

Intercepts are listed in table 4 for these curves and for the flattest and steepest curves which could be drawn, using (1), without conflicting with any of the runs. The extreme curves bracket the uncertainties in the experimental location of the equilibrium curve, but there is an additional uncertainty of 3,000 bars in the intercept as discussed above. All of the curves are metastable below the kyanite-sillimanite-andalusite triple point.

The entropy change of the reaction at 25°C, computed from the slopes with  $\Delta V = 5.7 \text{ cm}^3/\text{mol}$ , is compared in table 4 with the  $\Delta S$  found by Todd (1950) from low-temperature heat capacities. The difference between Todd's value and those calculated from the curvilinear extrapolations are less than the estimated uncertainties. Linear extrapolation leads to a serious discrepancy.

#### FIELDS OF ANDALUSITE AND MULLITE

Other stable assemblages in this system are andalusite and mullite plus quartz, neither of which was synthesized under the conditions described here. Mullite is stable at zero pressure and high temperature (Eitel, 1954, p. 691); mullite plus quartz is converted to sillimanite at a pressure of about 5,000 bars at 600°C (Kennedy, 1955). At higher temperatures this reaction takes place at pressures which are assumed to be moderate but which are unknown. Work on this transition is in progress in this laboratory.

Data on the location and shape of the andalusite field are in conflict. Andalusite, kyanite, and sillimanite have been found together in nature, for example at Goat Mountain, Idaho (Heitanen, 1956). This suggests that a triple point exists at a pressure and temperature realized in the earth. Roy (1954) synthesized andalusite at pressures below 1,000 bars. The molar volume of sillimanite appears to be definitely smaller than that of andalusite (Taylor, 1928, 1929), and hence pressure favors sillimanite. If sillimanite is also the high-temperature phase, the equilibrium curve between andalusite and sillimanite has a negative slope; this is compatible both with the existence of a triple point and with Roy's observations. But heat capacity data (Kelley, 1949; Todd, 1950) suggest that the  $\Delta S$  of the reaction changes sign at about 100°C and that andalusite is the high-temperature phase above that temperature.

The  $\Delta S$  of the reaction sillimanite = andalusite is small, and we believe that the above data can best be reconciled by neglecting the measurements of heat capacity. On this assumption, a tentative phase diagram of the composition  $\text{Al}_2\text{SiO}_5$  has been constructed (fig. 3); the relation of the andalusite field to those of sillimanite and kyanite is qualitatively the same as that proposed by Miyashiro (1949) and Thompson (1955). The diagram is complicated by the intersection of the sillimanite-mullite plus quartz and andalusite-sillimanite equilibrium curves. The slopes of these curves are hypothetical, as are the locations of the triple points.

#### GEOLOGICAL APPLICATIONS

The chemical potential of water determines whether aluminosilicates can be formed in most rocks at low temperatures. Hydrous phases, rich in alumina, take their place in many cases (Thompson, 1955). Were the chemical potential of water to have its highest possible value, the assemblage andalusite plus

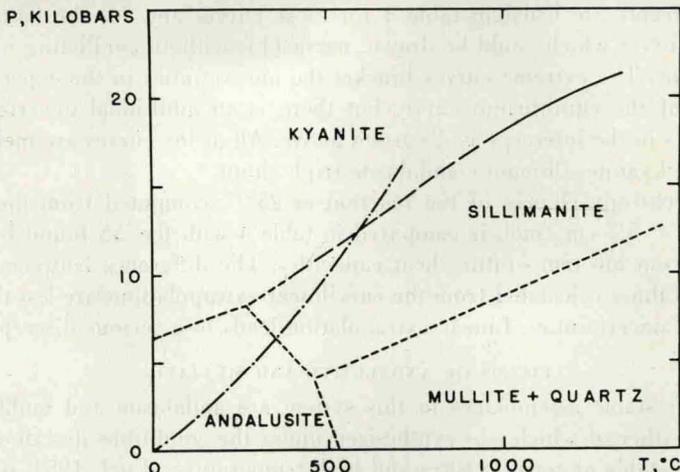


Fig. 3. Tentative phase diagram of the composition  $\text{Al}_2\text{SiO}_5$ . Phase boundaries indicated by short dashes are *not* experimentally determined, and no quantitative significance should be attached to them. The dot-dash curve indicates the *shape* of a typical geothermal gradient curve; its position has significance only at the origin.

quartz could not exist stably at pressures greater than a few hundred bars; pyrophyllite would appear in its place (Kennedy, 1955). We shall henceforth consider only cases in which either the temperature is sufficiently high or the chemical potential of water is sufficiently low so that one of the aluminosilicates may appear in the rock.

The stress mineral concept was introduced to account for the distribution in nature of kyanite, andalusite, and certain other minerals (Harker, 1939). The present work clearly demonstrates that kyanite can be formed in the absence of shear, but it is nevertheless a stress mineral in the sense that high pressures are necessary for its formation as a stable phase. The metastable prolongation of the steepest curve extrapolated by (1) intersects the pressure axis at 3,350 bars, and the stable boundary between the andalusite and kyanite fields must lie at higher pressures. Additional uncertainty in the extrapolated steepest curve is about 3,000 bars, but it is probable that kyanite is not stable under surface conditions.

A geothermal curve is superimposed on the phase diagram of the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  composition in figure 3. The gradient curve represents the pressures and temperatures that might be found in a vertical bore hole. In such a hole andalusite would be encountered in rocks of appropriate composition at shallow depths, and kyanite would appear at the greatest depths. Sillimanite would be found *above* kyanite if it appeared at all. This conclusion follows directly from the positive intercept of the kyanite-andalusite boundary; if the gradient curve is to enter the kyanite field at all, it must do so at elevated temperature and pressure.

Sillimanite-bearing rocks often occupy the central parts of regionally metamorphosed terrains, and kyanite occurs in rocks around the margin of the sillimanite zone. This spatial distribution of the aluminosilicates is observed