

Electrochemistry

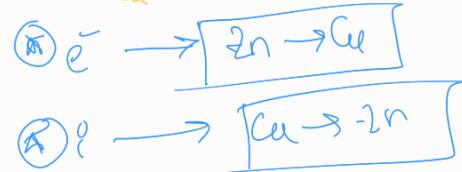


Galvanic Cells

- ⊗ Chemical to Electrical Energy
- ⊗ Spontaneous to non-spontaneous
- ⊗ $\Delta G < 0$

⊗ Anode = -ve (Zn) dissolves
cathode = +ve (Cu) deposited

⊗ $E_{cell} < 1.1 \text{ V}$



Electrolytic cells

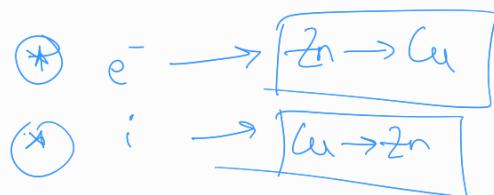
- ⊗ Electrical to chemical Energy

⊗ Non-spontaneous to spontaneous

⊗ $\Delta G > 0$

⊗ Anode = +ve (Cu) dissolves
cathode = -ve (Zn) deposited

⊗ $E_{cell} > 1.1 \text{ V}$



Electricity & Conductance

conductance due to ions in soln

Electrode Potential

$$E_{cell}^{\circ} = (E_{op}^{\circ})_{\text{anode}} + (E_{RP}^{\circ})_{\text{cathode}}$$

$$E_{cell}^{\circ} = (E_{RP}^{\circ})_{\text{cathode}} - (E_{op}^{\circ})_{\text{anode}}$$

NOTE

More than value of

E_{cell}° , More it is

Strongest Reducing agent \longleftrightarrow \longrightarrow lowest Oxidising agent

0

Lower Reducing agent \longleftrightarrow + \longrightarrow Strongest Oxidising agent

Gibb's Free Energy

$$\Delta G_r = -nF E_{cell} \Rightarrow \Delta G^{\circ} = -nF E_{cell}^{\circ}$$

$E_{cell} > 0, \Delta G < 0, \text{ Spontaneous.}$

$E_{cell} < 0, \Delta G > 0, \text{ Non-spontaneous.}$

Newnt Equ^r

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log Q \quad \left. \begin{array}{l} \\ \end{array} \right\} \begin{array}{l} \text{in solid and} \\ \text{liquid,} \\ \text{activity} = 1 \end{array}$$

$$\text{OR, } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log Q \quad \left. \begin{array}{l} \\ \end{array} \right\} \begin{array}{l} Q \rightarrow \text{Rxn Quotient.} \\ \text{in aq, activity} \\ = [\text{concentration}] \end{array}$$

(*) $-\log [H^+] = pH$

At Equilibrium, in newt equ^r $\rightarrow E_{\text{cell}} = 0$

Also, (*) $E_{\text{cell}}^{\circ} = -0.059 \log K_{\text{sp}}$

Concentration Cells

$E_{\text{cell}} > 0$

$(E_{RP})_{\text{cathode}} > (E_{RP})_{\text{anode}}$

For any type concentration cell, $E_{\text{cell}}^{\circ} = 0$

(*) $(E_{RP})_{\text{insoluble}} = (E_{RP})_{\text{soluble}} + \frac{0.059}{n} \log(K_{\text{sp}})$

(1) Electrolyte conc. cell

$$E_{\text{cell}} = 0 - \frac{0.059}{n} \log \left(\frac{C_1}{C_2} \right) \quad \begin{array}{l} (C_2 > C_1) \\ \text{anode} \\ \text{cathode} \end{array}$$

(2) Electrode conc. cell

$$E_{\text{cell}} = 0 - \frac{0.059}{n} \log \left(\frac{P_2}{P_1} \right) \quad \begin{array}{l} \text{cathode} \\ \text{anode} \end{array}$$

Electrolytic and Metallic Conductance

$$G_I = \frac{1}{R} \quad (\text{conductance}) \quad \text{Unit} \rightarrow \Omega^{-1} \text{ or Siemen}$$

$$\boxed{\text{Temp} \uparrow, G_I \downarrow}$$

(i) Solute-solute interaction $\uparrow, G_I \downarrow$

(ii) Solute-solvent interaction $\uparrow, G_I \downarrow$

(iii) Solvent-solvent interaction $\uparrow, G_I \downarrow$

Metallic/electronic conductance

$$\uparrow \uparrow, R \uparrow, G_I \downarrow$$

Electrolyte/ion Conductance

$$\uparrow \uparrow, R \downarrow, G_I \uparrow$$

Molar Conductivity (Λ_m)

$$\Lambda_m = \frac{K \times 1000}{m \text{ (mol/l)}}$$

$$S \text{ cm}^{-1}$$

$$\Lambda_m = \frac{K}{m \times 1000}$$

(s m^{-1})
 (mol/l)

$$\Lambda_m = \frac{K}{c} \rightarrow S \text{ cm}^{-1}$$

$$\downarrow$$

$$\rightarrow \text{mol cm}^{-3}$$

$$S \text{ cm}^{-1} \text{ mol}^{-1}$$

$$K = C_1 \times G^* \Rightarrow K = \frac{1}{R} \left(\frac{\lambda}{A} \right)$$

Effect of conc' of K and Λ_m

For both strong and weak electrolyte

(i) $K \downarrow, \downarrow$ in concentration for both strong and weak electrolyte

(ii) Becz, the number of ion per unit volume that carry the current in a soln decreases on dilution.

