Electrochemistry

- **Electrolysis**
  - Faraday's law
  - Ist law
  - IInd law
- **Electrolytic conduction.**
  - K
  - λ
  - Kohlrausch's law.
  - Strong / Weak Electrolytes
- **Nernst Equation.**
  - SHE
  - Daniel cell
  - E° cell
  - Nernst Eq^n.
- **Cell**
  - Primary
  - Secondary.
  - Fuel cell
  - Corrosion Prevention.

REDOX RXN

REDUCTION	OXIDATION
• Addition of Hydrogen.	• Addition of Oxygen.
• Removal of Oxygen.	• Removal of Hydrogen.
• Gain of e^-.	• Loss of e^-.
• Decreases in Oxidation No.	• Increases in Oxidation No.

Oxidation Question:

- H_2SO_4

$1\times2 + x - 2\times4 = 0$

$2 + x - 8 = 0$

$x = 6$

$KMnO_4$

$+1 + x - 2\times4 = 0$

$x - 7 = 0$

$x = 7$

$K_2Cr_2O_7$

$+1\times2 + 2x - 2\times7$

$2x - 12 = 0$

$x = 6$.

$Fe_2(SO_4)_3$

$2x - 2\times3 = 0$

$2x - 6 = 0$

$x = 3$

$NAuCl_4$

$-1 + x + -1\times4 = 0$

$x = 5$.

Calculation Of Oxidation No.

Hydrogen.

