

Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures

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*A summary of the thermodynamic data for minerals
at 298.15 K together with calculated values for
the functions $C_{P,T}^\circ$, $\Delta H_{f,T}^\circ$, $\Delta G_{f,T}^\circ$, S_T° , $(H_T^\circ - H_{298}^\circ)/T$,
and $(G_T^\circ - H_{298}^\circ)/T$ at temperatures up to 1,800 K*



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THERMODYNAMIC PROPERTIES OF MINERALS AND RELATED SUBSTANCES AT 298.15 K AND 1 BAR (10^5 PASCALS) PRESSURE AND AT HIGHER TEMPERATURES

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ABSTRACT

Selected values for the entropy (S°), molar volume (v°), and for the enthalpy and Gibbs free energy of formation (ΔH_f° , and ΔG_f°) are given for the elements, 133 oxides, and 212 other minerals and related substances at 298.15 K. For those materials for which high-temperature heat-capacity or heat-content data are also available ($(H_T^\circ - H_{298}^\circ)/T$, S_T° , $(G_T^\circ - H_{298}^\circ)/T$, C_p° , $\Delta H_{f,T}^\circ$, $\Delta G_{f,T}^\circ$ and $\log K_{f,T}$ are tabulated at 100 K intervals for temperatures up to 1,800 K. For substances that have solid-state phase changes or whose melting or boiling point is less than 1,800 K, we have also tabulated the properties listed above at the temperature of the phase change so that the enthalpy or entropy changes associated with the transformation form an integral part of the high-temperature tables.

INTRODUCTION

The purpose of these tables of thermodynamic properties is to present a critical summary of the available thermodynamic data for minerals and related substances in a convenient form for the use of earth scientists. To make the tables as useful as possible, we have tried (1) to include enough auxiliary data so that a single set of tables would suffice for most calculations, (2) to insure internal consistency, and (3) to provide the means for rapid revision and expansion as new data become available.

This compilation is divided into two sections. In the first section, we give values for the entropy (S_{298}°), molar volume (v_{298}°), the enthalpy of formation ($\Delta H_{f,298}^\circ$) and Gibbs free energy of formation ($\Delta G_{f,298}^\circ$), and the logarithm of the equilibrium constant of formation ($\log K_{f,298}$) for the reference elements, minerals, several oxides, and other substances of geological interest, where the subscript 298 implies 298.15 K. The tables in the second section contain values for the thermodynamic properties at 100 K intervals for temperatures up to 1,800 K. The data are arranged in order of their conventional mineralogical groups. Within each group (for example, the oxides), the listing is by alphabetical order of the chemical symbol of the principal cation.

The data have been taken from recent critical evaluations or have been evaluated by the present authors, and uncertainties have been assigned to the 298.15 K properties. The sources of data are indicated numerically

in the tables and listed in complete form following the tables. These tables entirely supersede those of an earlier report on the same subject matter by Robie and Waldbaum (1968).

The true differential heat capacity, C_p° , is rarely measured at temperatures above 400 K because of the ease with which the heat content, $H_T^\circ - H_{298}^\circ$, may be determined. From the heat-content measurements, one may derive approximate values for C_p° at high temperatures by differentiation of the $H_T^\circ - H_{298}^\circ$ versus temperature curve. Because many users find it more convenient to use analytical expressions for heat capacities rather than tabulated values, we have also provided equations for the heat capacities at high temperatures.

In order to derive values of C_p° from the experimental heat-content measurements, the measured values of $H_T^\circ - H_{298}^\circ$ were fitted to polynomials having six or fewer terms, and constrained so that at 298.15 K, $H_T^\circ - H_{298}^\circ$ was identically equal to 0 and that the first derivative of the fitted equation at 298.15 K had to equal the value of the heat capacity obtained by low-temperature calorimetry. This procedure forces the values of C_p° derived from the *heat-content* measurements to join smoothly with the more accurate directly measured values of C_p° determined by low-temperature calorimetry.

The least-squares fitting was done by computer, using either the program HINC written by D. W. Osborne of Argonne National Laboratory (D. W. Osborne, written com., 1975) or PHAS20 (Haas and Fisher, 1976). The equation used to fit the heat-content data was that suggested by Haas and Fisher (1976).

$$H_T^\circ - H_{298}^\circ = A + BT + CT^2 + D/T + ET^{1/2} + FT^3$$

The first four terms of this equation are those used by Kelley (1960). For most phases, only four or five terms have been used. In fitting the data, we have followed a general rule that the number of experimental points should be approximately three times the number of constants used in the equation. The tabulated values of the heat capacity, C_p° , at temperatures above 400 K were obtained by differentiation of the heat-content equation. The derived C_p° equation, and its range of validity, is listed at the bottom of each high-temperature table.

Thermodynamic properties of gases at high pressures have not been included in these tables. High pressure-high temperature functions of the most geologically important gases, H_2O and CO_2 , have been given by Bain (1964), Hilsenrath and others (1955), Robie (1966), and Burnham and others (1969).

PHYSICAL CONSTANTS AND ATOMIC WEIGHTS

The symbols and constants used in these tables are listed in table 1. The units adopted for reporting the thermodynamic properties are those of the International System of Units (SI) (Page and Vigoureux, 1972).

