

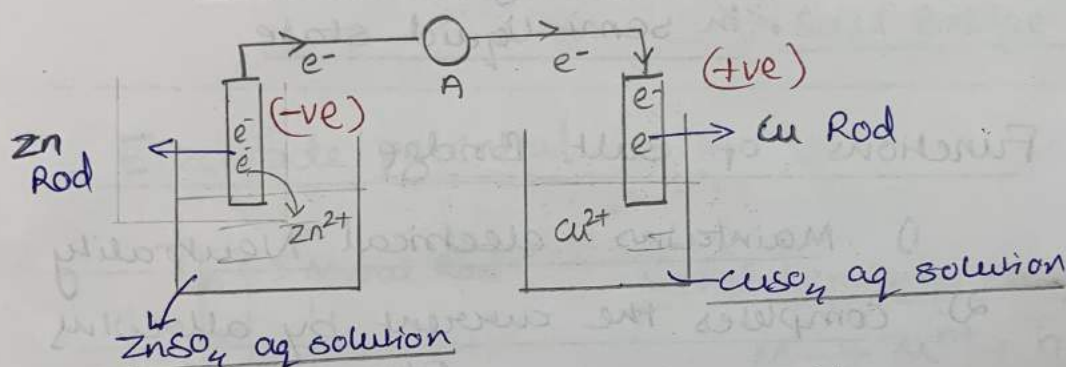
Electrochemistry

(1)

▶ Electrochemical cell / Galvanic cell / Voltaic cell

- chemical energy \rightarrow Electrical Energy
due to spontaneous Redox Rxn
 $\Delta G < 0$

• Zn-Cu cell \rightarrow Daniell cell

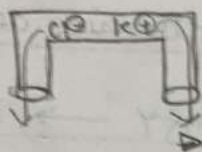


- $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$
oxidation
- oxidation half cell
- Left half cell
- -ve half cell
- Anode half cell
- $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
Reduction
- Reduction half cell
- +ve half cell
- Cathode half cell
- Right half cell

▶ Problem : After some time

- Left half cell +ve charge in solution prevent outward flow of e^-
- Right half cell -ve charge in solution prevent inward flow

10) Salt Bridge



Inverted U-tube glass

Electrolyte (Neutral)

Neutralises

The charges

→ here, $KCl / K_2SO_4 /$
 KNO_3 / NH_4Cl

• in Agar Agar Powder

• in semi liquid state

▷ Functions of Salt Bridge

- 1) Maintains electrical Neutrality
- 2) Completes the current by allowing Flow of e^-
- 3) Minimises the liquid-liquid Junction potential

▷ Conditions for electrolyte

i) inert Electrolyte

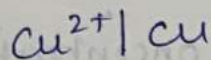
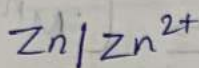
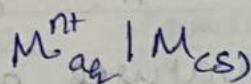
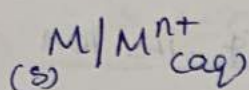
do not form precipitate (insoluble)

eg $AgCl$ (ppt)

because of KCl

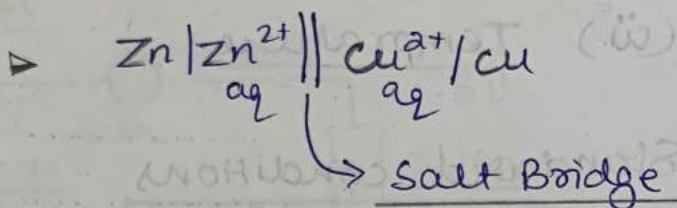
ii) Good Ionic Mobility & Equal Mobility of cation & Anion

