

culated for these reactions from the relation:  $f_i = \gamma_i P_i$ , using fugacity coefficient data tabulated by Robie (1962). The results of such calculations for  $P_F = 2000$  bars are shown in figure 1 with the curves for several specified oxygen buffer assemblages.

The calculated stability field of siderite thus obtained is a narrow wedge bounded by reactions (3), (4), and (7), with stable decompositions to hematite, to magnetite, and (below the graphite buffer curve) to magnetite + graphite. In a  $\text{CO}_2 + \text{CO}$  atmosphere, the breakdown of siderite to iron (reaction 6) lies in the condensed area below the graphite buffer curve where  $\text{CO}_2$  and  $\text{CO}$  do not exist (French and Eugster, 1965). The reaction is therefore metastable, and the siderite stability field is thus much smaller than those presented by Holland (1959) and Garrels (1960). The breakdown of siderite to wüstite is also metastable, in agreement with the calculations of Muan (1958) for 1 atm total pressure. The stability field of siderite does not intersect that of fayalite ( $\text{Fe}_2\text{SiO}_4$ ), the upper limit of which is bounded by the quartz + fayalite + magnetite (QFM) buffer curve (fig. 1). Reaction between siderite and quartz to produce fayalite is not stable at these pressures (French and Eugster, 1962; French, ms).

The system Fe-C-O contains three components; from the Phase Rule,  $F = 5 - P$ . Reactions (3) and (4), in which two solid phases are in equilibrium with a gas phase, are therefore divariant reaction surfaces in  $P_F$ - $f_{\text{O}_2}$ - $T$  space. Reaction (7), in which three solid phases and a gas coexist, is univariant and lies entirely within the region of the diagram

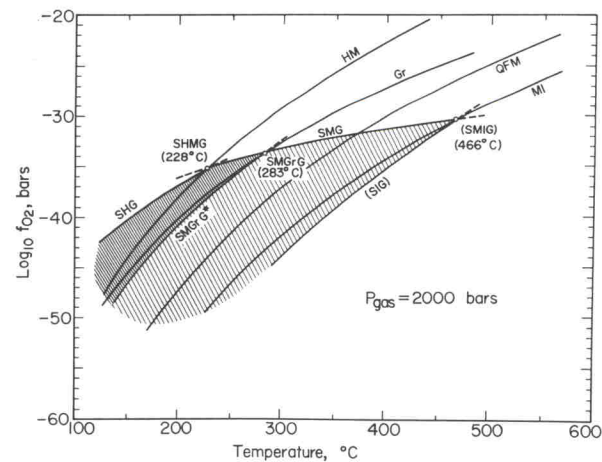


Fig. 1. Isobaric section at  $P_F = 2000$  bars, showing siderite stability relations calculated from thermodynamic data. The stable field of siderite (narrow ruling) is bounded by decomposition reactions to hematite (SHG), magnetite (SMG), and magnetite + graphite (SMGrG\*). The latter reaction lies entirely in the condensed region below the graphite buffer (Gr). Because of the reactions involving graphite, this field is much smaller than that calculated using reactions not involving graphite (wide ruling) (Holland, 1959; Garrels, 1960). Other solid lines (HM, Gr, QFM, and MI) designate solid-phase oxygen buffers.

where  $P_F = P_{O_2}$  (French and Eugster, 1965). The metastable reaction of siderite to iron + graphite +  $O_2$  (reaction 8) also lies in this region and is similarly univariant.

We may imagine addition of an inert ideal gas to the condensed region in such a manner that the value of  $P_F$  below the graphite buffer curve is always kept equal to the value of  $P_F = P_{CO_2} + P_{CO}$  above it. Under these conditions, the region below the graphite buffer curve is a four-component system Fe-C-O-gas, and the four-phase assemblage becomes a divariant surface in  $P_F$ - $P_{O_2}$ - $T$  space. The surface will have an orientation similar to that of other buffering assemblages (Eugster and Wones, 1962).

With this reservation, reaction (7) likewise becomes a divariant reaction surface in  $P_F$ - $P_{O_2}$ - $T$  space. The three divariant surfaces of reactions (3), (4), and (7) intersect in two univariant curves. The curve siderite + hematite + magnetite + gas (SHMG) is fixed by the intersection of reactions (3) and (4) with the hematite-magnetite (HM) buffer. The curve: siderite + magnetite + graphite + gas (SMGrG) is the mutual intersection of reactions (4) and (7) with the graphite buffer surface. This latter univariant curve is the only part of the surface of reaction (7) that is experimentally accessible. These univariant curves appear in figure 1 as isobaric invariant points, SHMG at 228°C and SMGrG at 283°C. (A third intersection, corresponding to a univariant curve for the equilibrium siderite + hematite + graphite + gas, is theoretically possible but appears to be metastable under reasonable experimental conditions.)

In the system Fe-C-O, assuming that a gas phase is always present, five phases (four solids plus gas) must coexist at a true invariant point. The point: siderite + magnetite + wüstite + iron + gas is apparently metastable, since it requires a minimum temperature of 560°C. It is uncertain if the equilibrium: siderite + hematite + magnetite + graphite + gas is metastable, or whether it is stable at temperatures too low to be meaningful or experimentally accessible (see French and Eugster, 1965).

The thermodynamic calculations are useful in predicting approximate stability relations in advance of actual experimental work. However, uncertainties in the thermodynamic data produce large uncertainties in calculated equilibrium temperatures of the invariant points. Calculations for the equilibrium point: siderite + hematite + magnetite + gas (SHMG) give *minimum* uncertainties of  $\pm 50^\circ\text{C}$  at  $P_F = 1$  bar and  $\pm 90^\circ\text{C}$  at  $P_F = 2000$  bars (for details, see French, 1970, p. 9-10). Under these conditions, significant discrepancies between calculated and experimentally determined equilibrium temperatures may reasonably be expected.

#### EXPERIMENTAL METHODS

In high-pressure hydrothermal studies of oxidation-reduction reactions, control of  $f_{O_2}$  is attained by surrounding the sample with an "oxygen buffer" consisting of one or more solid phases whose presence fixes the oxygen fugacity for any given temperature and total pressure (Eugster,