THE STABILITY OF GRAPHITE IN THE SYSTEM C-O.

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On the basis of the CCO-buffer equation (graphite-CO_2-CO-O_2) from French and Eugster (1965) :

$$\log fO_2 \; = \; - \frac{20586}{T} - 0.044 + \log P - \frac{0.028(P-1)}{T} \quad \text{for atm and K} \quad (1)$$

the stability of graphite can be calculated in the system C-O. The derivation of this equation was, however, based on the assumption that:

$$\log fCO_2 \; = \; \log P_{gas}$$
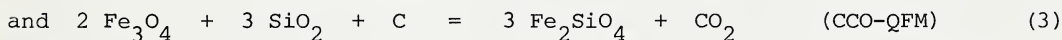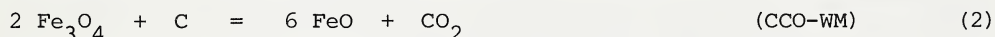
which also means that their assumptions were :

1) $\quad P_{CO_2} \; = \; P_{total} \;$ and $\; P_{CO} \; = \; 0,$

and 2) $\quad fCO_2 \; = \; P_{CO_2} \;$ (or that CO_2 is an ideal gas)

Recent experiments on PVT relations of CO_2 (Shmulovich and Shmonov (1975) and Holloway (1976)) however indicate a significant pressure dependence of the fugacity coefficient of carbon dioxide. Therefore it seemed desirable to determine the oxygen fugacity of the CCO-buffer experimentally.

Redox equilibria of the CCO-assemblage werde studied under controlled oxygen fugacities of the QFM- (quartz-fayalite-magnetite) and WM-(wüstite-magnetite) buffers respectively in the temperature range 800-1200°C and pressures up to 30 kbar.

Experiments were carried out to study the monovariant equilibria :

$$2 \; Fe_3O_4 \; + \; C \; = \; 6 \; FeO \; + \; CO_2 \qquad\qquad\qquad \text{(CCO-WM)} \qquad (2)$$

and $2 \; Fe_3O_4 \; + \; 3 \; SiO_2 \; + \; C \; = \; 3 \; Fe_2SiO_4 \; + \; CO_2 \qquad$ (CCO-QFM) $\qquad$ (3)

CO_2 was introduced in the form of $FeCO_3$ or $Ag(COO)_2$, both of which decomposed under the conditions of the experiment with liberation of CO_2.

Assuming that neither carbon is introduced into wüstite, magnetite, quartz or fayalite, nor iron into graphite or the carbon oxide species it appeared to be unnecessary to separate the buffer assemblages by membranes. The reagents were thus intimately mixed. The samples were welded in silver-palladium or platinum capsules and reacted in a piston cylinder apparatus. The run products were investigated microscopically and by X-ray diffractometry.

The results (figure 1) plot between theoretical estimates, assuming

1) ideal gas behavior after equation (1) (French and Eugster(1965)) (= "b")
and 2) real gas behavior of CO_2, applying a modified equation after Redlich and Kwong (Holloway(1976)) (= "c").

By least squares fit the present data for the CCO equilibrium may be expressed by :

$$\log fO_2 = 2.74 - \frac{19559}{T} + \frac{0.13\ (P-1)}{T} \quad \text{in bar and K, for } 5 < P < 30 \text{ kbar.}$$
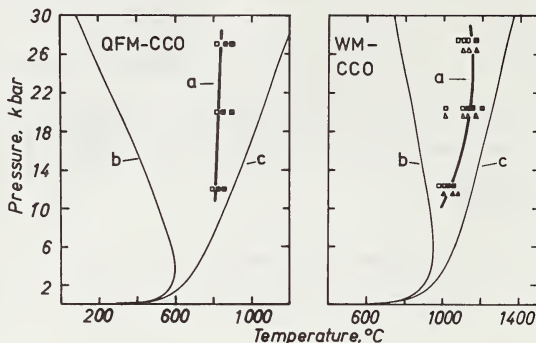

Figure 1.

Monovariant equilibria QFM-CCO and WM-CCO.

"a" = experimental results.
"b" = theoretical estimates assuming ideal gas behavior after equation (1), (French and Eugster,(1965)).
"c" = theoretical estimates assuming real gas behavior of CO_2 applying a modified equation after Redlich and Kwong "MRK". (Holloway,(1976)).

References :

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