H^+Cl^-

Electrolyte	Electrode	Anode prod.	cathode prod.
$CuSO_4$ (aq.)	Cu	Cu (dis.)	Cu(s) (pure
HCl (conc)	inert	Cl_2(g)	H_2(g).
H_2SO_4 (conc)	inert	S_2O_8 (semi solid)	H_2(g)

* Faraday's 1st law of electrolysis:

- weight of substances deposited or liberated at an electrode during electrolysis are directly proportional to electricity that passes through an electrolyte.

- if 'W gm' of substance deposited on passing Q coulombs of electricity, then

$$W \propto Q \qquad w = z \times Q$$

$$z = \frac{E}{96500} \qquad w = z \times I \times t$$

$$w = \frac{E}{96500} \cdot It \qquad \text{gm equiv.} = \frac{W}{E} = \frac{It}{96500}$$

$$\frac{W}{M} = \frac{It}{96500 \cdot n} \qquad W = E \cdot F$$

z = proportionality constant.
↳ Electrochemical equivalent of substance deposited.

here, n = n factor M = molecular weight.

Q:12 'W' gm of copper deposited in copper voltmeter when an electric current of 2 ampere is passed for 2 hours. If one ampere e. current passed for 4 hours in same voltameter, copper deposited will be.

→ $I = 2\text{amp}$ $t = 2\text{hr}$ $I = 1\text{amp}$ $t = 4\text{hrs}$

$W = It$ $W = It$

$= 2 \times 2$ $= 1 \times 4$

$\underline{\underline{W = 4}}$ $\underline{\underline{W = 4}}$.

$\therefore \underline{\underline{W}}$.

Q:13 $I = 9.65$ amp. $t = 10\text{min.}$ $w = 3\text{gm}$ $E = ?$

→ $\downarrow$ 600secs.

$$W = \frac{E}{96500} \cdot It \longrightarrow \cancel{3} = \frac{E}{96500}(9.65)(\overset{200}{\cancel{600}}) \quad \therefore E = \frac{\overset{\overset{50}{\cancel{100}}}{\cancel{96500}} \times \cancel{100}}{\cancel{965} \times \cancel{200}} \quad \underline{\underline{E = 50}}.$$

Q:14 electrochemical equivalent of substance is 0.0006735. its equivalent weight is?

→ $Z = 6735 \times 10^{-7}$ $Z = E/96500$.

$\therefore E = 6735 \times 10^{-7} \times 965 \times 10^{2}$

$= 6499275 \times 10^{-5} \longrightarrow 64.99275 \simeq \underline{\underline{65}}$.

Q:15 How many Faraday's are required to reduce one mole of MnO_4^- to Mn^{+2}? $\underline{n = 5}$.

→ $Mn^{+7} \longrightarrow Mn^{+2}$ 1F = charge per mole.

$W = E \cdot F \longrightarrow W = \frac{M}{n} \cdot F$.

$\therefore \frac{W}{M} = \frac{F}{n}$ (mole) $1 = \frac{F}{5}$

$\therefore \underline{\underline{F = 5}}$. $\underline{\underline{5F\ \text{req.}}}$

Q:16 ion reduced to element when it absorbs 6×10^{20} electrons. No. of equivalent ion is:

→ $1F = 10^{23} \times 6$ (e^-) over 1 mole.

F = charge / mole(e^-)

e^-(ion) = 6×10^{20}

$$F = \frac{\cancel{6} \times 10^{20}}{6 \times 10^{23}} \longrightarrow 1 \times 10^{-3} \qquad \underline{\underline{0.001}}.$$

Q:17 How many minutes will it take to plate out 5gm (Cr) from $Cr_2(SO_4)_3$ soln with 1.50 Amp current.

