American Mineralogist
Vol. 57, pp. 1375–1385 (1972)

DIASPORE–CORUNDUM EQUILIBRIUM DETERMINED BY EPITAXIS OF DIASPORE ON CORUNDUM

HERBERT HAAS, *Department of Geological Sciences*
Southern Methodist University, Dallas, Texas 75222

ABSTRACT

The pressure–temperature equilibrium curve between diaspore and corundum and vapor was experimentally determined above 390° C and 1.5 kbar in two ways, by observing presence or absence of epitaxial growth of diaspore crystallites on corundum grains and by recording weight changes on single crystals of corundum. Equilibrium points were used to derive thermodynamic data for diaspore, which allowed calculation of the equilibrium curve below 390° C. This curve passes through 1 bar at 220° C, 170 bar at 360°, 2400 bar at 405°, and 7500 bar at 460°.

INTRODUCTION

Diaspore, the aluminum hydroxide AlO[OH], is often reported to occur in pyrophyllite deposits (Espenshade and Potter, 1960; Zen, 1961); however, stable occurrence of pyrophyllite in contact with corundum is not known. An exact knowledge of the pressure–temperature equilibrium curve between diaspore and corundum can therefore give valuable information on the stability field of pyrophyllite. Thermodynamic data for diaspore are needed for the calculation of phase boundaries and additional thermodynamic data in mineral assemblages belonging to the system Al_2O_3–SiO_2–H_2O[1]. Presently thermodynamic data for diaspore are available at 298° K and 1 bar pressure (Robie and Waldbaum, 1968; Zen, 1971). Shortly before the revised version of this manuscript was submitted for publication, Zen (1972) published thermodynamic data at higher temperatures based on preliminary experimental data that were orally presented by this writer (Haas and Holdaway, 1970). Zen's data are in agreement with the data presented here.

The equilibrium curve has furthermore been studied with hydrothermal methods by Ervin and Osborn (1951), Kennedy (1959), Fyfe and Hollander (1964), and Matsushima *et al.* (1967). The results of previous studies are shown in Figure 3, together with the equilibrium curve determined in the present research. In some of these studies (Ervin and Osborn, 1951; Kennedy, 1959) precipitated gels with seeds

---

[1] The present diaspore—corundum study was made to provide the data needed in a broader investigation recently completed by this writer: *Equilibria in the system Al_2O_3–SiO_2–H_2O involving the stability limits of diaspore and pyrophyllite, and thermodynamic data of these minerals.* Ph.D. thesis, Southern Methodist University.

were used as starting materials, a method which does not necessarily indicate true stability relations between these minerals and may lead to the formation of metastable phases, *e.g.*, boehmite. A report by Matsushima *et al.* (1967) lists reversals of the reaction diaspore $\rightleftharpoons$ corundum + water in experiments where both minerals are present in the experimental charge only at pressures above 10 kbar. The extrapolation of the resulting high pressure equilibrium curve below 10 kbar is in agreement with the data presented in this work.

This work was performed with single crystals and pure mineral powders in grain sizes of 30 to 50 μm which is slightly smaller than the average grain size in fine grained rocks. Thus by selecting these starting materials a simulation of natural conditions was attempted.

All experiments were made in a conventional hydrothermal installation with externally heated rod bombs. This apparatus has pre-

