Thermodynamic Tabulations for Selected Phases in the System $CaO-Al_2O_3-SiO_2-H_2O$ at 101.325 kPa (1 atm) between 273.15 and 1800 K

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The standard thermodynamic properties of phases in the lime-alumina-silica-water system between 273.15 and 1800 K at 101.325 kPa (1 atm) were evaluated from published experimental data. Phases included in the compilation are boehmite, diaspore, gibbsite, kaolinite, dickite, halloysite, andalusite, kyanite, sillimanite, Ca-Al clinopyroxene, anorthite, gehlenite, grossular, prehnite, zoisite, margarite, wollastonite, cyclowollastonite (= pseudowollastonite), larnite, Ca olivine, hatrurite, and rankinite. The properties include heat capacity, entropy, relative enthalpy, and the Gibbs energy function of the phases and the enthalpies, Gibbs energies, and equilibrium constants for formation both from the elements and the oxides. Tabulated values are given at 50 K intervals with the 2-sigma confidence limit at 250 K intervals. Summaries for each phase give the temperature-dependent functions for heat capacity, entropy, and relative enthalpy and the experimental data used in the final evaluation.

Key words: Enthalpy; enthalpy of formation; entropy; equilibrium constant for formation; Gibbs energy function; Gibbs energy of formation; heat capacity; lime-alumina-silica-water; minerals; thermodynamic data.

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1. Introduction

The experimental data on the selected phases (table 1) in the lime-alumina-silica-water system were evaluated using the method of Haas and Fisher (1976). The goal was to produce a set of thermodynamic properties for each phase at a standard state of 1 atm (101.325 kPa) that is consistent with thermodynamic theory, the observed properties of each phase, and the observed phase relations among the phases. The experimental data used in the study came from a literature search through June 1979.

TABLE 1. Phases for which evaluated data are presented in this study

Chemical formula	State	Mineral name
$AlO(OH)$	orthorhombic	boehmite
$AlO(OH)$	orthorhombic	diaspore
$Al(OH)_3$	monoclinic	gibbsite
$Al_2Si_4O_{10}(OH)_2$	monoclinic	pyrophyllite
$Al_2Si_2O_5(OH)_4$	monoclinic	dickite
$Al_2Si_2O_5(OH)_4$	monoclinic	halloysite
$Al_2Si_2O_5(OH)_4$	monoclinic	kaolinite
Al_2SiO_5	orthorhombic	andalusite
Al_2SiO_5	triclinic	kyanite
Al_2SiO_5	orthorhombic	sillimanite
$CaAl_2SiO_6$	monoclinic	(Ca-Al clinopyroxene)
$CaAl_2Si_2O_8$	triclinic	anorthite
$Ca_2Al_2SiO_7$	tetragonal	gehlenite
$Ca_3Al_2Si_3O_{12}$	cubic	grossular
$Ca_2Al_2Si_3O_{10}(OH)_2$	orthorhombic	prehnite
$Ca_2Al_3Si_3O_{12}(OH)$	orthorhombic	zoisite
$CaAl_4Si_2O_{10}(OH)_2$	monoclinic	margarite
$CaSiO_3$	triclinic	cyclowollastonite (= "pseudowollastonite")
$CaSiO_3$	triclinic	wollastonite
Ca_2SiO_4, α	hexagonal, α	
Ca_2SiO_4, α'	orthorhombic, α'	
Ca_2SiO_4, β	monoclinic, β	larnite
Ca_2SiO_4, γ	orthorhombic, γ	(Ca olivine)
Ca_3SiO_5	crystal	(hatrurite and other polymorphs, undifferentiated)
$Ca_3Si_2O_7$	monoclinic	rankinite

2. Nomenclature

The following symbols were used in the text, tables, and data summaries.

Symbol	Units	Meaning
C_p°	J/(mol·K)	standard molar heat capacity
E°	volts	standard electrochemical potential in volts
$[G^\circ(T)-H^\circ(Tr)]/T$	J/(mol·K)	Gibbs energy function
$\Delta G^\circ_{f,e}$	J/mol	standard molar Gibbs energy of formation from the elements
$\Delta G^\circ_{f,ox}$	J/mol	standard molar Gibbs energy of formation from the oxides
H°	J/mol	standard molar enthalpy
$H^\circ(T)-H^\circ(298)$ or $H^\circ(T)-H^\circ(Tr)$	J/mol	relative standard molar enthalpy, base is H° at (Tr=298.15 K), 101.325 kPa
$\Delta H^\circ_{f,e}$	J/mol	standard molar enthalphy of formation from the elements
$\Delta H^\circ_{f,ox}$	J/mol	standard molar enthalpy of formation from the oxides
ΔH°_r	J	standard enthalpy of reaction
$\log K^\circ_{f,e}$		$\log_{10}$ of the standard equilibrium constant for formation from the elements
$\log K^\circ_{f,ox}$		$\log_{10}$ of the standard equilibrium constant for formation from the oxides
P	Pa	obsolute pressure in pascals
S°	J/(mol·K)	standard molar entropy
T	K	absolute temperature in kelvins
Tr	K	reference temperature, absolute scale, equals 298.15 K
V°	cm^3/mol	standard molar volume

Fundamental constants used in this evaluation are given in table 2.

Where possible, the data have been corrected to the International Practical Temperature Scale of 1968 (Comite International des Poids et Measures, 1969). For most phase equilibria, however, this was not possible because the necessary temperature calibration data were not supplied.

The "formula weights" have been calculated to be consistent with the 1975 relative atomic masses for the elements (Commission on Atomic Weights, 1976).

Table 3 gives the sources of data for the thermodynamic properties of the elements and oxides that were used as reference phases in the evaluation procedure. In addition, the Gibbs-energy change for H_2O(gas) between 101.325 kPa and the experimental pressure in experiments on phase equilibria were obtained from Fisher and Zen (1971).

TABLE 2. Fundamental constants and defined constants

Name	Symbol	Value of units
	Fundamental constants	
Avagadro constant	N	6.022094×10^{23} mol^{-1}
Faraday constant	F	96,487.0 J/(volts·mol)
Gas constant	R	8.3143 J/(mol·K)
Absolute temperature of the "ice point," 0 °C		273.15 K
	Defined units	
Standard atmosphere	atm	101.325 kPa
Standard bar	b	100.000 kPa
Thermochemical calorie	cal	4.1840 J

TABLE 3. Reference phases used in the evaluation and the sources for the thermodynamic values on these phases

Phase	$C_p^\circ(T)$	$S^\circ(298)$,$H^\circ_f(298)$,$G^\circ_f(298)$
Al (crystal, liquid)	a	b
Ca (α- and β-crystals, liquid, ideal gas)	a	b
H_2 (ideal gas)	a	b
O_2 (ideal gas)	a	b
Si (crystal, liquid)	a	b
Al_2O_3 (corundum)	c	b
CaO (lime)	c	b
H_2O (liquid, ideal gas)	c	b,d
SiO_2 (α- and β-quartz)	c	b

[a]Hultgren and others (1973).
[b]CODATA Task Group (1978).
[c]Stull and Prophet (1971) and Chase and others (1974, 1975).
[d]Fisher and Zen (1971).

3.1. Introduction

The details of the approach and the procedure are described by Haas and Fisher (1976) and by Haas (1974). The approach and procedure given there have been followed closely and will not be described here in detail. The following description summarizes the evaluation procedure:

1. Literature search

a. Review of literature for data that define thermodynamic properties of a phase or a group of phases.

b. Close scrutiny of each citation to determine:
(1) What was physically observed.
(2) With what precision was it observed.
2. Refinement cycle
a. Comparison of related data (heat capacity, relative enthalpy, enthalpies of formation, enthalpies of reaction, Gibbs energy of reaction, entropies) for phases in a chemical system using weighted, simultaneous, multiple, least-squares regression.
b. Review of the pertinent literature where data are found not to be in agreement.
c. Removal of assumed or apparently erroneous data from the set of data being fit by the regression.
d. Repeat of steps a through c until all discordant data have been identified and removed.
3. Preparation of tables using the smoothing functions and the variance-covariance matrix from the last execution of step 2a.

The mathematical model used in the regression in step 2a is based on eq (1) for the heat capacity at constant pressure and the known relations among heat capacity, enthalpy, entropy, and Gibbs energy for the ith phase in a group of chemically related phases. The constants $a_{2,i}$ and $a_{4,i}$ were reserved for the constants of integration to describe the enthalpy and entropy of the ith phase, respectively. Equation (1) is a restatement of Haas and Fisher's equation (6):

$$C^\circ_{p,i} = \frac{a_{1,i}}{T^2} + \frac{a_{3,i}}{T^{1/2}} + a_{5,i} + 2a_{6,i}T + a_{7,i}T^2 \qquad (1)$$

Equation (1) has no theoretical basis. Equation (1) is a smoothing function only and must be so considered. At the absolute zero of temperature the function is indeterminate. In our work, data at temperatures below 200 K were not considered. Above 200 K, the function readily describes most data. In order to avoid overfitting of the data, nonsignificant constants have been eliminated from the general equation wherever they were not needed to describe the properties of a phase. This is particularly common for the last term, $a_{7,i}T^2$, in eq (1). Removal of this term eliminated any rapid excursions of the calculated values in the temperature region around and above the highest experimental temperature. For some phases (examples in this study are grossular, dickite, halloysite, and kaolinite), the fitting produced functions that contain maxima in the tabulated heat capacities. Each case was examined to determine whether these maxima should be eliminated because they are not theoretically possible without some additional phenomenom. For the clays, the maxima occur at the highest tabulated heat capacities where the functions supply estimates only and no action was taken. Equation (1) has been fit within the temperature range presented for each phase in the appendix and should not be extended indiscriminately to higher or lower temperatures.

For grossular, the experimental heat capacities were measured at or below 978 K. The estimated values used in the fitting for the heat capacity above 1000 K joined smoothly with the experimental data below 1000 K and did not contain a maximum. Therefore, the maximum in the fitted function was a result of the constraints imposed on the thermal data by the phase equilibria that included observations up to 1523 K. In this case, no action was taken. The presence of the maximum emphasizes the need for measured high-temperature heat capacities. Until this has been accomplished, the tabulations are considered the best available.

3.2. Data Entry

Haas (1974) described the mechanics used to fit the model to discrete experimental observations in detail. The typical problem includes the following information:
1. Title for problem.
2. Control codes to identify the options used.
3. Number and labels for the phases in the problem.
4. Sets of data being fit.
   a. Name of the set and reference.
   b. Control codes related to the observation and to data editing.
   c. Label(s) for the phase(s), the stoichiometric coefficient(s) and any pertinent data on polymorphs.
   d. Data as given in the reference.
      (1) Temperature (and correction factor if needed to convert to kelvins).
      (2) Observed value (and correction factor if needed to convert to joules, volts, moles, etc.).
      (3) Precision.
      (4) Second independent variable (if needed).
5. Constants of eq (1) above for each of the reference phases as well as the trial constants for the phases for which the properties are being refined.
6. Control parameters for the error plots.

The input format is designed to reduce manual conversions before entry into the computer for fitting.

The class of data that is not discussed by Haas consists of bracketed observations like those typical of phase equilibria studies. As an example, let us consider reaction A, below.

$$CaAl_2Si_2O_8\text{(anorthite)} + Al_2O_3\text{(corundum)} + H_2O\text{(gas)} = CaAl_4Si_2O_{10}(OH)_2\text{(margarite)} \qquad (A)$$

Chatterjee (1974) determined that the equilibrium at 100 MPa was located between 743.15 and 773.15 K. If we consider no additional information, there is an equal probability of equilibrium occurring at any temperature between these two bracketing temperatures at 100 MPa. Therefore, if we neglect the errors associated with the measurement of temperature and pressure, the probability curve is a square wave whose bounds are at 743.15 K and 773.15 K. To consider the reaction to occur at the midpoint of the bracket, 758.15 K, is unwarranted; this would cause the fitting algorithms to give too much weight to the midpoints of bracketed data. We evaluated the phase equilibrium data by calculating the Gibbs energy of reaction at 101.325 kPa for each two experimentally measured bracketing pressures and temperatures as if each bracketing pressure and temperature represented equilibrium. This procedure does not define a square probability curve between the bracketing values but does define a nearly uniform probability between the bracketing values and allows a sufficient probability of occurrence outside the bracketing values to compensate for errors in measurement of pressure and temperature. The Gibbs energy for the reaction at 101.325 kPa for both bracketing temperatures (or bracketing pressures in some cases) is calculated using the following formula:

$$\Delta G^\circ(\text{reaction}) = \frac{1}{1000}\Delta V^\circ(\text{reaction, solids})\,(101.325\text{--}10^5) + \frac{(-1)}{1000}\int_{10^5}^{101.325} V^\circ(H_2O)dP_T \quad (2)$$

where ΔV° (reaction, solids) is the volume change between the solid product, margarite, and the solid reactants, anorthite and corundum, expressed in cm^3/mol. The difference (101.325–10^5) is the pressure difference in kPa. The factor 1000 is the conversion factor for cm^3/mol to J/(kPa·mol). The integral represents the Gibbs energy difference of H_2O between 10^5 and 101.325 kPa. The term (–1) is the stoichiometric coefficient of H_2O(gas) in reaction A. The Gibbs energy difference for H_2O at constant temperature was calculated from data in Fisher and Zen (1971). We expect to replace this method of estimation in the near future with one based on the *P-V-T* function proposed by Haar and others (in press). Equation 2 neglects the compressibility and thermal expansion of the solids. If thermal expansion and compressibility data are available for the solid phases, these corrections can be added.

3.3. Weighting of Experimental Data

Data were weighted by the reciprocal of the precision; the higher (smaller in magnitude) the precision, the higher (larger in magnitude) the weight. The use of weighting served two purposes. First, it allowed the simultaneous fitting of different properties that have large variations in magnitude. An example is the simultaneous fitting of enthalpy data that could exceed 7 MJ and electrochemical potentials that are more like 1.0 millivolt. Second, weighting constrained the solution towards the more precise observations. This was particularly desirable where precise data from low-temperature, adiabatic calorimetry were being matched with the less precise data from differential scanning calorimetry or from drop calorimetry.

In the first fitting of a data set from a particular reference, the author's stated precision was used. In subsequent cycles this would be modified if logic or other data showed the author's estimate to be unrealistically small.

Weighting of data within the above guideline was straightforward with two exceptions. The first exception is when the author makes many observations of a phenomenon but only reports an average value and the standard deviation. To enter one value, the average value, would underweight the work that went into the determination relative to the significance of discrete measurements on the same or other properties. We arbitrarily overcame this by making three entries: (1) the average value, (2) the average value less the deviation, and (3) the average value plus the deviation. All three entries had a weight equal to the stated standard deviation.

The second exception is related to the treatment of brackets in phase equilibria. As stated in the preceeding section, the Gibbs energy at 101.325 kPa for both temperature limits (or pressure limits or their combination that defines the bracket) was entered. The weight was calculated from the arbitrary decision that the precision for each bracket was the difference in Gibbs energy for the bracket with the constraint that the magnitude of the assigned precision was equal to or greater than the precision associated with the determination of the temperature (or pressure) of the limit of the bracket. In this fashion, we reduced the tendency of the regression to settle on the midpoint of a bracket. We will return to this point again when we consider the topic of data rejection.

3.4. Data Rejection

Data were rejected during the literature search and during the refinement cycles. Data were rejected during the literature search if there was a clear error in the measurement technique or if there was ambiguity in the identification of the reactants or products.

During the refinement cycle, where all data for all phases in the chemical system are simultaneously fit by the model, the model returns the weighted average of all the data. Error plots such as figure 1 are part of the printed output. On the error plots for each source and type of data, the weighted difference, calculated as (observed – calculated)/precision, is plotted as a function of temperature. These plots give a quick visual picture of the quality of the agreement between the function in the model, the other data in the refinement, and the specific data set. Ideally, the errors should be centered about the zero axis and should not exceed $\pm$ 2 units ($\pm$ 2s). Not attaining such an ideal plot can be the result of one or more of the following:

1. The function does not adequately describe the data.
2. Some set (or sets) of data is not consistent with the balance of the data considered.
3. The magnitude of the experimental precision is larger than that which the author stated. As a rule of thumb, if more than one third of the data plots outside the bounds of + 1 or –1 (equal to $\pm$ 1s), this leads to overweighting of the data set. More realistic precisions were entered in this situation.

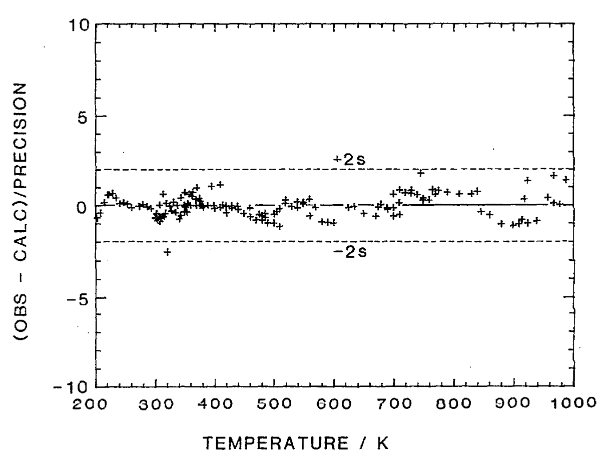

FIGURE 1. Parameter (observed value – calculated value)/precision as a function of temperature for the differential scanning calorimeter measurements of heat capacity for anorthite. Plus signs (+) indicate the data of Krupka and others (1979).

Error plots alert the evaluator to the existence of a conflict in the data sets. The evaluator must determine the source for the conflict and make the appropriate correction to the data. As an example, figure 2 is a combination of the error plots for reaction B. The relative errors for the silicic acid solubilities of Hemley and others (1980) and the reversed brackets of Thompson (1970) are shown. The data of Hemley and his coworkers plot systematically high for this reaction, but they are well within 1 sigma of the zero abscissa. The systematic discrepancy is caused by a minor misfit between these data and one or more of the enthalpies of solution and Gibbs energies of reaction in which either kaolinite or pyrophyllite is involved.

$$Al_2Si_2O_5(OH)_4(\text{kaolinite}) + 6SiO_2(\text{alpha quartz}) = Al_2Si_4O_{10}(OH)_2(\text{pyrophyllite}) + H_2O(\text{gas}) \quad (B)$$

However, the reversed observations of Thompson (1970) lie well outside the 2 sigma limits. Figure 3 shows the calculated Gibbs energy for reaction B and the experimental data cited on figure 2. As expected, the data of Hemley and coworkers lie near the calculated values. Because the calculated line also reflects the other data in the problem, particularly entropies and other phase equilibria, we conclude that data of Hemley and coworkers are consistent. However, both the magnitude and the slope of the reversed brackets of Thompson are not in agreement with the other data. A review of the experimental method suggests that the error may be due to the finely ground kaolinite and pyrophyllite ("less than 300 mesh," p. 454) that was used in the study and to the relatively short duration of the experiments ("usually 28 days" at 100 MPa, "for 1 week" at 200 and 400 MPa, p. 455–456). These data were not included in the evaluation. The above conjecture on the part of the evaluators is not proven; only detailed discussions with the authors or repetition of the experiments could prove the data are in error.

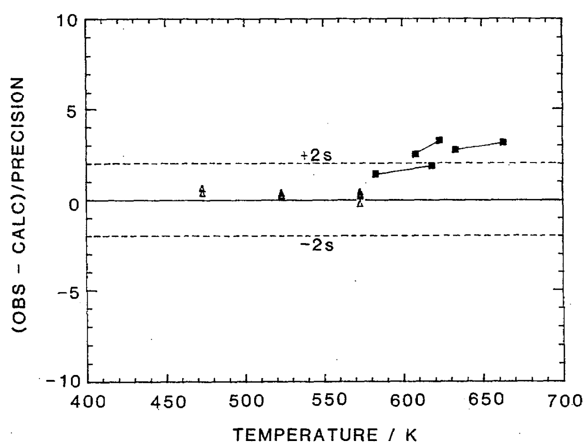

FIGURE 2. Parameter (observed value − calculated value)/precision as a function of temperature for the reaction: Kaolinite + 2 Quartz = Pyrophyllite + Steam. The open triangles were calculated from the silicic acid solubilities of Hemley and others (1980). The connected solid squares represent the brackets of Thompson (1970). The dashed lines represent two times the precision stated by the authors or two times the width of the Gibbs energy bracket, whichever is appropriate.

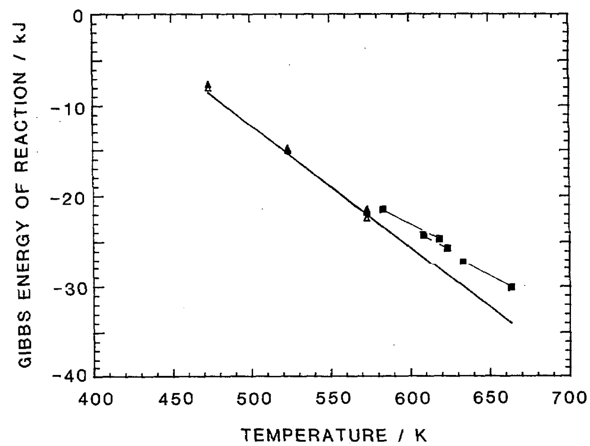

FIGURE 3. Gibbs energy of reaction as a function of absolute temperature for the reaction: Kaolinite + 2 Quartz = Pyrophyllite + Steam. The open triangles were calculated from the silicic acid solubilities of Hemley and others (1980). The connected solid squares represent the brackets of Thompson (1970). The solid line was calculated from the least-squares solution to the entire set of experimental observations.

Discordant data are readily identified. The cause of the disagreement is not always as straightforward as the identification. Fortunately, because sufficient related data were available for the phases in question, the right decision was made. In the discussions associated with the thermodynamic tables, all data used to produce the final results are given. Because of manpower and time, however, we have not included the much larger set of excluded data. The reference section contains all literature sources considered in the evaluation. References which contain indirect or supporting information on thermodynamic properties and references containing experimental data considered, but excluded from the evaluation, are marked with an asterisk (*) at the beginning of the citation.

3.5. Preparation of Tables and Summaries

Tables of thermodynamic data at 101.325 kPa between 273.15 K and 1800 K were prepared from the functions in the fitted model. The commonly used thermodynamic functions given below were tabulated:

C°_p	heat capacity
S°	entropy
$[G^\circ_T - H^\circ_{Tr}]/T$	Gibb's function
$H^\circ_T - H^\circ_{Tr}$	relative enthalpy
$\Delta H^\circ_{f,e}$	enthalpy of formation from the elements
$\Delta G^\circ_{f,e}$	Gibbs energy of formation from the elements
$\log K^\circ_{f,e}$	equilibrium constant for formation from the elements
$\Delta H^\circ_{f,ox}$	enthalpy of formation from the oxides
$\Delta G^\circ_{f,ox}$	Gibbs energy of formation from the oxides
$\log K^\circ_{f,ox}$	equilibrium constant for formation from the oxides

The summaries associated with each table contain functions for heat capacity, entropy, and relative enthalpy as obtained in fitting the model to the data. The summaries also cite those data used in the final evaluation that were directly pertinent to determine the properties of the phase in question. In the interest of saving manpower for more evaluations, data that were considered and rejected were not tabulated.

3.6. Confidence Limits

All evaluations must start with some base that is accepted without question. In this effort, the properties of the elements and the oxides cited in table 3 were used without question. The properties for the evaluated phases are determined relative to those reference values. In the course of the evaluation, we found no inconsistency of sufficient magnitude that would require us to consider reevaluating any of that reference base. This does not mean that the tabulated values are without error. For example, the uncertainty for the entropy at 298.15 K for Ca or CaO is about 1 percent (CODATA Task Group, 1978).

In preparing the tabulations, the 2-sigma confidence limits were given for the 298.15 K isotherm and for every isotherm that is a multiple of 250 K. These limits reflect only the variation in the final set of data on the chemical system. They do not include confidence limits on the reference data in table 3. For this reason the confidence limits for formation from the elements and the oxides is identical. If such a time arises when manpower is abundant or when other data centers adopt similar evaluation procedures, the imprecision in the reference base will be included in the tables.

4. Results

The appendix contains the thermodynamic properties and summaries for the phases listed in tables 1 and 3. The arrangement follows that of the JANAF Thermochemical Tables (Chase and others, 1974). The formula in the upper right of each table and summary is an alphabetical arrangement of atomic symbols. The more conventional formula is given elsewhere in the table or summary. In this set, aluminum (Al) compounds come first, followed by calcium, hydrogen, oxygen, and lastly silicon compounds. The index at the beginning of the appendix locates minerals within the alphabetized formulas.

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[1]References which begin with an asterisk (*) are not cited in the text or tables. They indicate additional literature sources which were considered in the evaluation.

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7. Appendix, Thermodynamic Tables, and Summaries

7.1. Mineral Index to Tables and Summaries

Mineral name and formula	Filing formula
Andalusite, Al_2SiO_5	Al_2O_5Si
Anorthite, $CaAl_2Si_2O_8$	$Al_2CaO_8Si_2$
Boehmite, AlO(OH)	$AlHO_2$
Ca-Al Clinopyroxene, $CaAl_2SiO_6$	Al_2CaO_6Si
Corundum, Al_2O_3	Al_2O_3
Cyclowollastonite, $CaSiO_3$	CaO_3Si
Diaspore, AlO(OH)	$AlHO_2$
Dickite, $Al_2Si_2O_5(OH)_4$	$Al_2H_4O_9Si_2$
Gehlenite, $Ca_2Al_2SiO_7$	$Al_2Ca_2O_7Si$
Gibbsite, $Al(OH)_3$	AlH_3O_3
Grossular, $Ca_3Al_2Si_3O_{12}$	$Al_2Ca_3O_{12}Si_3$
Halloysite, $Al_2Si_2O_5(OH)_4$	$Al_2H_4O_9Si_2$
Kaolinite, $Al_2Si_2O_5(OH)_4$	$Al_2H_4O_9Si_2$
Kyanite, Al_2SiO_5	Al_2O_5Si
Lime, CaO	CaO
Larnite, Ca_2SiO_4	Ca_2O_4Si
Margarite, $CaAl_4Si_2O_{10}(OH)_2$	$Al_4CaH_2O_{12}Si_2$
Ca Olivine, Ca_2SiO_4	Ca_2O_4Si
Prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$	$Al_2Ca_2H_2O_{12}Si_3$
Quartz, SiO_2	O_2Si
Rankinite, $Ca_3Si_2O_7$	$Ca_3O_7Si_2$
Sillimanite, Al_2SiO_5	Al_2O_5Si
Wollastonite, $CaSiO_3$	CaO_3Si
Zoisite, $Ca_2Al_3Si_3O_{12}(OH)$	$Al_3Ca_2HO_{13}Si_3$

7.2. Index to Tables and Summaries

Filing formula	Table title
Al	Al (reference state)
$AlHO_2$	AlO(OH) (reference state)
$AlHO_2$	AlO(OH), Boehmite
$AlHO_2$	AlO(OH), Diaspore
AlH_3O_3	$Al(OH)_3$, Gibbsite
Al_2CaO_6Si	$CaAl_2SiO_6$, Ca-Al Clinopyroxene
$Al_2CaO_8Si_2$	$CaAl_2Si_2O_8$, Anorthite
$Al_2Ca_2H_2O_{12}Si_3$	$Ca_2Al_2Si_3O_{10}(OH)_2$, Prehnite
$Al_2Ca_2O_7Si$	$Ca_2Al_2SiO_7$, Gehlenite
$Al_2Ca_3O_{12}Si_3$	$Ca_3Al_2Si_3O_{12}$, Grossular
$Al_2H_2O_{12}Si_4$	$Al_2Si_4O_{10}(OH)_2$, Pyrophyllite
$Al_2H_4O_9Si_2$	$Al_2Si_2O_5(OH)_4$, Dickite
$Al_2H_4O_9Si_2$	$Al_2Si_2O_5(OH)_4$, Halloysite
$Al_2H_4O_9Si_2$	$Al_2Si_2O_5(OH)_4$, Kaolinite
Al_2O_3	Al_2O_3, Corundum
Al_2O_5Si	Al_2SiO_5 (reference state)
Al_2O_5Si	Al_2SiO_5, Andalusite
Al_2O_5Si	Al_2SiO_5, Kyanite
Al_2O_5Si	Al_2SiO_5, Sillimanite
$Al_3Ca_2HO_{13}Si_3$	$Ca_2Al_3Si_3O_{12}(OH)$, Zoisite
$Al_4CaH_2O_{12}Si_2$	$CaAl_4SiO_{10}(OH)_2$, Margarite
Ca	Ca (reference state)
CaO	CaO, Lime
CaO_3Si	$CaSiO_3$ (reference state)
CaO_3Si	$CaSiO_3$, Cyclowollastonite (= "Pseudowollastonite")
CaO_3Si	$CaSiO_3$, Wollastonite
Ca_2O_4Si	Ca_2SiO_4 (reference table, Ca Olivine base)

Ca_2O_4Si	Ca_2SiO_4 (reference table, Larnite base)
Ca_2O_4Si	Ca_2SiO_4, (α' cyrstal)
Ca_2O_4Si	Ca_2SiO_4, Ca Olivine (γ crystal)
Ca_2O_4Si	Ca_2SiO_4, Larnite (β crystal)
Ca_3O_5Si	Ca_3SiO_5 (crystal)
$Ca_3O_7Si_2$	$Ca_3Si_2O_7$, Rankinite
H_2	H_2 *(ideal gas)*
H_2O	H_2O (reference table)
H_2O	H_2O (ideal gas)
O_2	O_2 (ideal gas)
O_2Si	SiO_2, Quartz (reference table)
Si	Si (reference table)

7.3. Tables and Summaries

Al

Reference state: crystals (face centered cubic) 273.15 K to 933 K
liquid 933 K to 1800 K

Al

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	23.844	26.241	-28.445	-602.	0.	0.	0.	--	--	--
298.15	24.307	28.350	-28.350	0.	0.	0.	0.	--	--	--
300.	24.338	28.500	-28.351	45.	0.	0.	0.	--	--	--
350.	25.049	32.308	-28.650	1281.	0.	0.	0.	--	--	--
400.	25.625	35.691	-29.322	2548.	0.	0.	0.	--	--	--
450.	26.157	38.741	-30.202	3842.	0.	0.	0.	--	--	--
500.	26.692	41.524	-31.197	5163.	0.	0.	0.	--	--	--
550.	27.255	44.094	-32.254	6512.	0.	0.	0.	--	--	--
600.	27.863	46.491	-33.342	7890.	0.	0.	0.	--	--	--
650.	28.525	48.747	-34.441	9299.	0.	0.	0.	--	--	--
700.	29.249	50.887	-35.540	10743.	0.	0.	0.	--	--	--
750.	30.039	52.932	-36.632	12225.	0.	0.	0.	--	--	--
800.	30.898	54.898	-37.712	13748.	0.	0.	0.	--	--	--
850.	31.828	56.798	-38.779	15316.	0.	0.	0.	--	--	--
900.	32.831	58.645	-39.832	16932.	0.	0.	0.	--	--	--
933.	33.533	59.840	-40.518	18027.	0.	0.	0.	--	--	--
933.	31.756	71.405	-40.518	28817.	0.	0.	0.	--	--	--
950.	31.756	71.978	-41.076	29357.	0.	0.	0.	--	--	--
1000.	31.756	73.607	-42.662	30945.	0.	0.	0.	--	--	--
1050.	31.756	75.157	-44.173	32532.	0.	0.	0.	--	--	--
1100.	31.756	76.634	-45.615	34120.	0.	0.	0.	--	--	--
1150.	31.756	78.045	-46.995	35708.	0.	0.	0.	--	--	--
1200.	31.756	79.397	-48.317	37296.	0.	0.	0.	--	--	--
1250.	31.756	80.693	-49.586	38884.	0.	0.	0.	--	--	--
1300.	31.756	81.939	-50.807	40472.	0.	0.	0.	--	--	--
1350.	31.756	83.137	-51.982	42059.	0.	0.	0.	--	--	--
1400.	31.756	84.292	-53.116	43647.	0.	0.	0.	--	--	--
1450.	31.756	85.407	-54.210	45235.	0.	0.	0.	--	--	--
1500.	31.756	86.483	-55.268	46823.	0.	0.	0.	--	--	--
1550.	31.756	87.525	-56.292	48411.	0.	0.	0.	--	--	--
1600.	31.756	88.533	-57.284	49999.	0.	0.	0.	--	--	--
1650.	31.756	89.510	-58.246	51586.	0.	0.	0.	--	--	--
1700.	31.756	90.458	-59.179	53174.	0.	0.	0.	--	--	--
1750.	31.756	91.379	-60.086	54762.	0.	0.	0.	--	--	--
1800.	31.756	92.273	-60.968	56350.	0.	0.	0.	--	--	--

Al (reference state) | Aluminum, crystal; Aluminum, liquid | Formula weight = 26.982 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (aluminum, crystal)

S° = 28.350 J/(mol·K) | ΔH_f° = 0.0 kJ/mol

V° = 9.999±0.001 cm^3/mol | ΔG_f° = 0.0 kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

Aluminum, crystal (temperature range 200 to 933 K)

a_1 = -2.05250×10^5	a_4 = -1.28573×10^2	a_6 = -4.07067×10^{-3}
a_2 = -8.70784×10^3	a_5 = 2.76424×10^1	a_7 = 1.57641×10^{-5}
a_3 = 0.0		

Aluminum, liquid (temperature range 933 to 1800 K)

a_1 = 0.0	a_4 = -1.45759×10^2	a_6 = 0.0
a_2 = -9.468×10^3	a_5 = 3.17565×10^1	a_7 = 0.0
a_3 = 0.0		

Critical Reaction

Melting:

Al(aluminum, crystal) = Al(aluminum, liquid)

T_m = 933 K (observed) | ΔS_m° = 11.565 J/(mol·K)

ΔH_m° = 10.790 kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for aluminum were taken from the following sources:

Property	Source
Heat capacity	Hultgren and others (1973)
Entropy	CODATA Task Group (1978)
Enthalpy of melting	Hultgren and others (1973)

AlO(OH)

Reference state: Diaspore 273.15 K to 571.86 K
Boehmite 571.86 K to 750 K

$AlHO_2$

Issued September, 1979

Temperature	C_p^o	S^o	$(G_T^o-H_{Tr}^o)/T$	$H_T^o-H_{Tr}^o$	Formation from the Elements $\Delta H_{f,e}^o$	$\Delta G_{f,e}^o$	$\log K_{f,e}^o$	Formation from the Oxides $\Delta H_{f,ox}^o$	$\Delta G_{f,ox}^o$	$\log K_{f,ox}^o$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	49.137	30.861	-35.543	-1279.	-999042.	-927511.	177.368	-18073.	-11819.	2.260
298.15	53.098	35.339	-35.339	0.	-999456.	-920945.	161.346	-18697.	-11219.	1.966
(2 sigma)	±0.094	±0.092	±0.092	±0.	±366.	±362.	±0.063	±366.	±362.	±0.063
300.	53.374	35.668	-35.340	98.	-999484.	-920457.	160.266	-18741.	-11172.	1.945
350.	60.067	44.416	-36.015	2940.	-1000083.	-907235.	135.397	-19891.	-9819.	1.465
400.	65.574	52.808	-37.594	6085.	-1000438.	-893944.	116.737	-40815.	-6856.	0.895
450.	70.202	60.806	-39.732	9483.	-1000594.	-880621.	102.220	-40739.	-2615.	0.304
480.90	72.717	65.552	-41.240	11692.	-1000607.	-872382.	94.757	-40652.	0.	0.000
500.	74.159	68.412	-42.223	13095.	-1000587.	-867290.	90.605	-40585.	1613.	-0.169
(2 sigma)	±0.369	±0.130	±0.093	±39.	±371.	±361.	±0.038	±371.	±361.	±0.038
550.	77.591	75.645	-44.935	16890.	-1000447.	-853966.	81.103	-40360.	5823.	-0.553
571.86	78.955	78.696	-46.168	18601.	-1000349.	-848146.	77.471	-40241.	7656.	-0.699
571.86	100.858	102.904	-46.167	32446.	-986505.	-848146.	77.471	-26397.	7656.	-0.699
600.	103.213	107.805	-48.944	35317.	-985726.	-841356.	73.246	-25601.	9313.	-0.811
650.	107.047	116.221	-53.797	40575.	-984227.	-829385.	66.650	-24096.	12162.	-0.977
700.	110.493	124.282	-58.546	46015.	-982603.	-817534.	61.005	-22484.	14891.	-1.111
750.	113.611	132.014	-63.188	51619.	-980872.	-805803.	56.121	-20774.	17502.	-1.219
(2 sigma)	±1.890	±0.989	±0.886	±867.	±886.	±689.	±0.048	±886.	±689.	±0.048

$AlHO_2$

AlO(OH) (reference state) Diaspore, Boehmite Formula weight = 59.988 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (diaspore)

$S° = 35.339 \pm 0.092$ J/(mol·K) $\Delta H_f^\circ = -999.456 \pm 0.366$ kJ/mol

$V° = 17.760 \pm 0.052$ cm^3/mol $\Delta G_f^\circ = -920.945 \pm 0.362$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

Diaspore (temperature range 200 to 571.86 K)

$a_1 = 2.43069\times10^5$	$a_4 = -1.021486\times10^3$	$a_6 = 0.0$
$a_2 = 1.04719\times10^5$	$a_5 = 1.505560\times10^2$	$a_7 = 0.0$
$a_3 = -1.73002\times10^3$		

Boehmite (temperature range 571.86 to 750 K)

$a_1 = 7.77111\times10^5$	$a_4 = -1.42636\times10^3$	$a_6 = 0.0$
$a_2 = 3.04561\times10^4$	$a_5 = 2.06903\times10^2$	$a_7 = 0.0$
$a_3 = -2.59274\times10^3$		

Critical Reactions

Inversion:

AlO(OH)(diaspore) = AlO(OH)(boehmite)

$T_i = 571.86$ K (calculated) $\Delta S_i^\circ = 24.208 \pm 1.8$ J/(mol·K)

$\Delta H_i^\circ = 13.844 \pm 0.7$ kJ/mol

Decomposition:

2AlO(OH)(diaspore) = Al_2O_3(corundum) + H_2O(gas)

$T_d = 480.90$ K (calculated) $\Delta S_d^\circ = 169.066 \pm 1.54$ J/(mol·K)

$\Delta H_d^\circ = 81.304 \pm 0.74$ kJ/mol

For detailed information on AlO(OH), refer to the appropriate tables on the individual phases.

