

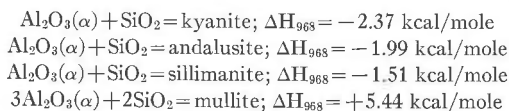
## THE THERMODYNAMIC PROPERTIES OF THE ALUMINUM SILICATES

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### ABSTRACT

The heats of formation, from the oxides, of the three polymorphs of  $\text{Al}_2\text{SiO}_5$  (kyanite, andalusite and sillimanite) and of mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , have been measured by oxide melt solution calorimetry at  $968^\circ\text{K}$ :



On the basis of these results, and of entropy, heat content and volume data taken from the literature, the P-T diagram for the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system has been calculated for a wide range of temperatures and pressures. This diagram is in reasonable agreement with recent high temperature-high pressure experimental work and with some data based on direct geological observations.

### INTRODUCTION

The problem of the thermodynamic properties of silicate minerals is one of considerable scientific and technological interest. While this field dates back to the early days of modern geochemistry, it has been stimulated greatly by the postwar development by Torgeson and Sahana (1948) of precision HF-solution calorimetry. By now this approach has been applied by a number of investigators.

However, even at its best, HF-solution calorimetry has proved to be a rather cumbersome method, and is providing significant new information at a relatively modest rate. Furthermore, it is becoming increasingly apparent that this method has very important limitations. This is due to the fact that hydrofluoric acid, even near  $100^\circ\text{C}$ ., is a poor solvent for many silicates and other minerals.

Recently Yokokawa and Kleppa (1964a, 1964b) have reported the development of new calorimetric methods which are likely to have an impact on this problem. In this approach the mineral and its component oxides are dissolved in an oxide melt in a calorimeter maintained at elevated temperatures. The heat of formation of the mineral is then calculated from the observed heats of solution. In a first application of this method to a slightly different problem Yokokawa and Kleppa (1964b) determined the enthalpy of transformation of several of the metastable forms of aluminum oxide to the stable corundum modification. During

the past year Navrotsky and Kleppa (1966) have determined the enthalpy of formation of magnesium-aluminum spinel from the component oxides.

In the present work these new high-temperature methods are applied to a study of the anhydrous aluminum silicates. The binary system  $\text{Al}_2\text{O}_3\text{-SiO}_2$  contains four well-defined compounds which all occur in nature. Three of these, *kyanite*, *sillimanite* and *andalusite*, have the composition  $\text{Al}_2\text{SiO}_5$  and are common in metamorphic rocks. This group presents an interesting and geologically important case of polymorphism. The fourth compound,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , mullite, occurs more rarely in nature, but is of great technological importance as a principal component of porcelains and related ceramic materials.

The problem of the thermodynamic properties of the aluminum silicates has attracted considerable attention during the past 15 years. For example, the low-temperature heat capacities of kyanite, andalusite and sillimanite were studied by Todd (1950), who also reported third law standard entropies for these substances at 25° C. More recently corresponding high-temperature heat content and entropy data have been published by Pankratz and Kelley (1964). For these minerals volume and thermal expansion data over a wide range of temperatures are given by Skinner, *et al.* (1961). For mullite third law entropy values as well as high-temperature enthalpies and entropies are contained in a recent report by Pankratz *et al.* (1963). However, there is as yet no reliable direct information on the enthalpies of formation of these compounds.

The compilation of thermodynamic data by Rossini *et al.* (1952) refers to an early investigation of the aluminum silicates by Neumann (1925) who measured the various heats of solution in aqueous HF. From these data the enthalpies of formation from the compound oxides were calculated to be of the order of -40 to -45 kcal/mole.

So far all attempts to repeat these calorimetric measurements in HF have failed. In recent years Neumann's data have been questioned also on other grounds, initially by Flood and Knapp (1957). On the basis of general chemical considerations as well as the appearance of ternary phase diagrams involving  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  these authors concluded that the aluminum silicates should be stable with respect to silica and corundum by 5 kcal/mole or less. Evidence in support of this view may be found, *e.g.*, in recent studies of phase relations involving the  $\text{Al}_2\text{SiO}_5$  polymorphs and, for mullite, in work on metallurgical equilibria involving this phase (Kay and Taylor, 1960; Rein and Chipman, 1963).