(iii) $\Lambda_m \uparrow, c \downarrow$ (strong electrolyte)

(iv) $\Lambda_m \uparrow, c \uparrow$ (for weak electrolyte)

(v) $c \downarrow, \alpha \uparrow$

Graph



Kohlrausch law

$$\Lambda_m^\circ = \Lambda_{ira}^\circ + \Lambda_{cl}^\circ$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

equilibrium constant

$$K_{eq} = \frac{C \alpha^\gamma}{1 - \alpha}$$

if $\alpha < 0.1$

$$K_{eq} = C \alpha^\gamma$$

Electrolysis

④ Electrolysis of Molten PbBr_2



④ Electrolysis of Molten NaCl



Oxidation of H_2O

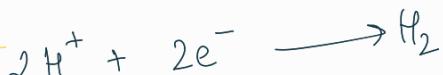


Reduction of H_2O



Electrolysis of Sulphuric Acid :-

Cathode



Anode

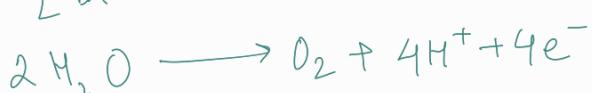


④ Electrolysis of NaBr :- (Same will be for NaCl)

Cathode



Anode



Faraday's Law :-

1st law :-

$$\frac{W}{E} = \frac{Q}{F}$$

Current Efficiency $\rightarrow \frac{\text{Actual Mass}}{\text{Theoretical Mass}} \times 100$

④ 2nd Law of Faraday :- Equivalent of A = Equivalent of B = . . .

Sparingly Soluble salt



$$2s \quad 3s$$

$$k_{sp} = (2s)^2 \times (3s)^3$$

$$\Rightarrow k_{sp} = 4s^2 \times 27s^3$$

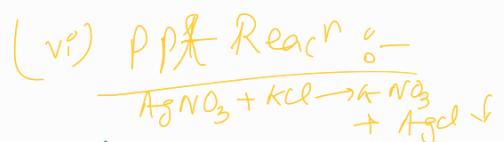
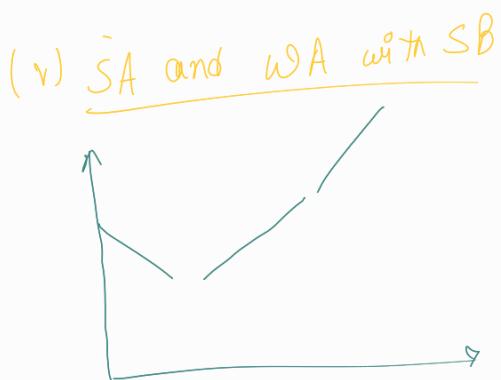
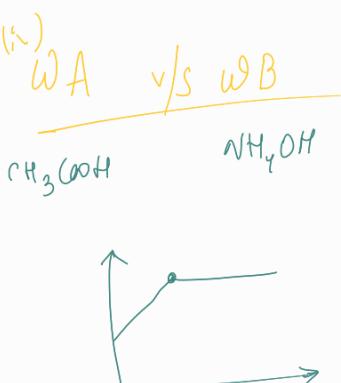
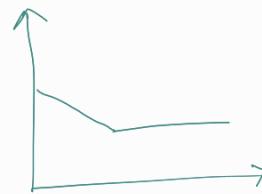
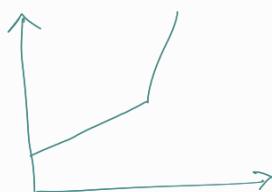
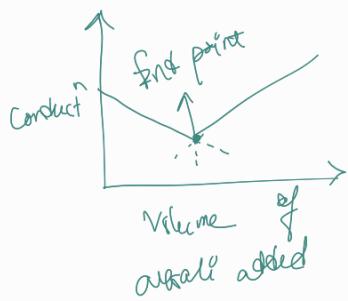
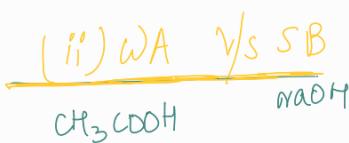
$$\therefore k_{sp} = 108s^5$$

Relate

formula

$$\sqrt[10]{m} = \frac{k \times 1000}{s}$$

Conductometric Titration



if $K^+ > Ag^+$



if $K^+ < Ag^+$