AlO(OH)

Boehmite (Orthorhombic, dimorphous with Diaspore)

$AlHO_2$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	60.442	42.920	-48.687	-1575.	-990306.	-922068.	176.328	-9337.	-6377.	1.220
298.15	65.489	48.435	-48.435	0.	-990424.	-915817.	160.447	-9664.	-6091.	1.067
(2 sigma)	±0.218	±0.513	±0.513	±0.	±725.	±682.	±0.119	±725.	±682.	±0.119
300.	65.846	48.841	-48.436	121.	-990428.	-915354.	159.377	-9686.	-6069.	1.057
350.	74.659	59.672	-49.271	3640.	-990351.	-902842.	134.742	-10158.	-5426.	0.810
400.	82.123	70.142	-51.230	7565.	-989927.	-890366.	116.270	-30303.	-3278.	0.428
449.32	88.437	80.059	-53.854	11775.	-989222.	-878130.	102.085	-29369.	0.	0.000
450.	88.518	80.193	-53.894	11835.	-989210.	-877962.	101.911	-29355.	44.	-0.005
500.	94.061	89.813	-57.008	16403.	-988247.	-865650.	90.434	-28244.	3253.	-0.340
(2 sigma)	±1.005	±0.581	±0.515	±114.	±739.	±670.	±0.070	±739.	±670.	±0.070
550.	98.917	99.011	-60.412	21230.	-987075.	-853446.	81.053	-26988.	6343.	-0.602
600.	103.213	107.805	-63.997	26285.	-985726.	-841356.	73.246	-25601.	9313.	-0.811
650.	107.047	116.221	-67.693	31543.	-984227.	-829385.	66.650	-24096.	12162.	-0.977
700.	110.493	124.282	-71.449	36983.	-982603.	-817534.	61.005	-22484.	14891.	-1.111
750.	113.611	132.014	-75.231	42587.	-980872.	-805803.	56.121	-20774.	17502.	-1.219
(2 sigma)	±1.890	±0.989	±0.555	±478.	±886.	±689.	±0.048	±886.	±689.	±0.048

$AlHO_2$

AlO(OH) Boehmite Formula weight = 59.988 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 48.440\pm0.510$ J/(mol·K) $\Delta H_f° = -990.42\pm0.73$ kJ/mol

$V° = 19.535\pm0.052$ cm^3/mol $\Delta G_f° = -915.82\pm0.68$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 800 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2a_6T + a_7T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2T^2) - 2a_3/T^{0.5} + a_4 + a_5\ln(T) + 2a_6T + a_7T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2a_3T^{0.5} + a_5T + a_6T^2 + a_7T^3/3$$

$a_1 = 7.77111\times10^5$ $a_4 = -1.42636\times10^3$ $a_6 = 0.0$

$a_2 = 3.04561\times10^4$ $a_5 = 2.06903\times10^2$ $a_7 = 0.0$

$a_3 = -2.59274\times10^3$

Critical Reactions

Inversion:

AlO(OH)(diaspore) = AlO(OH)(boehmite)

T_i = 571.86 K (calculated) $\Delta S_i° = 24.208\pm1.800$ J/(mol·K)

$\Delta H_i° = 13.844\pm0.700$ kJ/mol

Decomposition:

2 AlO(OH)(boehmite) = Al_2O_3(corundum) + H_2O(gas)

T_d = 449.32 K (calculated) $\Delta S_d° = 130.726\pm3.260$ J/(mol·K)

$\Delta H_d° = 58.738\pm1.464$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of boehmite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Shomate and Cook (1946)	heat capacity	isothermal calorimetry	10	200 - 296 K
Estimated values[a]	heat capacity	corresponding states technique	7	298 - 600 K
Shomate and Cook (1946)	entropy	isothermal calorimetry	1	298.15 K

a The heat capacity was estimated by a corresponding states method (Lyon and Giauque, 1949) from the heat-capacity data for diaspore from Perkins and others (1979) and the low-temperature heat capacity for boehmite from Shomate and Cook (1946).

The standard error of estimate to the heat capacity of Shomate and Cook (1946) is 0.2 J/(mol·K). The estimated heat-capacity values are a smooth extension of the data of Shomate and Cook. The standard error of estimate of the estimated heat capacity is 0.15 J/(mol·K). The fitted entropy at 298.15 K is 48.44 ± 0.51 J/(mol·K) or a departure of 0.01 from the experimental value of 48.45 ± 0.21 determined by Shomate and Cook.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Hemley and others (in press)[b]	H_4SiO_4 concentration	A	473-573	9	-75.671±1.059	-990.451

a Reaction:

A) 2 AlO(OH)(boehmite) + 2 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_2O_5(OH)_4$(kaolinite)

b Hemley and others (in press) measured the silicic-acid content of water that was equilibrated with boehmite and kaolinite between 473 K and 573 K at 100 MPa. Using their data for the solubility of quartz at the same conditions, the molar volumes of the solid phases, and heat data for H_2O(gas) of Fisher and Zen (1971), we calculated the free energy of reaction at 101.325 kPa and temperature for each of nine observations.

The phase-equilibrium study of Hemley and others (in press) was evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated and is shown in column 6 of Table 2. From this enthalpy of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for boehmite (column 7 of Table 2) was calculated and can be compared with the enthalpy of formation of -990.424±0.725 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of boehmite and presents the data in their poorest perspective.

The molar volume of boehmite was obtained from the compilation of Robie and others (1967).

AlO(OH)

Diaspore (orthorhombic, dimorphous with Boehmite)

$AlHO_2$

Issued September, 1979

Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ-H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ-H_{Tr}^\circ$ J/mol	Formation from the Elements $\Delta H_{f,e}^\circ$ J/mol	$\Delta G_{f,e}^\circ$ J/mol	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$ J/mol	$\Delta G_{f,ox}^\circ$ J/mol	$\log K_{f,ox}^\circ$
273.15	49.137	30.861	-35.543	-1279.	-999042.	-927511.	177.368	-18073.	-11819.	2.260
298.15	53.098	35.339	-35.339	0.	-999456.	-920945.	161.346	-18697.	-11219.	1.966
(2 sigma)	±0.094	±0.092	±0.092	±0.	±366.	±362.	±0.063	±366.	±362.	±0.063
300.	53.374	35.668	-35.340	98.	-999484.	-920457.	160.266	-18741.	-11172.	1.945
350.	60.067	44.416	-36.015	2940.	-1000083.	-907235.	135.397	-19891.	-9819.	1.465
400.	65.574	52.808	-37.594	6085.	-1000438.	-893944.	116.737	-40815.	-6856.	0.895
450.	70.202	60.806	-39.732	9483.	-1000594.	-880621.	102.220	-40739.	-2615.	0.304
480.90	72.717	65.552	-41.240	11692.	-1000607.	-872382.	94.757	-40652.	0.	0.000
500.	74.159	68.412	-42.223	13095.	-1000587.	-867290.	90.605	-40585.	1613.	-0.169
(2 sigma)	±0.369	±0.130	±0.093	±39.	±371.	±361.	±0.038	±371.	±361.	±0.038
550.	77.591	75.645	-44.935	16890.	-1000447.	-853966.	81.103	-40360.	5823.	-0.553
600.	80.603	82.528	-47.784	20847.	-1000197.	-840660.	73.186	-40072.	10009.	-0.871
650.	83.274	89.087	-50.711	24945.	-999858.	-827378.	66.489	-39727.	14168.	-1.139
700.	85.663	95.348	-53.677	29169.	-999449.	-814126.	60.751	-39330.	18300.	-1.366
750.	87.817	101.333	-56.656	33507.	-998984.	-800904.	55.780	-38886.	22401.	-1.560
(2 sigma)	±0.751	±0.323	±0.118	±178.	±420.	±360.	±0.025	±420.	±360.	±0.025

$AlHO_2$

Al0(OH) | Diaspore | Formula weight = 59.988 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 35.339 \pm 0.092$ J/(mol·K) $\quad \Delta H_f^\circ = -999.456 \pm 0.366$ kJ/mol

$V° = 17.760 \pm 0.052\ cm^3$/mol $\quad \Delta G_f^\circ = -920.945 \pm 0.362$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = 2.43069x10^5$ $\quad a_4 = -1.021486x10^3$ $\quad a_6 = 0.0$

$a_2 = 1.04719x10^5$ $\quad a_5 = 1.50556x10^2$ $\quad a_7 = 0.0$

$a_3 = -1.73002x10^3$

Critical Reactions

Inversion:

Al0(OH)(diaspore) = Al0(OH)(boehmite)

T_i = 571.86 K (calculated) $\quad \Delta S_i^\circ = 24.208 \pm 1.8$ J/(mol·K)

$\Delta H_i^\circ = 13.844 \pm 0.7$ kJ/mol

Decomposition:

2 Al0(OH)(diaspore) = Al_2O_3(corundum) + H_2O(gas)

T_d = 480.90 K (calculated) $\quad \Delta S_d^\circ = 169.060 \pm 1.54$ J/(mol·K)

$\Delta H_d^\circ = 81.304 \pm 0.74$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of diaspore.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King and Weller (1961)	heat capacity	isothermal calorimetry	10	206 - 296 K
Perkins and others (1979)	heat capacity	adiabatic calorimetry	15	203 - 345 K
Perkins and others (1979)	heat capacity	differential scanning calorimetry	19	340 - 509 K
Perkins and others (1979)	entropy	adiabatic calorimetry	1	298.15 K

The heat capacity measured by King and Weller (1961) was fit with a standard error of estimate of 0.25 J/(mol·K). The heat capacity of Perkins and others (1979) measured on an adiabatic calorimeter and differential scanning calorimeter were fit with a standard error of estimate of 0.26 and 0.78 J/(mol·K), respectively. The fitted entropy at 298.15 K is 35.339 ± 0.092 J/(mol·K) or a departure of .001 from the experimental value of 35.338 ± 0.0377 of Perkins and others.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Hemley and others (in press)[b]	H_4SiO_4 concentration	A	473-573	6	-57.885±0.441	-999.421
Hemley and others (in press)[b]	H_4SiO_4 concentration	B	523-598	4	-1.678±1.770	-999.837
Hemley and others (in press)[b]	H_4SiO_4 concentration	C	623-663	2	78.164±0.200	-999.855
Haas (1972)	gas-medium pressure apparatus	D	662-741	5 pair	81.322±0.875	-999.465
Haas and Holdaway (1973)	gas-medium pressure apparatus	E	618-722	4	311.486±3.224	-999.646

a Reactions:

A) 2 Al0(OH)(diaspore) + 2 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_2O_5(OH)_4$(kaolinite)

B) 2 Al0(OH)(diaspore) + 4 SiO_2(quartz, alpha) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite)

C) 2 Al0(OH)(diaspore) + SiO_2(quartz, alpha) = Al_2SiO_5(andalusite) + H_2O(gas)

D) 2 Al0(OH)(diaspore) = Al_2O_3(corundum) + H_2O(gas)

E) $Al_2Si_4O_{10}(OH)_2$(pyrophyllite) + 6 Al0(OH)(diaspore) = 4 Al_2SiO_5(andalusite) + 4 H_2O(gas)

$AlHO_2$

b Henley and others (in press) measured the silicic-acid content of water equilibrated with the mineral pairs A) diaspore-kaolinite, B) diaspore-pyrophyllite, and C) diaspore-andalusite at 100 and 200 MPa between 450 K and 700 K. Using their data for the solubility of quartz at the same conditions, the molar volumes of the solid phases, and the free-energy data for H_2O(gas) of Fisher and Zen (1971), the free energy of reactions A, B, and C was calculated for each observation.

The phase-equilibrium studies of Haas (1972) and Haas and Holdaway (1973) were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for diaspore (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -999.456±0.366 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of diaspore and presents the data in their poorest perspective. The phase-equilibria data cited above bracket the regression fit in free energy space.

The molar volume of diaspore was obtained from the compilation of Robie and others (1967).

$Al(OH)_3$

Gibbsite (monoclinic, trimorphous with Bayerite and Nordstrandite)

AlH_3O_3

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	84.735	60.714	-68.793	-2207.	-1292765.	-1166756.	223.119	-25183.	-9791.	1.872
298.15	91.729	68.440	-68.440	0.	-1293334.	-1155197.	202.385	-26766.	-8311.	1.456
(2 sigma)	±0.158	±0.344	±0.344	±0.	±628.	±637.	±0.112	±628.	±637.	±0.112
300.	92.226	69.009	-68.442	170.	-1293370.	-1154339.	200.988	-26879.	-8196.	1.427
350.	104.706	84.185	-69.612	5101.	-1294071.	-1131105.	168.808	-29700.	-4854.	0.724
400.	115.656	98.896	-72.358	10615.	-1294268.	-1107805.	144.664	-91780.	3219.	-0.420
450.	125.423	113.093	-76.100	16647.	-1294016.	-1084508.	125.886	-90793.	15038.	-1.746
500.	134.262	126.772	-80.488	23142.	-1293364.	-1061260.	110.869	-89500.	26731.	-2.793
(2 sigma)	±1.827	±0.473	±0.347	±141.	±644.	±652.	±0.068	±644.	±652.	±0.068
550.	142.361	139.954	-85.298	30061.	-1292350.	-1038096.	98.590	-87923.	38280.	-3.635
600.	149.861	152.666	-90.386	37368.	-1291011.	-1015039.	88.367	-86082.	49673.	-4.324
650.	156.868	164.941	-95.651	45038.	-1289375.	-992105.	79.727	-83993.	60903.	-4.894
700.	163.464	176.810	-101.027	53048.	-1287468.	-969308.	72.331	-81668.	71963.	-5.370
750.	169.716	188.303	-106.464	61379.	-1285312.	-946657.	65.931	-79120.	82849.	-5.770
(2 sigma)	±7.542	±2.016	±0.499	±1225.	±1377.	±731.	±0.051	±1377.	±731.	±0.051

AlH_3O_3

$Al(OH)_3$ Gibbsite Formula weight = 78.003 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 68.440 \pm 0.344$ J/(mol·K) $\Delta H_f° = -1293.334 \pm 0.628$ kJ/mol

$V° = 31.956 \pm 0.030$ cm^3/mol $\Delta G_f° = -1155.197 \pm 0.637$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 800 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 6.617044\times10^5$ $a_4 = -1.513072\times10^3$ $a_6 = 3.006455\times10^{-2}$

$a_2 = 2.582430\times10^4$ $a_5 = 2.208509\times10^2$ $a_7 = 0.0$

$a_3 = -2.667640\times10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of gibbsite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Hemingway and others (1977)	heat capacity	adiabatic calorimetry	23	200 - 480 K
Hemingway and others (1977)	entropy	adiabatic calorimetry	1	298.15 K

The heat-capacity measurements of Hemingway and others (1977) were fit with a standard error of estimate of 0.33 J/(mol·K),. The fitted entropy at 298.15 K is 68.440 ± 0.344 J/(mol·K), which agrees with the experimental value of 68.44 ± 0.14 J/(mol·K) reported by Hemingway and others (1977).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) kJ	$\Delta H_f°$(298.15 K) kJ/mol
Hemingway and Robie (1977)[b]	solution calorimetry (HF)	A	303.4	4	-486.096±2.514	-1293.578

a Reactions:

A) Al(aluminum, reference) + 3 H_2O(liquid) = $Al(OH)_3$(gibbsite) + 1.5 H_2(hydrogen, reference)

b Hemingway and Robie (1977) measured the enthalpy of solution of gibbsite in HF acid solution at 303.4 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of water, quartz, and aluminum metal in the HF acid solution. A correction was made for the enthalpy of vaporization of H_2 gas evolved during the dissolution of aluminum metal.

The molar volume of gibbsite was obtained from the compilation of Robie and others (1967).

$CaAl_2SiO_6$

Ca-Al Clinopyroxene (monoclinic, member of the Pyroxene Group)

Al_2CaO_6Si

Issued September, 1979

Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ-H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ-H_{Tr}^\circ$ J/mol	Formation from the Elements: $\Delta H_{f,e}^\circ$ J/mol	$\Delta G_{f,e}^\circ$ J/mol	$\log K_{f,e}^\circ$	Formation from the Oxides: $\Delta H_{f,ox}^\circ$ J/mol	$\Delta G_{f,ox}^\circ$ J/mol	$\log K_{f,ox}^\circ$
273.15	154.134	127.599	-142.251	-4002.	-3298437.	-3137609.	600.007	-77415.	-80492.	15.393
298.15	165.658	141.611	-141.611	0.	-3298956.	-3122865.	547.113	-77452.	-80772.	14.151
(2 sigma)	±2.737	±2.173	±2.173	±0.	±1912.	±1468.	±0.257	±1912.	±1468.	±0.257
300.	166.425	142.638	-141.614	307.	-3298986.	-3121772.	543.548	-77453.	-80793.	14.067
350.	183.805	169.673	-143.709	9087.	-3299427.	-3092193.	461.484	-77430.	-81350.	12.141
400.	196.556	195.089	-148.561	18611.	-3299333.	-3062589.	399.933	-77361.	-81914.	10.697
450.	206.375	218.830	-155.065	28694.	-3298878.	-3033020.	352.064	-77295.	-82488.	9.575
500.	214.215	240.994	-162.562	39216.	-3298178.	-3003516.	313.775	-77257.	-83067.	8.678
(2 sigma)	±2.064	±1.809	±2.079	±362.	±1823.	±1272.	±0.133	±1823.	±1272.	±0.133
550.	220.652	261.723	-170.645	50093.	-3297315.	-2974090.	282.455	-77256.	-83648.	7.944
600.	226.056	281.160	-179.053	61264.	-3296351.	-2944748.	256.363	-77299.	-84228.	7.333
650.	230.675	299.441	-187.618	72685.	-3295336.	-2915489.	234.291	-77388.	-84802.	6.815
700.	234.681	316.686	-196.227	84321.	-3294307.	-2886309.	215.379	-77524.	-85368.	6.370
750.	238.198	333.000	-204.806	96145.	-3294134.	-2857165.	198.990	-77707.	-85922.	5.984
(2 sigma)	±1.690	±1.540	±1.883	±725.	±1712.	±1173.	±0.082	±1712.	±1173.	±0.082
800.	241.318	348.474	-213.306	108135.	-3293065.	-2828069.	184.654	-77936.	-86462.	5.645
850.	244.110	363.189	-221.693	120272.	-3292101.	-2799037.	172.008	-78930.	-86982.	5.345
900.	246.629	377.215	-229.947	132541.	-3291262.	-2770058.	160.770	-78828.	-87458.	5.076
950.	248.917	390.611	-238.053	144931.	-3312076.	-2740729.	150.696	-78708.	-87941.	4.835
1000.	251.006	403.433	-246.004	157429.	-3311260.	-2710680.	141.591	-78570.	-88430.	4.619
(2 sigma)	±2.651	±1.330	±1.711	±999.	±1653.	±1187.	±0.062	±1653.	±1187.	±0.062
1050.	252.925	415.727	-253.795	170028.	-3310493.	-2680670.	133.356	-78418.	-88927.	4.424
1100.	254.695	427.534	-261.426	182719.	-3309781.	-2650695.	125.871	-78255.	-89431.	4.247
1150.	256.335	438.893	-268.896	195496.	-3317000.	-2620471.	119.025	-78083.	-89943.	4.085
1200.	257.860	449.835	-276.209	208351.	-3315466.	-2590220.	112.749	-77905.	-90463.	3.938
1250.	259.283	460.390	-283.366	221280.	-3313894.	-2560034.	106.978	-77722.	-90990.	3.802
(2 sigma)	±3.875	±1.385	±1.568	±1515.	±1872.	±1253.	±0.052	±1872.	±1253.	±0.052
1300.	260.615	470.586	-290.372	234278.	-3312286.	-2529911.	101.653	-77539.	-91524.	3.677
1350.	261.865	480.445	-297.230	247340.	-3310643.	-2499850.	96.725	-77356.	-92065.	3.562
1400.	263.042	489.990	-303.945	260463.	-3308968.	-2469852.	92.151	-77177.	-92613.	3.455
1450.	264.152	499.240	-310.521	273643.	-3307262.	-2439913.	87.895	-77003.	-93168.	3.356
1500.	265.202	508.213	-316.962	286877.	-3305525.	-2410034.	83.925	-76839.	-93728.	3.264
(2 sigma)	±4.952	±1.816	±1.461	±2416.	±2578.	±1370.	±0.048	±2578.	±1370.	±0.048
1550.	266.196	516.925	-323.272	300163.	-3303759.	-2380213.	80.213	-76685.	-94293.	3.178
1600.	267.140	525.392	-329.457	313496.	-3301964.	-2350450.	76.734	-76545.	-94864.	3.097
1650.	268.038	533.626	-335.519	326876.	-3300141.	-2320744.	73.469	-76421.	-95438.	3.021
1700.	268.893	541.641	-341.465	340299.	-3348799.	-2290643.	70.383	-76315.	-96016.	2.950
1750.	269.709	549.447	-347.296	353764.	-3346777.	-2259550.	67.444	-76231.	-96597.	2.883
(2 sigma)	±5.860	±2.463	±1.412	±3641.	±3711.	±1607.	±0.048	±3711.	±1607.	±0.048
1800.	270.488	557.056	-353.017	367270.	-3497557.	-2224591.	64.556	-76171.	-97180.	2.820
(2 sigma)	±6.024	±2.605	±1.411	±3918.	±3977.	±1677.	±0.049	±3977.	±1677.	±0.049

$CaAl_2SiO_6$ Ca-Al Clinopyroxene Formula weight = 218.125 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 141.600 \pm 2.200$ J/(mol·K) $\Delta H_f^\circ = -3298.9 \pm 1.9$ kJ/mol

$V° = 63.439 \pm 0.064$ cm^3/mol $\Delta G_f^\circ = -3122.9 \pm 1.5$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S^\circ(T)/[J/(mol \cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

$a_1 = -2.72024 \times 10^6$ $a_4 = -1.96633 \times 10^3$ $a_6 = 0.0$

$a_2 = 2.98963 \times 10^4$ $a_5 = 3.22040 \times 10^2$ $a_7 = 0.0$

$a_3 = -2.18582 \times 10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of Ca-Al clinopyroxene.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Thompson and others (1978)	heat capacity	differential scanning calorimeter	16	298.15 - 1000 K
Estimated values[a]	heat capacity	component summation	11	1000 - 2000 K

a Above 1000 K, the heat capacity of Ca-Al clinopyroxene was estimated by a summation of the average heat capacities of CaO-, SiO_2-, $(Al^{IV})_2O_3$-, and $(Al^{VI})_2O_3$-components derived from a number of sodium, potassium, and calcium aluminum silicates. (Al^{IV}) and (Al^{VI}) represent aluminum in tetrahedral and octahedral coordination, respectively.

The standard error of estimate of the fitted heat-capacity data of Thompson and others (1978) for synthetic Ca-Al clinopyroxene is 0.33 J/(mol·K). The estimated heat-capacity values above 1000 K were a smooth extension of the data of Thompson and others. The standard error of estimate for the estimated heat capacity from 1000 to 2000 K is 1.6 J/(mol·K).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Charlu and others (1978)[b]	solution calorimetry (borate salt)	A	970	1	75.069±1.006	-3301.339
Hays (1965)	solid-medium pressure apparatus	B	1473-1673	4 pair	-11.841±1.953	-3299.007

a Reactions:

A) $CaAl_2SiO_6$(clinopyroxene) = CaO(lime) + Al_2O_3(corundum) + SiO_2(quartz, alpha)

B) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) + Al_2O_3(corundum) = 3 $CaAl_2SiO_6$(clinopyroxene)

b Charlu and others (1978) measured the enthalpy of solution of synthetic Ca-Al clinopyroxene in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of lime, quartz, and corundum in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

The phase-equilibrium study of Hays (1965) (utilizing solid-medium pressure apparatus) was evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. This study complies with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated. These are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for Ca-Al clinopyroxene (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -3298.956±1.902 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of Ca-Al clinopyroxene and presents the data in their poorest perspective. Most of the phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume of Ca-Al clinopyroxene was obtained from the compilation of Robie and others (1967).

$CaAl_2Si_2O_8$

Anorthite (triclinic, member of the Feldspar Group)

$Al_2CaO_8Si_2$

Issued September, 1979

Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ-H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ-H_{Tr}^\circ$ J/mol	Formation from the Elements: $\Delta H_{f,e}^\circ$ J/mol	Formation from the Elements: $\Delta G_{f,e}^\circ$ J/mol	Formation from the Elements: log $K_{f,e}^\circ$	Formation from the Oxides: $\Delta H_{f,ox}^\circ$ J/mol	Formation from the Oxides: $\Delta G_{f,ox}^\circ$ J/mol	Formation from the Oxides: log $K_{f,ox}^\circ$
273.15	199.778	181.275	-200.110	-5145.	-4227236.	-4021095.	768.956	-95649.	-103103.	19.716
298.15	211.600	199.290	-199.290	0.	-4227833.	-4002200.	701.168	-95631.	-103786.	18.183
(2 sigma)	±0.146	±0.145	±0.145	±0.	±1118.	±1117.	±0.196	±1118.	±1117.	±0.196
300.	212.425	200.601	-199.294	392.	-4227869.	-4000800.	696.601	-95630.	-103837.	18.080
350.	232.294	234.897	-201.957	11529.	-4228466.	-3962898.	591.430	-95610.	-105206.	15.701
400.	248.139	266.989	-208.103	23555.	-4228460.	-3924954.	512.546	-95604.	-106578.	13.918
450.	260.828	296.975	-216.330	36290.	-4228007.	-3887039.	451.195	-95628.	-107948.	12.530
500.	271.072	325.005	-225.812	49597.	-4227233.	-3849193.	402.122	-95703.	-109314.	11.420
(2 sigma)	±0.417	±0.179	±0.145	±45.	±1119.	±1117.	±0.117	±1119.	±1117.	±0.117
550.	279.430	351.246	-236.035	63366.	-4226238.	-3811436.	361.980	-95850.	-110669.	10.510
600.	286.333	375.865	-246.673	77515.	-4225103.	-3773776.	328.536	-96087.	-112006.	9.751
650.	292.117	399.019	-257.510	91981.	-4223890.	-3736214.	300.246	-96424.	-113320.	9.106
700.	297.049	420.852	-268.405	106713.	-4222649.	-3698747.	276.004	-96871.	-114603.	8.552
750.	301.337	441.496	-279.262	121675.	-4222255.	-3661332.	254.998	-97429.	-115851.	8.069
(2 sigma)	±0.738	±0.333	±0.162	±174.	±1122.	±1121.	±0.078	±1122.	±1121.	±0.078
800.	305.152	461.068	-290.019	136839.	-4220960.	-3623980.	236.621	-98101.	-117058.	7.643
850.	308.631	479.673	-300.632	152185.	-4219765.	-3586706.	220.412	-100317.	-118209.	7.264
900.	311.888	497.407	-311.076	167698.	-4218685.	-3549499.	206.007	-100356.	-119260.	6.922
950.	315.015	514.354	-321.332	183371.	-4239245.	-3511956.	193.101	-100362.	-120310.	6.615
1000.	318.091	530.591	-331.392	199199.	-4238152.	-3473706.	181.448	-100331.	-121360.	6.339
(2 sigma)	±1.322	±0.471	±0.204	±324.	±1155.	±1135.	±0.059	±1155.	±1135.	±0.059
1050.	321.182	546.185	-341.251	215181.	-4237076.	-3435510.	170.907	-100257.	-122413.	6.090
1100.	324.344	561.199	-350.909	231318.	-4236011.	-3397365.	161.327	-100132.	-123471.	5.863
1150.	327.625	575.688	-360.369	247617.	-4242820.	-3358988.	152.570	-99948.	-124536.	5.657
1200.	331.066	589.704	-369.634	264083.	-4240806.	-3320603.	144.542	-99694.	-125610.	5.468
1250.	334.703	603.292	-378.710	280727.	-4238666.	-3282305.	137.160	-99358.	-126697.	5.294
(2 sigma)	±4.280	±0.729	±0.248	±747.	±1384.	±1156.	±0.048	±1384.	±1156.	±0.048
1300.	338.566	616.494	-387.603	297558.	-4236387.	-3244095.	130.349	-98927.	-127798.	5.135
1350.	342.684	629.347	-396.320	314588.	-4233954.	-3205976.	124.047	-98387.	-128919.	4.988
1400.	347.079	641.889	-404.867	331831.	-4231349.	-3167950.	118.198	-97724.	-130061.	4.853
1450.	351.774	654.149	-413.252	349301.	-4228556.	-3130020.	112.755	-96922.	-131230.	4.727
1500.	356.786	666.158	-421.483	367013.	-4225555.	-3092190.	107.680	-95964.	-132429.	4.612
(2 sigma)	±9.904	±1.759	±0.330	±2324.	±2674.	±1196.	±0.042	±2674.	±1196.	±0.042
1550.	362.132	677.944	-429.566	384985.	-4222328.	-3054463.	102.935	-94836.	-133662.	4.504
1600.	367.828	689.530	-437.510	403232.	-4218854.	-3016845.	98.490	-93518.	-134935.	4.405
1650.	373.886	700.940	-445.320	421774.	-4215114.	-2979339.	94.318	-91993.	-136252.	4.313
1700.	380.318	712.196	-453.004	440627.	-4312104.	-2941052.	90.367	-90244.	-137619.	4.229
1750.	387.136	723.318	-460.569	459812.	-4307481.	-2900793.	86.584	-88252.	-139041.	4.150
(2 sigma)	±18.260	±3.779	±0.595	±5706.	±5926.	±1455.	±0.043	±5926.	±1455.	±0.043
1800.	394.348	734.324	-468.020	479347.	-4455352.	-2856748.	82.901	-85998.	-140523.	4.078
(2 sigma)	±20.267	±4.307	±0.680	±6656.	±6862.	±1576.	±0.046	±6862.	±1576.	±0.046

$Al_2CaO_8Si_2$

$CaAl_2Si_2O_8$ | Anorthite | Formula weight = 278.209 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 199.29 \pm 0.15$ J/(mol·K) $\qquad \Delta H_f^\circ = -4227.8 \pm 1.1$ kJ/mol

$V° = 100.79 \pm 0.10$ cm^3/mol $\qquad \Delta G_f^\circ = -4002.2 \pm 1.1$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 3.18591\times10^6$ $\qquad a_4 = -5.35832\times10^3$ $\qquad a_6 = -1.46450\times10^{-1}$

$a_2 = 1.10301\times10^5$ $\qquad a_5 = 8.00971\times10^2$ $\qquad a_7 = 1.05663\times10^{-4}$

$a_3 = -9.44981\times10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of anorthite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Robie and others (1978)	heat capacity	adiabatic calorimetry	49	202 - 381 K
Krupka and others (1979)	heat capacity	differential scaning calorimetry	95	349 - 966 K
White (1919)	relative enthalpy	drop calorimetry	9	1173 - 1673 K
Robie and others (1978)	entropy	adiabatic calorimetry	1	298.15 K

The heat capacities of Robie and others (1978) and of Krupka and others (1979) were fit with a standard error of estimate of 0.4 and 1.36 J/(mol·K), respectively. The relative enthalpy measurements of White (1919) were fit with a standard error of estimate of 980 J/mol, or approximately 0.3 percent of the observed value. The fitted entropy value at 298.15 K is 199.29 ± 0.15 J/(mol·K) or a departure of 0.01 from the experimental value of 199.3 ± 0.3 J/(mol·K).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Kracek and Neuvonen (1952)[b]	solution calorimetry(HF)	A	347.85	1	43.275±1.447	-4226.665
Charlu and others (1978)[c]	solution calorimetry (borate salt)	B	970	2	95.089±1.988	-4228.375
					94.454±1.738	-4228.919
Newton (1965)	gas- and solid-medium pressure apparatus	C	843-1113	6 pair	-306.468±2.790	-4227.725
Boettcher (1970)	gas-medium pressure apparatus	C	898-928	1 pair	-308.308±4.088	-4227.418
Strens (1968)	gas-medium pressure apparatus	D	770-823	1 pair	-220.561±5.976	-4226.920
Boettcher (1970)	gas-medium pressure apparatus	D	853-933	2 pair	-213.025±2.944	-4228.428
Shmulovich (1974)	gas-medium pressure apparatus	E	1133-1153	1 pair	159.942±1.763	-4226.727
Huckenholz (1974)	unspecified	E	1125-1423	6 pair	158.750±2.236	-4227.919
Hays (1965)	solid-medium pressure apparatus	E	1473-1523	2 pair	156.099±6.608	-4230.570
Huckenholz (1974)	unspecified	F	848-858	1 pair	-49.366±0.328	-4228.137
Newton (1966b)	gas-medium pressure apparatus	F	803-923	2 pair	-51.708±3.042	-4225.795
Huckenholz (1974)	unspecified	G	888-958	2 pair	-50.101±0.499	-4227.971
Newton (1966b)	gas-medium pressure apparatus	G	973-1023	2 pair	-49.103±1.847	-4228.969
Boettcher (1970)	gas-medium pressure apparatus	G	893-1053	2 pair	-50.328±1.454	-4227.744
Storre and Nitsch (1974)	gas- and solid-medium pressure apparatus	H	788-833	2 pair	-89.818±1.710	-4228.388
Chatterjee (1971)	gas-medium pressure apparatus	I	763-893	3 pair	-94.087±0.931	-4227.976
Hays (1965)	solid-medium pressure apparatus	J	1473-1673	4 pair	-11.814±1.953	-4227.678
Boettcher (1970)	gas-medium pressure apparatus	K	1033-1053	1 pair	-102.037±0.996	-4228.292
Huckenholz (1974)	unspecified	K	1028-1263	3 pair	-102.895±1.257	-4227.434
Liou (1971)	gas-medium pressure apparatus	L	708-828	5 pair	-89.180±0.496	-4227.848
Kay and Taylor (1960)[d]	silica activity	M	1653	1	83.137±2.584	-4227.859
Kay and Taylor (1960)[d]	silica activity	N	1543	1	59.386±2.412	-4223.667

Reactions:

A) $CaAl_2Si_2O_8$(anorthite) + 3 H_2O(liquid) = CaO(lime) + 2 $Al(OH)_3$(gibbsite) + 2 SiO_2(quartz, alpha)

B) $CaAl_2Si_2O_8$(anorthite) = CaO(lime) + Al_2O_3(corundum) + 2 SiO_2(quartz, alpha)

C) 2 $Ca_3Al_2Si_3O_{12}$(grossular) + 6 $CaAl_2Si_2O_8$(anorthite) + Al_2O_3(corundum) + 3 H_2O(gas)
= 6 $Ca_2Al_3Si_3O_{12}(OH)$(zoisite)

D) $Ca_3Al_2Si_3O_{12}$(grossular) + 5 $CaAl_2Si_2O_8$(anorthite) + 2 H_2O(gas)
= 4 $Ca_2Al_3Si_3O_{12}(OH)$(zoisite) + SiO_2(quartz, alpha)

E) 2 $Ca_3Al_2Si_3O_{12}$(grossular) = $CaAl_2Si_2O_8$(anorthite) + 3 $CaSiO_3$(wollastonite) + $Ca_2Al_2SiO_7$(gehlenite)

F) $CaAl_2Si_2O_8$(anorthite) + 2 $CaSiO_3$(wollastonite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, alpha)

G) $CaAl_2Si_2O_8$(anorthite) + 2 $CaSiO_3$(wollastonite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, beta)

H) $CaAl_2Si_2O_8$(anorthite) + Al_2SiO_5(andalusite) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite) + SiO_2(quartz, alpha)

I) $CaAl_2Si_2O_8$(anorthite) + Al_2O_3(corundum) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite)

J) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) + Al_2O_3(corundum) = 3 $CaAl_2SiO_6$(clinopyroxene)

K) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) = $Ca_3Al_2Si_3O_{12}$(grossular) + Al_2O_3(corundum)

L) $CaAl_2Si_2O_8$(anorthite) + $CaSiO_3$(wollastonite) + H_2O(gas) = $Ca_2Al_2Si_3O_{10}(OH)_2$(prehnite)

M) 2 $CaAl_2Si_2O_8$(anorthite) = $Ca_2Al_2SiO_7$(gehlenite) + Al_2O_3(corundum) + 3 SiO_2(cristobalite, beta)

N) $CaAl_2Si_2O_8$(anorthite) + $CaSiO_3$(cyclowollastonite) = $Ca_2Al_2SiO_7$(gehlenite) + 2 SiO_2(cristobalite, beta)

b Kracek and Neuvonen (1952) measured the enthalpy of solution of lime and synthetic anorthite in HF acid at 374.15 K. To complete the thermodynamic cycle, their data were evaluated in combination with the recent data for the enthalpies of solution of water, quartz, and gibbsite in similar solutions (Barany, 1963; Bennington and others, 1978; Hemingway and Robie, 1977; Barany and Kelley, 1961; and Koehler and others, 1961).

c Charlu and others (1978) measured the enthalpy of solution of two samples of synthetic anorthite in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of lime, quartz, and corundum in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

d Kay and Taylor (1960) determined the activity of silica in the silicate liquid for the lime-alumina-silica system. Using the silica activity from their study and the measured temperatures and compositions of the silicate melts in equilibrium with either anorthite, gehlenite, and corundum or anorthite, cyclowollastonite, and gehlenite, we obtained the equilibrium constants for reactions M and N at the melt temperature and 101.325 kPa.

