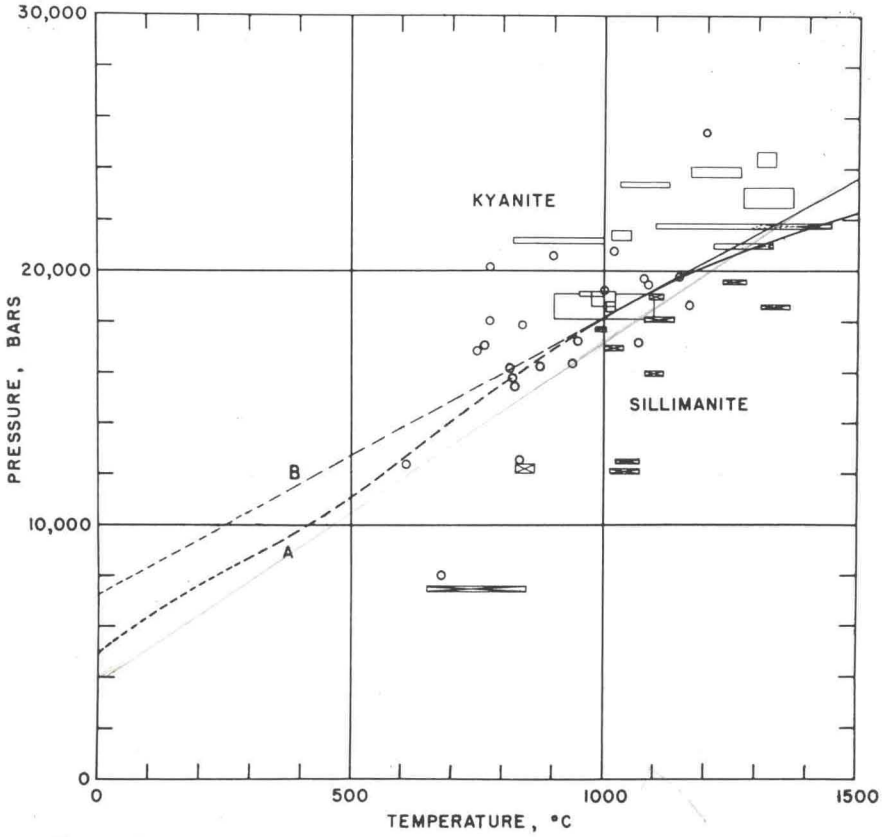

Fig. 2. Results of quenching experiments. Curve A is the "best" equilibrium curve. Curve B is a straight line extrapolation. Open boxes represent runs in which kyanite was produced, boxes with crosses represent runs in which sillimanite was produced, and circles represent runs which produced only quartz + corundum.

The synthetic crystals of sillimanite have the shape of stubby prisms, elongate parallel to the *c*-axis. Crystal outlines of the synthetic kyanite are less well-developed; it has the same mean index of refraction as natural kyanite (1.72). Crystals of both kyanite and sillimanite contain abundant inclusions of quartz and corundum.

RESULTS

The results of the quenching runs are given in table 2, and the positions of the runs are shown in figure 2. The uncertainties in pressure indicate the maximum fluctuation in pressure during the run. No uncertainty less than 100 bars is reported; although the precision of the pressure measurements is higher than this, uncertainties in the correction for the temperature of the coil and imperfect compensation for the effect of temperature on the resistance of the leads make this a more realistic estimate of the minimum uncertainty.

The uncertainties in temperature are determined by readings of the thermocouples at the ends of the capsules. The temperature recorded by each

thermocouple was averaged over the duration of the run, and the mean of the two readings was taken as the temperature of the run. The uncertainty is half the difference between the readings of the thermocouples. This is a generous estimate of the uncertainty in the temperature of the charge, for the metal capsule in which the charge is held tends to even out its temperature.

The uncertainties define a rectangle on the P-T plane, but the conditions of the run do not lie at a single point within it because of the thermal gradient and fluctuations in temperature during the run. It is incorrect to assume that the conditions of the run could be at either the high or low-temperature sides of the rectangles.

The most troublesome aspect of this investigation was the formation of quartz plus corundum. Runs in which these phases were the only products are shown as circles in figure 2; they formed from both andalusite and kaolinite. The assemblage persisted at high temperatures and was present in most of the runs in which kyanite or sillimanite was also formed. It was decidedly less abundant at the higher temperatures, however. Quartz and corundum were characteristically included in larger grains of kyanite or sillimanite; the converse relationship was not observed.

In the portion of the P-T plane where we were able to synthesize kyanite or sillimanite consistently, the assemblage quartz plus corundum seems clearly to be metastable. It is well-known that when kaolinite is dehydrated at low pressure, this assemblage appears as an intermediate stage in the reaction which eventually produces the stable assemblage, mullite plus quartz (Eitel, 1954, p. 1104, 1106). Since quartz and corundum occur as inclusions in aluminosilicate grains and become less abundant at high temperatures, where equilibrium should be most closely approached, it is inferred that the aluminosilicates grow at their expense. This is presumptive evidence that at high pressure the reaction proceeds in the same stepwise manner as the decomposition of kaolinite at low pressure. Both andalusite and kaolinite gave similar results.

It is perhaps less clear that quartz plus corundum is a metastable assemblage below 1000°C, but this is inferred from the stepwise nature of the reaction. Our failure to form kyanite or sillimanite consistently below 1000°C is interpreted as due to the slow rate at which early-formed quartz and corundum react at these temperatures. There is no way in which our runs can be separated into well-defined fields of aluminosilicates and quartz plus corundum; on the other hand the fields of kyanite and sillimanite can be cleanly separated. The stability of quartz plus corundum can only be established by demonstrating that they can be formed reversibly from kyanite and sillimanite. Lacking such evidence, and faced with ample evidence of the reluctance with which quartz and corundum combine, we regard them as metastable in all of our runs.

This conclusion is consistent with the thermochemical data on these minerals (table 3). From these data we estimate that if the heat of formation of sillimanite from the oxides is algebraically less than –500 to –1000 cal/mol, quartz plus corundum is a metastable assemblage under all of the conditions we have investigated. The uncertainty in this estimate is probably a few kilocalories per mole. Calorimetric determinations of the heat of formation of