

these values. In discussing the quartz-coesite boundary, MacDonald (1956) is careful to point out that "in order to demonstrate that this curve is actually the equilibrium curve, a detailed study should be made using coesite as a starting material and showing that coesite converts to quartz at pressures lower than those given by the curve." Another example, from Ervin and Osborne (1951), illustrates the point further. They state: "there is only one rigorous criterion for equilibrium . . . if while pressure and temperature remain constant, the crystals of one phase grow while crystals of a second phase disappear, then the first phase is stable with respect to the second." They continue: "therefore, this straightforward method fails, and the criterion set up for equilibrium is too rigorous for practical application in studies of this system." It is obvious that experimental workers are well aware that grave difficulties of this kind exist and in many instances have not yet been overcome. But the phase diagrams continue to be labeled erroneously as equilibrium diagrams with the added implication that the equilibrium is stable.

It is perhaps necessary to restate that an equilibrium boundary may correspond to metastable equilibrium. For example, *A* may be converted to *B* and vice versa, although there may exist a third phase *C* with lower free energy than either *A* or *B*. A phase or phase assemblage is in its stability field when the free energy of that phase or assemblage is lower than any equivalent phase or assemblage. Absolute proof that an assemblage is stable rather than metastable, and that a stability field is not a metastability field, is impossible (see Turner and Verhoogen [1960], p. 6-40). Excellent examples of metastable equilibria are demonstrated by Jamieson (1957) in his studies of the polymorphism of  $\text{CaCO}_3$  at high pressure.

*Example 1: Polymorphism of  $\text{SiO}_2$ .*—Consider crystallization of amorphous silica over a temperature range of 300°–600° C. at water pressures of 100 to 3,000 bars. There is a low-temperature region within which cris-

tobalite crystallizes and a high-temperature field of quartz. The position of the quartz-cristobalite boundary (F. W. Dickson, unpublished data) depends upon the duration of the experiment (e.g., in fig. 2, curve *A* might be the boundary for runs of 3 days, and curve *B* the boundary for runs of 3 weeks). If the sample is contaminated with alkali, quartz is formed in short experiments at low temperatures. Clearly, such results have little bearing on the stability relations of the polymorphs of silica; rather, they demonstrate the overshadowing influence of nucleation in determining which phases will crystallize in a given environment.

Kinetic studies (Carr and Fyfe, 1958) show that the progress of the reaction

amorphous silica  $\rightarrow$  cristobalite  $\rightarrow$

silica-K  $\rightarrow$  quartz

is relatively insensitive to temperature but sensitive to pressure. In the absence of catalysts, it may take months or years to convert cristobalite to quartz several hundred degrees below the upper stability limit of quartz.

In accounts of synthetic investigations of silicate systems, not infrequently cristobalite is listed as one of the constituent phases of so-called "equilibria," crystallized at temperatures within the stability field of quartz. Such data are immediately suspect as including assemblages known to be metastable.

*Example 2: The system  $\text{MgO-H}_2\text{O}$ .*—Although a half-dozen papers on the system  $\text{MgO-H}_2\text{O}$  have been published in the past nine years, the boundary between brucite and periclase has not been fixed with the precision merited by the accuracy now possible in control and measurement of pressure and temperature.

The first synthetic study was made by Bowen and Tuttle (1949), using the now familiar hydrothermal quenching apparatus. The starting materials used were brucite and periclase, so that equilibrium was approached from two directions. Their results, based on five experiments of two to three

hours' duration, are reproduced as curve *A* in figure 3.