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for anorthite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -4227.8±1.1 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of anorthite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate. The phase-equilibria studies also lack the precision to discriminate among the experimental enthalpies of solution; therefore, the three experimental enthalpies of solution were included in the study.

The molar volume of anorthite was obtained from the compilation of Robie and others (1967).

$Ca_2Al_2Si_3O_{10}(OH)_2$

Prehnite (orthorhombic)

$Al_2Ca_2H_2O_{12}Si_3$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	312.544	264.558	-294.028	-8050.	-6192637.	-5848224.	1118.359	-228741.	-221950.	42.444
298.15	331.110	292.745	-292.745	0.	-6193631.	-5816655.	1019.053	-229828.	-221279.	38.767
(2 sigma)	±0.538	±0.659	±0.659	±0.	±832.	±729.	±0.128	±832.	±729.	±0.128
300.	332.405	294.797	-292.751	614.	-6193691.	-5814315.	1012.362	-229906.	-221226.	38.519
350.	363.758	348.478	-296.919	18046.	-6194713.	-5750990.	858.288	-231888.	-219620.	32.776
400.	389.191	398.769	-306.541	36891.	-6194738.	-5687589.	742.722	-273429.	-214842.	28.055
450.	410.022	445.852	-319.433	56888.	-6193996.	-5624233.	652.843	-273009.	-207543.	24.091
500.	427.230	489.971	-334.305	77833.	-6192673.	-5560992.	580.952	-272505.	-200295.	20.925
(2 sigma)	±1.322	±0.879	±0.670	±232.	±924.	±667.	±0.070	±924.	±667.	±0.070
550.	441.543	531.382	-350.358	99563.	-6190923.	-5497905.	522.147	-271968.	-193100.	18.339
600.	453.505	570.330	-367.083	121948.	-6188871.	-5434992.	473.158	-271443.	-185953.	16.189
650.	463.534	607.037	-384.142	144881.	-6186625.	-5372259.	431.720	-270971.	-178849.	14.372
700.	471.950	641.706	-401.313	168275.	-6184274.	-5309704.	396.215	-270588.	-171778.	12.818
750.	479.006	674.515	-418.443	192054.	-6183569.	-5247244.	365.450	-270325.	-164730.	11.473
(2 sigma)	±1.721	±1.047	±0.726	±412.	±1011.	±615.	±0.043	±1011.	±615.	±0.043
800.	484.904	705.623	-435.428	216156.	-6181015.	-5184907.	338.539	-270210.	-157695.	10.296
850.	489.808	735.172	-452.198	240528.	-6178628.	-5122724.	314.804	-272418.	-150646.	9.258
900.	493.848	763.287	-468.706	265122.	-6176453.	-5060676.	293.714	-271399.	-143512.	8.329
950.	497.135	790.079	-484.921	289900.	-6196043.	-4998349.	274.828	-270395.	-136435.	7.502
1000.	499.759	815.648	-500.823	314825.	-6194136.	-4935363.	257.797	-269433.	-129409.	6.760
(2 sigma)	±3.589	±1.621	±0.793	±1184.	±1509.	±673.	±0.035	±1509.	±673.	±0.035
1050.	501.798	840.083	-516.401	339866.	-6192430.	-4872467.	242.392	-268537.	-122431.	6.091
1100.	503.316	863.464	-531.649	364996.	-6190946.	-4809647.	228.391	-267727.	-115493.	5.484
1150.	504.368	885.862	-546.566	390190.	-6205447.	-4746329.	215.585	-267023.	-108589.	4.932
1200.	505.001	907.342	-561.154	415426.	-6202577.	-4682951.	203.843	-266442.	-101713.	4.427
1250.	505.257	927.964	-575.417	440684.	-6199772.	-4619691.	193.046	-266000.	-94859.	3.964
(2 sigma)	±20.005	±4.369	±1.029	±4560.	±4671.	±1097.	±0.046	±4671.	±1097.	±0.046

$Al_2Ca_2H_2O_{12}Si_3$

$Ca_2Al_2Si_3O_{10}(OH)_2$ Prehnite Formula weight = 412.388 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

S° = 292.745±0.659 J/(mol·K) ΔH_f° = -6193.631±0.832 kJ/mol

V° = 140.326±0.650 cm^3/mol ΔG_f° = -5816.655±0.729 kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 298.15 to 1250 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol \cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

a_1 = 2.755226×10^6 a_4 = -6.270704×10^3 a_6 = -5.753272×10^{-2}

a_2 = 1.842781×10^5 a_5 = 9.460222×10^2 a_7 = 0.0

a_3 = -1.056051×10^4

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of prehnite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Perkins and others (1980)	heat capacity	adiabatic calorimetry	8	200 - 298 K
Perkins and others (1980)	heat capacity	differential scanning calorimetry	12	298 - 800 K
Perkins and others (1980)	entropy	adiabatic calorimetry	1	298.15 K

The compositionally adjusted heat capacities that were obtained from measurements on a natural prehnite sample by Perkins and others (1980) were fit with a standard error of estimate of 0.32 J/(mol·K). The fitted entropy at 298.15 K is 292.745 ± 0.659 J/(mol·K) or a departure of 0.01 J/mol from the compositionally adjusted value of 292.75 ± 0.29 J/(mol·K) reported by Perkins and others.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Liou (1971)	gas-medium pressure apparatus	A	708-828	5 pair	-89.180±0.496	-6193.616

a Reaction:

A) $CaAl_2Si_2O_8$(anorthite) + $CaSiO_3$(wollastonite) + H_2O(gas) = $Ca_2Al_2Si_3O_{10}(OH)_2$(prehnite)

The phase-equilibrium study of Liou (1971) (utilizing gas-medium pressure apparatus) was evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The study cited in Table 2 complies with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated and is shown in column 6 of Table 2. From this enthapy of reaction and the calculated enthalpies of formation of other phases in the reaction, the enthalpy of formation for prehnite (column 7 of Table 2) was calculated and can be compared with the enthalpy of formation of -6193.631±0.832 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of prehnite and presents the data in their poorest perspective. Most of the phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume for prehnite was taken from the study of Liou (1971).

$Ca_2Al_2SiO_7$

Gehlenite (tetragonal, member of the Melilite Group)

$Al_2Ca_2O_7Si$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	195.177	192.348	-210.688	-5010.	-3981198.	-3799542.	726.607	-125045.	-135392.	26.082
298.15	205.387	209.891	-209.891	0.	-3981707.	-3783001.	662.766	-125110.	-137428.	24.077
(2 sigma)	±0.571	±0.972	±0.972	±0.	±2458.	±2329.	±0.408	±2458.	±2329.	±0.408
300.	206.095	211.163	-209.895	381.	-3981738.	-3781768.	658.464	-125116.	-137504.	23.942
350.	223.063	244.258	-212.469	11126.	-3982231.	-3748392.	559.416	-125302.	-139555.	20.827
400.	236.577	274.959	-218.386	22630.	-3982209.	-3714983.	485.127	-125531.	-141576.	18.488
450.	247.476	303.476	-226.275	34740.	-3981819.	-3681500.	427.349	-125792.	-143566.	16.665
500.	256.370	330.026	-235.338	47344.	-3981176.	-3648274.	381.132	-126086.	-145526.	15.203
(2 sigma)	±1.044	±1.049	±0.975	±161.	±2487.	±2253.	±0.235	±2487.	±2253.	±0.235
550.	263.707	354.815	-245.085	60351.	-3980375.	-3615022.	343.326	-126418.	-147454.	14.004
600.	269.821	378.031	-255.207	73694.	-3979491.	-3581347.	311.827	-126794.	-149350.	13.002
650.	274.966	399.837	-265.502	87317.	-3978587.	-3548747.	285.181	-127220.	-151213.	12.152
700.	279.336	420.378	-275.839	101178.	-3977715.	-3515715.	262.346	-127699.	-153041.	11.420
750.	283.086	439.782	-286.127	115241.	-3978590.	-3482570.	242.555	-128236.	-154832.	10.783
(2 sigma)	±1.138	±1.178	±0.999	±341.	±2545.	±2166.	±0.151	±2545.	±2166.	±0.151
800.	286.336	458.158	-296.310	129478.	-3977689.	-3449639.	225.238	-128833.	-155586.	10.224
850.	289.184	475.604	-306.348	143868.	-3977001.	-3416659.	209.962	-130209.	-158296.	9.728
900.	291.711	492.206	-316.216	158391.	-3976547.	-3383711.	196.385	-130507.	-159939.	9.283
950.	293.982	508.040	-325.899	173034.	-3997856.	-3350390.	184.217	-130802.	-161566.	8.884
1000.	296.051	523.173	-335.387	187786.	-3997647.	-3316319.	173.227	-131097.	-163178.	8.524
(2 sigma)	±1.884	±1.226	±1.026	±513.	±2588.	±2103.	±0.110	±2588.	±2103.	±0.110
1050.	297.965	537.664	-344.676	202637.	-3997596.	-3282255.	163.283	-131392.	-164775.	8.197
1100.	299.763	551.567	-353.767	217581.	-3997709.	-3248189.	154.244	-131689.	-166357.	7.900
1150.	301.477	564.930	-362.659	232612.	-4013731.	-3213554.	145.964	-131987.	-167927.	7.627
1200.	303.136	577.795	-371.357	247727.	-4012289.	-3178794.	138.369	-132285.	-169483.	7.377
1250.	304.764	590.204	-379.864	262925.	-4010804.	-3144095.	131.384	-132583.	-171027.	7.147
(2 sigma)	±1.837	±1.299	±1.046	±798.	±2645.	±2079.	±0.087	±2645.	±2079.	±0.087
1300.	306.383	602.188	-388.186	273204.	-4009276.	-3109457.	124.939	-132879.	-172558.	6.933
1350.	308.011	613.782	-396.328	293563.	-4007701.	-3074378.	118.974	-133171.	-174079.	6.736
1400.	309.664	625.013	-404.295	309005.	-4006075.	-3040359.	113.437	-133455.	-175589.	6.551
1450.	311.358	635.909	-412.095	324531.	-4004395.	-3005899.	108.284	-133731.	-177089.	6.379
1500.	313.104	646.494	-419.733	340142.	-4002656.	-2971497.	103.477	-133994.	-173579.	6.219
(2 sigma)	±3.847	±1.312	±1.062	±957.	±2665.	±2102.	±0.073	±2665.	±2102.	±0.073
1550.	314.914	656.790	-427.215	355842.	-4000853.	-2937155.	98.981	-134241.	-180061.	6.068
1600.	316.798	666.818	-434.546	371634.	-3998978.	-2902372.	94.769	-134469.	-181536.	5.927
1650.	318.765	676.596	-441.733	387523.	-3997028.	-2868548.	90.814	-134674.	-183003.	5.793
1700.	320.823	686.142	-448.782	403512.	-4045503.	-2834035.	87.079	-134852.	-184465.	5.668
1750.	322.980	695.473	-455.698	419607.	-4043237.	-2798437.	83.529	-135000.	-185922.	5.549
(2 sigma)	±9.839	±1.580	±1.075	±1871.	±3085.	±2171.	±0.065	±3085.	±2171.	±0.065
1800.	325.241	704.603	-462.485	435812.	-4346538.	-2755057.	79.950	-135112.	-187375.	5.437
(2 sigma)	±11.442	±1.753	±1.078	±2313.	±3367.	±2191.	±0.064	±3367.	±2191.	±0.064

$Al_2Ca_2O_7Si$

$Ca_2Al_2SiO_7$ Gehlenite Formula weight = 274.204 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 209.89±0.97$ J/(mol·K) $\Delta H_f° = -3981.7±2.5$ kJ/mol

$V° = 90.24±0.18$ cm^3/mol $\Delta G_f° = -3783.0±2.3$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

$a_1 = 1.51047x10^6$ $a_4 = -3.82222x10^3$ $a_6 = -6.71533x10^{-2}$

$a_2 = 5.19543x10^4$ $a_5 = 5.88351x10^2$ $a_7 = 3.89086x10^{-5}$

$a_3 = -6.27433x10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of gehlenite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Weller and Kelley (1963)	heat capacity	isothermal calorimeter	10	206 - 296 K
Pankratz and Kelley (1964)	relative enthalpy	drop calorimeter	15	402 - 1801 K
Hemingway and Robie (1977)	entropy	adiabatic calorimeter	1	298.15 K

The standard error of estimate of the fitted heat-capacity data of Weller and Kelley (1963) for synthetic gehlenite is 0.14 J/(mol·K). The standard error of estimate of the fitted relative enthalpy measurements of Pankratz and Kelley (1964) is 420 J/(mol·K) or approximately 0.2 percent of the observed value. Hemingway and Robie (1977) calculated an entropy for gehlenite from the low-temperature heat-capacity data of Weller and Kelley (1963) after correcting their temperature scale. The fitted entropy at 298.15 K is 209.89 ± 0.97 J/(mol·K) or a departure of 0.09 from the experimental value of 209.8 ± 0.4 J/(mol·K) determined by Hemingway and Robie.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Shmulovich (1974)	gas-medium pressure apparatus	A	1133-1153	1 pair	159.942±1.763	-3980.604
Huckenholz (1974)	unspecified	A	1125-1423	6 pair	158.750±2.236	-3982.796
Hays (1965)	solid-medium pressure apparatus	A	1473-1523	2 pair	156.099±6.608	-3984.447
Hays (1965)	solid-medium pressure apparatus	B	1473-1673	4 pair	-11.814±1.953	-3981.555
Boettcher (1970)	gas-medium pressure apparatus	C	1033-1053	2 pair	-102.037±0.996	-3982.169
Huckenholz (1974)	unspecified	C	1028-1263	3 pair	-102.895±1.257	-3981.311
Kay and Taylor (1960)[b]	silica activity	D	1653	1	83.137±2.584	-3981.557
Kay and Taylor (1960)[b]	silica activity	E	1543	1	59.386±2.412	-3985.876

a Reactions:

A) 2 $Ca_3Al_2Si_3O_{12}$(grossular) = $CaAl_2Si_2O_8$(anorthite) + 3 $CaSiO_3$(wollastonite) + $Ca_2Al_2SiO_7$(gehlenite)

B) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) + Al_2O_3(corundum) = 3 $CaAl_2SiO_6$(clinopyroxene)

C) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) = $Ca_3Al_2Si_3O_{12}$(grossular) + Al_2O_3(corundum)

D) 2 $CaAl_2Si_2O_8$(anorthite) = $Ca_2Al_2SiO_7$(gehlenite) + Al_2O_3(corundum) + 3 SiO_2(cristobalite, beta)

E) $CaAl_2Si_2O_8$(anorthite) + $CaSiO_3$(cyclowollastonite) = $Ca_2Al_2SiO_7$(gehlenite) + 2 SiO_2(cristobalite, beta)

b Kay and Taylor (1960) determined the activity of silica in the silicate liquid for the lime-alumina-silica system. Using the silica activity from their study and the measured temperatures and compositions of the silicate melts in equilibrium with either anorthite, gehlenite, and corundum or anorthite, cyclowollastonite, and gehlenite, we obtained the equilibrium constants for reactions D and E at the melt temperature and 101.325 kPa.

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for gehlenite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -3981.707±2.458 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of gehlenite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate. However, the phase-equilibria studies have sufficient precision to indicate that they are incompatible with the enthalpy of formation of gehlenite at 298.15 K of -4007.570 ± 2.820 kJ/mol calculated from the enthalpy of solution measurements of Barany (1963). The sample-preparation procedure of Barany (1963) may have produced a contaminated sample, and his data were not used here.

The molar volume of gehlenite was obtained from the compilation of Robie and others (1967).

$Ca_3Al_2Si_3O_{12}$

Grossular (cubic, member of the Garnet Group)

$Al_2Ca_3O_{12}Si_3$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements			Formation from the Oxides		
					$\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	$\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$-\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	310.918	227.878	-257.251	-8023.	-6635402.	-6305187.	1205.744	-322988.	-314053.	60.057
298.15	330.509	255.971	-255.971	0.	-6636338.	-6274919.	1099.339	-323249.	-313224.	54.875
(2 sigma)	±0.149	±2.946	±2.946	±0.	±3220.	±2583.	±0.453	±3220.	±2583.	±0.453
300.	331.858	258.020	-255.978	613.	-6636393.	-6272675.	1092.169	-323267.	-313161.	54.526
350.	363.923	311.687	-260.142	18041.	-6637245.	-6211974.	927.086	-323667.	-311444.	46.480
400.	389.093	361.991	-269.764	36891.	-6637106.	-6151220.	803.266	-323956.	-309677.	40.440
450.	409.151	409.021	-282.654	56865.	-6636253.	-6090523.	706.970	-324191.	-307878.	35.737
500.	425.320	452.996	-297.514	77741.	-6634901.	-6029962.	629.945	-324425.	-306053.	31.973
(2 sigma)	±0.159	±2.947	±2.946	±24.	±3220.	±2247.	±0.235	±3220.	±2247.	±0.235
550.	438.472	494.171	-313.540	99347.	-6633217.	-5969548.	566.940	-324705.	-304203.	28.891
600.	449.239	532.800	-330.219	121549.	-6631337.	-5909295.	514.450	-325069.	-302323.	26.320
650.	458.092	569.120	-347.213	144239.	-6629373.	-5849205.	470.048	-325551.	-300409.	24.141
700.	465.391	603.344	-364.298	167332.	-6627416.	-5789266.	432.000	-326179.	-298453.	22.271
750.	471.415	635.664	-381.322	190757.	-6628051.	-5729355.	399.027	-326974.	-296446.	20.646
(2 sigma)	±0.602	±2.937	±2.945	±83.	±3216.	±2004.	±0.140	±3216.	±2004.	±0.140
800.	476.384	666.253	-398.183	214456.	-6626003.	-5669510.	370.181	-327958.	-294379.	19.221
850.	480.473	695.260	-414.812	238381.	-6624262.	-5609784.	344.735	-331297.	-292230.	17.958
900.	483.826	722.821	-431.165	262491.	-6622868.	-5550151.	322.122	-331431.	-289928.	16.827
950.	486.559	749.056	-447.211	286753.	-6643366.	-5490192.	301.872	-331597.	-287618.	15.814
1000.	488.769	774.072	-462.933	311138.	-6642485.	-5429523.	283.609	-331813.	-285298.	14.902
(2 sigma)	±1.190	±2.928	±2.939	±294.	±3211.	±2015.	±0.105	±3211.	±2015.	±0.105
1050.	490.538	797.963	-478.323	335622.	-6641917.	-5368890.	267.087	-332094.	-282965.	14.077
1100.	491.933	820.816	-493.375	360186.	-6641676.	-5308277.	252.069	-332454.	-280618.	13.325
1150.	493.013	842.709	-508.091	384811.	-6665387.	-5246826.	238.318	-332905.	-278252.	12.639
1200.	493.827	863.709	-522.474	409483.	-6663000.	-5185201.	225.706	-333455.	-275864.	12.008
1250.	494.419	883.881	-536.529	434190.	-6660657.	-5123674.	214.106	-334114.	-273452.	11.427
(2 sigma)	±1.531	±2.947	±2.933	±630.	±3233.	±2276.	±0.095	±3233.	±2276.	±0.095
1300.	494.826	903.281	-550.264	458921.	-6658360.	-5062240.	203.403	-334888.	-271010.	10.889
1350.	495.080	921.961	-563.687	483670.	-6656115.	-5000894.	193.496	-335784.	-268537.	10.390
1400.	495.209	939.968	-576.806	508427.	-6653923.	-4939630.	184.300	-336808.	-266028.	9.926
1450.	495.239	957.347	-589.630	533189.	-6651784.	-4878443.	175.740	-337963.	-263480.	9.492
1500.	495.192	974.135	-602.169	557950.	-6649699.	-4817329.	167.754	-339253.	-260890.	9.085
(2 sigma)	±1.687	±2.992	±2.929	±1002.	±3300.	±2719.	±0.095	±3300.	±2719.	±0.095
1550.	495.087	990.371	-614.431	582707.	-6647666.	-4756284.	160.286	-340681.	-258255.	8.703
1600.	494.942	1006.087	-626.426	607458.	-6645684.	-4695303.	153.286	-342251.	-255571.	8.344
1650.	494.772	1021.315	-638.163	632201.	-6643750.	-4634384.	146.712	-343963.	-252836.	8.004
1700.	494.592	1036.083	-649.650	656935.	-6793388.	-4572173.	140.486	-345819.	-250047.	7.683
1750.	494.414	1050.417	-660.897	681660.	-6791115.	-4506876.	134.523	-347820.	-247202.	7.379
(2 sigma)	±2.223	±3.046	±2.929	±1356.	±3409.	±3278.	±0.098	±3409.	±3278.	±0.098
1800.	494.250	1064.343	-671.911	706377.	-7247367.	-4429873.	128.551	-349968.	-244297.	7.089
(2 sigma)	±2.440	±3.058	±2.930	±1428.	±3437.	±3399.	±0.099	±3437.	±3399.	±0.099

$Al_2Ca_3O_{12}Si_3$

$Ca_3Al_2Si_3O_{12}$	Grossular	Formula weight = 450.452 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 256.00 \pm 2.90$ J/(mol·K) $\qquad \Delta H_f° = -6636.3 \pm 3.2$ kJ/mol

$V° = 125.30 \pm 0.06$ cm^3/mol $\qquad \Delta G_f° = -6274.9 \pm 2.6$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1600 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\, a_6\, T + a_7\, T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\, T^2) - 2\, a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\, a_6\, T + a_7\, T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\, a_3\, T^{0.5} + a_5\, T + a_6\, T^2 + a_7\, T^3/3$$

$a_1 = 1.77080 \times 10^6$ $\qquad a_4 = -6.53238 \times 10^3$ $\qquad a_6 = -9.66435 \times 10^{-2}$

$a_2 = 9.02292 \times 10^4$ $\qquad a_5 = 9.05362 \times 10^2$ $\qquad a_7 = 3.35314 \times 10^{-5}$

$a_3 = -1.07077 \times 10^4$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of grossular.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Westrum and others (1979)	heat capacity	adiabatic calorimeter	57	200 - 596 K
Krupka and others (1979)	heat capacity	differential scanning calorimeter	50	350 - 978 K
Estimated values[a]	heat capacity	component summation	11	1000 - 1800 K
Westrum and others (1979)	entropy	adiabatic calorimeter	1	298.15

a Above 1000 K, the heat capacity of grossular was estimated by totaling the average heat capacities of CaO-, SiO_2-, $(Al^{IV})_2O_3$-, and $(Al^{VI})_2O_3$-components derived from a number of sodium, potassium, and calcium aluminum silicates. (Al^{IV}) and (Al^{VI}) represent aluminum in tetrahedral and octahedral coordination.

The standard error of estimate of the fitted heat capacity of Westrum and others (1979) on a natural grossular and Krupka and others (1979) on a synthetic grossular is 0.84 and 6.4 J/(mol·K), respectively. The estimated heat-capacity values above 1000 K is a smooth extension of the data of Krupka and others (1979). The estimated heat capacity was fit with a standard error of estimate of 2.7 J/(mol·K). Westrum and others derived an entropy for grossular at 298.15 K of 254.68 ± 1.26 J/(mol·K), which has a departure of 1.32 from the fitted value of 256.0 ± 2.9 J/(mol·K). Haselton and Westrum (1979) reported heat-capacity data on synthetic grossular and obtained an entropy of 260.12 J/(mol·K) at 298.15 K. Neither the heat capacity nor entropy reported by Haselton and Westrum were used because the entropy is inconsistent with the phase-equilibria studies.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Charlu and others (1978)[b]	solution calorimetry (borate salt)	A	970	2	-316.703±5.089 -318.334±5.146	-6642.885 -6641.254
Boettcher (1970)	gas-medium pressure apparatus pressure apparatus	B	898-928	1 pair	-308.308±4.088	-6635.093
Newton (1965)	gas- and solid-medium pressure apparatus medium apparatus	B	843-1113	6 pair	-306.468±2.790	-6636.013
Boettcher (1970)	gas- and solid-medium pressure apparatus medium apparatus	C	853-933	2 pair	-213.025±2.944	-6639.311
Strens (1968)	gas-medium pressure apparatus	C	770-823	1 pair	-220.561±5.976	-6631.774
Shmulovich (1974)	gas-medium pressure apparatus	D	1133-1153	1 pair	159.942±1.763	-6636.890
Huckenholz (1974)	unspecified	D	1125-1423	6 pair	158.750±2.236	-6636.294
Hays (1965)	solid-medium pressure apparatus	D	1473-1523	2 pair	156.099±6.608	-6634.968
Huckenholz (1974)	unspecified	E	848-858	1 pair	-49.366±0.328	-6636.033
Newton (1966b)	gas-medium pressure apparatus	E	803-923	2 pair	50.708±3.042	6637.375
Huckenholz (1974)	unspecified	F	888-958	2 pair	-50.101+0.499	-6636.199
Newton (1966b)	solid-medium pressure apparatus	F	973-1023	2 pair	-49.103±1.847	-6635.201
Boettcher (1970)	gas-medium pressure apparatus	F	893-1053	2 pair	-50.328±1.454	-6636.426
Huckenholz (1974)	unspecified	G	1028-1263	3 pair	-102.895±1.257	-6636.736
Boettcher (1970)	gas-medium pressure apparatus	G	1033-1053	1 pair	-102.037±0.996	-6635.878

a Reactions:

A) $Ca_3Al_2Si_3O_{12}$(grossular) = 3 CaO(lime) + Al_2O_3(corundum) + 3 SiO_2(quartz, beta)

B) 2 $Ca_3Al_2Si_3O_{12}$(grossular) + 6 $CaAl_2Si_2O_8$(anorthite) + Al_2O_3(corundum) + 3 H_2O(gas) = 6 $Ca_2Al_3Si_3O_{12}(OH)$(zoisite)

C) $Ca_3Al_2Si_3O_{12}$(grossular) + 5 $CaAl_2Si_2O_8$(anorthite) + 2 H_2O(gas) = 4 $Ca_2Al_3Si_3O_{12}(OH)$(zoisite) + SiO_2(quartz, alpha)

D) 2 $Ca_3Al_2Si_3O_{12}$(grossular) = $CaAl_2Si_2O_8$(anorthite) + 3 $CaSiO_3$(wollastonite) + $Ca_2Al_2SiO_7$(gehlenite)

E) 2 $CaSiO_3$(wollastonite) + $CaAl_2Si_2O_8$(anorthite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, alpha)

F) 2 $CaSiO_3$(wollastonite) + $CaAl_2Si_2O_8$(anorthite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, beta)

G) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) = $Ca_3Al_2Si_3O_{12}$(grossular) + Al_2O_3(corundum)

b Charlu and others (1978) measured the enthalpy of solution of two samples of synthetic grossular in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of lime, quartz, and corundum in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for grossular (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -6636.338±3.220 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of grossular and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate.

The molar volume of grossular was obtained from the compilation of Robie and others (1967).

$Al_2Si_4O_{10}(OH)_2$

Pyrophyllite (monoclinic)

$Al_2H_2O_{12}Si_4$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	275.556	214.466	-240.562	-7128.	-5640881.	-5299642.	1013.453	-36683.	-24758.	4.734
298.15	294.349	239.424	-239.424	0.	-5642023.	-5268357.	922.994	-37708.	-23620.	4.138
(2 sigma)	±0.318	±0.992	±0.992	±0.	±1158.	±1043.	±0.183	±1158.	±1043.	±0.183
300.	295.656	241.249	-239.429	546.	-5642094.	-5266038.	916.898	-37781.	-23532.	4.097
350.	327.053	289.276	-243.150	16144.	-5643428.	-5203241.	776.541	-39606.	-21010.	3.136
400.	351.979	334.638	-251.780	33143.	-5643786.	-5140322.	671.257	-81004.	-15338.	2.003
450.	372.025	377.293	-263.380	51261.	-5643393.	-5077406.	589.370	-80498.	-7160.	0.831
500.	383.509	417.369	-276.796	70287.	-5642421.	-5014566.	523.868	-79981.	961.	-0.100
(2 sigma)	±1.312	±1.033	±0.994	±121.	±1170.	±1007.	±0.105	±1170.	±1007.	±0.105
550.	402.465	455.069	-291.306	90070.	-5640993.	-4951846.	470.287	-79504.	9032.	-0.858
600.	414.699	490.623	-306.449	110504.	-5639196.	-4889274.	425.649	-79092.	17062.	-1.485
650.	425.837	524.262	-321.921	131521.	-5637085.	-4826864.	387.891	-78753.	25060.	-2.014
700.	435.374	556.208	-337.525	153078.	-5634694.	-4764627.	355.541	-78478.	33035.	-2.465
750.	445.704	586.667	-353.127	175155.	-5632033.	-4702570.	327.516	-78245.	40992.	-2.855
(2 sigma)	±9.594	±1.569	±1.013	±806.	±1417.	±1023.	±0.071	±1417.	±1023.	±0.071
800.	457.143	515.828	-368.640	197750.	-5629101.	-4640700.	303.006	-78023.	48934.	-3.195
850.	467.948	543.864	-384.011	220876.	-5625882.	-4579022.	281.392	-80638.	56882.	-3.496
900.	479.332	570.930	-399.203	244555.	-5622349.	-4517543.	262.191	-78612.	64915.	-3.768
950.	491.469	597.168	-414.198	268821.	-5639980.	-4455876.	245.001	-76190.	72825.	-4.004
1000.	504.506	722.704	-428.988	293717.	-5635437.	-4393670.	229.502	-73323.	80595.	-4.210
(2 sigma)	±45.080	±7.811	±1.401	±6808.	±6890.	±1470.	±0.077	±6890.	±1470.	±0.077
1050.	513.566	747.655	-443.570	319289.	-5630337.	-4331705.	215.490	-69957.	88211.	-4.388
1100.	533.754	772.125	-457.950	345592.	-5624619.	-4269996.	202.765	-66035.	95653.	-4.542
1150.	550.161	796.208	-472.135	372685.	-5618218.	-4208563.	191.159	-61493.	102903.	-4.674
1200.	567.863	819.992	-486.134	400630.	-5611065.	-4147424.	180.533	-56264.	109941.	-4.786
1250.	585.927	843.555	-499.960	429494.	-5603089.	-4086600.	170.770	-50279.	116746.	-4.879
(±2 sigma)	±113.181	±24.351	±3.884	±25769.	±25776.	±4859.	±0.203	±25776.	±4859.	±0.203

$Al_2H_2O_{12}Si_4$

$Al_2Si_4O_{10}(OH)_2$ Pyrophyllite Formula weight = 360.314 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 239.424 \pm 0.992$ J/(mol·K) $\Delta H_f^\circ = -5642.023 \pm 1.158$ kJ/mol

$V° = 127.82 \pm 0.29$ cm^3/mol $\Delta G_f^\circ = -5268.357 \pm 1.043$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1000 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 6.069358 \times 10^6$ $a_4 = -9.850236 \times 10^3$ $a_6 = -3.960932 \times 10^{-1}$

$a_2 = 2.311270 \times 10^5$ $a_5 = 1.454512 \times 10^3$ $a_7 = 3.971889 \times 10^{-4}$

$a_3 = -1.774285 \times 10^4$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of pyrophyllite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Robie and others (1976)	heat capacity	adiabatic calorimetry	20	200 - 370 K
Krupka and others (1979)	heat capacity	differential scanning calorimetry	48	335 - 680 K
Robie and others (1976)	entropy	adiabatic calorimetry	1	298.15 K

The heat-capacity measurements of Robie and others (1976) and Krupka and others (1979) were fit with standard errors of estimate of 0.31 and 2.0 J/(mol·K), respectively. The fitted entropy at 298.15 K is 239.424 ± 0.992 J/(mol·K), which agrees with the experimental value of 239.4 ± 0.4 reported by Robie and others (1976).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Hemley and others (in press)[b]	H_4SiO_4 concentration	A	523-598	4	-1.678±1.644	-5643.386
Hemley and others (in press)[b]	H_4SiO_4 concentration	B	613-673	11	-78.080±1.616	-5642.283
Haas and Holdaway (1973)	gas-medium pressure apparatus	B	643-737	4	-76.968±0.615	-5642.872
Kerrick (1968)	gas-medium pressure apparatus	B	668-718	2	-79.382±1.273	-5643.589
Hemley and others (in press)[b]	H_4SiO_4 concentration	C	473-573	10	57.792±0.323	-5642.550
Haas and Holdaway (1973)	gas-medium pressure apparatus	D	618-722	4	311.486±3.224	-5643.168

a Reactions:

A) 2 AlO(OH)(diaspore) + 4 SiO_2(quartz, alpha) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite)

B) Al_2SiO_5(andalusite) + 3 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite)

C) $Al_2Si_2O_5(OH)_4$(kaolinite) + 2 SiO_2(quartz, alpha) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite) + H_2O(gas)

D) $Al_2Si_4O_{10}(OH)_2$(pyrophyllite) + 6 AlO(OH)(diaspore) = 4 Al_2SiO_5(andalusite) + 4 H_2O(gas)

b Hemley and others (in press) measured the silicic-acid content of water equilibrated with the mineral pairs 1) pyrophyllite-diaspore, 2) pyrophyllite-andalusite, and 3) pyrophyllite-kaolinite between 500 K and 700 K at 100 and 200 MPa. Using their data for the solubility of quartz under the same conditions, the molar volumes of the solid phases, and the free-energy data for H_2O(gas) of Fisher and Zen (1971), we calculated the free energy of reaction at 101.325 kPa and temperature for reactions A, B, and C for each observation.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for pyrophyllite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -5642.023±1.158 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of pyrophyllite and presents the data in their poorest perspective.

The phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume of pyrophyllite was obtained from the study by Krupka and others (1979).

$Al_2Si_2O_5(OH)_4$

$Al_2H_4O_9Si_2$

Dickite (monoclinic, polymorphous with Kaolinite, Nacrite, and Halloysite, member of the Kaolinite - Serpentine Group)

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	224.241	176.737	-197.985	-5804.	-4117368.	-3823141.	731.101	-47687.	-28734.	5.495
298.15	239.787	197.058	-197.058	0.	-4118475.	-3796160.	665.071	-49750.	-26906.	4.714
(2 sigma)	±0.736	±3.067	±3.067	±0.	±1237.	±1538.	±0.269	±1237.	±1538.	±0.269
300.	240.872	198.545	-197.063	445.	-4118545.	-3794160.	660.621	-49897.	-26764.	4.660
350.	267.038	237.716	-200.097	13167.	-4119921.	-3739973.	558.160	-53639.	-22607.	3.374
400.	287.841	274.786	-207.138	27059.	-4120419.	-3685652.	481.296	-136540.	-12136.	1.585
450.	304.298	309.677	-216.613	41879.	-4120241.	-3631311.	421.511	-135570.	3358.	-0.390
500.	317.245	342.436	-227.575	57430.	-4119559.	-3577018.	373.688	-134476.	18737.	-1.957
(2 sigma)	±1.677	±3.131	±3.070	±256.	±1263.	±1971.	±0.206	±1263.	±1971.	±0.206
550.	327.337	373.166	-239.429	73556.	-4118516.	-3522812.	334.568	-133345.	34003.	-3.229
600.	335.085	401.996	-251.787	90125.	-4117234.	-3468712.	301.978	-132254.	49168.	-4.280
650.	340.886	429.058	-264.394	107032.	-4115815.	-3414725.	274.410	-131266.	64245.	-5.163
700.	345.052	454.482	-277.073	124187.	-4114346.	-3360850.	250.790	-130438.	79252.	-5.914
750.	347.833	478.391	-289.705	141514.	-4112901.	-3307080.	230.325	-129815.	94207.	-6.561
(2 sigma)	±4.150	±3.286	±3.090	±650.	±1397.	±2627.	±0.183	±1397.	±2627.	±0.183
800.	349.429	500.896	-302.208	158950.	-4111545.	-3253403.	212.425	-129439.	109128.	-7.125
850.	350.002	522.102	-314.526	176440.	-4110334.	-3199807.	196.636	-130779.	124045.	-7.623
900.	349.686	542.103	-326.619	193936.	-4109320.	-3146277.	182.605	-130150.	139015.	-8.068
950.	348.591	560.983	-338.462	211396.	-4130058.	-3092405.	170.032	-129730.	153956.	-8.465
1000.	346.811	578.821	-350.038	228783.	-4129290.	-3037812.	158.679	-129547.	168881.	-8.821
(2 sigma)	±11.337	±4.041	±3.129	±2209.	±2532.	±3364.	±0.176	±2532.	±3364.	±0.176

$Al_2H_4O_9Si_2$

$Al_2Si_2O_5(OH)_4$ Dickite Formula weight = 258.160 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 197.058 \pm 3.067$ J/(mol·K) $\Delta H_f^\circ = -4118.475 \pm 1.237$ kJ/mol

$V° = 99.300 \pm 0.140$ cm^3/mol $\Delta G_f^\circ = -3796.160 \pm 1.538$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1000 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = 3.804450 \times 10^6$ $a_4 = -6.190732 \times 10^3$ $a_6 = -1.056632 \times 10^{-1}$

$a_2 = 1.379448 \times 10^5$ $a_5 = 9.083598 \times 10^2$ $a_7 = 0.0$

$a_3 = -1.119531 \times 10^4$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of dickite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King and Weller (1961)	heat capacity	isothermal calorimetry	10	206 - 296 K
Estimated values[a]	heat capacity		27	340 - 800 K
King and Weller (1961)	entropy	isothermal calorimetry	1	298.15 K

a Heat-capacity values for kaolinite from Hemingway and others (1978) were used.

