

## Experimental Control of Oxygen Fugacities by Graphite-Gas Equilibria

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**Abstract.** Control of oxygen fugacities in a  $\text{CO}_2 + \text{CO}$  atmosphere has been established experimentally by using a solid-phase buffer technique. Equilibration between the buffer and the enclosed sample is established by diffusion of the gas atmosphere through the buffer. The establishment of equilibrium by this method is indicated by the reversibility of experimental results in a study of the decomposition relations of siderite,  $\text{FeCO}_3$ . Precipitation of solid graphite from a  $\text{CO}_2 + \text{CO}$  atmosphere under reducing conditions provides a method for control of  $f_{\text{O}_2}$  values through equilibrium between crystalline graphite and the oxides of carbon in the gas phase. Equilibrium values of  $f_{\text{O}_2}$  are calculated from thermodynamic data for several values of  $P_{\text{gas}} = P_{\text{CO}_2} + P_{\text{CO}}$ . For values of  $P_{\text{gas}}$  greater than 100 bars, the following approximation may be used without serious error:

$$\log f_{\text{O}_2} = -(20,586/T) - 0.044 + \log P_{\text{gas}} - 0.028(P_{\text{gas}} - 1)/T$$

These results indicate two important consequences of the presence of graphite in igneous and metamorphic rocks. First, equilibrium between graphite and gas will buffer a value of  $f_{\text{O}_2}$  which is within the stability field of magnetite for most geological environments. Second, such buffering will also occur in systems with additional volatile components if the variance of the system is not changed by their introduction. In gas phases in the system C-H-O, equilibration with graphite allows approximate calculation of such ratios as  $\text{CO}_2/\text{CO}$ ,  $\text{H}_2\text{O}/\text{H}_2$ , and  $\text{CH}_4/\text{H}_2$ . A noteworthy result is that the value of  $\text{CH}_4/\text{H}_2$  in equilibrium with graphite will be large over a wide range of geological conditions; methane will become a significant-to-dominant component of the gas phase under moderately reducing conditions.

### Symbols.

$T$ ,	temperature in degrees Kelvin.
$P_s$ ,	isotropic pressure on solid phases.
$P_{\text{gas}}$ ,	total pressure of the gas phase. The unqualified term 'total pressure' refers to closed experimental systems in which $P_s = P_{\text{gas}}$ .
$P_i$ ,	partial pressure of component $i$ in the gas phase
$f_i$ ,	fugacity of component $i$ in the gas phase.
$\gamma_i$ ,	fugacity coefficient of component $i$ in the gas phase, defined by $\gamma_i = f_i/P_i$ .
$G_T^\circ$ ,	standard Gibbs free energy of formation of a compound from its elements at a specified temperature and unit fugacities of components occurring in the gaseous state.

$\Delta G^\circ$ ,	standard Gibbs free energy change in a reaction, equal to $\Sigma (G_T^\circ)_{\text{products}} - \Sigma (G_T^\circ)_{\text{reactants}}$ .
$K(T)$ ,	equilibrium constant of a reaction, written using fugacities of gaseous components; a function of $T$ only.
$\log N$ ,	logarithm of $N$ to the base 10.
$\ln N$ ,	logarithm of $N$ to the base $e$ .

**Introduction.** The method of using solid buffers for the control of oxygen fugacities in hydrothermal experiments at elevated pressures [Eugster, 1957; Eugster and Wones, 1962] has been applied successfully to studies of the stability of a number of iron-bearing minerals [see, e.g., Turnock and Eugster, 1962; Wones, 1963a, b; Ernst, 1960, 1962; Buddington and Lindsley, 1964] and to the melting relations of iron-rich liquids [Hamilton et al., 1964].

An oxygen buffer is an assemblage of solid phases ( $A$ ,  $B$ ,  $C$ , etc.) related to each other by reactions of the type

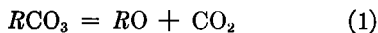
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For such assemblages,  $f_{O_2}$  is fixed if total pressure and temperature are known; values of  $f_{O_2}$  can be calculated from thermodynamic data [Eugster and Wones, 1962]. In the presence of water, oxygen buffers also define  $f_{H_2}$  and the  $f_{H_2O}/f_{H_2}$  ratio of the gas phase. Direct determinations of  $f_{H_2}$  for some buffers made by Shaw [1963] are in good agreement with the calculated data.

In hydrothermal experiments, the sample is contained in a sealed platinum or silver-palladium [Muan, 1963] tube and surrounded by the oxygen buffer. Equilibrium between the buffer and the sample is established by diffusion of hydrogen through the walls of the tube. The attainment of equilibrium is demonstrated by reversing the particular reaction under investigation. Throughout the experiment, the bulk composition of the sample does not change except for its hydrogen content.

Studies of the phase relations of carbonates pose a somewhat different problem. Decomposition reactions of divalent carbonates may be represented by two distinct equations [Jamieson and Goldsmith, 1960], in which  $R$  represents a divalent cation.



Reactions of the first type, in which oxidation does not occur, have been studied experimentally in carbon dioxide atmospheres, using samples contained in open tubes [see, e.g., Harker and Tuttle, 1955; Harker and Hutta, 1956; Goldsmith and Graf, 1957].