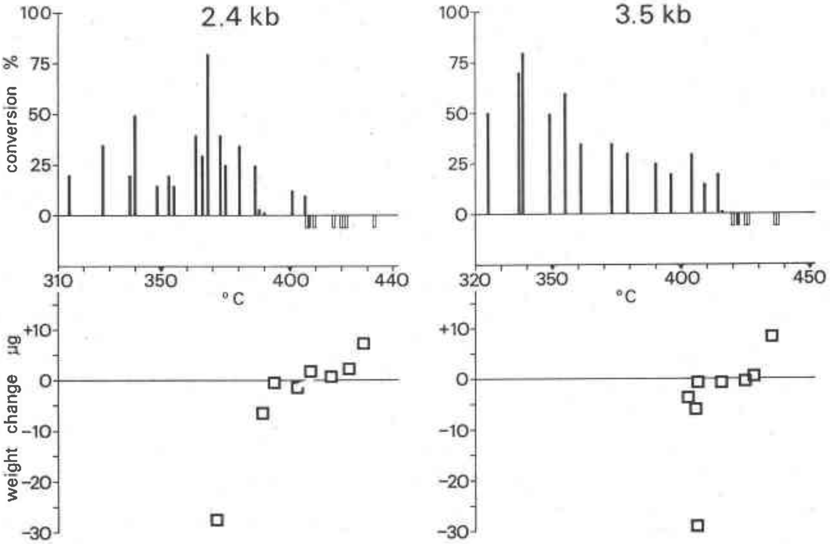

FIG. 1. Experimental results at 2.4 and 3.5 kbar. *Top:* Solid bars pointing upward represent percentage of corundum powder which converted to diaspore crystallites. Open bars pointing downward indicate temperature at which no diaspore growth can be detected. Solid bars pointing downward show runs where scanning electron photomicrographs were made and growth of corundum could be detected. *Bottom:* Squares indicate weight change of single corundum crystals during 30 days runs. For improved clarity the symbols to indicate weight change are drawn smaller than the actual tolerance range would require. Tolerances are ± 3 μg for the weight change. Thus the boxes should be about twice the drawn size. Considering both investigations the equilibrium temperature at 2.4 kbar is 405° C ± 7° and at 3.5 kbar 418° C ± 7°.

viously been described by Holdaway (1971). Equilibrium temperatures were determined at 1.75, 2.4, 3.5, 4.8, and 7.0 kbar pressure. Two independent methods were used to bracket the equilibrium temperature at each pressure. In every case the results of both methods agree. The first method involves a single crystal of corundum as reaction detector; in the second method epitaxial overgrowth of diaspore on small corundum grains serves as a stability indicator.

Experimental

Single-crystal method

This was first used on diaspore–corundum by Fyfe and Hollander (1964). In the present study most crystals were made from synthetic corundum and weighed about 50 mg. A few experiments were made with natural yellow sapphire of gem quality, and results of these experiments matched results obtained with synthetic corundum crystals. The crystals were weighed against reference weights at the lower and upper ends of the optical scale on a Mettler M-5 microbalance.[1] For each experiment a corundum crystal, 75 mg diaspore powder[2] and 75 mg water were sealed in a silver capsule by fusion welding. A typical run lasted 30 days at pressures of 2.4, 3.5, and 4.8 kbar. At 1.75 kbar, 50 days were needed to observe significant weight changes; at 7.0 kbar, 8 days sufficed. After a run the corundum crystal was extracted from the capsule and thoroughly cleaned, dried, checked under the microscope with crossed nicols for overgrowth other than corundum (if such overgrowth was present, *e.g.*, diaspore spines, and could not be cleaned away, the run was discarded), and re-weighed. The observed weight change was plotted against temperature, as shown at the bottom of Figure 1. A zero weight change indicates the temperature where both minerals, diaspore and corundum, are stable and in equilibrium. Weight gains were small; this is typical for refractory minerals like corundum. Weight losses rapidly increased when the temperatures of the runs were set 10° or more below the equilibrium temperature.

Powder Method. In this type of run the charge placed in the silver capsule consisted of 15 to 25 mg corundum powder[3] with a few percent diaspore seeds, or a multicomponent mixture containing corundum powder.[4] 35 mg water was

---

[1] Each crystal was weighed a minimum of six times in an uninterrupted sequence of weighings which included the reference weights. The individual crystal weighings were averaged if the deviations among them did not exceed 2.5 μg. If the weighing sequence showed deviations in excess of 2.5 μg the whole sequence was repeated, usually on a different day. Re-weighing special reference crystals at intervals of two months over the whole period of this investigation indicates a maximal weighing error of ± 3 μg.