TABLE 1.—*Symbols, constants, and conversion factors*

T	Temperature in kelvins.
K	Kelvin, the unit of temperature. It is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
J	Joule, the unit of energy (or work). One joule = 1/4.1840 thermochemical calories or 10 cm ³ •bar.
mol	Amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilograms of carbon 12. It is identical with the gfw (gram formula weight).
P	Pressure in bars. One bar = 10 ⁵ pascals or 0.1 MPa. The standard atmosphere is equal to 101325 pascals. The kilogram•cm ⁻² is equal to 98065.5 pascals.
°	Superscript indicates that the substance is in its standard state, 1 bar (10 ⁵ pascals) for a condensed phase.
H _T [°] - H ₂₉₈ [°]	Enthalpy at temperature T relative to 298.15 K in J•mol ⁻¹ , also called the heat content.
(H _T [°] - H ₂₉₈ [°])/T	Enthalpy function in J•mol ⁻¹ •K ⁻¹ .
S _T [°]	Entropy at temperature T, in J•mol ⁻¹ •K ⁻¹ .
(G _T [°] - H ₂₉₈ [°])/T	Gibbs energy function in J•mol ⁻¹ •K ⁻¹ .
C _P [°]	Heat capacity at constant pressure in J•mol ⁻¹ •K ⁻¹ .
V ₂₉₈ [°]	Volume of 1 mol of a substance at 1 bar pressure and at 298.15 K, in cm ³ , or J•bar ⁻¹ .
ΔH _m [°]	Enthalpy of melting at 1 bar pressure in J•mol ⁻¹ .
ΔH _b [°]	Enthalpy of vaporization to the ideal gas at 1 bar pressure at the normal boiling point in J•mol ⁻¹ .
ΔH _f [°]	Enthalpy of formation from the elements in their standard reference states in J•mol ⁻¹ .
ΔG _f [°]	Gibbs free energy of formation from the elements in their reference states in J•mol ⁻¹ .
K _f	Equilibrium constant of formation.
R	Gas constant, 8.3143 ± 0.0008 J•K ⁻¹ •mol ⁻¹ .
F	Faraday constant, 96,487.0 ± 1.0 J•V ⁻¹ •mol ⁻¹ .
A	Avogadro's number, (6.022094 ± 0.000008) × 10 ²³ mol ⁻¹ .
log	Common logarithm, base 10.
ln	Natural logarithm, base e = 2.71828 . . .
V	Volt.

Values for the gas constant (R) and the Faraday constant (F) used in the calculations are those adopted by the CODATA Task Group (1976), although their values differ slightly from the most recent least-squares evaluation of the physical constants by Cohen and Taylor (1973). For Avogadro's number (used in calculating molar volumes from X-ray cell dimensions), we have used the value of Deslattes and others (1974) 6.022094 ± 0.000008 × 10²³ mol⁻¹.

For convenience, we also give values for the atomic weights for 1975 (scale C¹² = 12.000) (Commission on Atomic Weights, 1976) in alphabetical order by their chemical symbol in table 2.

REFERENCE STATES AND TRANSITIONS

The reference states for ΔH_f[°], ΔG_f[°], and log K_f of the compounds are the elements in their standard states at 1 bar pressure (10⁵ pascals) and the

THERMODYNAMIC PROPERTIES OF MINERALS

TABLE 2.—Atomic weights for 1975

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Actinium	Ac	227.0278	Sodium	Na	22.98977
Silver	Ag	107.868	Niobium	Nb	92.9064
Aluminum	Al	26.98154	Neodymium	Nd	144.24
Americium	Am	(243)	Neon	Ne	20.179
Argon	Ar	39.948	Nickel	Ni	58.70
Arsenic	As	74.9216	Neptunium	Np	237.0482
Astatine	At	(210)	Oxygen	O	15.9994
Gold	Au	196.9665	Osmium	Os	190.2
Boron	B	10.81	Phosphorus	P	30.97376
Barium	Ba	137.33	Protactinium	Pa	231.0359
Beryllium	Be	9.01218	Lead	Pb	207.2
Bismuth	Bi	208.9804	Palladium	Pd	106.4
Bromine	Br	79.904	Polonium	Po	(209)
Carbon	C	12.011	Promethium	Pm	(145)
Calcium	Ca	40.08	Praseodymium	Pr	140.9077
Cadmium	Cd	112.41	Platinum	Pt	195.09
Cerium	Ce	140.12	Plutonium	Pu	(244)
Chlorine	Cl	35.453	Radium	Ra	226.0254
Cobalt	Co	58.9332	Rubidium	Rb	85.4678
Chromium	Cr	51.996	Rhenium	Re	186.207
Cesium	Cs	132.9054	Rhodium	Rh	102.9055
Copper	Cu	63.546	Radon	Rn	(222)
Dysprosium	Dy	162.50	Ruthenium	Ru	101.07
Erbium	Er	167.26	Sulfur	S	32.06
Europium	Eu	151.96	Antimony	Sb	121.75
Fluorine	F	18.9984	Scandium	Sc	44.9559
Iron	Fe	55.847	Selenium	Se	78.96
Francium	Fr	(223)	Silicon	Si	28.0855
Gallium	Ga	69.72	Samarium	Sm	150.4
Gadolinium	Gd	157.25	Tin	Sn	118.69
Germanium	Ge	72.59	Strontium	Sr	87.62
Hydrogen	H	1.0079	Tantalum	Ta	180.9479
Helium	He	4.0026	Terbium	Tb	158.9254
Hafnium	Hf	178.49	Technetium	Tc	(97)
Mercury	Hg	200.59	Tellurium	Te	127.60
Holmium	Ho	164.9304	Thorium	Th	232.0381
Iodine	I	126.9045	Titanium	Ti	47.90
Indium	In	114.82	Thallium	Tl	204.37
Iridium	Ir	192.22	Thulium	Tm	168.9342
Potassium	K	39.0983	Uranium	U	238.029
Krypton	Kr	83.80	Vanadium	V	50.9414
Lanthanum	La	138.9055	Tungsten	W	183.85
Lithium	Li	6.941	Xenon	Xe	131.30
Lutetium	Lu	174.97	Yttrium	Y	88.9059
Magnesium	Mg	24.305	Ytterbium	Yb	173.04
Manganese	Mn	54.9380	Zinc	Zn	65.38
Molybdenum	Mo	95.94	Zirconium	Zr	91.22
Nitrogen	N	14.0067			

stated temperature. The standard states for the condensed elements are the most stable form at 1 bar pressure and the stated temperature. For gaseous elements, the standard state is the ideal gas at 1 bar pressure. The reference pressure for the standard state adopted for these tables is the bar, that is, 10^5 pascals. The reasons for this choice are:

- In most modern high-pressure—high-temperature equilibrium studies on minerals, the pressure is measured in bars.
- The use of the bar as the standard pressure in conjunction with the joule for energy (or work) simplifies conversion of the Pv term ($\text{cm}^3 \cdot \text{bar}$) in high-pressure calculations of mineral equilibria. Thus, $1 \text{ joule} = 10.0 \text{ cm}^3 \cdot \text{bar}$ in contrast with $1 \text{ calorie} = 41.2929 \text{ cm}^3 \cdot \text{atm}$ in terms of older (non-SI) units.
- The *standard atmosphere* used as the reference pressure for most thermochemical measurements, with the frequent exception of the PvT properties of gases, is an arbitrarily adopted unit. In terms of the SI base unit of pressure, the *standard atmosphere* is equal to 101325 pascals.
- The effect of the change of reference pressure from 1 atmosphere, as used in an earlier edition of these tables (Robie and Waldbaum, 1968), to the present choice of 1 bar has an insignificant effect upon the tabulated values of the thermodynamic functions for the condensed phases and only a minor and constant effect for the gas phases.

