

the equilibrium relations between mordenite, analcime, and albite remains confused. The nature of the starting material profoundly influences the product synthesized. Clearly, some other approach would be desirable.

Example 5: The system $\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SiO}_2 + \text{H}_2\text{O}$.—Coombs *et al.* (1959) used some dozen starting materials in runs of around 30 days' duration. A high-temperature dehydration reaction



was consistently found, but the reaction temperature varied by as much as 150° C., and the width of the wairakite field varied by as much as 80° C. Epistilbite, or calcium mordenite, depending on the reactivity of the initial mix, appeared in the low-temperature field. The common natural lime zeolites, laumontite and heulandite, failed to appear at all. It was found that in runs of a week's duration wairakite would form and persist at temperatures where anorthite and quartz would be produced if the runs were of a month's duration. Moreover, even in runs of a month's duration, cristobalite was present among some of the reaction products.

SYNTHESIS AT HIGHER TEMPERATURES

The situation is only partly improved at higher temperatures, even though reactions might be expected to proceed faster. In work involving synthesis of aluminum silicates and hydrates from the composition $\text{Al}_2\text{O}_3\text{-4SiO}_2$, Carr and Fyfe (in press) have found that three different starting materials produce three different fields of synthesis. The upper limit of pyrophyllite at 15,000 psi varies from 440 to 530° C., and the higher-temperature phase produced is either mullite, corundum, or an andalusite-like phase (all with quartz). From some starting materials pyrophyllite could be synthesized at temperatures where, with longer runs, synthetic pyrophyllite produced the andalusite-like phase. Other workers have also reported different products. In the low-pressure region Roy and Osborne (1954) report mullite as the decomposition product

of pyrophyllite; Kennedy (1955) reports a mullite-sillimanite solid solution; and Roy (1954) has synthesized andalusite.

Yoder and Eugster (1955) used seven starting materials for work on the reaction

$$\text{muscovite} \rightleftharpoons \text{sanidine} +$$

corundum + water.

At 15,000 psi water pressure, the upper limit of muscovite was found to vary from below 600° C. to above 650° C. This range of 50°+ may not appear large, but it is perhaps of the same order as the span of some facies or subfacies. The same writers' work on phlogopite (1954), where the stability limit of phlogopite is above 1,000° C., is not free from evidence of disequilibrium in synthetic results. Yoder and Eugster state that "great care had to be exercised in evaluating the data." In some runs, mixtures of phlogopite and its breakdown products were synthesized more than 300° C. below the evaluated upper stability limit.

SYNTHESIS AT HIGH PRESSURES

A number of synthetic studies have recently been carried out at pressures of more than 10,000 bars. In some (Robertson, Birch, and MacDonald, 1957) the experimental apparatus is basically similar to that used at lower pressures. Many other results have been obtained from the squeezer apparatus (Griggs and Kennedy, 1956). From experience with the alumina-water and silica systems, it might be expected that high pressures would facilitate attainment of equilibrium. However, in most systems considered, the desired transformation involves conversion of metastable low-density phases to stable high-density phases. It would seem likely that the nucleus of a dense phase would be smaller than that of a less-dense phase and that the ΔV^* of nucleation would be such as to favor metastable nucleation of dense phases at high pressures. As yet, there have been too few experiments described to come to any conclusions. The writer's limited experience with the squeezer-type apparatus has, however, indicated that the problem of starting materials may

be just as critical at 15,000 bars as at lower pressures.

Most workers in the very high P - T region have been able to demonstrate reversibility under the extreme conditions used. Often the region of reversibility is tied into a region at lower temperatures where normal synthesis is used. It should be stressed that the two sets of data should converge if the time factor is comparable, but this convergence does not necessarily prove that equilibrium was established in the synthesis at lower temperatures.

DIRECT MEASUREMENT OF VAPOR PRESSURE

There are few mineral systems where direct measurements of vapor pressure are possible, and these will be systems where rather limited chemical rearrangement is involved. More complex reactions tend to be sluggish, and there are difficulties associated with such measurements over prolonged times. This method is likely to prove superior to synthetic methods, at least for simple systems, when quenching becomes difficult. A system such as $\text{MgO-H}_2\text{O}$ is typical.

Direct measurements of the vapor pressures of brucite-periclase mixtures have been made by Giauque and Archibald (1937), Kennedy (1957), and Fyfe (1958). All were impressed by the sluggish attainment of equilibrium, attributed to either adsorption or aging of the crystalline products. This work has done much to indicate the importance of grain size on the position of an equilibrium boundary. Giauque (1949) has discussed this problem in detail. Curves C and D of figure 3 represent the findings of Kennedy and Fyfe. It will be noticed that, as expected, the equilibrium curves from direct measurements are at lower temperatures than all obtained by synthesis.

REVERSIBLE CONVERSION OF MINERAL PHASES AND DISAPPEARANCE OF PHASES FROM MIXTURES

If the equilibrium temperature of a reaction $A \rightleftharpoons B$ is to be determined at pressure P , a simple method, in principle, is to take

a mixture of A and B and find at what temperatures only A or B remains. The method is beset by formidable difficulties associated mainly with extreme slowness of reactions. This writer is convinced, however, that valuable and reliable results can be obtained if the experimenter is willing to make experiments of months and not days. Bowen and Tuttle (1949), who used minerals extensively as starting materials, illustrate the method in their study of the reaction



They succeeded in producing talc from the right-hand assemblage at 750° C. and 15,000 psi and produced enstatite + cristobalite from talc at 800° C. and 15,000 psi. The equilibrium temperature for the reaction must be above 750° C. and below 800° C.

Kennedy (1959) was able to show that, if sufficient time is allowed, a mixture of diaspore and boehmite produces diaspore in the region where boehmite tends to appear metastably. The writer has found that at 300° C. a mixture of albite + quartz + analcime produces only albite, while the same mixture at 250° C. is unchanged in runs of 3 months. The latter result provides no information, but the former provides as much useful information as scores of synthesis runs. If a mixture of A and B is used, results may be obtained in a reasonable time, which would not be obtained if A or B were left to recrystallize by themselves. An excellent example of the use of this method is provided by Tuttle and Bowen (1958) in their study of the quartz-tridymite equilibrium. If the mixture is used, the nucleation barrier is removed, and the course of crystallization depends on the different solubilities of the two phases, the stable phase having the lower solubility. The only barrier to reaction involves the transfer of material.

Much less complete, but at times useful, data relate to destruction of a mineral phase. This approach sets a maximum limit to the stability. Yoder and Eugster (1954) made extensive use of data on the decomposition