Siderite ( $FeCO_3$ ) and rhodochrosite ( $MnCO_3$ ) are carbonates whose stability is governed by reactions of the second type. Such reactions must be studied under controlled fugacities of both  $CO_2$  and  $O_2$ . Since noble metal tubes are not sufficiently permeable to  $CO_2$  and  $CO$ , sealed tubes cannot be used for buffered experiments in a  $CO_2 + CO$  atmosphere. For this reason, siderite was studied experimentally [French and Eugster, 1962; French, 1964a] in unsealed silver tubes, allowing direct equilibration between the gas phase and the charge. Because of contamination problems, only those buffer assemblages

could be used which are possible decomposition products of the carbonate, i.e., pairs of iron oxides for siderite and of manganese oxides for rhodochrosite.

*Oxygen fugacities in a  $CO_2 + CO$  Atmosphere.* In a  $CO_2$  atmosphere, the value of  $f_{O_2}$  of the oxygen buffer will also fix the value of the  $CO_2/CO$  ratio through the decomposition of  $CO_2$  ( $CO_2 = CO + \frac{1}{2}O_2$ ). If  $CO_2$ ,  $CO$ , and  $O_2$  are the only species in the gas phase, the values of  $f_{CO}$  and  $f_{CO_2}$  may be calculated (see Eugster and Wones [1962], p. 93, for analogous calculations for a hydrothermal atmosphere). Since data on the fugacity coefficients  $\gamma_i$  of  $CO$  and  $CO_2$  in mixtures are not available, it is assumed that the values of  $\gamma_i$  are the same for each species in the mixture as for the pure components at the same temperature and total pressure (Lewis and Randall's rule; see Denbigh [1957], p. 127). Since the value of  $f_{O_2}$  at moderate temperatures is less than  $10^{-10}$  bar, we may assume that

$$P_{gas} = P_{CO_2} + P_{CO} \quad (3)$$

$$K_b(T) = f_{CO_2}/f_{CO}(f_{O_2})^{1/2} \quad (4)$$

Values of  $K_b$  are tabulated by Wagman *et al.* [1945].<sup>2</sup>

From these relations, the individual fugacities may be determined as

$$f_{CO_2} = \frac{K_b P_{gas} \gamma_{CO} \gamma_{CO_2} (f_{O_2})^{1/2}}{[K_b \gamma_{CO} (f_{O_2})^{1/2}] + \gamma_{CO_2}} \quad (5)$$

$$f_{CO} = \frac{P_{gas} \gamma_{CO} \gamma_{CO_2}}{[K_b \gamma_{CO} (f_{O_2})^{1/2}] + \gamma_{CO_2}} \quad (6)$$

These expressions are analogous to those obtained for  $f_{H_2O}$  and  $f_{H_2}$  in a hydrothermal atmosphere [see Eugster and Wones, 1962, p. 93].

Values of  $\log f_{CO}$  as a function of temperature are given in Figure 1 for a number of oxygen buffers at total pressures of 1 bar and 2000 bars. At  $P_{gas} = 1$  bar, the fugacities of all components are assumed equal to the partial pressures ( $\gamma_i = 1.00$ ). Fugacity data for  $CO_2$  are available to 1400 bars [Robie, 1962], based on Kennedy's [1954] experimental determinations of

<sup>2</sup> Wagman's tabulated values of  $\log K_b$  agree to within 0.01 with values calculated from more recent standard free energy data [Coughlin, 1954, JANAF tables]. Experimental measurements [Darken and Gurry, 1945, 1946] differ from these values by 3 to 4%.

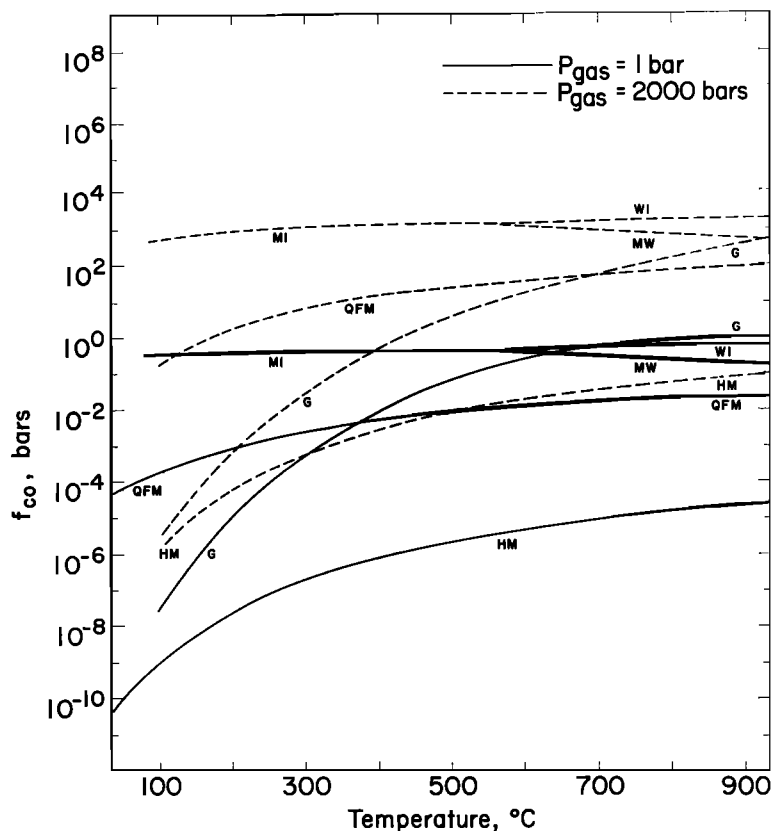


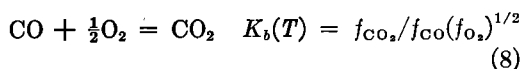
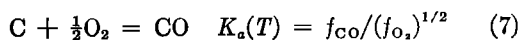
Fig. 1. Values of  $f_{\text{CO}}$  as a function of temperature in a  $\text{CO}_2 + \text{CO}$  atmosphere for several oxygen buffer assemblages. Data for graphite buffer calculated in this paper; other data from *Eugster and Wones* [1962]. Abbreviations: *G*, graphite; *HM*, hematite + magnetite; *MI*, magnetite + iron; *MW*, magnetite + wüstite; *WI*, wüstite + iron; *QFM*, quartz + fayalite + magnetite.

