

ElectrochemistryDeals energy conversion  $\rightarrow$  Chemical  $\leftrightarrow$  Electrical. $\rightarrow$  Conductance

Electrolytic

Metallic

- |   |   |
|---|---|
| 1. Temp $\uparrow$ , R $\downarrow$ so conductance $\uparrow$ | $\rightarrow$ T $\uparrow$ R $\downarrow$ so c.f. |
| 2. Conducting power low.                                      | $\rightarrow$ Cond. power comparatively high.     |
| 3. Follow Faraday law   | $\rightarrow$ X                                   |
- But - Both follow ohm's law.
4. due to friction & water transfer  $\rightarrow$  due to fee  $e^-$  & not matter transfer.

1. Conductance

$$C \text{ or } G = \frac{1}{R}$$

R =  $\Omega$ , Ohm, Volt/mAG = mho,  $\Omega^{-1}$  or Siemens (S)2. sp. conductance (conductivity) (G,  $\kappa$ )

$$\kappa = \frac{1}{\rho} = \frac{l}{Ra}$$

$$R = \rho \frac{l}{a}$$

 $\rho$  = specific resistance.  
or, resistivity. $\rho$  unit = (ohm-cm) $\kappa$  = (ohm-cm) $^{-1}$  or,  $S\text{m}^{-1}$  or,  $S\text{cm}^{-1}$ l = dist b/w electrode & a = dipped surface area of  
in cm electrode in  $\text{cm}^2$ .

## 3. For cell

$$l/a = \text{cell const (ct or } q^*)$$

\*\*

$$\kappa = C \times q^*$$

so, conductance of 1 ml /  $1\text{cm}^3$  is called specific conductance.4. Equivalent conductance ( $\Lambda_{eq}$  or  $\Lambda_{eq}$ )

$$\Lambda_{eq} = \kappa \times V$$

Volume of sol $^n$  in ml contains 1 g eq.  
electrolyte.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

$$\frac{\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}}{S \text{cm}^2 \text{eq}^{-1}}$$

5. Molar conductance

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

$$\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$$

$$\Lambda_m = \kappa \times V$$

Rel?  $\Lambda_m = \lambda_{eq} \times v$

⇒ Point to check order of electrolytic conductance:-

1. First check weak or strong electrolyte & strong >> weak if all are strong then
1. conc more cond. more.
2. if no. of ion more & more
3. mobility of ion more & more.

mobility  $\propto \frac{1}{\text{hydration}}$

hyd<sup>n</sup>  $\propto$  charge size.

Note

But in all ions conductance of H<sup>+</sup> is highest.

For weak acids-

By ost. dil<sup>n</sup> law  $\alpha \propto \sqrt{v} \propto \frac{1}{\sqrt{c}}$  & if conc same then strength check by eq. concept.

Factor affecting conductance.

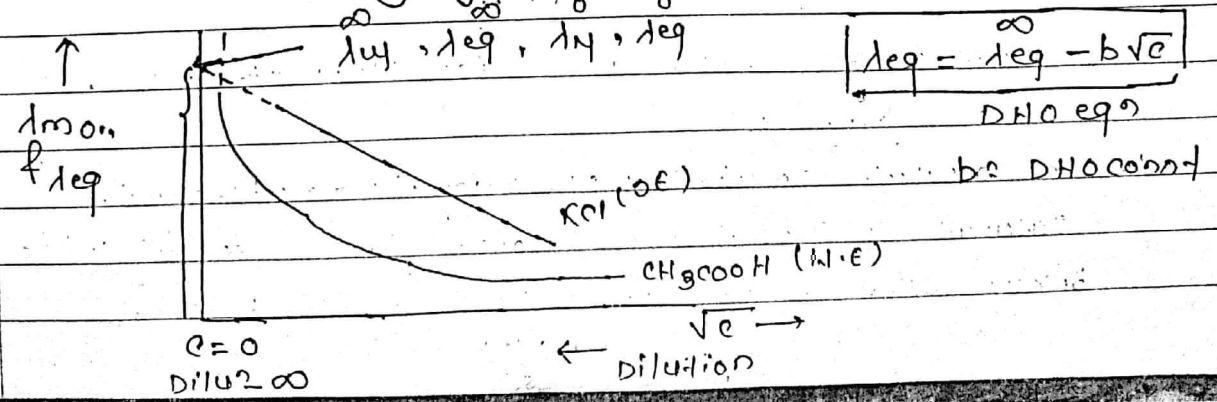
1. Intra ionic interaction force  $\downarrow$  so mobility  $\uparrow \Rightarrow c \uparrow \Rightarrow \lambda_{eq} \& \Lambda_m \uparrow$ .
2. hyd<sup>n</sup> or solvation:-
- sol<sup>n</sup>  $\uparrow \Rightarrow$  mobility  $\downarrow$  so  $c \downarrow$ .
3. viscosity :-  $\uparrow$  so mobility of ions  $\downarrow \Rightarrow c \downarrow$ .
4. Temp  $\uparrow \rightarrow$  internal R.E  $\uparrow$ , & III force  $\downarrow$  so mobility rapidly  $\uparrow$  & conductance  $\uparrow$ .

