

Fig. 4. Plot of  $P_T = P_{\text{CO}_2} + P_{\text{CO}}$  against  $T$ , showing location of the experimentally determined univariant curve: siderite + magnetite + graphite + gas (SMGrG). In each run symbol, the upper box denotes behavior of the siderite sample, the lower box denotes behavior of the buffer. Slight vertical displacements of run symbols have been made for visibility and do not indicate differences in run pressure. The dashed portion of the curve is extrapolated. The runs near zero pressure were made at 30 psi  $\text{CO}_2$  pressure and do not indicate a definite equilibrium decomposition temperature.

run (French and Rosenberg, 1965). The temperatures at which a sudden increase in production of magnetite from siderite was observed are virtually identical to those determined by the open-tube method used in this study (fig. 6) (French and Rosenberg, 1965). This agreement between results obtained by two different experimental methods strengthens the conclusion that the temperatures obtained do correspond to the stable equilibrium temperatures for the isobaric invariant points for the equilibrium: siderite + magnetite + graphite + gas.

#### DISCUSSION OF EXPERIMENTAL RESULTS

*Buffering and metastability in a  $\text{CO}_2 + \text{CO}$  gas phase.*—Buffering in a  $\text{CO}_2 + \text{CO}$  atmosphere involves mechanical diffusion of gas species

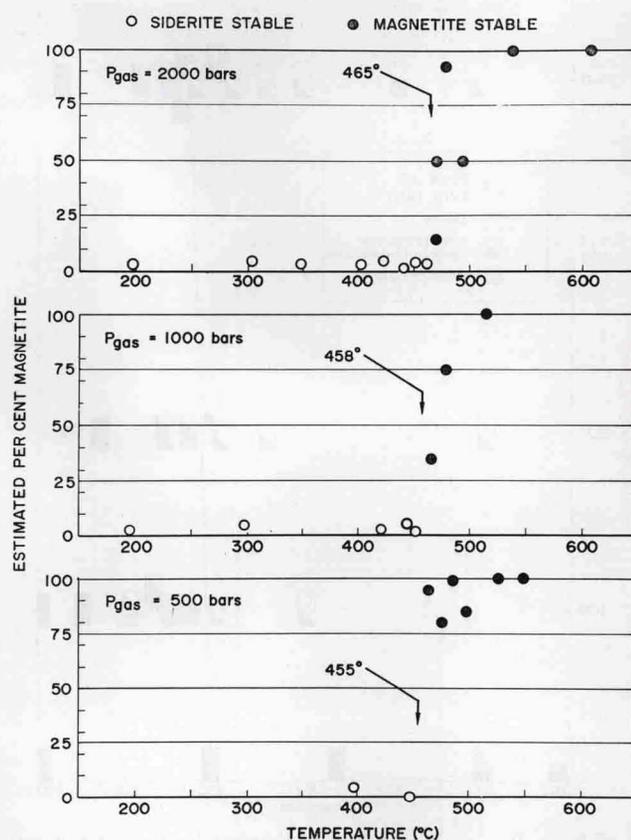


Fig. 5. Plot of estimated percentage of siderite sample decomposition as a function of temperature for runs used to locate the univariant curve: siderite + magnetite + graphite + gas (SMGrG). The equilibrium temperatures ( $455^\circ\text{--}465^\circ\text{C}$ ) are located by the sharp increase in decomposition with increasing temperature. Decomposition below this temperature is relatively constant and does not exceed 5 percent, but decomposition is virtually complete in several runs located above the equilibrium temperature and below  $500^\circ\text{C}$ .

through the solid buffer and requires that the necessary solid-gas equilibration reactions take place in times that are short compared to run duration (French and Eugster, 1965). If these conditions are not met at the reaction temperatures involved ( $300^\circ\text{--}500^\circ\text{C}$ ), then equilibrium will not be attained, and the determinations will not correspond to equilibrium siderite decomposition temperatures.

The problem of reaction and buffering by graphite is especially important. Considerable experimental evidence indicates that metastably low values of the  $\text{CO}_2/\text{CO}$  ratio may be preserved for significant periods, even at elevated temperatures, without precipitation of graphite (Muan, 1958; Bank and others, 1961; Bank and Verdurmen, 1963), although