW = 208.246

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.506	-118.860	-118.860	INFINITE
100	11.278	64.124	89.352	-2.523	-118.979	-120.062	262.394
200	12.918	72.557	79.041	-1.297	-119.087	-121.098	132.330
298	13.422	77.826	77.826	.000	-119.200	-122.064	89.475
300	13.428	77.909	77.826	.025	-119.202	-122.081	88.936
400	13.630	81.803	78.355	1.379	-119.400	-123.016	67.213
500	13.728	84.856	79.361	2.747	-119.797	-123.878	54.147
600	13.783	87.364	80.492	4.123	-120.395	-124.636	45.399
700	13.816	89.492	81.630	5.503	-120.805	-125.314	39.125
800	13.838	91.338	82.730	6.886	-121.342	-125.921	34.400
900	13.853	92.969	83.779	8.271	-121.780	-126.465	30.710
1000	13.864	94.429	84.772	9.656	-122.223	-126.963	27.748
1100	13.872	95.751	85.711	11.043	-124.667	-127.220	25.276
1200	13.878	96.958	86.599	12.431	-125.169	-127.429	23.208
1300	13.883	98.069	87.439	13.819	-125.649	-127.598	21.451
1400	13.886	99.098	88.236	15.207	-126.113	-127.731	19.940
1500	13.889	100.056	88.992	16.596	-126.564	-127.831	18.625
1600	13.892	100.953	89.712	17.985	-127.009	-127.901	17.470
1700	13.894	101.795	90.398	19.374	-127.451	-127.942	16.448
1800	13.896	102.589	91.054	20.764	-127.895	-127.959	15.536
1900	13.897	103.340	91.681	22.154	-128.347	-127.948	14.717
2000	13.898	104.053	92.282	23.543	-128.815	-127.916	13.978
2100	13.900	104.731	92.858	24.933	-129.298	-127.860	13.307
2200	13.901	105.378	93.413	26.323	-163.159	-126.554	12.572
2300	13.901	105.996	93.947	27.713	-163.499	-124.881	11.866
2400	13.902	106.586	94.461	29.104	-163.697	-123.194	11.218
2500	13.903	107.155	94.958	30.494	-164.355	-121.489	10.621
2600	13.903	107.700	95.437	31.884	-164.871	-119.764	10.067
2700	13.904	108.225	95.901	33.274	-165.444	-118.018	9.553
2800	13.904	108.731	96.350	34.665	-166.073	-116.250	9.074
2900	13.905	109.219	96.786	36.055	-166.752	-114.459	8.626
3000	13.905	109.690	97.208	37.446	-167.478	-112.645	8.206
3100	13.905	110.146	97.618	38.836	-168.248	-110.804	7.812
3200	13.906	110.588	98.017	40.227	-169.054	-108.939	7.440
3300	13.906	111.015	98.404	41.617	-169.892	-107.046	7.089
3400	13.906	111.431	98.781	43.008	-170.756	-105.129	6.758
3500	13.906	111.834	99.148	44.399	-171.642	-103.188	6.443
3600	13.907	112.225	99.506	45.789	-172.544	-101.217	6.145
3700	13.907	112.606	99.855	47.180	-173.459	-99.223	5.861
3800	13.907	112.977	100.196	48.571	-174.382	-97.206	5.591
3900	13.907	113.339	100.528	49.961	-175.311	-95.162	5.333
4000	13.907	113.691	100.853	51.352	-176.242	-93.095	5.086
4100	13.907	114.034	101.170	52.743	-177.171	-91.006	4.851
4200	13.908	114.369	101.480	54.133	-178.100	-88.894	4.626
4300	13.908	114.696	101.784	55.524	-179.023	-86.760	4.410
4400	13.908	115.016	102.081	56.915	-179.940	-84.599	4.202
4500	13.908	115.329	102.372	58.306	-180.852	-82.425	4.003
4600	13.908	115.634	102.657	59.697	-181.755	-80.227	3.812
4700	13.908	115.934	102.936	61.087	-182.652	-78.009	3.627
4800	13.908	116.226	103.210	62.478	-183.540	-75.775	3.450
4900	13.908	116.513	103.475	63.869	-184.420	-73.519	3.279
5000	13.908	116.794	103.742	65.260	-185.291	-71.249	3.114
5100	13.908	117.070	104.001	66.651	-186.153	-68.957	2.955
5200	13.908	117.340	104.255	68.041	-187.008	-66.650	2.801
5300	13.908	117.605	104.504	69.432	-187.855	-64.330	2.653
5400	13.909	117.865	104.749	70.823	-188.693	-61.990	2.509
5500	13.909	118.120	104.990	72.214	-189.524	-59.634	2.370
5600	13.909	118.370	105.227	73.605	-190.348	-57.268	2.235
5700	13.909	118.617	105.459	74.996	-191.166	-54.887	2.104
5800	13.909	118.858	105.688	76.387	-191.976	-52.485	1.978
5900	13.909	119.096	105.914	77.777	-192.782	-50.076	1.855
6000	13.909	119.330	106.135	79.168	-193.580	-47.648	1.736

Dec. 31, 1972

BARIUM DICHLORIDE ($BaCl_2$) (IDEAL GAS) GFW = 208.246 $BaCl_2$

Point Group C_{2v}

$S°_{298.15}$ = 77.83 ± 1.2 gibbs/mol

Ground State Quantum Weight = 1

$\Delta Hf°_0$ = -118.86 ± 4 (or ±1.6) kcal/mol

$\Delta Hf°_{298.15}$ = -119.2 ± 4 (or ±1.6) kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
255 (1)	[36] (1)	265 (1)

Bond Distance: Ba-Cl = 2.82 ± 0.03 Å

Bond Angle: Cl-Ba-Cl = [100° ± 20°]

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = 11.278 \times 10^{-113}\ g^3cm^6$

Heat of Formation

ΔHf°(298.15 K) is calculated from ΔHf°(c) by addition of ΔHs° = 86.0 ± 1.5 kcal/mol derived from third-law analysis of the vapor-pressure equation of Hildenbrand et al. (1, 2). The equation (1) summarized five torsion-effusion runs (83 total points) and is reasonably consistent with five boiling pressures in the mmHg range measured by Novikov (3). Other vapor pressure data (4-6) reviewed below are considered less reliable. ΔHf°(g) is assigned alternative uncertainties to reflect the discrepancies in ΔHf°(c). Equilibria derived from flame studies (7) yield ΔHf°(g) = -119.1 ± 3 and ΔHf°(c) = -205.1 ± 3 kcal/mol, which confirm the adopted values by an independent path. Mass spectra (8) at 1230 K showed that the saturated vapor consists predominantly of $BaCl_2$ with considerably less than 1% of dimer.

Source	Method	No. of Points	Range T, K	ΔHs°(298.15 K), kcal/mol 2nd Law	3rd Law	δS[a] gibbs/mol
(1, 2) Hildenbrand (1965)	Torsion effusion[b]	83[b]	1235-1440	85.1	86.01	-0.7
(3) Novikov (1964)	Boiling Point	5	1588-1710	75.6±4.2	86.30±0.7	-6.4±2.5
(4) Van Westenburg (1964)	Effusion	3	1244-1277	78.5±1.6	85.3 ±0.2	-5.4±1.3
(5) von Wartenburg (1922)	Boiling point	1	1819		>81	
(6) Maier (1925)	Static	4	1343-1487	85.4±3.8	76.6±0.9	6.1±2.7
(7) Schofield (1971)	Flame Kp[c]	8	2134-2535	- 9.5±8.7[c]	-13.5±2.4[c]	1.7±3.7

[a] δS = ΔS° (2nd Law) - ΔS° (3rd Law). [b] Pressures obtained from an equation summarizing 5 runs (83 total points).

[c] ΔHr° for $Ba(g) + 2\ HCl(g) \rightarrow BaCl_2(g) + 2\ H(g)$ yields ΔHf°(298.15 K) = 119.1 ± 3 kcal/mol.

Heat Capacity and Entropy

Vibrations ν_1 and ν_2 are the values quoted by Hildenbrand (9) and derived from IR spectra of molecules in matrix isolation (10). The bending mode was not observed; its value was calculated (10) from force-constant correlations as described for BaF_2 (11). Hastie et al. (12) assigned the bending mode to a band which they observed at 61 cm^{-1} in argon and 62 cm^{-1} in neon. This value would reduce S° by about 1.0 gibbs/mol; our assigned uncertainty includes this possibility. Agreement is better for ν_1 = 255 (9, 10) or 262 cm^{-1} (12, in Ne) and for ν_3 = 265±5 (13, gas), 260 (9, 10) or 268 cm^{-1} (12, in Ne). We adopt the gas-phase value (13) for ν_3.

Bond length is from gas-phase electron diffraction (14) which also gave the bond angle 180° ± 40°. Later studies (15) of electric and magnetic deflection of molecular beams revealed a permanent electric dipole moment and suggested a bond angle of the order of roughly 120°. Hastie et al. (12) estimated an angle of 120° ± 10° from relative intensities of ν_1 and ν_3. The matrix spectra (9, 10) were first interpreted to give an angle of 120° but reanalysis by Hemple (10) gave the angle 95.4°, estimated from the three fundamentals. We adopt 100° ± 20° and note that S° changes by only 0.2 gibbs/mol in the range 95° to 120°. The singlet ground state is based on magnetic deflection data (15). Principal moments of inertia are $I_A = 25.513 \times 10^{-39}$, $I_B = 54.94 \times 10^{-39}$ and $I_C = 80.46 \times 10^{-39}$ g cm^2.

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$BaCl_2$

Barium Monofluoride (BaF)

(Ideal Gas) GFW = 156.3384

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.233	- 76.526	- 76.526	INFINITE
100	7.068	50.482	65.846	- 1.536	- 76.583	- 78.782	172.177
200	7.808	55.602	59.569	- .753	- 76.798	- 80.895	88.398
298	8.305	58.823	58.823	.000	- 77.000	- 82.864	60.741
300	8.312	58.874	58.823	.015	- 77.004	- 82.900	60.393
400	8.571	61.305	59.153	.861	- 77.265	- 84.830	46.349
500	8.716	63.235	59.783	1.726	- 77.716	- 86.674	37.885
600	8.805	64.832	60.495	2.602	- 78.360	- 88.403	32.201
700	8.864	66.194	61.214	3.486	- 78.814	- 90.044	28.113
800	8.907	67.381	61.913	4.375	- 79.392	- 91.607	25.026
900	8.940	68.432	62.580	5.267	- 79.871	- 93.104	22.609
1000	8.967	69.375	63.213	6.162	- 80.352	- 94.550	20.664
1100	8.989	70.231	63.813	7.060	- 82.834	- 95.750	19.024
1200	9.009	71.014	64.380	7.960	- 83.373	- 96.900	17.648
1300	9.027	71.736	64.919	8.862	- 83.889	- 98.006	16.476
1400	9.044	72.405	65.430	9.765	- 84.387	- 99.074	15.466
1500	9.062	73.030	65.916	10.671	- 84.871	- 100.105	14.585
1600	9.081	73.615	66.379	11.578	- 85.347	- 101.106	13.810
1700	9.102	74.167	66.821	12.487	- 85.819	- 102.076	13.123
1800	9.125	74.687	67.244	13.398	- 86.292	- 103.019	12.508
1900	9.152	75.181	67.649	14.312	- 86.770	- 103.935	11.955
2000	9.183	75.652	68.037	15.229	- 87.259	- 104.826	11.455
2100	9.218	76.101	68.411	16.149	- 87.762	- 105.693	11.000
2200	9.259	76.530	68.770	17.073	- 121.637	- 105.308	10.461
2300	9.305	76.943	69.116	18.001	- 121.988	- 104.557	9.935
2400	9.357	77.340	69.451	18.934	- 122.392	- 103.791	9.452
2500	9.414	77.723	69.774	19.872	- 122.848	- 103.007	9.005
2600	9.476	78.093	70.087	20.817	- 123.356	- 102.204	8.591
2700	9.544	78.452	70.390	21.768	- 123.912	- 101.379	8.206
2800	9.617	78.801	70.684	22.726	- 124.517	- 100.535	7.847
2900	9.695	79.140	70.970	23.691	- 125.162	- 99.665	7.511
3000	9.778	79.470	71.248	24.665	- 125.846	- 98.776	7.196
3100	9.864	79.792	71.518	25.647	- 126.562	- 97.862	6.899
3200	9.955	80.106	71.782	26.638	- 127.305	- 96.924	6.620
3300	10.048	80.414	72.039	27.638	- 128.067	- 95.963	6.355
3400	10.145	80.715	72.290	28.648	- 128.846	- 94.979	6.105
3500	10.243	81.011	72.535	29.667	- 129.634	- 93.970	5.868
3600	10.344	81.301	72.774	30.696	- 130.427	- 92.939	5.642
3700	10.446	81.586	73.008	31.736	- 131.221	- 91.888	5.428
3800	10.550	81.866	73.238	32.786	- 132.012	- 90.814	5.223
3900	10.654	82.141	73.463	33.846	- 132.797	- 89.721	5.028
4000	10.758	82.412	73.683	34.916	- 133.571	- 88.605	4.841
4100	10.862	82.679	73.899	35.997	- 134.334	- 87.472	4.663
4200	10.966	82.942	74.111	37.089	- 135.083	- 86.320	4.492
4300	11.069	83.201	74.320	38.191	- 135.816	- 85.150	4.328
4400	11.171	83.457	74.524	39.303	- 136.533	- 83.963	4.170
4500	11.272	83.709	74.726	40.425	- 137.233	- 82.761	4.019
4600	11.371	83.958	74.924	41.557	- 137.915	- 81.543	3.874
4700	11.469	84.204	75.119	42.699	- 138.580	- 80.310	3.734
4800	11.564	84.446	75.310	43.851	- 139.227	- 79.062	3.600
4900	11.657	84.685	75.499	45.012	- 139.857	- 77.803	3.470
5000	11.748	84.922	75.685	46.182	- 140.470	- 76.531	3.345
5100	11.836	85.155	75.869	47.361	- 141.066	- 75.248	3.225
5200	11.922	85.386	76.050	48.549	- 141.645	- 73.949	3.108
5300	12.005	85.614	76.228	49.746	- 142.208	- 72.642	2.995
5400	12.085	85.839	76.404	50.950	- 142.756	- 71.325	2.887
5500	12.161	86.061	76.577	52.163	- 143.290	- 69.996	2.781
5600	12.235	86.281	76.749	53.382	- 143.811	- 68.659	2.680
5700	12.306	86.498	76.918	54.610	- 144.318	- 67.313	2.581
5800	12.374	86.713	77.085	55.844	- 144.812	- 65.957	2.485
5900	12.438	86.925	77.250	57.084	- 145.295	- 64.595	2.393
6000	12.500	87.135	77.413	58.331	- 145.765	- 63.223	2.303

Dec. 31, 1972

BARIUM MONOFLUORIDE (BaF) (IDEAL GAS) GFW = 156.3384 BaF

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 58.82 ± 0.05 gibbs/mol

ΔHf°_0 = -76.5 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -77.0 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X $^2\Sigma^+$	0	2	D $^2\Sigma^+$	24156.8	2
A $^2\Pi_{1/2}$	11646.9	2	D' $^2\Sigma^+$	26222.3	2
A $^2\Pi_{3/2}$	12278.2	2	E $^2\Sigma^+$	28139.7	2
B $^2\Sigma^+$	14062.5	2	F $^2\Sigma^+$	29411.3	2
C $^2\Pi$	19998.2	2	G $^2\Sigma^+$	31451.9	2
	20197.2	2	H $^2\Sigma^+$	31582.0	2

ω_e = 468.9 cm^{-1} $\omega_e x_e$ = 1.79 cm^{-1} σ = 1

B_e = 0.2164 cm^{-1} α_e = [0.00112] cm^{-1} r_e = 2.152 Å

Heat of Formation

ΔHf is obtained from a third law analysis of Kp data for three gaseous dissociation equilibria. The Kp data were derived from observations made on the condensed phase systems BaF_2 - B (1) and BaF_2 - Al (2) by the mass spectrometric-Knudsen effusion method. Results of a second and third law analysis of these data are given below. Also included below are results derived from two mass spectrometric studies (2, 3) of the heterogeneous reaction (D), and a value for the heat of dissociation of BaF which was determined from spectrophotometric studies (4, 5) of reaction equilibria in H_2-O_2-N_2 flames.

Investigator	Reaction	Range, K	Points	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(BaF, g) kcal/mol
Hildenbrand (1)	A	1418-1512	8	- 1.0	-6.6±0.5	-3.8±2.2	-78.0±1.5
Hildenbrand (1)	B	1418-1512	8	8.6	3.5±1.1	-3.5±5.7	-77.3±3.6
Ehlert et al. (2)	C	1175-1255	8[a]	26.0	23.0±0.2	-2.5±0.9	-75.6±3.0
Ehlert et al. (2)	D	1175-1255	8	-118.8	-96.4±1.1	18.4±3.6	-74.9±1.7
Zmbov and Margrave (3)	D	1428		-103.5			-71.3±3.0
Gurvich and Ryabova (4, 5)	E			145±6			-83.3±8.0

Reactions:
(A) $Ba(g) + BaF_2(g) \rightarrow 2\ BaF(g)$
(B) $2Ba(g) + BF_3(g) \rightarrow 2\ BaF(g) + BF(g)$
(C) $Ba(g) + AlF(g) \rightarrow BaF(g) + Al(g)$
(D) $2\ BaF(g) \rightarrow Ba(g) + BaF_2(c)$
(E) $BaF(g) \rightarrow Ba(g) + F(g)$

[a] One point rejected due to failure of a statistical test.

Auxiliary ΔHf data (all in kcal/mol) (6): Ba(g), 42.8; BaF_2(g), -192.1; BF_3(g), -271.42; BF(g), -27.7; AlF(g), -63.4; Al(g), 78.0; F(g), 18.86; BaF_2(c), -288.9.

It is believed that the Kp data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert et al. (2) determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. Further support for this belief is provided by the large positive drift that arises in the third law analysis of these Kp's. Also, it is felt that the results obtained from the flame-spectrophotometric studies (4, 5) are somewhat more uncertain than those derived from the Kp data for the three homogeneous reactions. Therefore, we choose to adopt a median value ΔHf°_{298}(BaF, g) = -77.0 ± 2.0 kcal/mol of the first three results. The adopted value corresponds to a dissociation energy of D°_0(Ba-F) = 137.9 kcal/mol (5.98 eV).

Gaydon (7) has reported a spectroscopic value for D°_0 of 3.8 eV which is considerably lower than the adopted thermochemical value. The spectroscopic value is based on a linear Birge-Sponer extrapolation of the thirteen known vibrational levels for the ground state ($^2\Sigma^+$). However, Gaydon (7) and later Hildenbrand (8) have shown that the linear extrapolation generally underestimates D°_0 when the bonding in the molecule is partially ionic. Correcting D°_0(LBX) for the ionic character of BaF with the ionicity parameter suggested by Hildenbrand (8), we obtain D°_0(Ba-F) = 6.9 eV which is somewhat high. Other values for D°_0 that have been reported are 5.94 (1) and 5.68 eV (9). Both of these values were calculated from the Rittner ionic model (10) for polarizable ions and show remarkably good agreement with the adopted value.

Heat Capacity and Entropy

The spectroscopic data, except for α_e, are given by Rosen (11) for ^{138}BaF. α_e is calculated from the Morse potential function. Corrections to these data to account for the natural isotopic abundances of barium were found to be negligible. The electronic states and levels are also taken from the compilation of Rosen (11).

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BaF

Barium Monofluoride Unipositive Ion (BaF^+)

(Ideal Gas) GFW = 156.3378

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.144	57.085	57.085	.000	35.900	29.067	-21.307
300	8.151	57.135	57.085	.015	35.905	29.025	-21.145
400	8.455	59.526	57.409	.847	36.127	26.694	-14.585
500	8.629	61.433	58.029	1.702	36.163	24.327	-10.633
600	8.737	63.016	58.732	2.570	36.008	21.977	-8.005
700	8.809	64.369	59.443	3.448	36.044	19.632	-6.129
800	8.861	65.549	60.134	4.332	35.958	17.295	-4.725
900	8.900	66.595	60.795	5.220	35.972	14.962	-3.633
1000	8.934	67.534	61.423	6.112	35.984	12.627	-2.760
1100	8.967	68.388	62.018	7.007	33.996	10.487	-2.083
1200	9.005	69.169	62.582	7.905	33.952	8.351	-1.521
1300	9.053	69.892	63.117	8.808	33.935	6.219	-1.046
1400	9.115	70.565	63.625	9.716	33.938	4.087	-.638
1500	9.197	71.197	64.109	10.632	33.961	1.954	-.285
1600	9.302	71.793	64.571	11.556	33.998	-.182	.025
1700	9.431	72.361	65.012	12.493	34.051	-2.319	.298
1800	9.587	72.904	65.436	13.444	34.115	-4.461	.542
1900	9.769	73.428	65.843	14.411	34.187	-6.605	.760
2000	9.976	73.934	66.235	15.398	34.266	-8.754	.957
2100	10.205	74.426	66.613	16.407	34.348	-10.908	1.135
2200	10.454	74.906	66.979	17.440	1.078	-11.839	1.176
2300	10.718	75.377	67.334	18.498	1.355	-12.431	1.181
2400	10.992	75.839	67.679	19.584	1.600	-13.036	1.187
2500	11.273	76.293	68.014	20.697	1.816	-13.650	1.193
2600	11.556	76.741	68.341	21.838	2.001	-14.274	1.200
2700	11.835	77.182	68.661	23.008	2.160	-14.901	1.206
2800	12.107	77.618	68.973	24.205	2.292	-15.537	1.213
2900	12.368	78.047	69.278	25.429	2.402	-16.174	1.219
3000	12.614	78.470	69.578	26.678	2.490	-16.817	1.225
3100	12.842	78.888	69.871	27.951	2.561	-17.463	1.231
3200	13.051	79.299	70.159	29.246	2.620	-18.110	1.237
3300	13.238	79.703	70.443	30.561	2.669	-18.757	1.242
3400	13.403	80.101	70.721	31.893	2.709	-19.408	1.248
3500	13.545	80.492	70.994	33.240	2.746	-20.057	1.252
3600	13.664	80.875	71.264	34.601	2.781	-20.709	1.257
3700	13.761	81.251	71.528	35.973	2.816	-21.363	1.262
3800	13.836	81.619	71.789	37.353	2.852	-22.016	1.266
3900	13.891	81.979	72.046	38.739	2.891	-22.672	1.271
4000	13.926	82.331	72.299	40.130	2.933	-23.328	1.275
4100	13.943	82.675	72.547	41.524	2.980	-23.985	1.279
4200	13.945	83.011	72.793	42.918	3.031	-24.643	1.282
4300	13.931	83.339	73.034	44.312	3.087	-25.302	1.286
4400	13.905	83.659	73.272	45.704	3.146	-25.962	1.290
4500	13.867	83.971	73.506	47.093	3.209	-26.627	1.293
4600	13.819	84.276	73.737	48.477	3.276	-27.290	1.297
4700	13.762	84.572	73.964	49.856	3.345	-27.955	1.300
4800	13.699	84.861	74.188	51.229	3.416	-28.620	1.303
4900	13.629	85.143	74.409	52.596	3.489	-29.288	1.306
5000	13.554	85.418	74.627	53.955	3.561	-29.959	1.310
5100	13.476	85.685	74.841	55.306	3.634	-30.633	1.313
5200	13.394	85.946	75.052	56.650	3.708	-31.303	1.316
5300	13.311	86.201	75.260	57.985	3.780	-31.976	1.319
5400	13.226	86.449	75.465	59.312	3.852	-32.653	1.322
5500	13.140	86.690	75.667	60.630	3.920	-33.329	1.324
5600	13.054	86.926	75.866	61.940	3.986	-34.006	1.327
5700	12.968	87.157	76.062	63.241	4.050	-34.686	1.330
5800	12.883	87.381	76.255	64.534	4.111	-35.365	1.333
5900	12.799	87.601	76.445	65.818	4.169	-36.048	1.335
6000	12.716	87.815	76.633	67.093	4.223	-36.730	1.338

Dec. 31, 1972

BARIUM MONOFLUORIDE UNIPOSITIVE ION (BaF^+) (IDEAL GAS) GFW = 156.3378 BaF^+

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

$S^\circ_{298.15}$ = [57.1 ± 2] gibbs/mol

ΔHf°_0 = 35.0 ± 10.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 35.9 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X\ ^1\Sigma^+$	0	1
$a\ ^3\Pi$	[9000]	6
$A'\ ^1\Pi$	[11000]	2
$B'\ ^1\Delta$	[13000]	2
$b\ ^3\Sigma^-$	[15000]	3
$A\ ^1\Sigma^+$	[16000]	1
$B\ ^1\Sigma^+$	[30000]	1

ω_e = [540] cm^{-1} $\omega_e x_e$ = [2.06] cm^{-1} σ = 1

B_e = [0.2371] cm^{-1} α_e = [0.00122] cm^{-1} r_e = [2.064] Å

Heat of Formation

The appearance potential (AP) of BaF^+ from BaF(g) has been measured mass spectrometrically as 4.9 eV (1) and 4.8 ± 0.3 eV (2). This latter value has been confirmed by Zmbov and Margrave (3). Combining these results with ΔHf°_0(BaF, g) = -76.5 ± 2.0 kcal/mol (4), we obtain $\Delta Hf^\circ_0(BaF^+$, g) equal to 36.5 and 34.2 ± 9.0 kcal/mol.

Hildenbrand (2) also reported an AP for BaF^+ from BaF_2(g) as 13.5 ± 1.0 eV. Green et al. (5) obtained an ionization efficiency curve for BaF^+ which extrapolates (high-energy portion) to 12.9 eV at zero ion current. Assuming the process to be $e^- + BaF_2(g) \rightarrow BaF^+(g) + F(g) + 2e^-$, we obtain $\Delta Hf^\circ_0(BaF^+$, g) values of 101.3 ± 25 and 87.5 kcal/mol by combining the above results with $\Delta Hf^\circ_0(BaF_2$, g) = -191.6 ± 1.5 kcal/mol and ΔHf°_0(F, g) = 18.36 ± 0.4 kcal/mol (4).

The two lower values for ΔHf°_0 are preferred here, since the dissociative ionization of BaF_2(g) most likely involved unknown kinetic energy factors. We choose to adopt $\Delta Hf^\circ_0(BaF^+$, g) = 35.0 ± 10.0 kcal/mol which gives $\Delta Hf^\circ_{298}(BaF^+$, g) = 35.9 ± 10.0 kcal/mol. The adopted heat of formation corresponds to an ionization potential for BaF(g) of 4.83 eV.

Heat Capacity and Entropy

The dissociation energy of $BaF^+(D^\circ_0$ = 145.4 kcal/mol) is slightly greater than that for BaF(D°_0 = 137.9 kcal/mol (4)) which implies somewhat stronger bonding in the ion. Thus, one would expect the internuclear distance (r_e) for the ground state of BaF^+ to be less than that for BaF. Barrow and Beale (6) postulated from a rotational analysis of the $F^2\Sigma^+ - X^2\Sigma^+$ band system of SrF a r_e for SrF^+ which was some 4% lower than that for SrF. We assume a similar decrease in r_e for BaF^+ and obtain r_e = 2.064 Å from r_e(BaF) = 2.152 Å (4). ω_e is calculated from Badger's rule (7) which can be written in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e - d_{ij})^3$. Molecular data for CsF (4), BaF (4), and BaO (8) were used to determine the constant d_{ij}. The product $x_e\mu^{1/2}$ has been shown to be constant within a group of similar molecules by Barrow and Caunt (9). Since $\mu^{1/2}(BaF^+) \cong \mu^{1/2}(BaF)$, we assume $x_e(BaF^+) = x_e(BaF)$ and obtain $\omega_e x_e$ equal to 2.06 cm^{-1} with our estimated value for ω_e. α_e is obtained from the other constants assuming a Morse potential function. The moment of inertia is 11.806 x 10^{-39} g cm^2.

BaF^+ has eight valence electrons; thus, the ground state configuration ($^1\Sigma^+$) and electronic levels for the A and B states are estimated from those for the isoelectronic molecule BaS (10). By analogy with the gaseous alkaline earth oxides (11), C_2 (4), and BeS (12), low-lying triplet states are to be expected. The two estimated triplet levels are based on those which have been observed directly in C_2 (4), BeS (12), and indirectly (through perturbative effects) in BaS (10). Also included are a $^1\Pi$ state at 11,000 cm^{-1} and a $^1\Delta$ state at 13,000 cm^{-1}. These levels are also estimated by analogy with those for C_2(4) and BeS (12). It is believed that our adopted electronic entropies for BaF^+ are most likely minimal values. Probable upper limits for the electronic contributions can be established by decreasing the triplet levels to 1000 cm^{-1} ($^3\Pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy by 3.8 eu and 2.1 eu at 2000 K and 4000 K, respectively. The enthalpy at 0 K is -2.20 kcal/mol.

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Barium Difluoride (BaF_2)

(Crystal) GFW = 175.3368

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.453	-288.591	-288.591	INFINITE
100	10.492	7.145	37.124	-2.998	-289.237	-285.067	623.014
200	15.726	16.435	24.576	-1.628	-289.175	-280.885	306.937
298	17.257	23.039	23.039	.000	-288.900	-276.873	202.953
300	17.281	23.146	23.040	.032	-288.894	-276.798	201.647
400	18.150	28.243	23.729	1.806	-288.612	-272.811	149.057
500	18.750	32.361	25.057	3.652	-288.485	-268.680	117.527
600	19.200	35.318	26.370	5.549	-288.525	-264.953	96.509
700	19.690	38.613	28.109	7.493	-288.344	-261.040	81.500
800	20.300	41.479	29.617	9.490	-288.247	-257.145	70.249
900	21.200	43.917	31.072	11.561	-287.985	-253.271	61.503
1000	22.600	46.216	32.472	13.744	-287.621	-249.433	54.514
1100	24.900	48.468	33.824	16.108	-289.083	-245.443	48.765
1200	31.200	50.837	35.141	18.835	-288.243	-241.507	43.984
1300	32.900	53.820	36.464	22.563	-286.384	-237.686	39.959
1400	27.250	56.000	37.785	25.501	-285.301	-233.985	36.527
1500	25.730	58.241	39.066	28.761	-283.886	-230.355	33.563
1600	25.730	59.901	40.317	31.334	-283.154	-226.812	30.981
1700	25.730	61.461	41.516	33.907	-282.421	-223.312	28.709
1800	25.730	62.932	42.665	36.480	-281.693	-219.857	26.694
1900	25.730	64.323	43.769	39.053	-280.974	-216.441	24.896
2000	25.730	65.643	44.830	41.626	-280.270	-213.062	23.282

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BARIUM DIFLUORIDE (BaF_2) (CRYSTAL) GFW = 175.3368 BaF_2

$S^\circ_{298.15}$ = 23.04 ± 0.10 gibbs/mol
Tt = 1240 K (α - β)
Tt = 1480 K (β - γ)
Tm = 1641 K

ΔHf°_0 = -288.6 ± 1.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -288.9 ± 1.0 kcal/mol
ΔHt° = 0.0 kcal/mol
ΔHt° = 0.639 ± 0.200 kcal/mol
ΔHm° = 5.583 ± 0.150 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 96.83 ± 0.50 kcal/mol

Heat of Formation

Guntz (1) measured the heat of neutralization of $Ba(OH)_2(aq)$ with HF(aq) as ΔH = -34.8 kcal/mol at 284 K. We estimate ΔCp = 106 gibbs/mol (2) for $Ba(OH)_2 \cdot 660\ H_2O + 2(HF \cdot 110\ H_2O) \rightarrow BaF_2(c) + 2\ H_2O(\ell)$ which gives ΔHr_{298} = -33.4 kcal/mol. This value leads to $\Delta Hf^\circ_{298}(BaF_2, c)$ = -288.3 kcal/mol when combined with $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 (3), $\Delta Hf^\circ_{298}(Ba(OH)_2 \cdot 660\ H_2O)$ = -237.9 (4), and $\Delta Hf^\circ_{298}(HF \cdot 110\ H_2O)$ = -76.81 kcal/mol (5). Petersen (6) investigated the same reaction but with $HF \cdot 200\ H_2O$ and found that 16% of the BaF_2 remained dissolved. After correcting for incomplete precipitation his final result was ΔH_{292} = -33.92 kcal/mol which gives $\Delta Hf^\circ_{298}(BaF_2, c)$ = -288.2 kcal/mol.

In the same study, Petersen (6) measured the heat of precipitation of BaF_2 from $BaCl_2(aq)$ with AgF(aq) as ΔH_{292} = -35.02 kcal/mol. We estimate ΔCp = 108 gibbs/mol (2) for $2(AgF \cdot 200\ H_2O) + BaCl_2 \cdot 400\ H_2O \rightarrow BaF_2(c) + 2AgCl(c)$ which gives ΔH_{298} = -34.4 kcal/mol. Combining this value with $\Delta Hf^\circ_{298}(AgCl, c)$ = -30.37 (7), $\Delta Hf^\circ_{298}(AgF \cdot 200\ H_2O)$ = -53.398 (7), and $\Delta Hf^\circ_{298}(BaCl_2 \cdot 400\ H_2O)$ = -207.938 kcal/mol (4), we obtain $\Delta Hf^\circ_{298}(BaF_2, c)$ = -288.4 kcal/mol. Petersen (6) also reported the heat of solution of BaF_2 as ΔH°_{soln} = 1.88 kcal/mol. From this result, we obtain $\Delta Hf^\circ_{298}(BaF_2, c)$ = -290.3 kcal/mol.

Stephen and Stephen (9) have selected a "best" value for the solubility of BaF_2 of 1.614 g/ℓ at 298 K which corresponds to $K_{sp} = 3.1196 \times 10^{-6}$. Using $\Delta Gf^\circ_{298}(Ba^{+2}, \infty\ aq)$ = -134.02 (4) and $\Delta Gf^\circ_{298}(F^-, \infty\ aq)$ = -66.96 kcal/mol (5), we calculate $\Delta Gf^\circ_{298}(BaF_2, c)$ = -275.45 kcal/mol. Based on the adopted functions, this value gives $\Delta Hf^\circ_{298}(BaF_2, c)$ = -287.5 kcal/mol.

Two equilibrium studies (10, 11) have also been reported. Second and third law analyses of these data are given below.

Investigator	Reaction	Temp Range, K	No. of Points	ΔHr_{298}, kcal/mol 2nd Law	ΔHr_{298}, kcal/mol 3rd Law	Drift eu	$\Delta Hf^\circ_{298}(BaF_2, c)$ kcal/mol
Domange (10)	A	1173-1373	3	41.0	62.5±3.4	16.9±1.0	-267.3
Hood and Woyski (11)	B	477-1033	9	5.9	5.8±1.0	-0.1±0.1	-279.8

Reaction: (A) $BaF_2(c) + H_2O(g) \rightarrow 2\ HF(g) + BaO(c)$ (B) $HF(g) + 0.5\ BaCl_2(c) \rightarrow HCl(g) + 0.5\ BaF_2(c)$

The large discrepancy which arises in the ΔHf values obtained from the equilibrium and calorimetric results is not well understood. Domange (10) has measured similar equilibria for CoF_2, MgF_2, and CaF_2 which are very consistent with JANAF heats of formation. Very recently, Finch et al. (12) attempted to determine the heat of precipitation of BaF_2 from $BaCl_2(aq)$ by dissolving a slight excess of NaF. X-ray diffraction studies of the precipitate showed the formation of BaClF and Ba_2ClF_3 along with BaF_2. We believe the equilibrium results of Hood and Woyski (11) may have been influenced by the formation of mixed halides. Also, it seems quite likely that the calorimetric results of Petersen (6) on the precipitation of BaF_2 from $BaCl_2(aq)$ with AgF(aq) would be similarly influenced. We choose to adopt $\Delta Hf^\circ_{298}(BaF_2, c)$ = -288.9 ± 1.0 kcal/mol which is a weighted value of the calorimetric results of Guntz (1) and Petersen (6) on the heat of neutralization of $Ba(OH)_2(aq)$, the heat of solution of $BaF_2(c)$ (6) and the K_{sp} value obtained from the solubility data of Stephen and Stephen (9). Barany et al. (8) determined the heat of solution of BaO(c) in HF(aq), which contained some dissolved silica, as ΔH = -73.04 kcal/mol. We assume this value refers to the reaction $BaO(c) + 2\ HF \cdot 4.41\ H_2O \rightarrow BaF_2(c) + H_2O(\ell)$, and we calculate $\Delta Hf^\circ_{298}(BaF_2, c)$ = -290.2 ± 2.0 kcal/mol with $\Delta Hf^\circ_{298}(BaO, c)$ = -132.3 kcal/mol (5). These results substantiate our adopted ΔHf° value.

Heat Capacity and Entropy

Cp below 298 K is based on the low temperature (14-300 K) heat capacities of Pitzer et al. (13). These data show an unusual leveling off of Cp above 274 K, and values in the range 274-300 K are obtained by graphical extrapolation of their low temperature data. $S^\circ_{298.15}$ is based on the adopted Cp's with S°_{15} = 0.09 eu.

Relative enthalpies have been reported by Efremova and Matizen (14) (757-2053 K) and Krestovnikov and Karetnikov (15) (288-1273 K). The enthalpy data of Efremova and Matizen (14) indicate the existence of a second order phase transition at 1240 K. We adopt their smoothed Cp data in the temperature range 800-1480 K. Cp's below 800 K are estimated graphically by comparison with those for $BaCl_2$, CaF_2, and SrF_2 (5). Cp data for $BaF_2(\gamma)$ are based on a JANAF curve fit of their relative enthalpies (1482-1596 K). The rapid rise in the enthalpy near the melting point (1641 K) is assumed to be due to premelting, and these points were not used in the fit. The maximum deviation of our adopted functions from those used in the fit is 0.5%. Kelley (16) has analyzed the enthalpy data of Krestovnikov and Karetnikov (15). His smoothed enthalpies are consistently 2-3% higher than those adopted. No second order phone transition was observed. These data are judged to be less reliable and are not used in our evaluation.

Transition Data

The transition temperatures are those reported by Efremova and Matizen (14). We assume the transition at 1240 K is of the second order type, since no discontinuity appears in their enthalpy data at this temperature. The heat of the β-γ transition is calculated as the difference between the adopted enthalpies for these two phases at 1480 K.

Melting Data

See $BaF_2(\ell)$ table for details.

Sublimination Data

See $BaF_2(g)$ table for details.

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BaF_2

Barium Difluoride (BaF_2)

(Liquid) GFW = 175.3368

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	17.257	28.980	28.980	- .000	- 279.946	- 269.690	197.688
300	17.281	29.087	28.981	.032	- 279.940	- 269.626	196.422
400	18.150	34.184	29.670	1.806	- 279.658	- 266.233	145.463
500	18.750	38.301	30.997	3.652	- 279.531	- 262.896	114.912
600	19.200	41.759	32.511	5.549	- 279.571	- 259.563	94.546
700	19.690	44.754	34.050	7.493	- 279.390	- 256.245	80.003
800	20.300	47.420	35.558	9.490	- 279.293	- 252.944	69.101
900	21.200	49.858	37.013	11.561	- 279.031	- 249.664	60.627
1000	22.600	52.156	38.413	13.743	- 278.668	- 246.420	53.855
1100	23.859	54.411	39.765	16.111	- 280.126	- 243.023	48.284
1200	23.859	56.487	41.073	18.497	- 279.627	- 239.672	43.650
1300	23.859	58.397	42.333	20.882	- 279.111	- 236.362	39.736
1400	23.859	60.165	43.545	23.268	- 278.580	- 233.095	36.388
1500	23.859	61.811	44.708	25.654	- 278.039	- 229.864	33.491
1600	23.859	63.351	45.326	28.040	- 277.494	- 226.671	30.962
1700	23.859	64.797	46.900	30.426	- 276.948	- 223.510	28.734
1800	23.859	66.161	47.932	32.812	- 276.407	- 220.384	26.758
1900	23.859	67.451	48.926	35.198	- 275.875	- 217.285	24.994
2000	23.859	68.675	49.883	37.584	- 275.358	- 214.215	23.408
2100	23.859	69.839	50.806	39.970	- 274.860	- 211.171	21.977
2200	23.859	70.949	51.696	42.356	- 307.740	- 206.923	20.556
2300	23.859	72.009	52.557	44.741	- 307.101	- 202.354	19.228
2400	23.859	73.025	53.388	47.127	- 306.521	- 197.813	18.013
2500	23.859	73.999	54.193	49.513	- 306.000	- 193.295	16.898
2600	23.859	74.935	54.973	51.899	- 305.538	- 188.796	15.870
2700	23.859	75.835	55.729	54.285	- 305.132	- 184.312	14.919
2800	23.859	76.703	56.463	56.671	- 304.782	- 179.846	14.038
2900	23.859	77.540	57.175	59.057	- 304.482	- 175.387	13.217
3000	23.859	78.349	57.868	61.443	- 304.230	- 170.942	12.453
3100	23.859	79.131	58.541	63.829	- 304.019	- 166.503	11.738
3200	23.859	79.889	59.196	66.215	- 303.845	- 162.070	11.069
3300	23.859	80.623	59.835	68.600	- 303.702	- 157.641	10.440
3400	23.859	81.335	60.457	70.986	- 303.585	- 153.217	9.849
3500	23.859	82.027	61.063	73.372	- 303.489	- 148.794	9.291

Dec. 31, 1972

BARIUM DIFLUORIDE (BaF_2) (LIQUID) GFW = 175.3368 BaF_2

$S^\circ_{298.15}$ = 28.980 gibbs/mol

Tm = 1641 K

Tb = 2545 K

$\Delta Hf^\circ_{298.15}$ = −279.946 kcal/mol

ΔHm° = 5.583 ± 0.150 kcal/mol

ΔHr° = 68.2 kcal/mol

Heat of Formation

ΔHf° is obtained from that of the crystal by addition of ΔHm° and the difference between ($H^\circ_{1641}-H^\circ_{298}$) for the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1100 K below which Cp follows that of the crystal. Cp is assumed constant in the temperature range 1100-3500 K and is based on a JANAF curve fit of the relative enthalpies of Efremova and Matizen (1) for the liquid (1641-1900 K). Some scatter was observed in these data at the higher temperatures, and these points were not included in the fit. The maximum deviation of the observed enthalpies which were used in the fit from those adopted is 0.29%.

Melting Data

Tm is the value selected by Efremova and Matizen (1) from their relative enthalpy data. These data show premelting starting near 1620 K and complete melting occurring at 1646 K. Other values for Tm that have been reported are 1627 (2), 1628 (3), 1627 (4), 1617 (5), and 1593 K (6). The selected Tm was obtained from measurements made on samples of BaF_2 contained in steel and molybdenum capsules. There were no indications of any reaction between the sample and container. Three of the lower values given above were determined from measurements on BaF_2 contained in either graphite (3, 4) or tantalum (2) crucibles. It has now been established by mass spectroscopy (7, 8) that the alkaline earth difluorides can be appreciably reduced by these materials near 1400 K. Thus, we prefer the higher value.

ΔHm° is obtained as the difference in the adopted functions for the liquid and crystal at Tm.

Vaporization Data

Tb is the calculated temperature at which ΔGr° = 0 for $BaF_2(\ell) \rightarrow BaF_2(g)$. ΔHv° is obtained from the difference in ΔHf°_{Tb} for the gas and liquid. Ruff and Le Boucher (9) derived Tb = 2533 K and ΔHv = 69.8 kcal/mol from an analysis of their vapor pressures (1960-2206 K).

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BaF_2

BARIUM DIFLUORIDE (BaF_2) (IDEAL GAS) GFW = 175.3368 BaF_2

Point Group = C_{2v}

$S^\circ_{298.15}$ = 71.98 ± 0.50 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -191.6 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -192.1 ± 1.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
413 (1)
[64] (1)
390 (1)

Bond Distance: Ba-F = 2.32 ± 0.03 Å

Bond Angle: F-Ba-F = [95]°

$\sigma = 2$

Product of Moments of Inertia: $I_AI_BI_C$ = $[6.8579 \times 10^{-114}]\ g^3cm^6$

Heat of Formation

$\Delta Hf^\circ_{298}(BaF_2, g)$ = -192.1 ± 1.5 kcal/mol is obtained from that of the crystal by addition of ΔHs° = 96.83 ± 0.50 kcal/mol. The selected ΔHs° is based on an analysis of six sets of vapor pressure data (1 - 5). The results of our analysis are given below.

Investigator	Method	Temp. Range, K	No. of Points	ΔHs°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} kcal/mol
Ruff and Le Boucher (1)	Dynamic B.P.	2061-2206	9	97.0[a]	86.79±0.88[a]	-4.9±0.8	-193.2±2.0
Green et al. (2)	Knudsen-Mass Spec.	1232-1503	20	96.5	98.17±0.45	1.2±0.6	-190.7±1.5
Bautista and Margrave (3)	Langmuir	1130-1250	10[b]	96.4	97.68±0.19	1.1±0.9	-191.2±1.2
Hart and Searcy (4)	Torsion-Effusion	1261-1548	49[c]	93.2	96.12±0.68	2.1±0.7	-192.8±1.7
Hart and Searcy (4)	Torsion-Langmuir	1315-1492	25[d]	93.7	96.47±0.38	2.0±0.8	-192.4±1.4
Hildenbrand et al. (5)	Torsion-Effusion	1265-1550	Equation	94.2	94.74±0.13	0.4	-194.2±1.1

[a] ΔH°_{298}(vaporization)

2[b], 4[c], and 3[d] points rejected due to failure of a statistical test.

A weighted value of these six results is adopted.

Heat Capacity and Entropy

The bond length is taken from the high-temperature electron diffraction studies of Akishin and Spiridonov (6). Although Akishin and Spiridonov (6) interpreted their results in terms of a linear configuration for BaF_2, recent electric-deflection experiments (7) and matrix isolation infrared studies (8, 9) clearly indicate that BaF_2 is bent. Calder et al. (8) estimated the bond angle as 100° from the changes in the bond angles with mass of the central atom for other alkaline earth difluorides. Baikov (10) estimated the angle as 115°. We prefer a slightly lower value (95°) than these, since these are indications that other heavy metal halides have bond angles below 100°. For example, bond angles for PbF_2 and $PbCl_2$ have been reported as 90° (11) and 96 ± 3° (12), respectively.

The symmetric (ν_1) and antisymmetric (ν_3) stretching frequencies are those observed by Calder et al. (8) in their study of infrared spectra of BaF_2 trapped in a krypton matrix. Other matrix frequencies in excellent agreement with the adopted ones have been reported by Snelson (9). Further confirmation of the adopted ν_3 is provided by observations of Baikov (13). He reported $\nu_3 = 415 \pm 7\ cm^{-1}$ which was observed in the infrared spectra of BaF_2 vapor at 1950 K. The bending frequency (ν_2) is that estimated by Calder et al. (8). This value is considerably less than that observed by Baikov (10) ($\nu_2 = 100\ cm^{-1}$). However, only the high frequency portion of this rather broad band was recorded. We have used our adopted frequencies in a valence bond calculation with the result $k/(k\delta/\ell^2) = 11.8$. This ratio of the stretching to bending force constants appears quite reasonable in comparison with those for other alkaline earth difluorides (14). Also, our adopted frequencies give thermodynamic functions which show good compatibility with the vapor pressure data (see Heat of Formation section).

The individual moments of inertia are: $I_A = 30.600 \times 10^{-39}$, $I_B = 18.459 \times 10^{-39}$, and $I_C = 12.141 \times 10^{-39}\ g\ cm^2$.

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BaF_2

Barium Difluoride (BaF_2)

(Ideal Gas) GFW = 175.3368

T, °K	Cp° gibbs/mol	S° gibbs/mol	-(G°-H°298)/T gibbs/mol	H°-H°298 kcal/mol	ΔHf° kcal/mol	ΔGf° kcal/mol	Log Kp
0	.000	.000	INFINITE	- 3.262	- 191.600	- 191.600	INFINITE
100	10.217	59.360	82.750	- 2.339	- 191.778	- 192.830	421.429
200	11.971	67.017	73.137	- 1.224	- 191.971	- 193.797	211.771
298	12.854	71.985	71.985	.000	- 192.100	- 194.666	142.694
300	12.864	72.064	71.985	.024	- 192.102	- 194.681	141.825
400	13.277	75.829	72.495	1.333	- 192.285	- 195.517	106.826
500	13.490	78.817	73.471	2.673	- 192.664	- 196.287	85.797
600	13.613	81.288	74.574	4.028	- 193.246	- 196.955	71.741
700	13.689	83.392	75.687	5.394	- 193.643	- 197.545	61.676
800	13.740	85.224	76.767	6.765	- 194.172	- 198.065	54.109
900	13.775	86.844	77.799	8.141	- 194.605	- 198.525	48.208
1000	13.800	88.297	78.777	9.520	- 195.045	- 198.938	43.478
1100	13.819	89.613	79.703	10.901	- 197.490	- 199.110	39.559
1200	13.833	90.816	80.580	12.284	- 197.994	- 199.234	36.285
1300	13.845	91.924	81.410	13.667	- 198.480	- 199.317	33.508
1400	13.853	92.950	82.199	15.052	- 198.950	- 199.364	31.122
1500	13.861	93.906	82.948	16.438	- 199.409	- 199.377	29.049
1600	13.867	94.801	83.661	17.824	- 199.864	- 199.361	27.231
1700	13.872	95.642	84.341	19.211	- 200.317	- 199.315	25.624
1800	13.876	96.435	84.991	20.599	- 200.774	- 199.244	24.192
1900	13.879	97.185	85.613	21.987	- 201.240	- 199.146	22.907
2000	13.882	97.897	86.210	23.375	- 201.721	- 199.023	21.748
2100	13.885	98.575	86.783	24.763	- 202.221	- 198.877	20.697
2200	13.887	99.221	87.333	26.152	- 236.098	- 197.479	19.618
2300	13.889	99.838	87.864	27.540	- 236.456	- 195.715	18.597
2400	13.891	100.429	88.375	28.929	- 236.873	- 193.936	17.660
2500	13.892	100.996	88.869	30.319	- 237.348	- 192.137	16.797
2600	13.894	101.541	89.346	31.708	- 237.883	- 190.318	15.998
2700	13.895	102.065	89.807	33.097	- 238.474	- 188.476	15.256
2800	13.896	102.571	90.254	34.487	- 239.120	- 186.614	14.566
2900	13.897	103.058	90.687	35.876	- 239.817	- 184.725	13.921
3000	13.898	103.530	91.107	37.266	- 240.561	- 182.815	13.318
3100	13.899	103.985	91.516	38.656	- 241.346	- 180.878	12.752
3200	13.899	104.427	91.912	40.046	- 242.168	- 178.914	12.219
3300	13.900	104.854	92.298	41.436	- 243.020	- 176.924	11.717
3400	13.900	105.269	92.673	42.826	- 243.899	- 174.908	11.243
3500	13.901	105.672	93.039	44.216	- 244.799	- 172.864	10.794
3600	13.902	106.064	93.395	45.606	- 245.713	- 170.794	10.369
3700	13.902	106.445	93.743	46.996	- 246.641	- 168.702	9.965
3800	13.902	106.815	94.082	48.386	- 247.577	- 166.582	9.581
3900	13.903	107.177	94.413	49.777	- 248.517	- 164.441	9.215
4000	13.903	107.529	94.737	51.167	- 249.459	- 162.271	8.866
4100	13.904	107.872	95.053	52.557	- 250.401	- 160.081	8.533
4200	13.904	108.207	95.362	53.948	- 251.340	- 157.866	8.215
4300	13.904	108.534	95.665	55.338	- 252.275	- 155.628	7.910
4400	13.904	108.854	95.961	56.729	- 253.205	- 153.370	7.618
4500	13.905	109.166	96.251	58.119	- 254.130	- 151.092	7.338
4600	13.905	109.472	96.535	59.509	- 255.048	- 148.792	7.069
4700	13.905	109.771	96.813	60.900	- 255.959	- 146.472	6.811
4800	13.905	110.064	97.086	62.290	- 256.863	- 144.131	6.562
4900	13.905	110.350	97.354	63.681	- 257.760	- 141.773	6.323
5000	13.906	110.631	97.617	65.072	- 258.650	- 139.398	6.093
5100	13.906	110.907	97.875	66.462	- 259.534	- 137.008	5.871
5200	13.906	111.177	98.128	67.853	- 260.410	- 134.553	5.657
5300	13.906	111.442	98.377	69.243	- 261.281	- 132.164	5.450
5400	13.906	111.701	98.621	70.634	- 262.145	- 129.724	5.250
5500	13.906	111.957	98.861	72.025	- 263.003	- 127.261	5.057
5600	13.907	112.207	99.097	73.415	- 263.858	- 124.765	4.870
5700	13.907	112.453	99.329	74.806	- 264.707	- 122.294	4.689
5800	13.907	112.695	99.558	76.197	- 265.550	- 119.788	4.514
5900	13.907	112.933	99.783	77.587	- 266.391	- 117.271	4.344
6000	13.907	113.167	100.304	78.978	- 267.226	- 114.735	4.179

Dec. 31, 1972

Barium Monoiodide (BaI) BaI

(Ideal Gas) GFW = 264.2445

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.481	- 9.390	- 9.390	INFINITE
100	8.322	57.107	74.408	- 1.730	- 9.410	- 13.577	29.672
200	8.783	63.061	67.404	- .868	- 9.745	- 17.619	19.253
298	8.896	66.593	66.593	.000	- 10.138	- 21.403	15.689
300	8.897	66.648	66.593	.016	- 10.146	- 21.472	15.642
400	8.948	69.215	66.943	.909	- 12.561	- 25.111	13.720
500	8.979	71.215	67.604	1.805	- 18.338	- 27.694	12.105
600	9.002	72.854	68.347	2.705	- 18.992	- 29.502	10.746
700	9.022	74.244	69.093	3.606	- 19.453	- 31.220	9.747
800	9.039	75.449	69.813	4.509	- 20.034	- 32.859	8.977
900	9.055	76.515	70.500	5.413	- 20.515	- 34.433	8.361
1000	9.071	77.470	71.150	6.320	- 20.995	- 35.954	7.858
1100	9.086	78.335	71.765	7.228	- 23.474	- 37.231	7.397
1200	9.100	79.126	72.346	8.137	- 24.010	- 38.457	7.004
1300	9.115	79.855	72.896	9.048	- 24.519	- 39.640	6.664
1400	9.129	80.531	73.417	9.960	- 25.011	- 40.785	6.367
1500	9.143	81.162	73.913	10.873	- 25.488	- 41.896	6.104
1600	9.157	81.752	74.384	11.789	- 25.956	- 42.974	5.870
1700	9.172	82.308	74.834	12.705	- 26.420	- 44.023	5.660
1800	9.186	82.832	75.264	13.623	- 26.883	- 45.045	5.469
1900	9.200	83.329	75.676	14.542	- 27.353	- 46.041	5.296
2000	9.214	83.802	76.070	15.463	- 27.835	- 47.014	5.137
2100	9.229	84.252	76.449	16.385	- 28.331	- 47.960	4.991
2200	9.245	84.681	76.814	17.309	- 62.202	- 47.657	4.734
2300	9.260	85.093	77.165	18.234	- 62.550	- 46.987	4.465
2400	9.277	85.487	77.503	19.161	- 62.953	- 46.302	4.216
2500	9.295	85.866	77.830	20.089	- 63.412	- 45.599	3.986
2600	9.313	86.231	78.146	21.020	- 63.927	- 44.877	3.772
2700	9.333	86.583	78.452	21.952	- 64.494	- 44.133	3.572
2800	9.355	86.923	78.749	22.886	- 65.115	- 43.368	3.385
2900	9.378	87.251	79.036	23.823	- 65.780	- 42.579	3.209
3000	9.402	87.570	79.316	24.762	- 66.489	- 41.768	3.043
3100	9.429	87.878	79.587	25.704	- 67.236	- 40.931	2.886
3200	9.457	88.178	79.851	26.648	- 68.015	- 40.071	2.737
3300	9.487	88.470	80.108	27.595	- 68.819	- 39.184	2.595
3400	9.520	88.753	80.358	28.545	- 69.647	- 38.275	2.460
3500	9.555	89.030	80.601	29.499	- 70.489	- 37.339	2.332
3600	9.591	89.300	80.839	30.456	- 71.342	- 36.380	2.209
3700	9.630	89.563	81.072	31.417	- 72.202	- 35.398	2.091
3800	9.671	89.820	81.298	32.382	- 73.065	- 34.392	1.978
3900	9.714	90.072	81.520	33.352	- 73.927	- 33.362	1.870
4000	9.760	90.318	81.737	34.325	- 74.785	- 32.313	1.765
4100	9.807	90.560	81.949	35.304	- 75.635	- 31.238	1.665
4200	9.856	90.797	82.157	36.287	- 76.478	- 30.145	1.569
4300	9.907	91.029	82.361	37.275	- 77.310	- 29.034	1.476
4400	9.960	91.258	82.560	38.268	- 78.131	- 27.901	1.386
4500	10.015	91.482	82.756	39.267	- 78.939	- 26.749	1.299
4600	10.071	91.703	82.948	40.271	- 79.733	- 25.580	1.215
4700	10.128	91.920	83.137	41.281	- 80.513	- 24.396	1.134
4800	10.187	92.134	83.322	42.297	- 81.279	- 23.193	1.056
4900	10.247	92.345	83.504	43.319	- 82.031	- 21.975	.980
5000	10.308	92.552	83.683	44.347	- 82.769	- 20.742	.907
5100	10.370	92.757	83.859	45.380	- 83.492	- 19.496	.835
5200	10.433	92.959	84.032	46.421	- 84.200	- 18.234	.766
5300	10.496	93.158	84.202	47.467	- 84.895	- 16.958	.699
5400	10.560	93.355	84.370	48.520	- 85.575	- 15.668	.634
5500	10.624	93.550	84.535	49.579	- 86.242	- 14.368	.571
5600	10.689	93.742	84.698	50.645	- 86.897	- 13.058	.510
5700	10.753	93.931	84.858	51.717	- 87.539	- 11.733	.450
5800	10.818	94.119	85.016	52.795	- 88.168	- 10.397	.392
5900	10.882	94.304	85.172	53.880	- 88.785	- 9.051	.335
6000	10.946	94.488	85.326	54.972	- 89.390	- 7.693	.280

June 30, 1974

BARIUM MONOIODIDE (BaI) (IDEAL GAS) GFW = 264.2445 BaI

Ground State Configuration $[^2\Sigma^+]$

$S°_{298.15}$ = 66.59 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = -9.39 ± 20 kcal/mol

$\Delta Hf°_{298.15}$ = -10.14 ± 20 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X $[^2\Sigma^+]$	0	2
C $[^2\Pi]$	17816.3 18568.8	2 2
D $[^2\Sigma^+]$	25764.4	2
E $[^2\Sigma^+]$	26753.3	2

ω_e = 152.2 cm^{-1} $\omega_e x_e$ = 0.29 cm^{-1} σ = 1

B_e = [0.0250] cm^{-1} α_e = [0.000059] cm^{-1} r_e = [3.20] Å

Heat of Formation

The adopted $\Delta Hf°_0$ = -9.39 ± 20 kcal/mol is calculated from a $D°_0$ value of 3.37 eV(77.7 kcal/mol) calculated by a linear Birge-Sponer extrapolation of ω_e and $\omega_e x_e$ data (1) with a correction for the ionic character of the molecule as described by Hildenbrand (2). Other values for $D°_0$, in kcal/mol, are 56 (3) predicted from a correlation of binding energies of Group II and Group III diatomic hydrides and halides, 71.7 (4) as a lower bound from a consideration of ionic bonding forces, and 66 (5) derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. $D°_0$ = 77.7 kcal/mol is adopted because the ratio of $D°_0(BaI)/D°_0(BaI_2)$ = 0.47 which is nearly the same as the ratio of 0.46 found for a series of mono- and difluorides (6) and for other alkaline earth halide systems (8). $\Delta Hf°_{298}$ = -10.14 ± 20 kcal/mol is calculated from the adopted $\Delta Hf°_0$ = -9.39 ± 20 kcal/mol.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen (1). The adopted value of r_e = 3.20 Å was estimated by Margrave (3) and is also the bond distance in $BaI_2(g)$ (7). B_e is calculated from the adopted r_e; α_e is calculated assuming a Morse potential function.

The electronic levels and their probable designation are those given by Rosen (1).

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8. JANAF Thermochemical Tables.

BaI

Barium Diiodide (BaI_2) BaI_2

(Crystal) GFW = 391.1490

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.596	- 144.490	- 144.490	INFINITE
100	16.480	20.210	55.530	- 3.532	- 144.561	- 144.309	315.388
200	17.980	32.210	41.175	- 1.793	- 144.608	- 144.042	157.402
298	18.520	39.470	39.470	.000	- 144.700	- 143.740	105.364
300	18.530	39.585	39.470	.034	- 144.702	- 143.733	104.710
400	19.010	44.981	40.203	1.911	- 148.719	- 143.254	78.271
500	19.490	49.275	41.602	3.836	- 159.229	- 140.895	61.585
600	19.960	52.870	43.188	5.809	- 159.258	- 137.223	49.984
700	20.440	55.983	44.799	7.829	- 159.049	- 133.570	41.702
800	20.920	58.743	46.372	9.897	- 158.916	- 129.936	35.497
900	21.400	61.235	47.887	12.013	- 158.637	- 126.329	30.677
1000	21.880	63.514	49.338	14.176	- 158.313	- 122.757	26.828
1100	22.375	65.623	50.724	16.389	- 159.941	- 119.023	23.648
1200	22.862	67.591	52.048	18.651	- 159.578	- 115.319	21.002
1300	23.340	69.440	53.315	20.961	- 159.143	- 111.647	18.770
1400	23.809	71.186	54.530	23.319	- 158.645	- 108.012	16.861
1500	24.270	72.845	55.696	25.723	- 158.088	- 104.415	15.213

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BARIUM DIIODIDE (BaI_2) (CRYSTAL) GFW = 391.1490 BaI_2

$S°_{298.15}$ = 39.47 ± 0.1 gibbs/mol
Tm = 984 ± 2 K

$\Delta Hf°_0$ = -144.5 ± 0.8 kcal/mol
$\Delta Hf°_{298.15}$ = -144.7 ± 0.8 kcal/mol
ΔHm° = 6.34 ± 0.13 kcal/mol
$\Delta Hs°_{298.15}$ = 72.3 kcal/mol

Heat of Formation

Ehrlich, Peik, and Koch (1) derived $\Delta Hf°_{298}(BaI_2, c)$ = -144.7 ± 0.4 kcal/mol from heat of solution measurements of Ba(c) and BaI_2(c) in 0.1 N HI. An auxiliary HI heat of solution value, -13.22 kcal/mol, calculated from data in reference (2) was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA key value of $\Delta Hf°_{298}(I^-$, aq. std. state) = -13.60 kcal/mol (3) in the $\Delta Hf°_{298}$(HI, aq solution) table, so that the above derived heat of formation of BaI_2(c) will be approximately -145.1 kcal/mol.

Combining $\Delta Hf°_{298}(Ba^{+2}$, aq, std. state) = -128.5 kcal/mol, selected by Parker (4), with the CODATA value for I^-(aq, std. state) (3) gives $\Delta Hf°_{298}(BaI_2$, aq, std. state) = -155.7 kcal/mol. Further combination with the heat of solution, -10.98 kcal/mol (5, 11), gives $\Delta Hf°_{298}(BaI_2, c)$ = -144.7 kcal/mol. This heat of solution value was based on several sets of data, one of which was that of Ehrlich et al. (1, 11).

We adopt -144.7 ± 0.8 kcal/mol because of the correlation of $\Delta Hf°_{298}(Ba^{+2}$, aq, std. state) with the evaluation of data for several barium compounds (4). See also the updated discussion in the heat of formation section for BaO(c) (12).

Heat Capacity and Entropy

Cp°(13.08 - 300.17 K) has been measured by Paukov, Khriplovich, and Smirnova (6). Our T^3 extrapolation agrees with their $S°_{13}$ = 0.619 gibbs/mol and $H°_{13} - H°_0$ = 6.01 cal/mol, and our smoothing and integration of their Cp data agrees with their $S°_{298}$ = 39.47 ± 0.1 gibbs/mol which is adopted.

The low-temperature heat capacities join smoothly with a linear extrapolation from $Cp°_{298}$ = 18.52 gibbs/mol to Dworkin and Bredig's reported Cp of 21.8 gibbs/mol at the adopted Tm of 984 K (7). This gives $H°_{984}-H°_{298}$ = 13.83 kcal/mol, in fair agreement with Dworkin and Bredig's drop calorimeter value of 13.9 kcal/mol (7).

Melting Data

Dworkin and Bredig (7) report ΔHm° = 6.34 kcal/mol (±2%) at Tm of 984 K from drop calorimetry; Emons and Loeffelholz (8) found 6.050 kcal/mol (± 5%) at a reported Tm of 981 K by high temperature cryoscopy. Hutchison (9) determined Tm to be 983 K, while Kubaschewski et al. (10) listed 985 K. We adopt ΔHm° = 6.34 ± 0.13 kcal/mol and Tm = 984 ± 2°K.

Heat of Sublimation

$\Delta Hs°_{298}$ is derived as the difference between the heats of formation of ideal gas and the crystal states at 298.15 K.

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BaI_2

Barium Diiodide (BaI_2) BaI_2

(Liquid) GFW = 391.1490

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.520	43.898	43.898	.000	- 140.029	- 140.390	102.908
300	18.530	44.013	43.899	.034	- 140.031	- 140.391	102.275
400	19.010	49.409	44.631	1.911	- 144.048	- 140.355	76.686
500	19.490	53.703	46.030	3.836	- 154.558	- 138.438	60.511
600	19.960	57.298	47.617	5.809	- 154.588	- 135.210	49.250
700	27.000	60.411	49.227	7.829	- 154.379	- 131.999	41.212
800	27.000	64.016	50.855	10.529	- 153.614	- 128.852	35.201
900	27.000	67.196	52.498	13.229	- 152.751	- 125.808	30.550
1000	27.000	70.041	54.112	15.929	- 151.890	- 122.860	26.851
1100	27.000	72.614	55.679	18.629	- 153.031	- 119.804	23.803
1200	27.000	74.964	57.190	21.329	- 152.230	- 116.818	21.275
1300	27.000	77.125	58.641	24.029	- 151.405	- 113.900	19.148
1400	27.000	79.126	60.034	26.729	- 150.565	- 111.046	17.335
1500	27.000	80.989	61.369	29.429	- 149.712	- 108.255	15.773
1600	27.000	82.731	62.651	32.129	- 148.852	- 105.517	14.413
1700	27.000	84.368	63.880	34.829	- 147.990	- 102.836	13.220
1800	27.000	85.911	65.062	37.529	- 147.130	- 100.204	12.166
1900	27.000	87.371	66.198	40.229	- 146.279	- 97.621	11.229
2000	27.000	88.756	67.292	42.929	- 145.441	- 95.084	10.390
2100	27.000	90.073	68.345	45.629	- 144.620	- 92.584	9.635
2200	27.000	91.329	69.362	48.329	- 177.176	- 88.900	8.831
2300	27.000	92.530	70.343	51.029	- 176.211	- 84.908	8.068
2400	27.000	93.679	71.292	53.729	- 175.304	- 80.958	7.372
2500	27.000	94.781	72.209	56.429	- 174.455	- 77.045	6.735
2600	27.000	95.840	73.098	59.129	- 173.664	- 73.165	6.150
2700	27.000	96.859	73.959	61.829	- 172.929	- 69.313	5.610
2800	27.000	97.841	74.795	64.529	- 172.249	- 65.487	5.112

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BARIUM DIIODIDE (BaI_2) (LIQUID) GFW = 391.1490 BaI_2

$S^\circ_{298.15}$ = 43.898 gibbs/mol
Tm = 984 ± 2 K
Tb = 2340 K

$\Delta Hf^\circ_{298.15}$ = -140.029 kcal/mol
ΔHm° = 6.34 ± 0.13 kcal/mol
ΔHv° = 43.88 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(BaI_2, \ell)$ = -140.029 kcal/mol is obtained from the sum of the heat of formation of the crystal, the heat of melting, and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 27.0 gibbs/mol, was determined by Dworkin and Bredig (1) from drop calorimetric measurements. This value is adopted and assumed constant over a 700-2800 K range. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S^\circ_{298}(BaI_2, \ell)$ = 43.898 gibbs/mol is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Vaporization Data

The temperature at which $\Delta Gr^\circ = 0$ for the reaction $BaI_2(\ell) = BaI_2(g)$ is 2340 K, the adopted Tb. Peterson and Hutchison (2) have extrapolated Knudsen effusion cell measurements in the 1154-1301 K range to obtain a normal boiling point of 2300 K.

ΔHv° = 43.88 kcal/mol is the calculated difference between the heats of formation of the ideal gas and the liquid at Tb. See $BaI_2(g)$ table for details.

References

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2. D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data 15, 320 (1970).

BaI_2

Barium Diiodide (BaI_2)

BaI_2

(Ideal Gas) GFW = 391.1490

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.741	-71.335	-71.335	INFINITE
100	12.663	68.604	95.221	-2.662	-71.391	-75.978	166.051
200	13.533	77.732	84.431	-1.340	-71.855	-80.393	87.850
298	13.734	83.180	83.180	.000	-72.400	-84.472	61.920
300	13.736	83.265	83.180	.025	-72.411	-84.546	61.592
400	13.811	87.228	83.720	1.403	-76.927	-88.361	48.278
500	13.846	90.314	84.742	2.786	-87.979	-90.164	39.411
600	13.866	92.841	85.887	4.172	-88.595	-90.543	32.980
700	13.877	94.979	87.037	5.559	-89.019	-90.837	28.360
800	13.885	96.832	88.148	6.947	-89.566	-91.057	24.876
900	13.890	98.468	89.206	8.336	-90.014	-91.216	22.150
1000	13.894	99.932	90.207	9.725	-90.464	-91.325	19.959
1100	13.897	101.256	91.152	11.115	-92.915	-91.194	18.119
1200	13.899	102.466	92.045	12.505	-93.424	-91.015	16.576
1300	13.901	103.578	92.890	13.895	-93.909	-90.794	15.264
1400	13.902	104.608	93.691	15.285	-94.379	-90.536	14.133
1500	13.903	105.567	94.451	16.675	-94.836	-90.247	13.149
1600	13.904	106.465	95.174	18.065	-95.286	-89.925	12.283
1700	13.905	107.308	95.863	19.456	-95.733	-89.577	11.516
1800	13.905	108.103	96.521	20.846	-96.183	-89.202	10.831
1900	13.906	108.854	97.151	22.237	-96.641	-88.801	10.214
2000	13.906	109.568	97.754	23.627	-97.113	-88.379	9.658
2100	13.906	110.246	98.333	25.018	-97.601	-87.928	9.151
2200	13.907	110.893	98.889	26.409	-131.466	-86.231	8.566
2300	13.907	111.511	99.424	27.799	-131.811	-84.166	7.998
2400	13.907	112.103	99.941	29.190	-132.213	-82.085	7.475
2500	13.908	112.671	100.438	30.581	-132.673	-79.988	6.993
2600	13.908	113.216	100.919	31.972	-133.191	-77.871	6.546
2700	13.908	113.741	101.385	33.362	-133.766	-75.732	6.130
2800	13.908	114.247	101.835	34.753	-134.395	-73.571	5.742
2900	13.908	114.735	102.272	36.144	-135.072	-71.386	5.380
3000	13.908	115.207	102.695	37.535	-135.796	-69.180	5.040
3100	13.908	115.663	103.106	38.926	-136.561	-66.946	4.720
3200	13.909	116.104	103.505	40.317	-137.361	-64.688	4.418
3300	13.909	116.532	103.894	41.707	-138.192	-62.403	4.133
3400	13.909	116.947	104.271	43.098	-139.048	-60.095	3.863
3500	13.909	117.351	104.639	44.489	-139.923	-57.758	3.607
3600	13.909	117.742	104.998	45.880	-140.813	-55.399	3.363
3700	13.909	118.124	105.348	47.271	-141.715	-53.016	3.131
3800	13.909	118.494	105.689	48.662	-142.624	-50.606	2.910
3900	13.909	118.856	106.022	50.053	-143.537	-48.171	2.699
4000	13.909	119.208	106.347	51.444	-144.451	-45.717	2.498
4100	13.909	119.551	106.665	52.835	-145.363	-43.234	2.305
4200	13.909	119.887	106.976	54.225	-146.274	-40.731	2.119
4300	13.909	120.214	107.280	55.616	-147.179	-38.211	1.942
4400	13.909	120.534	107.577	57.007	-148.078	-35.666	1.772
4500	13.909	120.846	107.869	58.398	-148.971	-33.099	1.608
4600	13.909	121.152	108.154	59.789	-149.856	-30.513	1.450
4700	13.909	121.451	108.434	61.180	-150.733	-27.913	1.298
4800	13.909	121.744	108.708	62.571	-151.603	-25.288	1.151
4900	13.909	122.031	108.977	63.962	-152.465	-22.647	1.010
5000	13.910	122.312	109.241	65.353	-153.320	-19.990	.874
5100	13.910	122.587	109.500	66.744	-154.166	-17.317	.742
5200	13.910	122.857	109.754	68.135	-155.006	-14.626	.615
5300	13.910	123.122	110.004	69.526	-155.838	-11.917	.491
5400	13.910	123.382	110.249	70.917	-156.663	-9.190	.372
5500	13.910	123.637	110.490	72.308	-157.482	-6.454	.256
5600	13.910	123.888	110.727	73.699	-158.296	-3.705	.145
5700	13.910	124.134	110.961	75.090	-159.104	-.935	.036
5800	13.910	124.376	111.190	76.481	-159.906	1.848	-.070
5900	13.910	124.614	111.415	77.872	-160.703	4.642	-.172
6000	13.910	124.848	111.637	79.263	-161.495	7.454	-.271

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BARIUM DIIODIDE (BaI_2) (IDEAL GAS) GFW = 391.1490 BaI_2

Point Group = C_{2v}
$S^\circ_{298.15}$ = [83.18 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -71.3 ± 4 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -72.4 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[111] (1)
[26] (1)
[185] (1)

Bond Distance: Ba-I = 3.20 ± 0.03 Å   Bond Angle: I-Ba-I = [170°]   σ = 2
Product of Moments of Inertia: $I_AI_BI_C = 2.1167 \times 10^{-112}\ g^3\ cm^6$

Heat of Formation

Winchell (1) has reported ΔH, ΔG, and ΔS for the vaporization of $BaI_2(\ell)$ at 1150 K derived from a mass spectrometric Knudsen effusion cell investigation (28 unpublished points in the range of 1019-1278 K). The spectra showed no evidence of BaI_2 polymers; also it was concluded that $BaI_2(\ell) = BaI_2(g)$ is the important vaporization. Peterson and Hutchison (2, 3) used a weight loss Knudsen effusion technique to observe vapor pressures at 18 temperatures in the range of 1154-1301 K. Their heat of vaporization, 53.6 ± 1.3 kcal/mole, is in good agreement with Winchell's value, 54 ± 4 kcal/mol.

Our second and third law analyses of these data follow.

Investigator	No. of Points	Temp. Range, K	ΔHv°_{298}, kcal/mol 2nd Law	3rd Law	Drift gibbs/mole
Winchell (1)	3[a]	1019-1278	62.16	68.07	5.1
Peterson and Hutchison (2)	18[b]	1154-1301	64.35 ± 1.5	67.61 ± 0.5	2.6 ± 1.2

[a] ΔG calculated at 1019 K and 1278 K from ΔH, ΔG, and ΔS values given at 1150 K to permit use of 2nd law.

[b] One point rejected by statistical tests.

We select ΔHv°_{298} = 67.6 ± 3 kcal/mol and combine this with $\Delta Hf^\circ_{298}(\ell)$ = -140.029 ± 0.9 kcal/mol to give the adopted $\Delta Hf^\circ_{298}(g)$ = -72.4 ± 4 kcal/mol.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from the work of Akishin et al. (4) who also judged the bond angle to be 180 ± 20°. The later electric deflection study of Buechler et al. (5) showed that all of the barium dihalide molecules are bent. Noting the trend in the magnitude of the bond angle in the alkaline earth-halide series, we have assumed a bond angle of 170°. The individual moments of inertia are: $I_A = 42.941 \times 10^{-38}$, $I_B = 42.826 \times 10^{-38}$, and $I_C = 1.1510 \times 10^{-39}\ g\ cm^2$.

In estimating the vibrational frequencies, the stretching force constants for gaseous BaF, BaF_2, BaCl, and $BaCl_2$ are calculated from their vibrational frequencies (6), using the valence force model. The trend in the ratio k(monohalide)/k_1 (dihalide) indicates that k(BaI)/$k_1(BaI_2)$ = 1 is a reasonable approximation, an approximation used by Brewer et al. (7). The stretching force constant for BaI(g) is calculated from the ground state vibrational frequency given by Rosen (8). The bending force constant is assumed to be 0.01 times the stretching force constant (7). The adopted vibrational frequencies are calculated from these estimated force constants. Other estimates for ν_1, ν_2, and ν_3, where a linear molecule was assumed, are 109, 26, 184 (7) and 106, 37, 178 (9).

We assign an uncertainty of ±2 gibbs/mol to the entropy to allow for error in the estimation of bond angle and of the vibrational frequencies.

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BaI_2

Barium Oxide (BaO) BaO

(Crystal) GFW = 153.3394

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.366	-130.696	-130.696	INFINITE
100	7.554	6.525	26.558	-2.003	-131.057	-128.835	281.563
200	10.375	12.882	18.233	-1.070	-131.093	-126.576	138.314
298	11.329	17.225	17.225	.000	-131.000	-124.375	91.167
300	11.341	17.295	17.225	.021	-130.998	-124.337	90.578
400	11.926	20.734	17.877	1.154	-130.912	-122.133	66.729
500	12.377	23.451	18.549	2.460	-130.873	-119.934	52.423
600	12.723	25.637	19.544	3.656	-131.050	-117.703	42.873
700	13.001	27.620	20.559	4.942	-131.215	-115.455	36.047
800	13.247	29.383	21.564	6.255	-131.425	-113.194	30.923
900	13.459	30.944	22.511	7.590	-131.441	-110.925	26.936
1000	13.660	32.373	23.427	8.946	-131.557	-108.657	23.747
1100	13.853	33.684	24.321	10.321	-135.210	-106.195	21.099
1200	14.031	34.897	25.134	11.715	-134.853	-103.729	18.892
1300	14.237	36.027	25.929	13.127	-134.512	-101.262	17.024
1400	14.377	37.036	26.588	14.557	-134.263	-98.795	15.423
1500	14.546	38.044	27.415	16.003	-133.188	-96.340	14.037
1600	14.714	39.026	28.111	17.466	-133.307	-93.927	12.827
1700	14.873	39.929	28.780	18.946	-132.971	-91.440	11.755
1800	15.041	40.786	29.423	20.442	-132.642	-89.001	10.806
1900	15.207	41.597	30.043	21.754	-132.705	-86.568	9.958
2000	15.362	42.381	30.640	23.482	-132.571	-84.145	9.195
2100	15.521	43.135	31.217	25.026	-133.438	-81.720	8.505
2200	15.680	43.860	31.776	26.586	-155.067	-78.388	7.787
2300	15.839	44.561	32.316	28.162	-155.260	-74.114	7.042
2400	15.996	45.238	32.841	29.754	-155.097	-70.152	6.388
2500	16.154	45.894	33.350	31.361	-154.873	-66.202	5.787
2600	16.311	46.531	33.845	32.985	-154.721	-62.258	5.233
2700	16.467	47.150	34.326	34.624	-154.566	-58.320	4.721
2800	16.624	47.751	34.795	36.279	-154.472	-54.387	4.245
2900	16.780	48.337	35.252	37.949	-154.412	-50.456	3.802
3000	16.936	48.909	35.697	39.634	-154.384	-46.527	3.389

Dec. 31, 1972; June 30, 1974

BARIUM OXIDE (BaO) (CRYSTAL) GFW = 153.3394 BaO

$S°_{298.15}$ = 17.225 ± 0.09 gibbs/mol

Tm = 2286 ± 15 K

$\Delta Hf°_0$ = -130.7 ± 0.5 kcal/mol

$\Delta Hf°_{298.15}$ = -131.0 ± 0.5 kcal/mol

ΔHm° = [14] kcal/mol

$\Delta Hs°_{298.15}$ = 101.4 ± 2 kcal/mol

Heat of Formation

ΔHf° is rounded from -130.98 ± 0.47 kcal/mol derived by Fitzgibbon et al. (1) from calorimetric reactions of HCl(aq) with Ba(c) and BaO(c). Combination of their two reactions yields $\Delta Hr°_{298}$ = -62.66 ± 0.47 kcal/mol for Ba(c) + $H_2O(\ell)$ → BaO(c) + H_2(g). Although the resulting ΔHr° is 1.3 kcal/mol less negative than that of NBS Technical Note 270-6 (2), it confirms Parker's selection (2) of key values for BaO and $BaCl_2$ from calorimetry involving aqueous HCl (3-5) instead of discrepant values derived from other reactions (6-8). Earlier HCl calorimetry gave ΔHf°(BaO, c) = -132.0 (3, 2) and -132.1 kcal/mol (4, 5). The new value (1) is preferred since both reactions were run in the same calorimeter on samples that were well characterized. The latter is particularly important since impurities were a major problem in studies of BaO (3, 4, 9-14) and Ba (2, 5-7).

Direct measurements of ΔHc of Ba(c) by Mah (6) gave -139.06 ± 0.7 kcal/mol. Combustion studies of Fitzgibbon et al. (1) suggest that the negative bias of 8 kcal/mol was due to partial dissolution of the crucible lining (MgO) in molten BaO formed in the combustion. Dissolution was eliminated in combustions on sintered MgO disks, but large amounts of BaO_2 were formed both in this case and with the use of BaO crucibles (1). This led the authors (1) to dismiss combustion calorimetry in favor of solution calorimetry. Parker (2) noted earlier that the combustion result was incompatible with data for $BaCl_2$(aq), $Ba(OH)_2$(aq and c), BaO_2(c) and $BaCO_3$(c); also a similar discrepancy existed for SrO(c). We find that the combustion value is incompatible with equilibrium data (19) for $BaCl_2$(ℓ and g).

ΔHf°($BaCl_2$, c) and ΔHf°(Ba^{2+}, aq) deserve an updated discussion. We combine ΔHr° = -127.95 ± 0.41 kcal/mol (1) for Ba(c) + 2 HCl(54.3 H_2O) = H_2(g) + $BaCl_2$ [in 148.9 HCl (55.0 H_2O)] with ΔHf°(HCl, 54.3 H_2O) = -39.52 ± 0.02 kcal/mol (16) and ΔH_{soln} = -2.09 ± 0.2 kcal/mol (17, 18, 2) for $BaCl_2$(c) in HCl(55 H_2O) to give ΔHf°($BaCl_2$, c) = -204.9 ± 0.5 kcal/mol. This confirms the JANAF (19) ΔHf°($BaCl_2$) of -205.2 kcal/mol based on the selection of Parker (2); the alternative uncertainty of ±0.6 kcal/mol should now be used instead of ±3 kcal/mol (19). The new ΔHf° for $BaCl_2$(1) yields ΔHf°(Ba^{2+}, aq) = -128.0 ± 0.6 kcal/mol, assuming $\Delta H°_{soln}$($BaCl_2$, c) = -3.0 ± 0.2 kcal/mol (many references) and ΔHf°(Cl^-, aq) = -39.933 ± 0.021 kcal/mol (16). This is consistent with Parker's selection of ΔHf°(Ba^{2+}, aq) = -128.5 kcal/mol (2).

Heat Capacity and Entropy

Cp° is based on data (1.4-310 K) of Gmelin (12) who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed Cp° above 240 K where the scatter increases rapidly. The entropy is obtained by integration of our adopted Cp° using S° = 0.0015 gibbs/mol at 4 K. The value S° = 15.75 ± 0.02 gibbs/mol reported by Gmelin (12) corresponds to neither 273.15 K nor 298.15 K and must be erroneous. Cp° data (56-299 K) of Anderson (13) differ by ±1.0% but average about 1.0% higher from 150 to 260 K.

Cp° above 300 K is from constrained fitting of enthalpy data (391-1299 K) of Lander (14). This calorimetry is subject to bias from a calibration based on Pt and from impurities in the two samples. Information is insufficient to assess the bias due to minor changes in the enthalpy of Pt (15). We apply crude corrections to the observed enthalpies for 27 mole % SrO in one sample and for about 2.8 mole % SiO_2 in the other sample. Deviations from the adopted curve are ±0.9% (first sample) and ±1.0% (second sample) except for -2.0% at 421 K.

Melting Data

See BaO(ℓ).

Heat of Sublimation

ΔHs° is calculated as the difference in ΔHf° between gas and crystal.

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BaO

Barium Oxide (BaO) BaO

(Liquid) GFW = 153.3394

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.300	23.077	23.077	.000	-117.502	-112.625	82.556
300	11.312	23.147	23.077	.021	-117.499	-112.594	82.025
400	11.926	26.489	23.528	1.184	-117.413	-110.975	60.634
500	12.377	29.201	24.400	2.400	-117.475	-109.362	47.802
600	12.720	31.489	25.396	3.656	-117.702	-107.716	39.235
700	13.001	33.472	26.411	4.942	-117.716	-106.053	33.111
800	13.242	35.224	27.405	6.255	-117.837	-104.377	28.515
900	13.459	36.796	28.363	7.590	-117.842	-102.693	24.937
1000	13.660	38.224	29.279	8.946	-117.833	-101.011	22.076
1100	13.850	39.535	30.152	10.321	-119.811	-99.133	19.696
1200	14.031	40.748	30.985	11.715	-119.831	-97.252	17.712
1300	14.207	41.878	31.780	13.127	-119.814	-95.371	16.033
1400	14.379	42.938	32.540	14.557	-119.764	-93.493	14.595
1500	14.548	43.935	33.267	16.003	-119.687	-91.619	13.349
1600	14.714	44.880	33.963	17.466	-119.589	-89.751	12.259
1700	16.000	45.850	34.634	19.066	-119.352	-87.893	11.299
1800	16.000	46.764	35.283	20.666	-119.119	-86.049	10.448
1900	16.000	47.629	35.910	22.266	-118.897	-84.218	9.687
2000	16.000	48.450	36.517	23.866	-118.689	-82.400	9.004
2100	16.000	49.231	37.104	25.466	-118.499	-80.589	8.387
2200	16.000	49.975	37.672	27.066	-151.688	-77.562	7.705
2300	16.000	50.686	38.222	28.666	-151.357	-74.200	7.051
2400	16.000	51.367	38.756	30.266	-151.086	-70.851	6.452
2500	16.000	52.020	39.274	31.866	-150.874	-67.513	5.902
2600	16.000	52.648	39.776	33.466	-150.721	-64.181	5.395
2700	16.000	53.252	40.264	35.066	-150.625	-60.854	4.926
2800	16.000	53.833	40.738	36.666	-150.586	-57.531	4.490
2900	16.000	54.395	41.200	38.266	-150.596	-54.206	4.085
3000	16.000	54.937	41.649	39.866	-150.653	-50.882	3.707
3100	16.000	55.462	42.086	41.466	-150.753	-47.555	3.353
3200	16.000	55.970	42.512	43.066	-150.889	-44.224	3.020
3300	16.000	56.462	42.927	44.666	-151.055	-40.888	2.708
3400	16.000	56.940	43.332	46.266	-151.248	-37.548	2.414
3500	16.000	57.404	43.728	47.866	-151.461	-34.201	2.136
3600	16.000	57.854	44.114	49.466	-151.689	-30.846	1.873
3700	16.000	58.293	44.491	51.066	-151.930	-27.486	1.624
3800	16.000	58.720	44.860	52.666	-152.179	-24.120	1.387
3900	16.000	59.135	45.221	54.266	-152.431	-20.747	1.163
4000	16.000	59.540	45.574	55.866	-152.685	-17.368	.949
4100	16.000	59.935	45.919	57.466	-152.937	-13.981	.745
4200	16.000	60.321	46.257	59.066	-153.187	-10.589	.551
4300	16.000	60.697	46.589	60.666	-153.432	-7.190	.365
4400	16.000	61.065	46.914	62.266	-153.670	-3.787	.188
4500	16.000	61.425	47.232	63.866	-153.903	-.378	.018
4600	16.000	61.776	47.545	65.466	-154.127	3.038	-.144
4700	16.000	62.121	47.851	67.066	-154.344	6.456	-.300
4800	16.000	62.457	48.152	68.666	-154.553	9.881	-.450
4900	16.000	62.787	48.447	70.266	-154.753	13.306	-.593
5000	16.000	63.111	48.737	71.866	-154.946	16.737	-.732

Dec. 31, 1972; June 30, 1974

BARIUM OXIDE (BaO) (LIQUID) GFW = 153.3394 BaO

$S°_{298.15}$ = [23.077] gibbs/mol
Tm = 2286 ± 15 K
Tb = [3360.6] K

$\Delta Hf°_{298.15}$ = [-117.502] kcal/mol
ΔHm° = [14] kcal/mol
ΔHv° = [70.71] kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference in $(H°_{2286}-H°_{298})$ between crystal and liquid.

Heat Capacity and Entropy

Cp° of the liquid is estimated as 8 gibbs/g-atom by comparison with other oxides. Cp° is taken from the crystal in the range 298 K up to the glass transition assumed at 1600 K. S° is calculated in a manner analogous to ΔHf°.

Melting Data

Foex (1) obtained Tm = 2010°C from a solar-furnace study using BaO as its own container. We adopt this result but increase it by 3° for conversion to IPTS-68. Foex showed that the much lower value (1918°C) of Schumacher (2, 3) probably resulted from contamination by WO_3 from tungsten supports of the sample. ΔHm° is estimated such that ΔSm° is 6 gibbs/mole.

Vaporization Data

Unlike the other alkaline-earth oxides, BaO(c) vaporizes mainly to BaO(g) with traces of Ba_2O_2 and Ba_2O. Mass-spectrometric studies (4) suggest that decomposition to Ba(g) and O(g) is not a major contributor even though the observed intensities of Ba^+ are almost comparable with those of BaO^+. Tb is the calculated T at which ΔGr° = 0 for BaO(c) = BaO(g); ΔHv° is the corresponding difference in ΔHf°.

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BaO

Barium Oxide (BaO) BaO

(Ideal Gas) GFW = 153.3394

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.154	-29.065	-29.065	INFINITE
100	6.969	48.298	62.887	-1.459	-29.122	-31.068	67.899
200	7.346	53.216	56.952	-.747	-29.367	-32.920	35.973
298	7.863	56.249	56.249	.000	-29.600	-34.613	25.372
300	7.871	56.297	56.249	.015	-29.604	-34.644	25.238
400	8.232	58.615	56.562	.821	-29.875	-36.287	19.826
500	8.457	60.478	57.165	1.656	-30.317	-37.843	16.541
600	8.601	62.034	57.851	2.510	-30.946	-39.287	14.310
700	8.698	63.367	58.546	3.375	-31.382	-40.646	12.690
800	8.766	64.534	59.223	4.248	-31.942	-41.930	11.455
900	8.816	65.569	59.872	5.128	-32.402	-43.150	10.478
1000	8.855	66.500	60.489	6.011	-32.866	-44.319	9.686
1100	8.885	67.346	61.074	6.898	-35.333	-45.246	8.990
1200	8.910	68.120	61.630	7.788	-35.857	-46.124	8.400
1300	8.931	68.834	62.157	8.680	-36.359	-46.959	7.894
1400	8.950	69.497	62.658	9.575	-36.845	-47.756	7.455
1500	8.967	70.115	63.134	10.470	-37.319	-48.519	7.069
1600	8.985	70.694	63.589	11.368	-37.786	-49.251	6.727
1700	9.003	71.239	64.023	12.267	-38.249	-49.953	6.422
1800	9.025	71.754	64.438	13.169	-38.715	-50.628	6.147
1900	9.052	72.243	64.836	14.073	-39.189	-51.276	5.898
2000	9.086	72.708	65.218	14.979	-39.674	-51.901	5.672
2100	9.129	73.152	65.586	15.890	-40.174	-52.500	5.464
2200	9.184	73.578	65.939	16.806	-74.047	-51.848	5.151
2300	9.254	73.988	66.280	17.727	-74.395	-50.831	4.830
2400	9.342	74.384	66.610	18.657	-74.794	-49.798	4.535
2500	9.449	74.767	66.929	19.596	-75.243	-48.749	4.262
2600	9.579	75.140	67.237	20.547	-75.739	-47.679	4.008
2700	9.733	75.505	67.537	21.513	-76.277	-46.589	3.771
2800	9.915	75.862	67.828	22.495	-76.855	-45.480	3.550
2900	10.124	76.213	68.111	23.497	-77.464	-44.347	3.342
3000	10.361	76.560	68.387	24.521	-78.097	-43.194	3.147
3100	10.629	76.904	68.656	25.570	-78.748	-42.020	2.962
3200	10.925	77.246	68.919	26.647	-79.406	-40.826	2.788
3300	11.249	77.587	69.176	27.756	-80.064	-39.610	2.623
3400	11.601	77.928	69.429	28.898	-80.715	-38.375	2.467
3500	11.977	78.270	69.677	30.077	-81.349	-37.121	2.318
3600	12.375	78.613	69.920	31.294	-81.960	-35.847	2.176
3700	12.791	78.958	70.160	32.552	-82.543	-34.558	2.041
3800	13.222	79.304	70.396	33.853	-83.090	-33.254	1.913
3900	13.664	79.654	70.629	35.197	-83.598	-31.937	1.790
4000	14.112	80.005	70.859	36.586	-84.063	-30.607	1.672
4100	14.560	80.359	71.086	38.020	-84.482	-29.264	1.560
4200	15.005	80.715	71.311	39.498	-84.853	-27.913	1.452
4300	15.442	81.074	71.534	41.020	-85.176	-26.552	1.350
4400	15.865	81.434	71.755	42.586	-85.449	-25.186	1.251
4500	16.270	81.795	71.974	44.193	-85.675	-23.814	1.157
4600	16.654	82.156	72.191	45.839	-85.853	-22.435	1.066
4700	17.012	82.519	72.407	47.523	-85.986	-21.056	.979
4800	17.342	82.880	72.622	49.241	-86.077	-19.673	.896
4900	17.641	83.241	72.835	50.990	-86.128	-18.292	.816
5000	17.908	83.600	73.046	52.768	-86.143	-16.907	.739
5100	18.140	83.957	73.257	54.571	-86.124	-15.521	.665
5200	18.339	84.311	73.466	56.395	-86.076	-14.139	.594
5300	18.502	84.662	73.674	58.237	-86.002	-12.754	.526
5400	18.631	85.009	73.881	60.094	-85.906	-11.374	.460
5500	18.727	85.352	74.086	61.962	-85.791	-9.993	.397
5600	18.790	85.690	74.290	63.838	-85.663	-8.618	.336
5700	18.824	86.023	74.493	65.719	-85.523	-7.244	.278
5800	18.828	86.350	74.695	67.602	-85.375	-5.870	.221
5900	18.806	86.672	74.895	69.484	-85.222	-4.502	.167
6000	18.759	86.988	75.094	71.362	-85.066	-3.133	.114

June 30, 1974

BARIUM OXIDE (BaO) (IDEAL GAS) GFW = 153.3394 BaO

Symmetry Number = 1

$S^\circ_{298.15}$ = 56.249 ± 0.08 gibbs/mol

ΔHf°_0 = -29.1 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -29.6 ± 2 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1-4)	$X^1\Sigma$	0.0	1	1.9397	0.31261	0.00139	669.81	2.054
(1)	$a^3\Pi$	17372.	6	2.289	0.2244	0.0014	448.3	2.4
(1)	$A'^1\Pi$	17568.	2	2.289	0.2244	0.0014	448.3	2.4
(5)	$^3\Sigma^+$	[14000]	3	[2.133]	[0.2583]	[0.0011]	[499.7]	[1.64]
(1, 6, 2)	$A^1\Sigma^+$	16722.	1	2.133	0.25832	0.00107	499.7	1.64
(5)	$^3\Sigma^+$	[22000]	3	[2.26]	[0.230]	[0.001]	[480]	[2]
(5)	$^3\Delta$	[22000]	6	"	"	"	"	"
(5)	$^1\Delta$	[24000]	2	"	"	"	"	"
(5)	$^3\Sigma^-$	[24000]	3	"	"	"	"	"
(5)	$^1\Sigma^-$	[24000]	1	"	"	"	"	"
(5)	$^1\Sigma^+$	[28000]	1	"	"	"	"	"
(5)	$^3\Pi$	[32000]	6	[2.20]	[0.243]	"	[488]	[3.6]
(2)	$B^1\Pi$	32775.	2	"	"	"	488.	3.6

Heat of Formation

We adopt D°_0 = 131.0 ± 2 kcal/mol and ΔHf°_{298} = -29.6 ± 2 kcal/mol based on equilibria and vaporization data analyzed below. The results are in excellent agreement, even though δS varies widely. D°_0 is confirmed also by values of 132 ± 5(electron impact, 17), ≥131.4(crossed-beam chemiluminescence, 18) and ∿131 kcal/mol (flame study, 1973, 7). We have adjusted the latter value to make it roughly consistent with our free energy functions. Less reliable data were reviewed by Schofield (19). Our analysis supports the conclusions of Brewer and Rosenblatt (20).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	3rd Law	ΔHf°_{298} kcal/mol	D°_0
(7) Kalff(1970)	Flame photometric	A	∿2680-2860	12	19.±4	49.±11	-4.7±2.5	-29.6±3	131.0
(8) Colin(1964)	Knudsen mass spec.	B	1934-2069	3	-11.±10	-29.±20	-6.8±2.0	-29.1±3	130.5
(9) Semenov(1972)	" " "	C	1423-1723	Eqn.	3.7	108.1	102.2±1.0	-28.8±2	130.2
(10) Newbury(1968)	Knudsen thermobal.	C	1563-1853	17	5.9±0.9	111.8±1.5	101.8±1.3	-29.2±2	130.6
	" " "	C	1503-1862	45	4.2±0.5	109.2±0.8	102.1±1.0	-28.9±2	130.3
	Knudsen mass spec.	C	1590-1892	11	4.8±0.2	110.1±0.3	101.7±1.1	-29.3±2	130.8
	" " "	C	1481-1917	38	5.5±0.3	111.4±0.5	101.8±1.4	-29.2±2	130.6
	" " "	C	1365-1910	29	6.1±0.4	112.1±0.6	102.1±1.6	-28.9±2	130.3
(11) Inghram(1955)	" " "	C	1530-1758	4	-2.8±6.1	99.±10	103.2±1.7	-27.8±2	129.2
(12) Shchukarev(1957)	Langmuir mass spec.	C	∿1173-1473	Eqn.	-6.1	93.3	101.4±1.6	-29.6±2	131.0
(13) Nikonov(1961)	Knudsen effusion	C	∿1140-1470	Eqn.	-2.0	97.2	99.8±0.5	-31.2±2	132.6
(14) Blewett(1939)	" "	C	1526-1800	12	-0.5±2.5	103.1±4.1	103.9±1.3	-27.1±3	128.5
(15) Herrmann(1937)	Langmuir	C	∿1200-1560	Eqn.	16.	124.	101.8±4.6	-29.2±3	130.7
(16) Claassen(1933)	"	C	1223-1475	7	-4.5±1.5	95.9±2.1	101.9±1.0	-29.1±2	130.5

[a] Reactions: A) $Ba(g) + CO_2(g) = BaO(g) + CO(g)$; B) $Ba(g) + SO(g) = BaO(g) + S(g)$; C) $BaO(c) = BaO(g)$.

[b] δS = ΔSr°(2nd Law) - ΔSr°(3rd Law).

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants of the observed states are from Field (1) and Rosen (2). The long-sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field (1) using a new method for assignment of perturbations. This study resolved the long-standing controversy over low-lying electronic levels and confirmed (1) that $X^1\Sigma^+$ is the ground state (4). We estimate the other potentially low-lying state ($^3\Sigma^+$) at 14000 cm^{-1} by assuming that it lies 3000 ± 2500 cm^{-1} (1, 5) below the isoconfigurational A state. Other predicted states and their vibrational-rotational constants are estimated in isoconfigurational groups by comparison with BeO, MgO, CaO and SrO (5). Comparisons are facilitated by listing the states in the isoconfigurational order of MgO (5). Our thermodynamic functions correspond to an "effective" ground state with g = 1 instead of g = 6 (10, 19). Our functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2\varepsilon_i/T)$.

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BaO

Bromine Monatomic (Br) Br

(Ideal Gas) GFW = 79.904

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.481	28.183	28.183	INFINITE
100	4.968	36.376	46.220	-.984	28.346	25.352	-55.407
200	4.968	39.820	42.258	-.488	28.257	22.383	-24.459
298	4.968	41.803	41.803	.000	26.735	19.695	-14.437
300	4.968	41.834	41.303	.009	26.728	19.652	-14.316
400	4.968	43.263	41.998	.506	23.104	18.040	-9.857
500	4.971	44.372	42.366	1.003	23.160	16.767	-7.329
600	4.979	45.279	42.778	1.500	23.213	15.483	-5.640
700	4.997	46.048	43.192	1.999	23.266	14.191	-4.431
800	5.026	46.717	43.591	2.500	23.319	12.891	-3.522
900	5.063	47.311	43.972	3.004	23.374	11.584	-2.813
1000	5.106	47.846	44.333	3.513	23.432	10.271	-2.245
1100	5.153	48.335	44.675	4.026	23.494	8.952	-1.779
1200	5.199	48.785	44.999	4.543	23.560	7.627	-1.389
1300	5.243	49.203	45.307	5.066	23.630	6.297	-1.059
1400	5.284	49.593	45.599	5.592	23.703	4.960	-.774
1500	5.320	49.959	45.878	6.122	23.780	3.619	-.527
1600	5.351	50.304	46.144	6.656	23.859	2.272	-.310
1700	5.377	50.629	46.398	7.192	23.940	.921	-.118
1800	5.398	50.937	46.642	7.731	24.023	-.436	.053
1900	5.415	51.229	46.876	8.272	24.108	-1.796	.207
2000	5.428	51.507	47.100	8.814	24.193	-3.163	.346
2100	5.437	51.772	47.316	9.357	24.280	-4.533	.472
2200	5.443	52.025	47.525	9.901	24.366	-5.907	.587
2300	5.446	52.267	47.726	10.445	24.451	-7.284	.692
2400	5.440	52.499	47.920	10.990	24.537	-8.666	.789
2500	5.445	52.721	48.107	11.535	24.622	-10.051	.879
2600	5.442	52.935	48.289	12.079	24.706	-11.439	.962
2700	5.437	53.140	48.465	12.623	24.790	-12.832	1.039
2800	5.432	53.338	48.635	13.166	24.872	-14.227	1.110
2900	5.425	53.528	48.801	13.709	24.953	-15.624	1.177
3000	5.418	53.712	48.962	14.251	25.033	-17.025	1.240
3100	5.410	53.890	49.118	14.793	25.112	-18.428	1.299
3200	5.402	54.061	49.269	15.333	25.189	-19.834	1.355
3300	5.393	54.227	49.417	15.873	25.265	-21.243	1.407
3400	5.384	54.388	49.561	16.412	25.340	-22.653	1.456
3500	5.375	54.544	49.701	16.950	25.413	-24.065	1.503
3600	5.366	54.695	49.838	17.487	25.484	-25.480	1.547
3700	5.356	54.842	49.971	18.023	25.555	-26.897	1.589
3800	5.347	54.985	50.101	18.558	25.624	-28.315	1.628
3900	5.338	55.124	50.228	19.093	25.691	-29.735	1.666
4000	5.329	55.259	50.352	19.626	25.757	-31.158	1.702
4100	5.320	55.390	50.474	20.158	25.821	-32.582	1.737
4200	5.312	55.518	50.592	20.690	25.884	-34.007	1.770
4300	5.303	55.643	50.708	21.221	25.946	-35.433	1.801
4400	5.295	55.765	50.822	21.751	26.007	-36.861	1.831
4500	5.287	55.884	50.933	22.280	26.066	-38.291	1.860
4600	5.279	56.000	51.042	22.808	26.124	-39.721	1.887
4700	5.271	56.114	51.149	23.336	26.180	-41.152	1.914
4800	5.264	56.224	51.253	23.862	26.235	-42.587	1.939
4900	5.256	56.333	51.356	24.388	26.289	-44.021	1.963
5000	5.249	56.439	51.456	24.914	26.342	-45.456	1.987
5100	5.242	56.543	51.555	25.438	26.393	-46.894	2.010
5200	5.235	56.645	51.652	25.962	26.443	-48.331	2.031
5300	5.229	56.744	51.747	26.485	26.492	-49.768	2.052
5400	5.222	56.842	51.841	27.008	26.540	-51.209	2.073
5500	5.216	56.938	51.932	27.530	26.587	-52.648	2.092
5600	5.210	57.032	52.023	28.051	26.632	-54.090	2.111
5700	5.205	57.124	52.111	28.572	26.676	-55.531	2.129
5800	5.199	57.214	52.198	29.092	26.720	-56.973	2.147
5900	5.193	57.303	52.284	29.611	26.762	-58.417	2.164
6000	5.188	57.390	52.369	30.131	26.803	-59.863	2.181

Sept. 30, 1961; June 30, 1974

BROMINE, MONATOMIC (Br) (IDEAL GAS) GFW = 79.904 Br

Ground State Configuration $^3P_{3/2}$

$S°_{298.15}$ = 41.803 ± 0.005 gibbs/mol

$\Delta Hf°_0$ = 28.183 ± 0.029 kcal/mol

$\Delta Hf°_{298.15}$ = 26.735 ± 0.039 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^3P_{3/2}$	0	4
$^3P_{1/2}$	3685.24	2

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for $\Delta Hf°_{298}$(Br, g) was derived using $D°_0(^{79}Br^{81}Br)$ = 15893.1 ± 2 cm^{-1}(45.4403 + 0.006 kcal/mol) from Horsley and Barrow (2). This value was calculated from the dissociation energies of $^{79}Br_2$ and $^{81}Br_2$. The convergence limit in the absorption spectrum of the $^3\Pi_{0+U}-^1\Sigma^+_g$ system corresponded to dissociation to a ground state bromine atom and a bromine atom in the $^3P_{1/2}$ excited state.

LeRoy and Berstein (3, 4) have calculated the dissociation energy of diatomic bromine from the vibrational spacings of the higher levels. The latter calculation (4), using the data of Horsley and Barrow (2), yielded $D°_0$ = 15895.5 ± 0.5 cm^{-1}.

The adopted ΔHf° value differs by 0.005 kcal/mol from the previous JANAF value (5).

Heat Capacity and Entropy

The electronic levels for Br(g) are those recommended by C. M. Sitterley (6) and were adopted by the ICSU-CODATA Task Group. We do not include the levels which lie above 63000 cm^{-1} (7) as they do not contribute to the values of the thermodynamic functions below 6000 K. The calculated value of $S°_{298}$ agrees with that adopted by CODATA (1). The $S°_{298}$ value is 0.002 gibbs/mol less than the previous JANAF value (5).

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Br

Lead Monobromide (PbBr) BrPb

(Ideal Gas) GFW = 287.104

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.425	19.100	19.100	INFINITE
100	7.968	55.820	72.789	-1.697	19.071	15.013	-32.810
200	8.640	61.605	65.897	-.859	18.721	11.084	-12.112
298	8.824	65.095	65.095	.000	16.951	7.584	-5.559
300	8.826	65.150	65.095	.016	16.939	7.526	-5.483
400	8.905	67.701	65.442	.903	13.054	5.174	-2.827
500	8.950	69.693	66.100	1.796	12.833	3.228	-1.411
600	8.980	71.328	66.840	2.693	12.595	1.330	-.485
700	9.003	72.714	67.582	3.592	11.178	-.337	.105
800	9.023	73.917	68.300	4.493	10.910	-1.964	.537
900	9.042	74.981	68.985	5.397	10.651	-3.557	.864
1000	9.059	75.935	69.633	6.302	10.400	-5.122	1.119
1100	9.077	76.799	70.246	7.208	10.156	-6.663	1.324
1200	9.097	77.590	70.825	8.117	9.923	-8.181	1.490
1300	9.119	78.319	71.374	9.028	9.695	-9.680	1.627
1400	9.145	78.995	71.894	9.941	9.470	-11.163	1.743
1500	9.174	79.627	72.389	10.857	9.248	-12.628	1.840
1600	9.207	80.220	72.860	11.776	9.025	-14.079	1.923
1700	9.245	80.780	73.310	12.699	8.804	-15.515	1.995
1800	9.286	81.309	73.740	13.625	8.581	-16.941	2.057
1900	9.330	81.812	74.151	14.556	8.358	-18.353	2.111
2000	9.378	82.292	74.546	15.491	8.133	-19.753	2.159
2100	9.428	82.751	74.926	16.432	-34.542	-19.589	2.039
2200	9.480	83.191	75.292	17.377	-34.674	-18.875	1.875
2300	9.533	83.613	75.645	18.327	-34.823	-18.153	1.725
2400	9.587	84.020	75.985	19.283	-34.988	-17.424	1.587
2500	9.641	84.413	76.315	20.245	-35.171	-16.690	1.459
2600	9.695	84.792	76.633	21.212	-35.370	-15.946	1.340
2700	9.749	85.159	76.942	22.184	-35.585	-15.196	1.230
2800	9.802	85.514	77.242	23.161	-35.817	-14.436	1.127
2900	9.854	85.859	77.533	24.144	-36.061	-13.667	1.030
3000	9.905	86.194	77.816	25.132	-36.319	-12.891	.939
3100	9.954	86.520	78.092	26.125	-36.589	-12.106	.853
3200	10.002	86.836	78.360	27.123	-36.871	-11.311	.773
3300	10.048	87.145	78.622	28.125	-37.160	-10.508	.696
3400	10.092	87.445	78.877	29.132	-37.457	-9.696	.623
3500	10.135	87.739	79.126	30.144	-37.761	-8.875	.554
3600	10.177	88.025	79.369	31.160	-38.069	-8.045	.488
3700	10.217	88.304	79.607	32.179	-38.379	-7.207	.426
3800	10.255	88.577	79.839	33.203	-38.691	-6.359	.366
3900	10.292	88.844	80.067	34.230	-39.005	-5.503	.308
4000	10.327	89.105	80.290	35.261	-39.317	-4.645	.254
4100	10.361	89.360	80.508	36.296	-39.629	-3.774	.201
4200	10.394	89.610	80.721	37.333	-39.938	-2.893	.151
4300	10.426	89.855	80.931	38.374	-40.244	-2.010	.102
4400	10.456	90.095	81.137	39.418	-40.545	-1.114	.055
4500	10.485	90.331	81.338	40.465	-40.842	-.217	.011
4600	10.514	90.561	81.536	41.515	-41.135	.691	-.033
4700	10.541	90.788	81.731	42.568	-41.421	1.601	-.074
4800	10.568	91.010	81.922	43.624	-41.702	2.522	-.115
4900	10.594	91.228	82.109	44.682	-41.977	3.445	-.154
5000	10.619	91.443	82.294	45.742	-42.246	4.374	-.191
5100	10.643	91.653	82.475	46.806	-42.510	5.308	-.227
5200	10.667	91.860	82.654	47.871	-42.766	6.250	-.263
5300	10.690	92.063	82.830	48.939	-43.016	7.197	-.297
5400	10.712	92.263	83.002	50.009	-43.261	8.145	-.330
5500	10.734	92.460	83.173	51.081	-43.499	9.099	-.362
5600	10.756	92.654	83.340	52.156	-43.732	10.058	-.393
5700	10.777	92.844	83.505	53.233	-43.960	11.018	-.422
5800	10.798	93.032	83.668	54.311	-44.181	11.989	-.452
5900	10.818	93.217	83.828	55.392	-44.399	12.957	-.480
6000	10.838	93.399	83.986	56.475	-44.611	13.927	-.507

June 30, 1962; Dec. 31, 1973

LEAD MONOBROMIDE (PbBr) (IDEAL GAS) GFW = 287.104 BrPb

Ground State Configuration $^2\Pi_{1/2}$

$S°_{298.15}$ = 65.10 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = 19.10 ± 10 kcal/mol

$\Delta Hf°_{298}$ = 16.95 ± 10 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8300]	2
A [$^2\Sigma$]	20884.3	[2]
B [$^2\Sigma$]	34523.7	[2]

ω_e = 206.56 cm^{-1}

$\omega_e x_e$ = 0.495 cm^{-1}

σ = 1

B_e = 0.0451 cm^{-1}

α_e = [0.00014] cm^{-1}

r_e = 2.546 Å

Heat of Formation

The adopted $\Delta Hf°_0$ = 19.10 ± 10 kcal/mol is calculated and rounded from the $D°_0$ value of 2.43 eV (56.04 kcal/mol) determined by Singh from emission spectra (1), $\Delta Hf°_0$ (Pb, g) = 46.91 ± 0.13 kcal/mol (2), and $\Delta Hf°_0$ (Br, g) = 28.188 kcal/mol (2). Rosen (3) and Gaydon (4) recommended 57 ± 9 kcal/mol and 58 ± 9 kcal/mol, respectively, for $D°_0$. A linear Birge-Sponer extrapolation of the ground state vibrational constants, as derived from absorption spectra (v, 0-11) observed by Morgan (5), gives a dissociation energy of 2.66 eV. Correction for the ionic character of PbBr as proposed by Hildenbrand (6) gives $D°_0$ = 2.44 eV which is in good agreement with the value determined by Singh (1). $\Delta Hf°_{298}$ = 16.95 ± 10 kcal/mol is calculated from the adopted $\Delta Hf°_0$ = 19.10 ± 10 kcal/mol.

Heat Capacity and Entropy

The vibrational constants are from the compilation of Rosen (3), corrected for the natural isotopic abundance of ^{79}Br and ^{81}Br. Analogous to PbF (2) and PbCl (2), a $^2\Pi_{3/2}$ state at 8300 cm^{-1} is added to the electronic states and levels listed by Rosen (3). The assignment of the first excited state remains uncertain; the choice appears to be between $^2\Sigma$, tentatively assigned to PbF (2) and PbCl (2), and $^2\Delta$, tentatively assigned to PbI (2). The $^2\Sigma$ state is adopted. The entropy is increased by 0.009 eu at 4000 K and 0.012 eu at 6000 K if the $^2\Delta$ state is used. The adopted value of B_e was determined by Lal and Khanna (7) and is adjusted for the natural abundance of the bromine isotopes. The value of r_e is calculated from the adopted B_e. The value of α_e is calculated assuming a Morse potential function.

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BrPb

Calcium Dibromide ($CaBr_2$) Br_2Ca

(Crystal) GFW = 199.888

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.935	31.000	31.000	.000	- 163.300	- 158.734	116.355
300	17.955	31.111	31.000	.033	- 163.312	- 158.705	115.617
400	18.640	36.378	31.714	1.866	- 170.356	- 155.705	85.073
500	18.990	40.577	33.081	3.748	- 170.003	- 152.083	66.475
600	19.240	44.061	34.629	5.659	- 169.631	- 148.534	54.103
700	19.510	47.345	36.194	7.595	- 169.241	- 145.048	45.286
800	19.950	49.678	37.718	9.567	- 169.158	- 141.591	38.681
900	20.520	52.059	39.161	11.590	- 168.885	- 138.162	33.550
1000	21.180	54.254	40.580	13.674	- 168.606	- 134.762	29.452
1100	21.970	56.309	41.918	15.831	- 168.309	- 131.393	26.105
1200	22.840	58.258	43.199	18.071	- 169.764	- 127.899	23.294
1300	23.760	60.122	44.429	20.401	- 169.059	- 124.437	20.920
1400	24.710	61.918	45.615	22.824	- 168.262	- 121.035	18.894
1500	25.650	63.655	46.760	25.342	- 167.372	- 117.692	17.148

June 30, 1974

CALCIUM DIBROMIDE ($CaBr_2$) (CRYSTAL) GFW = 199.888 Br_2Ca

$S^\circ_{298.15}$ = [31.0 ± 1.0] gibbs/mol
Tm = 1015 K

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = -163.3 ± 1.0 kcal/mol
ΔHm° = 6.95 ± 0.15 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 71.3 ± 3.0 kcal/mol

Heat of Formation

The adopted enthalpy of formation is the mean of three values derived from two independent paths. One path involves the heats of solution of Ca(c) and $CaBr_2$(c) in HBr·555 H_2O which were measured by Ehrlich et al. (1). Recalculation of their results using recent thermal data (2, 3) for aqueous HBr yields $\Delta Hf^\circ_{298}(CaBr_2, c)$ = -164.0 kcal/mol. The uncertainty in this value could approach ± 1.0 kcal/mol due primarily to the rather impure metal (99.3% free Ca) used in these measurements.

An alternate path used to obtain values for ΔHf° involves the results of measurements on the heat of solution of $CaBr_2$ (c) in aqueous solution. The work (4-6) reported in this area has been reviewed by Bichowsky and Rossini (7). Recalculation of these results using $\Delta Hf^\circ_{298}(Ca^{+2}, \infty\ aq)$ = -129.74 kcal/mol (8) and $\Delta Hf^\circ_{298}(Br^-, \infty\ aq)$ = -29.039 ± 0.036 kcal/mol (2) yields values for ΔHf° of $CaBr_2$(c) in kcal/mol of -162.3 (4), -160.2 (5), and -163.6 (6). The disagreement in these values is disturbing but can be mostly accounted for when one considers the difficulties involved in the preparation (6) of "pure" anhydrous $CaBr_2$.

A mean value (-163.3 kcal/mol) for $\Delta Hf^\circ_{298}(CaBr_2, c)$ of three results (1, 4, and 6) is preferred because of the difficulties reported in obtaining and keeping samples free of impurities. NBS (8) has selected essentially the same value (-163.2 kcal/mol) from their analysis of the available data.

Heat Capacity and Entropy

No low temperature Cp° data have been reported for $CaBr_2$; thus, the value of S°_{298} must be estimated. Application of the Berthelot principle (9) to the process $SrBr_2(c) + Ca(c) = CaBr_2(c) + Sr(c)$ gives S°_{298} = 31.7 ± 1.5 eu for $CaBr_2$. Auxiliary entropies are taken from the JANAF tables (10). Also, JANAF entropies (10) for the other three calcium dihalides suggest a value near 30.5 eu for $CaBr_2$. We adopt S°_{298} = 31 ± 1 eu which is the value selected by NBS (8). Other reported estimates for S°_{298} are 32.0 ± 2.8 eu (11), 32.2 ± 0.7 eu (12), and 33 eu (13).

Cp° at 298.15 K has not been measured. However, Janz et al. (14) measured relative enthalpies (434-1013 K) for $CaBr_2$ and reported the results in equation form. Their equation gives Cp° = 16.3 gibbs/mol at 298.15 K which appears to be too low by about 2 units when compared with JANAF Cp° data for several other alkaline earth dihalides. The only other enthalpy study that has been reported is that of Dworkin and Bredig (15) who measured $(H^\circ_{1015}-H^\circ_{298})$ = 14.00 kcal/mol at Tm in a copper block drop-calorimeter. We adopt this result. JANAF data (10) are used to obtain Cp° at 298.15 K from the process $CaCl_2(c) + 2\ KBr(c) = CaBr_2(c) + 2\ KCl(c)$ by assuming ΔCp = 0. Data in the temperature range 300-1013 K are estimated by comparison with those for CaF_2 and $CaCl_2$ (10). More weight is given to the results for $CaCl_2$, since it has the same crystal structure (15) as $CaBr_2$ and nearly the same melting temperature (1045 K) (10) and enthalpy $(H^\circ_{1045}-H^\circ_{298}$ = 14.2 kcal/mol) (10) at Tm as does $CaBr_2$. The Cp° estimates are also made so as to reproduce as closely as possible the adopted enthalpy at 1015 K. Our estimated Cp° data give a value of $(H^\circ_{1015}-H^\circ_{298})$ = 13.994 kcal/mol which agrees with the measured value (15) to within 6 calories. Cp° data above 1015 K are obtained by graphical extrapolation. The enthalpies obtained from the equation of Janz et al. (14) are systematically lower than our adopted values. The deviation is -0.4% at 1015 K; it increases at lower temperatures and reaches a maximum value of -2.7% at 600 K.

Melting Data

See $CaBr_2$ (ℓ) table.

Sublimation Data

ΔHs°_{298} is calculated as the difference in the adopted heats of formation for the gas and crystal at 298.15 K.

References

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Br_2Ca

Calcium Dibromide ($CaBr_2$) Br_2Ca

(Liquid) GFW = 199.888

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.935	35.340	35.339	.000	− 158.458	− 155.186	113.754
300	17.955	35.451	35.340	.033	− 158.470	− 155.165	113.038
400	18.640	40.718	36.353	1.866	− 165.515	− 152.600	83.377
500	18.990	44.917	37.420	3.748	− 165.161	− 149.411	65.307
600	19.240	48.401	38.968	5.659	− 164.789	− 146.296	53.288
700	27.000	51.387	40.534	7.597	− 164.398	− 143.245	44.723
800	27.000	54.992	42.121	10.297	− 163.587	− 140.272	38.320
900	27.000	58.172	43.731	12.997	− 162.637	− 137.415	33.369
1000	27.000	61.017	45.320	15.697	− 161.742	− 134.660	29.430
1100	27.000	63.590	46.866	18.397	− 160.902	− 131.994	26.225
1200	27.000	65.939	48.359	21.097	− 161.897	− 129.249	23.539
1300	27.000	68.101	49.795	23.797	− 160.822	− 126.571	21.279
1400	27.000	70.102	51.175	26.497	− 159.748	− 123.977	19.354
1500	27.000	71.964	52.500	29.197	− 158.676	− 121.460	17.697
1600	27.000	73.707	53.771	31.897	− 157.605	− 119.014	16.257
1700	27.000	75.344	54.993	34.597	− 156.535	− 116.634	14.994
1800	27.000	76.887	56.167	37.297	− 192.360	− 113.638	13.798
1900	27.000	78.347	57.296	39.997	− 191.071	− 109.298	12.572
2000	27.000	79.732	58.383	42.697	− 189.785	− 105.030	11.477
2100	27.000	81.049	59.432	45.397	− 188.501	− 100.823	10.493
2200	27.000	82.305	60.443	48.097	− 187.221	− 96.678	9.604
2300	27.000	83.505	61.420	50.797	− 185.946	− 92.591	8.798
2400	27.000	84.654	62.364	53.497	− 184.677	− 88.558	8.064
2500	27.000	85.757	63.278	56.197	− 183.414	− 84.579	7.394

June 30, 1974

CALCIUM DIBROMIDE ($CaBr_2$) (LIQUID) GFW = 199.888 Br_2Ca

$S^\circ_{298.15}$ = [35.340] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [−158.458] kcal/mol

Tm = 1015 K ΔHm° = 6.95 ± 0.15 kcal/mol

Tb = 2083 K ΔHv° = 48.0 kcal/mol

Heat of Formation

ΔHf° of $CaBr_2(\ell)$ is obtained from that of the crystal by addition of ΔHm° and the difference in the values of (H°_{1015}−H°_{298}) for the crystal and liquid. Toguri et al. (1) have reported a Kp value for the anion exchange equilibrium 0.5 $CaBr_2(\ell)$ + HCl(g) = 0.5 $CaCl_2(\ell)$ + HBr(g) at 1073 K. A third law analysis of this single value gives ΔHr°_{298} = −0.22 kcal/mol with JANAF functions. The third law heat leads to $\Delta Hf^\circ_{298}(\ell)$ = −157.9 kcal/mol which supports our adopted value by an independent path.

Heat Capacity and Entropy

Cp° of the liquid above 700 K is the value (27.0 gibbs/mol) determined by Dworkin and Bredig (2) from enthalpy measurements in the vicinity of the melting point. A similar enthalpy study (1013-1132 K) by Janz et al. (3) suggests only a slightly higher value (27.38 gibbs/mol) for Cp° of $CaBr_2(\ell)$. A glass transition is assumed at 700 K below which Cp° is that of the crystal.

The entropy at 298.15 K is obtained in a manner analogous to that of the heat of formation.

Melting Data

The adopted value of Tm is that measured calorimetrically by Dworkin and Bredig (2). Similar measurements by Janz et al. (3) gave essentially the same value (1013 K). Other reported values for Tm are 1018 K (4), 1003 K (5-7), and 1016 K (8).

ΔHm° is that measured by Dworkin and Bredig (2) in a copper block drop-calorimeter. Another calorimetrically determined value (ΔHm° = 6.86 ± 0.09 kcal/mol, 3) and one based on cryoscopic measurements (ΔHm° = 7.03 ± 0.35 kcal/mol, 4) bracket the selected value.

Vaporization Data

Tb is the temperature at which ΔGr° for the process $CaBr_2(\ell)$ = $CaBr_2(g)$ approaches zero. ΔHv° is the difference in the heats of formation of the gas and liquid at Tb. Peterson and Hutchison (9) obtained Tb = 2088 K from vapor pressure measurements on the liquid (1149-1321 K). This value is nearly identical to our result.

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Br_2Ca

Calcium Dibromide ($CaBr_2$) Br_2Ca

(Ideal Gas) GFW = 199.888

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.776	-88.546	-88.546	INFINITE
100	12.557	60.292	87.663	-2.737	-88.409	-92.770	202.749
200	13.969	69.521	76.509	-1.397	-88.782	-97.003	106.000
298	14.433	75.200	75.200	.000	-92.000	-100.612	73.750
300	14.438	75.289	75.200	.027	-92.018	-100.665	73.334
400	14.630	79.473	75.769	1.481	-99.441	-102.028	55.745
500	14.725	82.749	76.850	2.950	-99.501	-102.667	44.876
600	14.778	85.439	78.064	4.425	-99.565	-103.294	37.625
700	14.811	87.719	79.284	5.905	-99.631	-103.911	32.443
800	14.832	89.699	80.465	7.387	-100.038	-104.489	28.545
900	14.847	91.446	81.590	8.871	-100.304	-105.029	25.505
1000	14.858	93.011	82.655	10.356	-100.624	-105.537	23.065
1100	14.866	94.428	83.662	11.842	-100.998	-106.012	21.063
1200	14.872	95.722	84.614	13.329	-103.206	-106.297	19.359
1300	14.876	96.912	85.515	14.817	-103.343	-106.548	17.912
1400	14.880	98.015	86.369	16.304	-103.482	-106.790	16.671
1500	14.883	99.042	87.180	17.793	-103.621	-107.022	15.593
1600	14.886	100.002	87.951	19.281	-103.762	-107.244	14.649
1700	14.888	100.905	88.687	20.770	-103.903	-107.456	13.814
1800	14.889	101.756	89.390	22.259	-140.939	-106.981	12.989
1900	14.891	102.561	90.062	23.748	-140.861	-105.096	12.089
2000	14.892	103.325	90.706	25.237	-140.786	-103.217	11.279
2100	14.893	104.051	91.324	26.726	-140.713	-101.340	10.547
2200	14.894	104.744	91.919	28.215	-140.644	-99.467	9.881
2300	14.895	105.406	92.491	29.705	-140.579	-97.596	9.274
2400	14.896	106.040	93.042	31.194	-140.521	-95.728	8.717
2500	14.896	106.648	93.574	32.684	-140.463	-93.863	8.205
2600	14.897	107.232	94.089	34.174	-140.424	-91.999	7.733
2700	14.897	107.795	94.586	35.663	-140.391	-90.139	7.296
2800	14.898	108.336	95.067	37.153	-140.369	-88.277	6.890
2900	14.898	108.859	95.534	38.643	-140.359	-86.416	6.513
3000	14.899	109.364	95.987	40.133	-140.365	-84.557	6.160
3100	14.999	109.853	96.426	41.623	-140.389	-82.695	5.830
3200	14.899	110.326	96.853	43.113	-140.431	-80.833	5.521
3300	14.899	110.784	97.268	44.603	-140.496	-78.973	5.230
3400	14.900	111.229	97.672	46.093	-140.582	-77.107	4.956
3500	14.900	111.661	98.066	47.583	-140.694	-75.236	4.698
3600	14.900	112.081	98.449	49.073	-140.833	-73.365	4.454
3700	14.900	112.489	98.823	50.563	-140.999	-71.489	4.223
3800	14.901	112.886	99.188	52.053	-141.196	-69.607	4.003
3900	14.901	113.273	99.545	53.543	-141.425	-67.720	3.795
4000	14.901	113.651	99.892	55.033	-141.685	-65.829	3.597
4100	14.901	114.019	100.233	56.523	-141.978	-63.929	3.408
4200	14.901	114.378	100.565	58.013	-142.305	-62.021	3.227
4300	14.901	114.728	100.890	59.503	-142.667	-60.105	3.055
4400	14.901	115.071	101.209	60.993	-143.062	-58.179	2.890
4500	14.901	115.406	101.521	62.483	-143.493	-56.247	2.732
4600	14.902	115.733	101.826	63.973	-143.957	-54.302	2.580
4700	14.902	116.054	102.125	65.464	-144.454	-52.345	2.434
4800	14.902	116.368	102.419	66.954	-144.987	-50.384	2.294
4900	14.902	116.675	102.707	68.444	-145.551	-48.405	2.159
5000	14.902	116.976	102.989	69.934	-146.146	-46.416	2.029
5100	14.902	117.271	103.266	71.424	-146.773	-44.418	1.903
5200	14.902	117.560	103.538	72.915	-147.427	-42.404	1.782
5300	14.902	117.844	103.806	74.405	-148.110	-40.376	1.665
5400	14.902	118.123	104.068	75.895	-148.820	-38.340	1.552
5500	14.902	118.396	104.326	77.385	-149.554	-36.284	1.442
5600	14.902	118.665	104.580	78.875	-150.312	-34.221	1.336
5700	14.902	118.928	104.829	80.366	-151.090	-32.138	1.232
5800	14.902	119.188	105.075	81.856	-151.889	-30.043	1.132
5900	14.902	119.442	105.316	83.346	-152.707	-27.936	1.035
6000	14.902	119.693	105.553	84.836	-153.542	-25.819	.940

June 30, 1974

CALCIUM DIBROMIDE ($CaBr_2$) (IDEAL GAS) GFW = 199.888 Br_2Ca

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = [75.2 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -88.5 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -92.0 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[148](1)
[47](2)
330 (1)

Bond Distance: Ca-Br = 2.67 ± 0.03 Å

Bond Angle: Br-Ca-Br = 180°

σ = 2

Rotational Constant: B_o = 0.014797 cm^{-1}

Heat of Formation

The selection of ΔHf° = -92.0 ± 2.0 kcal/mol for $CaBr_2(g)$ is based on results derived from two independent means. Peterson and Hutchison (1, 2) have reported results of an extensive study of the vapor pressures (1149-1321 K) for liquid $CaBr_2$. Measurements were made by the Knudsen effusion method on a sample which had been prepared by direct union of high purity elements. X-ray diffraction patterns on the final product showed no metal or oxide lines. Schofield and Sugden (3) investigated the equilibrium Ca(g) + 2 HBr(g) = $CaBr_2$(g) + 2 H(g) in H_2-O_2-N_2 flames and reported Kp data for temperatures in the range 2137-2532 K. Results of our second and third law analysis of these data are tabulated below. We assume that the dibromide monomer is the only vapor species produced in the volatilization of $CaBr_2(\ell)$. Support for this assumption is provided by mass spectra for some of the other alkaline earth dihalides (4). These studies indicate that the saturated vapors consist predominately of the metal dihalide monomer and agree with predictions which were made by Brewer et al. (5) for these dihalide molecules. Included in the table for comparison are results of our analysis of older vapor pressure data (6, 7) which have been reviewed by Brewer et al. (5).

Reaction	Source	Method	No. of Points	Temp. Range, K	ΔHr°, kcal/mol 2nd Law	ΔHr°, kcal/mol 3rd Law	Drift eu	ΔHf°_{298} ($CaBr_2$, g)[a] kcal/mol
A	Peterson and Hutchison(1,2)	Knudsen Effusion	18[b]	1149-1321	65.7	67.70 ± 0.60	1.6 ± 1.3	-90.8 ± 1.6
B	Brewer (5,6)		1	990		68.9		-94.4
A	Brewer (5,7)	Boiling Point	2	1180;1480	62.5	64.76 ± 0.7	1.7	-93.7 ± 1.7
C	Schofield and Sugden (3)	Flame Kp	8[b]	2137-2532	-9.4	-14.38 ± 1.7	-2.1 ± 3.2	-93.2 ± 2.0

Reactions: (A) $CaBr_2(\ell) = CaBr_2(g)$

(B) $CaBr_2(c) = CaBr_2(g)$

(C) $Ca(g) + 2\ HBr(g) = CaBr_2(g) + 2\ H(g)$

[a] Third law values.

[b] One point rejected due to failure of a statistical test.

In the selection of ΔHf° no weight is given to those measurements made prior to 1965. Also, we note that Schofield and Sugden (3) reported in the same paper similar results for $SrCl_2$ and $BaCl_2$ which lead to ΔHf° values that are quite consistent with JANAF heats of formation (4). We, therefore, choose to select an average value of the results of Peterson and Hutchison (1, 2) and Schofield and Sugden (3). An earlier analysis (14) of the vapor pressure data (1, 2) with older functions (5) gave ΔHf° of -95.2 kcal/mol.

Heat Capacity and Entropy

The bond length is from the high-temperature electron diffraction work of Akishin and Spiridonov (8). Electron diffraction patterns (8) were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton et al. (9), using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $CaBr_2$ molecule. The absence of dipolar character is most reasonably explained by a linear and centrosymmetric configuration. We adopt a linear structure for $CaBr_2$. Its moment of inertia is 1.8917×10^{-37} g cm^2.

The antisymmetric stretching frequency (ν_3) was observed in the high-temperature infrared spectra of $CaBr_2$ vapor by Baikov (10). The symmetric stretching (ν_1) and bending (ν_2) frequencies are calculated from force constants by the valence force method (11). The observed value of ν_3 gives k = 1.028×10^5 dynes/cm which leads to ν_1 = 148 cm^{-1}. Other estimates that have been reported for ν_1 (in cm^{-1}) are 148 (10), 164 (5), and 172 (13). A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $CaCl_2$ (ratio = 81, 4) and $SrBr_2$ (ratio = [100], 4) suggests a value near 100 for $CaBr_2$. This value for the ratio gives $k\delta/\ell^2 = 1.028 \times 10^3$ dynes/cm, or ν_2 = 47 cm^{-1}. However, similar data for $BeBr_2$ (12) indicate that the value of the ratio could be as low as 41. This leads to a ν_2 = 73 cm^{-1} which agrees with the value (85 cm^{-1}) recommended by Krasnov and Svettsov (13). Brewer et al. (5) choose ν_2 = 52 cm^{-1}. We prefer the lowest value of ν_2 (47 cm^{-1}) at this time but include in the uncertainty (± 2.0 eu) assigned to the value of S°_{298} the possibility that the highest value (85 cm^{-1}) is correct. The singlet ground state is assigned by analogy with that for $BaCl_2$ (4).

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Br_2Ca

Magnesium Dibromide ($MgBr_2$) Br_2Mg

(Crystal) GFW = 184.113

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	17.486	28.000	28.000	.000	- 125.300	- 120.471	88.307
300	17.540	28.108	28.000	.032	- 125.312	- 120.440	87.740
400	18.470	33.290	28.700	1.836	- 132.362	- 117.352	64.118
500	19.059	37.478	30.051	3.714	- 132.009	- 113.639	49.671
600	19.462	40.989	31.589	5.640	- 131.640	- 110.000	40.068
700	19.830	44.017	33.153	7.605	- 131.261	- 106.423	33.227
800	20.209	46.689	34.681	9.606	- 130.881	- 102.901	28.111
900	20.619	49.093	36.151	11.647	- 130.499	- 99.427	24.144
1000	21.065	51.288	37.556	13.731	- 132.234	- 95.812	20.940
1100	21.545	53.318	38.898	15.862	- 131.807	- 92.193	18.317
1200	22.050	55.214	40.180	18.041	- 131.358	- 88.611	16.138
1300	22.570	57.000	41.405	20.272	- 130.885	- 85.067	14.301
1400	23.080	58.691	42.580	22.555	- 160.752	- 81.082	12.657
1500	23.590	60.301	43.708	24.888	- 159.824	- 75.424	10.989

June 30, 1966; June 30, 1974

MAGNESIUM DIBROMIDE ($MgBr_2$) (CRYSTAL) GFW = 184.113 Br_2Mg

$S^\circ_{298.15}$ = [28.0 ± 1.0] gibbs/mol
Tm = 984 ± 15 K

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = -125.3 ± 0.5 kcal/mol
ΔHm° = [9.4 ± 1.0] kcal/mol
$\Delta Hs^\circ_{298.15}$ = 52.9 ± 2.0 kcal/mol

Heat of Formation

The selected value for ΔHf° is that given in NBS Tech. Note 270-6 (1). This value is derived from the solution calorimetric measurements of Finch et al. (2). Their enthalpies for the reaction of crystalline MgO with aqueous HBr and solution of anhydrous $MgBr_2$ in the same solvent are combined to give ΔHr_{298} = 7.77 ± 0.40 kcal/mol for the process MgO(c) + 2 HBr(aq) = $MgBr_2(c) + H_2O(\ell)$. When this result is combined with auxiliary data (1, 3, and 4), the selected value is obtained. This value is confirmed by an independent means. Bichowsky and Rossini (5) give the heat of solution of $MgBr_2$ in 800 H_2O as -43.3 kcal/mol based on measurements by Beketoff (6). Correction of this value to 298.15 K and infinite dilution gives a value for ΔH°_{soln} which leds to ΔHf° = -125.4 kcal/mol when combined with $\Delta Hf^\circ_{298}(Mg^{+2}, \infty\ aq)$ = -111.58 kcal/mol (1) and $\Delta Hf^\circ_{298}(Br^-, \infty\ aq)$ = -29.039 ± 0.035 kcal/mol (4).

Two emf studies (7, 8) on the potential of the magnesium electrode in ether solution give results in disagreement with the calorimetric values. From these cell data we derive ΔHf° values of -118.8 kcal/mol (7) and -115.0 kcal/mol (8). These rather large discrepancies are taken as an indication that the electrodes are probably irreversible under these conditions. In fact one study (8) reported that from 10 to 20 hours were required before stable emf values were obtained.

Heat Capacity and Entropy

Cp° at 298.15 K is obtained from the process $MgCl_2(c) + 2\ NaBr(c) = MgBr_2(c) + 2\ NaCl(c)$ by assuming ΔCp° is zero. A comparison of the Cp° value (17.49 gibbs/mol) with those for other alkaline earth dihalides shows that it is reasonable. Cp° data above 300 K are estimated by comparison with similar data for $MgCl_2$ and CaI_2 (3).

Several estimates (9-12) lying in the range 27-30 eu for S°_{298} have been reported. Available experimental data for several other alkaline earth dihalides suggest a value for S°_{298} of $MgBr_2(c)$ near 28 eu. We tentatively adopt this value. It is also the value recommended by Kelley and King (10) and NBS (1).

Melting Data

The value of Tm is that determined from cooling curves by Kellner (13, 14). The uncertainty in these measurements is probably near ± 15 K.

ΔHm° is calculated from a ΔSm° = 9.5 eu by multiplication of Tm. ΔSm° is assumed the same as that for CaI_2 (3) which also has the hexagonal CdI_2 structure (15). Kelley (16) obtained a value of ΔHm° equal to 8.3 kcal/mol from an analysis of phase diagrams for the systems $MgBr_2$-MBr(M = Na, K, 14) and $MgBr_2$-LiBr (17). However, he implied that the value was somewhat uncertain. Furthermore, it is noted that several ΔHm° values listed by Kelley for other alkaline earth dihalides deviate considerably (1-3 kcal/mol) from those measured calorimetrically (18). Thus, we prefer the estimated value at this time. (See also $MgBr_2(\ell)$ table Heat of Formation Section.)

Heat of Sublimation

See $MgBr_2(g)$ table.