Roy, Roy, and Osborne (1953) used the same technique as Bowen and Tuttle, starting with a variety of natural and synthetic samples of brucite and periclase. Their equilibrium curve (*B* of fig. 3) is nearly 300° C. below that of Bowen and Tuttle. It is apparent that in the work of Bowen and Tuttle, either brucite persisted far above its stability limit, or periclase that had formed in some runs reverted to brucite during quenching. From the experience of Roy *et al.*, the latter alternative seems the more likely. As they had maintained the water pressure throughout the whole experi-

ment, including the quenching, it is further possible that the temperatures of their boundary might also be too high. Roy and Roy (1957) reinvestigated the system using both temperature and pressure quenching (i.e., the pressure was dropped simultaneously with the temperature). Their runs were as long as 168 hours, and they concluded that the work of 1953 was little in error. However, in this writer's opinion, a difficulty remains in that phases assumed present during the experiment might not be preserved during quenching, for release of pressure during quenching would allow reversion of brucite to periclase. Hence phase identification is based on textural evidence.

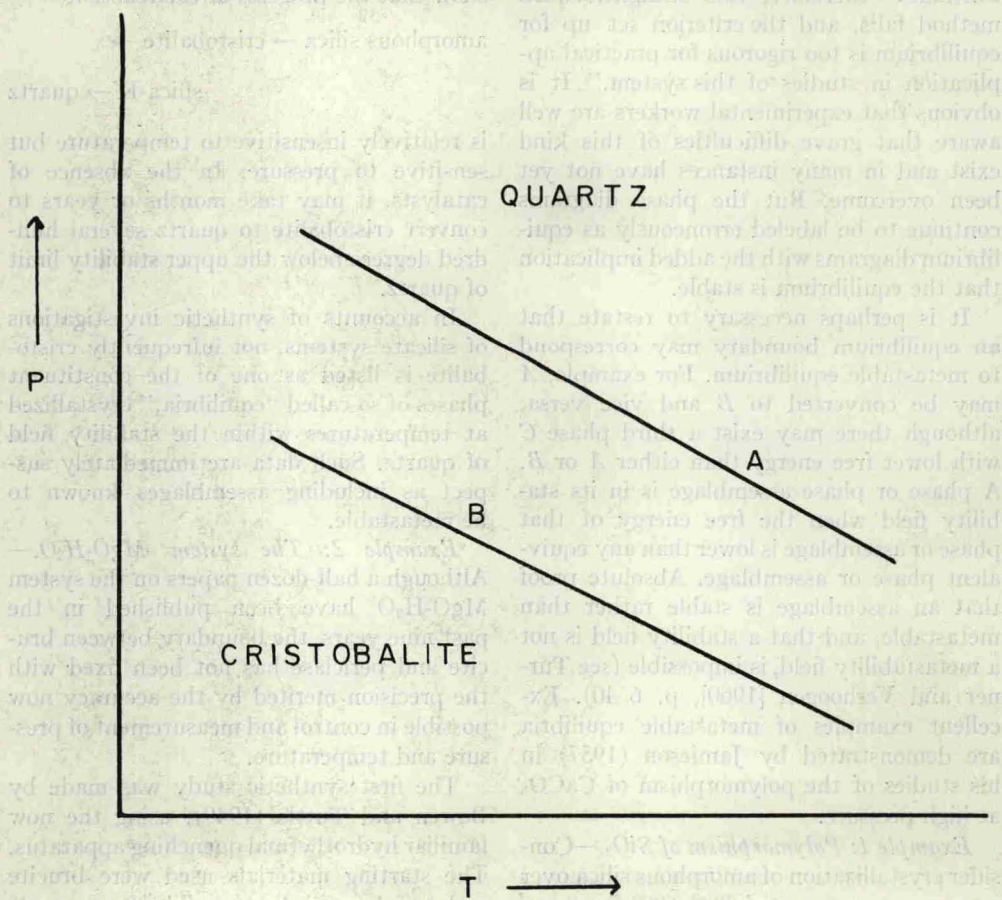


FIG. 2.—Phases synthesized from amorphous silica at low temperatures. Curve *A* might be that found when the experimental time is three days; curve *B* when this time is three weeks. Additional complexity due to regions where silica-*K* and tridymite may form are omitted.