All data listed in these tables have been corrected to the standard state $P=1$ bar. For a condensed phase (liquid or solid), it can be readily shown that the effect of changing the reference state from 1 atmosphere to 1 bar has only a trivial effect upon all the thermodynamic properties tabulated in this report *except* for ΔG_f° .

For a gaseous phase, the reference state is the ideal gas, that is, one that obeys the equation of state $Pv=RT$. From the equation of state, it follows that:

$$v=RT/P$$

from which

$$(\partial v/\partial T)_P=R/P, \text{ and } (\partial^2 v/\partial T^2)_P=0,$$

Then from standard thermodynamic relations

$$(\partial C_P/\partial P)_T=T(\partial^2 v/\partial T^2)_P=0$$

and

$$(\partial S/\partial P)_T=-(\partial v/\partial T)_P=-R/P$$

from which

$$dS=-(R/P)dP$$

For the change in pressure from $P=1$ atm (1.0135 bar) to 1.000 bar

$$\Delta S = -R \int_{1.013}^{1.000} (1/P)dP = 0.11 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Also, for an ideal gas,

$$dH = TdS + vdP = T(-R/P) dP + (RT/P)dP = 0.$$

Thus, for a gaseous phase, C_p° , $(H_T^\circ - H_{298}^\circ)/T$, and ΔH_f° are independent of pressure, but the numerical values of S° , ΔG_f° , and $(G_T^\circ - H_{298}^\circ)/T$ depend upon the choice of pressure. Similarly it can be shown that the change of the standard state from a pressure of 1 atmosphere to 1 bar does not affect the enthalpy of formation (from the elements in their reference states) but will cause a change in the Gibbs free energy of formation of a condensed phase if and only if one of the reference elements (usually oxygen) is a gas.

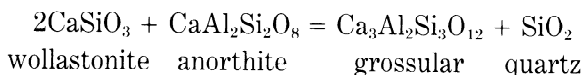
The entropies of the gaseous elements and compounds were converted to the standard state $P=1$ bar, using the above relations, before entering the various thermodynamic data into the data bank. Inasmuch as the computer program calculates $\Delta G_{f,T}^\circ$ from ΔH_f° and the entropies or Gibbs energy functions of the constituent elements, the values of $\Delta G_{f,T}^\circ$ are automatically corrected to the 1 bar standard state.

The National Bureau of Standards Technical Note 270 series, the JANAF thermochemical tables, and the CODATA tables have retained the use of the *standard atmosphere* as the reference pressure. The authors hope that in the near future the General Conference of Weights and Measures of the International Bureau of Weights and Measures will recommend the elimination of the standard atmosphere as the reference pressure.

Data are listed for the elements in their standard reference states, and for a few in nonstandard states; for example, S_2 gas and the diamond form of carbon. Melting and boiling points and their associated enthalpy changes are listed at the bottom of each table of high-temperature properties. A horizontal dashed line in the tables indicates a transition in the phase. A dashed line in the columns ΔH_f° , ΔG_f° , and $\log K_f$, indicates a transition in one of the reference elements. Transitions in the reference elements are also listed separately at the bottom of each table. Inasmuch as most of the high-temperature "heat-capacity" data are actually heat-content measurements and not true heat capacities (C_p°), we have followed the practice of Kelley (1960) and have treated all the high-temperature transitions as first order at a single temperature. At the transition temperature, the functions $(H_T^\circ - H_{298}^\circ)/T$, S_T° , and $\Delta H_{f,T}^\circ$ make a stepwise change; $\Delta G_{f,T}^\circ$ and $(G_T^\circ - H_{298}^\circ)/T$, are continuous, but their temperature derivatives change abruptly. For those elements (and their compounds) for which we have, of necessity, adopted a nonequilibrium phase as the reference state (for example, S_2 gas above 716.9 K), there will also be a discontinuity in both $\Delta G_{f,T}^\circ$ and $(G_T^\circ - H_{298}^\circ)/T$ at the transition temperature. These properties of the functions must be borne in mind when interpolating in the tables.

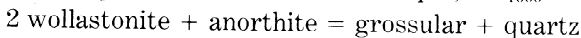
The reference state adopted for an element above its normal boiling or sublimation temperature is not necessarily its equilibrium state. Thus, at equilibrium, liquid sulfur boils at 1 bar pressure and approximately 716.9 K to a gas composed of S, S₂, S₄, S₆, S₈, etc., but for our reference table, we have assumed the gas phase to be only S₂. In these ambiguous cases, we have chosen either the dominant species in the gas or that species for which the best thermodynamic data are available as the reference state.

Enthalpies and Gibbs free energies of formation for multiple-oxide phases using the *binary oxides* as reference states have also been computed and tabulated, inasmuch as many mineralogical equilibria involve only binary or multiple-oxide phases; for example:



and because the enthalpies of formation of most multiple-oxide phases are determined using the binary oxides as the reactants. Tables of the thermodynamic functions for temperatures above 298.15 K for multiple-oxide phases calculated using the *binary oxides* as the reference phases immediately follow the appropriate table calculated from the elements and are differentiated by the heading "FORMATION FROM THE OXIDES" above the columns for ΔH_f° , ΔG_f° , and $\log K_f$ and by asterisks immediately to the right of the entries for ΔH_f° and ΔG_f° .