The heat-capacity measurements of King and Weller (1961) were fit with a standard error of estimate of 0.27 J/(mol·K). The estimated heat-capacity values were fit with a standard error of estimate of 1.66 J/(mol·K). The fitted entropy at 298.15 K is 197.058 ± 3.067 J/(mol·K), which agrees with the experimental value of 197.058 ± 1.255 reported by King and Weller (1961).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) kJ	ΔH_f°(298.15 K) kJ/mol
Barany and Kelley (1961)[b]	solution calorimetry (HF)	A	346.85	6	-3.642±1.215	-4118.615

a Reaction:

A) $Al_2Si_2O_5(OH)_4$(dickite) + H_2O = 2 SiO_2(quartz, alpha) + 2 $Al(OH)_3$(gibbsite)

b Barany and Kelley (1961) measured the enthalpy of solution of dickite in HF acid solution at 346.85 K. To complete the thermodynamic cycle, their data were evaluated in combination with the recent data for the enthalpies of solution of water, quartz, and gibbsite in similar solutions (Barany, 1963; Bennington and others, 1978; Hemingway and Robie, 1977; Barany and Kelley, 1961; and Koehler and others, 1961).

The molar volume of dickite was obtained from the compilation of Robie and others (1967).

$Al_2Si_2O_5(OH)_4$

$Al_2H_4O_9Si_2$

Halloysite (monoclinic, polymorphous with Kaolinite, Nacrite, and Dickite, member of the Kaolinite - Serpentine Group)

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	log $K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	log $K^\circ_{f,ox}$
273.15	230.416	182.502	-204.283	-5950.	-4100066.	-3807414.	728.094	-30385.	-13007.	2.487
298.15	245.245	203.334	-203.334	0.	-4101028.	-3780584.	662.342	-32303.	-11330.	1.985
(2 sigma)	±0.755	±3.067	±3.067	±0.	±1200.	±1508.	±0.264	±1200.	±1508.	±0.264
300.	246.270	204.854	-203.339	455.	-4101088.	-3778595.	657.911	-32440.	-11200.	1.950
350.	270.688	244.728	-206.432	13404.	-4102237.	-3724743.	555.887	-35955.	-7377.	1.101
400.	289.860	282.175	-213.585	27436.	-4102594.	-3670783.	479.355	-118715.	2733.	-0.357
450.	305.023	317.226	-223.175	42323.	-4102350.	-3616816.	419.829	-117679.	17853.	-2.072
500.	317.065	350.011	-234.237	57887.	-4101655.	-3562902.	372.214	-116572.	32853.	-3.432
(2 sigma)	±1.683	±3.132	±3.069	±257.	±1227.	±1948.	±0.204	±1227.	±1948.	±0.204
550.	326.629	380.696	-246.172	73988.	-4100636.	-3509073.	333.264	-115465.	47741.	-4.534
600.	334.194	409.454	-258.594	90516.	-4099396.	-3455348.	300.815	-114415.	62531.	-5.444
650.	340.121	436.448	-271.247	107380.	-4098019.	-3401733.	273.366	-113470.	77238.	-6.207
700.	344.686	461.828	-283.963	124506.	-4096579.	-3348226.	249.848	-112671.	91877.	-6.856
750.	348.105	485.732	-296.625	141830.	-4095137.	-3294823.	229.472	-112052.	106464.	-7.415
(2 sigma)	±4.156	±3.286	±3.090	±651.	±1365.	±2609.	±0.182	±1365.	±2609.	±0.182
800.	350.551	508.281	-309.156	159300.	-4093747.	-3241514.	211.649	-111642.	121017.	-7.902
850.	352.162	529.585	-321.502	176871.	-4092456.	-3188290.	195.928	-112900.	135562.	-8.331
900.	353.050	549.743	-333.627	194504.	-4091304.	-3135137.	181.959	-112134.	150155.	-8.715
950.	353.307	568.841	-345.508	212166.	-4111840.	-3081652.	169.441	-111512.	164709.	-9.056
1000.	353.010	586.958	-357.132	229826.	-4110800.	-3027459.	158.138	-111057.	179235.	-9.362
(2 sigma)	±11.384	±4.043	±3.129	±2213.	±2517.	±3351.	±0.175	±2517.	±3351.	±0.175

$Al_2H_4O_9Si_2$

$Al_2Si_2O_5(OH)_4$ Halloysite Formula weight = 258.160 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 203.334±3.067$ J/(mol·K) $\Delta H_f° = -4101.028±1.200$ kJ/mol

$V° =$ $\Delta G_f° = -3780.584±1.508$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1000 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = 1.936712x10^6$ $a_4 = -5.153860x10^3$ $a_6 = -7.258844x10^{-2}$

$a_2 = 8.41514x10^4$ $a_5 = 7.723004x10^2$ $a_7 = 0.0$

$a_3 = -8.729481x10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of halloysite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King and Weller (1961)	heat capacity	isothermal calorimetry	10	206 - 296 K
Estimated values[a]	heat capacity		27	340 - 800 K
King and Weller (1961)	entropy	isothermal calorimetry	1	298.15 K

a Heat-capacity values for kaolinite from Hemingway and others (1978) were used.

The heat capacity measured by King and Weller (1961) was fit with a standard error of estimate of 0.23 J/(mol·K). The estimated heat-capacity values were fit with a standard error of estimate of 1.5 J/(mol·K). The fitted entropy at 298.15 K is 203.334 ± 3.067 J/(mol·K), which agrees with the experimental value of 203.334 ± 1.255 J/(mol·K) reported by King and Weller (1961).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) kJ	$\Delta H_f°$(298.15 K) kJ/mol
Barany and Kelley (1961)[b]	solution calorimetry(HF)	A	346.85	6	-21.089±1.177	-4101.168

a Reaction:

A) $Al_2Si_2O_5(OH)_4$(halloysite) + H_2O(liquid) = 2 SiO_2(quartz, alpha) + 2 $Al(OH)_3$(gibbsite)

b Barany and Kelley (1961) measured the enthalpy of solution of halloysite in HF acid solution at 346.85 K. To complete the thermodynamic cycle, their data were evaluated in combination with the recent data for the enthalpies of solution of water, quartz, and gibbsite in similar solutions (Barany, 1963; Bennington and others, 1978, Hemingway and Robie, 1977; Barany and Kelley, 1961; and Koehler and others, 1961).

$Al_2Si_2O_5(OH)_4$

$Al_2H_4O_9Si_2$

Kaolinite (monoclinic, polymorphous with Dickite, Nacrite, and Halloysite, member of the Kaolinite - Serpentine Group)

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	$\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	$\log K^\circ_{f,ox}$
273.15	231.273	184.057	-205.919	-5972.	-4118841.	-3826613.	731.765	-49160.	-32207.	6.159
298.15	246.135	204.966	-204.966	0.	-4119780.	-3799823.	665.713	-51056.	-30570.	5.356
(2 sigma)	±0.771	±1.022	±1.022	±0.	±1065.	±982.	±0.172	±1065.	±982.	±0.172
300.	247.159	206.492	-204.971	456.	-4119839.	-3797838.	661.262	-51191.	-30442.	5.300
350.	271.445	246.495	-208.074	13447.	-4120946.	-3744071.	558.772	-54665.	-26705.	3.986
400.	290.400	284.030	-215.249	27512.	-4121271.	-3690202.	481.891	-137392.	-16686.	2.179
450.	305.345	319.131	-224.863	42420.	-4121005.	-3636329.	422.094	-136334.	-1660.	0.193
500.	317.201	351.940	-235.949	57995.	-4120299.	-3582510.	374.262	-135216.	13244.	-1.384
(2 sigma)	±1.682	±1.196	±1.028	±257.	±1110.	±975.	±0.102	±1110.	±975.	±0.102
550.	326.624	382.631	-247.904	74100.	-4119277.	-3528779.	335.135	-134106.	28036.	-2.663
600.	334.093	411.384	-260.342	90625.	-4118040.	-3475150.	302.538	-133059.	42729.	-3.720
650.	339.968	438.368	-273.009	107483.	-4116670.	-3421631.	274.965	-132121.	57340.	-4.608
700.	344.523	463.736	-285.736	124600.	-4115238.	-3368220.	251.339	-131330.	71883.	-5.364
750.	347.969	487.629	-298.407	141917.	-4113804.	-3314912.	230.871	-130718.	86375.	-6.016
(2 sigma)	±4.157	±1.555	±1.084	±650.	±1265.	±1050.	±0.073	±1265.	±1050.	±0.073
800.	350.476	510.171	-310.944	159381.	-4112419.	-3261698.	212.967	-130313.	100834.	-6.584
850.	352.178	531.473	-323.296	176951.	-4111129.	-3208568.	197.174	-131573.	115284.	-7.085
900.	353.184	551.635	-335.426	194588.	-4109973.	-3155510.	183.141	-130803.	129783.	-7.532
950.	353.585	570.744	-347.313	212259.	-4130500.	-3102119.	170.566	-130171.	144242.	-7.931
1000.	353.453	588.879	-358.942	229937.	-4129442.	-3048022.	159.212	-129699.	158672.	-8.288
(2 sigma)	±11.389	±2.826	±1.190	±2214.	±2444.	±1274.	±0.067	±2444.	±1274.	±0.067

$Al_2H_4O_9Si_2$

$Al_2Si_2O_5(OH)_4$ | Kaolinite | Formula weight = 258.160 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 205.0 \pm 1.00$ J/(mol·K) $\Delta H_f° = -4119.8 \pm 1.1$ kJ/mol

$V° = 99.52 \pm 0.52$ cm^3/mol $\Delta G_f° = -3799.8 \pm 1.0$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1000 K)

$$C_p°(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\, a_6\, T + a_7\, T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\, T^2) - 2\, a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\, a_6\, T + a_7\, T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\, a_3\, T^{0.5} + a_5\, T + a_6\, T^2 + a_7\, T^3/3$$

$a_1 = 1.49195 \times 10^6$ $a_4 = -4.97366 \times 10^3$ $a_6 = -6.77102 \times 10^{-2}$

$a_2 = 7.35514 \times 10^4$ $a_5 = 7.49175 \times 10^2$ $a_7 = 0.0$

$a_3 = -8.27864 \times 10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of kaolinite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King and Weller (1961)[a]	heat capacity	isothermal calorimeter	10	206 - 296 K
Hemingway and others (1978)	heat capacity	differential scanning calorimeter	27	340 - 800 K
King and Weller (1961)[a]	entropy	isothermal calorimeter	1	298.15 K

a The measurements were made on an impure natural sample of kaolinite. The observed heat-capacity and entropy values were assumed to equal the molar sum of the heat capacities and entropies, respectively, of the components. The stoichiometry used was: kaolinite, 0.970; pyrophyllite, 0.016; boehmite, 0.014.

The heat-capacity measurements of King and Weller (1961) and Hemingway and others (1978) were fit with a standard error of estimate of 0.52 and 1.6 J/(mol·K), respectively. The fitted entropy for 298.15 K is 205.0 ± 1.0 J/(mol·K), or a departure of 0.33 J/mol from the experimental value, corrected for composition, of 204.67 ± 0.42 J/(mol·K) reported by King and Weller.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Barany and Kelley (1961)[b]	solution calorimetry (HF)[b]	A	346.85	10	-2.362±1.304	-4119.894
					-2.403±1.116	-4119.853
Hemley and others (in press)[c]	H_4SiO_4 concentration	B	573-573	9	-75.671±1.059	-4119.572
Hemley and others (in press)[c]	H_4SiO_4 concentration	C	473-573	6	-57.885±0.441	-4119.844
Hemley and others (in press)[c]	H_4SiO_4 concentration	D	473-573	10	57.792±0.323	-4120.515

a Reactions:

A) $Al_2Si_2O_5(OH)_4$(kaolinite) + H_2O(gas) = 2 SiO_2(quartz, alpha) + 2 $Al(OH)_3$(gibbsite)

B) 2 $AlO(OH)$(boehmite) + 2 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_2O_5(OH)_4$(kaolinite)

C) 2 $AlO(OH)$(diaspore) + 2 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_2O_5(OH)_4$(kaolinite)

D) $Al_2Si_2O_5(OH)_4$(kaolinite) + 2 SiO_2(quartz, alpha) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite)+ H_2O(gas)

b Barany and Kelley (1961) measured the enthalpy of solution of kaolinite in HF acid solution at 346.85 K. To complete the thermodynamic cycle, their data were evaluated in combination with the recent data for the enthalpies of solution of water, quartz, and gibbsite in similar solutions (Barany, 1963; Bennington and others, 1978; Hemingway and Robie, 1977; Barany and Kelley, 1961; and Koehler and others, 1961).

c Hemley and others (in press) measured the silicic-acid content of water equilibrated with the mineral pairs A) boehmite-kaolinite, B) diaspore-kaolinite, and C) pyrophyllite-kaolinite at 100 and 200 MPa between 450 K and 600 K. Using their data for the solubility of quartz under the same conditions, the molar volumes of the solid phases, and the free-energy data for H_2O(gas) of Fisher and Zen (1971), we calculated the gibbs energies of reactions B, C, and D for each observation.

The phase-equilibrium studies of Hemley and others (in press) were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for kaolinite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -4119.780±1.065 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of kaolinite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate. The phase-equilibria studies are consistent with the experimental enthalpy of solution of Barany and Kelley (1961).

The molar volume of kaolinite was obtained from the compilation of Robie and others (1967).

Al_2O_3
Corundum (trigonal)

Al_2O_3

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	73.847	44.204	-51.223	-1917.	-1675326.	-1590109.	304.077	0.	0.	0.
298.15	79.393	50.917	-50.917	0.	-1675711.	-1582291.	277.211	0.	0.	0.
300.	79.772	51.409	-50.918	147.	-1675736.	-1581712.	275.400	0.	0.	0.
350.	88.678	64.405	-51.924	4368.	-1676206.	-1565999.	233.712	0.	0.	0.
400.	95.583	76.716	-54.261	8982.	-1676383.	-1550240.	202.440	0.	0.	0.
450.	101.075	88.303	-57.406	13903.	-1676343.	-1534473.	178.117	0.	0.	0.
500.	105.528	99.190	-61.046	19072.	-1676144.	-1518719.	158.659	0.	0.	0.
550.	109.195	109.425	-64.984	24443.	-1675833.	-1502991.	142.742	0.	0.	0.
600.	112.254	119.062	-69.093	29981.	-1675445.	-1487294.	129.480	0.	0.	0.
650.	114.833	128.151	-73.289	35660.	-1675011.	-1471632.	118.262	0.	0.	0.
700.	117.029	136.744	-77.518	41458.	-1674557.	-1456005.	108.648	0.	0.	0.
750.	118.914	144.884	-81.740	47358.	-1674103.	-1440410.	100.319	0.	0.	0.
800.	120.545	152.612	-85.930	53346.	-1673670.	-1424845.	93.033	0.	0.	0.
850.	121.967	159.963	-90.070	59409.	-1673275.	-1409305.	86.605	0.	0.	0.
900.	123.217	166.971	-94.150	65539.	-1672932.	-1393788.	80.893	0.	0.	0.
950.	124.323	173.663	-98.160	71728.	-1694168.	-1377895.	75.762	0.	0.	0.
1000.	125.310	180.066	-102.096	77970.	-1693699.	-1361261.	71.105	0.	0.	0.
1050.	126.197	186.201	-105.956	84258.	-1693201.	-1344652.	66.893	0.	0.	0.
1100.	127.003	192.091	-109.738	90588.	-1692679.	-1328066.	63.065	0.	0.	0.
1150.	127.740	197.753	-113.443	96957.	-1692134.	-1311505.	59.570	0.	0.	0.
1200.	128.421	203.204	-117.070	103361.	-1691570.	-1294968.	56.368	0.	0.	0.
1250.	129.056	208.460	-120.621	109798.	-1690986.	-1278455.	53.424	0.	0.	0.
1300.	129.655	213.533	-124.098	116266.	-1690385.	-1261965.	50.706	0.	0.	0.
1350.	130.226	218.437	-127.501	122763.	-1689766.	-1245499.	48.191	0.	0.	0.
1400.	130.774	223.183	-130.834	129288.	-1689130.	-1229057.	45.857	0.	0.	0.
1450.	131.307	227.781	-134.098	135840.	-1688477.	-1212637.	43.684	0.	0.	0.
1500.	131.829	232.242	-137.296	142419.	-1687807.	-1196240.	41.657	0.	0.	0.
1550.	132.345	236.573	-140.429	149023.	-1687120.	-1179866.	39.761	0.	0.	0.
1600.	132.859	240.783	-143.499	155653.	-1686413.	-1163514.	37.985	0.	0.	0.
1650.	133.376	244.879	-146.510	162309.	-1685687.	-1147184.	36.317	0.	0.	0.
1700.	133.898	248.868	-149.462	168991.	-1684940.	-1130877.	34.748	0.	0.	0.
1750.	134.428	252.757	-152.358	175699.	-1684172.	-1114592.	33.269	0.	0.	0.
1800.	134.969	256.552	-155.200	182434.	-1683380.	-1098330.	31.873	0.	0.	0.

Al_2O_3

Corundum   Formula weight = 101.926 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 50.917$ J/(mol·K) $\Delta H_f^\circ = -1675.711$ kJ/mol

$V° = 25.575 \pm 0.007$ cm^3/mol $\Delta G_f^\circ = -1582.291$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = 0.0$ $a_4 = -1.55092 \times 10^3$ $a_6 = -1.95913 \times 10^{-2}$

$a_2 = 1.7321 \times 10^4$ $a_5 = 2.33004 \times 10^2$ $a_7 = 9.44410 \times 10^{-6}$

$a_3 = -2.46518 \times 10^3$

Sources for Thermodynamic Properties

The thermodynamic properties for corundum were taken from the following sources:

Property	Source
Heat capacity	Stull and Prophet (1971), Chase and others (1974, 1975)
Entropy	CODATA Task Group (1978)
Enthalpy of formation from the elements	CODATA Task Group (1978)

The molar volume for corundum was taken from the compilation of Robie and others (1967).

Al_2SiO_5

Reference state: Kyanite 273.15 K to 430.46 K
Andalusite 430.46 K to 1016.9 K
Sillimanite 1016.9 K to 1800 K

Al_2O_5Si

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	113.775	74.123	-84.937	-2954.	-2593700.	-2456680.	469.792	-7809.	-5696.	1.089
298.15	122.348	84.465	-84.465	0.	-2594269.	-2444113.	428.198	-7859.	-5500.	0.964
(2 sigma)	±0.154	±0.439	±0.439	±0.	±433.	±389.	±0.068	±433.	±389.	±0.068
300.	122.936	85.224	-84.468	227.	-2594305.	-2443181.	425.395	-7862.	-5486.	0.955
350.	136.874	105.266	-86.018	6737.	-2594999.	-2417932.	360.856	-7934.	-5084.	0.759
400.	147.857	124.288	-89.624	13865.	-2595250.	-2392615.	312.443	-7984.	-4673.	0.610
430.46	153.475	135.347	-92.471	18456.	-2595232.	-2377184.	288.462	-8009.	-4420.	0.536
430.46	153.273	144.555	-92.471	22420.	-2591268.	-2377184.	288.462	-4045.	-4420.	0.536
450.	156.475	151.431	-94.882	25447.	-2591204.	-2367468.	274.808	-4065.	-4436.	0.515
500.	163.491	168.294	-101.389	33452.	-2590880.	-2342623.	244.732	-4127.	-4474.	0.467
(2 sigma)	±0.268	±0.729	±0.769	±615.	±643.	±410.	±0.043	±643.	±410.	±0.043
550.	169.117	184.150	-108.199	41773.	-2590381.	-2317821.	220.128	-4219.	-4505.	0.428
600.	173.663	199.067	-115.156	50346.	-2589764.	-2293069.	199.629	-4355.	-4525.	0.394
650.	177.367	213.118	-122.157	59[illegible]25.	-2589077.	-2268372.	182.288	-4548.	-4532.	0.364
700.	180.419	226.378	-129.132	68072.	-2588357.	-2243729.	167.429	-4806.	-4522.	0.337
750.	182.969	238.915	-136.037	77[illegible]59.	-2587634.	-2219138.	154.554	-5133.	-4490.	0.313
(2 sigma)	±0.316	±0.729	±0.486	±614.	±642.	±380.	±0.026	±642.	±380.	±0.026
800.	185.138	250.794	-142.841	86363.	-2586933.	-2194595.	143.292	-5533.	-4435.	0.290
850.	187.024	262.076	-149.526	95668.	-2586274.	-2170094.	133.358	-6723.	-4347.	0.267
900.	188.708	272.815	-156.079	105062.	-2585671.	-2145631.	124.529	-6844.	-4204.	0.244
950.	190.256	283.059	-162.495	114536.	-2606651.	-2120806.	116.610	-6968.	-4053.	0.223
1000.	191.726	292.856	-168.770	124086.	-2605925.	-2095254.	109.445	-7095.	-3897.	0.204
(2 sigma)	±0.492	±0.730	±0.429	±615.	±644.	±434.	±0.023	±644.	±434.	±0.023
1016.90	192.213	296.073	-170.859	127330.	-2605672.	-2086626.	107.183	-7138.	-3842.	0.197
1016.90	194.962	298.992	-170.859	130298.	-2602704.	-2086626.	107.183	-4170.	-3842.	0.197
1050.	195.912	305.252	-174.997	136768.	-2602107.	-2069837.	102.969	-4161.	-3832.	0.191
1100.	197.210	314.397	-181.127	146596.	-2601180.	-2044512.	97.086	-4148.	-3816.	0.181
1150.	198.361	323.189	-187.114	156486.	-2600227.	-2019231.	91.716	-4138.	-3802.	0.173
1200.	199.379	331.653	-192.961	166430.	-2599253.	-1993991.	86.796	-4133.	-3787.	0.165
1250.	200.278	339.811	-198.673	176422.	-2598262.	-1968792.	82.271	-4139.	-3773.	0.158
(2 sigma)	±0.572	±0.562	±0.433	±454.	±551.	±513.	±0.021	±551.	±513.	±0.021
1300.	201.069	347.681	-204.254	186456.	-2597256.	-1943633.	78.096	-4159.	-3758.	0.151
1350.	201.763	355.283	-209.707	196527.	-2596240.	-1918513.	74.232	-4195.	-3742.	0.145
1400.	202.368	362.632	-215.038	206631.	-2595216.	-1893430.	70.645	-4253.	-3724.	0.139
1450.	202.892	369.743	-220.251	216763.	-2594187.	-1868385.	67.306	-4334.	-3703.	0.133
1500.	203.342	376.629	-225.349	226919.	-2593154.	-1843375.	64.192	-4442.	-3680.	0.128
(2 sigma)	±0.879	±0.595	±0.437	±527.	±612.	±611.	±0.021	±612.	±611.	±0.021
1550.	203.723	383.303	-230.338	237096.	-2592118.	-1818399.	61.280	-4581.	-3652.	0.123
1600.	204.042	389.776	-235.219	247290.	-2591083.	-1793457.	58.550	-4753.	-3620.	0.118
1650.	204.303	396.059	-239.999	257499.	-2590048.	-1768547.	55.987	-4962.	-3581.	0.113
1700.	204.510	402.161	-244.679	267720.	-2639525.	-1743219.	53.563	-5209.	-3536.	0.109
1750.	204.668	408.092	-249.263	277949.	-2638354.	-1716874.	51.246	-5499.	-3482.	0.104
(2 sigma)	±1.208	±0.668	±0.448	±702.	±767.	±730.	±0.022	±767.	±730.	±0.022
1800.	204.779	413.859	-253.756	288186.	-2637182.	-1690563.	49.059	-5835.	-3420.	0.099
(2 sigma)	±1.276	±0.688	±0.450	±751.	±811.	±756.	±0.022	±811.	±756.	±0.022

Al_2O_5Si

Al_2SiO_5 (reference state) — Kyanite, Andalusite, Sillimanite — Formula weight = 162.046 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (kyanite)

$S° = 84.47±0.44$ J/(mol·K) — $\Delta H_f^\circ = -2594.27±0.43$ kJ/mol

$V° = 44.22±0.02$ cm^3/mol — $\Delta G_f^\circ = -2444.11±0.39$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

Kyanite (temperature range 200 to 430.46 K)

$a_1 = 0.0$	$a_4 = -2.23489\times10^3$	$a_6 = -1.29800\times10^{-2}$
$a_2 = 2.37951\times10^4$	$a_5 = 3.36114\times10^2$	$a_7 = 0.0$
$a_3 = -3.55746\times10^3$		

Andalusite (temperature range 430.46 to 1016.9 K)

$a_1 = 2.28751\times10^6$	$a_4 = -3.71202\times10^3$	$a_6 = -1.03545\times10^{-1}$
$a_2 = 8.75787\times10^4$	$a_5 = 3.134705\times10^2$	$a_7 = 0.0$
$a_3 = -6.75436\times10^3$		

Sillimanite (temperature range 1016.9 to 1800 K)

$a_1 = 0.0$	$a_4 = -2.050871\times10^3$	$a_6 = -9.470810\times10^{-3}$
$a_2 = 1.667620\times10^4$	$a_5 = 3.134705\times10^2$	$a_7 = 0.0$
$a_3 = -3.164868\times10^3$		

Critical Reactions

Inversions:

Al_2SiO_5(kyanite) = Al_2SiO_5(andalusite)

T_i = 430.46 K (calculated) — $\Delta S_i^\circ = 9.20±1.80$ J/(mol·K)

$\Delta H_i^\circ = 3.96±0.77$ kJ/mol

Al_2SiO_5(andalusite) = Al_2SiO_5(sillimanite)

T_i = 1016.9 K (calculated) — $\Delta S_i^\circ = 2.92±0.83$ J/(mol·K)

$\Delta H_i^\circ = 2.97±0.84$ kJ/mol

For detailed information on Al_2SiO_5, refer to the appropriate tables on the individual phases.

Al_2SiO_5

Andalusite (orthorhombic, polymorphous with Kyanite and Sillimanite)

Al_2O_5Si

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	113.630	83.456	-94.246	-2947.	-2589694.	-2455224.	469.514	-3803.	-4239.	0.811
298.15	121.991	93.775	-93.775	0.	-2590270.	-2442889.	427.984	-3860.	-4277.	0.749
(2 sigma)	±0.262	±0.728	±0.728	±0.	±641.	±484.	±0.085	±641.	±484.	±0.085
300.	122.573	94.531	-93.777	226.	-2590307.	-2441975.	425.185	-3864.	-4279.	0.745
350.	136.577	114.519	-95.323	6718.	-2591019.	-2417190.	360.746	-3953.	-4341.	0.648
400.	147.672	133.509	-98.921	13835.	-2591281.	-2392334.	312.407	-4014.	-4392.	0.574
450.	156.475	151.431	-103.769	21448.	-2591204.	-2367468.	274.808	-4065.	-4436.	0.515
500.	163.491	168.294	-109.387	29453.	-2590880.	-2342623.	244.732	-4127.	-4474.	0.467
(2 sigma)	±0.268	±0.729	±0.727	±38.	±643.	±410.	±0.043	±643.	±410.	±0.043
550.	169.117	184.150	-115.471	37774.	-2590381.	-2317821.	220.128	-4219.	-4505.	0.428
600.	173.663	199.067	-121.822	46347.	-2589764.	-2293069.	199.629	-4355.	-4525.	0.394
650.	177.367	213.118	-128.309	55126.	-2589077.	-2268372.	182.288	-4548.	-4532.	0.364
700.	180.419	226.378	-134.845	64073.	-2588357.	-2243729.	167.429	-4806.	-4522.	0.337
750.	182.969	238.915	-141.369	73159.	-2587634.	-2219133.	154.554	-5133.	-4490.	0.313
(2 sigma)	±0.316	±0.729	±0.726	±78.	±642.	±380.	±0.026	±642.	±380.	±0.026
800.	185.138	250.794	-147.840	82363.	-2586933.	-2194595.	143.292	-5533.	-4435.	0.290
850.	187.024	262.076	-154.231	91668.	-2586274.	-2170094.	133.358	-6723.	-4347.	0.267
900.	188.708	272.815	-160.523	101062.	-2585671.	-2145631.	124.529	-6844.	-4204.	0.244
950.	190.256	283.059	-166.705	110537.	-2606651.	-2120806.	116.610	-6968.	-4053.	0.223
1000.	191.726	292.856	-172.769	120087.	-2605925.	-2095254.	109.445	-7095.	-3897.	0.204
(2 sigma)	±0.492	±0.730	±0.725	±126.	±644.	±434.	±0.023	±644.	±434.	±0.023
1050.	193.163	302.245	-178.713	129709.	-2605167.	-2069739.	102.964	-7221.	-3734.	0.186
1100.	194.607	311.264	-184.534	139403.	-2604374.	-2044261.	97.074	-7342.	-3565.	0.169
1150.	196.094	319.947	-190.234	149170.	-2603544.	-2018820.	91.698	-7454.	-3391.	0.154
1200.	197.652	328.326	-195.814	159014.	-2602670.	-1993415.	86.771	-7551.	-3212.	0.140
1250.	199.307	336.427	-201.278	168937.	-2601747.	-1968049.	82.240	-7625.	-3029.	0.127
(2 sigma)	±0.568	±0.738	±0.724	±187.	±657.	±545.	±0.023	±657.	±546.	±0.023
1300.	201.080	344.279	-206.628	178946.	-2600767.	-1942720.	78.059	-7669.	-2845.	0.114
1350.	202.993	351.903	-211.868	189048.	-2599721.	-1917430.	74.190	-7676.	-2659.	0.103
1400.	205.061	359.322	-217.002	199248.	-2598600.	-1892180.	70.598	-7636.	-2474.	0.092
1450.	207.299	366.556	-222.035	209556.	-2597394.	-1866972.	67.256	-7541.	-2291.	0.083
1500.	209.721	373.624	-226.970	219981.	-2596092.	-1841807.	64.137	-7381.	-2112.	0.074
(2 sigma)	±1.915	±0.756	±0.724	±285.	±703.	±689.	±0.024	±703.	±689.	±0.024
1550.	212.339	380.543	-231.813	230532.	-2594683.	-1816687.	61.222	-7146.	-1940.	0.065
1600.	215.164	387.329	-236.567	241219.	-2593155.	-1791614.	58.490	-6826.	-1777.	0.058
1650.	218.204	393.996	-241.237	252052.	-2591496.	-1766591.	55.926	-6410.	-1625.	0.051
1700.	221.469	400.558	-245.827	263043.	-2640203.	-1741171.	53.500	-5887.	-1438.	0.046
1750.	224.967	407.027	-250.340	274203.	-2638102.	-1714759.	51.183	-5247.	-1358.	0.041
(2 sigma)	±4.592	±0.951	±0.727	±969.	±1182.	±852.	±0.025	±1182.	±852.	±0.025
1800.	228.703	413.417	-254.782	285543.	-2635825.	-1688410.	48.996	-4478.	-1257.	0.037
(2 sigma)	±5.280	±1.040	±0.729	±1205.	±1387.	±883.	±0.026	±1387.	±838.	±0.026

Al_2O_5Si

Al_2SiO_5 Andalusite Formula weight = 162.046 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 93.78 \pm 0.73$ J/(mol·K) $\Delta H_f° = -2590.27 \pm 0.64$ kJ/mol

$V° = 51.58 \pm 0.02$ cm^3/mol $\Delta G_f° = -2442.89 \pm 0.48$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p°(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\, a_6\, T + a_7\, T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\, T^2) - 2\, a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\, a_6\, T + a_7\, T^2/2$$

$$[H°(T) - H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\, a_3\, T^{0.5} + a_5\, T + a_6\, T^2 + a_7\, T^3/3$$

$a_1 = 2.28751 \times 10^6$ $a_4 = -3.71202 \times 10^3$ $a_6 = -1.03545 \times 10^{-1}$

$a_2 = 8.75787 \times 10^4$ $a_5 = 5.43227 \times 10^2$ $a_7 = 6.68935 \times 10^{-5}$

$a_3 = -6.75436 \times 10^3$

Critical Reactions

Inversion:

Al_2SiO_5(kyanite) = Al_2SiO_5(andalusite)

T_i = 430.46 K (calculated) $\Delta S_i° = 9.2 \pm 1.80$ J/(mol·K)

$\Delta H_i° = 3.96 \pm 0.77$ kJ/mol

Al_2SiO_5(andalusite) = Al_2SiO_5(sillimanite)

T_i = 1016.9 K (calculated) $\Delta S_i° = 2.92 \pm 0.83$ J/(mol·K)

$\Delta H_i° = 2.97 \pm 0.84$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of andalusite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Todd (1950)[a]	heat capacity	isothermal calorimetry	10	206 - 296 K
Pankratz and Kelly (1964)[a]	relative enthalpy	drop calorimetry	13	397 - 1600 K
Todd (1950)[a]	entropy	isothermal calorimetry	1	298.15 K

a The measurements were made on an impure natural sample of andalusite. The observed heat-capacity and entropy values were assumed to equal the molar sum of the heat capacities and entropies, respectively, of the components. The stoichiometry used was: andalusite, 0.9925; corundum, 0.0226; hematite, 0.00112; lime, 0.00058.

The heat capacity of Todd (1950) was fit with a standard error of estimate of 0.15 J/(mol·K). The relative enthalpy measured by Pankratz and Kelley (1964) was fit with a standard error of estimate of 93 J/mol or approximately 0.18 percent of the observed value. The fitted entropy at 298.15 K is 93.78 ± 0.73 J/(mol·K) or a departure of 0.56 J/mol from the experimental value of 93.22 ± 0.42 J/(mol·K) calculated from the data of Todd (1950).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Anderson and others (1977)[b]	solution calorimetry (borate salt)	A	973	1	-1.110±0.948	-2593.020
Hemley and others (in press)[c]	H_4SiO_4 concentration	B	723-773	10	-4.876±0.204	-2591.209
Hemley and others (in press)[c]	H_4SiO_4 concentration	C	623-663	2	78.164±0.200	-2589.472
Hemley and others (in press)[c]	H_4SiO_4 concentration	D	613-673	11	-78.080±1.616	-2590.320
Haas and Holdaway (1973)	gas-medium pressure apparatus	D	643-737	4	-76.968±0.615	-2591.119
Kerrick (1968)	gas-medium pressure apparatus	D	668-718	2	-79.383±1.273	-2588.704
Holdaway (1971)	gas-medium pressure apparatus	E	764-917	4	2.483±0.063	-2590.245
Holdaway (1971)	gas-medium pressure apparatus	F	650-858	6	4.215±0.179	-2590.032
Newton (1966a)	gas-medium pressure apparatus	F	973-1123	7	4.021±0.218	-2590.226
Storre and Nitsch (1974)	gas-medium pressure apparatus	G	788-833	4	-89.818±1.710	-2590.825
Haas and Holdaway (1973)	gas-medium pressure apparatus	H	618-722	4	311.486±3.224	-2589.982

a Reactions:

A) Al_2O_3(corundum) + SiO_2(quartz, beta) = Al_2SiO_5(andalusite)

B) Al_2O_3(corundum) + SiO_2(quartz, alpha) = Al_2SiO_5(andalusite)

C) 2 AlO(OH)(diaspore) + SiO_2(quartz, alpha) = Al_2SiO_5(andalusite) + H_2O(gas)

D) Al_2SiO_5(andalusite) + 3 SiO_2(quartz, alpha) + H_2O(gas) = $Al_2Si_4O_{10}(OH)_2$(pyrophyllite)

E) Al_2SiO_5(andalusite) = Al_2SiO_5(sillimanite)

F) Al_2SiO_5(kyanite) = Al_2SiO_5(andalusite)

G) $CaAl_2Si_2O_8$(anorthite) + Al_2SiO_5(andalusite) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite) + SiO_2(quartz, alpha)

H) $Al_2SiO_4O_{10}(OH)_2$(pyrophyllite) + 6 AlO(OH)(diaspore) = 4 Al_2SiO_5(andalusite) + 4 H_2O(gas)

b Anderson and others (1977) measured the enthalpy of solution of andalusite in lead borate salt melt at 974.15 K. To complete the thermodynamic cycle, their data were evaluated in combination with the enthalpies of solution of quartz and corundum (Charlu and others, 1978) and the changes in enthalpy of solution with temperature (Shearer and Kleppa, 1973) in the salt melt. Corrections were not made for the enthalpies of dilution and of mixing of the product melts.

c Hemley and others (in press) measured the silicic-acid content of water equilibrated with the mineral pairs: 1) andalusite-corundum, 2) andalusite-pyrophyllite, and 3) andalusite-diaspore between 600 K and 800 K at 100 and 200 MPa. Using their data for the solubility of quartz under the same conditions, the molar volumes of the solid phases, and the free-energy data for H_2O(gas) of Fisher and Zen (1971), we calculated the free energy of reaction at 101.325 kPa and temperature for reactions A, B, and C for each observation.

The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for andalusite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -2590.270±0.641 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of andalusite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate.

The molar volume of andalusite was obtained from the work of Winter and Ghose (1979).