During the past year Waldbaum (1965) has attempted to prepare a complete analysis of the thermodynamic properties of the mullite group compounds, based on all information so far available. Unfortunately,

due to the complete lack of heat of formation data, Waldbaum's analysis is inadequate in several important respects.

In the present communication we report new calorimetric data on the enthalpies of formation of all the four aluminum silicates, as determined by oxide melt solution calorimetry at 695° C. A preliminary note by Holm and Kleppa (1966) which covers the first results for the mineral kyanite has been published elsewhere. On the basis of our new data combined with the entropy, heat content, free energy and volume information referred to above, we shall be able to calculate a rather complete P-T diagram for the aluminum silicates valid for a wide range of temperatures and pressures. This diagram will be compared with relevant information derived from recent high pressure-high temperature phase stability work.

#### EXPERIMENTAL AND MATERIALS

The calorimeter used in the present work and the experimental procedures adopted were similar to those of Yokokawa and Kleppa. All experiments were performed at  $695 \pm 2^\circ$  C. Calibration was by the gold-drop method, based on the heat content equation for pure gold as given by Kelley (1960). The solvent was prepared from reagent grade lead (II) oxide, cadmium (II) oxide and boric acid in the ratio  $9\text{PbO} \cdot 3\text{CdO} \cdot 4\text{B}_2\text{O}_3$ , as recommended by Yokokawa and Kleppa. This melt is a good solvent for a variety of different oxides of basic, amphoteric and acid character (A. Navrotsky, 1966, priv. comm.).

In each solution experiment a small quartz or silicate sample (about 0.9 millimole quartz, about 0.5 millimole of each of the polymorphs and about 0.2 millimole mullite) was dissolved in 40 g of melt (about 250 millimoles of oxides). The solvent was renewed after each experiment.

In the case of kyanite, andalusite and sillimanite we had available small, powdered samples of the material originally used by Todd (1950), and later by Pankratz and Kelley (1964). These minerals had been specially prepared and purified by the Geophysical Laboratory of Washington, D. C. According to the chemical analysis given by Todd (1950) the kyanite and andalusite samples contain only very small amounts of impurities, of no significance within the experimental errors associated with the present work. The sample of sillimanite, on the other hand, was reported to contain 0.98%  $\text{Fe}_2\text{O}_3$  as the only significant impurity. We made a small correction for this impurity content, based on a value for the heat of solution of  $\text{Fe}_2\text{O}_3$  in the lead-cadmium-borate melt obtained by A. Navrotsky (1966, priv. comm.). In view of the impurity content of this sillimanite (I) we considered it desirable to check our results by use of a separate mineral sample. A small amount of a suitable sillimanite sample (II) was hand-picked from a mineralogical specimen from Or-

ville, North Dakota (Chicago Natural History Museum; M9122). According to a microprobe analysis carried out on another sillimanite sample from this specimen this should contain about 0.18% iron, *i.e.*, significantly less than I.

The mullite was a synthetic, powdered sample purchased from Tem-Pres Research, Inc., State College, Pennsylvania. According to the manufacturer this sample was prepared from Baker Analyzed Silicic Acid and Aluminum Hydroxide. From the weight and purity of the materials used the manufacturer states that any deviation from the stoichiometric ratio  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  should be less than 0.5%. The stoichiometric composition was assumed in the present work.

The sample of quartz was crystalline quartz from Brazil, of the type used in the oscillator plate industry. The content of impurities was entirely negligible, as shown by the analysis which is given by Holm and Kleppa (1966).

In all cases the "identity" of each mineral powder was checked by x-ray diffraction, by comparison with the ASTM data file. Prior to use all samples were carefully dried in air at 450° C.

The enthalpy change actually associated with each solution experiment was about 5 cal. We found that a precise determination of a heat effect of this small magnitude taxed our equipment and procedures to the limit, and required very effective performance of all control and measuring devices. Also, since each mineral sample behaved in a slightly different manner in the calorimeter, it was necessary to adjust experimental procedures somewhat from one sample to the other. In particular it was found to be difficult to obtain complete solution within reasonable periods of time of samples consisting of very fine particles, perhaps due to surface tension effects. Generally the most satisfactory performance of the calorimeter was achieved with powders drawn from the fraction -250 +325 mesh. The particle size problem was particularly acute in the case of andalusite, for which mineral all our sample was finer than 400 mesh. As a result of this complication we performed a large number of unsuccessful experiments with this mineral before optimal procedures had been worked out.

