



Fig. 6. Location of the univariant equilibrium: siderite + magnetite + graphite + gas, as determined by open-tube buffered runs (French, ms; rectangles) and by sealed-tube experiments (Rosenberg; circles) (from French and Rosenberg, 1965). The solid line indicates the univariant curve established from the open-tube buffered experiments; the sealed-tube experiments correspond virtually to the same curve. Stippled rectangles at left indicate the experimental uncertainty,  $\pm 7^{\circ}C$  in run temperature and  $\pm 5$  percent in total pressure.

there is little information about reaction rates at the high temperatures and pressures of the present experiments.

There is also little information about the rates of equilibration of  $CO_2 + CO$  atmospheres when graphite is present originally in the system. The reactions are sluggish and disequilibrium may persist for hours or even days at low temperatures. At higher temperatures, equilibration is attained or approached more quickly (Bradner and Urey, 1945; see also Mellor, 1924; Remy, 1956; for summaries), but catalysis may be required to promote reaction even at temperatures of  $500^{\circ}$  to  $600^{\circ}C$ .

It was not possible in the present study to measure directly the  $CO_2/CO$  ratio in the gas phase coexisting with the sample during a run, but indirect evidence indicates that the buffer assemblage does in fact control

the  $f_{O_2}$  value imposed on the sample (French, 1970). The experimental conditions, involving relatively high temperatures (300°-500°C), long reaction times (generally two weeks), and the presence of siderite, iron oxides, and an Ni-Co alloy reaction vessel as potential catalytic agents, offer optimum conditions for equilibration of the gas phase with the buffer. The following observations indicated that such buffering did in fact occur:

1. Complete reduction of the hematite-magnetite buffer to magnetite occurred during long runs near 400°C, indicating that extensive reaction does occur between the gas phase and buffer at these temperatures.

2. Distinctly different equilibrium decomposition temperatures are obtained, depending on whether the hematite-magnetite (HM) or magnetite-graphite (MGr) buffer assemblages are used.

3. Both hematite and magnetite are observed as decomposition products of siderite samples surrounded by a hematite-magnetite buffer.

4. In runs with the graphite buffer, graphite (or amorphous carbon) is observed to precipitate from the gas phase, indicating that metastably low  $CO_2/CO$  ratios are not maintained in the gas phase and that reaction between graphite and the gas does establish an equilibrium  $f_{O_2}$  (Rosenberg, 1963a; French and Rosenberg, 1965). A similar carbon phase occurs with magnetite in samples of siderite decomposed above the equilibrium temperature.

The temperatures determined for siderite decomposition are therefore believed to be equilibrium temperatures for the reactions indicated, a conclusion strengthened by the demonstration of reversibility at each equilibrium point. Reversibility was best demonstrated at the higher temperatures of the siderite + magnetite + graphite + gas curve, and these points are in good agreement with results from another experimental study which involved buffering by precipitated graphite (French and Rosenberg, 1965). Finally, the success of this buffering method and of the graphite buffer in particular has been well demonstrated in subsequent experimental studies, particularly in the determination of the rhodochrosite stability field (Huebner, 1969) and in investigations of complex metamorphic reactions involving C-H-O gas phases (Eugster and Skippen, 1968).

*Comparison with other investigators.*—Studies of siderite stability using hydrothermal techniques (Weidner and Tuttle, 1964; Weidner, ms; Johannes, 1968, 1969; Seguin, 1968) cannot be rigorously compared with the present investigations (for detailed discussion, see French, 1970, p. 31-35). In none of the studies was  $f_{O_2}$  explicitly controlled, and the values of  $f_{O_2}$  during the experiments are not known. Further, some investigations were carried out with a gas phase containing  $H_2O$  (Johannes, 1968, 1969; Seguin, 1968). In such cases, only the total pressures are specified, and the partial pressures of individual species, particularly  $CO_2$  and  $CO$ , are unknown.