When using the binary oxides as the reference states, one must remember that in this convention, ΔH_f° and ΔG_f° for these reference oxides are zero at all temperatures. For example, ΔG_{1000}° for the reaction



may be calculated from either the tabulated values of $\Delta G_{f,1000}^\circ$ (elements as reference states), or ΔG_{1000}° (oxides as reference states) for each of the phases in the above reaction. Thus:

$$\Delta G_{1000}^\circ (\text{oxides}) = \{[-304.53 + 0] - [-136.25 + 2(-91.18)]\} = 14.08 \text{ kJ}$$

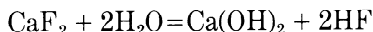
or

$$\Delta G_{1000}^\circ (\text{elements}) = \{[-5448.79 + (-729.98)] - [-3488.51 + 2(-1352.17)]\} \\ = 14.08 \text{ kJ}$$

Both calculations must obviously give the same result within the rounding error. However, in estimating the uncertainty in the resulting value of ΔG_f° for a reaction involving only oxide phases, one should use the uncertainties associated with the ΔG_f° values calculated from the oxides, inasmuch as this value usually corresponds more closely to the actual calorimetric reaction scheme from which the individual ΔG_f° values were obtained.

The user is cautioned not to mix values of ΔG_f° calculated from the elements for one phase with those obtained from the oxides for another in calculating ΔG_f° of a reaction involving the two phases, because a mean-

ingless result ensues. If a reaction involves both multiple-oxide phases and nonoxide phases, as in



fluorite steam portlandite

ΔG°_T for the reaction must be calculated using *only* values from the tabulated values of $\Delta G^\circ_{T,T}$ calculated from the elements.

SOURCES OF DATA

Many critical evaluations of thermochemical data have been particularly helpful in constructing these tables. For the thermodynamic functions of the elements at high temperatures, we have adopted the values selected by Hultgren and others (1973). The CODATA (1976) key values have been adopted when they differed significantly from those of Hultgren and others (1973). For the sulfides, arsenides, tellurides, selenides, and sulfosalts, the summaries by Mills (1974) and by Barton and Skinner (1977) have been very helpful. The tabulations by Kelley (1960) and by Kelley and King (1961) were particularly useful as a source of the pre-1960 heat-content and heat-capacity data. We have also relied heavily upon the critical evaluations of the National Bureau of Standards Technical Note 270 series (Wagman and others, 1968, 1969, 1971; Parker and others, 1971; Schumm and others, 1973) and of the JANAF thermochemical tables (Stull and Prophet, 1971; Chase and others, 1974, 1975).

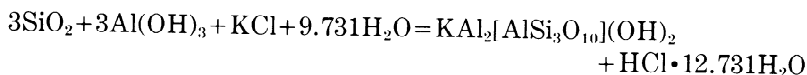
In evaluating the data for the silicates, we have accepted the revised values for ΔH°_f for those silicates given by Hemingway and Robie (1977), which include corrections for the effect of the particle size of quartz and for the incorrect value of ΔH°_f of gibbsite ($\text{Al}(\text{OH})_3$) used in earlier HF solution calorimetry studies. For those aluminum silicates for which definitive structural evidence of Al/Si disorder was available we have corrected the S°_{298} values for the configurational terms, that is, $S^\circ_0 \neq 0$, arising from frozen-in Al/Si disorder at 0 K, using the summary of Ulbrich and Waldbaum (1976) as a guide. We have also added a correction to the entropy of several manganese and iron compounds for which the accepted value of S°_{298} was based upon measurements of the heat capacity only above 50 K and for which other evidence indicated the existence of an unextracted magnetic contribution to S°_{298} below 50 K (see, for example, Robie, 1965, or Ulbrich and Waldbaum, 1976).

Values for the thermodynamic properties at 298.15 K for the more common aqueous ions are also listed in order to facilitate calculations of aqueous equilibria. The reference state for the free energies of the aqueous ions is the hypothetical ideal solution of unit molality. Values for ΔG°_f are listed on the basis of the usual convention that ΔG°_f , ΔH°_f , S° , and C_p° are identically 0 for aqueous H^+ ion in the hypothetical 1 molal ideal solution. A more complete discussion of the conventions adopted for

tabulating the thermodynamic properties of aqueous ions has been given by F. D. Rossini (1950, *Chemical thermodynamics*: New York, John Wiley, p. 320–370).

The molar volumes of the condensed phases are principally from the summary by Robie and others (1967), augmented by more recent precise X-ray measurements of unit-cell parameters. Although our principal sources of data for ΔH_f° , or ΔG_f° , have been solution or combustion calorimetry, for many compounds the best available data are values of ΔG_f° , calculated from solubilities, electrochemical cells, reduction equilibria, or decomposition pressure data; we have used these equilibrium studies to supplement the calorimetric data whenever possible. For the simpler gases, the thermodynamic constants calculated from spectroscopic data are usually the most precise.

In order to insure internal consistency in these tables and because of the complex nature of many of the reaction schemes used to obtain ΔH_f° , or ΔG_f° , we have corrected all the older data to the values adopted here. For multiple-oxide compounds, the heats of formation are most commonly measured utilizing the binary oxides as reference phases. However, stoichiometric K_2O cannot be prepared reproducibly, and FeO is thermodynamically unstable. Furthermore, $\alpha-Al_2O_3$, corundum, is insoluble in all common aqueous calorimetric solvents. Consequently, mixed sets of reactants such as the alkali halides, aluminum hydroxide (gibbsite), or an element have frequently been used as the reference phases in HF solution calorimetry for determining ΔH_f° of aluminosilicates. For example, Barany (1964) measured the enthalpy change for the reaction



and by utilizing literature data for the enthalpies of formation of the other phases, he calculated $\Delta H_{f,298}^\circ$ for muscovite. Accordingly, any improvement of ΔH_f° of quartz, gibbsite, sylvite, or aqueous HCl would alter the enthalpy of formation of muscovite. Recent measurements of $\Delta H_{f,298}^\circ$ of gibbsite by Hemingway and Robie (1977) have shown that the value of $\Delta H_{f,298}^\circ$ of gibbsite used by Barany (1964) to calculate the enthalpy of formation of muscovite was in error by $11230 \text{ J} \cdot \text{mol}^{-1}$, and accordingly we have corrected Barany's (1964) calorimetric value for $\Delta H_{f,298}^\circ$ of muscovite, and also several other aluminosilicates for which gibbsite was one of the reactants, to accord with this new $\Delta H_{f,298}^\circ$ of gibbsite.