[2] Diaspore origin: Chester, Massachusetts. Chemical analysis: Al_2O_3: 82.91%, SiO_2: 0.78%, Fe_2O_3: 0.43%, CaO: 0.35%, Na_2O: 0.06%, K_2O: 0.13%, MgO: 0.01%.

[3] Corundum, synthetic, ground to less than 325 mesh and elutriated to remove the finest fraction.

[4] Other components were pyrophyllite powder and either andalusite single crystals or kyanite powder. In such runs experimental data on these minerals were the principal objective.

added. The duration of most runs was the same as for the single crystal experiments. When the pressure and the temperature were in the stability field of diaspore, this mineral nucleated spontaneously on corundum in the form of fine whiskers or short, tabular prisms (Figure 4a, c). During prolonged experiments or at temperatures of 30° or more below equilibrium temperature these spines grew into orthorhombic–prismatic crystals (Figure 4b). At the same instance corrosion of the corundum grains could readily be observed. Whiskers and spines of diaspore began to form after runs of only two day's duration, and they grew in three distinct directions separated by 120° angles, all in the 0001 plane of corundum (Figure 4a). Naturally occurring overgrowth of diaspore on corundum with ordered growth directions was first observed by Kenngott (1866) and the mutual crystallographic orientations are reported by Schwiersch (1933) and Ervin (1952).

Proof of corundum stability above the temperature at which diaspore no longer nucleates was obtained by scanning electron microscope examination of a few powders from runs above the presumed equilibrium temperature. At magnifications of 1000x to 3500x steplike growth lines which appear compatible with the hexagonal–prismatic crystal form of corundum are clearly visible (Figure 4d). In all powder runs the corundum grains were routinely checked for the presence of diaspore growth under the optical microscope. If such growth was observed the percentage of conversion of corundum into diaspore was estimated by comparing the amount of grown diaspore crystallities with the residual corroded corundum grains. Since the indicated percentages of conversion are estimates only they may have an error of ±25 percent. In spite of this large tolerance one can observe an increase in the reaction rate as the experimental temperature is dropped to about 50 to 70° C below the observed

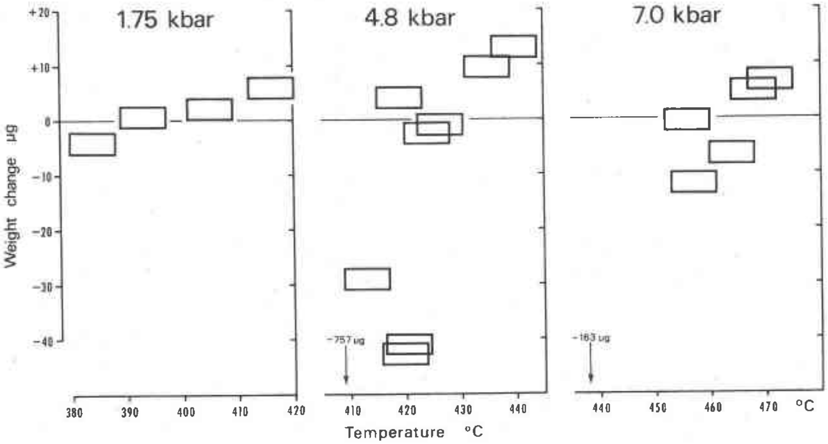

FIG. 2. Observed weight changes of single crystals of corundum at pressures not shown in Figure 1. The interpretation of these data is represented by horizontal bars along the equilibrium curve No. 1 in Figure 3. To improve clarity the error field for each experiment is reduced to about half of the actual temperature uncertainty of ± 5°.

equilibrium temperature. Further decrease of the experimental temperature causes the reaction rate to decrease again.