► Cell Representation

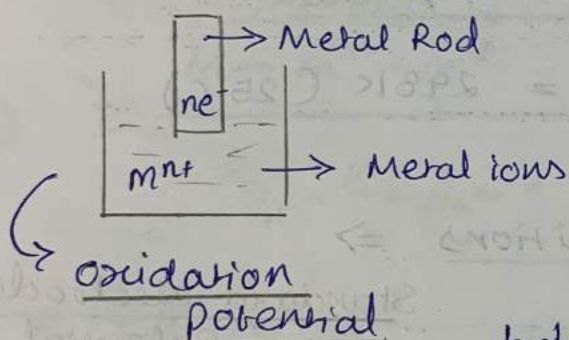


Oxidation
H.C

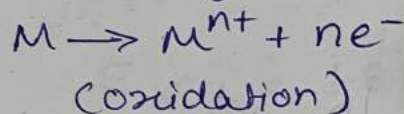
Reduction
H.C



Electrode potential



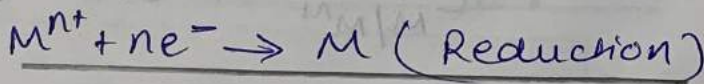
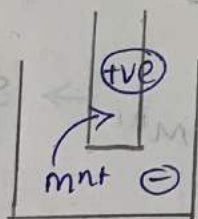
Metal tendency → oxidise



The potential difference
between the electrode
(metal)

& its electrolyte (under equilibrium)

is called Electrode potential



→ Reduction potential

Factors affecting electrode potential $[E]$

i) Nature of Metal & its ion

ii) concentration of ions $[M^{n+}]$

In case of gas \rightarrow partial pressure

(iii) Temperature

► Standard conditions

i) conc $[M^{n+}] = 1M$

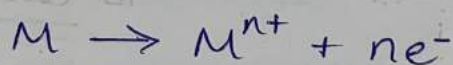
ii) $P_{\text{gas}} = 1\text{atm}/1\text{bar}$

iii) Temp = 298K (25°C)

• In standard conditions \Rightarrow

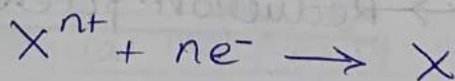
Standard electrode
 $[E^\circ]$ Potential

• Oxidation :



• $E_{M/M^{n+}} \rightarrow \text{OP}$ • $E^\circ_{M/M^{n+}} \rightarrow \text{SOP}$

• Reduction :

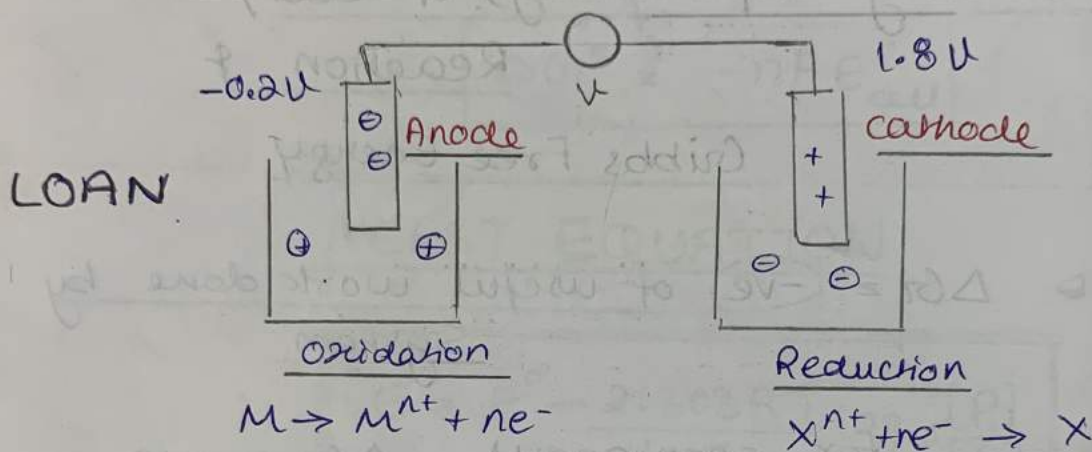


• $E_{X^{n+}/X} \rightarrow \text{RP}$ • $E^\circ_{X^{n+}/X} \rightarrow \text{SRP}$