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Br_2Mg

Magnesium Dibromide ($MgBr_2$) Br_2Mg

(Liquid) GFW = 184.113

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.486	35.971	35.971	.000	-117.210	-114.757	84.119
300	17.540	36.079	35.971	.032	-117.222	-114.741	83.589
400	18.470	41.260	36.671	1.836	-124.272	-112.450	61.440
500	19.059	45.449	38.021	3.714	-123.919	-109.534	47.877
600	19.462	48.960	39.559	5.640	-123.550	-106.693	38.863
700	25.000	51.988	41.124	7.605	-123.171	-103.913	32.443
800	25.000	55.326	42.695	10.105	-122.292	-101.223	27.653
900	25.000	58.271	44.265	12.605	-121.451	-98.639	23.953
1000	25.000	60.905	45.300	15.105	-122.770	-95.966	20.973
1100	25.000	63.287	47.283	17.605	-121.974	-93.326	18.542
1200	25.000	65.463	48.709	20.105	-121.204	-90.756	16.529
1300	25.000	67.464	50.075	22.605	-120.462	-88.248	14.836
1400	25.000	69.317	51.384	25.105	-150.112	-85.318	13.319
1500	25.000	71.041	52.638	27.605	-149.017	-80.729	11.762
1600	25.000	72.655	53.839	30.105	-147.923	-76.212	10.410
1700	25.000	74.170	54.991	32.605	-146.830	-71.762	9.226
1800	25.000	75.599	56.097	35.105	-145.738	-67.379	8.181
1900	25.000	76.951	57.159	37.605	-144.646	-63.054	7.253
2000	25.000	78.233	58.181	40.105	-143.557	-58.790	6.424

June 30, 1966; June 30, 1974

MAGNESIUM DIBROMIDE ($MgBr_2$) (LIQUID) GFW = 184.113 Br_2Mg

$S°_{298.15}$ = [35.971] gibbs/mol
Tm = 984 ± 15 K
Tb (to monomer) = 1431 K

$\Delta Hf°_{298.15}$ = [-117.210] kcal/mol
ΔHm° = [9.4 ± 1.0] kcal/mol
ΔHv° = 35.6 kcal/mol

Heat of Formation

ΔHf° for the liquid is derived from that for the crystal by addition of ΔHm° and the difference in the values of ($H°_{984}$-$H°_{298}$) for the crystal and liquid. The derived value is supported by results obtained from an equilibrium study (1) of the anion exchange reaction 0.5 $MgBr_2(\ell)$ + HCl(g) = 0.5 $MgCl_2(\ell)$ + HBr(g). A third law analysis of the Kp value reported for the equilibrium at 1073 K gives ΔHr_{298} = 0.05 kcal/mol which leads to $\Delta Hf(\ell)$ = -117.2 kcal/mol. In the same paper, Toguri et al. (1) reported similar data for the chloride-bromide salts of Ca, K, and Na. These results lead to ΔHf values for the molten bromides which show deviations from adopted JANAF values (2) of no more than 0.6 kcal/mol. Thus, although the exact agreement in the ΔHf° values for $MgBr_2(\ell)$ is fortuitous, it does tend to substantiate our thermal data.

Heat Capacity and Entropy

Cp° for the liquid is estimated as 25.0 gibbs/mol by analogy with measured Cp° data for molten $CaBr_2$ and $SrBr_2$ (2). The value is taken to be constant above the assumed glass transition at 700 K. Below 700 K Cp° is that of the crystal.

$S°_{298}$ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See $MgBr_2$(c) table.

Vaporization Data

Tb is the temperature at which ΔGr for the process $MgBr_2(\ell)$ = $MgBr_2(g)$ approaches zero. ΔHv° is the difference in the heats of formation of the gas and liquid at Tb.

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Br_2Mg

Magnesium Dibromide ($MgBr_2$) Br_2Mg

(Ideal Gas) GFW = 184.113

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	−3.588	−68.933	−68.933	INFINITE
100	11.871	57.698	83.866	−2.619	−68.786	−73.041	159.632
200	13.492	66.448	73.188	−1.348	−69.248	−77.251	84.416
298	14.032	71.922	71.922	.000	−72.400	−80.666	59.130
300	14.041	72.009	71.923	.026	−72.418	−80.717	58.802
400	14.372	76.099	72.478	1.448	−79.850	−81.963	44.782
500	14.543	79.327	73.536	2.895	−79.928	−82.482	36.053
600	14.651	81.989	74.730	4.356	−80.024	−82.985	30.227
700	14.715	84.253	75.933	5.824	−80.142	−83.469	26.060
800	14.758	86.221	77.098	7.298	−80.289	−83.935	22.930
900	14.788	87.961	78.211	8.775	−80.471	−84.380	20.490
1000	14.809	89.520	79.265	10.255	−82.810	−84.621	18.494
1100	14.825	90.932	80.262	11.737	−83.032	−84.794	16.847
1200	14.838	92.223	81.206	13.220	−83.279	−84.943	15.470
1300	14.847	93.411	82.100	14.704	−83.553	−85.070	14.301
1400	14.855	94.512	82.948	16.189	−114.218	−84.696	13.222
1500	14.861	95.537	83.753	17.675	−114.137	−82.591	12.033
1600	14.866	96.496	84.520	19.162	−114.056	−80.491	10.995
1700	14.871	97.397	85.251	20.649	−113.976	−78.394	10.078
1800	14.874	98.247	85.950	22.136	−113.897	−76.305	9.265
1900	14.877	99.052	86.618	23.623	−113.818	−74.217	8.537
2000	14.880	99.815	87.259	25.111	−113.741	−72.136	7.883
2100	14.882	100.541	87.874	26.599	−113.664	−70.059	7.291
2200	14.884	101.233	88.466	28.088	−113.588	−67.983	6.753
2300	14.886	101.895	89.036	29.576	−113.514	−65.910	6.263
2400	14.887	102.528	89.585	31.065	−113.440	−63.843	5.814
2500	14.888	103.136	90.115	32.553	−113.369	−61.779	5.401
2600	14.889	103.720	90.627	34.042	−113.298	−59.714	5.019
2700	14.891	104.282	91.122	35.531	−113.229	−57.657	4.667
2800	14.891	104.824	91.602	37.020	−113.162	−55.601	4.340
2900	14.892	105.346	92.067	38.510	−113.095	−53.544	4.035
3000	14.893	105.851	92.518	39.999	−113.032	−51.493	3.751
3100	14.894	106.339	92.956	41.488	−112.972	−49.442	3.486
3200	14.894	106.812	93.382	42.978	−112.913	−47.394	3.237
3300	14.895	107.271	93.796	44.467	−112.859	−45.349	3.003
3400	14.895	107.715	94.199	45.957	−112.807	−43.302	2.783
3500	14.896	108.147	94.591	47.446	−112.761	−41.259	2.576
3600	14.896	108.567	94.973	48.936	−112.719	−39.217	2.381
3700	14.897	108.975	95.346	50.425	−112.682	−37.175	2.196
3800	14.897	109.372	95.710	51.915	−112.650	−35.134	2.021
3900	14.897	109.759	96.066	53.405	−112.624	−33.096	1.855
4000	14.898	110.136	96.413	54.895	−112.605	−31.058	1.697
4100	14.898	110.504	96.752	56.384	−112.595	−29.021	1.547
4200	14.898	110.863	97.084	57.874	−112.591	−26.983	1.404
4300	14.899	111.214	97.408	59.364	−112.596	−24.943	1.268
4400	14.899	111.556	97.726	60.854	−112.609	−22.903	1.138
4500	14.899	111.891	98.037	62.344	−112.632	−20.864	1.013
4600	14.899	112.219	98.342	63.834	−112.665	−18.823	.894
4700	14.899	112.539	98.640	65.324	−112.708	−16.761	.780
4800	14.900	112.853	98.933	66.814	−112.764	−14.742	.671
4900	14.900	113.160	99.220	68.304	−112.830	−12.698	.566
5000	14.900	113.461	99.502	69.794	−112.908	−10.653	.466
5100	14.900	113.756	99.779	71.283	−113.001	−8.613	.369
5200	14.900	114.045	100.050	72.774	−113.104	−6.563	.276
5300	14.900	114.329	100.317	74.264	−113.221	−4.508	.186
5400	14.900	114.608	100.579	75.754	−113.353	−2.462	.100
5500	14.901	114.881	100.837	77.244	−113.499	−.403	.016
5600	14.901	115.149	101.090	78.734	−113.661	1.651	−.064
5700	14.901	115.413	101.339	80.224	−113.838	3.717	−.143
5800	14.901	115.672	101.584	81.714	−114.030	5.778	−.218
5900	14.901	115.927	101.825	83.204	−114.240	7.848	−.291
6000	14.901	116.178	102.062	84.694	−114.466	9.911	−.361

June 30, 1965; June 30, 1974

MAGNESIUM DIBROMIDE ($MgBr_2$) (IDEAL GAS) GFW = 184.113 Br_2Mg

Point Group [$D_{\infty h}$]
$S^\circ_{298.15}$ = [71.9 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = −68.9 ± 2.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −72.4 ± 2.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[179](1)
[70](2)
490 (1)

Bond Distance: Mg-Br = 2.34 ± 0.03 Å   Bond Angle: Br-Mg-Br = [180°]   σ = 2

Rotational Constant: B_0 = [0.01926] cm^{-1}

Heat of Formation

ΔHf°_{298} of the gas is obtained from that of the crystal by addition of ΔHs°_{298} = 52.9 ± 2.0 kcal/mol. The selected value for the heat of sublimation is derived from results of a mass spectrometric-Knudsen effusion study by Berkowitz and Marquart (1). The presence of ~2% dimer in the vapor phase over the solid at near 800 K was revealed by the mass spectral results. Berkowitz and Marquart (1), using $MgBr_2^+$-ion intensity as a measure of the monomer concentration, obtained a second law ΔHs = 50.3 kcal/mol at 751 K. This value when corrected to 298.15 K gives ΔHs°_{298} = 52.4 kcal/mol. Absolute partial pressures were also determined at 798 and 842 K by integrating the ion current during complete volatilization of the sample. A third law analysis of these two pressures gives a heat of sublimation equal to 53.4 kcal/mol which is in good agreement with the value obtained from the ion intensities by the second law. The drift in the third law analysis is 1.0 eu. The selected value of ΔHs°_{298} is an average of these two results.

Heat Capacity and Entropy

The bond length is from the electron-diffraction measurements of Akishin and Spiridonov (3). Their diffraction patterns for $MgBr_2$ were satisfactorily explained on the basis of a linear model. Klemperer et al. (4, 5) have performed electric quadrupole deflection experiments on several symmetrical triatomic dihalides in an attempt to determine which molecules possess permanent dipole moments. Their results on the geometrics of the alkaline earth dihalides have been summarized by Hayes (6) who pointed out that the linear form is favored by the light metal-heavy halogen combination. Thus, one would expect $MgBr_2$ to be linear, and we adopt this configuration. The moment of inertia is 1.453 x 10^{-37} g cm^2.

The antisymmetric stretching frequency (ν_3 = 490 cm^{-1}) has been observed in the infrared absorption spectrum of gaseous $MgBr_2$ by Randall et al. (7). The symmetric stretching (ν_1) and bending (ν_2) frequencies are calculated from force constants by the valence force method (8). The observed ν_3 frequency leads to k = 1.5 x 10^5 dynes/cm, or ν_1 = 179 cm^{-1}. A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $MgCl_2$(ratio = 88, 9), $CaBr_2$(ratio = [100], 9), and $SrBr_2$(ratio = [100], 9) suggests a value near 100 for $MgBr_2$. This value for the ratio gives $k\delta/\ell^2$ = 1.5 x 10^3 dynes/cm, or ν_2 = 70 cm^{-1}. Based on similar data for linear $BeBr_2$ (10), it is possible that the value of the ratio could be as low as 41. This ratio corresponds to a bending frequency of 109 cm^{-1}. We prefer the lower value of ν_2, since it is consistent with the observed value for $MgCl_2$(ν_2 = 88 cm^{-1}, 9). However, we do include in the uncertainty of the value for S°_{298} the possibility that the higher value is correct. Brewer et al. (2) used a value for the ratio of 10 and obtained ν_2 = 220 cm^{-1}. By comparison with the observed frequencies for $MgCl_2$ and $BeBr_2$(ν_2 = 220 cm^{-1}, 10) it is unlikely that the value for $MgBr_2$ is this high. Krasnov and Svettsov (11) have reported ν_1 = 188 cm^{-1} and ν_2 = 148 cm^{-1} based on force constant correlations. The ground state is assumed to be singlet by analogy with that for $BaCl_2$ (9).

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Br_2Mg

MAGNESIUM DIBROMIDE UNIPOSITIVE ION ($MgBr_2^+$) (IDEAL GAS) GFW = 184.11245 Br_2Mg^+

Point Group [$D_{\infty h}$]
$S^\circ_{298.15}$ = [76.9 ± 3.0] gibbs/mol
Ground State Configuration [$^2\Pi$]

ΔHf°_0 = 176.7 ± 6.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 174.8 ± 6.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Pi$	[25000]	4
$^2\Sigma$	[30000]	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[150](1)
[50](2)
[450](1)

Bond Distance: Mg-Br = [2.6] Å Bond Angle: Br-Mg-Br = [180]° σ = 2

Rotational Constant: B_o = [0.01560] cm^{-1}

Heat of Formation

Berkowitz and Marquart (1) have reported the appearance potential of $MgBr_2^+$ as $10.6_5 \pm 0.1_5$ eV(245.6 kcal/mol). Assuming this value refers to the direct ionization process $MgBr_2(g) + e^- = MgBr_2^+(g) + 2e^-$, we obtain $\Delta Hf^\circ_0(MgBr_2^+, g)$ = 176.7 ± 6.0 kcal/mol by combining it with $\Delta Hf^\circ_0(MgBr_2, g)$ = -68.9 ± 2.5 kcal/mol (2). The former value is adopted and corresponds to ΔHf°_{298} = 174.8 kcal/mol.

Heat Capacity and Entropy

A comparison of the dissociation energy (D°_0 = 91.0 kcal/mol) for $MgBr_2^+$ with that for $MgBr_2$(D°_0 = 160.3 kcal/mol, 2) suggests the existence of somewhat weaker bonding in the ion relative to the molecule. Thus, one would expect the bond length in the ion to be greater than that for $MgBr_2$. We assume a 10% increase in r_e for the ion. The correlation diagrams of Walsh (3) predict a linear configuration for $MgBr_2^+$(fifteen valence electrons). This prediction is supported by the fact several other fifteen valence electron molecules (BO_2, N_3, NCO, and NNO^+) are now known to be linear (2). We adopt a linear configuration for the ion. The moment of inertia is 1.7938×10^{-37} g cm^2.

The vibrational frequencies are estimated to be slightly less than those for $MgBr_2$ (2). The ground state electronic configuration is assumed to be $^2\Pi$ by analogy with those for the isoelectronic molecules (2) BO_2, N_3, NCO, and N_2O^+. Two excited states are also included based on those observed for BO_2 (2). The enthalpy at 0 K is -3.691 kcal/mol.

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Magnesium Dibromide Unipositive Ion ($MgBr_2^+$) Br_2Mg^+
(Ideal Gas) GFW = 184.11245

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	14.174	76.870	76.870	.000	174.800	163.572	- 119.901
300	14.181	76.957	76.870	.026	174.791	163.502	- 119.111
400	14.463	81.080	77.430	1.460	167.868	161.183	- 88.066
500	14.610	84.325	78.496	2.914	168.294	159.463	- 69.701
600	14.696	86.997	79.697	4.380	168.700	157.657	- 57.427
700	14.749	89.267	80.906	5.853	169.083	155.786	- 48.639
800	14.784	91.239	82.077	7.329	169.435	153.861	- 42.033
900	14.809	92.981	83.194	8.809	169.753	151.896	- 36.885
1000	14.826	94.543	84.252	10.291	167.913	150.079	- 32.800
1100	14.840	95.956	85.253	11.774	168.189	148.280	- 29.460
1200	14.850	97.248	86.199	13.259	168.440	146.458	- 26.674
1300	14.858	98.437	87.095	14.744	168.664	144.618	- 24.312
1400	14.864	99.538	87.945	16.230	138.497	143.240	- 22.361
1500	14.869	100.564	88.753	17.717	139.076	143.558	- 20.916
1600	14.873	101.524	89.521	19.204	139.653	143.836	- 19.647
1700	14.877	102.426	90.254	20.691	140.230	144.082	- 18.523
1800	14.880	103.276	90.954	22.179	140.807	144.291	- 17.519
1900	14.882	104.081	91.624	23.667	141.384	144.470	- 16.618
2000	14.884	104.844	92.266	25.156	141.959	144.617	- 15.803
2100	14.886	105.570	92.882	26.644	142.532	144.734	- 15.063
2200	14.888	106.263	93.475	28.133	143.105	144.827	- 14.387
2300	14.889	106.925	94.046	29.622	143.677	144.894	- 13.768
2400	14.890	107.558	94.595	31.111	144.248	144.934	- 13.198
2500	14.891	108.166	95.126	32.600	144.817	144.950	- 12.672
2600	14.892	108.750	95.639	34.089	145.384	144.945	- 12.184
2700	14.894	109.312	96.135	35.578	145.950	144.916	- 11.730
2800	14.895	109.854	96.615	37.067	146.514	144.867	- 11.307
2900	14.896	110.377	97.081	38.557	147.078	144.800	- 10.912
3000	14.897	110.882	97.533	40.047	147.639	144.711	- 10.542
3100	14.898	111.370	97.971	41.536	148.195	144.605	- 10.195
3200	14.900	111.843	98.397	43.026	148.751	144.479	- 9.867
3300	14.901	112.302	98.812	44.516	149.303	144.335	- 9.559
3400	14.903	112.746	99.215	46.007	149.853	144.179	- 9.268
3500	14.905	113.179	99.608	47.497	150.397	144.004	- 8.992
3600	14.908	113.598	99.991	48.988	150.936	143.813	- 8.731
3700	14.910	114.007	100.364	50.478	151.471	143.608	- 8.483
3800	14.914	114.405	100.728	51.970	152.002	143.390	- 8.247
3900	14.917	114.792	101.084	53.461	152.526	143.155	- 8.022
4000	14.921	115.170	101.431	54.953	153.043	142.906	- 7.808
4100	14.926	115.538	101.771	56.445	153.553	142.646	- 7.604
4200	14.931	115.898	102.103	57.938	154.057	142.374	- 7.409
4300	14.936	116.249	102.428	59.432	154.553	142.091	- 7.222
4400	14.942	116.593	102.746	60.926	155.041	141.798	- 7.043
4500	14.949	116.929	103.057	62.420	155.518	141.490	- 6.872
4600	14.956	117.257	103.363	63.915	155.987	141.175	- 6.707
4700	14.964	117.579	103.662	65.411	156.447	140.849	- 6.549
4800	14.972	117.894	103.955	66.908	156.895	140.511	- 6.398
4900	14.981	118.203	104.243	68.406	157.334	140.166	- 6.252
5000	14.991	118.506	104.525	69.904	157.760	139.811	- 6.111
5100	15.001	118.803	104.802	71.404	158.175	139.442	- 5.975
5200	15.012	119.094	105.074	72.905	158.579	139.073	- 5.845
5300	15.023	119.380	105.341	74.406	158.970	138.699	- 5.719
5400	15.035	119.661	105.604	75.909	159.348	138.307	- 5.598
5500	15.047	119.937	105.862	77.413	159.712	137.918	- 5.480
5600	15.060	120.208	106.116	78.919	160.063	137.515	- 5.367
5700	15.074	120.475	106.365	80.425	160.399	137.115	- 5.257
5800	15.088	120.737	106.611	81.934	160.723	136.701	- 5.151
5900	15.102	120.995	106.852	83.443	161.029	136.286	- 5.048
6000	15.117	121.249	107.090	84.954	161.320	135.855	- 4.949

June 30, 1974

Br_2Mg^+

Lead Dibromide ($PbBr_2$)

(Crystal) GFW = 367.008

Br_2Pb

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-4.597	-63.394	-63.394	INFINITE
100	16.300	19.023	54.353	-3.583	-63.471	-63.206	138.137
200	18.300	31.047	40.232	-1.837	-63.499	-62.934	68.771
298	19.020	38.511	38.510	.000	-66.300	-62.317	45.680
300	19.028	38.628	38.511	.035	-66.310	-62.292	45.380
400	19.420	44.156	39.262	1.957	-73.280	-59.501	32.510
500	20.240	48.573	40.696	3.939	-72.854	-56.106	24.524
600	21.220	52.349	42.330	6.011	-72.360	-52.800	19.233
700	22.242	55.696	44.005	8.184	-72.950	-49.395	15.422
800	23.265	58.733	45.659	10.459	-72.292	-46.073	12.587
900	24.288	61.532	47.269	12.837	-71.526	-42.841	10.403
1000	25.311	64.144	48.827	15.317	-70.652	-39.698	8.676

March 31, 1962; Dec. 31, 1973

LEAD DIBROMIDE ($PbBr_2$) (CRYSTAL) GFW = 367.008 Br_2Pb

$S^\circ_{298.15}$ = 38.51 ± 0.5 gibbs/mol
Tm = 644 ± 5 K

ΔHf°_0 = -63.4 ± 0.6 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -66.3 ± 0.6 kcal/mol
ΔHm° = 3.93 ± 0.2 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 41.35 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(PbBr_2, c)$ = -66.3 ± 0.6 kcal/mol is the rounded average of -66.350 kcal/mol calorimetrically determined by Braune and Koref (1) at about 293.15 K and five other values obtained from a second and third law analysis of electromotive force data (2, 3, 4). The auxiliary value $\Delta Hf^\circ_{298.15}(AgBr, c)$ = -23.99 kcal/mol (5) is used in the analysis.

				$-\Delta Hr_{298}$, kcal/mol			$-\Delta Hf^\circ_{298}(PbBr_2, c)$, kcal/mol	
Investigator	Reaction	No. of Points	Temp. Range, K	2nd Law	3rd Law	Drift eu	2nd Law	3rd Law
Krahmer (2)	A	5	273-292	17.88±0.06	18.52±0.04	-2.2±0.2	-65.86	-66.50
Cann and Sumner (3)	A	1	298		18.57			-66.57
Jahn-Held and Jellinek (4)	B	3	288-308	66.68±0.06	66.09±0.04	2.0±0.2	-66.68	-66.09

(A) $Pb(c) + 2\ AgBr(c) = PbBr_2(c) + 2\ Ag(c)$
(B) $Pb(c) + Br_2(\ell) = PbBr_2(c)$

Heat Capacity and Entropy

Cp° (18.4 - 297.0 K) has been measured by Latimer and Hoenshel (6). The enthalpy data of Ehrhardt (273-786 K) (7) and of Goodwin and Kalmus (298-860 K) (8) are discarded because the observed high Tm shows their samples were not pure. (See melting data discussion.) Linsey (16) measured the enthalpy (39 points) of $PbBr_2$ in the range 319-424 K using an ice calorimeter. The heat capacity data of Latimer and Hoenshel (6) is smoothed graphically. The enthalpy data was analyzed by Linsey (16) to yield heat capacity values from 273-644 K. Both sets of heat capacity values are adjusted graphically in the region 200-400 K so as to yield a smooth curve in the vicinity of 298 K. The adjustments are quite small such that the resulting enthalpy at 600 K differs by about 7 cal/mol from the smooth enthalpies reported by Linsey (16). The data of Linsey (16) did not indicate any transitions other than the solid-liquid transition at 644 K.

Latimer and Hoenshel (6) obtained $S^\circ_{15.85}$ = 2.4 eu after allowing for an approach to the T^3 rule. Kelley and King (10) later derived $S^\circ_{17.80}$ = 1.64 eu from the same data; this value is adopted. Combining this with $S^\circ_{298.15} - S^\circ_{17.80}$ = 36.883 eu derived from the adopted Cp° value gives $S^\circ_{298.15}$ = 38.511 ± 0.5 eu. A graphical extrapolation and integration of Cp gives $H^\circ_{17.80} - H^\circ_0$ = 0.0252 kcal/mol. This value may not be entirely consistent with the adopted $S^\circ_{17.80}$ value, but the error involved is undoubtedly small.

Melting Data

The older reported values of Tm have been summarized by Mellor (11). Seven determinations fall in the 636-653 K range and four more range from 753 to 772 K. Included in the high melting range are Tm = 763 K by Ehrhardt (7) and Tm = 761 K by Goodwin and Kalmus (8). Knowles (12), suggested that contamination of the $PbBr_2$ by PbO probably caused the high melting temperatures. The enthalpy measurements of Ehrhardt (7) and of Goodwin and Kalmus (8) are therefore judged not to represent $PbBr_2$. More recently, Blanc and Petit (13) have reported Tm = 640 K and ΔHm = 4.96 kcal/mol from a cryoscopic investigation. A visual polytherm technique was employed by Il'yasov (14) who found Tm = 649 K. Cola et al. (15) determined Tm = 644 K by differential thermal analysis and ΔHm = 4.41 ± 0.07 kcal/mol by differential scanning calorimetry. The enthalpy study by Linsey (16) gave Tm = 644 K and ΔHm° = 3.93 kcal/mol. We adopt these latter two values.

Heat of Sublimation

ΔHs°_{298} = 41.35 kcal/mol is the sum of the heat of fusion, the enthalpy difference of crystal and liquid between the melting point and 298.15 K, and ΔHv_{298}. See $PbBr_2(g)$ table.

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Br_2Pb

Lead Dibromide ($PbBr_2$) Br_2Pb

(Liquid) GFW = 367.008

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	19.020	41.558	41.558	.000	-63.913	-60.839	44.596
300	19.028	41.676	41.558	.035	-63.923	-60.820	44.307
400	26.800	47.205	42.309	1.958	-70.892	-58.333	31.872
500	26.800	53.136	43.909	4.638	-69.766	-55.326	24.183
600	26.800	58.072	45.875	7.318	-68.666	-52.540	19.138
700	26.800	62.203	47.920	9.998	-68.749	-49.748	15.532
800	26.800	65.782	49.934	12.678	-67.686	-47.106	12.869
900	26.800	68.938	51.873	15.358	-66.618	-44.598	10.830
1000	26.800	71.762	53.724	18.038	-65.544	-42.208	9.224
1100	26.800	74.316	55.481	20.718	-64.465	-39.927	7.933
1200	26.800	76.648	57.149	23.398	-63.379	-37.743	6.874
1300	26.800	78.793	58.733	26.078	-62.290	-35.650	5.993
1400	26.800	80.779	60.238	28.758	-61.201	-33.644	5.252
1500	26.800	82.628	61.669	31.438	-60.113	-31.712	4.620
1600	26.800	84.358	63.034	34.118	-59.029	-29.854	4.078
1700	26.800	85.983	64.337	36.798	-57.948	-28.063	3.608
1800	26.800	87.515	65.582	39.478	-56.873	-26.339	3.198
1900	26.800	88.964	66.775	42.158	-55.803	-24.670	2.838
2000	26.800	90.338	67.919	44.838	-54.740	-23.060	2.520

March 31, 1962; Dec. 31, 1973

LEAD DIBROMIDE ($PbBr_2$) (LIQUID) GFW = 367.008 Br_2Pb

$S^\circ_{298.15}$ = 41.558 gibbs/mol

Tm = 644 ± 5 K

Tb = 1185 K

$\Delta Hf^\circ_{298.15}$ = -63.913 kcal/mol

ΔHm° = 3.93 ± 0.2 kcal/mol

ΔHv° = 28.23 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(PbBr_2, \ell)$ = -63.913 kcal/mol is obtained from the sum of the heat of formation of the crystal, the heat of melting and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K, $H^\circ_{644}-H^\circ_{298}$. $\Delta Hf^\circ(\ell)$ can also be obtained from a second and third law analysis of emf measurements for the cell reaction $Pb(\ell) + Br_2(g) = PbBr_2(\ell)$. Results from three investigations are tabulated below. The auxiliary values, $\Delta Hf^\circ_{298}(Pb, \ell)$ = 1.025 kcal/mol (1) and $\Delta Hf^\circ_{298}(Br_2, g)$ = 7.387 kcal/mol (1), are used. The average result for $\Delta Hf^\circ_{298}(\ell)$ is -63.80 kcal/mol, in good agreement with the adopted value.

Investigator	No. of Points	Temp. Range K	$-\Delta Hr^\circ_{298}$, kcal/mol		Drift eu	$\Delta Hf^\circ_{298}(PbBr_2, \ell)$, kcal/mol	
			2nd Law	3rd Law		2nd Law	3rd Law
Salstrom and Hildebrand (2)	16	711-849	73.60±0.10	72.10±0.13	1.9±0.1	-65.19	-63.69
Lantratov and Shevlyakova (3)	1	862		72.36			-63.95
Bloom and Welch (4)	4	723-1000	74.22±0.33	68.79±1.63	6.3±0.4	-65.80	-60.38

Heat Capacity and Entropy

Ehrhardt (5) and Goodwin and Kalmus (6) have reported enthalpy measurements in the liquid temperature range. Their data is rejected because the high melting points observed indicated the samples were not entirely $PbBr_2$. See the $PbBr_2$(c) table discussion. Bizouard and Pauty (7) have measured 26.3 ± 0.6 gibbs/mol for the heat capacity of the molten salt. Linsey (9) reported a heat capacity value of 26.8 gibbs/mol based on enthalpy measurements from Tm to 924 K. This value is adopted and is assumed to represent the heat capacity up to 2000 K. A glass transition is assumed at 400°K below which the heat capacity is that of the crystal.

$S^\circ_{298.15}(PbBr_2, \ell)$ = 42.661 gibbs/mol is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Vaporization Data

Tb = 1185 K is calculated as the temperature at which $\Delta Gr^\circ = 0$ for the reaction $PbBr_2(\ell) = PbBr_2(g)$. ΔHv° = 28.23 kcal/mol is calculated as the difference between ΔHf° at Tb for the gas and the liquid. Bloom and Anthony (8) found an average value of ΔHv° = 29.8 ± 2.0 kcal/mol from mass spectrometric studies in the 660-735 K range. The present table gives ΔHv°_{700} = 34.50 kcal/mol.

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Br_2Pb

Br$_2$Pb

Lead Dibromide ($PbBr_2$)

(Ideal Gas) GFW = 367.008

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.582	- 21.029	- 21.029	INFINITE
100	11.901	66.930	92.899	- 2.597	- 21.135	- 25.661	56.081
200	13.263	75.717	82.325	- 1.321	- 21.633	- 30.003	32.786
298	13.603	81.089	81.089	.000	- 24.950	- 33.662	24.675
300	13.607	81.173	81.089	.025	- 24.970	- 33.716	24.562
400	13.736	85.108	81.625	1.393	- 32.494	- 35.096	19.176
500	13.798	88.180	82.640	2.770	- 32.673	- 35.728	15.617
600	13.832	90.699	83.779	4.152	- 32.869	- 36.320	13.229
700	13.852	92.833	84.924	5.536	- 34.248	- 36.688	11.455
800	13.866	94.684	86.031	6.922	- 34.479	- 37.021	10.114
900	13.875	96.317	87.085	8.309	- 34.704	- 37.325	9.064
1000	13.882	97.780	88.083	9.697	- 34.922	- 37.604	8.218
1100	13.887	99.103	89.025	11.086	- 35.134	- 37.862	7.523
1200	13.890	100.312	89.916	12.474	- 35.340	- 38.100	6.939
1300	13.893	101.423	90.759	13.864	- 35.541	- 38.321	6.442
1400	13.896	102.453	91.558	15.253	- 35.743	- 38.529	6.015
1500	13.898	103.412	92.317	16.643	- 35.945	- 38.720	5.642
1600	13.899	104.309	93.039	18.033	- 36.151	- 38.898	5.313
1700	13.900	105.152	93.727	19.423	- 36.360	- 39.063	5.022
1800	13.901	105.946	94.384	20.813	- 36.575	- 39.218	4.762
1900	13.902	106.698	95.012	22.203	- 36.795	- 39.358	4.527
2000	13.903	107.411	95.614	23.593	- 37.022	- 39.488	4.315
2100	13.904	108.089	96.192	24.983	- 79.704	- 38.053	3.960
2200	13.904	108.736	96.748	26.374	- 79.849	- 36.067	3.583
2300	13.905	109.354	97.283	27.764	- 80.017	- 34.072	3.238
2400	13.905	109.946	97.798	29.155	- 80.206	- 32.069	2.920
2500	13.906	110.514	98.295	30.545	- 80.420	- 30.061	2.628
2600	13.906	111.059	98.776	31.936	- 80.655	- 28.041	2.357
2700	13.906	111.584	99.241	33.327	- 80.911	- 26.014	2.106
2800	13.907	112.090	99.690	34.717	- 81.192	- 23.975	1.871
2900	13.907	112.578	100.127	36.108	- 81.490	- 21.926	1.652
3000	13.907	113.049	100.549	37.499	- 81.807	- 19.866	1.447
3100	13.907	113.505	100.960	38.889	- 82.143	- 17.796	1.255
3200	13.907	113.947	101.359	40.280	- 82.494	- 15.715	1.073
3300	13.908	114.374	101.747	41.671	- 82.859	- 13.623	.902
3400	13.908	114.790	102.124	43.061	- 83.237	- 11.519	.740
3500	13.908	115.193	102.492	44.452	- 83.626	- 9.404	.587
3600	13.908	115.585	102.850	45.843	- 84.024	- 7.278	.442
3700	13.908	115.966	103.200	47.234	- 84.429	- 5.141	.304
3800	13.908	116.337	103.541	48.625	- 84.840	- 2.990	.172
3900	13.908	116.698	103.873	50.015	- 85.258	- .830	.046
4000	13.908	117.050	104.198	51.406	- 85.678	1.334	- .073
4100	13.908	117.393	104.516	52.797	- 86.101	3.515	- .187
4200	13.909	117.729	104.827	54.188	- 86.525	5.709	- .297
4300	13.909	118.056	105.131	55.579	- 86.950	7.909	- .402
4400	13.909	118.376	105.428	56.970	- 87.374	10.123	- .503
4500	13.909	118.688	105.719	58.361	- 87.797	12.340	- .599
4600	13.909	118.994	106.004	59.751	- 88.220	14.573	- .692
4700	13.909	119.293	106.284	61.142	- 88.639	16.811	- .782
4800	13.909	119.586	106.558	62.533	- 89.057	19.059	- .868
4900	13.909	119.873	106.827	63.924	- 89.471	21.315	- .951
5000	13.909	120.154	107.091	65.315	- 89.882	23.580	- 1.031
5100	13.909	120.429	107.349	66.706	- 90.291	25.851	- 1.108
5200	13.909	120.699	107.604	68.097	- 90.695	28.135	- 1.182
5300	13.909	120.964	107.853	69.488	- 91.096	30.427	- 1.255
5400	13.909	121.224	108.098	70.879	- 91.495	32.721	- 1.324
5500	13.909	121.479	108.339	72.270	- 91.890	35.026	- 1.392
5600	13.909	121.730	108.576	73.661	- 92.282	37.336	- 1.457
5700	13.909	121.976	108.809	75.051	- 92.673	39.652	- 1.520
5800	13.909	122.218	109.038	76.442	- 93.059	41.983	- 1.582
5900	13.909	122.456	109.264	77.833	- 93.444	44.311	- 1.641
6000	13.909	122.690	109.486	79.224	- 93.826	46.643	- 1.699

March 31, 1962; Dec. 31, 1973

LEAD DIBROMIDE ($PbBr_2$) (IDEAL GAS) GFW = 367.008 Br$_2$Pb

Ground State Quantum Weight = [1]

Point Group = C_{2v}

$S^\circ_{298.15}$ = 81.09 ± 0.7 gibbs/mol

ΔHf°_0 = -21.03 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -24.95 ± 1.5 kcal/mol

Vibrational Frequencies and Degeneracies

ν_i, cm^{-1}
208 (1)
64 (1)
189 (1)

Bond Distance: Pb-Br = 2.6 ± 0.3 Å

Bond Angle: Br-Pb-Br = [95°]

$\sigma = 2$

Product of Moments of Inertia: $I_AI_BI_C = [6.4831 \times 10^{-112}]\ g^3cm^6$

Heat of Formation

$\Delta Hf^\circ_{298.15}$= -24.95 ± 1.5 kcal/mol is the sum of $\Delta Hf^\circ_{298.15}(\ell)$ = -63.913 ± 0.8 kcal/mol and $\Delta Hv^\circ_{298.15}(\ell)$ = 38.96 kcal/mol. The adopted heat of vaporization is from the second and third law analyses, tabulated below, of seven sets of liquid vapor pressure measurements, $PbBr_2(\ell) = PbBr_2(g)$. The overall average for ΔHv_{298} is 39.23 kcal/mol. The average value of the third law ΔHv_{298} is 38.96 kcal/mol. This is in good agreement with both the second and third law values from the data of Wartenberg and Bosse (1). The adopted heat of formation for $PbBr_2(g)$ yields a dissociation energy of D°_0 = 5.42 eV for the process $PbBr_2(g) = Pb(g) + 2\ Br(g)$.

Investigator	No. of Points	Temp. Range K	ΔHv°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu
Wartenberg and Bosse (1)	7[a]	1008-1191	38.05±0.19	39.02±0.12	0.9±0.2
Volmer (2)	11	684-841	39.36±0.11	38.93±0.08	-0.6±0.1
Greiner and Jellinek (3)	1	1043		38.90	
Jahn-Held and Jellinek (4)	3	1045-1153	41.85±6.54	38.68±0.73	-2.9±5.9
Bloom, et al. (5)	Equation	796-1133	39.56±0.48	38.81±0.30	-0.8±0.5
Murgulescu and Marta (6)	1	973		39.13	
Bloom and Hastie (7)	1	973		39.27	

[a] One point rejected by statistical test.

Heat Capacity and Entropy

Molecular dimensions are those given by Sutton (8). Beattie and Perry (9) observed the frequencies ν_1 = 200 cm^{-1} and ν_2 = 64 cm^{-1} in a gas phase Raman study of $PbBr_2$ in the presence of excess bromine; the $PbBr_2$ spectrum was superimposed on the resonance fluorescence spectrum of Br_2. The matrix isolation laser Raman spectroscopic study by Ozin and Vander Voet (10) gave ν_1 = 208 cm^{-1} and ν_3 = 189 cm^{-1}. Experimental conditions prevented observations below 90 cm^{-1} so ν_2 expected at about 65 cm^{-1} was not confirmed.

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Strontium Dibromide ($SrBr_2$) Br_2Sr

(Crystal) GFW = 247.428

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.317	- 168.538	- 168.538	INFINITE
100	15.377	15.524	50.028	- 3.450	- 168.659	- 168.325	367.873
200	17.602	27.100	35.940	- 1.768	- 168.738	- 167.978	183.558
298	18.368	34.282	34.282	.000	- 171.600	- 167.247	122.595
300	18.380	34.396	34.283	.034	- 171.611	- 167.219	121.819
400	18.890	39.755	35.010	1.898	- 178.646	- 164.293	89.766
500	19.320	44.017	36.399	3.809	- 178.317	- 160.744	70.261
600	19.760	47.577	37.974	5.762	- 177.994	- 157.259	57.282
700	20.290	50.661	39.570	7.763	- 177.677	- 153.829	48.028
800	20.930	53.410	41.131	9.823	- 177.361	- 150.445	41.100
900	21.750	55.921	42.637	11.955	- 177.204	- 147.084	35.717
1000	27.500	61.889	44.364	17.525	- 173.434	- 144.038	31.479
1100	27.500	64.510	46.078	20.275	- 174.410	- 141.034	28.021
1200	27.500	66.903	47.715	23.025	- 173.403	- 138.044	25.141
1300	27.500	69.104	49.277	25.775	- 172.398	- 135.138	22.719
1400	27.500	71.142	50.767	28.525	- 171.394	- 132.310	20.654
1500	27.500	73.039	52.189	31.275	- 170.392	- 129.554	18.876

June 30, 1974

STRONTIUM DIBROMIDE ($SrBr_2$) (CRYSTAL) GFW = 247.428 Br_2Sr

$S°_{298.15}$ = 34.3 ± 1.0 gibbs/mol
Tt = 918 K
Tm = 930 K

$\Delta Hf°_0$ = -168.5 ± 0.4 kcal/mol
$\Delta Hf°_{298.15}$ = -171.6 ± 0.4 kcal/mol
ΔHt° = 2.92 ± 0.05 kcal/mol
ΔHm° = 2.42 ± 0.05 kcal/mol
$\Delta Hs°_{298.15}$ = 74.3 ± 3.4 kcal/mol

Heat of Formation

The selected value for ΔHf° is derived from results of solution calorimetric measurements in aqueous acids performed by Ehrlich et al. (1). Their results on the heats of solution of Sr(c) and $SrBr_2$(c) in HBr·555 H_2O are combined with data for HBr(aq) (2, 3) in a thermochemical cycle to give $\Delta Hf°_{298}(SrBr_2, c)$ = -171.6 ± 0.4 kcal/mol. In the same paper, Ehrlich et al. (1) reported similar results for three (Ca, Sr, and Ba) of the alkaline earth dichlorides. We note that these results have been the basis for adopted JANAF heats of formation (4) for these dichlorides.

Independent values for ΔHf° can be obtained from measurements of the heat of solution of $SrBr_2$(c) in aqueous solution. The work (5-7) reported in this area was done several years ago, and the results have been conveniently summarized by Bichowsky and Rossini (8). Combining these results with $\Delta Hf°_{298}(Sr^{+2}, \infty\ aq)$ = -130.45 kcal/mol (9) and $\Delta Hf°_{298}(Br^-, \infty\ aq)$ = -29.039 ± 0.036 kcal/mol (2), we derive ΔHf° values for $SrBr_2$(c) in kcal/mol of -171.5 (5), -172.2 (6), and -171.6 (7). Deviations from our adopted value are at worst only 0.6 kcal/mol, and the results of two studies (5, 7) provide additional support for the selected value of ΔHf°. Also, our value for ΔHf° is essentially that (-171.5 kcal/mol) selected by NBS (9).

Heat Capacity and Entropy

Cp° data below 300 K are based primarily on the adiabatic calorimetry (60-302 K) of Taylor and Smith (10). These Cp° data show an unusual leveling off at near 18.0 gibbs/mol above 245 K. We adopt their Cp° data in the temperature range 60-245 K; values above 243 K are estimated by comparison with similar data for $SrCl_2$ and $BaCl_2$ (4). Our value for Cp° at 298.15 K (18.37 gibbs/mol) is roughly 0.4 gibbs/mol higher than the measured value of Taylor and Smith (10). Hüttig and Slonim (11) have reported mean heat capacity values over three temperature intervals (85-198, 196-271, and 276-368 K). Their measurements suggest a slightly higher value (18.8 gibbs/mol) for Cp° at 298.15 K than is adopted.

Taylor and Smith (10) reported $S°_{298}$ = 32.29 eu which was based on $S°_{60}$ = 6.68 eu. This latter value was obtained from Debye-Einstein functions which represented their Cp° data to only ± 1.8 percent from 60 to 100 K. A comparison of their extrapolated Cp° data with those which have been measured for $SrCl_2$, $BaCl_2$, and CaI_2 (4) indicates that the values for $SrBr_2$ decrease much more rapidly with temperature below 50 K than would be expected. We have made our own extrapolation to 0 K for $SrBr_2$ by comparison with the measured data for $SrCl_2$(7.4 to 60 K), $BaCl_2$(6 to 60 K), and CaI_2(13.1 to 60 K). Our extrapolation gives $S°_{60}$ = 8.7 eu, or $S°_{298}$ = 34.28 eu based on the adopted Cp° data (60-300 K). Our value for $S°_{298}$ is consistent with the estimates of 35 eu (12) and 33.8 eu (13), suggesting a possible uncertainty of ± 1 eu in the adopted value.

Taylor and Smith (10) measured relative enthalpy data (293-902 K) on a portion of the same sample used for their Cp° measurements. This sample was reported to contain less than 0.1% oxide and was investigated in a Bunsen ice calorimeter. Our analysis of their relative enthalpies by curve fitting techniques reveals the existence of considerable scatter in the data, and no weight is given to their results. The average deviation of 36 points in a Shomate type fit is 2.5%; the maximum deviation is -9.3% at 397 K. Also, these workers (10) were apparently unaware of the transition in $SrBr_2$ at 918 K, since their data set contains only two enthalpy points between 902-927 K. Relative enthalpies have also been measured by Dworkin and Bredig (14), and the results were reported in graphical form. The short temperature interval (846-902 K) over which these measurements were made for the α phase preclude derivation of accurate heat capacities. Dworkin and Bredig (14) also reported in the same paper enthalpy data for three (Ca, Sr, and Ba) of the alkaline earth dichlorides. A comparison of these enthalpies with those adopted by JANAF (4) indicates that their results are probably reliable to better than ± 2%. We adopt their measured value for $(H°_{918}-H°_{298})$ = 12.37 kcal/mol of the α phase at the transition temperature. Cp° values (300-918 K) are then estimated by comparison with those for $SrCl_2$ and $BaCl_2$ (4). These estimates are made so as to reproduce as closely as possible the adopted enthalpy at 918 K. Our estimated Cp° data give a value of $(H°_{918}-H°_{298})$ = 12.35 kcal/mol which agrees with the measured value of Dworkin and Bredig to within 20 calories. The enthalpies of Taylor and Smith (10) are roughly 2.5% higher than the adopted values at temperatures near the transition. Cp° data for the β phase (918-930 K) are taken from Dworkin and Bredig (14) and extrapolated above the melting point.

Transition Data

Existence of two forms of $SrBr_2$ has been shown by thermal analysis (15-18) and drop calorimetry (14). Values of Tt reported are 915 K (15-16), 920 K (17), 919 K (18), and 918 K (14). We adopt the latter value which is based on the drop calorimetry of Dworkin and Bredig (14). Several other investigators (10, 19-21) have mistakenly interpreted the transition as due to melting.

ΔHt° of 2.92 kcal/mol is derived from the enthalpy data of Dworkin and Bredig (14).

Melting Data

See $SrBr_2$(ℓ) table.

Heat of Sublimation

ΔHs_{298} is calculated as the difference in the adopted heats of formation for the gas and crystal at 298.15 K.

References

See $SrBr_2$(ℓ) table.

Br_2Sr

Strontium Dibromide ($SrBr_2$) Br_2Sr

(Liquid) GFW = 247.428

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	18.368	37.010	37.010	.000	- 168.521	- 164.981	120.934
300	18.380	37.123	37.010	.034	- 168.532	- 164.959	120.172
400	18.890	42.483	37.737	1.898	- 175.567	- 162.305	88.680
500	19.320	46.744	39.127	3.809	- 175.239	- 159.029	69.511
600	27.818	50.305	40.701	5.763	- 174.915	- 155.817	56.756
700	27.818	54.593	42.387	8.544	- 173.817	- 152.722	47.682
800	27.818	58.308	44.150	11.326	- 172.779	- 149.781	40.918
900	27.818	61.584	45.909	14.108	- 171.972	- 146.949	35.684
1000	27.818	64.515	47.625	16.890	- 170.991	- 144.221	31.519
1100	27.818	67.166	49.283	19.672	- 171.935	- 141.482	28.110
1200	27.818	69.587	50.876	22.453	- 170.896	- 138.759	25.271
1300	27.818	71.814	52.402	25.235	- 169.859	- 136.122	22.884
1400	27.818	73.875	53.863	28.017	- 168.823	- 133.566	20.851
1500	27.818	75.794	55.262	30.799	- 167.790	- 131.084	19.099
1600	27.818	77.590	56.602	33.581	- 166.757	- 128.671	17.576
1700	27.818	79.276	57.886	36.362	- 198.299	- 125.416	16.123
1800	27.818	80.866	59.119	39.144	- 196.926	- 121.169	14.712
1900	27.818	82.370	60.304	41.926	- 195.556	- 116.996	13.458
2000	27.818	83.797	61.443	44.708	- 194.191	- 112.899	12.337
2100	27.818	85.154	62.540	47.490	- 192.828	- 108.868	11.330
2200	27.818	86.448	63.598	50.271	- 191.471	- 104.902	10.421
2300	27.818	87.685	64.618	53.053	- 190.120	- 100.997	9.597
2400	27.818	88.869	65.604	55.835	- 188.777	- 97.150	8.847
2500	27.818	90.004	66.558	58.617	- 187.445	- 93.360	8.162
2600	27.818	91.096	67.481	61.399	- 186.123	- 89.622	7.533
2700	27.818	92.145	68.375	64.180	- 184.816	- 85.937	6.956
2800	27.818	93.157	69.242	66.962	- 183.526	- 82.297	6.424
2900	27.818	94.133	70.084	69.744	- 182.255	- 78.704	5.931
3000	27.818	95.076	70.901	72.526	- 181.006	- 75.156	5.475

June 30, 1974

STRONTIUM DIBROMIDE ($SrBr_2$) (LIQUID) GFW = 247.428 Br_2Sr

$S^\circ_{298.15}$ = [37.010] gibbs/mol
Tm = 930 K
Tb = 2419 K

$\Delta Hf^\circ_{298.15}$ = [-168.521] kcal/mol
ΔHm° = 2.42 ± 0.05 kcal/mol
ΔHv° = 46.4 kcal/mol

Heat of Formation

ΔHf° of $SrBr_2(\ell)$ is obtained from that of the crystal by addition of ΔHm° and the difference in the values of (H°_{930}-H°_{298}) for the crystal and liquid.

Heat Capacity and Entropy

Cp° for the liquid in the temperature range 600-3000 K is assumed constant at 27.818 gibbs/mol. This value is based on JANAF curve fits (deviations ± 0.1%) of the relative enthalpies (931-1002 K) reported by Dworkin and Bredig (1). Taylor and Smith (2) have also reported enthalpies (927-1118 K) for the liquid. These results suggest a somewhat higher value (28.36 gibbs/mol) for Cp°; however, the data are considered less reliable. (See $SrBr_2$(c) table for further discussion). The average deviation of the data of Taylor and Smith (2) from our adopted enthalpies is ±0.4%; the maximum deviation is 1.2% at 1067 K. A glass transition is assumed at 600 K below which Cp° is that of the crystal.

S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm is that observed by Dworkin and Bredig (1) from drop calorimetry. Other reported values for Tm are 926 K (3), 931 K (4), 924 K (5), and 928 K (6). Four other investigators (2, 7-10) have reported values of Tm near 916 K, but they have mistakenly interpreted the transition in $SrBr_2$ as that due to melting.

ΔHm° is calculated as the difference in the enthalpies of the liquid and β phase at Tm. The enthalpy of the liquid at Tm is based on JANAF curve fits of the enthalpy data reported by Dworkin and Bredig (1). We adopt their measured value of 15.6 kcal/mol for (H°_{930}-H°_{298}) of the β phase at Tm. A cryoscopic (4) determination of ΔHm° gave 2.6 ± 1.3 kcal/mol which agrees well with the adopted calorimetric value. Taylor and Smith (2) reported a calorimetric value of ΔHm° = 5.25 kcal/mol; however, this value also includes the heat of transition. Addition of our values for ΔHt° and ΔHm° gives 5.34 kcal/mol.

Vaporization Data

Tb is the temperature at which ΔGr for the process $SrBr_2(\ell) = SrBr_2(g)$ approaches zero. ΔHv° is the difference in the heats of formation of the gas and liquid at Tb. Peterson and Hutchison (10) obtained Tb = 2318 K from vapor pressure measurements on the liquid (1114-1304 K). However, the value is based on a rather long extrapolation and is probably uncertain to at least ± 100 K.

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Br_2Sr

Strontium Dibromide ($SrBr_2$) Br_2Sr

(Ideal Gas) GFW = 247.428

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.846	-93.767	-93.767	INFINITE
100	12.835	62.108	89.905	-2.780	-93.689	-98.013	214.206
200	14.182	71.525	78.592	-1.413	-94.083	-102.209	111.689
298	14.554	77.270	77.270	.000	-97.300	-105.763	77.527
300	14.558	77.360	77.271	.027	-97.318	-105.815	77.087
400	14.704	81.571	77.844	1.491	-104.753	-107.127	58.531
500	14.774	84.861	78.930	2.965	-104.861	-107.709	47.080
600	14.813	87.558	80.150	4.445	-105.011	-108.265	39.436
700	14.837	89.844	81.376	5.927	-105.213	-108.793	33.967
800	14.852	91.826	82.561	7.412	-105.472	-109.288	29.856
900	14.863	93.576	83.689	8.898	-105.961	-109.731	26.646
1000	14.871	95.142	84.758	10.385	-106.274	-110.132	24.069
1100	14.877	96.560	85.767	11.872	-108.513	-110.393	21.933
1200	14.881	97.855	86.721	13.360	-108.768	-110.552	20.134
1300	14.884	99.046	87.624	14.848	-109.025	-110.690	18.609
1400	14.887	100.149	88.480	16.337	-109.282	-110.808	17.298
1500	14.889	101.176	89.293	17.825	-109.542	-110.909	16.159
1600	14.891	102.137	90.066	19.314	-109.802	-110.991	15.161
1700	14.892	103.040	90.803	20.804	-142.636	-110.152	14.161
1800	14.894	103.891	91.506	22.293	-142.556	-108.244	13.143
1900	14.895	104.697	92.179	23.782	-142.479	-106.339	12.232
2000	14.895	105.461	92.825	25.272	-142.405	-104.440	11.413
2100	14.896	106.187	93.444	26.761	-142.335	-102.544	10.672
2200	14.897	106.880	94.039	28.251	-142.270	-100.651	9.999
2300	14.897	107.542	94.612	29.741	-142.211	-98.760	9.384
2400	14.898	108.177	95.164	31.231	-142.160	-96.871	8.821
2500	14.898	108.785	95.697	32.720	-142.120	-94.986	8.304
2600	14.899	109.369	96.211	34.210	-142.090	-93.100	7.826
2700	14.899	109.931	96.709	35.700	-142.075	-91.218	7.384
2800	14.900	110.473	97.191	37.190	-142.077	-89.333	6.973
2900	14.900	110.996	97.658	38.680	-142.098	-87.449	6.590
3000	14.900	111.501	98.111	40.170	-142.140	-85.565	6.233
3100	14.900	111.990	98.551	41.660	-142.207	-83.676	5.899
3200	14.901	112.463	98.978	43.150	-142.301	-81.787	5.586
3300	14.901	112.921	99.394	44.640	-142.425	-79.896	5.291
3400	14.901	113.366	99.798	46.130	-142.581	-77.999	5.014
3500	14.901	113.798	100.192	47.620	-142.772	-76.095	4.752
3600	14.901	114.218	100.576	49.110	-143.000	-74.189	4.504
3700	14.901	114.626	100.950	50.601	-143.264	-72.273	4.269
3800	14.901	115.024	101.315	52.091	-143.571	-70.350	4.046
3900	14.902	115.411	101.672	53.581	-143.920	-68.417	3.834
4000	14.902	115.788	102.020	55.071	-144.312	-66.479	3.632
4100	14.902	116.156	102.360	56.561	-144.747	-64.528	3.440
4200	14.902	116.515	102.693	58.051	-145.226	-62.566	3.256
4300	14.902	116.866	103.019	59.542	-145.748	-60.590	3.080
4400	14.902	117.208	103.337	61.032	-146.314	-58.602	2.911
4500	14.902	117.543	103.649	62.522	-146.923	-56.603	2.749
4600	14.902	117.871	103.955	64.012	-147.574	-54.588	2.594
4700	14.902	118.191	104.254	65.502	-148.265	-52.557	2.444
4800	14.902	118.505	104.548	66.993	-148.995	-50.517	2.300
4900	14.902	118.812	104.836	68.483	-149.762	-48.457	2.161
5000	14.902	119.113	105.119	69.973	-150.563	-46.380	2.027
5100	14.902	119.408	105.396	71.463	-151.399	-44.291	1.898
5200	14.903	119.698	105.668	72.954	-152.263	-42.182	1.773
5300	14.903	119.982	105.936	74.444	-153.156	-40.054	1.652
5400	14.903	120.260	106.198	75.934	-154.076	-37.914	1.534
5500	14.903	120.534	106.456	77.424	-155.019	-35.751	1.421
5600	14.903	120.802	106.710	78.915	-155.982	-33.577	1.310
5700	14.903	121.066	106.960	80.405	-156.965	-31.381	1.203
5800	14.903	121.325	107.205	81.895	-157.963	-29.167	1.099
5900	14.903	121.580	107.447	83.385	-158.976	-26.939	.998
6000	14.903	121.830	107.684	84.876	-160.000	-24.697	.900

June 30, 1974

STRONTIUM DIBROMIDE ($SrBr_2$) (IDEAL GAS) GFW = 247.428 Br_2Sr

Point Group $D_{\infty h}$
$S^\circ_{298.15}$ = [77.3 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -93.8 ± 3.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -97.3 ± 3.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[157](1)
[37](2)
[263](1)

Bond Distance: Sr-Br = 2.82 ± 0.03 Å Bond Angle: Br-Sr-Br = 180° σ = 2 Rotational Constant: B_o = 0.013265 cm^{-1}

Heat of Formation

Peterson and Hutchison (1, 2) have measured vapor pressures (1114-1304 K) for liquid $SrBr_2$ by the Knudsen effusion method. The vapor pressures were determined from observations of the time required for specific amounts of sample to be lost from stainless steel effusion cells. The sample of $SrBr_2$ used in this investigation was prepared by direct union of high purity elements. X-ray diffraction patterns on the final product showed no metal or oxide lines. Radii of the effusion cell orifices ranged from 0.16 mm to 0.38 mm. Results of second and third law analysis of these pressures are tabulated below. We assume that the dibromide monomer was the only vapor species present. Support for this assumption is provided by mass spectra for some of the other alkaline earth dihalides (3). These studies indicate that the saturated vapor consist predominantly of the metal dihalide monomer and agrees with predictions which were made by Brewer et al. (4) for the dihalide molecules. Also included in the table is a value for ΔHf° derived from a third law analysis of a single vapor pressure point determined by Stock and Heynemann (5) and tabulated by Brewer et al. (4).

Reference	Reaction	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} ($SrBr_2$, g)[b] kcal/mol
(1, 2)	A	13[a]	1147-1304	69.9	71.24±0.86	1.1±2.5	97.3±2.5
(4, 5)	A	1	1040		66.9		101.6

Reaction: $SrBr_2(\ell) = SrBr_2(g)$

[a] Two points rejected due to failure of a statistical test.

[b] Third law values based on $\Delta Hf^\circ_{298}(SrBr_2, \ell)$ = -168.521 kcal/mol (3).

The value $\Delta Hf^\circ_{298}(SrBr_2, g)$ = -97.3 ± 2.5 kcal/mol is preferred here rather than an average (-99.5 kcal/mol) of the two results, since it is impossible to assess the reliability of the measurement by Stock and Heynemann (5). However, our value does compare favorable with that (-98.0 kcal/mol) selected by NBS (6). The uncertainty of ±3.0 kcal/mol is assigned to reflect errors associated with the functions used in the analysis and with the auxiliary heat of formation data.

Heat Capacity and Entropy

The value of the bond length is that measured by Akishin and Spiridonov (7) in a high-temperature electron diffraction study. The molecular structure of $SrBr_2(g)$ has not been unambiguously established. Electron diffraction patterns (7) for $SrBr_2$ were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton et al. (8), using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $SrBr_2$ molecule. The absence of dipolar character is most reasonably explained by a linear and centrosymmetric configuration. We assume a linear structure for $SrBr_2$. Its moment of inertia is 2.1102 x 10^{-37} g cm^2.

Few infrared spectral studies (9-11) have been reported for the gaseous alkaline earth dibromides. The antisymmetric stretch (ν_3) and bending (ν_2) frequencies for $BeBr_2$ were observed by Snelson (9) in a neon matrix. Baikov (10) observed a band at 330 ± 5 cm^{-1} in the high-termperature infrared spectra of $CaBr_2$ vapor and assigned this band to ν_3. In a similar study on $MgBr_2(g)$ by Randall et al. (11) ν_3 was observed at 490 cm^{-1}. The only frequencies available for $SrBr_2$ are estimates (4, 10, and 12) which have been obtained by force constant calculations. The adopted vibrational frequencies are derived from estimated force constants by the valence force method (13). A comparison of values for the ratio of the stretching force constants for diatomic and triatomic strontium fluorides (ratio = 1.33, 3) and chlorides (ratio = 1.15, 3) suggests a value of near unity for the ratio of the bromides. Therefore, the stretching force constant for $SrBr_2$ is taken equal to that for SrBr(k = 1.154 x 10^5 dynes/cm) (4). Our values for ν_1 and ν_3 compare favorably with those estimated by a similar procedure (4) (ν_1 = 156 cm^{-1} and ν_3 = 262 cm^{-1}) and with those given by Krasnov and Svettsov (12, ν_1 = 158 cm^{-1} and ν_3 = 265 cm^{-1}). The estimated frequencies of Baikov (10) are roughly 12% lower than ours. A comparison of values for the ratio of the stretch to bend force constants for the bent molecules SrF_2(ratio = 50, 3) and $SrCl_2$(ratio = 78, 3) suggests a value near 100 for $SrBr_2$. Brewer (4) used this same value in his force constant calculations. This value for the ratio gives $k\delta/\ell^2$ = 1.154 x 10^3 dynes/cm, or ν_2 = 37 cm^{-1}. A comparison of similar data for the linear molecule $BeBr_2$ (9) indicates that the value of the ratio could be as low as 41. This leads to a ν_2 = 58 cm^{-1} which is excellent agreement with the value (56 cm^{-1}) recommended by Krasnov and Svettsov (12). We prefer the lower value of ν_2 at this time but include in the uncertainty (±2.0 gibbs/mol) assigned to the value of S°_{298} the possibility that the higher value is the correct one. The singlet ground state is assigned by analogy with that for $BaCl_2$ (3). Our adopted functions agree with those tabulated by Brewer et al. (4) to within 0.1 gibbs/mol in the range 298-2000 K.

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Br_2Sr

Magnesium Dibromide, Dimeric (Mg_2Br_4) Br_4Mg_2

(Ideal Gas) GFW = 368.226

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 7.401	- 176.791	- 176.791	INFINITE
100	25.136	78.841	136.738	- 5.790	- 176.824	- 181.679	397.059
200	27.750	98.116	113.031	- 2.983	- 177.483	- 186.534	203.835
298	30.834	110.237	110.237	.000	- 183.500	- 190.012	139.282
300	30.846	110.428	110.237	.057	- 183.531	- 190.051	138.452
400	31.253	119.365	111.453	3.165	- 198.131	- 189.224	103.387
500	31.445	126.362	113.761	6.301	- 198.045	- 187.007	81.741
600	31.551	132.105	116.354	9.451	- 198.009	- 184.806	67.316
700	31.615	136.974	118.960	12.610	- 198.022	- 182.604	57.012
800	31.657	141.199	121.432	15.773	- 198.101	- 180.399	49.283
900	31.656	144.929	123.884	18.941	- 198.251	- 178.177	43.267
1000	31.706	148.269	126.158	22.110	- 202.720	- 175.570	38.371
1100	31.722	151.291	128.308	25.282	- 202.956	- 172.849	34.342
1200	31.735	154.052	130.340	28.454	- 203.244	- 170.100	30.979
1300	31.742	156.592	132.263	31.628	- 203.586	- 167.322	28.129
1400	31.750	158.945	134.086	34.803	- 264.711	- 163.560	25.533
1500	31.755	161.136	135.817	37.978	- 264.346	- 156.349	22.780
1600	31.760	163.185	137.464	41.154	- 263.982	- 149.162	20.375
1700	31.764	165.111	139.034	44.330	- 263.620	- 141.993	18.254
1800	31.767	166.927	140.534	47.507	- 263.259	- 134.852	16.373
1900	31.770	168.644	141.969	50.684	- 262.898	- 127.725	14.692
2000	31.773	170.274	143.344	53.861	- 262.543	- 120.623	13.181
2100	31.775	171.824	144.663	57.038	- 262.188	- 113.538	11.816
2200	31.776	173.302	145.932	60.216	- 261.836	- 106.464	10.576
2300	31.778	174.715	147.153	63.393	- 261.487	- 99.408	9.446
2400	31.779	176.067	148.329	66.571	- 261.139	- 92.369	8.411
2500	31.780	177.365	149.465	69.749	- 260.795	- 85.347	7.461
2600	31.782	178.611	150.562	72.927	- 260.453	- 78.331	6.584
2700	31.783	179.811	151.623	76.105	- 260.115	- 71.338	5.774
2800	31.783	180.967	152.651	79.284	- 259.780	- 64.353	5.023
2900	31.784	182.082	153.647	82.462	- 259.448	- 57.375	4.324
3000	31.785	183.159	154.613	85.641	- 259.121	- 50.416	3.673
3100	31.785	184.202	155.550	88.819	- 258.801	- 43.461	3.064
3200	31.786	185.211	156.462	91.998	- 258.484	- 36.522	2.494
3300	31.787	186.189	157.348	95.176	- 258.176	- 29.594	1.960
3400	31.787	187.138	158.210	98.355	- 257.873	- 22.667	1.457
3500	31.787	188.059	159.050	101.534	- 257.580	- 15.756	.984
3600	31.788	188.955	159.868	104.712	- 257.298	- 8.850	.537
3700	31.788	189.826	160.666	107.891	- 257.023	- 1.951	.115
3800	31.789	190.674	161.444	111.070	- 256.760	4.941	- .284
3900	31.789	191.499	162.205	114.249	- 256.509	11.822	- .662
4000	31.789	192.304	162.947	117.428	- 256.272	18.696	- 1.021
4100	31.789	193.089	163.673	120.607	- 256.051	25.566	- 1.363
4200	31.790	193.855	164.382	123.786	- 255.844	32.431	- 1.688
4300	31.790	194.603	165.076	126.965	- 255.655	39.294	- 1.997
4400	31.790	195.334	165.756	130.144	- 255.482	46.156	- 2.293
4500	31.790	196.048	166.421	133.323	- 255.329	53.009	- 2.574
4600	31.790	196.747	167.073	136.502	- 255.196	59.862	- 2.844
4700	31.791	197.431	167.711	139.681	- 255.083	66.713	- 3.102
4800	31.791	198.100	168.338	142.860	- 254.996	73.554	- 3.349
4900	31.791	198.756	168.952	146.039	- 254.929	80.400	- 3.586
5000	31.791	199.398	169.554	149.218	- 254.886	87.245	- 3.813
5100	31.791	200.027	170.146	152.397	- 254.871	94.075	- 4.031
5200	31.791	200.645	170.726	155.576	- 254.880	100.922	- 4.242
5300	31.791	201.250	171.296	158.755	- 254.915	107.774	- 4.444
5400	31.792	201.845	171.857	161.935	- 254.979	114.605	- 4.638
5500	31.792	202.428	172.407	165.114	- 255.072	121.459	- 4.826
5600	31.792	203.001	172.946	168.293	- 255.197	128.298	- 5.007
5700	31.792	203.563	173.481	171.472	- 255.352	135.159	- 5.182
5800	31.792	204.116	174.004	174.651	- 255.537	142.005	- 5.351
5900	31.792	204.660	174.519	177.831	- 255.757	148.866	- 5.514
6000	31.792	205.194	175.026	181.010	- 256.010	155.709	- 5.672

June 30, 1974

MAGNESIUM DIBROMIDE, DIMERIC (Mg_2Br_4) (IDEAL GAS) GFW = 368.226 Br_4Mg_2

Point Group [D_{2h}]
$S^\circ_{298.15}$ = [110.2 ± 5.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -176.8 ± 5.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -183.5 ± 5.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[182](1)	[188](1)	[100](1)
[120](1)	[228](1)	[100](1)
[207](1)	[125](1)	[75](1)
[134](1)	[125](1)	[75](1)

Bond Distances: Mg-Br = [2.34] Å $Mg\text{-}Br'_{(bridge)}$ = [2.60] Å   σ = 4

Bond Angles: $Mg\text{-}Br'_{(bridge)}\text{-}Mg$ = [90]° $Br'_{(bridge)}\text{-}Mg\text{-}Br'_{(bridge)}$ = [90]°

$Br\text{-}Mg\text{-}Br'_{(bridge)}$ = [135]°

Product of Moments of Inertia: $I_AI_BI_C = [2.55322 \times 10^{-110}]\ g^3\ cm^6$

Heat of Formation

ΔHf° of the dimer is based on an analysis of mass spectrometric data reported by Berkowitz and Marquart (1). These studies have revealed the presence of approximately 2% dimer in the equilibrium vapor over $MgBr_2$(c) at around 800 K. The existence of the dimer was inferred from the observed ion intensities for $Mg_2Br_3^+$. Berkowitz and Marquart (1) reported a second law ΔHr_{803} of 12.9 kcal/mol for the process $MgBr_2(c) + MgBr_2(g) = Mg_2Br_4(g)$. When corrected to 298.15 K this value gives ΔHr° = 14.0 kcal/mol which leads to $\Delta Hf^\circ_{298}(Mg_2Br_4, g)$ = -183.7 kcal/mol. The absolute pressure of Mg_2Br_4(g) was also measured at 798 K by integrating the ion current during complete volatilization of a previously weighed sample. A third law analysis of the reported pressure gives ΔHs°_{298} = 67.4 kcal/mol for 2 $MgBr_2(c) = Mg_2Br_4(g)$. This value for the heat of sublimation leads to ΔHf°_{298}(dimer) = -183.2 kcal/mol which is in excellent agreement with the second law result. We adopt an average value (-183.5 kcal/mol) of these two results. The uncertainty in ΔHf° is estimated as ±5.0 kcal/mol, and the adopted ΔHf° value corresponds to a dimerization energy for $MgBr_2$(g) of 38.7 kcal/mol.

Heat Capacity and Entropy

The dimer molecule is assumed to have a bridge-bond structure of D_{2h} symmetry similar to that suggested by Thompson and Carlson (2) for the dimers of several transition metal dichlorides. The two outer Mg-Br bond lengths are assumed to be the same as that for $MgBr_2$(2.34 Å, 3). The four ring $Mg\text{-}Br'_{(bridge)}$ bond lengths are taken to be somewhat longer (2.6 Å). The four atoms which lie in the ring form a square. The $Br'_{(bridge)}\text{-}Mg\text{-}Br$ bond angle is estimated as 135°. The individual moments of inertia are: $I_A = 5.8027 \times 10^{-37}$, $I_B = 4.9058 \times 10^{-37}$, and $I_C = 8.9590 \times 10^{-38}\ g\ cm^2$.

The vibrational frequencies of the ring (first six listed) are taken equal to those for Na_2Br_2 (3). These frequencies were obtained by Berkowitz (4) from ionic model calculations. The remaining six frequencies are estimated by analogy with those for $MgBr_2$ and Mg_2Cl_4 (3). Following the observations made by Thompson and Carlson (2), all of the dimer frequencies are assumed to lie above the bending frequency ($\nu_2 = 70\ cm^{-1}$) of the monomer (3). Our adopted functions for the monomer and dimer reproduce the pressures measured by Berkowitz and Marquart (1) and show that the dimer becomes an increasing important vapor species with rising temperatures.

References

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Br_4Mg_2

Lead Tetrabromide ($PbBr_4$) Br_4Pb
(Ideal Gas) GFW = 526.816

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-6.185	-101.900	-101.900	INFINITE
100	20.683	76.336	123.327	-4.699	-102.169	-106.348	232.424
200	24.108	92.012	104.102	-2.418	-102.833	-110.282	120.510
298	25.007	101.837	101.837	.000	-109.073	-113.123	82.922
300	25.017	101.992	101.837	.046	-109.105	-113.147	82.428
400	25.363	109.243	102.824	2.568	-123.715	-111.490	60.916
500	25.529	114.922	104.696	5.113	-123.609	-108.449	47.403
600	25.621	119.586	106.801	7.671	-123.517	-105.425	38.401
700	25.677	123.540	108.917	10.236	-124.608	-102.226	31.916
800	25.713	126.971	110.964	12.806	-124.551	-99.033	27.054
900	25.738	130.001	112.914	15.378	-124.489	-95.846	23.275
1000	25.756	132.714	114.761	17.953	-124.420	-92.666	20.252
1100	25.769	135.169	116.506	20.529	-124.347	-89.495	17.781
1200	25.780	137.412	118.156	23.107	-124.266	-86.329	15.723
1300	25.787	139.476	119.718	25.685	-124.184	-83.170	13.982
1400	25.794	141.387	121.198	28.264	-124.102	-80.020	12.492
1500	25.799	143.167	122.604	30.844	-124.022	-76.874	11.200
1600	25.803	144.832	123.942	33.424	-123.947	-73.732	10.071
1700	25.806	146.396	125.217	36.005	-123.875	-70.594	9.076
1800	25.809	147.871	126.435	38.585	-123.811	-67.466	8.191
1900	25.812	149.267	127.600	41.166	-123.752	-64.335	7.400
2000	25.814	150.591	128.717	43.748	-123.701	-61.211	6.689
2100	25.816	151.850	129.789	46.329	-166.106	-56.535	5.884
2200	25.817	153.051	130.819	48.911	-165.976	-51.322	5.098
2300	25.819	154.199	131.811	51.493	-165.869	-46.111	4.382
2400	25.820	155.298	132.767	54.075	-165.785	-40.904	3.725
2500	25.821	156.352	133.689	56.657	-165.726	-35.704	3.121
2600	25.822	157.365	134.581	59.239	-165.690	-30.502	2.564
2700	25.823	158.339	135.443	61.821	-165.676	-25.306	2.048
2800	25.823	159.278	136.277	64.403	-165.688	-20.106	1.569
2900	25.824	160.185	137.086	66.986	-165.717	-14.904	1.123
3000	25.825	161.060	137.871	69.568	-165.767	-9.704	.707
3100	25.825	161.907	138.632	72.150	-165.837	-4.499	.317
3200	25.826	162.727	139.373	74.733	-165.922	.706	-.048
3300	25.826	163.521	140.092	77.316	-166.023	5.912	-.392
3400	25.826	164.292	140.793	79.898	-166.137	11.124	-.715
3500	25.827	165.041	141.475	82.481	-166.264	16.341	-1.020
3600	25.827	165.769	142.140	85.064	-166.401	21.560	-1.309
3700	25.827	166.476	142.788	87.646	-166.546	26.782	-1.582
3800	25.828	167.165	143.421	90.229	-166.698	32.012	-1.841
3900	25.828	167.836	144.038	92.812	-166.857	37.246	-2.087
4000	25.828	168.490	144.641	95.395	-167.020	42.472	-2.321
4100	25.829	169.128	145.231	97.977	-167.188	47.712	-2.543
4200	25.829	169.750	145.807	100.560	-167.357	52.959	-2.756
4300	25.829	170.358	146.371	103.143	-167.528	58.206	-2.958
4400	25.829	170.952	146.923	105.726	-167.699	63.461	-3.152
4500	25.829	171.532	147.463	108.309	-167.870	68.713	-3.337
4600	25.829	172.100	147.993	110.892	-168.041	73.975	-3.515
4700	25.830	172.655	148.512	113.475	-168.210	79.239	-3.685
4800	25.830	173.199	149.020	116.058	-168.380	84.503	-3.848
4900	25.830	173.732	149.519	118.641	-168.546	89.774	-4.004
5000	25.830	174.254	150.009	121.224	-168.710	95.048	-4.155
5100	25.830	174.765	150.489	123.807	-168.874	100.319	-4.299
5200	25.830	175.267	150.961	126.390	-169.033	105.602	-4.438
5300	25.830	175.759	151.424	128.973	-169.190	110.891	-4.573
5400	25.830	176.241	151.879	131.556	-169.347	116.171	-4.702
5500	25.831	176.715	152.326	134.139	-169.500	121.465	-4.827
5600	25.831	177.181	152.766	136.722	-169.652	126.752	-4.947
5700	25.831	177.638	153.198	139.305	-169.803	132.047	-5.063
5800	25.831	178.087	153.624	141.888	-169.950	137.350	-5.176
5900	25.831	178.529	154.042	144.471	-170.098	142.645	-5.284
6000	25.831	178.963	154.454	147.054	-170.244	147.937	-5.389

June 30, 1962; Dec. 31, 1973

LEAD TETRABROMIDE ($PbBr_4$) (IDEAL GAS) GFW = 526.816 Br_4Pb

Ground State Quantum Weight = [1]

Point Group = [T_d]

$S^\circ_{298.15}$ = [101.84 ± 3.0] gibbs/mol

ΔHf°_0 = [-101.9 ± 20] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-109.1 ± 20] kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[207] (1)
[59] (2)
[231] (3)
[73] (3)

Bond Distance: Pb-Br = [2.58] Å Bond Angle: Br-Pb-Br = [109° 28'] σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = [1.3063 x 10^{-110}] g^3cm^6

Heat of Formation

The adopted ΔHf°_0 = -101.9 ± 20 kcal/mol is derived from the dissociation energy for the process $PbBr_4(g) = Pb(g) + 4\ Br(g)$. D°_0 = 11.34 eV is estimated from an intercomparison of the lead mono-, di-, and tetra- halides (1). This adopted D°_0 value for $PbBr_4(g)$ is greater than the D°_0 value for $PbBr_2(g)$ by a factor of 2.09. The auxiliary values ΔHf°_0(Pb, g) = 46.91 kcal/mol (1) and ΔHf°_0(Br, g) = 28.188 kcal/mol (1) are used. ΔHf°_{298}($PbBr_4$, g) = -109.1 ± 20 kcal/mol is calculated from ΔHf°_0.

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya et al. (2). Later works (3, 4, 5) mistakenly cite this work as observed data and use a bond distance of 2.54 Å rather than the 2.58 Å originally published (2).

The individual moments of inertia are $I_A=I_B=I_C$ = 2.3552 x 10^{-37} g cm^2.

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Br_4Pb

Niobium Monocarbide ($NbC_{0.98}$)

$C_{0.98}Nb$

(Crystal) GFW = 104.6772

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.296	-32.993	-32.993	INFINITE
100	3.448	1.908	13.557	-1.165	-33.066	-32.936	71.981
200	6.567	5.315	8.588	-.655	-33.134	-32.771	35.810
298	8.660	8.357	8.357	.000	-33.200	-32.696	23.967
300	8.695	8.411	8.357	.016	-33.199	-32.693	23.817
400	10.010	11.105	8.716	.956	-33.099	-32.538	17.778
500	10.790	13.427	9.431	1.998	-32.983	-32.411	14.167
600	11.320	15.444	10.269	3.105	-32.871	-32.308	11.768
700	11.690	17.217	11.138	4.256	-32.772	-32.222	10.060
800	11.980	18.798	11.998	5.440	-32.682	-32.149	8.783
900	12.210	20.223	12.834	6.650	-32.604	-32.089	7.792
1000	12.410	21.520	13.639	7.881	-32.533	-32.035	7.001
1100	12.580	22.711	14.410	9.130	-32.470	-31.989	6.356
1200	12.740	23.812	15.148	10.397	-32.413	-31.947	5.818
1300	12.890	24.838	15.855	11.678	-32.362	-31.911	5.365
1400	13.027	25.798	16.531	12.974	-32.313	-31.877	4.976
1500	13.160	26.701	17.179	14.283	-32.270	-31.847	4.640
1600	13.290	27.555	17.801	15.606	-32.230	-31.821	4.347
1700	13.416	28.364	18.399	16.941	-32.196	-31.797	4.088
1800	13.540	29.135	18.974	18.289	-32.169	-31.774	3.858
1900	13.660	29.870	19.528	19.649	-32.152	-31.753	3.652
2000	13.780	30.574	20.063	21.021	-32.142	-31.732	3.467
2100	13.900	31.249	20.580	22.405	-32.142	-31.710	3.300
2200	14.020	31.898	21.080	23.801	-32.156	-31.691	3.148
2300	14.140	32.524	21.564	25.209	-32.181	-31.668	3.009
2400	14.260	33.129	22.033	26.629	-32.222	-31.645	2.882
2500	14.380	33.713	22.489	28.061	-32.281	-31.621	2.764
2600	14.500	34.279	22.931	29.505	-32.365	-31.592	2.656
2700	14.620	34.829	23.362	30.961	-32.483	-31.562	2.555
2800	14.740	35.363	23.781	32.429	-38.946	-31.408	2.451
2900	14.860	35.882	24.189	33.909	-38.858	-31.140	2.347
3000	14.980	36.388	24.588	35.401	-38.759	-30.876	2.249

December 31, 1973

NIOBIUM MONOCARBIDE ($NbC_{0.98}$) (CRYSTAL) GFW = 104.6772 $C_{0.98}Nb$

ΔHf°_0 = -33.0 ± 0.6 kcal/mol

$S^\circ_{298.15}$ = 8.36 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -33.2 ± 0.6 kcal/mol

Heat of Formation

There are five oxygen bomb calorimetry studies on NbC reported in the literature (1-5) and one CO(g) equilibrium study (6). The adopted ΔHf°_{298} value is derived from the calorimetric study of Huber et al. (3). These authors studied the combustion of eight NbC_x samples where x covers the range 0.686 to 0.984. For each composition six to eight combustions were performed. Huber et al. (3) reported that the combustions varied from 98.78 to 100% of completion. Corrections of the order 0.51% or less were made to the heat of combustion value to account for impurities in seven of the eight samples. The correction was 3.33% for the x = 0.984 sample. The calculated heats of formation were fitted to a quadratic equation by the least squares method by Huber et al. (3). Each value was weighted inversely proportional to the square of its uncertainty. Using the quadratic equation for ΔHf°_{298} and correcting for the JANAF value of $\Delta Hf^\circ_{298}(Nb_2O_5$, c) (7), we interpolate to x = 0.98, calculate and adopt ΔHf°_{298} = -33.20 ± 0.6 kcal/mol. Due to the large error in the data points, a linear equation can be chosen to fit the data without making a statistically significant difference (3).

Huber et al. (3) and Storms (8) have reanalyzed much of the calorimetric and equilibrium data (1-6) for NbC_x (x = 0.686 to 0.984). A graphical comparison of the results (i.e., ΔHf°_{298} values vs. x) indicated that the quadratic equation suggested by Huber et al. (3) is a satisfactory representation of the various ΔHf°_{298} results for NbC_x. The shortcomings of the various studies have been discussed by Huber et al. (3) and Storms (8). For comparison, the oxygen combustion study by Mah (1) leads to ΔHf°_{298} = -31.14 ± 0.8 kcal/mol for $NbC_{0.9445}$.

Heat Capacity and Entropy

There have been three low temperature heat capacity studies for NbC_x: Pankratz et al. (13) using a $NbC_{0.996}$ sample (52-296 K), Toth et al. (19) using five NbC_x samples where x = 0.77, 0.83, 0.86, 0.91, and 0.96 (1.5-18 K), and Sandernaw and Storms using three NbC_x samples where x = 0.702, 0.825, and 0.980 (7.5-320 K). In addition there are numerous high temperature heat capacity and enthalpy studies on various NbC_x samples (9-13, 15-18). The adopted heat capacity values are those suggested by Turchanin et al. (20). Their Cp° values were represented by a five term equation for the range 0-3000 K and is a compromise of the reported data mentioned, all adjusted to the composition $NbC_{0.98}$.

Phase Data

NbC has a face centered cubic structure of the NaCl type (8). The NbC phase exists, following the phase diagram of Storms (8), from roughly $NbC_{0.70}$ to near $NbC_{0.99}$. At the NbC-C eutectic temperature of 3573 ± 50 K, the phase limit is $NbC_{0.97}$.

References

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Methylene (CH_2)

(Ideal Gas) GFW = 14.02709

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.389	92.237	92.237	INFINITE
100	7.949	37.566	53.502	- 1.594	92.259	90.962	- 198.798
200	8.006	43.084	47.070	- .797	92.375	89.606	- 97.917
298	8.269	46.324	46.324	.000	92.350	88.248	- 64.688
300	8.276	46.375	46.324	.015	92.348	88.223	- 64.270
400	8.638	48.805	46.653	.861	92.254	86.861	- 47.458
500	9.002	50.772	47.286	1.743	92.118	85.527	- 37.384
600	9.370	52.445	48.010	2.661	91.958	84.223	- 30.678
700	9.753	53.918	48.751	3.617	91.787	82.948	- 25.898
800	10.144	55.246	49.481	4.612	91.617	81.697	- 22.319
900	10.528	56.463	50.190	5.646	91.452	80.466	- 19.540
1000	10.892	57.592	50.874	6.717	91.299	79.254	- 17.321
1100	11.228	58.646	51.533	7.823	91.156	78.056	- 15.508
1200	11.531	59.636	52.168	8.962	91.025	76.872	- 14.000
1300	11.802	60.570	52.779	10.129	90.899	75.697	- 12.726
1400	12.042	61.453	53.367	11.321	90.781	74.534	- 11.635
1500	12.252	62.291	53.934	12.536	90.666	73.378	- 10.691
1600	12.438	63.088	54.482	13.771	90.553	72.226	- 9.866
1700	12.601	63.847	55.010	15.023	90.444	71.085	- 9.139
1800	12.745	64.572	55.522	16.290	90.335	69.949	- 8.493
1900	12.873	65.264	56.016	17.571	90.228	68.820	- 7.916
2000	12.987	65.928	56.495	18.864	90.121	67.696	- 7.397
2100	13.088	66.564	56.960	20.168	90.014	66.579	- 6.929
2200	13.179	67.175	57.410	21.482	89.905	65.463	- 6.503
2300	13.261	67.762	57.848	22.804	89.796	64.357	- 6.115
2400	13.336	68.328	58.273	24.134	89.684	63.254	- 5.760
2500	13.403	68.874	58.686	25.471	89.570	62.152	- 5.433
2600	13.465	69.401	59.088	26.814	89.454	61.059	- 5.133
2700	13.522	69.910	59.479	28.164	89.337	59.968	- 4.854
2800	13.574	70.403	59.861	29.518	89.217	58.882	- 4.596
2900	13.622	70.880	60.233	30.878	89.095	57.804	- 4.356
3000	13.666	71.343	60.595	32.243	88.971	56.724	- 4.132
3100	13.706	71.792	60.949	33.611	88.845	55.652	- 3.923
3200	13.744	72.227	61.295	34.984	88.716	54.584	- 3.728
3300	13.779	72.651	61.633	36.360	88.583	53.518	- 3.544
3400	13.811	73.063	61.963	37.739	88.448	52.457	- 3.372
3500	13.842	73.463	62.286	39.122	88.309	51.400	- 3.210
3600	13.869	73.854	62.602	40.508	88.168	50.347	- 3.056
3700	13.895	74.234	62.911	41.896	88.021	49.300	- 2.912
3800	13.920	74.605	63.214	43.287	87.873	48.258	- 2.775
3900	13.942	74.967	63.510	44.680	87.719	47.218	- 2.646
4000	13.963	75.320	63.801	46.075	87.562	46.182	- 2.523
4100	13.982	75.665	64.086	47.472	87.401	45.146	- 2.407
4200	14.000	76.002	64.366	48.871	87.235	44.121	- 2.296
4300	14.017	76.332	64.641	50.272	87.065	43.094	- 2.190
4400	14.033	76.654	64.910	51.675	86.892	42.072	- 2.090
4500	14.047	76.970	65.175	53.079	86.713	41.052	- 1.994
4600	14.061	77.279	65.434	54.484	86.530	40.044	- 1.903
4700	14.073	77.581	65.690	55.891	86.343	39.036	- 1.815
4800	14.085	77.878	65.940	57.299	86.151	38.032	- 1.732
4900	14.096	78.168	66.187	58.708	85.955	37.032	- 1.652
5000	14.106	78.453	66.429	60.118	85.754	36.034	- 1.575
5100	14.115	78.733	66.668	61.529	85.547	35.039	- 1.502
5200	14.124	79.007	66.903	62.941	85.337	34.051	- 1.431
5300	14.132	79.276	67.134	64.354	85.122	33.072	- 1.364
5400	14.139	79.540	67.361	65.767	84.901	32.089	- 1.299
5500	14.146	79.800	67.585	67.181	84.675	31.114	- 1.236
5600	14.153	80.054	67.805	68.596	84.445	30.140	- 1.176
5700	14.159	80.305	68.022	70.012	84.210	29.171	- 1.118
5800	14.165	80.551	68.236	71.428	83.969	28.206	- 1.063
5900	14.170	80.794	68.447	72.845	83.724	27.252	- 1.009
6000	14.175	81.032	68.655	74.262	83.474	26.290	- .958

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1962; June 30, 1969; Dec. 31, 1972

METHYLENE (CH_2) (IDEAL GAS) GFW = 14.02709 CH_2

Point Group C_{2v}

$S^\circ_{298.15}$ = 46.32 ± 0.5 gibbs/mol

ΔHf°_0 = 92.24 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 92.35 ± 1.0 kcal/mol

Electronic Levels and Vibrational Frequencies

	ε_i, cm^{-1}	g_i	ω, cm^{-1}	C-H Distance	H-C-H Angle	$I_AI_BI_C$* $g^3\ cm^6$
$X\ ^3B_1$	0	3	[2954] (1) [1056] (1) [3123] (1)	1.029 Å	136°	4.506×10^{-120}
$a\ ^1A_1$	[2600]	1	[3026] (1) [1398] (1) [3074] (1)	1.11 Å	102.4°	13.53×10^{-120}
$b\ ^1B_1$	7100 + [2600]	1	[2931] (1) [761] (1) [3110] (1)	1.05 Å	140°	4.373×10^{-120}
$c\ ^1A_1$	27700 + [2600]	1	[2954] (1) [1056] (1) [3123] (1)	[1.029] Å	[136°]	4.506×10^{-120}

* Product of the Moments of Inertia = $I_AI_BI_C$

$\sigma = 2$

Heat of Formation

The electron impact data of Langer et al. (1) was reanalyzed by Prophet (2) to give $\Delta Hf^\circ_{298}(CH_2, g)$ = 95 ± 5 kcal/mol. Dibeler and Liston (3) reported the photoionization threshold for the process $CH_3CN \rightarrow CH_2^+ + HCN$ as 14.94 eV (344.55 kcal/mol). Using auxiliary data from (4) and (5), we obtain $\Delta Hf^\circ_0(CH_2, g)$ = 95 kcal/mol, which is a maximum value as the process is likely to occur with excess energy. $\Delta Hf^\circ_0(CH_2, g)$ values of 95.5 kcal/mol (a maximum) and 86.8 ± 6.0 kcal/mol have been obtained by Chupka et al. from the appearance threshold of CH_2^+ from $C_2H_4(g)$ by photoionization (6), and from chemical equilibria measured in a mass spectrometer (7), respectively. Chupka (8) and Dibeler et al. (9) have determined the photoionization threshold for the production of CH_2^+ from CH_4. If the latter value is corrected for rotational energy effects as suggested by Chupka (8), then both studies yield $\Delta Hf^\circ_0(CH_2, g)$ = 94.6 kcal/mol. Chupka (8) indicates that this is a maximum value since the process of H_2 elimination is likely to occur with excess energy in the products at the threshold.

Chupka and Lifshitz (10) have obtained the photoionization threshold for CH_2^+ from CH_3 as 15.09 ± 0.03 eV. Combining this with the spectroscopic ionization potential (4), they report $D_0(CH_2\text{-}H)$ = 4.694 ± 0.033 eV (108.25 ± 0.77 kcal/mol). Using $\Delta Hf^\circ_0(CH_3, g)$ = 35.64 kcal/mol and $\Delta Hf^\circ_0(H, g)$ = 51.63 kcal/mol from these tables yields $\Delta Hf^\circ_0(CH_2, g)$ = 92.24 ± 1.0 kcal/mol, which is adopted.

Heat Capacity and Entropy

Bernheim et al. (11), in examining the EPR spectra of CH_2 which was produced by the photolysis of diazirine and trapped in xenon at 4 K, concluded that the ground state of CH_2 is a triplet state and it is bent. In similar followup work, they deduced a bond angle of 137.7 ± 0.6° for CD_2 from a measurement of the isotropic component of the ^{13}C hyperfine interaction. Wasserman et al. (12), observing the EPR spectra on photolysis of diazomethane and diazirine at 4 K, concluded that CH_2 has a triplet ground state with a probable bond angle of 136 ± 8°. Wasserman et al. (13) also reported that their investigation of the EPR spectra of CD_2 and CHD supported their earlier conclusions (12). In these latter two works (12, 13), the bond angle was determined from the zero-field parameter. In more recent work by Wasserman et al. (14), the ^{13}C hyperfine structure was observed in the EPR spectrum of ground state $^{13}CD_2$ at 4 K. The authors conclude that ground state CH_2, by analogy, has an angle of 137-143°.

Herzberg and Johns (15) state that the electronic spectra of CH_2 and its isotopic derivatives is not only compatible with a linear ground state but it is also consistent with a bond angle of 136° if an ad hoc assumption of a heterogeneous predissociation of the excited state is made. Recent theoretical calculations indicate a bent ground state (16, 17). We adopt the triplet ground state, $X\ ^3B_1$, as bent with an angle of 136 ± 5° on the basis of the previously mentioned experimental work and weighted by the remarks of Herzberg and Johns (15). The bond length is 1.029 Å as reported by Herzberg (4). The bond lengths and angles for the $a\ ^1A_1$ and $b\ ^1B_1$ states are also from Herzberg and Johns (18).

The singlet electronic levels are firmly established (19). The unobserved singlet-triplet separation is likely to be less than 8000 cm^{-1}, as suggested by Herzberg (19). Many theoretical arguments yield energy separations within 10% of this value (16, 17, 20). Goldberg and Riter (24) estimate a value of 2600 ± 2000 cm^{-1} by calculations which allow for correlation energy effects in different states, all assumed to be linear, however. Foner and Hudson (21) suggest a "small" separation due to the absence of resolved structure in the CH_2 ionization curve. Carr, Eder, and Topor (22) via ketone photolysis deduced an energy gap of roughly 350-700 cm^{-1}. Halberstadt and McNesby (23) suggest 880 cm^{-1} based on ketone photolysis in the presence of methane and propane. The value chosen for the singlet-triplet energy separation is 2600 ± 2000 cm^{-1}. This value is intermediate between the experimental and theoretical suggestions.

The vibrational frequencies for the three lower lying states were calculated via the valence force field method using the force constants calculated by O'Neil, Schaeffer, and Bender (17). The geometry and vibrational levels for the $c\ ^1A_1$ state were estimated. The uncertainty in the entropy mainly reflects the uncertain position of the low lying electronic levels.

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CH_2

Tantalum Monocarbide (TaC)
(Crystal) GFW = 192.958

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.557	-34.387	-34.387	INFINITE
100	4.450	3.078	16.652	-1.357	-34.439	-34.340	75.051
200	6.977	6.976	10.879	-.781	-34.480	-34.221	37.395
298	8.793	10.127	10.127	.000	-34.440	-34.099	24.995
300	8.820	10.182	10.128	.016	-34.439	-34.097	24.840
400	9.958	12.886	10.488	.959	-34.354	-33.995	18.574
500	10.643	15.186	11.204	1.991	-34.264	-33.915	14.824
600	11.101	17.168	12.037	3.079	-34.190	-33.854	12.331
700	11.446	18.906	12.896	4.207	-34.133	-33.901	10.553
800	11.729	20.454	13.746	5.366	-34.087	-33.758	9.222
900	11.978	21.850	14.570	6.551	-34.048	-33.720	8.188
1000	12.205	23.124	15.363	7.761	-34.008	-33.686	7.362
1100	12.411	24.297	16.122	8.992	-33.972	-33.656	6.687
1200	12.614	25.385	16.849	10.243	-33.937	-33.627	6.124
1300	12.815	26.403	17.546	11.514	-33.904	-33.603	5.649
1400	13.012	27.360	18.213	12.806	-33.864	-33.580	5.242
1500	13.206	28.264	18.853	14.117	-33.816	-33.561	4.890
1600	13.393	29.122	19.468	15.447	-33.758	-33.548	4.582
1700	13.579	29.940	20.060	16.795	-33.691	-33.537	4.311
1800	13.764	30.721	20.631	18.162	-33.617	-33.530	4.071
1900	13.948	31.470	21.182	19.548	-33.540	-33.527	3.856
2000	14.132	32.190	21.714	20.952	-33.460	-33.528	3.664
2100	14.314	32.884	22.230	22.374	-33.376	-33.532	3.490
2200	14.496	33.554	22.730	23.815	-33.291	-33.544	3.332
2300	14.677	34.203	23.214	25.273	-33.202	-33.555	3.188
2400	14.858	34.831	23.685	26.750	-33.112	-33.572	3.057
2500	15.039	35.441	24.143	28.245	-33.021	-33.594	2.937
2600	15.219	36.035	24.589	29.758	-32.933	-33.619	2.826
2700	15.399	36.613	25.024	31.289	-32.849	-33.648	2.724
2800	15.579	37.176	25.448	32.838	-32.771	-33.678	2.629
2900	15.758	37.726	25.862	34.404	-32.706	-33.711	2.541
3000	15.938	38.263	26.266	35.989	-32.654	-33.747	2.458
3100	16.118	38.788	26.662	37.592	-32.621	-33.783	2.382
3200	16.297	39.303	27.049	39.213	-32.612	-33.821	2.310
3300	16.477	39.807	27.428	40.852	-41.346	-33.749	2.235
3400	16.656	40.302	27.799	42.508	-41.301	-33.517	2.154
3500	16.835	40.787	28.164	44.183	-41.239	-33.291	2.079
3600	17.014	41.264	28.521	45.875	-41.161	-33.065	2.007
3700	17.193	41.733	28.872	47.585	-41.067	-32.841	1.940
3800	17.372	42.193	29.216	49.314	-40.955	-32.618	1.876
3900	17.550	42.647	29.555	51.060	-40.828	-32.399	1.816
4000	17.729	43.094	29.888	52.824	-40.684	-32.185	1.759
4100	17.908	43.534	30.215	54.606	-40.524	-31.977	1.705
4200	18.086	43.967	30.537	56.405	-40.349	-31.768	1.653
4300	18.265	44.395	30.855	58.223	-40.157	-31.567	1.604
4400	18.443	44.817	31.167	60.058	-39.949	-31.370	1.558
4500	18.622	45.233	31.475	61.911	-39.725	-31.179	1.514
4600	18.801	45.645	31.779	63.783	-39.484	-30.990	1.472
4700	18.979	46.051	32.078	65.672	-39.227	-30.808	1.433

December 31, 1973

TANTALUM MONOCARBIDE (TaC) (CRYSTAL) GFW = 192.958 CTa

$S°_{298.15}$ = 10.13 ± 0.20 gibbs/mol
Tm = 4273 ± 200 K

$ΔHf°_0$ = -34.39 ± 0.9 kcal/mol
$ΔHf°_{298.15}$ = -34.44 ± 0.9 kcal/mol
ΔHm° = [25.0 ± 5.0] kcal/mol

Heat of Formation

There are eight oxygen bomb calorimetric studies on TaC reported in the literature (1-8) and one CO(g) equilibrium study (9). The adopted $ΔHf°_{298}$ value is derived from the calorimetric study of Huber et al. (6). These authors studied the combustion of ten TaC_x samples where x covers the range 0.724 to 0.998. For each composition seven or eight combustions were performed. Huber et al. (6) reported that the combustions varied from 94.83% to 100% completion but were usually greater than 99%. Corrections of the order 0.4% or less were made to the heat of combustion value to account for impurities. The calculated heats of formation for the ten compositions were fitted to both a quadratic and linear equation by the least squares method by Huber et al. (6). Each value was weighted inversely proportional to the square of its uncertainty. Using the linear equation for $ΔHf°_{298}$ and correcting for the JANAF value of $ΔHf°_{298}(Ta_2O_5$, c) (10), we extrapolate to x = 1.0, calculate, and adopt $ΔHf°_{298}$ = -34.44 ± 0.9 kcal/mol for TaC. The quadratic equation leads to a value of -33.94 ± 1.2 kcal/mol which is consistent with our adopted value.

Huber et al. (6) and Storms (11) have reanalyzed the calorimetric and equilibrium data (1-9) for TaC_x (x=0.724 to 0.998). A graphical comparison of the results (i.e., $ΔHf°_{298}$ values vs. x) indicated that the linear or quadratic equation suggested by Huber et al. (6) is a satisfactory representation of all the $ΔHf°_{298}$ results for TaC_x. The shortcomings of the various studies have been discussed by Huber et al. (6) and Storms (11). For comparison, the oxygen combustion study by Mah (8) led to a reported value of $ΔHf°_{298}$ = -35.4 ± 0.5 kcal/mol for $TaC_{0.996}$ based on six combustions.

Heat Capacity and Entropy

Kelley (12) measured the heat capacity of TaC in the region 54-294 K (32 points). The reported data refers to stoichiometric TaC with corrections for 0.03% free carbon having been made by Kelley (12, 13). The sample contained less than 0.02% impurities other than free carbon. Using the Debye function suggested by Kelley (12), we calculate and adopt $S°_{50}$ = 0.831 gibbs/mol and $H°_{50}-H°_0$ = 30.10 cal/mol.

Of the numerous enthalpy and heat capacity studies on TaC (14-24), the adopted Cp° values for T > 298 K are derived primarily from the studies of Pankratz et al. (21), Chang (23), Levinson (17), and Bolgar et al. (22). The heat capacity data for $200 \leq T \leq 298$ K are used to derive enthalpy values which in turn are used to constrain the high temperature enthalpy data. A polynomial curve fitting technique is used for the Pankratz et al. (21) and Levinson (17) data, with the above mentioned constraints, to obtain a smooth joining of the results near 298 K and to provide an equation suitable for extrapolation to Tm. Pankratz et al. (21) determined the enthalpy of $TaC_{1.008}$ in the region 405-1700 K (14 data points) while Levinson (17) studied $TaC_{1.007}$ in the range 1289-2778 K (15 data points). Both sets of data are corrected to the stoichiometric composition (TaC) assuming excess free carbon. These corrections are roughly 20 cal/mol at 1000 K and 90 cal/mol at 2500 K (10). Chang (23) determined the enthalpy of a reported stoichiometric TaC sample for 324-985 K (11 data points). Bolgar et al. (22) reported an equation for Cp° values as a function of T and x for the 1200-2400 K range. This equation was based on a study of four TaC_x compositions. We use this equation to extrapolate to the TaC composition.

The adopted tabulation yields enthalpy values for T < 1200 K which are very similar to those suggested by Pankratz et al. (21), the difference being no more than ±20 cal/mol. Above 1200 K, the data of Pankratz et al. (21) lies low approaching roughly 1% in the 1700-1800 K region. The Chang data (23) lies below the tabulated enthalpy values for T < 600 K. The average deviation is 0.94% with the maximum of -2.5% occurring at 324.4 K. The Levinson data (17) has an average deviation of 0.5% with considerable scatter. The Cp° values of Bolgar et al. (22) lie 0.21 gibbs/mol (1.64%) low at 1200 K and drift to 0.43 gibbs/mol (3.00%) high at 2200 K. The recent enthalpy data of Sheindlin et al. (24) has considerable scatter and deviates from our tabulated values by an average deviation of 6%.

Phase Data

TaC has a cubic structure of the NaCl type (11) and has a wide homogeneity range. From the phase diagram for the Ta-C system given by Storms (11), the temperature dependent homogeneity range extends from x=0.58 at 3603 ± 100 K to x=0.998 or possibly x=1.00. The phase boundary at a eutectic temperature of 3673 ± 50 K is $TaC_{0.98}$. A discussion of the phase diagram for TaC_x (x-0.00 to 1.6) is given by Storms (11).

Melting Data

Refer to TaC(ℓ) table.

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Tantalum Monocarbide (TaC)

(Liquid) GFW = 192.958

T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	8.793	16.319	16.319	.000	-8.115	-9.621	7.052
300	8.820	16.374	16.319	.016	-8.114	-9.630	7.015
400	9.958	19.078	16.680	.959	-8.030	-10.147	5.544
500	10.643	21.377	17.396	1.991	-7.940	-10.687	4.671
600	11.101	23.360	18.228	3.079	-7.865	-11.244	4.096
700	11.446	25.098	19.088	4.207	-7.809	-11.811	3.688
800	11.729	26.645	19.938	5.366	-7.763	-12.386	3.384
900	11.978	28.041	20.762	6.551	-7.723	-12.968	3.149
1000	12.205	29.315	21.554	7.761	-7.684	-13.553	2.962
1100	12.411	30.488	22.314	8.992	-7.648	-14.142	2.810
1200	12.614	31.577	23.041	10.243	-7.613	-14.733	2.683
1300	12.815	32.594	23.737	11.514	-7.579	-15.328	2.577
1400	13.012	33.551	24.404	12.806	-7.540	-15.924	2.486
1500	13.206	34.456	25.045	14.117	-7.492	-16.524	2.408
1600	13.393	35.314	25.660	15.447	-7.434	-17.130	2.340
1700	13.579	36.131	26.252	16.795	-7.366	-17.738	2.280
1800	13.764	36.913	26.823	18.162	-7.292	-18.350	2.228
1900	13.948	37.662	27.374	19.548	-7.216	-18.966	2.182
2000	14.132	38.382	27.906	20.952	-7.136	-19.587	2.140
2100	14.314	39.076	28.422	22.374	-7.051	-20.210	2.103
2200	14.496	39.746	28.921	23.815	-6.967	-20.841	2.070
2300	14.677	40.394	29.406	25.273	-6.877	-21.471	2.040
2400	14.858	41.023	29.877	26.750	-6.787	-22.108	2.013
2500	15.039	41.633	30.335	28.245	-6.697	-22.749	1.989
2600	15.219	42.226	30.781	29.758	-6.609	-23.392	1.966
2700	15.399	42.804	31.216	31.289	-6.525	-24.041	1.946
2800	16.000	43.368	31.640	32.838	-6.447	-24.690	1.927
2900	16.000	43.929	32.054	34.438	-6.348	-25.343	1.910
3000	16.000	44.471	32.459	36.038	-6.281	-25.999	1.894
3100	16.000	44.996	32.855	37.638	-6.251	-26.657	1.879
3200	16.000	45.504	33.242	39.238	-6.263	-27.315	1.866
3300	16.000	45.996	33.621	40.838	-15.036	-27.862	1.845
3400	16.000	46.474	33.992	42.438	-15.047	-28.248	1.816
3500	16.000	46.938	34.356	44.038	-15.060	-28.639	1.788
3600	16.000	47.389	34.711	45.638	-15.074	-29.027	1.762
3700	16.000	47.827	35.060	47.238	-15.090	-29.413	1.737
3800	16.000	48.254	35.402	48.838	-15.107	-29.798	1.714
3900	16.000	48.669	35.736	50.438	-15.126	-30.184	1.691
4000	16.000	49.074	36.065	52.038	-15.146	-30.570	1.670
4100	16.000	49.469	36.387	53.638	-15.168	-30.957	1.650
4200	16.000	49.855	36.703	55.238	-15.192	-31.339	1.631
4300	16.000	50.231	37.013	56.838	-15.218	-31.725	1.612
4400	16.000	50.599	37.318	58.438	-15.245	-32.109	1.595
4500	16.000	50.959	37.617	60.038	-15.274	-32.493	1.578
4600	16.000	51.310	37.911	61.638	-15.305	-32.874	1.562
4700	16.000	51.655	38.200	63.238	-15.337	-33.256	1.546
4800	16.000	51.991	38.484	64.838	-15.372	-33.635	1.531
4900	16.000	52.321	38.763	66.438	-15.408	-34.016	1.517
5000	16.000	52.645	39.037	68.038	-15.446	-34.395	1.503
5100	16.000	52.961	39.307	69.638	-15.487	-34.778	1.490
5200	16.000	53.272	39.573	71.238	-15.529	-35.154	1.477
5300	16.000	53.577	39.834	72.838	-15.573	-35.529	1.465
5400	16.000	53.876	40.091	74.438	-15.619	-35.904	1.453
5500	16.000	54.170	40.344	76.038	-15.668	-36.280	1.442
5600	16.000	54.458	40.594	77.638	-15.718	-36.655	1.431
5700	16.000	54.741	40.840	79.238	-15.771	-37.031	1.420
5800	16.000	55.019	41.082	80.838	-191.974	-36.980	1.393
5900	16.000	55.293	41.320	82.438	-192.029	-34.303	1.271
6000	16.000	55.562	41.555	84.038	-192.090	-31.634	1.152

December 31, 1973

TANTALUM MONOCARBIDE (TaC) (LIQUID) GFW = 192.958 CTa

$S^\circ_{298.15}$ = [16.319] gibbs/mol

Tm = 4273 ± 200 K

Td = 5581 K

$\Delta Hf^\circ_{298.15}$ = [-8.115] kcal/mol

ΔHm° = [25.0 ± 5.0] kcal/mol

Heat of Formation

The heat of formation of TaC(ℓ) at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between ($H^\circ_{4273}-H^\circ_{298}$) for TaC(c) and TaC(ℓ).

Heat Capacity and Entropy

The heat capacity for TaC(ℓ) is assumed to be 16.0 gibbs/mol for the entire liquid phase. A glass transition is assumed at 2800 K, below which the heat capacity values of the crystal are used. The entropy is calculated in a manner analogous to the heat of formation.

Melting Data

The phase diagram given by Storms (1) indicated a eutectic melting at 3673 ± 50 K. A congruent melting point was estimated by Storms (1) at roughly 4273 K for $TaC_{0.88}$. As an approximation due to the uncertainties in this area of the phase diagram, we adopt Tm = 4273 ± 200 K and assign this melting point to TaC. We assume a heat of melting ΔHm° = 25.0 ± 5.0 kcal/mol (ΔSm° = 5.85 gibbs/mol).

Decomposition Data

Using JANAF auxiliary data (2), we calculate Td as that temperature at which ΔGr° approaches zero for the reaction TaC(ℓ) = Ta(ℓ) + C(g). We calculate Td = 5581 K as the decomposition temperature.

References

1. E. K. Storms, "The Refractory Carbides," Academic Press, New York, 1967.
2. JANAF Thermochemical Tables: Ta(ℓ), 12-31-72; C(g), 3-31-61.

Trichromium Dicarbide (Cr_3C_2)

C_2Cr_3

(Crystal) GFW = 180.010

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.617	-20.603	-20.603	INFINITE
100	7.486	3.417	37.189	-3.377	-20.616	-20.608	45.040
200	17.858	12.099	22.421	-2.064	-20.593	-20.593	22.503
298	23.733	20.419	20.419	.000	-20.400	-20.628	15.121
300	23.820	20.566	20.420	.044	-20.394	-20.629	15.028
400	27.600	27.973	21.404	2.628	-20.051	-20.757	11.341
500	30.007	34.408	23.376	5.516	-19.664	-20.979	9.170
600	31.426	40.011	25.692	8.591	-19.295	-21.279	7.751
700	32.423	44.932	28.096	11.785	-18.967	-21.632	6.754
800	33.246	49.316	30.480	15.069	-18.680	-22.033	6.019
900	34.001	53.276	32.796	18.432	-18.439	-22.470	5.457
1000	34.734	56.896	35.028	21.869	-18.249	-22.930	5.011
1100	35.463	60.241	37.170	25.378	-18.126	-23.403	4.650
1200	36.197	63.358	39.224	28.961	-18.075	-23.884	4.350
1300	36.939	66.285	41.194	32.618	-18.108	-24.369	4.097
1400	37.690	69.050	43.086	36.349	-18.222	-24.844	3.878
1500	38.449	71.676	44.905	40.156	-18.423	-25.311	3.688
1600	39.217	74.182	46.657	44.039	-18.710	-25.764	3.519
1700	39.991	76.582	48.347	48.000	-19.080	-26.193	3.367
1800	40.771	78.890	49.980	52.038	-19.542	-26.599	3.230
1900	41.556	81.116	51.561	56.154	-20.091	-26.975	3.103
2000	42.346	83.267	53.093	60.349	-20.729	-27.323	2.986
2100	43.138	85.353	54.579	64.624	-21.453	-27.632	2.876
2200	43.920	87.377	56.024	68.976	-36.136	-27.442	2.726
2300	44.712	89.347	57.431	73.408	-35.708	-27.052	2.571
2400	45.504	91.267	58.801	77.919	-35.207	-26.687	2.430
2500	46.296	93.140	60.137	82.509	-34.629	-26.346	2.303

Dec. 31, 1973

TRICHROMIUM DICARBIDE (Cr_3C_2) (CRYSTAL) GFW = 180.010 C_2Cr_3

$\Delta Hf^\circ_0 = -20.6 \pm 3.0$ kcal/mol

$S^\circ_{298.15} = 20.42 \pm 0.10$ gibbs/mol $\Delta Hf^\circ_{298.15} = -20.4 \pm 3.0$ kcal/mol

Heat of Formation

Mah (1) determined the heat of combustion of $Cr_3C_2(c)$ using oxygen bomb calorimetry. She reported $\Delta Hc^\circ_{298} = -574.5 \pm 0.4$ kcal/mol based on the reaction $Cr_3C_2(c) + 17/4\ O_2(g) = 3/2\ Cr_2O_3(c) + 2\ CO_2(g)$. Using auxiliary JANAF data (2), we calculate $\Delta Hf^\circ_{298} = -20.4$ kcal/mol for $Cr_3C_2(c)$. Mah (1) reported that of the six combustion runs four were complete combustions whereas the other two were 99.17% and 98.57% complete. Corrections were made by Mah (1) for incomplete combustion, formation of small amounts of CO(g), and impurities. These corrections amount to less than 1.95% of the ΔE°_c value.

There are many equilibrium studies involving $Cr_3C_2(c)$ (3-13). Our analysis of a portion of these studies is tabulated below.

				ΔHr°_{298}, kcal/mol			
Reference	Reaction	Range, K	Method	2nd Law	3rd Law	Drift eu	ΔHf°_{298}* kcal/mol
4	A(14 pts.)**	1244-1382	CO equilibrium pressure	528.39	533.26	3.7±3.4	-21.29
8	A(18 pts.)	1316-1366	CO equilibrium pressure	495.46	526.56	23.0±6.4	-24.64
10	B(eqn)	880-1100	emf (CaF_2)	- 9.34	-12.60	-3.3	-12.60
11	B(eqn)	1073-1303	emf ($ThO_2 \cdot Y_2O_3$)	-12.70	-15.73	-2.5	-15.73
12	B(eqn)	885-1095	emf (CaF_2)	-15.42	-14.92	0.5	-14.92

Reaction A: $3\ Cr_2O_3(c) + 13\ C(c) = 2\ Cr_3C_2(c) + 9\ CO(g)$.

Reaction B: $3\ Cr(c) + 2\ C(c) = Cr_3C_2(c)$.

* Based on 3rd law ΔHr°.

** 1374 K point rejected due to statistical test.

The CO(g) equilibrium pressures measured by Heusler (3) in the range 1159-1369 K are higher than those of Kelley et al. (4) by a factor varying from 2.0 to 1.4 with increasing temperature. Three studies measured the chromium pressure in equilibrium with C(c) and $Cr_3C_2(c)$ (5, 7, 9). Reported heats of formation for Cr_3C_2 from these studies are -23.1 kcal/mol (5), -14.2 kcal/mol (7), and -22 kcal/mol (9). Alekseev and Shvartsman (6) studied the decarburization of the chromium carbides. Mah (1) analyzed their data and reported $\Delta Hf^\circ_{298} = -16.6$ kcal/mol for $Cr_3C_2(c)$.

The ΔHf° results are quite scattered with the emf results being roughly 5 kcal/mol more positive than the combustion and pressure equilibrium studies. Possible explanations for these discrepancies are discussed by Kulkarni and Worrell (16). We adopt $\Delta Hf^\circ_{298} = -20.4 \pm 3.0$ kcal/mol for $Cr_3C_2(c)$ based on the combustion study by Mah (1).

Heat Capacity and Entropy

The heat capacity of $Cr_3C_2(c)$ has been measured by Kelley et al. (4) [53-296 K, 29 pts.] and DeSorbo (14) [12-301 K, 65 pts.]. As reported by DeSorbo (14), the results of these two studies differ by no more than 0.1%. Using the Debye function 3D (300/T) as suggested by DeSorbo (14), we calculate and adopt $S^\circ_{12} = 0.0297$ gibbs/mol and $H^\circ_{12}-H^\circ_0 = 0.268$ cal/mol. The enthalpy has been measured by Kelley et al. (4) [481-1576 K, 17 pts.] and Oriani and Murphy (15) [297-1188 K, 11 pts.]. As stated by Oriani and Murphy (15), their results are somewhat lower than those of Kelley et al. (4); the maximum difference is 1.2% at 970 K. For T > 298 K, we base our adopted values on the enthalpy data of Kelley et al. (4). The enthalpy data is subjected to a curve fit procedure with the constraint that it join smoothly in the 298 K region with the enthalpy derived from the heat capacity data of Kelley et al. (4). The deviations between the tabulated and observed enthalpy average 0.26% with a maximum of 0.78% at the lowest observed temperature, 480.7 K.

Phase Data

Storms (17) has summarized the phase information for the Cr-Cr_3C_2 system and reported that Cr_3C_2 has an orthorhombic structure. The range of homogeneity is unknown (17).

Decomposition Data

The tentative phase diagram for the Cr-Cr_3C_2 system proposed by Storms (17) indicated that Cr_3C_2 has an incongruent melting point at 2168 K.

References

1. A. D. Mah, U. S. Bur. Mines, RI 7217, 1969.
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3. O. Heusler, Z. Anorg. Chem. 154, 353 (1926).
4. K. K. Kelley, F. S. Boericke, G. E. Moore, E. H. Huffman, and W. M. Bangert, U. S. Bur. Mines, Tech. Paper 662, 1949.
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14. W. DeSorbo, J. Amer. Chem. Soc. 75, 1825 (1953).
15. R. A. Oriani and W. K. Murphy, J. Amer. Chem. Soc. 76, 343 (1954).
16. A. D. Kulkarni and W. L. Worrell, Met. Trans. 3, 2363 (1972).
17. E. K. Storms, "The Refractory Carbides," Academic Press, New York, 1967.

C_2Cr_3

Heptachromium Tricarbide (Cr_7C_3)

C_3Cr_7

(Crystal) GFW = 400.005

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 8.221	- 39.075	- 39.075	INFINITE
100	19.219	9.436	85.010	- 7.557	- 38.978	- 39.142	85.544
200	40.013	29.970	52.340	- 4.474	- 38.775	- 39.361	43.012
298	50.131	48.036	48.036	.000	- 38.400	- 39.725	29.119
300	50.280	48.347	48.037	.093	- 38.389	- 39.731	28.944
400	56.576	63.743	50.093	5.460	- 37.841	- 40.259	21.997
500	60.438	76.807	54.164	11.322	- 37.283	- 40.933	17.892
600	62.979	88.059	58.897	17.497	- 36.792	- 41.712	15.194
700	64.999	97.921	63.782	23.897	- 36.371	- 42.559	13.288
800	66.828	106.721	68.609	30.489	- 36.007	- 43.469	11.875
900	68.596	114.694	73.294	37.260	- 35.709	- 44.426	10.788
1000	70.356	122.012	77.804	44.208	- 35.494	- 45.409	9.924
1100	72.127	128.801	82.135	51.332	- 35.399	- 46.403	9.219
1200	73.917	135.153	86.292	58.634	- 35.445	- 47.400	8.633
1300	75.727	141.141	90.283	66.116	- 35.658	- 48.391	8.135
1400	77.556	146.820	94.120	73.780	- 36.039	- 49.353	7.704
1500	79.401	152.234	97.815	81.628	- 36.603	- 50.288	7.327
1600	81.260	157.417	101.379	89.661	- 37.350	- 51.180	6.991
1700	83.132	162.400	104.823	97.880	- 38.280	- 52.014	6.687
1800	85.015	167.205	108.156	106.287	- 39.408	- 52.791	6.410
1900	86.907	171.852	111.387	114.883	- 40.727	- 53.498	6.154
2000	88.807	176.358	114.523	123.669	- 42.243	- 54.135	5.916
2100	90.715	180.737	117.573	132.645	- 43.953	- 54.684	5.691
2200	92.625	185.001	120.541	141.812	- 78.216	- 54.060	5.370
2300	94.534	189.161	123.434	151.170	- 77.214	- 52.979	5.034
2400	96.445	193.224	126.258	160.719	- 76.030	- 51.951	4.731
2500	98.355	197.200	129.016	170.459	- 74.658	- 50.978	4.456

Dec. 31, 1973

HEPTACHROMIUM TRICARBIDE (Cr_7C_3) (CRYSTAL) GFW = 400.005 C_3Cr_7

ΔHf°_0 = -39.1 ± 4.0 kcal/mol

$S^\circ_{298.15}$ = 48.04 ± 0.30 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -38.4 ± 4.0 kcal/mol

Heat of Formation

Mah (1) determined the heat of combustion of $Cr_7C_3(c)$ using oxygen bomb calorimetry. She reported ΔHc°_{298} = -1193.0 ± 0.9 kcal/mol based on the reaction $Cr_7C_3(c) + 33/4\ O_2(g) = 7/2\ Cr_2O_3(c) + 3\ CO_2(g)$. Using JANAF auxiliary data (2), we calculate ΔHf°_{298} = -38.4 kcal/mol for $Cr_7C_3(c)$. Mah (1) reported that the six combustion runs gave 99.09 to 99.84% completion of combustion. Corrections for incomplete combustion, formation of small amounts of CO(g), and impurities were made by Mah (1). These corrections amount to no more than 1.04% of the ΔEc° value.

The pressures of CO(g) in equilibrium with a Cr_2O_3-Cr_7C_3-$Cr_{23}C_6$ mixture have been measured by Kelley et al. (3) and Kulkarni and Worrell (4). Kelley et al. (3) also examined the Cr_2O_3-Cr_3C_2-Cr_7C_3 system. Kulkarni and Worrell (4) measured the CO pressure using a torsion effusion technique while Kelley et al. (3) measured the pressure manometrically. The results of our analyses are tabulated in the following table. In all cases we have assumed unit activity for the condensed species.

Reference	Range, K	Reaction	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$\Delta Hf^\circ_{298}(Cr_7C_3, c)$* kcal/mol
3	1307-1497	A (9 pts.)	994.44	970.74	-16.9±4.3	-41.53
4	1111-1250	B (11 pts.)[a]	220.48	218.99	- 1.3±0.6	-35.18
3	1505-1723	B (15 pts.)[b]	211.34	220.89	5.8±2.0	-35.81

Reaction A: $5\ Cr_2O_3(c) + 27\ Cr_3C_2(c) = 13\ Cr_7C_3(c) + 15\ CO(g)$.

Reaction B: $Cr_2O_3(c) + 3\ Cr_7C_3(c) = Cr_{23}C_6(c) + 3\ CO(g)$.

* Based on 3rd law ΔHr°.

[a] 1234.6, 1250.0 K points deleted due to statistical test; effective range is now 1111-1220 K.

[b] 1524 K point deleted due to statistical test.

We adopt ΔHf°_{298} = -38.4 ± 4.0 kcal/mol for $Cr_7C_3(c)$ based on the combustion data of Mah (1). The equilibrium studies by Kulkarni and Worrell (4) and Kelley et al. (3) are in reasonable agreement with the adopted value. Equilibrium studies involving $Cr_7C_3(c)$ by Hancock and Pidgeon (5), Alekseev and Shvartsman (6), and Bolgar et al. (7) are not considered (2).

Heat Capacity and Entropy

The heat capacity (54-295 K, 29 pts.) and enthalpy (480-1580 K, 15 pts.) have been measured by Kelley et al. (3). Using the Debye function suggested (3), we calculate S°_{50} = 1.679 gibbs/mol and $H^\circ_{50}-H^\circ_0$ = 62.66 cal/mol. The adopted heat capacity curve is based solely on the above mentioned study with the constraint that the heat capacity values derived from the enthalpy data join smoothly with the low temperature heat capacity values near 298 K. The observed Cp° values deviate from the adopted values within ±0.2% for T < 298 K. The enthalpy data agrees within ±0.35% with the tabulated values except for the 1263.4 K data (1.66% or ~1.0 kcal/mol too low) and the two points at 1545.1 and 1578.1 K which were not included in the polynomial curve fit (3). The polynomial is used to extrapolate Cp° values above 1500 K.

Phase Data

Storms (8) has summarized much of the phase data for the chromium carbides and reported a hexagonal structure for Cr_7C_3. The homogeneity range for Cr_7C_3 is not known (8).

Decomposition Data

The tentative phase diagram for the Cr-Cr_3C_2 system as proposed by Storms (8) indicated an incongruent melting at 2053 K.

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C_3Cr_7

Chromium Carbide ($Cr_{23}C_6$) C_6Cr_{23}

(Crystal) GFW = 1267.974

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 25.037	- 79.715	- 79.715	INFINITE
100	59.827	28.163	258.558	- 23.040	- 79.527	- 79.859	174.532
200	121.761	91.678	159.256	- 13.516	- 79.165	- 80.288	87.734
298	150.132	146.282	146.282	.000	- 78.500	- 80.973	59.354
300	150.500	147.212	146.285	.278	- 78.476	- 80.980	58.994
400	168.350	193.118	152.423	16.278	- 77.361	- 81.979	44.791
500	180.100	232.036	164.554	33.741	- 76.095	- 83.291	36.407
600	187.799	265.605	178.664	52.164	- 74.890	- 84.850	30.907
700	193.144	294.960	193.225	71.214	- 73.846	- 86.573	27.029
800	198.153	321.077	207.604	90.779	- 72.974	- 88.454	24.165
900	203.214	344.707	221.545	110.846	- 72.297	- 90.446	21.963
1000	208.447	366.386	234.959	131.427	- 71.887	- 92.496	20.215
1100	213.876	386.507	247.833	152.542	- 71.850	- 94.550	18.785
1200	219.486	405.356	260.182	174.208	- 72.260	- 96.592	17.592
1300	225.256	423.151	272.040	196.444	- 73.190	- 98.592	16.575
1400	231.161	440.060	283.442	219.264	- 74.659	- 100.487	15.687
1500	237.180	456.213	294.426	242.680	- 76.707	- 102.269	14.901
1600	243.295	471.715	305.025	266.704	- 79.333	- 103.897	14.192
1700	249.489	486.650	315.272	291.342	- 82.542	- 105.328	13.541
1800	255.750	501.087	325.196	316.604	- 86.376	- 106.564	12.939
1900	262.067	515.084	334.824	342.494	- 90.819	- 107.565	12.373
2000	268.431	528.688	344.179	369.019	- 95.887	- 108.327	11.837

Dec. 31, 1973

CHROMIUM CARBIDE ($Cr_{23}C_6$) (CRYSTAL) GFW = 1267.974 C_6Cr_{23}

$\Delta Hf^\circ_0 = -79.7 \pm 10.0$ kcal/mol

$S^\circ_{298.15} = 146.3 \pm 1.0$ gibbs/mol

$\Delta Hf^\circ_{298.15} = -78.5 \pm 10.0$ kcal/mol

Heat of Formation

Mah (1) determined the heat of combustion of $Cr_{23}C_6$(c) using oxygen bomb calorimetry. Using auxiliary JANAF data (2) and the value $\Delta Hc^\circ_{303.15} = -3604.2 \pm 1.5$ kcal/mol reported by Mah (1) for the combustion of $Cr_{23}C_6$, we calculate $\Delta Hf^\circ_{298} = -78.5$ kcal/mol for $Cr_{23}C_6$(c). The combustion equation is $Cr_{23}C_6(c) + 93/4\ O_2(g) = 23/2\ Cr_2O_3(c) + 6\ CO_2(g)$. The factor (23/2) makes the ΔHf value for $Cr_{23}C_6$ extremely sensitive to the corresponding value for Cr_2O_3(c). Of the nine combustion runs, Mah (1) reported complete combustion in three runs and 99.40 to 99.85% completion in the remaining six. Corrections for incomplete combustion, formation of small amounts of CO(g) and impurities were made by Mah (1). These corrections amount to no more than 0.7% of the ΔEc° value.

The pressures of CO(g) in equilibrium with a $Cr_{23}C_6$-Cr_2O_3-Cr mixture have been measured by Kelley et al. (3) and Kulkarni and Worrell (4). Our analysis of their data is tabulated below. Kulkarni and Worrell (4) measured the CO pressure using a torsion effusion technique while Kelley et al. (3) measured the pressure manometrically. In all cases unit activity is assumed for the condensed species.

Reference	Range, K	Comments**	Reaction	ΔH°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$\Delta Hf^\circ_{298}(Cr_{23}C_6,c)$* kcal/mol
4	1170-1307	1/4 mm	A(15 pts.)	466.37	462.43	-3.2±2.5	-78.53
4	1158-1286	1/3 mm	A(8 pts.)	450.14	462.31	9.9±7.2	-78.41
4	1156-1283	1/2 mm	A(9 pts.)	451.46	467.72	13.3±3.3	-83.82
3	1571-1772		A(18 pts.)[a]	459.47	467.19	4.6±4.0	-83.29

Reaction A: $Cr_{23}C_6 + 2\ Cr_2O_3(c) = 27\ Cr(c) + 6\ CO(g)$

* 3rd law value.

** effusion orifice diameter

[a] 1725, 1775 K points rejected due to statistical test.

We adopt $\Delta Hf^\circ_{298} = -78.5 \pm 10.0$ kcal/mol for $Cr_{23}C_6$(c) based on the combustion data of Mah (1), with excellent support in the equilibrium studies by Kulkarni and Worrell (4) for orifice diameters of 1/4 and 1/3 mm. Kulkarni and Worrell (4) concluded that equilibrium was not obtained in the cell with the 1/2 mm orifice in order to provide an explanation for the low pressures observed. Equilibrium studies involving $Cr_{23}C_6$(c) by Hancock and Pidgeon (5), Alekseev and Shvartsman (6), and Bolgar et al. (7) are not considered (2).

Heat Capacity and Entropy

The heat capacity (55-295 K, 29 pts.) and enthalpy (467-1697 K, 26 pts.) have been measured by Kelley et al (3). When the research was performed, Kelley et al. (3) considered the sample to be Cr_4C. All the data are corrected to the composition $Cr_{23}C_6$, assuming that the sample actually contained excess Cr. The contribution of the assumed free Cr was subtracted from the reported heat capacity and enthalpy values using JANAF data for Cr (2). These corrections amount to 0.6 gibbs/mol at 55 K and 5.0 gibbs/mol at 295 K for the heat capacity data and are in a range of 1.00-1.85 kcal/mol for the enthalpy data. We adopt $S^\circ_{50} = 4.861$ gibbs/mol and $H^\circ_{50}-H^\circ_0 = 181.6$ cal/mol. The enthalpy data are fit to a six term polynomial with a constraint to join smoothly in the 298 K region with the enthalpy derived from the heat capacity data. There is considerable scatter in the enthalpy data. Deviations of the observed data from the tabulated data are within ±0.6% except for the 486.5 K data point which is approximately 1% (500 cal/mol) too high. The enthalpy polynomial is used to extrapolate the results to 2000 K.

Phase Data

Storms (8) has summarized the phase information in the Cr-C system and reported that $Cr_{23}C_6$ has a complex face-centered-cubic structure. The range of homogeneity for $Cr_{23}C_6$ is unknown (8).

Decomposition Data

The tentative phase diagram of the Cr-Cr_3C_2 system proposed by Storms (8) indicated that $Cr_{23}C_6$ has an incongruent melting point at 1793 K.

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C_6Cr_{23}

Calcium Monoiodide (CaI) CaI

(Ideal Gas) GFW = 166.9845

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.392	-.650	-.650	INFINITE
100	7.771	53.293	70.031	-1.674	-.530	-4.749	10.379
200	8.534	58.970	63.222	-.850	-.838	-8.858	9.680
298	8.758	62.426	62.426	.000	-1.206	-12.719	9.323
300	8.761	62.481	62.427	.016	-1.213	-12.791	9.318
400	8.854	65.015	62.771	.898	-3.555	-16.520	9.026
500	8.902	66.997	63.426	1.786	-9.075	-19.231	8.406
600	8.932	68.623	64.160	2.677	-9.282	-21.243	7.738
700	8.953	70.001	64.899	3.572	-9.491	-23.221	7.250
800	8.970	71.198	65.613	4.468	-10.038	-25.138	6.867
900	8.983	72.255	66.293	5.365	-10.444	-27.002	6.557
1000	8.995	73.202	66.938	6.264	-10.903	-28.817	6.298
1100	9.005	74.060	67.547	7.164	-11.414	-30.585	6.077
1200	9.015	74.844	68.123	8.065	-13.760	-32.151	5.856
1300	9.024	75.566	68.668	8.967	-14.032	-33.672	5.661
1400	9.033	76.235	69.185	9.870	-14.305	-35.173	5.491
1500	9.042	76.858	69.676	10.774	-14.578	-36.655	5.341
1600	9.051	77.442	70.143	11.679	-14.851	-38.117	5.206
1700	9.060	77.991	70.589	12.584	-15.123	-39.563	5.086
1800	9.069	78.509	71.015	13.491	-52.289	-40.311	4.894
1900	9.079	79.000	71.422	14.398	-52.340	-39.645	4.560
2000	9.091	79.466	71.813	15.307	-52.392	-38.976	4.259
2100	9.104	79.910	72.188	16.216	-52.444	-38.304	3.986
2200	9.119	80.334	72.548	17.127	-52.499	-37.629	3.738
2300	9.136	80.739	72.896	18.040	-52.556	-36.952	3.511
2400	9.156	81.129	73.231	18.955	-52.617	-36.272	3.303
2500	9.179	81.503	73.554	19.872	-52.682	-35.590	3.111
2600	9.205	81.863	73.867	20.791	-52.753	-34.905	2.934
2700	9.235	82.211	74.170	21.713	-52.831	-34.217	2.770
2800	9.268	82.548	74.463	22.638	-52.916	-33.525	2.617
2900	9.306	82.874	74.747	23.566	-53.010	-32.831	2.474
3000	9.347	83.190	75.023	24.499	-53.117	-32.134	2.341
3100	9.392	83.497	75.292	25.436	-53.235	-31.432	2.216
3200	9.440	83.796	75.553	26.377	-53.368	-30.727	2.099
3300	9.493	84.087	75.807	27.324	-53.517	-30.017	1.988
3400	9.549	84.371	76.055	28.276	-53.682	-29.303	1.884
3500	9.609	84.649	76.296	29.234	-53.867	-28.582	1.785
3600	9.673	84.921	76.532	30.198	-54.071	-27.857	1.691
3700	9.739	85.187	76.763	31.169	-54.297	-27.127	1.602
3800	9.808	85.447	76.988	32.146	-54.546	-26.389	1.518
3900	9.880	85.703	77.208	33.131	-54.820	-25.644	1.437
4000	9.955	85.954	77.423	34.122	-55.116	-24.894	1.360
4100	10.031	86.201	77.635	35.122	-55.438	-24.132	1.286
4200	10.110	86.444	77.841	36.129	-55.786	-23.364	1.216
4300	10.189	86.682	78.044	37.144	-56.161	-22.590	1.148
4400	10.270	86.917	78.243	38.167	-56.560	-21.804	1.083
4500	10.352	87.149	78.439	39.198	-56.987	-21.009	1.020
4600	10.435	87.378	78.630	40.237	-57.438	-20.204	.960
4700	10.517	87.603	78.819	41.285	-57.915	-19.391	.902
4800	10.600	87.825	79.004	42.340	-58.417	-18.565	.845
4900	10.683	88.045	79.187	43.405	-58.942	-17.729	.791
5000	10.765	88.261	79.366	44.477	-59.490	-16.882	.738
5100	10.846	88.475	79.542	45.558	-60.060	-16.025	.687
5200	10.927	88.687	79.716	46.646	-60.652	-15.157	.637
5300	11.006	88.896	79.887	47.743	-61.262	-14.275	.589
5400	11.084	89.102	80.056	48.847	-61.890	-13.382	.542
5500	11.160	89.306	80.222	49.959	-62.536	-12.479	.496
5600	11.235	89.508	80.386	51.079	-63.196	-11.565	.451
5700	11.307	89.707	80.548	52.206	-63.870	-10.635	.408
5800	11.378	89.905	80.708	53.341	-64.558	-9.695	.365
5900	11.447	90.100	80.865	54.482	-65.255	-8.744	.324
6000	11.513	90.293	81.021	55.630	-65.963	-7.779	.283

June 30, 1974

CALCIUM MONOIODIDE (CaI) (IDEAL GAS) GFW = 166.9845 CaI

Ground State Configuration $[^2\Sigma^+]$

$S^\circ_{298.15}$ = 62.43 ± 0.05 gibbs/mol

ΔHf°_0 = -0.65 ± 20 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -1.21 ± 20 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	gi
X $[^2\Sigma^+]$	0	2
A $[^2\Pi]$	15585.1 15645.9	2 2
B $[^2\Sigma^+]$	15711.2	2
C $[^2\Pi]$	23314.0 23741.9	2 2
D $[^2\Sigma^+]$	31062.0	2

ω_e = 238.3 cm^{-1} $\omega_e x_e$ = 0.61 cm^{-1} σ = 1

B_e = [0.0667] cm^{-1} α_e = [0.00023] cm^{-1} r_e = [2.88] Å

Heat of Formation

The adopted ΔHf°_0 = -0.65 ± 20 kcal/mol is calculated from the D°_0 = 3 ± 1 eV(69 ± 23 kcal/mol) selected by Gaydon (1). A linear Birge-Sponer extrapolation of ω_e and $\omega_e x_e$ data (2) with a correction for the ionic character of the molecule as described by Hildenbrand (3) gave D°_0 = 66.5 kcal/mol. Other D°_0 values are 63.9 kcal/mol (4) as a lower bound from a consideration of ionic bonding forces and 64 kcal/mol (5) derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. Of the four ratios, D°_0(CaI)/D°_0(CaI_2), D°_0(CaI) = 69 kcal/mol gives 0.445 which is closest to 0.46 found for a series of mono- and difluorides (6) and for other alkaline earth halide systems (8). ΔHf°_{298} = -1.21 ± 20 kcal/mol is calculated from the adopted ΔHf°_0 = -0.65 ± 20 kcal/mol.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen (2). The value of r_e = 2.88 Å is assumed the same as the bond distance in CaI_2 (7). B_e is calculated from the adopted r_e. α_e is calculated assuming a Morse potential function.

The electronic levels and their probable designation are those given by Rosen (2).

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CaI

Calcium Diiodide (CaI_2) CaI_2

(Crystal) GFW = 293.8890

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	− 4.294	− 128.069	− 128.069	INFINITE
100	14.780	16.219	50.420	− 3.420	− 128.158	− 127.941	279.614
200	17.520	27.517	36.391	− 1.775	− 128.233	− 127.693	139.537
298	18.441	34.724	34.724	.000	− 128.300	− 127.416	93.398
300	18.450	34.839	34.725	.034	− 128.302	− 127.411	92.818
400	18.920	40.211	35.454	1.903	− 132.242	− 126.965	69.370
500	19.400	44.485	36.847	3.819	− 142.495	− 124.676	54.496
600	19.870	48.063	38.426	5.782	− 142.080	− 121.152	44.130
700	20.340	51.162	40.029	7.793	− 141.621	− 117.700	36.747
800	20.810	53.908	41.595	9.850	− 141.458	− 114.286	31.221
900	21.280	56.387	43.103	11.955	− 141.109	− 110.911	26.933
1000	21.750	58.653	44.547	14.106	− 140.768	− 107.573	23.510
1100	22.227	60.748	45.925	16.305	− 140.434	− 104.271	20.717
1200	22.700	62.703	47.243	18.552	− 141.888	− 100.846	18.367
1300	23.170	64.538	48.503	20.845	− 141.224	− 97.452	16.383
1400	23.640	66.272	49.711	23.186	− 140.515	− 94.111	14.691
1500	24.110	67.920	50.871	25.573	− 139.761	− 90.824	13.233

June 30, 1974

CALCIUM DIIODIDE (CaI_2) (CRYSTAL) GFW = 293.8890 CaI_2

$S^\circ_{298.15}$ = 34.72 ± 0.05 gibbs/mol
Tm = 1052 ± 2

ΔHf°_0 = −128.1 ± 0.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −128.3 ± 0.5 kcal/mol
ΔHm° = 10.00 ± 0.20 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 66.6 kcal/mol

Heat of Formation

Ehrlich, Peik, and Koch (1) derived $\Delta Hf^\circ_{298}(CaI_2, c)$ = −128.1 ± 0.4 kcal/mol from heat of solution measurements of Ca(c) and $CaI_2(c)$ in 0.1 N HI. An auxiliary HI heat of solution value, −13.22 kcal/mol, calculated from data in reference (2) was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA value of $\Delta Hf^\circ_{298}(I^-$ aq, std. state) = −13.60 kcal/mol (3) in the ΔHf°_{298}(HI, aq solution) table, so that the above derived heat of formation of $CaI_2(c)$ will be approximately −128.6 kcal/mol.