EXPERIMENTAL RESULTS

The estimated percentages are plotted against temperature in Figure 1, top. The equilibrium temperature lies between the highest temperature of diaspore growth and the lowest temperature at which the corundum grains show observable growth lines. Where optical microscopy did not yield a clear answer for runs close to the equilibrium temperature, high magnification pictures were made with the scanning electron microscope.[1] Since such pictures had to be kept at a small number, most experiments at temperatures significantly above the observed equilibrium temperature were investigated only optically, and checked for absence of diaspore nucleation and growth, and absence of corundum corrosion. These criteria proved to be a quick and reliable way to detect reaction in the stability field of diaspore, thus their absence can be accepted in the above circumstances as confirmation of corundum stability. The diaspore growth was successfully reversed by exposing diaspore–spined corundum grains to a second run with the temperature set 9° into the corundum stability field.[2] After the run, the spines were partly decomposed, frayed and disoriented.

It is thus possible to bracket the equilibrium temperature very closely; *e.g.*, for 2.4 kbar a run at 401° shows small diaspore spines (Figure 4c) and a run at 407° shows corundum growth (Figure 4d). The determined equilibrium temperature is 405°. The spines were identified by three criteria: a) refractive indices in oils, b) interpretation of X–ray diffraction patterns where a marked appearance of the major diaspore peaks occurred in runs with a microscopically observed diaspore growth of 30 precent or more, and c) by studying crystal forms on high magnification pictures. The results of this study are presented in Table 1 and as curve no. 1 in Figure 3. Below 390° this curve is calculated.

THERMODYNAMIC CALCULATIONS

The thermodynamic calculations are based on the experimental *P–T* values, tabulated thermodynamic data for corundum (Robie and Waldbaum, 1968), for water (Sharp, 1962; Burnham *et al.*, 1969;

---

[1] Type JSM, Japan Electron Optics Laboratory Co. Specimen coating: Palladium—Gold 40–60.

[2] At 3.5 kbar. Since the experimental temperatures are uncertain to ±5°, this run was therefore 4 to 14° above the equilibrium temperature.

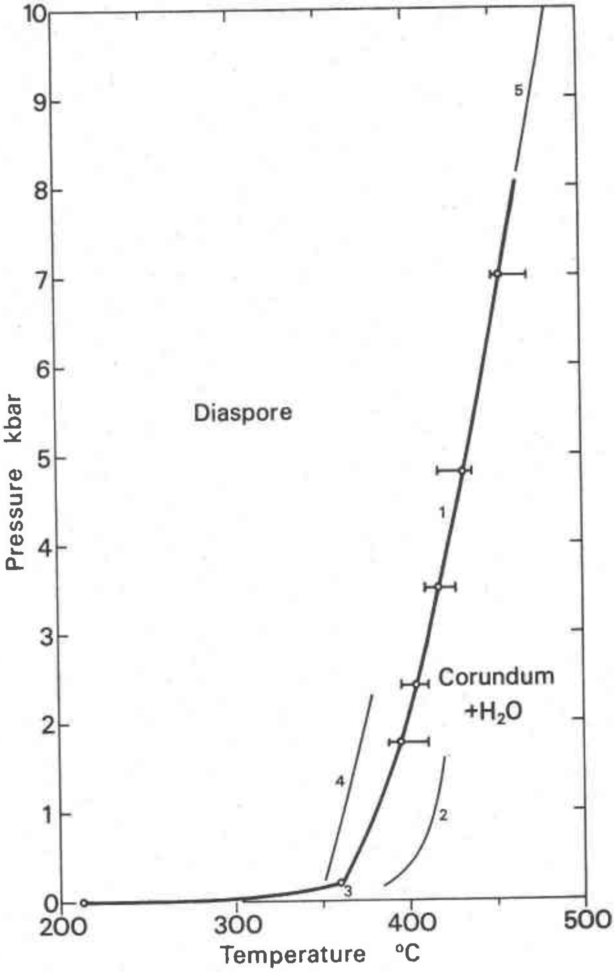

FIG. 3. Equilibrium curves for the reaction diaspore ⇄ corundum + water. *No. 1:* This report, between 390° and 470° C based on experimental data, from 220° to 390° C based on calculations. Horizontal bars indicate range of possible equilibrium temperature at each experimental pressure. *No. 2:* Reported by Ervin and Osborn (1951). *No. 3:* Equilibrium point by Fyfe and Hollander (1964). *No. 4:* Hydrothermal results of Kennedy (1959). *No. 5:* Piston-anvil results of Kennedy (1959).