- ★ ▷ Standard Reduction potential
is considered as standard Electrode potential

$$\boxed{SRP = -SOP}$$

- ▷ EMF of cell



eg $E_{M/M^{n+}} = -0.2V$ $E_{X^{n+}/X} = 1.8V$

- ▷ EMF of cell difference between
electrode of cell

$$\boxed{E_{cell} = E_{cathode} - E_{Anode}}$$

★ $E \rightarrow$ Reduction potential

$$\boxed{E_{cell} = E_{right} - E_{left}}$$

▷ $E^\circ_{\text{cell}} \rightarrow$ Standard EMF of cell

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

▷ Feasibility (Spontaneity) of cell / Reaction & Gibbs Free Energy

▷ $\Delta G =$ (-ve) of useful work done by System

for spontaneous

$$\Delta G = -ve$$

$$\Delta G = \ominus W_{\text{Electrical Done by cell}}$$

All electrical work is useful (Assumption)

• Electrical work

$$\Delta U = \frac{W}{q}$$

In n moles of e^- transferred

$$W = q \Delta U$$

$$q = 1.67 \times 10^{-19} \text{ C} \times n \times 6.022 \times 10^{23}$$

• 1F = charge on 1 mole electrons
 $\approx 96500 \text{ C}$

$$q = n \times 96500 \text{ C}$$

$$q = nF$$

$$\Delta V = E_{\text{cell}}$$

~~$$W = \Delta q$$~~

$$W = \Delta V \times q$$

$$\triangleright \boxed{W = nFE_{\text{cell}}}$$

$$\therefore \boxed{\Delta G = -nFE_{\text{cell}}}$$

$$\boxed{\Delta G^\circ = -nFE_{\text{cell}}^\circ}$$

NERST EQUATION

(L-3)

$$\boxed{E = E^\circ - \frac{2.303RT}{nF} \log_{10} \frac{[P]}{[R]}}$$

• E = Emf or Electrode potential at any conc & T

• E° = Standard EMF

• $R = 8.314 \text{ J/mol K}$

• $Q = \frac{[P]}{[R]}$

• $F = 96500 \text{ C}$

• n = no of electron lost/gain/transfer

• $[] \rightarrow \text{conc}$

• Pure solid & Pure liquid

$\text{conc} = 1$

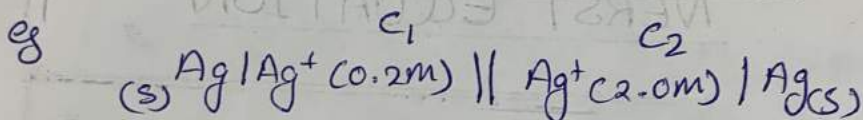
$$E = E^{\circ} - \frac{0.059}{n} \log_{10} \frac{[P]}{[R]}$$

used most of times

▷ conc are raised to stichometric coefficient

★ EMF of concentration cell

Same anode & cathode



$$E^{\circ}_{cell} = 0$$

For concentration cells

$$E_{cell} = -\frac{0.059}{n} \log_{10} \frac{[C_1]}{[C_2]}$$

$$\Delta G = \Delta G^{\circ} + 2.303 RT \log_{10} Q$$

$$-nFE_{cell} = -nFE^{\circ}_{cell} + \frac{2.303 RT}{nF} \log_{10} \frac{[P]}{[R]}$$

▷ $E_{cell} = E^{\circ}_{cell} - \frac{2.303 RT}{nF} \log_{10} \frac{[P]}{[R]}$

▷ Equilibrium constant from NERST Equation

at equilibrium $\Delta G = 0$

$$Q = K_{eq}$$

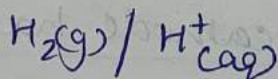
$$\underline{\Delta G = 0} \quad \therefore \quad \boxed{E_{cell} = 0}$$

$$\therefore \quad E_{cell}^{\circ} = \frac{2.303RT}{nF} \log_{10} K_c$$

$$\boxed{\log_{10} K_c = \frac{E_{cell}^{\circ} \times n}{0.059}}$$

▷ SHE (Standard Hydrogen Electrode) (L-4)

1) It is a gas-ion Electrode



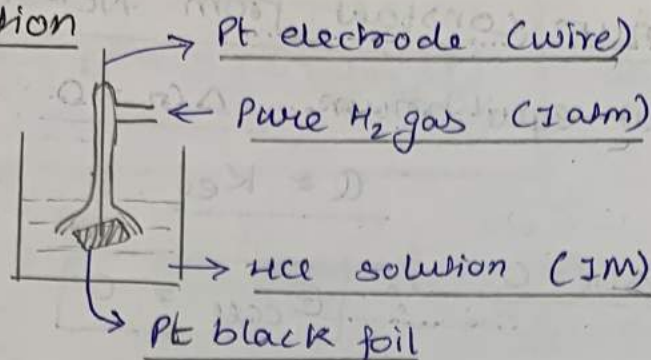
2) It is a reference Electrode as set by IUPAC