In this context as well as below the term "successful" is used to describe a run in which there was no significant drift of the calorimeter system during the experiment, and in which no undissolved sample could be detected after completion of the run.

## RESULTS

Yokokawa and Kleppa (1964b) reported the enthalpy of solution of  $\alpha\text{-Al}_2\text{O}_3$  (corundum) in the solvent melt at 705° C. to be  $7.6 \pm 0.2$  kcal/mole. This value was confirmed by Navrotsky and Kleppa (1966) who

found  $7.60 \pm 0.10$  kcal/mole at  $697^\circ$  C. In view of the agreement between these earlier investigations the heat of solution of alumina in the lead-cadmium-borate melt was not re-determined.

The heat of solution of quartz was measured both in the pure solvent and in melts containing 0.9 millimole of  $\text{Al}_2\text{O}_3$ . No difference was found within our experimental error. This shows that there is no significant energy of interaction between  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  in these rather dilute solutions. We have adopted for the heat of solution of quartz the value,  $-3.64 \pm 0.07$  kcal/mole, already given by Holm and Kleppa (1966).

We carried out five successful solution experiments with sillimanite I, and obtained the following enthalpies of solution: 5.63, 5.63, 5.62, 5.60, 5.52 kcal/mole. After correction for the reported content of  $\text{Fe}_2\text{O}_3$  we obtained a mean of 5.49 kcal/mole.

Two separate experiments were carried out with sillimanite II. These gave the values 5.49 and 5.41. Taking into account the small iron content the corrected mean is 5.43 kcal/mole. We have adopted  $5.47 \pm 0.07$  kcal/mole as our overall average for the heat of solution of sillimanite.<sup>1</sup>

In the case of andalusite we performed a total of four completely successful experiments and obtained the following values: 5.96, 5.96, 5.94 and 5.94, for a mean of 5.95 kcal/mole. This value may be associated with an uncertainty as large as  $\pm 0.10$  kcal/mole.

Finally, we carried out a total of five experiments with mullite, all of which were successful. These gave the following enthalpies of solution: 10.12, 10.11, 10.10, 10.05, 10.04 for a mean of  $10.08 \pm 0.10$  kcal/mole.

On the basis of these measurements, and the data for kyanite reported previously, we calculate the enthalpies of formation and of transformation which are summarized in Table I. In this table we have given also enthalpy data referred to the standard temperature of  $298^\circ$  K. These values have been calculated by use of published heat content information for the 6 substances involved. For quartz and corundum these data were taken from JANAF Thermochemical Tables (1960-65), while the values for the aluminum silicates are contained in the works of Pankratz and Kelley. The limits of error quoted in Table I are based on the procedure usually adopted in thermochemical work (square root of the sum of the squares). It will be noted that we estimate the errors associated with the polymorphic transformations to be somewhat smaller than those in the formation reactions. This is justified by the fact that the heats of

<sup>1</sup> Throughout the present section it will be noted that we quote experimental uncertainties which are larger than the indicated random error. This is due to the possibility of systematic errors for small heat effects. These errors arise from uncertainties associated with determination of the time of completion of the reaction period in the presence of small zero-drifts of the calorimeter system.

TABLE I. ENTHALPIES OF FORMATION AND OF TRANSFORMATION FOR INDICATED SOLID-SOLID REACTIONS

The following abbreviated symbols apply: Q=Quartz; C=Corundum; K=Kyanite; A=Andalusite; S=Sillimanite; M=Mullite.

Data in kcal/mole.

| Process | $\Delta H_{968}$  | $\Delta H_{298}$ |
|---------|-------------------|------------------|
| C+ Q=K  | $-2.37 \pm 0.15$  | -1.88            |
| C+ Q=A  | $-1.99 \pm 0.17$  | -1.34            |
| C+ Q=S  | $-1.51 \pm 0.15$  | -0.60            |
| 3C+2Q=M | $+5.44 \pm 0.35$  | +6.96            |
| K=A     | $+0.38 \pm 0.12$  | +0.54            |
| K=S     | $+0.86 \pm 0.10$  | +1.28            |
| A=S     | $+0.48 \pm 0.12$  | +0.74            |
| 3K=M+Q  | $+12.55 \pm 0.25$ | +12.60           |
| 3A=M+Q  | $+11.41 \pm 0.32$ | +10.98           |
| 3S=M+Q  | $+9.97 \pm 0.25$  | +8.76            |

transformation may be obtained directly from two heats of solution, while each formation value is based on three separate measurements.

