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12th Class Chemistry
Electrochemistry

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Electrochemistry :-

It is that branch of chemistry in which we are studies about the relationship b/w electrical energy and chemical energy and their interconversion.

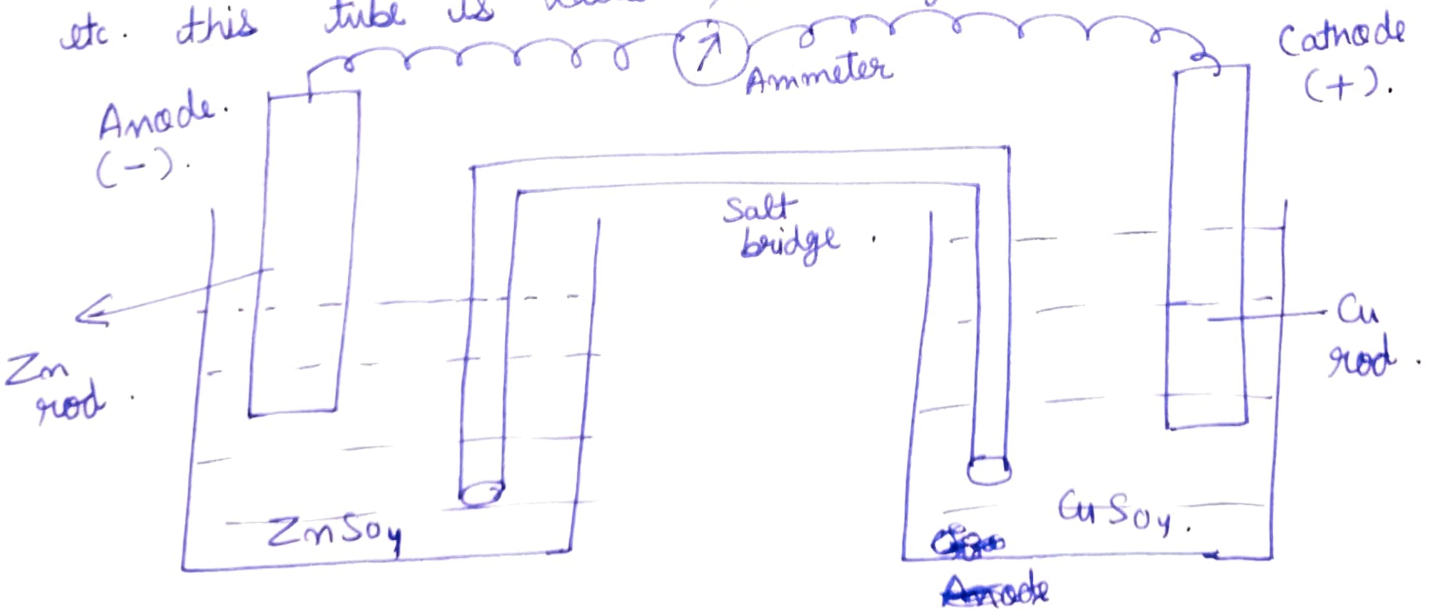
A chemical reax. in which electrons are lost by one substance and gained by another is called redox reax. In this transfer of electrons is the reason for electric current.

There are two types of cells - Electrochemical cells and Electrolytic cells.

=> Electrochemical cell :-

It is a device in which chemical energy of redox reax. is converted into electrical energy.

[It consists of two metallic electrodes dipping in electrolytic solutions. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCN. or KNO_3 or NH_4NO_3 (inert electrolyte) etc. this tube is called salt bridge.



$Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation).

$Cu^{+2} + 2e^- \longrightarrow Cu$. (Reduction).

Significance of Salt bridge :-

① It connects the Solution of two half-cells, thus Complete the cell circuit.

② It prevents transference or diffusion of the Solutions from one half-cell to other etc.

Note :- In Galvanic cell, oxidation occurs at anode and it is a negative plate, while reduction occurs at Cathode and it is a positive plate.

Nernst equation. :- It ~~is~~ gives the relation between electrode potential, temperature and Concentration of metal ions.

$$M^{n+} + ne^- \longrightarrow M.$$

$$\Rightarrow E_{Metal} = E^\circ_{Metal} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}.$$

$$\Rightarrow E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[oxi]}{[Red]}.$$

where $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$.

or

$E^\circ_{Right} - E^\circ_{Left}$.

Application :-

① To Calculate electrode Potential of a Cell.

$$aA + bB \xrightarrow{ne^-} cC + dD.$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[C]^c . [D]^d}{[A]^a . [B]^b}.$$

② To Calculate equilibrium Constant.

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_c.$$

③ Gibbs free energy and Cell Potential.

$$\Delta G^\circ = -nFE^\circ_{cell}.$$

or.

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

where. $F = 96500\ C$.

Relation b/w Cell Potential and equilibrium Constant.

$$E_{cell} = E^\circ_{cell} - \frac{2.303}{nF} \log K_c.$$

Example :- Depict the galvanic cell in which the Cell reax. is :- $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$

$\Rightarrow$ $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag.$

④

Conductances of Electrolytic or Ionic Solutions and its measurement :-

=> Resistance :-

$$R = \frac{V}{I}$$

where R = Resistance.

unit of Resistance = ohm or Ω.

where V = Voltage.

I = Current.

unit of Voltage = Volt (V).

" " current = Ampere (A).