Al_2SiO_5

Kyanite (triclinic, polymorphous with Andalusite and Sillimanite)

Al_2O_5Si

Issued September, 1979

Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ-H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ-H_{Tr}^\circ$ J/mol	Formation from the Elements: $\Delta H_{f,e}^\circ$ J/mol	Formation from the Elements: $\Delta G_{f,e}^\circ$ J/mol	Formation from the Elements: $\log K_{f,e}^\circ$	Formation from the Oxides: $\Delta H_{f,ox}^\circ$ J/mol	Formation from the Oxides: $\Delta G_{f,ox}^\circ$ J/mol	Formation from the Oxides: $\log K_{f,ox}^\circ$
273.15	113.775	74.123	-84.937	-2954.	-2593700.	-2456680.	469.792	-7809.	-5696.	1.089
298.15	122.348	84.465	-84.465	0.	-2594269.	-2444113.	428.198	-7859.	-5500.	0.964
(2 sigma)	±0.154	±0.439	±0.439	±0.	±433.	±389.	±0.068	±433.	±389.	±0.068
300.	122.936	85.224	-84.468	227.	-2594305.	-2443181.	425.395	-7862.	-5486.	0.955
350.	136.874	105.266	-86.018	6737.	-2594999.	-2417932.	360.856	-7934.	-5084.	0.759
400.	147.857	124.288	-89.624	13865.	-2595250.	-2392615.	312.443	-7984.	-4673.	0.610
450.	156.732	142.233	-94.483	21488.	-2595164.	-2367288.	274.787	-8025.	-4256.	0.494
500.	164.039	159.136	-100.111	29512.	-2594820.	-2341985.	244.665	-8067.	-3836.	0.401
(2 sigma)	±0.174	±0.436	±0.437	±31.	±432.	±382.	±0.040	±432.	±382.	±0.040
550.	170.145	175.066	-106.208	37871.	-2594282.	-2316726.	220.024	-8120.	-3410.	0.324
600.	175.305	190.098	-112.579	46511.	-2593599.	-2291522.	199.495	-8190.	-2979.	0.259
650.	179.705	204.308	-119.093	55389.	-2592813.	-2266381.	182.128	-8284.	-2541.	0.204
700.	183.483	217.767	-125.665	64471.	-2591958.	-2241302.	167.248	-8407.	-2095.	0.156
750.	186.744	230.540	-132.235	73729.	-2591064.	-2216286.	154.356	-8563.	-1639.	0.114
(2 sigma)	±0.160	±0.440	±0.435	±66.	±432.	±402.	±0.028	±432.	±402.	±0.028
800.	189.571	242.685	-138.761	83139.	-2590157.	-2191331.	143.079	-8757.	-1171.	0.076
850.	192.028	254.253	-145.217	92680.	-2589261.	-2166432.	133.133	-9710.	-685.	0.042
900.	194.168	265.291	-151.584	102336.	-2588396.	-2141585.	124.294	-9569.	-158.	0.009
950.	196.033	275.840	-157.848	112092.	-2609095.	-2116392.	116.367	-9412.	361.	-0.020
1000.	197.657	285.937	-164.002	121935.	-2608075.	-2090486.	109.196	-9245.	871.	-0.046
(2 sigma)	±0.306	±0.442	±0.434	±91.	±432.	±449.	±0.023	±432.	±449.	±0.023
1050.	199.070	295.616	-170.041	131854.	-2607020.	-2064632.	102.710	-9075.	1373.	-0.068
1100.	200.296	304.906	-175.961	141839.	-2605937.	-2038830.	96.816	-8905.	1866.	-0.089
1150.	201.356	313.833	-181.763	151881.	-2604832.	-2013077.	91.437	-8743.	2352.	-0.107
1200.	202.267	322.423	-187.446	161972.	-2603711.	-1987372.	86.508	-8591.	2831.	-0.123
1250.	203.044	330.696	-193.011	172106.	-2602578.	-1961715.	81.976	-8456.	3304.	-0.138
(2 sigma)	±0.564	±0.453	±0.434	±160.	±447.	±516.	±0.022	±447.	±516.	±0.022
1300.	203.700	338.672	-198.461	182275.	-2601438.	-1936103.	77.794	-8340.	3773.	-0.152
1350.	204.246	346.371	-203.798	192474.	-2600294.	-1910535.	73.923	-8249.	4237.	-0.164
1400.	204.693	353.807	-209.023	202698.	-2599150.	-1885009.	70.330	-8186.	4698.	-0.175
1450.	205.048	360.996	-214.140	212942.	-2598008.	-1859524.	66.987	-8155.	5157.	-0.186
1500.	205.321	367.953	-219.152	223201.	-2596871.	-1834078.	63.868	-8160.	5616.	-0.196
(2 sigma)	±0.865	±0.493	±0.435	±314.	±519.	±598.	±0.021	±519.	±598.	±0.021
1550.	205.516	374.689	-224.061	233472.	-2595742.	-1808671.	60.952	-8204.	6076.	-0.205
1600.	205.641	381.216	-228.871	243752.	-2594621.	-1783299.	58.219	-8292.	6538.	-0.213

Al_2O_5Si

Al_2SiO_5 Kyanite Formula weight = 162.046 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 84.47 \pm 0.44$ J/(mol·K) $\Delta H_f^\circ = -2594.27 \pm 0.43$ kJ/mol

$V° = 44.22 \pm 0.02$ cm^3/mol $\Delta G_f^\circ = -2444.11 \pm 0.39$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1600 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S^\circ(T)/[J/(mol \cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

$a_1 = 0.0$ $a_4 = -2.23489 \times 10^3$ $a_6 = -1.29800 \times 10^{-2}$

$a_2 = 2.37951 \times 10^4$ $a_5 = 3.36114 \times 10^2$ $a_7 = 0.0$

$a_3 = -3.55746 \times 10^3$

Critical Reactions

Inversion:

Al_2SiO_5(kyanite) = Al_2SiO_5(andalusite)

T_i = 430.46 (calculated) $\Delta S_i^\circ = 9.20 \pm 1.80$ J/(mol·K)

$\Delta H_i^\circ = 3.96 \pm 0.77$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of kyanite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Todd (1950)[a]	heat capacity	isothermal calorimetry	10	206 - 296 K
Pankratz and Kelley (1964)[a]	relative enthalpy	drop calorimetry	12	390 - 1503 K
Todd (1950)[a]	entropy	isothermal calorimetry	1	298.15 K

a The measurements were made on an impure natural sample of kyanite. The observed heat-capacity and entropy values were assumed to equal the molar sum of the heat capacities and entropies, respectively, of the components. The stoichiometry used in calculation: kyanite, 0.9928; corundum, 0.0091; hematite, 0.001; lime, 0.0014.

The standard error of estimate of the fitted heat capacity of Todd (1950) is 0.62 J/(mol·K). The standard error of estimate of the fitted relative enthalpy measurements of Pankratz and Kelley (1964) is 263 J/mol, or approximately 0.2 percent of the observed value. The fitted entropy of 298.15 K is 84.47 ± 0.44 J/(mol·K), or a departure of 0.7 J/mol from the experimental value of 83.77 ± 0.33 calculated from Todd (1950).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Anderson and Kleppa (1969)[b]	solution calorimetry (borate salt)	A	974	1	6.135±0.450	-2595.993
Storre and Nitsch (1974)	gas-medium pressure apparatus	B	803-933	6	-81.952±1.121	-2593.649
Newton (1966a)	gas-medium pressure apparatus	C	973-1123	7	4.021+0.218	-2594.313
Holdaway (1971)	gas-medium pressure apparatus	C	650-858	6	4.215±0.179	-2594.507

a Reactions:

A) Al_2SiO_5(kyanite) = Al_2O_3(corundum) + SiO_2(quartz, beta)

B) $CaAl_2Si_2O_8$(anorthite) + Al_2SiO_5(kyanite) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite) + SiO_2(quartz, alpha)

C) Al_2SiO_5(kyanite) = Al_2SiO_5(andalusite)

b Anderson and Kleppa (1969) measured the enthalpy of solution of kyanite in lead borate salt melt at 974.15 K. To complete the thermodynamic cycle, their data were evaluated in combination with the enthalpies of solution of quartz and corundum (Charlu and others, 1978) and the changes in enthalpy of solution with temperature (Shearer and Kleppa, 1973) in the salt melt. Corrections were not made for the enthalpies of dilution and of mixing of the product melts.

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for kyanite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -2594.269±0.433 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of kyanite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate.

The molar volume of kyanite was obtained from the work of Winter and Ghose (1979).

Al_2SiO_5

Sillimanite (orthorhombic, polymorphous with Kyanite and Andalusite)

Al_2O_5Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	116.803	85.519	-96.572	-3019.	-2587269.	-2453363.	469.158	-1378.	-2378.	0.455
298.15	124.533	96.090	-96.090	0.	-2587774.	-2441083.	427.667	-1363.	-2471.	0.433
(2 sigma)	±0.159	±0.550	±0.550	±0.	±537.	±443.	±0.078	±537.	±443.	±0.078
300.	125.064	96.862	-96.092	231.	-2587306.	-2440173.	424.872	-1363.	-2477.	0.431
350.	137.672	117.127	-97.664	6812.	-2588128.	-2415512.	360.495	-1363.	-2664.	0.398
400.	147.650	136.187	-101.300	13954.	-2588565.	-2390790.	312.205	-1399.	-2848.	0.372
450.	155.753	154.061	-106.180	21546.	-2588509.	-2366056.	274.644	-1470.	-3025.	0.351
500.	162.463	170.829	-111.816	29507.	-2588330.	-2341341.	244.598	-1577.	-3192.	0.333
(2 sigma)	±0.176	±0.548	±0.549	±32.	±537.	±406.	±0.042	±537.	±406.	±0.042
550.	168.102	186.585	-117.904	37775.	-2587383.	-2316663.	220.018	-1721.	-3347.	0.318
600.	172.900	201.423	-124.252	46303.	-2587312.	-2292031.	199.539	-1903.	-3487.	0.304
650.	177.022	215.430	-130.732	55054.	-2586653.	-2267450.	182.214	-2124.	-3610.	0.290
700.	180.591	228.682	-137.259	63996.	-2585937.	-2242922.	167.369	-2386.	-3715.	0.277
750.	183.700	241.250	-143.777	73105.	-2585192.	-2218447.	154.506	-2691.	-3799.	0.265
(2 sigma)	±0.161	±0.551	±0.547	±66.	±538.	±399.	±0.028	±538.	±399.	±0.028
800.	186.422	253.194	-150.245	82359.	-2584441.	-2194022.	143.255	-3040.	-3862.	0.252
850.	188.816	264.570	-156.638	91742.	-2583704.	-2169644.	133.330	-4153.	-3896.	0.239
900.	190.927	275.423	-162.938	101236.	-2583000.	-2145308.	124.510	-4173.	-3881.	0.225
950.	192.794	285.797	-169.133	110830.	-2603361.	-2120617.	116.600	-4178.	-3864.	0.212
1000.	194.447	295.729	-175.217	120512.	-2603003.	-2095205.	109.442	-4173.	-3848.	0.201
(2 sigma)	±0.309	±0.552	±0.546	±92.	±539.	±438.	±0.023	±539.	±438.	±0.023
1050.	195.912	305.252	-181.184	130272.	-2602107.	-2069837.	102.969	-4161.	-3832.	0.191
1100.	197.210	314.397	-187.032	140101.	-2601180.	-2044512.	97.086	-4148.	-3816.	0.181
1150.	198.361	323.189	-192.762	149990.	-2600227.	-2019231.	91.716	-4138.	-3802.	0.173
1200.	199.379	331.653	-198.374	159935.	-2599253.	-1993991.	86.796	-4133.	-3787.	0.165
1250.	200.278	339.811	-203.869	169926.	-2598262.	-1968792.	82.271	-4139.	-3773.	0.158
(2 sigma)	±0.572	±0.562	±0.546	±161.	±551.	±513.	±0.021	±551.	±513.	±0.021
1300.	201.069	347.681	-209.250	179960.	-2597256.	-1943633.	78.096	-4159.	-3758.	0.151
1350.	201.763	355.283	-214.519	190032.	-2596240.	-1918513.	74.232	-4195.	-3742.	0.145
1400.	202.368	362.632	-219.678	200135.	-2595216.	-1893430.	70.645	-4253.	-3724.	0.139
1450.	202.892	369.743	-224.731	210267.	-2594187.	-1868385.	67.306	-4334.	-3703.	0.133
1500.	203.342	376.629	-229.680	220423.	-2593154.	-1843375.	64.192	-4442.	-3680.	0.128
(2 sigma)	±0.879	±0.595	±0.547	±318.	±612.	±611.	±0.021	±612.	±611.	±0.021
1550.	203.723	383.303	-234.528	230600.	-2592118.	-1818399.	61.280	-4581.	-3652.	0.123
1600.	204.042	389.776	-239.279	240794.	-2591083.	-1793457.	58.550	-4753.	-3620.	0.118
1650.	204.303	396.059	-243.935	251003.	-2590048.	-1768547.	55.987	-4962.	-3581.	0.113
1700.	204.510	402.161	-248.500	261224.	-2639525.	-1743219.	53.563	-5209.	-3536.	0.109
1750.	204.668	408.092	-252.975	271454.	-2638354.	-1716874.	51.246	-5499.	-3482.	0.104
(2 sigma)	±1.208	±0.668	±0.550	±564.	±767.	±730.	±0.022	±767.	±730.	±0.022
1800.	204.779	413.859	-257.364	281690.	-2637182.	-1690563.	49.059	-5835.	-3420.	0.099
(2 sigma)	±1.276	±0.688	±0.551	±624.	±811.	±756.	±0.022	±811.	±756.	±0.022

Al_2SiO_5 Sillimanite Formula weight = 162.046 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 96.090 \pm 0.550$ J/(mol·K) $\Delta H_f^\circ = -2587.774 \pm 0.537$ kJ/mol

$V° = 50.049 \pm 0.014$ cm^3/mol $\Delta G_f^\circ = -2441.083 \pm 0.443$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 0.0$ $a_4 = -2.050871\times10^3$ $a_6 = -9.470810\times10^{-3}$

$a_2 = 1.66762\times10^4$ $a_5 = 3.134705\times10^2$ $a_7 = 0.0$

$a_3 = -3.164868\times10^3$

Critical Reactions

Inversion:

Al_2SiO_5(andalusite) = Al_2SiO_5(sillimanite)

T_i = 1016.90 K (calculated) $\Delta S_i^\circ = 2.92 \pm 0.83$ J/(mol·K)

$\Delta H_i^\circ = 2.97 \pm 0.84$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of sillimanite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Todd (1950)[a]	heat capacity	isothermal calorimetry	10	206 - 297 K
Pankratz and Kelley (1964)[a]	relative enthalpy	drop calorimetry	13	401 - 1496 K
Todd (1950)[a]	entropy	isothermal calorimetry	1	298.15 K

a The measurements were made on an impure natural sample of sillimanite. The observed heat-capacity and entropy values were assumed to equal the molar sum of the heat capacities and entropies, respectively, of the components. The stoichiometry used was: sillimanite, 0.9821; hematite, 0.0068; magnetite, 0.0032; $Mg_3(PO_4)$, 0.0027; MgF_2, 0.0017; MnO, 0.0009; quartz, 0.0008; whitlockite, 0.0007; P_2O_5(crystal), 0.0004.

The heat capacity measured by Todd (1950) was fit with a standard error of estimate of 0.61 J/(mol·K). The relative enthalpy measurements of Pankratz and Kelley (1964) were fit with a standard error of estimate of 2675 J/mol or approximately 1.3 percent of the observed value. The fitted entropy at 298.15 K is 96.09 ± 0.55 J/(mol·K), or a departure of 0.02 J/mol from the experimental value, corrected for composition, of 96.11 ± 0.42 calculated from the data of Todd (1950).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Charlu and others (1978)[b]	solution calorimetry (borate salt)	A	970	1	-0.432±0.583	-2585.979
Holdaway (1971)	gas-medium pressure apparatus	B	764-917	2 pair	2.483±0.063	-2587.799

a Reactions:

A) Al_2SiO_5(sillimanite) = Al_2O_3(corundum) + SiO_2(quartz, beta)

B) Al_2SiO_5(andalusite) = Al_2SiO_5(sillimanite)

b Charlu and others (1978) measured the enthalpy of solution of sillimanite in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of quartz and corundum in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

The phase-equilibrium study of Holdaway (1971) was evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen(1971) were used in the conversion. The study cited in Table 2 complies with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for sillimanite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -2587.774±0.537 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of sillimanite and presents the data in their poorest perspective.

The phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume of sillimanite was obtained from the work of Winter and Ghose (1979).

$Ca_2Al_3Si_3O_{12}(OH)$

Zoisite (orthorhombic, dimorphous with Clinozoisite, member of Epidote Group)

$Al_3Ca_2HO_{13}Si_3$

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	330.732	266.032	-297.244	-8526.	-6889989.	-6528649.	1248.477	-231737.	-227957.	43.592
298.15	350.863	295.885	-295.885	0.	-6891117.	-6495524.	1137.988	-232363.	-227583.	39.872
(2 sigma)	±0.563	±0.662	±0.662	±0.	±877.	±745.	±0.130	±877.	±745.	±0.130
300.	352.247	298.059	-295.891	650.	-6891186.	-6493069.	1130.543	-232408.	-227553.	39.621
350.	385.162	354.934	-300.307	19119.	-6892422.	-6426603.	959.117	-233583.	-226650.	33.826
400.	411.309	408.134	-310.498	39054.	-6892647.	-6360031.	830.534	-254578.	-224132.	29.269
450.	432.626	457.851	-324.140	60170.	-6892114.	-6293479.	730.528	-254640.	-220323.	25.574
500.	450.354	504.377	-339.863	82257.	-6891015.	-6227019.	650.532	-254705.	-216506.	22.618
(2 sigma)	±1.382	±0.852	±0.669	±220.	±977.	±654.	±0.068	±977.	±654.	±0.068
550.	465.329	548.022	-356.823	105160.	-6889496.	-6160690.	585.093	-254795.	-212682.	20.199
600.	478.137	589.074	-374.484	128754.	-6887679.	-6094513.	530.574	-254931.	-208848.	18.182
650.	489.204	627.793	-392.494	152944.	-6885661.	-6028497.	484.456	-255128.	-205001.	16.474
700.	498.846	664.408	-410.621	177651.	-6883526.	-5962640.	444.937	-255402.	-201135.	15.009
750.	507.305	699.119	-428.707	202809.	-6883014.	-5896866.	410.694	-255765.	-197247.	13.737
(2 sigma)	±2.438	±1.066	±0.728	±431.	±1135.	±520.	±0.036	±1135.	±520.	±0.036
800.	514.769	732.103	-446.647	228365.	-6880626.	-5831201.	380.738	-256231.	-193331.	12.623
850.	521.386	763.513	-464.370	254272.	-6878374.	-5765682.	354.315	-258959.	-189367.	11.637
900.	527.277	793.485	-481.828	280491.	-6876296.	-5700290.	330.836	-258388.	-185289.	10.754
950.	532.537	822.137	-498.990	306989.	-6906700.	-5634420.	309.802	-257751.	-181245.	9.966
1000.	537.247	849.575	-515.839	333736.	-6904672.	-5567510.	290.817	-257065.	-177236.	9.258
(2 sigma)	±6.928	±1.564	±0.777	±1237.	±1614.	±441.	±0.023	±1614.	±441.	±0.023
1050.	541.472	875.891	-532.362	360706.	-6902739.	-5500700.	273.645	-256345.	-173263.	8.619
1100.	545.270	901.170	-548.555	387876.	-6900917.	-5433980.	258.038	-255605.	-169324.	8.040
1150.	548.686	925.484	-564.418	415226.	-6914966.	-5366779.	243.767	-254859.	-165418.	7.514
1200.	551.761	948.902	-579.953	442739.	-6911523.	-5299540.	230.683	-254119.	-161546.	7.032
1250.	554.529	971.483	-595.166	470397.	-6908021.	-5232445.	218.652	-253395.	-157703.	6.590
(2 sigma)	±12.441	±3.342	±0.907	±3531.	±3630.	±736.	±0.031	±3630.	±736.	±0.031

$Al_3Ca_2HO_{13}Si_3$

$Ca_2Al_3Si_3O_{12}(OH)$ Zoisite Formula weight = 454.361 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 295.885 \pm 0.662$ J/(mol·K) $\Delta H_f° = -6891.117 \pm 0.877$ kJ/mol

$V° = 136.520 \pm 0.400$ cm^3/mol $\Delta G_f° = -6495.524 \pm 0.745$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1250 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

$a_1 = 0.0$ $a_4 = 5.391475 \times 10^3$ $a_6 = -1.984469 \times 10^{-2}$

$a_2 = 1.225488 \times 10^5$ $a_5 = 8.346223 \times 10^2$ $a_7 = 0.0$

$a_3 = -8.148754 \times 10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of zoisite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Perkins and others (1980)	heat capacity	adiabatic calorimetry	8	200 - 298 K
Perkins and others (1980)	heat capacity	differential scanning	11	298 - 730 K
Perkins and others (1980)	entropy	adiabatic calorimetry	1	298.15 K

The compositionally adjusted heat capacities that were obtained on a natural zoisite by Perkins and others (1980) using an adiabatic calorimeter and differential scanning calorimeter were fit with a standard error of estimate of 1.5 and 1.7 J/(mol·K), respectively. The fitted entropy at 298.15 K is 295.885 ± 0.662 J/(mol·K) or a departure of 0.03 J/mol from the compositionally adjusted value of 295.85 ± 0.29 reported by Perkins and others.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Newton (1965)	gas- and solid-medium pressure apparatus	A	843-1113	6 pair	-306.468±2.790	-6891.532
Boettcher (1970)	gas-medium pressure apparatus	A	898-928	1 pair	-308.308±4.088	-6891.225
Strens (1968)	gas-medium pressure apparatus	B	770-823	1 pair	-220.561±5.976	-6892.258
Boettcher (1970)	gas-medium pressure apparatus	B	853-933	2 pair	-213.025±2.944	-6890.374

a Reactions:

A) $2\ Ca_3Al_2Si_3O_{12}$(grossular) + $6\ CaAl_2Si_2O_8$(anorthite) + Al_2O_3(corundum) + $3\ H_2O$(gas) = $6\ Ca_2Al_3Si_3O_{12}(OH)$(zoisite)

B) $Ca_3Al_2Si_3O_{12}$(grossular) + $5\ CaAl_2Si_2O_8$(anorthite) + $2\ H_2O$(gas) = $4\ Ca_2Al_3Si_3O_{12}(OH)$(zoisite) + SiO_2(quartz, alpha)

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for zoisite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -6891.117±0.877 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of zoisite and presents the data in their poorest perspective. Most of the phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume of zoisite was obtained from the compilation of Robie and others (1967).

$CaAl_4Si_2O_{10}(OH)_2$

Margarite (monoclinic, Mica Group)

$Al_4CaH_2O_{12}Si_2$

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	Formation from the Elements $\Delta G^\circ_{f,e}$	Formation from the Elements $\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	Formation from the Oxides $\Delta G^\circ_{f,ox}$	Formation from the Oxides $\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	302.855	236.210	-264.893	-7835.	-6238317.	-5887259.	1125.823	-144791.	-137885.	26.368
298.15	323.444	263.642	-263.642	0.	-6239610.	-5855068.	1025.783	-145889.	-137203.	24.037
(2 sigma)	±0.515	±0.594	±0.594	±0.	±1023.	±949.	±0.166	±1023.	±949.	±0.166
300.	324.858	265.647	-263.648	600.	-6239691.	-5852682.	1019.042	-145967.	-137149.	23.880
350.	358.437	318.353	-267.734	17717.	-6241190.	-5788045.	863.818	-147949.	-135520.	20.225
400.	385.016	368.016	-277.197	36327.	-6241600.	-5723271.	747.382	-189497.	-130718.	17.070
450.	406.600	414.652	-289.906	56136.	-6241181.	-5658497.	656.821	-189092.	-123394.	14.323
500.	424.472	458.445	-304.593	76926.	-6240132.	-5593806.	584.380	-188597.	-116120.	12.131
(2 sigma)	±1.136	±0.710	±0.598	±160.	±1075.	±905.	±0.095	±1075.	±905.	±0.095
550.	439.497	499.626	-320.471	98535.	-6238608.	-5529243.	525.123	-188046.	-108899.	10.342
600.	452.281	538.430	-337.033	120838.	-6236732.	-5464836.	475.756	-187466.	-101729.	8.856
650.	463.263	575.076	-353.947	143733.	-6234608.	-5400596.	433.997	-186880.	-94608.	7.603
700.	472.773	609.764	-370.992	167140.	-6232323.	-5336526.	398.216	-186307.	-87532.	6.532
750.	481.059	642.671	-388.017	190990.	-6230788.	-5272587.	367.215	-185766.	-80496.	5.606
(2 sigma)	±0.978	±0.980	±0.644	±404.	±1191.	±856.	±0.060	±1191.	±856.	±0.060
800.	488.316	673.954	-404.918	215229.	-6228287.	-5208789.	340.099	-185270.	-73494.	4.799
850.	494.698	703.754	-421.627	239807.	-6225855.	-5145145.	316.182	-186269.	-66511.	4.087
900.	500.327	732.193	-438.097	264686.	-6223541.	-5081641.	294.931	-185057.	-59501.	3.453
950.	505.305	759.380	-454.296	289829.	-6264413.	-5017477.	275.880	-183797.	-52560.	2.890
1000.	509.714	785.413	-470.206	315207.	-6261914.	-4951913.	258.661	-182504.	-45686.	2.386
(2 sigma)	±1.983	±1.079	±0.711	±555.	±1253.	±866.	±0.045	±1253.	±866.	±0.045
1050.	513.622	810.379	-485.814	340792.	-6259413.	-4886475.	243.089	-181192.	-38878.	1.934
1100.	517.087	834.354	-501.116	366562.	-6256926.	-4821155.	228.937	-179875.	-32132.	1.526
1150.	520.158	857.408	-516.109	392495.	-6262342.	-4755667.	216.009	-178566.	-25445.	1.156
1200.	522.875	879.605	-530.795	418572.	-6258988.	-4690231.	204.160	-177275.	-18816.	0.819
1250.	525.276	900.999	-545.178	444777.	-6255586.	-4624936.	193.265	-176014.	-12239.	0.511
(2 sigma)	±3.932	±1.243	±0.762	±1007.	±1447.	±955.	±0.040	±1447.	±955.	±0.040

$Al_4CaH_2O_{12}Si_2$

$CaAl_4Si_2O_{10}(OH)_2$ Margarite Formula weight = 398.186 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 263.642±0.594$ J/(mol·K) $\Delta H^\circ_f = -6239.610±1.023$ kJ/mol

$V° = 133.800±0.100$ cm^3/mol $\Delta G^\circ_f = -5855.068±0.949$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1250 K)

$$C^\circ_p(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 0.0$ $a_4 = -5.406581\times10^3$ $a_6 = -2.514555\times10^{-2}$

$a_2 = 1.254512\times10^5$ $a_5 = 8.265040\times10^2$ $a_7 = 0.0$

$a_3 = -8.42743810^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of margarite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Perkins and others (1980)	heat capacity	differential scanning calorimetry	16	298 - 1000 K
Perkins and others (1980)	entropy	adiabatic calorimetry	1	298.15 K

The compositionally adjusted heat capacities of Perkins and others (1980), obtained from measurements on a natural margarite sample, were fit with a standard error of estimate of 1.6 J/(mol·K). The fitted entropy value at 298.15 K is 263.642 ± 0.594 J/(mol·K) or a departure of 0.01 J/mol from the compositionally adjusted value of 263.63 ± 0.26 J/(mol·K) reported by Perkins and others.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH°_r(298.15 K) Third Law, kJ	ΔH°_f(298.15 K) kJ/mol
Storre & Nitsch (1974)	gas- and solid-medium pressure apparatus	A	763-833	2 pair	-89.818±1.710	-6239.055
Chatterjee (1974)	gas-medium pressure apparatus	B	763-893	5 pair	-94.087±0.931	-6239.467

a Reactions:

A) $CaAl_2Si_2O_8$(anorthite) + Al_2SiO_5(andalusite) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite) + SiO_2(quartz, alpha)

B) $CaAl_2Si_2O_8$(anorthite) + Al_2O_3(corundum) + H_2O(gas) = $CaAl_4Si_2O_{10}(OH)_2$(margarite)

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthlapies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for margarite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -6239.610±1.023 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of margarite and presents the data in their poorest perspective. Most of the phase-equilibria data cited above bracket the regression fit in free-energy space.

The molar volume of margarite was obtained from the compilation of Robie and others (1967).

Ca

Reference state: alpha crystals (face-centered cubic) 273.15 K to 720 K
beta crystals (body-centered cubic) 720 K to 1112 K
liquid 1112 K to 1755 K
ideal monatomic gas 1755 K to 1800 K

Ca

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	25.180	39.404	-41.716	-631.	0.	0.	0.	--	--	--
298.15	25.341	41.616	-41.616	0.	0.	0.	0.	--	--	--
300.	25.354	41.773	-41.617	47.	0.	0.	0.	--	--	--
350.	25.743	45.709	-41.927	1324.	0.	0.	0.	--	--	--
400.	26.255	49.178	-42.620	2623.	0.	0.	0.	--	--	--
450.	26.900	52.307	-43.525	3952.	0.	0.	0.	--	--	--
500.	27.671	55.180	-44.549	5315.	0.	0.	0.	--	--	--
550.	28.560	57.858	-45.639	6721.	0.	0.	0.	--	--	--
600.	29.558	60.385	-46.763	8173.	0.	0.	0.	--	--	--
650.	30.657	62.794	-47.904	9678.	0.	0.	0.	--	--	--
700.	31.849	65.109	-49.051	11240.	0.	0.	0.	--	--	--
720.	32.351	66.013	-49.510	11882.	0.	0.	0.	--	--	--
720.	29.341	67.289	-49.510	12801.	0.	0.	0.	--	--	--
750.	30.581	68.512	-50.245	13700.	0.	0.	0.	--	--	--
800.	32.647	70.552	-51.451	15281.	0.	0.	0.	--	--	--
850.	34.712	72.593	-52.634	16965.	0.	0.	0.	--	--	--
900.	36.776	74.635	-53.800	18752.	0.	0.	0.	--	--	--
950.	38.840	76.679	-54.950	20642.	0.	0.	0.	--	--	--
1000.	40.903	78.724	-56.088	22636.	0.	0.	0.	--	--	--
1050.	42.966	80.769	-57.214	24733.	0.	0.	0.	--	--	--
1100.	45.029	82.816	-58.331	26933.	0.	0.	0.	--	--	--
1112.	45.524	83.307	-58.598	27476.	0.	0.	0.	--	--	--
1112.	29.275	90.968	-58.598	35995.	0.	0.	0.	--	--	--
1150.	29.275	91.952	-59.684	37108.	0.	0.	0.	--	--	--
1200.	29.275	93.198	-61.055	38571.	0.	0.	0.	--	--	--
1250.	29.275	94.393	-62.365	40035.	0.	0.	0.	--	--	--
1300.	29.275	95.541	-63.619	41499.	0.	0.	0.	--	--	--
1350.	29.275	96.646	-64.822	42963.	0.	0.	0.	--	--	--
1400.	29.275	97.711	-65.977	44427.	0.	0.	0.	--	--	--
1450.	29.275	98.738	-67.089	45890.	0.	0.	0.	--	--	--
1500.	29.275	99.730	-68.161	47354.	0.	0.	0.	--	--	--
1550.	29.275	100.690	-69.195	48818.	0.	0.	0.	--	--	--
1600.	29.275	101.620	-70.194	50282.	0.	0.	0.	--	--	--
1650.	29.275	102.521	-71.160	51745.	0.	0.	0.	--	--	--
1700.	29.275	103.395	-72.095	53209.	0.	0.	0.	--	--	--
1750.	29.275	104.243	-73.002	54673.	0.	0.	0.	--	--	--
1755.	29.275	104.327	-73.091	54819.	0.	0.	0.	--	--	--
1755.	20.851	191.628	-73.091	208032.	0.	0.	0.	--	--	--
1800.	20.862	192.156	-76.061	208971.	0.	0.	0.	--	--	--

Ca (reference state) — Calcium, alpha; Calcium, beta; Calcium, liquid; Calcium, ideal monatomic gas — Formula weight = 40.080 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (calcium, alpha)

$S° = 41.616$ J/(mol·K) $\Delta H_f° = 0.0$ kJ/mol

$V° = 26.190 \pm 0.04$ cm^3/mol $\Delta G_f° = 0.0$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

Calcium, alpha (temperature range 200 to 720 K)

$a_1 = -2.20152\times10^5$ $a_4 = 7.62562\times10^1$ $a_6 = 9.83620\times10^{-3}$

$a_2 = -1.42730\times10^4$ $a_5 = 0.0$ $a_7 = 9.72458\times10^{-6}$

$a_3 = 3.64127\times10^2$

Calcium, beta (temperature range 720 to 1112 K)

$a_1 = 0.0$ $a_4 = 3.71052\times10^1$ $a_6 = 2.05709\times10^{-2}$

$a_2 = -1.56800\times10^3$ $a_5 = 0.0$ $a_7 = 0.0$

$a_3 = -7.53816$

Calcium, liquid (temperature range 1112 to 1755 K)

$a_1 = 0.0$ $a_4 = -1.14367\times10^2$ $a_6 = 0.0$

$a_2 = -8.728\times10^3$ $a_5 = 2.92754\times10^1$ $a_7 = 0.0$

$a_3 = 0.0$

Calcium, ideal monatomic gas (temperature range 1755 to 1800 K)

$a_1 = 0.0$ $a_4 = 3.19488\times10^1$ $a_6 = -3.02477\times10^{-4}$

$a_2 = -6.07200\times10^3$ $a_5 = 2.14177\times10^1$ $a_7 = 2.25282\times10^{-7}$

$a_3 = -8.35017\times10^0$

Critical Reactions

Inversion:

Ca(calcium, alpha) = Ca(calcium, beta)

T_i = 720 K (observed) $\Delta S_i° = 1.2276$ J/(mol·K)

$\Delta H_i° = 0.919$ kJ/mol

Melting:

Ca(calcium, beta) = Ca(calcium, liquid)

T_m = 1112 K (observed) $\Delta S_m° = 7.661$ J/(mol·K)

$\Delta H_m° = 8.519$ kJ/mol

Vaporization:

Ca(calcium, liquid) = Ca(calcium, ideal monatomic gas)

T_v = 1755 K (observed) $\Delta S_v° = 87.301$ J/(mol·K)

$\Delta H_v° = 153.213$ kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for calcium were taken from the following sources:

Property	Source
Heat capacity	Hultgren and others (1973)
Entropy	CODATA Task Group (1978)
Enthalpy of inversion	Hultgren and others (1973)
Enthalpy of melting	Hultgren and others (1973)
Enthalpy of vaporization	Hultgren and others (1973)

CaO

Lime (cubic)

CaO

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	$\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	$\log K^\circ_{f,ox}$
273.15	40.605	34.475	-38.265	-1035.	-635131.	-606133.	115.911	0.	0.	0.
298.15	42.153	38.100	-38.100	0.	-635094.	-603480.	105.727	0.	0.	0.
300.	42.256	38.361	-38.101	78.	-635090.	-603284.	105.041	0.	0.	0.
350.	44.624	45.063	-38.625	2253.	-634931.	-597994.	89.246	0.	0.	0.
400.	46.380	51.142	-39.815	4530.	-634706.	-592732.	77.403	0.	0.	0.
450.	47.738	56.686	-41.387	6885.	-634444.	-587501.	68.195	0.	0.	0.
500.	48.821	61.774	-43.174	9300.	-634169.	-582300.	60.832	0.	0.	0.
550.	49.707	66.470	-45.081	11764.	-633898.	-577126.	54.811	0.	0.	0.
600.	50.446	70.827	-47.048	14268.	-633644.	-571977.	49.795	0.	0.	0.
650.	51.075	74.891	-49.035	16806.	-633419.	-566847.	45.552	0.	0.	0.
700.	51.617	78.696	-51.019	19374.	-633232.	-561733.	41.917	0.	0.	0.
750.	52.092	82.274	-52.985	21967.	-633927.	-556595.	38.765	0.	0.	0.
800.	52.513	85.649	-54.922	24582.	-633728.	-551447.	36.006	0.	0.	0.
850.	52.891	88.845	-56.824	27218.	-633621.	-546308.	33.572	0.	0.	0.
900.	53.235	91.878	-58.688	29871.	-633606.	-541173.	31.409	0.	0.	0.
950.	53.550	94.764	-60.511	32541.	-633686.	-536036.	29.473	0.	0.	0.
1000.	53.842	97.519	-62.293	35225.	-633860.	-530892.	27.731	0.	0.	0.
1050.	54.117	100.152	-64.034	37924.	-634129.	-525737.	26.154	0.	0.	0.
1100.	54.376	102.676	-65.733	40637.	-634494.	-520568.	24.720	0.	0.	0.
1150.	54.624	105.099	-67.393	43362.	-642827.	-515099.	23.397	0.	0.	0.
1200.	54.863	107.428	-69.012	46099.	-642442.	-509554.	22.180	0.	0.	0.
1250.	55.095	109.673	-70.594	48848.	-642049.	-504025.	21.062	0.	0.	0.
1300.	55.321	111.838	-72.139	51608.	-641649.	-498512.	20.030	0.	0.	0.
1350.	55.545	113.930	-73.648	54380.	-641242.	-493014.	19.076	0.	0.	0.
1400.	55.766	115.954	-75.123	57163.	-640828.	-487532.	18.190	0.	0.	0.
1450.	55.986	117.915	-76.565	59957.	-640406.	-482064.	17.366	0.	0.	0.
1500.	56.207	119.817	-77.976	62762.	-639976.	-476612.	16.597	0.	0.	0.
1550.	56.429	121.663	-79.355	65577.	-639537.	-471173.	15.878	0.	0.	0.
1600.	56.652	123.458	-80.705	68404.	-639090.	-465749.	15.205	0.	0.	0.
1650.	56.879	125.205	-82.028	71243.	-638633.	-460339.	14.573	0.	0.	0.
1700.	57.109	126.906	-83.323	74092.	-638167.	-454944.	13.979	0.	0.	0.
1750.	57.342	128.565	-84.592	76954.	-637691.	-449562.	13.419	0.	0.	0.
1800.	57.580	130.184	0.	0.	-790039.	-440270.	12.776	0.	0.	0.

CaO

CaO | Lime | Formula weight = 56.079 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 38.100$ J/(mol·K) $\Delta H_f^\circ = -635.094$ kJ/mol

$V° = 16.764 \pm 0.005$ cm^3/mol $\Delta G_f^\circ = -603.480$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = -2.55577 \times 10^5$ $a_4 = -4.20068 \times 10^2$ $a_6 = -3.08248 \times 10^{-3}$

$a_2 = -7.05800 \times 10^3$ $a_5 = 7.16851 \times 10^1$ $a_7 = 2.23862 \times 10^{-6}$

$a_3 = -4.31990 \times 10^2$

Sources for Thermodynamic Properties

The thermodynamic properties for lime were taken from the following sources:

Property	Source
Heat capacity	Stull and Prophet (1971) and Chase and others (1974, 1975)
Entropy	CODATA Task Group (1978)
Enthalpy of formation from the elements	CODATA Task Group (1978)

The molar volume of lime was obtained from the compilation of Robie and others (1967).