#### DISCUSSION

It is well known that the structures of the four aluminum silicates exhibit important similarities (see, *e.g.*, Bragg and Claringbull, 1965). However, there are significant minor differences, to which the observed heats of formation may be related. These differences are illustrated schematically in Table II, which has been taken from a review by Buerger (1961). From this table we note that the main structural difference between the  $Al_2SiO_5$  polymorphs may be described as follows:

In all of these polymorphs one of the two aluminum atoms is in a 6-coordinated position with respect to oxygen. However, the second aluminum atom assumes 6-coordination in kyanite, 5-coordination in andalusite and 4-coordination in sillimanite. Thus, with respect to oxygen coordination, andalusite clearly is intermediate between sillimanite and

TABLE II. SOME RELATIONS AMONG THE STRUCTURES OF THE ALUMINUM SILICATES

| Mineral     | Composition                               | Structure   |
|-------------|---|---|
| Kyanite     | $Al_2SiO_5$                               | $Al^{VI}Al^{VI}Si^{IV}O_5$                            |
| Andalusite  | $Al_2SiO_5$                               | $Al^{VI}Al^{V}Si^{IV}O_5$                             |
| Sillimanite | $Al_2SiO_5$                               | $Al^{VI}Al^{IV}Si^{IV}O_5$                            |
| Mullite     | $Al_2 \frac{1}{4}Si_{3/4}O_4 \frac{7}{8}$ | $Al^{VI}[Al^{IV}_{11/4}Si^{IV}_{3/4}]O_4 \frac{7}{8}$ |

kyanite. Our own heat data show that andalusite similarly is intermediate with respect to the enthalpy of formation. It is interesting to note that the difference in heat of formation even between the two end members of the group (sillimanite and kyanite) does not amount to more than about 1 kcal/mole.

The mullite structure may be derived from that of sillimanite by distributing the tetrahedrally coordinated aluminum and silicon atoms over their formerly ordered positions (Table II). At the same time the composition is adjusted by adding  $1/4$  Al, while removing  $1/4$  Si, and also  $1/8$  O from the oxygen sub-lattice. The constancy of (Al+Si) has been proved by  $x$ -ray density calculations (Agrell and Smith (1960)). The difference in heat of formation between one mole of sillimanite and the structurally equivalent amount of mullite ( $\text{Al}_2\text{Si}_3/4\text{O}_4\text{7/8}$ ) is, according to the data given in Table I,  $(3/8) 5.44 + 1.51 = 3.55$  kcal at  $968^\circ\text{K}$ . For one mole of silicon and aluminum atoms this amounts to 14.2 kcal/mole. This value is very close to the difference in heat of formation between one half mole of  $\text{Al}_2\text{O}_3$  and one mole of  $\text{SiO}_2$ , which at  $1000^\circ\text{K}$  is  $-202 + 216 = +14$  kcal (JANAF, 1960-65). This comparison strongly suggests that the difference in heat of formation between sillimanite and mullite in the main may be attributed to the difference in bond energy between silicon-oxygen on the one hand and aluminum-oxygen on the other.

On the basis of low-temperature heat capacity measurements Pankratz *et al.* (1963) give a third law standard entropy of mullite of  $60.8 \pm 0.8$  cal/deg mole at  $298^\circ$ . In view of the structure of mullite reviewed above this value must be viewed with suspicion, since it makes no allowance for the configurational entropy associated with distributing the Al and Si atoms over the 4-coordinated lattice positions.

From measurements of the activity of silica in silicate melts in equilibrium with corundum and mullite Rein and Chipman (1965) have calculated the free energy of formation of mullite from the component oxides to be  $-5,600$  cal/mole at  $1823^\circ\text{K}$ . This is in reasonable agreement with the earlier value of  $-5,800$  cal/mole given by Kay and Taylor (1960) based on essentially the same equilibrium measurement. Stoichiometric mullite may not be the phase in equilibrium with corundum and the silicate melt at  $1823^\circ$ . On the other hand, the appearance of the  $\text{Al}_2\text{O}_3$  phase diagram suggests relatively small departures from the stoichiometric mullite composition at this temperature (see phase diagram by Aramaki and Roy, 1962). Therefore we have neglected this complication. Assuming that the free energy value of Rein and Chipman (1965) applies to  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and making use of the high-temperature heat content data of Pankratz *et al.* (1963) and our own heat of forma-

tion value, we calculate the standard entropy of mullite to be

$$S_{298}^{\circ} = 64.43 \text{ cal/deg mole.}$$

We estimate the uncertainty in this value to be of the order of  $\pm 0.5$  cal/deg mole. This result is in serious disagreement with that of Pankratz *et al.*