METHODS OF CALCULATION

Having chosen what we believe are the currently "best available" values for $H_T^\circ - H_{298}^\circ$, or $C_p^\circ(T)$, S_{298}° , and either $\Delta H_{f,298}^\circ$ or $\Delta G_{f,298}^\circ$, we have calculated the Gibbs free energy function, and the enthalpy, free energy, and the equilibrium constant of formation at 100 K intervals using the following relations:

$$(G_T^\circ - H_{298}^\circ)/T = (H_T^\circ - H_{298}^\circ)/T - S_T^\circ \quad (1)$$

$$\Delta H_{f,T}^\circ = \Delta H_{f,298}^\circ + \Delta(H_T^\circ - H_{298}^\circ) \quad (2)$$

$$\Delta G_{f,T}^\circ = \Delta H_{f,298}^\circ + T\Delta[(G_T^\circ - H_{298}^\circ)/T] \quad (3)$$

and

$$\log K_{f,T} = -\Delta G_{f,T}^\circ/2.30258 RT = -\Delta G_{f,298}^\circ/19.1444T \quad (4)$$

These values together with C_p° , S_T° and $(H_T^\circ - H_{298}^\circ)/T$ are tabulated in the second section.

A Fortran IV program was used for the above calculations. The essential feature of the program is that internally consistent thermodynamic functions can be calculated for several hundred compounds in a single run of the computer. This consistency is accomplished by first calculating the thermodynamic functions for the reference elements and oxides and then holding these data in storage for later computations involving substances having these elements or oxides as reference phases. As new thermodynamic data become available, only a minimum number of changes in the data base are needed to prepare a completely revised set of internally consistent tables.

The input data supplied to the computer are the identifying name of the substance, the entropy, the enthalpy, and Gibbs free energy of formation at 298.15 K and their uncertainties, and the entropy and enthalpy increments, $S_T^\circ - S_{298}^\circ$ and $H_T^\circ - H_{298}^\circ$, at 100 K intervals, together with the number of atoms of each element in the chemical formula. Auxiliary data such as the melting and boiling points and enthalpies of melting and vaporization are also included. The program computes the formula weight of the compound on the basis of the atomic weights of the elements (1975 scale) and values for S_T° , $\Delta H_{f,T}^\circ$, $\Delta G_{f,T}^\circ$, $\log K_{f,T}$, C_p° , $(H_T^\circ - H_{298}^\circ)/T$, and $(G_T^\circ - H_{298}^\circ)/T$ at 100 K intervals up to 1,800 K.

Although the absolute value of $\Delta G_{f,T}^\circ$ or $\Delta H_{f,T}^\circ$ of the more complex compounds is rarely known more accurately than $\pm 1,000$ joules, these quantities are tabulated to the nearest 10 joules. This procedure is justified because the temperature derivatives of ΔG_f° , and ΔH_f° ,

$$(d\Delta G_f^\circ/dT)_p = -\Delta S_f^\circ \quad (5)$$

and

$$(d\Delta H_f^\circ/dT)_p = \Delta C_p^\circ \quad (6)$$

are calculated from the heat-content data, which are known independently of the enthalpy or Gibbs free energy of formation. The practice of rounding tabulated values of ΔG_f° or ΔH_f° on the basis of the uncertainty in the absolute value does not utilize the full accuracy of the heat-capacity information and destroys the necessary internal consistency between $\Delta H_{f,298}^\circ$ and the Gibbs free-energy function (eq. 3). Furthermore, in many instances, the *differences* between ΔH_f° or ΔG_f° for polymorphs are often known more accurately from phase-equilibria or calorimetric investigations than are the individual ΔH_f° or ΔG_f° values for a phase, so that

rounding off again tends to obscure small differences of major importance in calculations of geological interest.

The uncertainties assigned to the properties apply only to the values at 298.15 K and were taken principally from the original sources of experimental data. By convention, the uncertainty interval reported for calorimetric measurements is twice the standard deviation of the mean (Rossini, 1956, p. 319); that is,

$$\delta = 2[\sum (x_i - \bar{x})^2/n(n-1)]^{1/2} \quad (7)$$

where x_i is the value for an individual measurement, \bar{x} is the arithmetic mean of all the measurements, and n is the number of observations.

For substances where $\Delta H_{f,298}^\circ$ is the directly measured quantity, the free energy was calculated from

$$\Delta G_{f,298}^\circ = \Delta H_{f,298}^\circ - 298.15 \Delta S_{f,298}^\circ \quad (8)$$

and the uncertainty in the free energy was calculated from

$$\sigma_G = [(\sigma_H)^2 + (298\sigma_S)^2 + \sum (298n_i\sigma_{S_i})^2]^{1/2} \quad (9)$$

where σ_S is the uncertainty in the entropy of the substance, the σ_{S_i} are the uncertainties in the entropies of the i reference elements, and the n_i are the number of moles of each element in the chemical formula of the substance. Uncertainties derived in this manner were rounded upward to the nearest 10 joules.

For substances in which σ_G is less than σ_H , the basic quantities used in the calculation were $\Delta G_{f,298}^\circ$ and σ_G derived from electrochemical cell measurements, solubilities, or phase-equilibrium data. Hence, $\Delta H_{f,298}^\circ$ is a more indirectly derived quantity having a larger uncertainty. For these substances, σ_H was calculated from

$$\sigma_H = [(\sigma_G)^2 + (298\sigma_S)^2 + \sum (298n_i\sigma_{S_i})^2]^{1/2} \quad (10)$$

Camera-ready copy of the tables of the thermodynamic properties, and of the bibliography, were prepared from the output file (tape) of the FORTRAN IV program, using the WYLBUR text editor and the extended print facility at the Computer Center of the National Institutes of Health.

Several of the tables in the second section are incomplete because of the lack of adequate data on the enthalpies of formation or entropies at 298.15 K of these substances. The tables are nonetheless included, so that when such data become available, one may readily calculate the remaining functions using equations 2, 3, and 4 given above, or use equilibrium data and the third-law method to obtain the standard state enthalpy or Gibbs free energy change for the reaction (ΔH_r° , or ΔG_r°), following the procedures illustrated, for example, by Robie (1965).