3) It can act as both anode half cell or cathode half cell

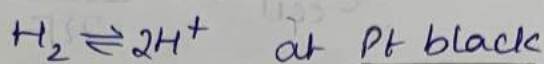
4) Its SRP or SOP is assumed to be 0

$$E_{H^+ / \frac{1}{2}H_2}^{\circ} = 0$$

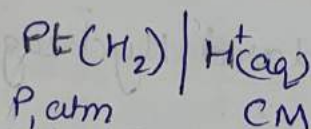
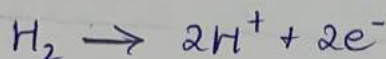
► Construction



CH_2 absorb / adsorb

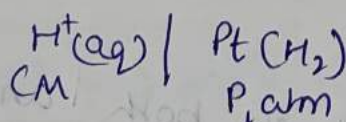
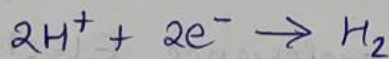


① SHE as Anode half cell



$E^\circ_{\text{H}_2/\text{H}^+} = 0$

② SHE as cathode half cell



► Use of SHE to determine standard Electrode Potential

1) We can Never find Absolute Potential of single Electrode

2) We find Relative EP wrt to SHE

Electrochemical Series

(L-05)

- Elements are arranged in order of
Increasing standard Reduction
Potential

<u>Reaction</u>	<u>Representation</u>	<u>SRP</u>
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	$E^\circ_{\text{Li}^+/\text{Li}}$	-3.05 V
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	$E^\circ_{\text{Zn}^{2+}/\text{Zn}}$	-0.76 V
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	$E^\circ_{\text{Fe}^{2+}/\text{Fe}}$	-0.45 V
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2}$	(0 V)
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$E^\circ_{\text{Cu}^{2+}/\text{Cu}}$	$+0.34 \text{ V}$
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$E^\circ_{\text{Ag}^+/\text{Ag}}$	$+0.80 \text{ V}$
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	$E^\circ_{\text{F}_2/\frac{1}{2}\text{F}_2^-}$	$+2.87 \text{ V}$