*P-V-T* relations. The values of  $\gamma_{\text{CO}_2}$  for 2000 bars were estimated by extrapolation of Robie's data. Values for  $\gamma_{\text{CO}}$  are taken from *Newton* [1935]. The effect of the extrapolations and uncertainties on the value of  $f_{\text{CO}}$  is probably less than an order of magnitude.

Derivation of the results for the 'graphite buffer' (Figure 1) is discussed in detail in the following section.

*Oxygen fugacities of the graphite buffer.* When the oxygen fugacity of a gas phase consisting primarily of  $\text{CO}$  and  $\text{CO}_2$  is reduced sufficiently, graphite may precipitate according to the reaction  $2\text{CO} = \text{C}_{(\text{gr})} + \text{CO}_2$  [see, e.g., *Muan*, 1958].

Equilibrium between graphite and such a gas phase is governed by two relations:



Hence, for a given temperature and total pressure, the presence of graphite defines the composition of the gas phase as well as the fugacities of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$ . In other words, the assemblage graphite + gas acts as an oxygen buffer.<sup>3</sup>

<sup>3</sup> The same conclusions are reached by applying the Gibbs phase rule ( $F + P = C + 2$ ) to the two-component system  $\text{C-O}$ . A two-phase assemblage (graphite + gas) has two degrees of freedom ( $F = 2$ ). If both temperature and total pressure are specified, the system becomes invariant, and the composition of the gas phase is uniquely determined.

In calculating oxygen fugacities of a gas phase in equilibrium with graphite, we must allow for the partial pressure of CO, which becomes significant at high temperatures and low total pressures [Muan, 1958]. The method of calculation used here is based on (7) and (8), which we can write:

$$K_a = \gamma_{\text{CO}} P_{\text{CO}} (f_{\text{O}_2})^{-1/2} \tag{7a}$$

$$K_b = \left[ \frac{\gamma_{\text{CO}_2} P_{\text{CO}_2}}{\gamma_{\text{CO}} P_{\text{CO}}} \right] (f_{\text{O}_2})^{-1/2} \tag{8a}$$

Eliminating  $f_{\text{O}_2}$  and combining with (3), we have

$$P_{\text{CO}_2} = \left[ \frac{K_b (\gamma_{\text{CO}})^2}{K_a \gamma_{\text{CO}_2}} \right] (P_{\text{CO}})^2 = P_{\text{gas}} - P_{\text{CO}}$$

and

$$P_{\text{CO}} = \frac{-1 + \left[ 1 + 4 P_{\text{gas}} \frac{K_b}{K_a} \left( \frac{\gamma_{\text{CO}}^2}{\gamma_{\text{CO}_2}} \right)^{1/2} \right]}{2 \frac{K_b}{K_a} \left( \frac{\gamma_{\text{CO}}^2}{\gamma_{\text{CO}_2}} \right)} \tag{9}$$

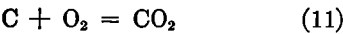
Values of  $K_a$  and  $K_b$  are obtained from tabulations [Wagman *et al.*, 1945]. Values of  $P_{\text{CO}}$  in equilibrium with graphite have been calculated from (9) for total pressures of 1, 100, 500, 1000, and 2000 bars.

From these data and the fugacity coefficients of the individual gases, the value of  $f_{\text{O}_2}$  in equilibrium with graphite can be calculated from the relation in (8).

$$\log f_{\text{O}_2} = 2 \left[ \log \frac{\gamma_{\text{CO}_2} P_{\text{CO}_2}}{\gamma_{\text{CO}} P_{\text{CO}}} - \log K_b \right] \tag{10}$$

Results are given in Table 1 and Figure 2.

A simpler but less rigorous method of obtaining the same results consists in combining (7) and (8) to obtain



$$\log K_c(T) = -\frac{\Delta G^0}{2.303RT} = \log f_{\text{CO}_2} - \log f_{\text{O}_2}$$

Rearranging, we obtain

$$\log f_{\text{O}_2} = \frac{\Delta G^0}{2.303RT} + \log f_{\text{CO}_2} \tag{12}$$

Equation 12 applies for a total pressure at which all compounds are in their respective standard

TABLE 1. Calculated Values of  $P_{\text{CO}}$  and  $\log f_{\text{O}_2}$  in Equilibrium with Graphite for Various Values of  $P_{\text{gas}} (= P_{\text{CO}_2} + P_{\text{CO}})$