\*\*

Dilution

- A. On Dil<sup>n</sup> conductance (Weak or strong) Both  $\uparrow$ .
1. For strong  $\uparrow$  Dil<sup>n</sup>  $\rightarrow$  III F  $\downarrow$  therefore conductance gradually  $\uparrow$ .
2. For weak  $\uparrow$  Dil<sup>n</sup> III F  $\downarrow$  &  $\alpha \uparrow$  so cond<sup>n</sup> rapidly  $\uparrow$ .
- B. on dil<sup>n</sup> specific conductance ( $\kappa$ )  $\downarrow$  b/c no. of ion/cm<sup>3</sup>  $\downarrow$ .
- C. on dilution  $\Lambda_m$  &  $\lambda_{eq}$  Both  $\uparrow$ .

Debye - HUCKEL Onsager graph



- Value of DHO Const ( $b$ ) depends on 1. Type of electrolyte (nature).  
2. solvent (3) Temp.

Drawback: We can never obtained  $\text{max}^y$  value of  $\lambda_m$  for weak electrolyte by extrapolating of curve because for W.E  $\alpha$  is always less than 1.

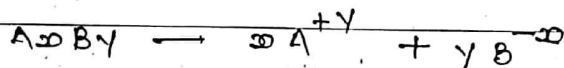
### Kohlrausch's law

(App. for both strong & weak electrolyte).

As to it, At  $\infty$  Dil<sup>n</sup>, electrolyte (Weak or strong) 100% dissociate then each ion make a definite contribution towards

eq. conductance of electrolyte irrespective to nature of other ion of electrolyte.

$$\lambda_{\text{eq}}^{\infty}(\text{AB}) = \lambda_{\text{eq}}^{\infty} \text{A}^+ + \lambda_{\text{eq}}^{\infty} \text{B}^-$$



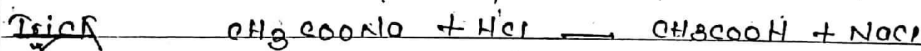
$$\lambda_{\text{eq}}^{\infty}(\text{A}_x\text{B}_y) = \frac{\lambda_{\text{M}}^{\infty} \text{A}^{+y}}{y} + \frac{\lambda_{\text{M}}^{\infty} \text{B}^{-x}}{x} \leftarrow \text{charge}$$

$$\lambda_{\text{M}}^{\infty}(\text{A}_x\text{B}_y) = x \lambda_{\text{M}}^{\infty} \text{A}^{+y} + y \lambda_{\text{M}}^{\infty} \text{B}^{-x}$$

↑ moles

### App?

1. To calculate  $\text{max}^m$  value of  $\lambda_m / \lambda_{\text{eq}}$  for weak electrolyte.



$$\lambda_{\text{eq}}^{\infty} + \lambda_{\text{eq}}^{\infty} = \infty + \lambda_{\text{eq}}^{\infty}$$