H → +1 → Non-Metal eg: (HCl) +1

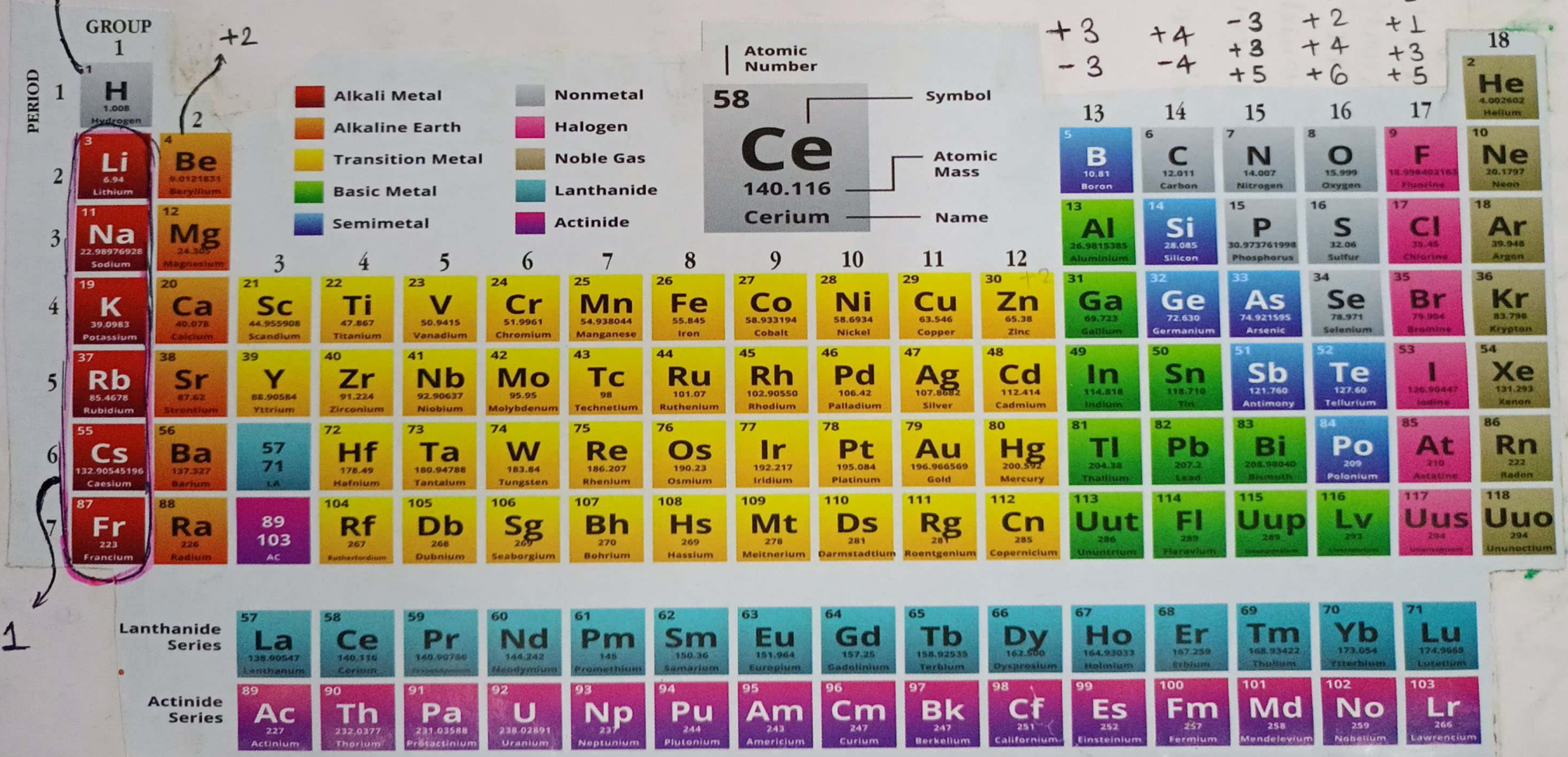
H → −1 → Metal eg: Na(H) −1

SO_2 → +4 SO_4 → −2

SO_3 → +6 NO_3 → −1

HNO_3 → +5 CO_3 → −2

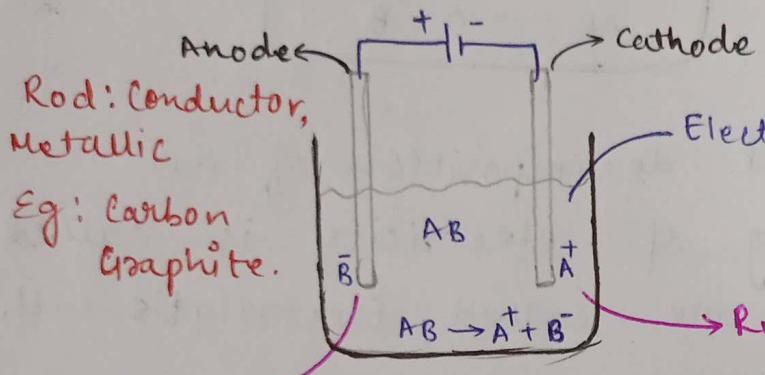
$AlCl_3$ → +3



CURRENT

Surface Conduction | Ionic Conduction.

Ionic Conduction: Chemical Effect of Current.



E⁻ Flow

- Conductors
- cheap
- Fast
- Initial cost is high.
- Maintance is high

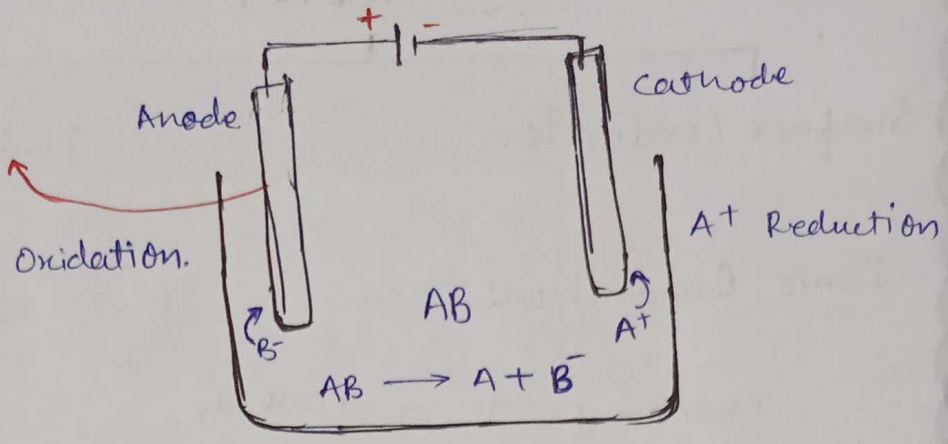
Ions Flows

- Electrodes, Electrolytes.
- costly
- slow
- Initial cost is less
- Reliable.