Fisher and Zen, 1971), the low temperature heat capacity data and the 298° K entropy of diaspore (King and Weller, 1961). Compressibility and thermal expansion of diaspore are not known. By assuming that the volume changes of diaspore and corundum cancel, the

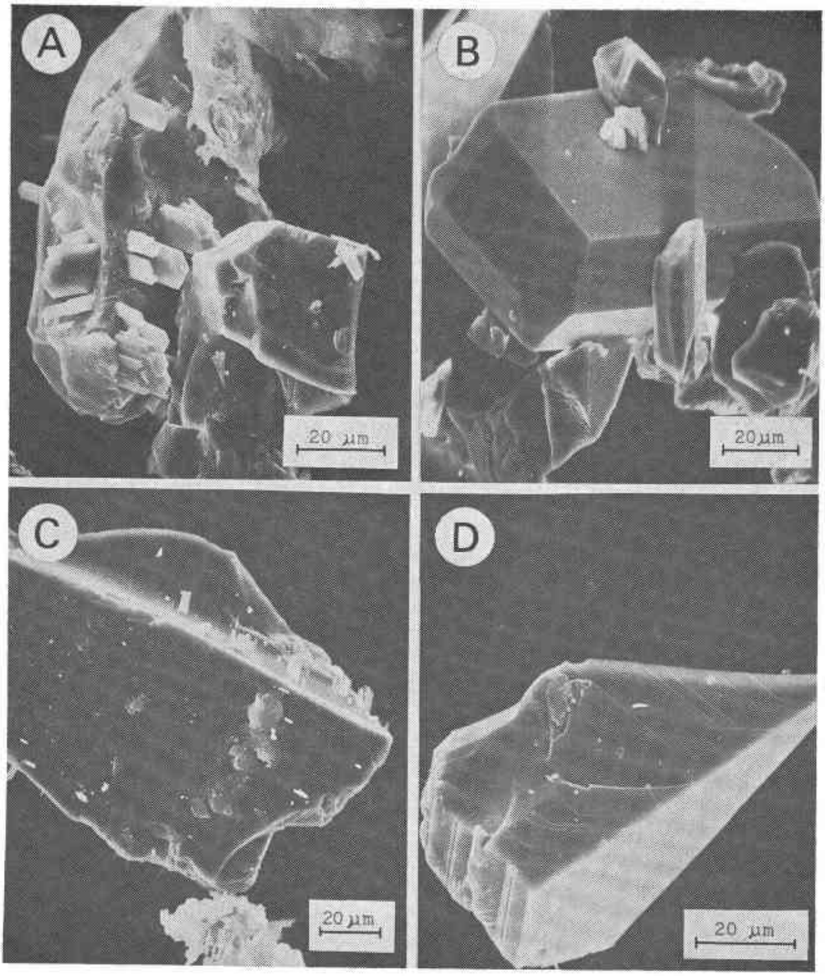

FIG. 4. Scanning electron photomicrographs. (A) Corundum grain after run of 50 days at 2.4 kbar and 380° C, 25° below the equilibrium temperature. Diaspore is growing epitaxially in two directions in the 0001 plane of corundum (the third direction is not visible in this picture). Orientations: *c* of corundum and *a* of diaspore vertical on picture, *c* of diaspore parallels elongation. (b) Euhedral diaspore crystal, nucleated and grown in 30 days at 2.4 kbar and 367° C, 38° below equilibrium temperature. Orientation of crystal: *c* horizontal, *b* approximately vertical and perpendicular to largest surface. (C) Diaspore growing on corundum grain. The spines are *ca.* 8 μm long and grew at 2.4 kbar and 401° C in 29 days, 4° below equilibrium temperature. (D) Corundum grain showing growth pattern which developed in 30 days at 2.4 kbar and 407° C, 2° above equilibrium temperature.

ΔV of the reaction is kept constant. The pressure effect on ΔS of the solid phases is assumed to be zero.

