10. Electrochemistry

- **Faraday's 1st Law**

The mass of substance deposited at an electrode is directly proportional to charge pass through it.

Mass $\propto$ Charge (Q)

$W \propto Q$

$W = ZQ$ (Z = electrochemical equivalent)

(Q = Charge in Coulombs)

$W = Z I t$

I = current in Ampere

t = time in seconds

$W = Z Q$ (Q = 1C) **Remember**

then $W = Z$

1 F charge deposits

1 g eq of any substance

So $W = \frac{E I t}{F}$ sec of substance

= No. of faradays

- **Faraday's 2nd Law**

If equal electricity is passed through two or more cells connected in series then the mass of substance deposited is directly proportional to equivalent mass

$W_1 \propto E_1$

$W_2 \propto E_2$

$$\frac{W_1}{E_1} = \frac{W_2}{E_2}$$

- Degree of dissociation : $\alpha = \frac{\lambda_{eq}}{\lambda^0_{eq}}$

- Kohlraush's law : $\Lambda^0_m = x\lambda^0_A + y\lambda^0_B$

- **Under standard conditions (E^o)**

$E^o_{cell} = E^o_{RP}(\text{cathode}) - E^o_{RP}(\text{anode})$ (or)

$E^o_{cell} = E^o_{OP}(\text{anode}) - E^o_{OP}(\text{cathode})$ (or)

$E^o_{cell} = E^o_{OP}(\text{anode}) + E^o_{RP}(\text{cathode})$

- Nernst Equation

$$E = E^\circ - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]}$$

& $E^\circ_{Cell} = E^\circ_{right} + E^\circ_{left}$ & $K_{eq.} = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$

$\Delta G = -nFE_{cell}$ &

$\Delta G^\circ = -nFE^\circ cell = -2.303\, RT \log K_c$

& $W_{max} = +nFE^\circ$ & $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

- **Application of Nernst Equation**

To find the $\mathbf{E_{cell}}$ of concentration cells

$E_{cell} = \frac{0.059}{n}\log_{10}\left(\frac{C_2}{C_1}\right)$ (for conc^n cell $\mathbf{E^o_{cell} = 0}$)

To find the pH of concentration cell

For the measurement of Eq. constant (**K**)

$$\boxed{E^0_{cell} = \frac{0.059}{n}\log_{10}K_C}$$

- Calculation of pH of an electrolyte by using a calomel electrode :

$$pH = \frac{E_{cell} - 0.2415}{0.0591}$$

- Thermodynamic efficiency of fuel cells :

$\eta = \frac{-\Delta G}{\Delta H} = \frac{-nFE^\circ_{cell}}{\Delta H}$ For $H_2 - O_2$ fuel cells it is 95%.

- $P = K_H.X$

Summing-up the Units of Different Quantities					
S.N.	Physical	Symbol	Expression	Commonly used Units	SI Units
1.	Resistance	Rq	$R = \frac{V}{I}$	omh (Ω)	omh (Ω)
2.	Conductance	G	$R = \frac{1}{R}$	omh^{-1} (Ω^{-1})	seimen(S)
3.	Specific resistance	ρ	$\rho = \frac{a}{1}$	ohm cm	ohm m
4.	Conductivity	k	$k = G\frac{l}{a} = \frac{1}{R}\frac{l}{a} = \frac{l}{p}$	$ohm^{-1}cm^{-1}$ ($\Omega^{-1}cm^{-1}$)	$S\ m^{-1}$
5.	Equivalent conductivity	Λ_{eq}	$\Lambda_{eq} = \frac{k}{normality}$	$ohm^{-1}cm^2\ eq^{-1}$($\Omega^{-1}cm^2eq^{-1}$)	$S\ m^2\ eq^{-1}$
6.	Molar conductivity	Λ_m	$\Lambda_m = \frac{k}{molarity}$	$ohm^{-1}cm^2\ eq^{-1}$($\Omega^{-1}cm^2eq^{-1}$) S	$m^2\ mol^{-1}$
7.	Cell constant	G*	$G^* = \frac{l}{a}$	cm^{-1}	m^{-1}

Effect of dilution on

Conductance → Increases

Λ_m & Λ_{eq} → Increases

Conductivity → Decreases

Debye–Huckel–Onsager equation :

$\Lambda_m = \Lambda^0{}_m - b\sqrt{C}$ (or) $\Lambda_{eq} = \Lambda^o_{eq} - b\sqrt{C}$

Λ_m = Molar conductance at given concentration

$\Lambda^0{}_m$ = Molar conductance at infinite dilution

C = concentration in molarity.

b = Constant value depends on type of electrolyte, solvent & temp.

- With dilution the Degree of dissociation of weak electrolyte increases, so Λ_m increases.