ELECTROLYSIS

* Metal - cathode deposited.
* Non Metal - Anode liberated / Evolved.

Metal conductor Graphite



The process of chemical decomposition of an electrolytes by the passing of electricity is called Electrolysis & the cell are called Electrolysis cell.

In the process of Electrolysis cation are converted into metal (+ve part) & deposited in cathode while (-ve part) or anionic part are deposited in or liberated in Anode.

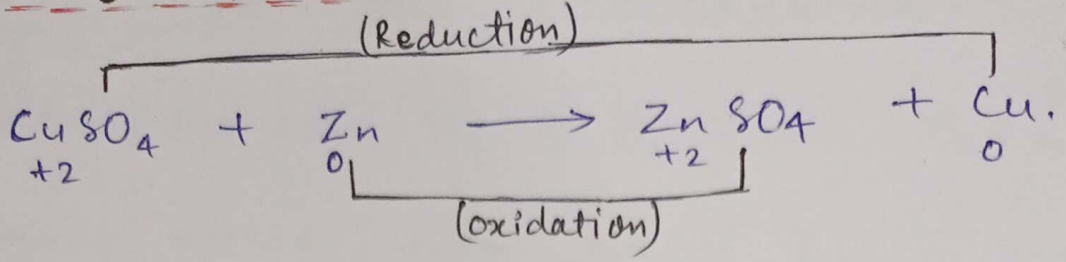
In the process of Electrolysis we can use Electrolytes. Electrolytes can maybe cation, anion or salt.

Electrolytes are of two types:

1) Strong Electrolytes → Which can dissociate above 95%.

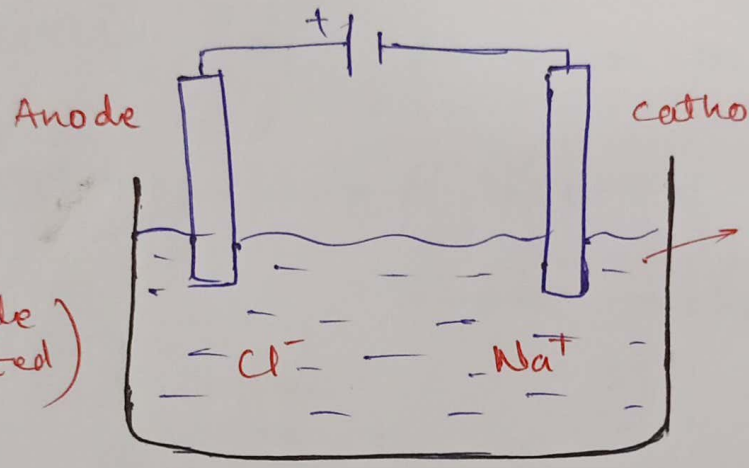
2) Weak Electrolytes → Which can only dissociate upto 5%.

Redox Couple



$Zn \longrightarrow ZnSO_4 + 2e^-$ Oxi. Half Rxn.

$CuSO_4 + 2e^- \longrightarrow Cu.$ Red. Half Rxn.



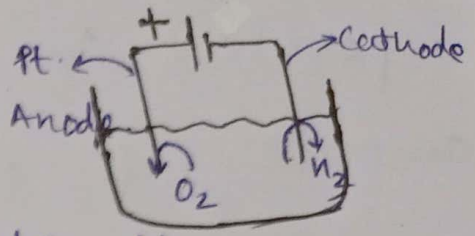
(Metal - cathode deposited)

(Non-metal - Anode liberated / Evolved)

Product Of Electrolysis :-

	At Cathode	At Anode
(i) Molten NaCl.	Na(metal)	Cl_2 (gas)
(ii) Aqueous NaCl.	H_2 (gas)	O_2 (gas)
(iii) Dil. H_2SO_4	H_2 (gas)	O_2 (gas)
(iv) Conc. H_2SO_4	H_2 (gas)	$S_2O_8^{2-}$

