NERNST EQUATION

- The cell potential of a galvanic cell depends on the concentrations of the reactants and products of the cell reaction.
- The cell potential generated under **non-standard conditions** can be calculated using **Nernst equation.**

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln Q$$

where

Q = reaction quotient

n = number of moles of e^-

Nernst Equation

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} \log Q$$

$$\frac{2.303\ (8.314\ \cancel{J}\ \cancel{mol}^{-1}\ \cancel{K}^{-1})\ (298.15\ \cancel{K})}{n(96495\ \cancel{J}\ V^{-1}\ \cancel{mol}^{-1})} \log Q$$

At 25 °C

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

- The Nernst equation for the general equation :

$$aA + bB \longrightarrow cC + dD$$

At 25 °C

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q

- Only species with concentration or partial pressure are included Q expression. Solid and liquid are excluded.

- E_{cell} could be increased by decreasing the Q, this can be done by
  - Increasing the concentration of reactant or
  - Decreasing the concentration of product

Uses of Nernst equation

- ✓ To calculate E_{cell} at non-standard condition.
- ✓ To predict spontaneity of a cell reaction at non-standard condition.
- ✓ To calculate concentration of ions or partial pressure of a gas in a galvanic cell at non-standard condition.
- ✓ To determine equilibrium constant, K.

Determination of E_{cell} and predict spontaneity of a cell reaction at non-standard condition

Example

$Mg(s) + 2Fe^{3+}(aq, 5.0\ M) \longrightarrow Mg^{2+}(aq, 10.0\ M) + 2Fe^{2+}(aq, 1.0\ M)$

anode (ox) : $Mg(s) \rightarrow Mg^{2+}(aq) + 2e-$

cathode (red) : $[Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)] \times 2$

$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$

Overall : $Mg(s) + 2Fe^{3+}(aq) \longrightarrow Mg^{2+}(aq) + 2Fe^{2+}(aq)$

Nernst equation :

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

n = 2

$$E_{cell} = E^o_{cell} - \frac{0.0592}{2} \log \frac{[Mg^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Mg/Mg^{2+}}$$

$$= +0.77 - (-2.37)$$

$$= +3.14\ V$$

Nernst equation :

$$E_{cell} = E^o_{cell} - \frac{0.0592}{2} \log \frac{[Mg^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$$

$$E_{cell} = 3.14 - \frac{0.0592}{2} \log \frac{(10.0)(1.0)^2}{(5.0)^2}$$

$$= +3.153\ V$$

$$E_{cell} > 0$$

∴ **The reaction occurs spontaneously.**

Determination of Ion Concentration

Example

Pt (*s*) | H_2 (g,1 atm) | H^+ (aq, ? M) || Ag^+ (aq,1 *M*) | Ag (*s*)

E_{cell} = + 0.98 V   at 298 K

Determine the H^+ ions concentration, and the pH of H^+ solution in the galvanic cell.

Solution :

cathode (red) : $[Ag^+(aq) + e^- \longrightarrow Ag(s)] \times 2$ $E^o_{red} = +0.80$ V

anode (ox) : $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$ $E^o_{red} = 0$ V

Overall : $2Ag^+(aq) + H_2(g) \longrightarrow 2Ag(s) + 2H^+(aq)$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = +0.80 - 0.00 = +0.80 \text{ V}$$

Nernst equation :

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2} \log \frac{[H^+]^2}{[Ag^+]^2 P_{H_2}}$$

$$0.98 = 0.80 - \frac{0.0592}{2} \log \frac{[H^+]^2}{(1)^2 (1)}$$

$$\log \frac{[H^+]^2}{(1)^2 (1)} = (0.80 - 0.98) \times \frac{2}{0.0592}$$

$$\log[H^+]^2 = -6.081$$

$$2\log[H^+] = -6.081$$

$$\log[H^+] = -3.041$$

$$[H^+] = \text{antilog}(-3.041) = 9.109 \times 10^{-4}\ M$$

$$pH = -\log[H^+]$$

$$= -(-3.041)$$

$$= 3.041$$

Determination of Equilibrium Constant , K

$$aA + bB \rightleftharpoons cC + dD$$

- As reactions proceed concentrations of products increase and reactants decrease.
- When the reactions reach **equilibrium**, no net reactions occur $\Rightarrow$ $Q = K$ and $E_{cell} = 0$,

Nernst equation :

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

$$0 = E^o_{cell} - \frac{0.0592}{2} \log K$$

$$E^o_{cell} = \frac{0.0592}{2} \log K$$

Example

Calculate the equilibrium constant (K) for the following reaction.

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

Solution :

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$= E^{o}_{Ag^{+}/Ag} - E^{o}_{Cu^{2+}/Cu}$$

$$= +0.80 - 0.34$$

$$= +0.46 \text{ V}$$

At equilibrium, $E_{cell} = 0$, $Q = K$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$$

$$0 = E^o_{cell} - \frac{0.0592}{2} \log K$$

$$E^o_{cell} = \frac{0.0592}{2} \log K$$

$$0.46 = \frac{0.0592}{2} \log K$$

$$\log K = 15.54$$

$$K = 3.467 \times 10^{15}$$