<i>T</i> , °K	<i>T</i> , °C	<i>P</i> <sub>CO</sub>	−log <i>f</i> <sub>O<sub>2</sub></sub>	−log <i>f</i> <sub>O<sub>2</sub></sub> *
<i>P</i> <sub>gas</sub> = 1 bar				
400	127	2.3 × 10 <sup>−7</sup>	51.53	51.51
500	227	4.2 × 10 <sup>−5</sup>	41.26	41.22
600	327	1.4 × 10 <sup>−3</sup>	34.40	34.35
700	427	0.016	29.51	29.45
800	527	0.099	25.89	25.78
900	627	0.35	23.16	22.92
1000	727	0.72	21.24	20.63
1100	827	0.93	19.95	18.76
1200	927	0.98	19.01	17.20
<i>P</i> <sub>gas</sub> = 100 bars				
400	127	2.0 × 10 <sup>−9</sup>	49.62	49.51
500	227	3.9 × 10 <sup>−4</sup>	39.29	39.22
600	327	0.013	32.40	32.36
700	427	0.16	27.49	27.46
800	527	1.0	23.82	23.78
900	627	4.3	20.97	20.92
1000	727	12.9	18.73	18.63
1100	827	29.4	16.93	16.76
1200	927	52.8	15.55	15.20
<i>P</i> <sub>gas</sub> = 500 bars				
400	127	3.1 × 10 <sup>−6</sup>	49.07	48.84
500	227	6.8 × 10 <sup>−4</sup>	38.62	38.55
600	327	0.025	31.69	31.68
700	427	0.31	26.75	26.87
800	527	2.0	23.03	23.10
900	627	8.6	20.20	20.23
1000	727	27.0	17.93	17.90
1100	827	66.9	16.09	16.07
1200	927	135	14.60	14.51
<i>P</i> <sub>gas</sub> = 1000 bars				
400	127	3.0 × 10 <sup>−6</sup>	48.73	48.58
500	227	7.2 × 10 <sup>−4</sup>	38.26	38.27
600	327	0.028	31.44	31.40
700	427	0.36	26.39	26.49
800	527	2.4	22.62	22.81
900	627	10.6	19.83	19.95
1000	727	34.6	17.56	17.66
1100	827	86.8	15.70	15.79
1200	927	182	14.20	14.22
<i>P</i> <sub>gas</sub> = 2000 bars				
400	127	3.0 × 10 <sup>−6</sup>	48.19	48.35
500	227	7.2 × 10 <sup>−4</sup>	37.75	38.03
600	327	0.026	30.85	31.15
700	427	0.36	25.90	26.23
800	527	2.6	22.24	22.55
900	627	11.8	19.38	19.68
1000	727	39.8	17.10	17.39
1100	827	104	15.24	15.51
1200	927	228	13.72	13.95

\* Approximate values from Eq. 15.