Application Of Electrolysis



1.) Production of H_2 & O_2 from H_2O

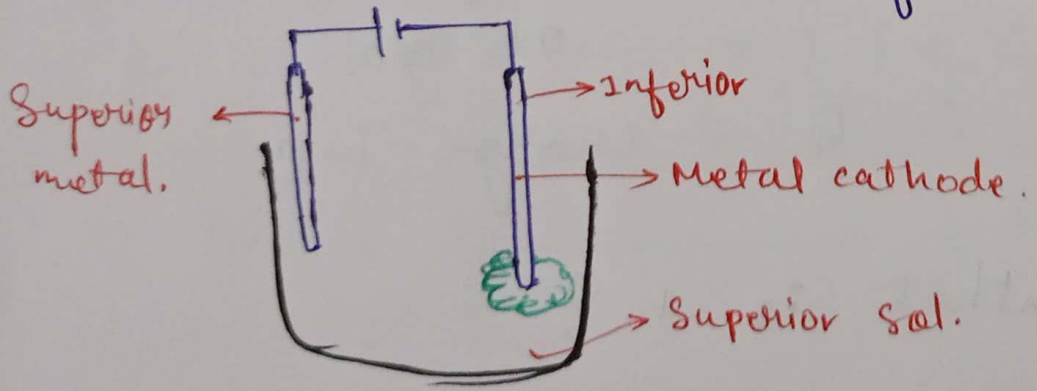
2.) Highly active meta, Na, K, Rb, Cs, Mg, Al.

Highly active non-metal. Cl_2, F_2, Br_2.

3.) Purification of copper (Cu).

4.) Purification of Al ⟶ Hell - Herold process.

5.) Electroplatting ⟶ A layer of speriour metal in inferior metal. surface.

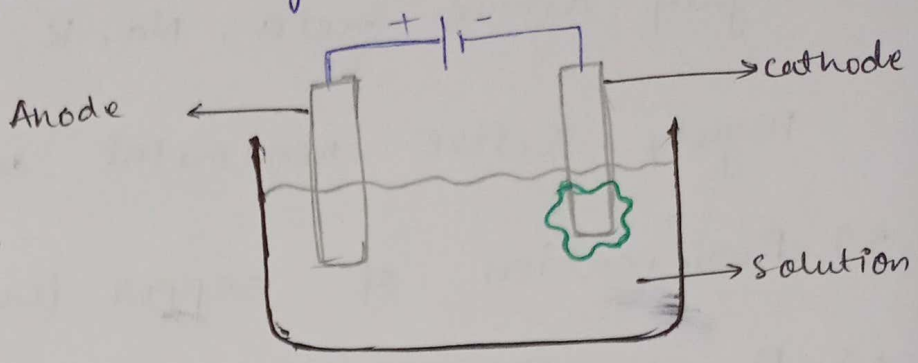


FARADAY'S 1'st LAW: The amount of substance deposited in cathode is directly proportional to the amount of charge passes through the solution.

$W \propto Q$

$W = ZQ$.

↳ Electrolysis Equivalent const.



$W = Z \times Q$.

$= \frac{E}{F} Q$.

E = Equivalent Mass.

$= \frac{Mw}{\text{Valency} \times \text{Ox. No.}}$

$w = \frac{Mw \times Q.}{Val \times F}$

$\therefore$ Mw = Molar mass of deposited sub.

$\therefore$ Valency = Deposited Metal Ox. No.

$\therefore$ Q. = Charge in C.

Q. What is F?

1 mole of e^- flow = 1F.

2 mole = 2F

1 mole of e^- = 1F

$1 \times 1.6 \times 10^{-19} \times 6.022 \times 10^{23}$ (C)

$= 96480$ C.

$1F \approx 96500C$

$\frac{dQ}{dt} = I$

$\int dQ = \int I\,dt$.

$Q = It$ —(1)

$Q = ne$. —(2)

$ne = It$.

$w = \frac{Mw \times I \times t}{Val \times F}$ OR $Val = \frac{Mw \times ne}{\text{Valency} \times F}$

Q. How much amount of charge flow when 1 mole of H_2O oxidise into O_2.

Sol. $H_2O \longrightarrow 2H^+ + O^{-2}$

$\hookrightarrow \frac{1}{2} O_2 + 2e^-$

1 mole $\longrightarrow$ 2 mole.

1 mole e^- = 1F

2 mole e^- = 2 F

= 2 x 96500 = 193000 coulumb.

