



Fig. 3. Plot of  $P_F = P_{\text{CO}_2} + P_{\text{CO}}$  against  $T$ , showing location of the experimentally determined univariant curve: siderite + hematite + magnetite + gas (SHMG). Dashed portions of the curve are extrapolated from runs made at 500 and 1000 bars. In each run symbol, upper box denotes behavior of the siderite sample, lower box denotes behavior of the buffer. Displacement of some run symbols vertically is for visibility only and does not indicate differences in run pressure. Runs near zero pressure were made at 30 psi  $\text{CO}_2$  pressure and do not locate a definite decomposition temperature.

An equilibrium temperature of  $363 \pm 10^\circ\text{C}$  is estimated on the basis of these two runs. The equilibrium temperature at  $P_F = 1000$  bars is bracketed by runs 49 ( $360^\circ\text{C}$ ) and 65 ( $370^\circ\text{C}$ ); the estimated equilibrium temperature is  $365 \pm 10^\circ\text{C}$ , indicating that the SHMG curve is virtually vertical between 500 and 1000 bars.

The equilibrium temperature for the SHMG curve at  $P_F = 2000$  bars was not definitely determined. Definite decomposition of the HM buffer to siderite was identified at temperatures below  $280^\circ\text{C}$  (table 2), but decomposition of siderite above this temperature could not be established clearly. Reactions were extremely sluggish at 2000 bars; several runs held for 5 weeks at about  $300^\circ\text{C}$  showed no detectable change in

either direction. In several runs at about 375°C, the HM buffer was completely reduced to magnetite during the experiment, while the siderite sample showed slight, but not significant, decomposition.

The reason for the anomalous behavior of the runs at 2000 bars is not definitely known. The high pressures may inhibit diffusion of gaseous reactants and products through the solid sample and buffer, thus producing a drastic reduction in reaction rates that are slow even at lower pressures. Such a kinetic explanation for the lack of reaction at 2000 bars is favored by the observed greater degree of reaction in both directions at lower pressures. Decomposition of the HM buffer to siderite appeared particularly favored by lower total pressures.

Small amounts of siderite, estimated generally at about 0.1 percent, were observed rarely in runs made above the equilibrium temperatures at 500 and 1000 bars, in which the siderite samples themselves showed definite decomposition. The small amounts of siderite in the buffers in these runs are not considered to represent stable formation of siderite at the run temperature. Such siderite could have formed: (1) during run-up of the bomb at temperatures within the stability field of siderite; (2) by contamination of the buffer by mechanical leakage of siderite from the sample. In these runs, decomposition of the siderite sample was regarded as the true indicator of reaction direction.

Siderite may, however, also develop metastably in the buffer. Since buffering results from diffusion of the fluid phase through the buffer, the portion of the buffer at the extreme ends of the tube will be exposed to the  $f_{O_2}$  of the bomb, which lies below that of the hematite-magnetite buffer (Eugster and Wones, 1962). At such lower  $f_{O_2}$  values, siderite is stable at higher temperatures (fig. 1) and could thus form in the buffer at temperatures above the true equilibrium temperature of the SHMG reaction. In all the experiments, however, nothing was observed to suggest that such formation of siderite did occur. No color boundary was observed in the buffer nor was there any apparent concentration of siderite at the ends of the sample tube.

Such metastable formation of siderite is illustrated by run 125 ( $P_F = 1000$  bars,  $T = 418^\circ\text{C}$ ). In this run, the siderite sample recrystallized into larger single crystals 5  $\mu\text{m}$  to 20  $\mu\text{m}$  in size; similar crystals of siderite are scattered through the buffer. Definite decomposition of the sample was indicated by a general red color and by the definite magnetism of the sample.

*The equilibrium: siderite + magnetite + graphite + gas (SMGrG).*

—The univariant equilibrium siderite + magnetite + graphite + gas (SMGrG) is defined by the intersection of three divariant surfaces: siderite + magnetite + gas (SMG); graphite + gas (the graphite buffer curve); and siderite + magnetite + graphite +  $O_2$  (SMGrG\*). The latter surface lies entirely within the condensed region below the graphite buffer (French and Eugster, 1965) and is only accessible at the univariant curve. Location of the univariant SMGrG curve was determined by the same