At experimental temperatures which are grouped around 700° K the entropy of diaspore was derived from the slope of the equilibrium curve and the known entropies of corundum and steam at the same conditions. The interpolation of the entropy curve between these points and the 298° K entropy is based on the integral

$$S^\circ = \int_0^T (C_p/T)\cdot dT.$$

Heat capacity data are available to 298°; the area under the $C_p/T = f_{(T)}$ curve to 700° K must equal the experimentally determined entropy. This procedure allows accurate estimation of the $C_p = f_{(T)}$ curve to 700° K because to satisfy the entropy requirements, C_p of diaspore can increase only from 13.65 to 14.0 calories per AlO[OH] between 400° and 700° K.[1] The assumption is made here that the entropies of corundum and water are correct.

The free energy of formation (ΔG°_f) of diaspore was derived directly from experimental equilibrium points and used together with corresponding S° values to calculate the enthalpy of formation (ΔH°_f) at these temperatures. These closely grouped data points were interpolated to obtain a ΔH°_f at 700° K. ΔH°_f at 298° K and at all other temperatures was based on this point by adding the difference between the heat contents of diaspore and the elements in diaspore. The heat content $[H_T - H_{298}]$ of diaspore was obtained by integration of the $C_p = f_{(T)}$ curve; the heat contents of the elements are tabulated in Robie and Waldbaum, (1968). ΔG°_f from 298° to 600° K was calculated from ΔH°_f and S° values. All 800° K values are based on extrapolated heat content and ΔG°_f curves, the two most linear functions. Results of the foregoing calculations are presented in Table 2, which is similar in format to mineral data tabulations by Robie and Waldbaum (1968).

The data in Table 2 were then used to calculate the equilibrium curve between 1 and 10,000 bars. (Figure 3 curve 1) In the range of experimental control this generated curve always passes within the interpreted reversals. At the water–steam equilibrium curve the diaspore–corundum curve shows a sharp bend with an average slope of 1.5 bars/degree below 200 bars. Fyfe and Hollander (1964) have

---

[1] The initial steepness of the C_p curve and its leveling off above 300° K may be explained with the hydrogen atoms acquiring most of their thermal motion below 300° K.

TABLE 1. POINTS ON THE EQUILIBRIUM CURVE DIASPORE - CORUNDUM

calculated:		
1 bar	220° C ±8°	
2	240°	
7	260°	
25	300°	
80	340°	
170	360°	
750	380°	
experimental:		
	best value	range
1750 bar	396° C	389 - 408° C
2400	405°	397 - 411°
3500	418°	412 - 426°
4800	433°	419 - 436°
7000	458°	455 - 468°
extrapolated (graphically and by calculation):		
10,000	482° C	

Table 2. THERMODYNAMIC PROPERTIES OF DIASPORE AlO[OH]

Temp. °K	S° cal	ΔG°_f kcal	ΔH°_f kcal	$[H^\circ_T - H^\circ_{298}]$ kcal
298	8.43 ± 0.5	-220.453 ±.500	-239.208 ±.200	0
400	12.34	-214.091	-239.540	1.356
500	15.40	-207.553	-239.879	2.728
600	17.92	-201.052	-240.259	4.112
700	20.14	-194.534	-240.679	5.506
800	22.41	-187.980	-240.897	7.156

S°	Third law entropy.
ΔG°_f	Free energy of formation from the elements.
ΔH°_f	Heat of formation from the elements.
$[H^\circ_T - H^\circ_{298}]$	Enthalpy at temperature T relative to 298° K (heat content).

Reference state for ΔG°_f and ΔH°_f are the elements in their standard state at one bar pressure and the stated temperature.

Tolerances apply to the results of this study only and do not include the uncertainties of the corundum and water data.

determined an experimental equilibrium point at 360° C on the critical curve of water (186 bars). The calculated curve passes within 4° of this point.