2. To calculate  $\alpha$  of weak electrolyte.

$$\alpha = \frac{\lambda_{\text{eq}}^y / \text{Moles}^0 \cdot \lambda_{\text{eq}}^0 / \text{M}}{\lambda_{\text{eq}}^{\infty} / \text{M} \cdot \lambda_{\text{eq}}^0 / \text{M}}$$

3. Calculate dissociation constant for weak electrolyte

$$K_a = c\alpha^2$$

4. To calculate solubility of sparingly soluble salt.

Saturated sol<sup>n</sup> of this salt consid<sup>r</sup> as  $\infty$  diluted sol<sup>n</sup>

because they are very less soluble.  $\therefore \lambda_m = \frac{\infty}{s}$

$$\lambda_{\text{M}}^{\infty} = \frac{R \times 1000}{s}$$

→  $K_{sol}^{\circ} = K_{solute} + K_{solvent}$

part B

1. electrode potential :- it develop b/w interface of metal and sol<sup>n</sup>.
2. standard cond<sup>n</sup> - IN case, 1 bar pressure = 1 atm and if Temp is not given th en 25°C (But not standard) at Ep is called S.E.P.

3. Value of Electrode potential (Ep) depends on:

1. Nature of electrolytic sol<sup>n</sup> & metal used (i) conc (ii) Temp.
- A. Oxid<sup>n</sup> potential w<sup>th</sup> tendency to get oxidised is called electrolytic sol<sup>n</sup> press<sup>n</sup> & developed potential = O.P.
- B. Red<sup>n</sup> potential :- Resistant (net) tendency of electrode to get reduced called osmotic press<sup>n</sup> of sol<sup>n</sup> and dev. potential = R.P.

⇒ A/c IUPAC, electrode potential is always consider as SRP.

Reference electrode

1. Primary ref. electrode :- S.H. Electrode, cat- cathode or anode depends on with which it coupled.

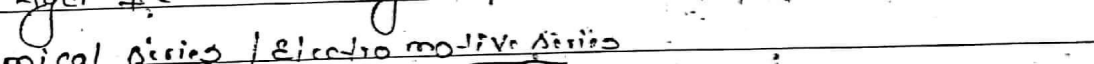
⇒ SRP & SOP both consider as (0).

2. secondary Ref. electrode :- [SRP or SOP ≠ 0]

1. calomel electrode (laboratory use) (Generally act as cathode.)



2. Ag/AgCl electrode :- (Industrial use)



Electrochemical series / Electro motive series

Best R.A  
-3.05

→ Li	Cs	Ag			
R	Fe	Pd ← Br <sub>2</sub>	Pt ← Cl <sub>2</sub>	Au → Best O.A Among metal.	→ F <sub>2</sub> (+1.5V)
Ba	Cd				
Sr	Co				
Ca	Ni				
Na	Sn				
Mg	Pb				
Al	H				
Mn	Cu				
Zn	Hg				

1. SRP = -SOP
2. Down the reactivity of metal ↓
3. But reactivity of non metal ↑

series in aq. sol<sup>n</sup>

3pp1-

1. Disp of metal ion by metal :- Above ion displac. Below ion from its aq. soln eg -  $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$ .

2. Disp of  $H^+$  from acidic soln :-

metal placed above  $H_2$  displac. it eg :-  $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

3. Disp of  $H_2$  gas from water by metal :-

1. metal from Li to Na in aq. disp  $H_2$  gas from cold water

2. metal from Mg to Al — " " " " Hot water

3. Iron can disp  $H_2$  from steam.

4. solubility of metal oxide :-

Electropositive chr. more then stability of metal oxide is more.

∴ Down the series stability of MO → ↓.