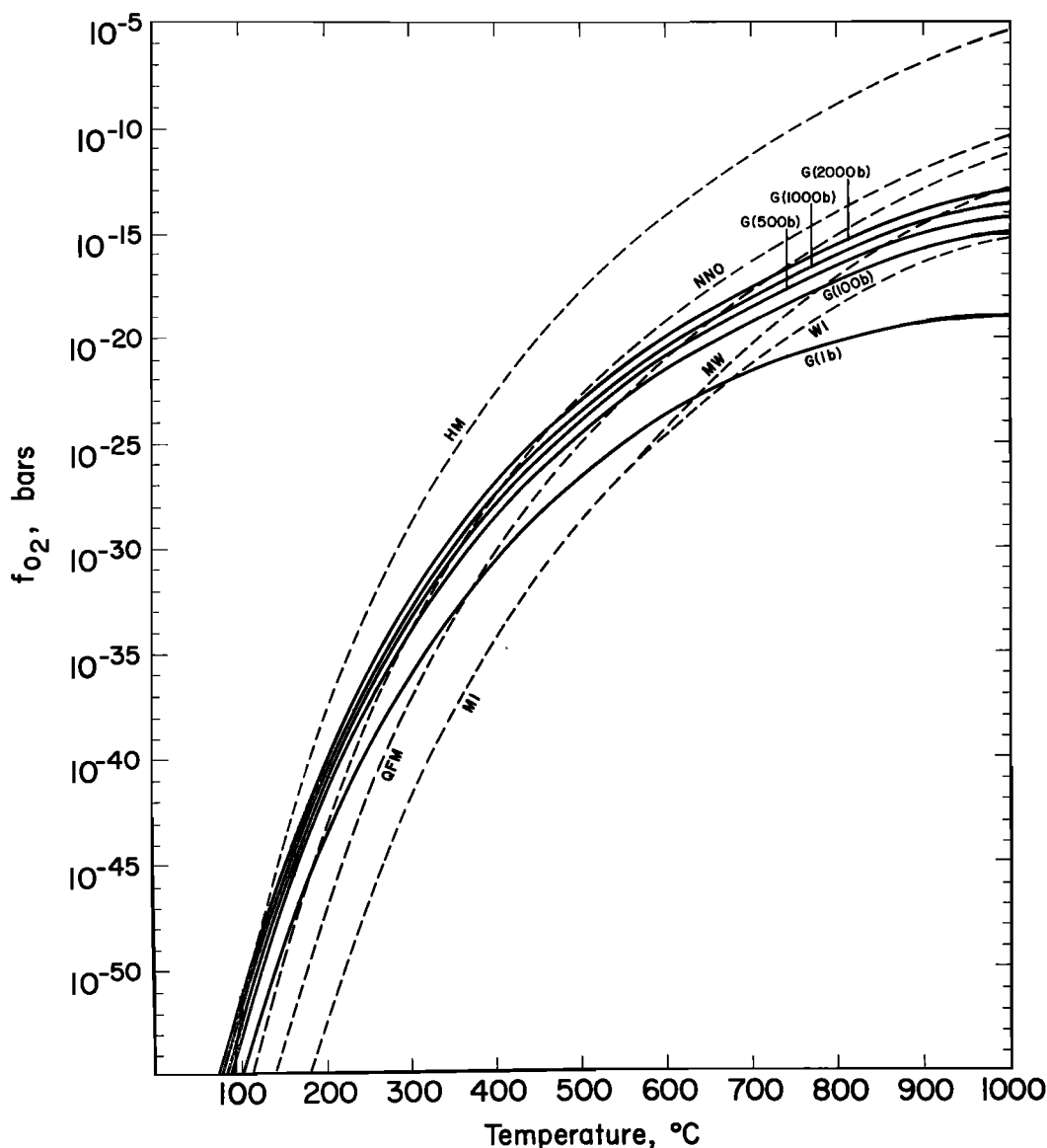


Fig. 2. Values of  $f_{O_2}$  for the graphite + gas buffer as a function of temperature for selected values of  $P_{gas} = P_{CO_2} + P_{CO}$ . Graphite + gas curves shown in solid lines; values of  $P_{gas}$  given in parentheses. The dashed lines indicate values of  $f_{O_2}$  for other buffering assemblages [Eugster and Wones, 1962] calculated for  $P_{gas} = 1$  bar; the effect of total pressure on this group of buffers is slight. Abbreviations: HM, hematite + magnetite; NNO, nickel + bunsenite; QFM, quartz + fayalite + magnetite; MI, magnetite + iron; MW, magnetite + wüstite; WI, wüstite + iron.

states; this will not be significantly different from 1 atm [Denbigh, 1957, pp. 120–124, 146]. An increase in total pressure will affect the free energy of reaction,  $\Delta G$ , because of the volume change of graphite with pressure. The effect of

this change on the value of  $K_e(T)$  may be calculated [see Eugster and Wones, 1962, pp. 91–92].

For the equilibrium represented by (11) at constant temperature,

$$\Delta G = \Delta G^0 + RT \ln K$$

$$= \Delta G^0 + RT[\ln f_{\text{CO}_2} - \ln f_{\text{O}_2}]$$

$$d\Delta G = 0 = \Delta V_s dP_s + RT \left( \frac{\partial \ln f_{\text{CO}_2}}{\partial P_{\text{gas}}} \right)_T dP_{\text{gas}}$$

$$- RT \left( \frac{\partial \ln f_{\text{O}_2}}{\partial P_{\text{gas}}} \right)_T dP_{\text{gas}}$$

When rearranged and integrated, this becomes

$$RT \ln \frac{f_{\text{O}_2}(P_2)}{f_{\text{O}_2}(P_1)}$$

$$= \Delta V_s(P_2 - P_1) + RT \ln \frac{f_{\text{CO}_2}(P_2)}{f_{\text{CO}_2}(P_1)}$$

Setting  $P_1 = 1$  atm, and substituting (12), we obtain

$$\log f_{\text{O}_2}(P_2) = \frac{\Delta G^0}{2.303RT} + \log f_{\text{CO}_2}(P_2)$$

$$+ \frac{\Delta V_s(P_2 - P_1)}{2.303RT} \quad (13)$$

$$\log f_{\text{O}_2} = \frac{G_T^0(\text{CO}_2)}{2.303RT}$$

$$+ \log f_{\text{CO}_2} - 0.028 \frac{P - 1}{T} \quad (14)$$

The molar volume of graphite (5.30 cm<sup>3</sup>) is here assumed to be independent of pressure.

While (14) is a rigorous expression, approximate values of  $\log f_{\text{O}_2}$  may be conveniently obtained by introducing the following simplifying assumptions: (a) that, at total pressures in excess of 100 bars,  $\log f_{\text{CO}_2} = \log P_{\text{gas}}$ ; (b) that  $G_T^0(\text{CO}_2) = -94,200 - 0.2T$  cal/mole [Kubaschewski and Evans, 1958]. Substituting in (14), we obtain the approximate expression

$$\log f_{\text{O}_2} \approx -(20,586/T) - 0.044$$

$$+ \log P_{\text{gas}} - 0.028(P_{\text{gas}} - 1)/T \quad (15)$$

A comparison of values of  $\log f_{\text{O}_2}$  calculated from (15) and (10) indicates that at temperatures above 500°K and total pressures in excess of 100 bars the approximations used do not introduce serious errors (Table 1). The calculated values of  $\log f_{\text{O}_2}$  for the graphite buffer at various total pressures (Table 1 and Figure 2) are believed accurate to at least  $\pm 0.5$ .

Figure 2 shows that for each value of  $P_{\text{gas}}$  =

$P_{\text{O}_2} + P_{\text{CO}}$  there is specified an isobarically univariant graphite + gas buffer curve. The family of such curves for different values of  $P_{\text{gas}}$  forms a surface in  $P_{\text{gas}}-P_{\text{O}_2}-T$  space. The surface has a shape and orientation similar to those of other buffering surfaces [Eugster and Wones, 1962]; higher temperatures and higher total pressures correspond to higher values of  $\log f_{\text{O}_2}$ . However, the effect of changes in total pressure on  $f_{\text{O}_2}$  is much more pronounced for the graphite buffer, particularly at lower pressures. At 700°C, for instance,  $f_{\text{O}_2}$  of the graphite buffer lies within the iron stability field at 1 bar pressure, but lies above the fayalite + magnetite + quartz buffer curve at 2000 bars. By contrast, increasing temperature makes the graphite buffer more reducing with respect to the iron oxide buffers.