ACKNOWLEDGMENTS

I thank Dr. Michael J. Holdaway for providing the diaspore chemical analysis and for his invaluable advice during the investigation and the preparation of this report. I am also grateful to Dr. Donald C. Thorstenson for constructive criticism of the manuscript. Thanks are extended to Drs. Emile A. Pessagno and James B. Urban (University of Texas at Dallas) for the opportunity to use the scanning electron microscope, and to Dr. Fouad Y. Michael for taking the pictures.

The financial support of NASA grant NCR-44-007-006 and the use of research equipment at the Institute for the Study of Earth and Man, at Southern Methodist University are gratefully acknowledged.

REFERENCES

BURNHAM, C. W., J. R. HOLLOWAY, AND N. F. DAVIS (1969) Thermodynamic properties of water to 1000° C and 10,000 bars. *Geol. Soc. Amer. Spec. Pap.* 132, 96 p.

ERVIN, JR., G., AND E. F. OSBORN (1951) The system Al_2O_3–H_2O. *J. Geol.* 59, 381–394.

——— (1952) Structural interpretation of the diaspore—corundum and boehmite–γ–Al_2O_3 transitions. *Acta Crystallogr.* 5, 103–108.

ESPENSHADE, G. H., AND D. B. POTTER (1960) Kyanite, Sillimanite, and Andalusite Deposits of the Southeastern States. *U.S. Geol. Surv. Prof. Pap.* 336, 121 p.

FISHER, J. R., AND E-AN ZEN (1971) Thermochemical calculations from hydrothermal phase equilibrium data and the free energy of H_2O. *Amer. J. Sci.* 270, 297–314.

FYFE, W. S., AND M. A. HOLLANDER (1964) Equilibrium dehydration of diaspore at low temperatures. *Amer. J. Sci.* 262, 709–712.

HAAS, H., AND M. J. HOLDAWAY (1970) Stability relations of corundum and diaspore in the medium pressure and temperature range. *EOS Trans. Amer. Geophys. Union,* 51, 437.

HOLDAWAY, M. J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *Amer. J. Sci.* 271, 97–131.

KENNEDY, G. C. (1959) Phase relations in the system Al_2O_3–H_2O at high temperatures and pressures. *Amer. J. Sci.* 257, 563–573.

KENNGOTT, A. (1866) *Die Minerale der Schweiz.* Leipzig.

KING, E. G., AND W. W. WELLER (1961) Low-temperature heat capacities and entropies at 298.15° K of diaspore, kaolinite, dickite and halloysite. *U. S. Bur. Mines Rep. Invest.* 5810, 6 p.

MATSUSHIMA, SHIGO, G. C. KENNEDY, JAGANNADHAM AKELLA, AND JOHN HAYGARTH (1967) A study of equilibrium relations in the systems Al_2O_3–SiO_2–H_2O. and Al_2O_3–H_2O. *Amer. J. Sci.* 265, 28–44.

ROBIE, R. A., AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15° K (25° C) and 1 atmosphere (1.013 bars) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* 1259, 256 p.

SCHWIERSCH, H. (1933) Thermischer Abbau der natürlichen Hydroxyde des Aluminiums und des dreiwertigen Eisens. Zugleich ein Beitrag zur Frage der Reaktionen im festen Zustande. *Chem. Erde,* **8,** 252–315.

SHARP, W. E. (1962) The thermodynamic functions for water in the range 10 to 1,000° C and 1 to 250,000 bars. *Univ. Calif. Lawrence Rad. Lab. Rep.* **7118,** 51 p.

ZEN, E-AN (1961) Mineralogy and petrology of the system Al_2O_3–SiO_2–H_2O in some pyrophyllite deposits of North Carolina. *Amer. Mineral.* **46,** 52–66.

——— (1971) Standard (298° K, 1 bar) enthalpy and Gibbs free energy of formation from the elements for 8 minerals, and 298° K, 1 bar third-law entropy for 6 minerals. *EOS Trans. Amer. Geophys. Union,* **52,** 381.

——— (1972) Gibbs free energy, enthalpy, and entropy of ten rock-forming minerals: calculations, discrepancies, implications. *Amer. Mineral.* **57,** 524–533.

Manuscript received, December 20, 1971; accepted for publication, June 5, 1972.