Combining $\Delta Hf^\circ_{298}(Ca^{+2}$, aq, std. state) = −129.74 kcal/mol, selected by Parker (4, 5), with the CODATA value for I^-(aq, std. state) (3) gives $\Delta Hf^\circ_{298}(CaI_2$, aq, std. state) = −156.94. Further combination with the heat of solution, −28.62 kcal/mol (5, 6) gives $\Delta Hf^\circ_{298}(CaI_2, c)$ = −128.32 kcal/mol. This heat of solution value was based on several sets of data, one of which was that of Ehrlich, et al. (1, 6).

We adopt −128.3 ± 0.5 kcal/mol because of the correlation of $\Delta Hf^\circ_{298}(Ca^{+2}$, aq, std. state) with the evaluation of data for several calcium compounds (4).

Heat Capacity and Entropy

Paukov, Khriplovich, and Korotkikh (7) have measured Cp°(13.10 – 309.18 K). Our T^3 extrapolation is in agreement with their values of S°_{13} = 0.516 gibbs/mol and $H^\circ_{13} - H^\circ_0$ = 4.99 cal/mol. The low temperature heat capacity joins smoothly with a linear extrapolation from Cp° = 18.31 gibbs/mol at 270 K to Cp° = 22.0 gibbs/mol at the adopted Tm = 1052 K. The linearly extrapolated heat capacity at 300 K is only 0.3% higher than the Paukov et al. (7) value and S°_{298} = 34.72 gibbs/mol in agreement with Paukov et al. (7). Dworkin and Bredig (8) determined the heat capacity of the crystal to be 23.2 gibbs/mol ± 5% near the melting point. By using the lower limit, Cp° = 22.0 gibbs/mol, of Dworkin and Bredig's value (8), $H^\circ_{1052} - H^\circ_{298}$ is brought down to 15.24 kcal/mol, about 0.7% higher than Dworkin and Bredig's drop calorimeter measurement of 15.1 ± 0.2% kcal/mol (8).

Melting Data

Dworkin and Bredig (8) measured ΔHm° = 10.00 kcal/mol ± 2% at Tm = 1052 K (Sm = 9.5 gibbs/mol) by drop calorimetry. Emons and Loeffelholz (9) determined ΔHm° = 6.65 kcal/mol ± 5% and Tm = 1053 K (Sm = 6.3 gibbs/mol) by high temperature cryoscopy. The two pair of investigators are in much better agreement with other salts (9). An entropy of melting criteria for choosing one of these values is not conclusive because the entropies of melting of CdI_2, $CdCl_2$, and $CdBr_2$ which have similar layer crystal structure range from 7.5 to 9.5 gibbs/mol (10). Hutchison (11) found Tm = 1018 K, noting that only approximate melting points were obtained.

Because drop calorimetry is a more direct measure of the heat of melting, we adopt ΔHm° = 10.00 ± 0.20 kcal/mol at Tm = 1052 ± 2 K.

Although unconfirmed by direct experimental evidence, the discrepancy in heat of melting and the adjustments required in joining low temperature and high temperature heat capacities might be explained by the existence of a solid state transition in CaI_2 similar to the transitions in $BaCl_2$, $SrBr_2$, or $SrCl_2$ (8).

Heat of Sublimation

ΔHs°_{298} is derived as the difference between the heats of formation of the ideal gas and liquid states.

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CaI_2

Calcium Diiodide (CaI_2) CaI_2

(Liquid) GFW = 293.8890

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	18.441	42.768	42.768	.000	- 119.543	- 121.058	88.738
300	13.450	42.882	42.768	.034	- 119.545	- 121.067	88.197
400	18.920	48.255	43.498	1.903	- 123.486	- 121.426	66.344
500	19.400	52.529	44.891	3.819	- 133.739	- 119.942	52.427
600	19.870	56.107	46.470	5.782	- 133.323	- 117.222	42.698
700	24.700	59.205	48.073	7.793	- 132.865	- 114.574	35.772
800	24.700	62.504	49.675	10.263	- 132.289	- 111.993	30.595
900	24.700	65.413	51.265	12.733	- 131.575	- 109.500	26.590
1000	24.700	68.015	52.812	15.203	- 130.915	- 107.083	23.403
1100	24.700	70.370	54.303	17.673	- 130.310	- 104.730	20.808
1200	24.700	72.519	55.733	20.143	- 131.541	- 102.277	18.627
1300	24.700	74.496	57.101	22.613	- 130.700	- 99.872	16.790
1400	24.700	76.326	58.410	25.083	- 129.862	- 97.532	15.225
1500	24.700	78.030	59.662	27.553	- 129.025	- 95.254	13.878
1600	24.700	79.624	60.860	30.023	- 128.189	- 93.028	12.707
1700	24.700	81.122	62.008	32.493	- 127.355	- 90.856	11.680
1800	24.700	82.534	63.110	34.963	- 163.416	- 88.052	10.691
1900	24.700	83.869	64.168	37.433	- 162.364	- 83.894	9.650
2000	24.700	85.136	65.185	39.903	- 161.314	- 79.793	8.719
2100	24.700	86.341	66.164	42.373	- 160.267	- 75.742	7.883
2200	24.700	87.490	67.107	44.843	- 159.224	- 71.742	7.127
2300	24.700	88.588	68.017	47.313	- 158.186	- 67.788	6.441
2400	24.700	89.639	68.896	49.783	- 157.154	- 63.879	5.817
2500	24.700	90.648	69.747	52.253	- 156.129	- 60.015	5.246

June 30, 1974

CALCIUM DIIODIDE (CaI_2) (LIQUID) GFW = 293.8890 CaI_2

$S^\circ_{298.15}$ = 42.768 gibbs/mol
Tm = 1052 ± 2 K
Tb = 2028 K

$\Delta Hf^\circ_{298.15}$ = -119.544 kcal/mol
ΔHm° = 10.00 ± 0.20 kcal/mol
ΔHv° = 42.88 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(CaI_2, \ell)$ = -119.544 kcal/mol is obtained from the sum of the heat of formation of the crystal, the heat of melting, and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 24.7 gibbs/mol, was derived by Dworkin and Bredig (1) from drop calorimetric measurements. This value is adopted and is assumed constant from 700 K to 2500 K. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S^\circ_{298}(CaI_2, \ell)$ = 42.768 gibbs/mol is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Vaporization Data

The temperature at which $\Delta Gr^\circ = 0$ for the reaction $CaI_2(\ell) = CaI_2(g)$ is 2028 K, the adopted Tb. Peterson and Hutchison (2) have extrapolated Knudsen effusion cell measurements in the 1076 - 1294 K range to obtain a normal boiling point of 1831 K.

ΔHv° = 42.88 kcal/mol is the calculated difference between the heats of formation of the ideal gas and the liquid at Tb. See $CaI_2(g)$ table for details.

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Calcium Diiodide (CaI_2) CaI_2

(Ideal Gas) GFW = 293.8890

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.827	-61.002	-61.002	INFINITE
100	12.816	63.194	90.822	-2.763	-60.901	-65.381	142.890
200	14.083	72.551	79.579	-1.406	-61.264	-69.731	76.198
298	14.492	78.263	78.263	.000	-61.700	-73.797	54.095
300	14.497	78.353	78.264	.027	-61.709	-73.872	53.816
400	14.665	82.550	78.835	1.486	-66.059	-77.717	42.463
500	14.748	85.832	79.918	2.957	-76.757	-79.612	34.798
600	14.794	88.525	81.135	4.434	-76.828	-80.177	29.204
700	14.823	90.808	82.358	5.915	-76.899	-80.730	25.205
800	14.842	92.789	83.541	7.399	-77.309	-81.242	22.194
900	14.855	94.538	84.667	8.884	-77.580	-81.718	19.844
1000	14.864	96.103	85.734	10.369	-77.905	-82.161	17.956
1100	14.871	97.520	86.742	11.856	-78.283	-82.569	16.405
1200	14.876	98.815	87.695	13.344	-80.496	-82.788	15.078
1300	14.880	100.005	88.597	14.831	-80.638	-82.973	13.949
1400	14.883	101.108	89.451	16.320	-80.781	-83.147	12.980
1500	14.886	102.135	90.263	17.808	-80.926	-83.312	12.139
1600	14.888	103.096	91.036	19.297	-81.071	-83.465	11.401
1700	14.890	103.999	91.772	20.786	-81.218	-83.610	10.749
1800	14.891	104.850	92.475	22.275	-118.260	-83.066	10.086
1900	14.893	105.655	93.148	23.764	-118.189	-81.113	9.330
2000	14.894	106.419	93.792	25.253	-118.120	-79.165	8.651
2100	14.895	107.146	94.411	26.743	-118.053	-77.218	8.036
2200	14.895	107.838	95.006	28.232	-117.991	-75.275	7.478
2300	14.896	108.501	95.578	29.722	-117.933	-73.334	6.968
2400	14.897	109.135	96.130	31.211	-117.882	-71.396	6.501
2500	14.897	109.743	96.662	32.701	-117.837	-69.461	6.072
2600	14.898	110.327	97.177	34.191	-117.801	-67.526	5.676
2700	14.898	110.889	97.674	35.681	-117.776	-65.594	5.309
2800	14.899	111.431	98.156	37.170	-117.763	-63.660	4.969
2900	14.899	111.954	98.623	38.660	-117.762	-61.727	4.652
3000	14.899	112.459	99.076	40.150	-117.778	-59.797	4.356
3100	14.900	112.948	99.515	41.640	-117.811	-57.862	4.079
3200	14.900	113.421	99.942	43.130	-117.863	-55.928	3.820
3300	14.900	113.879	100.358	44.620	-117.938	-53.991	3.576
3400	14.900	114.324	100.762	46.110	-118.035	-52.053	3.346
3500	14.900	114.756	101.156	47.600	-118.157	-50.108	3.129
3600	14.901	115.176	101.539	49.090	-118.307	-48.163	2.924
3700	14.901	115.584	101.913	50.580	-118.485	-46.213	2.730
3800	14.901	115.981	102.278	52.070	-118.693	-44.257	2.545
3900	14.901	116.368	102.635	53.560	-118.934	-42.294	2.370
4000	14.901	116.746	102.983	55.051	-119.205	-40.329	2.203
4100	14.901	117.114	103.323	56.541	-119.510	-38.349	2.044
4200	14.901	117.473	103.656	58.031	-119.850	-36.365	1.892
4300	14.902	117.823	103.981	59.521	-120.225	-34.377	1.747
4400	14.902	118.166	104.300	61.011	-120.634	-32.375	1.608
4500	14.902	118.501	104.611	62.501	-121.079	-30.363	1.475
4600	14.902	118.828	104.917	63.992	-121.556	-28.341	1.346
4700	14.902	119.149	105.216	65.482	-122.068	-26.311	1.223
4800	14.902	119.462	105.510	66.972	-122.615	-24.267	1.105
4900	14.902	119.770	105.798	68.462	-123.194	-22.211	.991
5000	14.902	120.071	106.080	69.952	-123.805	-20.144	.881
5100	14.902	120.366	106.357	71.443	-124.445	-18.066	.774
5200	14.902	120.655	106.630	72.933	-125.117	-15.975	.671
5300	14.902	120.939	106.897	74.423	-125.816	-13.868	.572
5400	14.902	121.218	107.160	75.913	-126.542	-11.747	.475
5500	14.902	121.491	107.418	77.403	-127.293	-9.617	.382
5600	14.902	121.760	107.671	78.894	-128.067	-7.473	.292
5700	14.903	122.023	107.921	80.384	-128.863	-5.310	.204
5800	14.903	122.283	108.166	81.874	-129.680	-3.135	.118
5900	14.903	122.537	108.408	83.364	-130.515	-.947	.035
6000	14.903	122.788	108.645	84.855	-131.367	1.258	-.046

June 30, 1974

CALCIUM DIIODIDE (CaI_2) (IDEAL GAS) GFW = 293.8890 CaI_2

Point Group = $D_{\infty h}$

$S^\circ_{298.15}$ = [78.26 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -61.0 ± 4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -61.7 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[117] (1)
[45] (2)
[316] (1)

Bond Distance: Ca-I = 2.88 ± 0.03 Å   Bond Angle: I-Ca-I = [180°]   σ = 2

Rotational Constant: B_o = 0.00801 cm^{-1}

Heat of Formation

Peterson and Hutchison (1, 2) used a weight loss Knudsen effusion technique to observe vapor pressures of the liquid at 18 temperatures ranging from 1076 K to 1294 K. Our second and third law analyses of these data, after rejection of one point due to failure of a statistical test, yield ΔHv°_{298} (2nd Law) = 60.83 ± 2.04 kcal/mol and ΔHv°_{298} (3rd Law) = 57.84 ± 0.98 kcal/mol with a drift of -2.6 ± 1.7 gibbs/mol. We adopt ΔHv°_{298} = 57.8 ± 3 kcal/mol and combine that with the adopted heat of formation of the liquid to obtain $\Delta Hf^\circ_{298}(CaI_2, g)$ = -61.7 ± 4 kcal/mol.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from Akishin et al. (3) who also judged that the bond angle was 180° ± 10-20°. We have assumed a linear structure.

To estimate the vibrational frequencies, the stretching force constants for gaseous CaF, CaF_2, CaCl, and $CaCl_2$ are calculated from the vibrational frequencies (4) using a valence force model. The trend in the ratio of k(monohalide)/k_1 (dihalide) indicates that k(CaI)/$k_1(CaI_2)$ = 1 is a reasonable approximation, an approximation which has been used by Brewer et al. (5). The stretching force constant for CaI(g) is calculated from the ground state vibrational frequency given by Rosen (6). The bending force constant is assumed to be 0.01 times the stretching force constant (5). The adopted vibrational frequencies are calculated from the estimated force constants. Other estimates for ν_1, ν_2, and ν_3 are 121, 77, 327 (7) and 118, 45, 321 (5).

We assign an uncertainty of ±2 gibbs/mol to the entropy to allow for error in bond angle and vibrational frequency estimates.

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CaI_2

Calcium Oxide (CaO)

(Crystal) GFW = 56.0794

	gibbs/mol			kcal/mol			
T, °K	$Cp°$	$S°$	$-(G°-H°_{298})/T$	$H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	- 1.613	- 150.994	- 150.994	INFINITE
100	3.517	1.487	16.531	- 1.504	- 151.467	- 149.165	325.999
200	8.049	5.507	9.996	- .898	- 151.750	- 146.726	160.335
298	10.067	9.133	9.133	.000	- 151.790	- 144.247	105.736
300	10.096	9.195	9.133	.019	- 151.790	- 144.200	105.050
400	11.144	12.261	9.544	1.087	- 151.714	- 141.680	77.410
500	11.707	14.814	10.350	2.232	- 151.581	- 139.184	60.837
600	12.065	16.982	11.279	3.421	- 151.420	- 136.720	49.800
700	12.322	18.862	12.231	4.641	- 151.242	- 134.284	41.925
800	12.524	20.521	13.166	5.884	- 151.391	- 131.845	36.018
900	12.694	22.006	14.067	7.145	- 151.389	- 129.402	31.423
1000	12.843	23.351	14.929	8.422	- 151.431	- 126.957	27.747
1100	12.978	24.581	15.751	9.713	- 151.517	- 124.507	24.737
1200	13.105	25.716	16.535	11.017	- 153.429	- 121.894	22.200
1300	13.224	26.770	17.282	12.334	- 153.261	- 119.273	20.052
1400	13.339	27.754	17.996	13.662	- 153.085	- 116.665	18.212
1500	13.450	28.678	18.677	15.001	- 152.901	- 114.070	16.620
1600	13.558	29.550	19.330	16.352	- 152.709	- 111.487	15.228
1700	13.665	30.375	19.955	17.713	- 152.509	- 108.917	14.002
1800	13.769	31.159	20.556	19.085	- 189.195	- 105.678	12.831
1900	13.873	31.906	21.134	20.467	- 188.760	- 101.050	11.623
2000	13.975	32.620	21.691	21.859	- 188.317	- 96.446	10.539
2100	14.076	33.305	22.228	23.262	- 187.869	- 91.863	9.560
2200	14.177	33.962	22.746	24.674	- 187.417	- 87.301	8.673
2300	14.277	34.594	23.248	26.097	- 186.960	- 82.761	7.864
2400	14.376	35.204	23.733	27.530	- 186.501	- 78.240	7.125
2500	14.475	35.793	24.204	28.972	- 186.041	- 73.739	6.446
2600	14.574	36.362	24.661	30.425	- 185.580	- 69.256	5.821
2700	14.672	36.914	25.104	31.887	- 185.122	- 64.791	5.244
2800	14.770	37.450	25.536	33.359	- 184.666	- 60.342	4.710
2900	14.868	37.970	25.955	34.841	- 184.215	- 55.909	4.213
3000	14.966	38.475	26.364	36.333	- 183.772	- 51.493	3.751
3100	15.063	38.968	26.763	37.834	- 183.337	- 47.090	3.320
3200	15.161	39.447	27.152	39.345	- 182.913	- 42.702	2.916
3300	15.258	39.915	27.532	40.866	- 182.502	- 38.328	2.538
3400	15.355	40.372	27.903	42.397	- 182.105	- 33.965	2.183
3500	15.452	40.819	28.265	43.937	- 181.724	- 29.614	1.849
3600	15.549	41.256	28.620	45.487	- 181.361	- 25.272	1.534

June 30, 1971; June 30, 1973

CALCIUM OXIDE (CaO) (CRYSTAL) GFW = 56.0794 CaO

ΔHf_0° = -150.99 ± 0.21 kcal/mol

$S^\circ_{298.15}$ = 9.133 ± 0.03 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -151.79 ± 0.21 kcal/mol

Tm = 3200 ± 50 K

ΔHm° = [19] kcal/mol

Heat of Formation

Huber and Holley (1) determined the heat of combustion of calcium metal in a bomb calorimeter and derived the heat of formation of calcium oxide (c) as -151.79 ± 0.21 kcal/mol which is adopted in the tabulation. The adopted value is in good agreement with the value, -151.9 kcal/mol (2) derived from solution calorimetry.

Heat Capacity and Entropy

Gmelin (3) measured low temperature Cp data from 4 to 300 K in an adiabatic calorimeter. We use his smoothed Cp values to derive S°_{298} = 9.133 ± 0.03 eu based on S° = 0.0001 eu at 4 K. Lander (4) determined high temperature enthalpy data from 563.6 to 1176.4 K by drop calorimetry. The low temperature Cp and high temperature enthalpy data are smoothly joined at 298 K by a polynomial curve fitting method. The deviations of the observed enthalpies from the adopted values are about 0.2-1%, except the enthalpy value at 753 K (2.0%). Heat capacities above 1200 K are extrapolated from the adopted Cp functions. The extrapolated Cp at the melting point (2887 K), 14.8 gibbs/mol, is in reasonable agreement with the value 2 x 7.25 gibbs/g-atom suggested by Kubaschewski (5).

Combination of the earlier low temperature Cp measurements of Nernst and Schwers (28-90 K) (6) and Parks and Kelley (87-293 K) (7) yields S°_{298} = 9.5 ± 0.2 eu, based on S°_{28} = 0.04 eu (8). These Cp measurements are less accurate than those of Gmelin (3), and are not adopted in the tabulation.

Fischer and Ertmer (9) determined high temperature enthalpy data by drop calorimetry in the temperature range from 0° to 1716°C. The accuracy was claimed to be approximately ±4%. We have not adopted their enthalpy data in the tabulation since the heat capacities which we derive from their data are always less than those of MgO (10) when the temperature is above 1000 K. The deviations between their enthalpy data and the adopted values are approximately 1.8% at 693 K, 3.3% at 1283 K and 5.3% at 1989 K.

Melting Data

Schneider (11) adjusted earlier melting points (12-15) to IPTS-48, yielding values ranging from 2565° to 2630°C. Recent studies by Foex (16, 17), using solar energy to melt the center of a rotating crucible of oxide, gave values higher by about 300°C. Apparently the earlier values were depressed by formation of tungstates with the tungsten supports of the sample. Unfortunately, Foex reported three values: 2910°C (16, 1965), 2950°C (16, 1968) and 2900°C (17, 1969). We adopt an intermediate value of 2927°C = 3200 K and arbitrarily assign an uncertainty of 50 K.

The heat of melting is assumed to be 19 kcal/mol which is calculated from the estimated ΔSm° = 6 eu at the melting point. The latter is estimated to be the same as that of MgO (10).

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CaO

Calcium Oxide (CaO)

(Liquid) GFW = 56.0794

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	10.067	14.895	14.895	.000	-133.206	-127.381	93.373
300	10.096	14.958	14.895	.019	-133.206	-127.345	92.771
400	11.144	18.023	15.306	1.087	-133.131	-125.401	68.516
500	11.707	20.576	16.112	2.232	-132.997	-123.482	53.974
600	12.065	22.744	17.041	3.421	-132.836	-121.594	44.290
700	12.322	24.624	17.993	4.641	-132.658	-119.734	37.383
800	12.524	26.283	18.928	5.884	-132.807	-117.871	32.201
900	12.694	27.768	19.829	7.145	-132.805	-116.005	28.170
1000	12.843	29.113	20.691	8.422	-132.847	-114.136	24.944
1100	12.978	30.344	21.513	9.713	-132.933	-112.261	22.304
1200	13.105	31.478	22.297	11.017	-134.845	-110.225	20.075
1300	13.224	32.532	23.044	12.334	-134.677	-108.180	18.187
1400	13.339	33.516	23.758	13.662	-134.501	-106.148	16.570
1500	13.450	34.440	24.439	15.001	-134.317	-104.129	15.172
1600	13.558	35.312	25.092	16.352	-134.125	-102.123	13.949
1700	13.665	36.137	25.718	17.713	-133.925	-100.129	12.872
1800	13.769	36.921	26.318	19.085	-170.612	-97.466	11.834
1900	13.873	37.668	26.896	20.467	-170.176	-93.414	10.745
2000	13.975	38.382	27.453	21.859	-169.734	-89.386	9.768
2100	14.076	39.067	27.990	23.262	-169.286	-85.379	8.886
2200	15.000	39.765	28.509	24.762	-168.746	-81.396	8.086
2300	15.000	40.431	29.013	26.262	-168.212	-77.438	7.358
2400	15.000	41.070	29.502	27.762	-167.686	-73.502	6.693
2500	15.000	41.682	29.977	29.262	-167.168	-69.589	6.084
2600	15.000	42.270	30.439	30.762	-166.660	-65.696	5.522
2700	15.000	42.836	30.888	32.262	-166.164	-61.823	5.004
2800	15.000	43.382	31.324	33.762	-165.680	-57.967	4.524
2900	15.000	43.908	31.749	35.262	-165.211	-54.127	4.079
3000	15.000	44.417	32.163	36.762	-164.760	-50.304	3.665
3100	15.000	44.909	32.566	38.262	-164.326	-46.496	3.278
3200	15.000	45.385	32.959	39.762	-163.913	-42.702	2.916
3300	15.000	45.846	33.343	41.262	-163.523	-38.922	2.578
3400	15.000	46.294	33.717	42.762	-163.157	-35.151	2.259
3500	15.000	46.729	34.083	44.262	-162.816	-31.391	1.960
3600	15.000	47.152	34.440	45.762	-162.503	-27.640	1.678
3700	15.000	47.563	34.789	47.262	-162.219	-23.898	1.412
3800	15.000	47.963	35.131	48.762	-161.965	-20.162	1.160
3900	15.000	48.352	35.465	50.262	-161.744	-16.436	.921
4000	15.000	48.732	35.792	51.762	-161.555	-12.712	.695
4100	15.000	49.102	36.112	53.262	-161.400	-8.992	.479
4200	15.000	49.464	36.425	54.762	-161.278	-5.277	.275
4300	15.000	49.817	36.733	56.262	-161.192	-1.563	.079
4400	15.000	50.162	37.034	57.762	-161.140	2.148	-.107
4500	15.000	50.499	37.329	59.262	-161.123	5.859	-.285

June 30, 1971; June 30, 1973

CALCIUM OXIDE (CaO) (LIQUID) GFW = 56.0794 CaO

$S^{\circ}_{298.15}$ = [14.895] gibbs/mol

$\Delta Hf^{\circ}_{298.15}$ = [-133.206] kcal/mol

Tm = 3200 ± 50 K

ΔHm° = [19] kcal/mol

Heat of Formation

$\Delta Hf^{\circ}_{298}(\ell)$ is calculated from $\Delta Hf^{\circ}_{298}(c)$ by adding ΔHm and the difference between $H^{\circ}_{3200}-H^{\circ}_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2100 K. Heat capacities of the liquid below 2100 K are assumed to be the same as those of the crystal. Above 2100 K the heat capacity is assumed to be constant at 7.50 gibbs/(g-atom).

The entropy at 298 K is calculated in a manner analogous to that of the heat of formation.

Melting Data

See CaO(c) table for details.

Decomposition

CaO does not vaporize simply to CaO(g); extensive dissociation of CaO(g) to Ca(g) was found mass-spectrometrically (1).

Reference

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Cobalt Monochloride (CoCl) ClCo

(Ideal Gas) GFW = 94.3862

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.258	46.078	46.078	INFINITE
100	7.131	50.226	65.820	-1.559	46.305	43.723	-95.558
200	7.942	55.424	59.447	-.805	46.239	41.154	-44.971
298	8.398	58.692	58.692	.000	46.100	38.686	-28.358
300	8.404	58.744	58.692	.016	46.097	38.640	-28.149
400	8.627	61.195	59.024	.868	45.921	36.180	-19.768
500	8.747	63.135	59.659	1.738	45.710	33.769	-14.760
600	8.819	64.736	60.376	2.616	45.462	31.403	-11.438
700	8.866	66.100	61.099	3.501	45.181	29.081	-9.079
800	8.900	67.286	61.799	4.389	44.767	26.817	-7.326
900	8.925	68.336	62.468	5.280	44.414	24.594	-5.972
1000	8.945	69.277	53.103	6.174	44.006	22.413	-4.898
1100	8.961	70.130	63.704	7.069	43.536	20.276	-4.028
1200	8.976	70.911	64.272	7.966	42.995	18.185	-3.312
1300	8.989	71.630	64.811	8.864	42.346	16.142	-2.714
1400	9.002	72.296	65.322	9.764	41.562	14.156	-2.210
1500	9.015	72.918	65.808	10.665	41.018	12.217	-1.780
1600	9.028	73.500	66.271	11.567	40.536	10.313	-1.409
1700	9.043	74.048	66.712	12.470	40.078	8.439	-1.085
1800	9.060	74.565	67.134	13.375	35.732	6.661	-.809
1900	9.078	75.055	67.538	14.282	35.215	5.061	-.582
2000	9.100	75.522	67.926	15.191	34.699	3.487	-.381
2100	9.124	75.966	68.298	16.102	34.184	1.938	-.202
2200	9.151	76.391	68.657	17.016	33.671	.415	-.041
2300	9.182	76.799	69.002	17.933	33.160	-1.085	.103
2400	9.217	77.190	69.335	18.853	32.652	-2.563	.233
2500	9.257	77.567	69.657	19.776	32.145	-4.020	.351
2600	9.301	77.931	69.968	20.704	31.643	-5.456	.459
2700	9.349	78.283	70.269	21.637	31.143	-6.874	.556
2800	9.404	78.624	70.562	22.574	30.647	-8.272	.646
2900	9.464	78.955	70.846	23.518	30.156	-9.654	.728
3000	9.530	79.277	71.121	24.467	29.670	-11.019	.803
3100	9.602	79.591	71.389	25.424	29.189	-12.368	.872
3200	9.680	79.897	71.650	26.388	-60.404	-12.865	.879
3300	9.765	80.196	71.905	27.360	-60.536	-11.378	.754
3400	9.857	80.489	72.153	28.341	-60.659	-9.885	.635
3500	9.956	80.776	72.395	29.332	-60.777	-8.392	.524
3600	10.061	81.058	72.632	30.332	-60.887	-6.892	.418
3700	10.173	81.335	72.864	31.344	-60.989	-5.391	.318
3800	10.291	81.608	73.090	32.367	-61.083	-3.888	.224
3900	10.416	81.877	73.312	33.403	-61.169	-2.381	.133
4000	10.546	82.142	73.529	34.451	-61.247	-.873	.048
4100	10.681	82.404	73.743	35.512	-61.315	.637	-.034
4200	10.821	82.663	73.952	36.587	-61.374	2.149	-.112
4300	10.965	82.919	74.158	37.676	-61.424	3.661	-.186
4400	11.113	83.173	74.360	38.780	-61.464	5.177	-.257
4500	11.263	83.425	74.558	39.899	-61.495	6.690	-.325
4600	11.416	83.674	74.754	41.033	-61.514	8.206	-.390
4700	11.571	83.921	74.946	42.182	-61.524	9.723	-.452
4800	11.726	84.166	75.136	43.347	-61.525	11.238	-.512
4900	11.881	84.410	75.322	44.527	-61.516	12.755	-.569
5000	12.035	84.651	75.507	45.723	-61.496	14.269	-.624
5100	12.189	84.891	75.688	46.934	-61.467	15.786	-.676
5200	12.340	85.129	75.868	48.161	-61.429	17.300	-.727
5300	12.488	85.366	76.044	49.402	-61.382	18.813	-.776
5400	12.633	85.600	76.219	50.658	-61.328	20.325	-.823
5500	12.774	85.834	76.392	51.929	-61.265	21.838	-.868
5600	12.910	86.065	76.563	53.213	-61.194	23.347	-.911
5700	13.041	86.295	76.731	54.510	-61.118	24.854	-.953
5800	13.167	86.523	76.898	55.821	-61.034	26.364	-.993
5900	13.287	86.749	77.063	57.144	-60.945	27.869	-1.032
6000	13.401	86.973	77.227	58.478	-60.851	29.374	-1.070

Dec. 31, 1973

COBALT MONOCHLORIDE (CoCl) (IDEAL GAS) GFW = 94.3862 ClCo

Ground State Configuration [$^3\Sigma$]

$S^\circ_{298.15}$ = 58.7 ± 1.5 gibbs/mol

ΔHf°_0 = 46.1 ± 3.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 46.1 ± 3.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	[3]	19868.1	[3]	21335.1	[3]	22182.5	[3]
[11000]	[3]	19945.8	[3]	21640.4	[3]	22402.7	[3]
17484.1	[3]	20969.1	[3]	22014.8	[3]	22966.2	[3]
19826.3	[3]	21263.9	[3]	22072.3	[3]	[25000]	[3]

ω_e = 421.2 cm^{-1} $\omega_e x_e$ = 0.74 cm^{-1} σ = 1 B_e = [0.17434] cm^{-1} α_e = [0.000459] cm^{-1} r_e = [2.09] Å

Heat of Formation

Kulkarni and Dadape (1) have studied the reaction of $CoCl_2$(g) with Co(c) by a transpiration method. They used highly purified argon as the carrier gas and condensed the gaseous products on a mullite cold finger. Chemical and x-ray analyses of the condensate showed the presence of metallic cobalt. The transport of the Co metal was ascribed to the disproportionation of CoCl(g) according to the reaction 2 CoCl(g) = Co(c) + $CoCl_2$(g). Partial pressures for CoCl(g) and $CoCl_2$(g) were reported for the temperature range 1395-1673 K. No consideration was given to possible dimerization of the dichloride. JANAF data (2) for $CoCl_2$(g) and Co_2Cl_4(g) are used to correct their $CoCl_2$ pressures for dimerization. The corrected pressures are 0.5% less than those of Kulkarni and Dadape (1) at 1395 K, and only 0.1% less at 1673 K. Hildenbrand (3) has also studied the disproportionation reaction of CoCl(g) by mass spectrometry. The monochloride was produced in the effusion cell (4) by vaporizing AgCl in the presence of metallic cobalt. The Ag^+ and $AgCl^+$ signals were also measured and used to derive equilibrium data for the process Ag(g) + CoCl(g) = AgCl(g) + Co(g). A comparison of the results of a second and third law analysis of these mass spectral data with those obtained from the transpiration study of Kulkarni and Dadape (1) is presented below.

Investigator	Reaction	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(CoCl, g)^a kcal/mol	D°_{298} kcal/mol
Kulkarni and Dadape (1)	A	9	1395-1673	83.3	79.65±1.8	-2.4±3.5	28.6±2.0	101.9
Hildenbrand (3)	B	7	1461-1605	20.0	14.19±0.53	-3.8±1.5	46.6±1.5$_b$	83.9
Hildenbrand (3)	C	7	1461-1605	6.21	9.87±0.35	2.4±1.1	45.6±1.5^b	84.9

Reactions: (A) $CoCl_2$(g) + Co(c) = 2 CoCl(g) (B) $CoCl_2$(g) + Co(g) = 2 CoCl(g) (C) Ag(g) + CoCl(g) = AgCl(g) + Co(g)

[a] Third law values. Auxiliary ΔHf°_{298} data (all in kcal/mol) $CoCl_2$(g), -22.4 ± 2.0; Co(g), 101.5 ± 0.5 (2).

[b] ΔHr°_{298} (Third Law) combined with D°_{298}(AgCl, g) = 75.0 ± 0.5 kcal/mol (4).

The two sets of measurements of Hildenbrand (3) lead to consistent values for ΔHf°, while the results of Kulkarni and Dadape (1) suggest a value roughly 20 kcal/mol lower. In the same paper, Kulkarni and Dadape (1) reported vapor pressures for $CoCl_2(\ell)$ which were also determined by their flow technique. These vapor pressures have been shown to be incompatible with JANAF data (see $CoCl_2$(g) table). Furthermore, their value for the bond dissociation energy (D°_{298} = 101.9 kcal/mol) of CoCl appears to be too high by comparison with similar data for other transition metal monochlorides. Values (5) of D° for the monochlorides of Cr, Mn, Ni, and Cu show a random variation of from 83.0 to 88.6 kcal/mol, suggesting a value for CoCl near 85 kcal/mol. The results of Hildenbrand (3) are in agreement with these predictions. It is further noted that Hildenbrand (4) has used a similar technique to study the monochlorides of Ca, Sr, and Ba. The results of these studies are quite consistent with JANAF heat of formation data (2). Thus, it appears that the method used by Hildenbrand (3, 4) is reliable, and we adopt an average value (ΔHf°_{298} = 46.1 kcal/mol) of his two results. The uncertainty is estimated to be ±3.0 kcal/mol. The adopted values for the ground state vibrational constants are judged to be of insufficient accuracy to warrant a Birge-Sponer calculation for D°_0(Co-Cl).

Heat Capacity and Entropy

The bond length is estimated as somewhat less than that for $CoCl_2$ (2). B_e is calculated from the value for r_e. The moment of inertia is 16.055 x 10^{-39} g cm^2. The value for α_e is obtained from the other constants assuming a Morse potential function.

Several band systems have been observed in the electronic spectrum (6-9) of CoCl. Vibrational constants for the upper and lower states of the various systems have been summarized by Rosen (5). However, since it is not certain which of the observed electronic transitions involve the ground state, no assignments were made. Also, confusion exists as to whether some of the systems belong to triplet-triplet transitions (7-9), an electronic triplet (8), or whether they are all separate systems (9). We adopt the vibrational constants for the ground state suggested by Herzberg (10). Comparison of these values with those listed by Rosen (5) for the lower states of other systems for CoCl indicate that the adopted ω_e value may be uncertain by as much as ±5 cm^{-1}. Krishnamurty (8) has shown that the ground state electronic configuration for CoCl is either $^5\Sigma$ or $^3\Sigma$. We prefer a triplet ground state, since the electronic configuration for Co^{+1} is ^3F (11). Other transition metal monochlorides (5) and the corresponding unipositive metal ions (11) have the same ground state multiplicities. If the ground state is a quintet, then the value of S°_{298} is increased by 1 eu. The adopted electronic levels in the range 17,000-23,000 cm^{-1} are taken from the compilation of Rosen (5). Each level is assumed to be a separate system and is assigned a quantum weight of 3. Two triplet levels are also included at 11,000 and 25,000 cm^{-1}, since Rao and Rao (9) are believed to have observed two components of a triplet-triplet transition near 14,000 cm^{-1}. By analogy with similar data for other transition metal monochlorides (5), the lower triplet level is not expected to lie below 10,000 cm^{-1}. The adopted upper levels and assumed quantum weights contribute 0.31 eu to the entropy of CoCl at 4000 K.

References

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ClCo

Nitrosyl Chloride (ONCl)

(Ideal Gas) GFW = 65.4591

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.715	12.815	12.815	INFINITE
100	8.369	52.210	71.328	- 1.912	12.577	13.592	- 29.705
200	9.741	58.442	63.465	- 1.005	12.425	14.674	- 16.034
298	10.657	62.517	62.517	.000	12.360	15.793	- 11.577
300	10.670	62.583	62.517	.020	12.359	15.814	- 11.521
400	11.269	65.739	62.943	1.118	12.339	16.970	- 9.272
500	11.730	68.305	63.767	2.269	12.346	18.128	- 7.924
600	12.114	70.479	64.709	3.462	12.371	19.282	- 7.023
700	12.437	72.371	65.671	4.690	12.407	20.431	- 6.379
800	12.707	74.050	66.616	5.947	12.451	21.573	- 5.894
900	12.932	75.560	67.527	7.230	12.502	22.711	- 5.515
1000	13.119	76.932	68.400	8.532	12.557	23.843	- 5.211
1100	13.278	78.190	69.234	9.853	12.615	24.968	- 4.961
1200	13.412	79.352	70.029	11.187	12.675	26.089	- 4.751
1300	13.528	80.430	70.788	12.534	12.737	27.204	- 4.573
1400	13.630	81.436	71.513	13.892	12.801	28.314	- 4.420
1500	13.719	82.380	72.206	15.260	12.865	29.420	- 4.286
1600	13.799	83.268	72.870	16.636	12.931	30.522	- 4.169
1700	13.871	84.106	73.507	18.019	12.997	31.620	- 4.065
1800	13.937	84.901	74.118	19.410	13.063	32.713	- 3.972
1900	13.998	85.656	74.706	20.806	13.130	33.804	- 3.888
2000	14.054	86.376	75.271	22.209	13.196	34.890	- 3.813
2100	14.108	87.063	75.816	23.617	13.263	35.972	- 3.744
2200	14.159	87.720	76.343	25.031	13.329	37.052	- 3.681
2300	14.207	88.351	76.851	26.449	13.395	38.129	- 3.623
2400	14.254	88.956	77.343	27.872	13.461	39.204	- 3.570
2500	14.299	89.539	77.819	29.300	13.525	40.274	- 3.521
2600	14.342	90.101	78.281	30.732	13.590	41.343	- 3.475
2700	14.385	90.643	78.729	32.168	13.654	42.409	- 3.433
2800	14.427	91.167	79.164	33.609	13.717	43.473	- 3.393
2900	14.468	91.674	79.586	35.053	13.780	44.536	- 3.356
3000	14.509	92.165	79.998	36.502	13.842	45.594	- 3.322
3100	14.549	92.641	80.398	37.955	13.904	46.652	- 3.289
3200	14.589	93.104	80.788	39.412	13.965	47.706	- 3.258
3300	14.629	93.554	81.168	40.873	14.026	48.760	- 3.229
3400	14.669	93.991	81.538	42.338	14.087	49.813	- 3.202
3500	14.708	94.417	81.900	43.807	14.147	50.860	- 3.176
3600	14.746	94.832	82.254	45.280	14.207	51.910	- 3.151
3700	14.787	95.236	82.599	46.756	14.268	52.957	- 3.128
3800	14.827	95.631	82.937	48.237	14.329	54.001	- 3.106
3900	14.866	96.017	83.267	49.722	14.391	55.045	- 3.085
4000	14.906	96.394	83.591	51.210	14.453	56.085	- 3.064
4100	14.946	96.762	83.908	52.703	14.516	57.125	- 3.045
4200	14.986	97.123	84.218	54.200	14.580	58.163	- 3.027
4300	15.027	97.476	84.522	55.700	14.646	59.202	- 3.009
4400	15.067	97.822	84.821	57.205	14.713	60.237	- 2.992
4500	15.108	98.161	85.113	58.714	14.781	61.269	- 2.976
4600	15.149	98.493	85.401	60.227	14.853	62.305	- 2.960
4700	15.190	98.820	85.683	61.744	14.925	63.335	- 2.945
4800	15.232	99.140	85.960	63.265	15.000	64.364	- 2.931
4900	15.274	99.454	86.232	64.790	15.077	65.389	- 2.916
5000	15.316	99.763	86.499	66.319	15.157	66.416	- 2.903
5100	15.359	100.067	86.762	67.853	15.240	67.441	- 2.890
5200	15.402	100.366	87.021	69.391	15.326	68.464	- 2.877
5300	15.445	100.659	87.276	70.934	15.414	69.485	- 2.865
5400	15.489	100.949	87.526	72.480	15.506	70.502	- 2.853
5500	15.533	101.233	87.773	74.031	15.601	71.524	- 2.842
5600	15.577	101.513	88.016	75.587	15.699	72.536	- 2.831
5700	15.622	101.790	88.255	77.147	15.800	73.550	- 2.820
5800	15.667	102.062	88.491	78.711	15.906	74.566	- 2.810
5900	15.713	102.330	88.723	80.280	16.014	75.573	- 2.799
6000	15.759	102.594	88.952	81.854	16.127	76.584	- 2.790

June 30, 1961; Dec. 31, 1965; Dec. 31, 1972.

NITROSYL CHLORIDE (ONCl) (IDEAL GAS) GFW = 65.4591 ClNO

Point Group C_s

ΔHf°_0 = 12.82 ± 0.1 kcal/mol

$S^\circ_{298.15}$ = 62.52 ± 0.04 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = 12.36 ± 0.1 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies, Degeneracies and Anharmonicity Constants

ν, cm^{-1}	X_{ii}, cm^{-1}	X_{ij}, cm^{-1}
1799.7 (1)	X_{11}= −17.8	X_{12} = 0.0
595.6 (1)	X_{22}= − 2.6	X_{23} =−4.3
330.9 (1)	X_{33}= − 1.0	X_{13} =−0.6

Bond Distance: O-N = 1.143 ± 0.012 Å N-Cl = 1.976 ± 0.005 Å

Bond Angle: O-N-Cl = 113.0° ± 0.7° σ = 1

Rotational Constants: A_0 = 2.8492 cm^{-1} B_0 = 0.19034 cm^{-1} C_0 = 0.17842 cm^{-1}

Heat of Formation

ΔHf°(298.15 K) is calculated from ΔHr° = 18.43 ± 0.06 kcal/mol derived by third-law analysis of equilibrium data (1) for 2 ONCl(g) → 2 NO(g) + Cl_2(g). Second-law analysis yields ΔHr° = 18.39 ± 0.07 and an entropy deviation of −0.09 ± 0.16 gibbs/mol from the third-law ΔSr°. Data analyzed cover a temperature range of 372.7 to 491.3 K and consist of a combination of three runs reported by Beeson and Yost (1). Combination is justified by the mutual consistency of the three runs, which involved excess NO, excess Cl_2, and roughly the stoichiometric ratio of NO and Cl_2, respectively. Earlier data reviewed by Bichowsky and Rossini (2) are considered less reliable.

Heat Capacity and Entropy

We list structural parameters which approximate the adopted rotational constants (3) obtained from microwave spectra of three isotopic molecules. These structural parameters are minor modifications of those given by Millen and Pannell (3). Changes are well within the ranges specified by the authors but give improved agreement with rotational constant A_0. Literature values include (O-N) = 1.139 ± 0.012 (3), 1.14 ± 0.02 (4, 7) and 1.17 ± 0.06 Å (5, 6); (N-Cl) = 1.975 ± 0.005 (3), 1.95 ± 0.01 (4), 1.95 ± 0.06 (5, 6) and 1.97 ± 0.01 Å (7, 6); and angle (O-N-Cl) = 113.33° ± 0.67° (3), 116° ± 2° (4), 114° ± 3° (5, 6) and 113° ± 2° (7, 6). The earlier values (4, 5, 7) resulted from electron-diffraction data (4) and two separate analyses (5, 7) of older microwave data (6). Rotational constants are adjusted for the natural isotopic abundance of Cl. A_0 is relatively uncertain.

Observed ν values and anharmonicity constants are from the gas-phase infrared study of Jones et al. (8), who reviewed earlier spectral data. Values of ν are adjusted for the natural isotopic abundance of chlorine. The anharmonicity constants differ from, and supersede, earlier values (9) used by Gordon (10) in calculating thermodynamic functions for ONCl.

New functions have been calculated through the courtesy of B. J. McBride (11), who used the above vibrational and rotational constants with first and second order corrections (method NRRAO2) in the NASA-Lewis computer program (12). We adopt these functions directly for 0 to 298.15 K and reproduce the functions at higher temperatures by integration of Cp°.

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ClNO

Lead Monochloride (PbCl)

(Ideal Gas) GFW = 242.6430

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.341	4.000	4.000	INFINITE
100	7.465	53.134	69.469	-1.633	3.937	1.761	-3.848
200	8.339	58.623	62.806	-.837	3.767	-.347	.379
298	8.660	62.022	62.022	.000	3.600	-2.331	1.709
300	8.664	62.075	62.022	.016	3.597	-2.368	1.725
400	8.805	64.589	62.364	.890	3.404	-4.329	2.364
500	8.881	66.563	63.013	1.775	3.189	-6.237	2.726
600	8.929	68.187	63.744	2.666	2.955	-8.099	2.950
700	8.963	69.566	64.480	3.560	1.541	-9.732	3.038
800	8.989	70.765	65.192	4.458	1.274	-11.324	3.094
900	9.012	71.825	65.871	5.358	1.015	-12.883	3.128
1000	9.032	72.775	66.515	6.260	.765	-14.414	3.150
1100	9.052	73.637	67.124	7.164	.521	-15.929	3.163
1200	9.073	74.425	67.700	8.071	.287	-17.404	3.170
1300	9.096	75.152	68.246	8.979	.058	-18.869	3.172
1400	9.122	75.827	68.763	9.890	-.168	-20.317	3.172
1500	9.151	76.458	69.256	10.803	-.392	-21.747	3.169
1600	9.185	77.049	69.724	11.720	-.616	-23.164	3.164
1700	9.222	77.607	70.172	12.640	-.839	-24.565	3.158
1800	9.263	78.136	70.600	13.565	-1.064	-25.956	3.151
1900	9.307	78.638	71.010	14.493	-1.290	-27.332	3.144
2000	9.354	79.116	71.403	15.426	-1.517	-28.697	3.136
2100	9.404	79.574	71.781	16.364	-44.195	-28.498	2.966
2200	9.455	80.012	72.146	17.307	-44.331	-27.748	2.757
2300	9.507	80.434	72.497	18.255	-44.483	-26.990	2.565
2400	9.561	80.840	72.836	19.208	-44.653	-26.225	2.388
2500	9.614	81.231	73.164	20.167	-44.841	-25.456	2.225
2600	9.667	81.609	73.482	21.131	-45.045	-24.676	2.074
2700	9.720	81.975	73.789	22.101	-45.266	-23.888	1.934
2800	9.771	82.329	74.088	23.075	-45.505	-23.092	1.802
2900	9.822	82.673	74.378	24.055	-45.758	-22.287	1.680
3000	9.871	83.007	74.660	25.039	-46.025	-21.473	1.564
3100	9.918	83.331	74.935	26.029	-46.305	-20.650	1.456
3200	9.964	83.647	75.202	27.023	-46.598	-19.818	1.354
3300	10.009	83.954	75.463	28.022	-46.900	-18.976	1.257
3400	10.051	84.254	75.717	29.025	-47.210	-18.124	1.165
3500	10.092	84.546	75.965	30.032	-47.529	-17.266	1.078
3600	10.131	84.830	76.207	31.043	-47.852	-16.395	.995
3700	10.169	85.109	76.444	32.058	-48.180	-15.516	.917
3800	10.205	85.380	76.676	33.077	-48.509	-14.629	.841
3900	10.239	85.646	76.902	34.099	-48.842	-13.733	.770
4000	10.272	85.905	77.124	35.125	-49.174	-12.831	.701
4100	10.303	86.159	77.342	36.153	-49.506	-11.919	.635
4200	10.334	86.408	77.554	37.185	-49.836	-10.997	.572
4300	10.363	86.652	77.763	38.220	-50.164	-10.071	.512
4400	10.390	86.890	77.968	39.258	-50.487	-9.130	.453
4500	10.417	87.124	78.169	40.298	-50.807	-8.190	.398
4600	10.443	87.353	78.366	41.341	-51.123	-7.237	.344
4700	10.468	87.578	78.560	42.387	-51.433	-6.282	.292
4800	10.492	87.799	78.750	43.435	-51.738	-5.315	.242
4900	10.515	88.015	78.937	44.485	-52.037	-4.346	.194
5000	10.538	88.228	79.120	45.538	-52.330	-3.372	.147
5100	10.560	88.437	79.301	46.593	-52.616	-2.388	.102
5200	10.581	88.642	79.479	47.650	-52.896	-1.398	.059
5300	10.602	88.844	79.653	48.709	-53.171	-.405	.017
5400	10.623	89.042	79.825	49.770	-53.439	.593	-.024
5500	10.643	89.237	79.995	50.833	-53.701	1.594	-.063
5600	10.662	89.429	80.162	51.899	-53.956	2.602	-.102
5700	10.681	89.618	80.326	52.966	-54.207	3.610	-.138
5800	10.700	89.804	80.488	54.035	-54.452	4.633	-.175
5900	10.716	89.987	80.647	55.106	-54.692	5.650	-.209
6000	10.736	90.167	80.804	56.179	-54.926	6.674	-.243

June 30, 1962; June 30, 1973

LEAD MONOCHLORIDE (PbCl) (IDEAL GAS) GFW = 242.6430 ClPb

Ground State Configuration $^2\Pi_{1/2}$

$S°_{298.15}$ = 62.02 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = 4.0 ± 12.0 kcal/mol

$\Delta Hf°_{298.15}$ = 3.6 ± 12.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X\ ^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	8274	2
$A\ [^2\Sigma]$	21866.9	[2]
$B\ ^2\Sigma^+$	34937.5	2

$\omega_e = 302.5\ cm^{-1}$

$B_e = 0.1172\ cm^{-1}$

$\omega_e x_e = 0.88\ cm^{-1}$

$\alpha_e = [0.00047]\ cm^{-1}$

$\sigma = 1$

$r_e = 2.180\ Å$

Heat of Formation

$\Delta Hf°_0$ is obtained from $D_0(Pb\text{-}Cl)$ = 3.1 ± 0.5 eV (71.5 kcal/mol) which is the recommended value given by Gaydon (1). D_0 is combined with $\Delta Hf°_0(Pb, g)$ = 46.91 ± 0.13 kcal/mol and $\Delta Hf°_0(Cl, g)$ = 28.587 ± 0.002 kcal/mol (2) to give $\Delta Hf°_0(PbCl, g)$ = 4.0 ± 12.0 kcal/mol. ΔHf° at 298 K is 3.6 ± 12.0 kcal/mol. The recommended value for D_0 is based mainly on results (D(LBX) = 3.2 eV) of a linear Birge-Sponer extrapolation of the observed vibrational levels (v, 0-18) (3) for the ground state of PbCl. This same value for D(LBX) is obtained from the results of two other spectrometric studies (4, 5), while the results of another similar study (6) lead to D(LBX) = 2.7 eV. The values of D(LBX) are increased by only 0.1 eV when corrected for the ionic character of PbCl by application of the Hildenbrand formula (7). Other spectroscopic values for D(LBS) based on linear Birge-Sponer extrapolations include 2.2 eV ($A^2\Sigma$, or $^2\Delta$) (5) and 2.4 eV ($B^2\Sigma$) (6). The dissociation products are assumed to be $Pb(^1D) + Cl(^2P)(A^2\Sigma$, or $^2\Delta)$ and $Pb(^3P) + Cl(^2P)$ $(B^2\Sigma)$. Also, Wieland and Newburgh (8) first reported D_0 = 3.12 eV from observations of predissociation, but later work (9) gave 3.05, or possibly 3.40 eV. It is to be noted that our ΔHf° values for PbCl and $PbCl_2$ (2) indicate no significant differences in the binding of these two molecules. The difference $D_0(PbCl\text{-}Cl) - D_0(Pb\text{-}Cl)$ is equal to only 2.2 kcal/mol.

Heat Capacity and Entropy

The vibrational constants, electronic states (except for $A^2\Sigma$), and levels are taken from the compilation of Rosen (10) for $Pb^{35}Cl$. The vibrational constants are adjusted for the natural isotopic abundances of chlorine. It is not clear whether the first excited state for PbCl is $^2\Sigma$ or $^2\Delta$. By analogy with that for PbF (11), we assume the first excited state to be $^2\Sigma$. However, if this state is $^2\Delta$, the entropy is increased by only 0.006 eu at 4000 K and 0.05 eu at 6000 K. The rotational constant is taken from the results of a rotational analysis of two bands of the A-X system for $^{208}Pb^{35}Cl$ by Singh and Singh (12). The rotational constant is adjusted for the natural isotopic abundances of lead and chlorine. The value for r_e is obtained from the adopted B_e value. The results of an earlier rotational analysis of the same bands by Rao and Rao (13) are in reasonable agreement with our adopted values. The value for α_e is estimated from the other constants assuming a Morse potential function. The moment of inertia is $23.889 \times 10^{-39}\ g\ cm^2$.

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Lead Monochloride Unipositive ion ($PbCl^+$)

(Ideal Gas) GFW = 242.6424

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	8.698	60.955	60.955	.000	178.200	171.100	− 125.419
300	8.702	61.008	60.955	.016	178.206	171.055	− 124.614
400	8.830	63.531	61.298	.893	178.513	168.625	− 92.133
500	8.899	65.510	61.949	1.780	178.797	166.120	− 72.611
600	8.943	67.137	62.682	2.672	179.062	163.560	− 59.577
700	8.975	68.518	63.420	3.568	178.145	161.146	− 50.312
800	9.001	69.718	64.134	4.467	178.377	158.702	− 43.355
900	9.022	70.779	64.814	5.368	178.616	156.229	− 37.939
1000	9.041	71.731	65.459	6.272	178.863	153.728	− 33.597
1100	9.058	72.593	66.069	7.177	179.118	151.202	− 30.041
1200	9.075	73.382	66.646	8.083	179.379	148.653	− 27.073
1300	9.090	74.109	67.193	8.992	179.648	146.082	− 24.559
1400	9.105	74.783	67.711	9.901	179.917	143.489	− 22.400
1500	9.119	75.412	68.204	10.813	180.189	140.880	− 20.526
1600	9.133	76.001	68.673	11.725	180.456	138.249	− 18.884
1700	9.147	76.555	69.120	12.639	180.724	135.604	− 17.433
1800	9.161	77.078	69.548	13.555	180.987	132.941	− 16.141
1900	9.174	77.574	69.958	14.471	181.246	130.265	− 14.984
2000	9.188	78.045	70.350	15.389	181.501	127.576	− 13.941
2100	9.201	78.494	70.727	16.309	139.301	126.425	− 13.157
2200	9.214	78.922	71.090	17.230	139.640	125.903	− 12.497
2300	9.227	79.332	71.440	18.152	139.958	125.168	− 11.894
2400	9.240	79.725	71.777	19.075	140.256	124.519	− 11.339
2500	9.253	80.102	72.102	20.000	140.531	123.856	− 10.827
2600	9.266	80.465	72.417	20.926	140.784	123.184	− 10.355
2700	9.279	80.815	72.722	21.853	141.018	122.502	− 9.916
2800	9.292	81.153	73.017	22.782	141.231	121.813	− 9.508
2900	9.306	81.479	73.303	23.711	141.425	121.117	− 9.128
3000	9.319	81.795	73.581	24.643	141.601	120.414	− 8.772
3100	9.332	82.101	73.851	25.575	141.760	119.703	− 8.439
3200	9.346	82.397	74.113	26.509	141.904	118.989	− 8.127
3300	9.360	82.685	74.369	27.445	142.036	118.272	− 7.833
3400	9.375	82.965	74.617	28.381	142.156	117.552	− 7.556
3500	9.389	83.237	74.860	29.319	142.266	116.824	− 7.295
3600	9.405	83.502	75.096	30.259	142.367	116.097	− 7.048
3700	9.421	83.759	75.327	31.200	142.462	115.366	− 6.814
3800	9.438	84.011	75.552	32.143	142.554	114.633	− 6.593
3900	9.455	84.256	75.772	33.088	142.641	113.898	− 6.383
4000	9.474	84.496	75.987	34.034	142.726	113.156	− 6.183
4100	9.493	84.730	76.198	34.983	142.811	112.416	− 5.992
4200	9.514	84.959	76.404	35.933	142.896	111.676	− 5.811
4300	9.536	85.183	76.605	36.885	142.983	110.929	− 5.638
4400	9.559	85.403	76.803	37.840	143.073	110.187	− 5.473
4500	9.583	85.618	76.996	38.797	143.166	109.434	− 5.315
4600	9.609	85.829	77.186	39.757	143.264	108.686	− 5.164
4700	9.637	86.036	77.372	40.719	143.368	107.931	− 5.019
4800	9.666	86.239	77.555	41.684	143.477	107.179	− 4.880
4900	9.697	86.438	77.734	42.652	143.592	106.421	− 4.747
5000	9.730	86.635	77.910	43.624	143.714	105.658	− 4.618
5100	9.764	86.828	78.083	44.598	143.844	104.898	− 4.495
5200	9.800	87.018	78.253	45.577	143.983	104.135	− 4.377
5300	9.839	87.205	78.420	46.559	144.128	103.367	− 4.262
5400	9.879	87.389	78.584	47.544	144.281	102.597	− 4.152
5500	9.920	87.571	78.746	48.534	144.442	101.822	− 4.046
5600	9.964	87.750	78.905	49.529	144.613	101.046	− 3.943
5700	10.010	87.927	79.062	50.527	144.790	100.262	− 3.844
5800	10.057	88.101	79.216	51.531	144.977	99.485	− 3.749
5900	10.106	88.273	79.368	52.535	145.171	98.696	− 3.656
6000	10.158	88.444	79.518	53.552	145.373	97.905	− 3.566

June 30, 1973

LEAD MONOCHLORIDE UNIPOSITIVE ION ($PbCl^+$) (IDEAL GAS) GFW = 242.6424 $ClPb^+$

Ground State Configuration [$^1\Sigma$]

$S^\circ_{298.15}$ = [61.0 ± 2.0] gibbs/mol

ΔHf°_0 = 177.1 ± 12.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 178.2 ± 12.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
$^3\Pi$	[30000]	6

ω_e = [283] cm^{-1}

B_e = [0.1062] cm^{-1}

$\omega_e x_e$ = [0.82] cm^{-1}

α_e = [0.00043] cm^{-1}

σ = 1

r_e = [2.29] Å

Heat of Formation

The $PbCl^+$ ion has been observed in several mass spectrometric studies (1-4) of the vapors in equilibrium with both solid and liquid $PbCl_2$. Electric deflection experiments of mass spectrometrically detected $PbCl_2$ beams by Büchler et al. (5) have shown neutral $PbCl_2$ to be the precursor of the ion. Reported values for the appearance potential (AP) of $PbCl^+$ are 11.7 (1) and 10.7 eV (2, 3, 4). The higher value of AP was obtained by the method of linear extrapolation; thus, it is judged to be somewhat less reliable. Also, the lower value was obtained with more sensitive equipment. Therefore, we adopt AP = 10.7 ± 0.5 eV for the process $PbCl_2(g) + e^- \rightarrow PbCl^+(g) + Cl(g) + 2e^-$, and we calculate $\Delta Hf^\circ_0(PbCl^+, g)$ = 177.1 ± 12.0 kcal/mol by combining the value for AP with $\Delta Hf^\circ_0(PbCl_2, g)$ = −41.1 ± 0.3 kcal/mol and $\Delta Hf^\circ_0(Cl, g)$ = 28.587 ± 0.002 kcal/mol (6). ΔHf° at 298 K is 178.2 kcal/mol, and the corresponding ionization potential for PbCl is 7.5 ± 1.0 eV. Our adopted ΔH is considered a maximum value, since unknown kinetic energy factors could have been involved in the dissociative ionization of $PbCl_2$.

Heat Capacity and Entropy

The dissociation energy of $PbCl^+$ (D_0 = 69.5 kcal/mol) is slightly less than that for PbCl (D_0 = 71.5 kcal/mol). This implies that somewhat weaker binding occurs in the ion relative to the neutral molecule. Thus, one might expect r_e ($PbCl^+$, g) > r_e(PbCl, g). We assume an increase in r_e of 5% and obtain $r_e(PbCl^+)$ = 2.29 Å with r_e(PbCl) = 2.180 Å (6). The value of B_e is obtained from the estimated value for r_e. Values for ω_e and $\omega_e x_e$ are estimated by a procedure similar to that given for SrF^+ (6). The constant term (d_{ij}) used in Badger's rule (7) is based on molecular data for PbCl, PbS, CsCl, and BaCl (6). The value of α_e is obtained from the other constants assuming a Morse potential function. The moment of inertia is 26.3601 x 10^{-39} g cm^2.

$PbCl^+$ has 10 valence electrons and is isoelectronic with the Group III A monochlorides. By analogy with the electronic states and levels for these isoelectronic molecules (6, 8), we estimate the ground state configuration to be $^1\Sigma$ with a triplet level lying at 30,000 cm^{-1}. The uncertainty in the latter value is believed to be no greater than 5000 cm^{-1}. If the triplet level is decreased to 25,000 cm^{-1}, the entropy increases only 0.01 eu at 4000 K and 0.14 eu at 6000 K. The enthalpy at 0 K is −2.357 kcal/mol.

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Strontium Monochloride (SrCl)

(Ideal Gas) GFW = 123.073

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.342	-29.325	-29.325	INFINITE
100	7.472	51.376	67.723	-1.635	-29.286	-31.566	68.987
200	8.345	56.865	61.055	-.837	-29.441	-33.799	36.934
298	8.664	60.270	60.270	.000	-29.600	-35.899	26.314
300	8.668	60.324	60.270	.016	-29.603	-35.938	26.181
400	8.809	62.839	60.612	.891	-29.803	-38.020	20.773
500	8.884	64.814	61.262	1.776	-30.043	-40.047	17.505
600	8.932	66.438	61.994	2.667	-30.329	-42.022	15.306
700	8.967	67.818	62.730	3.562	-30.664	-43.945	13.720
800	8.993	69.017	63.442	4.460	-31.057	-45.817	12.517
900	9.015	70.077	64.122	5.360	-31.678	-47.620	11.564
1000	9.035	71.028	64.766	6.263	-32.123	-49.368	10.789
1100	9.053	71.890	65.375	7.167	-34.491	-50.960	10.125
1200	9.069	72.679	65.951	8.073	-34.875	-52.441	9.551
1300	9.085	73.405	66.497	8.981	-35.258	-53.889	9.060
1400	9.100	74.079	67.015	9.890	-35.641	-55.307	8.634
1500	9.114	74.707	67.507	10.801	-36.023	-56.699	8.261
1600	9.129	75.296	67.975	11.713	-36.405	-58.065	7.931
1700	9.144	75.850	68.422	12.627	-69.360	-58.501	7.521
1800	9.160	76.373	68.850	13.542	-69.398	-57.861	7.025
1900	9.176	76.865	69.259	14.459	-69.437	-57.219	6.582
2000	9.194	77.340	69.651	15.377	-69.478	-56.575	6.182
2100	9.214	77.789	70.028	16.297	-69.521	-55.930	5.821
2200	9.236	78.218	70.391	17.220	-69.566	-55.282	5.492
2300	9.260	78.629	70.740	18.145	-69.615	-54.631	5.191
2400	9.288	79.024	71.077	19.072	-69.669	-53.978	4.915
2500	9.319	79.404	71.402	20.002	-69.731	-53.323	4.662
2600	9.353	79.770	71.717	20.936	-69.799	-52.665	4.427
2700	9.391	80.123	72.022	21.873	-69.880	-52.005	4.210
2800	9.432	80.466	72.318	22.814	-69.974	-51.340	4.007
2900	9.478	80.797	72.604	23.760	-70.083	-50.674	3.819
3000	9.527	81.119	72.883	24.710	-70.209	-50.003	3.643
3100	9.581	81.433	73.154	25.665	-70.354	-49.327	3.478
3200	9.638	81.738	73.417	26.626	-70.522	-48.646	3.322
3300	9.699	82.035	73.674	27.593	-70.713	-47.959	3.176
3400	9.764	82.326	73.924	28.566	-70.932	-47.266	3.038
3500	9.832	82.610	74.168	29.546	-71.178	-46.568	2.908
3600	9.903	82.888	74.406	30.533	-71.455	-45.860	2.784
3700	9.977	83.160	74.639	31.527	-71.763	-45.144	2.667
3800	10.055	83.427	74.867	32.528	-72.105	-44.421	2.555
3900	10.134	83.689	75.090	33.538	-72.481	-43.687	2.448
4000	10.217	83.947	75.308	34.555	-72.892	-42.944	2.346
4100	10.301	84.200	75.522	35.581	-73.338	-42.190	2.249
4200	10.387	84.450	75.732	36.615	-73.820	-41.426	2.156
4300	10.475	84.695	75.937	37.659	-74.336	-40.648	2.066
4400	10.564	84.937	76.139	38.710	-74.887	-39.857	1.980
4500	10.655	85.175	76.337	39.771	-75.471	-39.056	1.897
4600	10.746	85.410	76.532	40.841	-76.088	-38.239	1.817
4700	10.838	85.643	76.723	41.921	-76.735	-37.409	1.739
4800	10.931	85.872	76.911	43.009	-77.411	-36.566	1.665
4900	11.025	86.098	77.097	44.107	-78.115	-35.707	1.593
5000	11.118	86.322	77.279	45.214	-78.842	-34.834	1.523
5100	11.211	86.543	77.458	46.331	-79.593	-33.946	1.455
5200	11.305	86.761	77.635	47.456	-80.365	-33.043	1.389
5300	11.398	86.978	77.809	48.591	-81.154	-32.126	1.325
5400	11.490	87.192	77.981	49.736	-81.959	-31.194	1.262
5500	11.582	87.403	78.151	50.889	-82.778	-30.246	1.202
5600	11.672	87.613	78.318	52.052	-83.607	-29.284	1.143
5700	11.762	87.820	78.483	53.224	-84.445	-28.308	1.085
5800	11.851	88.025	78.645	54.405	-85.289	-27.314	1.029
5900	11.939	88.229	78.806	55.594	-86.137	-26.308	.975
6000	12.025	98.430	78.965	56.792	-86.988	-25.286	.921

Dec. 31, 1972

STRONTIUM MONOCHLORIDE (SrCl) (IDEAL GAS) GFW = 123.073 ClSr

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 60.27 ± 0.1 gibbs/mol

ΔHf°_0 = −29.32 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −29.6 ± 2 kcal/mol

Electronic Levels and Quantum Weights

	ε_i, cm^{-1}	g_i		ε_i, cm^{-1}	g_i
X $^2\Sigma^+$	0.0	2	D $^2\Sigma$	28622.3	2
A $^2\Pi$	14813.3	2	E $^2\Sigma$	32701.8	2
	15112.8	2	F $^2\Pi$	32909.4	2
B $^2\Sigma$	15779.5	2		32978.6	2
C $^2\Pi$	25244.7	2	G $^2\Delta$	34086.7	2
	25399.8	2		34112.8	2
			H $^2\Sigma$	34256.7	2

ω_e = 300.94 cm^{-1} $\omega_e x_e$ = 0.97 cm^{-1} σ = 1

B_e = [0.10271 ± 0.003] cm^{-1} α_e = [0.00043] cm^{-1} r_e = [2.55 ± 0.04] Å

Heat of Formation

ΔHf° is a weighted average of results from three gas-phase equilibrium reactions studied mass spectrometrically by Hildenbrand (1) and Potter et al. (2). Analyses of these data are summarized below. The overall range of values is less than 4 kcal/mol, suggesting the approximate uncertainty in ΔHf°. From the adopted ΔHf° we calculate D°_0 = 98.2 ± 2 kcal/mol. Independent methods give D°_0 = 98 ± 4 (3), ≥ 99 (4), 95.6 ± 1.6 (5), 97 ± 6 (6) and 88.1 kcal/mol (7).

Electron-impact data (3) gave D°_0(ClSr-Cl) = 112.8 ± 3.3 and we use $\Delta H^\circ_{atom}(SrCl_2)$ = 210.8 ± 3 kcal/mol to derive D°_0 = 98 ± 4 kcal/mol. Chemiluminescence from crossed beams of Sr atoms with Cl_2 gave an approximate lower limit to D°_0 of 99 kcal/mol (4). Flame studies gave D°_0 = 95.6 ± 1.6 kcal/mol (5) and D°_0(ClSr-Cl) = 114 ± 5 kcal/mol (6); we derive D°_0 = 97 ± 6 kcal/mol from the latter value using $\Delta H^\circ_{atom}(SrCl_2)$ = 210.8 ± 3 kcal/mol. Ryabova et al. (6, 5) considered the flames to involve $SrCl_2$, SrOHCl and SrOH as well as SrCl. Schofield and Sugden (8) inferred that the flames involved mainly $SrCl_2$ rather than SrCl as assumed in earlier flame studies. Gaydon (9) discounted a value of D°_0 derived from limited spectroscopic data on the ground state. Novikov and Gurvich (7) published additional emission spectra and derived D°_0 = 88.1 kcal/mol by parabolic extrapolation. This value should be considered as approximate in light of Gaydon's precautionary notes, especially since the observed levels extend only to about 0.3 of the dissociation limit. Hildenbrand (1) found that ionicity corrections bring the Birge-Sponer extrapolation into reasonable agreement with D°_0.

Source	Reaction[b]	Range T, K	ΔHr°(298.15 K), kcal/mol 2nd Law	 3rd Law	δS[a] gibbs/mol	ΔHf°(298.15 K) kcal/mol	D°_0
(1) Hildenbrand (1970)	A	1305-1416	16.3±4.2	14.93±0.6	1.5±3.1	-29.49±1.0	98.3
(2) Potter (1970)	A	1235-1540	13.6±1.1	13.97±0.5	-0.3±0.8	-29.97±1.0	98.8
(1) Hildenbrand (1970)	B	1305-1416	19.7±4.5	22.65±0.7	-2.2±3.3	-28.45±2.0	97.3
(2) Potter (1970)	B	1235-1540	7.9±4.7	18.79±2.6	-8.6±3.4	-32.31±3.2	101.1
(1) Hildenbrand (1970)	C	1061	-	2.07±2		-30.72±3.6	99.6

[a] δS = ΔSr°(2nd Law) − ΔSr°(3rd Law).

[b] Reactions: (A) Sr(g) + $SrCl_2$(g) = 2 SrCl(g); (B) Sr(g) + AlCl(g) = SrCl(g) + Al(g);
(C) Ca(g) + SrCl(g) = CaCl(g) + Sr(g).

Heat Capacity and Entropy

Electronic levels and vibrational constants are based on the review of Rosen (10) as modified by the additional data of Novikov and Gurvich (7). Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX_2(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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ClSr

Cobalt Dichloride ($CoCl_2$)

(Crystal) GFW = 129.8392

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°$_{298}$)/T (gibbs/mol)	H°−H°$_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.776	- 75.143	- 75.143	INFINITE
100	11.510	8.830	41.422	- 3.259	- 75.446	- 71.630	156.548
200	17.050	18.943	27.786	- 1.769	- 75.139	- 67.912	74.211
298	18.760	26.115	26.115	.000	- 74.700	- 64.457	47.249
300	18.780	26.231	26.115	.035	- 74.691	- 64.394	46.911
400	19.530	31.745	26.862	1.953	- 74.217	- 61.033	33.347
500	19.930	36.148	28.294	3.927	- 73.750	- 57.791	25.260
600	20.220	39.807	29.916	5.934	- 73.304	- 54.641	19.903
700	20.540	42.949	31.559	7.973	- 72.869	- 51.566	16.100
800	20.750	45.706	33.159	10.038	- 72.550	- 48.537	13.260
900	20.920	48.160	34.692	12.122	- 72.155	- 45.559	11.063
1000	21.090	50.373	36.151	14.222	- 71.803	- 42.624	9.315
1100	21.230	52.390	37.537	16.338	- 71.501	- 39.721	7.892
1200	21.350	54.242	38.853	18.467	- 71.260	- 36.843	6.710
1300	21.480	55.956	40.103	20.609	- 71.116	- 33.982	5.713
1400	21.600	57.553	41.293	22.763	- 71.098	- 31.126	4.859
1500	21.720	59.047	42.428	24.929	- 70.830	- 28.281	4.120

June 30,1973

COBALT DICHLORIDE ($CoCl_2$) (CRYSTAL) GFW = 129.8392 Cl_2Co

ΔHf°_0 = -75.1 ± 0.3 kcal/mol

$S^\circ_{298.15}$ = 26.12 ± 0.05 gibbs/mol
Tm = 1013 ± 2 K

$\Delta Hf^\circ_{298.15}$ = -74.7 ± 0.3 kcal/mol
ΔHm° = [10.7 ± 1.5] kcal/mol

Heat of Formation

The adopted value for ΔHf°_{298} of -74.7 kcal/mol is that given in NBS Technical Note 270-4 (1). This value is based mainly on results derived from heat of solution measurements on Co(c) (2) and $CoCl_2$(c) (3) in aqueous HCl (ΔHf°_{298}($CoCl_2$, c) = -74.9 ± 1.0 kcal/mol) and from a third law analysis of several sets of equilibrium data (4-11). Results of earlier heat of solution measurements on Co(c) (12, 13) in aqueous HCl are in reasonable agreement (±0.4 kcal/mol) with those used in our calculations (2), while the results of Thomsen (14) are some 2 kcal/mol more negative. Results of a second and third law analysis of the equilibrium data with JANAF functions are tabulated below. Auxiliary ΔHf data used in the analysis are (in kcal/mol): ΔHf°_{298}(HCl, g) = -22.063 ± 0.05 and ΔHf°_{298}($FeCl_2$, c) = -81.7 ± 0.1 (15).

Investigator	Reaction	Method	No. of Points	Temp. Range, K	ΔHr_{298}, kcal/mol 2nd Law	ΔHr_{298}, kcal/mol 3rd Law	Drift eu	$-\Delta Hf^\circ_{298}$($CoCl_2$, c) kcal/mol
Crut (4)	A	Static	1	718		23.4		67.5
Jellinek and Uloth (5)	A	Dynamic	3	673-873	36.5	30.46±1.59	-7.8±1.7	74.6±1.7
Sano (6)	A	Static	7	759-831	32.8	30.66±0.16	-2.8±0.4	74.8±0.3
Partington and Towndrow (7)	A	Static	5	673-773	32.9	30.91±0.30	-2.7±1.5	75.0±0.4
Shchukarev et al. (8)	A		10	573-973	28.8	29.91±0.39	1.4±0.2	74.0±0.5
Egan (9)	B	emf	2	673;723	-74.1	-75.09±0.10	-1.5	75.1±0.1
Hamby and Scott (10)	B	emf	1	973		-73.09		73.1
Sheldon and Gee (11)	C	emf	Equation	490-760	- 6.4	- 7.10±0.22	-1.1±0.02	74.6±0.3

Reactions:
(A) $CoCl_2(c) + H_2(g) = Co(c) + 2\ HCl(g)$
(B) $Co(c) + Cl_2(g) = CoCl_2(c)$
(C) $Fe(c) + CoCl_2(c) = FeCl_2(c) + Co(c)$

Three (5-7) of the five sets of equilibrium data on the H_2 reduction of $CoCl_2$(c) yield ΔHf° values which are in good agreement (±0.3 kcal/mol) with the value (-74.9 kcal/mol) obtained by solution calorimetry (2, 3). Also, the results obtained from our analysis of the recent electromotive force study of reaction (c) by Sheldon and Gee (11) provide further confirmation for the adopted value of ΔHf°.

Heat Capacity and Entropy

Cp° data below 300 K are based on the low temperature measurements of Chisholm and Stout (16) (11-300 K) and Kostryukova (17) (1.8-4 K). The Cp° data of Kostryakova (17) below 3 K involve bias due to the presence of trace amounts of water in the $CoCl_2$ sample. His results (17) contain a small anomaly near 2.8 K which presumably arises from the $CoCl_2 \cdot 6\ H_2O$ antiferromagnetic transition at 2.3 K (18). The effect of the hexahydrate on the Cp° data above 3 K is judged to be negligible. The Cp° data above 3 K are joined graphically with those of Chisholm and Stout at 11 K (16). The latter data set contains a lambda peak at 24.71 K. Cp° near the maximum is 4.1 gibbs/mol, and the enthalpy associated with the transition is on the order of a few calories. The existence of this anomaly has been confirmed from heat capacity measurements by Shalyt (19) (30-75 K, T_t = 24.9 K) and Trapeznikowa et al. (20) (13-130 K, T_t = 24.90 K). This anomaly is apparently associated with the cooperative ordering of the magnetic moments of the cobaltous ions. The latter two sets of Cp° data are judged to be less reliable than that of Chisholm and Stout (16) and are not used in the calculation of S°_{298}. S°_{298} is obtained from integration of the adopted Cp°'s and is based on $S^\circ_{3\ K}$ = 0.003 eu.

Cp° data above 300 K are estimated from Cp-T curves for $FeCl_2$ (15) and $MnCl_2$(21). The results of the only high temperature enthalpy study (22) reported for $CoCl_2$(c) have been analyzed by Kelley (21). However, a comparison of these Cp°'s with those for the isostructural chlorides $FeCl_2$ (15) and $MnCl_2$ (21) indicate that these values are probably too high by 3.5% at 400 K and 27.3% at 1000 K. Other comparisons (21, 23) exist which indicate that it is not unusual for the Cp° data of these Russian workers to be in error by several percent.

Melting Data

See $CoCl_2$(ℓ) table.

Heat of Sublimation

See $CoCl_2$(g) table.

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Cl_2Co

Cobalt Dichloride ($CoCl_2$)
(Liquid) GFW = 129.8392

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.760	35.617	35.617	.000	-64.894	-57.484	42.137
300	18.780	35.733	35.617	.035	-64.885	-57.438	41.844
400	19.530	41.246	36.364	1.953	-64.411	-55.028	30.066
500	19.930	45.649	37.795	3.927	-63.944	-52.735	23.050
600	20.220	49.308	39.418	5.934	-63.497	-50.536	18.408
700	23.700	52.449	41.060	7.972	-63.064	-48.411	15.114
800	23.700	55.614	42.686	10.342	-62.440	-46.353	12.663
900	23.700	58.405	44.280	12.712	-61.759	-44.382	10.778
1000	23.700	60.902	45.820	15.082	-61.137	-42.487	9.285
1100	23.700	63.161	47.295	17.452	-60.581	-40.649	8.076
1200	23.700	65.223	48.705	19.822	-60.099	-38.859	7.077
1300	23.700	67.120	50.049	22.192	-59.727	-37.106	6.238
1400	23.700	68.876	51.332	24.562	-59.493	-35.374	5.522
1500	23.700	70.512	52.557	26.932	-59.021	-33.668	4.905
1600	23.700	72.041	53.727	29.302	-58.489	-31.995	4.370
1700	23.700	73.478	54.847	31.672	-57.935	-30.354	3.902
1800	23.700	74.833	55.920	34.042	-61.271	-28.679	3.482
1900	23.700	76.114	56.950	36.412	-60.781	-26.880	3.092
2000	23.700	77.330	57.939	38.782	-60.294	-25.109	2.744

June 30, 1973

COBALT DICHLORIDE ($CoCl_2$) (LIQUID) GFW = 129.8392 Cl_2Co

$S°_{298.15}$ = [35.617] gibbs/mol
Tm = 1013 ± 2 K
$\Delta Hf°_{298.15}$ = [-64.894] kcal/mol
ΔHm° = [10.7 ± 1.5] kcal/mol

Heat of Formation

ΔHf° is obtained from that of the crystal by addition of the estimated value for ΔHm° and the difference between $(H°_{1013}-H°_{298})$ for the crystal and liquid. Independent values of ΔHf°(ℓ) (or ΔHf°(c)) can be obtained from a second and third law analysis of two sets (1, 2) of emf data for the formation cell of molten $CoCl_2$. Results of our analysis of these data are tabulated below.

Investigator	No. of Points	Temp. Range, K	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf(ℓ) kcal/mol	ΔHf(c) kcal/mol
Devoto and Guzzi (1)	4	1023-1173	-75.8	-65.77±1.2	9.2±1.8	-65.8	-75.6
Hamby and Scott (2)	2	1073-1173	-65.9	-63.67±0.3	2.0	-63.7	-73.5

Even though both data sets contain few points and show significant positive drift, we note that the average ΔHf(c) value (-74.6 kcal/mol) obtained from these results is in excellent agreement with our adopted value (-74.7 kcal/mol).

Heat Capacity and Entropy

Cp° is assumed constant at 23.70 gibbs/mol in the temperature range 700-2000 K and is estimated from liquid heat capacities (3) for $FeCl_2$, $MgCl_2$, $CaCl_2$, and $NiCl_2$ (4). A glass transition is assumed at 700 K below which Cp° is that of the crystal. $S°_{298}$ is obtained in a manner analogous to that for ΔHf°

Melting Data

Tm is that obtained by Schäfer and Krehl (5) from cooling curve measurements. Other reported values for Tm are 997 K (6) and 1008 K (7). Our adopted value for Tm is that selected by Brewer et al. (8), while Kelley (9) chose Tm = 1000 K. ΔHm° is calculated from ΔHm° = ΔSm° x Tm with ΔSm° = 3.51 ± 0.5 gibbs/g-atom. ΔSm° is estimated from similar data (3, 4) for the isostructural chlorides $FeCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$, and $CdCl_2$. Kelley (9) has analyzed freezing point depression data for several binary systems which involve $CoCl_2$. Unfortunately, the values of ΔHm° derived by Kelley (9) are very discrepant and probably of no use in defining ΔHm°. Reported values fall in the range 6.71-8.75 kcal/mol, and Kelley (9) recommended ΔHm° = 7.39 kcal/mol. This value is 3.31 kcal/mol less than our estimated value and is also inconsistent with ΔHf° values derived for the crystal and liquid from equilibrium data (See Heat of Formation Section for $CoCl_2$(c, ℓ)). The discrepancies which arise in Kelley's analysis of the freezing point data may be associated with the ability of the divalent cobalt ion to form complex ions.

Vaporization Data

See $CoCl_2$(g) table.

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Cl_2Co

Cobalt Dichloride ($CoCl_2$) Cl_2Co

(Ideal Gas) GFW = 129.8692

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.650	-22.717	-22.717	INFINITE
100	12.333	56.529	83.574	-2.705	-22.592	-23.545	51.458
200	13.792	65.662	72.556	-1.379	-22.449	-24.566	26.844
298	14.250	71.265	71.265	.000	-22.400	-25.619	18.779
300	14.256	71.353	71.265	.026	-22.400	-25.639	18.678
400	14.497	75.491	71.828	1.465	-22.405	-26.720	14.599
500	14.655	78.743	72.897	2.923	-22.454	-27.792	12.148
600	14.787	81.427	74.102	4.395	-22.543	-28.853	10.510
700	14.913	83.716	75.316	5.880	-22.662	-29.896	9.334
800	15.031	85.715	76.493	7.378	-22.910	-30.905	8.443
900	15.139	87.492	77.618	8.886	-23.091	-31.893	7.745
1000	15.233	89.092	78.687	10.405	-23.320	-32.860	7.182
1100	15.311	90.548	79.700	11.932	-23.607	-33.801	6.716
1200	15.374	91.883	80.661	13.467	-23.960	-34.712	6.322
1300	15.421	93.115	81.572	15.007	-24.418	-35.591	5.983
1400	15.455	94.260	82.438	16.551	-25.010	-36.428	5.687
1500	15.479	95.327	83.262	18.097	-25.362	-37.232	5.425
1600	15.494	96.326	84.047	19.646	-25.651	-38.013	5.192
1700	15.502	97.266	84.798	21.196	-25.917	-38.776	4.985
1800	15.505	98.152	85.515	22.746	-30.073	-39.456	4.791
1900	15.505	98.990	86.202	24.297	-30.402	-39.966	4.597
2000	15.502	99.786	86.862	25.847	-30.735	-40.462	4.421
2100	15.497	100.542	87.495	27.397	-31.068	-40.941	4.261
2200	15.492	101.263	88.105	28.947	-31.404	-41.403	4.113
2300	15.487	101.951	88.692	30.496	-31.742	-41.849	3.977
2400	15.482	102.610	89.258	32.044	-32.083	-42.281	3.850
2500	15.478	103.242	89.805	33.592	-32.427	-42.699	3.733
2600	15.475	103.849	90.334	35.140	-32.772	-43.103	3.623
2700	15.473	104.433	90.845	36.687	-33.121	-43.494	3.521
2800	15.471	104.996	91.341	38.234	-33.473	-43.871	3.424
2900	15.471	105.539	91.821	39.781	-33.827	-44.237	3.334
3000	15.473	106.063	92.287	41.329	-34.183	-44.591	3.248
3100	15.475	106.571	92.740	42.876	-34.543	-44.932	3.168
3200	15.478	107.062	93.180	44.424	-124.023	-44.425	3.034
3300	15.482	107.538	93.607	45.972	-124.051	-41.938	2.777
3400	15.487	108.001	94.024	47.520	-124.081	-39.448	2.536
3500	15.493	108.450	94.430	49.069	-124.116	-36.961	2.308
3600	15.500	108.886	94.825	50.619	-124.153	-34.468	2.093
3700	15.507	109.311	95.211	52.169	-124.195	-31.976	1.989
3800	15.515	109.725	95.588	53.720	-124.240	-29.485	1.696
3900	15.524	110.128	95.955	55.272	-124.290	-26.989	1.512
4000	15.533	110.521	96.315	56.825	-124.345	-24.494	1.338
4100	15.542	110.905	96.666	58.379	-124.403	-21.998	1.173
4200	15.551	111.279	97.009	59.933	-124.467	-19.500	1.015
4300	15.561	111.645	97.345	61.489	-124.535	-17.001	.864
4400	15.571	112.003	97.674	63.046	-124.607	-14.496	.720
4500	15.581	112.353	97.997	64.603	-124.686	-11.996	.583
4600	15.591	112.696	98.313	66.162	-124.767	-9.489	.451
4700	15.601	113.031	98.622	67.721	-124.855	-6.981	.325
4800	15.610	113.360	98.926	69.282	-124.947	-4.474	.204
4900	15.620	113.682	99.224	70.843	-125.046	-1.961	.087
5000	15.630	113.997	99.516	72.406	-125.148	.550	-.024
5100	15.639	114.307	99.803	73.965	-125.255	3.069	-.132
5200	15.648	114.611	100.085	75.534	-125.368	5.586	-.235
5300	15.657	114.909	100.362	77.095	-125.487	8.103	-.334
5400	15.666	115.202	100.634	78.665	-125.612	10.625	-.430
5500	15.674	115.489	100.901	80.232	-125.742	13.150	-.523
5600	15.683	115.772	101.164	81.800	-125.877	15.675	-.612
5700	15.690	116.049	101.423	83.369	-126.019	18.201	-.698
5800	15.698	116.322	101.678	84.938	-126.166	20.737	-.781
5900	15.705	116.591	101.928	86.508	-126.320	23.268	-.862
6000	15.712	116.855	102.175	88.079	-126.480	25.806	-.940

Dec. 31, 1973

COBALT DICHLORIDE ($CoCl_2$) (IDEAL GAS) GFW = 129.8392 Cl_2Co

Point Group $D_{\infty h}$

$S^\circ_{298.15}$ = [71.3 ± 2.0] gibbs/mol

T_b(to monomer) = 1360 K

ΔHf°_0 = -22.7 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -22.4 ± 2.0 kcal/mol

ΔHv° = [34.8] kcal/mol

ΔHs° = 52.3 ± 1.7 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$^4\Sigma_g^-$	0	[4]	$^4\Sigma_g^-$	[10425]	[4]
$^4\Phi_g$	[210]	[8]	$^4\Delta_g$	[14197]	[8]
$^4\Pi_g$	[2804]	[8]	$^4\Pi_g$	[21270]	[8]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[325] (1)
94.5 (2)
493 (1)

Bond Distance: Co-Cl = 2.117 Å Bond Angle: Cl-Co-Cl = 180° Rotational Constant: B_0 = 0.05305 cm^{-1} σ = 2

Heat of Formation

ΔHf° is calculated from ΔHs° = 52.3 ± 1.7 kcal/mol by addition of ΔHf°_{298}($CoCl_2$, c) = -74.7 ± 0.3 kcal/mol (1). The adopted value for ΔHs° is based on results of a second and third law analysis of extensive sublimation data reported by Hill et al. (2). These studies included both Knudsen-effusion and torsion-effusion measurements which were performed in platinum-10% rhodium effusion cells. Orifice diameters of the cells varied from 0.0518 cm to 0.1645 cm. The extent of dimerization (~1-2%) was also determined from mass spectrometric measurements, and the measured vapor pressures were corrected to represent equilibrium pressures of the monomer. Results of our analysis of sixty-four vapor pressure points measured in five different cells are given below. Derived ΔHf values show no significant trends with orifice size; thus, a mean value of the five results is adopted. Also included in this table is a value for ΔHf which was obtained from an analysis of equilibrium data (3) for CoO(c) + Cl_2(g) = $CoCl_2$(g) + $\frac{1}{2}$ O_2(g). Orlov (3) has not reported sufficient information to allow a small correction to be made for dimerization; even so, his results still give a value for ΔHf (-22.1 kcal/mol) which agrees fairly well with that adopted.

Reference	Method	Temp. Range K	No. of Points	ΔHs°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$-\Delta Hf^\circ_{298}$ kcal/mol
(2)	Knudsen Cell A	680-800	13		52.35±0.13	0.4±0.5	22.4±0.4
(2)	Knudsen-Cell B	697-814	14^a	51.0	52.29±0.10	0.5±0.4	22.4±0.4
(2)	Knudsen-Cell C	715-810	10	52.0	52.14±0.16	-0.0±0.9	22.6±0.5
(2)	Torsion-Cell A	759-834	10	56.7	52.38±0.52	-5.4±3.2	22.3±0.8
(2)	Torsion-Cell B	745-824	15	55.0	52.30±0.17	-3.4±0.4	22.4±0.5
(3)	Transpiration	1323-1523	Equation	16.6	34.77±2.1	12.7	22.1±2.2^b

^{a} Two points rejected due to failure of a statistical test. ^{b} ΔHf°_{298}(CoO, c) = -56.82 ± 0.10 kcal/mol (1).

Other vapor pressures for $CoCl_2$(c, ℓ) have been measured by static (4) and transpiration (5, 6) methods. In all three studies the presence of a small amount of dimer in the saturated vapor was not considered. JANAF pressures based on (a) selected values of the heats of sublimation and vaporization for the monomer and dimer, (b) the mass spectrometric value of 2ΔHs(monomer)- ΔHs(dimer) = -38.99 kcal/mol (see Co_2Cl_4(g) table) at 298 K, and (c) adopted entropies for the condensed and gaseous species are compared with the observed total pressures in the table given below.

Investigator	Method	Process	Temp. Range K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range
Maier (4)	Static	Sublimation	906-997	0.051-0.086	0.073-0.156
Maier (4)	Static	Vaporization	1022-1250	0.082-0.092	0.198-0.816
Kulkarni and Dadape (5)	Transpiration	Vaporization	1015-1144	0.090-0.092	0.531-0.743
Schäfer and Krehl (6)	Transpiration	Sublimation	925-1010	0.057-0.091	0.875-1.096
Schäfer and Krehl (6)	Transpiration	Vaporization	1019-1073	0.092	0.825-0.883

Our predictions agree reasonably well with the transpiration data of Schäfer and Krehl (6), while the static measurements of Maier (4) show significant deviations from our pressures, particularly at the lower temperatures. We note that JANAF analysis (1) of Maier's vapor pressures for $BaCl_2$, $AlCl_3$, and $FeCl_2$ indicate the existence of temperature dependent errors in his measurements; thus, the results for $CoCl_2$ are probably not reliable. Also, the transpiration data of Kulkarni and Dadape (5) show similar discrepancies. Our calculated pressure represents about one-half their measured value at a temperature (1015 K) near Tm = 1013 K.

Heat Capacity and Entropy

Measurements of the infrared (7-9) and electronic (10-12) spectra of both matrix-isolated and gaseous $CoCl_2$ have been interpreted on the basis of a linear structure of $D_{\infty h}$ symmetry. This structure is adopted, and the Co-Cl bond length is taken to be equal to the value determined by Tremmel et al. (13). The antisymmetric stretching frequency (ν_3) is that observed in the infrared absorption spectra of gaseous $CoCl_2$ by Leroi et al. (7). This value has been confirmed from results of two infrared matrix-isolation studies (8, 9). The doubly degenerate bending frequency (ν_2) was observed by Thompson and Carlson (8) in the infrared spectra of $CoCl_2$ isolated in an argon matrix. The infrared-inactive symmetric stretching frequency (ν_1) is estimated by comparison with similar data for $FeCl_2$ (1) and $NiCl_2$ (14). Some additional support for this value is provided by calculations of DeKock and Gruen (11). Assuming a linear model, they calculated ν_1 = 332 cm^{-1} from ν_3 = 493 cm^{-1}. Also, Clifton and Gruen (15) observed a vibrational spacing of 332 cm^{-1} in the fluorescence spectrum of argon matrix-isolated $CoCl_2$ which may be ν_1. A similar assignment for $NiCl_2$ was recently proposed by Gruen et al. (14) based on observations of the vibrational spacings in its fluorescence spectrum.

The electronic spectra of $CoCl_2$ have been extensively investigated both in the gas phase (10, 11, and 16) and in various matrices (9, 12, 15, and 17). Unfortunately, most of the results are conflicting and difficult to interpret. It is not certain whether the ground state configuration is $^4\Phi$, or $^4\Sigma$. Theoretical arguments based on a ligand-field model (12, 18) favor the former, but recently Lever and Hollebone (19) interpreted the electronic spectra of $CoCl_2$ in terms of an "orbital angular overlap" model and preferred the latter ground state configuration. Other problems associated with band assignments in the $CoCl_2$ spectra have been dealt with by Smith (18). The adopted states and levels comprise one of two sets of assignments proposed by Lever and Hollebone (19). The alternate functions derived from their second set of assignments (19) suggest that the adopted entropies may be biased by as much as +2 eu at 298 K and +0.2 eu at 4000 K. Functions based on the assignments of Smith (18) agree with those adopted to better than 1 eu at all temperatures.

References: See Co_2Cl_4(g) table.

Cl_2Co

Lead Dichloride ($PbCl_2$)
(Crystal) GFW = 278.096

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.421	32.500	32.500	.000	− 85.900	− 75.085	55.039
300	18.444	32.614	32.500	.034	− 85.893	− 75.018	54.651
400	19.143	38.016	33.232	1.914	− 85.495	− 71.453	39.040
500	19.334	42.362	34.637	3.862	− 85.073	− 67.991	29.719
600	20.526	46.039	36.239	5.880	− 84.614	− 64.616	23.536
700	21.217	49.255	37.873	7.968	− 85.274	− 61.132	19.086
800	21.909	52.133	39.479	10.124	− 84.725	− 57.720	15.768
900	22.600	54.754	41.032	12.349	− 84.104	− 54.380	13.205
1000	23.292	57.171	42.527	14.644	− 83.409	− 51.115	11.171
1100	23.983	59.423	43.962	17.008	− 82.641	− 47.922	9.521
1200	24.675	61.540	45.339	19.441	− 81.799	− 44.802	8.160
1300	25.366	63.542	46.663	21.943	− 80.885	− 41.755	7.020
1400	26.058	65.447	47.937	24.514	− 79.903	− 38.783	6.054
1500	26.749	67.269	49.166	27.154	− 78.852	− 35.860	5.228

March 31, 1962; June 30, 1973

LEAD DICHLORIDE ($PbCl_2$) (CRYSTAL) GFW = 278.096 Cl_2Pb

$S^\circ_{298.15}$ = 32.5 ± 0.5 gibbs/mol
Tm = 774 K

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = −85.9 ± 0.2 kcal/mol
ΔHm° = 5.23 ± 0.20 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 44.3 ± 0.1 kcal/mol

Heat of Formation

ΔHf° of −85.9 ± 0.2 kcal/mol is obtained from a third law analysis of six sets of electromotive force data (3, 4, 6, 7) for three different reactions, namely, (A) $Pb(c) + 2AgCl(c) = 2Ag(c) + PbCl_2(c)$, (B) $Pb(c) + Hg_2Cl_2(c) = 2Hg(\ell) + PbCl_2(c)$, and (C) $Pb(\ell) + Cl_2(g) = PbCl_2(c)$. Seven other sets of similar data (1, 2, 5) give ΔHf° values which are within ±0.2 kcal/mol of adopted value, while one set of emf data (7) for (D) $2CuCl(c) + Pb(c) = PbCl_2(c) + 2Cu(c)$ gives a ΔHf° value of −85.4 kcal/mol. Results of our analysis of these data are tabulated below. Also included in the table is a value for ΔHf° obtained from a third law analysis of equilibrium data (8) for (E) $PbCl_2(c) + H_2(g) = Pb(\ell) + 2HCl(g)$. Auxiliary heats of formation used in our analysis are (ΔHf°_{298} in kcal/mol): (AgCl, c) = −30.370 (9), (CuCl, c) = −33.0 ± 0.4 (10), (Pb, ℓ) = 1.025 (10), (Hg_2Cl_2, c) = −63.319 ± 0.05 (10), and (HCl, g) = −22.063 ± 0.05 (10). We assign an uncertainty of ±0.2 kcal/mol to ΔHf° to reflect the estimated error in the adopted value for S°_{298}.

Investigator	Reaction	No. of Points	Temp. Range K	$-\Delta Hr_{298}$, kcal/mol 2nd Law	3rd Law	Drift eu	$-\Delta Hf^\circ_{298}(PbCl_2, c)$ kcal/mol
Günther (1)	A	5	273-298	24.5	25.06±0.04	−1.8±0.3	85.8±0.1
	B	7	273-298	22.0	22.34±0.03	−1.3±0.3	85.7±0.1
Krahmer (2) Set I	A	5	273-294	24.8	25.26±0.03	−1.7±0.1	86.0±0.1
Set II	A	5	273-294	24.9	25.25±0.03	−1.4±0.2	86.0±0.1
Set I	B	5	273-298	22.2	22.36±0.02	−0.7±0.1	85.7±0.1
Set II	B	5	273-296	22.2	22.36±0.02	−0.7±0.3	85.7±0.1
Gerke (3)	A	5	278-318	25.1	25.17±0.03	−0.1±0.5	85.9±0.1
Set I	B	5	278-318	22.7	22.54±0.04	0.4±0.7	85.9±0.1
Set II	B	5	278-318	22.7	22.54±0.04	0.5±0.7	85.9±0.1
Jahn-Held and Jellinek (4)	A	3	288-308	25.2	25.17±0.02	0.2±0.9	85.9±0.1
Markov et al. (5)	C	Equation	673-771	82.1	86.87±0.55	−6.6	85.8±0.6
Delimarskii and Roms (6)	C	2	723;773	86.8	86.98±0.02	−0.2	85.9±0.1
Bugden and Shelton (7)	D	Equation	363-553	19.8	19.44±0.13	0.9	85.4±1.0
	A	Equation	293-573	24.9	25.20±0.80	−0.7	85.9±0.9
Parravano and Malquori (8)	E	3	633-773	23.3	33.7 ±2.4	14.7±7.8	76.8±2.5

Heat Capacity and Entropy

Cp° data below 298 K have been reported by Nerst (11) (15.6-87.7 K), Eucken (12) (106.5-290.7 K), and Brönsted (13) (283 K). We combine these results with Cp° = 18.52 gibbs/mol (14) at 330 K and obtain S°_{298} = 33.7 eu based on $S^\circ_{15.6}$ = 0.9 eu. Kelley and King (15) analyzed the same Cp°'s and found S°_{298} = 34.0 ± 1.0 eu. Data obtained from cell measurements on both the crystal and liquid (See Heats of Formation Sections for $PbCl_2$(c, ℓ)) allow independent calculations of S°_{298}. Thirteen of the 23 sets of emf data that we have analyzed are more compatible with a value for S°_{298} which is at least one eu less than that determined from the low temperature data. Since the cell measurements are judged to be more reliable, we adopt S°_{298} = 32.5 ± 0.5 eu and omit the Cp° data below 298 K.

Cp°'s above 300 K are based on the smoothed relative enthalpies of Alim et al. (16). Their measurements were made in an isothermal diphenyl ether calorimeter over the temperature range 400 to 950 K. The $PbCl_2$ was reported to have a purity of 99.96%, and samples of this material were sealed in platinum capsules for the drop experiments. Their enthalpies are fitted to a polynomial which represents the data to within ±0.4%. The calculated Cp°'s above 300 K are joined graphically with those of Eucken (12) at 298 K by comparison with the Cp°-T curve for $BaCl_2$(c) (10). Our adopted enthalpies are in reasonable agreement with those of Kelley (17). His results are based on the enthalpy measurements of Krestovnikov and Karetnikov (18), and most of the points agree with ours to better than a percent but show a maximum deviation of −1.3% at 500 K. Other enthalpy data that have been recently reported are those of Bloom and Tricklebank (19) (693-773 K) and Thompson and Flengas (20) (577-745 K). Both of these studies show rather poor agreement with our adopted results. Deviations from our values are −4.2% at 673 K to −5.0% at 773 K for (19), +0.1% at 680 K and −6.2% at 745 K for (20). Both drop investigations were conducted with quartz capsules which might have been slowly attacked by the $PbCl_2$ at the higher temperatures. The earlier enthalpy measurements of Goodwin and Kalmus (21) are considered less reliable and not included in our analysis.

Modestova (22) has reported the existence of a transition for $PbCl_2$ at 695 K based on differential thermal analysis and x-ray studies. This transition has not been observed by other workers, and we prefer not to include it. However, if it does exist, we speculate that the enthalpy associated with it is quite small; thus, our functions would be only slightly altered.

Melting Data

Tm of 774 K is from the enthalpy study of Alim et al. (16). Other values reported for Tm based on enthalpy measurements are 771 (21), 774 (18), 774 (19), and 772 (20). DTA measurements (24) gave Tm equal to 774 K, while cryoscopic studies (23) yielded 768 K. ΔHm° is calculated to be 5.23 kcal/mol from the adopted enthalpies for the crystal and liquid at Tm. Published values (all in kcal/mol) include 5.15 (21), 5.70 (23), 2.98 (18), 5.3 (19), 5.56 (20), and 5.03 (24).

Heat of Sublimation

(See $PbCl_2$(g) table).

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Cl_2Pb

Lead Dichloride ($PbCl_2$)

(Liquid) GFW = 278.096

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	18.421	36.661	36.661	.000	- 82.279	- 72.705	53.294
300	18.444	36.775	36.662	.034	- 82.272	- 72.646	52.922
400	19.143	42.177	37.393	1.914	- 81.875	- 69.496	37.971
500	26.650	46.523	38.798	3.862	- 81.452	- 66.450	29.045
600	26.650	51.382	40.503	6.527	- 80.346	- 63.554	23.149
700	26.650	55.490	42.358	9.192	- 80.429	- 60.650	18.936
800	26.650	59.049	44.227	11.857	- 79.371	- 57.898	15.817
900	26.650	62.188	46.052	14.522	- 78.310	- 55.277	13.423
1000	26.650	64.996	47.808	17.187	- 77.245	- 52.775	11.534
1100	26.650	67.536	49.488	19.852	- 76.176	- 50.380	10.010
1200	26.650	69.855	51.090	22.517	- 75.102	- 48.082	8.757
1300	26.650	71.988	52.617	25.182	- 74.025	- 45.874	7.712
1400	26.650	73.963	54.072	27.847	- 72.949	- 43.750	6.830
1500	26.650	75.801	55.460	30.512	- 71.874	- 41.700	6.076
1600	26.650	77.521	56.785	33.177	- 70.804	- 39.724	5.426
1700	26.650	79.137	58.053	35.842	- 69.737	- 37.812	4.861
1800	26.650	80.660	59.267	38.507	- 68.677	- 35.967	4.367
1900	26.650	82.101	60.431	41.172	- 67.622	- 34.178	3.931
2000	26.650	83.468	61.549	43.837	- 66.575	- 32.445	3.545

March 31, 1962; June 30, 1973

LEAD DICHLORIDE ($PbCl_2$) (LIQUID) GFW = 278.096 Cl_2Pb

$S°_{298.15}$ = 36.661 gibbs/mol
Tm = 774 K
Tb = 1226 K

$\Delta Hf°_{298.15}$ = -82.279 kcal/mol
ΔHm° = 5.23 ± 0.20 kcal/mol
ΔHv° = 30.2 kcal/mol

Heat of Formation

ΔHf° is obtained from that of the crystal by addition of ΔHm° and the difference between $(H°_{774}-H°_{298})$ for the crystal and liquid. Independent values of ΔHf°(ℓ) (or ΔHf°(c)) can be obtained from a second and third analysis of nine sets of emf data (1-9) for the formation cell of molten $PbCl_2$ ((A) Pb(ℓ) + Cl_2(g) = $PbCl_2$(ℓ)) and three sets of equilibrium data (10, 11) for (B) $PbCl_2$(ℓ) + H_2(g) = Pb(ℓ) + 2HCl(g). Results of our analysis of these data are tabulated below. Auxiliary heats of formation used in the analysis are $\Delta Hf°_{298}$(Pb, ℓ) = 1.025 kcal/mol (12) and $\Delta Hf°_{298}$(HCl, g) = -22.063 ± 0.05 kcal/mol (12). Five of the nine sets of emf data yield values for ΔHf°(c) which are in good agreement (±0.2 Kcal/mol) with the adopted value. Also, the results of the extensive emf measurements of Warner and Seifert (8) by the electronic commutator method are quite compatible with our adopted functions.

Investigator	Reaction	No. of Points	Temp. Range K	-ΔHr, kcal/mol 2nd Law	-ΔHr, kcal/mol 3rd Law	Drift eu	$-\Delta Hf°_{298}$, kcal/mol$^{(c)}$ (ℓ)	$-\Delta Hf°_{298}$, kcal/mol$^{(c)}$ (c)
Lorenz and Fox (1)	A	14	776-942	85.9	82.45±0.58	5.1±0.5	81.43	85.05
Hildenbrand and Ruhle (2)	A	7	774-880	88.9	82.95±0.62	7.2±0.3	81.93	85.55
Lorenz and Velde (3)	A	47^a	826-1016	87.1	83.18±0.52	4.4±0.2	82.16	85.78
Wachter and Hildenbrand (4)	A	18	772-855	84.9	83.31±0.11	2.0±0.3	82.29	85.91
Holub et al. (5)	A	3	843-923	86.0	83.08±0.27	3.3±0.2	82.06	85.68
Lantratov and Alabyyshev (6)	A	47^b	814-954	82.5	83.69±0.15	-1.4±0.1	82.67	86.29
Delimarskii and Roms (1)	A	2	823;873	83.5	83.56		82.54	86.16
Warner and Seifert (8)	A	Equation	775-1133	83.4	83.32±0.03	0.1	82.30	85.92
Hagemark and Hengstenberg (9)	A	Equation	773-893	84.6	83.51±0.15	1.3±0.1	82.49	86.11
Bagdasarian (10) Set I	B	10	876-978	40.0	38.89±0.36	-1.2±1.4	81.99	85.61
Set II	B	21	871-1220	44.2	38.08±1.26	-5.8±0.3	81.18	84.80
Jellinek and Rudat (11)	B	5	833-1133	37.8	38.62±0.51	0.8±1.1	81.72	85.34

$(3)^a$ and $(1)^b$ points rejected due to failure of a statistical test.

^{c} Third law values.

Heat Capacity and Entropy

Cp° is assumed constant at 26.65 gibbs/mol over the temperature range 500-2000 K and is based on the smoothed relative enthalpies (774-950 K) of Alim et al. (13). A glass transition is assumed at 500 K below which Cp° is that of the crystal. The smoothed enthalpies of Kelley (14) (800-1000 K) deviate by +4.0% from our values, while those of Thompson and Flengas (15) (813-945 K) deviate by ±1%. The enthalpies of Bloom and Tricklebank (16) are consistently lower than our values by -3.1% at 823 K, and the deviation increases to -12.6% at 1073 K. Warner and Seifert (8) have determined Cp° data for $PbCl_2$(ℓ) from their emf measurements. They reported values of (all in gibbs/mol) 25.7 (800 K), 26.2 (900 K), 26.5 (1000 K), and 26.7 (1100 K). Bizouard and Pauty (17) measured Cp° for the liquid as 24.7 gibbs/mol. The entropy at 298 K is calculated in a manner analogous to that of the heat of formation.

Vaporization Data

Tb is the temperature at which ΔGr = 0 for the process $PbCl_2$(ℓ) = $PbCl_2$(g). ΔHr° is calculated as the difference between $\Delta Hf°_{Tb}$ for the gas and liquid.

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Cl_2Pb

Lead Dichloride ($PbCl_2$)

(Ideal Gas) GFW = 278.096

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.355	-41.117	-41.117	INFINITE
100	10.608	62.615	86.970	-2.435	-41.316	-42.183	92.190
200	12.497	70.646	76.975	-1.266	-41.476	-42.979	46.966
298	13.189	75.787	75.786	.000	-41.600	-43.691	32.026
300	13.197	75.868	75.787	.024	-41.603	-43.704	31.838
400	13.490	79.710	76.309	1.361	-41.748	-44.383	24.250
500	13.635	82.738	77.302	2.718	-41.917	-45.023	19.680
600	13.717	85.231	78.422	4.086	-42.108	-45.626	16.619
700	13.767	87.350	79.550	5.460	-43.482	-46.006	14.364
800	13.800	89.191	80.643	6.838	-43.711	-46.351	12.663
900	13.823	90.817	81.684	8.220	-43.933	-46.667	11.332
1000	13.839	92.275	82.672	9.603	-44.150	-46.960	10.263
1100	13.851	93.594	83.606	10.987	-44.362	-47.231	9.384
1200	13.861	94.800	84.489	12.373	-44.567	-47.482	8.648
1300	13.868	95.910	85.325	13.759	-44.769	-47.717	8.022
1400	13.874	96.938	86.119	15.147	-44.970	-47.937	7.483
1500	13.878	97.895	86.872	16.534	-45.173	-48.140	7.014
1600	13.882	98.791	87.589	17.922	-45.380	-48.331	6.602
1700	13.885	99.633	88.273	19.311	-45.589	-48.507	6.236
1800	13.888	100.426	88.927	20.699	-45.806	-48.675	5.910
1900	13.890	101.177	89.552	22.088	-46.027	-48.828	5.616
2000	13.893	101.890	90.151	23.477	-46.256	-48.969	5.351
2100	13.894	102.568	90.726	24.867	-88.939	-47.547	4.948
2200	13.896	103.214	91.279	26.256	-89.088	-45.574	4.527
2300	13.898	103.832	91.812	27.646	-89.258	-43.591	4.142
2400	13.900	104.423	92.325	29.036	-89.451	-41.601	3.788
2500	13.902	104.991	92.820	30.426	-89.670	-39.604	3.462
2600	13.904	105.536	93.299	31.816	-89.911	-37.596	3.160
2700	13.907	106.061	93.762	33.207	-90.174	-35.580	2.880
2800	13.910	106.567	94.210	34.598	-90.462	-33.551	2.619
2900	13.915	107.055	94.645	35.989	-90.770	-31.514	2.375
3000	13.920	107.527	95.066	37.381	-91.098	-29.465	2.147
3100	13.926	107.983	95.476	38.773	-91.445	-27.406	1.932
3200	13.933	108.425	95.874	40.166	-91.810	-25.335	1.730
3300	13.942	108.854	96.261	41.559	-92.190	-23.250	1.540
3400	13.951	109.271	96.637	42.954	-92.582	-21.153	1.360
3500	13.963	109.675	97.004	44.350	-92.987	-19.050	1.190
3600	13.976	110.069	97.361	45.747	-93.401	-16.929	1.028
3700	13.991	110.452	97.710	47.145	-93.824	-14.799	.874
3800	14.007	110.825	98.050	48.545	-94.251	-12.658	.728
3900	14.025	111.189	98.382	49.946	-94.685	-10.504	.589
4000	14.045	111.545	98.707	51.350	-95.121	-8.343	.456
4100	14.068	111.892	99.024	52.756	-95.558	-6.169	.329
4200	14.092	112.231	99.335	54.164	-95.996	-3.983	.207
4300	14.117	112.563	99.639	55.574	-96.433	-1.789	.091
4400	14.145	112.888	99.936	56.987	-96.867	.423	-.021
4500	14.175	113.206	100.227	58.403	-97.298	2.634	-.128
4600	14.206	113.518	100.513	59.822	-97.724	4.862	-.231
4700	14.239	113.824	100.793	61.244	-98.145	7.095	-.330
4800	14.274	114.124	101.068	62.670	-98.560	9.340	-.425
4900	14.311	114.419	101.337	64.099	-98.969	11.592	-.517
5000	14.349	114.708	101.602	65.532	-99.370	13.850	-.605
5100	14.389	114.993	101.861	66.969	-99.763	16.122	-.691
5200	14.430	115.272	102.117	68.410	-100.148	18.400	-.773
5300	14.472	115.548	102.367	69.855	-100.526	20.682	-.853
5400	14.515	115.819	102.614	71.304	-100.896	22.972	-.930
5500	14.560	116.085	102.856	72.758	-101.257	25.269	-1.004
5600	14.605	116.348	103.095	74.216	-101.609	27.572	-1.076
5700	14.651	116.607	103.330	75.679	-101.954	29.876	-1.146
5800	14.698	116.862	103.561	77.147	-102.289	32.200	-1.213
5900	14.745	117.114	103.789	78.619	-102.618	34.517	-1.279
6000	14.793	117.362	104.013	80.096	-102.938	36.844	-1.342

March 31, 1962; June 30, 1973

LEAD DICHLORIDE ($PbCl_2$) (IDEAL GAS) GFW = 278.096 Cl_2Pb

Point Group = C_{2v}

$S^\circ_{298.15}$ = 75.8 ± 0.7 gibbs/mol

ΔHf°_0 = -41.1 ± 0.3 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -41.6 ± 0.3 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[22000]	3
$^1B_1$	31000	1

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
329 (1)
80 (1)
307 (1)

$\sigma = 2$

Bond Distance: Pb-Cl = 2.46 ± 0.02 Å Bond Angle: Cl-Pb-Cl = 96 ± 3°

Product of Moments of Inertia: $I_AI_BI_C = 5.9023 \times 10^{-113}\ g^3cm^6$

Heat of Formation

ΔHf° of -41.6 ± 0.3 kcal/mol is obtained from ΔHf°(c) = -85.9 ± 0.2 kcal/mol by addition of ΔHs°_{298}. The adopted value for ΔHs°_{298} is 44.3 ± 0.1 kcal/mol and is based on a third law analysis of six sets of vapor pressure data (4, 9, 11, 14, 15) for both the crystal and liquid. Results of our analysis of a total of eighteen sets of vp data are given below. Seven (1, 2, 3, 7, 8, 10, 12) of the remaining twelve sets yield ΔHf°(g) values which are within 0.3 kcal/mol of the adopted value. Mass spectrometric studies (16) of the equilibrium vapors over the condensed phases indicated that the predominant species is the monomer.

Investigator	Reaction	Temp. Range K	No. of Points	ΔHs°(or v), kcal/mol 2nd Law	ΔHs°(or v), kcal/mol 3rd Law	Drift eu	$\Delta Hf^\circ_{298}(PbCl_2, g)$ kcal/mol
Eastman and Duschak (1)	A	673-748	4	47.6	45.41±0.21	-3.2±0.1	40.5±0.4
	B	773-1223	19	42.5	40.93±0.49	-1.6±0.2	41.3±0.7
Wartenberg and Bosse (2)	B	1043-1227	7	37.6	40.62±0.42	2.6±0.8	41.7±0.6
Maier (3)	B	955-1266	12[a]	39.8	40.75±0.25	0.8±0.3	41.5±0.4
Volmer (4)	A	708-766	5	37.1	44.34±0.53	9.8±3.2	41.6±0.7
	B	783-865	7	44.3	40.69±0.30	-4.4±0.7	41.6±0.5
Greiner and Jellinek (5)	B	1033;1043	2	36.1	40.19±0.06	3.9	42.1±0.3
Niwa et al. (6)	A	653-733	7	49.0	45.13±0.31	-5.6±0.2	40.8±0.5
Tarasenkov and Kozhmyakov (7)	B	953-1215	9[a]	43.6	40.94±0.69	-2.5±0.9	41.3±0.9
Jahn-Held and Jellinek (8)	B	865-1272	18	38.9	40.60±0.50	1.6±0.5	41.7±0.7
Barton and Bloom (9)	B	950-1250	Equation	40.9	40.67±0.04	-0.2	41.6±0.3
Novikov and Polyachenok (10)	B	931-1154	4	41.0	40.74±0.24	-0.2±0.8	41.5±0.4
Bloom and Hastie (11)	B	923	1		40.70		41.6±0.3
George et al. (12)	B	821-1259	56[b]	39.9	40.73±0.24	0.8±0.1	41.5±0.4
Naryshkin et al. (13)	A	708-758	3	45.1	42.93±0.37	-3.0±6.8	43.0±0.6
	B	793-893	3	31.3	40.24±1.14	10.6±3.8	42.0±1.2
George et al. (14)	B	914-1249	Equation	40.2	40.69±0.12	0.5	41.6±0.3
Bloom et al. (15)	B	1071	1		40.63		41.6±0.3

Reactions: (A) $PbCl_2(c) = PbCl_2(g)$ (B) $PbCl_2(\ell) = PbCl_2(g)$ (1)[a] and (2)[b] points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The bond length is taken from the electron diffraction study of Lister and Sutton (17). Electric deflection experiments by Büchler et al. (18) showed that $PbCl_2$ possessed a permanent dipole moment; thus, the molecule must have a bent structure. Infrared studies (19) of matrix isolated $PbCl_2$ have led to a value for the bond angle of 96 ± 3° which we adopt. This value is based on the observed Cl isotopic splitting of the antisymmetrical stretching frequency (ν_3). The individual moments of inertia are: $I_A = 63.114 \times 10^{-39}$, $I_B = 39.346 \times 10^{-39}$, and $I_C = 23.768 \times 10^{-39}\ g\ cm^2$.

The vibrational frequencies are from the matrix infrared studies of Hastie et al. (19). Both of the stretching frequencies (ν_1 and ν_3) were observed in matrices of N_2, Ar, and Ne. The adopted values are gas-phase frequencies which were estimated by Hastie et al. (19) from their matrix data. Other matrix infrared (20) and matrix Raman (21) studies have led to stretching frequencies which deviate by less than 30 cm^{-1} from our adopted values. Also, ν_1 is in agreement with the value of 314 cm^{-1} which was observed by Beattie and Perry (22) in a gas-phase Raman study of $PbCl_2$ at 1000°C. The bending frequency (ν_2) is somewhat more uncertain than the stretching frequencies. Hastie et al. (19) observed a relatively weak band at 80 cm^{-1} when $PbCl_2$ was trapped in a neon matrix and assigned this band to ν_2. Gas-phase (22) and matrix (21) Raman studies have indicated that ν_2 lies much closer to 100 cm^{-1}. The gas-phase Raman spectrum (22) for $PbCl_2$ was obtained in the presence of an excess of chlorine to suppress decomposition and subsequent resonance fluorescence. We prefer the lower value (80 cm^{-1}) but assign an uncertainty of ±20 cm^{-1} which corresponds to 0.5 eu in S°_{298}.

The ground state is assumed to be $^1A_1$ based on an analogy with those for other Group IV A dichlorides (23). The upper $^1B_1$ level at 31000 cm^{-1} was observed by Hastie et al. (23). Also included is a triplet level ($^3B_1$) at 22000 cm^{-1}. The energy separation for the $^1B_1$-$^3B_1$ states (9000 cm^{-1}) is assumed to be similar to that observed for other Group IV A dichlorides (23).

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Lead Dichloride Unipositive Ion ($PbCl_2^+$)

(Ideal Gas) GFW = 278.0954

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	13.147	76.113	76.113	.000	195.100	191.424	- 140.318
300	13.155	76.194	76.113	.024	195.106	191.401	- 139.436
400	13.464	80.027	76.633	1.357	195.454	190.113	- 103.873
500	13.618	83.049	77.625	2.712	195.780	188.740	- 82.498
600	13.704	85.540	78.743	4.079	196.085	187.304	- 68.225
700	13.758	87.657	79.869	5.452	195.206	186.007	- 58.074
800	13.793	89.497	80.960	6.830	195.474	184.675	- 50.451
900	13.817	91.123	82.000	8.210	195.747	183.309	- 44.514
1000	13.835	92.580	82.987	9.593	196.027	181.912	- 39.757
1100	13.848	93.899	83.920	10.977	196.312	180.486	- 35.859
1200	13.858	95.104	84.802	12.362	196.602	179.035	- 32.607
1300	13.865	96.214	85.638	13.748	196.897	177.559	- 29.850
1400	13.871	97.242	86.431	15.135	197.192	176.060	- 27.484
1500	13.876	98.199	87.184	16.523	197.487	174.542	- 25.431
1600	13.880	99.094	87.900	17.910	197.775	173.001	- 23.631
1700	13.884	99.936	88.584	19.299	198.063	171.446	- 22.041
1800	13.887	100.730	89.237	20.687	198.343	169.870	- 20.625
1900	13.889	101.481	89.862	22.076	198.619	168.282	- 19.357
2000	13.891	102.193	90.460	23.465	198.887	166.679	- 18.214
2100	13.893	102.871	91.035	24.854	156.699	166.613	- 17.340
2200	13.895	103.517	91.588	26.244	157.048	167.076	- 16.597
2300	13.897	104.135	92.120	27.633	157.374	167.526	- 15.919
2400	13.899	104.726	92.633	29.023	157.678	167.962	- 15.295
2500	13.901	105.294	93.129	30.413	157.956	168.383	- 14.720
2600	13.903	105.839	93.607	31.803	158.211	168.795	- 14.188
2700	13.905	106.364	94.070	33.194	158.445	169.197	- 13.696
2800	13.908	106.870	94.518	34.584	158.653	169.593	- 13.237
2900	13.911	107.358	94.952	35.975	158.842	169.979	- 12.810
3000	13.914	107.829	95.374	37.366	159.010	170.361	- 12.411
3100	13.918	108.286	95.783	38.758	159.159	170.735	- 12.037
3200	13.923	108.728	96.181	40.150	159.290	171.106	- 11.686
3300	13.928	109.156	96.567	41.543	159.407	171.475	- 11.356
3400	13.934	109.572	96.944	42.936	159.510	171.841	- 11.046
3500	13.940	109.976	97.310	44.329	159.599	172.199	- 10.753
3600	13.947	110.369	97.668	45.724	159.679	172.560	- 10.476
3700	13.955	110.751	98.016	47.119	159.750	172.917	- 10.214
3800	13.963	111.123	98.356	48.515	159.816	173.272	- 9.965
3900	13.973	111.486	98.688	49.911	159.874	173.627	- 9.730
4000	13.983	111.840	99.013	51.309	159.928	173.974	- 9.506
4100	13.993	112.185	99.330	52.708	159.981	174.325	- 9.292
4200	14.004	112.523	99.640	54.108	160.032	174.675	- 9.089
4300	14.016	112.852	99.943	55.509	160.083	175.021	- 8.896
4400	14.029	113.175	100.240	56.911	160.135	175.374	- 8.711
4500	14.042	113.490	100.531	58.315	160.188	175.714	- 8.534
4600	14.055	113.799	100.816	59.719	160.244	176.061	- 8.365
4700	14.069	114.101	101.096	61.126	160.305	176.403	- 8.203
4800	14.084	114.398	101.370	62.533	160.368	176.747	- 8.047
4900	14.099	114.688	101.639	63.943	160.437	177.088	- 7.898
5000	14.114	114.973	101.902	65.353	160.509	177.423	- 7.755
5100	14.130	115.253	102.162	66.765	160.588	177.764	- 7.618
5200	14.146	115.527	102.416	68.179	160.673	178.102	- 7.485
5300	14.162	115.797	102.666	69.595	160.763	178.435	- 7.358
5400	14.179	116.062	102.911	71.012	160.858	178.768	- 7.235
5500	14.195	116.322	103.153	72.430	160.957	179.098	- 7.117
5600	14.212	116.578	103.390	73.851	161.065	179.426	- 7.002
5700	14.229	116.830	103.624	75.273	161.176	179.747	- 6.892
5800	14.246	117.077	103.854	76.696	161.293	180.081	- 6.786
5900	14.263	117.321	104.080	78.122	161.415	180.399	- 6.682
6000	14.280	117.561	104.303	79.549	161.541	180.718	- 6.583

June 30, 1973

LEAD DICHLORIDE UNIPOSITIVE ION ($PbCl_2^+$) (IDEAL GAS) GFW = 278.0954 Cl_2Pb^+

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [76.1 ± 2.0] gibbs/mol

ΔHf°_0 = 194.1 ± 12.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 195.1 ± 12.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	[2]
$^2B_1$	[20000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[300] (1)
[100] (1)
[350] (1)

Bond Distance: Pb-Cl = [2.30] Å

Bond Angle: Cl-Pb-Cl = [116]° σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [3.3791 x 10^{-113}] g^3cm^6

Heat of Formation

The appearance potential (AP) for $PbCl_2^+$ from $PbCl_2$(g) has been determined mass spectrometrically as (in eV) 11.2 ± 0.2 (1), 10.3 ± 0.2 (2), and 10.3 ± 0.5 (3). Hastie et al. (2) preferred the lower AP for $PbCl_2^+$, since this value was obtained with more sensitive equipment. Subsequent measurements by Hastie and Swingler (4) confirm the lower result. They reported an ionization efficiency curve for $PbCl_2^+$ from which we obtain AP = 10.0 eV by the linear extrapolation method. Also, molecular orbital calculations by Hastie and Margrave (5) indicated an ionization potential for $PbCl_2$ of 10.3 eV. We adopt a mean value from (2, 3, and 4) of 10.2 ± 0.5 eV (235.2 kcal/mol) for the process $PbCl_2(g) + e^- \rightarrow PbCl_2^+(g) + 2e^-$ which gives $\Delta Hf^\circ_0(PbCl_2^+, g)$ = 194.1 ± 12.0 kcal/mol when AP is combined with $\Delta Hf^\circ_0(PbCl_2, g)$ = -41.1 ± 0.3 kcal/mol (6). ΔHf° at 298 K is 195.1 kcal/mol.

Heat Capacity and Entropy

The correlation diagram of Walsh (7) predicts a bent configuration for $PbCl_2^+$, since the molecule has seventeen valence electrons. Also, Walsh (7) predicted that the apex angle for a non-hydride AB_2 molecule would decrease markedly in going from a 17- to an 18- electron molecule. We assume that the bond angle in $PbCl_2^+$ is 20° larger than that for $PbCl_2$ (6). The adopted value (116°) is consistent with JANAF bond angles for the isoelectronic molecules BCl_2(112°) and $AlCl_2$(120°) (6). The bond length is assumed to lie between that for PbCl and $PbCl_2$ (6). The individual moments of inertia are: $I_A = 57.849 \times 10^{-39}$, $I_B = 44.815 \times 10^{-39}$, and $I_C = 13.034 \times 10^{-39}$ g cm^2.

The vibrational frequencies are estimated by comparison with those for BCl_2, CCl_2, $SiCl_2$, and $PbCl_2$ (6). The ground state is assumed to be $^2A_1$ by analogy with that for the isoelectronic molecule NO_2 (8). MO calculations by Hastie and Margrave (5) for the Group III A dihalides predicted an upper $^2B_1$ state with the $^2A_1$-$^2B_1$ separation in the energy range 1-2 eV. We have included this state and estimated the $^2A_1$-$^2B_1$ separation (20,000 cm^{-1}) to be somewhat greater than that for $AlCl_2$ (15,000 cm^{-1}) (6), BCl_2 (11,000 cm^{-1}) (6), and NO_2 (<15,000 cm^{-1}) (8). The enthalpy at 0 K is -3.32 kcal/mol.

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Cl_2Pb^+

Strontium Dichloride (SrCl$_2$)

(Crystal) GFW = 158.526

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 3.882	− 198.268	− 198.268	INFINITE
100	12.977	9.909	42.556	− 3.265	− 198.667	− 194.543	425.172
200	16.906	20.452	29.059	− 1.721	− 198.439	− 190.499	208.167
298	18.066	27.440	27.440	.000	− 198.100	− 186.666	136.830
300	18.083	27.552	27.440	.033	− 198.094	− 186.596	135.935
400	18.855	32.866	28.160	1.883	− 197.733	− 182.817	99.886
500	19.436	37.136	29.542	3.798	− 197.370	− 179.129	78.297
600	19.995	40.730	31.115	5.769	− 197.010	− 175.515	63.931
700	20.693	43.862	32.717	7.802	− 196.646	− 171.961	53.689
800	21.700	46.686	34.289	9.918	− 196.264	− 168.462	46.022
900	23.178	49.322	35.814	12.157	− 195.992	− 164.996	40.066
1000	25.293	51.867	37.293	14.575	− 195.368	− 161.584	35.314
1100	29.400	56.105	38.877	18.951	− 194.713	− 158.294	31.450
1200	29.400	58.664	40.421	21.891	− 193.513	− 155.036	28.236
1300	29.400	61.017	41.916	24.831	− 192.315	− 151.878	25.533
1400	29.400	63.196	43.359	27.771	− 191.119	− 148.812	23.231
1500	29.400	65.224	44.750	30.711	− 189.925	− 145.832	21.248
1600	29.400	67.121	46.090	33.651	− 188.733	− 142.931	19.524
1700	29.400	68.904	47.380	36.591	− 220.116	− 139.199	17.895
1800	29.400	70.584	48.673	39.531	− 218.585	− 134.484	16.329
1900	29.400	72.174	49.821	42.471	− 217.057	− 129.852	14.936
2000	29.400	73.682	50.976	45.411	− 215.534	− 125.302	13.692

Dec. 31, 1972

STRONTIUM DICHLORIDE (SrCl$_2$) (CRYSTAL) GFW = 158.526 Cl$_2$Sr

$S^\circ_{298.15}$ = 27.44 ± 0.04 gibbs/mol

Tt = 1000 ± 10 K

Tm = 1147 ± 1 K

ΔHf°_0 = −198.27 ± 0.6 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −198.1 ± 0.6 kcal/mol

ΔHt° = [1.438 ± 0.3] kcal/mol

ΔHm° = 3.977 ± 0.15 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 83.5 ± 1.0 kcal/mol

Heat of Formation

ΔHf° is from NBS Technical Note 270-6 (1) and was selected by Parker in a manner analogous to that described (2) for ΔHf°(BaCl$_2$, c). The adopted value is essentially that derived by Ehrlich et al. (3) from their measurements of ΔH_{soln} of Sr(c) and SrCl$_2$(c) in HCl(550 H$_2$O). Earlier solution data for Sr (4) and SrCl$_2$ (5) are in good agreement.

Parker (2) rejected ΔHf° = −210 kcal/mol obtained by Siemonsen (6) from direct chlorination and ΔHf° = −201.0 kcal/mol which would result from SrO(c) based on Mah's direct combustion (7). Parker noted that these more negative values are inconsistent with data for SrCl$_2$(c, aq) and related compounds. They are also less consistent with equilibrium data discussed on the tables for SrCl$_2$(ℓ and g). Impurity effects are of concern in all these studies involving Sr(c), but the evidence favors the solution calorimetry.

Heat Capacity and Entropy

Cp° is based on adiabatic calorimetry (7.4-300 K) of Smith et al. (8) with omission of the point at 11.22 K which appears to be about 30% low. S° is calculated from Cp° using S°(7 K) = 0.012 gibbs/mol. Cp° above 300 K is from constrained fitting of enthalpy data (418-936 K for α-phase and 1034-1134 K for β-phase) from Dworkin and Bredig (9).

The transition near 1000 K is gradual and may be second order rather than first order as we have treated it. Gradual transitions also are observed for BaF$_2$, SrF$_2$ and perhaps CaF$_2$, all of which have α-phases of the fluorite structure. Reasonable Cp° curves are obtained by omitting from the curve fits those enthalpy data from about 50° below to 30° above Tt. The resulting gibbs-energy functions agree well with those obtained (9) by second-order analysis.

Deviations of the fitted data (9) from the adopted functions for α-phase are −0.5 to +0.3% except for +2.0% at 417.6 K. Data of Efremova and Matizen (10) deviate by +0.6 to +2.2% (805-959 K), while the equation of Janz et al. (11) agrees almost exactly near 850 K but deviates by −4.8% at 800 K. The β-phase deviations are −0.4 to +0.3% (9), 0.0 to −1.0% (10, 1047-1142 K) and −2 to 0% (11, 1050-1147 K).

Transition Data

Tt = 1000 K is arbitrarily selected as the peak of the gradual transition. Reported values include 1003 (9), 1002 (11) and 990 K (10). ΔHt° is calculated as the difference in the enthalpy curve fits (cf. above) at Tt. ΔHt° is assigned an uncertainty of 0.3 kcal/mol as a first-order transition, but the result is placed in brackets to emphasize that the transition may be second order. Reported values of ΔHt° include 1.65 (9) and 0.65 (11) kcal/mol.

Melting Data - see SrCl$_2$(ℓ).

Heat of Sublimation - see SrCl$_2$(g).

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Cl$_2$Sr

Strontium Dichloride ($SrCl_2$)

(Liquid) GFW = 158.526

T, °K	gibbs/mol Cp°	gibbs/mol S°	gibbs/mol −(G°−H°298)/T	kcal/mol H°−H°298	kcal/mol ΔHf°	kcal/mol ΔGf°	Log Kp
0							
100							
200							
298	18.066	32.462	32.462	.000	- 192.484	- 182.547	133.810
300	18.083	32.574	32.462	.033	- 192.477	- 182.486	132.941
400	18.855	37.888	33.182	1.883	- 192.117	- 179.209	97.915
500	19.436	42.160	34.564	3.798	- 191.753	- 176.023	76.940
600	19.995	45.752	36.137	5.769	- 191.393	- 172.911	62.983
700	20.693	48.884	37.739	7.802	- 191.030	- 169.860	53.033
800	21.700	51.708	39.311	9.918	- 190.647	- 166.863	45.585
900	25.000	54.653	40.855	12.418	- 190.114	- 163.916	39.804
1000	25.000	57.287	42.369	14.918	- 189.408	- 161.044	35.196
1100	25.000	59.670	43.835	17.418	- 190.629	- 158.131	31.418
1200	25.000	61.845	45.247	19.918	- 189.869	- 155.210	28.268
1300	25.000	63.846	46.601	22.418	- 189.111	- 152.352	25.613
1400	25.000	65.699	47.900	24.918	- 188.355	- 149.553	23.346
1500	25.000	67.424	49.145	27.418	- 187.601	- 146.808	21.390
1600	25.000	69.037	50.338	29.918	- 186.849	- 144.113	19.685
1700	25.000	70.553	51.483	32.418	- 218.672	- 140.558	18.070
1800	25.000	71.982	52.583	34.918	- 217.581	- 135.995	16.512
1900	25.000	73.333	53.639	37.418	- 216.493	- 131.491	15.125
2000	25.000	74.616	54.656	39.918	- 215.410	- 127.046	13.883
2100	25.000	75.835	55.636	42.418	- 214.330	- 122.655	12.765
2200	25.000	76.998	56.581	44.918	- 213.257	- 118.315	11.754
2300	25.000	78.110	57.493	47.418	- 212.190	- 114.022	10.835
2400	25.000	79.174	58.374	49.918	- 211.132	- 109.777	9.997
2500	25.000	80.194	59.227	52.418	- 210.086	- 105.576	9.229
2600	25.000	81.175	60.052	54.918	- 209.051	- 101.415	8.525
2700	25.000	82.118	60.852	57.418	- 208.033	- 97.295	7.875
2800	25.000	83.027	61.628	59.918	- 207.033	- 93.211	7.275
2900	25.000	83.905	62.381	62.418	- 206.054	- 89.165	6.720
3000	25.000	84.752	63.113	64.918	- 205.098	- 85.151	6.203

Dec. 31, 1972

STRONTIUM DICHLORIDE ($SrCl_2$) (LIQUID) GFW = 158.526 Cl_2Sr

$S^\circ_{298.15}$ = 32.462 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -192.484 kcal/mol

Tm = 1147 ± 1 K

ΔHm° = 3.877 ± 0.15 kcal/mol

Tb = 2331.0 K

ΔHv° = 59.31 kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference in ($H^\circ_{1147} - H^\circ_{298.15}$) between crystal and liquid. An independent value of ΔHf° for liquid (and crystal) may be derived from equilibrium data (1) for $Ca(\ell) + SrCl_2(\ell) \rightarrow Sr(\ell) + CaCl_2(\ell)$ at 1273 K. Our third-law analysis yields ΔHr°(298.15 K) = 6.5 ± 1.3 kcal/mol or ΔHf°(ℓ) = -191.5 ± 1.5 kcal/mol and ΔHf°(c) = -197.2 ± 1.5 kcal/mol. This confirms the adopted values as opposed to the more negative values (cf. $SrCl_2$, c).

Heat Capacity and Entropy

The constant Cp° of 25.0 gibbs/mol is a compromise chosen by comparison with $BaCl_2$ and $CaCl_2$. Our fits of the enthalpy data yield 26.8 (2) and 23.5 (3) gibbs/mol; the adopted value is roughly their mean. The value 26.7 gibbs/mol was also reported (4). Deviations from our adopted functions are ±0.3% (2, 1154-1204 K), +1.1 to -1.7% (3, 1152-1797 K) and -1.1 to -0.2% (4, equation, 1148-1287 K). Cp° is taken equal to that of the crystal from 298 to 800 K, the assumed glass transition. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Tm is selected from 1146 (2), 1147 ± 2 (3) and 1148 K (4) reported in the enthalpy studies. ΔHm° is obtained from the difference in the adopted enthalpy fits for liquid and β-phases. Published values include 3.85 (2, 3), 3.88 (2), 3.65 ± 0.17 (4) and 3.73 kcal/mol (5), the last value obtained by dynamic differential calorimetry.

Vaporization Data

Tb is calculated as the temperature at which ΔGr° = 0 for $SrCl_2(\ell) \rightarrow SrCl_2(g)$. ΔHv° is calculated as the corresponding ΔHr°.

