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

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

$$C + O_2 \rightleftharpoons CO_2$$

(1)

it is also necessary to take account of the competing Boudouard reaction ($C + \frac{1}{2}O_2 \rightleftharpoons CO$). Using the approach of French and Eugster (1965) this can be done by considering reaction (1) as a coupled system of the form:

$$2C + 2O_2 \overset{K_\alpha}{\rightleftharpoons} 2CO + O_2 \overset{K_\beta}{\rightleftharpoons} 2CO_2$$

(2)

For which the two thermodynamic equilibrium constants $K_\alpha$ and $K_\beta$ are defined by:

$$K_\alpha = \frac{(P_{CO})^2}{P_{O_2}}$$

(3)

$$K_\beta = \frac{(P_{CO_2})^2}{(P_{CO})^2 \cdot P_{O_2}}$$

(4)

where $P_{CO}$, $P_{CO_2}$ and $P_{O_2}$ 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 $P_{O_2}$ and combining we have:

$$\frac{(P_{CO})^2}{K_\alpha} = \frac{(P_{CO_2})^2}{(P_{CO})^2 \cdot K_\beta}$$

(5)

This can be rearranged to:

$$P_{CO_2} = (P_{CO})^2 \cdot \sqrt{\frac{K_\beta}{K_\alpha}}$$

(6)

The mixture fugacities of $P_{CO}$ and $P_{CO_2}$ can be expressed as the product of their partial pressures and the mixture fugacity coefficients $\gamma_{CO}^{P_{CO}}$ and $\gamma_{CO_2}^{P_{CO_2}}$ at those partial pressures, that is:
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 \( P = P_{CO} + P_{CO_2} \) (assuming that \( P_{O_2} \approx 0 \)) and the mole fractions in the gas mixture, that is:

\[
\begin{align*}
\mathbb{F}_{CO} &= f_{CO} \cdot \frac{P_{CO}}{P} \\
\mathbb{F}_{CO_2} &= f_{CO_2} \cdot \frac{P_{CO_2}}{P}
\end{align*}
\]  

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

\[
\begin{align*}
\mathbb{F}_{CO} &= \gamma_{CO} \cdot P_{CO} \\
\mathbb{F}_{CO_2} &= \gamma_{CO_2} \cdot P_{CO_2}
\end{align*}
\]  

where \( \gamma_{CO} \) and \( \gamma_{CO_2} \) are the pure gas fugacities of CO and CO\(_2\) at the total pressure \( P \), substituting into equation (6) we have:

\[
\gamma_{CO_2} \cdot P_{CO_2} = (\gamma_{CO} \cdot P_{CO})^2 \cdot \sqrt{\frac{K_\beta}{K_\alpha}}
\]  

Using \( P_{CO_2} = P - P_{CO} \) in equation (6) we can eliminate \( P_{CO_2} \) and rearrange to get a quadratic expression for \( P_{CO} \) of the form:

\[
\left( (\gamma_{CO})^2 \cdot \sqrt{\frac{K_\beta}{K_\alpha}} \right) \cdot (P_{CO})^2 + \gamma_{CO_2} \cdot P_{CO} - (\gamma_{CO_2} \cdot P) = 0
\]  

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

\[
P_{CO} = \frac{-\gamma_{CO_2} - \sqrt{\left(\gamma_{CO_2}\right)^2 + 4\gamma_{CO_2} \cdot (\gamma_{CO})^2 \cdot \sqrt{\frac{K_\alpha}{K_\beta}}}}{2(\gamma_{CO})^2 \cdot \sqrt{\frac{K_\alpha}{K_\beta}}}
\]
Replacing \( f_{\text{CO}} = \gamma_{\text{CO}} \cdot P_{\text{CO}} \) in the expression for the thermodynamic equilibrium constant \( K_{\alpha} \) in reaction (3) we can then write:

\[
K_{\alpha} = \frac{(\gamma_{\text{CO}} \cdot P_{\text{CO}}^2)}{f_{O_2}} = \exp \left( -\frac{\Delta G_{r_{\text{rxn}}}^{P_1,T_1}}{R \cdot T_1} \right) \tag{13}
\]

Where \( \Delta G_{r_{\text{rxn}}}^{P_1,T_1} \) 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:

\[
f_{O_2} = [\gamma_{\text{CO}} \cdot P_{\text{CO}}]^2 \cdot \exp \left( \frac{\Delta G_{r_{\text{rxn}}}^{P_1,T_1}}{R \cdot T_1} \right) \tag{14}
\]
REFERENCES