$CaSiO_3$

Reference state: Wollastonite 273.15 K to 1398 K
Cyclowollastorite 1398 K to 1800 K

CaO_3Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	83.472	73.538	-81.369	-2139.	-1634686.	-1556383.	297.628	-88990.	-89375.	17.091
298.15	87.562	81.028	-81.028	0.	-1634766.	-1549213.	271.415	-88974.	-89411.	15.664
(2 sigma)	±0.552	±0.678	±0.678	±0.	±702.	±608.	±0.106	±702.	±608.	±0.106
300.	87.843	81.571	-81.030	162.	-1634769.	-1548682.	269.649	-88972.	-89414.	15.568
350.	94.482	95.632	-82.125	4727.	-1634733.	-1534334.	228.987	-88943.	-89490.	13.356
400.	99.707	108.603	-84.635	9587.	-1634514.	-1520004.	198.492	-88925.	-89570.	11.697
450.	103.929	120.599	-87.973	14682.	-1634166.	-1505710.	174.778	-88926.	-89650.	10.406
500.	107.411	131.735	-91.799	19968.	-1633731.	-1491460.	155.812	-88954.	-89730.	9.374
(2 sigma)	±0.346	±0.692	±0.677	±77.	±710.	±575.	±0.060	±710.	±575.	±0.060
550.	110.331	142.113	-95.907	25413.	-1633240.	-1477256.	140.298	-89013.	-89805.	8.529
600.	112.813	151.822	-100.166	30994.	-1632717.	-1463099.	127.374	-89109.	-89873.	7.824
650.	114.948	160.938	-104.494	36689.	-1632182.	-1448986.	116.442	-89245.	-89931.	7.227
700.	116.802	169.526	-108.835	42484.	-1631651.	-1434914.	107.074	-89424.	-89977.	6.714
750.	118.427	177.641	-113.154	48365.	-1631974.	-1420842.	98.956	-89650.	-90009.	6.269
(2 sigma)	±0.624	±0.690	±0.675	±132.	±715.	±576.	±0.040	±715.	±576.	±0.040
800.	119.863	185.331	-117.427	54323.	-1631382.	-1406787.	91.854	-89923.	-90025.	5.878
850.	121.141	192.637	-121.638	60349.	-1630861.	-1392766.	85.589	-90954.	-90016.	5.532
900.	122.287	199.594	-125.777	66435.	-1630418.	-1378773.	80.022	-90916.	-89962.	5.221
950.	123.322	206.234	-129.839	72576.	-1630055.	-1364803.	75.042	-90855.	-89910.	4.944
1000.	124.262	212.584	-133.818	78766.	-1629776.	-1350850.	70.561	-90735.	-89862.	4.694
(2 sigma)	±0.509	±0.705	±0.673	±224.	±732.	±624.	±0.033	±732.	±624.	±0.033
1050.	125.121	218.668	-137.715	85001.	-1629584.	-1336909.	66.508	-90710.	-89818.	4.468
1100.	125.911	224.507	-141.528	91277.	-1629479.	-1322975.	62.823	-90631.	-89777.	4.263
1150.	126.642	230.120	-145.259	97591.	-1637335.	-1308763.	59.446	-90553.	-89740.	4.076
1200.	127.323	235.525	-148.908	103940.	-1636468.	-1294496.	56.348	-90476.	-89707.	3.905
1250.	127.961	240.735	-152.477	110322.	-1635589.	-1280265.	53.499	-90493.	-89676.	3.747
(2 sigma)	±1.512	±0.700	±0.673	±225.	±731.	±713.	±0.030	±731.	±713.	±0.030
1300.	128.562	245.766	-155.969	116735.	-1634699.	-1266070.	50.871	-90336.	-89648.	3.602
1350.	129.132	250.629	-159.386	123178.	-1633798.	-1251909.	48.439	-90276.	-89623.	3.468
1398.	129.654	255.149	-162.596	129389.	-1632923.	-1238346.	46.269	-90226.	-89601.	3.348
1398.	129.533	259.287	-162.596	135174.	-1627138.	-1238346.	46.269	-84442.	-89601.	3.348
1400.	129.558	259.472	-162.735	135433.	-1627101.	-1237790.	46.182	-84440.	-89608.	3.343
1450.	130.160	264.029	-166.149	141926.	-1626183.	-1223902.	44.090	-84402.	-89793.	3.235
1500.	130.730	268.452	-169.486	148448.	-1625250.	-1210046.	42.138	-84370.	-89980.	3.133
(2 sigma)	±6.721	±1.488	±0.658	±2099.	±2087.	±822.	±0.029	±2087.	±822.	±0.029
1550.	131.270	272.747	-172.748	154998.	-1624302.	-1196222.	40.312	-84317.	-90167.	3.039
1600.	131.783	276.923	-175.939	161575.	-1623341.	-1182428.	38.602	-84334.	-90355.	2.950
1650.	132.271	280.986	-179.061	168176.	-1622366.	-1168665.	36.997	-84332.	-90543.	2.866
1700.	132.735	284.941	-182.117	174802.	-1671886.	-1154481.	35.473	-84343.	-90732.	2.788
1750.	133.178	288.795	-185.110	181449.	-1670742.	-1139280.	34.006	-84368.	-90919.	2.714
(2 sigma)	±10.183	±2.602	±0.693	±4011.	±3988.	±1067.	±0.032	±3988.	±1067.	±0.032
1800.	133.601	292.553	-188.043	188119.	-1822415.	-1120188.	32.507	-84408.	-91106.	2.644
(2 sigma)	±10.918	±2.875	±0.718	±4512.	±4487.	±1155.	±0.034	±4487.	±1155.	±0.034

CaO_3Si

$CaSiO_3$ (reference state) Wollastonite, Cyclowollastonite Formula weight = 116.164 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (wollastonite)

$S° = 81.028 \pm 0.678$ J/(mol·K) $\Delta H_f^\circ = -1634.766 \pm 0.702$ kJ/mol

$V° = 39.930 \pm 0.200$ cm^3/mol $\Delta G_f^\circ = -1549.213 \pm 0.608$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

Wollastonite (temperature range 200 to 1398 K)

$a_1 = 0.0$ $a_4 = -1.212413\times10^3$ $a_6 = -9.115107\times10^{-3}$

$a_2 = 3.0259\times10^3$ $a_5 = 1.927733\times10^2$ $a_7 = 4.413189\times10^{-6}$

$a_3 = -1.7296\times10^3$

Cyclowollastonite (temperature range 1398 to 1800 K)

$a_1 = -9.739076\times10^3$ $a_4 = -1.024504\times10^3$ $a_6 = -3.621589\times10^{-4}$

$a_2 = -2.474400\times10^3$ $a_5 = 1.672547\times10^2$ $a_7 = 0.0$

$a_3 = -1.372368\times10^3$

Critical Reaction

Inversion:

$CaSiO_3$(wollastonite) = $CaSiO_3$(cyclowollastonite)

T_i = 1398 K (observed) $\Delta S_i^\circ = 4.138 \pm 1.42$ J/(mol·K)

$\Delta H_i^\circ = 5.785 \pm 1.76$ kJ/mol

For detailed information on $CaSiO_3$, refer to the appropriate tables on the individual phases.

$CaSiO_3$

Cyclowollastonite (=Pseudowollastonite, triclinic, dimorphous with Wollastonite)

CaO_3Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_r^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	83.890	79.740	-87.584	-2143.	-1627538.	-1550929.	296.585	-81842.	-83921.	16.048
298.15	87.450	87.244	-87.244	0.	-1627614.	-1543914.	270.487	-81822.	-84113.	14.736
(2 sigma)	±1.553	±0.915	±0.915	±0.	±932.	±784.	±0.137	±932.	±784.	±0.137
300.	87.696	87.785	-87.245	162.	-1627617.	-1543395.	268.729	-81821.	-84127.	14.648
350.	93.566	101.762	-88.336	4699.	-1627610.	-1529356.	228.244	-81819.	-84512.	12.613
400.	98.286	114.575	-90.826	9500.	-1627450.	-1515329.	197.881	-81861.	-84894.	11.086
450.	102.187	126.383	-94.129	14514.	-1627182.	-1501329.	174.270	-81942.	-85269.	9.898
500.	105.479	137.325	-97.909	19708.	-1626839.	-1487363.	155.384	-82062.	-85633.	8.946
(2 sigma)	±1.284	±0.890	±0.892	±228.	±952.	±713.	±0.074	±952.	±713.	±0.074
550.	108.306	147.514	-101.960	25054.	-1626447.	-1473434.	139.935	-82220.	-85982.	8.166
600.	110.766	157.046	-106.158	30533.	-1626026.	-1459542.	127.064	-82418.	-86316.	7.514
650.	112.932	165.999	-110.420	36126.	-1625593.	-1445686.	116.177	-82656.	-86631.	6.962
700.	114.857	174.440	-114.694	41822.	-1625161.	-1431863.	106.847	-82934.	-86927.	6.487
750.	116.582	182.424	-118.946	47609.	-1625579.	-1418034.	98.761	-83255.	-87201.	6.073
(2 sigma)	±1.586	±0.796	±0.810	±488.	±926.	±672.	±0.047	±926.	±672.	±0.047
800.	118.140	189.999	-123.152	53477.	-1625076.	-1404215.	91.686	-83618.	-87453.	5.710
850.	119.554	197.204	-127.298	59420.	-1624638.	-1390425.	85.445	-84741.	-87675.	5.388
900.	120.845	204.075	-131.374	65431.	-1624271.	-1376658.	79.899	-84769.	-87847.	5.098
950.	122.030	210.641	-135.374	71503.	-1623977.	-1362911.	74.938	-84776.	-88017.	4.840
1000.	123.123	216.928	-139.296	77632.	-1623758.	-1349176.	70.474	-84767.	-88188.	4.606
(2 sigma)	±1.833	±0.806	±0.728	±718.	±963.	±686.	±0.036	±963.	±686.	±0.036
1050.	124.133	222.960	-143.137	83814.	-1623619.	-1335451.	66.435	-84745.	-88360.	4.396
1100.	125.072	228.757	-146.898	90044.	-1623559.	-1321730.	62.764	-84712.	-88533.	4.204
1150.	125.945	234.336	-150.579	96320.	-1631454.	-1307730.	59.399	-84672.	-88707.	4.029
1200.	126.762	239.713	-154.182	102638.	-1630618.	-1293673.	56.312	-84626.	-88884.	3.869
1250.	127.527	244.904	-157.708	108995.	-1629764.	-1279651.	53.474	-84579.	-89062.	3.722
(2 sigma)	±3.771	±0.908	±0.676	±981.	±1173.	±735.	±0.031	±1173.	±735.	±0.031
1300.	128.245	249.920	-161.158	115390.	-1628893.	-1265664.	50.855	-84530.	-89242.	3.586
1350.	128.920	254.772	-164.536	121819.	-1628005.	-1251710.	48.432	-84483.	-89424.	3.460
1400.	129.558	259.472	-167.843	128281.	-1627101.	-1237790.	46.182	-84440.	-89608.	3.343
1450.	130.160	264.029	-171.082	134774.	-1626183.	-1223902.	44.090	-84402.	-89793.	3.235
1500.	130.730	268.452	-174.254	141297.	-1625250.	-1210046.	42.138	-84370.	-89980.	3.133
(2 sigma)	±6.721	±1.438	±0.663	±1903.	±2087.	±822.	±0.029	±2087.	±822.	±0.029
1550.	131.270	272.747	-177.362	147847.	-1624302.	-1196222.	40.312	-84347.	-90167.	3.039
1600.	131.783	276.923	-180.409	154423.	-1623341.	-1182428.	38.602	-84334.	-90355.	2.950
1650.	132.271	280.936	-183.395	161025.	-1622366.	-1168665.	36.997	-84332.	-90543.	2.866
1700.	132.735	284.941	-186.324	167650.	-1671886.	-1154481.	35.473	-84343.	-90732.	2.788
1750.	133.178	288.795	-189.197	174298.	-1670742.	-1139280.	34.006	-84368.	-90919.	2.714
(2 sigma)	±10.183	±2.602	±0.741	±3802.	±3988.	±1067.	±0.032	±3988.	±1067.	±0.032
1800.	133.601	292.553	-192.016	180967.	-1822415.	-1120188.	32.507	-84408.	-91106.	2.644
(2 sigma)	±10.918	±2.875	±0.773	±4300.	±4487.	±1155.	±0.034	±4487.	±1155.	±0.034

CaO_3Si

$CaSiO_3$ Cyclowollastonite Formula weight = 116.164 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 87.244 \pm 0.915$ J/(mol·K) $\Delta H_f^\circ = -1627.614 \pm 0.932$ kJ/mol

$V° = 40.080 \pm 0.280$ cm^3/mol $\Delta G_f^\circ = -1543.914 \pm 0.784$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\, a_6\, T + a_7\, T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\, T^2) - 2\, a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\, a_6\, T + a_7\, T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\, a_3\, T^{0.5} + a_5\, T + a_6\, T^2 + a_7\, T^3/3$$

$a_1 = -9.739076\times10^3$ $a_4 = -1.024504\times10^3$ $a_6 = -3.621589\times10^{-4}$

$a_2 = -2.474400\times10^3$ $a_5 = 1.672547\times10^2$ $a_7 = 0.0$

$a_3 = -1.372368\times10^3$

Critical Reactions

Inversion:

$CaSiO_3$(wollastonite) = $CaSiO_3$(cyclowollastonite)

T_i = 1398 K (observed) $\Delta S_i^\circ = 4.138 \pm 1.42$ J/(mol·K)

$\Delta H_i^\circ = 5.785 \pm 1.76$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of cyclowollastonite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Wagner (1932)	heat capacity	low-temperature calorimetry	7	201 - 295 K
Wagner (1932)	relative enthalpy	drop calorimetry	12	576 - 1558 K
White (1919)	relative enthalpy	drop calorimetry	28	373 - 1673 K
Parks and Kelley (1926)	specific heat	aneroid calorimetry	6	195 - 298 K
Robie and others (1979)	entropy		1	298.15

The heat-capacity measurements of Wagner (1932) were fit with a standard error of estimate of 0.70 J/(mol·K). The relative enthalpy measurements of Wagner (1932) and White (1919) were fit with standard error of estimate of 666 J/mol (0.97 percent of observed value) and 265 J/mol (0.35 percent of observed value), respectively. The specific heat measurements of Parks and Kelley (1926) were fit with a standard error of estimate of 1.1 J/(mol·K) or 1.3 percent of the observed value. The fitted entropy at 298.15 K is 87.244 ± 0.915 J/(mol·K) or a departure of 0.21 from the value of 87.45 ± 0.42 reported by Robie and others (1979).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Charlu and others (1978)[b]	solution calorimetry (borate salt)	A	970	1	-80.389±1.273	-1626.181
Kracek and others (1953)[c]	solution calorimetry (HF)	B	347.85	1	-6.526±4.183	-1628.240
Nacken (1930)[d]	solution calorimetry (HCl-HF)	B	314.85	4	-8.171±5.916	-1626.595
Kay and Taylor (1960)[e]	silica activity	C	1773	1	-86.058±2.771	-1626.253
Kay and Taylor (1960)[e]	silica activity	D	1543	1	59.386±2.412	-1623.448
Benz and Wagner (1961)	Emf	E	943-1003	10	-41.441±0.186	-1629.791

a Reactions:

A) CaO(lime) + SiO_2(quartz, beta) = $CaSiO_3$(cyclowollastonite)

B) $CaSiO_3$(cyclowollastonite) = $CaSiO_3$(wollastonite)

C) CaO(lime) + SiO_2(cristobalite, beta) = $CaSiO_3$(cyclowollastonite)

D) $CaSiO_3$(cyclowollastonite) + $CaAl_2Si_2O_8$(anorthite) = $Ca_2Al_2SiO_7$(gehlenite) + 2 SiO_2(cristobalite, beta)

E) 1/2 CaO(lime) + $CaSiO_3$(cyclowollastonite) = 1/2 $Ca_3Si_2O_7$(rankinite)

b Charlu and others (1978) measured the enthalpy of solution of cyclowollastonite in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of lime and quartz in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

c Kracek and others (1953) measured the enthalpy of solution of cyclowollastonite in HF acid solution at 347.85 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpy of solution of wollastonite.

d Nacken (1930) measured the enthalpy of solution of cyclowollastonite in HCl-HF acid solution at 314.85 K. To complete the thermodynamic cycle, the data were evaluted in combination with his enthalpy of solution of wollastonite.

e Kay and Taylor (1960) determined the activity of silica in the silicate liquid for the lime-alumina-silica system. Using the silica activity from their study and the measured temperature and composition of the silicate melt in equilibrium with anorthite, cyclowollastonite, and gehlenite, we obtained the equilibrium constants for reactions C and D at the melt temperature and 101.325 kPa.

Phase-equilibrium studies were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature. After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for cyclowollastonite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -1627.614±0.932 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of cyclowollastonite and presents the data in their poorest perspective. The phase-equilibria studies lack the precision to discriminate among the experimental enthalpies of solution.

The temperature of the experimentally observed inversion of wollastonite to cyclowollastonite at 101.325 kPa was entered as a fixed value in the regression and supplies an additional constraint on the free energy of cyclowollastonite and its dimorph. This inversion temperature is listed as "observed" in the section on critical reactions.

The molar volume of cyclowollastonite was obtained from the compilation of Robie and others (1967).

$CaSiO_3$

Wollastonite [triclinic, dimorphous with Cyclowollastonite (=Pseudowollastonite)]

CaO_3Si

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	$\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	$\log K^\circ_{f,ox}$
273.15	83.472	73.538	-81.369	-2139.	-1634686.	-1556383.	297.628	-88990.	-89375.	17.091
298.15	87.562	81.028	-81.028	0.	-1634766.	-1549213.	271.415	-88974.	-89411.	15.664
(2 sigma)	±0.552	±0.678	±0.678	±0.	±702.	±608.	±0.106	±702.	±608.	±0.106
300.	87.843	81.571	-81.030	162.	-1634769.	-1548682.	269.649	-88972.	-89414.	15.568
350.	94.482	95.632	-82.125	4727.	-1634733.	-1534334.	228.987	-88943.	-89490.	13.356
400.	99.707	108.603	-84.635	9587.	-1634514.	-1520004.	198.492	-88925.	-89570.	11.697
450.	103.929	120.599	-87.973	14682.	-1634166.	-1505710.	174.778	-88926.	-89650.	10.406
500.	107.411	131.735	-91.799	19968.	-1633731.	-1491460.	155.812	-88954.	-89730.	9.374
(2 sigma)	±0.346	±0.692	±0.677	±77.	±710.	±575.	±0.060	±710.	±575.	±0.060
550.	110.331	142.113	-95.907	25413.	-1633240.	-1477256.	140.298	-89013.	-89805.	8.529
600.	112.813	151.822	-100.166	30994.	-1632717.	-1463099.	127.374	-89109.	-89873.	7.824
650.	114.948	160.938	-104.494	36689.	-1632182.	-1448986.	116.442	-89245.	-89931.	7.227
700.	116.802	169.526	-108.835	42484.	-1631651.	-1434914.	107.074	-89424.	-89977.	6.714
750.	118.427	177.641	-113.154	48365.	-1631974.	-1420842.	98.956	-89650.	-90009.	6.269
(2 sigma)	±0.624	±0.690	±0.675	±132.	±715.	±576.	±0.040	±715.	±576.	±0.040
800.	119.863	185.331	-117.427	54323.	-1631382.	-1406787.	91.854	-89923.	-90025.	5.878
850.	121.141	192.637	-121.638	60349.	-1630861.	-1392766.	85.589	-90964.	-90016.	5.532
900.	122.287	199.594	-125.777	66435.	-1630418.	-1378773.	80.022	-90916.	-89962.	5.221
950.	123.322	206.234	-129.839	72576.	-1630055.	-1364803.	75.042	-90855.	-89910.	4.944
1000.	124.262	212.584	-133.818	78766.	-1629776.	-1350850.	70.561	-90785.	-89862.	4.694
(2 sigma)	±0.509	±0.705	±0.673	±224.	±732.	±624.	±0.033	±732.	±624.	±0.033
1050.	125.121	218.668	-137.715	85001.	-1629584.	-1336909.	66.508	-90710.	-89818.	4.468
1100.	125.911	224.507	-141.528	91277.	-1629479.	-1322975.	62.823	-90631.	-89777.	4.263
1150.	126.642	230.120	-145.259	97591.	-1637335.	-1308763.	59.446	-90553.	-89740.	4.076
1200.	127.323	235.525	-148.908	103940.	-1636468.	-1294496.	56.348	-90476.	-89707.	3.905
1250.	127.961	240.735	-152.477	110322.	-1635589.	-1280265.	53.499	-90403.	-89676.	3.747
(2 sigma)	±1.512	±0.700	±0.673	±225.	±731.	±713.	±0.030	±731.	±713.	±0.030
1300.	128.562	245.766	-155.969	116735.	-1634699.	-1266070.	50.871	-90336.	-89648.	3.602
1350.	129.132	250.629	-159.386	123178.	-1633798.	-1251909.	48.439	-90276.	-89623.	3.468
1400.	129.675	255.335	-162.729	129648.	-1632886.	-1237782.	46.182	-90225.	-89600.	3.343
1450.	130.197	259.894	-166.001	136145.	-1631964.	-1223687.	44.082	-90182.	-89578.	3.227
1500.	130.700	264.317	-169.205	142668.	-1631030.	-1209624.	42.123	-90151.	-89558.	3.119
(2 sigma)	±4.272	±0.845	±0.675	±711.	±1007.	±828.	±0.029	±1007.	±828.	±0.029
1550.	131.187	268.610	-172.343	149215.	-1630086.	-1195593.	40.291	-90131.	-89539.	3.017
1600.	131.663	272.783	-175.417	155786.	-1629130.	-1181592.	38.575	-90123.	-89520.	2.923
1650.	132.129	276.841	-178.429	162381.	-1628161.	-1167622.	36.964	-90128.	-89501.	2.833
1700.	132.587	280.793	-181.382	168999.	-1677689.	-1153231.	35.434	-90146.	-89482.	2.749
1750.	133.040	284.643	-184.277	175640.	-1676552.	-1137822.	33.962	-90178.	-89462.	2.670
(2 sigma)	±8.450	±1.576	±0.692	±2223.	±2349.	±991.	±0.030	±2349.	±991.	±0.030
1800.	133.491	288.397	-187.117	182303.	-1828231.	-1118523.	32.459	-90225.	-89441.	2.595
(2 sigma)	±9.455	±1.803	±0.702	±2664.	±2774.	±1039.	±0.030	±2774.	±1039.	±0.030

$CaSiO_3$ | Wollastonite | Formula weight = 116.164 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 81.028 \pm 0.678$ J/(mol·K) $\Delta H_f° = -1634.766 \pm 0.702$ kJ/mol

$V° = 39.930 \pm 0.200$ cm^3/mol $\Delta G_f° = -1549.213 \pm 0.608$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p°(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = 0.0$ $a_4 = -1.212413 \times 10^3$ $a_6 = -9.115107 \times 10^{-3}$

$a_2 = 3.025900 \times 10^3$ $a_5 = 1.927733 \times 10^2$ $a_7 = 4.413189 \times 10^{-6}$

$a_3 = -1.729600 \times 10^3$

Critical Reactions

Inversion:

$CaSiO_3$(wollastonite) = $CaSiO_3$(cyclowollastonite)

$T_i = 1398$ K (observed) $\Delta S_i° = 4.138 \pm 1.42$ J/(mol·K)

$\Delta H_i° = 5.785 \pm 1.76$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of wollastonite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Cristescu and Simon (1934)	heat capacity	low-temperature calorimetry	2	200 - 210 K
Cristescu (cited in Wagner, 1932)	heat capacity	low-temperature calorimetry	7	200 - 304 K
Gronow and Schwiete (1933)	relative enthalpy	drop calorimetry	5	573 - 1373 K
Southard (1941)	relative enthalpy	drop calorimetry	13	485 - 1423 K
Roth and Bertram (1929)	relative enthalpy	drop calorimetry	7	323 - 1157 K
White (1919)	relative enthalpy	drop calorimetry	18	373 - 1573 K
Wagner (1932)	relative enthalpy	drop calorimetry	11	566 - 1383 K
Hemingway and Robie (1977)	entropy		1	298.15 K

The heat capacities measured by Cristescu and Simon (1934) and Cristescu (cited in Wagner, 1932) were fit with a standard error of estimate of 0.07 and 1.0 J/(mol·K), respectively. The relative enthalpy measurements of Gronow and Schwiete (1933) were fit with a standard error of estimate of 761 J/mol or approximately 0.64 percent of the observed value. The relative enthalpy measurements of Southard (1941) were fit with a standard error of estimate of 147 J/mol or approximately 0.16 percent of the observed value. The relative enthalpy measurements of Roth and Bertram (1929) were fit with a standard error of estimate of 658 J/mol or approximately 1.5 percent of the observed value. The relative enthalpy measurements of White (1919) were fit with a standard error of estimate of 1033 J/mol or approximately 1.2 percent of the observed value. The relative enthalpy measurements of Wagner (1932) were fit with a standard error of estimate of 752 J/mol or approximately 0.65 percent of the observed value. The fitted entropy value at 298.15 K is 81.028 ± 0.678 J/(mol·K), or a departure of 0.97 J from the experimental value of 82.00 ± 0.40 J/(mol·K) given by Hemingway and Robie (1977).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Charlu and others (1978)[b]	solution calorimetry (borate salt)	A	970	1	87.754±1.551	-1633.556
Benz and Wagner (1961)	Emf	A	898-1148	12	87.606±0.384	-1636.310
Barany (1966)[c]	solution calorimetry (HF)	B	346.85	6	89.762±0.979	-1635.564
Kracek and others (1953)[d]	solution calorimetry (HF)	C	347.85	1	-6.526±4.183	-1634.150
Nacken (1930)[e]	solution calorimetry (HCl-HF)	C	314.85	6	-8.171±5.916	-1635.795
Newton (1966b)	gas-medium pressure apparatus	D	803-923	4	-51.708±0.304	-1633.747
Huckenholz (1974)	unspecified	D	848-858	2	-49.366±0.328	-1634.918
Newton (1966b)	gas-medium pressure apparatus pressure apparatus	E	973-1023	4	-49.102±1.847	-1635.334
Huckenholz (1974)	unspecified	E	888-958	4	-50.100±0.499	-1634.835
Boettcher (1970)	gas-medium pressure apparatus pressure apparatus	E	893-1053	4	-50.329±1.454	-1634.721
Liou (1971)	gas-medium pressure apparatus	F	708-828	10	-89.180±0.496	-1634.781
Hays (1965)	solid-medium pressure apparatus	G	1473-1523	4	-156.099±6.608	-1635.678
Huckenholz (1974)	unspecified	G	1125-1423	12	-158.750±2.236	-1634.794
Shmulovich (1974)	gas-medium pressure apparatus	G	1133-1153	2	-159.942±1.763	-1634.397

a Reactions:

A) $CaSiO_3$(wollastonite) = SiO_2(quartz, beta) + CaO(lime)

B) $CaSiO_3$(wollastonite) = SiO_2(quartz, alpha) + CaO(lime)

C) $CaSiO_3$(cyclowollastonite) = $CaSiO_3$(wollastonite)

D) $CaAl_2Si_2O_8$(anorthite) + 2 $CaSiO_3$(wollastonite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, alpha)

E) $CaAl_2Si_2O_8$(anorthite) + 2 $CaSiO_3$(wollastonite) = $Ca_3Al_2Si_3O_{12}$(grossular) + SiO_2(quartz, beta)

F) $CaAl_2Si_2O_8$(anorthite) + $CaSiO_3$(wollastonite) + H_2O(gas) = $Ca_2Al_2Si_3O_{10}(OH)_2$(prehnite)

G) $CaAl_2Si_2O_8$(anorthite) + $Ca_2Al_2SiO_7$(gehlenite) + 3 $CaSiO_3$(wollastonite) = 2 $Ca_3Al_2Si_3O_{12}$(grossular)

b Charlu and others (1978) measured the enthalpy of solution of wollastonite in lead borate salt melt at 970 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpies of solution of lime and quartz in the salt melt; corrections were not made for the enthalpies of dilution and of mixing of the product melts.

c Barany (1966) measured the enthalpy of solution of wollastonite in HF acid solution at 346.85 K. To complete the thermodynamic cycle, the data were evaluated in combination with the enthalpies of solution of lime (Barany, 1963) and of quartz (Hemingway and Robie, 1977; Bennington and others, 1978) in similar solutions.

d Kracek and others (1953) measured the enthalpy of solution of wollastonite in HF acid solution at 347.85 K. To complete the thermodynamic cycle, their data were evaluated in combination with their enthalpy of solution of cyclowollastonite.

e Nacken (1930) measured the enthalpy of solution of wollastonite in HCl-HF acid solution at 314.85 K. To complete the thermodynamic cycle, the data were evaluated in combination with his enthalpy of solution of cyclowollastonite.

Phase-equilibrium studies (utilizing gas- and solid-medium pressure apparatus) were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. Molar volumes of the phases and free-energy data for H_2O(gas) from Fisher and Zen (1971) were used in the conversion. The studies cited in Table 2 comply with the following criteria: 1) starting materials and reaction products were characterized, and 2) chemical equilibrium was demonstrated.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for wollastonite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -1634.766 ± 0.702 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of wollastonite and presents the data in their poorest perspective.

Most of the phase-equilibria data cited above bracket the regression fit in free-energy space. However, the phase-equilibria studies also lack sufficient precision to constrain the fit tightly, as the scatter in the calculated enthalpies of reaction and enthalpies of formation listed in Table 2 demonstrate. The phase-equilibria studies lack the precision to discriminate among the experimental enthalpies of solution.

The temperature of the experimentally observed inversion of wollastonite to cyclowollastonite was entered as a fixed value in the regression and supplies an additional constraint on the free energy of wollastonite and its dimorph. This inversion temperature is listed as "observed" in the section on critical reactions.

The molar volume of wollastonite was obtained from the compilation of Robie and others (1967) and the work of Evans (1977).

Ca_2SiO_4

Reference state: Ca Olivine 273.15 K to 1120 K
Alpha prime 1120 K to 1710 K
(crystal) 1710 K to 1800 K

Ca_2O_4Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ-H_{Tr}^\circ)/T$	$H_T^\circ-H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	120.737	109.706	-120.939	-3082.	-2316400.	-2209561.	422.535	-135573.	-136420.	26.088
298.15	125.690	120.499	-120.499	0.	-2316534.	-2199776.	385.391	-135648.	-136494.	23.913
(2 sigma)	±0.387	±2.045	±2.045	±0.	±2441.	±1881.	±0.330	±2441.	±1881.	±0.330
300.	126.025	121.278	-120.502	233.	-2316540.	-2199051.	382.889	-135654.	-136500.	23.767
350.	133.898	141.321	-122.057	6739.	-2316581.	-2179463.	325.267	-135859.	-136625.	20.390
400.	140.297	159.630	-125.634	13598.	-2316413.	-2159884.	282.052	-136118.	-136718.	17.853
450.	145.851	176.482	-130.350	20755.	-2316096.	-2140336.	248.444	-136412.	-136775.	15.876
500.	150.846	192.112	-135.763	28174.	-2315667.	-2120829.	221.561	-136721.	-136799.	14.291
(2 sigma)	±0.500	±2.055	±2.046	±78.	±2448.	±1522.	±0.159	±2448.	±1522.	±0.159
550.	155.417	206.706	-141.536	35833.	-2315156.	-2101369.	199.571	-137032.	-136792.	12.991
600.	159.629	220.413	-147.552	43710.	-2314586.	-2081959.	181.251	-137335.	-136756.	11.906
650.	163.510	233.345	-153.658	51790.	-2313981.	-2062598.	165.752	-137625.	-136696.	10.985
700.	167.074	245.595	-159.801	60056.	-2313360.	-2043284.	152.472	-137900.	-136614.	10.194
750.	170.322	257.234	-165.912	68492.	-2314415.	-2023941.	140.960	-138164.	-136513.	9.508
(2 sigma)	±0.411	±2.073	±2.048	±176.	±2460.	±1124.	±0.078	±2460.	±1124.	±0.078
800.	173.251	268.322	-171.958	77083.	-2313607.	-2004603.	130.887	-138421.	-136395.	8.906
850.	175.859	278.905	-177.950	85812.	-2312911.	-1985313.	122.002	-139393.	-136255.	8.373
900.	178.138	289.023	-183.842	94663.	-2312342.	-1966059.	114.107	-139233.	-136075.	7.898
950.	180.084	298.708	-189.634	103620.	-2311912.	-1946834.	107.044	-139026.	-135905.	7.473
1000.	181.690	307.987	-195.322	112666.	-2311636.	-1927627.	100.689	-138785.	-135747.	7.091
(2 sigma)	±1.356	±2.064	±2.052	±150.	±2453.	±860.	±0.045	±2453.	±860.	±0.045
1050.	182.952	316.884	-200.900	121783.	-2311529.	-1908430.	94.939	-138526.	-135601.	6.746
1100.	183.864	325.417	-206.357	130955.	-2311606.	-1889233.	89.712	-138264.	-135468.	6.433
1120.	184.130	328.733	-208.523	134635.	-2328467.	-1881432.	87.746	-138162.	-135418.	6.316
1120.	185.325	340.964	-208.523	148334.	-2314768.	-1881432.	87.746	-124463.	-135418.	6.316
1150.	186.612	345.879	-212.042	153913.	-2313877.	-1869836.	84.931	-124267.	-135714.	6.164
1200.	188.832	353.868	-217.736	163298.	-2312325.	-1850563.	80.553	-123891.	-136220.	5.929
1250.	191.147	361.623	-223.335	172798.	-2310685.	-1831356.	76.528	-123450.	-136742.	5.714
(2 sigma)	±2.130	±1.479	±1.845	±2837.	±1559.	±912.	±0.038	±1559.	±912.	±0.038
1300.	193.556	369.167	-228.848	182415.	-2308952.	-1812217.	72.816	-122940.	-137284.	5.516
1350.	196.060	376.518	-234.131	192155.	-2307118.	-1793146.	69.381	-122354.	-137846.	5.334
1400.	198.658	383.695	-239.393	202022.	-2305177.	-1774145.	66.194	-121688.	-138432.	5.165
1450.	201.351	390.713	-244.491	212022.	-2303124.	-1755216.	63.230	-120937.	-139043.	5.009
1500.	204.139	397.586	-249.430	222159.	-2300951.	-1736359.	60.465	-120095.	-139681.	4.864
(2 sigma)	±5.794	±1.476	±1.576	±2853.	±1596.	±1153.	±0.040	±1596.	±1153.	±0.040
1550.	207.020	404.326	-254.356	232438.	-2298652.	-1717577.	57.882	-119160.	-140349.	4.730
1600.	209.997	410.946	-259.156	242863.	-2296222.	-1698871.	55.462	-118125.	-141049.	4.605
1650.	213.067	417.454	-263.855	253439.	-2293654.	-1680243.	53.192	-116987.	-141783.	4.488
1700.	216.233	423.862	-268.457	264171.	-2341451.	-1661246.	51.044	-115741.	-142553.	4.380
1710.	216.877	425.132	-269.330	266336.	-2340863.	-1657246.	50.623	-115478.	-142711.	4.359
1710.	199.600	433.547	-269.330	280726.	-2326473.	-1657246.	50.623	-101088.	-142711.	4.359
1750.	199.600	438.162	-273.135	288710.	-2324801.	-1641611.	48.999	-100735.	-143689.	4.289
(2 sigma)	±34.005	±1.490	±1.409	±2981.	±1818.	±1429.	±0.043	±1818.	±1429.	±0.043
1800.	199.600	443.785	-277.846	298690.	-2628383.	-1614273.	46.845	-100338.	-144922.	4.206
(2 sigma)	±34.005	±1.700	±1.333	±3329.	±2346.	±1484.	±0.043	±2346.	±1484.	±0.043

Ca_2SiO_4 (reference state) | Ca-Olivine; Ca_2SiO_4, alpha prime; Ca_2SiO_4, alpha | Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 120.499 \pm 2.045$ J/(mol·K) $\Delta H_f^\circ = -2316.534 \pm 2.441$ kJ/mol

$V° = 59.110 \pm 0.360$ cm^3/mol $\Delta G_f^\circ = -2199.776 \pm 1.881$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

Ca-Olivine (temperature range 200 to 1120 K)

$a_1 = -2.360066\times10^6$ $a_4 = 2.391441\times10^2$ $a_6 = 1.065862\times10^{-1}$

$a_2 = -7.387180\times10^4$ $a_5 = 0.0$ $a_7 = -8.150119\times10^{-5}$

$a_3 = 1.656378\times10^3$

Ca_2SiO_4, alpha prime (temperature range 1120 to 1710 K)

$a_1 = 0.0$ $a_4 = -8.056381\times10^2$ $a_6 = 0.0$

$a_2 = -4.835440\times10^4$ $a_5 = 1.616203\times10^2$ $a_7 = 1.889700\times10^{-5}$

$a_3 = 0.0$

Ca_2SiO_4, alpha (temperature range 1710 to 1800 K)

$a_1 = 0.0$ $a_4 = -1.052325\times10^3$ $a_6 = 0.0$

$a_2 = -5.951\times10^4$ $a_5 = 1.996000\times10^2$ $a_7 = 0.0$

$a_3 = 0.0$

Critical Reactions

Inversions:

Ca_2SiO_4(Ca-Olivine) = Ca_2SiO_4(alpha prime)

T_i = 1120 K (observed) $\Delta S_i^\circ = 12.231 \pm 2.51$ J/(mol·K)

$\Delta H_i^\circ = 13.699 \pm 2.46$ kJ/mol

Ca_2SiO_4(alpha prime) = Ca_2SiO_4(alpha)

T_i = 1710 K $\Delta S_i^\circ = 8.415 \pm 2.49$ J/(mol·K)

$\Delta H_i^\circ = 14.390 \pm 3.39$ kJ/mol

For detailed information on Ca_2SiO_4, refer to the appropriate tables on the individual phases.