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Cl_2Sr

Strontium Dichloride ($SrCl_2$)

(Ideal Gas) GFW = 158.526

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	− 3.453	− 112.839	− 112.839	INFINITE
100	11.021	62.088	86.970	− 2.488	− 112.890	− 113.984	249.112
200	12.751	70.362	76.784	− 1.285	− 113.003	− 115.044	125.714
298	13.330	75.580	75.580	.000	− 113.100	− 116.019	85.044
300	13.337	75.662	75.580	.025	− 113.102	− 116.037	84.533
400	13.575	79.536	76.106	1.372	− 113.244	− 116.996	63.923
500	13.692	82.579	77.108	2.736	− 113.432	− 117.912	51.539
600	13.757	85.082	78.234	4.108	− 113.671	− 118.786	43.268
700	13.797	87.205	79.368	5.486	− 113.962	− 119.617	37.346
800	13.823	89.050	80.465	6.867	− 114.315	− 120.403	32.892
900	13.841	90.679	81.511	8.251	− 114.898	− 121.123	29.413
1000	13.854	92.138	82.502	9.635	− 115.308	− 121.794	26.618
1100	13.864	93.459	83.439	11.021	− 117.643	− 122.312	24.301
1200	13.871	94.665	84.325	12.408	− 117.996	− 122.721	22.350
1300	13.877	95.776	85.164	13.795	− 118.351	− 123.100	20.695
1400	13.881	96.804	85.959	15.183	− 118.707	− 123.452	19.272
1500	13.885	97.762	86.714	16.572	− 119.064	− 123.779	18.035
1600	13.888	98.659	87.433	17.960	− 119.424	− 124.081	16.949
1700	13.891	99.501	88.119	19.349	− 152.358	− 123.455	15.871
1800	13.893	100.295	88.773	20.739	− 152.377	− 121.755	14.783
1900	13.895	101.046	89.399	22.128	− 152.400	− 120.051	13.809
2000	13.896	101.759	90.000	23.517	− 152.428	− 118.349	12.933
2100	13.897	102.437	90.576	24.907	− 152.458	− 116.645	12.139
2200	13.899	103.083	91.130	26.297	− 152.495	− 114.939	11.418
2300	13.899	103.701	91.663	27.687	− 152.538	− 113.230	10.759
2400	13.900	104.292	92.177	29.077	− 152.590	− 111.520	10.155
2500	13.901	104.860	92.673	30.467	− 152.654	− 109.808	9.599
2600	13.902	105.405	93.152	31.857	− 152.729	− 108.092	9.086
2700	13.902	105.930	93.616	33.247	− 152.821	− 106.374	8.610
2800	13.903	106.435	94.065	34.638	− 152.930	− 104.650	8.168
2900	13.903	106.923	94.500	36.028	− 153.061	− 102.926	7.757
3000	13.904	107.395	94.922	37.418	− 153.215	− 101.195	7.372
3100	13.904	107.851	95.332	38.809	− 153.394	− 99.457	7.012
3200	13.905	108.292	95.730	40.199	− 153.604	− 97.715	6.674
3300	13.905	108.720	96.117	41.590	− 153.844	− 95.964	6.355
3400	13.905	109.135	96.494	42.980	− 154.119	− 94.205	6.055
3500	13.906	109.538	96.861	44.371	− 154.430	− 92.441	5.772
3600	13.906	109.930	97.218	45.761	− 154.780	− 90.663	5.504
3700	13.906	110.311	97.567	47.152	− 155.169	− 88.876	5.250
3800	13.906	110.682	97.907	48.542	− 155.601	− 87.080	5.008
3900	13.906	111.043	98.240	49.933	− 156.076	− 85.270	4.778
4000	13.907	111.395	98.564	51.324	− 156.596	− 83.448	4.559
4100	13.907	111.738	98.881	52.714	− 157.160	− 81.613	4.350
4200	13.907	112.074	99.191	54.105	− 157.769	− 79.765	4.151
4300	13.907	112.401	99.495	55.496	− 158.422	− 77.900	3.959
4400	13.907	112.721	99.792	56.886	− 159.120	− 76.016	3.776
4500	13.907	113.033	100.083	58.277	− 159.861	− 74.122	3.600
4600	13.907	113.339	100.367	59.668	− 160.643	− 72.207	3.431
4700	13.908	113.638	100.647	61.059	− 161.466	− 70.274	3.268
4800	13.908	113.931	100.920	62.449	− 162.329	− 68.328	3.111
4900	13.908	114.217	101.189	63.840	− 163.228	− 66.358	2.960
5000	13.908	114.498	101.452	65.231	− 164.160	− 64.373	2.814
5100	13.908	114.774	101.711	66.622	− 165.125	− 62.365	2.673
5200	13.908	115.044	101.964	68.013	− 166.120	− 60.340	2.536
5300	13.908	115.309	102.214	69.403	− 167.144	− 58.298	2.404
5400	13.908	115.569	102.459	70.794	− 168.192	− 56.235	2.276
5500	13.908	115.824	102.699	72.185	− 169.263	− 54.150	2.152
5600	13.908	116.075	102.936	73.576	− 170.353	− 52.049	2.031
5700	13.908	116.321	103.169	74.967	− 171.462	− 49.930	1.914
5800	13.908	116.563	103.397	76.358	− 172.585	− 47.784	1.801
5900	13.909	116.800	103.623	77.748	− 173.723	− 45.625	1.690
6000	13.909	117.034	103.844	79.139	− 174.871	− 43.442	1.582

Dec. 31, 1972

STRONTIUM DICHLORIDE ($SrCl_2$) (IDEAL GAS) GFW = 158.526 Cl_2Sr

Point Group C_{2v}

$S^\circ_{298.15}$ = 75.58 ± 1.2 gibbs/mol

Ground State Quantum Weight = 1

ΔHf°_0 = -112.84 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -113.1 ± 1.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
270 (1)	44 (1)	300 (1)

Bond Distance: Sr-Cl = 2.67 ± 0.03 Å

Bond Angle: Cl-Sr-Cl = 120° ± 20° $\sigma = 2$

Product of the Moments of Inertia: $I_AI_BI_C = 5.4423 \times 10^{-113}\ g^3cm^6$

Heat of Formation

ΔHf°(298.15 K) is calculated from ΔHf°(c) by addition of ΔHs° = 85.0 ± 1.5 kcal/mol derived by third-law analysis of the vapor-pressure equation of Hildenbrand et al. (1, 2). The equation (1) summarized five torsion-effusion runs (102 total points) and is reasonably consistent with three boiling pressures in the mmHg range measured by Novikov (3). Effusion studies (4-7) yield lower values of ΔHs°, but that of Loehman et al. (6) is consistent with the adopted value. Langmuir data (6) suggest that the sublimation coefficient is 0.3 ± 0.2. Equilibria derived from flame studies (8, 9) and mass-spectrometric effusion (10) confirm the adopted ΔHf° via independent paths (cf. below). Mass spectra (11) at 1220 K showed that the saturated vapor consists predominantly of $SrCl_2$ with considerably less than 1% of dimer.

Source	Method	Range T, K	ΔHs°(298.15 K), kcal/mol 2nd Law	ΔHs°(298.15 K), kcal/mol 3rd Law	δS[a] gibbs/mol	ΔHf°(298.15 K) kcal/mol
(1, 2) Hildenbrand (1965)	Torsion effusion[b]	1220-1425	84.0	85.00	-0.8	-113.1
(3) Novikov (1964)	Boiling Point	1620-1710	75.8±9.4	85.52±0.7	-5.8±5.6	-112.6
(4) Novikov (1970)	Total Effusion[b]	1337-1422	75.2	82.3	-5.1	
(5) Naryshkin (1968)	Effusion[b]	893-1141	75.6	78.0	-2.3	
(6) Loehman (1965)	Effusion	1195-1307	82.9±3.9	84.2±0.7	-1.0±3.1	-113.9
(6) Loehman (1965)	Langmuir[c]	968-1119	78.7±3.6	86.3±1.5	-7.4±3.5	-111.8
(7) Van Westenburg (1964)	Effusion	1175-1287	80.3±0.5	82.8±0.2	-2.0±0.4	
(8) Schofield (1971)	Flame Kp[d]	~2134-2350	-9.1±3.7[d]	- 1.6±0.8[d]	-3.3±1.6	-110.7±2
(9) Ryabova (1971)	Flame Kp[d]	1813-2209	9.0±25[d]	- 2.0±7.2[d]	5.5±12	-111.1±7
(10) Hildenbrand (1970)	Mass spec. Kp[e]	1661		3.7[e]		-112.7±2

[a] δS = ΔS°(2nd Law) - ΔS°(3rd Law). [b] Pressures obtained from an equation.

[c] Assuming a sublimation coefficient of 1.0; agreement with (1) requires α = 0.5.

[d] ΔHr° for $Sr(g) + 2\ HCl(g) = SrCl_2(g) + 2H(g)$. [e] ΔHr° for $Sr(g) + CaCl_2(g) = SrCl_2(g) + Ca(g)$.

Heat Capacity and Entropy

Vibrations ν_2 and ν_3 are the values quoted by Hildenbrand (10) and derived from IR spectra of molecules in matrix isolation (12). The bending mode was observed (13). Hastie et al. (14) failed to observe ν_2 but estimated a higher value of 60 ± 15 cm^{-1}. Agreement is better for ν_1 = 269 (10, 13) or 274 cm^{-1} (14) and for ν_3 = 300 ± 7 (15, gas), 300 (10, 13) or 307 cm^{-1} (14). We adopt a rounded value of 270 cm^{-1} for ν_1.

Bond length is from gas-phase electron diffraction (16) which also gave the bond angle 180° ± 30°. Later studies (17) of electric deflection of molecular beams revealed a permanent electric dipole moment, leading to the conclusion that $SrCl_2$ is bent. The matrix spectra (10, 12) were first interpreted to give an angle of 155° but reanalysis (13) gave the angle 112°, calculated from the three observed fundamentals. An angle of 130° ± 8° was derived by Hastie et al. (14) from the Cl-isotope splitting of ν_3. We adopt an intermediate value of 120° ± 20°. S° would change by +0.1 gibbs/mol for 112° and -1.3 gibbs/mol for 155°. The singlet ground state is taken by analogy with $BaCl_2(g)$. Principal moments of inertia are $I_A = 11.60 \times 10^{-39}$, $I_B = 62.95 \times 10^{-39}$ and $I_C = 74.55 \times 10^{-39}\ g\ cm^2$.

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Cl_2Sr

Cobalt Trichloride (CoCl$_3$)

(Ideal Gas) GFW = 165.2922

Cl$_3$Co

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°$_{298}$)/T (gibbs/mol)	H°−H°$_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-3.999	-38.669	-38.669	INFINITE
100	11.673	63.601	94.285	-3.068	-38.906	-38.310	83.726
200	15.809	73.033	81.451	-1.684	-39.068	-37.643	41.135
298	18.221	79.850	79.850	.000	-39.100	-36.934	27.074
300	18.252	79.963	79.850	.034	-39.100	-36.921	26.897
400	19.375	85.389	80.582	1.923	-39.070	-36.199	19.778
500	19.851	89.772	81.997	3.888	-39.038	-35.484	15.510
600	20.041	93.411	83.604	5.884	-39.038	-34.774	12.666
700	20.109	96.506	85.232	7.892	-39.073	-34.062	10.635
800	20.127	99.193	86.813	9.904	-39.250	-33.327	9.105
900	20.129	101.563	88.323	11.917	-39.371	-32.579	7.911
1000	20.127	103.684	89.755	13.929	-39.553	-31.817	6.954
1100	20.127	105.602	91.109	15.942	-39.803	-31.031	6.165
1200	20.132	107.354	92.391	17.955	-40.128	-30.220	5.504
1300	20.140	108.966	93.605	19.969	-40.563	-29.378	4.939
1400	20.152	110.459	94.756	21.983	-41.137	-28.496	4.448
1500	20.166	111.849	95.850	23.999	-41.472	-27.582	4.019
1600	20.181	113.151	96.891	26.016	-41.747	-26.646	3.640
1700	20.198	114.375	97.834	28.035	-41.998	-25.692	3.303
1800	20.215	115.530	98.832	30.056	-46.139	-24.658	2.994
1900	20.232	116.624	99.740	32.078	-46.453	-23.453	2.698
2000	20.249	117.662	100.611	34.102	-46.769	-22.236	2.430
2100	20.265	118.650	101.446	36.128	-47.084	-21.003	2.186
2200	20.280	119.593	102.250	38.155	-47.402	-19.753	1.962
2300	20.295	120.495	103.024	40.184	-47.719	-18.488	1.757
2400	20.309	121.359	103.770	42.214	-48.039	-17.210	1.567
2500	20.323	122.188	104.490	44.246	-48.361	-15.919	1.392
2600	20.335	122.986	105.186	46.279	-48.684	-14.615	1.229
2700	20.346	123.753	105.860	48.313	-49.010	-13.299	1.076
2800	20.356	124.494	106.512	50.348	-49.339	-11.968	.934
2900	20.366	125.208	107.144	52.384	-49.670	-10.630	.801
3000	20.374	125.899	107.758	54.421	-50.005	-9.279	.676
3100	20.382	126.567	108.354	56.459	-50.344	-7.916	.558
3200	20.389	127.214	108.934	58.498	-139.804	-5.706	.390
3300	20.395	127.842	109.497	60.537	-139.814	-1.515	.100
3400	20.400	128.450	110.046	62.577	-139.825	2.678	-.172
3500	20.404	129.042	110.580	64.617	-139.845	6.865	-.429
3600	20.408	129.617	111.101	66.657	-139.868	11.060	-.671
3700	20.411	130.176	111.609	68.698	-139.897	15.254	-.901
3800	20.413	130.720	112.105	70.739	-139.931	19.445	-1.118
3900	20.414	131.251	112.589	72.781	-139.972	23.642	-1.325
4000	20.415	131.767	113.062	74.822	-140.020	27.837	-1.521
4100	20.416	132.271	113.524	76.864	-140.073	32.032	-1.707
4200	20.416	132.763	113.976	78.905	-140.134	36.229	-1.885
4300	20.415	133.244	114.419	80.947	-140.201	40.429	-2.055
4400	20.414	133.713	114.852	82.988	-140.274	44.635	-2.217
4500	20.412	134.172	115.276	85.030	-140.355	48.834	-2.372
4600	20.410	134.621	115.692	87.071	-140.440	53.041	-2.520
4700	20.408	135.059	116.099	89.112	-140.534	57.250	-2.662
4800	20.406	135.489	116.499	91.152	-140.634	61.456	-2.798
4900	20.403	135.910	116.891	93.193	-140.742	65.671	-2.929
5000	20.400	136.322	117.275	95.233	-140.856	69.881	-3.055
5100	20.396	136.726	117.653	97.273	-140.974	74.102	-3.175
5200	20.393	137.122	118.023	99.312	-141.102	78.321	-3.292
5300	20.389	137.510	118.387	101.351	-141.236	82.538	-3.404
5400	20.385	137.891	118.745	103.390	-141.378	86.761	-3.511
5500	20.381	138.265	119.097	105.426	-141.526	90.990	-3.616
5600	20.376	138.633	119.442	107.466	-141.681	95.216	-3.716
5700	20.372	138.993	119.782	109.504	-141.844	99.444	-3.813
5800	20.367	139.347	120.116	111.541	-142.013	103.685	-3.907
5900	20.363	139.696	120.445	113.577	-142.190	107.918	-3.998
6000	20.358	140.038	120.769	115.613	-142.375	112.161	-4.085

Dec. 31, 1973

COBALT TRICHLORIDE (CoCl$_3$) (IDEAL GAS) GFW = 165.2922 Cl$_3$Co

Point Group [C_{3v}]

$S^\circ_{298.15}$ = [79.8 ± 2.0] gibbs/mol

Ground State Quantum Weight = [5]

ΔHf°_0 = -38.7 ± 2.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -39.1 ± 2.5 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[5]
[500]	[5]
[1000]	[5]
[5000]	[5]
[10000]	[5]

Vibrational Frequencies and Degeneracies

ν, cm^{-1}
[500] (1)
[250] (1)
[550] (2)
[150] (2)

Bond Distance: Co-Cl = [2.09] Å

Bond Angle: Cl-Co-Cl = [100]° σ = 3

Product of Moments of Inertia: $I_AI_BI_C$ = [7.8878 x 10^{-113}] g^{3}cm^6

Heat of Formation

Schäfer and Krehl (1) studied the reaction of chlorine with CoCl$_2$ by a transpiration method. They ascribed the enhanced volatility of CoCl$_2$(c, ℓ) in the presence of Cl$_2$ to the formation of gaseous CoCl$_3$ according to the reaction Cl$_2$(g) + 2 CoCl$_2$(g) = 2 CoCl$_3$(g). Partial pressures for the three species involved in the reaction were reported for the temperature range 918-1073 K. No consideration was given to possible dimerization of either the di- or trichloride. Subsequent measurements by Schäfer and Breil (2) have confirmed the increased volatility of CoCl$_2$(ℓ) in the presence of Cl$_2$. However, the latter study was conducted at only one temperature (1056 K). JANAF data (3) for CoCl$_2$(g) and Co$_2$Cl$_4$(g) are used to correct their pressures (1, 2) for dimerization of the dichloride. Our corrected CoCl$_2$ pressures are 5% less than those reported by Schäfer and Krehl (1) at 918 K and 11.4% less at 1073 K. We tentatively assume that dimerization of the trichloride is negligible over the temperature range investigated and treat the equilibrium pressures by the second and third law methods. Results of the analysis are: ΔHr_{298}(2nd Law) = -32.9 and ΔHr_{298} (3rd Law) = -33.36 ± 2.0 kcal/mol. The third law drift is -0.5 ± 2.9 eu. The measurements of Schäfer and Breil (2) at 1056 K give ΔHr_{298}(3rd Law) = -33.31 kcal/mol. Combining the average value for the third law heats of reaction with ΔHf°_{298}(CoCl$_2$, g) = -22.4 ± 2.0 kcal/mol (3), we obtain ΔHf°_{298}(CoCl$_3$, g) = -39.1 ± 2.5 kcal/mol. This value is adopted and corresponds to a bond dissociation energy of D°_{298}(CoCl$_2$-Cl) = 45.7 kcal/mol. A comparison of this value with that for the monochloride (D°_0(Co-Cl) = 84.4 kcal/mol) and dichloride (D°(CoCl-Cl) = 97.5 kcal/mol) clearly reveals the instability of the trichloride molecule.

Heat Capacity and Entropy

The structure of CoCl$_3$ is not known; however, it can be limited to two possibilities. The molecule has either a pyramidal structure of C_{3v} symmetry, or a planar structure of D_{3h} symmetry. By analogy with the geometries for PCl$_3$ (3), SiCl$_3$ (3), and TiF$_3$ (3, 4), we adopt the pyramidal structure. The bond length is taken equal to that for CoCl (3). The Cl-Co-Cl bond angle is estimated as 100°. The individual moments of inertia are: I_A = 60.355 x 10^{-39}, I_B = 36.151 x 10^{-39}, and I_C = 36.151 x 10^{-39} g cm^2.

The vibrational frequencies are estimated by comparison with those for PCl$_3$ (3), SiCl$_3$ (3), and TiF$_3$ (4). The ground state quantum weight is taken equal to that for Co^{+3} (5). The electronic levels are estimated from those for Fe^{+2} (5), since few levels have been observed in the spectrum of Co^{+3}. The Fe^{+2} ion is isoelectronic with Co^{+3}. The adopted upper levels and quantum weights contribute 0.65 eu at 298 K and 2.4 eu at 3000 K to the entropy of CoCl$_3$.

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3. JANAF Thermochemical Tables: CoCl$_2$(g), CoCl(g), and Co$_2$Cl$_4$(g), 12-31-73; PCl$_3$(g), 6-30-70; SiCl$_3$(g), 12-31-69; TiF$_3$(g), 6-30-68.
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Cl$_3$Co

Cobalt Dichloride, Dimeric (Co_2Cl_4) Cl_4Co_2

(Ideal Gas) GFW = 259.6784

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-7.217	-84.351	-84.351	INFINITE
100	24.099	76.985	133.619	-5.663	-84.437	-82.738	180.824
200	29.146	95.695	110.374	-2.936	-84.076	-81.184	88.714
298	30.457	107.620	107.620	.000	-83.800	-79.829	58.516
300	30.471	107.809	107.621	.056	-83.796	-79.805	58.138
400	31.014	116.659	108.824	3.134	-83.606	-78.506	42.894
500	31.309	123.614	111.111	6.251	-83.503	-77.243	33.763
600	31.515	129.341	113.686	9.393	-83.483	-75.995	27.681
700	31.684	134.212	116.279	12.553	-83.531	-74.745	23.336
800	31.831	138.453	118.791	15.729	-83.847	-73.454	20.067
900	31.959	142.210	121.189	18.919	-84.035	-72.142	17.519
1000	32.066	145.582	123.462	22.120	-84.330	-70.808	15.475
1100	32.155	148.643	125.614	25.331	-84.747	-69.437	13.796
1200	32.224	151.444	127.652	28.550	-85.304	-68.022	12.388
1300	32.278	154.025	129.583	31.776	-86.074	-66.553	11.189
1400	32.317	156.419	131.415	35.005	-87.117	-65.012	10.149
1500	32.344	158.650	133.157	38.239	-87.679	-63.414	9.239
1600	32.362	160.738	134.816	41.474	-88.120	-61.781	8.439
1700	32.373	162.700	136.399	44.711	-88.515	-60.119	7.729
1800	32.378	164.551	137.912	47.948	-96.690	-58.300	7.079
1900	32.380	166.301	139.361	51.186	-97.212	-56.149	6.459
2000	32.378	167.962	140.750	54.424	-97.740	-53.976	5.898
2100	32.375	169.542	142.084	57.662	-98.268	-51.776	5.388
2200	32.371	171.048	143.366	60.899	-98.803	-49.550	4.922
2300	32.367	172.487	144.601	64.136	-99.340	-47.297	4.494
2400	32.363	173.864	145.792	67.373	-99.881	-45.023	4.100
2500	32.360	175.185	146.942	70.609	-100.429	-42.726	3.735
2600	32.357	176.454	148.052	73.845	-100.979	-40.407	3.396
2700	32.356	177.675	149.127	77.080	-101.536	-38.068	3.081
2800	32.355	178.852	150.168	80.316	-102.098	-35.704	2.787
2900	32.355	179.987	151.177	83.551	-102.665	-33.325	2.511
3000	32.357	181.084	152.155	86.787	-103.237	-30.927	2.253
3100	32.360	182.145	153.106	90.023	-103.815	-28.506	2.010
3200	32.363	183.173	154.029	93.259	-282.635	-24.396	1.666
3300	32.368	184.169	154.928	96.496	-282.550	-16.328	1.081
3400	32.373	185.135	155.802	99.733	-282.469	-8.259	.531
3500	32.379	186.074	156.654	102.970	-282.400	-.200	.013
3600	32.386	186.986	157.483	106.209	-282.335	7.865	-.477
3700	32.394	187.873	158.293	109.448	-282.280	15.927	-.941
3800	32.402	188.737	159.083	112.687	-282.233	23.982	-1.379
3900	32.411	189.579	159.854	115.928	-282.196	32.043	-1.796
4000	32.420	190.400	160.607	119.170	-282.170	40.099	-2.191
4100	32.429	191.200	161.344	122.412	-282.152	48.154	-2.567
4200	32.439	191.982	162.064	125.655	-282.145	56.208	-2.925
4300	32.449	192.745	162.769	128.900	-282.148	64.263	-3.266
4400	32.459	193.492	163.459	132.145	-282.161	72.326	-3.592
4500	32.469	194.221	164.134	135.392	-282.186	80.376	-3.904
4600	32.479	194.935	164.796	138.639	-282.219	88.436	-4.202
4700	32.489	195.633	165.445	141.887	-282.265	96.497	-4.487
4800	32.499	196.318	166.081	145.137	-282.321	104.552	-4.760
4900	32.509	196.988	166.705	148.387	-282.391	112.617	-5.023
5000	32.518	197.645	167.317	151.638	-282.470	120.676	-5.275
5100	32.528	198.289	167.918	154.891	-282.557	128.746	-5.517
5200	32.537	198.920	168.508	158.144	-282.660	136.812	-5.750
5300	32.546	199.540	169.088	161.398	-282.774	144.876	-5.974
5400	32.555	200.149	169.657	164.653	-282.901	152.945	-6.190
5500	32.563	200.746	170.217	167.909	-283.039	161.021	-6.398
5600	32.572	201.333	170.768	171.166	-283.188	169.092	-6.599
5700	32.580	201.910	171.309	174.424	-283.352	177.164	-6.793
5800	32.587	202.476	171.841	177.682	-283.526	185.253	-6.981
5900	32.594	203.033	172.365	180.941	-283.715	193.331	-7.161
6000	32.601	203.581	172.881	184.201	-283.917	201.422	-7.337

Dec. 31, 1973

COBALT DICHLORIDE, DIMERIC (Co_2Cl_4) (IDEAL GAS) GFW = 259.6784 Cl_4Co_2

Point Group [D_{2h}]

$S°_{298.15}$ = [107.6 ± 4.0] gibbs/mol

$\Delta Hf°_0$ = -84.4 ± 7.0 kcal/mol

$\Delta Hf°_{298}$ = -83.8 ± 7.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i
0	[4]
[210]	[8]
[2804]	[8]
[10425]	[4]
[14197]	[8]
[21270]	[8]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[50] (1)	[125] (1)	323 (1)
[75] (1)	[150] (1)	[143](1)
[100] (1)	[175] (1)	289 (1)
[110] (1)	[200] (1)	432.5 (1)

Bond Distance: Co-Cl = [2.09] Å Co-Cl'(bridge) = [2.2] Å

Bond Angle: Co-Cl'(bridge)-Co = [90]° Cl'(bridge)-Co-Cl = [135]° Cl'(bridge)-Co-Cl'(bridge) = [90]° σ = 4

Product of Moments of Inertia: $I_AI_BI_C$ = [1.3492 x 10^{-111}]g^3cm^6

Heat of Formation

Mass spectrometric studies (1, 2) have indicated the presence of small amounts of dimer in the saturated vapor over $CoCl_2$(c). The existence of the dimeric species was inferred from the ion current intensities observed for $Co_2Cl_4^+$. This ion is believed to be produced by simple ionization of the dimer molecules. Schoonmaker et al. (1) have combined their mass spectral data with results of effusion vapor pressure measurements to give partial pressures for the monomer and dimer at 817 K. These results are analyzed by the third law method with JANAF free energy functions to give ΔH_{298}(dimerization) = -38.99 kcal/mol for the process 2 $CoCl_2(g) = Co_2Cl_4(g)$. This result is combined with $\Delta Hf°_{298}(CoCl_2, g)$ = -22.4 ± 2.0 kcal/mol (3) to give $\Delta Hf°_{298}(Co_2Cl_4, g)$ = -83.8 kcal/mol which we adopt. The uncertainty assigned to ΔHf is estimated to be ±7.0 kcal/mol and arises mainly from uncertainties in the values of $S°_{298}$ for dimer and ΔHf for the monomer.

Heat Capacity and Entropy

A bridge-bond structure of D_{2h} symmetry is assigned to Co_2Cl_4. A similar structure has been proposed for Be_2Cl_4(3) and other dimeric transition-metal dihalides (3-5). The Co_2Cl_2 ring system is assumed to be square and planar. The Cl-Co-Cl'(bridge) bond angle is estimated as 135°. The outer Co-Cl bond lengths are estimated from that for $CoCl_2$ (3), while the ring Co-Cl'(bridge) bond lengths are estimated to be somewhat larger. The individual moments of inertia are: $I_A = 2.3232 \times 10^{-37}$, $I_B = 2.0383 \times 10^{-37}$, and $I_C = 2.8491 \times 10^{-38}$ g cm^2.

The three observed vibrational frequencies (ν_9, ν_{11}, and ν_{12}) are taken from the matrix-infrared study of Thompson and Carlson (5). The rest of the frequencies except for ν_{10} are estimated by comparison with similar data for other dimeric molecules (3). The value for ν_{10} (143 cm^{-1}) was obtained by Thompson and Carlson (5) from a simplified normal coordinate analysis. Also, Leroi et al. (4) observed a band at 422 ± 10 cm^{-1} in the infrared spectrum of gaseous $CoCl_2$ near 1000 K. The band was assigned to an outer-bond stretching frequency of the dimer. This interpretation agrees with our adopted results. The electronic levels and quantum weights are arbitrarily taken equal to those for the monomer (3).

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$CoCl_2$(g) Table References

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Cl_4Co_2

Lead Tetrachloride ($PbCl_4$) Cl_4Pb

(Ideal Gas) GFW = 349.012

		gibbs/mol			kcal/mol		
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 5.604	- 131.600	- 131.600	INFINITE
100	17.762	67.947	111.230	- 4.328	- 132.139	- 129.023	281.980
200	22.333	81.907	93.346	- 2.288	- 132.153	- 125.878	137.553
298	24.028	91.191	91.191	.000	- 132.028	- 122.824	90.032
300	24.048	91.340	91.192	.044	- 132.025	- 122.767	89.435
400	24.775	98.371	92.145	2.490	- 131.891	- 119.701	65.402
500	25.139	103.943	93.967	4.988	- 131.773	- 116.667	50.995
600	25.345	108.546	96.024	7.513	- 131.676	- 113.655	41.399
700	25.471	112.463	98.100	10.054	- 132.760	- 110.468	34.490
800	25.555	115.870	100.113	12.606	- 132.702	- 107.288	29.310
900	25.612	118.884	102.034	15.164	- 132.637	- 104.114	25.282
1000	25.654	121.584	103.857	17.728	- 132.568	- 100.950	22.063
1100	25.685	124.031	105.581	20.295	- 132.494	- 97.792	19.429
1200	25.708	126.267	107.213	22.864	- 132.415	- 94.640	17.236
1300	25.727	128.325	108.759	25.436	- 132.333	- 91.496	15.382
1400	25.741	130.232	110.226	28.010	- 132.253	- 88.358	13.793
1500	25.753	132.009	111.619	30.584	- 132.174	- 85.224	12.417
1600	25.763	133.671	112.946	33.160	- 132.102	- 82.097	11.214
1700	25.771	135.233	114.212	35.737	- 132.032	- 78.970	10.152
1800	25.777	136.707	115.421	38.314	- 131.970	- 75.854	9.210
1900	25.783	138.100	116.578	40.892	- 131.914	- 72.736	8.367
2000	25.788	139.423	117.688	43.471	- 131.869	- 69.623	7.608
2100	25.792	140.681	118.753	46.050	- 174.278	- 64.961	6.761
2200	25.796	141.881	119.777	48.629	- 174.154	- 59.759	5.937
2300	25.799	143.028	120.763	51.209	- 174.054	- 54.559	5.184
2400	25.802	144.126	121.714	53.789	- 173.978	- 49.365	4.495
2500	25.804	145.179	122.632	56.369	- 173.930	- 44.176	3.862
2600	25.806	146.191	123.518	58.950	- 173.906	- 38.985	3.277
2700	25.808	147.165	124.376	61.530	- 173.907	- 33.797	2.736
2800	25.810	148.104	125.207	64.111	- 173.936	- 28.605	2.233
2900	25.812	149.010	126.012	66.692	- 173.987	- 23.415	1.765
3000	25.813	149.885	126.794	69.274	- 174.062	- 18.223	1.328
3100	25.814	150.731	127.552	71.855	- 174.159	- 13.027	.918
3200	25.815	151.551	128.289	74.437	- 174.277	- 7.829	.535
3300	25.817	152.345	129.006	77.018	- 174.413	- 2.623	.174
3400	25.817	153.116	129.704	79.600	- 174.566	2.588	- .166
3500	25.818	153.864	130.384	82.182	- 174.736	7.795	- .487
3600	25.819	154.592	131.046	84.763	- 174.918	13.017	- .790
3700	25.820	155.299	131.692	87.345	- 175.113	18.241	- 1.077
3800	25.821	155.988	132.323	89.927	- 175.316	23.467	- 1.350
3900	25.821	156.658	132.938	92.510	- 175.530	28.704	- 1.609
4000	25.822	157.312	133.539	95.092	- 175.752	33.940	- 1.854
4100	25.822	157.950	134.127	97.674	- 175.978	39.183	- 2.089
4200	25.823	158.572	134.701	100.256	- 176.209	44.433	- 2.312
4300	25.823	159.180	135.264	102.838	- 176.443	49.687	- 2.525
4400	25.824	159.773	135.814	105.421	- 176.679	54.958	- 2.730
4500	25.824	160.354	136.353	108.003	- 176.916	60.217	- 2.925
4600	25.825	160.921	136.881	110.586	- 177.152	65.492	- 3.112
4700	25.825	161.477	137.398	113.168	- 177.387	70.770	- 3.291
4800	25.825	162.020	137.906	115.751	- 177.622	76.052	- 3.463
4900	25.826	162.553	138.403	118.333	- 177.854	81.342	- 3.628
5000	25.826	163.075	138.891	120.916	- 178.083	86.629	- 3.787
5100	25.826	163.586	139.371	123.498	- 178.307	91.931	- 3.940
5200	25.826	164.088	139.841	126.081	- 178.529	97.235	- 4.087
5300	25.827	164.580	140.303	128.664	- 178.748	102.536	- 4.228
5400	25.827	165.062	140.757	131.246	- 178.963	107.846	- 4.365
5500	25.827	165.536	141.204	133.829	- 179.175	113.161	- 4.497
5600	25.827	166.002	141.642	136.412	- 179.381	118.475	- 4.624
5700	25.828	166.459	142.074	138.995	- 179.586	123.787	- 4.746
5800	25.828	166.908	142.498	141.577	- 179.785	129.124	- 4.866
5900	25.828	167.349	142.915	144.160	- 179.983	134.443	- 4.980
6000	25.828	167.783	143.326	146.743	- 180.178	139.776	- 5.091

June 30, 1962; Dec. 31, 1973

LEAD TETRACHLORIDE ($PbCl_4$) (IDEAL GAS) GFW = 349.012 Cl_4Pb

Ground State Quantum Weight = [1]

Point Group = T_d

$S^\circ_{298.15}$ = [91.19 ± 3.0] gibbs/mol

ΔHf°_0 = [-131.6 ± 20] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-132.0 ± 20] kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
331 (1)
90 (2)
352 (3)
103 (3)

Bond Distance: Pb-Cl = 2.43 Å   Bond Angle: Cl-Pb-Cl = [109° 28'] σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = [7.9668 x 10^{-112}] g^3cm^6

Heat of Formation

The adopted ΔHf°_0 = -131.6 ± 20 kcal/mol is derived from the dissociation energy for the process $PbCl_4(g) = Pb(g) + 4\ Cl(g)$. D°_0 = 12.70 eV is estimated from an intercomparison of the lead mono-, di-, and tetra- halides (1). The adopted D°_0 value for $PbCl_4(g)$ is greater than the D°_0 value for $PbCl_2(g)$ by a factor of 2.02. The auxiliary values ΔHf°_0(Pb, g) = 46.91 kcal/mol (1) and ΔHf°_0(Cl, g) = 28.587 kcal/mol (1) are used. $\Delta Hf^\circ_{298}(PbCl_4, g)$ = -132.0 ± 20 kcal/mol is calculated from ΔHf°_0.

Heat Capacity and Entropy

The bond distance is given by Lister and Sutton (2). The vibrational frequencies are those determined by Clark and Hunter (3) from Raman spectra of $PbCl_4$ in n-pentane solution. Clark and Hunter (3) also observed an electronic transition at 35,250 cm^{-1} which they claim is the lowest allowed electronic transition of the molecule. The present calculations assume a singlet electronic ground state.

The individual moments of inertia are: $I_A=I_B=I_C$ = 9.2703 x 10^{-38} g cm^2.

References

1. JANAF Thermochemical Tables: PbF(g), $PbF_2(g)$, $PbF_4(g)$, PbBr(g), $PbBr_2(g)$, PbI(g), and $PbI_2(g)$, 12-31-73; PbCl(g) and $PbCl_2(g)$, 6-30-73; Pb(g), 3-31-62; Cl(g), 6-30-72.
2. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941).
3. R. J. H. Clark and B. K. Hunter, J. Mol. Structure 9, 354 (1971).

Cl_4Pb

Chromium (Cr)

(Reference State) GFW = 51.996

T, °K	gibbs/mol Cp°	S°	−(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-.970	.000	.000	.000
100	2.381	1.025	9.975	-.895	.000	.000	.000
200	4.747	3.554	6.139	-.517	.000	.000	.000
298	5.601	5.645	5.645	.000	.000	.000	.000
300	5.610	5.680	5.645	.010	.000	.000	.000
400	6.030	7.353	5.870	.593	.000	.000	.000
500	6.365	8.737	6.309	1.214	.000	.000	.000
600	6.625	9.921	6.815	1.864	.000	.000	.000
700	6.830	10.958	7.334	2.536	.000	.000	.000
800	7.035	11.882	7.846	3.229	.000	.000	.000
900	7.290	12.725	8.342	3.945	.000	.000	.000
1000	7.615	13.509	8.820	4.690	.000	.000	.000
1100	8.000	14.253	9.280	5.470	.000	.000	.000
1200	8.410	14.966	9.724	6.290	.000	.000	.000
1300	8.871	15.658	10.154	7.154	.000	.000	.000
1400	9.351	16.332	10.572	8.065	.000	.000	.000
1500	9.847	16.994	10.978	9.025	.000	.000	.000
1600	10.356	17.646	11.374	10.035	.000	.000	.000
1700	10.875	18.289	11.762	11.096	.000	.000	.000
1800	11.402	18.926	12.142	12.210	.000	.000	.000
1900	11.937	19.557	12.516	13.377	.000	.000	.000
2000	12.477	20.183	12.884	14.598	.000	.000	.000
2100	13.023	20.805	13.246	15.873	.000	.000	.000
2200	9.400	23.595	13.675	21.824	.000	.000	.000
2300	9.400	24.013	14.115	22.764	.000	.000	.000
2400	9.400	24.413	14.536	23.704	.000	.000	.000
2500	9.400	24.797	14.939	24.644	.000	.000	.000
2600	9.400	25.165	15.325	25.584	.000	.000	.000
2700	9.400	25.520	15.696	26.524	.000	.000	.000
2800	9.400	25.862	16.053	27.464	.000	.000	.000
2900	9.400	26.192	16.397	28.404	.000	.000	.000
3000	7.356	53.939	17.142	110.393	.000	.000	.000
3100	7.478	54.183	18.333	111.134	.000	.000	.000
3200	7.595	54.422	19.457	111.888	.000	.000	.000
3300	7.708	54.657	20.520	112.653	.000	.000	.000
3400	7.819	54.889	21.527	113.430	.000	.000	.000
3500	7.928	55.117	22.484	114.217	.000	.000	.000
3600	8.036	55.342	23.393	115.015	.000	.000	.000
3700	8.146	55.564	24.260	115.824	.000	.000	.000
3800	8.257	55.782	25.087	116.644	.000	.000	.000
3900	8.371	55.998	25.876	117.476	.000	.000	.000
4000	8.489	56.212	26.632	118.319	.000	.000	.000
4100	8.611	56.423	27.356	119.174	.000	.000	.000
4200	8.738	56.632	28.051	120.041	.000	.000	.000
4300	8.870	56.839	28.718	120.921	.000	.000	.000
4400	9.008	57.045	29.359	121.815	.000	.000	.000
4500	9.151	57.249	29.977	122.723	.000	.000	.000
4600	9.300	57.451	30.572	123.646	.000	.000	.000
4700	9.454	57.653	31.146	124.583	.000	.000	.000
4800	9.613	57.854	31.700	125.537	.000	.000	.000
4900	9.777	58.054	32.236	126.506	.000	.000	.000
5000	9.945	58.253	32.754	127.492	.000	.000	.000
5100	10.116	58.451	33.256	128.495	.000	.000	.000
5200	10.290	58.650	33.743	129.515	.000	.000	.000
5300	10.466	58.847	34.214	130.553	.000	.000	.000
5400	10.644	59.045	34.672	131.609	.000	.000	.000
5500	10.822	59.241	35.117	132.682	.000	.000	.000
5600	11.000	59.438	35.550	133.773	.000	.000	.000
5700	11.178	59.634	35.971	134.882	.000	.000	.000
5800	11.353	59.830	36.380	136.009	.000	.000	.000
5900	11.526	60.026	36.780	137.153	.000	.000	.000
6000	11.695	60.221	37.169	138.314	.000	.000	.000

June 30, 1973

CHROMIUM (Cr) (REFERENCE STATE) GFW = 51.996 Cr

0 to 2130 K Crystal

2130 to 2955 K Liquid

2955 to 6000 K Ideal Monatomic Gas

See crystal, liquid, and monatomic gas tables for details.

Cr

Chromium (Cr)

(Crystal) GFW = 51.996

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-.970	.000	.000	.000
100	2.381	1.025	9.975	-.895	.000	.000	.000
200	4.747	3.554	6.139	-.517	.000	.000	.000
298	5.601	5.645	5.645	.000	.000	.000	.000
300	5.610	5.680	5.645	.010	.000	.000	.000
400	6.030	7.353	5.870	.593	.000	.000	.000
500	6.365	8.737	6.309	1.214	.000	.000	.000
600	6.625	9.921	6.815	1.864	.000	.000	.000
700	6.830	10.958	7.334	2.536	.000	.000	.000
800	7.035	11.882	7.846	3.229	.000	.000	.000
900	7.290	12.725	8.342	3.945	.000	.000	.000
1000	7.615	13.509	8.820	4.690	.000	.000	.000
1100	8.000	14.253	9.280	5.470	.000	.000	.000
1200	8.410	14.966	9.724	6.290	.000	.000	.000
1300	8.871	15.658	10.154	7.154	.000	.000	.000
1400	9.351	16.332	10.572	8.065	.000	.000	.000
1500	9.847	16.994	10.978	9.025	.000	.000	.000
1600	10.356	17.646	11.374	10.035	.000	.000	.000
1700	10.875	18.289	11.762	11.096	.000	.000	.000
1800	11.402	18.926	12.142	12.210	.000	.000	.000
1900	11.937	19.557	12.516	13.377	.000	.000	.000
2000	12.477	20.183	12.884	14.598	.000	.000	.000
2100	13.023	20.805	13.246	15.873	.000	.000	.000
2200	13.572	21.423	13.604	17.202	-4.622	.157	-.016
2300	14.125	22.039	13.957	18.587	-4.177	.364	-.035
2400	14.681	22.652	14.307	20.028	-3.676	.551	-.050
2500	15.240	23.262	14.653	21.524	-3.120	.716	-.063
2600	15.801	23.871	14.996	23.076	-2.508	.857	-.072
2700	16.364	24.478	15.336	24.684	-1.840	.974	-.079
2800	16.929	25.083	15.673	26.348	-1.116	1.065	-.083

June 30, 1973

CHROMIUM (Cr) (CRYSTAL) GFW = 51.996 Cr

$S^\circ_{298.15}$ = 5.645 ± 0.05 gibbs/mol
Tt = 311.5 K
Tm = 2130 ± 20 K

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
ΔHt° = 0.0002 kcal/mol
ΔHm° = [4.9 ± 1.0] kcal/mol
ΔHs° = 95.0 ± 1.0 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for $T \leq 10$ K are chosen to be the same as those adopted by Hultgren et al. (1). A graphical integration of these Cp° data yields S°_{10} = 0.005 gibbs/mol and $H^\circ_{10}-H^\circ_0$ = 0.0252 cal/mol. These data also match well with the Cp° studies of Clusius and Franzosini (2). The adopted Cp° values are based on the following studies.

Source	No. of Points	Method	Range, K
Clusius and Franzosini (2)	76	Cp°	14.10-274.43
Anderson (3)	23	Cp°	56.1 -291.1
Kalishevich et al. (4)	Smooth	Cp°	60-300
Beaumont et al. (5)	Graph	Cp°	268-324
Armstrong and Grayson-Smith (6)	Smooth	Cp°	273-1073
Hultgren and Land (7)	Smooth	drop	400-1500
Conway and Hein (8)	48	drop	1267.2108
Lucks and Deem (9)	17	drop	303-1884
Kohlhaas et al. (10)	Smooth	Cp°	320-1800
Jaeger and Rosenbohm (11)	26	drop	673-1339

The adopted Cp° values are obtained primarily by graphical techniques to insure smoothness of the curve and a reasonable representation of the sometimes diverse results. A ΔCp° = 0 is also adopted across Tt. Below 200 K, there is excellent agreement between three independent studies (2, 3, 4). Above 200 K these three studies drift apart by at most 0.06 gibbs/mol. Above 298 K, there are considerable differences in the various sets of data, differences of the order of 0.2 gibbs/mol being typical. In terms of enthalpy, the data of Jaeger and Rosenbohm (11) deviates from the adopted values by +150 to +350 cal/mol; the data of Lucks and Deem (9) by 0 to -450 cal/mol; the data of Hultgren and Land (7) by -13 to +60 cal/mol; and the data of Conway and Hein (8) by -190 to +250 cal/mol. Surprisingly the enthalpy study by Kirillin et al. (12) yields enthalpies which are crudely 2 kcal/mol less than the adopted values at 2000 K.

Melting Data

See Cr(ℓ) table for details.

Transition Data

Beaumont et al. (5) measured the heat capacity of 99.998% pure Cr in the region 268-324 K. The detailed Cp° measurements gave evidence of a lambda-type anomaly, the maximum occurring at 311.5 K. Beaumont et al. (5) estimated the heat associated with this transition to be 1.4 cal/mol. Garnier and Salamon (13) used an extension of the ac calorimetric method to determine latent heat and heat capacity simultaneously. They concluded that annealing the Cr sample decreases the transition temperature and sharpens the peak. They also concluded that the transition was first order with a latent heat of 0.19 ± 0.04 cal/mol at a transition temperature of 311.5 K. Garnier and Salamon (13) calculated a latent heat of 0.23 ± 0.05 cal/mol and 0.25 ± 0.08 cal/mol from expansivity data and neutron-diffraction data, respectively. Sze and Meaden (14) observed a large step in specific heat measurements (50%) and estimated a latent heat of 0.47 cal/mol.

We adopt Tt = 311.5 K and ΔHt° = 0.0002 kcal/mol based on the work by Garnier and Salamon (13). In addition we adopt ΔCp° = 0 across the transition. The nature of the transition is not understood at this time.

Sublimation Data

See Cr(g) table for details.

References

1. R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Cr table, October, 1966.
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Cr

Chromium (Cr)

(Liquid) GFW = 51.996

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.601	8.660	8.659	.000	6.239	5.340	-3.915
300	5.610	8.694	8.660	.010	6.239	5.335	-3.887
400	6.030	10.367	8.885	.593	6.239	5.033	-2.750
500	6.365	11.750	9.323	1.213	6.239	4.732	-2.068
600	6.626	12.935	9.829	1.863	6.239	4.430	-1.614
700	6.830	13.971	10.348	2.536	6.239	4.130	-1.289
800	7.035	14.896	10.860	3.229	6.239	3.828	-1.046
900	7.290	15.739	11.356	3.945	6.239	3.526	-.856
1000	7.615	16.523	11.834	4.689	6.239	3.225	-.705
1100	8.000	17.267	12.294	5.470	6.239	2.924	-.581
1200	8.410	17.980	12.738	6.290	6.239	2.623	-.478
1300	8.871	18.671	13.168	7.154	6.239	2.321	-.390
1400	9.400	19.346	13.586	8.065	6.239	2.020	-.315
1500	9.400	19.995	13.992	9.005	6.219	1.718	-.250
1600	9.400	20.602	14.386	9.945	6.149	1.420	-.194
1700	9.400	21.171	14.768	10.885	6.028	1.129	-.145
1800	9.400	21.709	15.139	11.825	5.854	.845	-.103
1900	9.400	22.217	15.498	12.765	5.627	.573	-.066
2000	9.400	22.699	15.847	13.705	5.346	.313	-.034
2100	9.400	23.158	16.184	14.645	5.011	.070	-.007
2200	9.400	23.595	16.511	15.585	.000	.000	.000
2300	9.400	24.013	16.828	16.525	.000	.000	.000
2400	9.400	24.413	17.136	17.465	.000	.000	.000
2500	9.400	24.797	17.435	18.405	.000	.000	.000
2600	9.400	25.165	17.725	19.345	.000	.000	.000
2700	9.400	25.520	18.007	20.285	.000	.000	.000
2800	9.400	25.862	18.282	21.225	.000	.000	.000
2900	9.400	26.192	18.549	22.165	.000	.000	.000
3000	9.400	26.510	18.809	23.105	-81.049	1.238	-.090
3100	9.400	26.819	19.062	24.045	-80.850	3.978	-.280
3200	9.400	27.117	19.309	24.985	-80.664	6.711	-.458
3300	9.400	27.406	19.550	25.925	-80.489	9.439	-.625
3400	9.400	27.687	19.785	26.865	-80.326	12.161	-.782
3500	9.400	27.959	20.015	27.805	-80.173	14.879	-.929

June 30, 1973

CHROMIUM (Cr) (LIQUID) GFW = 51.996 Cr

$S°_{298.15}$ = [8.660] gibbs/mol

Tm = 2130 ± 20 K

Tb = 2955 ± 20 K

$ΔHf°_{298.15}$ = [6.239] kcal/mol

ΔHm° = [4.9 ± 1.0] kcal/mol

ΔHv° = 81.142 kcal/mol

Heat of Formation

The heat of formation of Cr(ℓ) at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H°_{2130}-H°_{298}$ for Cr(c) and Cr(ℓ).

Heat Capacity and Entropy

The heat capacity for Cr(ℓ) is estimated as 9.4 gibbs/mol by analogy with other monatomic metals. The same value was adopted by Hultgren et al. (1). A glass transition is assumed at 1400 K. Below 1400 K, the Cp° values are those of the crystal. The entropy is calculated in a manner analogous to that used for the heat of formation.

Melting Data

The value for the heat of melting is adopted as ΔHm° = 4.9 ± 1.0 kcal/mol. This value is calculated from ΔSm° = 2.3 eu. This estimated entropy of melting is consistent with the recently accepted ΔSm° values for V (2, 2.49 eu), Nb (2, 2.33 eu), and Ta (2, 2.68 eu). This is in contrast to a value of ΔSm° = 1.9 eu used by Hultgren et al. (1).

The melting temperature is adopted as Tm = 2130 K as was chosen by Hultgren et al. (1). Values reported in the literature are:

Source	Year	T, K
Carlile, Christian, and Hume-Rothery (3)	1949	2133
Greenaway, Johnstone, and McQuillan (4)	1951	2118±10
Bloom, Putman, and Grant (5)	1952	2176±10
Haworth and Hume-Rothery (6)	1959	2122

Vaporization Data

The value for Tb is calculated as the temperature for which the free energy for the reaction Cr(ℓ) = Cr(g) approaches zero. The difference in the heat of formation of Cr(ℓ) and Cr(g) at Tb is ΔHv°.

References

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2. JANAF Thermochemical Tables: V(c), 6-30-73; Nb(c) and Ta(c), 12-31-72.
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Chromium (Cr)

(Ideal Gas) GFW = 51.996

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.481	94.489	94.489	INFINITE
100	4.968	36.207	46.051	- .984	94.911	91.392	- 199.738
200	4.968	39.651	42.089	- .488	95.029	87.810	- 95.954
298	4.968	41.635	41.634	.000	95.000	84.270	- 61.771
300	4.968	41.665	41.635	.009	94.999	84.204	- 61.342
400	4.968	43.094	41.829	.506	94.913	80.617	- 44.047
500	4.968	44.203	42.197	1.003	94.789	77.056	- 33.681
600	4.968	45.109	42.609	1.500	94.636	73.523	- 26.781
700	4.968	45.875	43.023	1.996	94.460	70.018	- 21.861
800	4.969	46.538	43.421	2.493	94.264	66.540	- 18.178
900	4.972	47.123	43.801	2.990	94.045	63.087	- 15.320
1000	4.980	47.648	44.160	3.488	93.798	59.659	- 13.039
1100	4.995	48.123	44.499	3.986	93.516	56.260	- 11.178
1200	5.023	48.559	44.819	4.487	93.197	52.886	- 9.632
1300	5.065	48.962	45.123	4.991	92.837	49.541	- 8.329
1400	5.124	49.340	45.410	5.501	92.436	46.226	- 7.216
1500	5.203	49.696	45.684	6.017	91.992	42.940	- 6.256
1600	5.299	50.034	45.946	6.542	91.507	39.686	- 5.421
1700	5.414	50.359	46.196	7.077	90.981	36.463	- 4.688
1800	5.544	50.672	46.436	7.625	90.415	33.272	- 4.040
1900	5.688	50.976	46.667	8.187	89.810	30.114	- 3.464
2000	5.841	51.271	46.890	8.763	89.165	26.988	- 2.949
2100	6.001	51.560	47.105	9.355	88.482	23.896	- 2.487
2200	6.165	51.843	47.314	9.963	83.139	20.994	- 2.086
2300	6.329	52.121	47.517	10.588	82.824	18.176	- 1.727
2400	6.492	52.394	47.715	11.229	82.525	15.372	- 1.400
2500	6.651	52.662	47.907	11.886	82.242	12.579	- 1.100
2600	6.805	52.926	48.095	12.559	81.975	9.798	- .824
2700	6.953	53.185	48.279	13.247	81.723	7.027	- .569
2800	7.094	53.441	48.459	13.950	81.486	4.265	- .333
2900	7.228	53.692	48.635	14.666	81.262	1.511	- .114
3000	7.356	53.939	48.808	15.395	.000	.000	.000
3100	7.478	54.183	48.977	16.137	.000	.000	.000
3200	7.595	54.422	49.143	16.891	.000	.000	.000
3300	7.708	54.657	49.307	17.656	.000	.000	.000
3400	7.819	54.889	49.468	18.432	.000	.000	.000
3500	7.928	55.117	49.626	19.220	.000	.000	.000
3600	8.036	55.342	49.782	20.018	.000	.000	.000
3700	8.146	55.564	49.935	20.827	.000	.000	.000
3800	8.257	55.782	50.086	21.647	.000	.000	.000
3900	8.371	55.998	50.235	22.478	.000	.000	.000
4000	8.489	56.212	50.381	23.321	.000	.000	.000
4100	8.611	56.423	50.526	24.176	.000	.000	.000
4200	8.738	56.632	50.669	25.044	.000	.000	.000
4300	8.870	56.839	50.810	25.924	.000	.000	.000
4400	9.008	57.045	50.950	26.818	.000	.000	.000
4500	9.151	57.249	51.087	27.726	.000	.000	.000
4600	9.300	57.451	51.223	28.648	.000	.000	.000
4700	9.454	57.653	51.358	29.586	.000	.000	.000
4800	9.613	57.854	51.491	30.539	.000	.000	.000
4900	9.777	58.054	51.623	31.509	.000	.000	.000
5000	9.945	58.253	51.754	32.495	.000	.000	.000
5100	10.116	58.451	51.883	33.498	.000	.000	.000
5200	10.290	58.650	52.011	34.518	.000	.000	.000
5300	10.466	58.847	52.139	35.556	.000	.000	.000
5400	10.644	59.045	52.265	36.611	.000	.000	.000
5500	10.822	59.241	52.390	37.685	.000	.000	.000
5600	11.000	59.438	52.514	38.776	.000	.000	.000
5700	11.178	59.634	52.637	39.885	.000	.000	.000
5800	11.353	59.830	52.759	41.011	.000	.000	.000
5900	11.526	60.026	52.881	42.155	.000	.000	.000
6000	11.695	60.221	53.002	43.316	.000	.000	.000

June 30, 1973

CHROMIUM (Cr) (IDEAL GAS) GFW = 51.996 Cr

Ground State Configuration $^7S_3$

$S^\circ_{298.15}$ = 41.63 ± 0.1 gibbs/mol

ΔHf°_0 = 94.5 ± 1.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 95.0 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	7	21847.88	5	24299.89	5	25359.62	9
7593.16	5	21856.94	3	24303.94	3	25548.64	11
7750.78	1	23163.27	1	24282.34	9	25771.40	13
7810.82	3	23512.00	3	24833.86	7	27891.38	137
7927.47	5	24093.16	5	24897.55	9	32251.66	238
8095.21	7	23305.01	5	25083.61	11	36788.34	186
8307.57	9	23386.35	7	24940.61	5	42721.05	366
20517.40	5	23498.84	9	25106.34	7	45623.05	300
20520.92	7	23933.90	9	25177.39	9	47284.76	246
20523.69	9	24056.11	11	24971.21	1	48084.41	276
20523.94	11	24200.23	13	25010.64	3	49658.34	194
20519.60	13	24277.06	1	25089.20	5	51822.23	187
21840.84	7	24286.54	3	25206.02	7	53551.61	195
						54444.45	115

Heat of Formation

The many vapor pressure studies are treated by a second and third law analysis and are tabulated below. In all cases the reaction of interest is Cr(c) → Cr(g), so that ΔHf°_{298}(Cr, g) by definition is ΔHr°_{298}.

Source	No. of Points	Range, K	Method	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu
Speiser, Johnston, and Blackburn (1)	15*	1283-1562	Langmuir	94.05±0.84	94.82	0.54±0.60
Gulbranson and Andrew (2)	9	1162-1282	Knudsen	98.51±2.16	95.28	-2.64±1.77
Burlakov (3)	10 10**	1292-1509 1187-1550	Langmuir	97.60±1.60 95.15±1.00	92.32 91.82	-3.71±1.12 -2.47±0.74
McCabe et al. (4)	9	1381-1505	Knudsen	101.14±2.87	94.90	-4.29±1.97
Piloyan et al. (5)	Equation	1502-1576	Knudsen	88.08	90.06	1.28
Nesmeyanov and Dyk Man (6)	15	1317-1558	Knudsen	93.14±5.70	93.99	0.59±3.95
Kubaschewski and Heymer (7)	Equation	1441-1672	Knudsen	92.50	94.79	1.48
Gulbranson and Andrew (8)	9	1273-1373	Knudsen	97.54±2.93	95.97	-1.19±2.23
Aldred and Myles (9)	Equation	1376-1592	Torsion-effusion	91.79	93.85	1.40
Dickson et al. (10)	15**	1559-1805	Knudsen	92.78±3.08	95.50	1.62±1.84

* Two points neglected due to failure of a statistical test.

** One point neglected due to failure of a statistical test.

Early studies by Greenwood (11) and Baur and Brunner (12) are not considered as their work leads to ΔHf°_{298} which are 10-15 kcal/mol too low when compared to the results listed above.

We adopt ΔHf°_{298} = 95.0 ± 1.0 kcal/mol for Cr(g). This value is representative of the more recent third law values tabulated above (7, 8, 9, 10).

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore (13). Above the level ε_i = 25771.40 cm^{-1}, the values of ε_i and g_i listed are average values calculated from those given by Moore (13). There are predicted levels which have not been observed and/or classified. It is anticipated that these levels will not significantly alter the entropy below 3000 K. The heat capacity and entropy values are very similar to those adopted by Hultgren et al. (14), the ST° values being within 0.001 gibbs/mol up to 3000 K.

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Cr

Chromium Mononitride (CrN) CrN

(Crystal) GFW = 66.0027

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.942	-27.836	-27.836	INFINITE
100	2.337	.920	18.657	-1.774	-28.189	-26.270	57.413
200	6.961	3.957	10.504	-1.309	-28.451	-24.232	26.480
298	12.590	9.013	9.013	.000	-28.000	-22.181	16.259
300	12.283	9.090	9.013	.023	-27.994	-22.145	16.132
400	11.730	12.376	9.464	1.165	-27.783	-20.229	11.053
500	11.890	15.010	10.317	2.346	-27.575	-18.365	8.028
600	12.050	17.192	11.288	3.543	-27.384	-16.541	6.025
700	12.210	19.052	12.263	4.756	-27.207	-14.748	4.605
800	12.360	20.702	13.222	5.984	-27.043	-12.960	3.546
900	12.520	22.167	14.136	7.228	-26.894	-11.231	2.727
1000	12.680	23.495	15.007	8.488	-26.766	-9.498	2.076
1100	12.840	24.711	15.834	9.764	-26.664	-7.776	1.545
1200	13.000	25.835	16.621	11.055	-26.593	-6.062	1.104
1300	13.150	26.881	17.371	12.364	-26.555	-4.353	.732
1400	13.310	27.862	18.095	13.687	-26.553	-2.646	.413
1500	13.475	28.786	18.768	15.026	-26.589	-.937	.137
1600	13.630	29.660	19.422	16.381	-26.661	.775	-.106
1700	13.790	30.491	20.049	17.752	-26.773	2.494	-.321
1800	13.950	31.284	20.651	19.139	-26.925	4.219	-.512
1900	14.120	32.043	21.231	20.542	-27.115	5.955	-.685
2000	14.300	32.772	21.799	21.964	-27.343	7.701	-.842
2100	14.430	33.473	22.330	23.400	-27.613	9.459	-.984
2200	14.590	34.147	22.851	24.850	-32.547	11.388	-1.131
2300	14.750	34.799	23.357	26.317	-32.455	13.383	-1.272
2400	14.930	35.431	23.847	27.801	-32.346	15.374	-1.400
2500	15.075	36.043	24.322	29.302	-32.223	17.360	-1.518

Dec. 31, 1973

CHROMIUM MONONITRIDE (CrN) (CRYSTAL) GFW = 66.0027 CrN

$S^\circ_{298.15}$ = 9.0 ± 0.5 gibbs/mol
Td = 1555 K

ΔHf°_0 = −27.8 ± 2.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −28.0 ± 2.0 kcal/mol
ΔHd° = 26.7 kcal/mol

Heat of Formation

Second and third law analyses of equilibrium nitrogen pressures for the reaction $Cr_2N(c) + 0.5\ N_2(g) = 2\ CrN(c)$ cited in a recent review (1) of the thermodynamic properties of the Cr-N system are made using revised thermal functions for Cr_2N (2) and CrN (see below). In calculating equilibrium constants for this reaction, the activities of Cr_2N and CrN are assumed to be unity at each temperature. Also, we have not taken into account in our analysis any variations in the compositions of the two nitrides (see Phase Data Section). Results of our analysis are tabulated below.

Investigator	No. of Points	Temp. Range, K	−ΔHr°, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(CrN, c)[a] kcal/mol
Valensi (3)	8	1083-1288	25.9	24.88±0.37	0.8±1.0	-27.4±1.7
Sano (4)	6	1104-1223	28.5	26.58±0.16	1.7±0.3	-28.3±1.1
Smith (5)	10[b]	1178-1351	13.0	25.0 ±1.2	-9.5	-27.5±1.6
Mills (6)	Equation	1173-1323	25.1	25.26±0.02	-0.2	-27.6±1.0

[a] Third Law values; auxiliary data used $\Delta Hf^\circ_{298}(Cr_2N, c)$ = −30.0 ± 3.0 kcal/mol (2).

[b] Data taken from reference (1); one point rejected due to failure of a statistical test.

The equilibrium pressures of Sano (4) are inconsistent with those of the other investigations, and no weight is given to these results. Reasons for these discrepancies have been presented by DeLuca and Leitnaker (1). Also, we note that the drifts are both positive and negative which provides support for our revised thermal functions for the two nitrides.

One calorimetric value for ΔHf° is available. Neumann et al. (7) measured ΔHf° directly by combination of the elements in a bomb calorimeter. Two samples of chromium (99.2-99.7% purity) were heated to temperatures near 1200 K in 25 atmospheres of nitrogen. Under these conditions (8), it is unlikely that significant amounts of subnitride (Cr_2N) were formed. Three series of experiments gave ΔHf° values in the range −(29.0-31.2) kcal/mol. Neumann et al. (7) recommended the value ΔHf°_{298}(CrN, c) = −29.5 ± 0.5 kcal/mol, since the more negative results were obtained under conditions (impure nitrogen) where some oxide was formed.

We adopt ΔHf° value of −28.0 ± 2.0 kcal/mol which is based mainly on the results from two equilibrium studies (3, 6) and to a lesser extent on the value determined by bomb calorimetry. Our adopted value agrees with that (−28.4 ± 1.5) selected by DeLuca and Leitnaker (1) but is 1.8 kcal/mol less negative than the NBS (9) value (−29.8).

Heat Capacity and Entropy

Only one low temperature heat capacity study (10) has been reported for CrN. These measurements covered the temperature range 73-315 K; unfortunately, the results are presented only in graphical form. Cp° values taken from the graph at 25° temperature intervals are used to obtain a value for S°_{298} by integration. This method leads to S°_{298} = 9.0 gibbs/mol with S°_{73} = 0.39 gibbs/mol. The latter value is obtained from the Debye function D(530/T).). The uncertainty in our value for S°_{298} is believed to be no greater than ±0.5 gibbs/mol. Previously published estimates of S°_{298} are 8.56 (1) and 7.85 (11). The low temperature data set (10) contains a lambda peak at 281.7 K with Cp° near the maximum equal to 75.1 gibbs/mol. Other transition temperatures have been reported as 286 K (12) and 287 K (13). The anomaly arises from an antiferromagnetic-paramagnetic transformation (12, 13) which is accompanied by an orthorhombic to cubic structural change (14).

Satoh (15) has measured the heat contents of three chromium nitride samples at three temperatures each (372.6, 598.8, and 784.2 K) in an ice calorimeter. DeLuca and Leitnaker (1) have reevaluated his heat contents and presented Cp° data for CrN in the temperature range 298-1400 K. Their values above 400 K are adopted and joined smoothly with the low temperature Cp° data (10) near 350 K. Cp° data above 1400 K are obtained by graphical extrapolation.

Phase Data

The homogeneity range of the CrN phase is not known; however, results of two recent studies (6, 12) indicate that it is probably much smaller than that for Cr_2N (2). Browne et al. (12) prepared samples of $Cr_{1.0}N_x$ with x ranging from 0.980 to 0.997 by equilibrating metallic chromium at temperatures from 1123 to 1321 K in one atmosphere of nitrogen. Mills (6), using a thermogravimetric technique, studied the temperature dependence of the lower limiting composition. At 1173 K in one atmosphere of nitrogen he found a limiting composition of $Cr_{1.0}N_{0.997}$, and the variation of composition with temperature was small. X-ray diffraction patterns (16, 17) for CrN have been interpreted in terms of a cubic structure (NaCl type). Other information on the chromium-chromium nitride system has been reviewed by Storms (8).

Decomposition Data

No information is available on the melting point of CrN. Upon heating we assume that the compound decomposes to its elements rather than melting. Td is the temperature at which ΔGr° for the process $CrN(c) = Cr(c) + 0.5\ N_2(g)$ approaches zero. ΔHd° is the negative of the heat of formation at Td.

References

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CrN

Chromium Mononitride (CrN) CrN

(Ideal Gas) GFW = 66.0027

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.398	120.608	120.608	INFINITE
100	6.957	47.378	61.406	-1.403	120.882	118.155	-258.227
200	7.040	52.213	55.737	-.705	120.854	115.421	-126.126
298	7.350	55.076	55.076	.000	120.700	112.785	-82.674
300	7.357	55.122	55.076	.014	120.697	112.736	-82.128
400	7.726	57.290	55.370	.768	120.520	110.109	-60.161
500	8.027	59.048	55.935	1.556	120.336	107.527	-47.000
600	8.250	60.532	56.581	2.371	120.144	104.983	-38.240
700	8.412	61.817	57.239	3.204	119.942	102.473	-31.993
800	8.532	62.948	57.853	4.052	119.725	99.991	-27.316
900	8.622	63.958	58.503	4.910	119.487	97.539	-23.686
1000	8.692	64.871	59.095	5.776	119.221	95.113	-20.787
1100	8.747	65.702	59.658	6.648	118.919	92.717	-18.421
1200	8.792	66.465	60.194	7.525	118.576	90.351	-16.455
1300	8.829	67.170	60.704	8.406	118.187	88.014	-14.796
1400	8.859	67.826	61.190	9.290	117.750	85.709	-13.380
1500	8.886	68.438	61.653	10.178	117.263	83.436	-12.157
1600	8.909	69.012	62.095	11.067	116.725	81.199	-11.091
1700	8.930	69.553	62.518	11.959	116.134	78.997	-10.156
1800	8.950	70.064	62.923	12.853	115.490	76.830	-9.328
1900	8.968	70.548	63.312	13.749	114.792	74.702	-8.593
2000	8.987	71.009	63.685	14.647	114.040	72.610	-7.934
2100	9.005	71.448	64.044	15.547	113.234	70.558	-7.343
2200	9.025	71.867	64.390	16.448	107.751	68.703	-6.825
2300	9.045	72.269	64.724	17.352	107.260	66.938	-6.361
2400	9.067	72.654	65.047	18.257	106.810	65.194	-5.937
2500	9.091	73.025	65.358	19.165	106.341	63.470	-5.549
2600	9.118	73.382	65.660	20.076	105.873	61.764	-5.192
2700	9.146	73.726	65.953	20.989	105.406	60.077	-4.863
2800	9.178	74.060	66.236	21.905	104.942	58.406	-4.559
2900	9.212	74.382	66.512	22.824	104.480	56.753	-4.277
3000	9.248	74.695	66.779	23.747	22.972	56.352	-4.105
3100	9.288	74.999	67.039	24.674	22.715	57.469	-4.052
3200	9.330	75.294	67.293	25.605	22.448	58.594	-4.002
3300	9.375	75.582	67.540	26.540	22.173	59.729	-3.956
3400	9.422	75.863	67.780	27.480	21.891	60.871	-3.913
3500	9.471	76.137	68.015	28.425	21.602	62.021	-3.873
3600	9.523	76.404	68.245	29.374	21.307	63.180	-3.836
3700	9.577	76.666	68.469	30.329	21.006	64.348	-3.801
3800	9.632	76.922	68.688	31.290	20.698	65.523	-3.768
3900	9.689	77.173	68.902	32.256	20.385	66.707	-3.738
4000	9.748	77.419	69.112	33.228	20.064	67.898	-3.710
4100	9.807	77.660	69.317	34.206	19.736	69.098	-3.683
4200	9.867	77.897	69.519	35.189	19.404	70.306	-3.658
4300	9.928	78.130	69.717	36.179	19.064	71.523	-3.635
4400	9.990	78.359	69.910	37.175	18.715	72.745	-3.613
4500	10.051	78.584	70.101	38.177	18.358	73.978	-3.593
4600	10.112	78.806	70.287	39.185	17.991	75.219	-3.574
4700	10.173	79.024	70.471	40.199	17.616	76.467	-3.556
4800	10.234	79.239	70.651	41.220	17.230	77.723	-3.539
4900	10.294	79.451	70.829	42.246	16.834	78.986	-3.523
5000	10.353	79.659	71.003	43.279	16.427	80.260	-3.508
5100	10.411	79.865	71.175	44.317	16.008	81.539	-3.494
5200	10.468	80.067	71.344	45.361	15.576	82.830	-3.481
5300	10.523	80.267	71.511	46.410	15.135	84.127	-3.469
5400	10.578	80.465	71.675	47.465	14.679	85.432	-3.458
5500	10.630	80.659	71.836	48.526	14.210	86.749	-3.447
5600	10.682	80.851	71.996	49.591	13.729	88.071	-3.437
5700	10.731	81.041	72.153	50.662	13.234	89.404	-3.428
5800	10.779	81.228	72.307	51.738	12.726	90.744	-3.419
5900	10.825	81.412	72.460	52.818	12.204	92.092	-3.411
6000	10.870	81.595	72.611	53.903	11.670	93.451	-3.404

Dec. 31, 1973

CHROMIUM MONONITRIDE (CrN) (IDEAL GAS) GFW = 66.0027 CrN

Ground State Configuration [$^4\Sigma$]

$S^\circ_{298.15}$ = [55.1 ± 2.0] gibbs/mol

ΔHf°_0 = 120.6 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 120.7 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i
0	[4]
[15000]	[8]
[20000]	[4]

ω_e = [1000] cm^{-1} $\omega_e x_e$ = [5.0] cm^{-1} σ = 1

B_e = [0.56115] cm^{-1} α_e = [0.00375] cm^{-1} r_e = [1.65] Å

Heat of Formation

Srivastava and Farber (1) have observed mass spectrometrically CrN(g) as one of the vapor species in equilibrium with the Cr-V-N system. A substitution reaction between VN and Cr was employed in the formation of gaseous mononitride in the temperature range 1900 to 2063 K. Ion intensities for the equilibrium species CrN, VN, Cr, V, and N_2 were measured and converted to partial pressures by means of an intensity-pressure relationship for Au(g). Results of a second and third law analysis of their pressure data (1) are given below.

Reaction	No. of Points	Temp. Range, K	ΔHr_{298}, kcal/mol		Drift eu	ΔHf°_{298}(CrN, g)^a, kcal/mol	
			2nd Law	3rd Law		2nd Law	3rd Law
A	7	1903-2063	-35.6	-27.18±0.75	4.3±2.3	130.6	122.2
B	7	1903-2063	21.3	22.42±0.33	0.6±1.3	118.1	119.2

Reactions: (A) $CrN(g) = Cr(g) + 0.5\ N_2(g)$

(B) $VN(g) + Cr(g) = CrN(g) + V(g)$

[a] Auxiliary ΔHf° data (2) used (in kcal/mol): Cr(g), 95.0 ± 1.0; VN(g), 125 ± 5; V(g), 123.2 ± 2.0.

We note that several of the log Kp values listed by Srivastava and Farber (1) for the two gas phase reactions are inconsistent with their reported partial pressure data. Since the third law method is relatively insensitive to errors in the equilibrium constant, we believe the two third law ΔHf° values are more reliable than those obtained by the second law. Thus, we adopt the average third law value of ΔHf°_{298}(CrN, g) = 120.7 ± 5.0 kcal/mol. Taking into account estimated errors in the pressure determinations and thermal functions, an overall uncertainty of ±5 kcal/mol is assigned. The adopted ΔHf° value corresponds to a dissociation energy of D°_{298}(CrN) = 87.3 kcal/mol.

Although no other experimental value for D° is available, two estimations have been reported. Gingerich (4), using empirical correlations of Colin and Goldfinger (3) and Pauling (6), predicted a value of D°_{298} = 96 kcal/mol for CrN(g) by both methods. This predicted value is in reasonable agreement with that determined experimentally by Srivastava and Farber (1) and reaffirms the usefulness of three empirical correlations (3-5) in predicting dissociation energies for gaseous diatomic mononitrides.

Heat Capacity and Entropy

The value of r_e(CrN) is obtained from the expression $r_e(MO) - r_e(MN) = -0.023$ Å with r_e(CrO) = 1.627 Å (2). Differences in the bond lengths (7) for the oxides and nitrides of As, B, P, Si, and Ti are used to establish the value of -0.023. B_e is calculated from the estimated value for r_e. The moment of inertia is calculated to be 4.9881×10^{-39} g cm^2. The value of α_e is obtained from the other constants assuming a Morse potential function. The values of ω_e and $\omega_e x_e$ are assumed to lie between those for VO (2) and AsN (7).

CrN is isoelectronic with VO; therefore, the ground state electronic configuration is taken to be the same as that for VO (2). Also, the electronic levels and quantum weights are estimated by analogy with those for VO (2). Further support for the quartet ground state of CrN is provided by the fact that the atomic levels for Cr^{+3} (8) are also quartets. Our adopted upper levels and quantum weights contribute 0.13 eu to the entropy of CrN at 4000 K.

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CrN

Chromium Monoxide (CrO) CrO

(Ideal Gas) GFW = 67.9954

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.110	44.898	44.898	INFINITE
100	6.957	49.409	63.558	-1.415	45.171	42.402	-92.669
200	7.098	54.257	57.831	-.715	45.145	39.626	-43.301
298	7.486	57.159	57.159	.000	45.000	36.946	-27.082
300	7.494	57.206	57.159	.014	44.997	36.897	-26.879
400	7.883	59.417	57.458	.783	44.828	34.221	-18.698
500	8.174	61.209	58.035	1.587	44.646	31.590	-13.808
600	8.380	62.718	58.693	2.415	44.446	28.997	-10.562
700	8.527	64.022	59.363	3.261	44.231	26.440	-8.255
800	8.634	65.168	60.019	4.119	43.997	23.913	-6.533
900	8.715	66.190	60.648	4.987	43.742	21.418	-5.201
1000	8.777	67.111	61.249	5.862	43.458	18.952	-4.142
1100	8.827	67.950	61.821	6.742	43.139	16.517	-3.282
1200	8.868	68.720	62.364	7.627	42.780	14.113	-2.570
1300	8.903	69.431	62.881	8.515	42.376	11.740	-1.974
1400	8.932	70.092	63.373	9.407	41.925	9.400	-1.467
1500	8.958	70.709	63.841	10.302	41.424	7.094	-1.034
1600	8.981	71.288	64.289	11.199	40.872	4.823	-.659
1700	9.001	71.833	64.717	12.098	40.269	2.588	-.333
1800	9.020	72.348	65.127	12.999	39.612	.390	-.047
1900	9.038	72.837	65.520	13.902	38.900	-1.770	.204
2000	9.055	73.301	65.897	14.807	38.134	-3.891	.425
2100	9.071	73.743	66.260	15.713	37.313	-5.972	.622
2200	9.087	74.165	66.610	16.621	31.814	-7.857	.780
2300	9.103	74.569	66.947	17.530	31.325	-9.649	.917
2400	9.119	74.957	67.273	18.441	30.835	-11.419	1.040
2500	9.135	75.330	67.588	19.354	30.344	-13.171	1.151
2600	9.151	75.688	67.893	20.268	29.852	-14.901	1.253
2700	9.168	76.034	68.188	21.184	29.359	-16.613	1.345
2800	9.186	76.368	68.474	22.102	28.866	-18.307	1.429
2900	9.205	76.690	68.752	23.022	28.371	-19.982	1.506
3000	9.224	77.003	69.022	23.943	-53.173	-20.404	1.486
3100	9.244	77.306	69.284	24.866	-53.469	-19.306	1.361
3200	9.265	77.599	69.539	25.792	-53.779	-18.200	1.243
3300	9.287	77.885	69.788	26.719	-54.099	-17.083	1.131
3400	9.310	78.162	70.030	27.649	-54.432	-15.957	1.026
3500	9.333	78.433	70.266	28.581	-54.774	-14.821	.925
3600	9.358	78.696	70.497	29.516	-55.126	-13.673	.830
3700	9.383	78.953	70.722	30.453	-55.489	-12.517	.739
3800	9.409	79.203	70.942	31.392	-55.862	-11.350	.653
3900	9.435	79.448	71.157	32.335	-56.246	-10.175	.570
4000	9.463	79.687	71.367	33.280	-56.640	-8.989	.491
4100	9.490	79.921	71.573	34.227	-57.045	-7.792	.415
4200	9.519	80.150	71.774	35.178	-57.460	-6.586	.343
4300	9.547	80.374	71.972	36.131	-57.887	-5.368	.273
4400	9.576	80.594	72.165	37.087	-58.326	-4.143	.206
4500	9.606	80.810	72.355	38.046	-58.777	-2.906	.141
4600	9.635	81.021	72.541	39.008	-59.242	-1.658	.079
4700	9.665	81.229	72.724	39.973	-59.719	-.401	.019
4800	9.695	81.433	72.903	40.941	-60.210	.866	-.039
4900	9.724	81.633	73.079	41.912	-60.715	2.142	-.096
5000	9.754	81.830	73.252	42.886	-61.234	3.430	-.150
5100	9.784	82.023	73.422	43.863	-61.769	4.730	-.203
5200	9.813	82.213	73.590	44.843	-62.318	6.037	-.254
5300	9.842	82.400	73.754	45.826	-62.883	7.360	-.303
5400	9.871	82.585	73.916	46.811	-63.464	8.688	-.352
5500	9.900	82.766	74.075	47.800	-64.059	10.031	-.399
5600	9.928	82.945	74.232	48.791	-64.670	11.382	-.444
5700	9.956	83.121	74.386	49.786	-65.297	12.746	-.489
5800	9.984	83.294	74.538	50.783	-65.939	14.122	-.532
5900	10.011	83.465	74.688	51.782	-66.597	15.506	-.574
6000	10.038	83.633	74.836	52.785	-67.269	16.905	-.615

Dec. 31, 1973

CHROMIUM MONOXIDE (CrO) (IDEAL GAS) GFW = 67.9954 CrO

Ground State Configuration $^5\Pi$

$S^\circ_{298.15}$ = 57.16 ± 1.5 gibbs/mol

ΔHf°_0 = 44.9 ± 10.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 45.0 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
X $^5\Pi$	0	10
B $^5\Pi$	16584.5	10

ω_e = 898.8 cm^{-1} $\omega_e x_e$ = 6.50 cm^{-1} σ = 1

B_e = 0.5286 cm^{-1} α_e = 0.0050 cm^{-1} r_e = 1.627 Å

Heat of Formation

Based on the adopted ground state vibrational constants, a linear Birge-Sponer extrapolation yields a dissociation energy, D°_0, of 3.796 eV (87.54 kcal/mol). Applying a correction for the ionicity in the Cr-O bond (1), we recalculate D°_0 = 4.017 eV (92.63 kcal/mol). This in turn corresponds to a ΔHf°_{298} value of 60.95 kcal/mol for CrO(g), using auxiliary data (2).

Huldt and Lagerqvist (3), using a spectroscopic flame technique, reported D°_0 = 4.4 ± 0.5 eV for CrO(g). This value was later corrected to D°_0 = 5.3 eV (122.9 kcal/mol) (4, 5). Grimley et al. (6) mentioned that in determining D°_0 values by the flame technique of Huldt and Lagerqvist (3) the calculation assumes that the only gaseous species containing Cr are Cr and CrO. Under the experimental conditions of Huldt and Lagerqvist (3), Grimley et al. (6) indicated that the $CrO_2(g)$ partial pressure cannot be neglected.

Grimley et al. (6) studied the vaporization of $Cr_2O_3(c)$ under neutral and oxidizing conditions using mass spectrometric methods. The reported partial pressure data for Cr(g), CrO(g), $CrO_2(g)$, O(g), and $O_2(g)$ may be analyzed in terms of many different chemical equilibria. Our analyses of four equilibria in the neutral and oxidizing conditions are tabulated below.

	Reaction	ΔHf°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}, kcal/mol 2nd Law	3rd Law
Neutral conditions	A*	-39.5	-44.9	-2.8±2.1	55.5	50.1
1842-2062 K	B	-108.2	-100.4	4.0±1.4	46.3	54.2
13 points	C	174.0	178.2	2.1±1.2	38.4	42.6
	D*	206.3	205.9	-0.2±1.4	40.9	40.5
Oxidizing conditions	A	-27.2	-43.7	-8.6±13.1	67.8	51.3
1893-1945 K	B	-46.9	-99.3	-27.3±4.0	107.6	55.2
3 points	C	192.2	181.0	- 5.8±4.4	56.6	45.4
	D	202.0	208.9	3.6±9.0	36.6	43.5

Reaction A: $Cr(g) + 1/2\ O_2(g) = CrO(g)$

B: $Cr(g) + O(g) = CrO(g)$

C: $1/2\ Cr_2O_3(c) = CrO(g) + 1/4\ O_2(g)$

D: $1/2\ Cr_2O_3(c) = CrO(g) + 1/2\ O(g)$

* One point rejected due to a statistical test (1842 K).

The drifts are less severe in the neutral system so that there is better agreement in the 2nd and 3rd law results for the neutral conditions than in the oxidizing system. Note that the 3rd law ΔHr°_{298} value are slightly more positive for the oxidizing than the neutral conditions for corresponding equilibria. There is also unfortunately a 10 kcal/mol difference in the calculated ΔHf°_{298} values between the gas phase (reactions A and B) and condensed phase (reactions C and D) equilibria. Grimley et al. (6) prefer the gas phase results while Brewer and Rosenblatt (7) prefer the condensed phase results. We adopt ΔHf°_{298} = 45.0 ± 10.0 kcal/mol for CrO(g) as a value which is representative of the 2nd and 3rd law results in the neutral system. The adopted ΔHf° value leads to D°_0 = 4.71 eV (108.6 kcal/mol).

Chizhikov et al. (8) also studied the vaporization of Cr_2O_3 via mass spectrometry in the range 1690-2020 K. They reported the detection of gaseous Cr, CrO, CrO_2, and O during the evaporation process. The reported smoothed partial pressures of CrO(g) and $CrO_2(g)$ lie higher than those reported by Grimley et al. (6) by a factor of 2-5, while the partial pressures of Cr(g) are less than a factor 2 different. This data was not analyzed.

Heat Capacity and Entropy

The spectroscopic work involving CrO(g) has been reviewed and referenced by Rosen (9). The adopted vibration and rotation constants as well as the electronic levels are those tabulated by Rosen (9). The ground state has not been firmly established. Weltner (10) suggested a possible $^3\Sigma^-$ ground state. The free energy functions used here are 1.02 gibbs/mol at 298 K and 1.57 gibbs/mol at 3000 K lower than those suggested by Brewer and Rosenblatt (7). The difference arises in that Brewer and Rosenblatt (7) approximated the CrO electronic levels with the Cr^{++} electronic levels. The latter has a singlet ground state and many levels lying below 600 cm^{-1}.

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CrO

Chromium Dioxide (CrO_2) CrO_2

(Ideal Gas) GFW = 83.9948

T, °K	Cp°	S°	-(G°-H°298)/T	H°-H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.679	-17.634	-17.634	INFINITE
100	8.457	54.181	72.908	-1.873	-17.597	-18.773	41.028
200	9.468	60.376	65.242	-.973	-17.771	-19.892	21.737
298	10.370	64.323	64.323	.000	-18.000	-20.884	15.309
300	10.387	64.387	64.323	.019	-18.004	-20.902	15.227
400	11.236	67.496	64.741	1.102	-18.215	-21.836	11.931
500	11.889	70.077	65.557	2.260	-18.409	-22.718	9.930
600	12.359	72.288	66.499	3.473	-18.601	-23.562	8.583
700	12.696	74.220	67.467	4.727	-18.797	-24.373	7.610
800	12.940	75.932	68.420	6.009	-19.006	-25.157	6.872
900	13.120	77.467	69.342	7.313	-19.232	-25.912	6.292
1000	13.256	78.857	70.225	8.632	-19.485	-26.641	5.822
1100	13.361	80.126	71.068	9.963	-19.773	-27.343	5.432
1200	13.443	81.292	71.872	11.303	-20.101	-28.016	5.102
1300	13.508	82.370	72.639	12.651	-20.474	-28.661	4.818
1400	13.561	83.373	73.370	14.005	-20.895	-29.276	4.570
1500	13.604	84.311	74.069	15.363	-21.368	-29.858	4.350
1600	13.639	85.190	74.736	16.725	-21.893	-30.407	4.153
1700	13.669	86.017	75.376	18.091	-22.470	-30.921	3.975
1800	13.694	86.800	75.989	19.459	-23.105	-31.401	3.813
1900	13.716	87.541	76.578	20.829	-23.797	-31.843	3.663
2000	13.734	88.245	77.144	22.202	-24.545	-32.249	3.524
2100	13.750	88.915	77.688	23.576	-25.351	-32.613	3.394
2200	13.764	89.555	78.213	24.952	-30.838	-32.783	3.257
2300	13.776	90.167	78.720	26.329	-31.317	-32.861	3.123
2400	13.787	90.754	79.209	27.707	-31.801	-32.916	2.997
2500	13.797	91.317	79.682	29.086	-32.290	-32.955	2.881
2600	13.805	91.858	80.140	30.466	-32.782	-32.971	2.771
2700	13.813	92.379	80.584	31.847	-33.279	-32.969	2.669
2800	13.819	92.882	81.014	33.229	-33.780	-32.948	2.572
2900	13.825	93.367	81.432	34.611	-34.286	-32.908	2.480
3000	13.831	93.835	81.837	35.994	-115.845	-31.614	2.303
3100	13.836	94.289	82.232	37.377	-116.160	-28.800	2.030
3200	13.840	94.728	82.616	38.761	-116.492	-25.979	1.774
3300	13.845	95.154	82.989	40.145	-116.839	-23.145	1.533
3400	13.848	95.568	83.353	41.530	-117.202	-20.301	1.305
3500	13.852	95.969	83.708	42.915	-117.578	-17.446	1.089
3600	13.855	96.359	84.054	44.300	-117.969	-14.578	.885
3700	13.858	96.739	84.392	45.686	-118.374	-11.701	.691
3800	13.861	97.109	84.721	47.072	-118.793	-8.811	.507
3900	13.863	97.469	85.044	48.458	-119.227	-5.914	.331
4000	13.865	97.820	85.359	49.845	-119.675	-3.003	.164
4100	13.868	98.162	85.667	51.231	-120.139	-.080	.004
4200	13.870	98.496	85.968	52.618	-120.616	2.854	-.148
4300	13.871	98.823	86.263	54.005	-121.109	5.803	-.295
4400	13.873	99.142	86.553	55.392	-121.619	8.757	-.435
4500	13.875	99.454	86.836	56.780	-122.144	11.727	-.570
4600	13.876	99.758	87.113	58.167	-122.687	14.710	-.699
4700	13.878	100.057	87.386	59.555	-123.246	17.703	-.823
4800	13.879	100.349	87.653	60.943	-123.823	20.708	-.943
4900	13.880	100.635	87.915	62.331	-124.417	23.721	-1.058
5000	13.881	100.916	88.172	63.719	-125.030	26.751	-1.169
5100	13.883	101.191	88.424	65.107	-125.662	29.795	-1.277
5200	13.884	101.460	88.673	66.495	-126.312	32.847	-1.381
5300	13.885	101.725	88.916	67.884	-126.980	35.918	-1.481
5400	13.886	101.984	89.156	69.272	-127.669	38.993	-1.578
5500	13.886	102.239	89.392	70.661	-128.374	42.090	-1.672
5600	13.887	102.489	89.623	72.050	-129.100	45.193	-1.764
5700	13.888	102.735	89.851	73.438	-129.845	48.311	-1.852
5800	13.889	102.977	90.075	74.827	-130.608	51.446	-1.939
5900	13.890	103.214	90.296	76.216	-131.389	54.589	-2.022
6000	13.890	103.447	90.513	77.605	-132.188	57.751	-2.104

Dec. 31, 1973.

CHROMIUM DIOXIDE (CrO_2) (IDEAL GAS) GFW = 83.9948 CrO_2

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [64.32 ± 3.0] gibbs/mol

Ground State Quantum Weight = [3]

ΔHf°_0 = -17.6 ± 10.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -18.0 ± 10.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
998 (1)
[300] (1)
1008 (1)

Bond Distance: Cr-O = [1.627] Å

Bond Angle: O-Cr-O = [110°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.326 x 10^{-115}] g^3cm^6

$\sigma = 2$

Heat of Formation

Grimley et al. (1) studied the vaporization of Cr_2O_3(c) under neutral and oxidizing conditions using mass spectrometric methods. In the range 1842-2062 K (IPTS-68) this study detected quantitatively Cr(g), CrO(g), CrO_2(g), O(g), and O_2(g). Of the many chemical equilibria which could be analyzed, we tabulate below our second and third law analyses of the equilibrium between CrO(g) and CrO_2(g).

	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(CrO_2, g)* kcal/mol
Neutral system, 13 points, 1842-2062 K				
Reaction A**	141.27	119.87	-10.3±3.6	-15.31
Reaction B**	71.11	64.41	- 3.4±2.8	-19.41
Oxidizing system, 3 points, 1893-1945 K				
Reaction A	120.97	122.48	0.8±9.2	-17.92
Reaction B	101.21		-17.9±0.1	-21.82

* ΔHf°_{298} value based on 3rd law ΔHr°_{298}.

** One point (1865 K) rejected due to a statistical test.

Reaction A: $CrO_2(g) = CrO(g) + O(g)$. Reaction B: $CrO_2(g) = CrO(g) + 1/2\ O_2(g)$.

We adopt ΔHf°_{298} = -18.0 ± 10.0 kcal/mol. This value is intermediate to the four results tabulated above with extra weight given to those of the neutral conditions. Our analysis of equations analogous to those treated in the CrO(g) table (3) yields the same trends as with CrO(g). The results are consistent with our adopted value.

Using auxiliary data (3), we calculate D°_0 = 9.98 eV(230.1 kcal/mol) corresponding to $CrO_2(g) = Cr(g) + 2\ O(g)$. This value is a factor of 2.12 greater than the D°_0 value of CrO(g) (3).

Chizhikov et al. (2) also studied the vaporization of Cr_2O_3 via mass spectrometry in the range 1690-2020 K. They reported the detection of gaseous Cr, CrO, CrO_2, and O during the evaporation process. The reported smoothed partial pressures of CrO(g) and CrO_2(g) lie higher than those of Grimley et al. (1) by a factor of 2-5, while the partial pressures of Cr(g) are less than a factor of two difference. This study was not further analyzed.

Mass spectrometric studies were made by Farber and Srivastava (7) on the reactions involved with vanadium and chromium additives in potassium-seeded H_2/O_2 flames. Equilibrium values at an average flame temperature of 2250 K for the reaction $CrO_2(g) + 2\ H_2O(g) = H_2CrO_4(g) + 2\ H(g)$ were analyzed by Farber and Srivastava (7). They calculated ΔHf°_{298} = -3.0 ± 7 kcal/mol for CrO_2(g). The experimental determination of ΔHf°_{298} for H_2CrO_4(g) also required the ΔHf°_{298} value for CrO(g). Adjusting the calculations of Farber and Srivastava (7) to be consistent with the JANAF ΔHf°_{298} value for CrO(g) (3), we recalculate ΔHf°_{298} = -11.0 kcal/mol for CrO_2(g).

Heat Capacity and Entropy

CrO_2(g) is assumed to have a molecular geometry similar to that observed for TiO_2(g), ZrO_2(g), and TaO_2(g) (3). The O-Cr-O bond is estimated as 110° while the Cr-O bond distance is estimated to be the same as that in CrO(g) (3). The symmetric and asymmetric stretching frequencies are obtained from the infrared spectra of gaseous tetrahedral CrO_2Cl_2 and CrO_2F_2 (4, 5). The bending frequency of 300 cm^{-1} is estimated, based on analogies with TaO_2(g) and WO_2(g) (3, 6). Refer also to the TiO_2(g) table (3). The electronic ground state is assumed to be $^3A_1$ as in WO_2(g) (6). The three principal moments of inertia are: $I_A = 12.30 \times 10^{-39}$, $I_B = 9.435 \times 10^{-39}$, and $I_C = 2.866 \times 10^{-39}$ g cm^2.

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CrO_2

Chromium Trioxide (CrO_3) CrO_3

(Ideal Gas) GFW = 99.9942

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.959	-68.876	-68.876	INFINITE
100	8.358	52.208	73.780	-2.157	-69.191	-68.100	148.832
200	10.944	58.747	64.741	-1.195	-69.654	-66.827	73.026
298	13.390	63.591	63.591	.000	-70.000	-65.361	47.911
300	13.430	63.674	63.591	.025	-70.005	-65.332	47.594
400	15.258	67.804	64.142	1.465	-70.214	-63.740	34.826
500	16.500	71.351	65.237	3.057	-70.340	-62.105	27.146
600	17.338	74.438	66.519	4.751	-70.428	-60.450	22.019
700	17.914	77.157	67.849	6.516	-70.502	-58.780	18.352
800	18.321	79.577	69.166	8.329	-70.579	-57.102	15.600
900	18.617	81.753	70.446	10.176	-70.669	-55.412	13.456
1000	18.838	83.726	71.677	12.050	-70.781	-53.710	11.738
1100	19.006	85.530	72.855	13.942	-70.927	-51.997	10.331
1200	19.137	87.190	73.982	15.850	-71.111	-50.267	9.155
1300	19.241	88.726	75.058	17.769	-71.342	-48.521	8.157
1400	19.324	90.155	76.086	19.697	-71.620	-46.756	7.299
1500	19.393	91.491	77.068	21.633	-71.951	-44.969	6.552
1600	19.449	92.744	78.009	23.575	-72.334	-43.158	5.895
1700	19.496	93.924	78.911	25.522	-72.771	-41.320	5.312
1800	19.535	95.040	79.777	27.474	-73.267	-39.457	4.791
1900	19.569	96.097	80.608	29.429	-73.821	-37.563	4.321
2000	19.598	97.102	81.408	31.388	-74.434	-35.642	3.895
2100	19.623	98.058	82.178	33.349	-75.105	-33.684	3.506
2200	19.645	98.972	82.921	35.312	-80.461	-31.539	3.133
2300	19.664	99.846	83.638	37.278	-80.809	-29.308	2.785
2400	19.681	100.683	84.331	39.245	-81.165	-27.059	2.464
2500	19.695	101.486	85.001	41.214	-81.528	-24.800	2.168
2600	19.709	102.259	85.650	43.184	-81.896	-22.522	1.893
2700	19.720	103.003	86.279	45.155	-82.272	-20.232	1.638
2800	19.731	103.721	86.889	47.128	-82.653	-17.926	1.399
2900	19.740	104.413	87.482	49.102	-83.042	-15.606	1.176
3000	19.749	105.083	88.057	51.076	-164.486	-12.037	.877
3100	19.756	105.730	88.617	53.051	-164.687	-6.950	.490
3200	19.764	106.358	89.162	55.027	-164.908	-1.861	.127
3300	19.770	106.966	89.692	57.004	-165.146	3.237	-.214
3400	19.776	107.556	90.209	58.981	-165.402	8.343	-.536
3500	19.781	108.129	90.713	60.959	-165.672	13.456	-.840
3600	19.786	108.687	91.204	62.937	-165.959	18.581	-1.128
3700	19.791	109.229	91.684	64.916	-166.262	23.710	-1.401
3800	19.795	109.757	92.153	66.896	-166.580	28.851	-1.659
3900	19.799	110.271	92.611	68.875	-166.914	33.994	-1.905
4000	19.802	110.772	93.058	70.855	-167.265	39.149	-2.139
4100	19.806	111.261	93.496	72.836	-167.632	44.316	-2.362
4200	19.809	111.739	93.925	74.816	-168.014	49.488	-2.575
4300	19.812	112.205	94.345	76.797	-168.413	54.677	-2.779
4400	19.814	112.660	94.756	78.779	-168.830	59.865	-2.974
4500	19.817	113.106	95.159	80.760	-169.264	65.069	-3.160
4600	19.819	113.541	95.554	82.742	-169.716	70.285	-3.339
4700	19.821	113.967	95.941	84.724	-170.186	75.507	-3.511
4800	19.823	114.385	96.321	86.706	-170.674	80.740	-3.676
4900	19.825	114.794	96.694	88.689	-171.180	85.977	-3.835
5000	19.827	115.194	97.060	90.671	-171.706	91.230	-3.988
5100	19.829	115.587	97.419	92.654	-172.252	96.499	-4.135
5200	19.831	115.972	97.772	94.637	-172.816	101.769	-4.277
5300	19.832	116.350	98.119	96.620	-173.399	107.062	-4.415
5400	19.833	116.720	98.460	98.604	-174.003	112.352	-4.547
5500	19.835	117.084	98.796	100.587	-174.625	117.666	-4.676
5600	19.836	117.442	99.125	102.571	-175.268	122.982	-4.800
5700	19.837	117.793	99.450	104.554	-175.929	128.312	-4.920
5800	19.839	118.138	99.769	106.538	-176.610	133.661	-5.036
5900	19.840	118.477	100.083	108.522	-177.309	139.013	-5.149
6000	19.841	118.810	100.393	110.506	-178.027	144.384	-5.259

Dec. 31, 1973.

CHROMIUM TRIOXIDE (CrO_3) (IDEAL GAS) GFW = 99.9942 CrO_3

Point Group [D_{3h}]

$S^\circ_{298.15}$ = [63.59 ± 4.0] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf°_0 = -68.9 ± 10.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -70.0 ± 10.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[875] (1)
[500] (1)
969 (2)
[425] (2)

Bond Distance: Cr-O = [1.627] Å

σ = [6]

Bond Angle: O-Cr-O = [120°]

Product of the Moments of Inertia = $I_AI_BI_C$ = [2.347×10^{-114}] g^3cm^6

Heat of Formation

The vaporization of Cr_2O_3 under oxidizing conditions was studied by Grimley, Burns, and Inghram (1) using mass spectrometric methods. The principal gaseous species observed were Cr, CrO, CrO_2, CrO_3, O, and O_2. The vapor pressures at three different temperatures (1893, 1914, and 1942 K, IPTS-68) are analyzed for four different reactions by the second and third law methods.

Reaction	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$\Delta Hf^\circ_{298}(CrO_3, g)$* kcal/mol
$Cr(g) + 3\ O(g) = CrO_3(g)$	-279.80	-332.47	-27.5±6.4	-58.79
$Cr(g) + 1.5\ O_2(g) = CrO_3(g)$	-220.52	-165.48	28.7±21.1	-70.48
$0.5\ Cr_2O_3(c) + 1.5\ O(g) = CrO_3(g)$	- 30.81	- 24.28	3.4±1.4	-70.04
$0.5\ Cr_2O_3(c) + 0.75\ O_2(g) = CrO_3(g)$	- 1.17	59.22	31.5±12.4	-75.88

* Based on third law ΔHr°_{298}.

The second law results are considered less reliable due to the small number of data points and the small temperature range studied (52 K). We adopt ΔHf°_{298} = -70.0 ± 10.0 kcal/mol for $CrO_3(g)$.

Washburn (3), in a mass spectrometric study of the sublimation of $CrO_3(c)$, stated that the gaseous Cr-containing molecules are in equilibrium among themselves but not with O(g). If the same situation were to hold in the study by Grimley et al. (1), a value intermediate to -70.04 and -75.88 kcal/mol might be more appropriate. However, the adopted value with its assigned uncertainty is still consistent with this possibility.

Mass spectrometric studies were made by Farber and Srivastava (6) on the reactions involved with vanadium and chromium additives in potassium-seeded H_2/O_2 flames. Equilibrium values at an average flame temperature of 2250 K for the reaction $CrO_3(g) + H_2O(g) = H_2CrO_4(g)$ were analyzed by Farber and Srivastava (6). They calculated ΔHf°_{298} = -64.6 ± 7 kcal/mol for $CrO_3(g)$. The experimental determination of ΔHf°_{298} for $H_2CrO_4(g)$ also required the ΔHf°_{298} value for CrO(g). Adjusting the calculations of Farber and Srivastava (6) to be consistent with the JANAF ΔHf°_{298} value for CrO(g) (2), we recalculate ΔHf°_{298} = -72.6 kcal/mol for $CrO_3(g)$.

Defining the dissociation by $CrO_3(g) = Cr(g) + 3O(g)$, we calculate D°_0 = 14.8 ± 0.4 eV (340.3 ± 10 kcal/mol). This compares with D°_0 = 4.71 eV for CrO(g) and D°_0 = 9.98 eV for $CrO_2(g)$ for similar dissociations (2).

Heat Capacity and Entropy

The molecular structure is assumed to be planar with D_{3h} symmetry. The three Cr-O bond distances are taken to be the same as in CrO(g) (2). The individual moments of inertia are $I_A = 21.10 \times 10^{-39}$ g cm^2 and $I_B=I_C = 10.55 \times 10^{-39}$ g cm^2.

Barraclough et al. (4) observed a vibrational frequency at 969 cm^{-1} in the infrared spectrum of $CrO_3(c)$ dispersed in a Nujol mull. This frequency was assigned to represent the stretching frequency of the two free Cr-O groups in crystalline CrO_3. We assume this frequency also represents the stretching mode in the vapor phase. This infrared work is supported by the infrared and Raman studies of Mattes (5). The remaining vibrational frequencies are those suggested by Grimley et al. (1). The electronic ground state is assumed to be a singlet.

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CrO_3

Chromium Subnitride (Cr_2N)

(Crystal) GFW = 117.9987

Cr_2N

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	15.790	15.500	15.500	.000	-30.000	-24.432	17.909
300	15.820	15.598	15.500	.029	-29.997	-24.397	17.773
400	17.550	20.408	16.144	1.706	-29.835	-22.553	12.322
500	18.340	24.412	17.409	3.501	-29.633	-20.756	9.073
600	19.000	27.814	18.867	5.368	-29.422	-19.000	6.921
700	19.660	30.792	20.362	7.301	-29.197	-17.279	5.395
800	20.310	33.460	21.335	9.300	-28.956	-15.593	4.260
900	20.970	35.890	23.264	11.364	-28.704	-13.939	3.385
1000	21.630	38.134	24.640	13.494	-28.451	-12.313	2.691
1100	22.290	40.226	25.963	15.690	-28.209	-10.709	2.128
1200	22.940	42.194	27.234	17.951	-27.988	-9.128	1.662
1300	23.600	44.056	28.457	20.278	-27.794	-7.565	1.272
1400	24.260	45.829	29.635	22.671	-27.634	-6.015	.939
1500	24.920	47.525	30.772	25.130	-27.509	-4.476	.652
1600	25.580	49.155	31.870	27.655	-27.422	-2.943	.402
1700	26.240	50.725	32.933	30.246	-27.375	-1.414	.182
1800	26.890	52.244	33.964	32.904	-27.370	.112	-.014
1900	27.430	53.712	34.965	35.619	-27.415	1.640	-.189
2000	28.080	55.136	35.938	38.395	-27.510	3.171	-.347
2100	28.670	56.520	36.886	41.232	-27.654	4.708	-.490
2200	29.300	57.868	37.809	44.131	-37.090	6.567	-.652
2300	29.860	59.183	38.710	47.089	-36.447	8.537	-.811
2400	30.420	60.466	39.590	50.103	-35.748	10.478	-.954
2500	31.000	61.719	40.450	53.174	-34.995	12.389	-1.083

Dec. 31, 1973.

CHROMIUM SUBNITRIDE (Cr_2N) (CRYSTAL) GFW = 117.9987 Cr_2N

$S^\circ_{298.15}$ = [15.5 ± 2.0] gibbs/mol
Td = 1810 K

ΔHf°_0 = Unknown
$\Delta Hf^\circ_{298.15}$ = -30.0 ± 3.0 kcal/mol
ΔHd° = 27.7 kcal/mol

Heat of Formation

Mah (1) has measured the heat of combustion of chromium subnitride at 303.15 K. Chemical analysis showed the sample to contain 87.66% total chromium, 11.51% nitrogen, and 2.54% acid-insoluble residue. Reevaluation of her analytical results indicates that the composition of the material was 96.77% $Cr_2N_{0.969}$, 0.69% Cr, 2.37% Cr_2O_3, and 0.17% Al_2O_3. For the process $Cr_2N_{0.969}(c) + 1.5\ O_2(g) = Cr_2O_3(c) + 0.4845\ N_2(g)$, we calculate $\Delta Hc^\circ_{298} = -241.2_9 \pm 1.5$ kcal/mol from Mah's data (1) at unit fugacities of oxygen and nitrogen. Impurity corrections are based on JANAF heat of formation data (2). When the value for ΔHc° is combined with the heat of formation for Cr_2O_3(2), one obtains $\Delta Hf^\circ_{298}(Cr_2N_{0.969}, c) = -29.9 \pm 3.5$ kcal/mol. The large uncertainty in this value arises from impurities in the subnitride sample, as well as from the uncertainty (±2.0 kcal/mol) in the ΔHf° of Cr_2O_3 (2).

All available equilibrium nitrogen pressures except those of one study (5) have been recently reviewed for the reaction $2\ Cr(c) + 0.5\ N_2(g) = Cr_2N(c)$. These results are reanalyzed by the second and third law methods using revised thermal functions for Cr_2N (see below). In calculating equilibrium constants for this reaction, the activities of Cr_2N and Cr are assumed to be unity at each temperature. Also, we have not taken into account in our analysis any variations in the composition of the subnitride (see Phase Data Section). Results of our analysis are tabulated below.

Investigator	No. of Points	Temp. Range, K	Drift eu	$\Delta Hf^\circ_{298}(Cr_2N, c)$ 2nd Law	3rd Law
Sano (4)	6	1229-1395	-3.7±0.2	-24.0	-28.8±0.5
Mozgovai and Samarin (5)	Equation	1600-1750	-14.0	-10.2	-33.8±1.7
Seybolt and Oriani (6)	5	1273-1673	-7.8±5.4	-21.3	-32.8±3.9
Tomilin and Savost'yanova(7)	Equation	1517-1724	-32.6	-20.3	-32.6±5.7
Mills (8)	Equation	1337-1653	- 2.1	-29.2	-32.3±0.5
Schwerdtfeger (9)	3	1373-1583	-3.7±0.7	-27.1	-32.5±0.8
Smith (10)	2	1333;1370	-13.4	-13.6	-31.7±0.7

The equilibrium pressures reported by Sano (4) are inconsistent with those of the other investigation, and no weight is given to these results. Reasons for the discrepancies have been suggested by DeLuca and Leitnaker (3).

We adopt ΔHf° of -30.0 ± 3.0 kcal/mol which is based on the second and third law results from the two equilibrium studies (8, 9) and the ΔHf° value determined by combustion calorimetry (1). Our adopted value agrees with that selected by NBS (-30.5) (11) but is 1.8 kcal/mol less negative than the selected value of DeLuca and Leitnaker (3).

Heat Capacity and Entropy

No low temperature heat capacity data for Cr_2N have been reported. As a result, a value of S°_{298} is estimated by analogy with entropies (2, 12, and 13) for other transition-metal subnitrides. For the reaction $2\ M(c) + 0.5\ N_2(g) = M_2N(c)$ (where M=Fe, Mo, Nb, Ta, and V), we calculate an average ΔSf° of -18.7 gibbs/mol. This value is combined with entropies for Cr and N_2 (2) to give 15.5 gibbs/mol as S°_{298} for $Cr_2N(c)$. Other reported estimates (in gibbs/mol) for S°_{298} are 14.3 (3) and 17.7 ± 1.0 (14).

The only high temperature enthalpy study reported for Cr_2N is that of Satoh (15). This worker measured heat contents ($H^\circ_T - H^\circ_{273}$) for three nitride samples at three temperatures each (372.6, 598.8, and 784.2 K) in an ice calorimeter. In light of more recent data on the stoichiometry of the Cr_2N_{1-x} phase, DeLuca and Leitnaker (3) have shown that the subnitride sample used by Satoh (15) was substoichiometric. The latter workers reevaluated the heat contents reported by Satoh (15) and presented Cp° data for Cr_2N in the temperature range 298-1800 K. A comparison of their value (17.0 gibbs/mol) for Cp° at 298.15 K with similar data for other transition-metal subnitrides (2, 12, and 13) indicates that it is probably too large by 1-2 gibbs/mol. We find a ΔCpf° of 1.1 gibbs/mol for several subnitrides (2, 12, and 13) which leads to a Cp° value of 15.79 gibbs/mol for Cr_2N at 298.15 K. This value is adopted and joined smoothly with the data of DeLuca and Leitnaker (3) near 400 K. Cp° data above 1800 K are obtained by graphical extrapolation.

Phase Data

Blix (16) has determined the structure of the subnitride phase as hexagonal by x-ray diffraction methods, and he indicated that the homogeneity limits extend from $CrN_{0.47}$ to $CrN_{0.66}$. On the other hand, Eriksson (17) has reported that the phase exists between $CrN_{0.38}$ and $CrN_{0.50}$. More recently, Mills (8), using a thermogravimetric technique, has examined the homogeneity limits of Cr_2N as a function of temperature. The upper limiting composition was determined to be $CrN_{0.49}$ with only a small variation with temperature. The lower limiting composition of Cr_2N varied widely with temperature in the range 1273-1373 K. At 1273 K, Mills (8) reported the limiting composition as $CrN_{0.41}$, while at 1373 K the composition was found to be $CrN_{0.37}$. Other information on the chromium-chromium nitride system has been reviewed by Storms (18).

Decomposition Data

No information is available on the melting point of Cr_2N. We assume that the subnitride decomposes prior to melting, according to the reaction $Cr_2N(c) \rightarrow 2\ Cr(c) + 0.5\ N_2(g)$. Td is the temperature at which ΔGr for the decomposition process approaches zero. ΔHd° is the negative of the heat of formation of Cr_2N at Td.

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Cr_2N

Dichromium Trioxide (Cr_2O_3)

(Crystal) GFW = 151.9902

Cr_2O_3

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 3.653	− 269.800	− 269.800	INFINITE
100	5.797	2.412	37.199	− 3.479	− 270.817	− 264.644	578.379
200	13.024	10.293	21.646	− 2.271	− 271.409	− 258.181	282.127
298	28.757	19.396	19.396	.000	− 271.200	− 251.701	184.502
300	29.140	19.575	19.397	.054	− 271.186	− 251.580	183.276
400	26.930	27.184	20.443	2.696	− 270.776	− 245.112	133.923
500	28.136	33.342	22.426	5.458	− 270.352	− 238.745	104.355
600	28.812	38.535	24.589	8.308	− 269.935	− 232.465	84.675
700	29.303	43.016	26.995	11.215	− 269.539	− 226.248	70.638
800	29.706	46.956	29.248	14.166	− 269.171	− 220.091	60.126
900	30.049	50.475	31.415	17.154	− 268.836	− 213.976	51.961
900	30.049	50.475	31.415	17.154	− 268.836	− 213.976	51.961
1000	30.356	53.657	33.483	20.175	− 268.546	− 207.896	45.436
1100	30.641	56.564	35.451	23.225	− 268.314	− 201.843	40.102
1200	30.911	59.242	37.323	26.302	− 268.149	− 195.807	35.661
1300	31.169	61.726	39.106	29.406	− 268.058	− 189.783	31.905
1400	31.419	64.045	40.805	32.536	− 268.047	− 183.764	28.687
1500	31.664	66.221	42.428	35.690	− 268.119	− 177.742	25.897
1600	31.904	68.272	43.980	38.868	− 268.276	− 171.712	23.455
1700	32.141	70.214	45.466	42.071	− 268.519	− 165.668	21.298
1800	32.375	72.057	46.893	45.296	− 268.855	− 159.609	19.379
1900	32.715	73.817	48.264	48.551	− 269.277	− 153.529	17.660
2000	33.023	75.503	49.584	51.838	− 269.782	− 147.427	16.110
2100	33.235	77.119	50.857	55.151	− 270.376	− 141.293	14.705
2200	33.447	78.670	52.086	58.485	− 280.312	− 134.818	13.393
2300	33.661	80.162	53.275	61.840	− 280.211	− 128.207	12.182
2400	33.875	81.599	54.425	65.217	− 280.097	− 121.599	11.073
2500	34.089	82.986	55.540	68.615	− 279.971	− 115.000	10.053
2600	34.304	84.327	56.621	72.035	− 279.829	− 108.402	9.112
2700	34.520	85.626	57.672	75.476	− 279.675	− 101.812	8.241
2800	34.736	86.885	58.693	78.939	− 279.507	− 95.227	7.433
2900	34.953	88.106	59.686	82.423	− 279.324	− 88.647	6.681
3000	35.171	89.297	60.653	85.930	− 441.225	− 79.601	5.799

Dec. 31, 1973

DICHROMIUM TRIOXIDE (Cr_2O_3) (CRYSTAL) GFW = 151.9902 Cr_2O_3

$S^\circ_{298.15}$ = 19.40 ± 0.3 gibbs/mol

Tm = 2603 ± 15 K

ΔHf°_0 = -269.8 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -271.2 ± 2.0 kcal/mol

ΔHm° = [31.0] kcal/mol

Heat of Formation

Two oxygen bomb calorimetric studies on Cr(c) led to reported values of ΔHf°_{298} = -272.6 ± 0.4 kcal/mol by Mah (1) and -271.0 ± 1.8 kcal/mol by Golutvin and Chin'k'uei (2) for Cr_2O_3(c). The seven combustion runs by Mah (1) involve corrections of 1-5% for incomplete combustion and 0.07% for impurities. Mah (1) reported that completions of combustion ranged from 95.30 to 98.90%. Of the fourteen runs by Golutvin and Chin'k'uei (2), seven had a completeness of combustion of 91.88 to 98.96%. Their reported ΔHf°_{298} value is based on an average of the results for these seven runs with no correction for incomplete combustion or impurities. These latter authors (2) also stated that there was no clear dependence between the heat of combustion and completeness of combustion. Early calorimetric studies led to reported values for ΔHf° of -267.8 (298 K, 3), -288.9 ± 1.0 (292 K, 4), and -268.9 ± 0.6 kcal/mol (294 K, 5).

There are many equilibrium studies involving Cr_2O_3(c). Our analysis of the more recent studies are tabulated below. The free energy of formation equation presented by Richardson and Jeffes (8) is representative of the earlier equilibrium studies (9).

Reference	Reaction	Temp. Range, K	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	ΔHf°_{298}, kcal/mol 2nd Law	ΔHf°_{298}, kcal/mol 3rd Law
8	A	873-1773	Eqn.	-270.62	-268.44	1.7	-270.62	-268.44
9	B(transpiration)	871-1427	4	-32.89±0.65	-31.61±0.65	1.1±0.5	-272.05	-268.22
10	B (static)	1313-1573	5(47)	-32.17±0.75	-32.36±0.19	-0.1±0.5	-269.89	-270.46
11	B (transpiration)	1493-1893	5	-32.85±0.94	-32.79±0.30	0.1±0.6	-271.94	-271.76
12	A (emf)	1000-1700	Eqn.	-264.60	-268.91	-3.3	-264.60	-268.91
13	A (emf)	1173-1523	Eqn.	-269.71	-270.32	-0.5	-269.71	-270.32

Reaction A: 2 Cr(c) + 3/2 O_2(g) = Cr_2O_3(c).

Reaction B: 2/3 Cr(c) + H_2O(g) = 1/3 Cr_2O_3(c) + H_2(g).

We adopt ΔHf°_{298} = -271.2 ± 2.0 kcal/mol for Cr_2O_3(c). This value is an average of two combustion studies (1, 2) and three equilibrium studies which have a small third law drift (10, 11, 13).

Kelley et al. (6) investigated experimentally the thermodynamic properties of the chromium carbides. They measured the CO(g) equilibrium pressure in four distinct systems. A combination of our analyses of these four equilibria (7) leads to ΔHf°_{298} = -269.9 kcal/mol for Cr_2O_3(c).

Heat Capacity and Entropy

The heat capacity of Cr_2O_3(c) was measured in the region 56-336 K by Anderson (14) and 100-350 K by Volger (15). Using the combination of Debye and Einstein functions suggested by Anderson (14), we calculate S°_{50} = 0.386 gibbs/mol and $H^\circ_{50}-H^\circ_0$ = 14.3 cal/mol. Both studies (14, 15) indicated a maximum in the Cp° curve at 305 K. The graphically displayed data of Volger (15) lies considerably higher than that of Anderson (14). Early heat capacity data (137-299 K) by Russell (16) is in good agreement with that of Anderson (14). Above 305 K the heat capacity values decrease rapidly (~5 gibbs/mol) until 325-340 K, at which point the values show little change with temperature. The adopted Cp° values below T = 330 K are based on the study by Anderson (14).

Enthalpy data on Cr_2O_3(c) were measured by Kelley et al. (298-1774 K, 6) and Laschschenko and Kompanskii (288-1428 K, 17). The adopted heat capacity values are those suggested by Kelley et al. (6), except that the values in the region 350-500 K are shifted slightly so as to join smoothly with the low temperature heat capacity results (14). The derived enthalpy values agree with the enthalpy data of Kelley et al. (6) to within ±0.5%, the maximum deviation of 25 cal or .5% occurring at 479 K.

Phase Data

Brewer (18) summarized the phase data and reported that Cr_2O_3 has a homogeneity range of x = 1.50-1.56 for CrO_x. Cr_2O_3 has the α-corundum structure and is antiferromagnetic with structural distortion occurring below the Curie temperature of 305 K.

Melting Data

Refer to Cr_2O_3(ℓ) table.

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Cr_2O_3

Dichromium Trioxide (Cr_2O_3) Cr_2O_3

(Liquid) GFW = 151.9902

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	24.320	30.018	30.018	.000	-243.398	-227.066	166.444
300	24.380	30.169	30.019	.045	-243.393	-226.965	165.344
400	26.940	37.569	31.010	2.624	-243.047	-221.537	121.042
500	28.136	43.728	32.956	5.386	-242.623	-216.209	94.505
600	28.812	48.921	35.196	8.235	-242.206	-210.966	76.844
700	29.308	53.401	37.484	11.142	-241.810	-205.789	64.250
800	29.706	57.342	39.725	14.093	-241.442	-200.670	54.821
900	30.049	60.861	41.881	17.082	-241.107	-195.595	47.497
1000	30.356	64.043	43.941	20.102	-240.817	-190.553	41.645
1100	30.641	66.950	45.902	23.152	-240.585	-185.538	36.863
1200	30.911	69.627	47.769	26.230	-240.420	-180.541	32.881
1300	31.169	72.112	49.547	29.334	-240.329	-175.556	29.514
1400	31.419	74.431	51.243	32.463	-240.318	-170.575	26.628
1500	31.664	76.607	52.862	35.617	-240.390	-165.591	24.127
1600	31.904	78.658	54.411	38.796	-240.547	-160.600	21.937
1700	32.141	80.599	55.895	41.998	-240.790	-155.594	20.003
1800	37.500	82.443	57.319	45.224	-241.125	-150.574	18.282
1900	37.500	84.471	58.695	48.974	-241.052	-145.546	16.742
2000	37.500	86.394	60.032	52.724	-241.094	-140.522	15.355
2100	37.500	88.224	61.331	56.474	-241.251	-135.488	14.100
2200	37.500	89.968	62.594	60.224	-250.771	-130.133	12.928
2300	37.500	91.635	63.820	63.974	-250.275	-124.661	11.846
2400	37.500	93.231	65.013	67.724	-249.788	-119.208	10.855
2500	37.500	94.762	66.172	71.474	-249.310	-113.780	9.947
2600	37.500	96.233	67.301	75.224	-248.838	-108.366	9.109
2700	37.500	97.648	68.398	78.974	-248.375	-102.973	8.335
2800	37.500	99.012	69.468	82.724	-247.920	-97.595	7.618
2900	37.500	100.328	70.509	86.474	-247.472	-92.233	6.951
3000	37.500	101.599	71.524	90.224	-409.129	-84.413	6.149
3100	37.500	102.829	72.515	93.974	-408.297	-73.600	5.189
3200	37.500	104.019	73.481	97.724	-407.498	-62.819	4.290
3300	37.500	105.173	74.424	101.474	-406.727	-52.061	3.448
3400	37.500	106.293	75.345	105.224	-405.987	-41.325	2.656
3500	37.500	107.380	76.244	108.974	-405.272	-30.611	1.911
3600	37.500	108.436	77.124	112.724	-404.585	-19.913	1.209
3700	37.500	109.464	77.984	116.474	-403.926	-9.237	.546
3800	37.500	110.464	78.826	120.224	-403.294	1.423	-.082
3900	37.500	111.438	79.650	123.974	-402.690	12.061	-.676
4000	37.500	112.387	80.456	127.724	-402.114	22.688	-1.240
4100	37.500	113.313	81.246	131.474	-401.566	33.303	-1.775
4200	37.500	114.217	82.021	135.224	-401.046	43.902	-2.284
4300	37.500	115.099	82.780	138.974	-400.556	54.496	-2.770
4400	37.500	115.961	83.524	142.724	-400.098	65.068	-3.232
4500	37.500	116.804	84.254	146.474	-399.672	75.637	-3.673

Dec. 31, 1973

DICHROMIUM TRIOXIDE (Cr_2O_3) (LIQUID) GFW = 151.9902 Cr_2O_3

$S^\circ_{298.15}$ = [30.018] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-243.398] kcal/mol

Tm = 2603 ± 15 K ΔHm° = [31.0] kcal/mol

Heat of Formation

The heat of formation of $Cr_2O_3(\ell)$ at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between ($H^\circ_{2603}-H^\circ_{298}$) for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for $Cr_2O_3(\ell)$ is estimated to be 7.5 gibbs/g-atom. A glass transition is assumed at 1800 K. Below 1800 K, the Cp° values are those of the crystal with the exception that the values below 500 K are a smooth extrapolation to Cp° = 24.32 gibbs/mol at 298.15 K. The entropy is calculated in a manner analogous to that used for the heat of formation.

Melting Data

The melting point is chosen to be Tm = 2603 ± 15 K, as suggested by Charlesworth (1). This result is based on the work by McNally et al. (2). The heat of melting is estimated by analogy with ΔSm° = 12.03 for corundum (3).

References

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Cr_2O_3

Hypofluorous Acid (HOF)

(Ideal Gas) GFW = 36.0058

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.411	-22.806	-22.806	INFINITE
100	7.950	45.323	61.483	-1.616	-23.085	-22.294	48.723
200	8.096	50.859	54.942	-.817	-23.286	-21.429	23.417
298	8.587	54.174	54.174	.000	-23.500	-20.472	15.007
300	8.598	54.227	54.174	.016	-23.504	-20.454	14.900
400	9.218	56.786	54.519	.907	-23.701	-19.406	10.603
500	9.777	58.905	55.190	1.857	-23.869	-18.313	8.005
600	10.236	60.729	55.965	2.859	-24.011	-17.188	6.261
700	10.614	62.337	56.762	3.902	-24.133	-16.040	5.008
800	10.933	63.775	57.551	4.980	-24.240	-14.878	4.064
900	11.211	65.079	58.316	6.087	-24.334	-13.701	3.327
1000	11.457	66.274	59.053	7.221	-24.415	-12.515	2.735
1100	11.677	67.376	59.760	8.378	-24.487	-11.322	2.249
1200	11.875	68.401	60.438	9.555	-24.549	-10.122	1.843
1300	12.053	69.358	61.088	10.752	-24.604	-8.917	1.499
1400	12.213	70.258	61.711	11.966	-24.653	-7.709	1.203
1500	12.357	71.105	62.309	13.194	-24.698	-6.496	.946
1600	12.486	71.907	62.884	14.436	-24.741	-5.283	.722
1700	12.602	72.667	63.437	15.691	-24.780	-4.064	.522
1800	12.705	73.391	63.971	16.956	-24.819	-2.846	.345
1900	12.799	74.080	64.485	18.232	-24.856	-1.623	.187
2000	12.882	74.739	64.981	19.516	-24.893	-.399	.044
2100	12.958	75.369	65.461	20.808	-24.930	.826	-.086
2200	13.026	75.974	65.925	22.107	-24.969	2.053	-.204
2300	13.088	76.554	66.375	23.413	-25.009	3.282	-.312
2400	13.144	77.112	66.810	24.725	-25.050	4.514	-.411
2500	13.194	77.650	67.233	26.041	-25.096	5.745	-.502
2600	13.241	78.168	67.644	27.363	-25.141	6.981	-.587
2700	13.283	78.669	68.043	28.689	-25.190	8.218	-.665
2800	13.321	79.153	68.431	30.020	-25.241	9.455	-.738
2900	13.356	79.621	68.809	31.354	-25.295	10.697	-.806
3000	13.388	80.074	69.177	32.691	-25.353	11.937	-.870
3100	13.418	80.514	69.536	34.031	-25.412	13.181	-.929
3200	13.445	80.940	69.885	35.374	-25.476	14.427	-.985
3300	13.470	81.354	70.227	36.720	-25.542	15.675	-1.038
3400	13.493	81.757	70.560	38.068	-25.611	16.924	-1.088
3500	13.515	82.148	70.885	39.419	-25.684	18.178	-1.135
3600	13.535	82.529	71.204	40.771	-25.760	19.433	-1.180
3700	13.553	82.900	71.515	42.126	-25.840	20.689	-1.222
3800	13.570	83.262	71.819	43.482	-25.922	21.949	-1.262
3900	13.586	83.615	72.117	44.840	-26.009	23.207	-1.301
4000	13.601	83.959	72.409	46.199	-26.098	24.471	-1.337
4100	13.615	84.295	72.695	47.560	-26.192	25.736	-1.372
4200	13.628	84.623	72.975	48.922	-26.288	27.004	-1.405
4300	13.641	84.944	73.249	50.286	-26.387	28.276	-1.437
4400	13.652	85.258	73.519	51.650	-26.490	29.546	-1.468
4500	13.663	85.564	73.783	53.016	-26.597	30.820	-1.497
4600	13.673	85.865	74.042	54.383	-26.705	32.100	-1.525
4700	13.682	86.159	74.297	55.751	-26.818	33.379	-1.552
4800	13.691	86.447	74.547	57.119	-26.933	34.662	-1.578
4900	13.700	86.730	74.793	58.489	-27.052	35.945	-1.603
5000	13.708	87.006	75.035	59.859	-27.173	37.230	-1.627
5100	13.715	87.278	75.272	61.230	-27.298	38.521	-1.651
5200	13.722	87.544	75.505	62.602	-27.425	39.812	-1.673
5300	13.729	87.806	75.735	63.975	-27.555	41.110	-1.695
5400	13.736	88.062	75.961	65.348	-27.689	42.401	-1.716
5500	13.742	88.315	76.183	66.722	-27.824	43.703	-1.737
5600	13.747	88.562	76.402	68.096	-27.964	45.004	-1.756
5700	13.753	88.806	76.618	69.471	-28.105	46.308	-1.776
5800	13.758	89.045	76.830	70.847	-28.249	47.616	-1.794
5900	13.763	89.280	77.039	72.223	-28.396	48.924	-1.812
6000	13.768	89.511	77.245	73.599	-28.546	50.236	-1.830

Dec. 31, 1960; Sept. 30, 1965; Dec. 31, 1972.

HYPOFLUOROUS ACID (HOF) (IDEAL GAS) GFW = 36.0058 FHO

Point Group C_s

ΔHf°_0 = -22.8 ± 1 kcal/mol

$S^\circ_{298.15}$ = 54.17 ± 0.05 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -23.5 ± 1 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
3578.5 (1)
1354.8 (1)
889.0 (1)

Bond Distance: H-O = 0.966 Å O-F = 1.442 Å

Bond Angle: H-O-F = 96.78°

$\sigma = 1$

Product of the Moments of Inertia: $I_AI_BI_C = 1.4741 \times 10^{-117}\ g^3cm^6$

Heat of Formation

ΔHf°_0 is the value derived by Berkowitz et al. (1) from photoionization data which gave 14.34 eV as the threshold of O^+ formation, $HOF + h\nu \rightarrow O^+ + HF + e^-$. The threshold of OH^+ formation, 15.07 eV for $HOF + h\nu \rightarrow OH^+ + F + e^-$, yields ΔHf°_0 = -21.7 kcal/mol assuming $\Delta Hf^\circ_0(OH^+)$ = 307.5 ± 0.5 kcal/mol from Dibeler et al. (2). The latter authors found 18.05 eV for $H_2O + h\nu \rightarrow OH^+ + H^+ + e^-$. Our adopted value for HOF differs by only 2.5 kcal/mol from the mean ΔHf°_0 of H_2O and F_2O, namely -25.3 kcal/mol.

Heat Capacity and Entropy

Vibrational frequencies are from gas-phase infrared spectra of Appelman and Kim (3); the values are confirmed by IR spectra of HOF isolated in a matrix of N_2 (4). Structural parameters are those derived by Pearson and Kim (5) from centrifugal distortion analysis of mm-wave rotational spectra (5, 6) of HOF and DOF. We use the atomic coordinates (5) to derive the principal moments of inertia $I_A = 0.1433 \times 10^{-39}$, $I_B = 3.1368 \times 10^{-39}$ and $I_C = 3.2801 \times 10^{-39}$ g cm^2 and their product; the corresponding bond distances are 0.96648 and 1.44215 Å, i.e., slightly longer than the rounded values (5) listed above. The earlier study (6) gave 0.964 ± 0.01 and 1.442 ± 0.001 Å and a bond angle of 97.2 ± 0.6°.

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Lead Monofluoride (PbF) FPb

(Ideal Gas) GFW = 226.1984

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.215	-18.700	-18.700	INFINITE
100	7.033	51.466	66.653	-1.519	-18.774	-21.006	45.908
200	7.703	56.532	60.452	-.784	-18.992	-23.150	25.297
298	8.221	59.714	59.714	.000	-19.184	-25.149	18.435
300	8.229	59.765	59.714	.015	-19.188	-25.186	18.348
400	8.514	62.175	60.041	.854	-19.386	-27.155	14.837
500	8.675	64.094	60.666	1.714	-19.602	-29.074	12.708
600	8.775	65.685	61.374	2.587	-19.836	-30.946	11.272
700	8.843	67.043	62.089	3.468	-21.250	-32.587	10.174
800	8.891	68.227	62.784	4.355	-21.517	-34.189	9.340
900	8.929	69.277	63.448	5.246	-21.778	-35.757	8.683
1000	8.959	70.219	64.079	6.140	-22.032	-37.297	8.151
1100	8.987	71.075	64.677	7.038	-22.280	-38.812	7.711
1200	9.013	71.858	65.243	7.938	-22.519	-40.303	7.340
1300	9.040	72.580	65.780	8.840	-22.754	-41.775	7.023
1400	9.069	73.251	66.290	9.746	-22.987	-43.231	6.749
1500	9.100	73.878	66.775	10.654	-23.218	-44.666	6.508
1600	9.135	74.466	67.238	11.566	-23.451	-46.090	6.296
1700	9.173	75.021	67.679	12.481	-23.684	-47.497	6.106
1800	9.214	75.546	68.102	13.400	-23.920	-48.893	5.936
1900	9.258	76.046	68.507	14.324	-24.156	-50.274	5.783
2000	9.305	76.522	68.896	15.252	-24.394	-51.641	5.643
2100	9.354	76.977	69.270	16.185	-67.084	-51.446	5.354
2200	9.405	77.413	69.630	17.123	-67.233	-50.699	5.036
2300	9.457	77.833	69.978	18.066	-67.398	-49.943	4.746
2400	9.509	78.236	70.314	19.014	-67.581	-49.179	4.478
2500	9.561	78.625	70.638	19.968	-67.783	-48.410	4.232
2600	9.613	79.001	70.953	20.926	-68.002	-47.631	4.004
2700	9.664	79.365	71.258	21.890	-68.237	-46.842	3.792
2800	9.714	79.718	71.553	22.859	-68.489	-46.046	3.594
2900	9.763	80.059	71.841	23.833	-68.756	-45.238	3.409
3000	9.811	80.391	72.120	24.812	-69.038	-44.423	3.236
3100	9.857	80.714	72.392	25.795	-69.332	-43.598	3.074
3200	9.901	81.027	72.657	26.783	-69.638	-42.763	2.921
3300	9.943	81.332	72.916	27.775	-69.954	-41.918	2.776
3400	9.983	81.630	73.168	28.772	-70.278	-41.063	2.639
3500	10.022	81.920	73.414	29.772	-70.609	-40.199	2.510
3600	10.059	82.203	73.654	30.776	-70.946	-39.324	2.387
3700	10.094	82.479	73.889	31.784	-71.287	-38.441	2.271
3800	10.128	82.748	74.118	32.795	-71.630	-37.547	2.159
3900	10.160	83.012	74.343	33.809	-71.976	-36.648	2.054
4000	10.190	83.270	74.563	34.827	-72.322	-35.740	1.953
4100	10.219	83.521	74.778	35.847	-72.668	-34.821	1.856
4200	10.247	83.768	74.989	36.870	-73.012	-33.891	1.764
4300	10.273	84.009	75.196	37.896	-73.354	-32.957	1.675
4400	10.298	84.246	75.399	38.925	-73.694	-32.012	1.590
4500	10.322	84.478	75.599	39.956	-74.029	-31.063	1.509
4600	10.345	84.705	75.794	40.989	-74.361	-30.103	1.430
4700	10.368	84.928	75.986	42.025	-74.688	-29.141	1.355
4800	10.389	85.146	76.175	43.063	-75.011	-28.163	1.282
4900	10.410	85.360	76.360	44.103	-75.329	-27.186	1.213
5000	10.430	85.571	76.542	45.145	-75.642	-26.202	1.145
5100	10.449	85.778	76.721	46.189	-75.950	-25.211	1.080
5200	10.468	85.981	76.897	47.235	-76.252	-24.209	1.017
5300	10.486	86.180	77.070	48.282	-76.550	-23.204	.957
5400	10.504	86.377	77.241	49.332	-76.843	-22.197	.898
5500	10.521	86.569	77.409	50.383	-77.130	-21.184	.842
5600	10.538	86.759	77.574	51.436	-77.413	-20.162	.787
5700	10.555	86.946	77.737	52.491	-77.692	-19.140	.734
5800	10.571	87.130	77.897	53.547	-77.965	-18.106	.682
5900	10.587	87.310	78.055	54.605	-78.236	-17.076	.633
6000	10.603	87.488	78.211	55.664	-78.502	-16.038	.584

June 30, 1962; Dec. 31, 1973

LEAD MONOFLUORIDE (PbF) (IDEAL GAS) GFW = 226.1984 FPb

Ground State Configuration $^2\Pi_{1/2}$

$S°_{298.15}$ = 59.71 ± 0.05 gibbs/mol

$\Delta Hf°_0$ = -18.70 ± 2.5 kcal/mol

$\Delta Hf°_{298.15}$ = -19.18 ± 2.5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	8264.7	2
A [$^2\Sigma$]	22566.6	[2]
B $^2\Sigma^+$	35643	2

ω_e = 507.2 cm^{-1}

B_e = 0.2288 cm^{-1}

$\omega_e x_e$ = 2.30 cm^{-1}

α_e = [0.0013] cm^{-1}

σ = 1

r_e = 2.058 Å

Heat of Formation

Rosen (1) lists $D°_0$ = 84.0 ± 2 kcal/mol derived from the mass spectrometric work of Zmbov, Hastie, and Margrave (2). The partial pressures and log K for the $PbF_2(g) + Pb(g) = 2PbF(g)$ reaction in the latter reference are inconsistent. Third law calculations show that the log K value corresponds to the heat of reaction given. The dissociation energy calculated by the linear Birge-Sponer extrapolation of the adopted ground state vibrational constants, as derived from emission and absorption spectra (ν, 0-13) (3, 4), is 3.44 eV. Correcting this value for the ionic character of PbF as suggested by Hildenbrand (5) gives $D°_0$ = 3.64 eV (83.9 kcal/mol). The upper limit of the value recommended by Gaydon (6) (3 ± 0.5 eV) falls at 80.7 kcal/mol. An intercomparison of the dissociation energies of the lead (7), mercury (1), and potassium (7) monohalides indicates that $D°_0$ = 84.0 ± 2 kcal/mol is reasonable. Combining this with $\Delta Hf°_0$(Pb, g) = 46.91 ± 0.13 kcal/mol (7) and $\Delta Hf°_0$(F, g) = 18.36 ± 0.40 kcal/mol (7) gives $\Delta Hf°_0$ (PbF, g) = -18.73 ± 2.5 kcal/mol. We adopt $\Delta Hf°_0$ (PbF, g) = -18.70 ± 2.5 kcal/mol which is consistent with the above. $\Delta Hf°_{298}$ (PbF, g) = -19.18 ± 2.5 kcal/mol is calculated from $\Delta Hf°_0$.

Heat Capacity and Entropy

The vibrational constants, the electronic states and levels, and the rotational constant are those recommended in Rosen (1) with the following modifications. The first excited state, unassigned in Rosen (1), is tentatively classed as a $^2\Sigma$ state in accordance with the preference for $^2\Sigma$ over $^2\Delta$ expressed by Barrow et al. (8). If the state is $^2\Delta$ rather than $^2\Sigma$, the entropy is increased by 0.005 eu at 4000 K and 0.05 eu at 6000 K. The C and higher electronic states (1) have been omitted; inclusion increases the entropy only by approximately 0.005 eu at 6000 K. The adopted B_e = 0.2288 cm^{-1} is obtained by an approximate correction to B_0 = 0.2281 cm^{-1} given in Rosen (1), and r_e = 2.058 Å calculated from B_e compares with r_0 = 2.061 Å given in Rosen (1). The value for α_e is calculated assuming a Morse potential function.