An important difference between the graphite buffer and other oxygen buffers is a consequence of the fact that the graphite buffer contains only one solid phase and that its buffering characteristic is due to the assemblage graphite + gas.<sup>4</sup> Therefore, the graphite buffer curves divide  $P_{\text{gas}}-P_{\text{O}_2}-T$  space into two distinctly different regions, a region above the graphite + gas curve, which represents the existence of a CO<sub>2</sub>-rich gas (graphite absent) and a region below the graphite buffer curve, which is condensed.

Consider, for instance, a fixed value of  $P_{\text{gas}}$ , e.g., 2000 bars (Figure 2), and a value of  $f_{\text{O}_2}$  and  $T$  above that of the 2000-bar graphite + gas buffer curve. Under these conditions, any bulk composition in the system C-O is represented by a gas phase consisting essentially of CO<sub>2</sub> and CO, the CO<sub>2</sub>/CO ratio of which is defined by the quantities  $P_{\text{gas}}$ ,  $T$ , and  $f_{\text{O}_2}$ . If the value of  $f_{\text{O}_2}$  in the gas is decreased until the graphite buffer curve at 2000 bars is reached, reduction of CO<sub>2</sub> and CO occurs and graphite is precipitated [Muan, 1958]. The value of  $f_{\text{O}_2}$  will remain fixed on the curve until all the oxides have been converted to graphite.

In the two-component system C-O, values of  $f_{\text{O}_2}$  below the graphite-gas curve therefore repre-

<sup>4</sup> The presence of a gas is not necessary to define the oxygen fugacity of, e.g., an Fe<sub>3</sub>O<sub>4</sub> + Fe<sub>2</sub>O<sub>3</sub> buffer for a specific temperature and total pressure. The gas phase is necessary only for the buffer to function, since the values of  $P_{\text{O}_2}$  specified are vanishingly small. By contrast, a gas phase (CO<sub>2</sub>) enters directly into the buffering reaction for the graphite buffer.

sent a system in which all carbon is present as graphite and the gas phase may contain only oxygen (the vapor pressure of graphite is neglected). The value of  $P_{\text{gas}}$  below the graphite + gas curve is no longer 2000 bars, but has become equal to  $P_{\text{O}_2}$ , or  $10^{-20}$  to  $10^{-30}$  bars. Hence, no gas can be present in the region below the curve, unless voids remain while the solid graphite supports a pressure of 2000 bars ( $P_{\text{gas}} \ll P_s$ ). The region below the graphite + gas curve is thus condensed in the sense that carbon oxides must be absent from the gas phase.

It is very important to realize that as long as graphite is present it is not possible to produce equilibrium values of  $f_{\text{O}_2}$  within the condensed region by the addition of other volatile components (e.g., hydrogen or a hydrogen-water mixture). To illustrate this point, consider a graphite-gas assemblage in equilibrium at  $P_{\text{gas}} = 2000$  bars (Figure 2). At constant total pressure, if  $f_{\text{O}_2}$  is suddenly reduced to a value below the graphite + gas curve by addition of a proper hydrogen + water mixture, a situation is produced in which  $P_{\text{gas}} = 2000$  bars  $> P_{\text{CO}_2} + P_{\text{CO}}$ . To re-establish equilibrium, graphite will precipitate from the gas, reducing the value of  $P_{\text{CO}_2} + P_{\text{CO}}$  to that value which corresponds to the particular graphite + gas curve which passes through the specified value of  $f_{\text{O}_2}$ . Regardless of the value of  $f_{\text{O}_2}$  originally established by the new mixture, equilibrium between graphite and gas will be maintained, although, under strongly reducing conditions, the value of  $P_{\text{CO}_2} + P_{\text{CO}}$  may become very small.

By contrast, if the value of  $f_{\text{O}_2}$  is fixed above the original graphite + gas curve, the graphite will oxidize, increasing the value of  $P_{\text{CO}_2} + P_{\text{CO}}$  until a new graphite + gas curve through the value of  $f_{\text{O}_2}$  is reached. If the graphite is completely oxidized before this value is attained, a divariant one-phase gas assemblage is produced.

In summary, all displacements from the equilibrium graphite + gas surface in  $P_{\text{gas}}-P_{\text{O}_2}-T$  space will produce changes in gas composition and in the magnitudes of  $P_{\text{CO}_2}$ ,  $P_{\text{CO}}$ , and  $f_{\text{O}_2}$  which tend to return to a new equilibrium position on the same surface. If graphite is removed by oxidation before equilibrium is attained, a one-phase gas assemblage is produced. The presence of additional volatile components in the system will add extra degrees of freedom to the equilibrium assemblage graphite + gas. For each addi-

tional component  $i$  introduced, an additional variable (e.g.,  $P_i$ ) must be independently specified if the value of  $f_{\text{O}_2}$  is to remain buffered by equilibrium between graphite and the gas phase. The effect of hydrogen as an additional component is discussed in a later section.

*Experimental determination of carbonate stabilities using oxygen buffers.* The techniques of using solid-phase buffers in a  $\text{CO}_2 + \text{CO}$  atmosphere to control  $f_{\text{O}_2}$  were applied to a study of the stability relations of siderite ( $\text{FeCO}_3$ ) [French, 1964a; French and Eugster, 1965].

Values of  $f_{\text{O}_2}$  along most of the solid-phase buffers used in earlier studies [Eugster and Wones, 1962] are metastable with respect to graphite. The two buffers used in the siderite study were graphite and hematite-magnetite mixtures.