However, this discrepancy is readily understood if we take into account the entropy of Al-Si disorder. If all the tetrahedrally coordinated aluminum atoms mix randomly with all the silicon atoms this entropy contribution amounts to  $-(16/3)R[(5/8)\ln(5/8) + (3/8)\ln(3/8)] = 7.0$  cal/deg mole. This number clearly is too large. Much better agreement with our new entropy value is obtained if we assume a model for the mullite structure, which, in the short-hand notation of Table II is written  $Al^{VI}Al^{IV}[Al_{1/4}^{IV}Si_{3/4}^{IV}]O_{4 \ 7/8}$ . In the random mixing approximation this model gives a configurational entropy of  $-(8/3)R[(1/4)\ln(1/4) + (3/4)\ln(3/4)\ln 3/4] = 3.0$  cal/deg mole. While this model certainly is not literally correct, this result strongly suggests that the majority of the tetrahedrally coordinated aluminum atoms in the mullite structure do not in fact exchange randomly with the silicon atoms. This appears to be consistent with the most recent X-ray structural work on mullite which indicates the presence of characteristic weak super-structure reflections (see, *e.g.*, Agrell and Smith, 1960 and Burnham, 1964).

#### CALCULATION OF THE TEMPERATURE-PRESSURE DIAGRAMS FOR THE BINARY SYSTEM $Al_2O_3-SiO_2$

If we allow for the variation of composition this is a two-component system in the sense of thermodynamics. Thus the maximum number of degrees of freedom is 4. However, since there is no indication of solid solubility of  $Al_2O_3$  or  $SiO_2$  in  $Al_2SiO_5$ , the composition variable may be neglected as long as we confine our attention to the three polymorphs proper. An important consequence of this is that the appearance of the P-T diagram for the equilibria among kyanite, sillimanite and andalusite will not depend on the presence of surplus amounts of  $SiO_2$  or  $Al_2O_3$ .

On the other hand, as soon as we consider equilibria involving mullite, this situation will be changed. Therefore the P-T relations in the system  $Al_2O_3-SiO_2$  requires the construction of two related diagrams, one valid for surplus quartz and one for surplus corundum.

We mentioned by way of introduction the geological interest in the three polymorphs of  $Al_2SiO_5$ . Stimulated by this interest a number of investigators have attempted to locate experimentally the kyanite-sillimanite, kyanite-andalusite and andalusite-sillimanite univariant boundaries in the P-T field, as well as the kyanite-andalusite-sillimanite



non-variant point. However, due to the extreme sluggishness of these phase transformations, there is as yet no general agreement about the location of these boundaries.

The new heat data reported in the present work will permit us to calculate, from non-equilibrium data, the P-T diagrams for this system over a wide range of temperatures and pressures.

The sources of the data actually used in these calculations are summarized in Table III. The volume data for mullite, quartz and corundum were taken from Robie (1962), while the other references have been given above.

TABLE III. SUMMARY OF DATA USED IN CALCULATING THE P-T DIAGRAM FOR THE SYSTEM  $\text{Al}_2\text{O}_3\text{-SiO}_2$

| Type of Data          | $\text{Al}_2\text{SiO}_5$    | Mullite                       | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ |
|-----------------------|------------------------------|-------------------------------|----------------|-------------------------|
| Enthalpy of formation | This work                    | This work                     | —              | —                       |
| Enthalpy increments   | Pankratz and Kelley (1964)   | Pankratz <i>et al.</i> (1963) | JANAF          | JANAF                   |
| Entropy of formation  | Todd (1950)                  | This work                     | JANAF          | JANAF                   |
| Entropy increments    | Pankratz and Kelley (1964)   | Pankratz <i>et al.</i> (1963) | JANAF          | JANAF                   |
| Volume                | Skinner <i>et al.</i> (1961) | Robie (1962)                  | Robie (1962)   | Robie (1962)            |

At zero pressure the calculation of the co-existence temperature for two phases of identical composition was based on the well known relation

$$\Delta G = \Delta H - T\Delta S$$

For equilibrium, we have  $\Delta G = 0$  and  $T_{\text{eq}} = \Delta H / \Delta S$ . At higher pressures the equilibrium states were calculated by the use of the relation

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$$

In the use of this relation we should, in a rigorous calculation, allow for the possible dependence of  $\Delta V$  on pressure. However, for reactions involving dense, incompressible solids at moderate pressures, this correction will be negligible within the limits of error of the present calculations.