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FPb

Strontium Monofluoride (SrF)

(Ideal Gas) GFW = 106.6184

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.219	-70.044	-70.044	INFINITE
100	7.040	49.045	64.275	-1.523	-70.015	-72.285	157.979
200	7.728	54.123	58.055	-.786	-70.219	-74.489	81.398
298	8.242	57.315	57.315	.000	-70.400	-76.539	56.105
300	8.249	57.366	57.315	.015	-70.404	-76.578	55.787
400	8.529	59.782	57.643	.856	-70.607	-78.605	42.948
500	8.687	61.703	58.269	1.717	-70.848	-80.578	35.221
600	8.785	63.297	58.978	2.591	-71.132	-82.498	30.050
700	8.851	64.656	59.694	3.473	-71.467	-84.366	26.340
800	8.898	65.841	60.390	4.361	-71.860	-86.164	23.544
900	8.934	66.891	61.055	5.252	-72.484	-87.932	21.353
1000	8.963	67.834	61.687	6.147	-72.931	-89.624	19.587
1100	8.988	68.690	62.285	7.045	-75.304	-91.161	18.112
1200	9.009	69.473	62.852	7.945	-75.692	-92.585	16.862
1300	9.028	70.194	63.389	8.846	-76.082	-93.977	15.799
1400	9.045	70.864	63.900	9.750	-76.472	-95.339	14.883
1500	9.061	71.489	64.385	10.655	-76.862	-96.673	14.085
1600	9.077	72.074	64.847	11.562	-77.253	-97.981	13.384
1700	9.092	72.625	65.289	12.471	-110.217	-98.360	12.645
1800	9.107	73.145	65.711	13.381	-110.266	-97.661	11.858
1900	9.122	73.638	66.115	14.292	-110.317	-96.959	11.153
2000	9.139	74.106	66.503	15.205	-110.369	-96.254	10.518
2100	9.156	74.552	66.876	16.120	-110.425	-95.548	9.944
2200	9.175	74.979	67.235	17.036	-110.484	-94.839	9.421
2300	9.196	75.387	67.580	17.955	-110.547	-94.126	8.944
2400	9.220	75.779	67.914	18.876	-110.616	-93.411	8.506
2500	9.246	76.156	68.236	19.799	-110.693	-92.692	8.103
2600	9.275	76.519	68.548	20.725	-110.778	-91.970	7.731
2700	9.307	76.870	68.849	21.654	-110.876	-91.245	7.386
2800	9.343	77.209	69.142	22.587	-110.986	-90.516	7.065
2900	9.382	77.537	69.426	23.523	-111.113	-89.782	6.766
3000	9.424	77.856	69.701	24.463	-111.257	-89.046	6.487
3100	9.470	78.166	69.970	25.408	-111.420	-88.302	6.225
3200	9.519	78.467	70.230	26.357	-111.607	-87.554	5.980
3300	9.572	78.761	70.484	27.312	-111.818	-86.798	5.748
3400	9.629	79.047	70.732	28.272	-112.057	-86.037	5.530
3500	9.688	79.327	70.974	29.238	-112.324	-85.267	5.324
3600	9.751	79.601	71.210	30.210	-112.621	-84.490	5.129
3700	9.817	79.869	71.440	31.188	-112.951	-83.704	4.944
3800	9.885	80.132	71.665	32.173	-113.315	-82.907	4.768
3900	9.956	80.390	71.886	33.165	-113.715	-82.104	4.601
4000	10.030	80.643	72.101	34.164	-114.149	-81.287	4.441
4100	10.106	80.891	72.313	35.171	-114.620	-80.460	4.289
4200	10.184	81.136	72.520	36.186	-115.127	-79.621	4.143
4300	10.264	81.376	72.723	37.208	-115.670	-78.768	4.003
4400	10.346	81.613	72.923	38.238	-116.248	-77.904	3.870
4500	10.429	81.847	73.118	39.277	-116.861	-77.026	3.741
4600	10.514	82.077	73.310	40.324	-117.507	-76.134	3.617
4700	10.599	82.304	73.499	41.380	-118.186	-75.227	3.498
4800	10.686	82.528	73.685	42.444	-118.894	-74.305	3.383
4900	10.773	82.749	73.868	43.517	-119.631	-73.369	3.272
5000	10.861	82.968	74.048	44.599	-120.393	-72.417	3.165
5100	10.949	83.183	74.225	45.689	-121.181	-71.451	3.062
5200	11.038	83.397	74.399	46.789	-121.989	-70.466	2.962
5300	11.126	83.608	74.571	47.897	-122.817	-69.467	2.865
5400	11.215	83.817	74.740	49.014	-123.662	-68.454	2.771
5500	11.303	84.023	74.907	50.140	-124.523	-67.424	2.679
5600	11.390	84.228	75.072	51.275	-125.394	-66.377	2.590
5700	11.477	84.430	75.234	52.418	-126.277	-65.315	2.504
5800	11.563	84.631	75.394	53.570	-127.165	-64.238	2.421
5900	11.649	84.829	75.553	54.731	-128.060	-63.147	2.339
6000	11.733	85.026	75.709	55.900	-128.959	-62.039	2.260

Dec. 31, 1972

STRONTIUM MONOFLUORIDE (SrF) (IDEAL GAS) GFW = 106.6184 FSr

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15} = 57.32 \pm 0.05$ gibbs/mol

$\Delta Hf^\circ_0 = -70.0 \pm 2.0$ kcal/mol

$\Delta Hf^\circ_{298.15} = -70.4 \pm 2.0$ kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2
$A\ ^2\Pi$	15067.8	2
	15348.5	2
$B\ ^2\Sigma$	17303.4	2
$C\ ^2\Pi$	27383.7	4
$D\ ^2\Sigma$	28296.6	2
$E\ ^2\Pi$	31528.7	2
	31614.8	2
$F\ ^2\Sigma$	32822.0	2
$G\ ^2\Pi$	34759.2	4

$\omega_e = 498.0$ cm^{-1}
$B_e = 0.2506$ cm^{-1}

$\omega_e x_e = 2.15$ cm^{-1}
$\alpha_e = [0.00148]$ cm^{-1}

$\sigma = 1$
$r_e = 2.0757 \pm 0.0005$ Å

Heat of Formation

Equilibrium constants for four dissociation equilibria have been determined from observations made on the condensed phase systems SrF_2-B (1), SrF_2-Al (2), and SrF_2-BaF_2-Al (2) by the mass spectrometric-Knudsen effusion method. Heats of reaction have been calculated from these Kp data by both the second and third law methods. Results of our analysis are given below. Also included below is a value for the heat of dissociation of SrF which was determined from spectrophotometric studies (3) of reaction equilibria in H_2-O_2-N_2 flames.

Investigator	Reaction	Range, K	Points	ΔHr_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}(SrF, g) kcal/mol
Hildenbrand (1)	A	1476-1585	10	23.4	25.1±0.9	1.2±4.7	-70.1±2.7
Hildenbrand (1)	B	1436-1525	9	4.3	2.0±0.7	-1.5±4.0	-71.0±1.0
Ehlert et al. (2)	C	1174-1290	9[a]	8.1	10.6±0.3	2.0±1.0	-70.0±4.0
Ehlert et al. (2)	D	1125-1292	10	-127.6	-116.5±1.5	9.1±2.7	-67.6±1.3
Ryabova and Gurvich (3)	E			132 ± 7			-73.9±8.0

Reactions:
(A) $2Sr(g) + BF_3(g) = 2SrF(g) + BF(g)$
(B) $Sr(g) + SrF_2(g) = 2SrF(g)$
(C) $Sr(g) + BaF(g) = Ba(g) + SrF(g)$
(D) $2SrF(g) = Sr(g) + SrF_2(c)$
(E) $SrF(g) = Sr(g) + F(g)$

[a] One point rejected due to failure of a statistical test.

Auxiliary ΔHf data (4) (in kcal/mol): Sr(g), 39.2; BF_3(g), -271.42; BF(g), -27.7; SrF_2(g), -183.1; BaF(g), -77.0; Ba(g), 42.8; SrF_2(c), -290.9; F(g), 18.86.

It is believed that the Kp data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert et al. (2) determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. This belief is further substantiated by the appearance of the rather large positive drift in the third law analysis of their Kp data for reaction (D). Also, it is felt that the ΔHf value obtained from the flame-spectrophotometric studies (3) is perhaps somewhat less reliable than the three values derived from the Kp data for the homogeneous reactions. Thus, a median value ΔHf°_{298}(SrF, g) = -70.4 ± 2.0 kcal/mol of the latter results is adopted. The adopted value corresponds to a dissociation energy of D°_0(Sr-F) = 127.7 kcal/mol (5.54 eV).

Spectroscopic values for D°_0 based on a linear Birge-Sponer extrapolation of the ground state ($X\ ^2\Sigma$) vibrational levels (v,0-4) have been reported as 3.2 (5) and 3.5 eV (6). However, it is well established now that the linear extrapolation (5, 6) generally underestimates D°_0 if the binding of the molecule is partially ionic. Based on the ionic character correction suggested by Hildenbrand (6), these values adjust to 4.9 and 5.4 eV. The latter value is now in reasonable agreement with the adopted thermochemical value. Other spectroscopic values (7) include 4.6 (from $X\ ^2\Sigma$), 4.7 (from $A\ ^2\Pi$), and 5.2 eV (from $C\ ^2\Pi$). The products of dissociation from the two excited states of SrF were assumed to be $Sr(^3P) + F(^2P)$.

Heat Capacity and Entropy

The spectroscopic data with the exception of the value for α_e are those given by Rosen (8). α_e is calculated from the other constants assuming a Morse potential function. The electronic states and levels are also taken from the compilation of Rosen (8).

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FSr

Strontium Monofluoride Unipositive Ion (SrF^+)

(Ideal Gas) GFW = 106.6178

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.100	55.625	55.625	.000	47.100	39.977	-29.304
300	8.108	55.675	55.625	.015	47.105	39.933	-29.091
400	8.424	58.055	55.947	.843	47.386	37.500	-20.489
500	8.608	59.956	56.565	1.695	47.633	34.999	-15.298
600	8.723	61.536	57.266	2.562	47.839	32.452	-11.821
700	8.800	62.887	57.975	3.439	47.995	29.874	-9.327
800	8.855	64.066	58.664	4.322	48.094	27.277	-7.452
900	8.897	65.111	59.323	5.209	47.963	24.688	-5.995
1000	8.930	66.050	59.950	6.101	48.009	22.099	-4.830
1100	8.960	66.903	60.544	6.995	46.131	19.617	-3.898
1200	8.989	67.684	61.107	7.893	46.236	17.201	-3.133
1300	9.022	68.405	61.641	8.793	45.342	14.778	-2.484
1400	9.061	69.075	62.148	9.697	46.449	12.346	-1.927
1500	9.112	69.701	62.631	10.606	46.559	9.907	-1.443
1600	9.176	70.291	63.091	11.520	46.672	7.459	-1.019
1700	9.257	70.850	63.532	12.442	14.218	5.910	-.760
1800	9.358	71.382	63.953	13.372	14.686	5.407	-.657
1900	9.478	71.891	64.357	14.314	15.163	4.879	-.561
2000	9.619	72.381	64.746	15.268	15.649	4.326	-.473
2100	9.731	72.854	65.121	16.238	16.145	3.746	-.390
2200	9.961	73.313	65.483	17.225	16.653	3.144	-.312
2300	10.159	73.760	65.833	18.231	17.175	2.519	-.239
2400	10.372	74.197	66.173	19.258	17.708	1.870	-.170
2500	10.597	74.625	66.502	20.306	18.253	1.199	-.105
2600	10.832	75.045	66.823	21.377	18.809	.506	-.043
2700	11.072	75.458	67.135	22.473	19.375	-.209	.017
2800	11.316	75.865	67.440	23.592	19.948	-.944	.074
2900	11.558	76.267	67.737	24.736	20.526	-1.700	.128
3000	11.797	76.663	68.028	25.903	21.106	-2.478	.180
3100	12.030	77.053	68.313	27.095	21.686	-3.273	.231
3200	12.254	77.439	68.592	28.309	22.261	-4.088	.279
3300	12.466	77.819	68.866	29.545	22.828	-4.920	.326
3400	12.666	78.194	69.135	30.802	23.384	-5.769	.371
3500	12.851	78.564	69.399	32.078	23.923	-6.633	.414
3600	13.020	78.929	69.659	33.372	24.444	-7.514	.456
3700	13.172	79.287	69.914	34.681	24.942	-8.409	.497
3800	13.308	79.641	70.165	36.006	25.415	-9.315	.536
3900	13.427	79.988	70.413	37.342	25.857	-10.236	.574
4000	13.529	80.329	70.656	38.690	26.267	-11.168	.610
4100	13.614	80.664	70.896	40.048	26.644	-12.108	.645
4200	13.684	80.993	71.133	41.413	26.984	-13.057	.679
4300	13.738	81.316	71.366	42.784	27.287	-14.013	.712
4400	13.778	81.632	71.596	44.160	27.551	-14.976	.744
4500	13.804	81.942	71.822	45.539	27.775	-15.947	.775
4600	13.816	82.246	72.046	46.920	27.960	-16.921	.804
4700	13.821	82.543	72.266	48.302	28.105	-17.897	.832
4800	13.813	82.834	72.483	49.684	28.211	-18.876	.859
4900	13.796	83.118	72.697	51.065	28.279	-19.858	.886
5000	13.771	83.397	72.908	52.443	28.309	-20.842	.911
5100	13.738	83.669	73.117	53.819	28.304	-21.827	.935
5200	13.699	83.936	73.322	55.190	28.264	-22.807	.959
5300	13.654	84.196	73.525	56.553	28.193	-23.767	.981
5400	13.604	84.451	73.725	57.921	28.091	-24.770	1.002
5500	13.550	84.700	73.922	59.279	27.958	-25.747	1.023
5600	13.493	84.944	74.117	60.631	27.801	-26.721	1.043
5700	13.433	85.182	74.309	61.977	27.619	-27.693	1.062
5800	13.370	85.415	74.498	63.317	27.415	-28.662	1.080
5900	13.306	85.643	74.685	64.651	27.190	-29.628	1.097
6000	13.241	85.866	74.870	65.979	26.946	-30.589	1.114

Dec. 31, 1972

STRONTIUM MONOFLUORIDE UNIPOSITIVE ION (SrF^+) (IDEAL GAS) GFW = 106.6178 FSr^+

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

$S°_{298.15}$ = [55.6 ± 2.0] gibbs/mol

$\Delta Hf°_0$ = 46.0 ± 10.0 kcal/mol

$\Delta Hf°_{298.15}$ = 47.1 ± 10.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$X\ ^1\Sigma^+$	0	1
$a\ ^3\Pi$	[10000]	6
$A'\ ^1\Pi$	[12000]	2
$B'\ ^1\Delta$	[15000]	2
$A\ ^1\Sigma^+$	[18000]	1
$b\ ^3\Sigma^-$	[20000]	3
$B\ ^1\Sigma^+$	[35000]	1

ω_e = [561] cm^{-1} $\omega_e x_e$ = [2.42] cm^{-1} σ = 1

B_e = [0.27265] cm^{-1} α_e = [0.00157] cm^{-1} r_e = [1.99] Å

Heat of Formation

The appearance potential (AP) of SrF^+ from SrF(g) has been measured mass spectrometrically by Hildenbrand (1), Green et al. (2), and Ehlert et al. (3) as 5.0 ± 0.3 eV, 4.9 ± 0.3 eV, and 5.2 ± 0.3 eV, respectively. For the process $e^- + SrF(g) \rightarrow SrF^+(g) + 2e^-$, the corresponding $\Delta Hf°_0(SrF^+, g)$ are derived to be 45.3 ± 9.0, 43.0 ± 9.0, and 49.9 ± 9.0 kcal/mol with $\Delta Hf°_0(SrF, g)$ = -70.0 ± 2.0 kcal/mol (4).

Hildenbrand (1) has also reported an AP of 13.0 ± 1.0 eV for SrF^+ from $SrF_2(g)$. Green et al. (2) obtained an ionization efficiency curve for SrF^+ which extrapolates (high-energy portion) to 10.5 eV at zero ion current. Assuming the process to be $e^- + SrF_2(g) \rightarrow SrF^+(g) + F(g) + 2e^-$, we obtain $\Delta Hf°_0(SrF^+, g)$ equal to 98.7 ± 25.0 and 41.1 kcal/mol by combining the above results with $\Delta Hf°_0(SrF_2, g)$ = -182.7 ± 1.0 kcal/mol and $\Delta Hf°_0(F, g)$ = 18.36 ± 0.4 kcal/mol (4).

The adopted $\Delta Hf°_0$ is based on the three mass spectral results (1, 2, 3) for the direct ionization process of SrF(g). The value of ΔHf at 298 K is 47.1 ± 10.0 kcal/mol, and the corresponding ionization potential for SrF(g) is 5.03 eV.

Heat Capacity and Entropy

The internuclear distance (r_e) is the value estimated by Barrow and Beale (5) from spectroscopic work on SrF. The value of ω_e is calculated from Badger's rule (6) which can be written in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e - d_{ij})^3$. Molecular data for the ground states of SrF (4), SrO (7), and RbF (8) were used to determine the constant d_{ij}. The product $x_e\mu^{1/2}$ has been shown to be constant within a group of similar molecules by Barrow and Caunt (9). Since $\mu^{1/2}(SrF^+) \cong \mu^{1/2}(SrF)$, we assume $x_e(SrF^+) = x_e(SrF)$ and obtain $\omega_e x_e$ equal to 2.42 cm^{-1} with our estimated value for ω_e(561 cm^{-1}). The value of α_e is obtained from the other constants assuming a Morse potential function. The moment of inertia is 10.266×10^{-39} g cm^2.

SrF^+ has eight valence electrons; thus, the ground state configuration ($^1\Sigma^+$) and electronic level for the B state are estimated from those for the isoelectronic molecule SrS (7). By analogy with the gaseous alkaline earth oxides (10), C_2 (4), BeS (11), and BaS (12), low lying triplet states are to be expected. The two estimated triplet levels are based on those which have been observed directly in C_2 (4), BeS (11), and indirectly (through perturbative effects) in BaS (12). Also included are additional states at 12,000 cm^{-1} ($^1\Pi$), 15,000 cm^{-1} ($^1\Delta$), and 18,000 cm^{-1} ($^1\Sigma$). These three levels are also estimated from those for C_2 (4), BeS (11), and BaS (12). The adopted electronic entropies are believed to represent minimal values. Probable upper limits for the electronic contributions can be established by decreasing the two triplet levels to 1000 cm^{-1} ($^3\Pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy by 3.9 eu and 2.6 eu at 2000 K and 4000 K, respectively. The enthalpy at 0 K is -2.192 kcal/mol.

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FSr^+

Lead Difluoride, Alpha (α-PbF_2) F_2Pb

(Crystal) GFW = 245.1968

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	$-(G°-H°_{298})/T$ (gibbs/mol)	$H°-H°_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	17.270	27.000	27.000	.000	- 161.800	- 150.789	110.531
300	17.300	27.107	27.000	.032	- 161.794	- 150.721	109.800
400	18.180	32.180	27.686	1.798	- 161.450	- 147.080	80.361
500	19.050	36.337	29.013	3.662	- 161.066	- 143.533	62.738
600	19.715	39.864	30.535	5.598	- 160.652	- 140.063	51.018
700	20.500	42.962	32.093	7.608	- 161.363	- 136.476	42.610
800	21.285	45.750	33.629	9.698	- 160.860	- 132.955	36.322
900	22.070	48.303	35.119	11.865	- 160.283	- 129.501	31.447
1000	22.855	50.669	36.557	14.112	- 159.627	- 126.115	27.562

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969; Dec. 31, 1973

LEAD DIFLUORIDE, ALPHA (α-PbF_2) (CRYSTAL) GFW = 245.1968 F_2Pb

$S°_{298.15}$ = [27.0 ± 2.0] gibbs/mol

Tt = 583 ± 1 K

$\Delta Hf°_0$ = unknown

$\Delta Hf°_{298.15}$ = -161.8 ± 1.0 kcal/mol

$\Delta Ht°$ = 0.3496 kcal/mol

Heat of Formation

Heats of formation derived from the enthalpy changes of different chemical reactions are tabulated below. Due to a lack of sample characterization we can only assume from sample preparation that the following reactions involve α-$PbF_2(c)$.

Reference	Chemical Reaction	Type of Data	$\Delta Hr°_{298}$ kcal/mol	$\Delta Hf°_{298}$ kcal/mol
1	$Pb(c) + F_2(g) = PbF_2(\alpha)$	emf	-159.7±0.5	-159.7±0.5
2	$PbO(c) + 2\ HF(40\%\ aq) = PbF_2(\alpha) + H_2O(\ell)$	calor.	- 22.9±0.3	-159.4±0.5
3	$PbF_2(\alpha) + 2\ Na(c) = Pb(c) + 2\ NaF(aq)$	emf	-112.2±0.2	-162.2±0.4
4	$PbF_2(\alpha) + Mg(c) = Pb(c) + MgF_2(c)$	calor.	-109.5±1.5	-159.2±2.0
5	$3/2\ PbF_2(c) + Al(c) = 3/2\ Pb(c) + AlF_3(c)$	calor.	-118.5±0.1	-161.6±1.0
6	$3/2\ PbF_2(c) + Al(c) = 3/2\ Pb(c) + AlF_3(c)$	calor.	-117.7±0.6	-162.2±1.0

The samples used by Gross et al. (4, 5) could easily be β-PbF_2 rather than α-PbF_2. Other reactions (7, 8, 9) have led to values near $\Delta Hf°_{298}$ = -161.8 kcal/mol (10); this value is adopted and is assigned an uncertainty of ±2 kcal/mol.

The adopted heat of formation is supported by measurements (11) of the reaction $PbF_2(c) + Be(c) = BeF_2(c) + Pb(c)$ from which the heat of formation of $BeF_2(c)$ agrees with that from the direct fluorination of beryllium metal if the adopted value for $\Delta Hf°_{298}(PbF_2,\ \alpha)$ is used.

Heat Capacity and Entropy

The enthalpy of α-$PbF_2(c)$ was measured by Linsey (12). Twenty data points (320-728 K) were obtained using a sample encapsulated in gold while fifteen were obtained (370-595 K) using a sample encapsulated in Nichrome V. We adopt the heat capacity values calculated by Linsey (12) and extrapolate linearly to 1000 K. It should be noted, however, that Linsey (12) adjusted his experimental enthalpy for α-$PbF_2(c)$ so that when the orthorhombic sample was heated above Tt, the resulting enthalpy was consistent with the cubic PbF_2 enthalpy.

There is no low temperature heat capacity data for α-$PbF_2(c)$. We estimate $S°_{298}$ = 27.0 ± 2.0 gibbs/mol.

Transition Data

The transition temperature is that obtained by Linsey (12) via enthalpy measurements on orthorhombic PbF_2. When heated above Tt, orthorhombic PbF_2 changes quickly to the cubic form. Upon cooling the transformation is very sluggish.

The heat of transition at room temperature, 240 ± 9 cal/mol, was determined by Linsey (12) by the differences in the heat of solution of the orthorhombic and cubic modifications in 1.0 M $Fe(NO_3)_3$. $\Delta Ht°$ is calculated from this value using the enthalpy differences ($H°_{583}-H°_{298}$) for the cubic and orthorhombic modifications.

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F_2Pb

Lead Difluoride, Beta (β-PbF_2) F_2Pb

(Crystal) GFW = 245.1968

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	17.750	27.351	27.350	.000	- 161.560	- 150.654	110.432
300	17.780	27.460	27.351	.033	- 161.553	- 150.586	109.702
400	18.350	32.650	28.055	1.838	- 161.170	- 146.987	80.310
500	19.260	36.828	29.404	3.712	- 160.776	- 143.488	62.719
600	21.780	40.516	30.952	5.739	- 160.271	- 140.074	51.022
700	35.250	44.653	32.592	8.443	- 160.288	- 136.585	42.644
800	25.320	48.752	34.376	11.501	- 158.817	- 133.313	36.419
900	22.570	51.481	36.131	13.815	- 158.093	- 130.171	31.610
1000	22.570	53.859	37.787	16.072	- 157.427	- 127.105	27.779
1100	22.570	56.010	39.347	18.329	- 156.761	- 124.105	24.657
1200	22.570	57.974	40.819	20.586	- 156.092	- 121.164	22.067
1300	22.570	59.780	42.209	22.843	- 155.424	- 118.281	19.885
1400	22.570	61.453	43.524	25.100	- 154.759	- 115.449	18.022
1500	22.570	63.010	44.772	27.357	- 154.097	- 112.662	16.415

Dec. 31, 1973

LEAD DIFLUORIDE, BETA (β-PbF_2) (CRYSTAL) GFW = 245.1968 F_2Pb

S_{29815} = 27.351

Tt = 583 ± 1 K

Tm = 1103 ± 2 K

$\Delta Hf^\circ_{298.15}$ = -161.56 ± 1.0 kcal/mol

ΔHt° = 0.3496 kcal/mol

ΔHm = 3.52 ± 0.3 kcal/mol

Heat of Formation

Linsey (1) determined the heat of transition at room temperature to be 240 ± 9 cal/mol from heat of solution measurements of the orthorhombic and cubic modifications in 1 M $Fe(NO_3)_3$. We calculate and adopt $\Delta Hf^\circ_{298}(PbF_2, \beta)$ by adding this heat of transition value to the ΔHf°_{298} value for $PbF_2(c, \alpha)$.

Other heat of formation values derived from the enthalpy changes of different chemical reactions are tabulated below. Due to a lack of sample characterization we can only assume from sample preparation and experimental conditions that the following reactions involve β-$PbF_2(c)$.

Reference	Chemical Reaction	Type of Data	ΔHr°_{298} kcal/mol	ΔHf°_{298} kcal/mol
2	$PbF_2(\beta) + H_2(g) = Pb(\ell) + 2\ HF(g)$	Press	32.0	-161.3
3	$PbF_2(\beta) + H_2O(g) = PbO(c) + 2\ HF(g)$	Press	30.06	-154.6
4	$1/2\ PbF_2(\beta) + 1/3\ Al(c) = 1/2\ Pb(\ell) + 1/3\ AlF_3(c)$	emf	-116.39	-162.0

The two studies by Gross et al. (5, 6) may well involve β-PbF_2. Kolesov et al. (7) used two PbF_2 samples which had been fused. These samples should then be in the β-modification. The results are considerably different from those given in the α-PbF_2 table (8) for α-PbF_2.

Heat Capacity and Entropy

Linsey (1) measured the enthalpy of cubic PbF_2. The enthalpy data (61 data points, 321-1164 K) revealed an anomaly in the enthalpy and heat capacity in the range 573-823 K. Linsey (1) interpreted the results in terms of a lambda-type (cooperative) transition in the heat capacity with a maximum at 716 K. We adopt the heat capacity values calculated and reported by Linsey (1).

Banashek et al. (8) measured the high temperature enthalpies (H°_T-$H^\circ_{293.16}$) in the range 670-1165 K. Their data is consistent with the interpretation of Linsey (1).

The entropy is calculated in a manner analogous to that used for ΔHt°.

Melting Data

See $PbF_2(\ell)$ table.

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F_2Pb

Lead Difluoride (PbF_2) F_2Pb

(Liquid) GFW = 245.1968

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	17.750	31.293	31.293	.000	− 147.409	− 123.233	90.332
300	17.780	31.403	31.293	.033	− 147.416	− 123.084	89.666
400	18.350	36.593	31.997	1.838	− 147.802	− 114.914	62.786
500	19.050	40.763	33.346	3.708	− 148.219	− 106.647	46.615
600	19.750	44.298	34.884	5.648	− 148.633	− 98.291	35.803
700	26.100	47.395	36.454	7.658	− 150.195	− 89.678	27.999
800	26.100	50.880	38.045	10.268	− 150.038	− 81.045	22.141
900	26.100	53.954	39.645	12.878	− 149.894	− 72.430	17.588
1000	26.100	56.704	41.216	15.488	− 149.760	− 63.830	13.950
1100	26.100	59.192	42.739	18.098	− 149.633	− 55.244	10.976
1200	26.100	61.463	44.206	20.708	− 149.508	− 46.667	8.499
1300	26.100	63.552	45.615	23.318	− 149.390	− 38.101	6.405
1400	26.100	65.486	46.966	25.928	− 149.279	− 29.546	4.612
1500	26.100	67.287	48.261	28.538	− 149.175	− 20.994	3.059

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969; Dec. 31, 1973

LEAD DIFLUORIDE (PbF_2) (LIQUID) GFW = 245.1968 F_2Pb

$S^\circ_{298.15}$ = [31.293] gibbs/mol

Tm = 1103 ± 4 K

$\Delta Hf^\circ_{298.15}$ = −147.409 kcal/mol

ΔHm° = 3.52 ± 0.5 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298.15}(\ell)$ is obtained from $\Delta Hf^\circ_{298.15}$ for cubic PbF_2 by adding ΔHm° and the difference between $H^\circ_{Tm}-H^\circ_{298.15}$ for the cubic crystal and liquid.

Heat Capacity and Entropy

The enthalpies ($H^\circ-H^\circ_{293.16}$) of $PbF_2(\ell)$ in the temperature range 1104-1165°K were determined by Banashek, Patsukova, and Rassonskaya (1). Based on their reported results the heat capacity of $PbF_2(\ell)$ is evaluated to be 24 ± 2 gibbs/mol by the least square method. Linsey (13) measured the enthalpy of $PbF_2(\ell)$ in the range 1105-1164 K (8 data points) and reported a constant heat capacity value of 26.10 gibbs/mol. We adopt this value and extrapolate to 700 K and 1500 K. A glass transition is assumed at 700 K below which the heat capacity values of cubic PbF_2 are used.

The entropy ($S^\circ_{298.15}$) is calculated in a manner analogous to that of the heat of formation.

Melting Data

Tm and ΔHm° are taken from the enthalpy data of Linsey (13). Our analysis of the enthalpy data of Banashek et al. (1) yields a heat of melting value of 2.98 kcal/mol.

Other values of Tm (°K) reported are 1091 (2, 11), 1097 (3, 4, 5) and 1128 (6). Using the freezing point data of binary systems PbF_2-$PbBr_2$ (5), PbF_2-$PbCl_2$ (5, 7), PbF_2-PbI_2 (5, 8), PbF_2-PbO (9), and PbF_2-NaF (10), Kelley (3) evaluated the corresponding values of ΔHm° (kcal/mol) as 1.70, 1.70, 1.96, 3.87, and 2.47. Other reported values of ΔHm° are 3.00 (1) and 4.16 (2) kcal/mol.

Vaporization Data

From mass spectroscopic study on the vapor species in PbF_2, Zmbov, Hastie, and Margrave (4) have shown that molten PbF_2 vaporizes partly as molecular PbF_2. There is considerable disproportionation, and at 988 K the vapor composition is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb (4, 12). Tb has been reported as 1565 K (11) where the vapor is expected to be a mixture of the above species.

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F_2Pb

Lead Difluoride (PbF_2) F_2Pb

(Ideal Gas) GFW = 245.1968

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.003	-103.249	-103.249	INFINITE
100	9.292	58.309	79.920	-2.161	-103.525	-104.406	228.179
200	11.020	65.290	71.009	-1.144	-103.811	-105.166	114.920
298	12.177	69.928	69.928	.000	-104.000	-105.788	77.545
300	12.193	70.003	69.928	.023	-104.003	-105.799	77.075
400	12.823	73.607	70.415	1.277	-104.171	-106.372	58.119
500	13.173	76.509	71.353	2.578	-104.350	-106.903	46.727
600	13.381	78.931	72.420	3.907	-104.543	-107.394	39.118
700	13.514	81.004	73.502	5.252	-105.919	-107.662	33.614
800	13.603	82.815	74.555	6.608	-106.150	-107.896	29.476
900	13.665	84.421	75.564	7.971	-106.377	-108.101	26.250
1000	13.710	85.863	76.523	9.340	-106.599	-108.281	23.665
1100	13.744	87.171	77.432	10.713	-106.817	-108.439	21.545
1200	13.770	88.368	78.294	12.089	-107.029	-108.575	19.774
1300	13.791	89.471	79.112	13.467	-107.240	-108.695	18.273
1400	13.807	90.494	79.889	14.847	-107.452	-108.800	16.985
1500	13.820	91.447	80.628	16.228	-107.666	-108.887	15.865
1600	13.831	92.339	81.333	17.611	-107.885	-108.963	14.884
1700	13.840	93.178	82.005	18.994	-108.109	-109.022	14.016
1800	13.847	93.969	82.648	20.379	-108.340	-109.072	13.243
1900	13.854	94.718	83.264	21.764	-108.577	-109.106	12.550
2000	13.859	95.429	83.854	23.149	-108.822	-109.126	11.925
2100	13.864	96.105	84.422	24.535	-151.524	-107.584	11.196
2200	13.868	96.750	84.968	25.922	-151.690	-105.488	10.479
2300	13.872	97.367	85.493	27.309	-151.879	-103.383	9.824
2400	13.875	97.957	86.000	28.696	-152.092	-101.270	9.222
2500	13.877	98.524	86.490	30.084	-152.330	-99.149	8.668
2600	13.880	99.068	86.964	31.472	-152.591	-97.016	8.155
2700	13.882	99.592	87.422	32.860	-152.874	-94.872	7.679
2800	13.884	100.097	87.865	34.248	-153.181	-92.720	7.237
2900	13.886	100.584	88.296	35.637	-153.508	-90.552	6.824
3000	13.887	101.055	88.713	37.025	-153.857	-88.378	6.438
3100	13.889	101.510	89.119	38.414	-154.222	-86.190	6.076
3200	13.890	101.951	89.513	39.803	-154.606	-83.989	5.736
3300	13.891	102.379	89.896	41.192	-155.004	-81.776	5.416
3400	13.892	102.793	90.269	42.581	-155.416	-79.549	5.113
3500	13.893	103.196	90.633	43.971	-155.840	-77.311	4.828
3600	13.894	103.588	90.987	45.360	-156.274	-75.060	4.557
3700	13.895	103.968	91.333	46.750	-156.717	-72.798	4.300
3800	13.896	104.339	91.671	48.139	-157.167	-70.522	4.056
3900	13.897	104.700	92.000	49.529	-157.624	-68.239	3.824
4000	13.897	105.052	92.322	50.918	-158.085	-65.943	3.603
4100	13.898	105.395	92.637	52.308	-158.550	-63.634	3.392
4200	13.899	105.730	92.944	53.698	-159.017	-61.311	3.190
4300	13.899	106.057	93.246	55.088	-159.485	-58.980	2.998
4400	13.900	106.376	93.540	56.478	-159.955	-56.635	2.813
4500	13.900	106.689	93.829	57.868	-160.424	-54.285	2.636
4600	13.900	106.994	94.112	59.258	-160.893	-51.920	2.467
4700	13.901	107.293	94.389	60.648	-161.361	-49.548	2.304
4800	13.901	107.586	94.661	62.038	-161.827	-47.158	2.147
4900	13.902	107.872	94.928	63.428	-162.292	-44.767	1.997
5000	13.902	108.153	95.190	64.818	-162.755	-42.366	1.852
5100	13.902	108.429	95.446	66.209	-163.215	-39.956	1.712
5200	13.903	108.699	95.699	67.599	-163.673	-37.529	1.577
5300	13.903	108.963	95.946	68.989	-164.129	-35.097	1.447
5400	13.903	109.223	96.190	70.379	-164.584	-32.663	1.322
5500	13.903	109.478	96.429	71.770	-165.035	-30.215	1.201
5600	13.904	109.729	96.665	73.160	-165.485	-27.757	1.083
5700	13.904	109.975	96.896	74.550	-165.934	-25.297	.970
5800	13.904	110.217	97.123	75.941	-166.379	-22.822	.860
5900	13.904	110.454	97.347	77.331	-166.825	-20.348	.754
6000	13.904	110.688	97.568	78.722	-167.268	-17.863	.651

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969; Dec. 31, 1973.

LEAD DIFLUORIDE (PbF_2) (IDEAL GAS) GFW = 245.1968 F_2Pb

Point Group = C_{2v}

$S°_{298.15}$ = 69.93 ± 0.8 gibbs/mol

Ground State Quantum Weight = [1]

$\Delta Hf°_0$ = -103.2 ± 2 kcal/mol

$\Delta Hf°_{298.15}$ = -104.0 ± 2 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

545.7 (1)
170 (1)
522.5 (1)

Bond Distance: Pb-F = 2.13 ± 0.02 Å Bond Angle: F-Pb-F = [90°] σ = 2

Product of the Moments of Inertia: $I_AI_BI_C = [4.5699 \times 10^{-114}]\ g^3cm^6$

Heat of Formation

Vapor pressure data for PbF_2 have previously been interpreted on the assumption that PbF_2 was the only species present in the gas phase (1, 2). Zmbov, Hastie, and Margrave (3) have studied the vapor species over PbF_2(c, ℓ) mass spectrometrically and shown that PbF_2 vaporizes only partly as molecular PbF_2 and there is considerable disproportionation. The vapor composition at 988 K is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb (3, 4). From extrapolation of the ion intensity data from 1043 to 988 K to the temperature region in which Nesmeyanov and Iofa (2) measured the saturated vapor pressures of PbF_2(c), 792-988 K, by Knudsen effusion method, the partial pressure of PbF_2(g), at 988 K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the heat of sublimation ($\Delta Hs°_{298}$) of PbF_2(c, β) is derived as 57.53 kcal/mol by the third law method, yielding $\Delta Hf°_{298}(PbF_2, g)$ = -104.0 ± 2 kcal/mol.

Due to lack of data on vapor compositions over PbF_2 at various temperatures, the total pressure measurements reported by Wartenberg and Bosse (1), using boiling point method, and those of Nesmeyanov and Iofa (2) are not used for evaluation.

The adopted $\Delta Hf°_{298}$ leads to a dissociation energy $D°_0$ = 8.10 eV for the process $PbF_2(g) = Pb(g) + 2F(g)$, using auxiliary data (5).

Heat Capacity and Entropy

The bond distance was determined by Akishin, Spiridonov, and Khodchenkov (6). The bond angle was estimated by Hauge et al. (7) from a Group IV A difluoride comparison. Hauge et al. (7) determined the vibrational frequencies from the infrared spectra of neon matrix isolated PbF_2(g).

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F_2Pb

Strontium Difluoride (SrF_2)

(Crystal) GFW = 125.6168

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 3.125	- 290.395	- 290.395	INFINITE
100	8.765	5.023	32.907	- 2.788	- 291.073	- 286.906	627.033
200	14.731	13.321	21.105	- 1.557	- 291.132	- 282.687	308.906
298	16.727	19.628	19.628	.000	- 290.900	- 278.581	204.205
300	16.755	19.732	19.628	.031	- 290.895	- 278.505	202.890
400	17.860	24.715	20.300	1.766	- 290.589	- 274.419	149.935
500	18.480	28.771	21.601	3.585	- 290.276	- 270.413	118.197
600	18.840	32.174	23.088	5.452	- 289.983	- 266.468	97.061
700	19.100	35.098	24.599	7.349	- 289.728	- 262.570	81.978
800	19.350	37.664	26.075	9.271	- 289.520	- 258.706	70.675
900	19.680	39.957	27.492	11.218	- 289.526	- 254.849	61.886
1000	20.500	42.071	28.846	13.225	- 289.304	- 251.007	54.858
1100	21.560	44.070	30.140	15.323	- 290.922	- 247.081	49.090
1200	23.200	46.012	31.382	17.556	- 290.426	- 243.115	44.277
1300	26.000	47.959	32.581	19.990	- 289.735	- 239.199	40.213
1400	34.400	50.128	33.755	22.922	- 288.550	- 235.351	36.740
1500	37.000	52.799	34.936	26.795	- 286.428	- 231.623	33.747
1600	30.100	54.923	36.121	30.083	- 284.895	- 228.024	31.147
1700	27.200	56.647	37.280	32.925	- 316.385	- 223.599	28.746
1800	25.650	58.151	38.398	35.555	- 315.175	- 218.178	26.490
1900	24.550	59.507	39.474	38.062	- 314.092	- 212.818	24.480
2000	23.800	60.745	40.507	40.477	- 313.106	- 207.513	22.676
2100	23.350	61.895	41.498	42.833	- 312.185	- 202.258	21.049
2200	23.100	62.975	42.450	45.154	- 311.306	- 197.045	19.575
2300	23.000	63.999	43.365	47.458	- 310.451	- 191.869	18.232
2400	23.000	64.978	44.245	49.758	- 309.610	- 186.732	17.004
2500	23.000	65.917	45.094	52.058	- 308.781	- 181.630	15.878

Dec. 31, 1972

STRONTIUM DIFLUORIDE (SrF_2) (CRYSTAL) GFW = 125.6168

F_2Sr

$S^\circ_{298.15}$ = 19.63 ± 0.05 gibbs/mol
Tt = [1421] K
Tt = [1484] K
Tm = 1750 ± 2 K

ΔHf°_0 = -290.4 ± 0.7 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -290.9 ± 0.7 kcal/mol
ΔHt° = [0.0] kcal/mol
ΔHt° = [0.0] kcal/mol
ΔHm° = 7.092 ± 0.150 kcal/mol
$\Delta H^\circ_{s_{298.15}}$ = 107.8 ± 0.3 kcal/mol

Heat of Formation

Guntz (1) measured the heat of neutralization of $Sr(OH)_2$ (aq) with HF(aq) as ΔH = -35.8 kcal/mol at 284 K. We estimate a ΔCp = 105 gibbs/mol for $Sr(OH)_2 \cdot 555\ H_2O + 2(HF \cdot 110\ H_2O) \rightarrow SrF_2(c) + 2\ H_2O(\ell)$ which gives ΔH_{298} = -34.1 kcal/mol. This value leads to $\Delta Hf^\circ_{298}(SrF_2, c)$ = -291.3 kcal/mol when combined with the following heats of formation: $\Delta Hf^\circ_{298}(H_2O, \ell)$ = -68.315 (2), $\Delta Hf^\circ_{298}(Sr(OH)_2 \cdot 555\ H_2O)$ = -240.1 (3), and $\Delta Hf^\circ_{298}(HF \cdot 110\ H_2O)$ = -76.78 kcal/mol (4).

Petersen (5) measured the heat of precipitation of SrF_2 from an aqueous $SrCl_2$ solution with AgF(aq) as ΔH = -34.5 kcal/mol at 293 K. We estimate a ΔCp = 108 gibbs/mol for $2(AgF \cdot 200\ H_2O) + SrCl_2 \cdot 400\ H_2O \rightarrow SrF_2(c) + 2\ AgCl(c)$ which gives ΔH_{298} = -34.0 kcal/mol. This value leads to $\Delta Hf^\circ_{298}(SrF_2, c)$ = -290.9 kcal/mol when combined with the following heats of formation: $\Delta Hf^\circ_{298}(AgCl, c)$ = -30.37 (6), $\Delta Hf^\circ_{298}(AgF \cdot 200\ H_2O)$ = -53.398 (6), and $\Delta Hf^\circ_{298}(SrCl_2 \cdot 400\ H_2O)$ = -209.871 kcal/mol (3).

Stephen and Stephen (7) have selected as a "best" value for the solubility of SrF_2 0.119 g/ℓ at 298 K which corresponds to $K_{sp} = 3.397 \times 10^{-9}$. Using $\Delta Gf^\circ_{298}(Sr^{+2}, \infty\ aq)$ = -133.71 (3) and $\Delta Gf^\circ_{298}(F^-, \infty\ aq)$ = -66.96 kcal/mol (4), we calculate $\Delta Gf^\circ_{298}(SrF_2, c)$ = -279.18 kcal/mol. Based on the adopted functions for SrF_2, this value gives $\Delta Hf^\circ_{298}(SrF_2, c)$ = -291.5 kcal/mol.

Very recently, Finch et al. (9) measured the heat of precipitation of SrF_2 from an aqueous $SrCl_2$ solution by addition of a slight excess of NaF. X-ray diffraction patterns showed the precipitate to be crystalline SrF_2. Reduction of their data gives ΔH°_{soln} = 0.42 kcal/mol for $SrF_2(c) \rightarrow Sr^{+2}(\infty, aq) + 2\ F^-(\infty, aq)$ from which we obtain $\Delta Hf^\circ_{298}(SrF_2, c)$ = -290.5 ± 0.5 kcal/mol with $\Delta Hf^\circ_{298}(Sr^{+2}, \infty\ aq)$ = -130.45 (3) and $\Delta Hf^\circ_{298}(F^-, \infty\ aq)$ = -79.82 kcal/mol (4).

The adopted heat of formation, $\Delta Hf^\circ_{298}(SrF_2, c)$ = -290.9 ± 0.7 kcal/mol, is a weighted value of these four results. Barany et al. (8) determined the heat of solution of SrO(c) in 20.1 wt % aqueous HF, which contained some dissolved silica, as -65.41 ± 0.30 kcal/mol. We assume this value refers to the process $SrO(c) + 2\ HF \cdot 4.41\ H_2O \rightarrow SrF_2(c) + 2\ H_2O(\ell)$ at 298 K, and we calculate $\Delta Hf^\circ_{298}(SrF_2, c)$ = -291.8 ± 2.0 kcal/mol with $\Delta Hf^\circ_{298}(SrO, c)$ = -141.5 kcal/mol (4). These results substantiate our adopted ΔHf° value.

Heat Capacity and Entropy

Cp below 300 K is based on the low-temperature (11-300 K) heat capacities for SrF_2 reported by Smith et al. (10). The sample purity was 99.9% by petrographic examination. We have fitted a smooth polynomial curve through their data and obtained $S^\circ_{298.15}$ = 19.63 ± 0.05 eu based on $S_{10.9}$ = 0.021 eu.

The only high temperature enthalpy data is that recently reported by Efremova and Matizen (11) in the temperature range 813-2126 K. Spectroscopic analysis showed the SrF_2 sample contained less than 0.04% of foreign metals. A second order transition was observed between the temperatures of 1421 and 1484 K. We adopt their smoothed Cp data in the temperature range 900-1750 K; Cp's above the melting point are obtained by graphical extrapolation. Cp data in the temperature range 300-900 K are estimated graphically by comparison with those for $BaCl_2$ and CaF_2 (4). Cp is assumed constant at 39.5 gibbs/mol over the temperature interval (1421-1484 K) of the transition (see further discussion in Transition Data). The observed enthalpies of Efremova and Matizen (11) deviate from our adopted ones by 1.4% at the lowest temperature (813 K) of their measurements and by only a few tenths of one percent at the higher temperatures.

Transition Data

Efremova and Matizen (11) reported that the phase transition for SrF_2 occurs over a short temperature interval (1421-1484 K). There are no discontinuities in their enthalpy data in this temperature range. Other alkaline earth dihalides (12), which have the calcium fluoride structure, are known to exhibit similar behavior, and this fact would seem to rule out the possibility that the observed transition resulted wholly from impurities. We speculate that the two crystalline forms, α and β, of SrF_2 are practically of the same energy content and can therefore coexist over this temperature interval.

We choose to tentatively adopt two transitions with zero enthalpies, pending resolution of the phases present at these temperatures by X-ray diffraction measurements. The adopted values are placed in brackets above to emphasize that there is no confirmatory evidence for their existence.

Melting Data

Kojima et al. (13) determined the melting point of a SrF_2 sample, which had been purified by passing anhydrous HF through the melt, as 1746 ± 1 K. Porter and Brown (14) found a melting point of 1736 ± 5 K for a sample of 99.8+ % purity, while Petit and Delbove (15) reported 1735 K. The adopted melting point, 1750 ± 2 K, is that determined by Efremova and Matizen (11) in their calorimetric studies of a high purity SrF_2 sample. The heat of melting, 7.092 ± 0.150 kcal/mol, is calculated as the difference between the adopted enthalpies of the liquid and crystal at Tm.

Sublimation Data

See $SrF_2(g)$ table for details.

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F_2Sr

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Strontium Difluoride (SrF_2)

(Liquid) GFW = 125.6168

T, °K	gibbs/mol			kcal/mol			
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	16.725	26.158	26.158	.000	- 280.125	- 269.752	197.734
300	16.755	26.262	26.158	.031	- 280.120	- 269.689	196.468
400	17.860	31.245	26.830	1.766	- 279.814	- 266.256	145.475
500	18.480	35.301	28.132	3.585	- 279.501	- 262.903	114.915
600	18.840	38.704	29.618	5.452	- 279.208	- 259.611	94.563
700	19.100	41.628	31.130	7.349	- 278.953	- 256.366	80.041
800	19.350	44.194	32.605	9.271	- 278.745	- 253.155	69.159
900	19.680	46.487	34.023	11.218	- 278.751	- 249.950	60.696
1000	20.500	48.601	35.376	13.225	- 278.529	- 246.762	53.930
1100	21.560	50.600	36.670	15.323	- 280.147	- 243.489	48.377
1200	23.673	52.542	37.912	17.556	- 279.650	- 240.176	43.742
1300	23.673	54.437	39.111	19.924	- 279.026	- 236.912	39.828
1400	23.673	56.191	40.269	22.291	- 278.406	- 233.696	36.482
1500	23.673	57.825	41.386	24.658	- 277.789	- 230.523	33.587
1600	23.673	59.352	42.461	27.026	- 277.177	- 227.393	31.060
1700	23.673	60.788	43.497	29.393	- 309.142	- 223.394	28.719
1800	23.673	62.141	44.496	31.760	- 308.195	- 218.379	26.515
1900	23.673	63.421	45.459	34.128	- 307.251	- 213.414	24.548
2000	23.673	64.635	46.387	36.495	- 306.313	- 208.499	22.784
2100	23.673	65.790	47.284	38.862	- 305.381	- 203.633	21.192
2200	23.673	66.891	48.150	41.229	- 304.455	- 198.810	19.750
2300	23.673	67.943	48.988	43.597	- 303.537	- 194.027	18.437
2400	23.673	68.951	49.799	45.964	- 302.629	- 189.286	17.237
2500	23.673	69.917	50.585	48.331	- 301.732	- 184.582	16.136
2600	23.673	70.846	51.346	50.699	- 300.848	- 179.913	15.123
2700	23.673	71.739	52.085	53.066	- 299.980	- 175.277	14.188
2800	23.673	72.600	52.802	55.433	- 299.129	- 170.675	13.322
2900	23.673	73.431	53.500	57.801	- 298.299	- 166.101	12.518
3000	23.673	74.233	54.177	60.168	- 297.493	- 161.559	11.770
3100	23.673	75.010	54.837	62.535	- 296.711	- 157.040	11.071
3200	23.673	75.761	55.479	64.902	- 295.958	- 152.547	10.418
3300	23.673	76.490	56.105	67.270	- 295.236	- 148.076	9.807
3400	23.673	77.196	56.715	69.637	- 294.548	- 143.627	9.232
3500	23.673	77.883	57.310	72.004	- 293.895	- 139.196	8.692

Dec. 31, 1972

STRONTIUM DIFLUORIDE (SrF_2) (LIQUID) GFW = 125.6168 F_2Sr

$S^\circ_{298.15}$ = 26.158 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -280.125 kcal/mol

Tm = 1750 ± 2 K

ΔHm° = 7.092 ± 0.150 kcal/mol

Tb = 2759 K

ΔHv° = 76.4 kcal/mol

Heat of Formation

The heat of formation is obtained from that of the crystal by adding the heat of melting and the difference between $H_{1750}-H_{298}$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for liquid SrF_2 is obtained from the enthalpy measurements of Efremova and Matizen (1). Cp is assumed to be constant in the temperature range 1200-3500 K. At 1200 K a glass transition is assumed below which Cp follows that of the crystal. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which ΔGr° = 0 for the vaporization process. The heat of vaporization is the difference in ΔHf°_{Tb} for the liquid and gas.

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F_2Sr

Strontium Difluoride

(Ideal Gas) GFW = 125.6168

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 3.192	- 182.662	- 182.662	INFINITE
100	9.998	57.351	80.239	- 2.289	- 182.774	- 183.839	401.781
200	11.696	64.821	70.827	- 1.201	- 182.976	- 184.832	201.974
298	12.665	69.694	69.694	.000	- 183.100	- 185.708	136.128
300	12.677	69.773	69.694	.023	- 183.103	- 185.725	135.300
400	13.153	73.493	70.198	1.318	- 183.237	- 186.578	101.941
500	13.405	76.457	71.164	2.647	- 183.414	- 187.394	81.910
600	13.551	78.915	72.257	3.995	- 183.640	- 188.170	68.541
700	13.642	81.012	73.361	5.355	- 183.922	- 188.903	58.978
800	13.703	82.838	74.434	6.723	- 184.268	- 189.593	51.794
900	13.746	84.454	75.459	8.095	- 184.849	- 190.219	46.191
1000	13.776	85.904	76.433	9.471	- 185.258	- 190.794	41.698
1100	13.799	87.218	77.354	10.850	- 187.595	- 191.217	37.991
1200	13.817	88.420	78.227	12.231	- 187.951	- 191.530	34.882
1300	13.830	89.526	79.054	13.613	- 188.312	- 191.813	32.247
1400	13.841	90.552	79.839	14.997	- 188.675	- 192.069	29.983
1500	13.850	91.507	80.586	16.382	- 189.041	- 192.298	28.018
1600	13.857	92.401	81.297	17.767	- 189.411	- 192.504	26.295
1700	13.863	93.241	81.975	19.153	- 222.357	- 191.781	24.655
1800	13.868	94.034	82.623	20.540	- 222.390	- 189.982	23.067
1900	13.873	94.784	83.243	21.927	- 222.427	- 188.180	21.646
2000	13.876	95.495	83.838	23.314	- 222.469	- 186.376	20.366
2100	13.879	96.172	84.410	24.702	- 222.516	- 184.572	19.209
2200	13.882	96.818	84.959	26.090	- 222.570	- 182.764	18.156
2300	13.884	97.435	85.488	27.478	- 222.631	- 180.952	17.194
2400	13.887	98.026	85.998	28.867	- 222.701	- 179.139	16.313
2500	13.888	98.593	86.491	30.256	- 222.783	- 177.323	15.502
2600	13.890	99.138	86.967	31.644	- 222.878	- 175.502	14.752
2700	13.891	99.662	87.427	33.034	- 222.987	- 173.677	14.058
2800	13.893	100.167	87.874	34.423	- 223.114	- 171.849	13.413
2900	13.894	100.655	88.306	35.812	- 223.263	- 170.015	12.813
3000	13.895	101.126	88.725	37.202	- 223.434	- 168.178	12.252
3100	13.896	101.582	89.133	38.591	- 223.630	- 166.332	11.726
3200	13.897	102.023	89.529	39.981	- 223.855	- 164.481	11.234
3300	13.898	102.450	89.914	41.370	- 224.111	- 162.621	10.770
3400	13.898	102.865	90.289	42.760	- 224.400	- 160.754	10.333
3500	13.899	103.268	90.654	44.150	- 224.725	- 158.875	9.921
3600	13.900	103.660	91.010	45.540	- 225.087	- 156.988	9.530
3700	13.900	104.041	91.357	46.930	- 225.489	- 155.092	9.161
3800	13.901	104.411	91.695	48.320	- 225.933	- 153.181	8.810
3900	13.901	104.772	92.026	49.710	- 226.421	- 151.264	8.477
4000	13.902	105.124	92.349	51.100	- 226.952	- 149.329	8.159
4100	13.902	105.468	92.665	52.491	- 227.527	- 147.382	7.856
4200	13.902	105.803	92.974	53.881	- 228.148	- 145.420	7.567
4300	13.903	106.130	93.276	55.271	- 228.813	- 143.441	7.290
4400	13.903	106.449	93.572	56.661	- 229.524	- 141.447	7.026
4500	13.903	106.762	93.861	58.052	- 230.277	- 139.439	6.772
4600	13.904	107.067	94.145	59.442	- 231.074	- 137.412	6.529
4700	13.904	107.366	94.423	60.832	- 231.913	- 135.366	6.294
4800	13.904	107.659	94.696	62.223	- 232.790	- 133.301	6.069
4900	13.904	107.946	94.964	63.613	- 233.707	- 131.219	5.853
5000	13.905	108.227	95.226	65.004	- 234.658	- 129.118	5.644
5100	13.905	108.502	95.484	66.394	- 235.645	- 127.001	5.442
5200	13.905	108.772	95.737	67.785	- 236.662	- 124.857	5.248
5300	13.905	109.037	95.985	69.175	- 237.709	- 122.696	5.059
5400	13.905	109.297	96.229	70.566	- 238.783	- 120.520	4.878
5500	13.906	109.552	96.469	71.956	- 239.882	- 118.318	4.702
5600	13.906	109.803	96.705	73.347	- 241.002	- 116.096	4.531
5700	13.906	110.049	96.937	74.737	- 242.143	- 113.856	4.365
5800	13.906	110.291	97.165	76.128	- 243.299	- 111.595	4.205
5900	13.906	110.528	97.390	77.519	- 244.471	- 109.317	4.049
6000	13.906	110.762	97.610	78.909	- 245.657	- 107.016	3.898

Dec. 31, 1972

STRONTIUM DIFLUORIDE (SrF_2) (IDEAL GAS) GFW = 125.6168 F_2Sr

Point Group = C_{2v}

ΔHf°_0 = -182.7 ± 1.0 kcal/mol

$S^\circ_{298.15}$ = 69.69 ± 0.50 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -183.1 ± 1.0 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
442 (1)
82 (1)
443 (1)

Bond Distance: Sr-F = 2.20 ± 0.03 Å

Bond Angle: F-Sr-F = 108°

σ = 2

Product of Moments of Inertia: $I_AI_BI_C = 4.0212 \times 10^{-114}\ g^3cm^6$

Heat of Formation

ΔHf is obtained from that of the crystal by addition of the adopted ΔH°_s = 107.8 ± 0.3 kcal/mol. Second and third law analyses of four sets of vapor pressure data for SrF_2(c, ℓ) are listed below.

Investigator	Method	Temp. Range, K	ΔH°_s, kcal/mol 2nd Law	ΔH°_s, kcal/mol 3rd Law	Drift eu	ΔHf°_{298} kcal/mol
Ruff and Le Boucher (1)	Dynamic B.P.	2095-2232	106.4[a]	96.1±0.8[a]	-4.8±3.1	-184.0±1.5
Bautista and Margrave (2)	Langmuir	1235-1319	104.5	108.0±0.5	2.8±2.9	-182.9±1.2
Green et al. (3)	Knudsen	1207-1563[b]	107.9	107.8±0.3	-0.07±0.38	-183.1±1.0
Hildenbrand (4)	Torsion-Effusion	1420-1710	103.8	106.5±0.4	1.7	-184.4±1.1

[a] ΔH°_v(298 K)

[b] Six of the 30 experimental points were rejected due to failure of a statistical test.

Note that the drifts are both positive and negative indicating the correctness of the functions used in the analysis. A weighted value of these four results is adopted.

Heat Capacity and Entropy

The bond length is that measured by Akishin and Spiridonov (5) in their high-temperature electron diffraction studies of the alkaline earth dihalide vapors. Although it was inferred from these measurements that all the dihalides are linear, recent results of electric-deflection experiments (6) and matrix isolation infrared spectra (1, 8) for SrF_2 can only be satisfactorily interpreted in terms of a molecule with a bent configuration. We adopt the vibrational frequencies and bond angle determined by Calder et al. (8) in their thorough investigation of the infrared spectra of isotopically enriched samples of SrF_2 trapped in krypton matrices. The uncertainty assigned to the entropy reflects possible errors due to matrix-shift effects in these frequencies. The adopted symmetric (ν_1) and antisymmetric (ν_3) stretching frequencies are in reasonable agreement with those determined by Snelson (7) for SrF_2 trapped in neon, argon, and krypton matrices. Also, the antisymmetric frequency is quite consistent with the value 455 ± 7 cm^{-1} observed by Baikov (9) in the infrared spectra of SrF_2 vapor at 2050 K. In an earlier paper, Baikov (10) reported observing under similar conditions a broad absorption band at 105 cm^{-1} which he assigned to the symmetric bending (ν_2) mode of SrF_2. We prefer the matrix value (82 cm^{-1}), since Baikov (10) recorded only the high-frequency (>90 cm^{-1}) portion of this band. Furthermore, Hastie et al. (11) have pointed out that in general bending frequencies are less influenced by matrix effects and in some cases may be shifted slightly upwards from the gas phase values.

The individual moments of inertia are: $I_A = 27.844 \times 10^{-39}$, $I_B = 19.985 \times 10^{-39}$, and $I_C = 7.359 \times 10^{-39}\ g\ cm^2$.

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F_2Sr

Lead Tetrafluoride (PbF_4) F_4Pb

(Ideal Gas) GFW = 283.1936

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-4.723	-269.759	-269.759	INFINITE
100	14.233	60.069	97.042	-3.697	-270.546	-267.534	584.695
200	19.018	71.553	81.618	-2.013	-270.865	-264.364	288.883
298	21.734	79.706	79.706	.000	-270.900	-261.159	191.435
300	21.771	79.841	79.706	.040	-270.900	-261.099	190.210
400	23.249	86.328	80.581	2.299	-270.833	-257.839	140.877
500	24.075	91.613	82.275	4.669	-270.750	-254.603	111.287
600	24.570	96.050	84.211	7.103	-270.670	-251.379	91.565
700	24.885	99.862	86.181	9.577	-271.768	-247.978	77.422
800	25.097	103.200	88.104	12.077	-271.721	-244.585	66.817
900	25.246	106.165	89.949	14.594	-271.670	-241.195	58.570
1000	25.354	108.831	91.707	17.124	-271.616	-237.813	51.974
1100	25.435	111.251	93.375	19.664	-271.559	-234.435	46.578
1200	25.497	113.467	94.958	22.211	-271.497	-231.061	42.082
1300	25.546	115.510	96.462	24.763	-271.437	-227.693	38.279
1400	25.585	117.405	97.891	27.320	-271.379	-224.332	35.020
1500	25.617	119.171	99.251	29.880	-271.325	-220.970	32.195
1600	25.643	120.825	100.548	32.443	-271.279	-217.617	29.725
1700	25.664	122.381	101.787	35.008	-271.239	-214.262	27.545
1800	25.682	123.848	102.973	37.576	-271.209	-210.917	25.609
1900	25.698	125.237	104.108	40.145	-271.186	-207.567	23.876
2000	25.711	126.555	105.198	42.715	-271.173	-204.216	22.316
2100	25.722	127.810	106.245	45.287	-313.619	-199.319	20.743
2200	25.732	129.007	107.253	47.859	-313.533	-193.879	19.260
2300	25.740	130.151	108.224	50.433	-313.470	-188.440	17.906
2400	25.748	131.247	109.160	53.007	-313.434	-183.005	16.665
2500	25.755	132.298	110.065	55.583	-313.425	-177.573	15.523
2600	25.760	133.308	110.939	58.158	-313.442	-172.137	14.469
2700	25.766	134.280	111.786	60.735	-313.481	-166.700	13.493
2800	25.770	135.218	112.606	63.311	-313.547	-161.264	12.587
2900	25.775	136.122	113.402	65.889	-313.635	-155.820	11.743
3000	25.778	136.996	114.174	68.466	-313.748	-150.382	10.955
3100	25.782	137.841	114.924	71.044	-313.878	-144.934	10.218
3200	25.785	138.660	115.653	73.623	-314.029	-139.481	9.526
3300	25.788	139.453	116.362	76.201	-314.197	-134.024	8.876
3400	25.791	140.223	117.052	78.780	-314.380	-128.560	8.264
3500	25.793	140.971	117.725	81.359	-314.579	-123.089	7.686
3600	25.795	141.697	118.381	83.939	-314.787	-117.613	7.140
3700	25.797	142.404	119.021	86.518	-315.009	-112.134	6.623
3800	25.799	143.092	119.645	89.098	-315.238	-106.645	6.133
3900	25.801	143.762	120.255	91.678	-315.478	-101.158	5.669
4000	25.802	144.416	120.851	94.258	-315.722	-95.660	5.227
4100	25.804	145.053	121.433	96.839	-315.973	-90.156	4.806
4200	25.805	145.675	122.003	99.419	-316.229	-84.643	4.404
4300	25.806	146.282	122.561	102.000	-316.486	-79.125	4.022
4400	25.808	146.875	123.107	104.581	-316.749	-73.601	3.656
4500	25.809	147.455	123.641	107.161	-317.013	-68.077	3.306
4600	25.810	148.022	124.165	109.742	-317.278	-62.540	2.971
4700	25.811	148.577	124.679	112.323	-317.545	-57.002	2.651
4800	25.812	149.121	125.182	114.904	-317.811	-51.448	2.342
4900	25.813	149.653	125.676	117.486	-318.078	-45.898	2.047
5000	25.813	150.175	126.161	120.067	-318.346	-40.343	1.763
5100	25.814	150.686	126.637	122.648	-318.614	-34.787	1.491
5200	25.815	151.187	127.104	125.230	-318.880	-29.209	1.228
5300	25.816	151.679	127.563	127.811	-319.147	-23.633	.975
5400	25.816	152.161	128.014	130.393	-319.415	-18.064	.731
5500	25.817	152.635	128.458	132.975	-319.681	-12.479	.496
5600	25.817	153.100	128.894	135.556	-319.949	-6.887	.269
5700	25.818	153.557	129.322	138.138	-320.217	-1.297	.050
5800	25.818	154.006	129.744	140.720	-320.483	4.305	-.162
5900	25.819	154.448	130.159	143.302	-320.752	9.899	-.367
6000	25.819	154.881	130.567	145.884	-321.021	15.504	-.565

June 30, 1962; Dec. 31, 1973.

LEAD TETRAFLUORIDE (PbF_4) (IDEAL GAS) GFW = 283.1936 F_4Pb

Point Group = [T_d]

$S^\circ_{298.15}$ = [79.71 ± 3.0] gibbs/mol

ΔHf°_0 = -269.8 ± 5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -270.9 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[564] (1)
[158] (2)
[570] (3)
[180] (3)

Bond Distance: Pb-F = [2.08] Å

Bond Angle: F-Pb-F = [109° 28'] σ = 12

Product of Moments of Inertia: $I_AI_BI_C$ = [4.8233×10^{-113}] g^3cm^6

Heat of Formation

A third law analysis of the partial pressure data at 988 K reported by Zmbov et al. (1) for the equilibrium 2 $PbF_2(g) = PbF_4(g) + Pb(g)$ gives ΔHr°_{298} = -16.15 kcal/mol. There are inconsistencies in the published results but the partial pressure data are correctly given (2). The second law heat of reaction derived by Zmbov et al. (1) from a graphical plot of six ion current quotient values vs. reciprocal temperature (approximately 1020 to 1110 K), when corrected to 298 K, is in agreement with the third law value of -16.15 kcal/mol. Combining this heat of reaction with $\Delta Hf^\circ_{298}(PbF_2, g)$ = -104.0 ± 1 kcal/mol (3) and ΔHf°_{298}(Pb, g) = 46.75 ± 0.13 kcal/mol (3) gives the adopted $\Delta Hf^\circ_{298}(PbF_4, g)$ = -270.9 ± 5 kcal/mol. The adopted heat of formation leads to a dissociation energy D°_0 = 16.96 eV for the process $PbF_4(g) = Pb(g) + 4\ F(g)$. This is consistent with D°_0 = 8.10 eV for $PbF_2(g)$ (3) and D°_0 = 3.64 eV for PbF(g) (3).

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya et al. (4). Later works (5, 6, 7) mistakenly cite this work as observed data. A band at 663 cm^{-1} was recently observed in an infrared study by Hauge et al. (8) and was assigned to matrix isolated PbF_4. Calculation with infrared active ν_3 = 663 cm^{-1} rather than 570 cm^{-1} decreases S°_{298} by 0.45 eu. Only the calculated frequencies are used for the present table pending more complete observation.

References

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F_4Pb

Hydrogen Monatomic (H) H

(Ideal Gas) GFW = 1.008

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.481	51.634	51.634	INFINITE
100	4.968	21.964	31.808	- .984	51.751	50.774	- 110.967
200	4.968	25.408	27.846	- .488	51.946	49.717	- 54.328
298	4.968	27.391	27.391	.000	52.103	48.589	- 35.616
300	4.968	27.422	27.391	.009	52.106	48.567	- 35.381
400	4.968	28.851	27.586	.506	52.255	47.364	- 25.879
500	4.968	29.960	27.954	1.003	52.403	46.124	- 20.161
600	4.968	30.866	28.366	1.500	52.550	44.855	- 16.338
700	4.968	31.631	28.779	1.996	52.695	43.561	- 13.600
800	4.968	32.295	29.178	2.493	52.839	42.246	- 11.541
900	4.968	32.880	29.558	2.990	52.980	40.914	- 9.935
1000	4.968	33.403	29.917	3.487	53.118	39.565	- 8.647
1100	4.968	33.877	30.255	3.984	53.252	38.204	- 7.590
1200	4.968	34.309	30.575	4.480	53.381	36.830	- 6.708
1300	4.968	34.707	30.878	4.977	53.506	35.446	- 5.959
1400	4.968	35.075	31.165	5.474	53.626	34.052	- 5.316
1500	4.968	35.418	31.437	5.971	53.740	32.650	- 4.757
1600	4.968	35.738	31.696	6.467	53.847	31.240	- 4.267
1700	4.968	36.039	31.943	6.964	53.951	29.824	- 3.834
1800	4.968	36.323	32.178	7.461	54.049	28.402	- 3.448
1900	4.968	36.592	32.404	7.958	54.143	26.975	- 3.103
2000	4.968	36.847	32.619	8.455	54.232	25.543	- 2.791
2100	4.968	37.089	32.827	8.951	54.317	24.106	- 2.509
2200	4.968	37.320	33.026	9.448	54.398	22.665	- 2.252
2300	4.968	37.541	33.217	9.945	54.475	21.221	- 2.016
2400	4.968	37.753	33.402	10.442	54.548	19.775	- 1.801
2500	4.968	37.955	33.580	10.939	54.618	18.323	- 1.602
2600	4.968	38.150	33.752	11.435	54.684	16.871	- 1.418
2700	4.968	38.338	33.918	11.932	54.748	15.415	- 1.248
2800	4.968	38.518	34.079	12.429	54.808	13.956	- 1.089
2900	4.968	38.693	34.236	12.926	54.866	12.498	- .942
3000	4.968	38.861	34.387	13.423	54.921	11.035	- .804
3100	4.968	39.024	34.534	13.919	54.973	9.571	- .675
3200	4.968	39.182	34.677	14.416	55.023	8.106	- .554
3300	4.968	39.335	34.816	14.913	55.070	6.639	- .440
3400	4.968	39.483	34.951	15.410	55.116	5.170	- .332
3500	4.968	39.627	35.082	15.907	55.158	3.701	- .231
3600	4.968	39.767	35.210	16.403	55.198	2.230	- .135
3700	4.968	39.903	35.335	16.900	55.236	.759	- .045
3800	4.968	40.036	35.457	17.397	55.271	- .714	.041
3900	4.968	40.165	35.576	17.894	55.304	- 2.188	.123
4000	4.968	40.290	35.693	18.390	55.335	- 3.662	.200
4100	4.968	40.413	35.806	18.887	55.364	- 5.138	.274
4200	4.968	40.533	35.917	19.384	55.390	- 6.613	.344
4300	4.968	40.650	36.026	19.881	55.414	- 8.091	.411
4400	4.968	40.764	36.133	20.378	55.437	- 9.568	.475
4500	4.968	40.876	36.237	20.874	55.456	- 11.047	.536
4600	4.968	40.985	36.339	21.371	55.475	- 12.523	.595
4700	4.968	41.092	36.439	21.868	55.491	- 14.001	.651
4800	4.968	41.196	36.537	22.365	55.505	- 15.480	.705
4900	4.968	41.299	36.633	22.862	55.517	- 16.959	.756
5000	4.968	41.399	36.727	23.358	55.527	- 18.439	.806
5100	4.968	41.497	36.820	23.855	55.536	- 19.918	.854
5200	4.968	41.594	36.911	24.352	55.542	- 21.398	.899
5300	4.968	41.688	37.000	24.849	55.547	- 22.876	.943
5400	4.968	41.781	37.088	25.346	55.550	- 24.358	.986
5500	4.968	41.872	37.174	25.842	55.551	- 25.837	1.027
5600	4.968	41.962	37.258	26.339	55.551	- 27.318	1.066
5700	4.968	42.050	37.342	26.836	55.548	- 28.796	1.104
5800	4.968	42.136	37.424	27.333	55.544	- 30.277	1.141
5900	4.968	42.221	37.504	27.830	55.539	- 31.756	1.176
6000	4.968	42.305	37.584	28.326	55.531	- 33.236	1.211

Dec. 31, 1960; Sept. 30, 1965; June 30, 1974

HYDROGEN MONATOMIC (H) (IDEAL GAS) GFW = 1.0080 H

Ground State Configuration $^2S_{1/2}$

$S^\circ_{298.15}$ = 27.391 ± 0.004 gibbs/mol

ΔHf°_0 = 51.634 ± 0.001 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 52.103 ± 0.001 kcal/mol

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for ΔHf°_{298}(H, g) was derived using $D^\circ_0(H_2)$ = 36118.3 ± 1 cm^{-1}(103.267 ± 0.001 kcal/mol) from Herzberg (2).

Other experimental values for $D^\circ_0(H_2)$ were obtained by Herzberg and Monfils (36113.0 ± 0.3 cm^{-1}, 3) and Beutler (36116 ± 6 cm^{-1}, 4).

Heat Capacity and Entropy

The electronic levels for H(g) are given in the compilation by Moore (5). We include only the ground state in our calculations as the remaining levels lie above 80000 cm^{-1} and do not contribute to the values of the thermodynamic functions below 6000 K. The calculated value of S°_{298} agrees with that adopted by CODATA (1).

References

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5. C. E. Moore, U.S. Natl. Bur. Std., Circ. 467, 1949.

H

Iodine Monatomic (I)

I

(Ideal Gas) GFW = 126.9045

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.481	25.613	25.613	INFINITE
100	4.968	37.755	47.599	- .984	25.745	22.699	- 49.608
200	4.968	41.199	43.636	- .488	25.653	19.683	- 21.508
298	4.968	43.182	43.182	.000	25.517	16.780	- 12.300
300	4.968	43.213	43.182	.009	25.514	16.726	- 12.185
400	4.968	44.642	43.377	.506	23.425	13.889	- 7.588
500	4.968	45.751	43.745	1.003	18.160	12.004	- 5.247
600	4.968	46.656	44.157	1.500	18.209	10.768	- 3.922
700	4.968	47.422	44.570	1.996	18.256	9.524	- 2.974
800	4.968	48.086	44.969	2.493	18.302	8.274	- 2.260
900	4.969	48.671	45.348	2.990	18.347	7.018	- 1.704
1000	4.970	49.194	45.707	3.487	18.391	5.757	- 1.258
1100	4.973	49.668	46.046	3.984	18.435	4.491	- .892
1200	4.977	50.101	46.366	4.482	18.478	3.221	- .587
1300	4.983	50.500	46.669	4.980	18.522	1.948	- .328
1400	4.992	50.869	46.956	5.478	18.564	.672	- .105
1500	5.004	51.214	47.229	5.978	18.608	- .608	.089
1600	5.018	51.537	47.488	6.479	18.652	- 1.890	.258
1700	5.034	51.842	47.735	6.982	18.696	- 3.175	.408
1800	5.052	52.130	47.971	7.486	18.742	- 4.463	.542
1900	5.072	52.404	48.197	7.992	18.789	- 5.753	.662
2000	5.093	52.665	48.414	8.500	18.837	- 7.047	.770
2100	5.114	52.914	48.623	9.011	18.887	- 8.342	.868
2200	5.137	53.152	48.823	9.523	18.938	- 9.640	.958
2300	5.160	53.381	49.016	10.038	18.991	- 10.940	1.040
2400	5.182	53.601	49.203	10.555	19.045	- 12.242	1.115
2500	5.204	53.813	49.383	11.074	19.101	- 13.548	1.184
2600	5.226	54.017	49.557	11.596	19.158	- 14.855	1.249
2700	5.247	54.215	49.726	12.120	19.217	- 16.164	1.308
2800	5.267	54.406	49.890	12.645	19.277	- 17.475	1.364
2900	5.286	54.591	50.049	13.173	19.339	- 18.788	1.416
3000	5.304	54.771	50.203	13.702	19.401	- 20.105	1.465
3100	5.321	54.945	50.354	14.234	19.465	- 21.423	1.510
3200	5.336	55.114	50.500	14.766	19.530	- 22.743	1.553
3300	5.351	55.279	50.642	15.301	19.595	- 24.064	1.594
3400	5.364	55.439	50.781	15.837	19.662	- 25.389	1.632
3500	5.376	55.594	50.916	16.374	19.729	- 26.714	1.668
3600	5.387	55.746	51.048	16.912	19.796	- 28.042	1.702
3700	5.397	55.894	51.177	17.451	19.863	- 29.373	1.735
3800	5.406	56.038	51.303	17.991	19.932	- 30.704	1.766
3900	5.414	56.178	51.426	18.532	20.000	- 32.037	1.795
4000	5.420	56.315	51.547	19.074	20.068	- 33.373	1.823
4100	5.426	56.449	51.665	19.616	20.136	- 34.708	1.850
4200	5.431	56.580	51.780	20.159	20.204	- 36.047	1.876
4300	5.436	56.708	51.893	20.702	20.272	- 37.389	1.900
4400	5.439	56.833	52.004	21.246	20.339	- 38.731	1.924
4500	5.442	56.955	52.113	21.790	20.406	- 40.072	1.946
4600	5.444	57.075	52.219	22.334	20.473	- 41.417	1.968
4700	5.445	57.192	52.324	22.879	20.539	- 42.764	1.989
4800	5.446	57.307	52.427	23.423	20.605	- 44.111	2.008
4900	5.446	57.419	52.527	23.968	20.670	- 45.460	2.028
5000	5.446	57.529	52.626	24.513	20.734	- 46.810	2.046
5100	5.446	57.637	52.724	25.057	20.798	- 48.162	2.064
5200	5.444	57.742	52.819	25.602	20.861	- 49.516	2.081
5300	5.443	57.846	52.913	26.146	20.923	- 50.869	2.098
5400	5.441	57.948	53.005	26.690	20.984	- 52.223	2.114
5500	5.439	58.048	53.096	27.234	21.045	- 53.580	2.129
5600	5.437	58.146	53.185	27.778	21.104	- 54.939	2.144
5700	5.434	58.242	53.273	28.322	21.163	- 56.297	2.159
5800	5.431	58.336	53.360	28.865	21.220	- 57.656	2.173
5900	5.428	58.429	53.445	29.408	21.277	- 59.017	2.186
6000	5.425	58.520	53.529	29.951	21.333	- 60.377	2.199

Dec. 31, 1961; June 30, 1974

IODINE MONATOMIC (I) (IDEAL GAS) GFW = 126.9045 I

Ground State Configuration $^3P_{3/2}$

$S^\circ_{298.15}$ = 43.182 ± 0.005 gibbs/mol

ΔHf°_0 = 25.613 ± 0.010 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 25.517 ± 0.010 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^3P_{3/2}$	0	4
$^3P_{1/2}$	7603.15	2

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for ΔHf°_{298}(I, g) was derived using $D^\circ_0(I_2)$ = 12440.9 ± 1.1 cm^{-1}(35.5700 ± 0.0031 kcal/mol) from LeRoy (2), LeRoy and Berstein (3), and Brown (4). LeRoy (2), LeRoy and Berstein (3), and a recent work by LeRoy and Berstein (5) obtained the dissociation energy from the analysis of the distribution of the uppermost vibrational levels. Their calculations were based on the data of Brown (4), with reference to the study by Verma (6).

The adopted ΔHf° value differs by 0.02 kcal/mol from the previous JANAF value (7).

Heat Capacity and Entropy

The electronic levels for I(g) are those given in the compilation by Moore (8). We do not include the levels which lie above 54000 cm^{-1} as they do not contribute to the values of the thermodynamic functions below 5000 K. Inclusion of these higher levels reduces the heat capacity by 0.004 gibbs/mol at 6000 K. The calculated value of S°_{298} agrees with that adopted by CODATA (1). The S°_{298} value is also 0.002 gibbs/mol less than the previous JANAF value (7).

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2. R. J. LeRoy, J. Chem. Phys. 52, 2678 (1970).
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8. C. E. Moore, U.S. Natl. Bur. Std., Circ. 467, 1949.

I

IPb

Lead Monoiodide (PbI)
(Ideal Gas) GFW = 334.1045

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°$_{298}$)/T (gibbs/mol)	H°−H°$_{298}$ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.471	26.500	26.500	INFINITE
100	8.265	57.466	74.711	-1.724	26.459	22.322	-48.784
200	8.759	63.393	67.726	-.867	26.125	18.310	-20.009
298	8.880	66.917	66.917	.000	25.750	14.553	-10.668
300	8.881	66.972	66.917	.016	25.743	14.484	-10.552
400	8.934	69.535	67.266	.907	23.396	10.862	-5.935
500	8.965	71.532	67.927	1.803	17.856	8.258	-3.610
600	8.987	73.168	68.668	2.700	17.615	6.362	-2.317
700	9.005	74.555	69.413	3.600	16.195	4.697	-1.466
800	9.020	75.758	70.132	4.501	15.925	3.073	-.840
900	9.035	76.822	70.818	5.404	15.662	1.482	-.360
1000	9.050	77.774	71.466	6.308	15.408	-.079	.017
1100	9.066	78.638	72.080	7.214	15.161	-1.617	.321
1200	9.083	79.427	72.660	8.121	14.923	-3.130	.570
1300	9.103	80.155	73.209	9.030	14.692	-4.625	.778
1400	9.127	80.831	73.729	9.942	14.462	-6.103	.953
1500	9.154	81.461	74.224	10.856	14.236	-7.563	1.102
1600	9.186	82.053	74.695	11.773	14.008	-9.009	1.231
1700	9.221	82.611	75.144	12.693	13.782	-10.440	1.342
1800	9.261	83.139	75.574	13.617	13.553	-11.860	1.440
1900	9.303	83.641	75.985	14.545	13.324	-13.266	1.526
2000	9.349	84.119	76.380	15.478	13.094	-14.660	1.602
2100	9.398	84.576	76.760	16.415	-29.588	-14.488	1.508
2200	9.448	85.015	77.125	17.358	-29.727	-13.767	1.368
2300	9.500	85.436	77.477	18.305	-29.882	-13.038	1.239
2400	9.553	85.841	77.817	19.258	-30.054	-12.301	1.120
2500	9.607	86.233	78.146	20.216	-30.245	-11.559	1.011
2600	9.661	86.610	78.464	21.179	-30.451	-10.808	.908
2700	9.714	86.976	78.773	22.148	-30.673	-10.048	.813
2800	9.767	87.330	79.072	23.122	-30.913	-9.279	.724
2900	9.820	87.674	79.363	24.101	-31.166	-8.501	.641
3000	9.871	88.008	79.646	25.086	-31.432	-7.716	.562
3100	9.922	88.332	79.921	26.076	-31.710	-6.921	.488
3200	9.972	88.648	80.188	27.070	-31.999	-6.117	.418
3300	10.021	88.956	80.449	28.070	-32.296	-5.302	.351
3400	10.069	89.255	80.704	29.075	-32.601	-4.480	.288
3500	10.115	89.548	80.953	30.084	-32.912	-3.648	.228
3600	10.161	89.834	81.195	31.098	-33.227	-2.807	.170
3700	10.206	90.113	81.433	32.116	-33.546	-1.959	.116
3800	10.250	90.385	81.665	33.139	-33.864	-1.099	.063
3900	10.292	90.652	81.892	34.166	-34.184	-.232	.013
4000	10.334	90.913	82.114	35.197	-34.502	.637	-.035
4100	10.375	91.169	82.332	36.233	-34.818	1.523	-.081
4200	10.416	91.419	82.545	37.272	-35.132	2.415	-.126
4300	10.455	91.665	82.754	38.316	-35.442	3.308	-.168
4400	10.494	91.906	82.960	39.363	-35.747	4.215	-.209
4500	10.532	92.142	83.161	40.415	-36.046	5.126	-.249
4600	10.570	92.374	83.359	41.470	-36.341	6.046	-.287
4700	10.606	92.602	83.553	42.528	-36.628	6.966	-.324
4800	10.643	92.825	83.744	43.591	-36.909	7.902	-.360
4900	10.678	93.045	83.931	44.657	-37.184	8.836	-.394
5000	10.713	93.261	84.116	45.727	-37.452	9.777	-.427
5100	10.747	93.474	84.297	46.800	-37.712	10.724	-.460
5200	10.781	93.683	84.476	47.876	-37.966	11.677	-.491
5300	10.814	93.888	84.651	48.956	-38.212	12.637	-.521
5400	10.847	94.091	84.824	50.039	-38.452	13.600	-.550
5500	10.878	94.290	84.995	51.125	-38.685	14.562	-.579
5600	10.910	94.486	85.162	52.214	-38.911	15.532	-.606
5700	10.941	94.680	85.328	53.307	-39.132	16.504	-.633
5800	10.971	94.870	85.491	54.403	-39.346	17.486	-.659
5900	11.000	95.058	85.651	55.501	-39.554	18.466	-.684
6000	11.029	95.243	85.809	56.603	-39.757	19.450	-.708

June 30, 1962; Dec. 31, 1973

LEAD MONOIODIDE (PbI) (IDEAL GAS) GFW = 334.1045 IPb

Ground State Configuration $^2\Pi_{1/2}$

$S^\circ_{298.15}$ = 66.92 ± 0.05 gibbs/mol

ΔHf°_0 = 26.50 ± 9 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 25.75 ± 9 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8300]	2
A [$^2\Delta$]	20528.5	[4]
B [$^2\Sigma$]	33488	[2]

ω_e = 160.5 cm^{-1} $\omega_e x_e$ = 0.25 cm^{-1} σ = 1

B_e = [0.02861] cm^{-1} α_e = [0.00006] cm^{-1} r_e = [2.736] Å

Heat of Formation

ΔHf°_0(PbI, g) = 26.50 ± 9 kcal/mol is calculated from D°_0 = 46 ± 9 kcal/mol with ΔHf° (Pb, g) = 46.91 ± 0.13 kcal/mol (1) and ΔHf°_0(I, g) = 25.633 kcal/mol (1). The dissociation energy is uncertain. Both Rosen (2) and Gaydon (3) referred to the most probable value of D°_0 = 1.98 eV determined by Wieland and Newburgh (4) from emission and absorption spectra. Interpretation is difficult and Wieland and Newburgh (4, 5) have given possible values of 2.84, 1.98, and 1.36 eV with 1.98 eV given as the most probable value. The linear Birge-Sponer extrapolation of the adopted ground state vibrational constants, derived from emission and absorption spectra (v, 0-36) (5), gives a dissociation energy of 3.18 eV. Correction for the ionic character of PbI as suggested by Hildenbrand (6) gives D°_0 = 2.7 eV (62.3 kcal/mol). This is in better agreement with the original D°_0 = 2.84 eV given by Wieland and Newburgh (5) than it is with D°_0 = 1.98 eV recommended later (4). An intercomparison of the dissociation energies of lead (1), mercury (2), and potassium (1) halides suggests a D°_0 value near 45 kcal/mol. The rounded value D°_0 = 2.0 ± 0.4 eV (46 ± 9 kcal/mol) listed by Gaydon (3) is adopted. $\Delta Hf^\circ_{298.15}$(PbI, g) = 25.75 ± 9 kcal/mol is calculated from the selected ΔHf°_0 (PbI, g) = 26.5 ± 9 kcal/mol.

Heat Capacity and Entropy

The vibrational constants are taken from the compilation of Rosen (2). The electronic states and levels are from Rosen (2) except that the $^2\Pi_{3/2}$ state at 8300 cm^{-1} is added in analogy to PbF (1) and PbCl (1). The value of r_e = 2.736 Å is estimated from a comparison of the sums of the ionic radii of the lead halides with the adopted r_e values for PbF, PbCl, and PbBr (1). B_e is calculated from the adopted r_e. The value for α_e is estimated assuming a Morse potential function.

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IPb

Strontium Monoiodide (SrI)

(Ideal Gas) GFW = 214.5245

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.459	-6.650	-6.650	INFINITE
100	8.181	55.625	72.807	-1.718	-6.594	-10.827	23.663
200	8.733	61.515	65.842	-.865	-6.920	-14.954	16.340
298	8.875	65.033	65.033	.00C	-7.288	-18.813	13.790
300	8.877	65.088	65.034	.016	-7.296	-18.885	13.757
400	8.940	67.652	65.383	.908	-9.650	-22.616	12.357
500	8.978	69.651	66.044	1.804	-15.214	-25.324	11.069
600	9.005	71.290	66.786	2.703	-15.506	-27.320	9.951
700	9.028	72.680	67.531	3.604	-15.844	-29.264	9.136
800	9.048	73.887	68.252	4.508	-16.239	-31.154	8.511
900	9.067	74.954	68.938	5.414	-16.862	-32.977	8.008
1000	9.085	75.910	69.588	6.322	-17.307	-34.743	7.593
1100	9.102	76.777	70.203	7.231	-19.675	-36.355	7.223
1200	9.118	77.569	70.784	8.142	-20.059	-37.854	6.894
1300	9.135	78.300	71.335	9.055	-20.441	-39.321	6.610
1400	9.151	78.977	71.857	9.969	-20.822	-40.759	6.363
1500	9.168	79.609	72.353	10.885	-21.203	-42.171	6.144
1600	9.184	80.202	72.825	11.802	-21.582	-43.555	5.949
1700	9.202	80.759	73.275	12.722	-54.535	-44.012	5.658
1800	9.221	81.285	73.706	13.643	-54.570	-43.392	5.268
1900	9.241	81.784	74.118	14.566	-54.607	-42.770	4.920
2000	9.263	82.259	74.513	15.491	-54.644	-42.147	4.606
2100	9.287	82.711	74.893	16.419	-54.682	-41.521	4.321
2200	9.314	83.144	75.258	17.349	-54.722	-40.894	4.062
2300	9.344	83.559	75.610	18.281	-54.765	-40.264	3.826
2400	9.378	83.957	75.950	19.218	-54.813	-39.632	3.609
2500	9.416	84.341	76.278	20.157	-54.867	-38.999	3.409
2600	9.457	84.711	76.595	21.101	-54.927	-38.362	3.225
2700	9.503	85.069	76.902	22.049	-54.998	-37.724	3.054
2800	9.553	85.415	77.200	23.002	-55.080	-37.082	2.894
2900	9.608	85.751	77.489	23.960	-55.176	-36.438	2.746
3000	9.667	86.078	77.770	24.923	-55.287	-35.791	2.607
3100	9.730	86.396	78.043	25.893	-55.416	-35.138	2.477
3200	9.797	86.706	78.309	26.869	-55.565	-34.482	2.355
3300	9.868	87.009	78.568	27.853	-55.737	-33.820	2.240
3400	9.943	87.304	78.821	28.843	-55.934	-33.154	2.131
3500	10.021	87.594	79.067	29.841	-56.157	-32.480	2.028
3600	10.102	87.877	79.308	30.848	-56.409	-31.801	1.931
3700	10.186	88.155	79.544	31.862	-56.690	-31.113	1.838
3800	10.272	88.428	79.774	32.885	-57.003	-30.417	1.749
3900	10.361	88.696	79.999	33.916	-57.349	-29.713	1.665
4000	10.451	88.959	80.220	34.957	-57.729	-29.001	1.585
4100	10.542	89.218	80.436	36.007	-58.143	-28.276	1.507
4200	10.635	89.473	80.648	37.065	-58.591	-27.542	1.433
4300	10.728	89.725	80.856	38.134	-59.073	-26.799	1.362
4400	10.822	89.972	81.061	39.211	-59.589	-26.042	1.294
4500	10.916	90.217	81.262	40.298	-60.138	-25.273	1.227
4600	11.010	90.458	81.459	41.394	-60.719	-24.491	1.164
4700	11.103	90.695	81.653	42.500	-61.331	-23.698	1.102
4800	11.195	90.930	81.844	43.615	-61.972	-22.890	1.042
4900	11.286	91.162	82.031	44.739	-62.640	-22.069	.984
5000	11.376	91.391	82.216	45.872	-63.334	-21.234	.928
5100	11.464	91.617	82.399	47.014	-64.051	-20.386	.874
5200	11.551	91.840	82.578	48.165	-64.791	-19.523	.821
5300	11.636	92.061	82.755	49.324	-65.548	-18.644	.769
5400	11.718	92.280	82.929	50.492	-66.323	-17.750	.718
5500	11.799	92.495	83.101	51.668	-67.114	-16.846	.669
5600	11.877	92.709	83.271	52.852	-67.917	-15.926	.622
5700	11.952	92.919	83.438	54.043	-68.730	-14.989	.575
5800	12.026	93.128	83.603	55.242	-69.552	-14.039	.529
5900	12.096	93.334	83.767	56.448	-70.380	-13.075	.484
6000	12.164	93.538	83.928	57.661	-71.213	-12.096	.441

June 30, 1974

STRONTIUM MONOIODIDE (SrI) (IDEAL GAS) GFW = 214.5245 ISr

Ground State Configuration $^2\Sigma^+$

$S^\circ_{298.15}$ = 65.03 ± 0.05 gibbs/mol

ΔHf°_0 = 6.65 ± 20 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 7.29± 20 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
X $^2\Sigma^+$	0	2
A $^2\Pi$	14422.7 14815.9	2 2
B $^2\Sigma$	14748.8	2
C $^2\Pi$	22666.1 23223.4	2 2
D $^2\Sigma$	28928.3	2

ω_e = 173.9 cm^{-1} $\omega_e x_e$ = 0.42 cm^{-1} σ = 1

B_e = [0.0354] cm^{-1} α_e = [0.00011] r_e = [3.03] Å

Heat of Formation

The adopted ΔHf°_0 = -6.65 ± 20 kcal/mol is obtained from D°_0 = 71.5 kcal/mol calculated from the ratio $D^\circ_0(SrI)/D^\circ_0(SrI_2)$ = 0.46. This value for the ratio was found for a series of mono- and difluorides (1) and for other alkaline earth halide systems (2). Other values for D°_0 in kcal/mol are 54.6 obtained from a linear Birge-Sponer extrapolation of ω_e and $\omega_e x_e$ data (3) with a correction for the ionic character of the molecule as described by Hildenbrand (4), 67.3 obtained by Krasnov and Karaseva (5) as a lower bound from a consideration of ionic bonding forces, and 65 obtained by Mims, Lin, and Herm (6) as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. ΔHf°_{298} = -7.29 ± 20 kcal/mol is calculated from the adopted ΔHf°_0 = -6.65 kcal/mol.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen (3). The value of r_e = 3.03 Å is assumed the same as the bond distance in SrI_2 (7). B_e is calculated from the adopted r_e. α_e is calculated assuming a Morse potential function.

The electronic levels and their designations are from Ashrafunnisa, Rao, and Rao (8, 9) and Reddy, Reddy, and Rao (10). The data are similar to the values in Rosen (2) but are more complete. The D $^2\Sigma$ level is confirmed by Shah, Petal, and Darji (11).

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Lead Diiodide (PbI_2) I_2Pb

(Crystal) GFW = 461.009

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 4.661	- 41.783	- 41.783	INFINITE
100	16.680	22.399	57.866	- 3.547	- 41.821	- 41.722	91.184
200	18.020	34.496	43.466	- 1.794	- 41.849	- 41.615	45.474
298	18.540	41.787	41.787	.000	- 41.920	- 41.486	30.410
300	18.550	41.902	41.787	.034	- 41.922	- 41.483	30.221
400	18.847	47.286	42.519	1.907	- 45.873	- 41.187	22.504
500	19.214	51.524	43.911	3.806	- 56.170	- 39.044	17.066
600	20.008	55.090	45.484	5.764	- 55.799	- 35.653	12.986
700	21.210	58.260	47.086	7.822	- 56.510	- 32.139	10.034
800	22.730	61.189	48.668	10.017	- 55.937	- 28.693	7.839
900	24.481	63.967	50.215	12.377	- 55.195	- 25.331	6.151
1000	26.306	66.640	51.724	14.915	- 54.268	- 22.060	4.821

March 31, 1962; Dec. 31, 1973

LEAD DIIODIDE (PbI_2) (CRYSTAL) GFW = 461.009 I_2Pb

$S^\circ_{298.15}$ = 41.79 ± 0.05 gibbs/mol
Tm = 683 ± 2 K

ΔHf°_0 = -41.78 ± 0.10 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -41.92 ± 0.10 kcal/mol
ΔHm° = 5.6 ± 0.2 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 41.16 kcal/mol

Heat of Formation

Koref and Braune (1) determined $\Delta Hf^\circ_{296}(PbI_2, c)$ = -41.850 kcal/mol by heat of solution calorimetry. Third law analyses of emf data at 298.15 K reported by Gerke (2) and Cann and Taylor (3) for the reaction $Pb(c) + I_2(c) = PbI_2(c)$ lead to $\Delta Hf^\circ_{298}(PbI_2, c)$ = -41.923 and -41.925 kcal/mol, respectively. $\Delta Hf^\circ_{298}(PbI_2, c)$ = -41.92 ± 0.10 kcal/mol is adopted.

Heat Capacity and Entropy

McBride (4) measured the low temperature heat capacity (4.52-291.00 K) of PbI_2. Enthalpies have been measured by Ehrhardt (5) (448-776 K), Magnus (6) (373-523 K), and Linsey (7) (323-877 K). The enthalpy data of Linsey (7) is subjected to a curve fitting procedure subject to the constraint that it join smoothly in the region of 298 K with the enthalpy derived from the heat capacity data of McBride (4). S°_{10} = 0.662 eu is adopted from McBride (4). The data of Linsey (7) did not indicate any transitions other than the solid-liquid transition at 683 K.

Melting Data

Germann and Metz (8), van Klooster and Stearns (9), and Popovkin, Odin, and Novoselova (10) determined Tm = 685 ± 1 K. Blanc and Petit (11) found Tm = 680°K. Sumarokova and Modestova (12) found PbI_2 to exist in two crystalline forms with the α-β transition at 645 K. On a DTA cooling curve, Popovkin, Odin, and Novoselova (10) observed a peak at 656 K which they attribute to the β-α transition. Modestova and Sumarokova (13) observed the β-form to melt at 669 K. Ehrhardt's (5) drop calorimetry data and his interpretation of the enthalpy increase at 648 K as indicating the melting point are consistent with the existence of a β-phase. The observation by Novoselova, Odin, and Popovkin (14) that only the α-form crystallizes on cooling melts of the PbI_2 rich region of the PbI_2-PbSe system is consistent with the interpretation that the reference state for Ehrhardt's work is α-PbI_2. The enthalpy measurements by Linsey (7) led to a reported value of Tm = 683 K. This value is adopted.

From a plot of Ehrhardt's enthalpy data, ΔHm = 5.43 to 5.52 kcal/mol at 685 K is obtained. Kelley (15) derived 5.57, 5.67, and 5.80 kcal/mol from phase diagram information and also gives 6.01 kcal/mol (16). Another analysis (17) has resulted in ΔHm = 5.20 kcal/mol. Blanc and Petit's (11) value of 3.87 kcal/mol is too low. The enthalpy data of Linsey (7) was analyzed to yield ΔHm = 5.6 kcal/mol. ΔHm° = 5.6 ± 0.2 kcal/mol is adopted.

Heat of Sublimation

ΔHs°_{298} is calculated from the difference between the adopted values for ΔHf°_{298} of the gas and crystal. Refer to $PbI_2(g)$ table.

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I_2Pb

Lead Diiodide (PbI_2)

(Liquid) GFW = 461.009

I_2Pb

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.540	47.539	47.539	.000	-37.686	-38.967	28.564
300	18.550	47.653	47.539	.034	-37.688	-38.975	28.393
400	18.847	53.038	48.271	1.907	-41.639	-39.254	21.448
500	25.950	57.847	49.686	4.080	-51.662	-37.698	16.478
600	25.950	62.578	51.453	6.675	-50.654	-35.000	12.749
700	25.950	66.579	53.335	9.270	-50.828	-32.279	10.078
800	25.950	70.044	55.212	11.865	-49.855	-29.695	8.112
900	25.950	73.100	57.033	14.460	-48.878	-27.234	6.613
1000	25.950	75.834	58.779	17.055	-47.894	-24.881	5.438
1100	25.950	78.308	60.444	19.650	-46.905	-22.628	4.496
1200	25.950	80.566	62.028	22.245	-45.910	-20.464	3.727
1300	25.950	82.643	63.535	24.840	-44.910	-18.384	3.091
1400	25.950	84.566	64.969	27.435	-43.912	-16.382	2.557
1500	25.950	86.356	66.336	30.030	-42.914	-14.450	2.105

March 31, 1962; Dec. 31, 1973

LEAD DIIODIDE (PbI_2) (LIQUID) GFW = 461.009 I_2Pb

$S^\circ_{298.15}$ = 47.539 gibbs/mol

Tm = 683 ± 2 K

Tb = 1105 K

$\Delta Hf^\circ_{298.15}$ = -37.686 kcal/mol

ΔHm° = 5.6 + 0.2 kcal/mol

ΔHv° = 28.34 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(PbI_2, \ell)$ = -37.686 kcal/mol is obtained from the sum of the heat formation of the crystal, the heat of melting, and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K, $H_{683}-H_{298}$. $\Delta Hf(\ell)$ can also be obtained from a second and third law analysis of emf data for the cell reaction $Pb(\ell) + I_2(g) = PbI_2(\ell)$ as reported by Murgulescu, Sternberg, and Terzi (1) in the form of an equation covering a range of 723 to 923 K. The enthalpy changes for the reaction are ΔHr_{298} = -57.65 ± 0.18 kcal/mol (2nd law) and -52.74 ± 1.08 kcal/mol with a drift of 5.8 ± 0.2 eu. With auxiliary data $\Delta Hf^\circ_{298}(Pb, \ell)$ = 1.025 kcal/mol (2) and $\Delta Hf^\circ_{298}(I_2, g)$ = 14.924 kcal/mol (2), $\Delta Hf^\circ_{298}(PbI_2, \ell)$ = -41.70 kcal/mol and -36.79 kcal/mol from the second and third law calculations, respectively.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 25.95 gibbs/mol from 460 to 2000 K and is based on a linear least squares fit of the liquid range enthalpy measurements (683-877 K) of Linsey (4). The enthalpy measurements of Ehrhardt (3) for the liquid range covered a smaller temperature region (687-776 K) and are considered less reliable. A least squares fit of the Ehrhardt data (3) leads to a heat capacity value of 32.5 gibbs/mol. A glass transition is assumed at 460 K below which the heat capacity is that of the crystal.

$S^\circ_{298}(PbI_2, \ell)$ = 47.539 eu is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Vaporization Data

Tb = 1105 K is calculated as the temperature at which ΔGr° = 0 for the reaction $PbI_2(c) = PbI_2(g)$. ΔHv° = 28.34 kcal/mol is calculated as the difference between ΔHf° at Tb for the gas and the liquid.

References

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2. JANAF Thermochemical Tables: Pb(ℓ), 3-31-62; $I_2(g)$, 9-30-61.
3. O. Ehrhardt, Wied. Ann. 24 215 (1885).
4. C. W. Linsey, Ph.D. Dissertation, North Texas State University, 1970.

I_2Pb

Lead Diiodide (PbI_2) I_2Pb

(Ideal Gas) GFW = 461.009

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-3.761	.277	.277	INFINITE
100	12.860	71.219	98.012	-2.679	.207	-4.577	10.002
200	13.607	80.438	87.163	-1.345	-.240	-9.194	10.047
298	13.770	85.908	85.908	.000	-.760	-13.481	9.882
300	13.772	85.993	85.908	.025	-.771	-13.559	9.878
400	13.831	89.964	86.449	1.406	-5.214	-17.599	9.616
500	13.860	93.054	87.472	2.791	-16.025	-19.665	8.595
600	13.875	95.582	88.620	4.178	-16.225	-20.374	7.421
700	13.884	97.722	89.771	5.566	-17.606	-20.858	6.512
800	13.890	99.576	90.883	6.954	-17.840	-21.306	5.820
900	13.894	101.213	91.942	8.344	-18.068	-21.726	5.276
1000	13.897	102.677	92.944	9.733	-18.290	-22.120	4.834
1100	13.900	104.001	93.890	11.123	-18.506	-22.493	4.469
1200	13.901	105.211	94.783	12.513	-18.716	-22.845	4.161
1300	13.903	106.324	95.629	13.903	-18.921	-23.180	3.897
1400	13.904	107.354	96.430	15.294	-19.127	-23.501	3.669
1500	13.904	108.313	97.191	16.684	-19.334	-23.806	3.469
1600	13.905	109.211	97.914	18.074	-19.545	-24.096	3.291
1700	13.906	110.054	98.604	19.465	-19.759	-24.374	3.133
1800	13.906	110.849	99.262	20.856	-19.979	-24.640	2.992
1900	13.907	111.600	99.892	22.246	-20.206	-24.894	2.863
2000	13.907	112.314	100.495	23.637	-20.438	-25.135	2.747
2100	13.907	112.992	101.074	25.028	-63.126	-23.811	2.478
2200	13.908	113.639	101.631	26.418	-63.279	-21.937	2.179
2300	13.908	114.257	102.166	27.809	-63.453	-20.053	1.905
2400	13.908	114.849	102.683	29.200	-63.649	-18.160	1.654
2500	13.908	115.417	103.181	30.591	-63.870	-16.263	1.422
2600	13.908	115.963	103.662	31.982	-64.113	-14.353	1.207
2700	13.908	116.487	104.127	33.372	-64.379	-12.435	1.007
2800	13.909	116.993	104.578	34.763	-64.667	-10.504	.820
2900	13.909	117.481	105.014	36.154	-64.974	-8.564	.645
3000	13.909	117.953	105.438	37.545	-65.301	-6.615	.482
3100	13.909	118.409	105.849	38.936	-65.645	-4.652	.328
3200	13.909	118.851	106.248	40.327	-66.006	-2.680	.183
3300	13.909	119.279	106.637	41.718	-66.381	-.693	.046
3400	13.909	119.694	107.015	43.109	-66.769	1.303	-.084
3500	13.909	120.097	107.383	44.499	-67.169	3.311	-.207
3600	13.909	120.489	107.741	45.890	-67.578	5.330	-.324
3700	13.909	120.870	108.091	47.281	-67.995	7.360	-.435
3800	13.909	121.241	108.432	48.672	-68.417	9.404	-.541
3900	13.909	121.602	108.765	50.063	-68.846	11.459	-.642
4000	13.909	121.954	109.091	51.454	-69.278	13.517	-.739
4100	13.909	122.298	109.409	52.845	-69.713	15.597	-.831
4200	13.909	122.633	109.720	54.236	-70.150	17.685	-.920
4300	13.909	122.960	110.024	55.627	-70.588	19.776	-1.005
4400	13.909	123.280	110.321	57.018	-71.026	21.884	-1.087
4500	13.910	123.593	110.613	58.409	-71.463	24.002	-1.166
4600	13.910	123.898	110.898	59.800	-71.899	26.130	-1.241
4700	13.910	124.197	111.178	61.191	-72.332	28.260	-1.314
4800	13.910	124.490	111.452	62.582	-72.764	30.410	-1.385
4900	13.910	124.777	111.721	63.973	-73.193	32.563	-1.452
5000	13.910	125.058	111.985	65.364	-73.620	34.724	-1.518
5100	13.910	125.334	112.244	66.755	-74.043	36.894	-1.581
5200	13.910	125.604	112.499	68.146	-74.464	39.074	-1.642
5300	13.910	125.869	112.748	69.536	-74.882	41.265	-1.702
5400	13.910	126.129	112.994	70.927	-75.297	43.463	-1.759
5500	13.910	126.384	113.235	72.318	-75.709	45.661	-1.814
5600	13.910	126.634	113.472	73.709	-76.118	47.870	-1.868
5700	13.910	126.881	113.705	75.100	-76.525	50.086	-1.920
5800	13.910	127.123	113.934	76.491	-76.929	52.315	-1.971
5900	13.910	127.360	114.160	77.882	-77.331	54.544	-2.020
6000	13.910	127.594	114.382	79.273	-77.731	56.783	-2.068

March 31, 1962; Dec. 31, 1973

LEAD DIIODIDE (PbI_2) (IDEAL GAS) GFW = 461.009 I_2Pb

Ground State Quantum Weight = [1]

Point Group = C_{2v}

$S°_{298.15}$ = [85.91 ± 2.0] gibbs/mol

$\Delta Hf°_0$ = 0.28 ± 1.0 kcal/mol

$\Delta Hf°_{298.15}$ = -0.76 ± 1.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[100] (1)

[40] (1)

[160] (1)

Bond Distance: Pb-I = 2.79 ± 0.02 Å

Bond Angle: Br-Pb-Br = [95°]

σ = 2

Product of Moments of Inertia: $I_AI_BI_C$ = [2.9478 x 10^{-111}] g^3cm^6

Heat of Formation

The adopted value of $\Delta Hf°_{298}$ = -0.76 ± 1.0 kcal/mol is the average of results from third law analyses of two sets (1, 2) of sublimation data and one set (3) of vaporization data. Auxiliary data $\Delta Hf°_{298}(PbI_2, c)$ = -41.92 kcal/mol (4) and $\Delta Hf°_{298}(PbI_2, \ell)$ = -37.686 kcal/mol (4) are used in the calculations. The adopted heat of formation for $PbI_2(g)$ yields a dissociation energy of $D°_0$ = 4.29 eV for the process $PbI_2(g) = Pb(g) + 2 I(g)$.

				ΔHs°(or v), kcal/mol			
Investigator	Reaction	No. of Points	Temp. Range, K	2nd Law	3rd Law	Drift eu	$-\Delta Hf°_{298}(PbI_2, g)^*$ kcal/mol
Niwa et al. (1)	A	7	579-650	39.77±0.37	41.54±0.16	2.9±0.60	0.38
Duncan and Thomas (2)	A	13	563-613	39.44±0.40	40.24±0.09	1.4±0.7	1.69
Jellinek and Rudat (3)	B	4	923-1073	35.19±0.52	37.49±0.32	2.3±0.6	0.20

(A) $PbI_2(c) = PbI_2(g)$

(B) $PbI_2(\ell) = PbI_2(g)$

* $\Delta Hf°_{298.15}(PbI_2, g)$ calculated from 3rd law values

Heat Capacity and Entropy

Molecular dimensions are those given by Sutton (5). Vibrational frequencies are estimated by comparison with the corresponding values for $HgI_2(g)$ (4) and with the lead dihalide series (4). The electronic ground state is assumed to be $^1A_1$ based on analogy with $PbCl_2(g)$ (4).

References

1. K. Niwa, M. Sato, and M. Yosiyama, J. Chem. Soc. Japan 60, 918 (1939).
2. J. F. Duncan and F. G. Thomas, J. Chem. Soc. 1964, 360 (1964).
3. K. Jellinek and A. Rudat, Z. physik. Chem. 143, 55 (1929).
4. JANAF Thermochemical Tables: $PbI_2(c)$, 12-31-73; $PbI_2(\ell)$, 12-31-73; $HgI_2(g)$, 3-31-62; $PbF_2(g)$, 12-31-73; $PbCl_2(g)$, 6-30-73; $PbBr_2(g)$, 12-31-73.
5. L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

Strontium Diiodide (SrI_2) I_2Sr

(Crystal) GFW = 341.4290

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 4.522	- 134.048	- 134.048	INFINITE
100	16.110	18.861	54.055	- 3.519	- 134.294	- 133.922	292.687
200	17.930	30.728	39.714	- 1.797	- 134.140	- 133.747	146.151
298	18.630	38.031	38.031	.000	- 134.200	- 133.536	97.884
300	18.650	38.146	38.031	.034	- 134.202	- 133.532	97.278
400	19.309	43.600	38.770	1.932	- 138.135	- 133.161	72.756
500	19.945	47.977	40.188	3.895	- 148.354	- 130.948	57.237
600	20.620	51.675	41.802	5.924	- 148.004	- 127.496	46.441
700	21.270	54.902	43.447	8.018	- 147.630	- 124.116	38.749
800	21.930	57.786	45.063	10.179	- 147.188	- 120.782	32.996
900	22.584	60.407	46.624	12.404	- 146.544	- 117.491	28.531
1000	23.240	62.820	48.124	14.695	- 146.453	- 114.244	24.968
1100	23.894	65.066	49.564	17.052	- 147.832	- 110.938	22.041
1200	24.550	67.173	50.944	19.474	- 147.159	- 107.614	19.599
1300	25.213	69.164	52.270	21.962	- 146.419	- 104.347	17.542
1400	25.873	71.057	53.545	24.517	- 145.617	- 101.140	15.789
1500	26.529	72.864	54.773	27.137	- 144.751	- 97.995	14.278

June 30, 1974

STRONTIUM DIIODIDE (SrI_2) (CRYSTAL) GFW = 341.4290 I_2Sr

$S^\circ_{298.15}$ = 38.03 ± 0.2
Tm = 811 ± 10 K

ΔHf°_0 = -134.0 ± 0.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -134.2 ± 0.5 kcal/mol
ΔHm° = 4.70 ± 0.09 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 68.5 kcal/mol

Heat of Formation

Ehrlich, Peik, and Koch (1) derived $\Delta Hf^\circ_{298}(SrI_2, c)$ = -133.8 ± 0.4 kcal/mol from heat of solution measurements of Sr(c) and $SrI_2(c)$ in 0.1 N HI. An auxiliary HI heat of solution value, -13.22 kcal/mole, calculated from data in reference (2) was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA key value of $\Delta Hf^\circ_{298}(I^-$, aq, std. state) = -13.60 kcal/mol (3) in the ΔHf°_{298}(HI, aq solution) table, so that the above derived heat of formation of $SrI_2(c)$ will be approximately -134.3 kcal/mol.

Combining $\Delta Hf^\circ_{298}(Sr^{+2}$, aq, std. state) = -130.45 kcal/mol, selected by Parker (4, 5), with the CODATA value for I^-(aq, std. state) (3) gives $\Delta Hf^\circ_{298}(SrI_2$, aq, std. state) = -157.65 kcal/mol. Further combination with the heat of solution, -23.43 kcal/mol (5), gives $\Delta Hf^\circ_{298}(SrI_2, c)$ = -134.22 kcal/mol. This heat of solution value is based solely on the work of Ehrlich, et al. (6).

To be consistant with the selection of the heats of formation of $BaI_2(c)$ and $CaI_2(c)$, we adopt $\Delta Hf^\circ_{298.15}(SrI_2, c)$ = -134.2 ± 0.5 kcal/mol calculated via the combination of aqueous ions.

Heat Capacity and Entropy

Cp°(13.5 - 300.9 K) has been measured by Paukov, Rakhmenkulov, and Vrublevskaya and smoothed values have been published (7). Starting values of entropy and enthalpy, S°_{14} and $H^\circ_{14}-H^\circ_0$, were not given. Our T^3 extrapolation leads to S°_8 = 0.148 gibbs/mol and $H^\circ_8-H^\circ_0$ = 0.891 cal/mol, which, when combined with our Cp extrapolation from 14 K to 8 K and with the Paukov, et al. (7) data, gives $S^\circ_{298.15}$ = 38.03 gibbs/mol and $H^\circ_{298.15}-H^\circ_0$ = 4522 cal/mol. Paukov, et al. (7) gave 37.42 ± 0.06 gibbs/mol and 4516 ± 7 cal/mol for the entropy and enthalpy at 298.15 K. Inasmuch as our integration of their data gives $S^\circ_{298} - S^\circ_{14}$ = 37.26 gibbs/mol it appears unlikely that their published value for S°_{298} is correct.

The low temperature heat capacity joins smoothly with a linear extrapolation from Cp° = 18.45 at 270 K to Cp° = 22.0 at the adopted Tm of 811 K. The linearly extrapolated heat capacity at 298 K is 0.6% higher than the published smoothed value (7). Dworkin and Bredig (8) determined the heat capacity of the crystal near the melting point to be 22.9 ± 5%. The graphically selected Cp°_{811} = 22.0 is within the experimental error and gives $H^\circ_{811} - H^\circ_{298}$ = 10.42 kcal/mol, in agreement with Dworkin and Bredig's measured value of 10.4 kcal/mol (8).

Melting Data

Emons and Loeffelholz (9) determined ΔHm° = 4.580 kcal/mol (±5%) and Tm = 802 K by high temperature cryoscopy, in good agreement with the drop calorimetry ΔHm° = 4.70 kcal/mol (±2%) and Tm = 811 K by Dworkin and Bredig (8). Hutchison (10) found Tm = 793 K, noting that his melting point data were only approximate.

Because drop calorimetry is a more direct measure of the heat of melting, we adopt ΔHm° = 4.70 ± 0.09 kcal/mol at Tm = 811 ± 10 K.

Heat of Sublimation

ΔHs°_{298} is derived as the difference between the heats of formation of the ideal gas and the crystal state at 298.15 K.

References

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3. ICSU-CODATA Task Group, J. Chem. Thermodynamics 4, 331 (1972).
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9. H. H. Emons and B. Loeffelholz, Wiss. Z. Hochsch. Chem. Leuna-Merseburg 6, 261 (1964).
10. J. F. Hutchison, U.S. At. Energy Comm. IS-T-50, 1965.

Strontium Diiodide (SrI_2) I_2Sr

(Liquid) GFW = 341.4290

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	18.630	41.214	41.214	.000	- 131.154	- 131.439	96.347
300	18.650	41.329	41.214	.034	- 131.155	- 131.441	95.754
400	19.300	46.783	41.954	1.932	- 135.089	- 131.388	71.787
500	26.300	51.161	43.371	3.895	- 145.348	- 129.494	56.602
600	26.300	55.956	45.081	6.525	- 144.357	- 126.418	46.048
700	26.300	60.010	46.932	9.155	- 143.417	- 123.503	38.559
800	26.300	63.522	48.791	11.785	- 142.536	- 120.719	32.979
900	26.300	66.620	50.603	14.415	- 141.887	- 118.026	28.661
1000	26.300	69.391	52.346	17.045	- 141.062	- 115.419	25.225
1100	26.300	71.897	54.011	19.675	- 142.163	- 112.784	22.408
1200	26.300	74.186	55.598	22.305	- 141.282	- 110.152	20.061
1300	26.300	76.291	57.110	24.935	- 140.401	- 107.593	18.088
1400	26.300	78.240	58.551	27.565	- 139.523	- 105.103	16.407
1500	26.300	80.054	59.924	30.195	- 138.646	- 102.676	14.960
1600	26.300	81.752	61.236	32.825	- 137.770	- 100.305	13.701
1700	26.300	83.346	62.490	35.455	- 169.470	- 97.085	12.481
1800	26.300	84.849	63.691	38.085	- 168.255	- 92.862	11.275
1900	26.300	86.271	64.842	40.715	- 167.044	- 88.707	10.204
2000	26.300	87.620	65.948	43.345	- 165.836	- 84.617	9.247
2100	26.300	88.904	67.011	45.975	- 164.632	- 80.585	8.387
2200	26.300	90.127	68.034	48.605	- 163.434	- 76.612	7.611
2300	26.300	91.296	69.020	51.235	- 162.242	- 72.691	6.907
2400	26.300	92.415	69.972	53.865	- 161.058	- 68.822	6.267
2500	26.300	93.489	70.891	56.495	- 159.885	- 65.004	5.683
2600	26.300	94.521	71.780	59.125	- 158.723	- 61.231	5.147

June 30, 1974

STRONTIUM DIIODIDE (SrI_2) (LIQUID) GFW = 341.4290 I_2Sr

$S^\circ_{298.15}$ = 41.214 gibbs/mol

Tm = 811 ± 10 K

T_b = 2181 K

$\Delta Hf^\circ_{298.15}$ = -131.154 kcal/mol

ΔHm° = 4.70 ± 0.09 kcal/mol

ΔHv° = 45.35 kcal/mol

Heat of Formation

$\Delta Hf^\circ_{298}(SrI_2, \ell)$ = -131.154 kcal/mol is obtained from the sum of the heat of formation of the crystal, the heat of melting, and the enthalpy difference of the crystal and the liquid between the melting point and 298.15 K.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 26.3 gibbs/mol, was determined by Dworkin and Bredig (1) from drop calorimeter measurements. This value is adopted and assumed constant over a 500-2600 K range. A glass transition is assumed at 500 K below which the heat capacity is that of the crystal.

$S^\circ_{298}(SrI_2, \ell)$ = 41.214 gibbs/mol is calculated from the crystal entropy in a manner similar to the heat of formation calculation.

Vaporization Data

The temperature at which $\Delta Gr^\circ = 0$ for the reaction $SrI_2(\ell) = SrI_2(g)$ is 2181 K, the adopted Tb. Peterson and Hutchison (2) have extrapolated Knudsen effusion cell measurements in the 1061-1308 K range to obtain a normal boiling point of 2046 K.

ΔHv° = 45.35 kcal/mol is the calculated difference between the heats of formation of the ideal gas and the liquid at Tb. See $SrI_2(g)$ table for details.

References

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2. D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data 15, 320 (1970).

I_2Sr

Strontium Diiodide (SrI_2) I_2Sr

(Ideal Gas) GFW = 341.4290

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-3.954	-64.980	-64.980	INFINITE
100	13.400	65.621	93.963	-2.834	-64.909	-69.413	151.702
200	14.420	75.314	82.464	-1.430	-65.273	-73.797	80.641
298	14.674	81.128	81.128	.000	-65.700	-77.885	57.091
300	14.677	81.219	81.128	.027	-65.709	-77.961	56.794
400	14.774	85.456	81.705	1.500	-70.067	-81.835	44.712
500	14.820	88.758	82.798	2.980	-80.809	-83.753	36.609
600	14.845	91.463	84.023	4.464	-80.964	-84.329	30.717
700	14.861	93.753	85.254	5.949	-81.169	-84.875	26.499
800	14.871	95.738	86.443	7.436	-81.431	-85.387	23.327
900	14.878	97.489	87.575	8.923	-81.925	-85.847	20.847
1000	14.883	99.057	88.646	10.411	-82.242	-86.266	18.853
1100	14.886	100.476	89.658	11.899	-84.485	-86.542	17.194
1200	14.889	101.771	90.614	13.388	-84.745	-86.718	15.793
1300	14.891	102.963	91.519	14.877	-85.005	-86.871	14.604
1400	14.893	104.067	92.376	16.366	-85.268	-87.005	13.582
1500	14.894	105.094	93.190	17.856	-85.531	-87.121	12.694
1600	14.895	106.056	93.965	19.345	-85.796	-87.217	11.913
1700	14.896	106.959	94.703	20.835	-118.636	-86.393	11.107
1800	14.897	107.810	95.408	22.325	-118.561	-84.498	10.259
1900	14.898	108.616	96.082	23.814	-118.491	-82.607	9.502
2000	14.898	109.380	96.728	25.304	-118.423	-80.723	8.821
2100	14.899	110.107	97.348	26.794	-118.359	-78.838	8.205
2200	14.899	110.800	97.943	28.284	-118.301	-76.959	7.645
2300	14.900	111.462	98.517	29.774	-118.249	-75.080	7.134
2400	14.900	112.096	99.070	31.264	-118.205	-73.203	6.666
2500	14.900	112.704	99.603	32.754	-118.172	-71.330	6.236
2600	14.901	113.289	100.118	34.244	-118.150	-69.456	5.838
2700	14.901	113.851	100.616	35.734	-118.144	-67.584	5.471
2800	14.901	114.393	101.099	37.224	-118.154	-65.709	5.129
2900	14.901	114.916	101.566	38.714	-118.184	-63.837	4.811
3000	14.901	115.421	102.020	40.204	-118.236	-61.963	4.514
3100	14.902	115.910	102.460	41.694	-118.312	-60.085	4.236
3200	14.902	116.383	102.888	43.185	-118.415	-58.206	3.975
3300	14.902	116.842	103.304	44.675	-118.549	-56.321	3.730
3400	14.902	117.286	103.708	46.165	-118.716	-54.434	3.499
3500	14.902	117.718	104.103	47.655	-118.917	-52.539	3.281
3600	14.902	118.138	104.487	49.145	-119.156	-50.641	3.074
3700	14.902	118.546	104.861	50.636	-119.432	-48.735	2.879
3800	14.902	118.944	105.227	52.126	-119.750	-46.818	2.693
3900	14.902	119.331	105.583	53.616	-120.111	-44.894	2.516
4000	14.902	119.708	105.932	55.106	-120.515	-42.964	2.347
4100	14.902	120.076	106.272	56.597	-120.961	-41.015	2.186
4200	14.903	120.435	106.605	58.087	-121.453	-39.059	2.032
4300	14.903	120.786	106.931	59.577	-121.989	-37.095	1.885
4400	14.903	121.129	107.250	61.067	-122.569	-35.114	1.744
4500	14.903	121.464	107.562	62.558	-123.191	-33.117	1.608
4600	14.903	121.791	107.868	64.048	-123.856	-31.107	1.478
4700	14.903	122.112	108.167	65.538	-124.561	-29.086	1.353
4800	14.903	122.425	108.461	67.028	-125.306	-27.046	1.231
4900	14.903	122.733	108.749	68.519	-126.087	-24.990	1.115
5000	14.903	123.034	109.032	70.009	-126.904	-22.918	1.002
5100	14.903	123.329	109.309	71.499	-127.754	-20.832	.893
5200	14.903	123.618	109.582	72.990	-128.635	-18.728	.787
5300	14.903	123.902	109.849	74.480	-129.544	-16.603	.685
5400	14.903	124.181	110.112	75.970	-130.480	-14.461	.585
5500	14.903	124.454	110.370	77.460	-131.440	-12.307	.489
5600	14.903	124.723	110.624	78.951	-132.420	-10.135	.396
5700	14.903	124.986	110.874	80.441	-133.420	-7.941	.304
5800	14.903	125.246	111.119	81.931	-134.436	-5.730	.216
5900	14.903	125.500	111.361	83.422	-135.465	-3.503	.130
6000	14.903	125.751	111.599	84.912	-136.508	-1.256	.046

June 30, 1974

STRONTIUM DIIODIDE (SrI_2) (IDEAL GAS) GFW = 341.4290 I_2Sr

Point Group = $D_{\infty h}$
$S^\circ_{298.15}$ = [81.13 ± 2.0] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°_0 = -65.0 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -65.7 ± 1.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[111] (1)
[31] (2)
[219] (1)

Bond Distance: Sr-I = 3.03 ± 0.03 Å Bond Angle: I-Sr-I = [180] σ = 2
Rotational Constant: B_o = 0.00723 cm^{-1}

Heat of Formation

Peterson and Hutchison (1, 2) used a weight loss Knudsen effusion technique to observe vapor pressures of the liquid at 20 temperatures ranging from 1061 to 1308 K. Our second and third law analyses of these data give ΔHv°_{298} (2nd law) = 65.72 ± 1.48 kcal/mol and ΔHv°_{298} (3rd law) = 65.48 ± 0.68 kcal/mol with a drift of -0.2 ± 1.2 gibbs/mol. We adopt ΔHv°_{298} = 65.5 ± 0.7 kcal/mol and combine this with the adopted heat of formation of the liquid to obtain $\Delta Hf^\circ_{298}(SrI_2, g)$ = -65.7 ± 1.5 kcal/mol.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from Akishin et al. (3) who also judged that the bond angle was 180° ± 10°. We have assumed a linear structure.

An analysis of the trend of the ratio of the stretching force constants, k(monohalide)/k_1(dihalide), has indicated that k(SrI)/$k_1(SrI_2)$ = 1 is a reasonable approximation (4). The bending force constant is taken as 0.01 times the stretching force constant. These approximations have been used by Brewer et al. (5). Our vibrational frequencies calculated from the force constants, using k for SrI calculated from the ground state vibrational frequency given by Rosen (6), are in exact agreement with those calculated by Brewer et al. (5), which are adopted. Other estimates of ν_1, ν_2, and ν_3 are 111, 49, and 220 (7).

We assign an uncertainty of ±2 gibbs/mol to the entropy to allow for error in bond angle and vibrational frequency estimates.

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5. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).
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I_2Sr

Lead Tetraiodide (PbI_4) I_4Pb

(Ideal Gas) GFW = 714.8180

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 6.603	- 52.300	- 52.300	INFINITE
100	22.756	84.700	133.589	- 4.889	- 52.467	- 57.140	124.880
200	24.922	101.351	113.724	- 2.474	- 53.011	- 61.609	67.323
298	25.409	111.411	111.411	.000	- 53.649	- 65.698	48.158
300	25.414	111.568	111.412	.047	- 53.662	- 65.772	47.915
400	25.595	118.908	112.411	2.599	- 62.106	- 69.428	37.934
500	25.680	124.629	114.304	5.163	- 83.261	- 69.250	30.269
600	25.726	129.316	116.427	7.733	- 83.175	- 66.457	24.207
700	25.754	133.284	118.559	10.308	- 84.268	- 63.485	19.821
800	25.773	136.724	120.619	12.884	- 84.215	- 60.518	16.533
900	25.785	139.761	122.581	15.462	- 84.159	- 57.561	13.978
1000	25.794	142.478	124.437	18.041	- 84.096	- 54.608	11.935
1100	25.801	144.937	126.190	20.621	- 84.029	- 51.663	10.265
1200	25.806	147.182	127.848	23.201	- 83.958	- 48.723	8.874
1300	25.810	149.248	129.415	25.782	- 83.881	- 45.789	7.698
1400	25.813	151.160	130.901	28.363	- 83.809	- 42.862	6.691
1500	25.816	152.941	132.312	30.945	- 83.737	- 39.941	5.819
1600	25.818	154.608	133.654	33.526	- 83.671	- 37.021	5.057
1700	25.820	156.173	134.933	36.108	- 83.610	- 34.107	4.385
1800	25.821	157.649	136.154	38.690	- 83.556	- 31.199	3.788
1900	25.822	159.045	137.323	41.272	- 83.510	- 28.292	3.254
2000	25.823	160.369	138.442	43.855	- 83.470	- 25.389	2.774
2100	25.824	161.629	139.516	46.437	- 125.888	- 20.931	2.178
2200	25.825	162.831	140.549	49.020	- 125.771	- 15.938	1.583
2300	25.826	163.979	141.543	51.602	- 125.678	- 10.946	1.040
2400	25.826	165.078	142.501	54.185	- 125.607	- 5.957	.542
2500	25.827	166.132	143.425	56.767	- 125.564	- .976	.085
2600	25.827	167.145	144.318	59.350	- 125.543	4.007	- .337
2700	25.828	168.120	145.182	61.933	- 125.546	8.990	- .728
2800	25.828	169.059	146.018	64.516	- 125.573	13.975	- 1.091
2900	25.829	169.966	146.828	67.099	- 125.620	18.960	- 1.429
3000	25.829	170.841	147.614	69.681	- 125.690	23.944	- 1.744
3100	25.829	171.688	148.377	72.264	- 125.777	28.935	- 2.040
3200	25.829	172.508	149.118	74.847	- 125.882	33.926	- 2.317
3300	25.830	173.303	149.839	77.430	- 126.003	38.925	- 2.578
3400	25.830	174.074	150.541	80.013	- 126.138	43.923	- 2.823
3500	25.830	174.823	151.224	82.596	- 126.285	48.929	- 3.055
3600	25.830	175.550	151.890	85.179	- 126.444	53.936	- 3.274
3700	25.830	176.258	152.539	87.762	- 126.612	58.946	- 3.482
3800	25.830	176.947	153.172	90.345	- 126.786	63.967	- 3.679
3900	25.831	177.618	153.790	92.928	- 126.969	68.991	- 3.866
4000	25.831	178.272	154.394	95.511	- 127.156	74.009	- 4.044
4100	25.831	178.910	154.984	98.094	- 127.347	79.048	- 4.214
4200	25.831	179.532	155.561	100.677	- 127.542	84.087	- 4.376
4300	25.831	180.140	156.126	103.261	- 127.738	89.119	- 4.530
4400	25.831	180.734	156.679	105.844	- 127.937	94.166	- 4.677
4500	25.831	181.314	157.220	108.427	- 128.136	99.220	- 4.819
4600	25.831	181.882	157.750	111.010	- 128.335	104.277	- 4.954
4700	25.831	182.438	158.269	113.593	- 128.532	109.327	- 5.084
4800	25.831	182.982	158.778	116.176	- 128.730	114.397	- 5.209
4900	25.832	183.514	159.278	118.759	- 128.926	119.464	- 5.328
5000	25.832	184.036	159.768	121.343	- 129.121	124.533	- 5.443
5100	25.832	184.548	160.248	123.926	- 129.313	129.606	- 5.554
5200	25.832	185.049	160.721	126.509	- 129.506	134.684	- 5.661
5300	25.832	185.541	161.184	129.092	- 129.695	139.772	- 5.764
5400	25.832	186.024	161.640	131.675	- 129.884	144.863	- 5.863
5500	25.832	186.498	162.087	134.258	- 130.071	149.945	- 5.958
5600	25.832	186.964	162.527	136.842	- 130.256	155.033	- 6.050
5700	25.832	187.421	162.960	139.425	- 130.441	160.129	- 6.140
5800	25.832	187.870	163.386	142.008	- 130.624	165.234	- 6.226
5900	25.832	188.312	163.805	144.591	- 130.806	170.333	- 6.310
6000	25.832	188.746	164.217	147.174	- 130.988	175.440	- 6.390

June 30, 1962; Dec. 31, 1973.

LEAD TETRAIODIDE (PbI_4) (IDEAL GAS) GFW = 714.8180 I_4Pb

Ground State Quantum Weight = [1]

Point Group = [T_d]

$S^\circ_{298.15}$ = [111.41 ± 3.0] gibbs/mol

ΔHf°_0 = [-52.3 ± 20] kcal/mol

$\Delta Hf^\circ_{298.15}$ = [-53.6 ± 20] kcal/mol

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[137] (1)

[37] (2)

[168] (3)

[48] (3)

Bond Distance: Pb-I = [2.77] Å

Bond Angle: I-Pb-I = [109° 28']

$\sigma = 12$

Product of Moments of Inertia: $I_AI_BI_C = [8.0044 \times 10^{-110}]\ g^3cm^6$

Heat of Formation

The adopted $\Delta Hf^\circ_0 = -52.3 \pm 20$ kcal/mol is derived from the dissociation energy for the process $PbI_4(g) = Pb(g) + 4\ I(g)$. $D^\circ_0 = 8.75$ eV is estimated from an intercomparison of the lead mono-, di-, and tetra- halides (1). This adopted D°_0 value for $PbI_4(g)$ is greater than the D°_0 value for $PbI_2(g)$ by a factor of 2.04. The auxiliary values $\Delta Hf^\circ_0(Pb, g) = 46.91$ kcal/mol (1) and $\Delta Hf^\circ_0(I, g) = 25.633$ kcal/mol (1) are used. $\Delta Hf^\circ_{298}(PbI_4, g) = -53.6 \pm 20$ kcal/mol is calculated from ΔHf°_0.

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya et al. (2). Later works (3, 4, 5) mistakenly cite this work as observed data.

The individual moments of inertia are $I_A=I_B=I_C = 4.3097 \times 10^{-37}\ g\ cm^2$.

References

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Vanadium Subnitride ($VN_{0.465}$)

(Crystal) GFW = 57.4545

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.105	-31.114	-31.114	INFINITE
100	2.545	1.190	11.394	-1.020	-31.308	-30.368	66.368
200	5.367	3.926	6.973	-.609	-31.498	-29.349	32.071
298	6.902	6.384	6.384	.000	-31.600	-28.269	20.722
300	6.924	6.427	6.384	.013	-31.601	-28.248	20.579
400	7.810	8.549	6.668	.753	-31.636	-27.124	14.820
500	8.369	10.355	7.229	1.563	-31.626	-25.996	11.363
600	8.799	11.919	7.883	2.422	-31.582	-24.874	9.060
700	9.168	13.304	8.561	3.320	-31.517	-23.761	7.419
800	9.504	14.550	9.233	4.254	-31.433	-22.658	6.190
900	9.822	15.688	9.888	5.220	-31.336	-21.567	5.237
1000	10.128	16.739	10.521	6.218	-31.230	-20.487	4.478
1100	10.427	17.718	11.131	7.246	-31.113	-19.419	3.858
1200	10.720	18.638	11.719	8.303	-30.991	-18.361	3.344
1300	11.010	19.508	12.285	9.390	-30.864	-17.313	2.911
1400	11.296	20.334	12.831	10.505	-30.734	-16.276	2.541
1500	11.581	21.123	13.357	11.649	-30.603	-15.248	2.222
1600	11.865	21.880	13.866	12.821	-30.470	-14.229	1.944
1700	12.147	22.607	14.359	14.022	-30.337	-13.218	1.699
1800	12.428	23.310	14.837	15.251	-30.203	-12.214	1.483
1900	12.650	23.988	15.301	16.505	-30.077	-11.218	1.290
2000	12.900	24.643	15.752	17.782	-29.959	-10.228	1.118
2100	13.130	25.278	16.190	19.084	-29.854	-9.245	.962
2200	13.370	25.894	16.618	20.409	-35.233	-8.241	.819
2300	13.600	26.494	17.034	21.757	-35.190	-7.015	.667
2400	13.840	27.078	17.440	23.130	-35.124	-5.791	.527
2500	14.040	27.647	17.837	24.523	-35.038	-4.570	.400
2600	14.250	28.201	18.225	25.938	-34.933	-3.354	.282
2700	14.480	28.744	18.605	27.374	-34.804	-2.141	.173
2800	14.700	29.274	18.976	28.833	-34.654	-.934	.073
2900	14.920	29.794	19.341	30.314	-34.483	.267	-.020
3000	15.130	30.303	19.698	31.817	-34.290	1.462	-.107
3100	15.330	30.803	20.048	33.340	-34.077	2.650	-.187
3200	15.540	31.293	20.391	34.883	-33.845	3.831	-.262
3300	15.750	31.774	20.729	36.448	-33.592	5.005	-.331
3400	15.960	32.247	21.061	38.033	-33.317	6.171	-.397
3500	16.170	32.713	21.387	39.640	-33.022	7.328	-.458

Dec. 31, 1973

VANADIUM SUBNITRIDE ($VN_{0.465}$) (CRYSTAL) GFW = 57.4545

$S^\circ_{298.15}$ = 6.384 ± 0.010 gibbs/mol

Td = 2875 K

ΔHf°_0 = −31.1 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −31.6 ± 1.5 kcal/mol

ΔHd° = 34.3 kcal/mol

Heat of Formation

Pankratz et al. (1) measured the heat of combustion of vanadium subnitride at 303.15 K. The composition of their sample was $VN_{0.465}$ which corresponds to the nitrogen-rich boundary of the subnitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.74 weight percent VO and trace amounts of CaO and Mo as impurities. The composition of the combustion products fell between V_2O_4 and V_2O_5. JANAF heat of formation data (2) for these two oxides are used to correct their combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction are roughly 3 cal/g subnitride greater than those used by Pankratz et al. (1). Impurity corrections for VO and Mo are also based on JANAF heat of formation data (2) and amount to 9.03 and 0.37 cal/g subnitride, respectively. For the process $VN_{0.465}(c) + 1.25\ O_2(g) = 0.5\ V_2O_5(c) + 0.2325\ N_2(g)$ we obtain ΔHc° = −153.69 ± 0.75 kcal/mol at unit fugacities of oxygen and nitrogen. When this value is combined with the heat of formation of V_2O_5 (2), that for vanadium subnitride is $\Delta Hf^\circ_{298}(VN_{0.465}, c) = -31.6 \pm 1.5$ kcal/mol. We adopt this value and include in the overall uncertainty (±1.5 kcal/mol) the error associated with correcting the combustion values to correspond to the pentoxide as the final state. The only other value for ΔHf° is derived from dissociation pressure data for $VN_{0.43}$ which were reported by Brauer and Schnell (3) for the temperature range 1655-1873 K (corrected to IPTS-68). JANAF functions for $VN_{0.465}$ are used to analyze these pressures by the third law method. These calculations lead to ΔHf° for the subnitride phase of −25.2 ± 1.7 kcal/mol. The second law value is ΔHf°_{298} = −10.7 kcal/mol; the third law drift is 8.3 ± 1.1 eu. These results show considerable scatter and are believed to be less reliable than those obtained by combustion calorimetry.

Heat Capacity and Entropy

Pankratz et al. (1) have measured low temperature heat capacities (3 to 307 K) for $VN_{0.465}$ in an adiabatic calorimeter. The composition of the subnitride sample was similar to that employed in their combustion work. Their Cp° data are adopted and used to obtain a value (6.384 eu) for S°_{298}. This latter value is based on S°_0 = 0.004 eu.

In the same paper, Pankratz et al. (1) reported measurements of the high temperature enthalpies (401-1794 K) for $VN_{0.465}$ which were obtained in a copper-block drop calorimeter. The subnitride sample was the same as that used in their combustion work and was contained in Pt-Rh alloy capsules during the "drop" experiments. Temperature measurements were based on the IPTS-68 scale. A technique employing orthogonal polynomials is used to fit their experimental enthalpies by computer. The curve is constrained to join smoothly with the low temperature Cp° data near 298 K. The average deviation of the smoothed enthalpies from the experimental values is ±0.46%; the maximum deviation is +0.73% at 702 K. Cp° data above 1800 K are obtained by graphical extrapolation. No anomalies are observed in either the low temperature Cp° data, or the high temperature enthalpies.

Phase Data

In a review of vanadium binary systems, Rostoker and Yamamoto (4) have questioned the existence of a subnitride phase, since Muthmann et al. (5) were unable to recognize its presence. However, several recent investigations (1, 3, 6-8) have reported the preparation of the subnitride at temperatures in excess of 1300 K. Using x-ray techniques, Brauer and Schnell (3) and Hahn (6) found that the phase had an extensive homogeneity range which extends from about $VN_{0.37}$ to $VN_{0.49}$ (27 to 33 atomic percent nitrogen). Pankratz et al. (1) reported the composition of the nitrogen-rich phase boundary as $VN_{0.465}$. These results are in agreement with the earlier x-ray work (3, 6). The structure of vanadium subnitride has been determined to be hexagonal (6, 7). Further information on the vanadium-vanadium nitride system has been reviewed by Storms (9).

Decomposition Data

No information is available on the melting behavior of $VN_{0.465}$ at elevated temperatures. Mass spectrometric evidence (10) has been presented which indicates that vanadium mononitride decomposes to its elements rather than melting. By analogy with VN, we assume the process $VN_{0.465}(c) = V(\ell) + 0.2325\ N_2(g)$ to be the mode of decomposition upon heating the solid. Td is the temperature at which ΔGr for the above process approaches zero. ΔHd° is the negative of the heat of formation of $VN_{0.465}$ at Td.

