

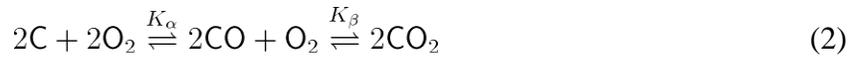
ELECTRONIC ANNEX EA6: RELATIONSHIP OF OXYGEN FUGACITY AND THE GRAPHITE BUFFER

In determining the f_{O_2} dependence of graphite buffer reaction:



it is also necessary to take account of the competing Boudouard reaction ($\text{C} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}$).

Using the approach of French and Eugster (1965) this can be done by considering reaction (1) as a coupled system of the form:



For which the two thermodynamic equilibrium constants K_α and K_β are defined by:

$$K_\alpha = \frac{(\mathbb{F}_{\text{CO}})^2}{\mathbb{F}_{\text{O}_2}} \quad (3)$$

$$K_\beta = \frac{(\mathbb{F}_{\text{CO}_2})^2}{(\mathbb{F}_{\text{CO}})^2 \cdot \mathbb{F}_{\text{O}_2}} \quad (4)$$

where \mathbb{F}_{CO} , \mathbb{F}_{CO_2} , and \mathbb{F}_{O_2} , are the mixture fugacities of CO, CO₂ and O₂ at the partial pressures P_{CO} , P_{CO_2} , and P_{O_2} , respectively. Expressing each of these equations in terms of \mathbb{F}_{O_2} , and combining we have:

$$\frac{(\mathbb{F}_{\text{CO}})^2}{K_\alpha} = \frac{(\mathbb{F}_{\text{CO}_2})^2}{(\mathbb{F}_{\text{CO}})^2 \cdot K_\beta} \quad (5)$$

This can be rearranged to:

$$\mathbb{F}_{\text{CO}_2} = (\mathbb{F}_{\text{CO}})^2 \cdot \sqrt{\frac{K_\beta}{K_\alpha}} \quad (6)$$

The mixture fugacities of \mathbb{F}_{CO} and \mathbb{F}_{CO_2} , can be expressed as the product of their partial pressures and the mixture fugacity coefficients $\gamma_{\text{CO}}^{P_{\text{CO}}}$ and $\gamma_{\text{CO}_2}^{P_{\text{CO}_2}}$ at those partial pressures, that is:

$$\begin{aligned}\mathbb{F}_{\text{CO}} &= \gamma_{\text{CO}}^{P_{\text{CO}}} \cdot P_{\text{CO}} \\ \mathbb{F}_{\text{CO}_2} &= \gamma_{\text{CO}_2}^{P_{\text{CO}_2}} \cdot P_{\text{CO}_2}\end{aligned}\quad (7)$$

Using the Lewis Randall gas fugacity mixing rules we can replace the mixture fugacities with the product of the corresponding pure gas fugacities f_{CO} and f_{CO_2} , at the total pressure $P = P_{\text{CO}} + P_{\text{CO}_2}$ (assuming that $P_{\text{O}_2} \sim 0$) and the mole fractions in the gas mixture, that is:

$$\begin{aligned}\mathbb{F}_{\text{CO}} &= f_{\text{CO}} \cdot \frac{P_{\text{CO}}}{P} \\ \mathbb{F}_{\text{CO}_2} &= f_{\text{CO}_2} \cdot \frac{P_{\text{CO}_2}}{P}\end{aligned}\quad (8)$$

Rewriting the pure gas fugacities in terms of the respective fugacity coefficients equation (7) can be rewritten as:

$$\begin{aligned}\mathbb{F}_{\text{CO}} &= \gamma_{\text{CO}} \cdot P_{\text{CO}} \\ \mathbb{F}_{\text{CO}_2} &= \gamma_{\text{CO}_2} \cdot P_{\text{CO}_2},\end{aligned}\quad (9)$$

where γ_{CO} and γ_{CO_2} are the pure gas fugacities of CO and CO₂ at the total pressure P , substituting into equation (6) we have:

$$\gamma_{\text{CO}_2} \cdot P_{\text{CO}_2} = (\gamma_{\text{CO}} \cdot P_{\text{CO}})^2 \cdot \sqrt{\frac{K_{\beta}}{K_{\alpha}}}\quad (10)$$

Using $P_{\text{CO}_2} = P - P_{\text{CO}}$ in equation (66) we can eliminate P_{CO_2} and rearrange to get a quadratic expression for P_{CO} of the form:

$$\left((\gamma_{\text{CO}})^2 \cdot \sqrt{\frac{K_{\beta}}{K_{\alpha}}} \right) \cdot (P_{\text{CO}})^2 + \gamma_{\text{CO}_2} \cdot P_{\text{CO}} - (\gamma_{\text{CO}_2} \cdot P) = 0\quad (11)$$

Solving for P_{CO} we have the real solution:

$$P_{\text{CO}} = \frac{-\gamma_{\text{CO}_2} - \sqrt{(\gamma_{\text{CO}_2})^2 + 4\gamma_{\text{CO}_2} \cdot (\gamma_{\text{CO}})^2 \cdot \sqrt{\frac{K_{\alpha}}{K_{\beta}}}}{2(\gamma_{\text{CO}})^2 \cdot \sqrt{\frac{K_{\alpha}}{K_{\beta}}}}\quad (12)$$

Replacing $f_{\text{CO}} = \gamma_{\text{CO}} \cdot P_{\text{CO}}$ in the expression for the thermodynamic equilibrium constant K_{α} in reaction (3) we can then write:

$$K_{\alpha} = \frac{(\gamma_{\text{CO}} \cdot P_{\text{CO}}^2)}{f_{\text{O}_2}} = \exp\left(-\frac{\Delta G_{\text{rxn}}^{P_1, T_1}}{R \cdot T_1}\right) \quad (13)$$

Where $\Delta G_{\text{rxn}}^{P_1, T_1}$ is the Gibbs free energy of reaction for the oxidation of graphite to CO at pressure P_1 , and temperature T_1 . This can be rearranged to give the desired expression for the f_{O_2} dependence of graphite buffer reaction (1), that is:

$$f_{\text{O}_2} = [\gamma_{\text{CO}} \cdot P_{\text{CO}}]^2 \cdot \exp\left(\frac{\Delta G_{\text{rxn}}^{P_1, T_1}}{R \cdot T_1}\right) \quad (14)$$

REFERENCES

- French, B. M. and Eugster, H. P. (1965) Experimental control of oxygen fugacities by graphite-gas equilibria. *J. Geophys. Res.* **70**, 1529-1539.