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

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

$$\mathsf{C} + \mathsf{O}_2 \rightleftharpoons \mathsf{CO}_2 \tag{1}$$

it is also necessary to take account of the competing Boudouard reaction ($\mathsf{C} + \frac{1}{2}\mathsf{O}_2 \rightleftharpoons \mathsf{CO}$). Using the approach of French and Eugster (1965) this can be done by considering reaction (1) as a coupled system of the form:

$$2\mathsf{C} + 2\mathsf{O}_2 \overset{K_\alpha}{\rightleftharpoons} 2\mathsf{CO} + \mathsf{O}_2 \overset{K_\beta}{\rightleftharpoons} 2\mathsf{CO}_2 \tag{2}$$

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

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

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

where $\mathbb{F}_{\mathsf{CO}}$, $\mathbb{F}_{\mathsf{CO}_2}$ and $\mathbb{F}_{\mathsf{O}_2}$ are the mixture fugacities of CO, CO_2 and O_2 at the partial pressures P_{CO}, P_{CO_2} and P_{O_2}, respectively. Expressing each of these equations in terms of $\mathbb{F}_{\mathsf{O}_2}$ and combining we have:

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

This can be rearranged to:

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

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

$$\begin{aligned} \mathbb{F}_{\mathrm{CO}} &= \gamma_{\mathrm{CO}}^{P_{\mathrm{CO}}} \cdot P_{\mathrm{CO}} \\ \mathbb{F}_{\mathrm{CO}_2} &= \gamma_{\mathrm{CO}_2}^{P_{\mathrm{CO}_2}} \cdot P_{\mathrm{CO}_2} \end{aligned} \tag{7}$$

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 $P = P_{\mathrm{CO}} + P_{\mathrm{CO}_2}$ (assuming that P_{O_2} ~ 0) and the mole fractions in the gas mixture, that is:

$$\begin{aligned} \mathbb{F}_{\mathrm{CO}} &= f_{\mathrm{CO}} \cdot \frac{P_{\mathrm{CO}}}{P} \\ \mathbb{F}_{\mathrm{CO}_2} &= f_{\mathrm{CO}_2} \cdot \frac{P_{\mathrm{CO}_2}}{P} \end{aligned} \tag{8}$$

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

$$\begin{aligned} \mathbb{F}_{\mathrm{CO}} &= \gamma_{\mathrm{CO}} \cdot P_{\mathrm{CO}} \\ \mathbb{F}_{\mathrm{CO}_2} &= \gamma_{\mathrm{CO}_2} \cdot P_{\mathrm{CO}_2} \end{aligned} \tag{9}$$

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

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

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

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

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

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

Replacing $\mathbf{f}_{\mathsf{CO}} = \gamma_{\mathsf{CO}} \cdot P_{\mathsf{CO}}$ in the expression for the thermodynamic equilibrium constant K_α in reaction (3) we can then write:

$$K_\alpha = \frac{(\gamma_{\mathsf{CO}} \cdot P^2_{\mathsf{CO})}}{\mathbf{f}_{\mathsf{O}_2}} = \exp\left(-\frac{\Delta G^{P_1,T_1}_{rxn}}{R \cdot T_1}\right) \tag{13}$$

Where $\Delta G^{P_1,T_1}_{rxn}$ 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:

$$\mathbf{f}_{\mathsf{O}_2} = [\gamma_{\mathsf{CO}} \cdot P_{\mathsf{CO}}]^2 \cdot \exp\left(\frac{\Delta G^{P_1,T_1}_{rxn}}{R \cdot T_1}\right) \tag{14}$$

REFERENCES

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