Q. How much charge flow when 1 mole of FeO

$\overset{+2}{\uparrow}$ $\qquad$ $\overset{+3}{\uparrow}$

$FeO \longrightarrow \frac{1}{2} Fe_2O_3 + 1e^-$

1 mole $\longrightarrow \frac{1}{2} Fe_2$.

1 mole e^- = 1F

= 96500 C.

Q. 1 mole of ~~AgN~~ e^- flow from the solution of $AgNO_3$, $CuSO_4$ & $AlCl_3$. So, what is the molar ratio of Ag, Al & Cu ?

Sol. $AgNO_3 \longrightarrow Ag^+$ $\qquad$ 1 mole e^- = 1 mole Ag.

~~2 mole e^- = 1 mole~~

$CuSO_4 \longrightarrow Cu^{+2}$ $\qquad$ 2 mole e^- = 1 mole Cu.

1 mole = $\frac{1}{2}$ mole Cu.

$AlCl_3 \longrightarrow Al^{+3}$ $\qquad$ 3 mole of e^- = 1 mole Al.

1 mole e^- = 1/3 mole Al

Ag : Cu : Al

$1^{\times 6} : \frac{1}{2}^{\times 6} : \frac{1}{3} \times 6.$

6 : 3 : 2.

Q. The amount of substance in gram when 0.4F of charge flow from solution of $AgNO_3$, $CuSO_4$ & $FeCl_3$.

Sol: $Q = 0.4F$

$W = ?$

$Mw = 108$

Valency = 1.

$$W = \frac{Mw \times Q}{Valency \times F}$$

$$= \frac{108 \times 0.4F}{1 \times F}$$

$$= 43.2\ g.$$

$AgNO_3 \longrightarrow Ag^+$

0.4 mole of e^-

1 mole of e^- = 1 mole of Ag.

0.4 mole e^- = 0.4 mole of Ag.

↓

$= 0.4 \times 108\ g.$

$CuSO_4 \longrightarrow Cu^{+2}$

Cu valency = +2.

Mw = 63.5

Q = 0.4.

2 mole of e^- = 1 mole of Cu.

1 mole of e^- = $\frac{1}{2}$ mole of Cu.

0.4 mole of e^- = $\frac{1}{2} \times 0.4 \times 63.5\ g.$

$$W = \frac{Mw \times Q}{val \times F}$$

$$= \frac{63.5 \times 0.4F}{2 \times F}$$

$FeCl_3 \longrightarrow Fe^{+3}$

Val $\longrightarrow$ 3

Mw $\longrightarrow$ 56.

Q $\longrightarrow$ 0.4

Q. An electric current of 100 A flow for 5 hours in a molten NaCl solution, so amount of Na deposited & amount of Cl_2 liberated at STP ? (in l)

Sol: $I = 100\ A.$

$t = 5\ hr.$

$= 5 \times 60 \times 60\ sec$

$$w = \frac{Mw \times I \times t}{Val \times F}$$

$$= \frac{23 \times 100 \times 5 \times 60 \times 60}{1 \times 96500}$$

$$W_{Na} = 429.01\ g.$$

$NaCl \longrightarrow Na^+ + Cl^-$

$Na^+ \downarrow$, $Cl^- \downarrow$

g { $1e^-$ Na. , val = 1 , Mw = 23 } l. { Cl_2 , val = 2 , Mw = 71 }

$$W_{Cl} = \frac{Mw \times I \times t}{Val \times F}$$

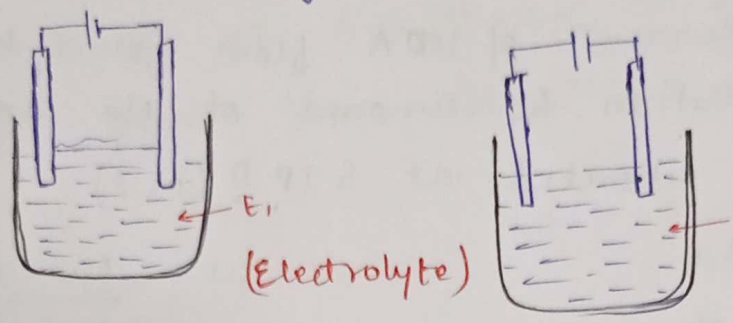
$$= \frac{71 \times 100 \times 5 \times 60 \times 60}{2 \times 96500}$$

$$W_{Cl} = 662.17\ g.$$

$$= \frac{662.17}{71} \times 22.4\ l$$

$= 208.91$ lit. at STP. of Cl_2

FARADAY'S 2nd LAW : When same amount flows b/w electrodes then, the amt. of substances deposited or liberated at electrode is Directly proportional to it's Equivalent weight.