52 amu

→ $Cr_2(SO_4)_3 \rightarrow Cr = +3$ nfact $= 3$.

mole chromium = 5/52.

$$\frac{W}{M} = \frac{It}{96500 \cdot n} \qquad \therefore \frac{5}{52} = \frac{\overset{0.1}{\cancel{\overset{0.5}{\cancel{1.50}}}} \times t}{96500 \times (\cancel{3})}$$

$$t = \frac{\overset{24125}{\cancel{\overset{48250}{\cancel{96500}}}} \times 10}{\underset{26\,13}{\cancel{52}}} \qquad t = \underline{\underline{18557 \text{ secs}}}$$

for mins,

$$t = \frac{18557}{60} \longrightarrow 309.2$$

$\Rightarrow$ $\underline{\underline{309}}$ mins

Q:18 ratio of wts of H_2 and Mg deposited by same amount of electricity from aq. H_2SO_4 and fused $MgSO_4$ are:

→ (eq wt H) $1 : \frac{\overset{12}{\cancel{24}}}{\cancel{2}}$ (eq. wt Mg) (n-fact).

$\underline{\underline{1:12}}$.

Q:19 Ag removed electrolytically from 200ml of 0.1N solⁿ of $AgNO_3$ by current of 0.1 Ampere. How long will it take to remove half of silver from solution.

→

(Z) * Electrochemical equivalent:

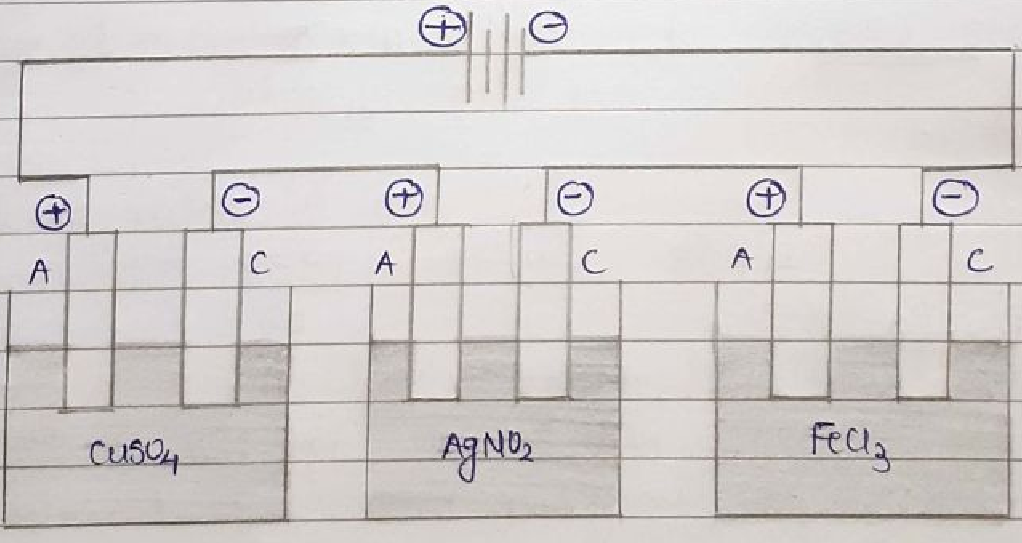
- If $I = 1$ ampere and $t = 1$ second, then $w = Z$.

So, electrochemical equivalence may be defined as amount of substance deposited by passing one ampere of current for one second or by passing one coulomb of charge through electrolyte.

* Faraday's 2nd law of electrolysis:

- when same quantity of electricity is passed through different electrolytes, amount of different substances deposited at electrodes is directly proportional to their equivalent mass (E).

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



eg: Q:

distil water = weakly H_2O
(ions)

Q:21. wt ratio of Al(3) and Ag(+1) deposited using same quantity of current is?

→ n fact for Al = +3 (27 amu) . n fact for Ag = +1. (108 amu).

$$\frac{W_1}{W_2} = \frac{\overset{9}{\cancel{27}}/\cancel{3}}{108}$$

9:108.

