



FIG. 3.—“Equilibrium” curves for the reaction brucite \rightarrow periclase + water. Curve *A* from Bowen and Tuttle (1949); *B* from Roy, Roy, and Osborne (1953); *C* from Fyfe (1958); *D* from Kennedy (1955); and *E* and *F* from thermodynamic calculations of MacDonald (1955). The differences in curves *E* and *F* are attributed to effect of particle size.

As will be discussed later, subsequent work by Kennedy (1956) and Fyfe (1958), using different methods, produced results indicating even lower "equilibrium" temperatures.

A major difficulty encountered in this system is due to speed of reaction. When reaction rates become comparable with feasible quenching rates, the synthetic method loses sharpness. Fortunately, this difficulty seldom arises. It probably applies mainly to reactions in two-component systems, such as oxide-water and oxide-carbon dioxide.

Example 3: The system $Al_2O_3-H_2O$.—In this system, extensively studied by Ervin and Osborne (1951), the difficulty is one of nucleation; it arose particularly with regard to equilibrium between diaspore and boehmite, polymorphs of $Al_2O_3 \cdot H_2O$. The writers were well aware that metastable crystallization was occurring, and the observations they made represent a reproducible phenomenon. Alumina gel and γ -alumina were used as starting materials, both being unstable species. To obtain reasonable results, it was found necessary to add seed crystals. In the majority of runs, only diaspore seeds were added, but in some, seeds of diaspore, boehmite, and corundum were used. As Ervin and Osborne emphasize: "the possibility of metastable growth under these conditions must be kept in mind." If seeds of only one phase are added, the experiment is prejudiced in favor of that phase. If seeds of several phases are added, in a short run the phase which dominantly forms will be controlled by rates of propagation of nuclei and growth.

In their equilibrium diagram Ervin and Osborne indicate a large stability field of boehmite. Subsequent work of Kennedy (1959), who had access to entropy data, presents convincing evidence that the phase boehmite is always metastable although this might be impossible to prove by direct synthesis. The conversion of boehmite to diaspore in the low-pressure region would take excessive time in the absence of diaspore seeds, but with long runs Kennedy was able to form diaspore from boehmite-diaspore mixtures in the region of boehmite synthesis.

Example 4: The system $NaAlSi_3O_8 + SiO_2 + H_2O$.—In this system, neglecting the high-pressure field of jadeite + quartz, only three phases are known to occur with free quartz, namely, albite, analcime, and sodium-mordenite. Reasoning purely from the respective water contents, we might expect that at low temperatures mordenite would be stable, followed by analcime and albite at high temperatures. What relations have been found experimentally?

Barrer and White (1952) studied the crystallization of highly reactive gels, which in some cases had been dried or thickened by evaporation so that in all probability they would contain nuclei. From the most siliceous composition Barrer found that at low temperatures analcime dominated; at 210° C. mordenite was the major phase, and this in turn passed to albite at 360° C. Some analcime was erratically scattered through reaction products dominated by mordenite. Fyfe (1955), using an oxide mix, found a low-temperature field of mordenite, which at 220° C. was succeeded by analcime which in turn passed to albite at 300° C. The analcime-albite boundary was diffuse; but for no good reason the upper limit of analcime was selected as the defining criterion. Barrer and Fyfe used short-run times.

Subsequently, more detailed work was reported in Coombs, Ellis, Fyfe, and Taylor (1959). A study of kinetics indicated that analcime was the phase tending to grow metastably in the albite field, and accordingly, the analcime-albite boundary was reduced to 280° C. in agreement with findings of Sand, Roy, and Osborne (1957). Coombs *et al.* found that with oxide mixes containing amorphous silica, mordenite again appeared as the stable phase up to 230° C. But when quartz was substituted for the more reactive amorphous silica, mordenite was not found at temperatures as low as 115° C., and analcime was synthesized. In mixes where sodium bicarbonate was used as the source of soda, mordenite was synthesized up to 275° C., above which albite became stable. Although one may attempt to explain these observations (cf. Coombs *et al.*), it is clear from this array of data that our understanding of