★ SRP ↑ Tendency to get Reduce ↑
Oxidising Agent ↑

★ $\text{F}_2 \rightarrow$ Best oxidising agent

★ $\text{Li}^+ \rightarrow$ Best Reducing agent

60-1)
▷ To Find spontaneity of Galvanic cell

▷ $E_{\text{mf}} > 0$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$$

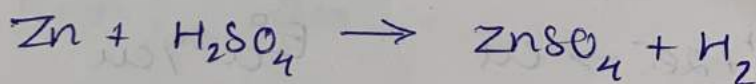
$$E_{\text{cell}}^{\circ} > 0$$

$$E_{\text{cathode}}^{\circ} > E_{\text{Anode}}^{\circ}$$

★ Cathode should be lower than
Anode in Electrochemical Series

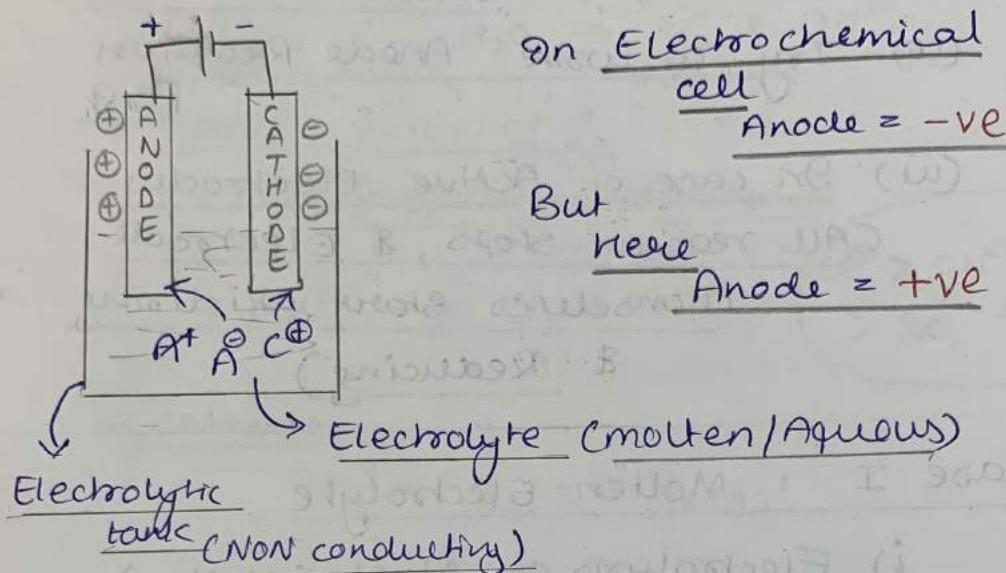
★ Metals above H in the series

displaces H_2 from diluted
Mineral Acid



▷ Electrolytic cell → Electrolysis (L-6)

electrical energy → chemical energy



- Cations → $C^+ \rightarrow$ cathode
 $C^+ + e^- \rightarrow C$ (Reduction)
- Anions → $A^- \rightarrow$ Anode
 $A^- \rightarrow A + e^-$ (Oxidation)

▷ Factors on which products at Electrode depends

- 1) Nature of Electrolyte
- 2) Medium of Electrolyte
- 3) Concentration of Electrolyte → conc. or dil.
- 4) Nature of Electrode - Active or Inert

- Inert → Platinum/Graphite
- Active → metal electrode

► Rules for Product formation

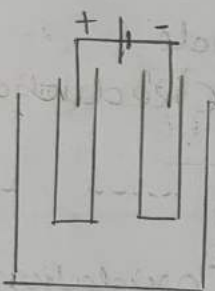
(i) Assume Inert (Pt) Electrode
unless mentioned

(ii) Try to write Anode Reaction
First

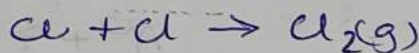
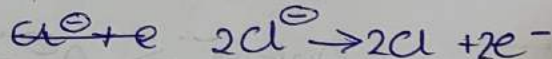
(iii) In case of Active Electrodes
Cathode reaction stops, & Electrode
themselves start oxidising
& Reducing)

► Case I : Molten Electrolyte

i) Electrolysis of NaCl (molten)
with Pt Electrode

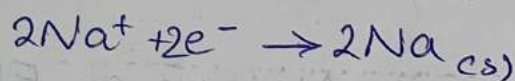


• Anode oxidation



(secondary change)

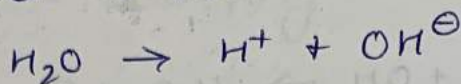
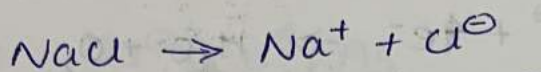
• Cathode Reduction



► Case II Aqueous Electrolyte

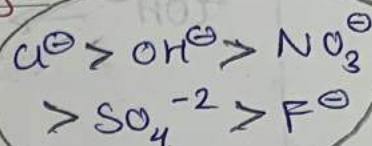
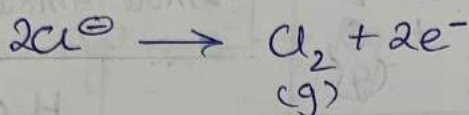
i) Electrolysis of NaCl with Pt
(aq) electrode