From the relation given above, we note that if experimental uncertainties in  $\Delta S$  are neglected, the possible error in our values for  $\Delta H$  gives rise to a proportional error in  $T_{\text{eq}}$ . The errors in the entropy data are believed to be small. They should not materially increase the uncertainties estimated below.

For kyanite-sillimanite, with an uncertainty in  $\Delta H$  of  $\pm 100$  cal/mole

(Table I), and an entropy of transformation of the order of 3 cal/deg mole (Todd (1960)), the uncertainty in  $T_{eq}$  amounts to about  $\pm 30^\circ$ . For kyanite-andalusite the uncertainty is about  $\pm 50^\circ$ , and for andalusite-sillimanite of the order of  $\pm 100$  to  $200^\circ$ . These larger uncertainties principally reflect the smaller values of  $\Delta S$  for these transformations.

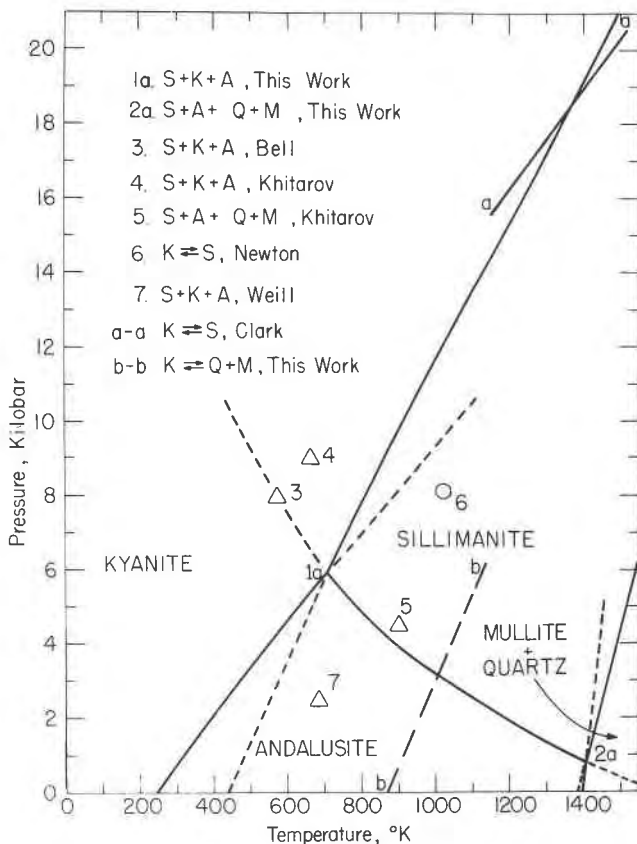
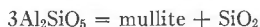


FIG. 1. P-T diagram for the system  $Al_2O_3-SiO_2$  in the presence of quartz calculated from thermodynamic data and compared with selected data obtained in high pressure-high temperature work.

The calculated P-T diagram for the  $Al_2O_3-SiO_2$  system in the presence of quartz is given in Fig. 1 along with some selected experimental data. Our diagram indicates that the non-variant point for the three polymorphs is at 705  $^\circ K$ . and 5.9 kilobar. We estimate, again largely on the basis of the uncertainties in the enthalpy data, the probable errors in these values to be  $\pm 65^\circ$  and  $\pm 1.0$  kilobar, respectively.

Our new heat data indicate that all the  $\text{Al}_2\text{SiO}_5$  polymorphs become unstable at elevated temperatures, and decompose according to the reactions



For sillimanite and andalusite this reaction should take place near  $1400^\circ\text{K}$  at atmospheric pressure, while for kyanite it should occur (metastably) near  $900^\circ\text{K}$ .