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Vanadium Mononitride (VN) NV

(Crystal) GFW = 64.9481

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.488	-51.243	-51.243	INFINITE
100	3.612	1.997	15.520	-1.352	-51.571	-49.690	108.598
200	7.092	5.669	9.681	-.802	-51.808	-47.708	52.132
298	9.078	8.906	8.906	.000	-51.900	-45.671	33.477
300	9.130	8.963	8.906	.017	-51.901	-45.632	33.243
400	10.348	11.769	9.281	.995	-51.884	-43.542	23.790
500	11.038	14.156	10.023	2.066	-51.800	-41.466	18.125
600	11.522	16.212	10.887	3.195	-51.678	-39.409	14.355
700	11.907	18.018	11.780	4.367	-51.534	-37.377	11.670
800	12.240	19.630	12.662	5.574	-51.375	-35.365	9.661
900	12.543	21.089	13.519	6.814	-51.208	-33.373	8.104
1000	12.827	22.426	14.343	8.082	-51.037	-31.401	6.863
1100	13.099	23.661	15.135	9.379	-50.863	-29.446	5.850
1200	13.362	24.812	15.894	10.702	-50.689	-27.506	5.010
1300	13.620	25.892	16.622	12.051	-50.517	-25.582	4.301
1400	13.873	26.911	17.321	13.426	-50.347	-23.670	3.695
1500	14.123	27.876	17.993	14.825	-50.182	-21.770	3.172
1600	14.370	28.796	18.639	16.250	-50.020	-19.882	2.716
1700	14.620	29.675	19.263	17.700	-49.863	-18.003	2.314
1800	14.830	30.516	19.865	19.172	-49.713	-16.133	1.959
1900	15.050	31.324	20.447	20.666	-49.575	-14.270	1.641
2000	15.280	32.102	21.010	22.183	-49.448	-12.415	1.357
2100	15.500	32.852	21.556	23.722	-49.336	-10.567	1.100
2200	15.720	33.579	22.086	25.283	-54.710	-8.699	.864
2300	15.930	34.282	22.601	26.865	-54.666	-6.608	.628
2400	16.140	34.964	23.102	28.469	-54.602	-4.519	.412
2500	16.350	35.628	23.590	30.093	-54.519	-2.434	.213
2600	16.560	36.273	24.066	31.739	-54.417	-.354	.030
2700	16.770	36.902	24.529	33.405	-54.294	1.724	-.140
2800	16.980	37.515	24.982	35.093	-54.151	3.796	-.296
2900	17.190	38.115	25.425	36.801	-53.989	5.863	-.442
3000	17.400	38.701	25.858	38.531	-53.805	7.924	-.577
3100	17.600	39.275	26.281	40.281	-53.602	9.978	-.703
3200	17.800	39.837	26.696	42.051	-53.381	12.025	-.821
3300	18.000	40.388	27.103	43.841	-53.141	14.066	-.932
3400	18.210	40.928	27.501	45.652	-52.879	16.099	-1.035
3500	18.410	41.459	27.893	47.483	-52.598	18.123	-1.132

Dec. 31, 1973

VANADIUM MONONITRIDE (VN) (CRYSTAL) GFW = 64.9481 NV

$S°_{298.15}$ = 8.91 ± 0.10 gibbs/mol
Td = 2619 K

$\Delta Hf°_0$ = -51.2 ± 1.2 kcal/mol
$\Delta Hf°_{298.15}$ = -51.9 ± 1.2 kcal/mol
ΔHd° = 54.4 kcal/mol
$\Delta Hs°_{298}$ = 176.9 ± 5.9 kcal/mol

Heat of Formation

Mah (1) measured the heat of combustion of vanadium mononitride at 303.15 K. The composition of the sample was $VN_{1.00}$ which corresponds to the nitrogen-rich boundary of the mononitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.07 weight percent of unreacted vanadium. The composition of the combustion products ranged from $VO_{2.231}$ to $VO_{2.298}$. X-ray diffraction patterns showed the solid combustion products to be a mixture of V_2O_4 and V_2O_5. JANAF heat of formation data (2) for these two oxides are used to correct Mah's combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction agree with those of Mah (1) to within 0.1 cal/g mononitride. For the process $VN(c) + 1.25\ O_2(g) = 0.5\ V_2O_5(c) + 0.5\ N_2(g)$, we obtain ΔHc° = -133.41 ± 0.43 kcal/mol at unit fugacities of oxygen and nitrogen. When this value is combined with the heat of formation of V_2O_5 (2), that for vanadium mononitride is $\Delta Hf°_{298}(VN, c)$ = -51.9 ± 1.2 kcal/mol. We adopt this value and include in the overall uncertainty (±1.2 kcal/mol) the error associated with correcting the combustion values for the $V_2O_4(c)$ formed to $V_2O_5(c)$ as the final state.

Other values for ΔHf° can be derived from the results of dissociation pressure measurements (3), emf data (4), and equilibrium data (5) obtained by an effusion-mass spectrometric technique. Results of a second and third law analysis of these data are summarized below.

Investigator	Method	Reaction	No. of Points	Temp. Range, K	$\Delta Hr°_{298}$, kcal/mol 2nd Law	$\Delta Hr°_{298}$, kcal/mol 3rd Law	Drift eu	$-\Delta Hf°_{298}(VN, c)$[a] kcal/mol
Slade and Higson (3)	Static	A	2	1476-1544	-68.8	-41.1±1.8	-18.3	41.1
Voleinik and Shabdenov (4)	emf	A	Equation	363-403	-54.4	-55.5±0.1	- 2.7	55.5±0.1
Farber and Srivastava (5)	Mass Spec	B	13	1900-2412	173.5	181.7±1.6	3.8±0.8	58.5±3.6

Reactions: (A) $V(c) + 0.5\ N_2(g) = VN(c)$ (B) $VN(c) = V(g) + 0.5\ N_2(g)$

[a] Third law values; auxiliary data used $\Delta Hf°_{298}(V, g)$ = 123.2 ± 2.0 kcal/mol (2).

Results obtained from the dissociation pressures of Slade and Higson (3) are obviously not reliable. Two other more extensive sets of dissociation pressure data (6, 7) have been reported for the mononitride phase. Brauer and Schnell (6) measured the nitrogen dissociation pressures for $VN_{0.72}$ between 1573 and 1873 K, while Kozheurov et al. (7) determined equilibrium pressures for VN_x (x = 0.55-0.9) at temperatures in the range 1573-1923 K. Unfortunately, these compositions are significantly different from $VN_{1.00}$, and thus the data are probably of no use in defining the heat of formation of the mononitride at its nitrogen-rich phase boundary. The third law values of ΔHf° obtained from the emf (4) and mass spectral (5) data are 3.6 and 6.6 kcal/mol, respectively, more negative than our adopted value. However, since the thermal functions used in the analysis of the mass spectral data (5) are based on extrapolated data, the second law value ($\Delta Hf°_{298}$ = -50.3 kcal/mol) is probably more reliable. This value is in much better agreement with that obtained by combustion calorimetry.

Heat Capacity and Entropy

Shomate and Kelley (8) measured the low temperature (52.6-296.3 K) heat capacities for VN. The purity of the mononitride sample based on an analysis for vanadium by permanganate titration was found to be 99.76 weight percent. Their Cp° data corrected to 1969 Atomic Weight Scale are adopted. The value of $S°_{298}$ is obtained from the adopted Cp° data and is based on $S°_{52}$ = 0.47 eu. This latter value is calculated from the Debye function D(351/T) which was suggested by Shomate and Kelley (8).

High temperature enthalpies for VN have been reported by King (9) for the temperature range 408-1611 K. The sample was identical to that employed by Shomate and Kelley (8) and was contained in platinum-rhodium alloy capsules for the "drop" experiments. His experimental enthalpies are corrected to refer to the 1969 Atomic Weight Scale. Also, his reported temperatures are corrected to the IPTS-68 scale. A technique based on orthogonal polynomials is used to fit the corrected enthalpies by computer. The curve is constrained to join smoothly with the low temperature Cp° data (8) near 298 K. Our smoothed enthalpies show an average deviation of ±0.4% from the experimental values (9). The maximum deviation is +2.1% at 408 K. No anomalies are observed in either the low temperature Cp° data (8) or the high temperature enthalpies (9). Cp° data above 1613 K are obtained by graphical extrapolation. Satoh (10) has measured the mean specific heats of VN over three temperature intervals by means of an ice calorimeter. However, the sample used in his study was impure (97.93% VN), and we believe the results are probably not reliable. They do show considerable scatter from our adopted results; deviations are in the range of ±1-5%.

Phase Data

The mononitride phase has been prepared by several workers (1, 5-8, and 11-13) at temperatures as high as 1600 K. X-ray data (6, 11) and dissociation pressure measurements (7) have shown that the phase has an extensive homogeneity range. Although Kozheurov et al. (7) were unable to obtain $VN_{1.00}$ at 1273 K, Brauer and Schnell (6) and Hahn (11) reported that the composition of the mononitride phase extends from $VN_{0.72}$ to $VN_{1.00}$ (42 to 50 atomic percent nitrogen) at 1273-1873 K. The dissociation pressure data of Kozheurov et al. (7) indicate that the vanadium-rich phase boundary decreases from $VN_{0.7}$ at 1573 K to $VN_{0.56}$ at 1923 K. The structure of the mononitride is face-centered cubic (6, 11). Further information on the vanadium-vanadium nitride system has been reviewed by Storms (14).

Decomposition Data

The melting point of VN has been reported to be approximately 2323 K by Rostoker and Yamamoto (15). However, Farber and Srivastava (5) in their mass spectrometric studies observed solid nitride at temperatures as high as 2412 K. Liquid vanadium metal, presumably formed from decomposition of the nitride, was deposited in the sample. We assume that VN decomposes to its elements prior to melting. Td is the temperature at which the ΔGr for the decomposition reaction $VN(c) \rightarrow V(\ell) + 0.5\ N_2(g)$ approaches zero. ΔHd° is the negative of the heat of formation of VN(c) at Td.

NV

Sublimation Data

The value for ΔHs° is obtained from the difference in the heats of formation for the crystal and gas.

References (see VN(g) table).

Vanadium Mononitride (VN) NV

(Ideal Gas) GFW = 64.9481

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.103	125.042	125.042	INFINITE
100	6.957	48.034	62.115	- 1.408	125.273	122.550	- 267.833
200	7.055	52.871	56.420	- .710	125.185	119.845	- 130.960
298	7.444	55.753	55.753	.000	125.000	117.262	- 85.955
300	7.453	55.799	55.753	.014	124.996	117.214	- 85.390
400	7.921	58.009	56.051	.783	124.804	114.649	- 62.641
500	8.293	59.818	56.629	1.595	124.628	112.131	- 49.012
600	8.556	61.355	57.292	2.438	124.465	109.648	- 39.939
700	8.738	62.689	57.970	3.303	124.303	107.190	- 33.466
800	8.865	63.864	58.634	4.184	124.135	104.757	- 28.618
900	8.956	64.914	59.275	5.075	123.953	102.346	- 24.853
1000	9.022	65.861	59.887	5.974	123.755	99.955	- 21.845
1100	9.072	66.723	60.470	6.879	123.537	97.586	- 19.389
1200	9.110	67.515	61.024	7.788	123.297	95.237	- 17.345
1300	9.141	68.245	61.552	8.701	123.033	92.909	- 15.619
1400	9.166	68.923	62.055	9.616	122.743	90.603	- 14.144
1500	9.187	69.556	62.534	10.534	122.426	88.318	- 12.868
1600	9.208	70.150	62.992	11.454	122.083	86.055	- 11.755
1700	9.229	70.709	63.429	12.375	121.712	83.814	- 10.775
1800	9.251	71.237	63.848	13.299	121.314	81.597	- 9.907
1900	9.275	71.738	64.251	14.226	120.885	79.402	- 9.133
2000	9.302	72.214	64.637	15.154	120.423	77.231	- 8.439
2100	9.333	72.669	65.009	16.086	119.928	75.083	- 7.814
2200	9.367	73.104	65.367	17.021	113.928	72.984	- 7.250
2300	9.405	73.521	65.712	17.960	113.328	71.136	- 6.759
2400	9.448	73.922	66.046	18.902	112.731	69.315	- 6.312
2500	9.495	74.309	66.369	19.849	112.137	67.519	- 5.902
2600	9.546	74.682	66.682	20.801	111.545	65.745	- 5.526
2700	9.601	75.043	66.985	21.759	110.959	63.995	- 5.180
2800	9.660	75.394	67.279	22.722	110.378	62.266	- 4.860
2900	9.722	75.734	67.564	23.691	109.801	60.558	- 4.564
3000	9.788	76.064	67.842	24.666	109.230	58.870	- 4.289
3100	9.857	76.386	68.113	25.649	108.665	57.200	- 4.033
3200	9.928	76.701	68.376	26.638	108.105	55.549	- 3.794
3300	10.002	77.007	68.633	27.634	107.553	53.915	- 3.571
3400	10.078	77.307	68.884	28.638	107.008	52.299	- 3.362
3500	10.156	77.600	69.129	29.650	106.469	50.697	- 3.166
3600	10.234	77.887	69.368	30.669	105.937	49.111	- 2.981
3700	10.314	78.169	69.602	31.697	- 1.334	47.720	- 2.819
3800	10.394	78.445	69.831	32.732	- 1.443	49.047	- 2.821
3900	10.475	78.716	70.055	33.776	- 1.556	50.378	- 2.823
4000	10.555	78.982	70.275	34.827	- 1.673	51.711	- 2.825
4100	10.635	79.244	70.491	35.887	- 1.796	53.046	- 2.828
4200	10.714	79.501	70.702	36.954	- 1.924	54.386	- 2.830
4300	10.793	79.754	70.910	38.030	- 2.056	55.728	- 2.832
4400	10.870	80.003	71.114	39.113	- 2.194	57.073	- 2.835
4500	10.945	80.248	71.314	40.203	- 2.338	58.422	- 2.837
4600	11.019	80.490	71.511	41.302	- 2.486	59.775	- 2.840
4700	11.091	80.727	71.704	42.407	- 2.641	61.129	- 2.843
4800	11.161	80.962	71.895	43.520	- 2.801	62.488	- 2.845
4900	11.229	81.192	72.082	44.639	- 2.968	63.848	- 2.848
5000	11.294	81.420	72.267	45.765	- 3.139	65.215	- 2.851
5100	11.357	81.644	72.448	46.898	- 3.317	66.582	- 2.853
5200	11.417	81.865	72.627	48.037	- 3.499	67.956	- 2.856
5300	11.475	82.083	72.804	49.181	- 3.687	69.332	- 2.859
5400	11.530	82.298	72.978	50.332	- 3.882	70.710	- 2.862
5500	11.582	82.510	73.149	51.487	- 4.081	72.096	- 2.865
5600	11.631	82.719	73.318	52.648	- 4.287	73.482	- 2.868
5700	11.678	82.926	73.485	53.813	- 4.498	74.874	- 2.871
5800	11.721	83.129	73.649	54.983	- 4.715	76.267	- 2.874
5900	11.762	83.330	73.812	56.157	- 4.936	77.665	- 2.877
6000	11.800	83.528	73.972	57.336	- 5.163	79.067	- 2.880

Dec. 31, 1973

VANADIUM MONONITRIDE (VN) (IDEAL GAS) GFW = 64.9481 NV

Ground State Configuration [$^3\Delta$]

$S^\circ_{298.15}$ = [55.8 ± 2.0] gibbs/mol

ΔHf°_0 = 125.0 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 125.0 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	[6]	[12000]	[2]	[16000]	[6]	[21000]	[2]
[1000]	[2]	[13000]	[3]	[18000]	[2]	[22000]	[6]
[3000]	[1]	[14000]	[6]	[19000]	[2]	[24000]	[2]
[10000]	[6]	[15000]	[1]	[20000]	[6]	[25000]	[6]
						[28000]	[6]

ω_e = [1025] cm^{-1}

B_e = [0.5905] cm^{-1}

$\omega_e x_e$ = [4.41] cm^{-1}

α_e = [0.00354] cm^{-1}

σ = 1

r_e = [1.612] Å

Heat of Formation

Dissociation energies for the diatomic Group III-VI transition-metal nitrides have been estimated by Gingerich (1) and provide support for the existence of these gaseous molecules. Very recently, mass-spectrometric evidence (2) has been presented which verifies the existence of VN(g). Using an effusion-mass spectrometric technique, Farber and Srivastava (2) observed the VN^+ ion as one of the vapor species in equilibrium with solid VN in the temperature range 1900-2412 K. The molecular precursor of this ion is assumed to be VN(g). Results of effusion weight loss and mass spectrometric experiments (2) were combined to yield partial pressures for the species involved in the following two reactions: (A) VN(c) = VN(g) and (B) VN(g) = V(g) + 0.5 N_2(g). During the course of these experiments, the ion intensities for each species did not show any variation with time. This implies that the mononitride phase remained at near unit activity during their measurements. Results of a second and third law analyses of these partial pressure data are tabulated below.

Reference	Reaction	Temp. Range, K	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	$\Delta Hf^\circ_{298}(VN, g)^a$ kcal/mol
(2)	A	1900-2412	13	174.3	185.4±2.4	5.2±1.4	133.5±3.6
(2)	B	1900-2412	12^b	- 1.9	- 3.6±1.6	-0.8±1.4	126.8±3.6

[a] Third Law Values; Auxiliary ΔHf°_{298} data used in kcal/mol VN(c), -51.9±1.2; V(g), 123.2±2.0 (3).

[b] One point rejected due to failure of a statistical test.

The third law value of 126.8 ± 3.6 kcal/mol for ΔHf° is considered to be more reliable than that (133.5 kcal/mol) derived from the sublimation data, since the results for the gas phase reaction (B) show the least drift. Also, Farber and Srivastava (2) reported a second law value determined from ion intensity plots of ΔHr = 3 ± 5 kcal/mol for reaction (B) at 2162 K. Using auxiliary data (3), this value leads to ΔHf°_{298}(VN, g) = 122.0 ± 7.0 kcal/mol. We adopt ΔHf°_{298}(VN, g) = 125.0 ± 5.0 kcal/mol which is a weighted average of the third law value derived from reaction (B) and the second law value based on ion intensity plots. The adopted ΔHf° value corresponds to a bond dissociation energy (D°_{298}) of 111.2 kcal/mol. This compares favorably with the value (116 kcal/mol) estimated by Gingerich (1).

Heat Capacity and Entropy

The value of r_e(VN) is obtained from the expression r_e(MO)-r_e(MN) = -0.023 Å with r_e(VO) = 1.589 Å (3). Differences in the bond lengths (4) for the oxides and nitrides of As, B, P, Si, and Ti are used to establish the value -0.023. Be is calculated from the estimated value for r_e. The moment of inertia is 4.7401×10^{-39} g cm^2. The value of α_e is obtained from the other constants assuming a Morse potential function. The values of ω_e and $\omega_e x_e$ are assumed to lie between those for TiO(g) and AsN(g) (4). VN is isoelectronic with TiO. Farber and Srivastava (2) have estimated a somewhat higher value (1065 cm^{-1}) for ω_e. However, their estimate is based partially on estimated JANAF data (3) for ZrN(g).

The ground state electronic configuration ($^3\Delta$), upper electronic levels and quantum weights are estimated by analogy with those for TiO (3, 5). It is possible, however, that the ground state for VN is $^1\Delta$. VN is also isoelectronic with ScF and ZrO which both have singlet ground states (5). If the adopted ground state and first excited state are interchanged, then the value of S°_{298} is reduced by 1.94 eu. Our adopted upper levels and quantum weights contribute 0.61 and 1.11 eu to the entropy of VN(g) at 2000 and 4000 K, respectively.

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NV

Nb

Niobium (Nb)

(Reference State) GFW = 92.9064

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.256	.000	.000	.000
100	4.168	3.001	13.660	-1.066	.000	.000	.000
200	5.519	6.424	9.246	-.564	.000	.000	.000
298	5.902	8.715	8.715	.000	.000	.000	.000
300	5.906	8.752	8.715	.011	.000	.000	.000
400	6.069	10.475	8.949	.610	.000	.000	.000
500	6.190	11.842	9.395	1.223	.000	.000	.000
600	6.297	12.980	9.901	1.848	.000	.000	.000
700	6.398	13.959	10.412	2.483	.000	.000	.000
800	6.497	14.819	10.910	3.127	.000	.000	.000
900	6.595	15.590	11.388	3.782	.000	.000	.000
1000	6.692	16.290	11.844	4.446	.000	.000	.000
1100	6.789	16.933	12.278	5.120	.000	.000	.000
1200	6.883	17.527	12.691	5.804	.000	.000	.000
1300	6.974	18.082	13.084	6.497	.000	.000	.000
1400	7.072	18.602	13.460	7.199	.000	.000	.000
1500	7.185	19.094	13.819	7.912	.000	.000	.000
1600	7.315	19.562	14.164	8.636	.000	.000	.000
1700	7.462	20.009	14.495	9.375	.000	.000	.000
1800	7.625	20.440	14.813	10.129	.000	.000	.000
1900	7.801	20.857	15.120	10.901	.000	.000	.000
2000	7.990	21.262	15.417	11.690	.000	.000	.000
2100	8.192	21.657	15.705	12.499	.000	.000	.000
2200	8.410	22.043	15.984	13.329	.000	.000	.000
2300	8.650	22.422	16.256	14.182	.000	.000	.000
2400	8.919	22.796	16.521	15.060	.000	.000	.000
2500	9.234	23.166	16.779	15.967	.000	.000	.000
2600	9.616	23.535	17.032	16.908	.000	.000	.000
2700	10.106	23.907	17.280	17.894	.000	.000	.000
2800	8.000	26.577	17.564	25.236	.000	.000	.000
2900	8.000	26.858	17.880	26.036	.000	.000	.000
3000	8.000	27.129	18.184	26.836	.000	.000	.000
3100	8.000	27.392	18.477	27.636	.000	.000	.000
3200	8.000	27.646	18.759	28.436	.000	.000	.000
3300	8.000	27.892	19.032	29.236	.000	.000	.000
3400	8.000	28.131	19.296	30.036	.000	.000	.000
3500	8.000	28.362	19.552	30.836	.000	.000	.000
3600	8.000	28.588	19.800	31.636	.000	.000	.000
3700	8.000	28.807	20.040	32.436	.000	.000	.000
3800	8.000	29.020	20.274	33.236	.000	.000	.000
3900	8.000	29.228	20.501	34.036	.000	.000	.000
4000	8.000	29.431	20.722	34.836	.000	.000	.000
4100	8.000	29.628	20.936	35.636	.000	.000	.000
4200	8.000	29.821	21.146	36.436	.000	.000	.000
4300	8.000	30.009	21.350	37.236	.000	.000	.000
4400	8.000	30.193	21.549	38.036	.000	.000	.000
4500	8.000	30.373	21.743	38.836	.000	.000	.000
4600	8.000	30.549	21.932	39.636	.000	.000	.000
4700	8.000	30.721	22.117	40.436	.000	.000	.000
4800	8.000	30.889	22.298	41.236	.000	.000	.000
4900	8.000	31.054	22.475	42.036	.000	.000	.000
5000	8.000	31.216	22.649	42.836	.000	.000	.000
5100	8.000	31.374	22.318	43.636	.000	.000	.000
5200	8.646	63.649	23.379	209.405	.000	.000	.000
5300	8.700	63.815	24.140	210.273	.000	.000	.000
5400	8.751	63.978	24.877	211.145	.000	.000	.000
5500	8.800	64.139	25.589	212.023	.000	.000	.000
5600	8.846	64.298	26.279	212.905	.000	.000	.000
5700	8.891	64.455	26.947	213.792	.000	.000	.000
5800	8.933	64.610	27.595	214.683	.000	.000	.000
5900	8.973	64.763	28.224	215.578	.000	.000	.000
6000	9.012	64.914	28.834	216.478	.000	.000	.000

Dec. 31, 1972; Dec. 31, 1973

NIOBIUM (Nb) (REFERENCE STATE) GFW = 92.9064 Nb

0 to 2750 K Crystal

2750 to 5136.06 K Liquid

5136.06 to 6000 K Ideal Monatomic Gas

See crystal, liquid, and monatomic gas for details.

Nb

Niobium (Nb) Nb

(Crystal) GFW = 92.9064

T, °K	C_p°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.256	.000	.000	.000
100	4.168	3.001	13.660	-1.066	.000	.000	.000
200	5.519	6.424	9.246	-.564	.000	.000	.000
298	5.902	8.715	8.715	.000	.000	.000	.000
300	5.906	8.752	8.715	.011	.000	.000	.000
400	6.069	10.475	8.949	.610	.000	.000	.000
500	6.190	11.842	9.395	1.223	.000	.000	.000
600	6.297	12.980	9.901	1.848	.000	.000	.000
700	6.398	13.959	10.412	2.483	.000	.000	.000
800	6.497	14.819	10.910	3.127	.000	.000	.000
900	6.595	15.590	11.388	3.782	.000	.000	.000
1000	6.692	16.290	11.844	4.446	.000	.000	.000
1100	6.789	16.933	12.278	5.120	.000	.000	.000
1200	6.883	17.527	12.691	5.804	.000	.000	.000
1300	6.974	18.082	13.084	6.497	.000	.000	.000
1400	7.072	18.602	13.460	7.199	.000	.000	.000
1500	7.185	19.094	13.819	7.912	.000	.000	.000
1600	7.315	19.562	14.164	8.636	.000	.000	.000
1700	7.462	20.009	14.495	9.375	.000	.000	.000
1800	7.625	20.440	14.813	10.129	.000	.000	.000
1900	7.801	20.857	15.120	10.901	.000	.000	.000
2000	7.990	21.262	15.417	11.690	.000	.000	.000
2100	8.192	21.657	15.705	12.499	.000	.000	.000
2200	8.410	22.043	15.984	13.329	.000	.000	.000
2300	8.650	22.422	16.256	14.182	.000	.000	.000
2400	8.919	22.796	16.521	15.060	.000	.000	.000
2500	9.234	23.166	16.779	15.967	.000	.000	.000
2600	9.616	23.535	17.032	16.908	.000	.000	.000
2700	10.106	23.907	17.280	17.894	.000	.000	.000
2800	10.670	24.285	17.523	18.932	-6.304	.116	-.009
2900	11.315	24.670	17.763	20.031	-6.005	.340	-.026
3000	12.048	25.066	18.000	21.198	-5.638	.553	-.040
3100	12.877	25.474	18.234	22.443	-5.193	.752	-.053
3200	13.809	25.897	18.467	23.777	-4.659	.936	-.064

Dec. 31, 1972; Dec. 31, 1973

NIOBIUM (Nb) (CRYSTAL) GFW = 92.9064 Nb

$S^\circ_{298.15}$ = 8.72 ± 0.1 gibbs/mol
Tm = 2750 ± 10 K

ΔHf°_0 = 0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol
ΔHm° = 6.43 ± 0.2 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 175.2 ± 4.0 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for T < 10 are chosen to be the same as those adopted by Hultgren et al. (1). A graphical integration of these Cp° data yields S°_{10} = 0.029 gibbs/mol and $H^\circ_{10}-H^\circ_0$ = 0.19 cal/mol. The work by DaSilva et al. (2, 3) on the low temperature (1-10 K) heat capacity of annealed and unannealed niobium wires in magnetic fields supports this choice. Clusius et al. (4) measured the heat capacity (61 pts.) in the region 11-274 K. This data is smoothed graphically and is constrained to join smoothly with the Cp° values for T ≤ 10 K. Deviations up to 4% occur between the observed and adopted Cp° values for T < 80 K. The deviations here parallel the deviations obtained in our analysis of the heat capacity for Ta (5). The deviations decrease steadily with increasing temperature up to 274 K.

There are numerous high temperature heat capacity and enthalpy measurements for Nb(c). The various studies are listed below.

Reference	Temperature Range, K	Method
Jaeger and Veenstra (6)	273-1873	drop
Fieldhouse et al. (7)	454-1882	drop
Gel'd and Kusenko (8)	433-1840	drop
Lowenthal (9)	1400-2350	modul
Kraftmakher (10)	1300-2700	modul
Hawkins and Orr (11)	358-1415	drop
Kirillin et al. (12)	600-2600	drop
Conway and Hein (13)	1273-2593	drop
Makarenko and Trukhanov (14)	1100-2400	pulse
Cezairliyan (15)	1500-2700	pulse
Sheindlin et al. (16)	1650-2707	drop

The adopted Cp° values for T > 298 K are obtained by a combination of graphical and polynomial curve fitting techniques. A polynomial curve fit procedure is used on the enthalpy data of Hawkins and Orr (11) with the constraint that it join smoothly in the 298 K region with the enthalpy derived from the Clusius et al. (4) heat capacity data. Above 1300 K, a heat capacity curve is adopted through graphical procedures. The adopted curve is chosen so as to be intermediate between the Cp° values of Cezairliyan (15) and the higher Cp° values implied from the enthalpy data of Kirillin et al. (12) and Sheindlin et al. (16). In general there is good agreement between the various sets of data.

The heat capacity values near Tm are the smoothed values suggested by Cezairliyan (15). In comparison with the adopted Cp° values, Cezairliyan's smoothed data lies low by 1.9% at 1500 K with the difference steadily decreasing to zero at 2600 K. The smoothed results of Cezairliyan (15) are used for extrapolation to 3200 K. The Cp° values reported by Makarenko and Trukhanov (14) are linear in the region 1100-2400 K whereas the adopted Cp° values are nonlinear; the Cp°-T curve being concave upward in this region. The Cp° values of Makarenko and Trukhanov (14) are within -0.4% to +0.8% of the adopted values in the region 1400-2100 K but drift to -3% at 1100 K and 2400 K. In comparing enthalpies, Kirillin et al. (12) reported smoothed values (12) which are 15 cal/mol or 0.8% lower than our tabulated values at 600 K and drift to 849 cal/mol or 4.5% higher at 2700 K. The enthalpy results of Sheindlin et al. (16) lie above the JANAF values by 0.9% in the region 1700-2700 K (82 cal/mol at 1700 K and 181 cal/mol at 2700 K).

Melting Data

See Nb(ℓ) table for details.

Sublimation Data

ΔHs°_{298} for Nb(c) = Nb(g) is simply ΔHf°_{298} for Nb(g). See Nb(g) table for details.

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Nb

Nb

Niobium (Nb)

(Liquid) GFW = 92.9064

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.902	11.317	11.317	.000	7.107	6.331	-4.641
300	5.906	11.354	11.317	.011	7.107	6.326	-4.608
400	6.069	13.077	11.551	.610	7.107	6.066	-3.314
500	6.190	14.444	11.998	1.223	7.107	5.806	-2.538
600	6.297	15.582	12.503	1.848	7.106	5.545	-2.020
700	6.398	16.561	13.014	2.483	7.106	5.285	-1.650
800	6.497	17.422	13.512	3.127	7.107	5.025	-1.373
900	6.595	18.192	13.990	3.782	7.106	4.765	-1.157
1000	6.692	18.892	14.446	4.446	7.107	4.505	-.984
1100	6.789	19.535	14.380	5.120	7.107	4.245	-.843
1200	6.883	20.129	15.293	5.804	7.107	3.984	-.726
1300	6.974	20.684	15.686	6.497	7.106	3.724	-.626
1400	7.072	21.204	16.062	7.199	7.106	3.464	-.541
1500	7.185	21.696	16.421	7.912	7.106	3.203	-.467
1600	7.315	22.164	16.766	8.636	7.107	2.944	-.402
1700	7.462	22.611	17.097	9.375	7.107	2.683	-.345
1800	8.000	23.043	17.415	10.129	7.107	2.423	-.294
1900	8.000	23.475	17.723	10.929	7.135	2.161	-.249
2000	8.000	23.885	18.021	11.729	7.146	1.900	-.208
2100	8.000	24.276	18.309	12.529	7.137	1.637	-.170
2200	8.000	24.648	18.589	13.329	7.107	1.376	-.137
2300	8.000	25.004	18.860	14.129	7.054	1.116	-.106
2400	8.000	25.344	19.123	14.929	6.976	.860	-.078
2500	8.000	25.671	19.379	15.729	6.869	.607	-.053
2600	8.000	25.984	19.627	16.529	6.728	.360	-.030
2700	8.000	26.286	19.868	17.329	6.542	.118	-.010
2800	8.000	26.577	20.102	18.129	.000	.000	.000
2900	8.000	26.858	20.331	18.929	.000	.000	.000
3000	8.000	27.129	20.553	19.729	.000	.000	.000
3100	8.000	27.391	20.769	20.529	.000	.000	.000
3200	8.000	27.645	20.980	21.329	.000	.000	.000
3300	8.000	27.892	21.136	22.129	.000	.000	.000
3400	8.000	28.130	21.386	22.929	.000	.000	.000
3500	8.000	28.362	21.582	23.729	.000	.000	.000
3600	8.000	28.586	21.774	24.529	.000	.000	.000
3700	8.000	28.807	21.961	25.329	.000	.000	.000
3800	8.000	29.020	22.144	26.129	.000	.000	.000
3900	8.000	29.228	22.323	26.929	.000	.000	.000
4000	8.000	29.431	22.498	27.729	.000	.000	.000
4100	8.000	29.628	22.670	28.529	.000	.000	.000
4200	8.000	29.821	22.838	29.329	.000	.000	.000
4300	8.000	30.009	23.002	30.129	.000	.000	.000
4400	8.000	30.193	23.164	30.929	.000	.000	.000
4500	8.000	30.373	23.322	31.729	.000	.000	.000
4600	8.000	30.549	23.477	32.529	.000	.000	.000
4700	8.000	30.721	23.629	33.329	.000	.000	.000
4800	8.000	30.889	23.779	34.129	.000	.000	.000
4900	8.000	31.054	23.926	34.929	.000	.000	.000
5000	8.000	31.216	24.070	35.729	.000	.000	.000
5100	8.000	31.374	24.212	36.529	.000	.000	.000
5200	8.000	31.530	24.351	37.329	-154.969	2.054	-.086
5300	8.000	31.682	24.488	38.129	-165.037	5.266	-.217
5400	8.000	31.831	24.622	38.929	-165.109	8.460	-.343
5500	8.000	31.978	24.755	39.729	-165.187	11.695	-.465

Dec. 31, 1972; Dec. 31, 1973

NIOBIUM (Nb) (LIQUID) GFW = 92.9064 Nb

$S^\circ_{298.15}$ = 11.317 gibbs/mol

Tm = 2750 ± 10 K

Tb = 5136.06 K

$\Delta Hf^\circ_{298.15}$ = 7.107 kcal/mol

ΔHm° = 6.43 ± 0.20 kcal/mol

ΔHv° = 164.929 kcal/mol

Heat of Formation

The heat of formation of Nb(ℓ) at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{2750}-H^\circ_{298}$ for Nb(c) and Nb(ℓ).

Heat Capacity and Entropy

The enthalpy measurements on Nb(ℓ) by Sheindlin et al. (7) and Margrave (8) do not extend over a sufficiently wide temperature range such that a heat capacity value could be derived. Therefore, the heat capacity for Nb(ℓ) is estimated as 8.0 cal/mol by analogy with other monatomic metals. The entropy at 298.15K is calculated in a manner analogous to that used in calculating the heat of formation. A glass transition is assumed at 1800K. The heat capacity values used below 1800 K are those of Nb(c).

Melting Data

Melting point determinations for Nb have been numerous, with most reported values in the range 2680-2795 K (IPTS-68 scale). A prime cause for diversity in the results is that the melting point is quite sensitive to impurities, especially gases such as oxygen and nitrogen. These effects have been documented by Schofield (1) and Pemsler (2). The value chosen for Tm is 2750 ± 10 K as reported by Cezairliyan (3) using a subsecond pulse heating method. This value is consistent with the heat capacity values near Tm which are also based on related work by Cezairliyan (4). Other values in this range (corrected to IPTS-68 scale) are 2746 K by Schofield (1), 2745 K by Pemsler (2), and 2738 K by Buehler (5). Kocherzhinskii and Kobzenko (6) have reported a Tm value of 2793 K, using a sample purified by electron zone fusion.

The value chosen for ΔHm° is 6.43 ± 0.20 kcal/mol as determined by Cezairliyan (3) using a pulse heating technique. Adopting this value gives consistency between the Cp° values near Tm, ΔHm°, and Tm as all these values are dependent upon the same heating technique. Sheindlin et al. (7) reported ΔHm° = 6.597 ± 0.170 kcal/mol based on enthalpy measurements on Nb(c) and Nb(ℓ) obtained from levitation calorimetry techniques. In the vicinity of Tm, the adopted enthalpy values for Nb(c) and Nb(ℓ) lie roughly 200 cal/mol lower than those reported by Sheindlin et al. (7). Margrave (8), also using levitation techniques, reported a value ΔHm° = 7.9 kcal/mol. It is felt that Margrave's value was calculated from a measured enthalpy of Nb(ℓ) at Tm and the enthalpy of Nb(c) at Tm as suggested by Hultgren et al. (9). Our enthalpy values at Tm for Nb(c) would reduce Margrave's value to roughly 7.4 kcal/mol for ΔHm°.

Martynyuk and Tsapkov (10) measured the enthalpies of Nb(c) and Nb(ℓ) at the melting point using the method of pulse heating. They reported a heat of melting value of 7.89 kcal/mol for an Nb sample which was reported to be 99.94% pure. No Tm value was reported.

Vaporization Data

Tb is the temperature at which the Gibbs energy change for the reaction Nb(ℓ) = Nb(g) approaches zero. The difference between ΔHf°(Nb, g) and ΔHf°(Nb, ℓ) at Tb is ΔHv°. Thus Tb is calculated as 5136.06 K and ΔHv° is 164.929 kcal/mol. The uncertainty in the boiling point is probably of the order of ±100 K. Also refer to Nb(g) table.

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Nb

Niobium (Nb)

(Ideal Gas) GFW = 92.9064

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.997	174.459	174.459	INFINITE
100	6.888	36.738	50.855	-1.412	174.854	171.481	-374.770
200	7.154	41.618	45.149	-.706	175.058	168.019	-183.603
298	7.208	44.490	44.490	.000	175.200	164.534	-120.606
300	7.207	44.535	44.490	.013	175.202	164.467	-119.814
400	7.086	46.595	44.772	.729	175.319	160.871	-87.896
500	6.893	48.155	45.299	1.428	175.405	157.249	-68.733
600	6.704	49.395	45.882	2.108	175.460	153.611	-55.953
700	6.540	50.416	46.459	2.770	175.487	149.967	-46.822
800	6.402	51.280	47.009	3.417	175.490	146.321	-39.973
900	6.284	52.027	47.526	4.051	175.469	142.676	-34.646
1000	6.185	52.684	48.009	4.674	175.428	139.035	-30.386
1100	6.102	53.269	48.462	5.288	175.368	135.398	-26.901
1200	6.034	53.797	48.885	5.895	175.291	131.767	-23.998
1300	5.981	54.278	49.281	6.496	175.199	128.144	-21.543
1400	5.941	54.720	49.654	7.092	175.093	124.528	-19.440
1500	5.915	55.129	50.006	7.684	174.972	120.920	-17.618
1600	5.902	55.510	50.338	8.275	174.839	117.322	-16.025
1700	5.903	55.868	50.653	8.865	174.690	113.731	-14.621
1800	5.917	56.205	50.952	9.456	174.527	110.150	-13.374
1900	5.943	56.526	51.237	10.049	174.348	106.578	-12.259
2000	5.981	56.832	51.509	10.645	174.155	103.016	-11.257
2100	6.030	57.125	51.769	11.246	173.947	99.465	-10.351
2200	6.089	57.406	52.019	11.851	173.722	95.923	-9.529
2300	6.157	57.679	52.259	12.464	173.482	92.392	-8.779
2400	6.234	57.942	52.491	13.083	173.223	88.872	-8.093
2500	6.317	58.198	52.714	13.711	172.944	85.363	-7.462
2600	6.407	58.448	52.930	14.347	172.639	81.866	-6.881
2700	6.501	58.691	53.139	14.992	172.298	78.381	-6.344
2800	6.599	58.930	53.341	15.647	165.611	75.025	-5.856
2900	6.700	59.163	53.538	16.312	165.476	71.792	-5.410
3000	6.802	59.392	53.729	16.987	165.351	68.564	-4.995
3100	6.906	59.616	53.916	17.673	165.237	65.339	-4.606
3200	7.011	59.837	54.097	18.368	165.132	62.119	-4.243
3300	7.115	60.055	54.274	19.075	165.039	58.901	-3.901
3400	7.218	60.269	54.448	19.791	164.955	55.686	-3.579
3500	7.319	60.479	54.617	20.518	164.882	52.473	-3.277
3600	7.419	60.687	54.783	21.255	164.819	49.262	-2.991
3700	7.517	60.892	54.945	22.002	164.766	46.053	-2.720
3800	7.612	61.093	55.104	22.758	164.722	42.845	-2.464
3900	7.705	61.292	55.260	23.524	164.688	39.639	-2.221
4000	7.795	61.488	55.414	24.299	164.663	36.432	-1.991
4100	7.882	61.682	55.564	25.083	164.647	33.227	-1.771
4200	7.966	61.873	55.712	25.876	164.640	30.021	-1.562
4300	8.047	62.061	55.857	26.676	164.640	26.816	-1.363
4400	8.125	62.247	56.001	27.485	164.649	23.611	-1.173
4500	8.200	62.431	56.141	28.301	164.665	20.406	-.991
4600	8.272	62.612	56.280	29.125	164.689	17.199	-.817
4700	8.341	62.790	56.417	29.956	164.720	13.993	-.651
4800	8.408	62.967	56.551	30.793	164.757	10.786	-.491
4900	8.471	63.141	56.684	31.637	164.801	7.577	-.338
5000	8.532	63.312	56.815	32.487	164.851	4.368	-.191
5100	8.591	63.482	56.944	33.343	164.907	1.158	-.050
5200	8.646	63.649	57.071	34.205	.000	.000	.000
5300	8.700	63.815	57.197	35.072	.001	.000	.000
5400	8.751	63.978	57.321	35.945	.000	.000	.000
5500	8.800	64.139	57.444	36.823	.000	.000	.000
5600	8.846	64.298	57.565	37.705	.000	.000	.000
5700	8.891	64.455	57.684	38.592	.000	.000	.000
5800	8.933	64.610	57.802	39.483	.000	.000	.000
5900	8.973	64.763	57.919	40.378	.000	.001	.000
6000	9.012	64.914	58.034	41.278	.000	.000	.000

June 30, 1972; Dec. 31, 1973

NIOBIUM (Nb) (IDEAL GAS) GFW = 92.9064 Nb

Ground State Configuration $^6D_{1/2}$

$S^\circ_{298.15}$ = 44.49 ± 0.10 gibbs/mol

ΔHf°_0 = 174.5 ± 4.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 175.2 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	2	9043.14	6	12018.25	6	14211.30	4
154.19	4	9497.52	8	12136.86	8	14899.26	6
391.99	6	8827.00	8	12357.70	10	18254.79	186
695.25	8	9328.88	10	13012.20	12	23795.36	168
1050.26	10	9439.08	4	12102.12	10	27536.63	224
1142.79	4	10237.51	6	12502.97	12	30778.99	214
1586.90	6	10126.06	2	12288.25	4	33099.63	316
2154.11	8	11318.09	4	12692.12	6	35508.99	158
2805.36	10	10922.74	8	12982.38	8	37614.24	248
4998.17	2	11044.08	10	13145.71	10	39251.44	228
5297.92	4	11247.88	12	13404.77	6	41451.31	236
5965.45	6	11524.65	14	13515.20	8	44504.84	166
8410.90	2	11344.70	6	13929.15	2	47368.66	148
8705.32	4						

Heat of Formation

A second and third law analysis of six reported vapor pressure studies is tabulated below. Five studies (1-5) used the Langmuir free evaporation method while one study (6) used the integral variation of the Knudsen method.

Investigator	Reaction	Temp, K (IPTS-68)	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} kcal/mol
Koch et al. (1)	A	2744-3146	15*	146.2	168.4	7.5±1.5	175.5
Speiser et al. (2)	B	2307-2600	14**	175.8	172.5	-1.3±1.6	172.5
Kaufman (3)	B	2456-2691	8	182.8	175.7	-2.8±5.3	175.7
Woerner and Wakefield (4)	B	2253-2604	Equation	183.4	174.8	-3.6	174.8
Reimann and Grant (5)	B	2370-2685	Equation	175.0	177.7	1.1	177.7
Vlasov (6)	B	2553-2684	4	143.1	191.4	18.4±4.8	191.4

* 2939.9 K point deleted due to a statistical test

** 2307, 2328, 2584 K points deleted due to a statistical test.

A = vaporization

B = sublimation

ΔHf°_{298} value is calculated from the third law ΔHf°_{298}.

We adopt ΔHf°_{298} = 175.2 kcal/mol for Nb(g) which is a rounded average of four results (2, 3, 4, 5). With a drift of 7.5 eu in that data, Shchukarev et al. (7) reported a heat of sublimation of Nb(c), determined at 2243-2393 K, of 172 ± 5 kcal/mol. Our tabulations give ΔHs°_{2300} = 173.5 kcal/mol. The same workers (7) later reported ΔHs°_{298} = 173 kcal/mol based on a second law analysis of Nb^+ ion currents at temperatures above 2573 K.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore (8). Above the level ε_i = 14899.26 cm^{-1}, the values of ε_i and g_i listed are average values calculated from those given by Moore (8). There are predicted electronic levels which have not been observed (8). These levels are assumed to lie above 20,000 cm^{-1} and thus will not significantly affect the entropy at temperatures below 3000 K. The heat capacity and entropy values are very similar to those adopted by Hultgren (9), being the same at 298 K and differing by 0.39 gibbs/mol in Cp and 0.03 gibbs/mol in S° at 5500 K.

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Niobium Monoxide (NbO) NbO

(Crystal) GFW = 108.9058

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°₂₉₈)/T (gibbs/mol)	H°−H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	9.826	11.000	11.000	.000	− 100.300	− 93.676	68.666
300	9.844	11.061	11.000	.018	− 100.299	− 93.635	68.213
400	10.524	13.995	11.396	1.040	− 100.232	− 91.422	49.951
500	10.953	16.392	12.163	2.115	− 100.136	− 89.230	39.002
600	11.282	18.419	13.041	3.227	− 100.026	− 87.060	31.711
700	11.560	20.179	13.937	4.369	− 99.908	− 84.908	26.510
800	11.823	21.740	14.817	5.538	− 99.782	− 82.774	22.613
900	12.065	23.147	15.666	6.733	− 99.649	− 80.656	19.586
1000	12.301	24.430	16.479	7.951	− 99.508	− 78.552	17.168
1100	12.528	25.613	17.256	9.193	− 99.360	− 76.464	15.192
1200	12.753	26.713	17.999	10.457	− 99.204	− 74.389	13.548
1300	12.975	27.742	18.709	11.743	− 99.039	− 72.328	12.159
1400	13.195	28.712	19.389	13.052	− 98.865	− 70.280	10.971
1500	13.412	29.630	20.042	14.382	− 98.683	− 68.245	9.943
1600	13.629	30.502	20.668	15.734	− 98.493	− 66.221	9.045
1700	13.845	31.335	21.272	17.108	− 98.300	− 64.210	8.255
1800	14.061	32.133	21.853	18.503	− 98.103	− 62.210	7.553
1900	14.276	32.899	22.414	19.920	− 97.905	− 60.222	6.927
2000	14.490	33.636	22.957	21.358	− 97.706	− 58.244	6.365
2100	14.703	34.348	23.483	22.818	− 97.508	− 56.275	5.857
2200	14.917	35.037	23.992	24.299	− 97.313	− 54.317	5.396
2300	15.131	35.705	24.487	25.801	− 97.122	− 52.367	4.976
2400	15.344	36.354	24.968	27.325	− 96.937	− 50.425	4.592
2500	15.557	36.984	25.436	28.870	− 96.763	− 48.491	4.239
2600	15.770	37.599	25.892	30.437	− 96.603	− 46.562	3.914
2700	15.983	38.198	26.337	32.024	− 96.471	− 44.641	3.613
2800	16.195	38.783	26.771	33.633	− 102.675	− 42.607	3.326

Dec. 31, 1973

NIOBIUM MONOXIDE (NbO) (CRYSTAL) GFW = 108.9058 NbO

$S^\circ_{298.15}$ = [11.0 ± 2.0] gibbs/mol

Tm = 2210 ± 15 K

ΔHf°_0 = unknown

$\Delta Hf^\circ_{298.15} = -100.3 \pm 3.0$ kcal/mol

$\Delta Hm^\circ = 20.4 \pm 5.0$ kcal/mol

$\Delta Hs^\circ_{298} = 147.8 \pm 5.0$ kcal/mol

Heat of Formation

There are two reported oxygen bomb calorimetric studies for NbO(c). The results must be interpreted in light of impure samples, incomplete combustion to Nb_2O_5(c), and the possible nonstoichiometry of the reactants and products. Morozova and Getskina (1) reported ΔHc°_{291} = 255.0 kcal/mol while Kusenko and Gel'd (2) reported ΔHc°_{298} = 263.2 kcal/mol for the combustion of NbO(c). Using auxiliary data (3), we calculate $\Delta Hf^\circ_{298} = -99.5$ and -95.4 kcal/mol for NbO(c). Schaefer and Liedmeier (4), using Cl_2 bomb calorimetry, reported a value of -97 ± 1 kcal/mol, based on $\Delta Hf^\circ_{298}(NbOCl_3, c) = -210.2$ kcal/mol.

A second and third law analysis of the majority of the reported smoothed emf data is tabulated below. Note that the heats of formation for NbO(c) calculated from the third law ΔHr° values are roughly 3 kcal/mol more negative than the adopted value. There is, however, excellent agreement within the equilibrium data; the third law ΔHf°_{298} values average -100.3 kcal/mol with a spread of only 1.8 kcal/mol. We adopt $\Delta Hf^\circ_{298} = 100.3 \pm 3.0$ kcal/mol based on an average of the equilibrium studies (5-11). The reason for the discrepancy between the equilibrium and combustion results is not known at this time (8).

Reference	Temp, K	Reaction	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	ΔHf°_{298}(NbO, c) 3rd Law, kcal/mol
5	1245-1379	A	-35.56	-36.38	-0.63	-100.02
6	1115-1347	A	-35.34	-37.60	-1.80	-101.24
7	1123-1323	A	-38.62	-36.20	1.98	- 99.84
8	1030-1300	B	-11.17	- 3.19	6.62	-100.99
9	1000-1400	A	-37.82	-35.91	1.60	- 99.55
10	1073-1373	A	-36.95	-36.46	0.40	-100.10
11	1177-1388	C	- 9.69	- 9.72	-0.03	-100.12

Reactions:
A $Nb(c) + Fe_{0.95}O = NbO(c) + 0.95\ Fe(c)$
B $Nb(c) + 0.2\ Ta_2O_5(c) = 0.4\ Ta(c) + NbO(c)$
C $Nb(c) + 1/3\ Cr_2O_3(c) = NbO(c) + 2/3\ Cr(c)$

Heat Capacity and Entropy

Gel'd and Kusenko (12) measured the enthalpy of NbO(c) and reported fourteen data points in the range 420-1702 K (IPTS-68). A Shomate-type equation is used to represent the data. The average deviation between the data and calculated values is 0.31%; the maximum deviation of 0.62% occurs at 1518 K. This equation is used to obtain extrapolated values of Cp° up to Tm.

There is no low temperature heat capacity data reported in the literature for T < 298 K. In order to have the third law results of the equilibrium data agree with the combustion data an entropy value of the order of 13-14 gibbs/mol would be necessary. At this point, however, the third law drifts would be all positive. S°_{298} = 10.2 gibbs/mol would lead to a more satisfying variation in the third law drifts for the condensed phase equilibrium data but an intermediate value S°_{298} = 11.0 gibbs/mol gives better consistency with the vapor pressure data. For more details refer to the NbO(g) and NbO_2(g) tables (3).

Phase Data

Brauer (13) reported a homogeneity range of x = 0.89-1.04 for NbO_x. NbO(c) has a cubic structure, a NaCl type with ordered vacancies (13, 14). Further information may be found in the review of the Nb-O system by Elliott (15).

Melting Data

See NbO(ℓ) table for details.

Sublimation Data

The mass spectrometric study by Shchukarev et al. (16) indicated that NbO(c) at elevated temperatures yields NbO(g) and NbO_2(g). In the range 1873-2473 K, the concentration of NbO in the vapor phase over NbO(c, ℓ) varied in the range 5-30% (16). A sublimation heat, ΔHs°_{298}, is calculated as the difference between the ΔHf°_{298} values for NbO(g) and NbO(c), $\Delta Hs^\circ_{298} = 147.8 \pm 5.0$ kcal/mol.

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NbO

NbO

Niobium Monoxide (NbO)

(Liquid) GFW = 108.9058

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	9.826	19.893	19.893	.000	-80.484	-76.511	56.084
300	9.844	19.954	19.893	.018	-80.483	-76.487	55.720
400	10.524	22.888	20.289	1.040	-80.416	-75.163	41.067
500	10.953	25.285	21.056	2.115	-80.319	-73.860	32.284
600	11.282	27.312	21.934	3.227	-80.210	-72.579	26.437
700	11.560	29.072	22.831	4.369	-80.092	-71.317	22.266
800	11.823	30.633	23.710	5.538	-79.965	-70.072	19.143
900	12.065	32.040	24.559	6.733	-79.833	-68.843	16.717
1000	12.301	33.323	25.372	7.951	-79.692	-67.629	14.780
1100	12.528	34.506	26.149	9.193	-79.544	-66.430	13.198
1200	12.753	35.606	26.892	10.457	-79.388	-65.245	11.883
1300	12.975	36.636	27.602	11.743	-79.223	-64.073	10.772
1400	13.195	37.605	28.283	13.052	-79.048	-62.914	9.821
1500	15.000	38.523	28.935	14.382	-78.866	-61.768	9.000
1600	15.000	39.491	29.565	15.882	-78.529	-60.639	8.283
1700	15.000	40.400	30.176	17.382	-78.209	-59.530	7.653
1800	15.000	41.258	30.768	18.882	-77.907	-58.440	7.096
1900	15.000	42.069	31.341	20.382	-77.627	-57.367	6.599
2000	15.000	42.838	31.897	21.882	-77.366	-56.308	6.153
2100	15.000	43.570	32.436	23.382	-77.127	-55.261	5.751
2200	15.000	44.268	32.958	24.882	-76.913	-54.225	5.387
2300	15.000	44.935	33.464	26.382	-76.724	-53.198	5.055
2400	15.000	45.573	33.955	27.882	-76.563	-52.178	4.751
2500	15.000	46.185	34.433	29.382	-76.434	-51.166	4.473
2600	15.000	46.774	34.896	30.882	-76.341	-50.156	4.216
2700	15.000	47.340	35.346	32.382	-76.296	-49.150	3.978
2800	15.000	47.885	35.785	33.882	-82.610	-48.029	3.749
2900	15.000	48.412	36.211	35.382	-82.384	-46.797	3.527
3000	15.000	48.920	36.626	36.882	-82.160	-45.574	3.320

Dec. 31, 1973

NIOBIUM MONOXIDE (NbO) (LIQUID) GFW = 108.9058 NbO

$S^\circ_{298.15}$ = 19.893 gibbs/mol

Tm = 2210 ± 15 K

$\Delta Hf^\circ_{298.15}$ = -80.484 kcal/mol

ΔHm° = 20.4 ± 5.0 kcal/mol

Heat of Formation

The heat of formation of NbO(ℓ) is calculated from ΔHf°_{298}(NbO, c) plus the heat of melting (ΔHm°) and the enthalpy differences ($H^\circ_{2210}-H^\circ_{298}$) for the crystal and liquid.

Heat Capacity and Entropy

There is no data reported in the literature concerning the heat capacity or enthalpy of NbO(ℓ). We estimate a constant value of Cp° = 15.0 gibbs/mol for the liquid phase. A glass transition is also assumed at 1500 K so as to insure the proper thermodynamic relationship between crystal values and extrapolated liquid values. At temperatures below 1500 K, Cp° values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the heat of formation.

Melting Data

Elliott (1) reported the melting point of NbO(c) as Tm = 2222 K (IPTS-68). Measurements by Kolchin and Sumarokova (2) gave Tm = 2212 K (IPTS-68). The vapor pressure study of NbO(c, ℓ) by Shchukarev et al. (3) gave Tm = 2207 K. We adopt Tm = 2210 ± 15 K in order to maintain good consistency with the vapor pressure data.

Since the crystal structure of NbO(c) is a defect NaCl structure, we can estimate ΔHm° = 13.9 kcal/mol based on ΔSm° = 6.27 eu as observed for NaCl (4). The data of Shchukarev et al. (3) are more consistent with ΔHm° = 20.4 kcal/mol, as determined from our analysis of the vapor pressures over NbO(c, ℓ) (4). We adopt ΔHm° = 20.4 ± 5.0 kcal/mol. This leads to ΔSm° = 9.23 eu which is roughly 3 eu greater than the NaCl value (4).

Vaporization Data

The vapors over NbO(ℓ) have been shown by Shchukarev et al. (3) to be NbO(g) and NbO_2(g). At 2300 K, the rates of the vapor pressures NbO_2(g):NbO(g) is 1.00:0.23 (3).

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4. JANAF Thermochemical Tables: NaCl(c), 9-30-64; NbO(g), 12-31-73.

NbO

Niobium Monoxide (NbO)

(Ideal Gas) GFW = 108.9058

T, °K	gibbs/mol			kcal/mol			Log Kp
	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	
0	.000	.000	INFINITE	-2.099	47.695	47.695	INFINITE
100	6.956	49.388	63.423	-1.404	47.853	45.284	-98.968
200	7.043	54.224	57.751	-.705	47.701	42.763	-46.729
298	7.358	57.090	57.089	.000	47.500	40.382	-29.601
300	7.365	57.135	57.090	.014	47.496	40.338	-29.386
400	7.735	59.306	57.383	.769	47.297	37.983	-20.753
500	8.034	61.065	57.949	1.558	47.108	35.677	-15.594
600	8.253	62.550	58.595	2.373	46.920	33.407	-12.169
700	8.412	63.835	59.254	3.207	46.730	31.170	-9.732
800	8.529	64.967	59.899	4.054	46.534	28.961	-7.912
900	8.617	65.976	60.519	4.912	46.330	26.776	-6.502
1000	8.684	66.883	61.111	5.777	46.117	24.615	-5.380
1100	8.737	67.718	61.675	6.648	45.895	22.476	-4.466
1200	8.780	68.480	62.210	7.524	45.663	20.357	-3.707
1300	8.815	69.185	62.720	8.404	45.421	18.257	-3.069
1400	8.844	69.839	63.206	9.287	45.170	16.177	-2.525
1500	8.868	70.450	63.668	10.172	44.907	14.115	-2.057
1600	8.890	71.023	64.110	11.060	44.633	12.072	-1.649
1700	8.909	71.563	64.533	11.950	44.343	10.046	-1.291
1800	8.927	72.072	64.938	12.842	44.036	8.037	-.976
1900	8.944	72.555	65.326	13.736	43.710	6.045	-.695
2000	8.961	73.015	65.699	14.631	43.366	4.072	-.445
2100	8.978	73.452	66.058	15.528	43.002	2.116	-.220
2200	8.996	73.870	66.404	16.426	42.614	.178	-.018
2300	9.014	74.271	66.737	17.327	42.204	-1.742	.166
2400	9.035	74.655	67.059	18.229	41.767	-3.643	.332
2500	9.057	75.024	67.370	19.134	41.301	-5.526	.483
2600	9.081	75.380	67.672	20.041	40.801	-7.389	.621
2700	9.108	75.723	67.963	20.950	40.255	-9.232	.747
2800	9.137	76.055	68.246	21.862	33.354	-10.939	.854
2900	9.169	76.376	68.521	22.778	32.995	-12.514	.943
3000	9.203	76.687	68.788	23.696	32.637	-14.077	1.025
3100	9.240	76.989	69.048	24.618	32.281	-15.628	1.102
3200	9.279	77.283	69.301	25.544	31.926	-17.168	1.173
3300	9.321	77.570	69.547	26.474	31.573	-18.693	1.238
3400	9.365	77.849	69.787	27.409	31.222	-20.215	1.299
3500	9.412	78.121	70.021	28.347	30.873	-21.724	1.356
3600	9.460	78.386	70.250	29.291	30.528	-23.221	1.410
3700	9.511	78.646	70.473	30.240	30.186	-24.709	1.460
3800	9.563	78.901	70.692	31.193	29.847	-26.187	1.506
3900	9.617	79.150	70.906	32.152	29.512	-27.659	1.550
4000	9.671	79.394	71.115	33.117	29.180	-29.121	1.591
4100	9.727	79.633	71.320	34.087	28.853	-30.574	1.630
4200	9.784	79.869	71.520	35.062	28.530	-32.020	1.666
4300	9.841	80.099	71.717	36.043	28.211	-33.456	1.700
4400	9.899	80.326	71.910	37.030	27.896	-34.888	1.733
4500	9.957	80.549	72.100	38.023	27.587	-36.311	1.764
4600	10.015	80.769	72.286	39.022	27.282	-37.726	1.792
4700	10.073	80.985	72.469	40.026	26.981	-39.136	1.820
4800	10.130	81.198	72.648	41.036	26.686	-40.540	1.846
4900	10.187	81.407	72.825	42.052	26.395	-41.940	1.871
5000	10.243	81.613	72.999	43.074	26.109	-43.331	1.894
5100	10.298	81.817	73.170	44.101	25.828	-44.716	1.916
5200	10.352	82.017	73.338	45.133	-139.418	-44.045	1.851
5300	10.405	82.215	73.503	46.171	-139.757	-42.205	1.740
5400	10.457	82.410	73.667	47.214	-140.097	-40.363	1.634
5500	10.507	82.602	73.827	48.262	-140.437	-38.512	1.530
5600	10.556	82.792	73.986	49.316	-140.778	-36.657	1.431
5700	10.604	82.979	74.142	50.374	-141.119	-34.795	1.334
5800	10.650	83.164	74.296	51.436	-141.460	-32.925	1.241
5900	10.694	83.347	74.446	52.503	-141.801	-31.051	1.150
6000	10.737	83.527	74.597	53.575	-142.143	-29.171	1.063

Dec. 31, 1973

NIOBIUM MONOXIDE (NbO) (IDEAL GAS) GFW = 108.9058 NbO

Ground State Configuration $[^4\Sigma^-]$

$S^\circ_{298.15}$ = 57.09 ± 0.85 gibbs/mol

ΔHf°_0 = 47.7 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 47.5 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$X[^4\Sigma^-]$	0	4
$[^4\Pi]$	15000	8
$[^4\Sigma^-]$	21316.2	4

ω_e = 989.03 cm^{-1}

B_e = 0.432 cm^{-1}

$\omega_e x_e$ = 3.83 cm^{-1}

α_e = 2.1 x 10^{-3} cm^{-1}

σ = 1

r_e = 1.691 Å

Heat of Formation

Using the adopted vibrational constants (ω_e and $\omega_e x_e$), we calculate D°_0 = 7.855 eV as the dissociation energy of NbO(g) based on the linear Birge-Sponer extrapolation of the ground state. Applying a correction for the ionicity in the Nb-O bond as suggested by Hildenbrand and Murad (1), we recalculate D°_0 = 8.032 eV. This latter value corresponds to ΔHf°_{298}(NbO, g) = 48.03 kcal/mol, assuming dissociation to normal atoms, while the former yields 52.11 kcal/mol.

Shchukarev, Semenov, and Frantseva (2, 3) have investigated mass spectrometrically the composition of the vapors over NbO(c, ℓ) and NbO_2(c, ℓ). In their first work (2), the authors reported that, besides NbO sublimation at 1773-1923 K, the reaction 2 NbO(c) = Nb(c) + NbO_2(g) occurs. A second law ΔHs° = 138 ± 3 kcal/mol was reported for the range 1773-1923 K. Using auxiliary data (5), we calculate ΔHf°_{298}(NbO, g) = 47.2 ± 3.0 kcal/mol, assuming the ΔHs° reported value refers to 1900 K.

Shchukarev et al. (3) measured the vapor pressures of NbO and NbO_2 over NbO(c, ℓ) and NbO_2(c, ℓ) by the effusion method coupled with a mass spectrometer. The results are summarized in the following table.

Reaction	Range, K	ΔHr°_{298}, kcal/mol		Drift eu	ΔHf°_{298}, kcal/mol	
		2nd Law	3rd Law		2nd Law	3rd Law
NbO(c) = NbO(g)	1773-2210	148.0	147.5	-0.24	47.7	47.2
NbO(ℓ) = NbO(g)	2210-2473	128.1	128.0	-0.04	47.6	47.5

We adopt ΔHf°_{298} = 47.5 ± 5.0 kcal/mol for NbO(g). The adopted value is an average value based on the second and third law results tabulated above. It is interesting to note that the adjusted Birge-Sponer result shows excellent agreement with the adopted ΔHf°_{298}. The adopted ΔHf°_{298} leads to a dissociation energy D°_0 = 8.05 eV.

Heat Capacity and Entropy

The spectroscopic work involving NbO(g) has been reviewed and referenced by Rosen (4). The adopted vibrational and rotational constants as well as the electronic levels are those tabulated by Rosen (4). As indicated in Rosen (4), the data suggest a $^4\Sigma^-$ ground state as in VO(g) (5). However, a possible ground state $^2\Delta$ as in TaO(g) (5) is not definitely excluded. The recent reviews by Cheetham and Barrow (6) and Weltner (7) favor a $^2\Delta$ ground state. Using a $^2\Delta$ ground state and $^2\Delta$-$^2\Delta$ transition at 21316.2 cm^{-1} produces the same thermodynamic functions as does a $^4\Sigma^-$ ground state and a $^4\Sigma$-$^4\Sigma$ transition at 21316.2 cm^{-1}. Green et al. (9) studied the infrared absorption spectra of isotopic NbO isolated in an Ar matrix. Green et al. (9) reported that a partial analysis of the observed bands supported the assignment of a $^4\Sigma^-$ electronic ground state for NbO.

The free energy functions used here are approximately 0.85 gibbs/mol at 298 K and 2.90 gibbs/mol at 3000 K lower than those proposed by Brewer and Rosenblatt (8). The difference arises from the fact that Brewer and Rosenblatt (8) approximated the NbO electronic levels by using Nb^{++} electronic levels (which included low lying levels) whereas we have used the observed NbO electronic levels.

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Niobium Dioxide (NbO_2) NbO_2

(Crystal) GFW = 124.9052

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.216	-188.885	-188.885	INFINITE
100	5.053	2.695	23.016	-2.032	-189.585	-185.415	405.224
200	10.736	8.118	14.201	-1.217	-189.968	-181.063	197.856
298	13.731	13.027	13.027	.000	-190.000	-176.675	129.506
300	13.768	13.112	13.028	.025	-189.999	-176.593	128.648
400	15.148	17.287	13.587	1.480	-189.854	-172.143	94.054
500	16.190	20.786	14.686	3.050	-189.628	-167.739	73.319
600	17.125	23.820	15.961	4.716	-189.344	-163.387	59.514
700	18.058	26.530	17.281	6.475	-188.978	-159.088	49.670
800	19.000	29.003	18.593	8.328	-188.555	-154.848	42.302
900	19.952	31.296	19.879	10.275	-188.077	-150.662	36.585
1000	20.913	33.448	21.129	12.318	-187.525	-146.533	32.025
1100	22.200	36.240	22.349	15.280	-186.076	-142.471	28.306
1200	19.850	38.172	23.589	17.500	-185.388	-138.536	25.231
1300	19.850	39.761	24.772	19.485	-184.953	-134.652	22.637
1400	19.850	41.232	25.896	21.470	-184.534	-130.798	20.419
1500	19.850	42.601	26.965	23.455	-184.133	-126.974	18.500
1600	19.850	43.882	27.982	25.440	-183.749	-123.176	16.825
1700	19.850	45.086	28.953	27.425	-183.385	-119.401	15.350
1800	19.850	46.220	29.881	29.410	-183.043	-115.647	14.041
1900	19.850	47.293	30.770	31.395	-182.725	-111.912	12.873
2000	19.850	48.312	31.622	33.380	-182.429	-108.194	11.823
2100	19.850	49.280	32.440	35.365	-182.158	-104.488	10.874
2200	19.850	50.203	33.226	37.350	-181.915	-100.795	10.013
2300	19.850	51.086	33.984	39.335	-181.699	-97.114	9.228
2400	19.850	51.931	34.714	41.320	-181.514	-93.439	8.509
2500	19.850	52.741	35.419	43.305	-181.364	-89.774	7.848
2600	19.850	53.520	36.100	45.290	-181.252	-86.111	7.238
2700	19.850	54.269	36.759	47.275	-181.191	-82.453	6.674
2800	19.850	54.991	37.398	49.260	-187.491	-78.681	6.141

Dec. 31, 1973

NIOBIUM DIOXIDE (NbO_2) (CRYSTAL) GFW = 124.9052 NbO_2

$S^\circ_{298.15}$ = 13.03 ± 0.07 gibbs/mol
Tt_1 = 1090 ± 20 K
Tt_2 = 1200 K
Tm = 2175 ± 15 K

ΔHf°_0 = -188.9 ± 2.0 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -190.0 ± 2.0 kcal/mol
ΔHt°_1 = 0.818 kcal/mol
ΔHt°_2 = 0.000 kcal/mol
ΔHm° = 22.0 ± 5.0 kcal/mol
$\Delta Hs^\circ_{298.15}$ = 143.1 ± 5.0 kcal/mol

Heat of Formation

There are three oxygen bomb calorimetric studies for NbO_2(c). As with NbO(c), the combustion results must be interpreted in light of impure samples, possible incomplete combustion, and possible nonstoichiometry. The following ΔHc° results have been reported for the oxygen combustion of one mole of NbO_2(c) to yield Nb_2O_5(c): 37.0 ± 0.4 kcal/mol (291 K) by Morozova and Getskina (1), 37.6 ± 2.6 kcal/mol (298 K) by Kusenko and Gel'd (2), and 36.67 ± 0.10 kcal/mol (298 K) by Mah (3). Using the value ΔHc°_{298} = 37.0 ± 2.0 kcal/mol and $\Delta Hf^\circ_{298}(Nb_2O_5$, c) = -454.0 ± 1.0 kcal/mol (4), we calculate and adopt ΔHf°_{298} = -190.0 ± 2.0 kcal/mol for NbO_2(c).

There are numerous equilibrium studies involving NbO_2. Early work involved the reduction of niobium oxides with hydrogen by Grube et al. (5), Süe (6), and Schaefer and Breil (7), and the carbon reduction of Nb_2O_5 by Süe (8). The more recent emf equilibrium studies are analyzed and tabulated in the following table.

Reference	Temp, K	Reaction	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} kcal/mol
9	1673-1823	$NbO_2(c)+H_2(g)=NbO(c)+H_2O(g)$	36.35	32.39	-2.3	-190.4
10	1100-1300	$NbO_2(c)+Nb(c)=2\ NbO(c)$	-11.96	-9.59	2.0	-187.8
11	1074-1175	$Nb_2O_5(c)+C(c)=2\ NbO_2(c)+CO(g)$	38.43	45.87	6.6	-190.3
12	1177-1351	$NbO(c)+1/3Cr_2O_3(c)=NbO_2(c)+2/3\ Cr(c)$	2.32	1.78	-0.4	-188.9

Heat Capacity and Entropy

King (13) measured the heat capacity of NbO_2(c) in the region 53-298 K. Using the combination of Debye and Einstein functions suggested by King (13), we calculate S°_{51} = 0.616 gibbs/mol and $H^\circ_{51}-H^\circ_0$ = 23 cal/mol. The enthalpy data of Gel'd and Kusenko (14), and King and Christensen (15), indicated a transition in the region 1000-1200 K. We adopt the reported enthalpy equations of King and Christensen (15) for the ranges 1090-1200 K and 1200-1800 K. The latter equation is extrapolated to Tm. For the region 298-1090 K, we use a five term polynomial to fit the enthalpy data of King and Christensen (15) with constraints to join smoothly with the enthalpy derived from the King data (13). The deviations are +0.34 to -0.87% in the range 298-1090 K. In the same range, the Gel'd and Kusenko data (14) lies approximately 2-3% higher, while above T = 1200 K, it is 0.5-2.5% high.

Phase Data

Brauer (16) reported a homogeneity range of x = 1.94 to 2.05 for NbO_x. A recent study by Janninck and Whitmore (17), using isopiestic reduction techniques at 1373 K; reported x = 1.9975 to 2.003.

Brauer (16), Magneli et al. (18), Terao (19), and Marinder (20) have shown that at room temperature NbO_2 has a deformed rutile structure. NbO_2 is similar to V_2O_4 in terms of crystal structure (21).

Transition Data

Electric conductivity and thermoelectric power measurements and a DTA and x-ray diffraction study indicated a phase transition in the region 1068-1173 K (17, 21, 22). In this region, the structure of NbO_2 transforms from a deformed rutile to a rutile structure. The evidence suggested that the transition is not sharp but is acutally spread over at least 50° (21).

The enthalpy data of King and Christensen (15) and Gel'd and Kusenko (14) are consistent with the above interpretation. We treat this transition as first order with Tt_1 = 1090 ± 20 K and add an artificial transition Tt_2 = 1200 K as in King and Christensen (15). This combination reproduces the reported enthalpy data (15). The value ΔHt°_1 = 0.818 kcal/mol is calculated as the difference between the enthalpies of the two "phases" at 1090 K associated with the transition at Tt_1.

Melting Data

See NbO_2(ℓ) table.

Sublimation Data

The heat of sublimation, ΔHs°_{298}, is calculated as the difference in the ΔHf°_{298} values for NbO_2(g) and NbO_2(c).

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NbO_2

Niobium Dioxide (NbO_2)

(Liquid) GFW = 124.9052

NbO_2

T, °K	gibbs/mol Cp°	S°	−(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	13.731	22.188	22.188	- .000	- 169.902	- 159.309	116.776
300	13.768	22.273	22.188	.025	- 169.901	- 159.243	116.009
400	15.198	26.447	22.748	1.480	- 169.757	- 155.709	85.076
500	16.190	29.947	23.847	3.050	- 169.531	- 152.222	66.536
600	17.125	32.981	25.122	4.716	- 169.247	- 148.786	54.195
700	18.058	35.691	26.441	6.475	- 168.881	- 145.403	45.397
800	19.000	38.164	27.754	8.328	- 168.458	- 142.079	38.814
900	19.952	40.457	29.040	10.275	- 167.979	- 138.809	33.708
1000	22.500	42.608	30.290	12.318	- 167.427	- 135.596	29.634
1100	22.500	44.753	31.509	14.568	- 166.690	- 132.449	26.315
1200	22.500	46.711	32.695	16.818	- 165.972	- 129.369	23.561
1300	22.500	48.512	33.844	19.068	- 165.272	- 126.347	21.241
1400	22.500	50.179	34.952	21.318	- 164.588	- 123.379	19.260
1500	22.500	51.731	36.019	23.568	- 163.922	- 120.459	17.551
1600	22.500	53.183	37.047	25.818	- 163.273	- 117.581	16.061
1700	22.500	54.548	38.037	28.068	- 162.644	- 114.745	14.751
1800	22.500	55.834	38.990	30.318	- 162.037	- 111.945	13.592
1900	22.500	57.050	39.909	32.568	- 161.454	- 109.179	12.558
2000	22.500	58.204	40.795	34.818	- 160.893	- 106.443	11.632
2100	22.500	59.302	41.650	37.068	- 160.357	- 103.732	10.796
2200	22.500	60.349	42.477	39.318	- 159.849	- 101.049	10.038
2300	22.500	61.349	43.276	41.568	- 159.366	- 98.387	9.349
2400	22.500	62.306	44.049	43.818	- 158.918	- 95.744	8.719
2500	22.500	63.225	44.798	46.068	- 158.503	- 93.123	8.141
2600	22.500	64.107	45.523	48.318	- 158.126	- 90.513	7.608
2700	22.500	64.957	46.228	50.568	- 157.800	- 87.920	7.117
2800	22.500	65.775	46.911	52.618	- 163.835	- 85.221	6.652
2900	22.500	66.564	47.575	55.068	- 163.333	- 82.421	6.211
3000	22.500	67.327	48.221	57.318	- 162.836	- 79.640	5.802

Dec. 31, 1973

NIOBIUM DIOXIDE (NbO_2) (LIQUID) GFW = 124.9052 NbO_2

$S^\circ_{298.15}$ = 22.188 gibbs/mol

Tm = 2175 ± 15 K

$\Delta Hf^\circ_{298.15}$ = -169.902 kcal/mol

ΔHm° = 22.0 ± 5.0 kcal/mol

Heat of Formation

The heat of formation of $NbO_2(\ell)$ is calculated from $\Delta Hf^\circ_{298}(NbO_2, c)$ plus the heat of melting (ΔHm°) and the enthalpy differences ($H^\circ_{2210}-H^\circ_{298}$) for the crystal and the liquid.

Heat Capacity and Entropy

There is no data reported in the literature concerning the heat capacity or enthalpy of $NbO_2(\ell)$. We estimate a constant value of Cp° = 7.5 gibbs/g-atom or 22.5 gibbs/mol for the liquid phase. A glass transition is assumed at 1000 K below which the Cp° values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the heat of formation.

Melting Data

Elliott (1) reported the melting point of $NbO_2(c)$ as Tm = 2191 K (IPTS-68) and stated that $NbO_2(c)$ melts without decomposition. The vapor pressure study of $NbO_2(c, \ell)$ by Shchukarev et al. (2) gave Tm = 2173 K (IPTS-68) with congruent melting. We adopt Tm = 2175 ± 15 K in order to maintain good consistency with the vapor pressure data. A value of Tm = 2357 K reported by Kolchin and Sumarokova (3) appears too high.

The vapor pressure data of Shchukarev et al. (2) suggests ΔHm° = 22.0 kcal/mol which we adopt. This leads to ΔSm° = 10.11 gibbs/mol.

Vaporization Data

The vapors over $NbO_2(\ell)$ have been shown by Shchukarev et al. (2) to be NbO(g), $NbO_2(g)$, and O(g). At 2300 K, the ratio of the vapor pressures $NbO_2(g)$: NbO(g) is 1.00:0.07.

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NbO_2

Niobium Dioxide (NbO_2)

(Ideal Gas) GFW = 124.9052

NbO_2

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.690	-47.159	-47.159	INFINITE
100	8.457	54.833	73.665	-1.883	-47.236	-48.280	105.516
200	9.517	61.037	65.948	-.982	-47.533	-49.212	53.776
298	10.494	65.019	65.019	.000	-47.800	-49.977	36.634
300	10.512	65.084	65.020	.019	-47.805	-49.990	36.418
400	11.382	68.233	65.443	1.116	-48.018	-50.685	27.693
500	12.025	70.846	66.269	2.288	-48.190	-51.331	22.437
600	12.476	73.080	67.223	3.514	-48.344	-51.945	18.921
700	12.794	75.029	68.202	4.779	-48.492	-52.533	16.402
800	13.022	76.753	69.165	6.070	-48.643	-53.101	14.506
900	13.189	78.297	70.095	7.381	-48.801	-53.649	13.028
1000	13.314	79.693	70.986	8.707	-48.966	-54.177	11.840
1100	13.411	80.967	71.837	10.043	-49.143	-54.691	10.866
1200	13.486	82.137	72.647	11.388	-49.330	-55.187	10.051
1300	13.545	83.219	73.419	12.740	-49.528	-55.667	9.358
1400	13.593	84.225	74.155	14.097	-49.737	-56.132	8.763
1500	13.632	85.164	74.858	15.458	-49.960	-56.581	8.244
1600	13.665	86.045	75.530	16.823	-50.196	-57.014	7.788
1700	13.692	86.874	76.173	18.191	-50.449	-57.432	7.383
1800	13.715	87.657	76.790	19.561	-50.722	-57.835	7.022
1900	13.735	88.399	77.382	20.934	-51.016	-58.223	6.697
2000	13.751	89.104	77.950	22.308	-51.331	-58.595	6.403
2100	13.766	89.776	78.497	23.684	-51.669	-58.949	6.135
2200	13.778	90.416	79.025	25.061	-52.034	-59.288	5.890
2300	13.789	91.029	79.533	26.440	-52.424	-59.610	5.664
2400	13.799	91.616	80.025	27.819	-52.845	-59.912	5.456
2500	13.808	92.180	80.500	29.199	-53.300	-60.199	5.263
2600	13.815	92.721	80.959	30.581	-53.791	-60.463	5.082
2700	13.822	93.243	81.405	31.962	-54.334	-60.710	4.914
2800	13.828	93.746	81.837	33.345	-61.236	-60.820	4.747
2900	13.834	94.231	82.256	34.728	-61.601	-60.798	4.582
3000	13.839	94.700	82.663	36.112	-61.970	-60.763	4.427
3100	13.843	95.154	83.058	37.496	-62.343	-60.717	4.281
3200	13.847	95.593	83.443	38.880	-62.721	-60.659	4.143
3300	13.851	96.020	83.818	40.265	-63.102	-60.590	4.013
3400	13.854	96.433	84.183	41.650	-63.488	-60.508	3.889
3500	13.857	96.835	84.539	43.036	-63.876	-60.415	3.773
3600	13.860	97.225	84.886	44.422	-64.268	-60.309	3.661
3700	13.863	97.605	85.224	45.808	-64.664	-60.194	3.556
3800	13.865	97.975	85.555	47.195	-65.062	-60.067	3.455
3900	13.868	98.335	85.878	48.581	-65.464	-59.932	3.359
4000	13.870	98.686	86.194	49.968	-65.869	-59.786	3.267
4100	13.872	99.028	86.503	51.355	-66.277	-59.628	3.178
4200	13.874	99.363	86.805	52.742	-66.687	-59.462	3.094
4300	13.875	99.689	87.101	54.130	-67.099	-59.282	3.013
4400	13.877	100.008	87.391	55.517	-67.515	-59.098	2.935
4500	13.878	100.320	87.674	56.905	-67.932	-58.901	2.861
4600	13.880	100.625	87.953	58.293	-68.351	-58.693	2.789
4700	13.881	100.924	88.226	59.681	-68.773	-58.479	2.719
4800	13.882	101.216	88.493	61.069	-69.196	-58.255	2.652
4900	13.883	101.502	88.756	62.457	-69.621	-58.027	2.588
5000	13.884	101.783	89.013	63.846	-70.047	-57.786	2.526
5100	13.885	102.058	89.267	65.234	-70.476	-57.534	2.465
5200	13.886	102.327	89.515	66.623	-235.874	-55.226	2.321
5300	13.887	102.592	89.759	68.012	-236.372	-51.743	2.134
5400	13.888	102.851	89.999	69.400	-236.877	-48.259	1.953
5500	13.889	103.106	90.235	70.789	-237.387	-44.758	1.779
5600	13.889	103.356	90.467	72.178	-237.904	-41.253	1.610
5700	13.890	103.602	90.696	73.567	-238.426	-37.739	1.447
5800	13.891	103.844	90.920	74.956	-238.953	-34.209	1.289
5900	13.892	104.081	91.141	76.345	-239.485	-30.676	1.136
6000	13.892	104.315	91.359	77.734	-240.023	-27.131	.988

Dec. 31, 1973

NIOBIUM DIOXIDE (NbO_2) (IDEAL GAS) GFW = 124.9052 NbO_2

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [65.02 ± 2.00] gibbs/mol

Ground State Quantum Weight = [2]

$\Delta Hf^\circ_0 = -47.2 \pm 5.0$ kcal/mol

$\Delta Hf^\circ_{298.15} = -47.8 \pm 5.0$ kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[970] (1)
[300] (1)
[930] (1)

Bond Distance: [1.691] Å

Bond Angle: [110°]

$\sigma = 2$

Product of the Moment of Inertia: $I_A I_B I_C = [4.383 \times 10^{-115}]\ g^3cm^6$

Heat of Formation

Shchukarev et al. (1-4) measured the vapor pressures of NbO and NbO_2 over NbO(c, ℓ) and NbO_2(c, ℓ) by the effusion method coupled with a mass spectrometer. An analysis of the reported smoothed results is presented in the following table (4).

		ΔHr°_{298}, kcal/mol		Drift	ΔHf°_{298}, kcal/mol	
Reaction	Range, K	2nd Law	3rd Law	eu	2nd Law	3rd Law
$NbO_2(c) = NbO_2(g)$	1773-2175	142.0	143.4	0.69	-48.0	-46.6
$NbO_2(\ell) = NbO_2(g)$	2175-2473	124.2	123.7	-0.22	-46.8	-46.3
$2NbO(c) = NbO_2(g)+Nb(c)$	1773-2210	147.8	149.9	1.03	-52.8	-50.7
$2NbO(\ell) = NbO_2(g)+Nb(c)$	2210-2473	119.7	111.1	-3.73	-41.3	-49.9

We adopt $\Delta Hf^\circ_{298}(NbO_2, g) = -47.8 \pm 5.0$ kcal/mol. This value is an average value of the 2nd and 3rd law results for the sublimation and vaporization of NbO_2. This adopted ΔHf°_{298} value leads to $D^\circ_0 = 14.73$ eV for the process $NbO_2(g) = Nb(g) + 2\ O(g)$. The D°_0 value is 1.83 times as great as the dissociation energy of NbO(g) (8.05 eV, 2).

The earlier less complete studies by Shchukarev et al. (1-3) are in fair agreement with the above conclusions. Using a platinum strip to vaporize NbO_2(c) in a mass spectrometer at temperatures of 1500 to 1880 K, Shchukarev et al. (1) reported a second law sublimation heat, $\Delta Hs^\circ_{1700} = 142 \pm 3$ kcal/mol. Using auxiliary data (6), we calculate $\Delta Hf^\circ_{298}(NbO_2, g) = -38.8$ kcal/mol. The mass spectrometric investigation of the NbO(c) evaporation by Shchukarev et al. (2) led to a reported value $\Delta Hr^\circ_{1800} = 140 \pm 3$ kcal/mol for the process $2\ NbO(c) = Nb(c) + NbO_2(g)$. Using auxiliary data (6), we calculate $\Delta Hf^\circ_{298}(NbO_2, g) = -53.3$ kcal/mol. NbO_2 pressures were obtained (1938-2122 K) by the differential effusion method using the radioactive tracer ^{95}Nb (3). The pressures agree within 5% of those obtained in the more complete study (4). Golubtsov et al. (5) also measured the vapor pressure of NbO_2(g) over NbO_2(c) in the range 1489-1905 K by using labelled atoms in a Knudsen cell. The same authors also studied the dissociation of Nb_2O_5 in vacuo in the range 1432-1756 K, the process being $Nb_2O_5(c) \rightarrow 2\ NbO_2(g) + 1/2\ O_2(g)$. These latter data (5) are not considered.

Heat Capacity and Entropy

The vibrational frequencies and geometry of NbO_2(g) are estimated based on existing and estimated data for related metal dioxides such as TiO_2(g), TaO_2(g), and WO_2(g) (6). The Nb-O bond distance is assumed to be the same as in NbO(g) (6). The ground state quantum weight of 2 is adopted so as to be consistent with TaO_2(g) (6).

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NbO_2

Diniobium Pentoxide (Nb_2O_5)

(Crystal) GFW = 265.8098

T, °K	gibbs/mol $Cp°$	 $S°$	 $-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	 $\Delta Hf°$	 $\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	- 5.327	- 451.629	- 451.629	INFINITE
100	13.015	8.202	56.222	- 4.802	- 453.219	- 443.092	968.375
200	25.316	21.398	35.532	- 2.827	- 453.986	- 432.590	472.712
298	31.546	32.815	32.815	.000	- 454.000	- 422.065	309.382
300	31.625	33.010	32.816	.058	- 453.996	- 421.867	307.330
400	34.654	42.566	34.098	3.387	- 453.623	- 411.206	224.672
500	36.769	50.536	36.610	6.963	- 453.061	- 400.664	175.130
600	38.417	57.392	39.516	10.725	- 452.388	- 390.246	142.147
700	39.678	63.413	42.508	14.633	- 451.663	- 379.946	118.625
800	40.640	68.776	45.463	18.651	- 450.918	- 369.755	101.012
900	41.376	73.607	48.326	22.753	- 450.165	- 359.654	87.336
1000	41.946	77.997	51.077	26.920	- 449.403	- 349.635	76.413
1100	42.390	82.017	53.709	31.138	- 448.639	- 339.697	67.492
1200	42.741	85.721	56.225	35.395	- 447.866	- 329.826	60.069
1300	43.019	89.153	58.627	39.683	- 447.096	- 320.020	53.800
1400	43.241	92.349	60.923	43.997	- 446.335	- 310.275	48.436
1500	43.419	95.339	63.119	48.330	- 445.589	- 300.582	43.795
1600	43.562	98.146	65.221	52.679	- 444.864	- 290.938	39.740
1700	43.677	100.790	67.237	57.041	- 444.163	- 281.338	36.168
1800	43.769	103.290	69.171	61.414	- 443.497	- 271.780	32.999
1900	43.842	105.658	71.029	65.795	- 442.868	- 262.257	30.166
2000	43.900	107.908	72.817	70.182	- 442.279	- 252.770	27.621
2100	43.944	110.051	74.540	74.574	- 441.733	- 243.305	25.321
2200	43.978	112.097	76.201	78.970	- 441.245	- 233.870	23.233
2300	44.003	114.052	77.804	83.369	- 440.812	- 224.455	21.328

Dec. 31, 1972

DINIOBIUM PENTOXIDE (Nb_2O_5) (CRYSTAL) GFW = 265.8098 Nb_2O_5

$S°_{298.15}$ = 32.82 ± 0.3 gibbs/mol

Tm = 1785 ± 30 K

$\Delta Hf°_0$ = -451.6 ± 1 kcal/mol

$\Delta Hf°_{298.15}$ = -454.0 ± 1 kcal/mol

$\Delta Hm°$ = 24.92 ± 0.5 kcal/mol

Heat of Formation

The many $\Delta Hf°_{298}(Nb_2O_5$, c) investigations suffer from uncertainties concerning the polymorphic state of the samples employed and the oftentimes incomplete impurity analysis of the samples (1). Thus, there is considerable scatter in the following tabulation for the heat of formation values, all of which are based on heat of combustion studies.

Source	Nb(c) purity, %	% completion *	$\Delta Hf°_{298}$ kcal/mol
Muthmann et al. (2)			-442.8
Becker and Roth (3)	98.8	96.34-96.94	-459.9±0.7**
Humphrey (4)	99.69	97.63-99.38	-454.0±0.6**
Morozova and Getskina (5)			-472.6±1.0
Morozova and Stolyarova (6)	99.49		-454.8±0.8
Kusenko and Gel'd (7)			-458.6±5.0
Kusenko and Gel'd (8)	99.01	99.1 -99.33	-455.1±0.5
Huber et al. (9)	99.45	98.78-100	-454.4±1.6
Kornilov et al. (10)	98.47-99.35	99.48-99.96	-453.5±0.4
Kornilov et al. (11)	98.47-99.35	99.48-99.96	-453.5±0.4
Lavrent'ev et al. (12)			-456.9

* Percent completion refers to extent of reaction 2Nb(c) + 2.5 O_2(g) = Nb_2O_5(c).

** Values adjusted by Kubaschewski and Catterall (13) to more satisfactorily correct for incomplete reaction to form Nb_2O_5.

The value chosen for $\Delta Hf°_{298}(Nb_2O_5$, c) is -454.0 ± 1 kcal/mol. This value is representative of the work by Humphrey (4), Kornilov et al. (10, 11), Huber et al. (9), Kusenko and Gel'd (8), and Morozova and Stolyarova (6). These works have discussed sample purity and have percentage conversions of Nb to Nb_2O_5(c) of the order of 97% or better. Based on the discussion by Reisman and Holtzberg (1), this $\Delta Hf°_{298}$ value is for the high temperature α-phase of Nb_2O_5(c). The heat capacity and enthalpy work, also dealing with the α-phase of Nb_2O_5, indicated no phase changes in the range 53-297 K and 381-1785 K (14, 15, 16).

Recently, $\Delta Gf°$ values for Nb_2O_5(c) in the range 1050-1300 K were calculated from measured emf values in an oxygen concentration cell and the known $\Delta Gf°$ values of Cr_2O_3(17). The reported smoothed $\Delta Gf°$ values were treated by a third law analysis, yielding $\Delta Hf°_{298}(Nb_2O_5$, c) = -451.6 kcal/mol with a drift equivalent to an entropy error of -4.8 eu.

Heat Capacity and Entropy

King (14) measured the heat capacity of the high temperature α-phase Nb_2O_5 from 53.24 to 296.64 K and fitted the data (29 data points) with a combination of Debye and Einstein functions. These functions fit the data over the entire measured temperature range with a maximum deviation of 0.6% (14), and are used to calculate $S°_{50}$ = 2.42 gibbs/mol.

Orr (15), using the same material as King (14), measured the enthalpy from 381.4 to 1809.2 K. Gel'd and Kusenko (16) also measured the enthalpy from 461 to 1828 K. Combining this data (15, 16) with a portion of the King data (a Cp fit, then integrated), a six term polynomial fit is used to represent the enthalpy data, yielding a deviation of -0.99% to +0.81% for the Orr data and -0.64% to +1.10% for the Gel'd and Kusenko data. Two points (644 K, 734 K) of the Gel'd and Kusenko data are not used as they deviate from the polynomial-fitted values by 2-3%. Enthalpy values corresponding to temperatures greater than 1750 K but less than Tm are considered to be involved in premelting (15). Enthalpy values for 1785 ≤ T ≤ 2300 K are obtained by extrapolating the values obtained from the polynomial fit. The chosen heat capacity values are obtained by differentiating the enthalpy polynomial fit for the range 298-2300 K. For temperatures 50-298 K, the King data was fit to a six term polynomial.

The existing experimental data (14, 15, 16) did not indicate any transitions other than a crystal-liquid transition. Lacking thermodynamic information for the other crystal phases of Nb_2O_5 (1), we assume that there is little difference in the heat capacity and enthalpy values for the various crystal phases. Thus the values tabulated here apply to all crystal Nb_2O_5 phases. The data for Ta_2O_5(c) presented in these tables is treated in the same manner as discussed here so as to maintain consistency between Nb_2O_5(c, ℓ) and Ta_2O_5(c, ℓ).

Melting Data

See Nb_2O_5(ℓ) table for details.

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Nb_2O_5

Diniobium Pentoxide (Nb_2O_5)

(Liquid) GFW = 265.8098

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°₂₉₈)/T (gibbs/mol)	H°−H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	31.546	40.987	40.987	.000	- 437.589	- 408.090	299.138
300	31.625	41.182	40.987	.058	- 437.585	- 407.908	297.161
400	34.654	50.738	42.270	3.387	- 437.212	- 398.064	217.492
500	36.769	58.707	44.782	6.963	- 436.650	- 388.339	169.743
600	38.417	65.563	47.687	10.725	- 435.977	- 378.738	137.955
700	39.678	71.584	50.680	14.633	- 435.252	- 369.256	115.287
800	40.640	76.948	53.634	18.651	- 434.507	- 359.881	98.315
900	41.376	81.779	56.498	22.753	- 433.754	- 350.597	85.137
1000	41.946	86.169	59.249	26.920	- 432.992	- 341.395	74.612
1100	42.390	90.188	61.881	31.138	- 432.228	- 332.275	66.017
1200	57.900	93.892	64.396	35.395	- 431.455	- 323.221	58.867
1300	57.900	98.527	66.846	41.185	- 429.184	- 314.293	52.837
1400	57.900	102.818	69.264	46.975	- 426.946	- 305.541	47.697
1500	57.900	106.812	71.636	52.765	- 424.743	- 296.946	43.265
1600	57.900	110.549	73.952	58.555	- 422.578	- 288.497	39.407
1700	57.900	114.059	76.209	64.345	- 420.449	- 280.181	36.020
1800	57.900	117.369	78.405	70.135	- 418.365	- 271.991	33.024
1900	57.900	120.499	80.539	75.925	- 416.327	- 263.914	30.357
2000	57.900	123.469	82.612	81.715	- 414.335	- 255.947	27.969
2100	57.900	126.294	84.625	87.505	- 412.391	- 248.073	25.817
2200	57.900	128.988	86.581	93.295	- 410.509	- 240.295	23.871
2300	57.900	131.561	88.481	99.085	- 408.685	- 232.600	22.102
2400	57.900	134.026	90.328	104.875	- 406.934	- 224.978	20.487
2500	57.900	136.389	92.123	110.665	- 405.266	- 217.437	19.008
2600	57.900	138.660	93.870	116.455	- 403.686	- 209.952	17.648
2700	57.900	140.845	95.569	122.245	- 402.211	- 202.528	16.394
2800	57.900	142.951	97.224	128.035	- 413.463	- 194.926	15.215
2900	57.900	144.983	98.836	133.825	- 411.643	- 187.151	14.104
3000	57.900	146.946	100.407	139.615	- 409.835	- 179.441	13.072
3100	57.900	148.844	101.939	145.405	- 408.038	- 171.789	12.111
3200	57.900	150.682	103.434	151.195	- 406.253	- 164.200	11.214
3300	57.900	152.464	104.893	156.985	- 404.478	- 156.666	10.376
3400	57.900	154.193	106.317	162.775	- 402.715	- 149.182	9.589
3500	57.900	155.871	107.709	168.565	- 400.960	- 141.753	8.851
3600	57.900	157.502	109.070	174.355	- 399.215	- 134.368	8.157
3700	57.900	159.088	110.400	180.145	- 397.480	- 127.035	7.504
3800	57.900	160.632	111.702	185.935	- 395.753	- 119.746	6.887
3900	57.900	162.136	112.976	191.725	- 394.033	- 112.511	6.305
4000	57.900	163.602	114.224	197.515	- 392.323	- 105.316	5.754
4100	57.900	165.032	115.445	203.305	- 390.620	- 98.159	5.232
4200	57.900	166.427	116.643	209.095	- 388.923	- 91.049	4.738
4300	57.900	167.790	117.816	214.885	- 387.233	- 83.969	4.268
4400	57.900	169.121	118.967	220.675	- 385.550	- 76.942	3.822
4500	57.900	170.422	120.096	226.465	- 383.873	- 69.945	3.397
4600	57.900	171.695	121.204	232.255	- 382.200	- 62.980	2.992
4700	57.900	172.940	122.292	238.045	- 380.535	- 56.061	2.607
4800	57.900	174.159	123.360	243.835	- 378.873	- 49.173	2.239
4900	57.900	175.353	124.409	249.625	- 377.215	- 42.332	1.888
5000	57.900	176.522	125.439	255.415	- 375.563	- 35.516	1.552

Dec. 31, 1972

DINIOBIUM PENTOXIDE (Nb_2O_5) (LIQUID) GFW = 265.8098

$S^\circ_{298.15}$ = 40.987 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -437.589 kcal/mol

Tm = 1785 ± 30 K

ΔHm° = 24.92 ± 0.5 kcal/mol

Heat of Formation

The heat of formation of $Nb_2O_5(\ell)$ at 298.15 K is calculated from that of the crystal by adding ΔH_m° and the difference between $H^\circ_{1785} - H^\circ_{298}$ for $Nb_2O_5(c)$ and $Nb_2O_5(\ell)$.

Heat Capacity and Entropy

Orr (1) and Gel'd and Kusenko (2) reported enthalpy measurements at temperatures greater than Tm. The work of Orr (1) indicates a Cp value of 57.90 gibbs/mol based on two enthalpy points in the liquid region. The three enthalpy points of Gel'd and Kusenko (2) deviate by +0.06%, -0.86%, and -0.37% from the linear representation of the Orr data. Thus, the constant Cp value of 57.90 gibbs/mol is chosen for the liquid phase. A glass transition is also chosen at 1200 K so as to insure the proper thermodynamic relationship between crystal values and extrapolated liquid value. At temperatures below 1200 K, the heat capacity values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the heat of formation.

Melting Data

The enthalpy work of Orr (1) and Gel'd and Kusenko (2) provide information as to the heat of fusion. The heat capacity discussion for $Nb_2O_5(c)$ and $Nb_2O_5(\ell)$ provide details as to the fitting of the data in the crystal and liquid regions. The heat of fusion is then calculated to be ΔH_m° = 24.31 ± 0.5 kcal/mol at a melting point of 1785 K ($H^\circ_{1785} - H^\circ_{298}$ = -60.759 kcal/mol for the crystal). This melting point, although it is consistent with the enthalpy work (1, 2), is 21 K greater than the value reported by Holtzberg et al. (3) and is greater than most Tm values cited by Charlesworth (4) and Schneider (5). Reisman and Holtzberg (6) attributed this high value of 1785 K to an impure sample. The melting point, Tm, is chosen to be 1785 K strictly on the basis of being consistent with the two sets of enthalpy data. More data is necessary to accurately define consistent values for Tm, ΔHm°, and enthalpy values in the liquid and crystal regions.

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Oxygen Monatomic (O) 0

(Ideal Gas) GFW = 15.9994

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.607	58.983	58.983	INFINITE
100	5.665	32.465	43.265	-1.080	59.164	57.987	-126.730
200	5.434	36.338	38.951	-.523	59.373	56.727	-61.988
298	5.237	38.467	38.467	.000	59.553	55.389	-40.601
300	5.234	38.499	38.467	.010	59.556	55.363	-40.332
400	5.134	39.990	38.671	.528	59.719	53.941	-29.472
500	5.081	41.129	39.353	1.038	59.864	52.479	-22.939
600	5.049	42.053	39.479	1.544	59.992	50.990	-18.573
700	5.029	42.829	39.903	2.048	60.107	49.481	-15.449
800	5.015	43.500	40.312	2.550	60.210	47.955	-13.101
900	5.006	44.090	40.699	3.051	60.304	46.417	-11.272
1000	4.999	44.617	41.065	3.552	60.391	44.870	-9.806
1100	4.994	45.093	41.410	4.051	60.471	43.314	-8.606
1200	4.990	45.527	41.735	4.550	60.546	41.751	-7.604
1300	4.986	45.927	42.043	5.049	60.617	40.182	-6.755
1400	4.984	46.296	42.333	5.548	60.683	38.607	-6.027
1500	4.982	46.640	42.609	6.046	60.746	37.028	-5.395
1600	4.980	46.961	42.871	6.544	60.806	35.445	-4.842
1700	4.979	47.263	43.121	7.042	60.863	33.858	-4.353
1800	4.978	47.548	43.359	7.540	60.916	32.268	-3.918
1900	4.978	47.817	43.587	8.038	60.966	30.675	-3.528
2000	4.978	48.072	43.805	8.535	61.014	29.079	-3.178
2100	4.978	48.315	44.014	9.033	61.059	27.482	-2.860
2200	4.978	48.547	44.214	9.531	61.101	25.882	-2.571
2300	4.980	48.768	44.408	10.029	61.141	24.280	-2.307
2400	4.981	48.980	44.594	10.527	61.178	22.677	-2.065
2500	4.983	49.183	44.773	11.025	61.212	21.071	-1.842
2600	4.986	49.379	44.947	11.524	61.245	19.465	-1.636
2700	4.990	49.567	45.114	12.022	61.274	17.858	-1.446
2800	4.994	49.749	45.277	12.522	61.302	16.250	-1.268
2900	4.999	49.924	45.434	13.021	61.328	14.641	-1.103
3000	5.004	50.094	45.586	13.521	61.351	13.030	-.949
3100	5.010	50.258	45.735	14.022	61.374	11.419	-.805
3200	5.017	50.417	45.878	14.523	61.394	9.807	-.670
3300	5.024	50.571	46.018	15.025	61.413	8.194	-.543
3400	5.032	50.722	46.154	15.528	61.430	6.581	-.423
3500	5.041	50.868	46.287	16.032	61.447	4.967	-.310
3600	5.050	51.010	46.416	16.537	61.463	3.354	-.204
3700	5.060	51.148	46.542	17.042	61.477	1.740	-.103
3800	5.070	51.283	46.665	17.549	61.491	.126	-.007
3900	5.080	51.415	46.785	18.056	61.505	-1.490	.084
4000	5.091	51.544	46.903	18.565	61.517	-3.106	.170
4100	5.102	51.670	47.017	19.074	61.529	-4.721	.252
4200	5.114	51.793	47.130	19.585	61.542	-6.338	.330
4300	5.126	51.913	47.239	20.097	61.554	-7.953	.404
4400	5.137	52.031	47.347	20.610	61.565	-9.570	.475
4500	5.149	52.147	47.452	21.125	61.577	-11.187	.543
4600	5.161	52.260	47.556	21.640	61.589	-12.803	.608
4700	5.174	52.371	47.657	22.157	61.601	-14.420	.671
4800	5.186	52.480	47.756	22.675	61.613	-16.038	.730
4900	5.198	52.587	47.854	23.194	61.626	-17.658	.788
5000	5.210	52.693	47.950	23.714	61.639	-19.276	.843
5100	5.222	52.796	48.044	24.236	61.652	-20.893	.895
5200	5.234	52.897	48.136	24.759	61.666	-22.513	.946
5300	5.246	52.997	48.227	25.283	61.680	-24.130	.995
5400	5.257	53.095	48.316	25.808	61.695	-25.751	1.042
5500	5.269	53.192	48.404	26.334	61.711	-27.369	1.088
5600	5.280	53.287	48.490	26.862	61.726	-28.990	1.131
5700	5.291	53.380	48.575	27.390	61.743	-30.611	1.174
5800	5.302	53.473	48.659	27.920	61.760	-32.229	1.214
5900	5.313	53.563	48.741	28.451	61.778	-33.851	1.254
6000	5.323	53.653	48.822	28.983	61.796	-35.471	1.292

June 30, 1962; June 30, 1974

OXYGEN MONATOMIC (O) (IDEAL GAS) GFW = 15.9994 0

Ground State Configuration $^3P_2$

$S°_{298.15}$ = 38.467 ± 0.005 gibbs/mol

$\Delta Hf°_0$ = 58.983 ± 0.024 kcal/mol

$\Delta Hf°_{298.15}$ = 59.553 ± 0.024 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	158.5	3
$^3P_0$	226.5	1
$^1D_2$	15867.5	5
^1S_o	33792.4	1

Heat of Formation

ΔHf° is the value adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions (1). The adopted value for $\Delta Hf°_{298}$(O, g) was derived using $D°_0(O_2)$ = 41260 ± 15 cm^{-1}(117.97 ± 0.04 kcal/mol) from Brix and Herzberg (2). The products of dissociation were assumed to be O atoms in their ground states. This calculation is discussed by Gaydon (3). The adopted ΔHf° value differs by 0.006 kcal/mol from the previous JANAF value (6).

Heat Capacity and Entropy

The electronic levels for O(g) are those given in the compilation by Moore (4) and reevaluated by Sitterley (5). We do not include the levels which lie above 73000 cm^{-1} as they do not contribute to the values of the thermodynamic functions below 6000 K. The calculated value of $S°_{298}$ agrees with that adopted by CODATA (1). The $S°_{298}$ value is 0.001 gibbs/mol less than the previous JANAF value (6).

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0

Strontium Oxide (SrO)

(Crystal) GFW = 103.6194

T, °K	gibbs/mol Cp°	 S°	 −(G°−H°298)/T	kcal/mol H°−H°298	 ΔHf°	 ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.073	- 141.016	- 141.016	INFINITE
100	5.963	3.643	21.956	- 1.831	- 141.441	- 139.135	304.080
200	9.658	9.162	14.231	- 1.014	- 141.561	- 136.772	149.457
298	10.853	13.270	13.270	.000	- 141.500	- 134.424	98.536
300	10.870	13.337	13.270	.020	- 141.498	- 134.381	97.896
400	11.587	16.569	13.706	1.145	- 141.388	- 132.024	72.134
500	12.078	19.210	14.551	2.330	- 141.268	- 129.696	56.690
600	12.440	21.446	15.518	3.556	- 141.161	- 127.393	46.403
700	12.730	23.386	16.507	4.815	- 141.082	- 125.105	39.059
800	12.978	25.102	17.476	6.101	- 141.043	- 122.826	33.555
900	13.198	26.643	18.410	7.410	- 141.218	- 120.533	29.270
1000	13.402	28.045	19.305	8.740	- 141.202	- 118.236	25.840
1100	13.593	29.331	20.158	10.090	- 143.095	- 115.830	23.013
1200	13.776	30.522	20.973	11.458	- 142.991	- 113.356	20.645
1300	13.953	31.631	21.751	12.845	- 142.873	- 110.891	18.642
1400	14.126	32.672	22.494	14.249	- 142.741	- 108.436	16.928
1500	14.295	33.652	23.205	15.670	- 142.595	- 105.990	15.443
1600	14.462	34.580	23.888	17.108	- 142.436	- 103.555	14.145
1700	14.627	35.462	24.543	18.562	- 174.836	- 100.225	12.885
1800	14.790	36.302	25.173	20.033	- 174.308	- 95.851	11.638
1900	14.952	37.106	25.780	21.520	- 173.768	- 91.507	10.526
2000	15.112	37.877	26.366	23.023	- 173.217	- 87.192	9.528
2100	15.272	38.619	26.932	24.542	- 172.656	- 82.904	8.628
2200	15.431	39.333	27.479	26.078	- 172.085	- 78.644	7.813
2300	15.590	40.022	28.010	27.629	- 171.506	- 74.410	7.071
2400	15.748	40.689	28.524	29.196	- 170.921	- 70.200	6.393
2500	15.906	41.335	29.024	30.778	- 170.333	- 66.017	5.771
2600	16.063	41.962	29.509	32.377	- 169.740	- 61.855	5.199
2700	16.220	42.571	29.982	33.991	- 169.149	- 57.717	4.672
2800	16.376	43.164	30.442	35.621	- 168.560	- 53.600	4.184
2900	16.533	43.741	30.891	37.266	- 167.976	- 49.505	3.731
3000	16.689	44.304	31.329	38.927	- 167.400	- 45.429	3.310
3100	16.845	44.854	31.756	40.604	- 166.833	- 41.372	2.917
3200	17.001	45.391	32.174	42.296	- 166.279	- 37.335	2.550
3300	17.157	45.917	32.582	44.004	- 165.740	- 33.314	2.206
3400	17.313	46.431	32.982	45.728	- 165.220	- 29.309	1.884
3500	17.468	46.935	33.374	47.467	- 164.719	- 25.320	1.581
3600	17.624	47.430	33.757	49.221	- 164.241	- 21.343	1.296

Dec. 31, 1972

STRONTIUM OXIDE (SrO) (CRYSTAL) GFW = 103.6194 OSr

ΔHf°_0 = -141.0 ± 0.8 kcal/mol

$S^\circ_{298.15}$ = 13.27 ± 0.1 gibbs/mol $\Delta Hf^\circ_{298.15}$ = -141.5 ± 0.8 kcal/mol

Tm = 2938 ± 20 K ΔHm° = [18] kcal/mol

Heat of Formation

ΔHf° is from NBS Technical Note 270-6 (1). The adopted value was derived (2) from ΔHf° = -198.1 kcal/mol for $SrCl_2$(c), ΔH_{soln} of $SrCl_2$ in HCl(aq), and calorimetric data for ΔHr of SrO(c) + (x+2)HCl(n H_2O) → [$SrCl_2$(aq) + H_2O(aq) + x HCl(n' H_2O)]. Data of Adami and Conway (3) yield ΔHf°(SrO, c) = -141.3 kcal/mol, while those of Monaenkova and Vorob'ev (4) yield -141.7 kcal/mol. Flidlider et al. (5) derived -140.5 kcal/mol from their (unpublished) data for SrO(c) and similar measurements for Sr(c) by Guntz and Benoit (6). Brisi and Abbattista (7) omit the mole ratios necessary for treatment of their data, but an approximate calculation suggests consistency with the adopted value. We omit from this discussion the early data which Parker (1, 2) reviewed in selecting the adopted value.

Direct measurements of ΔHc of Sr(c) by Mah (8) gave -144.44 ± 0.4 kcal/mol. The negative bias of about 3 kcal/mol presumably resulted from inadequate allowance for side reactions, e.g., with combustion products of Mylar used to contain the Sr. Parker (2) noted that the combustion value is incompatible with data for $SrCl_2$(c) and related compounds. We find that the combustion value is also less consistent with equilibrium data for $SrCl_2$(ℓ and g). There is a similar, but much larger, discrepancy for Ba compounds (cf. BaO, crystal). Although impurity effects are of concern in all studies, the evidence predominantly favors the solution calorimetry.

Heat Capacity and Entropy

Cp° is based on data (1.4-310 K) of Gmelin (9) who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed Cp° above 250 K where the scatter increases significantly. The entropy is obtained by integration of our adopted Cp° using S° = 0.0003 gibbs/mol at 4 K. Gmelin reported S°(273.15 K) = 12.40 ± 0.02 gibbs/mol compared with 12.33 from our integration. Cp° data (58-298 K) of Anderson (10) are lower at all temperatures with deviations ranging from -4.7% (61 K) to -0.3% (223 K) and -0.7% (298 K).

Cp° above 300 K is from constrained fitting of enthalpy data (363-1266 K) of Lander (11). The calorimeter (11) was calibrated with Pt, but details are lacking to assess the bias due to minor changes in the enthalpy of Pt (12). Deviations of Lander's data from the adopted curve range from -0.7 to +1.1%.

Melting Data - see SrO(ℓ).

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Strontium Oxide (SrO)

(Liquid) GFW = 103.6194

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	10.853	19.323	19.323	.000	-123.636	-118.365	86.764
300	10.870	19.390	19.323	.020	-123.634	-118.332	86.205
400	11.587	22.622	19.759	1.145	-123.523	-116.581	63.697
500	12.078	25.263	20.604	2.330	-123.403	-114.858	50.205
600	12.440	27.498	21.571	3.556	-123.296	-113.160	41.218
700	12.730	29.438	22.559	4.815	-123.218	-111.477	34.805
800	12.978	31.155	23.529	6.101	-123.179	-109.804	29.997
900	13.198	32.696	24.463	7.410	-123.354	-108.117	26.254
1000	13.402	34.097	25.357	8.740	-123.337	-106.424	23.259
1100	13.593	35.384	26.211	10.090	-125.231	-104.624	20.787
1200	13.776	36.574	27.026	11.458	-125.127	-102.755	18.714
1300	13.953	37.684	27.804	12.845	-125.009	-100.895	16.962
1400	14.126	38.724	28.547	14.249	-124.877	-99.045	15.462
1500	14.295	39.705	29.258	15.670	-124.731	-97.205	14.163
1600	14.462	40.633	29.940	17.108	-124.572	-95.375	13.028
1700	14.627	41.514	30.596	18.562	-156.972	-92.650	11.911
1800	14.790	42.355	31.226	20.033	-156.444	-88.881	10.792
1900	14.952	43.159	31.833	21.520	-155.904	-85.143	9.794
2000	15.112	43.930	32.418	23.023	-155.353	-81.433	8.899
2100	16.000	44.711	32.985	24.623	-154.710	-77.753	8.092
2200	16.000	45.455	33.535	26.223	-154.075	-74.104	7.362
2300	16.000	46.166	34.069	27.823	-153.447	-70.483	6.697
2400	16.000	46.847	34.588	29.423	-152.829	-66.888	6.091
2500	16.000	47.500	35.091	31.023	-152.223	-63.321	5.536
2600	16.000	48.128	35.581	32.623	-151.629	-59.776	5.025
2700	16.000	48.732	36.056	34.223	-151.052	-56.254	4.553
2800	16.000	49.314	36.520	35.823	-150.493	-52.753	4.118
2900	16.000	49.875	36.971	37.423	-149.955	-49.272	3.713
3000	16.000	50.418	37.410	39.023	-149.439	-45.809	3.337
3100	16.000	50.942	37.838	40.623	-148.949	-42.362	2.987
3200	16.000	51.450	38.255	42.223	-148.488	-38.932	2.659
3300	16.000	51.943	38.663	43.823	-148.057	-35.515	2.352
3400	16.000	52.420	39.060	45.423	-147.660	-32.111	2.064
3500	16.000	52.884	39.449	47.023	-147.298	-28.719	1.793
3600	16.000	53.335	39.828	48.623	-146.974	-25.335	1.538
3700	16.000	53.773	40.199	50.223	-146.689	-21.959	1.297
3800	16.000	54.200	40.562	51.823	-146.446	-18.591	1.069
3900	16.000	54.615	40.917	53.423	-146.245	-15.230	.853
4000	16.000	55.020	41.265	55.023	-146.088	-11.874	.649
4100	16.000	55.416	41.605	56.623	-145.974	-8.519	.454
4200	16.000	55.801	41.938	58.223	-145.905	-5.168	.269
4300	16.000	56.178	42.265	59.823	-145.880	-1.816	.092
4400	16.000	56.545	42.586	61.423	-145.898	1.534	-.076
4500	16.000	56.905	42.900	63.023	-145.960	4.885	-.237
4600	16.000	57.257	43.208	64.623	-146.063	8.240	-.391
4700	16.000	57.601	43.511	66.223	-146.207	11.595	-.539
4800	16.000	57.938	43.808	67.823	-146.390	14.955	-.681
4900	16.000	58.268	44.099	69.423	-146.609	18.316	-.817
5000	16.000	58.591	44.386	71.023	-146.863	21.685	-.948

Dec. 31, 1972

STRONTIUM OXIDE (LIQUID) GFW = 103.6194 OSr

$S^\circ_{298.15}$ = [19.323] gibbs/mol

$\Delta Hf^\circ_{298.15}$ = [-123.636] kcal/mol

Tm = 2938 ± 20 K

ΔHm° = [18] kcal/mol

Heat of Formation

ΔHf° is calculated from that of the crystal by addition of ΔHm° and the difference in ($H^\circ_{2938} - H^\circ_{298.15}$) between crystal and liquid.

Heat Capacity and Entropy

Cp° of the liquid is estimated as 8 gibbs/g-atom by comparison with other oxides. Cp° is taken from the crystal in the range from 298 K up to the glass transition assumed at 2000 K. S° is calculated in a manner analogous to ΔHf°.

Melting Data

Foex (1, 2) obtained Tm = 2660°C from a solar-furnace study using SrO as its own container. We adopt this result but increase it by 5° for conversion to IPTS-68. The much lower value (2420°C) of Schumacher (3, 4) probably resulte from contamination by WO_3 from tungsten supports of the sample. ΔHm° is estimated such that ΔSm° is 6 gibbs/mol. Phase data for the binary system $SrO-SrZrO_3$ (2) yield ΔHm = 10 ± 2 kcal/mol assuming ideal behavior in the liquid. Comparison with the very non-ideal behavior of other mixed oxides suggests that the SrO data (2) are not inconsistent with ΔHm° = 18 kcal/mol.

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OSr

Strontium Oxide (SrO)

OSr

(Ideal Gas) GFW = 103.6194

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-2.161	-2.803	-2.803	INFINITE
100	6.973	46.977	61.630	-1.465	-2.775	-4.803	10.496
200	7.383	51.908	55.666	-.752	-2.999	-6.759	7.386
298	7.909	54.958	54.958	.000	-3.200	-8.554	6.270
300	7.918	55.007	54.958	.015	-3.204	-8.587	6.256
400	8.276	57.338	55.274	.826	-3.407	-10.351	5.655
500	8.498	59.211	55.880	1.665	-3.632	-12.061	5.272
600	8.641	60.773	56.569	2.523	-3.894	-13.723	4.999
700	8.738	62.113	57.267	3.392	-4.205	-15.337	4.789
800	8.808	63.285	57.948	4.269	-4.575	-16.904	4.618
900	8.864	64.326	58.600	5.153	-5.175	-18.404	4.469
1000	8.917	65.262	59.220	6.042	-5.599	-19.851	4.338
1100	8.977	66.115	59.809	6.937	-7.948	-21.145	4.201
1200	9.057	66.399	60.367	7.838	-8.311	-22.329	4.067
1300	9.168	67.628	60.898	8.749	-8.668	-23.482	3.948
1400	9.322	68.313	61.403	9.673	-9.016	-24.609	3.842
1500	9.527	68.963	61.886	10.615	-9.350	-25.711	3.746
1600	9.789	69.586	62.348	11.581	-9.663	-26.791	3.660
1700	10.108	70.188	62.791	12.575	-42.524	-26.947	3.464
1800	10.482	70.777	63.219	13.604	-42.437	-26.033	3.161
1900	10.905	71.354	63.632	14.673	-42.315	-25.125	2.890
2000	11.364	71.925	64.032	15.786	-42.154	-24.225	2.647
2100	11.849	72.491	64.422	16.947	-41.951	-23.333	2.428
2200	12.344	73.054	64.801	18.156	-41.707	-22.453	2.230
2300	12.835	73.614	65.172	19.415	-41.420	-21.584	2.051
2400	13.308	74.170	65.535	20.723	-41.094	-20.728	1.888
2500	13.750	74.722	65.892	22.076	-40.735	-19.887	1.739
2600	14.152	75.270	66.242	23.471	-40.346	-19.060	1.602
2700	14.505	75.810	66.536	24.905	-39.935	-18.249	1.477
2800	14.804	76.344	66.925	26.371	-39.510	-17.453	1.362
2900	15.048	76.867	67.259	27.864	-39.079	-16.673	1.257
3000	15.237	77.381	67.588	29.378	-38.649	-15.908	1.159
3100	15.373	77.883	67.912	30.909	-38.227	-15.156	1.069
3200	15.459	78.372	68.231	32.451	-37.824	-14.420	.985
3300	15.501	78.849	68.546	34.000	-37.445	-13.694	.907
3400	15.503	79.312	68.856	35.550	-37.098	-12.980	.834
3500	15.472	79.761	69.161	37.099	-36.787	-12.276	.767
3600	15.413	80.196	69.462	38.644	-36.518	-11.579	.703
3700	15.332	80.617	69.757	40.181	-36.296	-10.889	.643
3800	15.233	81.025	70.049	41.709	-36.124	-10.204	.587
3900	15.121	81.419	70.335	43.227	-36.005	-9.525	.534
4000	14.999	81.800	70.617	44.733	-35.942	-8.847	.483
4100	14.872	82.169	70.894	46.227	-35.935	-8.169	.435
4200	14.742	82.526	71.167	47.707	-35.985	-7.492	.390
4300	14.610	82.871	71.435	49.175	-36.093	-6.811	.346
4400	14.480	83.206	71.699	50.629	-36.257	-6.129	.304
4500	14.352	83.530	71.958	52.071	-36.476	-5.442	.264
4600	14.228	83.844	72.213	53.500	-36.751	-4.748	.226
4700	14.108	84.148	72.464	54.917	-37.078	-4.049	.188
4800	13.993	84.444	72.710	56.322	-37.456	-3.342	.152
4900	13.883	84.732	72.953	57.716	-37.881	-2.630	.117
5000	13.779	85.011	73.191	59.099	-38.352	-1.905	.083
5100	13.680	85.233	73.426	60.472	-38.866	-1.170	.050
5200	13.586	85.548	73.656	61.835	-39.420	-.427	.018
5300	13.498	85.806	73.883	63.189	-40.011	.331	-.014
5400	13.415	86.057	74.106	64.535	-40.635	1.096	-.044
5500	13.337	86.303	74.326	65.872	-41.291	1.876	-.075
5600	13.264	86.542	74.542	67.202	-41.975	2.666	-.104
5700	13.195	86.776	74.754	68.525	-42.684	3.468	-.133
5800	13.131	87.005	74.964	69.841	-43.416	4.286	-.162
5900	13.070	87.229	75.170	71.151	-44.167	5.114	-.189
6000	13.013	87.448	75.372	72.456	-44.935	5.957	-.217

June 30, 1974

STRONTIUM OXIDE (SrO) (IDEAL GAS) GFW = 103.6194 OSr

Symmetry Number = 1

$S^\circ_{298.15}$ = 54.958 ± 0.1 gibbs/mol

ΔHf°_0 = -2.8 ± 4 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -3.2 ± 4 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1-4)	$X^1\Sigma^+$	0.0	1	1.9199	0.33798	0.00219	653.2	3.92
(1)	$a^3\Pi$	9055	6	2.195	0.2584	0.0020	463.5	1.61
(1)	$A'^1\Pi$	9794	2	2.184	0.2610	0.0023	460.3	1.61
(5)	$^3\Sigma^+$	[8000]	3	[2.021]	[0.3047]	[0.0011]	[619.6]	[0.9]
(1, 4)	$A^1\Sigma^+$	10870.	1	2.021	0.30471	0.00112	619.6	0.9
(5)	$^3\Sigma^+$	[22000]	3	[2.14]	[0.272]	[0.002]	[480]	[2.6]
(5)	$^3\Delta$	[22000]	6	"	"	"	"	"
(5)	$^1\Delta$	[24000]	2	"	"	"	"	"
(5)	$^3\Sigma^-$	[24000]	3	"	"	"	"	"
(5)	$^1\Sigma^-$	[24000]	1	"	"	"	"	"
(4)	$C^1\Sigma^+$	28546.	1	2.132	0.2742	0.0021	480.2	2.6
(5)	$^3\Pi$	[23000]	6	[2.06]	[0.2936]	[0.0015]	[520]	[3.2]
(4)	$B^1\Pi$	24636.	2	2.060	0.2936	0.0015	519.9	3.24

Heat of Formation

We adopt D°_0 = 101.0 ± 4 and ΔHf°_{298} = -3.2 ± 4 kcal/mol based on the equilibria analyzed below. Greatest weight is given to the conventional mass-spectrometric studies (7, 8). We give "<" or ">" for the resulting D°_0 values which we feel may be biased. The JANAF differences in ΔHf°_{298} for MoO_3-MoO_2 and WO_3-WO_2 may be biased by ∿4 and ∿-3 kcal/mol, respectively; this would cause bias of the opposite sign in D°_0 values derived from reactions C and D. With these adjustments our analyses would be comparable with those of Brewer and Rosenblatt (10) based on a $^1\Sigma$ ground state.

Less reliable data were reviewed by Drowart et al. (8) and Schofield (11). Subsequent studies include two new techniques: nonisothermal Langmuir mass-spectrometry (9) and crossed-beam reaction threshold (12). The former yields D°_0 = 98.3 and >96 kcal/mol (see reactions E and F below). JANAF data for the reaction SrO(c) = Sr(g) + O(g) suggest that the P_O assumed (9) for reaction F is too large. JANAF pressures for Sr(g) and O(g) may be combined with the estimated composition (3) of 5% SrO(g) to calculate Kp for reaction F and D°_0 = 93.5 ± 8 kcal/mol. D°_0 would increase to 97 kcal/mol if the beam in the magnetic-deflection experiment (3) contained 10% SrO(g) rather than 5%. The crossed-beam reaction (12) was interpreted to give D°_0 = 112.5(+3.5 to -0.7) kcal/mol. We assume this value has a positive bias. Finally, Kalff (13) used spectrometry of CO-N_2O flames to derive D°_0 = 93.6 ± 2.3 kcal/mol. This value becomes ∿99 kcal/mol when adjusted to be consistent with the JANAF free energy functions.

Source	Method	Reaction[a]	Range T/K	No. of Points	δS[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	ΔHr°_{298}/(kcal/mol) 3rd Law	ΔHf°_{298} kcal/mol	D°_0 kcal/mol
(7) Colin(1964)	Knudsen mass spec.	A	1931-2170	5	9.5±7.1	42.±15	22.6±2.8	-3.3±3	101.2
(8) Drowart(1964)	" " "	B	2156-2321	4	-40.±10	-73.±22	16.3±5.8	-4.1±6	101.9
	" " "	C	1987-2233	8	-2.5±6.1	40.±13	45.4±2.6	1.5±6	>96.4
	" " "	D	2326	1	-	-	44.9	-4.2±5	<102.0
(9) Asano(1972)	Langmuir mass spec.[c]	E[d]	1747-1850	Eqn.	-3.8	134.2	141.0±0.7	-0.5±3	98.3
	" " "	F[d]	" "	"	3.3	102.9	97.0	1.8±3	>96.0
(3) Kaufman(1965)	Magnetic deflection	F	∿2500	1	-	-	94.5	4.3±8	93.5

[a] Reactions: A) Sr(g) + SO(g) = SrO(g) + S(g); B) Sr(g) + O_2(g) = SrO(g) + O(g); C) Sr(g) + MoO_3(g) = SrO(g) + MoO_2(g); D) Sr(g) + WO_3(g) = SrO(g) + WO_2(g); E) SrO(c) = SrO(g); F) SrO(g) = Sr(g) + O(g).

[b] $\delta S = \Delta Sr^\circ$(2nd Law) - ΔSr°(3rd Law). [c] Nonisothermal. [d] $P_O = 0.4273 P_{Sr}$ assumed.

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants of the observed states are from Field (1) and Rosen (4). The long-sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field (1) using a new method for assignment of perturbations. This study resolved the long-standing controversy over low-lying electronic levels and confirmed (1) that $X^1\Sigma^+$ is the ground state (3). We estimate the other potentially low-lying state ($^3\Sigma^+$) at 8000 cm^{-1} by assuming that it lies 3000 ± 2500 cm^{-1} (1, 5) below the isoconfigurational A state. Other predicted states and their vibrational-rotational constants are estimated in isoconfigurational groups by comparison with BeO, MgO, CaO and BaO (5). Comparisons are facilitated by listing the states in the isoconfigurational order of MgO (5, 6). Our thermodynamic functions correspond to an "effective" ground state with 1<g<2 instead of g = 3 (11). Our functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2\varepsilon_i/T)$.

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OSr

Tanatum Monoxide (TaO) OTa

(Ideal Gas) GFW = 196.9465

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	− 2.095	46.300	46.300	INFINITE
100	6.956	49.915	63.914	− 1.400	46.411	43.875	− 95.888
200	7.026	54.748	58.259	− .702	46.221	41.403	− 45.243
298	7.314	57.601	57.601	.000	46.000	39.087	− 28.651
300	7.320	57.646	57.601	.014	45.996	39.044	− 28.444
400	7.681	59.802	57.893	.764	45.779	36.759	− 20.084
500	7.988	61.550	58.455	1.548	45.574	34.529	− 15.093
600	8.237	63.029	59.097	2.359	45.372	32.339	− 11.779
700	8.447	64.315	59.752	3.194	45.172	30.183	− 9.424
800	8.637	65.456	60.395	4.048	44.973	28.054	− 7.664
900	8.813	66.483	61.016	4.921	44.780	25.951	− 6.302
1000	8.978	67.421	61.610	5.810	44.592	23.870	− 5.217
1100	9.130	68.283	62.178	6.716	44.406	21.806	− 4.332
1200	9.268	69.084	62.720	7.636	44.222	19.760	− 3.599
1300	9.392	69.831	63.239	8.569	44.038	17.729	− 2.981
1400	9.503	70.531	63.735	9.514	43.855	15.712	− 2.453
1500	9.601	71.190	64.210	10.469	43.675	13.708	− 1.997
1600	9.691	71.813	64.666	11.434	43.499	11.717	− 1.600
1700	9.775	72.403	65.104	12.407	43.325	9.735	− 1.251
1800	9.856	72.964	65.525	13.389	43.148	7.764	− .943
1900	9.936	73.499	65.931	14.379	42.963	5.803	− .668
2000	10.018	74.010	66.322	15.376	42.772	3.852	− .421
2100	10.103	74.501	66.700	16.382	42.574	1.912	− .199
2200	10.193	74.973	67.065	17.397	42.368	− .020	.002
2300	10.289	75.428	67.419	18.421	42.157	− 1.942	.185
2400	10.391	75.868	67.762	19.455	41.938	− 3.854	.351
2500	10.498	76.295	68.095	20.499	41.710	− 5.758	.503
2600	10.610	76.709	68.418	21.555	41.474	− 7.652	.643
2700	10.727	77.111	68.733	22.622	41.225	− 9.537	.772
2800	10.847	77.504	69.039	23.700	40.962	− 11.412	.891
2900	10.970	77.886	69.338	24.791	40.682	− 13.277	1.001
3000	11.094	78.260	69.629	25.894	40.380	− 15.133	1.102
3100	11.218	78.626	69.913	27.010	40.053	− 16.978	1.197
3200	11.342	78.984	70.191	28.138	39.696	− 18.812	1.285
3300	11.463	79.335	70.463	29.278	30.591	− 20.523	1.359
3400	11.582	79.679	70.729	30.430	30.257	− 22.066	1.418
3500	11.697	80.016	70.989	31.594	29.934	− 23.601	1.474
3600	11.807	80.348	71.245	32.770	29.621	− 25.126	1.525
3700	11.913	80.672	71.495	33.956	29.316	− 26.642	1.574
3800	12.012	80.991	71.741	35.152	29.019	− 28.150	1.619
3900	12.106	81.305	71.982	36.358	28.731	− 29.652	1.662
4000	12.193	81.612	72.219	37.573	28.450	− 31.146	1.702
4100	12.274	81.914	72.452	38.796	28.176	− 32.631	1.739
4200	12.349	82.211	72.681	40.027	27.909	− 34.112	1.775
4300	12.416	82.503	72.906	41.266	27.647	− 35.584	1.809
4400	12.477	82.789	73.127	42.510	27.390	− 37.052	1.840
4500	12.532	83.070	73.345	43.761	27.138	− 38.514	1.870
4600	12.580	83.346	73.559	45.017	26.891	− 39.969	1.899
4700	12.622	83.617	73.771	46.277	26.646	− 41.420	1.926
4800	12.658	83.883	73.978	47.541	26.404	− 42.865	1.952
4900	12.689	84.144	74.183	48.808	26.165	− 44.308	1.976
5000	12.714	84.401	74.385	50.078	25.928	− 45.744	1.999
5100	12.735	84.653	74.584	51.351	25.692	− 47.174	2.022
5200	12.750	84.900	74.780	52.625	25.457	− 48.602	2.043
5300	12.762	85.143	74.973	53.901	25.223	− 50.021	2.063
5400	12.769	85.382	75.164	55.177	24.989	− 51.441	2.082
5500	12.772	85.616	75.352	56.454	24.756	− 52.853	2.100
5600	12.772	85.846	75.537	57.732	24.521	− 54.263	2.118
5700	12.769	86.072	75.720	59.009	24.286	− 55.668	2.134
5800	12.763	86.294	75.900	60.285	− 152.098	− 56.643	2.134
5900	12.754	86.512	76.078	61.561	− 152.333	− 54.997	2.037
6000	12.743	86.727	76.254	62.836	− 152.573	− 53.344	1.943

Dec. 31, 1973

TANTALUM MONOXIDE (TaO) (IDEAL GAS) GFW = 196.9464 OTa

Ground State Configuration $^2\Delta_{3/2}$

$S^\circ_{298.15}$ = 57.60 ± 0.50 gibbs/mol

ΔHf°_0 = 46.3 ± 15.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 46.0 ± 15.0 kcal/mol

Electronic Levels and Quantum Weights

State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i	State	ε_i, cm^{-1}	g_i
$X^2\Delta_{3/2}$	0.00	2	$^2\Phi_{7/2}$	22918.75	4	$^2\Delta_{5/2}$	27290.63	2
$^2\Delta_{5/2}$	3505.43	2	$^2\Pi_{1/2}$	23341.74	2	$^2\Delta_{3/2}$	32373.60	2
$^2\Delta_{3/2}$	10860.95	4	$^2\Phi_{5/2}$	24058.42	2	$^2\Delta_{5/2}$	35785.83	4
$^2\Pi_{1/2}$	11062	4	$^2\Pi_{3/2}$	25593.13	2	$^2\Delta_{5/2}$	35886.20	2
$^2\Phi_{5/2}$	12852.02	4	$^2\Phi_{7/2}$	26121.50	2	$^2\Delta_{5/2}$	36615	4
$^2\Delta_{3/2}$	13569.27	4	$^2\Delta_{3/2}$	26673.04	2	$^2\Delta_{5/2}$	36785	4
$^2\Phi_{5/2}$	15880.62	4						

ω_e = 1028.69 cm^{-1} $\qquad$ $\omega_e x_e$ = 3.51 cm^{-1} $\qquad$ σ = 1

B_e = 0.402840 cm^{-1} $\qquad$ α_e = 0.00182 cm^{-1} $\qquad$ r_e = 1.6872 Å

Heat of Formation

Based on the adopted ground state vibrational constants, a linear Birge-Sponer extrapolation yields a dissociation energy, D°_0, of 9.28 eV (214.02 kcal/mol). Applying a correction for the ionicity in the Ta-O bond (1), we recalculate D°_0 = 8.67 eV (199.94 kcal/mol). This in turn leads to a ΔHf°_{298} value of 45.52 kcal/mol for TaO(g) using auxiliary data (2).

Inghram, et al. (3) and Krikorian and Carpenter (4) have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta-Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2. Results of our second and third law analysis of these and other data are presented below. ΔHf°_{298} in the table refers to the heat of formation of TaO(g).

Reference	Reaction	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	ΔHf°_{298}, kcal/mol 2nd Law	ΔHf°_{298}, kcal/mol 3rd Law
3	A*	1	2022	-	147.31	-	-	+49.51
4	A	2	1927-2034	162.80	175.47	6.4	+65.00	+77.67
3	B*	5	2151-2278	193.95	144.81	-22.3±14.1	+100.30	+51.26
4	B	3	2180-2271	166.53	172.90	2.8±7.9	+ 72.98	+79.35
16	C	graph	1900-2900	54.15	93.33	17.5	54.15	93.33

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections (4, 5).

A: 0.6 Ta(c) + 0.2 Ta_2O_5(c) = TaO(g) B: 0.6 Ta(c) + 0.2 Ta_2O_5(ℓ) = TaO(g) C: Ta(c) + 1/2 O_2(g) = TaO(g)

The discrepancies here are rather severe and indicate considerable uncertainty in the system studied. In addition to the standard difficulties in a Knudsen cell system and the subsequent assumptions used for a second and third law analysis, there is an additional problem of oxygen diffusing through the walls of the Ta Knudsen cell, followed by volatilization of TaO(g) from the outer surfaces (4, 6). Based on JANAF ΔHf°_{298} values for Ta_2O_5(c) and Ta_2O_5(ℓ), ΔHr°_{298} for reaction (A) should be 4.25 kcal/mol more positive than reaction (B). The third law results of Krikorian and Carpenter (4) for reactions (A) and (B) differ by 2.57 kcal/mol but the second law results differ by 3.73 kcal/mol in the wrong direction. The third law results of Inghram et al. (3) differ by 2.50. It is interesting to note that, if the pressures reported by Krikorian and Carpenter (4) are multiplied by a factor of 1000, a third law analysis yields results in excellent agreement with the third law results of Inghram et al. (3). Second law values would still be in disagreement, however, and serious third law drifts would still be present. Drowart et al. (16) observed the vapors over a Ta wire at various oxygen pressures in the range 1900-2900 K. Our analysis of their graphically displayed results does not clarify the situation as there is again a large third law drift. Inghram et al. (3) also measured the ion currents corresponding to ZrO(g) and TaO(g) over mixtures of ZrO_2(c) and Ta(c) in a Ta Knudsen cell. The reaction was stated as ZrO_2(c) + Ta(c) = ZrO(g) + TaO(g). A second law analysis of seven data points yielded ΔHr°_{2200} = 317 ± 7 kcal/mol as reported by Inghram et al. (3). Using JANAF auxiliary data (2), this leads to ΔHf°_{298}(TaO, g) = 51 ± 12 kcal/mol, where ±12 kcal/mol reflects the additional uncertainty in ΔHf°_{298} for ZrO(g). Goldstein, Walsh, and White (7), in studying the vaporization of Nd_2O_3 from Ta Knudsen effusion cells in the range 2040-2450 K, determined the heat of reaction for Nd_2O_3(c) + Ta(c) = 2 NdO(g) + TaO(g). They reported a value of D°_0 = 9.36 ± 0.2 eV for TaO(g). This leads to ΔHf°_{298}(TaO, g) = 29.6 ± 5.0 kcal/mol.

Brewer and Rosenblatt (17) have suggested free energy functions which are 1.38 to 2.14 gibbs/mol more positive than those adopted here (298-3000 K). The reason for the difference is that Brewer and Rosenblatt (17) based their functions on low lying electronic states as observed in the Ta^{++} ion. The ΔHf°_{298} values derived from the third law would increase by roughly 3.5-4.2 kcal/mol with the drift becoming more positive by 2-3 eu, if we were to use Brewer and Rosenblatt's free energy functions.

Due to the large scatter in the mass spectrometric results, we prefer not to average the resulting ΔHf° values but to rely on correlations with VO(g) and NbO(g). There has been good agreement for VO(g) and NbO(g) between the adopted JANAF ΔHf°_{298} value and the value derived from the Birge-Sponer result corrected for ionicity (2). Thus we adopt ΔHf°_{298}(TaO, g) = 46.0 ± 15.0 kcal/mol, which is a rounded value based on the adjusted Birge-Sponer result. The adopted ΔHf°_{298} value corresponds to a dissociation energy D°_0 = 8.55 ± 0.65 eV.

Heat Capacity and Entropy

The band spectrum attributable to TaO(g) has been observed by many investigators (8-13). Weltner and McLeod (14) studied TaO spectroscopically in the infrared, visible, and near-ultraviolet regions by means of matrix isolation techniques. Sixteen electronic transitions were observed from the X $^2\Delta_{3/2}$ state, determined to be the ground state. Cheetham and Barrow (15) characterized nineteen electronic states from a rotational analysis of the emission spectrum of TaO in the region 2740-9500 Å. The combination of the results of these latter two studies as given by Cheetham and Barrow (15) provides the adopted vibrational and rotational constants as well as the electronic levels. Cheetham and Barrow (15) indicated the possibility of other low lying states based on the early work by Kiess and Stowell (8).