a) conc NaCl



• Anode oxidation

Preferential discharge



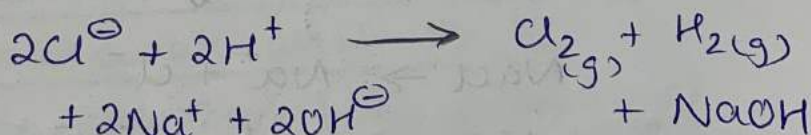
• cathode



$\text{Cl}_{2(g)}$ at anode & $\text{H}_{2(g)}$ at cathode

pH increase

Net reaction

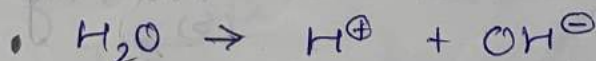


pH = Basic

Castner Kellner cell

b) Dilute NaCl

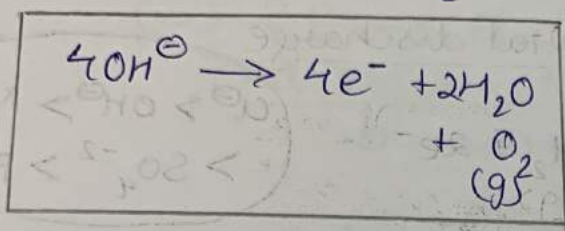
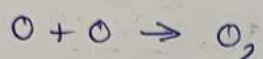
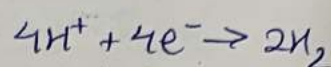
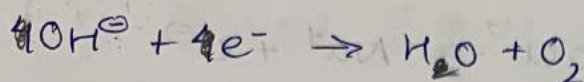
Pt electrode



Large quantity

• Anode: $\text{Cl}^- / \text{OH}^-$

Cathode: $\text{Na}^+ / \text{OH}^-$
 H^+



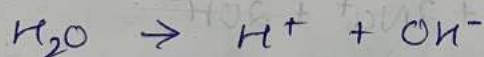
H_2 2mole	O_2 4mole	Cl_2 2mole	e^-
H_2O 2mole e^-			

★ 4mole e^- for 1 mole O_2

• $\text{PH} \rightarrow \text{constant}$

• conc of NaCl \rightarrow constant

③ Aq NaCl with Hg as cathode
(conc) (Amalgum)

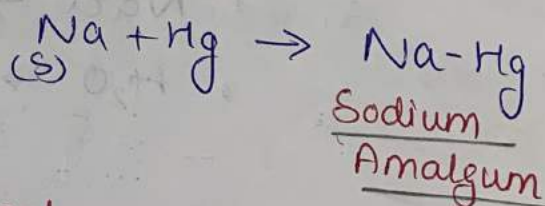
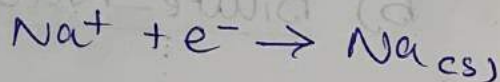
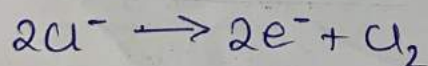


Anode: (Pt)

$\text{OH}^- / \text{Cl}^-$

Cathode: (Hg)

Na^+ / H^+

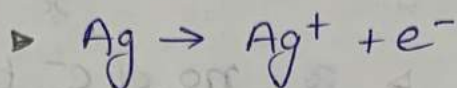


• $\text{PH} \rightarrow \text{No effect}$

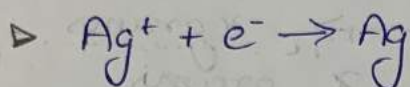
• conc of NaCl \rightarrow No effect

④ aq NaCl with Ag electrode (Active)

▷ Anode $\text{Cl}^- / \text{OH}^- / \text{Ag}$
(Active)



▷ Cathode $\text{Na}^+ / \text{H}^+ / \text{Ag}^+$



* This process is used in electrorefining

Cathode \rightarrow pure metal

Anode \rightarrow impure metal

▷ Faraday's Law of Electrolysis

(07)

▷ 1) The mass of a substance deposited or the mass of gas liberated at a particular electrode is directly proportional to amount of charge passing through solution (electrolyte)

$$m \propto Q$$

$$m = ZQ$$

$Z \rightarrow$ constant

ECE Electrochemical Equivalent

$$Q = it$$

$$m = Zit$$

$Z \rightarrow$ depends upon cation or Anion

$$Z = \frac{E}{F}$$

$E \rightarrow$ equivalent weight

$$F = 96500 \text{ C}$$

$\triangleright E = \frac{\text{molar mass}}{x}$

$\triangleright x = \text{no of } e^- \text{ transferred}$

$$\begin{array}{lcl} 1 \text{ mole } e^- & \longrightarrow & x \text{ grams} \\ 1F & \longrightarrow & x \text{ grams} \end{array}$$

unitary method

$$1C \longrightarrow \frac{x}{96500} \text{ gram}$$

$$\text{it} \longrightarrow \frac{x}{96500} \text{ gram}$$

• Electrochemical Equivalent

$$m = ZQ$$

when 1F charge passed

$$\text{mass deposited} = Z$$

IInd Law

If same amount of electric charge is passed through different electrolytes, then the amount of substance deposited / liberated

is directly proportional to its Equivalent weight

$$m = ZQ = \frac{E}{F} \times Q$$

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

$$m \propto E_{eq} wt$$

(08)