5. Disp of Non metal by non metal :-

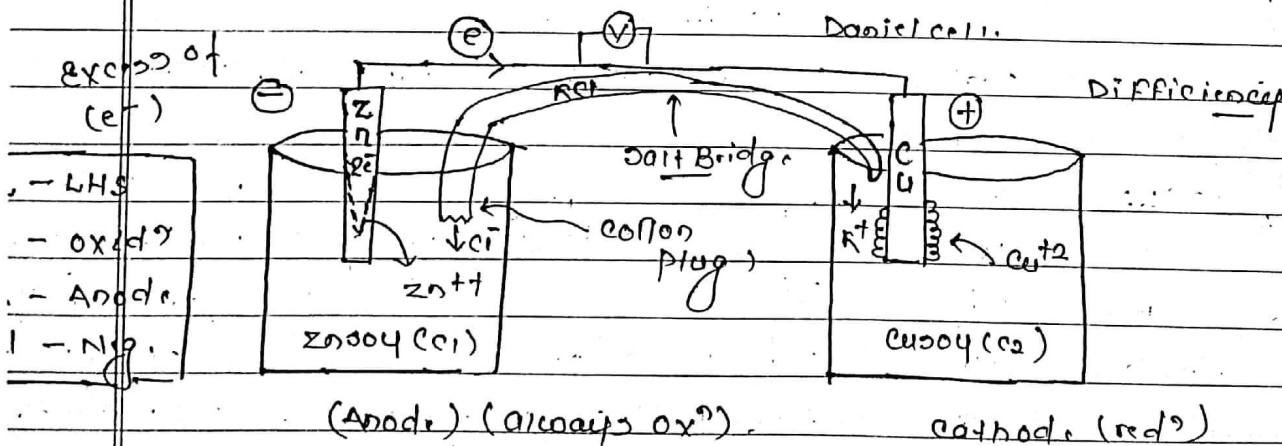
Below displac. upper anion. eg :-  $2KI + Cl_2 \rightarrow 2KCl + I_2$

Electrochemical cell

1. Electrolytic cell (Voltameter)  
(Electrical → Chemical)

2. Galvanic cell / Voltaic cell  
(Chemical energy → Electrical)  
if Zn in anode & Cu is cathode then Galvanic cell is called

Daniel cell.



(Anode) (always ox<sup>n</sup>)

cathode (red<sup>n</sup>)

⇒  $\Delta G = -ln \frac{u}{u} = -ln e^{e\Delta} = -QV$

$\Delta G = -nFE$     n = no. of mol. transferred  
F = Faraday const.

$E_{cell} = (E_{oxi})_A + (E_{red})_c$

$E_{cell} = (E_{red})_c - (E_{red})_A$

- If  $E_{cell} = +ve$  then then  $\Delta G = -ve$  & rxn should be spontaneous.
- At eq<sup>m</sup>  $\Delta G = 0$  &  $E_{cell} = 0$  But  $\Delta G^{\circ}$  &  $E^{\circ}_{cell} \neq 0$ .

Efficiency of cell

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE_{cell}}{\Delta H}$$

Some imp. result

1. Current flow - Cathode to anode (external circuit) but Anode to cathode in internal circuit (Salt bridge).
2. cell rxn are spontaneous & exothermic so temp of soln ↑.
3. Salt Bridge (i) maintain electrical neutrality of both electrode.  
(ii) connect different electrolytic soln & complete internal circuit & prevent liq. liq. junction potential which always oppos. emf of cell)

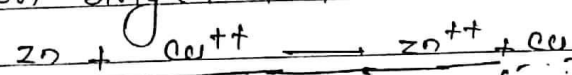
Note

1.  $E^{\circ}$  is intrinsic property. (intensive property)
2. If electrode potential of two half cell rxn given then for 3rd half cell rxn firstly convert  $E^{\circ} \rightarrow \Delta G^{\circ}$  then apply Hess's law of thermodynamics.

Nernst's eq

(always write rxn)

- use on single electrode as well as cell rxn



$T = 25^{\circ}C$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \left( \frac{[P]}{[R]} \right) \Rightarrow Q = \frac{[Anode]}{[Cathode]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log Q \quad n = \text{no. of mol. } e^{-} \text{ transferred}$$

F = Faraday const

→  $\Delta G = \Delta G^{\circ} + 2.303RT \log Q$  At eq<sup>m</sup>

$E_{cell} = 0$  &  $Q = K$   $E^{\circ}_{cell} = \frac{0.059}{n} \log K$

$\Delta G = 0$   $\Delta G^{\circ} = -2.303RT \log K$