OTa

The electronic states listed by Cheetham and Barrow (15) are actually sublevels as indicated by the Ω value. The quantum weight of 2 is assigned if the two sublevels which are part of the same state are present (i.e. similar ω_e and $\omega_e x_e$ values for the same Λ state but different Ω value). If the two sublevels of a particular Λ state are not accounted for then a quantum weight of 4 is assigned to that sublevel which is tabulated.

References: See TaO_2(g) table.

Titanium Monoxide, Alpha (α-TiO)

(Crystal) GFW = 63.8994

T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 1.476	- 128.986	- 128.986	INFINITE
100	3.051	1.370	15.147	- 1.379	- 129.369	- 127.240	278.092
200	7.333	4.920	9.121	- .840	- 129.638	- 124.986	136.579
298	9.550	8.310	8.310	.000	- 129.700	- 122.638	89.933
300	9.575	8.369	8.310	.018	- 129.700	- 122.645	89.347
400	10.750	11.299	8.702	1.039	- 129.652	- 120.298	65.728
500	11.530	13.786	9.475	2.155	- 129.548	- 117.971	51.565
600	12.150	15.944	10.373	3.339	- 129.407	- 115.669	42.132
700	12.690	17.858	11.312	4.582	- 129.239	- 113.392	35.403
800	13.190	19.586	12.240	5.876	- 129.054	- 111.141	30.362
900	13.660	21.167	13.146	7.215	- 128.854	- 108.913	26.448
1000	14.120	22.630	14.022	8.508	- 128.643	- 106.709	23.321
1100	14.570	23.997	14.867	10.043	- 128.416	- 104.526	20.767
1200	15.010	25.283	15.682	11.522	- 129.113	- 102.327	18.636
1300	15.450	26.502	16.468	13.045	- 128.733	- 100.110	16.830
1400	15.880	27.653	17.226	14.611	- 128.327	- 97.924	15.287
1500	16.310	28.773	17.959	16.221	- 127.896	- 95.767	13.953
1600	16.740	29.839	18.669	17.873	- 127.447	- 93.638	12.790
1700	17.170	30.867	19.356	19.569	- 126.976	- 91.540	11.768
1800	17.590	31.860	20.023	21.307	- 126.487	- 89.470	10.863
1900	18.020	32.823	20.672	23.087	- 125.981	- 87.428	10.056
2000	18.440	33.758	21.303	24.910	- 129.906	- 85.259	9.317
2100	18.860	34.669	21.919	26.775	- 129.344	- 83.039	8.642
2200	19.280	35.555	22.516	28.682	- 128.743	- 80.849	8.032
2300	19.710	36.421	23.103	30.632	- 128.101	- 78.586	7.477
2400	20.130	37.269	23.676	32.624	- 127.420	- 76.550	6.971
2500	20.550	38.099	24.236	34.658	- 126.700	- 74.446	6.508

Dec. 31, 1960; Mar. 31, 1967; Dec. 31, 1973.

TITANIUM MONOXIDE, ALPHA (α-TiO) (CRYSTAL) GFW = 63.8994 OTi

$S°_{298.15}$ = 8.31 ± 0.5 gibbs/mol
Tt = [1265] K

$ΔHf°_0$ = -128.9 ± 3 kcal/mol
$ΔHf°_{298.15}$ = -129.7 ± 3 kcal/mol
ΔHt° = [1.0] kcal/mol
$ΔHs°_{298.15}$ = 142.7 ± 4 kcal/mol

Heat of Formation

Recent data tend to support our speculation (1) that previous calorimetric data refer to ill-defined states of TiO(α, β). New combustion calorimetry (2) at 1100 K gave $ΔHf°_{298}$ = -129.9 ± 1.1 kcal/mol which is ∼5 kcal/mol more negative than two earlier combustion studies (3, 4) near room temperature. The difference was attributed (2) to use of samples consisting of α-phase (2) or mainly β-phase (3, 4). This interpretation is reasonable but unproved; it is neither confirmed nor refuted by incomplete published descriptions of the samples. Previously, the samples (3, 4) were assumed to be α-phase since similar material gave a discontinuity in enthalpy data above 1200 K.

Lyon (5) proposed that ΔHf may be affected by vacancy concentration, which varies from ∼14 to 15% (5) in samples of stoichiometric β-TiO obtained at normal pressure. Samples with vacancy concentrations down to 0% have been prepared (6) at high pressure. PVT data (6) allowed calculation (5) of values of ΔH for TiO(β, 0% vacancies) → TiO(β, 14% vacancies). These values, if valid, suggest that ΔHf should be quite different for vacancy-free β-TiO and significantly different even for the normal range of vacancy concentrations. Ideal ordered α-TiO, containing 1/6 or 16.7% vacancies, should involve additional changes in volume (5) and ΔHf. In summary, the discrepancy in ΔHf may arise from sample differences - phase, composition and vacancy concentration - or from bias in the reaction calorimetry.

Our choice of ΔHf° is influenced by ΔGf° values derived from oxygen potentials (7, 8) over TiO_x(0 < x < 1.5). We use solid-state emf data (7) for many compositions in the range 0.6 < x < 1.5; these are converted to $Δ\bar{G}(O_2)$ with the authors' results (7) for the reference couples Ta/Ta_2O_5 and "$TiO_{1.3}$", then integrated over appropriate ranges of x in order to get ΔGr°. For reaction C relating TiO(β) to Ti_2O_3 we get ΔGr° = -38.70(1300 K), -37.48(1400 K), -36.82(1500 K), -36.18(1600 K) and -35.52(1700 K) kcal/mol with an estimated uncertainty of ±1 kcal/mol (∼3%). Combination with ΔGf° (1) of Ti_2O_3 yields ΔGf°(TiO, β) = -131.5 + 23.5 (T/1000); hopefully, the uncertainty does not exceed 1.5 kcal/mol, based on a revised uncertainty of 1 kcal/mol for Ti_2O_3.

Approximate values of ΔGf°(TiO) may be derived from $TiO_{0.334}$(c) and Ti(c). Calorimetric data (10) yield ΔGf°($TiO_{0.334}$) = -46.1 + 8.40 (T/1000) for 1200 < T < 1700; this equation excludes the added disordering entropy (10) which now is known to be included, at least partially, in order-disorder transitions of the alloy near 800 K (11). $Δ\bar{G}(O_2)$ in the range 0.334 < x < 0.5 is approximated by limiting values, i.e. the mean from x < 0.334 and the univariant value (7) at x = 0.6, in order to get negative and positive limits for ΔGf°(TiO). These limits differ by 1 to 2.5 kcal/mol at 1300 to 1700 K; mean ΔGf° values are -102.0 (1300 K), -96.8(1400 K), -92.6(1500 K), -88.3(1600 K) and -85.0 kcal/mol (1700 K). Equilibration with Ca/CaO and Mg/MgO (8) near 1200 K gave $Δ\bar{G}(O_2)$ for x < 0.3; we combine these by interpolation with values (7) at x > 0.6 to give ΔGf°(TiO) = -107.3(1173 K), -106.6(1200 K) and -103.8 kcal/mol (1273 K). ΔGf° values derived from Ti(c) and $TiO_{0.334}$(c) are relatively uncertain, perhaps by 5 kcal/mol, due to gaps in $Δ\bar{G}(O_2)$ and to greater uncertainty in emf and x.

ΔHf° values from ΔHc° and from 3rd-law analyses of ΔGr° are compared below. ΔHf° from Ti_2O_3 (7, 8) is consistent with the new ΔHc° (2) but ∼5 kcal/mol more negative than the earlier value (3) which we assume to refer to β-TiO. ΔHf° from Ti_2O_3 (7, 8) and from ΔHc° (3) could be made consistent if, as proposed by Charlu et al. (2), ΔSt° and S°(β) were increased by 3 gibbs/mol [see β-TiO (9)]. If (3) instead of (2) were correct for α-TiO, $Δ\bar{G}(O_2)$ would have to be 14% larger than observed. The more uncertain ΔHf° from $TiO_{0.334}$ (7, 8) is very temperature dependent (large δS); it agrees with (2) at 1250 K and with (3) at 1700 K. ΔHf° from Ti (7-9) is even more negative than (2). We adopt ΔHf° = -129.7 kcal/mol (2) but increase the uncertainty to ±3 kcal/mol to allow for possible uncertainties in the samples.

Source	Method	Reaction[a]	Range T/K	δS[b] gibbs/mol	$ΔHr°_{298}$ kcal/mol	$ΔHf°_{298}$, kcal/mol		
						Authors	JANAF[c] TiO(α)	TiO(β)
(2) Charlu et al. (1974)	ΔHc°	A	1100→298	-	-96.05±1.1	-129.86	-129.7	[-128.7]
(3) Humphrey (1951)	ΔHc°	B	303→298	-	-101.61±0.12	-123.9±0.3	[-125.2]	-124.2
(4) Ariya (1957)	ΔHc°	B	298	-	-99.5	-124.5±0.4	[-127.3]	-126.3
(7, 9) From Ti_2O_3	Emf, ΔGr°	C	1300-1700	2.9	-52.77	-	[-130.0]	-129.0
(7, 9) From $TiO_{0.334}$	Emf, ΔGr°	D	1200-1700	-18.	-127.5	-	[-128.5]	-127.5
(7-9) From Ti(β)	Emf, $Δ\bar{G}(O_2)$	D	1273	-	-133.2	-	[-134.2]	-133.2
		E	1173-1200	-2.5	-135.4	-	-135.4	[-134.4]

[a] Reactions: A) TiO(α?) + 1/2 O_2(g) = TiO_2(rutile); B) TiO(β?) + 1/2 O_2 = TiO_2(rutile); C) TiO(β) + 1/4 O_2(g) = 1/2 Ti_2O_3(c);
D) Ti(β) + 1/2 O_2(g) = TiO(β); E) Ti(β) + 1/2 O_2(g) = TiO(α?).

[b] δS = ΔSr°(2nd law) - ΔSr°(3rd law).

[c] ΔHf° in brackets calculated from ΔHt° = [1.0] kcal/mol.

Heat Capacity and Entropy

Cp° is from data (52.6-296 K) of Shomate (12) and enthalpy data (357-1771 K) of Naylor (13). $S°_{298.15}$ = 8.31 is calculated from Cp° based on $S°_{50}$ = 0.23 gibbs/mol. Ideal, ordered α-TiO should have no configurational entropy at absolute zero (14). We assume that Cp°(α) = Cp°(β) and fit the enthalpy data (357-1200 K and 1273-1771 K) by a single curve after subtracting the apparent ΔHt = 0.83 kcal/mol from points above Tt. The single curve gives larger deviations than separate fits of the two regions, but the increases are of marginal significance.

Recent Cp° data (60-298 K) for $TiO_{1.01}$ (15) are larger at all temperatures with deviations of 2-3% at 110-250 K increasing to 5% at 298 K and 7% at 60 K. The new data yield $S°_{298}$ = 8.55 gibbs/mol of TiO. We know nothing about the TiO sample (15), but it also may have been used to obtain enthalpies (700-2300 K) which are not yet published (16). Shomate (12), Naylor (13) and later Humphrey (3, see ΔHf°) all used the same sample, 99.2% pure with Si and C as impurities. The (O/Ti) ratio was ∼0.994 (17). Vacancy concentration is unknown and the phase is uncertain.

Transition Data and Phase Data - See β-TiO.

Heat of Sublimation - This is the difference in ΔHf° for TiO(g) and TiO(α).

References - See TiO(β).

OTi

Titanium Monoxide, Beta (β-TiO)

(Crystal) GFW = 63.8994

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	9.550	9.101	9.100	.000	- 128.700	- 121.924	89.373
300	9.575	9.160	9.101	.018	- 128.700	- 121.882	98.791
400	10.750	12.089	9.492	1.039	- 128.652	- 119.614	65.354
500	11.530	14.576	10.267	2.155	- 128.548	- 117.365	51.301
600	12.150	16.734	11.169	3.339	- 128.407	- 115.143	41.941
700	12.690	18.649	12.103	4.582	- 128.239	- 112.946	35.263
800	13.190	20.376	13.031	5.876	- 128.054	- 110.773	30.262
900	13.660	21.957	13.936	7.219	- 127.854	- 108.625	26.378
1000	14.120	23.420	14.812	8.608	- 127.643	- 106.500	23.275
1100	14.570	24.787	15.657	10.043	- 127.416	- 104.395	20.741
1200	15.010	26.074	16.472	11.522	- 128.113	- 102.275	18.627
1300	15.450	27.293	17.258	13.045	- 127.733	- 100.138	16.835
1400	15.880	28.453	18.017	14.611	- 127.327	- 98.031	15.303
1500	16.310	29.564	18.750	16.221	- 126.898	- 95.953	13.980
1600	16.740	30.630	19.459	17.873	- 126.447	- 93.903	12.827
1700	17.170	31.658	20.147	19.565	- 125.976	- 91.884	11.813
1800	17.590	32.651	20.814	21.307	- 125.487	- 89.893	10.915
1900	18.020	33.614	21.462	23.087	- 124.981	- 87.929	10.114
2000	18.440	34.549	22.093	24.910	- 126.906	- 85.839	9.380
2100	18.860	35.458	22.708	26.775	- 128.344	- 83.699	8.711
2200	19.280	36.345	23.308	28.682	- 127.743	- 81.588	8.105
2300	19.710	37.212	23.894	30.632	- 127.101	- 79.504	7.555
2400	20.130	38.060	24.466	32.624	- 126.420	- 77.448	7.053
2500	20.550	38.890	25.027	34.658	- 125.700	- 75.423	6.593

Mar. 31, 1967; Dec. 31, 1973.

TITANIUM MONOXIDE, BETA (β-TiO) (CRYSTAL) GFW = 63.8994 OTi

$S^\circ_{298.15}$ = [9.10] gibbs/mol
Tt = [1265] K
Tm = 2023 ± 30 K

$\Delta Hf^\circ_{298.15}$ = -128.7 ± 3 kcal/mol
ΔHt° = [1.0] kcal/mol
ΔHm° = [10] kcal/mol

Heat of Formation

ΔHf° is calculated from that of α-TiO by adding ΔHt° to the difference in ($H^\circ_{1265}-H^\circ_{298}$) between α- and β-TiO. ΔGf° data for β-TiO are reviewed on the table for α-TiO (9). Values of ΔHf° derived from ΔGf° depend on the value of S° (see Entropy). There are additional references on ΔGf° which deserve comment. Solid-state emf data of Hoch et al. (18) are insufficient to yield ΔGf°(β), especially in the direct way used by Drowart et al. (19). Their intepretation is inconsistent with phase diagrams (20, 17) and extensive emf data (7) which show bivariant behavior in which $\Delta\bar{G}(O_2)$ is a strong function of (O/Ti). It is not useful to reinterpret the emf data (18); they show a temperature dependence of the wrong sign and we do not know the necessary electrode compositions. The often quoted ΔGf° of Kubaschewski and Dench (21) is not an independent value since it assumes the correctness of the calorimetric data of the Bureau of Mines (3, 12, 13). Kubaschewski's reassessment (22, 8) of $\Delta\bar{G}(O_2)$ is superseded (9) due to new data (7).

Heat Capacity and Entropy

We assume Cp°(β) = Cp°(α) as discussed on the table for α-TiO. S° is calculated in a manner analogous to that of ΔHf°. S° might be too low by as much as 3 or 4 gibbs/mol (2) due to a possible uncertainty in ΔHt° (see Transition Data). The possibility exists because experimental samples (2-4, 12, 13) were not adequately characterized as to phase and vacancy concentration.

Phase Data

Stoichiometric TiO has been identified in two crystalline forms. High-temperature β-TiO has a cubic NaCl-type structure (23), while low-temperature α-TiO has a closely related monoclinic structure (24, 25). Ideal α-TiO is an ordered array in which 1/6 of the lattice sites are vacant; half of the Ti and O atoms are missing alternately in every third (110) plane (24). β-TiO obtained at normal pressures appears to have a lower and somewhat variable (∿14-15%) vacancy concentration (5), depending on conditions of preparation. Vacancy concentration can be reduced to arbitrary values (including zero) at high pressure by quenching from high temperature (6). The process is reversed on reheating at normal pressure. Vacancy concentration (6, 26) and vacancy disorder (20, 25-27) in β-TiO appear to increase with increasing temperature, but definite conclusions are hampered since most data are for samples quenched to room temperature. Hilti (25) claimed two transitions: α→cubic (vacancy superlattice)→cubic (random vacancies). Jostsons and McDougall (20) designated the β- and α-phases as γ and γ' in order to avoid confusion with other Ti-O alloys. The relatively wide homogeneity ranges of α- and β-TiO are summarized in recent phase diagrams (20, 17) and emf studies (7). Limits of stability of α-TiO and the identity of its adjacent phases are less well established (20, 17) than for β-phase. TiO is metallic, exhibiting weak paramagnetism (27) and superconductivity with Tc below 1 K (26). Ordering of the vacancies by annealing had little effect on Tc (26).

Transition Data

The nature and kinetics of α⇌β are crucial since we lack definite knowledge of the phases used in thermochemical studies. The transition α→β is more rapid than the reverse one. β-TiO is readily retained by quenching, but α can be obtained only by annealing (23-30) for several hours below Tt. Moreover, there is disagreement as to whether the transition α→β proceeds directly (20) or via an intermediate peritectic decomposition, e.g. Ti_2O + β-TiO_{1+x} (17). Emf data (7) seem more consistent with the latter, but none of the evidence is definitive (17, 20, 24, 27-30). Lyon (5) suggested that peritectic decomposition is an alternative to direct reduction of vacancy concentration on going from α to β (see Phase Data). The difference in vacancy concentration, if real, may preclude direct equilibrium between ideal α and normal β. This could invalidate calculation of ΔSt from ΔHt (5).

Approximate ranges for Tt include 1235-1270 K from enthalpy data (13); 1235-1273 K from thermal analysis (29); between 1223 and 1263 K (20, 24), between 1223 and 1288 K (29), and between 1173 and 1223 K (28, 30), each based on the presence of α in samples quenched from various annealing temperatures. Later resistivity data (27) on Pearson's samples (28) suggest that Tt is between 1233 and 1303 K. Hilti (25) reported 1253 K for the first transition and 1523 K for the second. The latter transition is not apparent in the enthalpy data (13).

We adopt Tt = 1265 K and arbitrarily take ΔHt° = 1.0 kcal/mol. The apparent enthalpy difference (ΔH = 0.83 kcal/mol) at Tt is equal to ΔHt° only if Naylor's sample (13) was originally α-TiO and returned to α-form during drop calorimetry from above Tt. Charlu et al. (2) proposed instead, based on the difference in ΔHc° values, that ΔHt° = ∿5 kcal/mol and ΔSt° = ΔHt°/Tt = ∿4 gibbs/mol. The resulting increase in S°(β) would change our third-law analysis of ΔGr° for reactions C and D (see α-TiO). It would minimize the discrepancy between ΔHc° (3, 4) and the third-law ΔHf° but would more than double the discrepancy (δS) in the temperature dependence of ΔGf°(β) derived from Ti_2O_3 (7, 9). We prefer to minimize δS even though the larger value is compatible with the estimated uncertainty in ΔGf°(β).

Entropy calculations are available for processes somewhat related to α⇌β. The configurational entropy of TiO(β) with random vacancies was shown to be 2.0 gibbs/mol (14). ΔS of 1.5 to 2.3 gibbs/mol for TiO(β, 0% vacancies) → TiO(β, 14.4% vacancies) was calculated by Lyon (5) from compressibility, thermal expansion and a PV isotherm (6). Taylor and Doyle (6) reported observing β-TiO, presumably with much reduced vacancy concentration, at 56.4 kbar and 1153 K. This yields ΔT ≤ -80° assuming the Tt > 1233 K at 1 atm. We estimate ΔV = -0.16 cm^3/mol from the densities (6, 23) observed at 25°C and combine it with ΔP to calculate ΔS = ∿2.6 gibbs/mol for α→β. This calculation is highly uncertain; it is invalid if the transition is not an equilibrium one.

Melting Data - See TiO(ℓ).

References - See TiO(ℓ).

OTi

Titanium Monoxide (TiO)

(Liquid) GFW = 63.8994

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	9.550	14.374	14.374	- .000	- 118.054	- 112.850	82.722
300	9.575	14.433	14.374	.018	- 118.054	- 112.818	82.188
400	10.750	17.362	14.765	1.039	- 118.006	- 111.077	60.690
500	11.530	19.849	15.540	2.155	- 117.902	- 109.357	47.800
600	12.150	22.008	16.442	3.335	- 117.761	- 107.661	39.216
700	12.690	23.922	17.376	4.582	- 117.593	- 105.991	33.092
800	13.190	25.649	18.304	5.876	- 117.406	- 104.346	28.506
900	13.660	27.230	19.209	7.219	- 117.206	- 102.725	24.945
1000	14.120	28.693	20.085	8.608	- 116.997	- 101.127	22.101
1100	14.570	30.060	20.931	10.042	- 116.771	- 99.550	19.779
1200	15.010	31.347	21.746	11.522	- 117.467	- 97.957	17.840
1300	16.000	32.628	22.534	13.122	- 117.010	- 96.351	16.198
1400	16.000	33.813	23.298	14.722	- 116.571	- 94.778	14.796
1500	16.000	34.917	24.036	16.322	- 116.151	- 93.236	13.585
1600	16.000	35.959	24.749	17.922	- 115.753	- 91.721	12.528
1700	16.000	36.920	25.437	19.522	- 115.377	- 90.231	11.600
1800	16.000	37.834	26.100	21.122	- 115.026	- 88.763	10.777
1900	16.000	38.700	26.741	22.722	- 114.701	- 87.312	10.043
2000	16.000	39.520	27.359	24.322	- 113.849	- 85.725	9.358
2100	16.000	40.301	27.957	25.922	- 118.551	- 84.075	8.750
2200	16.000	41.045	28.535	27.522	- 118.257	- 82.442	8.190
2300	16.000	41.756	29.095	29.122	- 117.965	- 80.820	7.680
2400	16.000	42.437	29.637	30.722	- 117.676	- 79.210	7.213
2500	16.000	43.091	30.162	32.322	- 117.390	- 77.614	6.785
2600	16.000	43.718	30.671	33.922	- 117.106	- 76.029	6.391
2700	16.000	44.322	31.166	35.522	- 116.825	- 74.454	6.027
2800	16.000	44.904	31.646	37.122	- 116.547	- 72.890	5.689
2900	16.000	45.465	32.113	38.722	- 116.271	- 71.333	5.376
3000	16.000	46.008	32.567	40.322	- 115.997	- 69.789	5.084
3100	16.000	46.532	33.009	41.922	- 115.726	- 68.252	4.812
3200	16.000	47.040	33.440	43.522	- 115.457	- 66.728	4.557
3300	16.000	47.533	33.859	45.122	- 115.190	- 65.208	4.319
3400	16.000	48.010	34.269	46.722	- 114.925	- 63.697	4.094
3500	16.000	48.474	34.668	48.322	- 114.662	- 62.196	3.884
3600	16.000	48.925	35.058	49.922	- 216.027	- 60.436	3.669
3700	16.000	49.363	35.438	51.522	- 215.740	- 56.119	3.315
3800	16.000	49.790	35.810	53.122	- 215.468	- 51.811	2.980
3900	16.000	50.205	36.174	54.722	- 215.210	- 47.506	2.662
4000	16.000	50.611	36.530	56.322	- 214.967	- 43.209	2.361
4100	16.000	51.006	36.878	57.922	- 214.738	- 38.917	2.074
4200	16.000	51.391	37.219	59.522	- 214.523	- 34.633	1.802
4300	16.000	51.768	37.553	61.122	- 214.321	- 30.353	1.543
4400	16.000	52.136	37.881	62.722	- 214.131	- 26.078	1.295
4500	16.000	52.495	38.201	64.322	- 213.954	- 21.804	1.059

Dec. 31, 1960; Mar. 31, 1967; Dec. 31, 1973.

TITANIUM MONOXIDE (TiO)   (LIQUID)   GFW = 63.8994 OTi

$S^\circ_{298.15}$ = [14.374] gibbs/mol $\Delta Hf^\circ_{298.15}$ = [-118.054] kcal/mol

Tm = 2023 ± 30 K   ΔHm° = [10] kcal/mol

Heat of Formation

ΔHf° is calculated from that of β-TiO by addition of ΔHm° and the difference in $(H^\circ_{2023}-H^\circ_{298})$ for β and liquid.

Heat Capacity and Entropy

S° is calculated in a manner analogous to that of ΔHf°. Cp° is estimated as 8 gibbs/g-atom. Below the assumed glass transition at 1200 K, Cp° is taken to be the same as that of the crystal.

Melting Data

Tm was observed to be 1750°C (31), 1760 ± 25°C (32) and >1750°C (33). Incipient melting, partial melting and complete melting were observed (29) at approximately 1710°, 1730° and 1760°C, respectively. We adopt 1750 ± 30°C and estimate ΔHm° such that ΔSm° is 2.5 gibbs/g-atom. TiO does not melt congruently (17, 20, 29, 32, 33); there are various interpretations of the liquidus curve.

Vaporization Data

The vapor over TiO(c, ℓ) is mainly TiO and Ti, so the residue increases in (O/Ti) ratio (34).

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Titanium Monoxide (TiO)
(Ideal Gas) GFW = 63.8994

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.302	12.888	12.888	INFINITE
100	8.097	47.308	62.595	-1.529	13.180	10.716	-23.419
200	7.593	52.727	56.477	-.750	13.152	8.243	-9.007
298	7.762	55.776	55.775	.000	13.000	5.860	-4.295
300	7.768	55.824	55.776	.014	12.997	5.815	-4.237
400	8.131	58.108	56.085	.809	12.818	3.449	-1.884
500	8.433	59.957	56.680	1.638	12.636	1.127	-.493
600	8.646	61.514	57.359	2.493	12.447	-1.158	.422
700	8.792	62.859	58.051	3.365	12.244	-3.409	1.064
800	8.894	64.040	58.727	4.250	12.020	-5.631	1.538
900	8.967	65.092	59.377	5.143	11.770	-7.822	1.899
1000	9.021	66.039	59.997	6.043	11.492	-9.984	2.182
1100	9.062	66.901	60.586	6.947	11.188	-12.116	2.407
1200	9.094	67.691	61.145	7.855	9.920	-14.183	2.583
1300	9.120	68.420	61.677	8.766	9.688	-16.183	2.721
1400	9.141	69.097	62.183	9.679	9.440	-18.164	2.836
1500	9.158	69.728	62.666	10.594	9.175	-20.126	2.932
1600	9.174	70.320	63.126	11.510	8.890	-22.070	3.015
1700	9.190	70.876	63.565	12.428	8.584	-23.996	3.085
1800	9.206	71.402	63.986	13.348	8.254	-25.903	3.145
1900	9.223	71.900	64.390	14.270	7.901	-27.792	3.197
2000	9.242	72.374	64.777	15.193	3.076	-29.507	3.224
2100	9.264	72.825	65.150	16.118	2.699	-31.126	3.239
2200	9.290	73.257	65.509	17.046	2.321	-32.729	3.251
2300	9.319	73.670	65.854	17.976	1.943	-34.313	3.261
2400	9.353	74.068	66.188	18.910	1.566	-35.880	3.267
2500	9.390	74.450	66.511	19.847	1.189	-37.434	3.272
2600	9.433	74.819	66.824	20.788	.814	-38.972	3.276
2700	9.479	75.176	67.127	21.734	.441	-40.494	3.278
2800	9.530	75.522	67.420	22.684	.069	-42.004	3.279
2900	9.585	75.857	67.705	23.640	-.299	-43.497	3.278
3000	9.644	76.183	67.983	24.601	-.664	-44.981	3.277
3100	9.707	76.500	68.252	25.569	-1.025	-46.451	3.275
3200	9.773	76.809	68.515	26.543	-1.382	-47.914	3.272
3300	9.842	77.111	68.771	27.523	-1.734	-49.362	3.269
3400	9.913	77.406	69.020	28.511	-2.082	-50.799	3.265
3500	9.987	77.695	69.264	29.506	-2.424	-52.229	3.261
3600	10.063	77.977	69.502	30.509	-104.386	-53.383	3.241
3700	10.140	78.254	69.735	31.519	-104.689	-51.963	3.069
3800	10.218	78.525	69.963	32.537	-104.999	-50.536	2.906
3900	10.296	78.792	70.186	33.562	-105.315	-49.097	2.751
4000	10.375	79.053	70.404	34.596	-105.639	-47.651	2.604
4100	10.453	79.310	70.618	35.637	-105.969	-46.196	2.462
4200	10.531	79.563	70.828	36.686	-106.304	-44.737	2.328
4300	10.608	79.812	71.034	37.743	-106.645	-43.267	2.199
4400	10.684	80.057	71.237	38.808	-106.991	-41.790	2.076
4500	10.759	80.298	71.435	39.880	-107.341	-40.303	1.957
4600	10.831	80.535	71.631	40.960	-107.695	-38.805	1.844
4700	10.902	80.769	71.823	42.046	-108.054	-37.305	1.735
4800	10.970	80.999	72.011	43.140	-108.415	-35.795	1.630
4900	11.037	81.226	72.197	44.240	-108.781	-34.284	1.529
5000	11.100	81.449	72.380	45.347	-109.148	-32.757	1.432
5100	11.161	81.670	72.560	46.460	-109.519	-31.224	1.338
5200	11.219	81.887	72.737	47.579	-109.892	-29.687	1.248
5300	11.275	82.101	72.912	48.704	-110.266	-28.141	1.160
5400	11.327	82.313	73.084	49.834	-110.644	-26.587	1.076
5500	11.377	82.521	73.254	50.970	-111.021	-25.025	.994
5600	11.424	82.726	73.421	52.110	-111.402	-23.464	.916
5700	11.467	82.929	73.586	53.254	-111.782	-21.886	.839
5800	11.508	83.129	73.749	54.403	-112.165	-20.305	.765
5900	11.546	83.326	73.909	55.556	-112.548	-18.719	.693
6000	11.581	83.520	74.068	56.712	-112.933	-17.127	.624

Dec. 31, 1960; Mar. 31, 1967; Dec. 31, 1973.

TITANIUM MONOXIDE (TiO) (IDEAL GAS) GFW = 63.8994 OTi

Symmetry number = 1

$S^\circ_{298.15}$ = 55.776 ± 0.06 gibbs/mol

ΔHf°_0 = 12.89 ± 2 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 13.0 ± 2 kcal/mol

Electronic and Molecular Constants

Source	State	ε_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
(1, 2)	$X^3\Delta$	0.0	2	1.620	0.5354	0.00303	1008.26	4.13
		96.4	2					
		197.5	2					
(3, 4)	$E^3\Pi$	11800.	6	[1.654]	[0.5134]	[0.0029]	919.	[3.8]
(1, 2)	$A^3\Phi$	14019.4	2	1.664	0.50734	0.00318	867.71	3.94
		14192.3	2					
		14360.7	2					
(2, 4)	$B^3\Pi$	16226.4	2	1.663	0.5079	[0.0032]	873.	4.
		16248.0	2					
		16264.2	2					
(1, 2)	$C^3\Delta$	19341.7	2	1.695	0.4889	0.0029	837.86	4.546
		19437.4	2					
		19531.6	2					
(1,3-7)	$a^1\Delta$	[1000.]	2	1.616	0.5377	[0.003]	1016.3	3.93
(1, 4)	$d^1\Sigma^+$	[3219.]	1	1.600	0.5490	0.00337	1023.8	4.64
(1, 4)	$b^1\Pi$	[12273.]	2	1.654	0.5134	0.00286	918.7	3.75
(1, 4)	$c^1\Phi$	[18841.]	2	1.639	0.5228	[0.0032]	916.7	4.33
(8, 5, 4)	$f^1\Delta$	[20069.]	2	1.670	0.5037	[0.003]	[933.]	[4.2]
(9, 5, 4)	$e^1\Sigma$	[27517.]	1	1.694	0.4892	0.0025	853.9	4.7

Heat of Formation

ΔHf°_{298} = 13.0 ± 2 kcal/mol and D°_0 = 158.5 ± 2 kcal/mol are selected from reactions A, B, C and E (16) which are summarized below. The first three are isomolecular exchange reactions studied by mass spectrometry (13, 14). Reaction E is obtained from univariant Ti_2O_3-Ti_3O_5 by combining Knudsen effusion with the pressure ratio (TiO_2/TiO) = 0.246 obtained from mass spectrometry (16). We use the same analysis (16) for (17,E), although the condensed phase may not be univariant. We presume that the smaller D°_0 = 145.4 kcal/mol from reaction D is due to bias in the mass-spectrometric values (15) for the partial pressure of O(g). Larger values of D°_0 from sublimation (17, 19) and vaporization (18) of TiO are subject to bias due to presence of species other than TiO in the vapor and to unknown liquid activities. Activities of TiO in TiO_x(c) are very close to unity at x=1.0-1.1 and 1900 K according to emf data (20).

The analysis of Drowart et al. (14) was the key to resolution of the discrepancy in D°_0 (21); later studies (13, 16) confirmed their analysis. Our analysis uses D°_0(GeO, g) = 156.4 ± 1.5, D°_0(ScO, g) = 160.4 ± 2.0, and D°_0(YO, g) = 170.4 ± 2.5 kcal/mol with other auxiliary data and newly calculated free-energy functions, all of which are essentially consistent with Drowart et al. (14, 22). Our selected D°_0(TiO) = 158.5 ± 2 kcal/mol may be compared with 174.5 and 156.3 kcal/mol calculated by linear Birge-Sponer extrapolation of present (1) and older (23) vibrational constants of $X^3\Delta$. Kushawaha (24) used the older constants in construction of RKRV potential energy curves and thereby estimated D°_0 = 165.4 kcal/mol. He also derived D°_0 = 167.8 ± 20 kcal/mol from a chemiluminescent reaction (10), but we dismiss this since auxiliary data for KO and TiCl were estimates.

Source	Method	Reaction[a]	Range T/K	No. of Points	$\delta S^{\circ b}$ gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	3rd Law	ΔHf°_{298} kcal/mol	D°_0
(13) Hampson (1971)	Mass spec.	A	2145-2418	9	-6.4±5.0	-11.5±11.3	3.2±2.8	11.7±3.4	159.8
	Mass spec.	B	∿2023-2417	24[c]	0.2±1.5	- 2.6±3.3	-3.0±1.5	14.0±2.7	157.4
(14) Drowart (1969)	Mass spec.	B	1951-2463	Eqn.	0.0±0.1	- 3.0	-3.0	14.0±2.4	157.4
	Mass spec.	C	2313	1	-	-	-12.0	13.0±3.0	158.5
(15) Balducci (1972)	Mass spec.	D	2015-2240	12, 6	-0.2±2.6	145.2±5.4	146.5±1.6	26.1±2	145.4
(16) Wu (1972)	Knudsen eff.	E	1937-2044	12	-2.0±3.6	150.6±7.1	154.7±0.8	12.3±3.5	159.1
(17) Groves (1955)	Knudsen eff.	E	1971-2085	15	0.0±12	152.0±25	152.0±2.8	9.7±3.6	161.8
	Knudsen eff.	F	1847-1968	8	11 ± 3	157.1±5	135.1±3	6.4±4	165.0
(18) Berkowitz (1957)	Mass spec.	G	2027-2072	2	48	225.	125.5±4	7.5±7	164.0

[a] Reactions are A) TiO(g) + Ge(g) = Ti(g) + GeO(g); B) TiO(g) + Sc(g) = Ti(g) + ScO(g);
C) TiO(g) + Y(g) = Ti(g) + YO(g); D) TiO(g) = Ti(g) + O(g) from difference of two observed reactions
TiO_2 = O + TiO and TiO_2 + Ti = 2TiO;
E) 2 Ti_2O_3(c) = Ti_3O_5(β) + TiO(g); F) TiO(high) = TiO(g); G) TiO(ℓ) → TiO(g).

[b] δS° = ΔSr°(2nd law) - ΔSr°(3rd law). [c] Extreme points selected from large data set.

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational-rotational constants are from Rosen (1) as supplemented (4) by extensive new data (2, 3, 5, 8, 9). Additional states near 32000 cm^{-1} (10, 3) are omitted since their effect is negligible. We estimate unknown spectroscopic constants from known values for states arising from like molecular-orbital configurations (11). Although $^3\Delta$ is the ground state (6), several authors (1-3, 12) noted that energy levels of all singlet states are approximate due to uncertainty in the low-lying $a^1\Delta$. We revise $a^1\Delta$ from 581 cm^{-1} (6) to 1000 ± 400 cm^{-1} based on the temperature dependence of band intensities (6, 7), the requirement that $b^1\Pi$ lie above $E^3\Pi$ observed at 11894 cm^{-1} in a Ne-matrix (3), and the assumption that $f^1\Delta$ (8, 4) is the perturber of $C^3\Delta$ (5). The new E and f states confirm empirical predictions (11) which suggest additional unobserved levels at ∿13000 ($^3\Sigma$) and 15000 cm^{-1} ($^1\Sigma$). We omit these states since their predicted energies are less well established and their contributions to Cp° and S° would be quite small. The functions are calculated using first-order anharmonic corrections to Q^i_r and Q^i_v in the partition function $Q = Q_t \sum_i Q^i_r Q^i_v g_i \exp(-c_2 \varepsilon_i / T)$.

References - See TiO(ℓ).

Vanadium Monoxide (VO)

(Crystal) GFW = 66.9408

OV

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 1.651	- 102.704	- 102.704	INFINITE
100	3.321	1.608	16.990	- 1.538	- 103.056	- 100.975	220.681
200	8.150	5.506	10.243	- .948	- 103.252	- 98.797	107.960
298	10.875	9.324	9.324	.000	- 103.200	- 96.613	70.819
300	10.910	9.391	9.324	.020	- 103.197	- 96.572	70.353
400	11.850	12.682	9.766	1.166	- 103.020	- 94.389	51.572
500	12.345	15.381	10.628	2.377	- 102.811	- 92.255	40.325
600	12.794	17.672	11.616	3.634	- 102.581	- 90.165	32.843
700	13.227	19.677	12.627	4.935	- 102.333	- 88.116	27.511
800	13.647	21.471	13.622	6.279	- 102.065	- 86.103	23.522
900	14.054	23.102	14.586	7.664	- 101.780	- 84.124	20.428
1000	14.451	24.603	15.514	9.089	- 101.479	- 82.178	17.960
1100	14.839	25.999	16.404	10.554	- 101.162	- 80.263	15.947
1200	15.219	27.306	17.259	12.057	- 100.832	- 78.378	14.275
1300	15.594	28.539	18.080	13.598	- 100.491	- 76.520	12.864
1400	15.963	29.709	18.869	15.176	- 100.140	- 74.689	11.660
1500	16.330	30.822	19.629	16.790	- 99.781	- 72.884	10.619
1600	16.693	31.888	20.362	18.441	- 99.413	- 71.104	9.712
1700	17.053	32.911	21.070	20.129	- 99.038	- 69.345	8.915
1800	17.412	33.896	21.756	21.852	- 98.657	- 67.609	8.209
1900	17.767	34.847	22.420	23.611	- 98.275	- 65.895	7.580
2000	18.123	35.767	23.064	25.405	- 97.891	- 64.201	7.016
2100	18.476	36.660	23.690	27.235	- 97.510	- 62.526	6.507
2200	18.829	37.527	24.300	29.101	- 102.602	- 60.844	6.044
2300	19.180	38.372	24.893	31.001	- 102.264	- 58.954	5.602
2400	19.531	39.196	25.472	32.937	- 101.893	- 57.077	5.198
2500	19.881	40.000	26.037	34.907	- 101.491	- 55.219	4.827
2600	20.231	40.787	26.589	36.913	- 101.056	- 53.377	4.487

Dec. 31, 1973

VANADIUM MONOXIDE (VO) (CRYSTAL) GFW = 66.9408 OV

$S^\circ_{298.15}$ = 9.32 ± 0.2 gibbs/mol
Tm = 2063 ± 10 K

ΔHf°_0 = -102.7 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -103.2 ± 1.5 kcal/mol
ΔHm° = [13.0] kcal/mol

Heat of Formation

The adopted heats of formation for the vanadium oxides, and in particular VO(c), are based on the combustion studies by Mah and Kelley (1). The adopted value is ΔHf°_{298}(VO, c) = -103.2 kcal/mol, as reported by Mah and Kelley (1). For more details, refer to the V_2O_5(c) table (2). We increase their stated uncertainty limits of ±0.3 kcal/mol to ±1.5 kcal/mol so as to more adequately include all uncertainties in the experimental procedure, rather than just the scatter in the final results.

Other heat of formation results for VO(c) derived from combustion studies are reported as -102 kcal/mol by Samsonov (3) and -102 ± 1 kcal/mol by Vol'f and Ariya (4). However, the latter study (4) also reported a corresponding result for V_2O_5(c) which is 5.4 kcal/mol more negative than the adopted JANAF value (2). Older work by Kobayashi (5) involving water vapor equilibrium on vanadium and its oxides and by Mixter (6) involving sodium peroxide fusions are not considered.

Heat Capacity and Entropy

Todd and Bonnickson (7) measured the heat capacity of VO(c) in the region 55-296 K. The sample, estimated to be 98.2% pure, was prepared by heating a mixture of V(c) and V_2O_3(c) in a hydrogen atmosphere. The heat capacity results showed an anomaly similar to that found by Anderson (8) for V_2O_3(c). Todd and Bonnickson (7) concluded that the ∿20 cal/mol in excess to that expected for a smooth Cp° curve in the region 168-191 K was evidence of either an incomplete reaction in preparing VO(c) or subsequent disproportionation. Experimental data in this region was not reported. Using the Debye function D(398/T) as suggested by Todd and Bonnickson (7), we calculate S°_{50} = 0.297 gibbs/mol and $H^\circ_{50}-H^\circ_0$ = 11.051 cal/mol. The data are graphically curve fitted assuming a smooth sequence of "data points" in the region 168-191 K. Near 298.15 K the heat capacity data of Todd and Bonnickson (7) and the derivative of the smoothed enthalpy data of Orr (9) were constrained to join smoothly. Orr (9) used the same sample as did Todd and Bonnickson (7) and measured the enthalpy (fourteen data points) in the region 394-1698 K. The heat capacities derived from the Orr (9) data were extrapolated to Tm and above.

The heat capacity, entropy, and enthalpy values at 298.15 K reported by Chernyaev et al. (10) for VO_x, where x = 0.86, 0.99, 1.24, and 1.30, led to values for VO(c) which are considerably lower than our adopted values. For example, the S°_{298} value derived from the data of Chernyaev et al. (10, 22) is roughly 1.3 gibbs/mol lower than our adopted value.

Phase Data

Vanadium monoxide crystallizes in the cubic NaCl-type structure and is stable over a wide range of composition, roughly between the limit $VO_{0.80}$ and $VO_{1.30}$. Details and many references may be found in Stringer (20) and Alexander and Carlson (21).

Transition Data

There exists a large volume of literature dealing with transitions in the vanadium oxide condensed phases. These various oxides show widely varying electric and magnetic properties, as is discussed by Adler (11). In the case of VO(c), which has a wide homogeneity range, the reported data in the region of 120 K is conflicting. Sample purity, stoichiometry, and preparation undoubtedly play a major role in the appearance or lack of appearance of a possible transition. Much of the literature does not provide adequate sample characterization for an unequivical analysis of the data.

Conductivity measurements by Morin (12) on single crystals of VO(c) and numerous measurements, including NMR, by Warren et al. (13) indicated a transition in the region 114-126 K and 88-125 K, respectively. The transition was described by Morin (12) as a semiconductor-metal type. This is further discussed by Zhuze et al. (14) and Hyland (15). However, Kawano et al. (16) and Takei and Koide presented evidence on electric and magnetic properties and thermoelectric power for various vanadium monoxides within its homogeneity range which did not indicate any transition. Recent studies by Warren et al. (18) also indicated no evidence of a transition and, in addition, stated that the sample used in a previous study (13) was mainly V_2O_3(c) as determined by x-ray analysis. Many more references on this subject may be found in the compilation by Neuberger (19) and in a review of the V-O system by Stringer (20).

We conclude that there is no transition below Tm for VO(c) based primarily on the work cited above (16-18).

Melting Data

Refer to VO(ℓ) table for details.

Sublimation Data

At temperatures approaching Tm, VO(c) is reported to yield a vapor containing V(g), VO(g), and VO_2(g) (2).

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OV

Vanadium Monoxide (VO) OV

(Liquid) GFW = 66.9408

T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	10.875	16.524	16.524	.000	- 88.647	- 84.207	61.726
300	10.910	16.592	16.524	.020	- 88.645	- 84.180	61.325
400	11.850	19.883	16.967	1.166	- 88.467	- 82.717	45.194
500	12.345	22.582	17.828	2.377	- 88.258	- 81.303	35.537
600	12.794	24.872	18.816	3.634	- 88.029	- 79.933	29.115
700	13.227	26.877	19.827	4.935	- 87.780	- 78.603	24.541
800	13.647	28.671	20.822	6.279	- 87.513	- 77.310	21.120
900	14.054	30.302	21.786	7.664	- 87.227	- 76.051	18.468
1000	14.451	31.803	22.714	9.089	- 86.927	- 74.826	16.353
1100	14.839	33.199	23.604	10.554	- 86.610	- 73.631	14.629
1200	15.000	34.507	24.459	12.057	- 86.280	- 72.466	13.198
1300	15.000	35.707	25.279	13.557	- 85.979	- 71.327	11.991
1400	15.000	36.819	26.064	15.057	- 85.706	- 70.210	10.960
1500	15.000	37.854	26.816	16.557	- 85.462	- 69.112	10.070
1600	15.000	38.822	27.536	18.057	- 85.245	- 68.030	9.292
1700	15.000	39.731	28.227	19.557	- 85.057	- 66.959	8.608
1800	15.000	40.589	28.890	21.057	- 84.900	- 65.899	8.001
1900	15.000	41.400	29.527	22.557	- 84.776	- 64.847	7.459
2000	15.000	42.169	30.140	24.057	- 84.687	- 63.801	6.972
2100	15.000	42.901	30.731	25.557	- 84.636	- 62.758	6.531
2200	15.000	43.599	31.300	27.057	- 90.094	- 61.692	6.129
2300	15.000	44.265	31.849	28.557	- 90.156	- 60.400	5.739
2400	15.000	44.904	32.380	30.057	- 90.221	- 59.104	5.382
2500	15.000	45.516	32.893	31.557	- 90.289	- 57.806	5.053
2600	15.000	46.104	33.390	33.057	- 90.360	- 56.506	4.750
2700	15.000	46.671	33.872	34.557	- 90.433	- 55.202	4.468
2800	15.000	47.216	34.338	36.057	- 90.508	- 53.895	4.207
2900	15.000	47.742	34.792	37.557	- 90.587	- 52.587	3.963
3000	15.000	48.251	35.232	39.057	- 90.668	- 51.275	3.735
3100	15.000	48.743	35.660	40.557	- 90.750	- 49.960	3.522
3200	15.000	49.219	36.076	42.057	- 90.836	- 48.644	3.322
3300	15.000	49.681	36.481	43.557	- 90.923	- 47.324	3.134
3400	15.000	50.128	36.876	45.057	- 91.013	- 46.001	2.957
3500	15.000	50.563	37.261	46.557	- 91.104	- 44.676	2.790

Dec. 31, 1973

VANADIUM MONOXIDE (VO) (LIQUID) GFW = 66.9408 OV

$S^\circ_{298.15}$ = [16.524] gibbs/mol

Tm = 2063 ± 10 K

$\Delta Hf^\circ_{298.15}$ = [-88.647] kcal/mol

ΔHm° = [13.0] kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding ΔHm° and the difference between $(H^\circ_{2063}-H^\circ_{298})$ for the crystal and liquid.

Heat Capacity and Entropy

Cp° is estimated as 7.5 gibbs/g-atom. Below the assumed glass transition temperature at 1200 K, Cp° is taken from the crystal. The entropy is derived in a manner analogous to that for the heat of formation.

Melting Data

Alexander and Carlson (1) proposed a phase diagram for the V-VO system based on melting point determinations, differential thermal analysis, metallographic observations, and x-ray parametric measurements. These authors (1) reported that VO(c) melts congruently at 2063 ± 10 K. We adopt this value for Tm. In a phase diagram proposed by Stringer (2) a melting temperature of ∿1998 K was suggested but the melting was not congruent.

VO(c) has a sodium chloride structure and is stable over a wide range of composition, as is discussed, for example by Stringer (2). ΔHm° is estimated based on ΔSm° = 6.3 gibbs/mol as in NaCl (3). Since VO(c) has a defect structure, a comparison with the ΔSm° value of NaCl is not entirely satisfactory. We make this comparison, however, pending further data.

Vaporization Data

There is no data available in the literature dealing with the vaporization of VO(ℓ). We anticipate substantial decomposition to occur during heat treatment of VO(ℓ). See VO(g) table for further information (3).

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OV

OV

Vanadium Monoxide (VO)

(Ideal Gas) GFW = 66.9408

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.097	30.550	30.550	INFINITE
100	6.957	47.466	61.483	-1.402	30.781	28.276	-61.796
200	7.035	52.300	55.820	-.704	30.692	25.788	-28.180
298	7.337	55.160	55.160	.000	30.500	23.421	-17.168
300	7.344	55.205	55.160	.014	30.496	23.377	-17.030
400	7.710	57.369	55.452	.767	30.281	21.037	-11.494
500	8.011	59.123	56.016	1.553	30.066	18.750	-8.196
600	8.236	60.604	56.661	2.366	29.851	16.508	-6.013
700	8.400	61.887	57.318	3.198	29.630	14.301	-4.465
800	8.522	63.017	57.961	4.045	29.401	12.126	-3.313
900	8.614	64.026	58.580	4.902	29.158	9.982	-2.424
1000	8.685	64.938	59.171	5.767	28.898	7.865	-1.719
1100	8.741	65.768	59.733	6.638	28.622	5.775	-1.147
1200	8.786	66.531	60.268	7.515	28.326	3.711	-.676
1300	8.824	67.235	60.778	8.395	28.007	1.672	-.281
1400	8.856	67.891	61.262	9.279	27.664	-.341	.053
1500	8.884	68.502	61.725	10.166	27.295	-2.328	.339
1600	8.910	69.077	62.167	11.056	26.901	-4.291	.586
1700	8.934	69.618	62.589	11.948	26.482	-6.228	.801
1800	8.959	70.129	62.994	12.843	26.034	-8.139	.988
1900	8.984	70.614	63.382	13.740	25.554	-10.024	1.153
2000	9.010	71.075	63.756	14.640	25.043	-11.884	1.299
2100	9.039	71.516	64.115	15.542	24.497	-13.717	1.428
2200	9.070	71.937	64.461	16.447	18.444	-15.499	1.540
2300	9.104	72.341	64.795	17.356	17.791	-17.027	1.618
2400	9.142	72.729	65.117	18.268	17.138	-18.526	1.687
2500	9.183	73.103	65.429	19.185	16.487	-19.999	1.748
2600	9.228	73.464	65.731	20.105	15.836	-21.446	1.803
2700	9.277	73.813	66.024	21.030	15.188	-22.867	1.851
2800	9.329	74.152	66.309	21.961	14.543	-24.264	1.894
2900	9.385	74.480	66.585	22.896	13.900	-25.639	1.932
3000	9.444	74.799	66.853	23.838	13.261	-26.991	1.966
3100	9.505	75.110	67.115	24.785	12.626	-28.322	1.997
3200	9.570	75.413	67.369	25.739	11.993	-29.634	2.024
3300	9.637	75.708	67.617	26.699	11.367	-30.925	2.048
3400	9.706	75.997	67.860	27.666	10.744	-32.197	2.070
3500	9.776	76.279	68.096	28.640	10.127	-33.451	2.089
3600	9.848	76.556	68.327	29.622	9.515	-34.687	2.106
3700	9.921	76.826	68.553	30.610	-97.839	-35.726	2.110
3800	9.995	77.092	68.775	31.606	-98.033	-34.045	1.958
3900	10.069	77.353	68.991	32.609	-98.231	-32.360	1.813
4000	10.143	77.608	69.203	33.620	-98.437	-30.668	1.676
4100	10.217	77.860	69.412	34.638	-98.649	-28.971	1.544
4200	10.290	78.107	69.616	35.663	-98.867	-27.269	1.419
4300	10.363	78.350	69.816	36.696	-99.093	-25.561	1.299
4400	10.434	78.589	70.013	37.736	-99.324	-23.849	1.185
4500	10.504	78.824	70.206	38.783	-99.563	-22.131	1.075
4600	10.572	79.056	70.396	39.836	-99.808	-20.405	.969
4700	10.639	79.284	70.582	40.897	-100.060	-18.677	.868
4800	10.704	79.509	70.766	41.964	-100.318	-16.942	.771
4900	10.766	79.730	70.947	43.038	-100.584	-15.206	.678
5000	10.827	79.948	71.125	44.117	-100.856	-13.460	.588
5100	10.886	80.163	71.300	45.203	-101.135	-11.708	.502
5200	10.942	80.375	71.472	46.294	-101.420	-9.953	.418
5300	10.995	80.584	71.642	47.391	-101.710	-8.189	.338
5400	11.047	80.790	71.810	48.493	-102.009	-6.425	.260
5500	11.096	80.993	71.975	49.600	-102.311	-4.649	.185
5600	11.142	81.193	72.138	50.712	-102.621	-2.872	.112
5700	11.186	81.391	72.298	51.829	-102.937	-1.089	.042
5800	11.227	81.586	72.457	52.949	-103.259	.702	-.026
5900	11.266	81.778	72.613	54.074	-103.585	2.497	-.092
6000	11.302	81.968	72.767	55.203	-103.917	4.299	-.157

Dec. 31, 1973

VANADIUM MONOXIDE (VO) (IDEAL GAS) GFW = 66.9408 OV

Ground State Configuration $^4\Sigma^-$

$S^\circ_{298.15}$ = 55.16 ± 0.3 gibbs/mol

ΔHf°_0 = 30.5 ± 5.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 30.5 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X $^4\Sigma^-$	0	4
B $^4\Pi$	12706.3	8
C $^4\Sigma^-$	17420.3	4
	23890	[4]

ω_e = 1012.36 cm^{-1} $\omega_e x_e$ = 5.26 cm^{-1} σ = 1

B_e = 0.54825 cm^{-1} α_e = 0.00352 cm^{-1} r_e = 1.589 Å

Heat of Formation

Based on the adopted ground state vibrational constants, a linear Birge-Sponer extrapolation yields a dissociation energy of D°_0 = 6.039 eV (139.3 kcal/mol) for VO(g). Applying a correction for the ionicity in the V-O bond (1), we recalculate D°_0 = 6.495 eV (149.8 kcal/mol). This latter value leads to a ΔHf°_{298} value of 31.6 kcal/mol using auxiliary data (2).

Berkowitz, Chupka, and Inghram (3) determined the composition and partial pressures of the vapor over VO(c) by employing a mass spectrometer to analyze the vapors effusing from a tungsten Knudsen cell containing VO(c). The vapors detected mass spectrometrically at 1945 K were reported to be V(g), VO(g), and VO_2(g). The VO^+ intensity was determined in two sets of experiments using the temperature variation method. Berkowitz et al. (3) analyzed these results using second law methods and reported ΔHr°(T) = 125.2 kcal/mol (1690-1945 K) and 124.6 kcal/mol (1680-1950 K) for the reaction VO(c) = VO(g). Assigning these heats of reaction to an intermediate temperature of 1800 K, we calculate ΔHf°_{298} values for VO(g) of 30.1 and 30.4 kcal/mol, respectively, using auxiliary data (2). Berkowitz et al. (3) also used the absolute pressure method and determined the partial pressure of VO(g) at two temperatures, 1875 K and 1875 K (corrected to IPTS-68). The two absolute pressure data points differ in value by ~25%. A third law analysis of these two data points leads to ΔHf°_{298} values for VO(g) of 23.6 and 24.7 kcal/mol. We prefer the second law results of Berkowitz et al. (3) due to the fact that each result is based on multiple data points (~6) which cover a temperature range of 260 K.

Coppens, Smoes, and Drowart (4) used a combination of mass spectrometric and Knudsen cell techniques to determine the partial pressures necessary to define the equilibrium in the system VO(g) + Ge(g) = GeO(g) + V(g). The authors analyzed eight data points in the range 1927-2145 K by the third law method and reported ΔHr°_0 = 7.60 ± 0.38 kcal/mol which actually applies to the reverse reaction (14). The free energy functions used by Coppens et al. (4) for VO are very similar to those adopted here. Using auxiliary data (2, 5), we calculate ΔHf°_{298} = 29.1 kcal/mol for VO(g).

An effusion-mass spectrometric investigation of the vapors in equilibrium with V_2O_3(c) was conducted by Farber, Uy, and Srivastava (6). Their study, using an aluminum cell, showed that the vapors at 2270 K contained V(g), VO(g), and VO_2(g) as well as Al(g), AlO(g), and Al_2O(g). A third law analysis of the data at 2270 K yields ΔHr°_{298} = -26.5 kcal/mol for the reaction AlO(g) + V(g) = VO(g) + Al(g). Using auxiliary data (2), we calculate ΔHf°_{298} = 38.7 kcal/mol for VO(g). Farber et al. (6), however, reported the use of a more recent determination of ΔHf°_{298} for AlO(g) (7). If this latter value (+16.57 kcal/mol) is used, then the ΔHf°_{298} value for VO(g) is 35.3 kcal/mol.

Frantseva and Semenov (8) studied the evaporation of V_2O_3(c) by a mass spectrometer used in conjunction with a double effusion chamber. They reported a D°_0 value for VO(g) which is dependent, however, on their D°_0 value for VO_2(g) (2). The mass spectrometric study by Shchukarev et al. (9) detected VO(g) above V_2O_4(c) and V_2O_3(c) but there was insufficient data reported to permit the calculation of a ΔHf°_{298} value for VO(g).

We adopt ΔHf°_{298} = 30.5 kcal/mol for VO(g). This value is a rounded average of the two second law treatments from Berkowitz et al. (3) and the results from Coppens et al. (4). Each of these three sets of experiments involve multiple data points. Most of the remaining studies each involved only one data point. However, it should be noted that the ΔHf°_{298} derived from the Hildenbrand correction to the linear Birge-Sponer extrapolation is within 1.1 kcal/mol of the adopted value. The adopted heat of formation leads to a dissociation energy of D°_0 = 150.9 kcal/mol or 6.542 eV.

Heat Capacity and Entropy

Much of the spectroscopic work involving VO(g) has been reviewed and referenced by Rosen (10) and Weltner (11). The adopted vibrational and rotational constants as well as the electronic levels are those tabulated by Rosen (10). The EPR work of Kasai (12) and the optical absorption study by Richards and Barrow (13) established that the ground state was $^4\Sigma^-$. As reported in Rosen (10), there is evidence from matrix studies indicating a transition at 23890 cm^{-1}. We assume this level has a quantum weight of 4. The full weight of 8 is assigned to the B $^4\Pi$ state, rather than estimating the splitting. The free energy functions used here are approximately 3 gibbs/mol less than those proposed by Brewer and Rosenblatt (14). The difference arises from the fact that Brewer and Rosenblatt approximated the VO electronic levels by using V^{++} electronic levels (which include many low lying levels) whereas we have used the observed VO electronic levels.

References

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OV

Tantalum Dioxide (TaO_2) O_2Ta

(Ideal Gas) GFW = 212.9458

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.692	-47.259	-47.259	INFINITE
100	8.457	56.762	75.615	-1.885	-47.384	-48.535	106.073
200	9.527	62.969	67.887	-.984	-47.718	-49.558	54.155
298	10.516	66.957	66.957	.000	-48.000	-50.399	36.942
300	10.534	67.023	66.958	.019	-48.005	-50.412	36.725
400	11.407	70.178	67.382	1.118	-48.229	-51.180	27.964
500	12.047	72.796	68.210	2.293	-48.408	-51.896	22.684
600	12.495	75.035	69.166	3.521	-48.571	-52.578	19.151
700	12.810	76.986	70.146	4.787	-48.729	-53.233	16.620
800	13.035	78.712	71.111	6.080	-48.888	-53.867	14.716
900	13.200	80.257	72.043	7.392	-49.049	-54.480	13.229
1000	13.324	81.654	72.935	8.719	-49.213	-55.073	12.036
1100	13.418	82.929	73.787	10.056	-49.387	-55.652	11.057
1200	13.492	84.100	74.598	11.402	-49.569	-56.213	10.238
1300	13.552	85.192	75.371	12.754	-49.763	-56.758	9.542
1400	13.600	86.188	76.108	14.112	-49.965	-57.290	8.943
1500	13.641	87.128	76.812	15.474	-50.173	-57.805	8.422
1600	13.675	88.009	77.485	16.840	-50.386	-58.307	7.964
1700	13.706	88.839	78.128	18.209	-50.606	-58.795	7.559
1800	13.735	89.624	78.745	19.581	-50.837	-59.270	7.196
1900	13.762	90.367	79.338	20.956	-51.084	-59.733	6.871
2000	13.789	91.074	79.907	22.333	-51.346	-60.182	6.576
2100	13.816	91.747	80.455	23.713	-51.622	-60.616	6.308
2200	13.843	92.390	80.983	25.096	-51.916	-61.038	6.064
2300	13.872	93.006	81.492	26.482	-52.223	-61.446	5.839
2400	13.903	93.597	81.984	27.871	-52.548	-61.838	5.631
2500	13.935	94.166	82.460	29.263	-52.892	-62.221	5.439
2600	13.969	94.713	82.921	30.658	-53.255	-62.585	5.261
2700	14.005	95.241	83.368	32.057	-53.641	-62.937	5.094
2800	14.042	95.751	83.801	33.459	-54.052	-63.274	4.939
2900	14.081	96.244	84.222	34.865	-54.491	-63.595	4.793
3000	14.122	96.722	84.630	36.275	-54.962	-63.900	4.655
3100	14.164	97.186	85.028	37.690	-55.468	-64.190	4.525
3200	14.208	97.636	85.415	39.108	-56.016	-64.464	4.403
3300	14.252	98.074	85.792	40.531	-65.322	-64.607	4.279
3400	14.297	98.500	86.159	41.959	-65.865	-64.577	4.151
3500	14.343	98.915	86.519	43.391	-66.407	-64.532	4.030
3600	14.389	99.320	86.868	44.827	-66.949	-64.470	3.914
3700	14.435	99.715	87.210	46.268	-67.490	-64.393	3.804
3800	14.482	100.101	87.544	47.714	-68.029	-64.301	3.698
3900	14.528	100.477	87.871	49.165	-68.566	-64.198	3.598
4000	14.573	100.846	88.191	50.620	-69.103	-64.080	3.501
4100	14.618	101.206	88.504	52.079	-69.639	-63.947	3.409
4200	14.663	101.559	88.810	53.544	-70.171	-63.802	3.320
4300	14.706	101.904	89.111	55.012	-70.703	-63.641	3.235
4400	14.749	102.243	89.406	56.485	-71.233	-63.474	3.153
4500	14.790	102.575	89.694	57.962	-71.761	-63.291	3.074
4600	14.830	102.900	89.978	59.443	-72.287	-63.094	2.998
4700	14.869	103.220	90.256	60.928	-72.812	-62.889	2.924
4800	14.906	103.533	90.530	62.416	-73.335	-62.672	2.854
4900	14.942	103.841	90.798	63.909	-73.855	-62.448	2.785
5000	14.976	104.143	91.062	65.405	-74.374	-62.211	2.719
5100	15.009	104.440	91.322	66.904	-74.892	-61.959	2.655
5200	15.040	104.732	91.577	68.407	-75.407	-61.704	2.593
5300	15.070	105.019	91.828	69.912	-75.921	-61.431	2.533
5400	15.098	105.301	92.074	71.421	-76.433	-61.157	2.475
5500	15.124	105.578	92.317	72.932	-76.943	-60.866	2.419
5600	15.149	105.851	92.557	74.445	-77.454	-60.572	2.364
5700	15.172	106.119	92.792	75.961	-77.962	-60.267	2.311
5800	15.193	106.383	93.024	77.480	-254.616	-59.525	2.243
5900	15.213	106.643	93.253	79.000	-255.120	-56.159	2.080
6000	15.232	106.899	93.478	80.522	-255.627	-52.781	1.923

Dec. 31, 1973

TANTALUM DIOXIDE (TaO_2) (IDEAL GAS) GFW = 212.9458 O_2Ta

Point Group C_{2v}

$S^\circ_{298.15}$ = [66.96 ± 2.80] gibbs/mol

ΔHf°_0 = -47.3 ± 15.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -48.0 ± 15.0 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
X^2B_1	0	2
$^2A_1$	11618	2
$^2A_2$	16236	2

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
971 (1)
[300] (1)
912 (1)

σ = 2

Bond Distance: Ta-O = [1.69] Å Bond Angle: O-Ta-O = [110°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [6.169 x 10^{-115}] g^3cm^6

Heat of Formation

Inghram, et al. (1) and Krikorian and Carpenter (2) have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta-Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2. As in the case with TaO(g) (5), the absolute pressures of TaO_2(g) calculated from both studies differ by a factor of roughly 1000 in the range 2022-2279 K (IPTS-68). Results of our second and third law analysis of these and other data are presented below.

Reference	Reaction	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	ΔHf°_{298}, kcal/mol 2nd Law	ΔHf°_{298}, kcal/mol 3rd Law
1	A*	2	2022,2023	-	156.13	-	-	-39.47
1	B*	4	2151-2209	51.67	150.86	45±41	-	-36.25
2	B	1	2271	-	184.67	-	-	- 2.44
1	C*	4	2022-2179	70.72	70.05	-0.3±4.5	-49.44	-48.10
2	C	1	2271	-	81.03	-	-	-70.06
3	D	graph	1909-2860	-19.83	26.38	20.6±2.8	-19.83	26.38

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections (2, 4); procedure increases ΔHr° by ~3 kcal/mol.

ΔHf°_{298} refers to the heat of formation of TaO_2(g).

A: 0.2 Ta(c) + 0.4 Ta_2O_5(c) = TaO_2(g)

B: 0.2 Ta(c) + 0.4 Ta_2O_5(ℓ) = TaO_2(g)

C: 0.5 Ta(c) + 0.5 TaO_2(g) = TaO(g)

D: Ta(c) + O_2(g) = TaO_2(g)

As was observed in the TaO(g) table (5), the results of the second and third law analysis show considerable scatter. We adopt ΔHf°_{298}(TaO_2, g) = -48.0 kcal/mol based primarily on our analysis of the data from Inghram et al. (1) for the reaction 0.5 Ta(c) + 0.5 TaO_2(g) = TaO(g). For this reaction we adopt a rounded result of ΔHr°_{298} = 70.0 kcal/mol. The adopted ΔHf°_{298} value leads to a dissociation energy D°_0 = 15.3 eV (3520 kcal/mol) for the process TaO_2(g) = Ta(g) + 2 O(g). This value is 1.8 times the dissociation energy of TaO(g) (5).

Heat Capacity and Entropy

The electronic levels and vibrational frequencies are those reported by Weltner and McLeod (7). The results were based on a matrix isolation study of TaO_2 trapped in argon and neon matrices at 20 K and 4 K, respectively. The infrared spectrum was interpreted to favor a bent molecule in the ground state. Kaufman et al. (8) reported that TaO_2(g) is bent based on the deflection of molecular beams of TaO_2 by an electrostatic quadrupole. This latter result is dependent, however, on there being no low lying electronic states. The bending frequency for the ground state has not been observed but is estimated to be 300 cm^{-1} based on the observed ν_2 = 285 cm^{-1} value for the $^2A_1$ state (7). The Ta-O bond distance is estimated to be the same as in TaO(g) (5) whereas the bond angle is estimated to be 110°.

It should be noted that the free energy functions used here are roughly 2-4 gibbs/mole more positive than that suggested by Brewer and Rosenblatt (6) for linear TaO_2; the third law ΔHr°_{298} values in the above table would change by ~4.5 kcal/mol.

References for TaO_2(g)

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O_2Ta

Titanium Dioxide, Anatase (TiO_2)

O_2Ti

(Crystal) GFW = 79.8988

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.062	-223.195	-223.195	INFINITE
100	4.577	2.300	21.320	-1.902	-223.603	-219.757	480.277
200	10.306	7.290	13.045	-1.151	-224.266	-215.467	235.451
298	13.217	11.928	11.928	.000	-224.360	-211.122	154.756
300	13.255	12.010	11.928	.024	-224.360	-211.040	153.742
400	15.199	16.117	12.475	1.457	-224.256	-206.611	112.867
500	16.237	19.636	13.564	3.036	-224.054	-202.222	88.391
600	16.943	22.668	14.835	4.700	-223.811	-197.679	72.077
700	17.365	25.313	16.147	6.416	-223.559	-193.576	60.437
800	17.653	27.652	17.442	8.168	-223.315	-189.311	51.717
900	17.860	29.744	18.694	9.944	-223.089	-185.073	44.942
1000	18.010	31.634	19.395	11.738	-222.886	-180.860	39.527
1100	18.120	33.355	21.042	13.545	-222.707	-176.666	35.100
1200	18.210	34.936	22.135	15.361	-223.491	-172.450	31.407
1300	18.250	36.397	23.176	17.186	-223.237	-168.207	28.278
1400	18.340	37.753	24.170	19.017	-222.999	-163.984	25.599
1500	18.390	39.021	25.118	20.854	-222.778	-159.776	23.279
1600	18.430	40.209	26.024	22.695	-222.577	-155.581	21.251
1700	18.460	41.327	26.892	24.539	-222.396	-151.400	19.464
1800	18.490	42.383	27.724	26.387	-222.244	-147.229	17.875
1900	18.510	43.383	28.522	28.237	-222.116	-143.065	16.456
2000	18.530	44.333	29.289	30.089	-226.462	-138.754	15.162

June 30, 1962; Sept. 30, 1966, Dec. 31, 1973.

TITANIUM DIOXIDE, ANATASE (TiO_2) (CRYSTAL) GFW = 79.8988 O_2Ti

$S^\circ_{298.15}$ = 11.928 ± 0.08 gibbs/mol

Tm = [1949 ± 60 K] (anatase → liquid)

ΔHf°_0 = −223.2 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = −224.36 ± 0.5 kcal/mol

ΔHm° = [13.86] kcal/mol

Heat of Formation

ΔHf° is calculated from that of TiO_2(rutile) using ΔHr°(968 K) = −1.57 ± 0.19 kcal/mol for anatase → rutile. Navrotsky and Kleppa (1), using oxide-melt calorimetry, derived ΔHr° from the difference in ΔH_{soln} between anatase and rutile. Reduction of their value using JANAF enthalpies yields ΔHr°_{298} = −1.44 ± 0.3 and ΔHf°_{298}(anatase) = −224.26 ± 0.5 kcal/mol. Uncertainties in the enthalpies and in ΔHf°(rutile) contribute significantly to the overall uncertainty. Kybett and Margrave (2) derived ΔHf°_{298} = −223 ± 1 kcal/mol from fluorine calorimetry. Their reaction was TiO_2(anatase) + 2 F_2(g) → TiF_4(c) + O_2(g), but they gave no experimental data. Kybett's results for anatase and rutile may be combined to yield ΔHr°_{298} = −2 ± 1.4 kcal/mol for anatase → rutile; this is consistent with the adopted value. Values for ΔGr(≈ΔHr) of −0.2 to −0.3 kcal/mol for anatase → rutile were derived by Schuiling and Vink (12) from relative solubilities in aqueous NaCl at 200° and 300°C. We suspect that this less negative result arises from saturating solid phases which differ in physical form and chemical composition from standard-state macrocrystalline anatase (see Phase Data).

Heat Capacity and Entropy

Cp° below 300 K is based on data of Shomate (3, 52-296 K) and his Debye-Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of Cp° based on S°(50 K) = 0.45 gibbs/mol.

Cp° above 300 K is from constrained fitting of enthalpy data (739-1305 K) of Naylor (4). Naylor's points at 418 and 546 K are omitted due to positive bias in this temperature range. Enthalpy data (580-1001 K) of Lietz (5) deviate by −3.7 ± 1.25 at all temperatures. Similar discrepancies exist in Lietz' data for TiO_2(rutile). These discrepancies and the bias in Naylor's data near room temperature are discussed on the table for rutile (6). The choice between Naylor (4) and Lietz (5) is not clear-cut, but we feel that Naylor's data lead to more reasonable values of Cp°. New data on a well-characterized sample are needed.

The two discrepant studies (4, 5) do agree that the enthalpy of anatase is slightly larger than that of rutile at all temperatures in the observed region. Our adopted Cp° reproduces the approximate enthalpy difference between anatase and rutile as observed by each author (4, 5).

Phase Data

Both anatase and rutile have tetragonal crystal structures, but in anatase the elongated unit cell contains four molecules compared with two in the unit cell of rutile. Anatase transforms exothermally and irreversibly to rutile at temperatures above ∿1200 K (7-9). The rate of transformation is relatively slow and is governed by the nature and amount of impurities (7). Certain impurities markedly decrease the transformation temperature, which can be as low as 700 K in the presence of an alkali flux (10). These observations led to the conclusion that anatase is a metastable phase which persists up to a temperature sufficient to activate the crystal rearrangement. This was confirmed by the calorimetric data of Navrotsky and Kleppa (1), who concluded that anatase is metastable with respect to rutile at all temperatures.

Lietz (5) reported a transition in anatase at ∿913 K based on his enthalpy data and on changes in prism angles measured by Schröder (11). We reject Lietz' Tt, since his ΔHt° is not distinguishable from his experimental scatter. Lietz' data for rutile and anatase exhibit remarkably similar deviations in this temperature region. Schröder's data have the same deficiency. Lattice parameter data (13) show scatter but no obvious change in this temperature region.

Characterization of anatase samples is particularly important for interpreting physical and chemical properties. Anatase precipitated from acidic sulfate solutions consists of agglomerates of very small crystals with large amounts of water and SO_3 (14). X-ray and electron diffraction show the major lines of anatase but fail to show the impurities, suggesting that the latter are present in noncrystalline form. These precipitates (14) lose water near 150°C and SO_3 near 650°C; crystal growth starts near 600°C. Precipitates from other media give anatase at lower temperatures (15), but calcination temperatures of at least 650°C are needed for complete conversion of these precipitates into pure, macrocrystalline anatase. This suggests an alternative explanation for reports (5, 11) of Tt ∿645°C.

Melting Data

Tm is hypothetical in the sense that metastable anatase probably will convert to rutile (see Phase Data) before it can be superheated to the melting point. Tm is calculated as the temperature at which ΔG° = 0 for TiO_2(anatase) → TiO_2(ℓ). ΔHm° is the calculated difference in ΔHf° at Tm.

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O_2Ti

O_2Ti

Titanium Dioxide, Rutile (TiO_2)

(Crystal) GFW = 79.8988

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 2.064	- 224.637	- 224.637	INFINITE
100	4.422	2.424	21.424	- 1.900	- 225.301	- 221.207	483.447
200	10.041	7.363	13.138	- 1.155	- 225.710	- 216.925	237.045
298	13.170	12.020	12.020	.000	- 225.800	- 212.589	155.832
300	13.214	12.102	12.020	.024	- 225.800	- 212.507	154.811
400	15.018	16.174	12.563	1.444	- 225.709	- 208.086	113.693
500	16.062	19.647	13.642	3.002	- 225.528	- 203.701	89.038
600	16.714	22.637	14.898	4.644	- 225.307	- 199.356	72.615
700	17.152	25.248	16.194	6.338	- 225.077	- 195.049	60.897
800	17.466	27.560	17.473	8.070	- 224.853	- 190.776	52.117
900	17.700	29.631	18.711	9.828	- 224.645	- 186.528	45.295
1000	17.890	31.506	19.898	11.608	- 224.456	- 182.303	39.842
1100	18.040	33.219	21.032	13.405	- 224.287	- 178.095	35.384
1200	18.170	34.794	22.114	15.216	- 225.076	- 173.865	31.665
1300	18.290	36.253	23.146	17.039	- 224.824	- 169.608	28.514
1400	18.390	37.612	24.132	18.873	- 224.583	- 165.371	25.815
1500	18.480	38.884	25.073	20.716	- 224.356	- 161.149	23.479
1600	18.560	40.079	25.974	22.568	- 224.144	- 156.941	21.437
1700	18.640	41.207	26.837	24.428	- 223.949	- 152.747	19.637
1800	18.710	42.274	27.666	26.296	- 223.775	- 148.565	18.038
1900	18.780	43.288	28.461	28.170	- 223.623	- 144.390	16.609
2000	18.850	44.253	29.227	30.052	- 227.939	- 140.071	15.306
2100	18.920	45.174	29.965	31.941	- 227.805	- 135.679	14.120
2200	18.980	46.056	30.676	33.836	- 227.672	- 131.297	13.043
2300	19.040	46.901	31.363	35.737	- 227.537	- 126.919	12.060
2400	19.100	47.713	32.028	37.644	- 227.402	- 122.545	11.159
2500	19.160	48.494	32.671	39.557	- 227.267	- 118.181	10.331

June 30, 1962; Sept. 30, 1966; Dec. 31, 1973.

TITANIUM DIOXIDE, RUTILE (TiO_2) (CRYSTAL) GFW = 79.8988 O_2Ti

$S^\circ_{298.15}$ = 12.02 ± 0.04 gibbs/mol
Tm = 2130 ± 20 K

ΔHf°_0 = -224.64 ± 0.3 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -225.8 ± 0.3 kcal/mol
ΔHm° = [16 ± 4] kcal/mol

Heat of Formation

ΔHf° is the value obtained by Mah et al. (1) in an unusually thorough study by oxygen calorimetry. Eighteen combustions (1) of three well-characterized samples of titanium metal led to a selected value of -225.8 ± 0.1 kcal/mol. This is comparable with other oxygen-combustion values of -225.5 ± 0.2 (2), -224.9 ± 0.4 (3) and -225.3 ± 0.3 (4) and a fluorine-combustion value of -225 ± 1 (5) derived from the reaction TiO_2(rutile) + 2 F_2(g) → TiF_4(c) + O_2(g). No experimental data were given in the latter study (5).

The 1967 JANAF Table (6) assigned an uncertainty of ±1 kcal/mol to ΔHf° due to possible uncertainty in corrections for oxygen deficiency in the rutile produced by combustion (1, 3). The atomic ratio O/Ti in the combustion product was determined by ignition to constant weight in air (1, 2) or in wet oxygen (3) at 1000°C. Ratios obtained were 1.985 to 1.994 (1), 2.00 (2) and about 1.95 (3). Mah's corrections to the stoichiometric composition correspond to about -0.8 to -1.7 kcal/mol in ΔHf°. Our opinion of the reliability of these corrections has changed due to new information on the crystal structure, ΔGf° and ΔSf° of oxygen-deficient compositions (7, 8). Mah's O/Ti ratios are at compositions where there appears to be hysteresis in measurements of the oxygen potential near 1300 K (7). The full range of the hysteresis corresponds to less than 20% of the oxygen potential. We assume that this percentage is an upper limit for error which might be introduced in the corrections of ΔGf° and ΔHf° from the observed O/Ti ratios to the stoichiometric composition. Thus, we assign an uncertainty of ±0.3 kcal/mol to ΔHf° = -225.8, but note that the less negative value of -224.9 ± 0.4 kcal/mol (3) is one of several alternatives for minimizing the deviation from integral values of ΔGr° (7) relating rutile to Ti_3O_5 at 1304 K.

Heat Capacity and Entropy

Cp° below 300 K is based on data of Sandin and Keesom (9, 0.3-20 K), Dugdale et al. (10, 12-270 K) and Shomate (11, 52-298 K). Smoothed values rather than data points were reported in the first two studies (9, 10) and only in the range 20-50 K by Dugdale (10). Dugdale's deviation plot indicates that the smooth curves (10, 11) agree within about ±0.3% above 77 K, but at lower temperatures the data of Shomate show a positive bias increasing to over 2% at 52 K. We adopt Dugdale's curve below 80 K and calculate S° by polynomial integrations of Cp°. The extrapolation below 0.3 K is insignificant. Cp° data (69-295 K) of McDonald and Seltz (12) are omitted since they are roughly 3% higher than the adopted curve.

Cp° above 300 K is from constrained fitting of enthalpy data (763-1746 K) of Naylor (13). The point at 394 K is omitted due to positive bias (∿6%) in the drop calorimeter at the lowest temperature; a similar bias is observed in Naylor's data for the four other titanium oxides and in materials such as MgF_2 studied at nearly the same time. This bias and the low purity (97.9%) of Naylor's sample are unfortunate; they favor the selection of two more recent enthalpy studies (14, 15) which conflict with that of Naylor. The adopted curve is favored, however, by four enthalpy points observed at 965 K by Navrotsky et al. (16) and by comparisons with Cp° for GeO_2, MnO_2 and V_2O_4, which have the same tetragonal-SnO_2 crystal structure as rutile.

Enthalpy data of Lietz (15, 578-1283 K) deviate from the adopted curve by ∿-3% at all temperatures; similar deviations occur in his data for TiO_2(anatase). Data of Slyusar et al. (14, 645-1990 K) deviate by ∿-4% below 1136 K and by -1.7 to +3.4% at higher temperatures. The discontinuity of almost 3% in the data near 1100 K seems to correspond to the temperature at which the authors switched container materials and temperature sensors (14). Data for Ti_2O_3, Ti_3O_5 and Ti_4O_7 (14) also have discontinuities in this region; the data below the discontinuity for Ti_2O_3 show a negative bias like rutile. Moreover, the authors (14) report Tm = 2014 K, which is ∿100° too low for rutile. Other data are too scattered (17) and too uncertain (18, 19) to help resolve the difference with Naylor (13).

These discrepancies cause us to reject the data of Slyusar et al. (14) and to consider as coincidence the agreement with Lietz (15). These two data sets yield Cp° values deviating from the adopted curve by -0.8 gibbs/mol at 700 K, 0.0 at 1100 K, and +3 at 2000 K. New data on a pure sample of rutile are needed to resolve the disagreement. We note that use of the rejected Cp° curve is one of several alternatives for minimizing the deviation from equilibria (7) relating rutile to Ti_3O_5 at 1304 K.

Melting Data

See TiO_2(ℓ).

Heat of Sublimation

ΔHs°_{298} = 152.8 ± 3 kcal/mol is calculated from ΔHf°(TiO_2, g). Sublimation makes TiO_2(c) deficient in oxygen.

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O_2Ti

Titanium Dioxide (TiO_2) O_2Ti

(Liquid) GFW = 79.8988

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	13.170	17.291	17.291	- .000	- 213.684	- 202.045	148.103
300	13.214	17.372	17.291	.024	- 213.684	- 201.973	147.137
400	15.013	21.445	17.834	1.444	- 213.593	- 198.079	108.225
500	16.062	24.917	18.912	3.002	- 213.412	- 194.221	84.894
600	16.714	27.908	20.168	4.644	- 213.192	- 190.403	69.354
700	17.152	30.519	21.464	6.338	- 212.961	- 186.623	58.266
800	17.466	32.831	22.744	8.070	- 212.733	- 182.877	49.960
900	17.700	34.907	23.981	9.828	- 212.529	- 179.156	43.505
1000	17.890	36.777	25.169	11.608	- 212.340	- 175.458	38.346
1100	18.040	38.489	26.303	13.405	- 212.171	- 171.778	34.129
1200	18.172	40.065	27.385	15.216	- 212.961	- 168.074	30.611
1300	18.290	41.524	28.417	17.039	- 212.709	- 164.345	27.629
1400	18.370	42.883	29.402	18.873	- 212.467	- 160.634	25.076
1500	24.000	44.539	30.357	21.273	- 211.684	- 156.959	22.869
1600	24.000	46.088	31.292	23.673	- 210.924	- 153.334	20.945
1700	24.000	47.543	32.206	26.073	- 210.189	- 149.758	19.253
1800	24.000	48.915	33.096	28.473	- 209.483	- 146.224	17.754
1900	24.000	50.212	33.963	30.873	- 208.805	- 142.729	16.418
2000	24.000	51.443	34.807	33.273	- 212.603	- 139.115	15.202
2100	24.000	52.614	35.627	35.673	- 211.958	- 135.455	14.097
2200	24.000	53.731	36.425	38.073	- 211.320	- 131.829	13.096
2300	24.000	54.798	37.201	40.473	- 210.686	- 128.230	12.185
2400	24.000	55.819	37.955	42.873	- 210.058	- 124.656	11.351
2500	24.000	56.799	38.690	45.273	- 209.436	- 121.112	10.588
2600	24.000	57.740	39.404	47.673	- 208.818	- 117.591	9.884
2700	24.000	58.646	40.100	50.073	- 208.206	- 114.094	9.235
2800	24.000	59.519	40.778	52.473	- 207.599	- 110.620	8.634
2900	24.000	60.361	41.439	54.873	- 206.997	- 107.164	8.076
3000	24.000	61.175	42.084	57.273	- 206.400	- 103.732	7.557
3100	24.000	61.961	42.712	59.673	- 205.807	- 100.318	7.072
3200	24.000	62.723	43.326	62.073	- 205.219	- 96.929	6.620
3300	24.000	63.462	43.925	64.473	- 204.635	- 93.553	6.196
3400	24.000	64.178	44.510	66.873	- 204.056	- 90.194	5.798
3500	24.000	64.874	45.082	69.273	- 203.480	- 86.856	5.424
3600	24.000	65.550	45.641	71.673	- 304.534	- 83.267	5.055
3700	24.000	66.208	46.188	74.073	- 303.938	- 77.130	4.556
3800	24.000	66.848	46.723	76.473	- 303.358	- 71.010	4.084
3900	24.000	67.471	47.247	78.873	- 302.794	- 64.902	3.637
4000	24.000	68.079	47.761	81.273	- 302.247	- 58.810	3.213

June 30, 1962; Sept. 30, 1966; Dec. 31, 1973.

TITANIUM DIOXIDE (TiO_2) (LIQUID) GFW = 79.8988 O_2Ti

$S^\circ_{298.15}$ = [17.291] gibbs/mol

Tm = 2130 ± 20 K

$\Delta Hf^\circ_{298.15}$ = [-213.684] kcal/mol

ΔHm° = [16 ± 4] kcal/mol

Heat of Formation

ΔHf° is calculated from that of TiO_2(rutile) by adding ΔHm° to the difference in ($H^\circ_{2130}-H^\circ_{298}$) between rutile and liquid.

Heat Capacity and Entropy

Cp° is estimated as 8 gibbs/g-atom by comparison with MgF_2, $CaCl_2$, V_2O_4 and WO_3. Below the assumed glass transition at 1400 K, Cp° is taken to be the same as that of TiO_2(rutile). S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Schneider (1) reviewed eleven melting point studies and converted the values to IPTS-48. Eight of the results fall in the range 2113 ± 10 K for measurements in air. Brauer and Littke (2), using an atmosphere of oxygen-argon mixtures, found 2103 ± 15 K in air, 2113 ± 15 K with oxygen at 300 torr, 2133 ± 15 K at 500 torr and 2143 ± 15 K at higher oxygen pressures. The authors (2) interpreted the sharp increase in Tm with increased oxygen pressure as being due to suppression of the oxygen deficiency in TiO_2. The residue of the sample melted in air gave an oxygen stoichiometry of 1.996 compared with 2.000 at higher oxygen pressures; the color showed a corresponding change from dark blue to bright yellow. The oxygen deficiency may have been even greater if there was significant reoxidation during cooling to room temperature. Schneider (1) questioned the attainment of black-body conditions in the temperature measurements; in fact, Brauer and Littke (2) tried to compensate for the change in sample color by use of similarly colored compounds in calibrations of the pyrometer. We wonder if this eliminated all relative bias in the melting temperatures.

Tm = 2130 ± 20 K is adopted. This is intermediate between the data in air and those at highest oxygen pressures. ΔHm° is estimated such that ΔSm° = 7.5 gibbs/mol, or 2.5 gibbs/g-atom, based on observed data for isostructural V_2O_4. The resulting ΔHm° of 16 ± 4 kcal/mol may be compared with approximate values of ΔHm° derived from binary phase data. We obtain 12 kcal/mol from the binary with Al_2O_3 (3), 14 kcal/mol from BaO (4) and ZrO_2 (5), 16 kcal/mol from Ta_2O_5 (6), and 21 kcal/mol from WO_3 (7). These values are derived by calculating apparent ΔHm values assuming activity coefficients of unity and then extrapolating the apparent values to (Tm-T) = 0 in order to minimize activity effects. We omit other binary systems which deviate grossly from ideality. Uncertainties in the binary results are estimated to be about ±5 kcal/mol.

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Titanium Dioxide (TiO_2)

O_2Ti

(Ideal Gas) GFW = 79.8988

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.714	-72.487	-72.487	INFINITE
100	8.592	51.644	70.377	-1.903	-72.594	-73.352	160.311
200	9.616	58.136	63.085	-.989	-72.744	-74.115	80.989
298	10.552	62.151	62.151	.000	-73.000	-74.736	54.783
300	10.569	62.216	62.151	.020	-73.004	-74.747	54.453
400	11.419	65.378	62.576	1.121	-73.232	-75.292	41.137
500	12.050	67.998	63.406	2.296	-73.434	-75.763	33.125
600	12.495	70.236	64.362	3.524	-73.627	-76.235	27.769
700	12.808	72.188	65.344	4.791	-73.824	-76.654	23.933
800	13.033	73.913	66.309	6.083	-74.040	-77.045	21.048
900	13.198	75.458	67.242	7.395	-74.278	-77.406	18.797
1000	13.322	76.856	68.134	8.721	-74.543	-77.739	16.990
1100	13.417	78.130	68.986	10.059	-74.833	-78.044	15.506
1200	13.491	79.301	69.797	11.404	-76.086	-78.285	14.258
1300	13.550	80.383	70.570	12.756	-76.307	-78.459	13.190
1400	13.597	81.389	71.308	14.114	-76.542	-78.617	12.273
1500	13.636	82.328	72.011	15.475	-76.797	-78.756	11.475
1600	13.668	83.210	72.684	16.841	-77.071	-78.877	10.774
1700	13.695	84.039	73.328	18.207	-77.368	-78.981	10.154
1800	13.718	84.822	73.945	19.580	-77.691	-79.067	9.600
1900	13.737	85.565	74.537	20.952	-78.041	-79.134	9.103
2000	13.755	86.270	75.106	22.327	-82.864	-79.029	8.636
2100	13.770	86.941	75.654	23.703	-83.243	-78.827	8.204
2200	13.784	87.582	76.182	25.081	-83.627	-78.609	7.809
2300	13.797	88.195	76.691	26.460	-84.014	-78.372	7.447
2400	13.810	88.783	77.182	27.840	-84.405	-78.117	7.113
2500	13.822	89.347	77.658	29.222	-84.802	-77.843	6.806
2600	13.835	89.889	78.113	30.605	-85.201	-77.562	6.520
2700	13.849	90.411	78.564	31.989	-85.605	-77.260	6.254
2800	13.864	90.915	78.996	33.375	-86.012	-76.944	6.006
2900	13.879	91.402	79.415	34.762	-86.423	-76.610	5.773
3000	13.897	91.873	79.823	36.150	-86.838	-76.265	5.556
3100	13.916	92.329	80.219	37.541	-87.254	-75.904	5.351
3200	13.936	92.771	80.604	38.934	-87.673	-75.535	5.159
3300	13.959	93.200	80.979	40.328	-88.095	-75.149	4.977
3400	13.984	93.617	81.345	41.725	-88.519	-74.749	4.805
3500	14.011	94.023	81.701	43.125	-88.947	-74.340	4.642
3600	14.040	94.418	82.049	44.528	-190.994	-73.652	4.471
3700	14.071	94.803	82.389	45.933	-191.393	-70.388	4.158
3800	14.104	95.179	82.720	47.342	-191.804	-67.114	3.860
3900	14.140	95.546	83.045	48.754	-192.226	-63.827	3.577
4000	14.177	95.904	83.362	50.170	-192.665	-60.529	3.307
4100	14.215	96.255	83.672	51.590	-193.114	-57.218	3.050
4200	14.256	96.598	83.975	53.013	-193.574	-53.901	2.805
4300	14.300	96.934	84.273	54.441	-194.044	-50.568	2.570
4400	14.345	97.263	84.564	55.873	-194.524	-47.229	2.346
4500	14.390	97.586	84.850	57.310	-195.012	-43.874	2.131
4600	14.437	97.903	85.131	58.752	-195.507	-40.504	1.924
4700	14.485	98.214	85.406	60.193	-196.011	-37.131	1.727
4800	14.534	98.519	85.676	61.649	-196.521	-33.744	1.536
4900	14.584	98.819	85.941	63.105	-197.037	-30.355	1.354
5000	14.634	99.114	86.201	64.565	-197.559	-26.946	1.178
5100	14.684	99.405	86.457	66.031	-198.085	-23.525	1.008
5200	14.735	99.690	86.709	67.502	-198.615	-20.100	.845
5300	14.786	99.972	86.957	68.978	-199.148	-16.661	.687
5400	14.837	100.248	87.200	70.459	-199.685	-13.213	.535
5500	14.887	100.521	87.440	71.946	-200.221	-9.751	.387
5600	14.937	100.790	87.676	73.437	-200.763	-6.290	.245
5700	14.987	101.055	87.908	74.933	-201.304	-2.810	.108
5800	15.036	101.316	88.137	76.434	-201.847	.680	-.026
5900	15.084	101.573	88.363	77.940	-202.390	4.175	-.155
6000	15.131	101.827	88.585	79.451	-202.933	7.679	-.280

June 30, 1962; Sept. 30, 1966; Dec. 31, 1973.

TITANIUM DIOXIDE (TiO_2) (IDEAL GAS) GFW = 79.8988 O_2Ti

Point Group C_{2v}

$S^\circ_{298.15}$ = 62.15 ± 1.0 gibbs/mol

ΔHf°_0 = -72.49 ± 3 kcal/mol

ΔHf°_0 = -73.0 ± 3 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0	1	18880	[3]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
962 (1)	[270] (1)	935 (1)

Bond Distance: TiO = [1.62 ± 0.08] Å

Bond Angle: O-Ti-O = 110° ± 15°

σ = 2

Product of the Moments of Inertia: $I_AI_BI_C$ = [3.1153 x 10^{-115}] g^3cm^6

Heat of Formation

ΔHf° = -73.0 ± 3 kcal/mol is selected from the ten data sets analyzed below. These include four different reactions studied by Knudsen effusion or mass spectrometry. Our adopted value is consistent with all but two of the data sets, namely reactions C (2) and D (5). We presume that the less negative ΔHf° = -59.1 from reaction C is due to bias in the mass-spectrometric values (2) for the partial pressure of O(g). The more negative ΔHf° = -86.0 from the sublimation reaction D corresponds to effusion pressures too large by a factor of ∿25; allowance for the activity of TiO_2 in the oxygen-deficient condensed phase (5) increases the discrepancy. Gross mass transport from the cell by species other than TiO_2 may have occurred (3), since mass-spectrometric pressures (3, 6) are fairly consistent with our ΔHf°. We give little weight to reactions D and E due to problems in interpretation of the vapor composition (5, 6) and the activity of oxygen-deficient TiO_2(c, ℓ).

Activity effects appear to be minor for TiO_2 in TiO_x(c) in the range 1.833 < x < 1.889. Univariant, two-phase systems involving the crystals Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15} and Ti_9O_{17} occur in this region. Our calculations based on emf data (9) yield a(TiO_2) ≥ ∿0.7 at 1900 K; these values change only slowly with x and T. Sublimation experiments in this region may involve hysteresis, but the degree should be less than that found in equilibration data (10) near 1300 K.

Drowart et al. (11) provided the key improvement in ΔHf° by reinterpretation of the congruent vaporization (4) of Ti_3O_5(c). Gilles and co-workers (1, 12) confirmed the congruency of vaporization and gave supportive mass-spectrometric data. We use JANAF auxiliary data (7) with D°_0(TiO) = 158.5 ± 2 kcal/mol to recalculate the vaporization (4) as described in (1, 11). Resulting partial pressures of TiO_2, TiO and O(g) are analyzed in terms of reaction C. Third-law analysis yields our selected value of ΔHf° and D°_0(TiO_2) = 302.8 ± 3 kcal/mol. D°_0 would decrease by ∿1 kcal/mol if D°_0(TiO) were increased by 2 kcal/mol in the recalculation. The conclusion (1) that the ionization cross-section ratio (TiO/TiO_2) = 2.2 is unchanged in our recalculation; even larger ratios may be expected at low ionizing potentials (13).

Source	Method	Reaction[a]	Range T/K	No. of Points	δS°[b] gibbs/mol	ΔHr°_{298}/(kcal/mol) 2nd Law	ΔHr°_{298}/(kcal/mol) 3rd Law	ΔHf°_{298} kcal/mol	D°_0 kcal/mol
(1) Hampson (1971)	Mass spec.	A	2145-2318	5	-2.2±4.0	-19.7±8.9	-17.6±1.0	-74.4±3	304.2
(2) Balducci (1972)	Mass spec.	A	2165-2500	6	4.6±0.4	- 4.2±0.9	-14.8±1.2	-72.2±3	302.0
(3) Berkowitz (1957)	Mass spec.	A ?	2194	1	-	-	-10.8	-76.2±4	306.0
(1) Hampson (1971)	Mass spec.	B	1893	7	-	-	2.5±0.5	-72.8±7	302.6
(2) Balducci (1972)	Mass spec.	C	2015-2240	12	4.4±2.5	141.0±5.3	131.6±1.0	-59.1±3	288.9
(4) Wahlbeck (1967)	Effusion	C	1837-2014	Eqn.	3.5	152.3	145.6±0.7	-73.0±3	302.8
(5) Groves (1955)	Effusion	D	1849-2010	14	-5.5±4.0	129.2±7.7	139.8±1.3	-86.0	315.8
(3) Berkowitz (1957)	Mass spec.	D	1881	3	-	-	152.3±3.2	-73.5	303.3
(6) Semenov (1969)	Mass spec.	D	1850-2050	Eqn.	-3.6	142.7	149.8±1.0	-75.0	305.8
(6) Semenov (1969)	Mass spec.	E	2263-2538	6	-7.2±2.9	122.8±6.9	139.9±1.8	-73.8	303.6

[a] Reactions are A) $TiO_2(g) + Ti(g) = 2\ TiO(g)$; B) $TiO(g) + WO_3(g) = TiO_2(g) + WO_2(g)$; C) $TiO_2(g) = TiO(g) + O(g)$; D) $TiO_2(rutile) = TiO_2(g)$; E) $TiO_2(\ell) = TiO_2(g)$.

[b] δS° = ΔSr°(2nd law) - ΔSr°(3rd law).

Heat Capacity and Entropy

The electronic levels, bond angle and stretching frequencies are from infrared and emission spectra of TiO_2 isolated in rare-gas matrices (14). We assume the emission at 5295 Å to be a forbidden triplet-singlet transition due to its similarity with CeO_2 (15). Frequency ν_1 was observed both in infrared and emission spectra. The bond angle was derived (14) from ν_3 using splittings observed for the five Ti isotopes. Earlier electric-deflection experiments (16) at 2500 K had shown that the populated electronic states were polar (i.e., nonlinear). We estimate the bond length to be the same as that of ground-state TiO (7). Principal moments of inertia are $I_A = 12.107 \times 10^{-39}$, $I_B = 3.356 \times 10^{-39}$ and $I_C = 2.750 \times 10^{-39}$ g cm^2.

The bending frequency is estimated as 270 ± 80 cm^{-1} from the following information. A value of 272 cm^{-1} is derived from the three-constant valence-force field (17) using ν_1, ν_3 and $(k\delta/\ell^2)/k_1$ = 0.040 transferred from isoelectronic CaF_2 (18). The resulting value of k_{12}/k_1 is similar to that of CaF_2. The inferior two-constant cental-force field gives ν_2 = 325 cm^{-1}. Bending modes have been observed (19) for excited electronic states of TaO_2 (285 and 291 cm^{-1}) and WO_2 (300 cm^{-1}). These molecules have stretching frequencies quite similar to TiO_2, but the excited states may be linear rather than bent as are the ground states. We estimate that S° is uncertain by about 0.7 and 0.3 gibbs/mol due to uncertainties in ν_2 and the structural parameters, respectively.

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O_2Ti

Vanadium Dioxide (VO_2)

(Ideal Gas) GFW = 82.9402

O_2V

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-2.690	-55.106	-55.106	INFINITE
100	8.457	53.187	72.019	-1.883	-55.110	-56.118	122.645
200	9.517	59.392	64.302	-.982	-55.344	-57.044	62.335
298	10.494	63.374	63.374	.000	-55.600	-57.823	42.385
300	10.512	63.439	63.374	.019	-55.605	-57.837	42.134
400	11.382	66.587	63.797	1.116	-55.832	-58.545	31.988
500	12.025	69.200	64.624	2.288	-56.027	-59.200	25.876
600	12.476	71.435	65.577	3.514	-56.206	-59.818	21.789
700	12.794	73.383	66.556	4.779	-56.383	-60.406	18.860
800	13.022	75.107	67.519	6.070	-56.567	-60.969	16.656
900	13.189	76.651	68.450	7.381	-56.763	-61.507	14.936
1000	13.314	78.048	69.341	8.707	-56.975	-62.023	13.555
1100	13.411	79.321	70.191	10.043	-57.206	-62.517	12.421
1200	13.486	80.491	71.001	11.388	-57.458	-62.988	11.472
1300	13.545	81.573	71.773	12.740	-57.734	-63.438	10.665
1400	13.593	82.579	72.510	14.097	-58.036	-63.866	9.970
1500	13.632	83.518	73.213	15.458	-58.366	-64.271	9.364
1600	13.665	84.399	73.885	16.823	-58.723	-64.654	8.831
1700	13.692	85.228	74.528	18.191	-59.108	-65.012	8.358
1800	13.715	86.012	75.144	19.561	-59.525	-65.347	7.934
1900	13.735	86.754	75.736	20.934	-59.976	-65.658	7.552
2000	13.751	87.459	76.305	22.308	-60.463	-65.946	7.206
2100	13.766	88.130	76.852	23.684	-60.986	-66.207	6.890
2200	13.778	88.771	77.379	25.061	-67.025	-66.418	6.598
2300	13.789	89.383	77.888	26.440	-67.666	-66.376	6.307
2400	13.799	89.970	78.379	27.819	-68.313	-66.305	6.038
2500	13.808	90.534	78.854	29.199	-68.965	-66.209	5.788
2600	13.815	91.076	79.314	30.581	-69.620	-66.086	5.555
2700	13.822	91.597	79.759	31.962	-70.281	-65.937	5.337
2800	13.828	92.100	80.191	33.345	-70.945	-65.763	5.133
2900	13.834	92.585	80.610	34.728	-71.615	-65.566	4.941
3000	13.839	93.054	81.017	36.112	-72.288	-65.346	4.760
3100	13.843	93.508	81.413	37.496	-72.965	-65.103	4.590
3200	13.847	93.948	81.798	38.880	-73.648	-64.840	4.428
3300	13.851	94.374	82.172	40.265	-74.333	-64.555	4.275
3400	13.854	94.787	82.537	41.650	-75.023	-64.247	4.130
3500	13.857	95.189	82.893	43.036	-75.715	-63.921	3.991
3600	13.860	95.579	83.240	44.422	-76.412	-63.574	3.859
3700	13.863	95.959	83.579	45.808	-183.859	-63.027	3.723
3800	13.865	96.329	83.909	47.195	-184.154	-59.756	3.437
3900	13.868	96.689	84.232	48.581	-184.464	-56.481	3.165
4000	13.870	97.040	84.548	49.968	-184.789	-53.196	2.906
4100	13.872	97.383	84.857	51.355	-185.130	-49.901	2.660
4200	13.874	97.717	85.159	52.742	-185.485	-46.599	2.425
4300	13.875	98.044	85.455	54.130	-185.855	-43.285	2.200
4400	13.877	98.363	85.745	55.517	-186.241	-39.968	1.985
4500	13.878	98.674	86.029	56.905	-186.641	-36.638	1.779
4600	13.880	98.980	86.307	58.293	-187.055	-33.297	1.582
4700	13.881	99.278	86.580	59.681	-187.485	-29.951	1.393
4800	13.882	99.570	86.847	61.069	-187.928	-26.594	1.211
4900	13.883	99.857	87.110	62.457	-188.386	-23.233	1.036
5000	13.884	100.137	87.368	63.846	-188.856	-19.857	.868
5100	13.885	100.412	87.621	65.234	-189.341	-16.470	.706
5200	13.886	100.682	87.869	66.623	-189.837	-13.078	.550
5300	13.887	100.946	88.114	68.012	-190.345	-9.669	.399
5400	13.888	101.206	88.354	69.400	-190.868	-6.261	.253
5500	13.889	101.461	88.590	70.789	-191.399	-2.833	.113
5600	13.889	101.711	88.822	72.178	-191.944	.598	-.023
5700	13.890	101.957	89.050	73.567	-192.499	4.039	-.155
5800	13.891	102.198	89.275	74.956	-193.065	7.496	-.282
5900	13.892	102.436	89.496	76.345	-193.640	10.957	-.406
6000	13.892	102.669	89.713	77.734	-194.225	14.432	-.526

Dec. 31, 1973

VANADIUM DIOXIDE (VO_2) (IDEAL GAS) GFW = 82.9402 O_2V

Point Group [C_{2v}]

$S^\circ_{298.15}$ = [63.37 ± 1.40] gibbs/mol

Ground State Quantum Weight [2]

ΔHf°_0 = -55.1 ± 10.0 kcal/mol

ΔHf°_{298} = -55.6 ± 10.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}

[970] (1)

[300] (1)

[930] (1)

Bond Distance: V-O = [1.589] Å

σ = 2

Bond Angle: O-V-O = [110°]

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.858 x 10^{-115}] g^3cm^6

Heat of Formation

Four independent mass spectrometric studies lead to values for $\Delta Hf^\circ_{298}(VO_2, g)$ (1, 2, 3, 4). Shchukarev et al. (2) studied the composition of the vapor above V_2O_4 during evaporation from the surface of a platinum strip. A second law sublimation heat, ΔHs° = 104 ± 2 kcal/mol, was reported for the range 1500-1800 K. Assuming the reported value corresponds to 1700 K and using auxiliary data (5), we calculate $\Delta Hf^\circ_{298}(VO_2, g)$ = -62.3 ± 2.0 kcal/mol. The sublimation was described by 0.5 $V_2O_4(c) = VO_2(g)$. More recent related work (3) yields a ΔHf°_{298} value approximately 6 kcal/mol more positive. This latter work and other investigations are summarized in the following table.

Reference	Reaction	No. of Points	Temp. Range, K	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298}, kcal/mol* 2nd Law	3rd Law
3	A	Equation	1673-1818	114.29	114.32	0.02	-56.26	-56.23
3	B	Equation	1818-2273	104.90	103.77	-0.58	-54.30	-55.43
1	C	2	1948	-	-16.23	-	-	-45.97
4	C	1	2270	-	-12.86	-	-	-49.34
4	D	1	2270	-	-40.14	-	-	-32.94 (-39.73)**

*ΔHf°_{298} is the heat of formation of $VO_2(g)$.

**Value is based on recent determination by Farber et al. (8) for $\Delta Hf^\circ_{298}(AlO, g)$.

Reactions:
(A) 0.5 $V_2O_4(c) = VO_2(g)$
(B) 0.5 $V_2O_4(\ell) = VO_2(g)$
(C) $V(g) + VO_2(g) = 2\ VO(g)$
(D) $2\ AlO(g) + V(g) = 2\ Al(g) + VO_2(g)$

We adopt ΔHf°_{298} = -55.6 kcal/mol for $VO_2(g)$. This value is an average of the second and third law results of Frantseva and Semenov (3). These results are independent of the VO(g) data and show small third law drifts. The results of our analysis for reaction (C) for the data of Berkowitz et al. (1) and Farber et al. (4) show good agreement in ΔHr°_{298} but lead to values for ΔHf°_{298} which are 6-10 kcal/mol less negative than our adopted value. Killingbeck (6) studied the evaporation of V_2O_3 from a molybdenum effusion chamber and reported ΔHr°_{298} = 279.5 ± 5 kcal/mol for $V_2O_3(c) = VO(g) + VO_2(g)$. Using auxiliary data (5), we calculate ΔHf°_{298} = -42.3 ± 5.0 kcal/mol for $VO_2(g)$.

The adopted ΔHf°_{298} value corresponds to a dissociation energy D°_0 = 295.5 kcal/mol (12.8 eV) for the process $VO_2(g) = V(g) + 2\ O(g)$. This D°_0 value is 1.96 times the dissociation energy of VO(g) (5).

Heat Capacity and Entropy

The vibrational frequencies and geometry of $VO_2(g)$ are estimated based on existing and estimated data for related metal dioxides such as $TiO_2(g)$, $TaO_2(g)$, and $WO_2(g)$ (5). The V-O bond distance is assumed to be the same as in VO(g) (5).

The ground state quantum weight of 2 is adopted so as to be consistent with $TaO_2(g)$ (5). This introduces an uncertainty of ±1.38 eu in S°_{298}. The estimation of ν_2 at 300 cm^{-1} results in an uncertainty of 0.72 eu in S°_{298} for ±100 cm^{-1}. The estimates for $VO_2(g)$ are such that the third law drifts as indicated in the above table are small. Nevertheless, until more data is available for $VO_2(g)$, the uncertainty in the entropy must be considered as ±1.4 gibbs/mol for a bent molecule. The free energy functions suggested by Brewer and Rosenblatt (7) are roughly 3-4 eu lower than those adopted here. The main reason for the difference is that Brewer and Rosenblatt (7) treated $VO_2(g)$ as a linear molecule.

The electronic levels of the V^{+4} ion as reported by Moore (9) consist of a ground state with quantum weight four and an excited state at 620 cm^{-1} with a quantum weight six. The next excited state is listed at ~148000 cm^{-1}. Inclusion of an estimated state for $VO_2(g)$ at 620 cm^{-1} with a quantum weight of six would raise S°_{298} by 1.06 eu. This is within the estimated uncertainty of S°_{298}.

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O_2V

Dititanium Trioxide (Ti_2O_3)

(Crystal) GFW = 143.7982

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 3.367	- 361.450	- 361.450	INFINITE
100	6.256	2.643	34.393	- 3.175	- 362.567	- 356.229	778.537
200	16.920	10.476	20.391	- 1.983	- 363.335	- 349.538	381.957
298	22.900	18.464	18.464	.000	- 363.500	- 342.721	251.221
300	22.990	18.606	18.464	.042	- 363.499	- 342.592	249.578
400	28.090	25.879	19.423	2.583	- 363.261	- 335.647	183.389
500	31.130	33.308	21.447	5.930	- 362.302	- 328.837	143.734
600	32.610	39.126	23.920	9.124	- 361.573	- 322.212	117.365
700	33.540	44.228	26.464	12.435	- 360.801	- 315.712	98.570
800	34.170	48.750	28.973	15.822	- 360.031	- 309.325	84.503
900	34.630	52.803	31.399	19.263	- 359.283	- 303.030	73.586
1000	34.980	56.470	33.726	22.744	- 358.570	- 296.819	64.870
1100	35.260	59.818	35.948	26.257	- 357.894	- 290.675	57.752
1200	35.500	62.896	38.067	29.795	- 359.132	- 284.517	51.818
1300	35.700	65.746	40.088	33.355	- 358.285	- 278.335	46.792
1400	35.870	68.398	42.017	36.934	- 357.461	- 272.217	42.495
1500	36.030	70.878	43.859	40.529	- 356.662	- 266.155	38.779
1600	36.180	73.208	45.621	44.140	- 355.893	- 260.145	35.534
1700	36.310	75.406	47.309	47.764	- 355.157	- 254.185	32.678
1800	36.440	77.485	48.928	51.402	- 354.463	- 248.266	30.144
1900	36.550	79.458	50.484	55.051	- 353.810	- 242.384	27.881
2000	36.670	81.336	51.980	58.712	- 362.095	- 236.229	25.814
2100	36.780	83.128	53.421	62.385	- 361.480	- 229.948	23.931
2200	36.880	84.841	54.810	66.068	- 360.865	- 223.702	22.223
2300	36.990	86.483	56.152	69.761	- 360.246	- 217.481	20.665
2400	37.090	88.059	57.449	73.465	- 359.625	- 211.284	19.240
2500	37.190	89.575	58.704	77.179	- 359.003	- 205.119	17.931
2600	37.280	91.036	59.919	80.903	- 358.377	- 198.976	16.725
2700	37.380	92.445	61.098	84.636	- 357.751	- 192.856	15.611
2800	37.470	93.806	62.242	88.378	- 357.123	- 186.760	14.577
2900	37.560	95.122	63.353	92.130	- 356.494	- 180.681	13.617
3000	37.660	96.397	64.433	95.891	- 355.862	- 174.631	12.722

Dec. 31, 1960; March 31, 1967; June 30, 1967; June 30, 1973

DITITANIUM TRIOXIDE (Ti_2O_3) (CRYSTAL) GFW = 143.7982 O_3Ti_2

$S^\circ_{298.15}$ = 18.46 ± 0.05 gibbs/mol
Tt = 470 ± 20 K
Tm = 2115 ± 10 K

ΔHf°_0 = -361.45 ± 2 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -363.5 ± 2 kcal/mol
ΔHt° = 0.272 kcal/mol
ΔHm° = [25] kcal/mol

Heat of Formation

Humphrey (1) measured ΔHr°(298.15 K) = -88.11 ± 0.1 kcal/mol for the reaction Ti_2O_3(c) + 0.5 O_2(g) = 2 TiO_2(rutile) using bomb calorimetry. When combined with ΔHf°(298.15 K) = -225.8 kcal/mol for rutile, this yields -363.5 ± 2 kcal/mol as the adopted ΔHf°(298.15 K) for Ti_2O_3. The less negative value of -362.8 ± 0.6 kcal/mol was obtained by Ariya et al. (2) from their heats of combustion of various compositions in the Ti-O system. Ariya et al. (2) used an estimated correction for the formation of TiO_{2-x}, while Humphrey (1) obtained values of 0.1 to 1.3 kcal/mol by grinding the product and reburning it with white oil. Most of the assigned uncertainty arises from this problem [see TiO_2(rutile) for further details].

Heat Capacity and Entropy

Cp° is based on data of Sjöstrand and Keesom (3, 0.4-20 K) and Paukov and Berezovskii (4, 12-305 K). The two sets of data disagree in the region of overlap. Paukov (4) appears to have a positive bias at the lowest temperatures (12-18 K), so we adopt a curve which shifts gradually from Sjöstrand at 10 K to Paukov at 30 K. Deviations of Paukov (4) from the adopted Cp° are +36% (12 K) and +3% (20 K). Earlier data of Shomate (5, 53-296 K) deviate by +0.6% to +4.1% with extreme deviations of 3.0% at 53 K and 2.9 to 4.1% in a "hump" observed by Shomate near 240 K. No hump was found by Paukov. S° is derived from Cp° based on an extrapolation which is negligible.

Cp° between 298 K and 470 K is a smooth extrapolation of the low-temperature curve using the approximate shape found by Barros et al. (6, 150-700 K) via differential scanning calorimetry (Perkin-Elmer DSC-1B). The DSC data (6) have a positive bias of ~10%, over twice as large as we might expect for this apparatus so the results do not help establish Cp° between 298 K and T_t. Data measured by a conduction-type calorimeter (7, 323-523 K) have a large negative bias near 400 K. Drop-calorimetric data (8, 375-472 K) deviate from the adopted enthalpies by +5 to +2%.

Cp° above the λ-transition is derived from enthalpy data (8, 487-1750 K) by fitting only the region above 549 K. Maximum deviations from the adopted curve are ±0.4% in the fitted region and +0.9% at 526 K. Enthalpy data (493-1082 K) reported graphically by Erofeeva et al. (9) deviate by about -6 to -2%.

Slyusar et al. (15) recently reported new enthalpy data for Ti_2O_3, Ti_3O_5, Ti_4O_7 and TiO_2. The new data for Ti_3O_5 and TiO_2 are in reasonable agreement with existing JANAF Tables (16), but those for Ti_2O_3 cross the adopted values near 1100 K and deviate by -4.5 ± 1% (672-878 K) and +3.4 ± 1.1% (1158-2027 K). It appears that the two temperature regions may not belong to the same statistical population. Large negative deviations persist at the lower temperatures even when the data (15) are fitted assuming ΔHt° = 0. The transition vanishes for Ti_2O_3 samples doped with 4% V_2O_3 (6) and may be affected by other impurities or non-stoichiometry. We feel that Slyusar et al. (15) have not characterized their sample adequately. We tentatively reject their data pending new measurements on a well-characterized sample.

Transition Data

We arbitrarily choose T_t = 470 ± 20 K and derive ΔHt° as the difference between the adopted enthalpy curves at that temperature. Reported values of ΔHt° include 0.380 ± 0.025 (6), 0.036 (7) and 0.215 kcal/mol (8); each derives from different data and different base lines.

Convenience dictates that we treat the electrical transition as first order although recent Cp° data (6) suggest a gradual λ-type anomaly peaking near 470 K and extending from about 380 to 560 K. There is no change in the corundum-type symmetry, but the lattice parameters shift rapidly in this temperature range (10, 11). Honig (11) summarized evidence on the nature of the change from semiconductor to semimetal and noted that the transition can be explained without invoking antiferromagnetic ordering. Recent studies (6, 12-14) are consistent with this interpretation.

Melting Data

See $Ti_2O_3(\ell)$.

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O_3Ti_2

Dititanium Trioxide (Ti_2O_3)

(Liquid) GFW = 143.7982

		gibbs/mol		kcal/mol			
T, °K	Cp°	S°	−(G°−H°$_{298}$)/T	H°−H°$_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	22.670	30.384	30.384	.000	− 339.020	− 321.795	235.882
300	22.830	30.525	30.384	.042	− 339.019	− 321.688	234.350
400	28.470	37.978	31.362	2.647	− 338.717	− 315.943	172.623
500	31.130	44.648	33.367	5.640	− 338.112	− 310.316	135.639
600	32.610	50.466	35.743	8.834	− 337.383	− 304.825	111.033
700	33.540	55.568	38.219	12.145	− 336.611	− 299.460	93.496
800	34.170	60.090	40.675	15.532	− 335.841	− 294.206	80.373
900	34.630	64.143	43.062	18.973	− 335.093	− 289.046	70.190
1000	34.980	67.810	45.356	22.454	− 334.380	− 283.968	62.061
1100	35.260	71.158	47.552	25.967	− 333.704	− 278.959	55.424
1200	35.500	74.236	49.649	29.505	− 334.942	− 273.935	49.890
1300	35.700	77.086	51.651	33.065	− 334.095	− 268.886	45.204
1400	35.870	79.738	53.564	36.644	− 333.270	− 263.903	41.197
1500	37.500	82.325	55.396	40.394	− 332.317	− 258.981	37.733
1600	37.500	84.746	57.156	44.144	− 331.408	− 254.120	34.711
1700	37.500	87.019	58.846	47.894	− 330.547	− 249.317	32.052
1800	37.500	89.162	60.471	51.644	− 329.741	− 244.563	29.694
1900	37.500	91.190	62.035	55.394	− 328.987	− 239.852	27.589
2000	37.500	93.113	63.541	59.144	− 337.183	− 234.872	25.666
2100	37.500	94.943	64.994	62.894	− 336.491	− 229.771	23.913
2200	37.500	96.688	66.395	66.644	− 335.809	− 224.708	22.323
2300	37.500	98.355	67.748	70.394	− 335.133	− 219.673	20.874
2400	37.500	99.951	69.057	74.144	− 334.466	− 214.664	19.548
2500	37.500	101.481	70.324	77.894	− 333.808	− 209.689	18.331
2600	37.500	102.952	71.551	81.644	− 333.156	− 204.737	17.210
2700	37.500	104.367	72.740	85.394	− 332.513	− 199.809	16.173
2800	37.500	105.731	73.894	89.144	− 331.877	− 194.906	15.213
2900	37.500	107.047	75.015	92.894	− 331.249	− 190.019	14.320
3000	37.500	108.318	76.104	96.644	− 330.629	− 185.161	13.489
3100	37.500	109.548	77.163	100.394	− 330.014	− 180.320	12.713
3200	37.500	110.739	78.194	104.144	− 329.407	− 175.508	11.987
3300	37.500	111.893	79.197	107.894	− 328.806	− 170.707	11.305
3400	37.500	113.012	80.176	111.644	− 328.213	− 165.922	10.665
3500	37.500	114.099	81.129	115.394	− 327.624	− 161.162	10.063

Dec. 31, 1960; March 31, 1967; June 30, 1967; June 30, 1973

DITITANIUM TRIOXIDE (Ti_2O_3) (LIQUID) GFW = 143.7982 O_3Ti_2

$S^\circ_{298.15}$ = [30.384] gibbs/mol

Tm = 2115 ± 10 K

$\Delta Hf^\circ_{298.15}$ = [−339.020]kcal/mol

ΔHm° = [25] kcal/mol

Heat of Formation

ΔHf°(298.15 K) is calculated from that of the crystal by adding ΔHm° and the difference between ($H^\circ_{2115}-H^\circ_{298}$) for crystal and liquid.

Heat Capacity and Entropy

Cp° is estimated as 7.5 gibbs/g-atom. Below the assumed glass transition at 1400 K, Cp° is taken from the crystal; the high-temperature curve is extrapolated down to 298.15 K. S° is derived in a manner analogous to that of ΔHf°.

Melting Data

Tm is the value quoted by Wahlbeck and Gilles (1) based on work of K. D. Carlson. The adopted value is converted to IPTS-68. ΔHm° is estimated such that ΔSm° is 12 gibbs/mol as observed (2) for Al_2O_3(α, corundum). Other reported melting points were summarized earlier (3). Slyusar et al. (4) recently obtained Tm = 2043 K in an enthalpy study, but we tentatively reject this work (see Ti_2O_3, crystal).

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Divanadium Trioxide (V_2O_3)

(Crystal) GFW = 149.881

O_3V_2

T, °K	Cp°	S°	−(G°−H°₂₉₈)/T	H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 4.177	− 290.146	− 290.146	INFINITE
100	6.842	3.385	42.851	− 3.947	− 291.191	− 284.977	622.816
200	19.146	14.524	25.578	− 2.211	− 291.377	− 278.547	304.382
298	25.087	23.439	23.438	.000	− 291.300	− 272.249	199.564
300	25.158	23.594	23.439	.046	− 291.295	− 272.131	198.247
400	28.093	31.285	24.468	2.727	− 290.907	− 265.796	145.224
500	29.577	37.736	26.495	5.620	− 290.382	− 259.577	113.461
600	30.432	43.210	28.836	8.624	− 289.811	− 253.468	92.326
700	31.088	47.952	31.236	11.701	− 289.229	− 247.459	77.260
800	31.701	52.143	33.592	14.841	− 288.640	− 241.532	65.984
900	32.324	55.913	35.866	18.042	− 288.046	− 235.678	57.230
1000	32.973	59.352	38.045	21.307	− 287.444	− 229.892	50.243
1100	33.649	62.526	40.128	24.637	− 286.828	− 224.166	44.538
1200	34.349	65.484	42.119	28.037	− 286.198	− 218.497	39.794
1300	35.072	68.262	44.025	31.508	− 285.554	− 212.882	35.789
1400	35.813	70.888	45.850	35.052	− 284.896	− 207.316	32.363
1500	36.569	73.384	47.603	38.671	− 284.224	− 201.798	29.402
1600	37.338	75.769	49.290	42.366	− 283.534	− 196.326	26.817
1700	38.117	78.056	50.915	46.139	− 282.827	− 190.897	24.541
1800	38.906	80.257	52.484	49.990	− 282.105	− 185.509	22.524
1900	39.702	82.382	54.002	53.920	− 281.375	− 180.162	20.723
2000	40.504	84.438	55.473	57.931	− 280.637	− 174.856	19.107
2100	41.311	86.434	56.400	62.021	− 279.896	− 169.584	17.649
2200	42.123	88.375	58.287	66.193	− 290.096	− 164.300	16.322
2300	42.940	90.265	59.636	70.446	− 289.425	− 158.597	15.070
2400	43.758	92.110	60.951	74.781	− 288.681	− 152.922	13.925
2500	44.581	93.913	62.234	79.198	− 287.864	− 147.284	12.876
2600	45.406	95.677	63.486	83.697	− 286.973	− 141.678	11.909
2700	46.233	97.406	64.710	88.279	− 286.006	− 136.107	11.017
2800	47.062	99.103	65.909	92.944	− 284.964	− 130.573	10.192

Dec. 31, 1973

DIVANADIUM TRIOXIDE (V_2O_3) (CRYSTAL) GFW = 149.8810 O_3V_2

$S^\circ_{298.15}$ = 23.44 ± 0.3 gibbs/mol
Tt = 168.8 ± 0.2 K
Tm = 2340 ± 20 K

ΔHf°_0 = −290.1 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −291.3 ± 1.5 kcal/mol
ΔHt° = 0.388 kcal/mol
ΔHm° = [28.0] kcal/mol

Heat of Formation

The adopted heats of formation for the vanadium oxides, and in particular V_2O_3(c), are based on the combustion studies by Mah and Kelley (1). The adopted value is $\Delta Hf^\circ_{298}(V_2O_3$, c) = −291.3 kcal/mol as reported by Mah and Kelley (1). For more details refer to the V_2O_5(c) table (2). We assign an uncertainty limit of ±1.5 kcal/mol.

Charlu and Kleppa (3) reported a heat of formation value of −291.0 ± 0.9 kcal/mol for V_2O_3 based on oxidation studies to V_2O_5(c) in a high temperature microcalorimeter. An advantage of this technique is that complete oxidation to V_2O_5(c) was achieved whereas in the study by Mah and Kelley (1) a mixture of the two oxides V_2O_4 and V_2O_5 was obtained. Other combustion studies have been reported by Siemonsen and Ulich (4) and Vol'f and Ariya (5). Additional heat of formation values may be obtained from the sodium peroxide fusion studies by Mixter (6) and Ruff and Friedrich (7) and the following equilibrium studies involving vanadium and its oxides: H_2O/H_2 by Kobayashi (8), Müller (9), and Karasev, Polyakov, and Samarin (10); and CO/CO_2 by Spencer and Justice (11). As an example, the study by Spencer and Justice (11) leads to ΔHf°_{298} = −287.9 kcal/mol for V_2O_3(c). The analysis, based on data in the range 1024-1169 K, indicates a third law drift of −0.96 ± 0.43 eu.

Heat Capacity and Entropy

Anderson (12) measured the heat capacity of V_2O_3(c) in the range 57-287 K. The data indicated an anomaly in the region 165-182 K. This heat capacity data is joined smoothly at 298 K with the high temperature heat capacity values as derived from the enthalpy measurements of Cook (13). The adopted Cp° values are based on these two studies (12, 13). Using the combination of Debye and Einstein functions as suggested by Anderson (12), we calculate S°_{50} = 0.783 gibbs/mol and $H^\circ_{50}-H^\circ_0$ = 0.0284 kcal/mol. There is considerable scatter in the data of Cook (13); the deviations from the adopted values range from −0.8 to 0.6% except for the data point at 369.1 K which is −1.4% low ($\sim$25 cal/mol).

Khlyustov et al. (14) measured the heat capacity of V_2O_3 in the region 120-190 K. For T < Tt, this latter study lies above the Anderson data by $\sim$7% while for T > Tt, it is $\sim$10% higher. Three other studies examined the heat capacity in the range 343-573 K (15, 16, 17). These latter three studies indicated irregularities in the Cp° values in the region of investigation. We do not adopt these works, pending further independent verification.

Phase Data

A review of the literature of the V-O system by Stringer (18) stated that V_2O_3 has a homogeneity range of roughly $VO_{1.44}$ to $VO_{1.65}$. On cooling V_2O_3(c) through Tt, the crystal undergoes a structural distortion from hexagonal corundum to monoclinic. Numerous references as to the homogeneity range and crystal structure are contained, for example, in the reviews by Stringer (18) and Adler (19) as well as in the x-ray study by Minomura and Nagasaki (20).

Transition Data

The heat capacity data of Anderson (12) indicated an anomaly at 168.8 K. The anomaly appeared similar to a λ-type transition and a smooth curve is easily drawn joining the heat capacity data on either side of the transition. Anderson (12) made five measurements to determine the energy necessary to heat V_2O_3(c) through the transition. The mean enthalpy of the five measurements from 161.3 to 180.0 K was reported as 692.2 ± 2.4 cal/mol. Subtracting the calculated base heat in this same region, we calculate ΔHt° = 0.388 kcal/mol. We adopt Tt = 168.8 K and ΔHt° = 0.388 kcal/mol, and consider it to be first order.

Khlyustov et al. (14) reported heat capacity data in the region 123-184 K and reported a transition which resembled a λ-type with a maximum at 165.66 K with ΔHt° = 0.356 kcal/mol. Although both heat capacity studies (12, 14) appeared to indicate a second order transition, Minomura and Nagasaki (20) determined through x-ray measurements that V_2O_3(c) undergoes a discontinuous volume contraction ($\sim$3%) at Tt, indicative of a first order transition. Austin (21) and Feinlieb and Paul (22) studied the pressure dependence of Tt and reported $(\frac{dTt}{dP})_{Tt}$ values. Using the Clausius-Clapeyron equation for a first order transition with ΔV from Minomura and Nagasaki (20), we calculate ΔHt = 0.863 and 1.020 kcal/mol, respectively. The calorimetric value for ΔHt° is more reliable than these latter two determinations. For further information on this transition, the review by Adler (19) is suggested. There are indications of possible transitional behavior above room temperature (15, 16, 17, 19). We adopt only regular behavior above 298.15 K.

Melting Data: See V_2O_3(ℓ) table for details.

Sublimation Data

The experimental evidence indicated that, although V_2O_3(c) sublimes congruently, the vapors do not contain V_2O_3(g) (23).

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O_3V_2

O_3V_2

Divanadium Trioxide (V_2O_3)

(Liquid) GFW = 149.8810

T, °K	gibbs/mol Cp°	S°	−(G°−H°298)/T	kcal/mol H°−H°298	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	25.087	36.389	36.388	.000	− 261.246	− 246.056	180.364
300	25.158	36.544	36.389	.046	− 261.241	− 245.962	179.183
400	28.093	44.235	37.418	2.727	− 260.853	− 240.922	131.634
500	29.577	50.686	39.445	5.620	− 260.328	− 235.998	103.155
600	30.432	56.160	41.786	8.624	− 259.757	− 231.185	84.209
700	31.088	60.902	44.186	11.701	− 259.175	− 226.470	70.707
800	31.701	65.093	46.542	14.841	− 258.586	− 221.839	60.603
900	32.324	68.863	48.816	18.042	− 257.992	− 217.279	52.762
1000	32.973	72.302	50.995	21.307	− 257.390	− 212.788	46.505
1100	33.649	75.476	53.078	24.637	− 256.774	− 208.358	41.397
1200	34.349	78.434	55.069	28.037	− 256.144	− 203.984	37.150
1300	35.072	81.212	56.975	31.508	− 255.501	− 199.663	33.566
1400	35.813	83.838	58.800	35.052	− 254.842	− 195.392	30.502
1500	36.440	86.331	60.553	38.667	− 254.174	− 191.169	27.853
1600	37.500	88.718	62.239	42.366	− 253.480	− 186.992	25.542
1700	37.500	90.992	63.865	46.116	− 252.795	− 182.857	23.508
1800	37.500	93.135	65.432	49.866	− 252.175	− 178.760	21.704
1900	37.500	95.163	66.944	53.616	− 251.625	− 174.697	20.095
2000	37.500	97.086	68.403	57.366	− 251.147	− 170.662	18.649
2100	37.500	98.916	69.813	61.116	− 250.747	− 166.647	17.343
2200	37.500	100.661	71.176	64.866	− 261.369	− 162.602	16.153
2300	37.500	102.327	72.494	68.616	− 261.201	− 158.116	15.024
2400	37.500	103.923	73.771	72.366	− 261.042	− 153.635	13.990
2500	37.500	105.454	75.008	76.116	− 260.892	− 149.165	13.040
2600	37.500	106.925	76.207	79.866	− 260.750	− 144.699	12.163
2700	37.500	108.340	77.371	83.616	− 260.615	− 140.237	11.351
2800	37.500	109.704	78.502	87.366	− 260.487	− 135.780	10.598
2900	37.500	111.020	79.601	91.116	− 260.369	− 131.328	9.897
3000	37.500	112.291	80.669	94.866	− 260.257	− 126.880	9.243
3100	37.500	113.521	81.709	98.616	− 260.150	− 122.435	8.632
3200	37.500	114.712	82.722	102.366	− 260.053	− 117.997	8.059
3300	37.500	115.865	83.709	106.116	− 259.960	− 113.560	7.521
3400	37.500	116.985	84.671	109.866	− 259.875	− 109.123	7.014
3500	37.500	118.072	85.610	113.616	− 259.794	− 104.692	6.537

Dec. 31, 1973

DIVANADIUM TRIOXIDE (V_2O_3) (LIQUID) GFW = 149.8810 O_3V_2

$S^\circ_{298.15}$ = [36.389] gibbs/mol

Tm = 2340 ± 20 K

$\Delta Hf^\circ_{298.15}$ = [−261.246] kcal/mol

ΔHm° = [28.0] kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding ΔHm° and the difference between ($H^\circ_{2340}-H^\circ_{298}$) for the crystal and the liquid.

Heat Capacity and Entropy

Cp° for the liquid phase is estimated to be a constant 7.5 gibbs/g-atom. Below the assumed glass transition temperature at 1600 K, Cp° is taken from the crystal. The entropy is derived in a manner analogous to that for the heat of formation.

Melting Data

Tm = 2340 ± 20 K is the value extracted from the V-O phase diagram proposed by Stringer (1). This value is adopted and corrected to IPTS-68. ΔHm° is estimated such that ΔSm° is 12 gibbs/mol as observed (2) for Al_2O_3(α, corundum).

Vaporization Data

There is no evidence as to the existence of V_2O_3(g) and thus we do not report any heat of vaporization. See VO(g) and VO_2(g) tables for more information (2).

References

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2. JANAF Thermochemical Tables: Al_2O_3(α, c), 6-30-72; VO(g) and VO_2(g), 12-31-73.

O_3V_2

Divanadium Tetroxide (V_2O_4) O_4V_2

(Crystal) GFW = 165.8804

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	- 4.326	- 339.058	- 339.058	INFINITE
100	8.821	4.458	44.668	- 4.021	- 340.375	- 332.198	726.019
200	21.576	14.898	27.093	- 2.439	- 341.063	- 323.686	353.707
298	27.581	24.743	24.743	.000	- 341.100	- 315.133	230.998
300	27.674	24.914	24.744	.051	- 341.097	- 314.972	229.457
400	32.333	39.929	26.843	5.235	- 338.561	- 306.690	167.567
500	34.242	47.362	30.224	8.569	- 337.961	- 298.789	130.600
600	35.480	53.718	33.623	12.057	- 337.283	- 291.016	106.002
700	36.371	59.256	36.898	15.651	- 336.573	- 283.362	88.470
800	37.155	64.165	40.005	19.328	- 335.846	- 275.811	75.348
900	37.800	68.579	42.939	23.076	- 335.112	- 268.349	65.164
1000	38.404	72.593	45.706	26.887	- 334.377	- 260.970	57.035
1100	38.955	76.279	48.320	30.755	- 333.643	- 253.666	50.399
1200	39.486	79.692	50.794	34.677	- 332.915	- 246.427	44.880
1300	39.993	82.872	53.141	38.651	- 332.197	- 239.249	40.221
1400	40.489	85.855	55.372	42.675	- 331.491	- 232.125	36.236
1500	40.973	88.664	57.499	46.748	- 330.800	- 225.052	32.790
1600	41.450	91.324	59.531	50.870	- 330.122	- 218.026	29.781
1700	41.920	93.851	61.476	55.038	- 329.460	- 211.039	27.131
1800	42.386	96.260	63.342	59.253	- 328.819	- 204.091	24.780
1900	42.848	98.564	65.135	63.515	- 328.205	- 197.178	22.681
2000	43.306	100.774	66.862	67.823	- 327.619	- 190.299	20.795
2100	43.760	102.893	68.528	72.176	- 327.068	- 183.445	19.091
2200	44.210	104.944	70.137	76.575	- 337.497	- 176.570	17.541

June 30, 1973; Dec. 31, 1973

DIVANADIUM TETROXIDE (V_2O_4) (CRYSTAL) GFW = 165.8804 O_4V_2

$S^\circ_{298.15}$ = 24.74 ± 0.50 gibbs/mol
Tt = 340 ± 5 K
Tm = 1818 ± 15 K

ΔHf°_0 = -339.1 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = -341.1 ± 1.5 kcal/mol
ΔHt° = 2.15 ± 0.2 kcal/mol
ΔHm° = 26.785 ± 0.6 kcal/mol

Heat of Formation

The adopted ΔHf° values for the vanadium oxides, and in particular V_2O_4(c), are based on the combustion studies by Mah and Kelley (1). The adopted value is -341.1 kcal/mol which was obtained by rounding the reported value of Mah and Kelley (1). For more details refer to the V_2O_5(c) table (2). Charlu and Kleppa (3) reported a heat of formation value of ΔHf°_{298} = -342.4 ± 0.78 kcal/mol based on oxidation studies to V_2O_5(c) in a high temperature microcalorimeter. The combustion by this technique yielded complete oxidation to V_2O_5(c) as opposed to the method of Mah and Kelley (1), whereby ΔHf for V_2O_4(c) was determined simultaneously with that for V_2O_5(c) due to incomplete combustion of V(c). A combustion study by Siemonsen and Ulich (4) led to the reported value of -342 ± 2 kcal/mol for ΔHf°_{293}(V_2O_4, c). Additional thermodynamic data which relates V_2O_4(c) with V_2O_3(c) or V_2O_5(c) is contained in the sodium oxide fusion studies by Mixter (5), the H_2O-H_2 equilibrium study by Müller (6), the CO-CO_2 equilibrium study by Spencer and Justice (7), and the reduction of V_2O_5(c) with SO_2 by Flood and Kleppa (8). See V_2O_3(c) table for some additional information (2).

Heat Capacity and Entropy

Anderson (9) measured the heat capacity of V_2O_4 (reported purity of 99.5% or better) in the range 61.4-279.4 K. Using the combination of Debye and Einstein functions suggested by Anderson (9), we calculate S°_{60} = 1.48 gibbs/mol and $H^\circ_{60}-H^\circ_0$ = 63.66 cal/mol The data of Anderson (9) shows considerable scatter from our adopted values, with a ±2.0% deviation being typical for this data. Cook (10) measured the enthalpy of V_2O_4 in the range 315-1856 K. The enthalpy data for T < Tt appears too high to be fully consistent with Cp° data of Anderson (9). The adopted Cp° values in the region 280-340 K join smoothly with a positive power polynomial fit of the data of Anderson (4) and lead to enthalpy values at 315.5, 322.8, and 323.0 K which are roughly 48, 34, and 39 cal/mol, respectively, less than the data of Cook (10). This is a difference of 5-10%. The enthalpy data in the region Tt-Tm K are fit to a Kelley type equation and then differentiated to yield our adopted Cp° values. The data of Cook (10) also shows considerable scatter, with deviations ranging from -0.69% to +1.12%.

Three Cp° studies concentrated on the region near Tt but presented only graphical data (11, 12, 13). Kawakubo and Nakagawa (11) reported Cp° values between 30°C and 90°C which are roughly 18% higher than our adopted values below the transition and 25% higher above the transition. Ryder et al. (12) and Chandrashekhar et al. (13) measured Cp° values in the range 40-375 K and 150-730 K. These latter two works agree well graphically in their region of overlap. The Cp° values above Tt are very similar to our adopted values; at 500 K the adopted values are less than 0.1 gibbs/mol higher while at 700 K, roughly 0.75 gibbs/mol lower. Below Tt, the differences are more substantial; the adopted values lying approximately 1.5 gibbs/mol higher.

Phase Data

Minomura and Nagasaki (14) referenced earlier x-ray data and provided additional data to show that V_2O_4 undergoes a structural distortion to lower symmetry on cooling through a transition temperature of 340 K; tetragonal rutile to a monoclinic structure with the unit cell doubling in size. Recent crystallographic investigations by Kawada et al. (15) verified the doubling of the size of the unit cell and also detected considerable distortion of the shape of the unit cell. The literature review on the V-O system by Stringer (16) indicated that there are a series of oxides between V_3O_5 and V_2O_4. These oxides may be considered as members of a homologous series with V_2O_4(VO_2) being the series limit (16). Numerous references on phase data are contained in the reviews by Stringer (16), Adler (17), and Neuberger (18).

