

Electrode potential and cell emf

Electrode Potential

- **Origin of Electrode Potential:**

- Arises due to the tendency of a metal to lose or gain electrons when in contact with its own ion solution.
- Metal atoms tend to dissolve as cations, leaving behind excess electrons, creating a potential difference.
- The equilibrium between oxidation and reduction reactions defines the electrode potential.

- **Nernst Equation:**

- Used to calculate the electrode potential of a half-cell under non-standard conditions.
- Formula:

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

Where:

- E = Electrode potential at given conditions
- E° = Standard electrode potential
- R = Universal gas constant (8.314 J/mol·K)
- T = Temperature in Kelvin
- n = Number of electrons involved
- F = Faraday's constant (96485 C/mol)
- Q = Reaction quotient

- **Example:**

- Consider a Zn/Zn²⁺ half-cell at 25°C with $[Zn^{2+}] = 0.01M$.
- Standard electrode potential: $E_{Zn^{2+}/Zn}^\circ = -0.76V$
- Using Nernst equation:

$$E = -0.76 - \frac{0.0591}{2} \log(0.01)$$

$$E = -0.76 + 0.02955 \times 2$$

$$E = -0.70V$$

- **Formula for Cell EMF:**

$$E_{\text{cell}} = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

- **Problem:**

Calculate the cell potential for a Daniell cell at 25°C when $[Zn^{2+}] = 0.001M$ and $[Cu^{2+}] = 0.1M$.

Given:

- $E_{Zn^{2+}/Zn}^\circ = -0.76V$
- $E_{Cu^{2+}/Cu}^\circ = 0.34V$

Solution:

1. Calculate standard EMF:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= 0.34 - (-0.76) = 1.10V \end{aligned}$$

2. Apply Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \\ &= 1.10 - \frac{0.0591}{2} \log \frac{0.001}{0.1} \\ &= 1.10 - \frac{0.0591}{2} \log(10^{-2}) \\ &= 1.10 - \frac{0.0591}{2} \times (-2) \\ &= 1.10 + 0.0591 = 1.16V \end{aligned}$$

Final Answer: $E_{\text{cell}} = 1.16V$