Electrode potential and cell emf - Electrode Potential Overview

Derivation of the Nernst Equation

The Nernst equation is derived using the fundamental thermodynamic relationship between Gibbs free energy, reaction quotient, and electrode potential.

Step 1: Relationship Between Gibbs Free Energy and Electrode Potential

The change in Gibbs free energy (ΔG) for an electrochemical reaction is related to the cell potential by:

$$\Delta G = -nFE$$

where:

- ΔG = Gibbs free energy change
- n = Number of electrons transferred
- F = Faraday's constant (96485 C/mol)
- E = Electrode potential

Similarly, under standard conditions:

$$\Delta G^\circ = -nFE^\circ$$

where E° is the standard electrode potential.

Step 2: Gibbs Free Energy and Equilibrium Relationship

From thermodynamics:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where:

- R = Universal gas constant (8.314 J/mol·K)
- T = Absolute temperature in Kelvin
- Q = Reaction quotient

Substituting $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$:

$$-nFE = -nFE^\circ + RT \ln Q$$

Step 3: Expressing the Nernst Equation

Dividing throughout by $-nF$:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

This is the **Nernst equation** in its general form.

Step 4: Simplified Form at 25°C (298K)

At **room temperature** (298 K), substituting values:

$$\frac{RT}{F} = \frac{(8.314 \times 298)}{96485} = 0.0257V$$

So the equation becomes:

$$E = E^\circ - \frac{0.0257}{n} \ln Q$$

Converting natural logarithm to base 10:

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

where **0.0591V** is the constant at 25°C.

This is the most commonly used form of the **Nernst equation** in electrochemistry.