HALITE

FORMULA WEIGHT 58.443

NaCl: Crystals 298.15 to melting point 1073.8 K. Liquid 1073.8 to fictive boiling point 1791 K.

TEMP.	$(H_T^o - H_{298}^o)/T$	S_T^o	$-(G_T^o - H_{298}^o)/T$	C_P^o	FORMATION FROM THE ELEMENTS		
					ENTHALPY	FREE ENERGY	Log K_f
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	72.12	72.12	50.51	-411.260	-384.212	67.313
UNCERTAINTY		0.21	0.21		0.110	0.110	0.019
400	13.100	87.22	74.12	52.34	-413.461	-374.837	48.949
500	21.124	99.09	77.97	54.14	-413.024	-365.229	38.155
600	26.775	109.12	82.34	55.94	-412.352	-355.730	30.969
700	31.070	117.88	86.81	57.73	-411.456	-346.356	25.846
800	34.515	125.71	91.20	59.53	-410.352	-337.136	22.013
900	37.389	132.82	95.43	61.33	-409.064	-328.064	19.040
1000	39.877	139.37	99.49	63.12	-407.593	-319.133	16.670
1073.80	41.702	144.11	102.41	64.45	-380.693	-313.098	15.231
1073.80	67.925	170.33	102.41	68.55	-352.535	-313.098	15.231
1100	67.934	171.89	103.96	68.46	-377.527	-310.967	14.767
1200	67.964	177.83	109.87	68.14	-472.918	-302.951	13.187
1300	67.965	183.27	115.30	67.82	-470.082	-288.905	11.608
1400	67.943	188.29	120.35	67.50	-467.285	-275.089	10.264
1500	67.903	192.93	125.03	67.17	-464.521	-261.445	9.104
1600	67.847	197.26	129.41	66.85	-461.794	-248.002	8.096
1700	67.779	201.30	133.52	66.53	-459.103	-234.720	7.212

MELTING POINT	1073.8 K	BOILING POINT	1791 K
ENTHALPY OF MELTING	28.158 kJ	ENTHALPY OF VAPORIZATION	164.787 kJ
$H_{298}^o - H_0^o$	10.611 kJ	MOLAR VOLUME	2.7015 J/bar 27.015 cm ³

TRANSITIONS IN REFERENCE STATE ELEMENTS

SODIUM..... M. P. 370.98, B. P. 1175 K.

HEAT CAPACITY EQUATIONS

$$C_P^o = 45.151 + 1.7974 \times 10^{-2} T$$

(EQUATION VALID FROM 298 - 1073.8 K)

$$C_P^o = 72.008 - 3.2228 \times 10^{-3} T$$

(EQUATION VALID FROM 1073.8 - 1791 K)

SODIUM (REFERENCE STATE)

FORMULA WEIGHT 22.990

Na: Body-centered cubic crystals 298.15 to melting point 370.98 K. Liquid 370.98 to fictive boiling point 1175 K. Ideal monatomic gas 1175 to 1800 K. The equilibrium boiling point of the real gas is 1154 K.

TEMP.	$(H_T^0 - H_{298}^0)/T$	S_T^0	$-(G_T^0 - H_{298}^0)/T$	C_p^0	FORMATION FROM THE ELEMENTS		
					ENTHALPY	GIBBS FREE ENERGY	Log K_f
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	51.30	51.30	28.23	0.000	0.000	0.000
UNCERTAINTY		0.02	0.02				
370.98	5.808	57.63	51.82	31.97	.000	.000	.000
370.98	12.811	64.63	51.82	31.84	.000	.000	.000
400	14.188	67.15	52.96	31.51	.000	.000	.000
500	17.554	74.07	56.52	30.55	.000	.000	.000
600	19.655	79.57	59.91	29.80	.000	.000	.000
700	21.063	84.13	63.07	29.27	.000	.000	.000
800	22.066	88.01	65.94	28.95	.000	.000	.000
900	22.823	91.41	68.59	28.84	.000	.000	.000
1000	23.428	94.45	71.02	28.94	.000	.000	.000
1100	23.943	97.23	73.29	29.26	.000	.000	.000
1175	24.295	99.15	74.85	29.65	.000	.000	.000
1175	107.367	182.22	74.85	20.79	.000	.000	.000
1200	105.564	182.66	77.10	20.79	.000	.000	.000
1300	99.043	184.32	85.28	20.79	.000	.000	.000
1400	93.453	185.86	92.41	20.79	.000	.000	.000
1500	88.609	187.30	98.69	20.79	.000	.000	.000
1600	84.370	188.64	104.27	20.79	.000	.000	.000
1700	80.630	189.90	109.27	20.90	.000	.000	.000
1800	77.306	191.09	113.78	20.79	.000	.000	.000

MELTING POINT	370.98 K	BOILING POINT	1175 K
ENTHALPY OF MELTING	2.598 kJ	ENTHALPY OF VAPORIZATION	97.610 kJ
$H_{298}^0 - H_0^0$	6.460 kJ	MOLAR VOLUME	2.3812 J/bar 23.812 cm ³

TRANSITIONS IN REFERENCE STATE ELEMENTS

HEAT CAPACITY EQUATION

$$C_p^0 = 37.482 - 1.9183 \times 10^{-2} T + 1.0644 \times 10^{-5} T^2$$

(EQUATION VALID FROM 370.98 - 1175 K)

REFERENCE 107 35

COMPILED
7-24-76

PROPERTIES AT HIGH TEMPERATURES

45

CHLORINE (REFERENCE STATE)

FORMULA WEIGHT 70.906

 Cl₂: Ideal diatomic gas 298.15 to 1800 K.

