

sillimanite give values of about -50 kilocalories per mole (Kubaschewski and Evans, 1956).

TABLE 3  
Thermochemical Data Used in Calculations  
The room-temperature data were taken from the compilation of  
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|                                            | Kyanite                    | Sillimanite                | Andalusite                 | Quartz                    | Corundum                   |
|--------------------------------------------|----------------------------|----------------------------|----------------------------|---------------------------|----------------------------|
| Entropy, cal/mol°C.                        |                            |                            |                            |                           |                            |
| 300 °K                                     | 20.02 ± 0.1 <sup>8</sup>   | 22.97 ± 0.1 <sup>8</sup>   | 22.28 ± 0.1 <sup>8</sup>   | 10.0 ± 0.1 <sup>8</sup>   | 12.16 ± 0.02 <sup>4</sup>  |
| 1600 °K                                    | 90.85 ± 0.6 <sup>2,8</sup> | 92.17 ± 0.6 <sup>2,8</sup> | 94.27 ± 0.6 <sup>2,8</sup> | 35.9 ± 0.2 <sup>2,3</sup> | 57.53 ± 0.1 <sup>2,4</sup> |
| Volume, cm <sup>3</sup> /mol.              |                            |                            |                            |                           |                            |
| 300 °K                                     | 43.3 ± 1.0 <sup>5</sup>    | 49.0 ± 1.0 <sup>7</sup>    | 51.6 ± 1.0 <sup>1</sup>    | 22.6 ± 0.03 <sup>9</sup>  | 25.5 ± 0.2 <sup>9</sup>    |
| Enthalpy, kcal/mol.                        |                            |                            |                            |                           |                            |
| H <sub>1600 °K</sub> - H <sub>300 °K</sub> | 57.7 ± 0.6 <sup>2</sup>    | 56.3 ± 0.6 <sup>2</sup>    | 56.8 ± 0.6 <sup>2</sup>    | 21.1 ± 0.1 <sup>2</sup>   | 37.0 ± 0.1 <sup>2</sup>    |

#### References.

- <sup>1</sup> Hey and Taylor, 1931; MacDonald and Merriam, 1938.
- <sup>2</sup> Kelley, 1949.
- <sup>3</sup> Kelley, 1950.
- <sup>4</sup> Kerr, Johnston, and Hallett, 1950.
- <sup>5</sup> Naray-Szabo, Taylor, and Jackson, 1929.
- <sup>6</sup> Palache, Berman, and Frondel, 1944.
- <sup>7</sup> Taylor, 1928; Taylor, 1929.
- <sup>8</sup> Todd, 1950.
- <sup>9</sup> Wyckoff, 1926; Gibbs, 1926.

The minerals in this system are among the best refractories known, and they are extraordinarily reluctant to take part in chemical reaction. Metastable persistence of kyanite and sillimanite outside their respective fields of stability made the demonstration of the reversibility of the reaction extremely difficult. Natural kyanite held for four days at 1000°C and one atmosphere showed no sign of reaction; this run is 18,000 bars below the equilibrium curve. The reaction was reversed at higher temperature. Synthetic sillimanite produced in run 88 was completely converted to kyanite at 1220°C and 23,900 bars. Natural kyanite, after grinding for 60 hours, was converted to a mixture of kyanite and sillimanite at 18,600 bars and 1340°C. The reaction was thus reversed at points about 3000 bars from the equilibrium curve. This is the maximum uncertainty in its position.

Metastable formation of kyanite or sillimanite in the field of the other is known to have occurred only in run 90 (table 2). Subsequent runs showed that the kyanite formed in this run was metastable, and it is not shown in figure 2.

The preliminary results published by Griggs and Kennedy (1956) show an equilibrium curve between kyanite and sillimanite which lies at slightly over 20,000 bars at 1000°C; our curve lies at 18,000 bars at the same temperature.

