

The experiments of Weidner (Weidner and Tuttle, 1964; Weidner, ms) are more comparable with the present study because they were performed in an atmosphere of $\text{CO}_2 + \text{CO}$, but they were carried out in sealed tubes without external buffers. In Weidner's experiments, the decomposition of siderite between 500 bars and 10 kb was used to locate two reactions: (1) siderite + hematite = magnetite + gas; (2) siderite = magnetite + graphite + gas. Ideally, these reactions should correspond, respectively, to the SHMG and SMGrG curves determined in the present study.

Decomposition temperatures determined in these experiments (Weidner and Tuttle, 1964; Weidner, ms) are significantly higher than those observed for analogous reactions in the present study (French, 1965; French and Rosenberg, 1965) (fig. 7). Because of slow reaction rates at lower temperatures and pressures, Weidner did not determine the SHMG curve below about 3 kb. Extrapolating his determined curve to the lower pressures attained in the present study (fig. 7) gives approximately similar decomposition temperatures, although the slopes of the two curves are

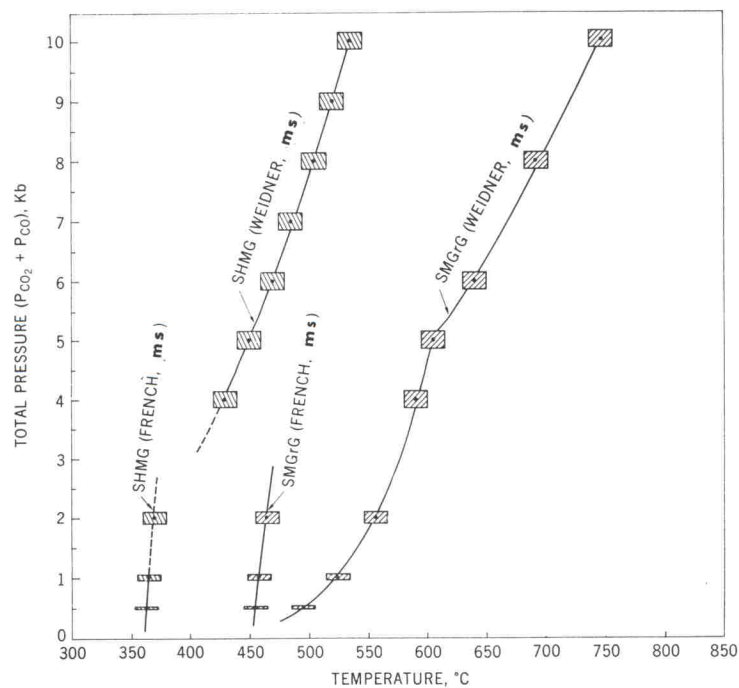


Fig. 7. Location of the two univariant curves: siderite + hematite + magnetite + gas (SHMG) and siderite + magnetite + graphite + gas (SMGrG) as determined by open-tube buffered experiments (French, ms) and by sealed-tube experiments (Weidner and Tuttle, 1964; Weidner, ms). The greatest discrepancy is for the SMGrG curve, for which Weidner's determined equilibrium temperatures below 2000 bars are 50° to 90°C higher than those determined here. The break in slope of Weidner's SMGrG curve has been interpreted as indicating a polymorphic transition in siderite (Weidner and Tuttle, 1964), but no corresponding break is evident in the SHMG curve.

distinctly different. The disagreement is more severe for the reaction: siderite + magnetite + graphite + gas (fig. 7). The temperatures determined by Weidner are from 60° to 90°C higher than those determined here.

The exact causes of the large temperature difference in the two investigations are not clear. Nor is it obvious why the results of Weidner's sealed-tube experiments also differ greatly from the apparently similar sealed-tube experiments of Rosenberg (French and Rosenberg, 1965).

The sealed-tube technique differs from the present experimental method in several ways that may affect the interpretation of the results (for details, see French, 1970):

1. There is no direct control of f_{O_2} , and it must be assumed that f_{O_2} is buffered during the run as the necessary phases are produced by reaction. However, the decomposition of siderite to magnetite or hematite produces a gas phase with high contents of CO which correspond to f_{O_2} values that are metastably low with respect to the graphite buffer (French and Eugster, 1965; French, 1970). At metastably low values of f_{O_2} , the decomposition of siderite to magnetite will take place at temperatures above the true equilibrium temperature (see fig. 1).

2. The reactions are not reversed, and only the decomposition of siderite is used to locate the equilibrium temperature.

3. Compaction of the sample tube and charge occurs during pressurization. This effect may reduce reaction rates by restricting the removal of volatile products produced in the solid sample. Further, during run-up, part of the external pressure is supported by the solid sample. These effects produce a complex and uncertain pressure-temperature history in the sample until sufficient decomposition has occurred to equalize the internal and external gas pressures.

4. Decomposition of the sample during run-up is necessary to produce internal gas pressure in the sample tube. The potential presence of decomposition products in *all* runs makes it difficult to recognize the true equilibrium temperature from the amount of sample decomposition. The estimated equilibrium temperature is thus a function of the value chosen for the amount of sample decomposition during run-up (French and Rosenberg, 1965), and, if this value is too high, the resulting equilibrium temperatures determined will also be too high.

It is believed that the open-tube buffered methods used in the present study (French, 1965; French and Eugster, 1965; French and Rosenberg, 1965) are superior to the sealed-tube technique for determining the stability relations of carbonates which involve oxidation reactions. The open-tube method permits direct calculation and control of f_{O_2} . Further, the open tubes minimize any kinetic problems that may arise from sample compaction and also allow extensive equilibration and reaction by mechanical diffusion of the gas phase through the charge. Most importantly, using the open-tube method, sample decomposition below the equilibrium temperature is negligible, and the true decomposition temperatures