* Difference b/w metallic and electrolytic conductance:

Metallic conductance	Electrolytic conductance
• due to movement of electron	• due to movement of ion.
• no chemical changes in conductor	• chemical changes seen in electrolyte b'coz of chem. rxn
• no involvement of any kind of matter.	• Involves transfer of matter as ion
• metallic conduction decrease with increase in temp.	• electrolytic conductance increase with increase in temp

Board

* General terms related to electrolytic conductance:

1.) **Resistance (R):** every conducting material offers some obstruction to flow of electricity which is called Resistance.

→ denoted by R and it's unit is Ohm.

→ resistance of any object is directly proportional to its length 'l' and inversely proportional to its area of cross-section A.

inverse of Ohm = <u>mho</u>

$R \propto \frac{l}{A}$ $\quad R = \rho\frac{l}{A}$ → where, ρ(rho) is a constant called Specific resistance or resistivity.

→ unit Ohm·cm.

II.) **Conductance (G):** inverse of resistance is called conductance.

$G = \frac{1}{R}$ → unit ⇒ Ohm^{-1} or mho.
also Siemens (S).

Sir → Rate flow of charge in electrolytic solⁿ.

III.) **Conductivity (K):** inverse of resistivity is specific conductance known as conductivity.

→ represent by K (Kappa)
→ SI unit: S/m
→ also S/cm

$K = \frac{1}{\rho}$ $\qquad K = \frac{1}{R}\cdot\boxed{\frac{l}{A}}$ → cell constant
→ G^*

Sir → Conductance due to all ions present in 1 ml of electrolytic solⁿ.

So; Conductivity = Conductance × cell constant.

* **NOTE:**
- after dilution of an electrolytic solution conductivity decreases.

(2.12 2.13 Start
2.11 2.14 eq. 2.4
2.15
2.16

IV.) **Molar conductivity (Λ_m):** molar conductivity of a solution is defined as conducting power of ions produced by dissolving 1 mole of an electrolyte in solution.

$\Lambda_m = K \times V$ $\Lambda_m = \frac{K \times 1000}{M}$

unit : ohm^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}

here:
K = conductivity V = volume (cm^3)
M = molarity (molar concn of solution)

* NOTE:
- after dilution molar conductivity increase.

V.) **Limiting molar conductivity (Λ_m°):** value of molar conductivity when concentration approach zero is known as limiting molar conductivity or molar conductivity at infinite dilution.
$\underbrace{\text{infinite dilution}} \rightarrow$ concn = 0.

VI.) **Equivalent conductivity (Λ_{eq}):** $\Lambda_{eq} = \frac{K \times 1000}{N}$
here,
N = normality of solution.

* Relation b/w Λ_m and Λ_{eq}:

$\Lambda_{eq} = \frac{K \times 1000}{N}$ $\Lambda_{eq} = \frac{K \times 1000}{M \times n}$ $\therefore$ $\Lambda_m = \Lambda_{eq} \cdot n$ fact.

Q:22 specific conductance of salt of 0.01 M concⁿ is 1.061×10^{-4} $\Omega^{-1}cm^{-1}$ molar conduc. of solⁿ is:

→ $\Lambda_m = \frac{K \times 1000}{M}$

$= \frac{1.061 \times 10^{-4} \times 10^{3}}{1 \times 10^{-2}}$

$= \frac{1.061 \times 10^{-1}}{10^{-2}} \longrightarrow 1.061 \times 10^{1}$

$\longrightarrow \underline{\underline{10.61}}$.

Q:23 specific conductance of N/10 KCl at 25°C is 0.0112 ohm⁻¹ cm⁻¹, Resistance is 55ohm at same temp. cell constant will be?

→ $K = \frac{1}{R} \cdot G^*$ $\longrightarrow$ $112 \times 10^{-4} = \frac{1}{55} \cdot G^*$

$G^* = 6160 \times 10^{-4}$

$= \underline{\underline{0.616\ cm^{-1}}}$

Q:24 electrical resistance of column of 0.05 mol/ltr NaOH solⁿ of diameter 1cm length 50cm is 5.55×10^3 ohm. calculate resistivity, conductivity and molar conductivity.

