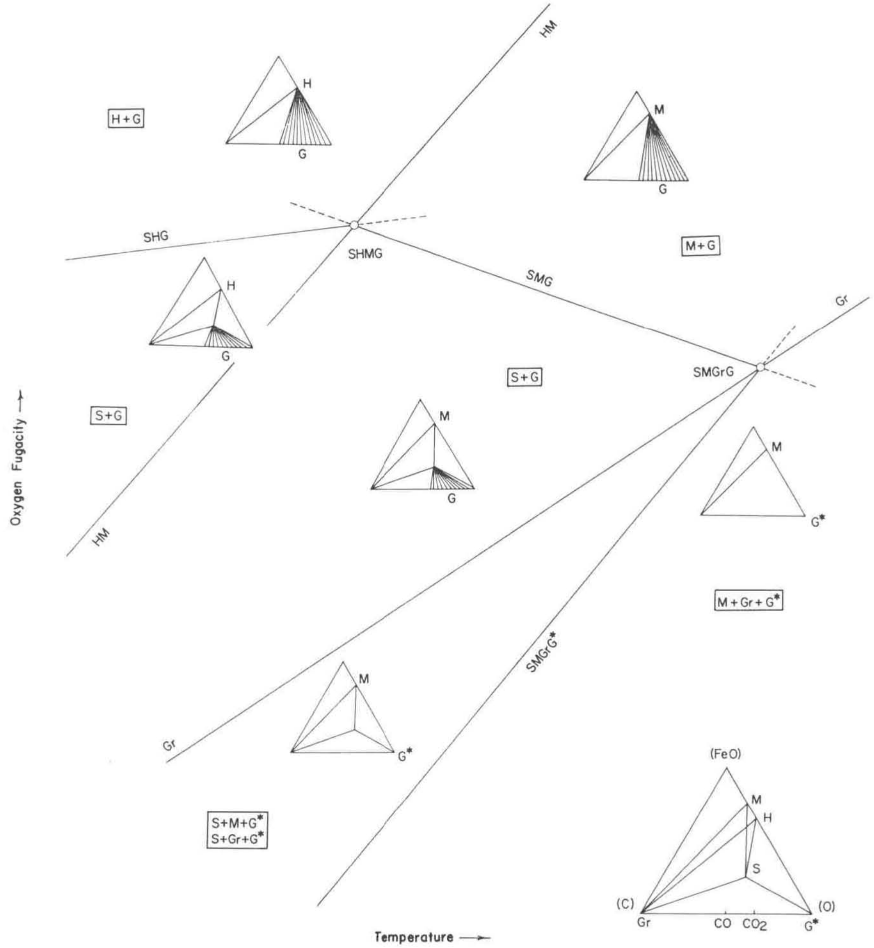

Fig. 10. Schematic isobaric section through the system Fe–C–O, showing stable assemblages as a function of log f_{O_2} and T. All solid phases coexist with a gas phase. Stable univariant equilibria are shown by solid lines; metastable extensions are dashed. Boxes indicate assemblages stable in each region. Above the graphite buffer curve (Gr), $P_F = P_{CO_2} + P_{CO}$, the gas phase is variable in composition, and an assemblage of one solid + gas is divariant. Below the graphite buffer curve, $P_F = P_{O_2}$, and two solids + gas form a divariant assemblage.

f_{O_2}, and most of the siderite + gas field occupies an area between 10^{-24} and 10^{-30} bars. The quartz–fayalite–magnetite buffer curve, which is the upper limit of stability of fayalite (Fe_2SiO_4), lies entirely in the condensed region below the graphite buffer curve over the entire temperature range for which siderite is stable (Eugster and Wones, 1962; French and Eugster, 1965). Accordingly, the stability fields of siderite + gas and of fayalite

+ gas do not intersect, and the possible reaction of siderite + quartz to form fayalite is not stable.[2]

Changes in the value of P_{CO_2} appear to have only a slight effect on the stability of siderite between 500 and 2000 bars; the equilibrium temperatures of the two univariant curves vary less than 10°C in that interval. By contrast, siderite stability is strongly affected by changes in the value of log f_{O_2}. For example, at 500 bars, a change in log f_{O_2} of 1.0 will change the equilibrium temperature of the assemblage siderite + magnetite + gas by more than 50°C. This effect is more striking at higher total pressures, where the SMG curve becomes flatter. Small changes in f_{O_2} will produce similarly large temperature variations in the assemblage, siderite + hematite + gas.

The isobaric sections demonstrate that, regardless of total pressure, an increase in f_{O_2} at constant temperature favors the decomposition of siderite to hematite or magnetite. The attitude of the SHG surface indicates that a temperature increase at constant P_F and f_{O_2} promotes the formation of siderite from hematite. However, because of the negative slope of the SMG curve at constant P_F, an increase in temperature under the same conditions will promote decomposition of siderite to magnetite.

COMPARISON OF EXPERIMENTAL RESULTS WITH THERMODYNAMIC CALCULATIONS

The experimentally determined univariant curves generally lie about 150°C above curves calculated from thermodynamic data (table 4). The experimental curves have considerably steeper slopes (higher values of dP_F/dT) than do their calculated counterparts. This difference may reflect in part the uncertainty in the equilibrium temperature. When the curves are steep, small uncertainties in the temperature determinations produce disproportionate uncertainties in the calculated slopes (see Burnham and Jahns, 1962, fig. 7).

Because all the experimentally determined isobaric invariant points lie on the divariant reaction surface: siderite + magnetite + gas, the experimental data may be used to calculate values of $\Delta H°$ and $\Delta G°$ for the decomposition of siderite to magnetite (eq 4) by computing values for

$$\log K_4 = 3 \log f_{CO_2} - \tfrac{1}{2} \log f_{O_2} \qquad (4)$$

and applying the relationships:

$$\Delta H° = -2.303R(d \log K/d(1/T)) \qquad (15)$$

$$\Delta G° = -2.303R\,T \log K. \qquad (16)$$

In theory, such experimentally determined values of $\Delta H°$ and $\Delta G°$ would allow a more accurate determination of the values of $\Delta H°_{f,T}$ and $\Delta G°_{f,T}$

[2] Recently redetermined values for f_{O_2} along the quartz–fayalite–magnetite buffer (Wones and Gilbert, 1969) are slightly more positive than those used here (Eugster and Wones, 1962). These new values extend the fayalite stability field to slightly higher f_{O_2} values and bring it closer to the siderite stability field (see fig. 1). However, calculations based on the new data do not indicate that there is any intersection or overlap of the two fields.