In the present investigation, the effects of the variables, temperature, total pressure, and composition, have been examined in those portions of the $CaCO_3$–$MgCO_3$ system that have the greatest petrological significance. A quantitative three-dimensional (P-T-X) view of the phase relations in the Ca-rich half of the system will be developed, and the petrologic implications will be considered.

EXPERIMENTAL METHODS

Apparatus.—Most of the present experiments were done by the "quenching" method in cold-seal vessels (Tuttle, 1949) and piston-cylinder apparatus (Boyd and England, 1960) using the 1 in.-diameter pressure vessel. Talc was used as a pressure medium in the majority of piston-cylinder runs. A graphite heater sleeve of 0.54 in.-inner diameter was immersed in the talc. Talc is useful up to above 800°C but loses water and plasticity above that temperature. A few runs at higher temperatures were made with an all-carbonate pressure medium assembly to avoid decomposition of the sample charge by water freed from the decomposition of talc as will be discussed shortly.

Encapsulation.—The sample charges were sealed in capsules welded from gold and, in a few runs, from platinum tubing. Gold is considerably less permeable to hydrogen than platinum and hence was preferable from the standpoint of carbonate decomposition problems resulting from small amounts of absorbed moisture in the talc pressure medium. The flattened welded capsules were 0.030 in. thick and $\frac{1}{8}$ in. long with the short dimension along the greatest temperature gradient. The capsules contained about two mg of sample, which was sufficient for analysis.

Temperature measurement and control.—Chromel-alumel or platinum-platinum 10 percent rhodium thermocouples were in contact with the sample capsules in the piston-cylinder arrangement. A 0.001 in. platinum foil separated the capsule and thermocouple to prevent any contamination effect by the gold on the thermocouple. Pt-Pt 10 percent Rh couples were used above 750°C. Temperatures were controlled automatically to $\pm$ 2°C by a Minneapolis-Honeywell Electronik-18 controller. Run durations ranged from a few minutes to a few days. At the end of a piston-cylinder run the samples were quenched to 100°C in a few seconds by turning off the heater current. A pressure correction for the emf of the thermocouples should be considered. Pt-Pt 10 percent Rh couples, which have the larger correction, were used in a few runs at 12 kb and temperatures to 1150°C. The largest correction that would be applied, according to the estimates of Hanneman and Strong (1965), would be about 15° and would not seriously affect the interpretation of any of the runs. Chromel-alumel has a smaller correction than Pt-Pt 10 percent Rh, according to Hanneman and Strong. No correction was made for pressure on the emf of the thermocouples.

Temperatures in the cold-seal runs at 2 kb were measured with exterior chromel-alumel couples placed a small fraction of an inch from the sample. The results of cold-seal runs were consistent with those of the piston-cylinder runs.

Pressure measurement.—Pressure measurement in a solid-pressure piston-cylinder apparatus requires some discussion in each individual application at the present state of technology. Most of the present runs were made in the following manner. First the desired nominal pressure was applied to the assembly. The true pressure at this stage will be somewhat less than nominal, owing to the "in-stroke" friction which is likely to be about 7 to 10 percent of the nominal pressure. Next the temperature was raised to the desired run value. The gauge measuring the oil pressure in the master ram always responded to heating with an immediate 10 to 15 bar (1-1.5 kb nominal sample pressure) rise. The immediate thermal expansion effect and the slower subsequent gauge rise due to gradual heating of the press were held at 15 bars. The increase of pressure due to thermal expansion was considered nearly to compensate for the frictional pressure loss, and no friction correction was applied. Thus the sample pressure is subject to an uncertainty of the order of $\pm$ 500 bars in absolute magnitude, and greater accuracy in locating the absolute pressures of the reaction curves of the present study cannot be claimed. The relative uncertainty among runs that are all made the same way should be considerably less than 500 bars, however. It is on the relative differences in pressure parameters that the interpretation of this paper is mainly based. The absolute pressure location of the present determination of the pure calcite-aragonite transition at 575°C agrees precisely with the gas-media apparatus point of Clark (1957), which should be a valid determination according to our interpretation and lends considerable support to the frictional compensation assumption.

In all the runs the solid pressure on the carbonate sample was greater than the decomposition CO_2 pressure at the temperature of the run. In an effectively plastic material decomposition does not occur under such circumstances (see for example Goldsmith and others, 1962).

Starting material.—Fine-grained precipitated $CaCO_3$ (calcite) and well crystallized anhydrous $MgCO_3$ were used as starting material in most of the present runs (Goldsmith and Heard, 1961). Intimate mixtures of the compositions $Ca_{95} Mg_5$, $Ca_{90} Mg_{10}$, $Ca_{80} Mg_{20}$, and $Ca_{70} Mg_{30}$ were used to determine the effect of pressure on the calcite-dolomite solvus and the effect of $MgCO_3$ on the calcite-aragonite transition. In addition, most of the charges contained a small amount (about 5 percent) of Li_2CO_3 flux. This substance was highly effective in promoting reaction, as shown by large crystal growth in fluxed runs, much better-equilibrated samples with sharper X-ray powder patterns from fluxed runs in a comparison series of runs made with and without flux, and ease of reversal of the main boundaries in the presence of flux. Li_2CO_3 has a 1-atm simple eutectic melting relation with $CaCO_3$ at 670° with little or no solid solution (Eitel and Skaliks, 1929). In runs much above 670°C the flux must have melted and dissolved significant amounts of $CaCO_3$ and $MgCO_3$. A simple phase rule analysis shows that magnesian calcite must have the same composition in equilibrium with dolomite whether or not a third phase capable of digesting $CaCO_3$ and $MgCO_3$ is present, as long