Q, I, T] same.

container / Electrodes vessel - same.

then $\left[\frac{E_1}{E_2} = \frac{W_1}{W_2}\right]$ → Equivalent weight.

$\therefore \left[\frac{W_1}{W_2} = \frac{At.w}{Val\,w} \times \frac{Val_w}{At.w}\right]$

Q. 4.5 gm of aluminium deposited when with $AlCl_3$ it is then what is the amt. of Cu deposited from $CuSO_4$ when same amt. of current passes through electrodes ?

Sol: Given, $W_{Al} = 4.5$ | $W_{Cu} = ?$

$At.Al = 27.$ | $At.Al = 63.50.$

$Valency_{Al} = +3$ | $Valency_{Cu} = +2$

$\therefore \frac{W_{Al}}{W_{Cu}} = \frac{27}{3} \times \frac{2}{63.5}$

$= \frac{\overset{0.5}{\cancel{4.5}} \times \overset{1}{\cancel{3}} \times 63.5}{\underset{1}{\cancel{9}}\,\cancel{27} \times 2} = W_{Cu}$

$W_{Cu} = 15.87$ gm.

ELECTROLYTIC CONDUCTION ~

current flows ⟶ from Ions.

= Ohm's law.

$V = IR$.

Resistance $R = \frac{V}{I}$ → Pt. difference, → current

$= R = \rho \frac{l}{A}$ (Ω) unit

($1 L = 1000 cm^3$)

$\rho = \frac{R \times A}{l}$ (Ω cm) unit.

when $\rho = \frac{R \times A}{l}$ → $1 cm^2$, → $1 cm$

Specific Resistance.

$\frac{1}{R} = G$ ⟶ conductance (Ω^{-1} / seimen)

$\frac{1}{\rho} = K$ (kappa) ($Ohm^{-1} cm^{-1}$) ($\Omega^{-1} cm^{-1}$).

= conductivity

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

$\left[K = \frac{1}{R} \frac{l}{A}\right]$ ← cell constant

(specific conductance)*

$K = G \times G^*$

*Cell const. $= \frac{l}{A} = (cm^{-1})$

Molar conductivity

$$\lambda_m = \frac{K \times 10^3}{M}$$ → Molarity (mol cm^{-3})

$$= \frac{Ohm^{-1}\ cm^{-1}\ cm^3}{mol.}$$

$$= (Ohm^{-1}\ cm^2\ mol^{-1})$$

Equivalent Conductivity

$$\lambda_{eq} = \frac{K \times 10^3}{N}$$

$$= \frac{Ohm^{-1}\ cm^{-1}\ cm^3}{gram\ eq.}$$

$$= (Ohm^{-1}\ cm^2\ gram\ eq^{-1})$$

⇒ Relation b/w λ_m & λ_{eq} :-

Since, $N = M \times V.F$

$$\therefore \lambda_{eq} = \frac{K \times 10^3}{M \times V.F} \rightarrow \lambda_m$$

$$\therefore \left[\lambda_{eq} = \frac{\lambda_m}{V.F}\right].$$

$$\lambda_{eq} \times V.F = \lambda_m$$

→ Resistance (R) :- The ratio of applied potential difference to the (upon) current. 'ohm'

→ Conductance (G) :- Reciprocal of resistance ($1/R$) Ohm^{-1}/seimens.