=> Resistivity or specific resistance :-

$$R \propto \frac{l}{A}$$

- $R = \rho \frac{l}{A}$.

or $\rho = \frac{RA}{l}$

where ρ = Resistivity.

A = Area

l = Length.

unit of resistivity = Ω m.

=> Conductance :-

The ease with which current flows through a conductor is known as its Conductance.

(It is inverse of Resistance).

$$G = \frac{1}{R} = \frac{A}{\rho l}$$

or $G = K\frac{A}{l}$ [where K = Conductivity, $K = \frac{1}{\rho}$].

S.I unit of Conductance (G) = Siemens (S) or ohm^{-1}.

=> Conductivity (specific conductance) :-

$$K = \frac{1}{\rho}$$

S.I unit of Conductivity is $S m^{-1}$.

or $S cm^{-1}$.

Note :-
[It always decreases with decrease in Concentration for weak and strong electrolytes].

=> Cell Constant (G^*) :-

$$G^* = \frac{l}{A} = RK$$

[~~where~~ ∵ $R = \rho\frac{l}{A}$.

$\Rightarrow \frac{l}{A} = \frac{R}{\rho}$

and $K = \frac{1}{\rho}$]

S.I unit of cell Constant is m^{-1}.

Note :-
=> K is also Called Kappa.

$$K = G G^* = \frac{A}{\rho l} \times \frac{l}{A} = \frac{1}{\rho}.$$

(Cap m)

Molar Conductivity :- (Λ_m)

It is defined as the conductance of that volume of Solution which Contains one ~~or~~ mole of the electrolyte Such that, entire Solution is in between the two electrodes kept one Centimetre apart and have large cross-sectional area, So as to Contain the electrolyte

or.

The conductance of 1 mole electrolytic Solution. i.e Called Λm.

Thus, molar conductance.

$$\Lambda_m = \frac{K \times 1000}{\text{Molarity}} \quad \text{or} \quad \lambda_m = KV.$$

It increases with decrease in Concentration (or increase on dilution). Its unit is $S m^2 mol^{-1}$ or $S cm^2 mol^{-1}$.

when $C \rightarrow 0$ (concentration), $\Lambda_m = \Lambda^\circ_m$, i.e. when Concentration. approches zero, the molar conductivity reaches a limiting value known as limiting molar conductivity (Λ°_m)

The variation in Λm with Concentration is different for strong and weak electrolytes. Such Variation for KCl (strong electrolyte) and CH_3COOH (weak electrolyte has been depicted below:-

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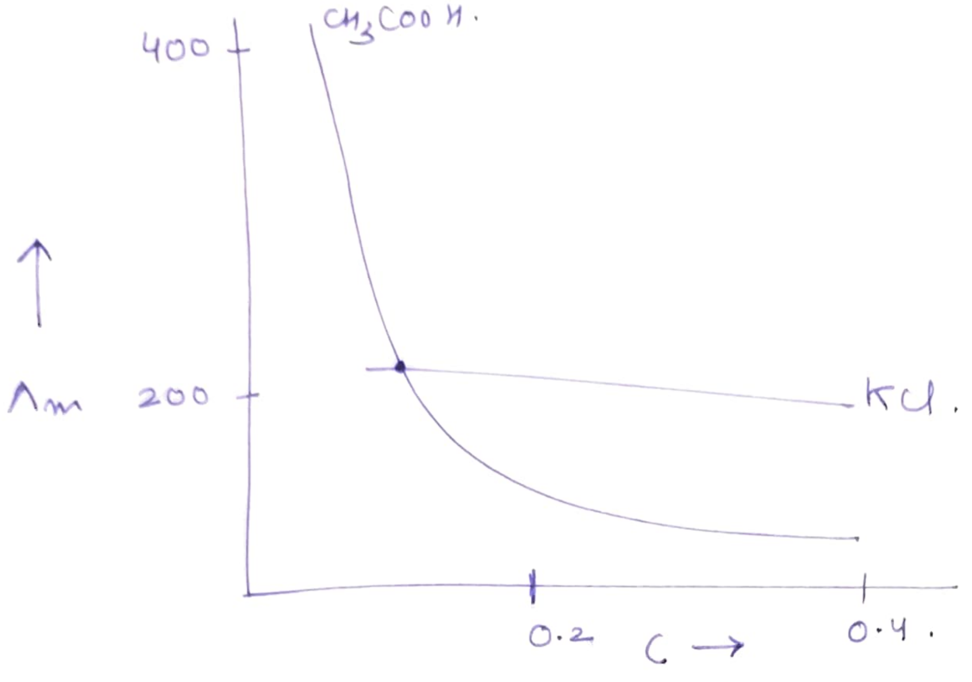

Kohlrausch's law of independent migration of ions :-

This law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte.

$$\Lambda^\circ_m = \Lambda^\circ_+ \text{Cations} + \Lambda^\circ_- \text{Anions}.$$

Degree of Dissociation (α) :-

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m}$$

where Λ^c_m = molar conductance of concentration c.

Λ°_m = molar conductance ~~of concentration~~ at infinite dilution.

Dissociation Constant (K_a) :-

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

Applications of Kohlrausch's law :-

① The molar conductivity of weak electrolytes at infinite dilution can be calculated by using Kohlrausch's law.

② Degree of dissociation of weak electrolyte (like acetic acid) at a given concentration can be calculated.

③ Knowing the degree of dissociation (α,) the dissociation constant (K) of the weak electrolyte at a given concentration of the solution can be calculated.