→ area = $\pi r^2 \rightarrow 3.14 \times (0.5)^2 \rightarrow 0.785\ cm^2$

length = 50cm

$R = \frac{\rho l}{A} \rightarrow \rho = \frac{RA}{l} \longrightarrow \frac{\overset{111}{\cancel{5.55}} \times \overset{2}{\cancel{10^{3}}} \times 0.785}{\cancel{50}}$

$\rho = 87.135\ \Omega\ cm$.

- $K = \frac{1}{\rho} = \frac{1}{87.135} \rightarrow \underline{0.01148}$ $S \cdot cm^{-1}$

- $\Lambda_m = \frac{K \times 1000}{C} \rightarrow \frac{0.01148 \times 1000}{0.05} = \underline{229.6}$ $cm^2 mol^{-1}$

* Variation of Λ_m and K with concⁿ (effect of dilution):

→ Variation of conductivity (K) with concⁿ:

- conductivity decreases with decrease in concentration, this is because number of ions per unit volume that carry current in solution decrease on dilution.

→ Variation of molar conductivity (Λ_m) with concⁿ:

- molar conductivity ($\Lambda_m = K \cdot V$) is increased with increase in dilution or decrease in concentration, this is because molarity decreases with increase in total volume 'V' of solution.

- the trend of variation in molar conductivity with concentration for strong and weak electrolyte is totally different.

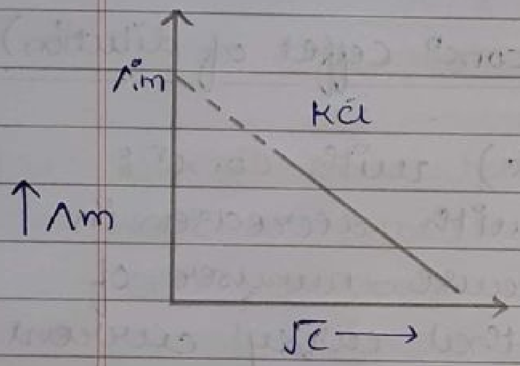
CASE:1 for strong electrolytes, Λ_m increases slowly with dilution and can be represented by Debye, Huckel and Onsager equation:

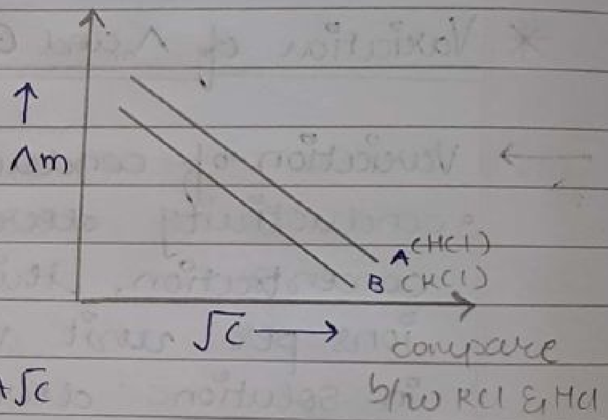
$$\Lambda_m = \Lambda^\circ_m - A C^{1/2}$$

(only for strong electrolyte)

- A = constant depending on nature of solvent and temperature.

- In case of strong electrolyte it is possible to determine molar conductivity at infinite dilution (Λ_m°) by extrapolation of curve $\underline{\Lambda_m}$ Vs $\underline{\sqrt{C}}$.





$$\therefore \Lambda_m = \boxed{\Lambda_m^\circ} - A\sqrt{C}$$

$$y = \boxed{c} - mx$$

Intercept [limiting molar conductivity]

CASE: II for weak electrolyte, molar conductivity increases steply with dilution. On contrary, value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of curve becomes almost parallel to y-axis when concentration approaches to zero.