Ca_2SiO_4

Reference state: Larnite 273.15 K to 970 K
Alpha prime 970 K to 1710 K
(crystal) 1710 K to 1800 K

Ca_2O_4Si

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	log $K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	log $K^\circ_{f,ox}$
273.15	122.972	115.710	-127.219	-3144.	-2306625.	-2201426.	420.980	-125798.	-128285.	24.532
298.15	128.401	126.719	-126.719	0.	-2306697.	-2191794.	383.993	-125811.	-128512.	22.515
(2 sigma)	±0.238	±1.286	±1.286	±0.	±1328.	±1039.	±0.182	±1328.	±1039.	±0.182
300.	128.775	127.514	-126.721	238.	-2306699.	-2191081.	381.501	-125813.	-128529.	22.379
350.	137.745	148.065	-128.324	6910.	-2306574.	-2171816.	324.126	-125852.	-128979.	19.249
400.	144.975	166.946	-131.988	13984.	-2306191.	-2152589.	281.099	-125897.	-129422.	16.901
450.	150.963	184.378	-136.853	21386.	-2305628.	-2133421.	247.641	-125944.	-129860.	15.074
500.	156.030	200.553	-142.424	29065.	-2304940.	-2114323.	220.882	-125995.	-130293.	13.612
(2 sigma)	±0.464	±1.283	±1.284	±68.	±1333.	±883.	±0.092	±1333.	±883.	±0.092
550.	160.388	215.634	-148.402	36978.	-2304174.	-2095298.	198.995	-126050.	-130720.	12.415
600.	164.190	229.756	-154.599	45094.	-2303366.	-2076344.	180.762	-126114.	-131142.	11.417
650.	167.544	243.033	-160.896	53389.	-2302545.	-2057459.	165.339	-126189.	-131558.	10.572
700.	170.532	255.561	-167.215	61842.	-2301736.	-2038637.	152.125	-126277.	-131967.	9.848
750.	173.216	267.420	-173.503	70437.	-2302633.	-2019798.	140.671	-126382.	-132370.	9.219
(2 sigma)	±0.665	±1.311	±1.281	±209.	±1355.	±764.	±0.053	±1355.	±764.	±0.053
800.	175.645	278.677	-179.728	79160.	-2301693.	-2000974.	130.650	-126507.	-132765.	8.669
850.	177.856	289.393	-185.866	87998.	-2300888.	-1982204.	121.811	-127370.	-133147.	8.182
900.	179.879	299.617	-191.904	96942.	-2300226.	-1963478.	113.957	-127118.	-133494.	7.748
950.	181.741	309.393	-197.832	105983.	-2299712.	-1944785.	106.932	-126826.	-133856.	7.360
970.	182.445	313.187	-200.171	109625.	-2299549.	-1937314.	104.325	-126699.	-134005.	7.216
970.	179.400	314.763	-200.171	111153.	-2298021.	-1937314.	104.325	-125171.	-134005.	7.216
1000.	180.517	320.244	-203.692	116552.	-2297913.	-1926160.	100.612	-125062.	-134280.	7.014
(2 sigma)	±5.830	±1.359	±1.284	±468.	±1402.	±772.	±0.040	±1402.	±772.	±0.040
1050.	182.454	329.098	-209.454	125626.	-2297850.	-1907575.	94.897	-124846.	-134746.	6.703
1100.	184.486	337.632	-215.087	134799.	-2297925.	-1888989.	89.701	-124583.	-135224.	6.421
1150.	186.612	345.879	-220.596	144076.	-2313877.	-1869836.	84.931	-124267.	-135714.	6.164
1200.	188.832	353.868	-225.983	153462.	-2312325.	-1850563.	80.553	-123891.	-136220.	5.929
1250.	191.147	361.623	-231.254	162961.	-2310685.	-1831356.	76.528	-123450.	-136742.	5.714
(2 sigma)	±2.130	±1.479	±1.285	±847.	±1559.	±912.	±0.038	±1559.	±912.	±0.038
1300.	193.556	369.167	-236.414	172578.	-2308952.	-1812217.	72.816	-122940.	-137284.	5.516
1350.	196.060	376.518	-241.468	182318.	-2307118.	-1793146.	69.381	-122354.	-137846.	5.334
1400.	198.658	383.695	-246.420	192186.	-2305177.	-1774145.	66.194	-121688.	-138432.	5.165
1450.	201.351	390.713	-251.275	202186.	-2303124.	-1755216.	63.230	-120937.	-139043.	5.009
1500.	204.139	397.586	-256.038	212322.	-2300951.	-1736359.	60.465	-120095.	-139681.	4.864
(2 sigma)	±5.794	±1.476	±1.294	±903.	±1596.	±1153.	±0.040	±1596.	±1153.	±0.040
1550.	207.020	404.326	-260.713	222601.	-2298652.	-1717577.	57.882	-119160.	-140349.	4.730
1600.	209.997	410.946	-265.304	233026.	-2296222.	-1698871.	55.462	-118125.	-141049.	4.605
1650.	213.067	417.454	-269.817	243602.	-2293654.	-1680243.	53.192	-116987.	-141783.	4.488
1700.	216.233	423.862	-274.253	254334.	-2341451.	-1661246.	51.044	-115741.	-142553.	4.380
1710.	216.877	425.132	-275.132	256500.	-2340863.	-1657246.	50.623	-115478.	-142711.	4.359
1710.	199.600	433.547	-275.132	270890.	-2326473.	-1657246.	50.623	-101088.	-142711.	4.359
1750.	199.600	438.162	-278.806	278874.	-2324801.	-1641611.	48.999	-100735.	-143689.	4.289
(2 sigma)	±34.005	±1.490	±1.300	±1242.	±1818.	±1429.	±0.043	±1818.	±1429.	±0.043
1800.	199.600	443.785	-283.311	288854.	-2628383.	-1614273.	46.845	-100338.	-144922.	4.206
(2 sigma)	±34.005	±1.700	±1.301	±1934.	±2346.	±1484.	±0.043	±2346.	±1484.	±0.043

Ca_2O_4Si

Ca_2SiO_4 (reference state) | Larnite; Ca_2SiO_4, alpha prime; Ca_2SiO_4, alpha | Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 126.719 \pm 1.286$ J/(mol·K) | $\Delta H_f^\circ = -2306.697 \pm 1.328$ kJ/mol

$V° = 51.600 \pm 0.540$ cm^3/mol | $\Delta G_f^\circ = -2191.794 \pm 1.039$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

Larnite (temperature range 200 to 970 K)

a_1 = 0.0	a_4 = -1.538485×10^3	a_6 = 0.0
a_2 = -2.120900×10^3	a_5 = 2.496890×10^2	a_7 = 0.0
a_3 = -2.094286×10^3		

Ca_2SiO_4, alpha prime (temperature range 970 to 1710 K)

a_1 = 0.0	a_4 = -8.056381×10^2	a_6 = 0.0
a_2 = -4.835440×10^4	a_5 = 1.616203×10^2	a_7 = 1.889700×10^{-5}
a_3 = 0.0		

Ca_2SiO_4, alpha (temperature range 1710 to 1800 K)

a_1 = 0.0	a_4 = -1.052325×10^3	a_6 = 0.0
a_2 = -5.951000×10^4	a_5 = 1.996000×10^2	a_7 = 0.0
a_3 = 0.0		

Critical Reactions

Inversions:

Ca_2SiO_4(larnite) = Ca_2SiO_4(alpha prime)

T_i = 970 K (calculated) | $\Delta S_i^\circ = 1.576 \pm 1.93$ J/(mol·K)

$\Delta H_i^\circ = 1.528 \pm 0.61$ kJ/mol

Ca_2SiO_4(alpha prime) = Ca_2SiO_4(alpha)

T_i = 1710 K | $\Delta S_i^\circ = 8.415 \pm 2.49$ J/(mol·K)

$\Delta H_i^\circ = 14.390 \pm 3.39$ kJ/mol

For detailed information on Ca_2SiO_4, refer to the appropriate tables on the individual phases.

Ca_2SiO_4

Alpha

Ca_2O_4Si

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Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ - H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ - H_{Tr}^\circ$ J/mol	Formation from the Elements $\Delta H_{f,e}^\circ$ J/mol	Formation from the Elements $\Delta G_{f,e}^\circ$ J/mol	Formation from the Elements $\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$ J/mol	Formation from the Oxides $\Delta G_{f,ox}^\circ$ J/mol	Formation from the Oxides $\log K_{f,ox}^\circ$
1650.	199.600	426.418	--	--	-2278342.	-1679721.	53.176	-101675.	-141261.	4.472
1700.	199.600	432.376	--	--	-2326892.	-1661161.	51.041	-101181.	-142468.	4.378
1750.	199.600	438.162	--	--	-2324801.	-1641611.	48.999	-100735.	-143689.	4.289
(2 sigma)	±34.005	±1.490	±--	±--	±1818.	±1429.	±0.043	±1818.	±1429.	±0.043
1800.	199.600	443.785	--	--	-2628383.	-1614273.	46.845	-100338.	-144922.	4.206
(2 sigma)	±34.005	±1.700	±--	±--	±2346.	±1484.	±0.043	±2346.	±1484.	±0.043

Ca_2SiO_4, alpha Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S°$ = ± J/(mol·K) ΔH_f° = ± kJ/mol

$V°$ = ± cm^3/mol ΔG_f° = ± kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 1650 to 1800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

a_1 = 0.0 a_4 = -1.052325×10^3 a_6 = 0.0

a_2 = -5.95100×10^4 a_5 = 1.996000×10^2 a_7 = 0.0

a_3 = 0.0

Critical Reactions

Inversion:

Ca_2SiO_4(alpha prime) = Ca_2SiO_4(alpha)

T_i = 1710 K (observed) ΔS_i° = 8.415±2.49 J/(mol·K)

ΔH_i° = 14.390±3.387 kJ/mol

Primary Experimental Data Used in the Analysis

Table 1 provides the sources for the primary data used in evaluating the thermodynamic properties of Ca_2SiO_4, alpha.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Coughlin and O'Brien (1957)	relative enthalpy	drop calorimetry	5	1715 - 1816 K

The relative enthalpy measurements of Coughlin and O'Brien (1957) were fit with a standard error of estimate of 287 J/mol or approximately 0.1 percent of the observed value.

The temperature of the experimentally observed inversion of alpha prime-Ca_2SiO_4 to alpha-Ca_2SiO_4 was entered as a fixed value in the regression and supplies constraint on the free energy of Ca_2SiO_4, alpha. This inversion temperature is listed as "observed" in the section on critical reactions.

Ca_2SiO_4

Alpha prime (orthorhombic, pseudohexagonal, dimorphous with Larnite)

Ca_2O_4Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ - H_{Tr}^\circ)/T$	$H_T^\circ - H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
950.	178.675	311.033	--	--	-2298123.	-1944753.	106.930	-125237.	-133824.	7.358
1000.	180.517	320.244	--	--	-2297913.	-1926160.	100.612	-125062.	-134280.	7.014
(2 sigma)	±5.830	±1.359	±--	±--	±1402.	±772.	±0.040	±1402.	±772.	±0.040
1050.	182.454	329.098	--	--	-2297850.	-1907575.	94.897	-124846.	-134746.	6.703
1100.	184.486	337.632	--	--	-2297925.	-1888989.	89.701	-124583.	-135224.	6.421
1150.	186.612	345.879	--	--	-2313877.	-1869836.	84.931	-124267.	-135714.	6.164
1200.	188.832	353.868	--	--	-2312325.	-1850563.	80.553	-123891.	-136220.	5.929
1250.	191.147	361.623	--	--	-2310685.	-1831356.	76.528	-123450.	-136742.	5.714
(2 sigma)	±2.130	±1.479	±--	±--	±1559.	±912.	±0.038	±1559.	±912.	±0.038
1300.	193.556	369.167	--	--	-2308952.	-1812217.	72.816	-122940.	-137284.	5.516
1350.	196.060	376.518	--	--	-2307118.	-1793146.	69.381	-122354.	-137846.	5.334
1400.	198.658	383.695	--	--	-2305177.	-1774145.	66.194	-121688.	-138432.	5.165
1450.	201.351	390.713	--	--	-2303124.	-1755216.	63.230	-120937.	-139043.	5.009
1500.	204.139	397.586	--	--	-2300951.	-1736359.	60.465	-120095.	-139681.	4.864
(2 sigma)	±5.794	±1.476	±--	±--	±1596.	±1153.	±0.040	±1596.	±1153.	±0.040
1550.	207.020	404.326	--	--	-2298652.	-1717577.	57.882	-119160.	-140349.	4.730
1600.	209.997	410.946	--	--	-2296222.	-1698871.	55.462	-118125.	-141049.	4.605
1650.	213.067	417.454	--	--	-2293654.	-1680243.	53.192	-116987.	-141783.	4.488
1700.	216.233	423.862	--	--	-2341451.	-1661246.	51.044	-115741.	-142553.	4.380
1750.	219.492	430.177	--	--	-2338447.	-1641283.	48.990	-114382.	-143361.	4.279
(2 sigma)	±12.653	±1.996	±--	±--	±2858.	±1432.	±0.043	±2858.	±1432.	±0.043

Ca_2O_4Si

Ca_2SiO_4, alpha prime

Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 116.049 \pm 13.62$ J/(mol·K)

$V° = 52.298$ cm^3/mol[a]

$\Delta H_f° = -2198.074 \pm 7.537$ kJ/mol

$\Delta G_f° = -2079.989 \pm 3.536$ kJ/mol

a Molar volume measured at 1023 K.

Equations at Reference Pressure, 101.325 kPa (Temperature range 950 to 1750 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

$a_1 = 0.0$ | $a_4 = -8.056381\times10^2$ | $a_6 = 0.0$

$a_2 = -4.835440\times10^4$ | $a_5 = 1.616203\times10^2$ | $a_7 = 1.889700\times10^{-5}$

$a_3 = 0.0$

Critical Reactions

Inversion:

Ca_2SiO_4(larnite) = Ca_2SiO_4(alpha prime)

T_i = 970 K (observed) $\Delta S_i° = 1.576 \pm 1.93$ J/(mol·K)

$\Delta H_i° = 1.528 \pm 0.61$ kJ/mol

Inversion:

Ca_2SiO_4(Ca-olivine) = Ca_2SiO_4(alpha prime)

T_i = 1120 K (observed) $\Delta S_i° = 12.231 \pm 2.51$ J/(mol·K)

$\Delta H_i° = 13.699 \pm 2.46$ kJ/mol

Inversion:

Ca_2SiO_4(alpha prime) = Ca_2SiO_4(alpha)

T_i = 1710 K (observed) $\Delta S_i° = 8.415 \pm 2.49$ J/(mol·K)

$\Delta H_i° = 14.390 \pm 3.387$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of Ca_2SiO_4 (alpha prime).

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Coughlin and O'Brien (1957)	relative enthalpy	drop calorimetry	12	974 - 1690 K

The relative enthalpy measurements of Coughlin and O'Brien (1957) were fit with a standard error of estimate of 274 J/(mol·K) or approximately 0.14 percent of the observed value.

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) Third Law, kJ	$\Delta H_f°$(298.15 K) kJ/mol
Benz and Wagner (1961)	Emf	A	971-1143	10	-5.517±0.379	-2198.122
Carlson (1931)	phase equilibria	B	1523	1	11.669±0.145	-2197.975

a Reactions:

A) 1/2 CaO(lime) + 1/2 $Ca_3Si_2O_7$(rankinite) = Ca_2SO_4(alpha prime)

B) Ca_2SiO_4(alpha prime) + CaO(lime) = Ca_3SiO_5

Phase-equilibrium studies were evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. The temperatures of the experimentally observed polymorphic transitions of larnite to alpha prime-Ca_2SiO_4, Ca-olivine to alpha prime-Ca_2SiO_4, and alpha prime-Ca_2SiO_4 to alpha-Ca_2SiO_4 were entered as fixed values in the regression and supply additional constraints on the free energy of alpha prime-Ca_2SiO_4 and its polymorphs. These inversion temperatures are listed as "observed" in the section on critical reactions.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each reaction. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for alpha prime-Ca_2SiO_4 (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -2198.074±7.537 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of alpha prime-Ca_2SiO_4 and presents the data in their poorest perspective.

The molar volume measured at 1023 K was taken from the work of Douglas (1952).

Ca_2SiO_4

Ca Olivine (gamma Ca_2SiO_4, orthorhombic, polymorphous with Bredigite and Larnite)

Ca_2O_4Si

Issued Sept[illegible]

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	Formation from the Elements: $\Delta G^\circ_{f,e}$ J/mol	Formation from the Elements: log $K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\Delta G^\circ_{f,ox}$ J/mol	Formation from the Oxides: log $K^\circ_{f,ox}$
273.15	120.737	109.706	-120.989	-3082.	-2316400.	-2209561.	422.535	-135573.	-136420.	26.088
298.15	125.690	120.499	-120.499	0.	-2316534.	-2199776.	385.391	-135648.	-136494.	23.913
(2 sigma)	±0.387	±2.045	±2.045	±0.	±2441.	±1881.	±0.330	±2441.	±1881.	±0.330
300.	126.025	121.278	-120.502	233.	-2316540.	-2199051.	382.889	-135654.	-136500.	23.767
350.	133.898	141.321	-122.067	6739.	-2316581.	-2179463.	325.267	-135859.	-136625.	20.390
400.	140.297	159.630	-125.634	13598.	-2316413.	-2159884.	282.052	-136118.	-136718.	17.853
450.	145.851	176.432	-130.360	20755.	-2316096.	-2140336.	248.444	-136412.	-136775.	15.876
500.	150.846	192.112	-135.763	28174.	-2315667.	-2120829.	221.561	-136721.	-136799.	14.291
(2 sigma)	±0.500	±2.055	±2.046	±78.	±2448.	±1522.	±0.159	±2448.	±1522.	±0.159
550.	155.417	206.706	-141.556	35833.	-2315156.	-2101369.	199.571	-137032.	-136792.	12.991
600.	159.629	220.413	-147.562	43710.	-2314586.	-2081959.	181.251	-137335.	-136756.	11.906
650.	163.510	233.315	-153.668	51790.	-2313981.	-2062598.	165.752	-137625.	-136696.	10.985
700.	167.074	245.595	-159.801	60056.	-2313360.	-2043284.	152.472	-137900.	-136614.	10.194
750.	170.322	257.234	-165.912	68492.	-2314415.	-2023941.	140.960	-138164.	-136513.	9.508
(2 sigma)	±0.411	±2.073	±2.048	±176.	±2460.	±1124.	±0.078	±2460.	±1124.	±0.078
800.	173.251	268.322	-171.968	77083.	-2313607.	-2004603.	130.887	-138421.	-136395.	8.906
850.	175.859	278.905	-177.950	85812.	-2312911.	-1985313.	122.002	-139393.	-136255.	8.373
900.	178.138	289.023	-183.842	94663.	-2312342.	-1966059.	114.107	-139233.	-136075.	7.898
950.	180.084	298.708	-189.634	103620.	-2311912.	-1946834.	107.044	-139026.	-135905.	7.473
1000.	181.690	307.937	-195.322	112666.	-2311636.	-1927627.	100.689	-138735.	-135747.	7.091
(2 sigma)	±1.356	±2.064	±2.052	±150.	±2453.	±860.	±0.045	±2453.	±860.	±0.045
1050.	182.952	316.834	-200.900	121783.	-2311529.	-1908430.	94.939	-138526.	-135601.	6.746
1100.	183.864	325.417	-206.367	130955.	-2311606.	-1889233.	89.712	-138254.	-135468.	6.433
1150.	184.422	333.604	-211.723	140164.	-2327625.	-1869469.	84.914	-138016.	-135347.	6.148
(2 sigma)	±2.879	±2.064	±2.052	±321.	±2455.	±826.	±0.038	±2455.	±826.	±0.038

Ca_2O_4Si

Ca_2SiO_4, gamma | Calcium Olivine | Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 120.499±2.045$ J/(mol·K) | $\Delta H_f° = -2316.534±2.441$ kJ/mol

$V° = 59.110±0.360$ cm^3/mol | $\Delta G_f° = -2199.776±1.881$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1150 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5\ \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = -2.360066\times10^6$ | $a_4 = 2.391441\times10^2$ | $a_6 = 1.065862\times10^{-1}$

$a_2 = 7.387180\times10^4$ | $a_5 = 0.0$ | $a_7 = -8.150119\times10^{-5}$

$a_3 = 1.656378\times10^3$

Critical Reactions

Inversion:

Ca_2SiO_4(Ca-olivine) = Ca_2SiO_4(alpha prime)

T_i = 1120 K (observed) | $\Delta S_i° = 12.231±2.51$ J/(mol·K)

$\Delta H_i° = 13.699±2.46$ kJ/mol

Primary Experimental Data Used in the Analysis

Table 1 provides the sources for the primary data used in evaluating the thermodynamic properties of Ca-olivine.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King (1957)	heat capacity	isothermal calorimetry	10	206 - 296 K
Coughlin and O'Brien (1957)	relative enthalpy	drop calorimetry	18	405 - 1113 K
King (1957)	entropy	isothermal calorimetry	1	298.15 K

The heat-capacity values of King (1957) were fit with a standard error of estimate of 0.56 J/(mol·K). The relative enthalpy measurements of Coughlin and O'Brien (1957) were fit with a standard error of estimate of 232 J/mol or approximately 0.93 percent of the observed value. The fitted entropy at 298.15 K is 120.499 ± 2.045 J/(mol·K), or a departure of 0.001 from the experimental value of 120.50 ± 0.84 reported by King (1957).

The temperatures of the experimentally observed inversion of Ca-olivine to alpha prime-Ca_2SiO_4 was entered as a fixed value in the regression and supplies a constraint on the free energy of Ca-olivine and its polymorphs. This inversion temperature is listed as "observed" in the section on critical reactions.

The molar volume of Ca olivine was obtained from the compilation of Robie and others (1967).

Ca_2SiO_4

Larnite (beta Ca_2SiO_4, monoclinic, polymorphous with Ca Olivine and Bredigite)

Ca_2O_4Si

Issued September [illegible]

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	Formation from the Elements: $\Delta G^\circ_{f,e}$ J/mol	Formation from the Elements: $\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\Delta G^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\log K^\circ_{f,ox}$
273.15	122.972	115.710	-127.219	-3144.	-2306625.	-2201426.	420.980	-125798.	-128285.	24.532
298.15	128.401	126.719	-126.719	0.	-2306697.	-2191794.	383.993	-125811.	-128512.	22.515
(2 sigma)	±0.238	±1.286	±1.286	±0.	±1328.	±1039.	±0.182	±1328.	±1039.	±0.182
300.	128.775	127.514	-126.721	238.	-2306699.	-2191081.	381.501	-125813.	-128529.	22.379
350.	137.745	148.065	-128.324	6910.	-2306574.	-2171816.	324.126	-125852.	-128979.	19.249
400.	144.975	166.946	-131.988	13984.	-2306191.	-2152589.	281.099	-125897.	-129422.	16.901
450.	150.963	184.378	-136.853	21386.	-2305628.	-2133421.	247.641	-125944.	-129860.	15.074
500.	156.030	200.553	-142.424	29065.	-2304940.	-2114323.	220.882	-125995.	-130293.	13.612
(2 sigma)	±0.464	±1.283	±1.284	±68.	±1333.	±883.	±0.092	±1333.	±883.	±0.092
550.	160.388	215.634	-148.402	36978.	-2304174.	-2095298.	198.995	-126050.	-130720.	12.415
600.	164.190	229.756	-154.599	45094.	-2303366.	-2076344.	180.762	-126114.	-131142.	11.417
650.	167.544	243.033	-160.896	53389.	-2302545.	-2057459.	165.339	-126189.	-131558.	10.572
700.	170.532	255.561	-167.215	61842.	-2301736.	-2038637.	152.125	-126277.	-131967.	9.848
750.	173.216	267.420	-173.503	70437.	-2302633.	-2019798.	140.671	-126382.	-132370.	9.219
(2 sigma)	±0.665	±1.311	±1.281	±209.	±1355.	±764.	±0.053	±1355.	±764.	±0.053
800.	175.645	278.677	-179.728	79160.	-2301693.	-2000974.	130.650	-126507.	-132765.	8.669
850.	177.856	289.393	-185.866	87998.	-2300888.	-1982204.	121.811	-127370.	-133147.	8.182
900.	179.879	299.617	-191.904	96942.	-2300226.	-1963478.	113.957	-127118.	-133494.	7.748
950.	181.741	309.393	-197.832	105983.	-2299712.	-1944785.	106.932	-126826.	-133856.	7.360
1000.	183.462	318.760	-203.646	115114.	-2299351.	-1926114.	100.610	-126500.	-134234.	7.012
(2 sigma)	±0.791	±1.370	±1.285	±390.	±1403.	±773.	±0.040	±1403.	±773.	±0.040

Ca_2O_4Si

Ca_2SiO_4, beta — Larnite — Formula weight = 132.163 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 126.719 \pm 1.286$ J/(mol·K) $\Delta H_f° = -2306.697 \pm 1.328$ kJ/mol

$V° = 51.600 \pm 0.540$ cm^3/mol $\Delta G_f° = -2191.794 \pm 1.039$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1000 K)

$$C_p°(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 0.0$ $a_4 = -1.538485\times10^3$ $a_6 = 0.0$

$a_2 = -2.120900\times10^3$ $a_5 = 2.496890\times10^2$ $a_7 = 0.0$

$a_3 = -2.094286\times10^3$

Critical Reactions

Inversion:

Ca_2SiO_4(larnite) = Ca_2SiO_4(alpha prime)

T_i = 970 K (observed) $\Delta S_i° = 1.576 \pm 1.93$ J/(mol·K)

$\Delta H_i° = 1.528 \pm 0.61$ kJ/mol

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of larnite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Todd (1951)	heat capacity	isothermal calorimetry	10	206 - 296 K
Coughlin and O'Brien (1957)	relative enthalpy	drop calorimetry	10	406 - 965 K
Hemingway and Robie (1977)	entropy		1	298.15 K

The heat capacity measured by Todd (1951) was fit with a standard error of estimate of 0.13 J/(mol·K). The relative enthalpy measurements of Coughlin and O'Brien (1957) were fit with a standard error of estimate of 102 J/mol or approximately 0.16 percent of the observed value. The fitted entropy at 298.15 K is 126.719 ± 1.286 J/(mol·K) which agrees with the experimental value of 126.7 ± 0.8 J/(mol·K) reported by Hemingway and Robie (1977).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	$\Delta H_r°$(298.15 K) kJ	$\Delta H_f°$(298.15 K) kJ/mol
Brunauer and others (1956)[b]	solution calorimetry ($HF-HNO_3$)	A	296.15	1	-8.637±0.831	-2306.681
King (1951)[c]	solution calorimetry (HF)[c]	B	346.85	6	126.069±1.971	-2306.954
Benz and Wagner (1961)	Emf	C	943-963	3	-2.678±0.088	-2312.720

a Reactions:

A) Ca_3SiO_5 = Ca_2SiO_4(larnite) + CaO(lime)

B) Ca_2SiO_4(larnite) = SiO_2(quartz, alpha) + 2 CaO(lime)

C) 1/2 CaO(lime) + 1/2 $Ca_3Si_2O_7$(rankinite) = Ca_2SiO_4(larnite)

b Brunauer and others (1956) measured the difference in the heat of solution of Ca_3SiO_5 and a 1:1 molar mixture of larnite and lime.

c King (1951) measured the heat of solution of larnite in HF acid at 346.85 K. To complete the thermodynamic cycle, his data were evaluated in combination with the more recent data for the enthalpies of solution of lime (Barany, 1963) and of quartz (Hemingway and Robie, 1977; Bennington and others, 1978) in similar solutions.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for larnite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -2306.697±1.320 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of larnite and presents the data in their poorest perspective.

The temperatures of well-defined experimentally observed polymorphic transitions were entered as fixed values in the regression and supply additional constraints on the free energy of larnite and its polymorphs. These inversion temperatures are listed as "observed" in the section on critical reactions.

The molar volume of larnite was obtained from the compilation of Robie and others (1967).

Ca_3SiO_5
(crystal)

Ca_3O_5Si

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	Formation from the Elements: $\Delta G^\circ_{f,e}$ J/mol	Formation from the Elements: $\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\Delta G^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\log K^\circ_{f,ox}$
273.15	164.410	153.834	-169.268	-4202.	-2933125.	-2799938.	535.434	-117167.	-120665.	23.075
298.15	171.604	168.600	-168.600	0.	-2933137.	-2787747.	488.401	-117157.	-120985.	21.196
(2 sigma)	±0.858	±0.311	±0.311	±0.	±1700.	±1699.	±0.298	±1700.	±1699.	±0.298
300.	172.099	169.653	-168.603	318.	-2933132.	-2786845.	485.232	-117157.	-121009.	21.070
350.	183.906	197.115	-170.744	9230.	-2932784.	-2762485.	412.278	-117131.	-121653.	18.156
400.	193.347	222.310	-175.637	18669.	-2932088.	-2738201.	357.572	-117087.	-122302.	15.971
450.	201.110	245.546	-182.131	28537.	-2931152.	-2714019.	315.035	-117024.	-122957.	14.273
500.	207.630	267.032	-189.562	38760.	-2930059.	-2689951.	281.017	-116945.	-123621.	12.915
(2 sigma)	±3.398	±1.120	±0.352	±456.	±1956.	±1662.	±0.174	±1956.	±1662.	±0.174
550.	213.200	287.139	-197.532	49284.	-2928875.	-2665997.	253.195	-116854.	-124293.	11.804
600.	218.023	305.901	-205.789	60067.	-2927651.	-2642153.	230.020	-116755.	-124973.	10.880
650.	222.248	323.523	-214.175	71076.	-2926429.	-2618411.	210.418	-116654.	-125662.	10.098
700.	225.983	340.133	-222.584	82284.	-2925247.	-2594762.	193.623	-116556.	-126359.	9.429
750.	229.313	355.839	-230.949	93668.	-2926642.	-2571085.	179.066	-116465.	-127062.	8.849
(2 sigma)	±2.885	±2.341	±0.762	±1230.	±2641.	±1494.	±0.104	±2641.	±1494.	±0.104
800.	232.301	370.736	-239.224	105209.	-2925300.	-2547427.	166.330	-116385.	-127771.	8.343
850.	235.000	384.902	-247.380	116893.	-2924178.	-2523845.	155.097	-117039.	-128480.	7.895
900.	237.451	398.404	-255.398	128705.	-2923286.	-2500323.	145.115	-116571.	-129166.	7.497
950.	239.686	411.303	-263.267	140635.	-2922633.	-2476844.	136.186	-116061.	-129879.	7.141
1000.	241.733	423.650	-270.980	152671.	-2922226.	-2453393.	128.152	-115515.	-130621.	6.823
(2 sigma)	±6.077	±2.573	±1.167	±1574.	±3111.	±1343.	±0.070	±3111.	±1343.	±0.070
1050.	243.614	435.491	-278.533	154805.	-2922070.	-2429956.	120.884	-114938.	-131390.	6.536
1100.	245.349	446.854	-285.928	177030.	-2922172.	-2406521.	114.276	-114336.	-132188.	6.277
1150.	246.955	457.806	-293.165	139338.	-2946150.	-2382234.	108.204	-113713.	-133013.	6.042
1200.	248.444	468.348	-300.246	201723.	-2943950.	-2357763.	102.631	-113075.	-133866.	5.827
1250.	249.828	478.519	-307.174	214181.	-2941709.	-2333384.	97.507	-112425.	-134745.	5.631
(2 sigma)	±13.495	±2.928	±1.355	±2905.	±4069.	±1222.	±0.051	±4069.	±1222.	±0.051
1300.	251.118	488.343	-313.955	226705.	-2939429.	-2309096.	92.781	-111768.	-135651.	5.451
1350.	252.322	497.843	-320.590	239291.	-2937114.	-2284896.	88.408	-111107.	-136582.	5.285
1400.	253.449	507.040	-327.086	251936.	-2934764.	-2260783.	84.351	-110447.	-137538.	5.132
1450.	254.504	515.952	-333.446	264635.	-2932383.	-2236754.	80.577	-109790.	-138517.	4.990
1500.	255.495	524.597	-339.674	277385.	-2929971.	-2212808.	77.057	-109141.	-139519.	4.858
(2 sigma)	±22.484	±5.096	±1.450	±6898.	±7440.	±1212.	±0.042	±7440.	±1212.	±0.042
1550.	256.425	532.990	-345.775	290183.	-2927531.	-2188943.	73.767	-108501.	-140542.	4.736
1600.	257.301	541.145	-351.754	303026.	-2925062.	-2165157.	70.685	-107875.	-141585.	4.622
1650.	258.126	549.076	-357.614	315912.	-2922566.	-2141448.	67.793	-107265.	-142648.	4.516
1700.	258.904	556.793	-363.359	328838.	-2970553.	-2117366.	65.059	-106675.	-143729.	4.416
1750.	259.638	564.309	-368.993	341802.	-2967863.	-2092311.	62.452	-106107.	-144828.	4.323
(2 sigma)	±32.378	±8.831	±1.803	±13515.	±13732.	±2231.	±0.067	±13732.	±2231.	±0.067
1800.	260.331	571.633	-374.521	354801.	-3423647.	-2055563.	59.651	-105563.	-145942.	4.235
(2 sigma)	±34.435	±9.712	±1.934	±15153.	±15328.	±2614.	±0.076	±15328.	±2614.	±0.076

Ca_3O_5Si

Ca_3SiO_5 (reference)

Ca_3SiO_5
(Hatrurite and others polymorphs, undifferentiated)[a]

Formula weight = 228.323 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 168.600 \pm 0.311$ J/(mol·K)

$\Delta H_f^\circ = -2933.13 \pm 1.700$ kJ/mol

$V° = 72.742$ cm^3/mol

$\Delta G_f^\circ = -2787.747 \pm 1.699$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = -6.525972\times10^{4}$ $a_4 = -2.053310\times10^{3}$ $a_6 = -2.325287\times10^{-3}$

$a_2 = -4.046000\times10^{3}$ $a_5 = 3.339197\times10^{2}$ $a_7 = 0.0$

$a_3 = -2.766085\times10^{3}$

Critical Reactions

Decomposition:

CaO(lime) + Ca_2SiO_4(alpha prime) = Ca_3SiO_5

T_d = 1522.75 K (calculated) $\Delta S_d^\circ = 7.114$ J/(mol·K)

$\Delta H_d^\circ = 10.834$ kJ/mol

a Data insufficient to evaluate properties of individual polymorphs. Equation constants and tabular data represent averaged properties of all polymorphs in temperature range of stability at 101.325 kPa.

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of Ca_3SiO_5.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
Todd (1951)	heat capacity	isothermal calorimetry	9	206 - 297 K
Gronow and Schwiete (1933)	relative enthalpy	drop calorimetry	12	576 - 1558 K
Todd (1951)	entropy	isothermal calorimetry	1	298.15 K

The heat-capacity values of Todd (1951) were fit with a standard error of estimate of 0.19 J/(mol·K). The relative enthalpy measurements of Gronow and Schwiete (1933) were fit with a standard error of estimate of 1021 J/mol or approximately 0.46 percent of the observed value. The fitted entropy value at 298.15 K is 168.600 ± 0.311 J/(mol·K) or a departure of 0.003 from the experimental value of 168.6 ± 1.25 reported by Todd (1951).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Brunauer and others (1956)[b]	solution calorimetry (HCl-HNO_3)	A	296.15	1	-8.637±0.831	-2933.153
Carlson (1931)	phase equilibria	B	1523	1	11.669±0.145	-2933.136

a Reactions:

A) Ca_3SiO_5 = Ca_2SiO_4(larnite) +CaO(lime)

B) Ca_2SiO_4(alpha prime) + CaO(lime) = Ca_3SiO_5

b Brunauer and others (1956) measured the difference in the heat of solution of Ca_3SiO_5 and a 1:1 molar mixture of larnite and lime.

The phase-equilibrium study of Carlson (1931) was evaluated after converting the data to free energies of reaction at 101.325 kPa and temperature. After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated and is shown in column 6 of Table 2. From this enthalpy of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for Ca_3SiO_5 (column 7 of Table 2) was calculated and can be compared with the enthalpy of formation of -2933.13±1.70 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of Ca_3SiO_5 and presents the data in their poorest perspective.

The molar volume was taken from the work of Yamaguchi and Miyabe (1960).