TEMP. K	$(H_T^0 - H_{298}^0)/T$ J/mol·K	S_T^0 J/mol·K	$-(G_T^0 - H_{298}^0)/T$ J/mol·K	C_P^0 J/mol·K	FORMATION FROM THE ELEMENTS GIBBS		
					ENTHALPY kJ/mol	FREE ENERGY kJ/mol	Log K _f
298.15	0.000	223.08	223.08	33.98	0.000	0.000	0.000
UNCERTAINTY		0.04	0.04				
400	8.830	233.26	224.43	35.26	.000	.000	.000
500	14.198	241.22	227.02	36.03	.000	.000	.000
600	17.882	247.84	229.96	36.54	.000	.000	.000
700	20.574	253.50	232.93	36.88	.000	.000	.000
800	22.629	258.44	235.81	37.13	.000	.000	.000
900	24.251	262.82	238.57	37.31	.000	.000	.000
1000	25.565	266.76	241.19	37.45	.000	.000	.000
1100	26.650	270.34	243.69	37.56	.000	.000	.000
1200	27.563	273.61	246.05	37.65	.000	.000	.000
1300	28.342	276.63	248.29	37.73	.000	.000	.000
1400	29.016	279.42	250.40	37.80	.000	.000	.000
1500	29.603	282.03	252.43	37.87	.000	.000	.000
1600	30.123	284.48	254.36	37.95	.000	.000	.000
1700	30.585	286.78	256.19	38.03	.000	.000	.000
1800	31.001	288.96	257.96	38.11	.000	.000	.000

MELTING POINT	172.16 K	BOILING POINT	239.10 K
ENTHALPY OF MELTING	6.406 kJ	ENTHALPY OF VAPORIZATION	20.410 kJ
$H_{298}^0 - H_0^0$	9.180 kJ	MOLAR VOLUME	2478.9200 J/bar 24789.200 cm ³
TRANSITIONS IN REFERENCE STATE ELEMENTS			

HEAT CAPACITY EQUATION

$$C_P^0 = 46.956 - 4.0158 \times 10^{-3} T + 9.9274 \times 10^{-7} T^2 - 2.0495 \times 10^{-9} T^3$$

(EQUATION VALID FROM 298 - 1800 K)

REFERENCE 107 35

 COMPILED
3-11-76

CORUNDUM

FORMULA WEIGHT 101.962

Al₂O₃: (Corundum), crystals 298.15 to melting point 2345 K.

TEMP. K	(H _T ^o -H ₂₉₈ ^o)/T J/mol·K	S _T ^o J/mol·K	-(G _T ^o -H ₂₉₈ ^o)/T J/mol·K	C _p ^o J/mol·K	FORMATION FROM THE ELEMENTS GIBBS		
					ENTHALPY kJ/mol	FREE ENERGY kJ/mol	Log K _f
298.15	0.000	50.92	50.92	79.01	-1675.700	-1582.228	277.201
UNCERTAINTY		0.10	0.10		1.300	1.320	0.231
400	22.575	76.85	54.27	96.39	-1676.304	-1550.162	202.431
500	38.372	99.47	61.10	105.95	-1675.984	-1518.654	158.653
600	50.187	119.38	69.19	112.19	-1675.264	-1487.257	129.478
700	59.377	137.02	77.64	116.65	-1674.404	-1455.990	108.648
800	66.756	152.83	86.07	120.04	-1673.565	-1424.841	93.033
900	72.833	167.13	94.30	122.73	-1672.865	-1393.793	80.894
1000	77.935	180.18	102.25	124.94	-1693.698	-1361.288	71.107
1100	82.294	192.17	109.88	126.79	-1692.719	-1328.080	63.066
1200	86.070	203.28	117.21	128.38	-1691.635	-1294.993	56.370
1300	89.378	213.61	124.23	129.77	-1690.457	-1261.964	50.707
1400	92.307	223.27	130.96	130.99	-1689.203	-1229.065	45.857
1500	94.924	232.34	137.42	132.08	-1687.872	-1196.232	41.657
1600	97.277	240.90	143.62	133.07	-1686.481	-1163.513	37.985
1700	99.409	249.00	149.59	133.96	-1685.029	-1130.906	34.749
1800	101.352	256.68	155.33	134.78	-1683.527	-1098.329	31.873

MELTING POINT	2345	K	BOILING POINT	K
ENTHALPY OF MELTING		kJ	ENTHALPY OF VAPORIZATION	kJ
H ₂₉₈ ^o - H ₀ ^o	10.016	kJ	MOLAR VOLUME	2.5575 J/bar 25.575 cm ³

TRANSITIONS IN REFERENCE STATE ELEMENTS

ALUMINUM... M. P. 933 K.

HEAT CAPACITY EQUATION

$$C_p^o = 1.5736 \times 10^{-2} + 7.1899 \times 10^{-4} T - 9.8804 \times 10^{-7} T^{-0.5} - 1.8969 \times 10^{-6} T^{-2}$$

(EQUATION VALID FROM 298 - 1900 K)

REFERENCE	285	50	35	COMPILED
	50	66	159	7-21-76

ANDALUSITE

FORMULA WEIGHT 162.047

 Al_2SiO_5 : Crystals 298.15 to 1800 K.

TEMP.	$(H_T^0 - H_{298}^0)/T$	S_T^0	$-(G_T^0 - H_{298}^0)/T$	C_p^0	FORMATION FROM THE ELEMENTS GIBBS		
					ENTHALPY	FREE ENERGY	Log K_f
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	93.22	93.22	122.70	-2587.525	-2439.892	427.458
UNCERTAINTY		0.42	0.42		2.100	2.100	0.368
400	34.900	133.31	98.41	148.98	-2588.377	-2389.267	312.005
500	59.384	168.35	108.97	164.49	-2587.831	-2339.541	244.409
600	77.800	199.29	121.49	174.61	-2586.609	-2289.984	199.360
700	92.157	226.77	134.61	181.61	-2585.102	-2240.674	167.201
800	103.675	251.37	147.69	186.74	-2583.546	-2191.567	143.094
900	113.133	273.60	160.47	190.73	-2582.100	-2142.649	124.356
1000	121.063	293.87	172.81	194.06	-2602.164	-2092.364	109.294
1100	127.835	312.51	184.67	197.05	-2600.393	-2041.471	96.941
1200	133.723	329.78	196.06	199.93	-2598.472	-1990.739	86.654
1300	138.928	345.90	206.97	202.86	-2596.362	-1940.168	77.957
1400	143.607	361.04	217.43	205.96	-2594.099	-1889.788	70.509
1500	147.871	375.36	227.49	209.33	-2591.597	-1839.555	64.059
1600	151.826	388.99	237.16	213.03	-2588.828	-1789.522	58.422

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H_{298}^0 - H_0^0$	17.096 kJ	MOLAR VOLUME	5.1530 J/bar 51.530 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

ALUMINUM... M. P. 933 K.

