Electrochemistry and the Redox Potential

R. Corn - - Chem M3LC

1. Nernst Equation for reduction-oxidation (Redox) reactions

For example, consider the reaction: $Fe^{3+} + Ce^{3+} \rightarrow Fe^{2+} + Ce^{4+}$

$\Delta G = -nFE_{cell}$

$\Delta G = \Delta G^0 + RTlnQ$

These two equations are combined to become the Nernst Equation:

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF}lnQ$$

where $\Delta G^0 = -nFE_{cell}^0$

The cell potential is related to the ΔG of the reaction.

2. Half Cell Reactions and the Redox Potential

The cell potential can be calculated from the difference between two Half Cell Potentials:

$Fe^{3+} + e \rightarrow Fe^{2+}$

$E_{Fe} = E_{Fe}^0 - \frac{RT}{F}ln\frac{[Fe^{2+}]}{[Fe^{3+}]}$

$Ce^{4+} + e \rightarrow Ce^{3+}$

$E_{Ce} = E_{Ce}^0 - \frac{RT}{F}ln\frac{[Ce^{3+}]}{[Ce^{4+}]}$

$E_{cell} = E_{Fe} - E_{Ce}$

Half Cells are written as reductions. The E^0s are tabulated based on the normal hydrogen electrode (NHE) scale, which defines E_H^0 as zero:

$H^+ + e \rightarrow \frac{1}{2}H_{2(g)}$ $\quad$ $E_H = E_H^0 + \frac{RT}{F}ln\frac{{P_{H_2}}^{1/2}}{[H^+]}$ $\quad$ $E_H^0 = 0$

E_{Fe} is called the Half Cell Potential, or the **Redox Potential** for the Fe^{2+}/ Fe^{3+} couple.

The Redox Potential can be measured in any aqueous system, and sets the concentration ratios of ALL of the redox species in the solution.

3. Electrochemical Alpha Fractions

The total concentration of Fe in a solution is given by C_{Fe}^{TOT}:

$$C_{Fe}^{TOT} = [Fe^{2+}] + [Fe^{3+}]$$

This concentration is divided into the oxidized and reduced forms. The fraction of the total Fe in each form is called the alpha fraction:

$$\alpha_{Fe^{2+}} = \frac{[Fe^{2+}]}{C_{Fe}^{TOT}} \qquad \alpha_{Fe^{3+}} = \frac{[Fe^{3+}]}{C_{Fe}^{TOT}} \qquad \alpha_{Fe^{2+}} + \alpha_{Fe^{3+}} = 1$$

Using the Fe half cell reaction, we can derive equations for the two alpha fractions that depend on the value of E_{Fe}:

$$\alpha_{Fe^{2+}} = \left[1 + exp\left(\frac{F}{RT}(E_{Fe} - E_{Fe}^{0})\right)\right]^{-1}$$

$$\alpha_{Fe^{3+}} = \left[1 + exp\left(-\frac{F}{RT}(E_{Fe} - E_{Fe}^{0})\right)\right]^{-1}$$