$Ca_3Si_2O_7$

Rankinite (monoclinic)

$Ca_3O_7Si_2$

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements $\Delta H^\circ_{f,e}$ J/mol	Formation from the Elements $\Delta G^\circ_{f,e}$ J/mol	Formation from the Elements $\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$ J/mol	Formation from the Oxides $\Delta G^\circ_{f,ox}$ J/mol	Formation from the Oxides $\log K^\circ_{f,ox}$
273.15	204.957	192.235	-211.434	-5244.	-3973011.	-3790325.	724.826	-246438.	-250177.	47.841
298.15	214.369	210.600	-210.600	0.	-3973202.	-3773595.	661.118	-246524.	-250513.	43.889
(2 sigma)	±0.714	±2.938	±2.938	±0.	±3200.	±2466.	±0.432	±3200.	±2466.	±0.432
300.	215.016	211.928	-210.604	397.	-3973210.	-3772357.	656.825	-246527.	-250537.	43.622
350.	230.408	246.277	-213.281	11549.	-3973134.	-3738880.	557.997	-246621.	-251199.	37.489
400.	242.564	277.868	-219.407	23384.	-3972631.	-3705446.	483.881	-246747.	-251845.	32.888
450.	252.365	307.024	-227.544	35766.	-3971835.	-3672093.	426.245	-246911.	-252472.	29.306
500.	260.390	334.042	-236.859	48591.	-3970851.	-3638840.	380.147	-247128.	-253079.	26.439
(2 sigma)	±1.088	±2.959	±2.937	±180.	±3224.	±2027.	±0.212	±3224.	±2027.	±0.212
550.	267.039	359.181	-246.850	61782.	-3969762.	-3605691.	342.440	-247411.	-253661.	24.091
600.	272.596	382.662	-257.200	75277.	-3968632.	-3572643.	311.026	-247773.	-254214.	22.131
650.	277.270	404.671	-267.706	89027.	-3967516.	-3539689.	284.453	-248223.	-254733.	20.471
700.	281.217	425.367	-278.236	102992.	-3966461.	-3506820.	261.682	-248774.	-255214.	19.044
750.	284.560	444.887	-288.702	117139.	-3968011.	-3473913.	241.945	-249435.	-255652.	17.805
(2 sigma)	±1.207	±3.038	±2.943	±452.	±3277.	±1607.	±0.112	±3277.	±1607.	±0.112
800.	287.391	463.345	-299.045	131439.	-3966857.	-3441012.	224.675	-250213.	-256041.	16.718
850.	289.785	480.841	-309.229	145870.	-3965965.	-3408175.	209.441	-252550.	-256368.	15.754
900.	291.805	497.464	-319.229	160412.	-3965349.	-3375383.	195.902	-252738.	-256587.	14.892
950.	293.498	513.288	-329.029	175045.	-3965020.	-3342618.	183.790	-252934.	-256796.	14.120
1000.	294.905	528.379	-338.622	189757.	-3964990.	-3309862.	172.889	-253147.	-256994.	13.424
(2 sigma)	±0.964	±3.117	±2.959	±697.	±3339.	±1474.	±0.077	±3339.	±1474.	±0.077
1050.	296.062	542.797	-348.004	204532.	-3965267.	-3277100.	163.027	-253390.	-257180.	12.794
1100.	296.995	556.592	-357.174	219359.	-3965859.	-3244317.	154.060	-253670.	-257354.	12.221
1150.	297.730	569.811	-366.134	234228.	-3990389.	-3210660.	145.833	-253997.	-257515.	11.697
1200.	298.287	582.494	-374.887	249129.	-3988804.	-3176793.	138.282	-254378.	-257660.	11.216
1250.	298.684	594.679	-383.436	264054.	-3987242.	-3142991.	131.338	-254822.	-257787.	10.772
(2 sigma)	±0.930	±3.157	±2.980	±844.	±3379.	±1725.	±0.072	±3379.	±1725.	±0.072
1300.	298.936	606.399	-391.788	278995.	-3985708.	-3109251.	124.931	-255333.	-257896.	10.362
1350.	299.057	617.684	-399.947	293945.	-3984205.	-3075570.	119.001	-255919.	-257984.	9.982
1400.	299.058	628.560	-407.918	308899.	-3982737.	-3041944.	113.496	-256586.	-258048.	9.628

$Ca_3Si_2O_7$ Rankinite Formula weight = 288.407 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 210.600 \pm 2.938$ J/(mol·K) $\Delta H_f^\circ = -3973.202 \pm 3.20$ kJ/mol

$V° = 96.506$ cm^3/mol $\Delta G_f^\circ = -3773.595 \pm 2.466$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1400 K)

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 3.397203\times10^5$ $a_4 = -2.971338\times10^3$ $a_6 = -2.103545\times10^{-2}$

$a_2 = 1.106750\times10^4$ $a_5 = 4.732091\times10^2$ $a_7 = 0.0$

$a_3 = -4.318802\times10^3$

Primary Experimental Data Used in the Analysis

Tables 1 and 2 provide the sources for the primary data used in evaluating the thermodynamic properties of rankinite.

Table 1. Sources for Heat Capacity, Relative Enthalpy, Entropy, and Related Data

Source	Data Type	Method	No. of Points	Range
King (1957)	heat capacity	isothermal calorimetry	10	206 - 296 K
Estimated values	heat capacity	component summation	12	400 - 1500 K
King (1957)	entropy	isothermal calorimetry	1	298.15 K

The heat capacity measured by King (1957) was fit with a standard error of estimate of 0.28 J/(mol·K). The estimated heat-capacity values were fit with a standard error of estimate of 5.33 J/(mol·K). The fitted entropy at 298.15 K is 210.600 ± 2.938 J/(mol·K), or a departure of 0.27 J/mol from the experimental value of 210.87 ± 1.26 reported by King (1957).

Table 2. Sources for the Enthalpy and Free Energy of Reaction and Related Data, and Enthalpies Calculated After Fitting

Source	Method	Reaction[a]	Range T/K	No. of Points	ΔH_r°(298.15 K) Third Law, kJ	ΔH_f°(298.15 K) kJ/mol
Benz and Wagner (1961)	Emf	A	943-963	3	-2.678±0.088	-3961.156
Benz and Wagner (1961)	Emf	B	971-1143	10	-5.517±0.379	-3973.106
Benz and Wagner (1961)	Emf	C	943-1003	10	-41.441±0.186	-3968.856

a Reactions:

A) 1/2 CaO(lime) + 1/2 $Ca_3Si_2O_7$(rankinite) = Ca_2SiO_4(larnite)

B) 1/2 CaO(lime) + 1/2 $Ca_3Si_2O_7$(rankinite) = Ca_2SiO_4(alpha prime)

C) 1/2 CaO(lime) + $CaSiO_3$(cyclowollastonite) = 1/2 $Ca_3Si_2O_7$(rankinite)

Phase-equilibrium studies of Benz and Wagner (1961) were evaluated after the data were converted to free energies of reaction at 101.325 kPa and temperature.

After fitting, as a test of consistency, the average enthalpy of reaction at 298.15 K and 101.325 kPa was calculated for each source. These enthalpies are shown in column 6 of Table 2. From these enthalpies of reaction and the calculated enthalpies of formation of other phases in the reactions, the enthalpy of formation for rankinite (column 7 of Table 2) was calculated for each source and can be compared with the enthalpy of formation of -3973.202±3.20 kJ/mol obtained from the fit. This calculation assigns the error of fit entirely to the heat of formation of rankinite and presents the data in their poorest perspective.

The molar volume was taken from the work of Saburi and others (1976).

H_2

Reference Table: Ideal diatomic gas 273.15 K to 1800 K

H_2

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	$\Delta G^\circ_{f,e}$ J/mol	$\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	$\Delta G^\circ_{f,ox}$ J/mol	$\log K^\circ_{f,ox}$
273.15	28.513	128.058	-130.683	-717.	0.	0.	0.	--	--	--
298.15	28.822	130.570	-130.570	0.	0.	0.	0.	--	--	--
300.	28.839	130.748	-130.570	53.	0.	0.	0.	--	--	--
350.	29.127	135.219	-130.923	1504.	0.	0.	0.	--	--	--
400.	29.221	139.116	-131.709	2963.	0.	0.	0.	--	--	--
450.	29.244	142.559	-132.727	4425.	0.	0.	0.	--	--	--
500.	29.250	145.641	-133.867	5887.	0.	0.	0.	--	--	--
550.	29.263	148.429	-135.066	7350.	0.	0.	0.	--	--	--
600.	29.293	150.977	-136.287	8814.	0.	0.	0.	--	--	--
650.	29.345	153.323	-137.509	10280.	0.	0.	0.	--	--	--
700.	29.417	155.500	-138.717	11748.	0.	0.	0.	--	--	--
750.	29.511	157.533	-139.904	13222.	0.	0.	0.	--	--	--
800.	29.623	159.441	-141.066	14700.	0.	0.	0.	--	--	--
850.	29.751	161.241	-142.201	16184.	0.	0.	0.	--	--	--
900.	29.895	162.945	-143.306	17675.	0.	0.	0.	--	--	--
950.	30.052	164.566	-144.383	19174.	0.	0.	0.	--	--	--
1000.	30.220	166.112	-145.431	20681.	0.	0.	0.	--	--	--
1050.	30.397	167.590	-146.451	22196.	0.	0.	0.	--	--	--
1100.	30.584	169.009	-147.445	23720.	0.	0.	0.	--	--	--
1150.	30.777	170.372	-148.412	25254.	0.	0.	0.	--	--	--
1200.	30.975	171.686	-149.354	26798.	0.	0.	0.	--	--	--
1250.	31.179	172.955	-150.273	28352.	0.	0.	0.	--	--	--
1300.	31.387	174.182	-151.169	29916.	0.	0.	0.	--	--	--
1350.	31.597	175.370	-152.044	31491.	0.	0.	0.	--	--	--
1400.	31.810	176.523	-152.898	33076.	0.	0.	0.	--	--	--
1450.	32.024	177.643	-153.732	34672.	0.	0.	0.	--	--	--
1500.	32.239	178.733	-154.547	36278.	0.	0.	0.	--	--	--
1550.	32.455	179.793	-155.344	37896.	0.	0.	0.	--	--	--
1600.	32.670	180.827	-156.125	39524.	0.	0.	0.	--	--	--
1650.	32.885	181.836	-156.888	41163.	0.	0.	0.	--	--	--
1700.	33.099	182.820	-157.637	42812.	0.	0.	0.	--	--	--
1750.	33.311	183.783	-158.370	44473.	0.	0.	0.	--	--	--
1800.	33.522	184.724	-159.089	46143.	0.	0.	0.	--	--	--

H_2, ideal gas | Hydrogen, ideal diatomic gas | Formula weight = 2.016 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 130.570$ J/(mol·K) $\Delta H^\circ_f = 0.0$ kJ/mol

$V° = 24789.200 \pm 3.4$ cm^3/mol $\Delta G^\circ_f = 0.0$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (temperature range 200 to 1800 K)

$$C^\circ_p(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = -5.1040600\times10^5$	$a_4 = 1.29375\times10^2$	$a_6 = 5.85357\times10^{-3}$
$a_2 = -1.8603165\times10^4$	$a_5 = 7.44240$	$a_7 = -1.38995\times10^{-6}$
$a_3 = 4.1016500\times10^2$		

Sources for Thermodynamic Properties

The thermodynamic properties for hydrogen were taken from the following sources:

Property	Source
Heat capacity	Hultgren and others (1973)
Entropy	CODATA Task Group (1978)

H_2O

Reference state: liquid 273.15 K to 373.15 K
ideal gas 373.15 K to 1800 K

H_2O

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Temperature (K)	C_p° J/(mol·K)	S° J/(mol·K)	$(G_T^\circ - H_{Tr}^\circ)/T$ J/(mol·K)	$H_T^\circ - H_{Tr}^\circ$ J/mol	Formation from the Elements $\Delta H_{f,e}^\circ$ J/mol	$\Delta G_{f,e}^\circ$ J/mol	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$ J/mol	$\Delta G_{f,ox}^\circ$ J/mol	$\log K_{f,ox}^\circ$
273.15	75.884	63.307	-70.218	-1888.	-286613.	-241274.	46.139	0.	0.	0.
298.15	75.254	69.921	-69.921	0.	-285808.	-237160.	41.549	0.	0.	0.
300.	75.230	70.386	-69.922	139.	-285749.	-236858.	41.241	0.	0.	0.
350.	75.469	81.981	-70.837	3900.	-284178.	-228834.	34.152	0.	0.	0.
373.15	76.003	86.831	-71.681	5653.	-283447.	-225197.	31.524	0.	0.	0.
373.15	34.048	196.318	-71.681	46509.	-242592.	-225197.	31.524	0.	0.	0.
400.	34.245	198.691	-80.127	47425.	-242865.	-223936.	29.243	0.	0.	0.
450.	34.669	202.748	-93.530	49148.	-243368.	-221539.	25.716	0.	0.	0.
500.	35.154	206.426	-104.639	50893.	-243861.	-219088.	22.888	0.	0.	0.
550.	35.686	209.801	-114.048	52664.	-244340.	-216587.	20.570	0.	0.	0.
600.	36.253	212.930	-122.159	54463.	-244804.	-214043.	18.634	0.	0.	0.
650.	36.846	215.855	-129.255	56290.	-245251.	-211462.	16.993	0.	0.	0.
700.	37.458	218.608	-135.540	58147.	-245681.	-208846.	15.584	0.	0.	0.
750.	38.082	221.213	-141.165	60036.	-246093.	-206201.	14.361	0.	0.	0.
800.	38.715	223.691	-146.247	61956.	-246488.	-203528.	13.289	0.	0.	0.
850.	39.352	226.057	-150.872	63907.	-246864.	-200832.	12.342	0.	0.	0.
900.	39.989	228.325	-155.113	65891.	-247224.	-198113.	11.498	0.	0.	0.
950.	40.624	230.504	-159.024	67906.	-247566.	-195375.	10.742	0.	0.	0.
1000.	41.254	232.604	-162.650	69953.	-247891.	-192620.	10.061	0.	0.	0.
1050.	41.878	234.632	-166.030	72032.	-248200.	-189849.	9.444	0.	0.	0.
1100.	42.494	236.594	-169.193	74141.	-248492.	-187063.	8.883	0.	0.	0.
1150.	43.100	238.496	-172.165	76281.	-248769.	-184265.	8.370	0.	0.	0.
1200.	43.695	240.343	-174.968	78451.	-249031.	-181455.	7.899	0.	0.	0.
1250.	44.278	242.139	-177.619	80650.	-249278.	-178634.	7.465	0.	0.	0.
1300.	44.848	243.887	-180.134	82878.	-249511.	-175803.	7.064	0.	0.	0.
1350.	45.404	245.590	-182.527	85135.	-249730.	-172964.	6.692	0.	0.	0.
1400.	45.945	247.251	-184.809	87418.	-249936.	-170117.	6.347	0.	0.	0.
1450.	46.472	248.872	-186.990	89729.	-250129.	-167263.	6.025	0.	0.	0.
1500.	46.982	250.456	-189.079	92065.	-250310.	-164403.	5.725	0.	0.	0.
1550.	47.477	252.005	-191.084	94427.	-250480.	-161536.	5.444	0.	0.	0.
1600.	47.954	253.520	-193.012	96813.	-250638.	-158665.	5.180	0.	0.	0.
1650.	48.415	255.003	-194.868	99222.	-250786.	-155788.	4.932	0.	0.	0.
1700.	48.858	256.455	-196.658	101654.	-250923.	-152907.	4.698	0.	0.	0.
1750.	49.283	257.877	-198.387	104108.	-251051.	-150023.	4.478	0.	0.	0.
1800.	49.689	259.271	-200.059	106582.	-251170.	-147134.	4.270	0.	0.	0.

H_2O

H_2O (reference state) | H_2O, water; H_2O, ideal gas | Formula weight = 18.015 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 69.921$ J/(mol·K) | $\Delta H_f^\circ = -285.808$ kJ/mol

$V° = 18.069 \pm 0.003$ cm^3/mol | $\Delta G_f^\circ = -237.160$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol \cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

H_2O, water (temperature range 200 to 373.15 K)

$a_1 = 6.6170441 \times 10^5$	$a_4 = -1.5130719 \times 10^3$	$a_6 = 3.0064551 \times 10^{-2}$
$a_2 = -1.1932000 \times 10^4$	$a_5 = 2.2085094 \times 10^2$	$a_7 = 0.0$
$a_3 = -2.6676397 \times 10^3$		

H_2O, ideal gas (temperature range 373.15 to 1800 K)

$a_1 = -1.310770 \times 10^5$	$a_4 = 1.55636 \times 10^2$	$a_6 = 1.29775 \times 10^{-2}$
$a_2 = -1.499822 \times 10^4$	$a_5 = 1.04381 \times 10^1$	$a_7 = -4.46885 \times 10^{-6}$
$a_3 = 2.99108 \times 10^2$		

Critical Reaction

Inversion:

H_2O, water = H_2O, ideal gas

$T_i = 373.15$ K (observed) | $\Delta S_i^\circ = 109.487$ J/(mol·K)

$\Delta H_i^\circ = 40.856$ kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for water and the ideal gas were taken from the following sources:

Property	Source
Heat capacity	Stull and Prophet (1971) and Chase and others (1974, 1975)
Entropy	CODATA Task Group (1978)
Enthalpy of formation from the elements	CODATA Task Group (1978)

H_2O
Ideal Gas

H_2O

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements $\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	Formation from the Oxides $\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	33.540	185.790	-188.864	-840.	-241592.	-229710.	43.927	0.	0.	0.
298.15	33.632	188.731	-188.731	0.	-241836.	-228611.	40.052	0.	0.	0.
300.	33.640	188.939	-188.732	62.	-241854.	-228529.	39.790	0.	0.	0.
350.	33.897	194.143	-189.142	1750.	-242357.	-226269.	33.769	0.	0.	0.
373.15	34.048	196.318	-189.520	2537.	-242592.	-225197.	31.524	0.	0.	0.
400.	34.245	198.691	-190.057	3453.	-242865.	-223936.	29.243	0.	0.	0.
450.	34.669	202.748	-191.246	5176.	-243368.	-221539.	25.716	0.	0.	0.
500.	35.154	206.426	-192.583	6921.	-243861.	-219088.	22.888	0.	0.	0.
550.	35.686	209.801	-193.997	8692.	-244340.	-216587.	20.570	0.	0.	0.
600.	36.253	212.930	-195.446	10491.	-244804.	-214043.	18.634	0.	0.	0.
650.	36.846	215.855	-196.904	12318.	-245251.	-211462.	16.993	0.	0.	0.
700.	37.458	218.608	-198.357	14175.	-245681.	-208846.	15.584	0.	0.	0.
750.	38.082	221.213	-199.795	16064.	-246093.	-206201.	14.361	0.	0.	0.
800.	38.715	223.691	-201.211	17984.	-246488.	-203528.	13.289	0.	0.	0.
850.	39.352	226.057	-202.604	19935.	-246864.	-200832.	12.342	0.	0.	0.
900.	39.989	228.325	-203.970	21919.	-247224.	-198113.	11.498	0.	0.	0.
950.	40.624	230.504	-205.310	23934.	-247566.	-195375.	10.742	0.	0.	0.
1000.	41.254	232.604	-206.622	25981.	-247891.	-192620.	10.061	0.	0.	0.
1050.	41.878	234.632	-207.908	28060.	-248200.	-189849.	9.444	0.	0.	0.
1100.	42.494	236.594	-209.168	30169.	-248492.	-187063.	8.883	0.	0.	0.
1150.	43.100	238.496	-210.402	32309.	-248769.	-184265.	8.370	0.	0.	0.
1200.	43.695	240.343	-211.611	34479.	-249031.	-181455.	7.899	0.	0.	0.
1250.	44.278	242.139	-212.796	36678.	-249278.	-178634.	7.465	0.	0.	0.
1300.	44.848	243.887	-213.959	38906.	-249511.	-175803.	7.064	0.	0.	0.
1350.	45.404	245.590	-215.099	41163.	-249730.	-172964.	6.692	0.	0.	0.
1400.	45.945	247.251	-216.217	43446.	-249936.	-170117.	6.347	0.	0.	0.
1450.	46.472	248.872	-217.316	45757.	-250129.	-167263.	6.025	0.	0.	0.
1500.	46.982	250.456	-218.394	48093.	-250310.	-164403.	5.725	0.	0.	0.
1550.	47.477	252.005	-219.453	50455.	-250480.	-161536.	5.444	0.	0.	0.
1600.	47.954	253.520	-220.494	52841.	-250638.	-158665.	5.180	0.	0.	0.
1650.	48.415	255.003	-221.518	55250.	-250786.	-155788.	4.932	0.	0.	0.
1700.	48.858	256.455	-222.524	57682.	-250923.	-152907.	4.698	0.	0.	0.
1750.	49.283	257.877	-223.514	60136.	-251051.	-150023.	4.478	0.	0.	0.
1800.	49.689	259.271	-224.488	62610.	-251170.	-147134.	4.270	0.	0.	0.

H_2O | H_2O, ideal gas | Formula weight = 18.015 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 188.731$ J/(mol·K) $\Delta H_f^\circ = -241.836$ kJ/mol

$V° = 24789.200 \pm 3.4$ cm^3/mol $\Delta G_f^\circ = -228.611$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (temperature range 200 to 1800 K)

$$C_p^\circ(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\ a_6\ T + a_7\ T^2$$

$$S^\circ(T)/[J/(mol \cdot K)] = -a_1/(2\ T^2) - 2\ a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\ a_6\ T + a_7\ T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\ a_3\ T^{0.5} + a_5\ T + a_6\ T^2 + a_7\ T^3/3$$

$a_1 = -1.310770 \times 10^5$ $a_4 = 1.55636 \times 10^2$ $a_6 = 1.29775 \times 10^{-2}$

$a_2 = -1.499812 \times 10^4$ $a_5 = 1.04381 \times 10^1$ $a_7 = -4.46885 \times 10^{-6}$

$a_3 = 2.99188 \times 10^2$

Critical Reaction

Inversion:

H_2O, water = H_2O, ideal gas

$T_i = 373.15$ K (observed) $\Delta S_i^\circ = 109.487$ J/(mol·K)

$\Delta H_i^\circ = 40.856$ kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for the ideal gas were taken from the following sources:

Property	Source
Heat capacity	Stull and Prophet (1971) and Chase and others (1974, 1975)
Entropy	CODATA Task Group (1978)
Enthalpy of formation from the elements	CODATA Task Group (1978)

O_2

Reference Table: Ideal diatomic gas 273.15 K to 1800 K

O_2

Issued September, 1979

Temperature	C°_p	S°	$(G^\circ_T-H^\circ_{Tr})/T$	$H^\circ_T-H^\circ_{Tr}$	Formation from the Elements			Formation from the Oxides		
					$\Delta H^\circ_{f,e}$	$\Delta G^\circ_{f,e}$	$\log K^\circ_{f,e}$	$\Delta H^\circ_{f,ox}$	$\Delta G^\circ_{f,ox}$	$\log K^\circ_{f,ox}$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	29.199	202.468	-205.148	-732.	0.	0.	0.	--	--	--
298.15	29.377	205.033	-205.033	0.	0.	0.	0.	--	--	--
300.	29.391	205.214	-205.033	54.	0.	0.	0.	--	--	--
350.	29.836	209.778	-205.393	1535.	0.	0.	0.	--	--	--
400.	30.320	213.793	-206.197	3039.	0.	0.	0.	--	--	--
450.	30.805	217.392	-207.244	4567.	0.	0.	0.	--	--	--
500.	31.274	220.662	-208.425	6119.	0.	0.	0.	--	--	--
550.	31.722	223.664	-209.676	7694.	0.	0.	0.	--	--	--
600.	32.145	226.443	-210.959	9291.	0.	0.	0.	--	--	--
650.	32.545	229.032	-212.250	10908.	0.	0.	0.	--	--	--
700.	32.921	231.457	-213.537	12545.	0.	0.	0.	--	--	--
750.	33.275	233.741	-214.808	14200.	0.	0.	0.	--	--	--
800.	33.607	235.899	-216.059	15872.	0.	0.	0.	--	--	--
850.	33.919	237.946	-217.287	17560.	0.	0.	0.	--	--	--
900.	34.212	239.893	-218.489	19263.	0.	0.	0.	--	--	--
950.	34.487	241.750	-219.665	20981.	0.	0.	0.	--	--	--
1000.	34.744	243.526	-220.814	22712.	0.	0.	0.	--	--	--
1050.	34.985	245.227	-221.936	24455.	0.	0.	0.	--	--	--
1100.	35.209	246.860	-223.032	26210.	0.	0.	0.	--	--	--
1150.	35.419	248.429	-224.103	27976.	0.	0.	0.	--	--	--
1200.	35.613	249.941	-225.148	29752.	0.	0.	0.	--	--	--
1250.	35.793	251.399	-226.169	31537.	0.	0.	0.	--	--	--
1300.	35.960	252.806	-227.167	33331.	0.	0.	0.	--	--	--
1350.	36.112	254.166	-228.142	35133.	0.	0.	0.	--	--	--
1400.	36.252	255.482	-229.095	36942.	0.	0.	0.	--	--	--
1450.	36.378	256.756	-230.027	38757.	0.	0.	0.	--	--	--
1500.	36.492	257.991	-230.938	40579.	0.	0.	0.	--	--	--
1550.	36.594	259.189	-231.830	42406.	0.	0.	0.	--	--	--
1600.	36.683	260.353	-232.704	44238.	0.	0.	0.	--	--	--
1650.	36.760	261.483	-233.559	46075.	0.	0.	0.	--	--	--
1700.	36.826	262.581	-234.396	47914.	0.	0.	0.	--	--	--
1750.	36.880	263.649	-235.217	49757.	0.	0.	0.	--	--	--
1800.	36.922	264.689	-236.021	51602.	0.	0.	0.	--	--	--

O_2

O_2, ideal gas — Oxygen, ideal diatomic gas — Formula weight = 31.999 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

$S° = 205.033$ J/(mol·K) — $\Delta H_f° = 0.0$ kJ/mol

$V° = 24789.200 \pm 3.4$ cm^3/mol — $\Delta G_f° = 0.0$ kJ/mol

Equations at Reference Pressure, 101.325 kPa (Temperature range 200 to 1800 K)

$$C_p°(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

$a_1 = 1.84663 \times 10^5$	$a_4 = -3.75052 \times 10^1$	$a_6 = 3.17977 \times 10^{-3}$
$a_2 = -6.32300 \times 10^3$	$a_5 = 3.54525 \times 10^1$	$a_7 = -1.85549 \times 10^{-6}$
$a_3 = -1.70675 \times 10^2$		

Sources for Thermodynamic Properties

The thermodynamic properties for oxygen were taken from the following sources:

Property	Source
Heat capacity	Hultgren and others (1973)
Entropy	CODATA Task Group (1978)

SiO_2

Quartz (below 844 K, trigonal; above 844 K, hexagonal)

O_2Si

Issued September, 1979

Temperature	C_p°	S°	$(G_T^\circ - H_{Tr}^\circ)/T$	$H_T^\circ - H_{Tr}^\circ$	Formation from the Elements $\Delta H_{f,e}^\circ$	$\Delta G_{f,e}^\circ$	$\log K_{f,e}^\circ$	Formation from the Oxides $\Delta H_{f,ox}^\circ$	$\Delta G_{f,ox}^\circ$	$\log K_{f,ox}^\circ$
(K)	J/(mol·K)	J/(mol·K)	J/(mol·K)	J/mol	J/mol	J/mol		J/mol	J/mol	
273.15	42.184	37.653	-41.633	-1087.	-910565.	-860875.	164.626	0.	0.	0.
298.15	44.748	41.460	-41.460	0.	-910699.	-856321.	150.024	0.	0.	0.
300.	44.928	41.737	-41.461	83.	-910707.	-855984.	149.040	0.	0.	0.
350.	49.357	49.005	-42.025	2443.	-910859.	-846849.	126.385	0.	0.	0.
400.	53.140	55.849	-43.329	5008.	-910884.	-837702.	109.393	0.	0.	0.
450.	56.463	62.304	-45.082	7750.	-910796.	-828559.	96.177	0.	0.	0.
500.	59.443	68.410	-47.113	10649.	-910608.	-819430.	85.605	0.	0.	0.
550.	62.160	74.204	-49.314	13690.	-910329.	-810325.	76.958	0.	0.	0.
600.	64.671	79.722	-51.620	16861.	-909963.	-801249.	69.755	0.	0.	0.
650.	67.015	84.992	-53.986	20154.	-909517.	-792207.	63.663	0.	0.	0.
700.	69.224	90.040	-56.382	23560.	-908995.	-783203.	58.443	0.	0.	0.
750.	71.320	94.888	-58.789	27074.	-908398.	-774238.	53.923	0.	0.	0.
800.	73.321	99.555	-61.192	30691.	-907730.	-765315.	49.970	0.	0.	0.
844.	75.015	103.526	-63.296	33954.	-907085.	-757500.	46.881	0.	0.	0.
844.	67.386	104.430	-63.296	34718.	-906322.	-757500.	46.881	0.	0.	0.
850.	67.446	104.908	-63.588	35122.	-906276.	-756442.	46.485	0.	0.	0.
900.	67.948	108.777	-65.992	38507.	-905895.	-747639.	43.392	0.	0.	0.
950.	68.450	112.464	-68.341	41917.	-905514.	-738858.	40.625	0.	0.	0.
1000.	68.952	115.988	-70.636	45352.	-905131.	-730096.	38.136	0.	0.	0.
1050.	69.454	119.365	-72.877	48812.	-904745.	-721354.	35.885	0.	0.	0.
1100.	69.956	122.607	-75.064	52297.	-904353.	-712630.	33.840	0.	0.	0.
1150.	70.459	125.728	-77.199	55808.	-903955.	-703924.	31.973	0.	0.	0.
1200.	70.961	128.737	-79.285	59343.	-903550.	-695236.	30.263	0.	0.	0.
1250.	71.463	131.644	-81.321	62904.	-903137.	-686565.	28.690	0.	0.	0.
1300.	71.965	134.457	-83.311	66490.	-902713.	-677910.	27.239	0.	0.	0.
1350.	72.467	137.182	-85.256	70100.	-902279.	-669272.	25.896	0.	0.	0.
1400.	72.969	139.827	-87.158	73736.	-901834.	-660650.	24.649	0.	0.	0.
1450.	73.471	142.396	-89.019	77397.	-901375.	-652044.	23.489	0.	0.	0.
1500.	73.973	144.895	-90.840	81083.	-900904.	-643455.	22.407	0.	0.	0.
1550.	74.475	147.329	-92.623	84795.	-900418.	-634881.	21.395	0.	0.	0.
1600.	74.977	149.702	-94.370	88531.	-899917.	-626323.	20.447	0.	0.	0.
1650.	75.479	152.016	-96.082	92292.	-899400.	-617782.	19.557	0.	0.	0.
1700.	75.981	154.277	-97.760	96079.	-949376.	-608806.	18.706	0.	0.	0.
1750.	76.483	156.487	-99.407	99890.	-948683.	-598799.	17.873	0.	0.	0.
1800.	76.986	158.649	-101.022	103727.	-947967.	-588813.	17.087	0.	0.	0.

O_2Si

SiO_2 (reference state) Quartz, alpha; Quartz, beta Formula weight = 60.085 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s) (quartz, alpha)

$S° = 41.460$ J/(mol·K) $\Delta H_f° = -910.699$ kJ/mol

$V° = 22.688 \pm 0.001$ cm^3/mol $\Delta G_f° = -856.321$ kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p°(T)/[J/(mol \cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2 a_6 T + a_7 T^2$$

$$S°(T)/[J/(mol \cdot K)] = -a_1/(2 T^2) - 2 a_3/T^{0.5} + a_4 + a_5 \ln(T) + 2 a_6 T + a_7 T^2/2$$

$$[H°(T)-H°(298.15K)]/(J/mol) = -a_1/T + a_2 + 2 a_3 T^{0.5} + a_5 T + a_6 T^2 + a_7 T^3/3$$

Quartz, alpha (temperature range 200 to 844 K)

$a_1 = 0.0$	$a_4 = -5.29232 \times 10^2$	$a_6 = 1.09962 \times 10^{-2}$
$a_2 = 1.05800 \times 10^3$	$a_5 = 8.32101 \times 10^1$	$a_7 = 0.0$
$a_3 = -7.77338 \times 10^2$		

Quartz, beta (temperature range 844 to 1800 K)

$a_1 = 0.0$	$a_4 = -3.00994 \times 10^2$	$a_6 = 5.0208 \times 10^{-3}$
$a_2 = -1.801085 \times 10^4$	$a_5 = 5.89107 \times 10^1$	$a_7 = 0.0$
$a_3 = 0.0$		

Critical Reaction

Inversion:

SiO_2(quartz, alpha) = SiO_2(quartz, beta)

$T_i = 844$ K $\Delta S_i° = 0.904$ J/(mol·K)

$\Delta H_i° = 0.764$ kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for quartz were taken from the following sources:

Property	Source
Heat capacity	Stull and Prophet (1971) and Chase and others (1974, 1975)
Entropy	CODATA Task Group (1978)
Enthalpy of formation from the elements	CODATA Task Group (1978)

The molar volume of quartz was obtained from the compilation of Robie and others (1967).

Si

Reference state: crystals 273.15 K to 1685 K
liquid 1685 K to 1800 K

Si

Issued September, 1979

Temperature (K)	C°_p J/(mol·K)	S° J/(mol·K)	$(G^\circ_T-H^\circ_{Tr})/T$ J/(mol·K)	$H^\circ_T-H^\circ_{Tr}$ J/mol	Formation from the Elements: $\Delta H^\circ_{f,e}$ J/mol	Formation from the Elements: $\Delta G^\circ_{f,e}$ J/mol	Formation from the Elements: $\log K^\circ_{f,e}$	Formation from the Oxides: $\Delta H^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\Delta G^\circ_{f,ox}$ J/mol	Formation from the Oxides: $\log K^\circ_{f,ox}$
273.15	19.154	17.097	-18.888	-489.	0.	0.	0.	--	--	--
298.15	19.946	18.810	-18.810	0.	0.	0.	0.	--	--	--
300.	19.999	18.934	-18.810	37.	0.	0.	0.	--	--	--
350.	21.222	22.113	-19.059	1069.	0.	0.	0.	--	--	--
400.	22.146	25.010	-19.624	2154.	0.	0.	0.	--	--	--
450.	22.875	27.662	-20.372	3280.	0.	0.	0.	--	--	--
500.	23.470	30.104	-21.225	4439.	0.	0.	0.	--	--	--
550.	23.970	32.365	-22.136	5626.	0.	0.	0.	--	--	--
600.	24.398	34.469	-23.077	6835.	0.	0.	0.	--	--	--
650.	24.771	36.437	-24.030	8065.	0.	0.	0.	--	--	--
700.	25.100	38.285	-24.983	9312.	0.	0.	0.	--	--	--
750.	25.394	40.027	-25.928	10574.	0.	0.	0.	--	--	--
800.	25.659	41.675	-26.861	11851.	0.	0.	0.	--	--	--
850.	25.901	43.238	-27.779	13140.	0.	0.	0.	--	--	--
900.	26.122	44.724	-28.680	14440.	0.	0.	0.	--	--	--
950.	26.327	46.142	-29.562	15752.	0.	0.	0.	--	--	--
1000.	26.517	47.498	-30.425	17073.	0.	0.	0.	--	--	--
1050.	26.693	48.796	-31.269	18403.	0.	0.	0.	--	--	--
1100.	26.859	50.041	-32.094	19742.	0.	0.	0.	--	--	--
1150.	27.015	51.239	-32.901	21089.	0.	0.	0.	--	--	--
1200.	27.162	52.392	-33.689	22443.	0.	0.	0.	--	--	--
1250.	27.302	53.503	-34.459	23805.	0.	0.	0.	--	--	--
1300.	27.435	54.577	-35.213	25173.	0.	0.	0.	--	--	--
1350.	27.561	55.614	-35.949	26548.	0.	0.	0.	--	--	--
1400.	27.682	56.619	-36.669	27929.	0.	0.	0.	--	--	--
1450.	27.797	57.592	-37.374	29316.	0.	0.	0.	--	--	--
1500.	27.908	58.537	-38.064	30709.	0.	0.	0.	--	--	--
1550.	28.015	59.454	-38.739	32107.	0.	0.	0.	--	--	--
1600.	28.118	60.345	-39.401	33510.	0.	0.	0.	--	--	--
1650.	28.217	61.211	-40.048	34919.	0.	0.	0.	--	--	--
1685.	28.285	61.804	-40.494	35908.	0.	0.	0.	--	--	--
1685.	25.522	91.805	-40.494	86459.	0.	0.	0.	--	--	--
1700.	25.522	92.031	-40.948	86841.	0.	0.	0.	--	--	--
1750.	25.522	92.771	-42.418	88117.	0.	0.	0.	--	--	--
1800.	25.522	93.490	-43.827	89394.	0.	0.	0.	--	--	--

Si (reference state) — Silicon, crystal; Silicon, liquid — Formula weight = 28.086 g/mol

Summary of Critical Data

Data at Reference Temperature, 298.15 K (±2s)

S° = 18.810 J/(mol·K) — ΔH_f° = 0.0 kJ/mol

V° = 12.056±0.002 cm^3/mol — ΔG_f° = 0.0 kJ/mol

Equations at Reference Pressure, 101.325 kPa

$$C_p^\circ(T)/[J/(mol\cdot K)] = a_1/T^2 + a_3/T^{0.5} + a_5 + 2\,a_6\,T + a_7\,T^2$$

$$S^\circ(T)/[J/(mol\cdot K)] = -a_1/(2\,T^2) - 2\,a_3/T^{0.5} + a_4 + a_5\ln(T) + 2\,a_6\,T + a_7\,T^2/2$$

$$[H^\circ(T)-H^\circ(298.15K)]/(J/mol) = -a_1/T + a_2 + 2\,a_3\,T^{0.5} + a_5\,T + a_6\,T^2 + a_7\,T^3/3$$

Silicon, crystal (temperature range 200 to 1685 K)

$a_1 = -4.48020\times10^5$	$a_4 = -4.82356\times10^2$	$a_6 = 2.81373\times10^{-4}$
$a_2 = -3.83500\times10^3$	$a_5 = 3.17050\times10^1$	$a_7 = 0.0$
$a_3 = -1.77189\times10^2$		

Silicon, liquid (temperature range 1685 to 1800 K)

$a_1 = 0.0$	$a_4 = -9.78143\times10^1$	$a_6 = 0.0$
$a_2 = -7.610\times10^3$	$a_5 = 2.55224\times10^1$	$a_7 = 0.0$
$a_3 = 0.0$		

Critical Reaction

Melting:

Si(silicon, crystal) = Si(silicon, liquid)

T_m = 1685 K — ΔS_m° = 30.001 J/(mol·K)

ΔH_m° = 50.551 kJ/mol

Sources for Thermodynamic Properties

The thermodynamic properties for silicon were taken from the following sources:

Property	Source
Heat capacity	Hultgren and others (1973)
Entropy	CODATA Task Group (1978)
Enthalpy of melting	Hultgren and others (1973)