#### EXTRAPOLATION OF THE EQUILIBRIUM CURVE TO LOWER TEMPERATURES

The equilibrium curve between kyanite and sillimanite is located between 1000°C and 1300°C by this work. These temperatures are too high for im-

mediate geological application, and it is desirable to extrapolate the curve to lower temperatures. High-temperature heat capacity data (Kelley, 1949) show that  $\Delta S$ , the entropy change of the reaction, depends on temperature at one atmosphere; hence a curvilinear extrapolation is required. Differences in thermal expansion and compressibility of kyanite and sillimanite,  $\Delta\alpha$  and  $\Delta\beta$  respectively, will be neglected. This introduces only a small error insofar as these quantities affect  $\Delta V$ , the volume change of the reaction.  $\Delta\alpha$  is likely to be less than  $10^{-5}$  deg $^{-1}$ , and  $\Delta\beta$  can hardly exceed  $10^{-6}$  bars $^{-1}$ . The correction to  $\Delta V$  is thus unlikely to exceed 3 percent at the highest temperatures and pressures. But the entropy change of the reaction is dependent on  $\Delta\alpha$  through the relation  $(\partial\Delta S/\partial P)_T = -\Delta(V\alpha) = -\bar{V}\Delta\alpha$ , where  $\bar{V}$  is a mean volume.  $\bar{V}$  is about 45 cm $^3$ /mol, and with  $\Delta\alpha$  assumed to be  $10^{-5}$  deg $^{-1}$ , we find that  $\Delta S$  changes by about 9 dj (decijoules)/mol $^{\circ}$ C in 20,000 bars. This is about 8 percent of the entropy change at room temperature or 15 percent of the change at 1100 $^{\circ}$ C.

The equilibrium curve is given by the equation

$$(1) \quad P(T) = P(T_0) + (\Delta S/\Delta V)_0 (T - T_0) + \frac{1}{\Delta V} \int_{T_0}^T \Delta S(T) dT$$

where  $\Delta S(T)$  is chosen to vanish at  $T = T_0$ .  $(\Delta S/\Delta V)_0$  and  $P(T_0)$  are fixed by the equilibrium pressures at two temperatures. These were chosen to be 1300 and 1600 $^{\circ}$ K. The integral in (1) was evaluated from the high-temperature entropy data given by Kelley (1949).

The non-linearity of the equilibrium curve is contained in the third term on the right of (1), and this term is subject to large uncertainties that do not affect the others. The high-temperature entropy data are estimated to be uncertain by about 20 dj. Random errors tend to cancel in the integration, but the integral is nevertheless subject to an uncertainty of perhaps 30 percent. Further errors are introduced by neglect of  $\Delta\alpha$  and  $\Delta\beta$ . Finally,  $\Delta V = 5.7 \pm 1.3$  cm $^3$ /mol (table 3); the uncertainty in this factor is almost 25 percent. Combining these independent errors, we estimate the uncertainty in this term to be about 3,000 bars at 25 $^{\circ}$ C and 1500 bars at 500 $^{\circ}$ C.

Utilizing (1), curve A in figure 2 was extrapolated to room temperature; it was fitted to the experimental data between 1000 $^{\circ}$ C and 1300 $^{\circ}$ C by placing it about halfway between adjacent points in the kyanite and sillimanite fields. Curve B in figure 2 is a linear extrapolation.

TABLE 4  
Parameters of the Equilibrium Curves at 25 $^{\circ}$ C

| Curve                                             | Intercept<br>(bars) | $\frac{dP}{dT}$ at 25 $^{\circ}$ C.<br>(bars/ $^{\circ}$ C) | $\Delta S$ at 25 $^{\circ}$ C.<br>(dj/mol/ $^{\circ}$ C) |
|---------------------------------------------------|---------------------|-------------------------------------------------------------|----------------------------------------------------------|
| "A"                                               | 5650                | $19 \pm 5$                                                  | $108 \pm 24$                                             |
| Steepest                                          | 3650                | $21 \pm 5$                                                  | $119 \pm 25$                                             |
| Flattest                                          | 7550                | $18 \pm 5$                                                  | $100 \pm 23$                                             |
| "B"                                               | 7600                | 11                                                          | $63 \pm 14$                                              |
| From Low-Temperature Heat Capacities (Todd, 1950) |                     |                                                             | 123 $\pm$ 6                                              |