Electrolytic conductance

Metallic conductor

1) current flows due to flow of e^-

2) No chemical decomposition of conductor

3) Resistance is due to collisions with kernels

2) Resistance increase on increasing Temp

Electrolytic conductor

i) current flow due to flow of ions

2) chemical Decomposition occurs

3) Resistance is due to interactions
 i) solute-solute interaction
 ii) solute-solvent interaction
 iii) solvent-solvent interaction (viscous force)

Resistance decrease on increasing Temp

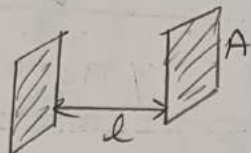
General Terms

① Resistance R unit ohm Ω

② Conductance $C = \frac{1}{R}$ unit mho siemens S

③ Specific resistance or Resistivity (ρ) $R = \rho \frac{L}{A}$ $\rho = R \frac{A}{L}$

A & l for electrolytic conductor



$$\text{cell constant} = \frac{l}{A}$$

▷ Resistivity $\rho = R \frac{A}{L}$ unit = ohm cm

④ conductivity or Specific conductance (K) $K = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$

K unit = $\text{ohm}^{-1} \text{cm}^{-1}$

$$K = \text{conductance} \times \text{cell constant}$$

conductivity depends upon concentration

⑤ Molar conductivity (Λ_m)

conductance due to all the ions of that volume of electrolyte which contains 1 mole of electrolyte

$$\Lambda_m = K \times \text{Volume}$$

$$M = \frac{n}{V}$$

when $n=1$

→ which contains 1 mole electrolyte

$$(L) V = \frac{1}{M}$$

$$V_{(\text{cm}^3)} = \frac{1000}{M}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

⑥ Equivalent conductivity

Solution contains 1 gm equivalent

$$\Lambda_e = \frac{\kappa \times 1000}{N}$$

$$N = M \times x$$

x = valency factor

unit = $\text{Scm}^2\text{eq}^{-1}$

$$\therefore \Lambda_e = \frac{\Lambda_m}{x}$$

▷ Variation of conductance / conductivity (κ) / molar & equivalent conductivity with concentration (09)

i) Conductance : strong electrolyte / weak electrolyte

conc $\downarrow \Rightarrow$ dilution $\uparrow \rightarrow$ conductance \uparrow

• weak electrolyte dilution $\uparrow \rightarrow \alpha \uparrow$
 \therefore no of ions \uparrow degree of Dissociation