The appropriate P-T curves for these decompositions are indicated in Fig. 1. In drawing these curves we have assumed that mullite is a phase of fixed composition at all temperatures and pressures, thus neglecting the complications which arise from the possible departures from stoichiometry. Our data indicate a sillimanite-andalusite-mullite-silica non-variant point at about  $1410^\circ\text{K}$  and 0.8 kilobar. Note, however, that the mentioned rather large uncertainty in the calculated sillimanite-andalusite curve raises doubts about the location and even about the existence of this non-variant point.

Finally we present in Fig. 2 the corresponding calculated P-T diagram for the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system in the presence of surplus corundum. It will be noted that at atmospheric pressure mullite (+corundum) becomes unstable with respect to andalusite near  $1300^\circ$ , and with respect to sillimanite at a slightly lower temperature. Metastably mullite (+corundum) may transform to kyanite near  $900^\circ\text{K}$  and 1 bar.

#### COMPARISON WITH EQUILIBRIUM DATA

In the present discussion we shall refer in the main to the recent experimental investigations of Clark (1961), of Bell (1963) and of Kharitov *et al.* (1963). Clark determined the phase boundary for the sillimanite-kyanite equilibrium at temperatures from  $900$  to  $1500^\circ\text{C}$ . and from about 16 to 24 kilobar. We have included his results in Fig. 1 (line a-a). It will be noted that our own calculated curve crosses Clark's at about 18.5 kilobar and  $1375^\circ\text{K}$ . Within the uncertainty of Clark's data, and of our own calculation, the agreement is excellent. The slope of Clark's curve is 13.2 bars/degree. This slope is too low to be consistent with the available thermodynamic data, as pointed out by Newton (1966).

Using a shear squeezer Bell recently determined the kyanite-andalusite-sillimanite non-variant point to be  $300 \pm 50^\circ\text{C}$ . and  $8.0 \pm 0.5$  kilobar (1966). This is not far from our own calculated values. The separation between some of Bell's points, particularly at lower temperatures, is sufficiently large so that the phase boundaries could very well be drawn to give a non-variant point near  $325^\circ\text{C}$ . and 7 kilobar. This is illustrated in Fig. 3, in which Bell's points are plotted along with our calculated curves. This figure suggests a small systematic difference. However,

when the many uncertainties both in Bell's work and in our own are taken into account, the agreement must be considered to be quite good.

Khitarov *et al.* (1963) used a "simple squeezer" and reports sillimanite-kyanite and sillimanite-andalusite curves which lie somewhat above those calculated in the present work. Khitarov's kyanite-sillimanite curve

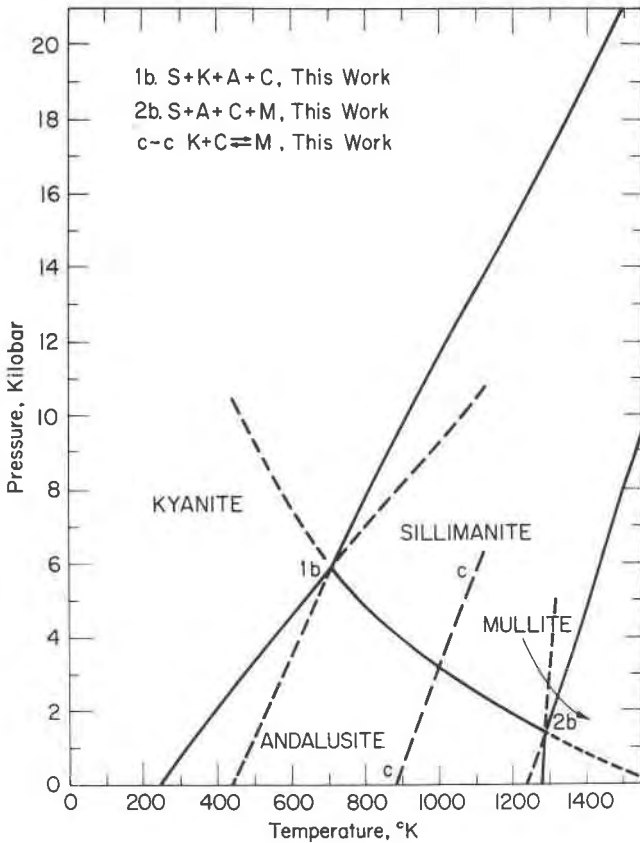


FIG. 2. P-T diagram for the system  $\text{Al}_2\text{O}_3\text{-SiO}_2$  in the presence of corundum calculated from thermodynamic data.

clearly has a too low slope ( $dP/dT$ ) to be consistent with Clark's data and with the Clausius-Clapeyron relation. His sillimanite-andalusite-mullite-quartz non-variant point is completely out of line in view of our thermodynamic data.