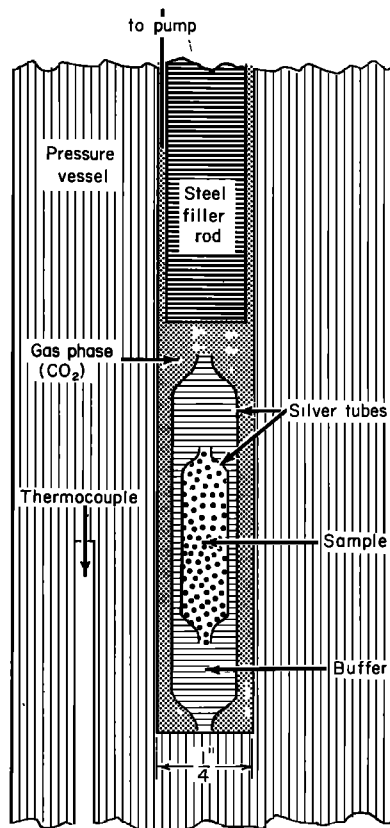


Fig. 3. Cutaway sketch of experimental apparatus. The sample (heavy dots) is enclosed in a solid-phase buffer (horizontal ruling). Buffering of the sample is established by diffusion of the  $\text{CO}_2$ -rich gas phase through the buffer.

The experimental arrangement is shown in Figure 3. The sample (usually synthetic siderite) is contained in a small (0.120-in. O.D.) silver tube; this inner tube is surrounded by a buffer mixture contained in a larger (0.173-in. O.D.) silver tube. Since neither  $\text{CO}_2$  nor  $\text{CO}$  will diffuse through silver, the ends of both tubes are crimped but left unsealed, in contrast to the method of preparation of samples run in a hydrothermal atmosphere. The charge is then placed in a Tuttle 'test-tube' type bomb, into which  $\text{CO}_2$  is supplied by an external pumping system. Temperatures are controlled and measured in the same manner as in earlier hydrothermal experiments.

During the run,  $\text{CO}_2$  from the atmosphere diffuses through the buffer; the  $\text{CO}_2/\text{CO}$  ratio to which the sample is subjected is thereby adjusted to the value specified by the  $f_{\text{O}_2}$  of the buffer. The attainment of equilibrium by this method was indicated by the consistency and reversibility of runs.

In these experiments,  $\text{Fe}_3\text{O}_4$  is added to the graphite buffer, so that, with both buffer mixtures, a single run will indicate the location of the reversible equilibrium with respect to run temperature by two reactions. If the run temperature lies within the stability field of  $\text{FeCO}_3$ , the sample is unchanged while  $\text{FeCO}_3$  forms in the buffer ( $\text{Fe}_3\text{O}_4 + \text{Fe}_3\text{O}_4$  or  $\text{Fe}_3\text{O}_4 + \text{C}_{(\text{gr})}$ ); if the run temperature lies above the stability field of siderite, the buffer remains unaffected while the sample decomposes to the respective buffer assemblages. (It must be emphasized that magnetite plays no part in buffering  $f_{\text{O}_2}$  when graphite is also present, and thus it is not correct to speak of a 'magnetite-graphite' buffer.)

Figure 4 presents stability data for siderite at a gas pressure of 1000 bars, as determined by French [1964a]. Only the two isobaric invariant points, siderite + hematite + magnetite + gas and siderite + magnetite + graphite + gas, are accessible by this method; the curves bounding the stability field of siderite + gas have been calculated approximately from thermodynamic data.

It is possible that rates of equilibration between graphite and gas (represented by equations 7, 8, and 11) are slow enough so that a gas phase with metastably low  $\text{CO}_2/\text{CO}$  ratios could be maintained without precipitation of graphite, particularly at low temperatures

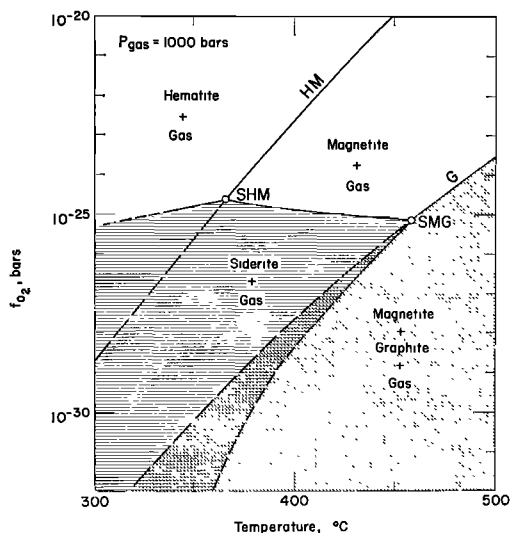


Fig. 4. Isobaric section through the stability field of siderite + gas at  $P_{\text{gas}} = 1000$  bars. Only the two isobaric invariant points, siderite + hematite + magnetite + gas (SHM) and siderite + magnetite + graphite + gas (SMG) were determined. The stability field of the assemblage siderite + gas (horizontal ruling) is bounded by the three univariant curves, siderite + hematite + gas, siderite + magnetite + gas, and siderite + magnetite + graphite + gas. The latter curve lies entirely within the condensed region below the graphite + gas buffer curve (slanted dashed area). HM designates the hematite-magnetite buffer and G the graphite + gas buffer for this value of  $P_{\text{gas}}$ .