• Strong electrolyte

on dilution Force of attraction b/w solute ions decreases

therefor ions move more readily
 \therefore conductance \uparrow

(ii) conductivity (κ) : conductance due to all ions present in 1ml electrolyte

dilution \uparrow concentration \downarrow

\therefore $\kappa \downarrow$

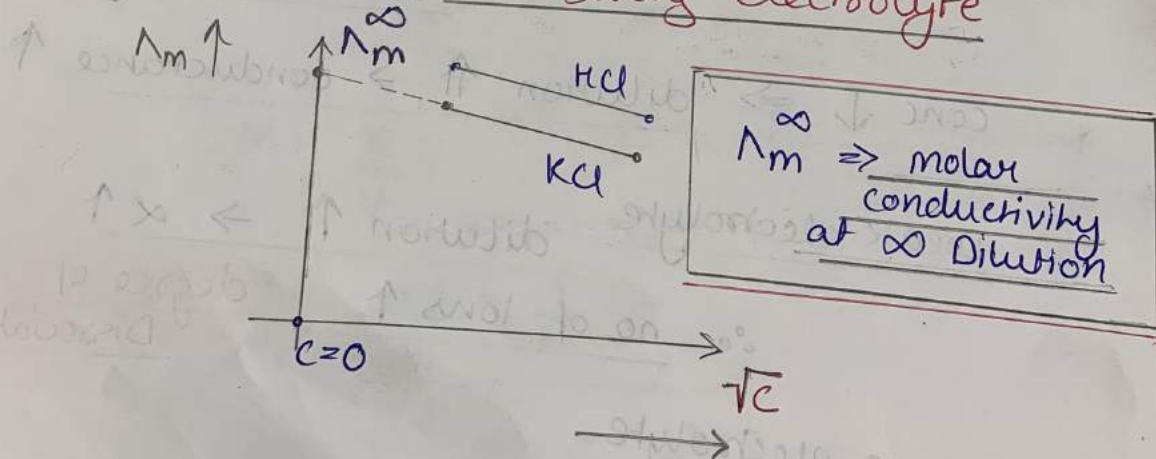
because no of ions in 1ml decreases

(iii) molar conductivity (Λ_m)

depends more on M

$\star \therefore$ on dilution \uparrow $\Lambda_m \uparrow$
also $\Lambda_e \uparrow$

Case I : Variation of Λ_m with conc for strong electrolyte



$\Lambda_m^\infty =$ Limiting molar conductivity

$$\Delta \left(\Lambda_m^\infty \text{ HCl} \right) > \left(\Lambda_m^\infty \text{ KCl} \right)$$

H⁺ moves more readily than K⁺

$$y = mx + c$$

$$\Lambda_m = -b\sqrt{c} + \Lambda_m^\infty$$

★

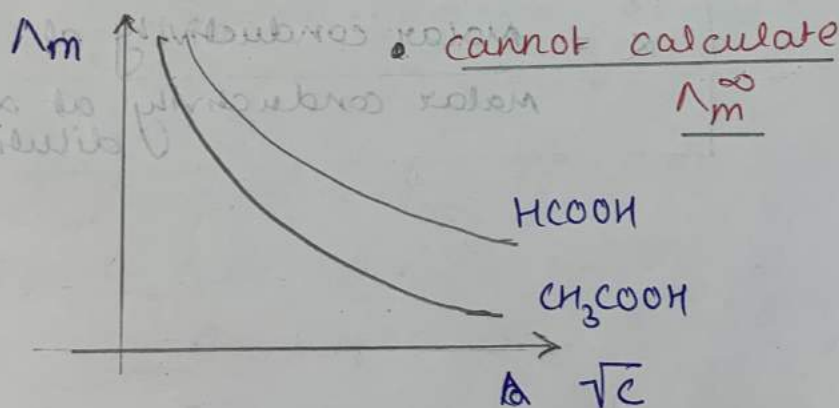
$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

b → slope

Strong electrolyte

b → depends on solvent

Case II : Variation of Λ_m with conc for weak electrolyte

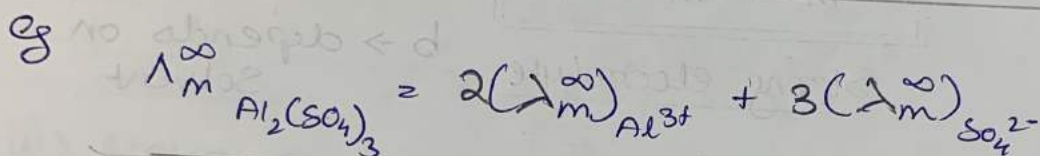


► Kohlrausch's Law: for both strong & weak electrolyte

$$(\Lambda_m^\infty)_{\text{electrolyte}} = (\Lambda_m^\infty)_{\text{cation}} + (\Lambda_m^\infty)_{\text{anion}}$$

if we have μ_+ cations & μ_- anions

$$(\Lambda_m^\infty)_{\text{electrolyte}} = \mu_+ (\Lambda_m^\infty)_{\text{anions}} + \mu_- (\Lambda_m^\infty)_{\text{cations}}$$



Degree of Dissociation

$$\alpha = \frac{\text{molar conductivity at conc } c (\Lambda_m^c)}{\text{molar conductivity at } \infty \text{, dilution } (\Lambda_m^\infty)}$$