SILICON.... M. P. 1685 K.

HEAT CAPACITY EQUATION

$$C_p^0 = 4.0843 \times 10^2 - 0.11050 T + 3.5897 \times 10^{-5} T^2 - 4.4199 \times 10^{-8} T^3$$

(EQUATION VALID FROM 298 - 1600 K)

REFERENCE	205	120	285 267	COMPILED 10-12-77
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QUARTZ

FORMULA WEIGHT 60.085

SiO₂: Alpha quartz 298.15 to 844 K. Beta quartz 844 to 1800 K.

Beta quartz is metastable above 1140 K.

TEMP. K	$(H_T^0 - H_{298}^0)/T$ J/mol·K	S_T^0 J/mol·K	$-(G_T^0 - H_{298}^0)/T$ J/mol·K	C_P^0 J/mol·K	FORMATION FROM THE ELEMENTS GIBBS		
					ENTHALPY kJ/mol	FREE ENERGY kJ/mol	Log K _f
298.15	0.000	41.46	41.46	44.59	-910.700	-856.288	150.019
UNCERTAINTY		0.20	0.20		1.000	1.100	0.193
400	12.575	55.91	43.34	53.44	-910.848	-837.660	109.388
500	21.376	68.51	47.13	59.47	-910.540	-819.395	85.602
600	28.152	79.81	51.66	64.47	-909.897	-801.219	69.753
700	33.667	90.09	56.42	68.99	-908.952	-783.176	58.442
800	38.350	99.58	61.23	73.24	-907.711	-765.287	49.968
844	40.059	103.76	63.69	75.06	-907.160	-757.697	46.894
844	40.623	104.31	63.69	67.39	-906.684	-757.697	46.894
900	42.356	108.35	65.99	67.96	-906.260	-747.572	43.388
1000	44.967	115.56	70.59	68.96	-905.502	-729.982	38.131
1100	47.194	122.18	74.99	69.96	-904.732	-712.474	33.833
1200	49.132	128.31	79.18	70.97	-903.937	-695.017	30.253
1300	50.851	134.03	83.18	71.97	-903.108	-677.649	27.228
1400	52.393	139.40	87.01	72.97	-902.241	-660.349	24.638
1500	53.800	144.47	90.67	73.97	-901.321	-643.096	22.395
1600	55.092	149.28	94.19	74.98	-900.352	-625.920	20.434
1700	56.291	153.85	97.56	75.98	-949.834	-608.355	18.693
1800	57.413	158.22	100.81	76.98	-948.460	-588.298	17.072

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H_{298}^0 - H_0^0$	6.916 kJ	MOLAR VOLUME	2.2688 J/bar 22.688 cm ³

TRANSITIONS IN REFERENCE STATE ELEMENTS

SILICON.... M. P. 1685 K.

HEAT CAPACITY EQUATIONS

$$C_P^0 = 44.603 + 3.7754 \times 10^{-2} T - 1.0018 \times 10^{-6} T^2$$

(EQUATION VALID FROM 298 - 844 K)

$$C_P^0 = 58.928 + 1.0031 \times 10^{-2} T$$

(EQUATION VALID FROM 844 - 1800 K)

REFERENCE	247	35	35	COMPILED
		278	284	7-16-76

ANDALUSITE

FORMULA WEIGHT 162.047

Al₂SiO₅: Crystals 298.15 to 1800 K.

TEMP.	FORMATION FROM THE OXIDES							
					GIBBS			
	(H _T ⁰ -H ₂₉₈ ⁰)/T	S _T ⁰	-(G _T ⁰ -H ₂₉₈ ⁰)/T	C _P ⁰	ENTHALPY	FREE ENERGY	Log K _f	
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol		
298.15	0.000	93.22	93.22	122.70	-1.125 *	-1.376 *	0.241	
UNCERTAINTY		0.42	0.42		1.260	1.260	0.221	
400	34.900	133.31	98.41	148.98	-1.225 *	-1.445 *	0.189	
500	59.384	168.35	108.97	164.49	-1.307 *	-1.492 *	0.156	
600	77.800	199.29	121.49	174.61	-1.448 *	-1.508 *	0.131	
700	92.157	226.77	134.61	181.61	-1.746 *	-1.508 *	0.113	
800	103.675	251.37	147.69	186.74	-2.267 *	-1.438 *	0.094	
900	113.133	273.60	160.47	190.73	-2.975 *	-1.283 *	0.074	
1000	121.063	293.87	172.81	194.06	-2.964 *	-1.094 *	0.057	
1100	127.835	312.51	184.67	197.05	-2.942 *	-0.919 *	0.044	
1200	133.723	329.78	196.06	199.93	-2.900 *	-0.729 *	0.032	
1300	138.928	345.90	206.97	202.86	-2.817 *	-0.555 *	0.022	
1400	143.607	361.04	217.43	205.96	-2.655 *	-0.373 *	0.014	
1500	147.871	375.36	227.49	209.33	-2.404 *	-0.229 *	0.008	
1600	151.826	388.99	237.16	213.03	-1.995 *	-0.090 *	0.003	

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
H ₂₉₈ ⁰ - H ₀ ⁰	17.096 kJ	MOLAR VOLUME	5.1530 J/bar 51.530 cm ³

TRANSITIONS IN REFERENCE STATE OXIDES

SiO₂..... ALPHA - BETA TRANSITION 844 K.

HEAT CAPACITY EQUATION

$$C_P^0 = 4.0843 \times 10^{-2} - 0.11050 T + 3.5897 \times 10^{-5} T^2 - 4.4199 \times 10^{-8} T^{-0.5}$$

(EQUATION VALID FROM 298 - 1600 K)

REFERENCE	205	120	285 267	COMPILED 10-12-77
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