Transition Data

Minomura and Nagasaki (14) reported that the structural distortion occurs at 340 K. This value is consistent with the enthalpy data of Cook (10). Kawakubo and Nakagawa (11) measured the temperature dependence of five physical properties through the transition point and concluded that the transition occurs at 338 K. We adopt Tt = 340 ± 5 K.

Using our adopted enthalpy values for T < Tt and T >Tt, we calculate and adopt ΔHm° = 2.15 ± 0.20 kcal/mol. Ryder et al. (12) reported a value of 2.040 ± 0.010 kcal/mol and Chandrashekhar et al. (13), a value of 2.24 kcal/mol. The values of ΔHm° = 1.60 and 1.50 kcal/mol reported by Klemm and Grimm (19) and Kawakubo and Nakagawa (11), respectively, are considered too low. In our tabulation, the transition is treated as being first order. Controversy exists concerning the order of the transition, as discussed by Adler (17). Additional references may be found in Stringer (16), Adler (17), and Neuberger (18).

Melting Data: See V_2O_4(ℓ) table.

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O_4V_2

Divanadium Tetroxide (V_2O_4)

(Liquid) GFW = 165.8804

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	28.700	41.461	41.461	.000	- 318.392	- 297.409	218.007
300	28.800	41.639	41.462	.053	- 318.387	- 297.279	216.568
400	32.333	50.464	42.641	3.129	- 317.959	- 290.301	158.613
500	34.242	57.897	44.969	6.464	- 317.358	- 283.453	123.897
600	35.480	64.253	47.666	9.952	- 316.680	- 276.734	100.800
700	36.371	69.791	50.440	13.545	- 315.970	- 270.133	84.339
800	37.155	74.700	53.171	17.223	- 315.243	- 263.636	72.022
900	37.800	79.114	55.813	20.971	- 314.509	- 257.227	62.463
1000	38.404	83.128	58.346	24.781	- 313.775	- 250.902	54.835
1100	38.966	86.815	60.769	28.650	- 313.040	- 244.651	48.608
1200	51.000	90.228	63.084	32.573	- 312.311	- 238.466	43.431
1300	51.000	94.310	65.331	37.673	- 310.467	- 232.387	39.068
1400	51.000	98.090	67.537	42.773	- 308.685	- 226.448	35.350
1500	51.000	101.608	69.693	47.873	- 306.967	- 220.635	32.146
1600	51.000	104.900	71.791	52.973	- 305.311	- 214.935	29.359
1700	51.000	107.992	73.831	58.073	- 303.717	- 209.334	26.912
1800	51.000	110.907	75.810	63.173	- 302.191	- 203.826	24.748
1900	51.000	113.664	77.731	68.273	- 300.739	- 198.401	22.821
2000	51.000	116.280	79.593	73.373	- 299.361	- 193.053	21.096
2100	51.000	118.768	81.400	78.473	- 298.063	- 187.768	19.541
2200	51.000	121.141	83.153	83.573	- 307.791	- 182.497	18.129
2300	51.000	123.408	84.854	88.673	- 306.731	- 176.826	16.802
2400	51.000	125.578	86.506	93.773	- 305.683	- 171.197	15.590
2500	51.000	127.660	88.111	98.873	- 304.647	- 165.618	14.478
2600	51.000	129.661	89.671	103.973	- 303.621	- 160.076	13.456
2700	51.000	131.585	91.188	109.073	- 302.605	- 154.574	12.512
2800	51.000	133.440	92.664	114.173	- 301.599	- 149.109	11.638
2900	51.000	135.230	94.101	119.273	- 300.605	- 143.680	10.828
3000	51.000	136.959	95.501	124.373	- 299.619	- 138.285	10.074

June 30, 1973

DIVANADIUM TETROXIDE (V_2O_4) (LIQUID) GFW = 165.8804 O_4V_2

$S°_{298.15}$ = 41.461 gibbs/mol

Tm = 1818 ± 15 K

$\Delta Hf°_{298.15}$ = -318.392 kcal/mol

ΔHm° = 26.785 ± 0.6 kcal/mol

Heat of Formation

The heat of formation of $V_2O_4(\ell)$ at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H°_{1818}-H°_{298}$ for $V_2O_4(c)$ and $V_2O_4(\ell)$.

Heat Capacity and Entropy

Cook (1) measured the enthalpy of $V_2O_4(\ell)$ in the region 1829.7-1856.8 K and represented the data by the equation $H°_T-H°_{298}$ = 51.00 T-5910 cal/mol. Thus Cp° for the liquid is adopted as 51.00 gibbs/mol. Since the enthalpy measurements only cover a range of 39 K in the liquid region, the value of Cp° should not be viewed as a precise value. A glass transition is assumed at 1200 K. Below 1200 K, the Cp° values are those of the crystal with the exception that the values of Cp° between 298 and 340 K are a smooth extrapolation of the crystal values above T_t. The entropy is calculated in a manner analogous to the heat of formation.

Melting Data

The melting point of $V_2O_4(c)$ is adopted as 1818 K, based on the enthalpy data of Cook (1). The heat of melting is calculated from the difference in $H°_{1818}-H°_{298}$ for $V_2O_4(\ell)$ and $V_2O_4(c)$.

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Ditantalum Pentoxide (Ta_2O_5)

(Crystal) GFW = 441.8910

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 5.507	- 486.603	- 486.603	INFINITE
100	13.882	8.869	58.205	- 4.934	- 488.241	- 478.008	1044.685
200	25.887	22.505	36.990	- 2.897	- 489.022	- 467.395	510.745
298	32.274	34.205	34.205	.000	- 489.000	- 456.761	334.815
300	32.347	34.405	34.206	.060	- 488.995	- 456.561	332.605
400	35.257	44.140	35.513	3.451	- 488.605	- 445.804	243.576
500	37.491	52.255	38.072	7.092	- 488.038	- 435.164	190.210
600	39.300	59.257	41.033	10.935	- 487.354	- 424.652	154.679
700	40.734	65.427	44.085	14.939	- 486.587	- 414.260	129.338
800	41.873	70.943	47.104	19.071	- 485.758	- 403.988	110.364
900	42.791	75.928	50.034	23.305	- 484.877	- 393.819	95.632
1000	43.679	80.486	52.855	27.631	- 483.946	- 383.748	83.868
1100	44.174	84.672	55.559	32.024	- 482.995	- 373.776	74.262
1200	44.711	88.539	58.149	36.469	- 482.030	- 363.888	66.273
1300	45.177	92.137	60.626	40.963	- 481.056	- 354.081	59.526
1400	45.588	95.500	62.998	45.502	- 480.069	- 344.353	53.756
1500	45.956	98.658	65.272	50.080	- 479.067	- 334.692	48.765
1600	46.289	101.635	67.452	54.692	- 478.052	- 325.100	44.407
1700	46.595	104.450	69.546	59.336	- 477.026	- 315.573	40.570
1800	46.878	107.122	71.560	64.010	- 476.003	- 306.105	37.166
1900	47.143	109.663	73.499	68.711	- 474.993	- 296.694	34.128
2000	47.392	112.088	75.369	73.438	- 473.994	- 287.338	31.399
2100	47.628	114.406	77.173	78.189	- 473.008	- 278.026	28.935
2200	47.855	116.627	78.916	82.964	- 472.043	- 268.766	26.699
2300	48.072	118.759	80.602	87.760	- 471.091	- 259.548	24.663
2400	48.282	120.809	82.235	92.578	- 470.162	- 250.366	22.799
2500	48.484	122.784	83.818	97.416	- 469.260	- 241.232	21.088
2600	48.682	124.690	85.353	102.274	- 468.384	- 232.126	19.512
2700	48.874	126.531	86.845	107.152	- 467.545	- 223.056	18.055
2800	49.062	128.312	88.294	112.049	- 466.745	- 214.015	16.705

Dec. 31, 1972

DITANTALUM PENTOXIDE (Ta_2O_5) (CRYSTAL) GFW = 441.891 O_5Ta_2

$S^\circ_{298.15}$ = 34.21 ± 0.3 gibbs/mol

Tm = 2058 ± 30 K

ΔHf°_0 = -486.6 ± 1 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -489.0 ± 1 kcal/mol

ΔHm° = [28.7 ± 4.0] kcal/mol

Heat of Formation

The ΔHf°_{298} values for Ta_2O_5(c) show scatter due to uncertainties concerning the polymorphic state of the sample and/or the incomplete specification of sample purity (1). The reported values for $\Delta Hf^\circ_{298}(Ta_2O_5, c)$ based on bomb calorimetry studies are as follows:

Source	Ta(c) purity, %	% run*	$\Delta Hf^\circ_{298}(Ta_2O_5, c)$ kcal/mol
Muthmann et al. (2)			309.5
Moose and Parr (3)	99.96	>99.9	-498.3
Sieverts et al. (4)			-480.5
Becker and Roth (5)	99.9	72.92-93.83	-486.0±0.5
Neumann et al. (6)			-499.9±1.0
Humphrey (7)	99.89	97.23-99.93+	-489.0±0.5**
Huber et al. (8)	99.80		-487.7±0.9
Kornilov et al. (9)	99.16, 99.7	99.5 -99.9	-489.3±0.4
Smirnova and Ormont (10)			-480.0±0.8

* Refers to extent of reaction 2Ta(c) + 5/2 O_2(g) = Ta_2O_5(c)

** The reported value of -488.8±0.5 was corrected by Huber et al. (8) in order to have the value based on the current atomic weight of Ta.

The value chosen for $\Delta Hf^\circ_{298}(Ta_2O_5, c)$ is -489.0 ± 0.5 based primarily on the work by Humphrey (7) and Kornilov et al. (9). Worrell (17), using a high temperature galvanic cell, obtained ΔGf° values of Ta_2O_5 in the range 1050-1300 K which are approximately 0.6-1.1 kcal/mol more negative than the values tabulated here. Ignatowicz and Davies (12) using a galvanic cell approach reported ΔGf° values for Ta_2O_5 in the range 1073-1373 K. Barbi (11, 13) determined ΔGf° based on emf measurements in the range 1079-1776 K while Rezukhina and Kravchenko (16) worked in the range 1200-1350 K. A third law analysis of the reported smoothed results yields the following:

	ΔHf°_{298}, kcal/mol	drift, eu
Barbi (11)	-484.6	0.85
Ignatowicz and Davies (12)	-487.5	-0.65
Barbi (13)*	-484.7	+0.95
Rezukhina and Kravchenko (16)	-487.3	+0.83

* Actual experimental data was analyzed.

These latter three works (12, 13, 16) did not specify purity of sample or the state of polymorphism.

Based on the recent critical review by Reisman and Holtzberg (1), this discussion has been concerned with the low temperature β-phase of Ta_2O_5. Even though two ΔHf°_{298} studies (9, 10) apparently deal with the high temperature α-phase, there does not appear to be any difference in the ΔHf°_{298} values for the α-phase or β-phase, within experimental error (1).

Heat Capacity and Entropy

Kelley (14) measured the heat capacity of Ta_2O_5(c) from 53.4 K to 294.2 K and fitted the data (29 data points) with a combination of Debye and Einstein functions. These functions were used to calculate S°_{50} = 2.47 gibbs/mol. Orr (15) measured the enthalpy of Ta_2O_5(c) from 395.6 K to 1802.6 K (15 data points). Nine data points at the high temperature end of the Kelley data were fitted by a four term polynomial, and integrated to yield enthalpy values in the vicinity of 298.15 K. These enthalpy values were combined with the Orr data, fitted to a six term polynomial, and extrapolated to 2800 K. The complete Kelley data was also fitted by a six term polynomial. The Nb_2O_5 heat capacity and enthalpy data presented in these tables are treated in the same manner so as to maintain consistency between the results for Nb_2O_5 and Ta_2O_5.

The Ta_2O_5(c) sample used by Kelley (14) and Orr (15) was the same. Presumably both were using the low temperature β-phase of Ta_2O_5, as discussed by Reisman and Holtzberg (1) and Orr (15). The enthalpy data of Orr (15) did not conclusively indicate any phase transitions, i.e. the β → α transition, in the vicinity of 1633 K, as reported by Reisman and Holtzberg (1).

Melting Data

See Ta_2O_5(ℓ) table for details.

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O_5Ta_2

Ditantalum Pentoxide (Ta_2O_5)

(Liquid) GFW = 441.8910

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	32.274	43.750	43.750	.000	- 467.775	- 438.382	321.343
300	32.347	43.950	43.751	.060	- 467.770	- 438.200	319.228
400	35.257	53.685	45.058	3.451	- 467.381	- 428.397	234.065
500	37.491	61.800	47.617	7.092	- 466.813	- 418.712	183.019
600	39.300	68.802	50.578	10.935	- 466.130	- 409.154	149.034
700	40.734	74.972	53.630	14.939	- 465.362	- 399.717	124.797
800	41.873	80.488	56.649	19.071	- 464.533	- 390.399	106.652
900	42.791	85.473	59.579	23.305	- 463.652	- 381.184	92.564
1000	43.679	90.031	62.400	27.631	- 462.721	- 372.068	81.315
1100	44.174	94.217	65.104	32.024	- 461.770	- 363.051	72.131
1200	44.711	98.084	67.694	36.469	- 460.806	- 354.117	64.493
1300	45.177	101.682	70.171	40.963	- 459.831	- 345.265	58.044
1400	58.000	105.045	72.543	45.502	- 458.844	- 336.491	52.529
1500	58.000	109.047	74.845	51.302	- 456.620	- 327.828	47.764
1600	58.000	112.790	77.101	57.102	- 454.416	- 319.313	43.616
1700	58.000	116.306	79.305	62.902	- 452.235	- 310.937	39.974
1800	58.000	119.621	81.453	68.702	- 450.086	- 302.687	36.751
1900	58.000	122.757	83.546	74.502	- 447.977	- 294.556	33.882
2000	58.000	125.732	85.581	80.302	- 445.905	- 286.538	31.311
2100	58.000	128.562	87.561	86.102	- 443.870	- 278.616	28.996
2200	58.000	131.260	89.486	91.902	- 441.880	- 270.796	26.901
2300	58.000	133.838	91.359	97.702	- 439.924	- 263.064	24.997
2400	58.000	136.307	93.181	103.502	- 438.013	- 255.411	23.258
2500	58.000	138.675	94.954	109.302	- 436.149	- 247.847	21.667
2600	58.000	140.949	96.679	115.102	- 434.331	- 240.348	20.203
2700	58.000	143.138	98.360	120.902	- 432.570	- 232.921	18.854
2800	58.000	145.248	99.997	126.702	- 430.867	- 225.558	17.606
2900	58.000	147.283	101.592	132.502	- 429.231	- 218.251	16.448
3000	58.000	149.249	103.148	138.302	- 427.670	- 211.003	15.372
3100	58.000	151.151	104.666	144.102	- 426.190	- 203.805	14.368
3200	58.000	152.992	106.148	149.902	- 424.803	- 196.656	13.431
3300	58.000	154.777	107.595	155.702	- 440.964	- 189.416	12.544
3400	58.000	156.509	109.008	161.502	- 439.592	- 181.813	11.687
3500	58.000	158.190	110.389	167.302	- 438.227	- 174.254	10.881
3600	58.000	159.824	111.740	173.102	- 436.872	- 166.727	10.122
3700	58.000	161.413	113.061	178.902	- 435.527	- 159.242	9.406
3800	58.000	162.960	114.354	184.702	- 434.189	- 151.789	8.730
3900	58.000	164.466	115.620	190.502	- 432.859	- 144.381	8.091
4000	58.000	165.935	116.859	196.302	- 431.539	- 137.003	7.485
4100	58.000	167.367	118.074	202.102	- 430.227	- 129.652	6.911
4200	58.000	168.765	119.264	207.902	- 428.919	- 122.340	6.366
4300	58.000	170.129	120.431	213.702	- 427.619	- 115.049	5.847
4400	58.000	171.463	121.576	219.502	- 426.327	- 107.801	5.355
4500	58.000	172.766	122.699	225.302	- 425.039	- 100.574	4.885
4600	58.000	174.041	123.801	231.102	- 423.757	- 93.371	4.436
4700	58.000	175.288	124.884	236.902	- 422.482	- 86.204	4.008
4800	58.000	176.509	125.946	242.702	- 421.209	- 79.061	3.600
4900	58.000	177.705	126.991	248.502	- 419.942	- 71.957	3.209
5000	58.000	178.877	128.017	254.302	- 418.679	- 64.868	2.835

Dec. 31, 1972

DITANTALUM PENTOXIDE (Ta_2O_5) (LIQUID) GFW = 441.891 O_5Ta_2

$S^\circ_{298.15}$ = 43.750 gibbs/mol

$\Delta Hf^\circ_{298.15}$ = -467.775 kcal/mol

Tm = 2058 ± 30 K

ΔHm° = [28.7 ± 4] kcal/mol

Heat of Formation

The heat of formation of $Ta_2O_5(\ell)$ at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{2058} - H^\circ_{298}$ for $Ta_2O_5(c)$ and $Ta_2O_5(\ell)$.

Heat Capacity and Entropy

The heat capacity for $Ta_2O_5(\ell)$ is estimated to be 58.00 gibbs/mol by analogy with $Nb_2O_5(\ell)$. A glass transition temperature is assumed at 1400 K. The heat capacity values used below 1400 K are those of $Ta_2O_5(c)$. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the heat of formation.

Melting Data

The melting point of β-Ta_2O_5 is chosen as 2058 ± 30 K based on work by Reisman et al. (1). The melting point data and the Ta_2O_5 polymorphism are discussed by Reisman and Holtzberg (2). The heat of fusion, ΔHm°, is estimated from the entropy of fusion for Nb_2O_5 as reported in these tables. Using the Nb_2O_5 entropy of fusion value of 24.92 eu and a melting temperature of 2058 K, the heat of fusion for Ta_2O_5 is calculated to be 28.7 ± 4 kcal/mol.

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Trititanium Pentoxide, Alpha (α-Ti_3O_5) O_5Ti_3

(Crystal) GFW = 223.6970

T, °K	gibbs/mol $Cp°$	$S°$	$-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	$\Delta Hf°$	$\Delta Gf°$	Log Kp
0	.000	.000	INFINITE	- 5.523	- 584.629	- 584.629	INFINITE
100	11.022	5.034	56.684	- 5.165	- 586.408	- 575.972	1258.786
200	27.353	18.083	34.023	- 3.188	- 587.545	- 565.012	617.416
298	37.000	30.920	30.920	.000	- 587.750	- 553.891	406.013
300	37.160	31.149	30.921	.069	- 587.747	- 553.681	403.356
400	43.700	42.837	32.469	4.147	- 587.300	- 542.377	296.341
500	46.400	52.925	35.579	8.673	- 586.540	- 531.233	232.202
600	48.000	61.531	39.205	13.396	- 585.702	- 520.250	189.501
700	49.250	69.028	42.942	18.261	- 584.840	- 509.410	159.045
800	50.200	75.668	46.625	23.234	- 583.992	- 498.694	136.237
900	51.000	81.629	50.189	28.296	- 583.173	- 488.079	118.522
1000	51.600	87.034	53.608	33.426	- 582.402	- 477.555	104.370
1100	52.200	91.981	56.874	38.617	- 581.676	- 467.103	92.805
1200	52.700	96.544	59.992	43.862	- 583.807	- 456.605	83.159
1300	53.200	100.783	62.969	49.158	- 582.796	- 446.048	74.987
1400	53.600	104.740	65.813	54.498	- 581.803	- 435.568	67.995
1500	54.000	108.452	68.533	59.878	- 580.835	- 425.156	61.945

Dec. 31, 1960; Mar. 31, 1967; Dec. 31, 1973.

TRITITANIUM PENTOXIDE, ALPHA (α-Ti_3O_5) (CRYSTAL) GFW = 223.697 O_5Ti_3

$\Delta Hf°_0$ = -584.6 ± 1.0 kcal/mol

$S°_{298.15}$ = 30.92 ± 0.4 gibbs/mol

$\Delta Hf°_{298.15}$ = -587.75 ± 1.0 kcal/mol

Tt = 450 ± 20 K ($\alpha \rightarrow \beta$)

$\Delta Ht°$ = [3.17 ± 1.2] kcal/mol

Heat of Formation

$\Delta Hf°_{298}$ = -587.75 kcal/mol is calculated from that of TiO_2(rutile) using $\Delta Hc°$ = -89.65 ± 0.05 kcal/mol determined by Humphrey (1) from combustion calorimetry. Ariya et al. (2) reported $\Delta Hf°$ = -587.0 ± 1.0 kcal/mol derived from their own values of $\Delta Hc°$ for $Ti_3O_{5.03}$ and Ti(c). Tests for incomplete combustion were made by grinding the product and igniting it to constant weight in air (1) or in moist oxygen (2). Humphrey (1) reported that his rutile was bright yellow in color and did not gain weight. This implies an atomic ratio (O/Ti) $\geq$ 2.00, compared with the value of ~1.95 reported by Ariya et al. (2). New high-temperature calorimetry by Charlu et al. (9) gave $\Delta Hc°_{1100}$ = -93.57 ± 1.3 kcal/mol after linear correction to (O/Ti) = 2.00 from 1.97 produced by combustion. Our reduction to 298 K and $Ti_3O_5(\alpha)$ yields $\Delta Hc°$ = -90.36 ± 2.5 kcal/mol, including an assumed uncertainty allowance of 1% for the weight gains.

The calorimetric data are compared below with new high-temperature data for $\Delta Gr°$ (3, 4). Emf data (4) for reaction B are consistent with the adopted $\Delta Hf°$, but integrated values of $\Delta Gr°$ for reaction A yield $\Delta Hf°$ more negative by 1.8 kcal/mol. Perhaps coincidentally, the $\Delta Hc°$ of Ariya et al. (2) yields $\Delta Hf°$ more negative by 1.9 kcal/mol when combined with the JANAF $\Delta Hf°$ (5) for TiO_2(rutile). Merritt et al. (3) obtained $\Delta Gr°$ for the combustion reaction A by integrating extensive data for equilibrium oxygen potentials of the many stable phases and solid solutions between TiO_2 and Ti_3O_5. They determined the oxide composition by mass during equilibration with ($H_2 + H_2O$) gas mixtures of known oxygen potential. Gross hysteresis was observed in three regions of composition. Oxygen potentials in these regions were deduced with a reasonable assumption, combined with Zador's emf data for oxygen-deficient rutile, and integrated to yield $\Delta Gr°$(1304 K) = -56.14 ± 0.43 kcal/mol for reaction A. We obtain $\Delta Gr°$ = -57.30 kcal/mol at 1273 K and -51.15 at 1473 K by similar integrations of oxygen potentials derived from emf data relative to Fe/FeO and Cr/Cr_2O_3 reported by Suzuki and Sambongi (4).

Suzuki and Sambongi (4) also reported solid-state emf data which relate Ti_3O_5 to Ti_2O_3. We convert their (graphical) emf data (4) to oxygen potentials using the authors' self-consistent data for the reference couples. The results for reaction B yield $\Delta Hr°$ and $\Delta Sr°$ values consistent with our adopted tables. Third-law values of $\Delta Hr°_{298}$ of -42.29, -42.15 and -42.13 kcal/mol agree with -42.52 (1), -42.8 ± 1.3 (2) and -42.0 (9) which can be calculated from combustion calorimetry.

The discrepancy in reaction A may be due to undetected bias (2% too small in magnitude) in $\Delta Gr°$, but alternative possibilities include bias in S° (see Ti_3O_5, β), $\Delta Hc°$ or enthalpy (see TiO_2, rutile).

Source	Method	Reaction[a]	Range T/K	δS[b] gibbs/mol	$\Delta Hr°_{298}$ kcal/mol	$\Delta Hf°_{298}$, kcal/mol Authors	JANAF
(1) Humphrey (1951)	$\Delta Hc°$	A	303→298	-	-89.65±0.05	-586.9±0.7	-587.75±0.9
(2) Ariya et al. (1957)	$\Delta Hc°$	A	293	-	-87.7	-587.0±1.0	-589.7
(9) Charlu et al. (1974)	$\Delta Hc°$	A	1100→298	-	-90.36±2.5	-586.3	-587.0±2.7
(3) Merritt et al. (1973)	$\Delta\bar{G}(O_2)$	A	1304	-	-87.81±0.6[c]	-	-589.6±1.1
(4) Suzuki et al. (1972)	$\Delta\bar{G}(O_2)$, Emf	A	1273-1473	-3.5	-87.81±1[c]	-	-589.6±1.4
(4) Suzuki et al. (1972)	Emf, Cr/Cr_2O_3	B[d]	~ 940-1740	0.6	-42.29[c]	-	-587.5[d]
	Emf, Ta/Ta_2O_5	B[d]	~1100-1750	0.0	-42.15[c]	-	-587.4[d]
	Emf, "$TiO_{1.3}$"	B[d]	~1300-1700	0.0	-42.13[c]	-	-587.4[d]

[a] Reactions: A = $Ti_3O_5(\alpha, \beta) + 1/2\ O_2 \rightarrow 3\ TiO_2$(rutile); B = $3/2\ Ti_2O_3(\alpha, \beta) + 1/4\ O_2 \rightarrow Ti_3O_5(\alpha, \beta)$.

[b] $\delta S = \Delta Sr°$(2nd Law) - $\Delta Sr°$(3rd Law). [c] Third-law $\Delta Hr°$ reduced to $Ti_3O_5(\alpha)$.

[d] $\Delta Gr°$ from integration of $\Delta\bar{G}(O_2)$ assuming negligible homogeneity range for Ti_2O_3. Alternative $\Delta Gr°$, assuming a linear variation of $\Delta\bar{G}(O_2)$ for $1.42 < x < 1.56$, changes δS by ~0.2 and $\Delta Hr°$ and $\Delta Hf°$ by ~-0.3.

Heat Capacity and Entropy

Cp° below 300 K is based on data of Shomate (6, 53-297 K) and his Debye-Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of Cp° based on S°(50 K) = 0.87 gibbs/mol. Our assigned entropy uncertainty of ±0.4 gibbs/mol includes an additional contribution because the sample gave weak, fuzzy x-ray lines and was only 99.1% pure. Apparently there are new Cp° data (12-300 K) which are unpublished and not yet available (10). Cp° is extrapolated smoothly from 300 K to 450 K and to higher temperatures where $Ti_3O_5(\beta)$ is the stable form. Our extrapolation probably represents the lower limit for the true Cp° below Tt, while the curve of Furukawa and Reilly (7) is an upper limit. The equations reported by Naylor (8) yield even higher enthalpies and fail to join properly with the low-temperature data at 298 K. This is due to complications in the enthalpy data (see below) and to positive bias in the drop calorimeter in this temperature range (5).

Naylor (8) measured enthalpy data (326-1340 K) which revealed a transition at ~450 K. When the samples were heated above this temperature, they did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10%. The change in the enthalpy curve seemed to depend on both the temperature and time of heating above Tt. Regrinding was the only method found for returning the sample to its original state. X-ray diffraction at room temperature revealed no difference between these two states, but failure to detect a difference may be due to the weak, fuzzy x-ray lines (6, 8). Possible explanations for the anomalous enthalpy data are noted in Transition Data.

Transition Data

See $Ti_3O_5(\beta)$.

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O_5Ti_3

Trititanium Pentoxide, Beta (β-Ti_3O_5)

O_5Ti_3

(Crystal) GFW = 223.6970

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	41.573	37.672	37.671	.000	−584.653	−552.807	405.218
300	41.600	37.929	37.672	.077	−584.642	−552.609	402.575
400	42.500	50.091	39.318	4.297	−584.053	−542.020	296.146
500	44.000	59.740	42.406	8.637	−583.477	−531.579	232.353
600	45.200	67.566	46.040	13.097	−582.904	−521.254	189.867
700	46.400	74.920	49.573	17.677	−582.327	−511.025	159.549
800	47.600	81.200	53.229	22.377	−581.752	−500.880	136.834
900	48.800	86.876	56.657	27.197	−581.175	−490.804	119.183
1000	50.000	92.080	59.943	32.137	−580.595	−480.795	105.077
1100	51.200	96.902	63.086	37.197	−579.999	−470.840	93.547
1200	52.400	101.408	66.094	42.377	−582.195	−460.830	83.929
1300	53.600	105.550	68.975	47.677	−581.160	−450.759	75.779
1400	54.800	109.566	71.739	53.097	−580.107	−440.768	68.807
1500	56.000	113.487	74.396	58.637	−578.979	−430.853	62.775
1600	57.200	117.140	76.954	64.297	−577.801	−421.013	57.508
1700	58.400	120.644	79.422	70.077	−576.575	−411.253	52.870
1800	59.600	124.016	81.806	75.977	−575.312	−401.566	48.757
1900	60.800	127.270	84.114	81.997	−574.011	−391.948	45.084
2000	62.000	130.419	86.351	88.137	−586.015	−381.941	41.737
2100	63.200	133.473	88.522	94.397	−584.507	−371.769	38.690
2200	64.400	136.441	90.633	100.777	−583.017	−361.675	35.929
2300	65.600	139.330	92.688	107.277	−581.357	−351.651	33.414
2400	66.800	142.148	94.690	113.897	−579.592	−341.696	31.116
2500	68.000	144.899	96.644	120.637	−577.722	−331.827	29.008

Mar. 31, 1967; Dec. 31, 1973.

TRITITANIUM PENTOXIDE, BETA (β-Ti_3O_5) (CRYSTAL) GFW = 223.697 O_5Ti_3

$S^\circ_{298.15}$ = [37.672] gibbs/mol

Tt = 450 ± 20 K (α→β)

Tm = 2050 ± 20 K

$\Delta Hf^\circ_{298.15}$ = [−584.653] kcal/mol

ΔHt° = [3.17 ± 1.2] kcal/mol

ΔHm° = [41] kcal/mol

Heat of Formation

ΔHf° is calculated from that of $Ti_3O_5(\alpha)$ by adding ΔHt° to the difference in $(H^\circ_{450}-H^\circ_{298})$ between the α- and β-phases. Experimental data for ΔGr° of the β-phase are analyzed on the table for the α-phase.

Heat Capacity and Entropy

Cp° of the β-phase is derived from fitting of enthalpy data of Naylor (1, 504-1340 K) and Slyusar et al. (2, 580-1994 K). Naylor's data below 482 K are omitted due to thermal hysteresis in the transition; even the points near 500 K show unusual scatter. The new data of Slyusar et al. (2) are suspect due to a discontinuity of almost 4% at ~1250 K where the authors switched container materials and temperature sensors. Their data (2) for Ti_2O_3 and TiO_2(rutile) show similar discontinuities and appear to have a bias of about −4% below 1100 K. Their data for Ti_3O_5 do not differ significantly from those of Naylor (1), so we combine the two sets.

S° is calculated in a manner analogous to that of ΔHf°. The uncertainty in S° may be as large as ±2.6 gibbs/mol due to uncertainty in ΔHt°, if significant fractions of the β-phase failed to revert to the α-phase during drop calorimetry (1, 2). Naylor's data (1) suggest that this may be the case, but Slyusar et al. (2) make no mention of the problem (see Transition Data). Excluding this possible uncertainty, we estimate that S° of $Ti_3O_5(\beta)$ is uncertain by ±0.6 gibbs/mol.

Transition Data and Phase Data

Ti_3O_5 has been identified in three crystalline structures. Low-temperature α-Ti_3O_5 is monoclinic (3), high-temperature β-Ti_3O_5 is a pseudobrookite type with slight monoclinic distortion (3), and metastable γ-Ti_3O_5 (4) is analogous to V_3O_5 (3, 4). Based on its similarity to V_3O_5, γ is the lowest member of the homologous series of phases Ti_nO_{2n-1} with structures related to rutile (9, 10). The magnetic anomaly, observed near 250 K in γ-Ti_3O_5 (4), corresponds to those observed at lower temperatures in Ti_4O_7 and higher homologues. We give the subsequent phase observations because they may have bearing on the anomalous enthalpy data and the discrepancy in ΔGf° at high temperatures.

Our designations for the stable phases α and β are reversed from those of Asbrink et al. (4). These phases were called M-type (our α), D-type and D'-type (our β) by Iwasaki et al. (11). D- and D'-types differed only in their low-temperature oxidation products; D-type gave rutile, while D'-type gave mixtures of anatase and rutile (11). D-type was obtained by H_2-reduction of anatase and D'-type by action of H_2 on rutile and Ti or CO on either anatase or rutile. D-type presumably is metastable; Iwasaki et al. (11) postulated free energy diagrams to explain conversion of D-type to other forms. The observations also can be explained by assuming that conversion of D-type is hindered kinetically, like TiO_2(anatase)→TiO_2(rutile), until gradually activated at elevated temperature. X-ray patterns of D-type, though not well defined, were similar to those of D'-type (11). Thus, D-type is not the Ti_nO_{2n-1} homologue (γ-Ti_3O_5), as postulated (11) on the basis of oxidation behavior. D- and D'-types may have the same crystal structure but differ in degree of ordering or content of impurities.

Enthalpy data of Naylor (1) gave Tt ~450 K for α→β. X-ray diffraction (4-6), DTA (5), magnetic susceptibility (4, 6), and electrical conductivity (5) confirm the transition temperature. The transition is reversible (3, 5-7) but exhibits thermal hysteresis of about ±20° (5, 6). More important to interpretation of enthalpy measurements is the observation that the β-phase is stabilized (5, 3) at room temperature by small amounts of impurities such as Fe, W and Mg. Samples doped with 5% Fe did not transform; those with 2% Fe gave a much-reduced endotherm (DTA) at ~75° below the normal Tt (5). Accidental contamination by W stabilized the β-form (5).

ΔHt° = 3.17 kcal/mol is calculated at Tt from the difference in enthalpy between our β-phase curve fit and our adopted α-phase. Alternative enthalpy curves (8) gave ΔHt° = 2.48 kcal/mol. These calculations assume that the β-phase reverted completely to α-phase at room temperature during drop calorimetry (1, 2). Naylor's anomalous enthalpies (1) for the α-phase suggest that part of his sample may have been stabilized in the β-form due to impurities. Other metastable phases may have been present. If the drop-calorimetric samples did not revert completely to α-phase, the true value of ΔHt° should be larger than the value calculated on the assumption of complete reversion. ΔGr° data (see Ti_3O_5, α) tend to favor an entropy greater than or equal to the adopted value, but DTA data (5) gave ΔHt° = 1.6 ± 0.4 kcal/mol, opposite to the expected direction. We emphasize this unsatisfactory situation by placing ΔHt° in brackets and assigning an uncertainty of ±1.2 kcal/mol. The seeming contradictions should be resolved easily by study of a well-characterized sample in an adiabatic calorimeter or an accurate differential-scanning calorimeter.

Melting Data and Sublimation Data

See Ti_3O_5(ℓ).

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O_5Ti_3

Trititanium Pentoxide (Ti_3O_5)

(Liquid) GFW = 223.6970

O_5Ti_3

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	41.578	55.556	55.556	.000	- 547.098	- 520.584	381.598
300	41.600	55.813	55.557	.077	- 547.087	- 520.420	379.125
400	42.800	67.945	57.203	4.297	- 546.498	- 511.618	279.535
500	44.000	77.624	60.351	8.637	- 545.924	- 502.966	219.846
600	45.200	85.753	63.924	13.097	- 545.349	- 494.430	180.096
700	46.400	92.810	67.558	17.677	- 544.772	- 485.989	151.733
800	47.600	99.085	71.113	22.377	- 544.197	- 477.633	130.483
900	48.800	104.760	74.542	27.197	- 543.620	- 469.344	113.972
1000	50.000	109.964	77.827	32.137	- 543.040	- 461.123	100.778
1100	51.200	114.786	80.970	37.197	- 542.444	- 452.957	89.994
1200	52.400	119.292	83.978	42.377	- 544.640	- 444.736	80.998
1300	53.600	123.534	86.859	47.677	- 543.625	- 436.453	73.374
1400	54.800	127.550	89.624	53.097	- 542.552	- 428.251	66.853
1500	64.000	131.966	92.301	59.497	- 540.564	- 420.156	61.217
1600	64.000	136.096	94.910	65.897	- 538.646	- 412.188	56.302
1700	64.000	139.976	97.448	72.297	- 536.800	- 404.343	51.982
1800	64.000	143.634	99.914	78.697	- 535.037	- 396.604	48.154
1900	64.000	147.094	102.307	85.097	- 533.356	- 388.959	44.741
2000	64.000	150.377	104.629	91.497	- 545.100	- 380.942	41.627
2100	64.000	153.500	106.882	97.897	- 543.512	- 372.769	38.795
2200	64.000	156.477	109.069	104.297	- 541.942	- 364.679	36.228
2300	64.000	159.322	111.193	110.697	- 540.382	- 356.657	33.890
2400	64.000	162.046	113.255	117.097	- 538.837	- 348.697	31.753
2500	64.000	164.658	115.260	123.497	- 537.307	- 340.811	29.794
2600	64.000	167.169	117.208	129.897	- 535.787	- 332.981	27.990
2700	64.000	169.584	119.104	136.297	- 534.282	- 325.207	26.324
2800	64.000	171.911	120.948	142.697	- 532.790	- 317.492	24.781
2900	64.000	174.157	122.744	149.097	- 531.310	- 309.820	23.349
3000	64.000	176.327	124.495	155.497	- 529.842	- 302.210	22.016
3100	64.000	178.426	126.201	161.897	- 528.385	- 294.642	20.772
3200	64.000	180.457	127.865	168.297	- 526.940	- 287.136	19.610
3300	64.000	182.427	129.488	174.697	- 525.505	- 279.662	18.521
3400	64.000	184.337	131.074	181.097	- 524.082	- 272.230	17.499
3500	64.000	186.193	132.622	187.497	- 522.667	- 264.851	16.538
3600	64.000	187.996	134.135	193.897	- 826.140	- 256.710	15.584
3700	64.000	189.749	135.615	200.297	- 824.661	- 240.916	14.230
3800	64.000	191.456	137.062	206.697	- 823.229	- 225.163	12.950
3900	64.000	193.118	138.478	213.097	- 821.843	- 209.440	11.737
4000	64.000	194.739	139.864	219.497	- 820.506	- 193.756	10.586

Mar. 31, 1967; Dec. 31, 1973.

TRITITANIUM PENTOXIDE (Ti_3O_5) (LIQUID) GFW = 223.697 O_5Ti_3

$S^\circ_{298.15}$ = [55.556] gibbs/mol

Tm = 2050 ± 20 K

$\Delta Hf^\circ_{298.15}$ = [-547.098] kcal/mol

ΔHm° = [41] kcal/mol

Heat of Formation

ΔHf° is calculated from that of $Ti_3O_5(\beta)$ by adding ΔHm° to the difference in $(H^\circ_{2050}-H^\circ_{298})$ between the β-phase and liquid.

Heat Capacity and Entropy

Cp° is estimated as 8 gibbs/g-atom. Below the assumed glass transition at 1400 K, Cp° is taken to be the same as that of $Ti_3O_5(\beta)$. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

$Ti_3O_5(\beta)$ melts incongruently at 2047 ± 10 K according to Wahlbeck and Gilles (1). Their phase diagram (1) suggests that melting starts at 2047 K and completes near 2077 K. The latter value is close to the melting point of 2083 K reported by Slyusar et al. (2), but is almost 90° above the value of ∿1990 K which may be interpolated from the liquidus curve of Brauer and Littke (3) for the Ti-O system. Conversion of the value of Wahlbeck and Gilles (1) to IPTS-68 yields 2050 K, which is adopted.

Sublimation and Vaporization Data

$Ti_3O_5(\beta)$ is the congruently vaporizing crystalline phase in the Ti-O system according to the studies of Gilles and coworkers (4-6). Studies of liquid samples (7) showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal reaction (4) in congruent vaporization is $Ti_3O_5 \rightarrow TiO(g) + 2\ TiO_2(g)$.

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O_5Ti_3

Divanadium Pentoxide (V_2O_5)

(Crystal) GFW = 181.8798

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	− 5.140	− 368.334	− 368.334	INFINITE
100	12.583	7.544	56.924	− 4.938	− 370.101	− 360.164	787.137
200	24.169	20.125	33.855	− 2.746	− 370.527	− 349.574	381.996
298	31,214	31.202	31.202	.000	− 370.600	− 339.255	248.679
300	31.316	31.395	31.203	.058	− 370.597	− 339.059	247.004
400	36.078	41.106	32.494	3.445	− 370.213	− 328.594	179.535
500	38.660	49.462	35.073	7.194	− 369.563	− 318.261	139.112
600	40.228	56.655	38.085	11.142	− 368.803	− 308.069	112.214
700	41.404	62.947	41.197	15.225	− 367.993	− 298.011	93.043
800	42.364	68.540	44.272	19.415	− 367.152	− 288.075	78.696
900	43.200	73.580	47.253	23.694	− 366.294	− 278.237	67.565
1000	43.900	78.167	50.118	28.049	− 365.428	− 268.499	58.680
1100	44.600	82.384	52.862	32.474	− 364.557	− 258.850	51.429
1200	45.300	86.295	55.487	36.969	− 363.680	− 249.278	45.400
1300	46.000	89.949	57.999	41.534	− 362.799	− 239.780	40.311
1400	46.700	93.383	60.405	46.169	− 361.914	− 230.351	35.959
1500	47.400	96.629	62.713	50.874	− 361.027	− 220.984	32.197

June 30, 1973

DIVANADIUM PENTOXIDE (V_2O_5) (CRYSTAL) GFW = 181.8798 O_5V_2

$S^\circ_{298.15}$ = 31.2 ± 0.5 gibbs/mol
Tm = 943 ± 10 K

ΔHf°_0 = −368.3 ± 1.5 kcal/mol
$\Delta Hf^\circ_{298.15}$ = −370.6 ± 1.5 kcal/mol
ΔHm° = 15.42 ± 0.75 kcal/mol

Heat of Formation

A review (1) of early experimental studies led to a value of −373 kcal/mol for $\Delta Hf^\circ_{298.15}$(V_2O_5, c). More recent combustion studies on V(c) have led to the following $\Delta Hf^\circ_{298.15}$ values for V_2O_5(c).

Source	Year	$\Delta Hf^\circ_{298.15}$(V_2O_5, c), kcal/mol
Vol'f and Ariya (2)	1959	−376 ± 2
Golutvin and Kozlovskaya (3)	1960	−370 ± 1
Mah and Kelley (4)	1961	−370.6 ± 0.5
Volkova and Gel'd (5)	1963	−371.9 ± 1.0

We adopt −370.6 ± 1.5 kcal/mol as the heat of formation of V_2O_5(c) at 298.15 K. This value is the Mah and Kelley result (4) but it is also in good agreement with the results of Golutvin and Kozlovskaya (3) and Volkova and Gel'd (5). The same value was recently adopted by NBS (6).

The combustion of vanadium and its oxides, as reported by Mah and Kelley (4), led to two problems: (1) the oxide products liquefy before the pentoxide composition is obtained and (2) the oxide products are corrosive and cause a container problem. The combustion of vanadium led to varying mixtures of V_2O_4(rutile) and V_2O_5. This was verified by x-ray diffraction. The heat of formation values for V_2O_4 and V_2O_5 were derived from the same set of experiments (4).

Heat Capacity and Entropy

Using a V_2O_5 sample with a reported purity of 99.5% or better, Anderson (7) measured the heat capacity in the range 56.8-289.5 K. Using the combination of Debye and Einstein functions suggested by Anderson (7), we calculate S°_{60} = 2.81 gibbs/mol and $H^\circ_{60}-H^\circ_0$ = 130.59 cal/mol. Cook (8) measured the enthalpy of V_2O_5 in the range 372-1513 K. The enthalpy data are fit to a Kelley type equation with the constraint that the data join smoothly with a portion of the integrated data of Anderson (7). The enthalpy data appear to lie too high in comparison with the integrated data of Anderson (7). A better fit is obtained by neglecting the 289.5 K data point of Anderson. The Anderson data show considerable scatter and deviate from our adopted Cp° values by ±4% below 65 K and ±1.8% between 65 and 280 K. The 289.5 K data point is 2.7% lower than the adopted value. The Cook data deviates from the adopted enthalpy values by roughly 8% (200 cal/mol) at 372.6 K with the difference decreasing to 2 cal/mol at 754.4 K. In the range 771.1-921.1 K the enthalpy difference ranges from −121 to +139 cal/mol.

Melting Data

The melting point of V_2O_5 is adopted as Tm = 943 ± 10 K as derived from the enthalpy studies of Cook (8). The heat of melting is calculated to be ΔHm° = 15.42 ± 0.75 kcal/mol based on our analyses of Cook's enthalpy data. Refer to the heat capacity discussion for V_2O_5(c) and V_2O_5(ℓ) for details. By way of comparison, Kohlmüller and Leitner (9) reported Tm = 937.9 K and ΔHm° = 14.5 kcal/mol while Pantony and Vasu (10) reported Tm = 951.12 K and ΔHm° = 13.8 kcal/mol. The latter two studies (9, 10) involved cryoscopic techniques. Murphy and West (11) reported Tm = 943 K based on DTA measurements and Holtzberg et al. (12) determined Tm = 947 ± 5 K in their study of the phases in the K_2O-V_2O_5 system.

The variance in the reported Tm values is probably attributable to the presence of V_2O_4(c). Refer to the discussion in the section on Sublimation Data in the V_2O_5(c) table and Decomposition Data in the V_2O_5(ℓ) table.

Sublimation Data

Using a combination of Knudsen effusion and mass spectrometric techniques, Berkowitz et al. (13) concluded that V_2O_5(c) did not "vaporize" invariantly. The temperature range investigated was not reported. Their conclusion was based on two observations: (1) some reduced vanadium oxide species were present in the gas phase, and (2) oxygen was also found to be effusing from the Knudsen cell. Chizhikov et al. (14) studied the dissociation of V_2O_5 at temperatures below Tm using mass spectrometry. They assumed reduced vanadium oxides, in addition to V_4O_{10}, were present in the vapor upon dissociation of V_2O_5(c) in vacuum. We conclude that there is no invariant sublimation process for V_2O_5(c) and thus we do not calculate a ΔHs°_{298} value. For related discussion refer to V_2O_5(ℓ) table.

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O_5V_2

Divanadium Pentoxide (V_2O_5)

(Liquid) GFW = 181.8798

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	31.214	45.879	45.879	.000	− 356.407	− 329.436	241.483
300	31.316	46.072	45.879	.058	− 356.404	− 329.269	239.872
400	36.078	55.783	47.171	3.445	− 356.020	− 320.272	174.989
500	38.660	64.138	49.750	7.194	− 355.371	− 311.406	136.116
600	45.600	71.338	52.762	11.145	− 354.607	− 302.683	110.252
700	45.600	78.367	55.931	15.705	− 353.320	− 294.133	91.832
800	45.600	84.456	59.124	20.265	− 352.109	− 285.763	78.067
900	45.600	89.827	62.243	24.825	− 350.970	− 277.537	67.395
1000	45.600	94.631	65.246	29.385	− 349.900	− 269.435	58.885
1100	45.600	98.978	68.118	33.945	− 348.893	− 261.439	51.943
1200	45.600	102.945	70.858	38.505	− 347.951	− 253.530	46.174
1300	45.600	106.595	73.468	43.065	− 347.076	− 245.697	41.305
1400	45.600	109.975	75.956	47.625	− 346.266	− 237.930	37.142
1500	45.600	113.121	78.330	52.185	− 345.523	− 230.218	33.543
1600	45.600	116.064	80.598	56.745	− 344.846	− 222.554	30.400
1700	45.600	118.828	82.766	61.305	− 344.233	− 214.929	27.631
1800	45.600	121.435	84.843	65.865	− 343.691	− 207.338	25.174
1900	45.600	123.900	86.834	70.425	− 343.227	− 199.776	22.979
2000	45.600	126.239	88.746	74.985	− 342.839	− 192.239	21.007
2100	45.600	128.464	90.585	79.545	− 342.533	− 184.715	19.223
2200	45.600	130.585	92.355	84.105	− 353.257	− 177.157	17.599
2300	45.600	132.612	94.062	88.665	− 353.195	− 169.155	16.073
2400	45.600	134.553	95.709	93.225	− 353.148	− 161.150	14.675
2500	45.600	136.414	97.300	97.785	− 353.116	− 153.155	13.389
2600	45.600	138.203	98.839	102.345	− 353.096	− 145.155	12.201
2700	45.600	139.924	100.329	106.905	− 353.089	− 137.157	11.102
2800	45.600	141.582	101.773	111.465	− 353.095	− 129.158	10.081
2900	45.600	143.182	103.174	116.025	− 353.115	− 121.159	9.131
3000	45.600	144.728	104.533	120.585	− 353.145	− 113.160	8.244

June 30, 1973

DIVANADIUM PENTOXIDE (V_2O_5) (LIQUID) GFW = 181.8798 O_5V_2

$S^\circ_{298.15}$ = 45.879 gibbs/mol

Tm = 943 ± 10 K

Td = 1963 K

$\Delta Hf^\circ_{298.15}$ = −356.407 kcal/mol

ΔHm° = 15.42 ± 0.75 kcal/mol

Heat of Formation

The heat of formation of $V_2O_5(\ell)$ at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{943}-H^\circ_{298}$ for $V_2O_5(c)$ and $V_2O_5(\ell)$.

Heat Capacity and Entropy

Cook (1) measured the enthalpy of V_2O_5 in the range 372-1513 K. In the liquid region (T > 943 K), Cook (1) represented his data by a straight line with a slope of Cp° = 45.60 gibbs/mol. We adopt this value for $V_2O_5(\ell)$. A glass transition is assumed at 600 K. The heat capacity values used below 600 K are those of $V_2O_5(c)$. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the heat of formation.

Decomposition Data

Polyakov (2) measured the weight loss of molten V_2O_5 in the range 700-1200°C for various oxygen flows. The oxygen pressure was greater than the dissociation pressure of V_2O_5. The vapor pressure was calculated by extrapolating to zero oxygen flow and assuming the vapor was monomeric $V_2O_5(g)$. Polyakov (2) assumed no loss of oxygen. Pak (3) proposed a method of calculating vapor pressures from experimental results obtained by the entrainment method with allowance for diffusion. Using Polyakov's data and assuming that the vapor phase is the dimeric molecule $V_4O_{10}(g)$, Pak (3) calculated a heat of vaporization ΔHv°_{298} which is 1.4 kcal/mol more positive than Polyakov's reported value of 32.3 kcal/mol V_2O_5. Semenov et al. (4) determined the vapor pressure of $V_4O_{10}(g)$ over $V_2O_5(\ell)$ at 1215-1530 K by an improved transfer technique in an oxygen carrier stream. The reported heat of vaporization was calculated to be 3.5 kcal/mol more positive than Polyakov's value.

Pantony and Vasu (5) stated that molten V_2O_5 attains a constant weight under fixed oxygen pressure and temperature in a reasonably short length of time while in pure nitrogen it is converted into $V_2O_4(c)$. Pantony and Vasu (5) studied gravimetrically the dissociation equilibrium of $V_2O_5(\ell)$ and confirmed its existence by cryoscopic methods. They concluded that the vapor pressure ascribed to $V_2O_5(g)$ or $V_4O_{10}(g)$ and measured by a transpiration-weight loss method is due to the loss of oxygen arising from the following dissociation $V_2O_5(soln) \rightleftarrows V_2O_4(soln) + 1/2\ O_2(g)$.

An effusion-mass spectrometric investigation of the vapor in equilibrium with V_2O_5 in the range 1000-1200 K led Farber et al. (6) to the conclusion that the vapor contained not only $V_4O_{10}(g)$, significant amounts of $V_4O_8(g)$, but also other vanadium oxides. We conclude that there is decomposition upon heating $V_2O_5(\ell)$ in an inert atmosphere or in vacuo. The use of an oxygen atmosphere suppresses the decomposition but in the transpiration-weight loss experiment it has not been verified that the weight loss is indeed $V_4O_{10}(g)$. We calculate a decomposition temperature, Td, as that temperature at which the free energy approaches zero for the reaction $V_2O_5(\ell) \rightleftarrows V_2O_4(\ell) + 1/2\ O_2(g)$.

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O_5V_2

Tetratitanium Heptoxide (Ti_4O_7)

O_7Ti_4

(Crystal) GFW = 303.5958

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0							
100							
200							
298	49.830	47.500	47.500	.000	− 813.700	− 767.989	562.951
300	50.000	47.809	47.501	.092	− 813.697	− 767.706	559.273
400	57.340	63.280	49.560	5.488	− 813.262	− 752.424	411.105
500	61.870	76.600	53.669	11.466	− 812.427	− 737.308	322.277
600	64.810	88.157	58.476	17.809	− 811.390	− 722.380	263.127
700	66.840	98.308	63.456	24.397	− 810.269	− 707.633	220.933
800	68.350	107.337	68.387	31.160	− 809.139	− 693.051	189.333
900	69.510	115.457	73.174	38.055	− 808.037	− 678.603	164.787
1000	70.460	122.831	77.776	45.054	− 806.988	− 664.279	145.178
1100	71.260	129.585	82.183	52.141	− 805.994	− 650.053	129.154
1200	71.960	135.816	86.396	59.303	− 808.808	− 635.768	115.789
1300	72.580	141.600	90.423	66.530	− 807.436	− 621.406	104.468
1400	73.140	147.000	94.274	73.817	− 806.090	− 607.149	94.780
1500	73.670	152.064	97.959	81.157	− 804.778	− 592.984	86.398
1600	74.160	156.835	101.491	88.549	− 803.507	− 578.902	79.074
1700	74.620	161.344	104.881	95.988	− 802.287	− 564.904	72.623
1800	75.060	165.622	108.137	103.472	− 801.135	− 550.975	66.897
1900	75.490	169.692	111.271	111.000	− 800.047	− 537.107	61.781
2000	75.910	173.575	114.290	118.570	− 816.819	− 522.683	57.116
2100	76.310	177.288	117.202	126.181	− 815.776	− 507.996	52.868
2200	76.700	180.847	120.014	133.832	− 814.717	− 493.370	49.012
2300	77.090	184.265	122.734	141.521	− 813.634	− 478.787	45.495
2400	77.470	187.554	125.367	149.249	− 812.533	− 464.245	42.275

Dec. 31, 1973.

TETRATITANIUM HEPTOXIDE (Ti_4O_7) (CRYSTAL) GFW = 303.5958 O_7Ti_4

$S^\circ_{298.15}$ = 47.5 ± 3 gibbs/mol
Tt = 130 ± 8 K
Tt = 150 ± 3 K
Tm = 1950 ± 20 K

ΔHf°_0 = unknown
$\Delta Hf^\circ_{298.15}$ = −813.7 ± 1.5 kcal/mol
ΔHt° = unknown
ΔHt° = unknown
ΔHm° = [54] kcal/mol

Heat of Formation

ΔHf° is calculated from that of $Ti_3O_5(\beta)$ using ΔHr°_{298} = −34.16 kcal/mol for 4/3 $Ti_3O_5(\beta)$ + 1/6 $O_2(g) \rightarrow Ti_4O_7(c)$. ΔHr° is derived by the third-law method from two concordant studies (1, 2) of high-temperature equilibria. Merritt et al. (1) obtained isothermal gravimetric equilibrium over the two-phase system Ti_3O_5-Ti_4O_7 using (H_2 + H_2O) gas mixtures of known oxygen potential. Integration yields ΔGr°(1304 K) = −20.29 ± 0.16 kcal/mol. Suzuki and Sambongi (2) reported solid-state emf data relative to the couple Cr/Cr_2O_3 over a range of ∿500°. We convert their (graphical) emf data (2) to oxygen potentials, using the authors' self-consistent data for Cr/Cr_2O_3, and integrate to get ΔGr°. Vasil'eva and Shaulova (3) reported an equation for the oxygen potential based on their emf data relative to $Fe/Fe_{0.95}O$ over a range of ∿90°. Equilibration data of Porter (4) are not considered because of the likelihood of oxidation during quenching of the composition (1).

Third-law analyses of the equilibria for 4/3 $Ti_3O_5(\beta)$ + 1/6 $O_2(g) \rightarrow Ti_4O_7(c)$ are summarized below. Merritt et al. (1) agree closely with Suzuki and Sambongi (2) but the earlier emf study (3) yields a ΔHf° which is 1.9 kcal/mol less negative. All three studies agree with the earlier conclusion of Wahlbeck and Gilles (5) that Ti_4O_7 is stable with respect to disproportionation into $Ti_3O_5(\beta)$ and TiO_2(rutile). We dismiss the ΔHf° derived from Vasil'eva (3) since it implies the contrary when combined with our adopted S° and Cp°. We adopt ΔHf° = −813.7 ± 1.5 kcal/mol, where the uncertainty includes the possibility that ΔHt° and S° of $Ti_3O_5(\beta)$ are biased (6).

Source	Method	Range T/K	δS[a] gibbs/mol	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	ΔHf°_{298}[b] kcal/mol
(1) Merritt et al. (1973)	Gravimetric	1304	-	-	-34.10	-813.63
(2) Suzuki (1972)	Emf	∿1273-1773	0.1	-34.0	-34.20	-813.74
(3) Vasil'eva (1969)	Emf	1168-1257	2.0	-29.8	-32.31	-811.84

[a] δS = ΔSr° (2nd Law) − ΔSr° (3rd Law). [b] Based on ΔHr° (3rd Law).

Heat Capacity and Entropy

Cp° is based on constrained fitting of enthalpy data (679-1937 K) of Slyusar et al. (6). The constraints required that the enthalpy be zero at the reference temperature (298.15 K) and that Cp° = 50 gibbs/mol and dCp°/dT ∿0.09 gibbs/(mol K) at 300 K. The latter values are estimated by comparison with TiO_2, Ti_3O_5, Ti_2O_3 and TiO (6). Deviations of the data from the resulting fit have a pattern (6) similar to that found with the authors' data (7) for $Ti_3O_5(\beta)$. The enthalpies of Slyusar et al. (7) for TiO_2, Ti_2O_3, Ti_3O_5 and Ti_4O_7 are less than satisfactory due to inconsistencies in H near 1200 K and in the reported values of Tm (6). Our constraints for Ti_4O_7 are an attempt to minimize the effects of the inconsistencies. They lead to a reasonable variation of Cp° with temperature. We assume that there are no phase transitions above 298 K since two transitions are known to occur at low temperature.

S°(298 K) = 47.5 ± 3 gibbs/mol is derived from the emf data of Suzuki and Sambongi (2). The uncertainty includes the possibility that ΔHt° and S° of $Ti_3O_5(\beta)$ are biased (6); excluding this possibility, we estimate an uncertainty of ±1.5 gibbs/mol. S°(298 K) = 49.5 gibbs/mol can be derived from the less reliable data of Vasil'eva and Shaulova (3). These authors (3) derived S°(298 K) = 42 gibbs/mol, which is clearly too low. Unfortunately, the entropy derived from Cp° data (12-300 K) of Berezovskii et al. (11) is unpublished and not yet available. These workers also measured Cp° of the higher homologues Ti_5O_9, Ti_6O_{11} and Ti_9O_{17}.

Transition Data and Phase Data

Transition temperatures near 130 K and 150 K were found by use of DTA (8), electrical conductivity (8), magnetic susceptibility (9), and x-ray diffraction (8, 10). The three crystalline phases are triclinic; the two transitions involve no change in symmetry but only rearrangements of atoms within the unit cell (10). There is obvious thermal hysteresis in the transition near 130 K. DTA endotherms (8) suggest that ΔHt°(150 K) is considerably larger than ΔHt°(130 K). ΔHt° values presumably were obtained with the Cp° data (11), but these are not yet available.

Ti_4O_7 is the lowest stable phase in the homologous series of structures Ti_nO_{2n-1} related to rutile. Phases exist with n=4,5,6,7,8,9 and certain higher integer values. These were reviewed in detail by Bursill and Hyde (12) in terms of the persistent structural phenomenon - crystallographic shear. Equilibrium data (1, 2) emphasize that ΔGr° is negative, but very small in magnitude, for formation of Ti_nO_{2n-1} from its two nearest neighbors. Kinetic limitations can cause hysteresis in measured properties (1).

Melting Data

See $Ti_4O_7(\ell)$.

Sublimation Data

$Ti_4O_7(c)$ vaporizes incongruently such that the residue approaches the congruently vaporizing composition of $Ti_3O_5(\beta)$. See $Ti_3O_5(\ell)$.

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O_7Ti_4

Tetratitanium Heptoxide (Ti_4O_7)

(Liquid) GFW = 303.5958

T, °K	gibbs/mol Cp°	S°	−(G°−H°₂₉₈)/T	kcal/mol H°−H°₂₉₈	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	49.830	69.567	69.566	.000	− 768.651	− 729.519	534.752
300	50.000	69.875	69.567	.092	− 768.648	− 729.277	531.277
400	57.340	85.347	71.627	5.488	− 768.213	− 716.202	391.314
500	61.870	98.667	75.736	11.466	− 767.378	− 703.291	307.408
600	64.810	110.223	80.542	17.809	− 766.341	− 690.571	251.540
700	66.840	120.375	85.522	24.397	− 765.220	− 678.030	211.691
800	68.350	129.403	90.454	31.160	− 764.090	− 665.655	181.848
900	69.510	137.523	95.240	38.055	− 762.988	− 653.414	158.671
1000	70.460	144.897	99.843	45.054	− 761.939	− 641.296	140.155
1100	71.260	151.651	104.250	52.141	− 760.944	− 629.277	125.026
1200	71.960	157.882	108.463	59.303	− 763.759	− 617.199	112.407
1300	72.580	163.667	112.490	66.531	− 762.387	− 605.043	101.717
1400	88.000	170.188	116.381	75.331	− 759.527	− 593.050	92.579
1500	88.000	176.260	120.173	84.131	− 756.755	− 581.255	84.689
1600	88.000	181.939	123.858	92.931	− 754.077	− 569.639	77.809
1700	88.000	187.274	127.433	101.731	− 751.496	− 558.193	71.761
1800	88.000	192.304	130.898	110.531	− 749.027	− 546.895	66.402
1900	88.000	197.062	134.256	119.331	− 746.668	− 535.731	61.623
2000	88.000	201.576	137.511	128.131	− 762.210	− 524.075	57.268
2100	88.000	205.869	140.664	136.931	− 759.977	− 512.218	53.307
2200	88.000	209.963	143.722	145.731	− 757.769	− 500.477	49.718
2300	88.000	213.875	146.688	154.531	− 755.575	− 488.831	46.450
2400	88.000	217.620	149.566	163.331	− 753.402	− 477.273	43.462
2500	88.000	221.212	152.360	172.131	− 751.250	− 465.819	40.722
2600	88.000	224.664	155.075	180.931	− 749.112	− 454.443	38.199
2700	88.000	227.985	157.714	189.731	− 746.995	− 443.148	35.870
2800	88.000	231.185	160.282	198.531	− 744.896	− 431.934	33.714
2900	88.000	234.273	162.780	207.331	− 742.814	− 420.781	31.711
3000	88.000	237.257	165.213	216.131	− 740.749	− 409.715	29.848
3100	88.000	240.142	167.584	224.931	− 738.699	− 398.708	28.109
3200	88.000	242.936	169.895	233.731	− 736.666	− 387.789	26.485
3300	88.000	245.644	172.150	242.531	− 734.647	− 376.915	24.962
3400	88.000	248.271	174.350	251.331	− 732.645	− 366.100	23.533
3500	88.000	250.822	176.499	260.131	− 730.654	− 355.358	22.190
3600	88.000	253.301	178.598	268.931	−1135.181	− 343.604	20.860
3700	88.000	255.712	180.650	277.731	−1133.106	− 321.649	18.999
3800	88.000	258.059	182.656	286.531	−1131.094	− 299.750	17.240
3900	88.000	260.345	184.619	295.331	−1129.144	− 277.896	15.573
4000	88.000	262.573	186.540	304.131	−1127.260	− 256.095	13.992

Dec. 31, 1973.

TETRATITANIUM HEPTOXIDE (Ti_4O_7) (LIQUID) GFW = 303.5958 O_7Ti_4

$S^\circ_{298.15}$ = [69.566] gibbs/mol

Tm = 1950 ± 20 K

$\Delta Hf^\circ_{298.15}$ = [−768.651] gibbs/mol

ΔHm° = [54] kcal/mol

Heat of Formation

ΔHf° is calculated from that of Ti_4O_7(c) by adding ΔHm° to the difference in ($H^\circ_{1950}-H^\circ_{298}$) between crystal and liquid.

Heat Capacity and Entropy

Cp° is estimated as 8 gibbs/g-atom. Below the assumed glass transition at 1300 K, Cp° is taken to be the same as that of the crystal. S° is calculated in a manner analogous to that of ΔHf°.

Melting Data

Hampson and Gilles (1) reported that Tm < 1943 K, which is in reasonable agreement with Tm ~1955 K obtained from the liquidus curve of Brauer and Littke (2). The value of 1993 K reported by Slyusar et al. (3) is over 40° higher than our adopted value of 1950 ± 20 K. Ti_4O_7 probably melts incongruently, but the data (2) are not completely conclusive on this point.

Vaporization Data

Studies of liquid samples (4) showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal products (1) of vaporization are TiO_2(g) and TiO(g).

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Lead Sulfide (PbS)

(Crystal) GFW = 239.26

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.751	- 23.554	- 23.554	INFINITE
100	9.500	9.870	31.963	- 2.209	- 23.599	- 23.410	51.161
200	11.380	17.189	22.902	- 1.143	- 23.529	- 23.248	25.404
298	11.816	21.832	21.832	.000	- 23.500	- 23.117	16.945
300	11.820	21.905	21.832	.022	- 23.500	- 23.115	16.839
400	12.060	25.336	22.298	1.215	- 24.058	- 22.963	12.546
500	12.300	28.053	23.187	2.433	- 24.451	- 22.644	9.898
600	12.520	30.315	24.191	3.674	- 24.757	- 22.252	8.105
700	12.750	32.263	25.209	4.938	- 26.163	- 21.600	6.744
800	12.980	33.981	26.200	6.225	- 39.422	- 22.202	6.065
900	13.210	35.523	27.151	7.534	- 39.265	- 20.059	4.871
1000	13.430	36.926	28.060	8.866	- 39.080	- 17.934	3.919
1100	13.660	38.217	28.925	10.221	- 38.867	- 15.831	3.145
1200	13.880	39.415	29.750	11.598	- 38.625	- 13.745	2.503
1300	14.110	40.535	30.537	12.998	- 38.356	- 11.682	1.964
1400	14.330	41.589	31.289	14.420	- 38.066	- 9.642	1.505
1500	14.550	42.585	32.009	15.864	- 37.754	- 7.623	1.111
1600	14.750	43.531	32.700	17.329	- 37.424	- 5.624	.768
1700	14.950	44.431	33.364	18.814	- 37.077	- 3.646	.469
1800	15.150	45.291	34.003	20.319	- 36.716	- 1.692	.205

June 30, 1973

LEAD SULFIDE (PbS) (CRYSTAL) GFW = 239.26 PbS

$S^\circ_{298.15}$ = 21.83 ± 0.4 gibbs/mol

Tm = 1386.5 ± 1.5 K

ΔHf°_0 = -23.6 ± 0.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = -23.5 ± 0.5 kcal/mol

ΔHm° = 4.5 ± 1.5 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 55.0 ± 1.5 kcal/mol

Heat of Formation

Second and third law analyses are made of the equilibrium data of Jellinek et al. (1), Sudo (2), and Stubbles and Birchenall (3), the free energies (via EMF measurements) of Kapustinskii and Makolkin (4) and of Kiukkola and Wagner (5), and the EMF data reported by Thompson and Flengas (6). The results of our analyses using auxiliary data (7) are summarized in the following table.

Investigator	Reaction	Temp. K	No. of Points	ΔHr°_{298}, kcal/mol 2nd Law	3rd Law	Drift eu	ΔHf°_{298} kcal/mol
(1) Jellinek et al. (1929)	A	788-1273	7	-18.4±0.8	-18.60	-0.16±0.80	-22.5
(2) Sudo (1950)	A	855-1048	Equation	-18.0	-20.12	-2.2	-24.0
(3) Stubbles and Birchenall (1959)	A	859-1193	30	-19.3±0.1	-19.76	-0.42±0.12	-23.6
(4) Kapustinskii and Makolkin (1938)	B	288-308	3	-17.7±0.5	-16.63	3.7±1.6	-21.5
(5) Kiukkola and Wagner (1957)	C	523-573	2	-24.7	-23.84	1.5	-23.5
(5) Kiukkola and Wagner (1957)	D	600-700	4	-24.5±0.2	-24.79	-0.45±0.32	-23.4
(6) Thompson and Flengas (1971)	E	773-1071	12	-40.7±0.5	-39.63	1.2±0.6	-23.2

Reactions:
(A) $Pb(\ell) + H_2S(g) = PbS(c) + H_2(g)$
(B) $Pb(c) + H_2S(g) = PbS(c) + H_2(g)$
(C) $Pb(c) + S(\ell) = PbS(c)$
(D) $Pb(\ell) + S(\ell) = PbS(c)$
(E) $Pb(\ell) + 1/2\ S_2(g) = PbS(c)$

The experiments of Jellinek et al. (1) are unsatisfactory (8) and are superseded by two later studies (2, 3) of the same equilibrium. The free energies of Kapustinskii and Makolkin (4) may be dismissed as biased on the basis of inconsistencies in both ΔHf° and entropy (drift). The other studies (2, 3, 5, 6) are consistent with the adopted ΔHf°(298.15 K) of -23.5 ± 0.5 kcal/mol.

We also calculate ΔHf° = -23.5 kcal/mol from ΔHr(293 K) = -13.38 ± 0.2 kcal/mol for the reaction $Pb(NO_3)_2(3000\ H_2O) + H_2S(aq) \rightarrow PbS(c) + 2\ HNO_3(2000\ H_2O)$ studied calorimetrically by Zeumer and Roth (9). The uncertainty of this calorimetric ΔHf° may approach ±1 kcal/mol due to the auxiliary data (10) and approximations used in our calculation. Recent DTA data (11) for $Pb(c) + S(\ell) \rightarrow PbS(c)$ gave ΔHr(480 K) = -23.4 ± 0.3 kcal/mol, which we reduce to ΔHf°(298.15 K) = -22.5 ± 1 kcal/mol. The uncertainty assigned (11) to ΔHr appears to be too optimistic. Korshunov (12) obtained ΔHf° = -22.38 kcal/mol by combustion of S-Mg-Pb mixtures in a bomb, but the chemical reactions probably were not characterized adequately.

Heat Capacity and Entropy

Cp° is from the work of Parkinson and Quarrington (13) (Cp° given as smoothed values, 20-260 K) and of Anderson (14) (54-289 K) which were graphically smoothed and extrapolated to 300 K. The data of Parkinson and Quarrington and Anderson are in good agreement; Anderson's values show more scatter. The largest deviation of the Parkinson and Quarrington values from the adopted values is +0.4% at 210 K. Anderson's points are mostly within less than ±1% of the selected values.

Above 300 K, Cp° values are derived from the drop-calorimeter enthalpies of Thompson and Flengas (15) (353-1281 K) with constraint to join smoothly with the low temperature data. The observed enthalpies differ from the adopted values by +4% at 400 K; above 500 K the deviation is generally within ±0.4%.

Also considered were the low temperature heat capacities measured by Eastman and Rodebush (16) (64-283 K) and Kelley's equations (17) which are based on the work of Bornemann and Hengstenberg (18) (273-873 K). The Eastman and Rodebush data appears to be high above 200 K. At 900 K the enthalpy calculated from Kelley's equation is 4% higher than the adopted value.

S°(20 K) of 0.83 gibbs/mol given by Kelley and King (19) is adopted here.

Melting Data - See PbS(ℓ) table.

Sublimation Data - See PbS(g) table.

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PbS

Lead Sulfide (PbS)

(Liquid) GFW = 239.26

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	11.816	24.091	24.090	.00C	- 20.092	- 20.383	14.941
300	11.820	24.164	24.091	.022	- 20.092	- 20.384	14.850
400	12.060	27.595	24.557	1.215	- 20.649	- 20.458	11.178
500	12.300	30.312	25.446	2.433	- 21.042	- 20.365	8.902
600	12.520	32.574	26.450	3.674	- 21.348	- 20.199	7.357
700	12.750	34.522	27.467	4.938	- 22.755	- 19.773	6.173
800	12.980	36.240	28.459	6.225	- 36.014	- 20.601	5.628
900	16.000	37.782	29.410	7.534	- 35.857	- 18.683	4.537
1000	16.000	39.467	30.333	9.134	- 35.404	- 16.799	3.671
1100	16.000	40.992	31.234	10.734	- 34.946	- 14.962	2.973
1200	16.000	42.384	32.106	12.334	- 34.481	- 13.164	2.398
1300	16.000	43.665	32.947	13.934	- 34.012	- 11.406	1.918
1400	16.000	44.851	33.755	15.534	- 33.544	- 9.686	1.512
1500	16.000	45.955	34.532	17.134	- 33.076	- 7.998	1.165
1600	16.000	46.987	35.279	18.734	- 32.611	- 6.341	.866
1700	16.000	47.957	35.996	20.334	- 32.149	- 4.713	.606
1800	16.000	48.872	36.686	21.934	- 31.693	- 3.114	.378
1900	16.000	49.737	37.351	23.534	- 31.241	- 1.538	.177
2000	16.000	50.558	37.991	25.134	- 30.795	.014	.002

June 30, 1973

LEAD SULFIDE (PbS) (LIQUID) GFW = 239.26 PbS

$S^\circ_{298.15}$ = 24.091 gibbs/mol

Tm = 1386.5 ± 1.5 K

$\Delta Hf^\circ_{298.15}$ = -20.092 kcal/mol

ΔHm° = 4.5 ± 1.5 kcal/mol

Heat of Formation

The heat of formation of PbS(ℓ) at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{1386.5}-H^\circ_{298}$ for PbS(c) and PbS(ℓ).

Heat Capacity and Entropy

The heat capacity of PbS(ℓ) is estimated to be 16.0 gibbs/mol. This appears reasonable as the Cp° value for PbO(ℓ) is 15.535 gibbs/mol (12). A glass transition is assumed at 900 K. Below this temperature, the heat capacity values used are those of PbS(c). The entropy at 298.15 K is calculated in a manner similar to that for $\Delta Hf^\circ_{298.15}$.

Melting Data

Employing cryoscopic measurements, Pelton and Flengas (1) and Bell and Flengas (2) determined the melting point of PbS to be 1113.4°C and 1111.9°C, respectively. Pelton and Flengas (1) estimated an accuracy of ±1°C. Miller and Komarek (3), in studying the retrograde solubility in the Pb-S system, reported Tm = 1113.3 ± 0.5°C. The latter authors have summarized many early determinations of Tm which were in the range 1103-1135°C. We adopt 1386.5 ± 1.5 K for Tm of PbS.

Kelley (4) adopted ΔHm° = 4.150 kcal/mol based on melting point data obtained by Friedrich (5) for the PbS-Cu_2S system and by Truthe (6) for the PbS-$PbCl_2$system. Maier (7) recalculated ΔHm° from Friedrich's data and obtained 4.155 kcal/mol. Kelley (4) also calculated ΔHm° = 5.03 kcal/mol from data on the PbS-Ag_2S system obtained by Friedrich. Other inconclusive works are discussed by Kelley (4). In the preceding calculations ΔHm° was derived from a graph of log x versus 1/T where x is the mole fraction of PbS in the melt and T is the liquidus temperature.

We calculate a ΔHm value for each melting point-composition data pair and plot this value against ΔT, the melting point depression of PbS. The resulting plot is extrapolated to ΔT = 0 to obtain ΔHm°. Friedrich's data then yields ΔHm° = 4.33 ± 0.15 kcal/mol. Truthe's data has considerable scatter but indicates a value of 4-6 kcal/mol for ΔHm°. An analysis of the data reported by Kohlmeyer and Monzer (8) for the PbS-PbO system yields ΔHm° = 5 ± 1 kcal/mol. Unfortunately, these three studies necessitate long extrapolations as the ΔT values are in the range 60-550 K. However, these three binary systems form simple, single eutectic phase diagrams and all are consistent with a ΔHm° value of 4.5 kcal/mol.

Recent work by Pelton and Flengas (1) on PbS-alkali halide systems involved ΔT values of 2-17 K so that a much shorter extrapolation is possible. An analysis of their data is tabulated below.

System	No. of data pts.	ΔHm°, kcal/mol
PbS-NaCl	3	8.5
PbS-KCl	10	4.5
PbS-RbCl	2	4.3
PbS-CsCl	2	4.6

Even in the PbS-KCl system, the scatter is such that it is impossible to precisely define ΔHm°. We adopt a value of ΔHm° = 4.5 ± 1.5 kcal/mol. This value is consistent with all systems discussed above except for PbS-NaCl.

It should be noted that our analyses treated all systems as though no association, dissociation, or compound formation occurs in the melt. It is possible that the occurrence of any or all of these factors would cause the data to be consistent with a ΔHm° which might be larger than the adopted value and even outside our uncertainty limits. For example, Pelton and Flengas (1) discussed their results in the PbS-alkali halide systems in terms of an estimated ΔHm° = 8.7 kcal/mol. Their conclusions need modifications with use of our adopted ΔHm° = 4.5 kcal/mol. In addition Blachnik and Kluge (9) have compared ΔHm° and Tm values for A(IV) B(VI) compounds, using ΔHm° = 8.7 kcal/mol for PbS. In assigning a constant ΔSm° value for GeS, SnS, and PbS, a difficulty arises in that PbS does not have the same crystal structure as GeS and SnS (9). Thus, ΔSm° is not necessarily expected to be the same for all three species.

Decomposition Data

Kohlmeyer (10, 11) reported that, although PbS(ℓ) had an apparent boiling point of 1617 K, the vaporization did not yield solely PbS(g). Decomposition occurred to yield sulfide molecules in the melt which were rich in Pb. The temperature at which ΔG° approaches zero for PbS(ℓ) = PbS(g) is calculated to be 1593 K. A similar calculation for the reaction PbS(ℓ) = Pb(ℓ) + 1/2 S S_2(g) yields 1999 K.

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PbS

Lead Sulfide (PbS)

(Ideal Gas) GFW = 239.26

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°298)/T (gibbs/mol)	H°−H°298 (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	- 2.254	31.943	31.943	INFINITE
100	7.119	51.617	67.174	- 1.556	32.054	28.069	- 61.346
200	7.920	56.802	60.816	- .803	31.811	24.170	- 26.411
298	8.385	60.062	60.062	.000	31.500	20.484	- 15.015
300	8.391	60.114	60.062	.016	31.494	20.416	- 14.873
400	8.622	62.563	60.394	.867	30.594	16.799	- 9.178
500	8.746	64.501	61.029	1.736	29.852	13.435	- 5.872
600	8.822	66.103	61.745	2.615	29.184	10.216	- 3.721
700	8.872	67.467	62.467	3.500	27.399	7.319	- 2.285
800	8.908	68.654	63.168	4.389	13.742	3.223	- .881
900	8.935	69.705	63.837	5.281	13.482	1.024	- .467
1000	8.957	70.648	64.472	6.176	13.230	.654	- .143
1100	8.975	71.502	65.073	7.073	12.965	- .593	.118
1200	8.991	72.284	65.642	7.971	12.748	- 1.315	.331
1300	9.005	73.004	66.181	8.871	12.517	- 3.019	.507
1400	9.018	73.672	66.592	9.772	12.286	- 4.206	.657
1500	9.031	74.295	67.173	10.674	12.056	- 5.376	.783
1600	9.043	74.878	67.642	11.578	11.825	- 6.530	.892
1700	9.056	75.427	68.084	12.483	11.592	- 7.670	.986
1800	9.069	75.945	68.506	13.389	11.354	- 8.793	1.068
1900	9.084	76.435	68.911	14.297	11.114	- 9.910	1.140
2000	9.101	76.902	69.299	15.206	10.869	- 11.010	1.203
2100	9.122	77.346	69.671	16.117	- 31.830	- 10.547	1.098
2200	9.146	77.771	70.030	17.031	- 31.988	- 9.529	.947
2300	9.174	78.178	70.375	17.947	- 32.166	- 8.505	.808
2400	9.208	78.569	70.709	18.866	- 32.362	- 7.470	.680
2500	9.248	78.946	71.031	19.788	- 32.578	- 6.430	.562
2600	9.294	79.310	71.342	20.715	- 32.811	- 5.380	.452
2700	9.348	79.661	71.644	21.647	- 33.059	- 4.321	.350
2800	9.409	80.002	71.936	22.585	- 33.324	- 3.253	.254
2900	9.479	80.334	72.220	23.530	- 33.600	- 2.173	.164
3000	9.557	80.656	72.496	24.481	- 33.889	- 1.082	.079
3100	9.644	80.971	72.764	25.441	- 34.184	.015	- .001
3200	9.739	81.279	73.026	26.410	- 34.488	1.122	- .077
3300	9.844	81.580	73.280	27.389	- 34.793	2.240	- .148
3400	9.958	81.876	73.529	28.379	- 35.100	3.369	- .217
3500	10.081	82.166	73.771	29.381	- 35.406	4.501	- .281
3600	10.212	82.452	74.009	30.396	- 35.706	5.647	- .343
3700	10.352	82.734	74.241	31.424	- 36.002	6.801	- .402
3800	10.500	83.012	74.468	32.467	- 36.286	7.962	- .458
3900	10.655	83.286	74.690	33.524	- 36.562	9.129	- .512
4000	10.817	83.558	74.909	34.598	- 36.823	10.304	- .563
4100	10.985	83.827	75.123	35.688	- 37.070	11.485	- .612
4200	11.160	84.094	75.333	36.795	- 37.301	12.675	- .660
4300	11.338	84.359	75.540	37.920	- 37.514	13.863	- .705
4400	11.521	84.622	75.744	39.063	- 37.708	15.063	- .748
4500	11.708	84.883	75.944	40.224	- 37.882	16.264	- .790
4600	11.896	85.142	76.141	41.405	- 38.034	17.470	- .830
4700	12.086	85.400	76.335	47.604	- 38.164	18.674	- .868
4800	12.277	85.656	76.527	43.822	- 38.273	19.887	- .905
4900	12.468	85.911	76.716	45.059	- 38.359	21.101	- .941
5000	12.657	86.165	76.902	46.315	- 38.423	22.312	- .975
5100	12.845	86.418	77.086	47.590	- 38.464	23.529	- 1.008
5200	13.030	86.669	77.268	48.884	- 38.481	24.747	- 1.040
5300	13.212	86.919	77.448	50.196	- 38.476	25.963	- 1.071
5400	13.389	87.167	77.625	51.527	- 38.449	27.180	- 1.100
5500	13.562	87.415	77.801	52.874	- 38.402	28.392	- 1.128
5600	13.729	87.651	77.975	54.239	- 38.333	29.608	- 1.156
5700	13.890	87.905	78.147	55.620	- 38.245	30.816	- 1.182
5800	14.045	88.148	78.317	57.017	- 38.137	32.031	- 1.207
5900	14.192	88.389	78.486	58.428	- 38.012	33.235	- 1.231
6000	14.323	88.629	78.653	59.855	- 37.868	34.444	- 1.255

June 30, 1973

LEAD SULFIDE (PbS) (IDEAL GAS) GFW = 239.26

PoS

Symmetry Number = 1

S°_{298} = 60.062 ± 0.005 gibbs/mol

ΔHf°_0 = 31.9 ± 1.5 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 31.5 ± 1.5 kcal/mol

Electronic and Molecular Constants

State	ε_i, cm^{-1}	g_i	r_e, Å	B_e cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
X 0^+	0	1	2.287	0.11633	0.000425	429.40	1.30
a 1	14821.9	2	2.562	0.09267	0.000374	285.9	0.88
A 0^+	18708.9	1	2.513	0.09634	0.000262	260.83	0.363
B 1	21774.5	2	2.467	0.09992	0.000602	282.17	0.856
C,0^+	23150.7	1	[2.522]	[0.09561]	[0.000347]	303.93	1.436
C 1	24952.3	2	[2.549]	[0.09358]	[0.000297]	283.95	1.171
D 1	29587.4	2	2.447	0.10269	0.00064	297.83	1.365
E 0^+	34000	1	[2.585]	[0.09095]	[0.000429]	[262.32]	[1.114]

Heat of Formation

Vago and Barrow (1) observed the convergence in the E-X system at 2715Å. The dissociation energy for PbS(g) is calculated to be 81.85 ± 0.40 kcal/mol. Barrow, Fry, and LeBargy (2) analyzed the PbS absorption spectrum in terms of type C coupling and assigned the electronically excited E state to be 0^+. If the non-crossing rule is applicable (2), then the most likely dissociation products are Pb($^3P_1$) and S($^3P_1$). The corresponding ΔHf°_{298}(PbS, g) value is 32.00 ± 0.40 kcal/mol, using auxiliary data (3).

Colin and Drowart (4) have studied the sublimation and dissociation of PbS by means of a Knudsen effusion cell coupled with a mass spectrometer. A second and third law analysis by Colin and Drowart (4) of four sets of experiments (865-1100 K) yielded an average value of 55.7 ± 1.6 kcal/mol for the heat of sublimation. It is anticipated that this result is roughly 0.5 kcal/mol too large since the free energy functions for the sublimation used by Colin and Drowart (4) are approximately 0.5 cal/mol greater than those presently adopted at 1000 K (3).

Colin and Drowart (4) presented data for 13 experiments in which either Pb, S_2, or both Pb and S_2 partial pressures were measured in addition to the PbS partial pressure. The missing pressure is calculated using the formula $[P(Pb)/P(S_2)][GFW(S_2)/GFW(Pb)]^{1/2} = 2$ as in Colin and Drowart (4). A second and third law analysis of these data is included in the following table. Also included is our analysis of 10 sublimation studies by other workers.

Source	Reaction	Range, K	No. Pts.	Method	ΔHr°_{298}, kcal/mol 2nd Law	ΔHr°_{298}, kcal/mol 3rd Law	Drift eu	ΔHf°_{298} ^{c} kcal/mol
Colin and Drowart (4)	A	990-1043	5	calc. P(S_2)	30.20±14.63	29.04	-1.1±14.3	33.12
	A	979-1118	4	calc. P(Pb)	36.48±10.22	28.31	-7.9±9.9	33.96
	A	1012-1182	4	all P meas.	21.97±4.67	29.32	6.8±4.3	32.85
	B	979-1182	13*	Knudsen-mass spec.	55.25±0.69	55.55	0.3±0.7	32.05
Schenck and Albers (5)	B	1123-1268	12*	Entrainment	59.48±0.66	55.00	-3.6±0.5	31.50
Veselowskii (6)	B	978-1069	6	Knudsen	55.38±0.44	54.88	-0.5±0.4	31.38
Hsiao and Schlecten (7)	B	776-927	**	Langmuir	53.16	57.24	4.8	33.74
Miller and Abdeev (8)	B	825-1025	**		54.56	54.95	0.4	31.45
Sudo (9)	B	1048-1193	10	Knudsen	57.66±1.16	56.12	-1.3±1.0	32.62
Isakova et al. (10)	B	1113-1378	11	Entrainment	57.27±1.35	54.34	-2.3±1.1	30.84
Hansen and Munir (11)	B	977-1020	12	torsion-effusion	55.99±0.87	54.55	-1.5±0.9	31.05
			17*	torsion-effusion	57.71±0.53	54.55	-3.2±0.5	31.05
Hansen and Munir (11)	B	860-975	20	torsion-Langmuir	53.58±1.94	54.68	1.2±2.2	31.18
			7	torsion-Langmuir	53.69±0.70	54.55	0.9±0.7	31.05

(A) $PbS(g) = Pb(g) + 1/2\ S_2(g)$ (B) $PbS(c) = PbS(g)$ ^{c} Heat of formation for PbS(g) based on the third law analysis.

** Actual data not presented, smoothed data used. * One point rejected due to statistical test.

The value adopted for ΔHf°_{298}(PbS, g) is 31.5 kcal/mol with an accompanying uncertainty of ±1.5 kcal/mol. Most of the uncertainty is attributable to the possible decomposition and/or reaction during sublimation. Colin and Drowart (4) and Isakova et al. (10) considered the effect of decomposition whereas many of the other investigators analyzed their data in terms of PbS(g) formation only. In addition, Hansen and Munir (11) attest to the congruency of sublimation using x-ray observations on samples which had lost at least 30% of their initial weight as a result of heating. The adopted ΔHf°_{298} is somewhat of a compromise between the spectroscopic work (1), the mass spectrometric work (4), and the bulk of the sublimation studies. The corresponding dissociation energy for PbS(g) is 82.4±1.5 kcal/mol.

A value of 86.5 kcal/mol for the dissociation energy of PbS(g) is calculated by applying the Hildenbrand formula (12) to the linear Birge-Sponer extrapolation of the ground state vibrational levels. Using auxiliary data (3), a ΔHf°_{298} value of 27.4 kcal/mol is obtained.

Heat Capacity and Entropy

The tabulated electronic and molecular constants are taken from Rosen (13), as reviewed and compiled by Barrow. The constants came from the work of Bell and Harvey (14), Rochester and Howell (15), Vago and Barrow (1), and Barrow, Fry, and LeBargy (2). The state designations are those which are consistent with type C coupling. In this case, the state designations Σ, Π, etc. no longer have meaning. The estimated values in the tabulation are derived from comparisons of known values in the PbS(g) and PbO(g) systems (3). The functions are calculated from the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i e^{-(c_2 \varepsilon_i/T)}$; the values for Q_r^i and Q_v^i were calculated with first order anharmonic corrections.

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PbS

Tantalum (Ta)

(Reference State) GFW = 180.947

T, °K	gibbs/mol Cp°	S°	$-(G°-H°_{298})/T$	kcal/mol $H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.358	.000	.000	.000
100	4.719	3.858	15.058	- 1.120	.000	.000	.000
200	5.756	7.549	10.454	- .581	.000	.000	.000
298	6.046	9.912	9.912	.000	.000	.000	.000
300	6.049	9.949	9.912	.011	.000	.000	.000
400	6.176	11.708	10.151	.623	.000	.000	.000
500	6.298	13.099	10.606	1.246	.000	.000	.000
600	6.416	14.258	11.121	1.882	.000	.000	.000
700	6.504	15.254	11.642	2.528	.000	.000	.000
800	6.563	16.127	12.149	3.182	.000	.000	.000
900	6.613	16.902	12.635	3.841	.000	.000	.000
1000	6.676	17.602	13.097	4.505	.000	.000	.000
1100	6.759	18.242	13.536	5.177	.000	.000	.000
1200	6.850	18.834	13.953	5.857	.000	.000	.000
1300	6.929	19.386	14.350	6.546	.000	.000	.000
1400	6.979	19.902	14.729	7.242	.000	.000	.000
1500	7.007	20.384	15.090	7.941	.000	.000	.000
1600	7.036	20.837	15.435	8.643	.000	.000	.000
1700	7.096	21.265	15.765	9.350	.000	.000	.000
1800	7.200	21.674	16.082	10.064	.000	.000	.000
1900	7.329	22.066	16.387	10.791	.000	.000	.000
2000	7.455	22.445	16.681	11.530	.000	.000	.000
2100	7.580	22.812	16.964	12.281	.000	.000	.000
2200	7.708	23.168	17.238	13.046	.000	.000	.000
2300	7.846	23.513	17.503	13.823	.000	.000	.000
2400	7.997	23.850	17.761	14.615	.000	.000	.000
2500	8.166	24.180	18.011	15.423	.000	.000	.000
2600	8.358	24.504	18.254	16.249	.000	.000	.000
2700	8.578	24.824	18.492	17.096	.000	.000	.000
2800	8.830	25.140	18.724	17.966	.000	.000	.000
2900	9.120	25.455	18.950	18.863	.000	.000	.000
3000	9.452	25.770	19.172	19.791	.000	.000	.000
3100	9.830	26.085	19.390	20.755	.000	.000	.000
3200	10.260	26.404	19.604	21.759	.000	.000	.000
3300	10.000	29.402	19.849	31.522	.000	.000	.000
3400	10.000	29.700	20.135	32.522	.000	.000	.000
3500	10.000	29.990	20.412	33.522	.000	.000	.000
3600	10.000	30.272	20.682	34.522	.000	.000	.000
3700	10.000	30.546	20.945	35.522	.000	.000	.000
3800	10.000	30.812	21.201	36.522	.000	.000	.000
3900	10.000	31.072	21.451	37.522	.000	.000	.000
4000	10.000	31.325	21.695	38.522	.000	.000	.000
4100	10.000	31.572	21.933	39.522	.000	.000	.000
4200	10.000	31.813	22.165	40.522	.000	.000	.000
4300	10.000	32.049	22.392	41.522	.000	.000	.000
4400	10.000	32.279	22.614	42.522	.000	.000	.000
4500	10.000	32.503	22.832	43.522	.000	.000	.000
4600	10.000	32.723	23.044	44.522	.000	.000	.000
4700	10.000	32.938	23.252	45.522	.000	.000	.000
4800	10.000	33.149	23.456	46.522	.000	.000	.000
4900	10.000	33.355	23.656	47.522	.000	.000	.000
5000	10.000	33.557	23.852	48.522	.000	.000	.000
5100	10.000	33.755	24.045	49.522	.000	.000	.000
5200	10.000	33.949	24.233	50.522	.000	.000	.000
5300	10.000	34.140	24.418	51.522	.000	.000	.000
5400	10.000	34.326	24.600	52.522	.000	.000	.000
5500	10.000	34.510	24.779	53.522	.000	.000	.000
5600	10.000	34.690	24.954	54.522	.000	.000	.000
5700	10.000	34.867	25.126	55.522	.000	.000	.000
5800	9.963	65.484	25.369	232.670	.000	.000	.000
5900	10.000	65.655	26.050	233.668	.000	.000	.000
6000	10.033	65.823	26.712	234.670	.000	.000	.000

Dec. 31, 1972

TANTALUM (Ta) (REFERENCE STATE) GFW = 180.947 Ta

0 to 3258 K Crystal

3258 to 5786 K Liquid

5786 to 6000 K Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

Ta

Tantalum (.Ta)
(Crystal) GFW = 180.947

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	-1.358	.000	.000	.000
100	4.719	3.858	15.058	-1.120	.000	.000	.000
200	5.756	7.549	10.454	-.581	.000	.000	.000
298	6.046	9.912	9.912	.000	.000	.000	.000
300	6.049	9.949	9.912	.011	.000	.000	.000
400	6.176	11.708	10.151	.623	.000	.000	.000
500	6.298	13.099	10.606	1.246	.000	.000	.000
600	6.416	14.258	11.121	1.882	.000	.000	.000
700	6.504	15.254	11.642	2.528	.000	.000	.000
800	6.563	16.177	12.149	3.182	.000	.000	.000
900	6.613	16.902	12.635	3.841	.000	.000	.000
1000	6.676	17.602	13.097	4.505	.000	.000	.000
1100	6.759	18.242	13.536	5.177	.000	.000	.000
1200	6.850	18.834	13.953	5.857	.000	.000	.000
1300	6.929	19.386	14.350	6.546	.000	.000	.000
1400	6.979	19.902	14.729	7.242	.000	.000	.000
1500	7.007	20.384	15.090	7.941	.000	.000	.000
1600	7.036	20.837	15.435	8.643	.000	.000	.000
1700	7.096	21.265	15.765	9.350	.000	.000	.000
1800	7.200	21.674	16.082	10.064	.000	.000	.000
1900	7.329	22.066	16.387	10.791	.000	.000	.000
2000	7.455	22.445	16.681	11.530	.000	.000	.000
2100	7.580	22.812	16.964	12.281	.000	.000	.000
2200	7.708	23.168	17.238	13.046	.000	.000	.000
2300	7.846	23.513	17.503	13.823	.000	.000	.000
2400	7.997	23.850	17.761	14.615	.000	.000	.000
2500	8.166	24.180	18.011	15.423	.000	.000	.000
2600	8.358	24.504	18.254	16.249	.000	.000	.000
2700	8.578	24.824	18.492	17.096	.000	.000	.000
2800	8.830	25.140	18.724	17.966	.000	.000	.000
2900	9.120	25.455	18.950	18.863	.000	.000	.000
3000	9.452	25.770	19.172	19.791	.000	.000	.000
3100	9.830	26.085	19.390	20.755	.000	.000	.000
3200	10.262	26.404	19.604	21.759	.000	.000	.000
3300	10.747	26.727	19.815	22.809	-8.713	.113	-.007
3400	11.295	27.056	20.023	23.911	-8.611	.379	-.024
3500	11.908	27.392	20.229	25.070	-8.452	.641	-.040
3600	12.592	27.737	20.433	26.295	-8.227	.898	-.054
3700	13.352	28.092	20.635	27.591	-7.931	1.147	-.068
3800	14.191	28.459	20.336	28.968	-7.554	1.388	-.080
3900	15.116	28.840	21.036	30.432	-7.090	1.617	-.091
4000	16.131	29.235	21.236	31.994	-6.528	1.834	-.100

Dec. 31, 1972

TANTALUM (Ta) (CRYSTAL) GFW = 180.947 Ta

$S^\circ_{298.15}$ = 9.91 ± 0.05 gibbs/mol

Tm = 3258 ± 10 K

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

ΔHm° = 8.74 ± 1.0 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for $T \leq 10$ K are chosen to be the same as those adopted by Hultgren et al. (1). A graphical integration of these Cp° data yields S°_{10} = 0.025 gibbs/mol. The adopted Cp° values for the range $10 \leq T \leq$ Tm are based on the following experimental data.

	temperature range, K	method
Kelley (2)	53-295	Cp°
Clusius and Losa (3)	10-273	Cp°
Sterrett and Wallace (4)	12-550	Cp°
Jaeger and Veenstra (5)	300-1554	drop, enthalpy
Oetting and Navritil (6)	533-1383	drop, enthalpy
Cezairliyan (7)	1900-3200	Cp°, pulse heating

The data of Cezairliyan (7), reported as smoothed Cp° values and represented by a third-order polynomial, yields Cp° values from 3200 K to Tm by extrapolation. These smooth Cp° values, as reported by Cezairliyan (7), are adopted for the range 1900-3200 K. Using a polynomial fit for each enthalpy data set (5, 6), Cp° values are obtained which define the region 298-1500 K. A polynomial, constrained at 10 K, is used to produce smoothed Cp°·values in the range 10-298 K based on the three low temperature studies (3, 4, 5).

For T < 100 K, the tabulated values do not agree well with the experimental data. In this region the deviations from the tabulated values are ±5% for Clusius and Losa (3), -0.3 to +1.9% for Kelley (2), and -1.7 to 2.8% for Sterrett and Wallace (4). The deviations are due in part to experimental scatter (3) and a poor match of experimental data at 10 K.

Many other experimental studies have been referenced by Gmelin (8) and Hultgren et al. (1). In addition, Cezairliyan (7) has compared graphically many of the investigations. The Cp° data and enthalpy data are all in generally good agreement. The importance of the recent Cezairliyan study (7) is that it gives added evidence to the deviation from a linear Cp-T relationship above 1000 K.

Melting Data

The melting point of Ta is chosen as 3258 ± 10 K based on the subsecond pulse heating technique of Cezairliyan (7). This choice is made so as to have a Tm consistent with Cp° data at temperatures near Tm (see heat capacity discussion). Other Tm values covering the range 3053-3273 K are referenced by Charlesworth (9); while additional references are found in Gmelin (8). Hultgren et al. (1) recommends a Tm value of 3287 K.

The heat of fusion, ΔHm°, for Ta has been measured by Lebedev, Savvatimskii, and Smirnov (10). They reported a ΔHm° value of 8.74 ± 0.5 kcal/mol based on measurements made during electrical explosion in thin wires. We adopt this value for ΔHm°. Based on ΔHm° = 8.74 kcal/mol and Tm = 3258 K, the entropy of melting, ΔSm°, is calculated to be 2.68 gibbs/mol. This compares with ΔSm° = 2.33 gibbs/mol for Nb, as reported in these tables.

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Tantalum (Ta)
(Liquid) GFW = 180.947

T, °K	Cp°	S°	-(G°-H°₂₉₈)/T	H°-H°₂₉₈	ΔHf°	ΔGf°	Log Kp
	gibbs/mol	gibbs/mol	gibbs/mol	kcal/mol	kcal/mol	kcal/mol	
0							
100							
200							
298	6.046	12.091	12.091	.000	7.476	6.826	-5.004
300	6.049	12.129	12.091	.011	7.476	6.823	-4.970
400	6.176	13.887	12.330	.623	7.476	6.604	-3.608
500	6.298	15.278	12.785	1.246	7.477	6.387	-2.792
600	6.416	16.437	13.300	1.882	7.476	6.169	-2.247
700	6.504	17.433	13.821	2.528	7.477	5.951	-1.858
800	6.563	18.306	14.328	3.182	7.476	5.733	-1.566
900	6.613	19.082	14.814	3.841	7.476	5.515	-1.339
1000	6.676	19.781	15.276	4.505	7.476	5.297	-1.158
1100	6.759	20.422	15.715	5.177	7.476	5.079	-1.009
1200	6.850	21.014	16.133	5.857	7.476	4.861	-.885
1300	6.929	21.565	16.530	6.546	7.477	4.644	-.781
1400	6.979	22.081	16.908	7.242	7.476	4.425	-.691
1500	7.007	22.563	17.269	7.941	7.477	4.208	-.613
1600	7.036	23.016	17.614	8.643	7.477	3.990	-.545
1700	7.096	23.444	17.945	9.350	7.476	3.771	-.485
1800	7.200	23.853	18.262	10.064	7.476	3.554	-.431
1900	7.329	24.246	18.566	10.791	7.476	3.335	-.384
2000	7.455	24.625	18.860	11.530	7.476	3.118	-.341
2100	7.580	24.991	19.143	12.281	7.477	2.900	-.302
2200	10.000	25.347	19.417	13.046	7.476	2.682	-.266
2300	10.000	25.791	19.685	14.046	7.699	2.459	-.234
2400	10.000	26.217	19.948	15.046	7.907	2.227	-.203
2500	10.000	26.625	20.207	16.046	8.099	1.986	-.174
2600	10.000	27.017	20.461	17.046	8.273	1.738	-.146
2700	10.000	27.395	20.711	18.046	8.426	1.484	-.120
2800	10.000	27.759	20.956	19.046	8.556	1.224	-.096
2900	10.000	28.109	21.197	20.046	8.659	.961	-.072
3000	10.000	28.448	21.433	21.046	8.731	.694	-.051
3100	10.000	28.776	21.665	22.046	8.767	.425	-.030
3200	10.000	29.094	21.892	23.046	8.763	.156	-.011
3300	10.000	29.402	22.115	24.046	.000	.000	.000
3400	10.000	29.700	22.334	25.046	.000	.000	.000
3500	10.000	29.990	22.548	26.046	.000	.000	.000
3600	10.000	30.272	22.759	27.046	.000	.000	.000
3700	10.000	30.546	22.966	28.046	.000	.000	.000
3800	10.000	30.812	23.169	29.046	.000	.000	.000
3900	10.000	31.072	23.368	30.046	.000	.000	.000
4000	10.000	31.325	23.564	31.046	.000	.000	.000
4100	10.000	31.572	23.756	32.046	.000	.000	.000
4200	10.000	31.813	23.945	33.046	.000	.000	.000
4300	10.000	32.049	24.131	34.046	.000	.000	.000
4400	10.000	32.278	24.313	35.046	.000	.000	.000
4500	10.000	32.503	24.493	36.046	.000	.000	.000
4600	10.000	32.723	24.669	37.046	.000	.000	.000
4700	10.000	32.938	24.843	38.046	.000	.000	.000
4800	10.000	33.149	25.014	39.046	.000	.000	.000
4900	10.000	33.355	25.182	40.046	.000	.000	.000
5000	10.000	33.557	25.348	41.046	.000	.000	.000
5100	10.000	33.755	25.510	42.046	.000	.000	.000
5200	10.000	33.949	25.671	43.046	.000	.000	.000
5300	10.000	34.139	25.829	44.046	.000	.000	.000
5400	10.000	34.326	25.984	45.046	.000	.000	.000
5500	10.000	34.510	26.138	46.046	.000	.000	.000
5600	10.000	34.690	26.289	47.046	.000	.000	.000
5700	10.000	34.867	26.438	48.046	.000	.000	.000
5800	10.000	35.041	26.585	49.046	-176.348	.224	-.008
5900	10.000	35.212	26.730	50.046	-176.346	3.269	-.121
6000	10.000	35.380	26.872	51.046	-176.348	6.312	-.230

Dec. 31, 1972

TANTALUM (Ta) (LIQUID) GFW = 180.947 Ta

$S^\circ_{298.15}$ = 12.080 gibbs/mol

Tm = 3258 ± 10 K

Tb = 5786 K

$\Delta Hf^\circ_{298.15}$ = 7.486 kcal/mol

ΔHm° = 8.74 ± 1.0 kcal/mol

ΔHv° = 176.148 kcal/mol

Heat of Formation

The heat of formation of Ta(ℓ) at 2 8.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{3258} - H^\circ_{298}$ for Ta(c) and Ta(ℓ).

Heat Capacity and Entropy

The heat capacity for Ta(ℓ) is estimated as 10.0 cal/mol by analogy with other monatomic metals. The same value was adopted by Hultgren et al. (1) and Stull and Sinke (2). A glass transition is assumed at 2200 K. Below this temperature, the heat capacity values used are those of Ta(c). The entropy at 298.15 K is calculated in a manner similar to that for $\Delta Hf^\circ_{298.15}$.

Melting Data

See Ta(c) table for details.

Vaporization Data

Tb is the temperature at which the Gibbs energy change for the reaction Ta(ℓ) → Ta(g) approaches zero. The difference between ΔHf°(Ta, g) and ΔHf°(Ta, ℓ) at Tb is ΔHv°. Thus, Tb is calculated to be 5786 K and ΔHv° is 176.148 kcal/mol. The uncertainty in the boiling point is probably of the order of ±200 K.

References

1. R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Ta table, August, 1971.
2. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956.

Ta

Tantalum (Ta)

(Ideal Gas) GFW = 180.947

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 1.482	186.776	186.776	INFINITE
100	4.968	38.813	48.662	- .985	187.035	183.540	- 401.125
200	4.968	42.256	44.697	- .488	186.993	180.051	- 196.751
298	4.985	44.242	44.242	.000	186.900	176.665	- 129.499
300	4.986	44.272	44.242	.009	186.898	176.601	- 128.654
400	5.081	45.717	44.438	.512	186.789	173.185	- 94.624
500	5.278	46.871	44.813	1.029	186.683	169.797	- 74.218
600	5.541	47.855	45.240	1.569	186.587	166.429	- 60.622
700	5.827	48.731	45.677	2.138	186.510	163.076	- 50.915
800	6.109	49.528	46.109	2.735	186.453	159.732	- 43.637
900	6.376	50.263	46.530	3.359	186.418	156.394	- 37.978
1000	6.621	50.947	46.938	4.009	186.404	153.059	- 33.451
1100	6.843	51.589	47.332	4.683	186.406	149.724	- 29.747
1200	7.043	52.193	47.712	5.377	186.420	146.390	- 26.661
1300	7.221	52.764	48.079	6.090	186.444	143.053	- 24.049
1400	7.377	53.305	48.433	6.820	186.478	139.714	- 21.810
1500	7.514	53.819	48.775	7.565	186.524	136.372	- 19.869
1600	7.633	54.308	49.106	8.323	186.580	133.027	- 18.171
1700	7.738	54.774	49.426	9.091	186.641	129.677	- 16.671
1800	7.831	55.219	49.735	9.870	186.706	126.325	- 15.338
1900	7.915	55.644	50.035	10.657	186.766	122.968	- 14.145
2000	7.992	56.052	50.326	11.453	186.823	119.609	- 13.070
2100	8.062	56.444	50.608	12.255	186.874	116.248	- 12.098
2200	8.129	56.820	50.882	13.065	186.919	112.883	- 11.214
2300	8.192	57.183	51.148	13.881	186.958	109.517	- 10.407
2400	8.252	57.533	51.407	14.703	186.988	106.150	- 9.666
2500	8.310	57.871	51.659	15.531	187.008	102.781	- 8.985
2600	8.367	58.198	51.904	16.365	187.016	99.412	- 8.356
2700	8.421	58.515	52.143	17.205	187.009	96.042	- 7.774
2800	8.475	58.822	52.376	18.049	186.983	92.673	- 7.233
2900	8.527	59.121	52.603	18.900	186.937	89.306	- 6.730
3000	8.579	59.411	52.825	19.755	186.864	85.941	- 6.261
3100	8.630	59.693	53.042	20.615	186.760	82.578	- 5.822
3200	8.680	59.967	53.255	21.481	186.622	79.220	- 5.410
3300	8.730	60.235	53.462	22.351	177.729	75.978	- 5.032
3400	8.780	60.497	53.665	23.227	177.605	72.897	- 4.686
3500	8.831	60.752	53.864	24.107	177.485	69.819	- 4.360
3600	8.881	61.001	54.059	24.993	177.371	66.744	- 4.052
3700	8.931	61.245	54.250	25.884	177.262	63.673	- 3.761
3800	8.982	61.484	54.437	26.779	177.157	60.604	- 3.486
3900	9.034	61.718	54.621	27.680	177.058	57.539	- 3.224
4000	9.085	61.948	54.801	28.586	176.964	54.475	- 2.976
4100	9.138	62.173	54.978	29.497	176.875	51.414	- 2.741
4200	9.190	62.393	55.152	30.414	176.792	48.355	- 2.516
4300	9.243	62.610	55.323	31.335	176.713	45.298	- 2.302
4400	9.296	62.823	55.491	32.262	176.640	42.243	- 2.098
4500	9.349	63.033	55.656	33.194	176.572	39.189	- 1.903
4600	9.401	63.239	55.819	34.132	176.510	36.137	- 1.717
4700	9.454	63.442	55.979	35.075	176.453	33.086	- 1.538
4800	9.506	63.641	56.136	36.023	176.401	30.036	- 1.368
4900	9.557	63.838	56.292	36.976	176.354	26.987	- 1.204
5000	9.608	64.031	56.445	37.934	176.312	23.939	- 1.046
5100	9.658	64.222	56.595	38.897	176.275	20.892	- .895
5200	9.706	64.410	56.744	39.866	176.244	17.846	- .750
5300	9.753	64.595	56.890	40.839	176.217	14.800	- .610
5400	9.799	64.778	57.034	41.816	176.194	11.755	- .476
5500	9.843	64.958	57.177	42.798	176.176	8.710	- .346
5600	9.885	65.136	57.317	43.785	176.163	5.665	- .221
5700	9.925	65.311	57.456	44.775	176.153	2.621	- .100
5800	9.963	65.484	57.593	45.770	.000	.000	.000
5900	10.000	65.655	57.728	46.768	.000	.000	.000
6000	10.033	65.823	57.862	47.769	.000	.000	.000

Dec. 31, 1972

TANTALUM (Ta) (IDEAL GAS) GFW = 180.947 Ta

Ground State Configuration $^4F_{3/2}$

$S°_{298.15}$ = 44.24 ± 0.1 gibbs/mol

$\Delta Hf°_0$ = 186.8 ± 0.5 kcal/mol

$\Delta Hf°_{298.15}$ = 186.9 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	4	9975.81	4	15114.14	12	24464.40	178
2010.10	6	11243.63	6	15391.01	10	27069.76	194
3963.92	8	12234.76	8	17224.47	6	33208.26	232
5621.04	10	13351.45	10	17383.12	8	38215.11	214
6049.42	2	10950.22	4	17384.65	4	40824.27	162
6068.91	4	11792.13	2	19178.45	6	44807.65	140
9253.43	6	11796.14	6	17993.74	6	43058.29	174
9705.38	8	12865.97	6	18504.72	2	46653.36	248
10690.32	10	15903.77	4	19657.78	4	53050.07	134
9758.97	2	14875.70	6	22506.24	90		

Heat of Formation

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

			$\Delta Hs°_{298}$, kcal/mol		drift
Source	Range, K	Points	2nd Law	3rd Law	gibbs/mol
Edwards, Johnston, and Blackburn (1)	2628-2952	7	190.0±3.0	186.9	-1.1±1.1
Langmuir and Malter (2)	2004-3269	16*	183.0	186.9	1.5
Fiske (3)	2637-2854	7	151.9±10.1	182.6	11.2±3.7
Gebhardt, Seghezzi, and Keil (4)	2904-3155	8**	233.1	190.3	-14.2

* Only smooth data was reported; however, 16 refers to the number of experimental determinations.

** Only smooth data reported.

These four studies are based on the Langmuir method.

Babeliowsky (5) reported a heat of sublimation value of 168.4 ± 4.0 kcal/mol. This value is based on mass spectrometric vaporization studies and is calculated by the second law method. Sasaki et al. (6), also using a mass spectrometer, reported a heat of sublimation value of 185.4 ± 0.3 kcal/mol as an average value in the range 2550-2770 K. The value chosen for the heat of sublimation which, in this case, is the heat of formation of Ta(g) is 186.9 ± 0.5 kcal/mol, based on the work of Edwards et al. (1) and Langmuir and Malter (2).

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore (7). Above the level ε_i = 19657.78 cm^{-1}, the values of ε_i and g_i listed are average values calculated from those given by Moore (7). There are predicted electronic levels which have not been observed (7). These levels are assumed to lie above 20000 cm^{-1} and thus will not significantly affect the entropy at temperatures below 3000 K. The heat capacity and entropy values are very similar to those adopted by Hultgren et al. (8), being identical at 298 K and differing by 0.154 gibbs/mol in Cp° and 0.04 gibbs/mol in S° at 6000 K.

References

1. J. W. Edwards, H. L. Johnston, and P. E. Blackburn, J. Amer. Chem. Soc. 73, 4727 (1951).
2. D. B. Langmuir and L. Malter, Phys. Rev. 55, 748 (1939).
3. R. Fiske, Phys. Rev. 61, 513 (1942).
4. E. Gebhardt, H. Seghezzi, and H. Keil, Z. Metallk. 53, 524 (1962).
5. T. P. Babeliowsky, Physica 28, 1160 (1962).
6. N. Sasaki, K. Kubo, and M. Asano, Shitsuryo Bunsiki 18, 1189 (1970).
7. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. II, 1952.
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Ta

Vanadium (V)

(Reference State) GFW = 50.9414

	gibbs/mol			kcal/mol			
T, °K	Cp°	S°	$-(G°-H°_{298})/T$	$H°-H°_{298}$	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.109	.000	.000	.000
100	3.136	1.717	11.637	-.992	.000	.000	.000
200	5.228	4.674	7.439	-.553	.000	.000	.000
298	5.950	6.915	6.915	.000	.000	.000	.000
300	5.958	6.952	6.915	.011	.000	.000	.000
400	6.270	8.713	7.153	.624	.000	.000	.000
500	6.440	10.131	7.612	1.260	.000	.000	.000
600	6.570	11.317	8.133	1.910	.000	.000	.000
700	6.700	12.339	8.662	2.574	.000	.000	.000
800	6.850	13.243	9.180	3.251	.000	.000	.000
900	7.020	14.060	9.677	3.944	.000	.000	.000
1000	7.190	14.808	10.153	4.655	.000	.000	.000
1100	7.380	15.502	10.608	5.383	.000	.000	.000
1200	7.600	16.154	11.044	6.132	.000	.000	.000
1300	7.825	16.771	11.461	6.903	.000	.000	.000
1400	8.080	17.360	11.861	7.698	.000	.000	.000
1500	8.320	17.926	12.247	8.518	.000	.000	.000
1600	8.570	18.470	12.619	9.363	.000	.000	.000
1700	8.850	18.998	12.979	10.234	.000	.000	.000
1800	9.130	19.512	13.327	11.132	.000	.000	.000
1900	9.450	20.014	13.666	12.061	.000	.000	.000
2000	9.780	20.507	13.996	13.022	.000	.000	.000
2100	10.150	20.993	14.317	14.018	.000	.000	.000
2200	11.043	23.970	14.643	20.520	.000	.000	.000
2300	11.043	24.461	15.059	21.624	.000	.000	.000
2400	11.043	24.931	15.461	22.728	.000	.000	.000
2500	11.043	25.382	15.849	23.832	.000	.000	.000
2600	11.043	25.815	16.224	24.937	.000	.000	.000
2700	11.043	26.232	16.587	26.041	.000	.000	.000
2800	11.043	26.633	16.939	27.145	.000	.000	.000
2900	11.043	27.021	17.280	28.250	.000	.000	.000
3000	11.043	27.395	17.611	29.354	.000	.000	.000
3100	11.043	27.757	17.932	30.458	.000	.000	.000
3200	11.043	28.108	18.245	31.563	.000	.000	.000
3300	11.043	28.448	18.549	32.667	.000	.000	.000
3400	11.043	28.778	18.845	33.771	.000	.000	.000
3500	11.043	29.098	19.133	34.875	.000	.000	.000
3600	11.043	29.409	19.414	35.980	.000	.000	.000
3700	6.905	58.611	19.737	143.831	.000	.000	.000
3800	7.022	58.796	20.763	144.528	.000	.000	.000
3900	7.142	58.980	21.740	145.236	.000	.000	.000
4000	7.265	59.163	22.674	145.956	.000	.000	.000
4100	7.389	59.344	23.566	146.689	.000	.000	.000
4200	7.514	59.523	24.420	147.434	.000	.000	.000
4300	7.640	59.701	25.238	148.192	.000	.000	.000
4400	7.766	59.878	26.023	148.962	.000	.000	.000
4500	7.892	60.054	26.778	149.745	.000	.000	.000
4600	8.016	60.229	27.503	150.540	.000	.000	.000
4700	8.140	60.403	28.201	151.348	.000	.000	.000
4800	8.262	60.576	28.874	152.168	.000	.000	.000
4900	8.383	60.747	29.523	153.001	.000	.000	.000
5000	8.501	60.918	30.149	153.845	.000	.000	.000
5100	8.616	61.087	30.754	154.701	.000	.000	.000
5200	8.729	61.256	31.339	155.568	.000	.000	.000
5300	8.839	61.423	31.905	156.446	.000	.000	.000
5400	8.946	61.589	32.453	157.336	.000	.000	.000
5500	9.050	61.754	32.984	158.235	.000	.000	.000
5600	9.150	61.918	33.499	159.145	.000	.000	.000
5700	9.246	62.081	33.999	160.065	.000	.000	.000
5800	9.340	62.243	34.485	160.995	.000	.000	.000
5900	9.429	62.403	34.957	161.933	.000	.000	.000
6000	9.515	62.562	35.416	162.880	.000	.000	.000

June 30, 1973

VANADIUM (V) (REFERENCE STATE) GFW = 50.9414 V

0 - 2190 K Crystal

2190 - 3693.8 K Liquid

3693.8 - 6000 K Ideal Gas

See crystal, liquid, monatomic gas tables for details.

V

Vanadium (V)

(Crystal) GFW = 50.9414

T, °K	Cp° (gibbs/mol)	S° (gibbs/mol)	−(G°−H°₂₉₈)/T (gibbs/mol)	H°−H°₂₉₈ (kcal/mol)	ΔHf° (kcal/mol)	ΔGf° (kcal/mol)	Log Kp
0	.000	.000	INFINITE	-1.109	.000	.000	.000
100	3.136	1.717	11.637	-.992	.000	.000	.000
200	5.228	4.674	7.439	-.553	.000	.000	.000
298	5.950	6.915	6.915	.000	.000	.000	.000
300	5.958	6.952	6.915	.011	.000	.000	.000
400	6.270	8.713	7.153	.624	.000	.000	.000
500	6.440	10.131	7.612	1.260	.000	.000	.000
600	6.570	11.317	8.133	1.910	.000	.000	.000
700	6.700	12.339	8.662	2.574	.000	.000	.000
800	6.850	13.243	9.180	3.251	.000	.000	.000
900	7.020	14.060	9.677	3.944	.000	.000	.000
1000	7.190	14.808	10.153	4.655	.000	.000	.000
1100	7.390	15.502	10.608	5.383	.000	.000	.000
1200	7.600	16.154	11.044	6.132	.000	.000	.000
1300	7.325	16.771	11.461	6.903	.000	.000	.000
1400	8.030	17.360	11.861	7.698	.000	.000	.000
1500	8.320	17.926	12.247	8.518	.000	.000	.000
1600	8.570	18.470	12.619	9.363	.000	.000	.000
1700	8.850	18.993	12.979	10.234	.000	.000	.000
1800	9.130	19.512	13.327	11.132	.000	.000	.000
1900	9.450	20.014	13.666	12.061	.000	.000	.000
2000	9.780	20.507	13.996	13.022	.000	.000	.000
2100	10.150	20.993	14.317	14.018	.000	.000	.000
2200	10.595	21.475	14.632	15.055	-5.465	.025	-.002
2300	11.055	21.956	14.940	16.138	-5.486	.275	-.026
2400	11.515	22.437	15.242	17.266	-5.462	.525	-.048
2500	11.975	22.916	15.540	18.441	-5.391	.774	-.068
2600	12.435	23.395	15.832	19.661	-5.276	1.018	-.086
2700	12.890	23.872	16.121	20.928	-5.113	1.257	-.102

June 30, 1973

VANADIUM (V) (CRYSTAL) GFW = 50.9414 V

$S^\circ_{298.15}$ = 6.92 ± 0.10 gibbs/mol

Tm = 2190 ± 20 K

ΔHf°_0 = 0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 0 kcal/mol

ΔHm° = 5.46 ± 1.50 kcal/mol

$\Delta Hs^\circ_{298.15}$ = 123.2 ± 2.0 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for temperatures below 10 K are those chosen by Hultgren (1). A graphical integration yields S°_{10} = 0.0253 gibbs/mol and $H^\circ_{10}-H^\circ_0$ = 0.147 cal/mol. The adopted heat capacity values for 10 ≤ T ≤ 320 K are obtained graphically, based on the following three works.

Source	Year	Range, K	Purity of Vanadium
Anderson (2)	1936	54-297	reported ≥ 99.5%
Clusius et al. (3)	1960	10-274	99.5%; remainder oxygen
Bieganski and Stalinski (4)	1961	25-340	99.8%; metallic impurities <0.08%

The low temperature (T < 50 K) results of Clusius et al. (3) do not join smoothly with the values adopted for T < 10 K. This mismatch is in part due to the oxygen impurity in the vanadium sample used by Clusius et al. (3). In order to effect a smooth joining of the Cp° values, a graphical representation of Cp(lattice)/T^3 versus T for the Hultgren data (1) and the Clusius et al. data (3) was used to derive adjusted Cp° values. The three data sets (2, 3, 4) are in reasonably good agreement; two sets (2, 4) lie predominantly above the adopted values while the remaining set (3) lies below. Above 100 K, the three data sets differ from the adopted Cp° values by roughly 1%, with the difference decreasing as T increases.

For the region 320 ≤ T ≤ 2190, there are four works upon which the adopted Cp° values are based.

Source	Year	Method	Range, K	Purity of Vanadium
Kohlhaas, Braun, and Vollmer (5)	1965	Cp°	320-1800	99.74%
Jaeger and Veenstra (6)	1934	drop	565-1928	reported as "purest"
Golutvin and Kozlovskaya (7)	1962	drop	488-1485	0.1%C, 0.07%O, 0.03%N
Berezin, Chekovskoii, and Sheindlin (8)	1971	levitation	1989-2284	0.06% total impurities

The heat capacity values reported by Kohlhaas et al. (5) are 1-2% lower than the adopted values below 950 K; 0.3% higher in the region 950-1300 K; and 7% lower above 1600 K. The results of Golutvin and Kozlovskaya (7) show considerable scatter and lie roughly 2-10% above the tabulated enthalpy values. The enthalpy data of Jaeger and Veenstra (6) do not join smoothly with that of Berezin et al. (8). In the region 1500-2000 K the adopted enthalpy values are a compromise between the latter two sets of data. Below roughly 1100 K the adopted enthalpy and that reported by Jaeger and Veenstra (6) differ at most by ± 15 cal/mol. From 1300-1800 K the difference increases from 70 cal/mol to 308 cal/mol or from 1.0% to 2.6%. The enthalpy at 2190 K (Tm) is very close to that which is obtained from a linear fit of the Berezin et al. data (8). Whereas the two sets of data (6, 8) separately indicate a Cp° value near Tm to be at least 11 gibbs/mol, the compromise yields 10.5 gibbs/mol.

Melting Data

See V(ℓ) for details.

Transition Data

The literature indicates differences in opinion as to the possibility of a transition in the region 175-325 K and near 1825 K. Although there are no detailed enthalpy measurements in the 1825 K region, Barnes (9) used field-electron emission techniques to show that an allotropic transformation does not occur in vanadium in this region if the samples are of high purity. Earlier work concerning a possible transition in this region was referenced by Barnes (9).

Documentation exists in the literature as to the observation of anomalies in the temperature dependence of some physical properties of vanadium in the range 175-325 K. Although the anomaly was attributed by different workers to an antiferromagnetic transition, a small distortion of the body-centered cubic crystal structure, and impurities, Finkel' et al. (10) recently ascribed the anomaly to a second order phase transition at 230 K. Using low temperature x-ray diffraction techniques in the study of a single crystal of vanadium, Finkel' et al. (10) observed a decrease in crystal lattice symmetry from body-centered cubic (T > 230 K) to tetragonal (T < 230 K). Nevertheless, Crangle and Smith (11) measured the specific heat of polycrystalline vanadium and confirmed the results of Clusius et al. (3) that no appreciable anomaly in Cp° exists in vanadium between 175 and 265 K. We do not adopt a ΔCp or ΔHt value in the two previously mentioned regions.

Sublimation Data

See V(g) for details.

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V

Vanadium (V)

(Liquid) GFW = 50.9414

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0							
100							
200							
298	5.950	8.730	8.730	.000	4.271	3.730	- 2.734
300	5.958	8.767	8.730	.011	4.271	3.726	- 2.715
400	6.270	10.528	8.968	.624	4.271	3.545	- 1.937
500	6.440	11.946	9.427	1.260	4.271	3.363	- 1.470
600	6.570	13.132	9.948	1.910	4.271	3.182	- 1.159
700	6.700	14.154	10.478	2.574	4.271	3.000	- .937
800	6.850	15.058	10.995	3.251	4.271	2.819	- .770
900	7.020	15.875	11.492	3.944	4.271	2.638	- .641
1000	7.190	16.623	11.969	4.655	4.271	2.456	- .537
1100	7.380	17.317	12.424	5.383	4.271	2.274	- .452
1200	7.600	17.969	12.859	6.132	4.271	2.093	- .381
1300	7.825	18.586	13.276	6.903	4.271	1.911	- .321
1400	8.080	19.175	13.676	7.698	4.271	1.730	- .270
1500	11.043	19.741	14.062	8.518	4.271	1.548	- .226
1600	11.043	20.454	14.439	9.623	4.531	1.358	- .185
1700	11.043	21.123	14.813	10.727	4.764	1.152	- .148
1800	11.043	21.754	15.181	11.831	4.970	.934	- .113
1900	11.043	22.351	15.543	12.936	5.146	.705	- .081
2000	11.043	22.918	15.898	14.040	5.289	.467	- .051
2100	11.043	23.457	16.245	15.144	5.397	.223	- .023
2200	11.043	23.970	16.585	16.249	.000	.000	.000
2300	11.043	24.461	16.916	17.353	.000	.000	.000
2400	11.043	24.931	17.241	18.457	.000	.000	.000
2500	11.043	25.382	17.557	19.561	.000	.000	.000
2600	11.043	25.815	17.867	20.666	.000	.000	.000
2700	11.043	26.232	18.169	21.770	.000	.000	.000
2800	11.043	26.633	18.464	22.874	.000	.000	.000
2900	11.043	27.021	18.752	23.979	.000	.000	.000
3000	11.043	27.395	19.034	25.083	.000	.000	.000
3100	11.043	27.757	19.310	26.187	.000	.000	.000
3200	11.043	28.108	19.579	27.292	.000	.000	.000
3300	11.043	28.449	19.843	28.396	.000	.000	.000
3400	11.043	28.778	20.101	29.500	.000	.000	.000
3500	11.043	29.098	20.353	30.604	.000	.000	.000
3600	11.043	29.409	20.601	31.709	.000	.000	.000
3700	11.043	29.711	20.843	32.813	- 106.747	.181	- .011
3800	11.043	30.006	21.080	33.917	- 106.340	3.065	- .176
3900	11.043	30.293	21.313	35.022	- 105.943	5.938	- .333
4000	11.043	30.572	21.541	36.126	- 105.559	8.803	- .481
4100	11.043	30.845	21.764	37.230	- 105.188	11.657	- .621
4200	11.043	31.111	21.984	38.335	- 104.828	14.502	- .755
4300	11.043	31.371	22.199	39.439	- 104.482	17.339	- .881
4400	11.043	31.625	22.410	40.543	- 104.148	20.169	- 1.002
4500	11.043	31.873	22.618	41.647	- 103.827	22.990	- 1.117

June 30, 1973

VANADIUM (V) (LIQUID) GFW = 50.9414 V

$S^\circ_{298.15}$ = 8.730 gibbs/mol
Tm = 2190 ± 20 K
Tb = 3693.8 K

$\Delta Hf^\circ_{298.15}$ = 4.271 kcal/mol
ΔHm° = 5.46 ± 1.50 kcal/mol
ΔHv° = 106.773 kcal/mol

Heat of Formation

The heat of formation of V(ℓ) at 298.15 K is calculated from that of the crystal by adding ΔHm° and the difference between $H^\circ_{2190}-H^\circ_{298}$ for V(c) and V(ℓ). Refer to V(g) table for an additional ΔHf°_{298} value as derived from effusion-mass spectrometric work (10).

Heat Capacity and Entropy

Enthalpy data in the liquid phase have been reported by Treverton and Margrave (1) and Berezin et al. (2). Using levitation calorimetry, Treverton and Margrave (1) determined the enthalpy of V(ℓ) in the range 2205-2638 K. They reported a least squares analysis of the enthalpy data in the form $H_T^\circ-H^\circ_{298}$ = 11.6527 T-5837.7 where T is degrees Kelvin and the enthalpy difference is in cal/mol. The standard deviation of the experimental points from the calculated ones was ±167 cal/mol. Berezin et al. (2) also used a form of levitation calorimetry and measured enthalpies in the region 1990-2325 K. For the liquid region their data were represented by $H_T^\circ-H^\circ_{298}$ = 11.043 T-3776, with a standard deviation of ±90 cal/mol. These two works agree remarkably well for the Cp° value of V(ℓ). In the measured enthalpy region, the Treverton and Margrave data (1) lie lower than the Berezin et al. data (2) by roughly 600-700 cal/mol. The two linear representations of the data intersect at 3380 K. We adopt the enthalpy values of Berezin et al. (2) since this work contains enthalpy data surrounding the melting point and a Tm value which is our adopted value.

Melting Data

The adopted value of the heat of fusion, ΔHm° = 5.46 ± 1.50 kcal/mol is based on the work by Berezin et al. (2). The actual value is calculated by taking the difference in the adopted value of $H^\circ_{2190}-H^\circ_{298}$ for V(ℓ) and V(c). Refer to the heat capacity discussion in the tables for V(c) and V(ℓ).

Preliminary results of experiments by Berezin et al..(2) indicated that Tm for 99.96% pure vanadium was close to 2190 K. Representative values of Tm reported in the literature are tabulated below.

Source	Purity of V	Tm,K
Storms and McNeal (3)	0.33% O, 0.078% N, 0.15% of 7 other impurities	2161 ± 10
Oriani and Jones (4)	99.8-99.9%	2192 ± 2
Kocherzhinskii et al. (5)	purity not given, purified by electron zone fusion	2223
Adenstedt et al. (6)	99.8%	2173 ± 25
McPherson (7)	purity not given	2193

We adopt Tm = 2190 ± 20 K principally since it is consistent with the work upon which ΔHm° is based. The adopted Tm value is also suggested by Charlesworth (8) in his compilation of elemental melting points.

Vaporization Data

The vaporization of V(ℓ) was studied by Farber and Srivastava (10). Refer to V(g) table for details. Kant and Lin (9), using a combination of effusion and mass-spectrometric techniques, reported the ratio of observed ion intensities relating to V_2(g) and V(g) and corresponding to the vaporization of vanadium in the range 2060-2316 K: This ratio is of the order of 10^{-6} which suggests that at least in this region the contribution of V_2(g) in the vapor phase may be neglected. Linearly extrapolating these data to Tb the V_2 partial pressure is of the order of 10^5 smaller than the V partial pressure.

Tb is calculated as the temperature at which the Gibbs energy change for the reaction V(ℓ) → V(g) approaches zero. The difference between ΔHf°(V, g) and ΔHf°(V, ℓ) at Tb is ΔHv°. Thus, Tb is calculated to be 3693.8 K and ΔHv° is 106.773 kcal/mol. The uncertainty in Tb is probably of the order of ±50 K.

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V

Vanadium (V)

(Ideal Gas) GFW = 50.9414

T, °K	Cp°	S°	−(G°−H°298)/T	H°−H°298	ΔHf°	ΔGf°	Log Kp
	gibbs/mol			kcal/mol			
0	.000	.000	INFINITE	−1.890	122.419	122.419	INFINITE
100	6.702	36.262	49.372	−1.311	122.881	119.427	−261.006
200	6.683	40.962	44.127	−.633	123.120	115.862	−126.608
298	6.217	43.544	43.543	.000	123.200	112.279	−82.303
300	6.209	43.582	43.544	.011	123.200	112.211	−81.746
400	5.891	45.319	43.783	.615	123.191	108.548	−59.308
500	5.783	46.619	44.225	1.197	123.137	104.893	−45.849
600	5.804	47.674	44.715	1.775	123.065	101.251	−36.881
700	5.875	48.573	45.203	2.359	122.985	97.621	−30.479
800	5.949	49.363	45.675	2.950	122.899	94.004	−25.681
900	6.003	50.067	46.124	3.548	122.804	90.398	−21.952
1000	6.032	50.701	46.551	4.150	122.695	86.802	−18.971
1100	6.038	51.276	46.955	4.754	122.571	83.219	−16.534
1200	6.026	51.801	47.337	5.357	122.425	79.648	−14.506
1300	6.003	52.283	47.699	5.959	122.256	76.090	−12.792
1400	5.974	52.727	48.043	6.558	122.060	72.546	−11.325
1500	5.942	53.138	48.369	7.153	121.835	69.017	−10.056
1600	5.912	53.520	48.679	7.746	121.583	65.503	−8.947
1700	5.886	53.878	48.974	8.336	121.302	62.007	−7.972
1800	5.865	54.214	49.256	8.923	120.991	58.528	−7.106
1900	5.850	54.530	49.525	9.509	120.648	55.067	−6.334
2000	5.842	54.830	49.783	10.094	120.272	51.625	−5.641
2100	5.843	55.115	50.030	10.678	119.860	48.203	−5.017
2200	5.851	55.387	50.268	11.262	113.942	44.826	−4.453
2300	5.868	55.648	50.496	11.848	113.424	41.696	−3.962
2400	5.893	55.898	50.716	12.436	112.908	38.588	−3.514
2500	5.926	56.139	50.928	13.027	112.395	35.503	−3.104
2600	5.968	56.372	51.133	13.622	111.885	32.436	−2.727
2700	6.018	56.598	51.331	14.221	111.380	29.391	−2.379
2800	6.076	56.818	51.523	14.826	110.881	26.363	−2.058
2900	6.142	57.033	51.710	15.436	110.386	23.353	−1.760
3000	6.216	57.242	51.891	16.054	109.900	20.360	−1.483
3100	6.296	57.447	52.066	16.680	109.422	17.384	−1.226
3200	6.384	57.648	52.238	17.314	108.951	14.422	−.985
3300	6.478	57.846	52.405	17.957	108.490	11.475	−.760
3400	6.577	58.041	52.568	18.609	108.038	8.543	−.549
3500	6.682	58.233	52.727	19.272	107.597	5.623	−.351
3600	6.792	58.423	52.882	19.946	107.166	2.715	−.165
3700	6.905	58.611	53.035	20.631	.000	.000	.000
3800	7.022	58.796	53.184	21.327	.000	.000	.000
3900	7.142	58.980	53.330	22.035	.000	.000	.000
4000	7.265	59.163	53.474	22.756	.000	.000	.000
4100	7.389	59.344	53.615	23.488	.000	.000	.000
4200	7.514	59.523	53.753	24.234	.000	.000	.000
4300	7.640	59.701	53.889	24.991	.000	.000	.000
4400	7.766	59.878	54.024	25.761	.000	.000	.000
4500	7.892	60.054	54.156	26.544	.000	.000	.000
4600	8.016	60.229	54.286	27.340	.000	.000	.000
4700	8.140	60.403	54.414	28.148	.000	.000	.000
4800	8.262	60.576	54.541	28.968	.000	.000	.000
4900	8.383	60.747	54.665	29.800	.000	.000	.000
5000	8.501	60.918	54.789	30.644	.000	.000	.000
5100	8.616	61.087	54.911	31.500	.000	.000	.000
5200	8.729	61.256	55.031	32.367	.000	.000	.000
5300	8.839	61.423	55.150	33.246	.000	.000	.000
5400	8.946	61.589	55.268	34.135	.000	.000	.000
5500	9.050	61.754	55.384	35.035	.000	.000	.000
5600	9.150	61.918	55.499	35.945	.000	.000	.000
5700	9.246	62.081	55.613	36.865	.000	.000	.000
5800	9.340	62.243	55.726	37.794	.000	.000	.000
5900	9.429	62.403	55.838	38.733	.000	.000	.000
6000	9.515	62.562	55.949	39.680	.000	.000	.000

June 30, 1973

VANADIUM (V) (IDEAL GAS) GFW = 50.9414 V

Ground State Configuration $^4F_{3/2}$

$S^\circ_{298.15}$ = 43.54 ± 0.20 gibbs/mol

ΔHf°_0 = 122.4 ± 2.0 kcal/mol

$\Delta Hf^\circ_{298.15}$ = 123.2 ± 2.0 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i	ε_i, cm^{-1}	g_i
0.00	4	8412.94	2	13801.53	4	22994.61	210
137.38	6	8476.20	4	13810.90	2	27221.15	162
323.42	8	8578.52	6	14514.75	4	32690.11	352
553.02	10	8715.72	8	14548.83	6	37164.15	460
2112.32	2	9544.54	2	14910.04	8	38876.69	252
2153.20	4	9636.96	4	14949.30	10	41568.79	460
2220.13	6	9824.58	6	15000.84	12	43986.17	376
2311.37	8	10892.50	8	15062.94	14	45807.86	306
2424.89	10	11100.65	10	17325.75	266	48676.78	330
						50996.16	360

Heat of Formation

The vapor pressure over vanadium was measured by Edwards et al. (1) using the Knudsen method and by Farber and Srivastava (6) using effusion-mass spectrometric techniques. Our second and third law analysis is tabulated below, where reaction (A) refers to the sublimation V(c) = V(g) and reaction (B), the vaporization V(ℓ) = V(g).

reference	reaction	no. pts	range	ΔHr°_{298}, kcal/mol 2nd law	3rd law	drift, eu
1	A	12*	1666-1882 K	121.67±0.99	122.95	0.72±0.55
6	A	7	1900-2155 K	121.60±1.48	123.45	0.91±0.73
6	B	6	2198-2412 K	113.04±5.34	119.18	2.65±2.30

*A statistical test discounted the 1766 K data point.

We adopt ΔHf°_{298} = 123.2 kcal/mol for V(g). This value, which is identical to ΔHs°_{298}, is a median of the two sublimation studies. Hultgren et al. (2) reported a third law value of 123.089 ± 0.250 kcal/mol based on a Knudsen vapor pressure study in the range 1771-1880 K by Saxer (3). This result is consistent with our adopted value.

The results of Kant and Lin (5) indicated that the partial pressure of $V_2(g)$ is negligible in the temperature ranges studied above.

Heat Capacity and Entropy

The electronic energy levels and quantum weights are obtained from Moore (4). Above the level ε_i = 15062.94 cm^{-1}, the values of ε_i and g_i tabulated are average values calculated from those given by Moore (4). The heat capacity and entropy values are very similar to those adopted by Hultgren et al. (2), being identical at 298.15 K and differing by 0.045 gibbs/mol in Cp° and 0.0.7 gibbs/mol in S° at 3800 K. There are predicted levels which have not been observed and/or classified. It is not expected that S°_{298} would be effected by the missing states, but that in the range 3000-6000 K, an error of 0.2-0.3 eu might result.

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