and growth again are effective. But for rapid reaction there must be some significant difference between the two curves, and significant supersaturation is necessary. This implies that transformation of $A(H_2O)$ to B, or vice versa, is likely to be a slow process near the equilibrium temperature. At large distances from this equilibrium temperature there is a much better chance of the stable phase forming. It would be fortuitous if the kinetic factors should so change at the equilibrium temperature that a true boundary of equilibrium could be obtained by such a synthesis; it is much more likely that one phase will appear over too wide a range. Ostwald's step rule, so commonly illustrated in synthesis, emphasizes this point.

port the principle. Unpublished data of the writer indicate that epidote is stable relative to its high-temperature breakdown products in much of the region studied by Ehlers (1953).

It should be noted that a fundamental difference exists between most studies of dry melts and those systems considered here. In dry-melt studies the common starting material is a homogeneous glass. The free-energy relations of this system would be similar to those indicated in figure 1 if the curve for $B + H_2O$ represents glass, and the curve for $A \cdot H_2O$ represents the solid phases. The important feature is that, near the melting point, the glass does not have the large "excess free energy" that is characteristic of the mix. Crystallization of met-

TABLE 1

FREE ENERGY OF FORMATION OF STABLE AND METASTABLE EQUIVA-
LENTS FROM TYPICAL STARTING MATERIALS AT 298° K

Reaction	$\Delta G°$ (kcal)	Ref.*
SiO_2 (glass)$\rightarrow SiO_2$ (cristobalite)	-1.2	a
SiO_2 (glass)$\rightarrow SiO_2$ (quartz)	-1.5	a
$CaO + SiO_2$ (glass)$\rightarrow CaSiO_3$ (wollastonite)	-22.9	a
$CaO + SiO_2$ (glass)$\rightarrow CaSiO_3$ (pseudowollastonite)	-22.1	a
$2MgO + 2SiO_2$ (glass)$\rightarrow 2MgSiO_3$	-21.98	a
$2MgO + 2SiO_2$ (glass)$\rightarrow Mg_2SiO_4 + SiO_2$ (quartz)	-19.5	b
$CaO + CO_2$ (gas)$\rightarrow CaCO_3$ (calcite)	-31.12	a
$CaO + CO_2$ (gas)$\rightarrow CaCO_3$ (aragonite)	-30.87	a

* References: (a) Rossini et al. (1952); (b) Fyfe et al. (1958) p. 23.

In table 1 free energies of formation of some phases from oxide mixes are shown. It will be noted that the free-energy differences between stable or metastable phases are normally trivial compared with the free energy of formation from the oxides. It is not surprising, for example, that aragonite can be easily grown where calcite is stable.

Goldsmith (1953) has stressed the relation between structure and ease of crystallization in his simplexity principle which suggests that phases with a large entropy will crystallize with greater ease than equivalent low-entropy phases. With some of the cases discussed by Goldsmith (e.g., jadeite), it is now known that failure to crystallize in early studies was due to experimental conditions being outside the fields of stability. But many cases (e.g., epidote) sup-

astable phases from the glass near the melting point is likely to be much less common, but it is not impossible. Further, all barriers dependent on transfer must be reduced at elevated temperatures.

STARTING MATERIALS IN SYNTHESIS

The master of chemical synthesis is the organic chemist, and perhaps the geologist has learned too little from his experience. In a typical issue of *Chemical Abstracts* there will be about twenty compounds listed with formula $C_4H_8O_2$. It is probable that an organic chemist could synthesize many of these at 1 atmosphere and the boiling point of alcohol, yet many will be metastable. The remarkable array of organic compounds results in part from the shrewd choice of arrangement of carbon atoms which the

chemist looks for in his starting materials. There are differences in the two problems, but perhaps some experimental geologists have been slow to realize that they can completely change the products of a synthesis by changing the type of starting materials.

What factors have commonly determined the choice of starting materials in experimental studies on mineral equilibria? There is little doubt that impatience and longevity are influential. Barrer (1950), while studying silicate synthesis, was one of the first to make extensive use of coprecipitated gels, and found that phases such as orthoclase (probably disordered) could be synthesized at temperatures below 200° C. in hours. With such materials crystallization of phases is readily achieved, but the chance of these phases being metastable is maximal. Unfortunately, the second stage, transformation of the metastable to the stable form, may be a much less facile reaction and require times of a different order of magnitude. Observation that A crystallized in 5 hours and remained unchanged for 5 weeks may appear at first glance strong evidence that A is already at the bottom of the energy well; but common experience indicates that this line of reasoning may be invalid (e.g., persistence of metastable cristobalite and boehmite and disordered feldspars).

In choosing starting materials for synthesis, there is clearly an impasse. The most reactive materials, while sometimes producing stable phases, are also likely to produce metastable phases. The most desirable materials are likely to be so low in free energy that they do not react in a reasonable time. There are, however, ways of bypassing this situation, which will be mentioned below.

In recent synthetic studies, it is becoming a common practice to employ a variety of starting materials of the same bulk composition. Inspection of the products from each may indicate that one material produces phases more compatible with petrological observation than the others and hence may be producing equilibrium products. How-

ever, such selection of the "best" results is unsatisfactory and only emphasizes the fundamental limitations of the synthetic method. To quote from careful work on muscovite by Yoder and Eugster (1955): "It should be clearly stated that considerable judgment on the part of the experimenters is involved in the interpretation of the results." In the same paper the statement "although it is common for minerals to grow metastably below their stability limit, metastable growth above their stability limits has not been observed" implies judgment with which this writer does not agree. The statement accords with the common synthesis of cristobalite in the quartz stability field and the failure of quartz to appear in the cristobalite field; but it conflicts with the equally common formation of aragonite in the calcite stability field. Working irrationally on the above assumption, the writer previously identified the maximum temperature at which analcime could be synthesized as the temperature of univariant equilibrium for the reaction, analcime + quartz $\leftrightarrows$ albite + water. Subsequent work on kinetics proved this judgment invalid. The low-temperature assemblage, analcime + quartz, grows in the region where the high-temperature phase albite is stable.

PROOF OF EQUILIBRIUM IN SYNTHESIS

An equilibrium boundary between two phases A and B exists only if A can be converted to B and B to A by infinitesimal changes in P or T from the values given by the boundary curve. In practice, reaction rates become appreciable only when P or T depart widely from the equilibrium value, if reaction is anticipated in short times of days or weeks.

Yoder and Eugster (1955) showed that the reaction

muscovite $\leftrightarrows$ sanidine + corundum + water

goes from left to right at 650° C. and from right to left at 350° C. at $P_{H_2O} = 15,000$ psi. The equilibrium boundary is between