Very recently a single, carefully measured point on the sillimanite-kyanite curve has been determined hydrothermally by Newton (1966). His point,  $750^\circ\text{C}$ . and  $8.1 \pm 0.3$  kilobar, lies about 4 kilobar below our own calculated curve, and falls well outside the estimated limits of errors.

Finally it should be mentioned that occasionally all the three polymorphs of  $\text{Al}_2\text{SiO}_5$  may occur together in nature, as in the Pritchard formation in Idaho. According to Hietanen (1956), the geological conditions under which the three polymorphs are found together suggest a temperature of crystallization of about  $400^\circ\text{C}$ . This estimate, which is

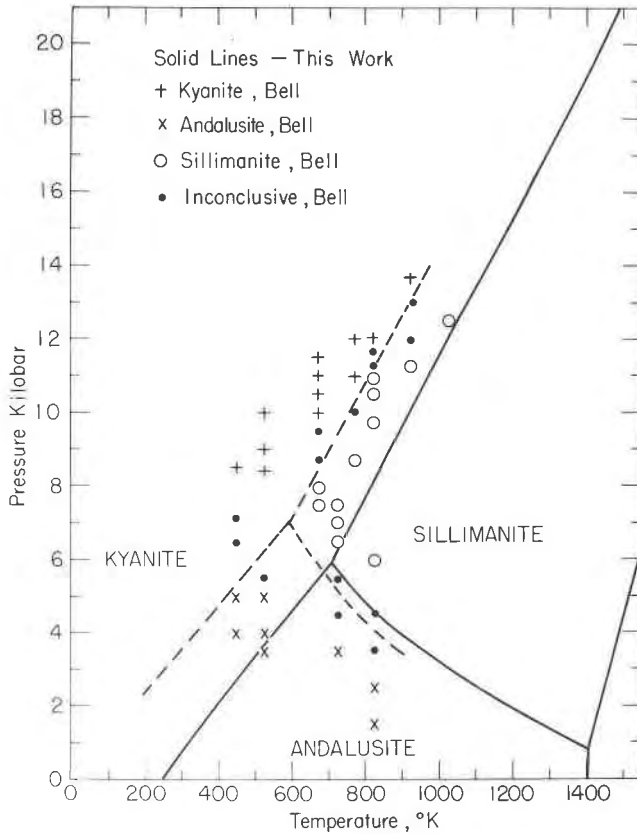


FIG. 3. Calculated P-T diagram for the system  $\text{Al}_2\text{O}_3\text{-SiO}_2$  compared with high pressure-high temperature data of Bell (1963).

based on the association on the three polymorphs with epidote and a plagioclase of composition  $\text{An}_{36}$ , is very consistent with our own calculated non-variant point temperature of  $430^\circ\text{C}$ .

#### POSTSCRIPT

After the present work had been completed and submitted for publication Weill (1966) has published a study of the stability relations in

the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system based on solubility measurements at 800 and 1000° C. By use of the Temkin (1945) model Weill calculates the activity of  $\text{SiO}_2$  in cryolite melts which are simultaneously saturated with corundum and  $\text{Al}_2\text{SiO}_5$  (or mullite). The activities in turn allow an evaluation of the Gibbs free energy changes associated with the phase transformations and a calculation of the P-T diagram.

Some of the details in Weill's calculation are open to question. For example, it seems very unlikely that  $\text{Na}^+$ ,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  will be statistically distributed over the cation sites in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{Na}_3\text{AlF}_6$  mixture as assumed in the Temkin model. On the other hand, Weill's calculation is relatively insensitive to the statistical model adopted. Generally his results confirm that the free energy changes associated with the polymorphic transformations at 800-1000° C. are indeed quite small, and his P-T diagram is similar in appearance to the one given above. However, according to Weill the field of stability of andalusite is significantly reduced compared to kyanite and sillimanite, and the kyanite-sillimanite-andalusite non-variant point is calculated to occur at about 410° C. and 2.4 kilobar. This point is shown in Fig. 1.

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