[Muan, 1958; P. E. Rosenberg, 1962, unpublished data]. However, the experimental data [French, 1964a; French and Rosenberg, 1965] indicate that equilibrium is attained through precipitation of graphite during runs of long (two weeks) duration.

In other studies of siderite stability performed in sealed unbuffered tubes, the bulk composition is constant ( $\text{FeCO}_3$ ). Some decomposition of the sample to oxides is necessary to produce gas pressure within the sample tube. However,  $f_{\text{O}_2}$  is neither constant nor exactly known for such decompositions, and magnetite or hematite may be in equilibrium with siderite over a wide range of  $T$  and  $f_{\text{O}_2}$  (see Figure 4). Unless  $f_{\text{O}_2}$  is known, the results of such experiments must be treated with caution.

*Graphite as an oxygen buffer in igneous and metamorphic rocks.* The control of oxygen fugacities in a vapor phase through equilibration with graphite has great significance in the study



of mineral assemblages produced by igneous or metamorphic processes. Recent studies of the behavior of oxygen in rocks [Chinner, 1960; Mueller, 1960; Kranck, 1961; Zen, 1963] have concentrated on iron-bearing minerals whose composition and stability relations are influenced by the  $f_{O_2}$  of the vapor phase with which they coexist [Eugster, 1959]. One difficulty with such assemblages is that equilibrium between two or more solid phases is generally required to specify the value of  $f_{O_2}$  present; such equilibrium may often be difficult to demonstrate texturally [Zen, 1963]. Moreover, if the assemblages contain carbonates or hydrous silicates, the  $f_{O_2}$  will be influenced by the fugacities of additional gas components such as  $H_2O$  and  $CO_2$ .

More recently, several researchers have called attention to the possible role of graphite and related carbonaceous matter in controlling the value of  $f_{O_2}$  in such diverse mineral assemblages as metamorphosed sediments [Miyashiro, 1964; Mueller and Condie, 1964] and meteorites [Mueller, 1964]. The  $f_{O_2}$  values permitted by graphite for total pressures of 10 bars and 10 kilobars were calculated approximately by Miyashiro [1964], assuming ideal behavior for all gas components.

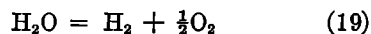
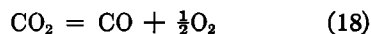
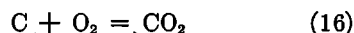
The importance of graphite in natural assemblages is that only a single solid phase is required to control the value of  $f_{O_2}$  in a  $CO_2 + CO$  atmosphere. Furthermore, since the buffering reaction occurs only in the system C-O, the effect of graphite upon  $f_{O_2}$  will be independent of the presence of other solid phases or gases. Introduction of other volatile components will create a situation in which  $P_{gas} > P_{CO_2} + P_{CO}$ .

The presence of graphite in a mineral assemblage therefore defines a relationship between the three parameters  $T$ ,  $f_{O_2}$ , and  $(P_{CO_2} + P_{CO})$  whereby, if any two are known, the third is completely determined without regard to other components in the system or other phases in the mineral assemblage. Because of the low gram-molecular weight of graphite, even trace amounts of graphite will exert a very large buffering effect with respect to changes in the composition of the gas phase.

For a fairly wide range of values of  $P_{CO_2} + P_{CO}$ , the occurrence of graphite in a mineral assemblage formed at moderate temperatures indicates a value of  $f_{O_2}$  within the stability field of magnetite. This feature has been proposed as

an explanation of the apparent reduction during metamorphism and of the preservation of steep gradients in  $f_{O_2}$  over relatively short distances [Zen, 1963; Miyashiro, 1964].

Most geological considerations have assumed a gas phase composed dominantly of  $H_2O$  and  $CO_2$ . However, if such a phase is equilibrated with graphite, two buffering reactions, involving both oxygen and hydrogen, are established. The equilibria involved in the system C-H-O may be described by the following four independent reactions, which involve methane ( $CH_4$ ) as well as the other components of the gas phase:



In the three-component system C-H-O, the assemblage graphite + gas will have three degrees of freedom. At a fixed temperature and total gas pressure, the system therefore becomes univariant. Thus the fugacities of all volatile components in the gas may be specified uniquely in terms of one fugacity, e.g.,  $f_{O_2}$ .

The equilibria in this system have been calculated in detail for a variety of temperatures and total pressures [French, 1965]. Preliminary results indicate that methane will be a significant component of the gas phase over a wide range of geologically reasonable conditions; at temperatures below about 800°C, the ratio  $f_{CH_4}/f_{H_2}$  will be greater than unity. Further, it appears that methane will become dominant in a gas phase coexisting with graphite at values of  $f_{O_2}$  corresponding to the lower part of the magnetite stability field where  $Fe_2SiO_4$  may become a stable phase [Eugster, 1959]. Such calculations do, however, neglect the possibility of polymerization of methane in the vapor phase to produce more complex paraffin-group hydrocarbons or other organic materials [see, e.g., Mueller, 1964].

The great potential significance of graphite in natural mineral assemblages indicates that more detailed identification and study of the carbonaceous matter in sediments and metamorphic rocks is required. In such studies, an exact distinction must be made between crystalline graphite and amorphous organic matter

with which it is often confused and from which it may develop by metamorphism [French, 1964b]. The calculations here apply only to crystalline graphite; they are not rigorously applicable to organic matter of uncertain character, although such material may be significant in producing and maintaining reducing values of  $f_{O_2}$  during metamorphism.

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