$Ca_{80} Mg_{20}$. The possibility of quenching through a two-phase field with the preservation of two phases was considered. A few runs were made in the present study in an effort to locate a two-phase field (see runs MC 102 at 960°C, MC 103 at 1050°C, and MC 104 at 1150° in table 3). The lower temperature runs produced a single magnesian calcite, but the run at 1150°C produced a sample that gave an X-ray diffraction pattern of a rather non-homogeneous magnesian calcite, indicating either a range of compositions or an ill-defined multiphase assemblage. This sample was visibly different from all the other runs in the system, with a texture strongly indicative of having crystallized from a melt. There seems little doubt that this sample as well as the 1150° runs of Goldsmith and Heard had melted. The subsequent rapid crystallization in a two-component system could account for the inhomogeneous or two-phase result, and one would expect somewhat different compositional results as a function of cooling rate. We have not been able to observe the existence of a two-calcite field in quenching experiments.

It will be shown in the next section that the calcite I $\rightleftharpoons$ II equilibrium in the pressure-temperature projection of the $MgCO_3$–saturated system must nearly coincide with the pure calcite I $\rightleftharpoons$ II transition because of the low differential solubility of $MgCO_3$ in the two phases. The approximate location of a two-calcite phase field may be sketched in the temperature-composition projection on this basis. The elevated pressures necessary to prevent carbonate decomposition in the higher temperature range will produce a lowering of the temperature of the calcite I $\rightleftharpoons$ II equilibrium according to our favored interpretation, assuming a first-order transition. The solvus would be intersected slightly below 900°, and the schematic relation is shown in figure 6.

Demonstration of equilibrium.—The unequivocal interpretation of the phase relations depends on a clear-cut demonstration of the attainment of equilibrium. Carbonates are in general more reactive than silicates, and solid solution equilibrium can be achieved in runs of hours' or days' duration at temperatures in the range 500 to 800°C. Some feeling for the time necessary to equilibrate $CaCO_3$–$MgCO_3$ solid solutions at 780°C in an unfluxed run is provided in the present study. A 2 kb cold seal run on unfluxed $Ca_{80}Mg_{20}$ mix at 780°C for 17 hr yielded a value of 14.6 mole percent $MgCO_3$ in the calcite. An unfluxed run at the same conditions for 63.5 hr yielded 15.4 mole percent. A fluxed run of the same duration yielded the same result. Fluxed runs in the piston-cylinder device at higher pressures for 1 day each were highly consistent with the longer cold-seal vessel runs. Hence there is a strong presumption of chemical equilibrium in the 780° runs. Similarily, Harker and Tuttle (1955) found that 8 hr at 800°C was not sufficient to give a final solid solution value but that 48 hr was long enough. The presence of Li_2CO_3 greatly shortens the time required. Some of the runs showed that equilibrium is attained in 3 hr or less at 780° in the presence of Li_2CO_3.

The calcite-aragonite and solvus curves were verified at 450°C, near the low end of the temperature span of the present investigation. A fluxed
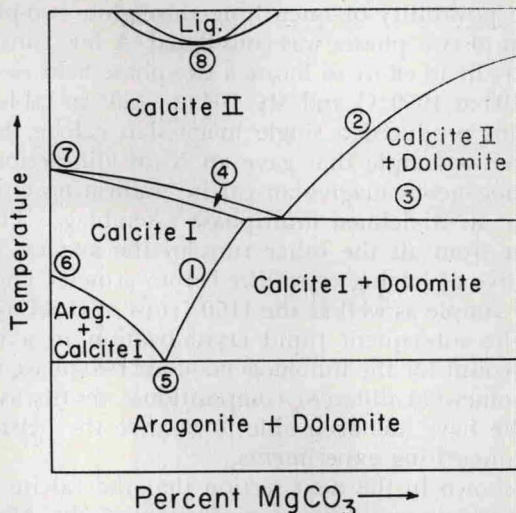
Fig. 7. Schematic isobaric section of the system $CaCO_3$–$MgCO_3$. See text for explanation of numbered curves and points.

run with a pure aragonite from Herrungrund, Hungary, and the Dover Plains, N.Y. dolomite made only 1 kb below the Mg-saturated calcite-aragonite boundary (run MC 45, table 3) reacted completely to yield a magnesian calcite at the identical composition deduced from the solvus runs. It is considered that this run demonstrates the equilibrium nature of the calcite-aragonite boundary deduced in the present study and indicates a high degree of confidence in the equilibrium nature of the solvus deduced. A similar reversal was made at 650°C with equally gratifying results (Run MC 95, table 3).

Summary of phase relations.—Figure 7 is a schematic isobaric phase diagram in the system $CaCO_3$–$MgCO_3$. Curves 1 and 2 are the solvus, above and below the calcite I $\rightleftharpoons$ II transformation, which is at the temperature of curve 3 at the pressure of this diagram. The field labeled 4 is the postulated two-phase field of calcite I and calcite II (see fig. 6), terminating at point 7, which is the value for the transition in pure $CaCO_3$. Point 5 is an invariant point and represents the intersection of the isobaric plane with the calcite I-aragonite -dolomite curve. The solvus is terminated at point 5 at this particular pressure by the formation of aragonite. Point 6 represents the temperature of the calcite-aragonite transformation in pure $CaCO_3$, or in other words, the equivalent of point 5 in the absence of $MgCO_3$. No field of solid solution of $MgCO_3$ in aragonite is indicated. The curves above point 8 represent a possible configuration for the melting relations suggested by the run at 1150°C. Inasmuch as pure $CaCO_3$ melts at about 1300°C at 10 kb, it is apparent that $MgCO_3$ lowers the melting temperatures, and assuming no decomposition, the melting loop is of the general form indicated.

Figure 8 is a true representation of the system at 1, 9, and 20 kb. The three isobaric sections are shown on the one diagram so that the relative