→ Specific Resistance (ρ) :- It is denoted by 'ρ' (ohm cm)

→ Specific conductance (K) :- Reciprocal of specific resistance ($Ohm^{-1}\ cm^{-1}$)

→ Molar Conductivity (λ_m) :- The conductance of all the ions produced by one mole of electrolytes present in the given solution. ($Ohm^{-1}\ cm^2\ mol^{-1}$)

→ Equivalent conductance (λ_{eq}) - It is defined as the conductance of all the ions produced by one gram equivalent of electrolytes in the given volume of solution.

Factor Affecting Electrolytic Conductance:

(i) Inter ionic attraction – If

(ii) Polarity of the sol. – If the solution have high polar then ~~tt~~ ions will move frequently.

(iii) Viscosity of Medium – On the increasing of viscosity the conductivity decreases.

(iv) Temperature :- $T \propto \frac{1}{M}$ AND $\lambda \propto \frac{1}{M}$

(v) Dillution : On dillution the conductivity increases as the movement of ions becomes easier due to per unit no. of atoms decreases.

According to Debye Hackle Onsager :-

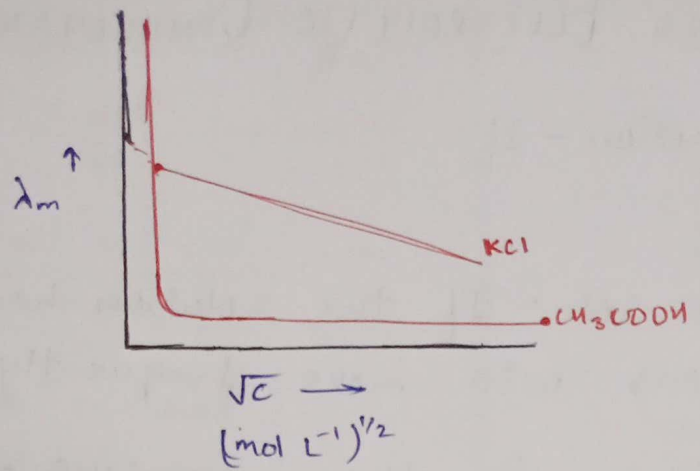
$$\lambda m = \lambda^{\circ} m - b\sqrt{c}$$

- λm : Molar conductivity.
- $\lambda^{\circ} m$: Molar conductivity at infinite dillution
- b : Random constant
- c : concentration.

Types Of Electrolytes :-

- Weak Electrolytes :- $AB \rightleftharpoons A^{+} + B^{-}$
  (5% Dissociation)
  Eg: CH_3COOH, NH_4OH

- Strong Electrolytes :- $AB \longrightarrow A^{+} + B^{-}$
  (100% Dissociation)
  Eg: KCl, NaCl, $CaCl_2$



KOHLRAUSCH'S LAW :- (Only applicable for infinite dilution)

State that Equivalent conductivity of an electrolyte at infinite dilution is the sum of equivalent ionic conductive of cations & Anions.

$$\lambda^{\infty}_{eq} = \lambda^{\infty}_{eq\,cat} + \lambda_{eq\,cat.}$$

For $A_x B_y \longrightarrow x A^{+y} + y B^{-x}$

$$\lambda^{\infty}_{eq} = \frac{1}{x}\lambda^{\infty}_{m(cat)} + \frac{1}{y}\lambda^{\infty}_{m\,(Ani.)}$$

For $A_x B_y \longrightarrow x A^{+y} + y B^{-x}$

$$\lambda^{\infty}_{m} = x\lambda^{\infty}_{m\,(cat)} + y\lambda^{\infty}_{m(Ani)}$$

where, $\lambda^{\infty}_{eq(cation)}$ - limiting eq. conductivity of cation.

$\lambda^{\infty}_{eq\,(Anion)}$ - limiting eq. conductivity of Anion.

$\lambda^{\infty}_{m\,(cation)}$ - limiting molar conductivity of cation.

$\lambda^{\infty}_{m\,(anion)}$ - limiting molar conductivity of Anion.

And x = Coefficient factor for cation.

y = Coefficient factor for anion.

Application of Kohlrausch's law

(i) To calculate conductance of weak electrolytes.

(ii) To calculate degree of dissociation.

i.e $\alpha = \frac{\lambda_m}{\lambda_m^\infty} \times 100\%$ $\quad$ $\alpha = \frac{\lambda_{eq}}{\lambda_{eq}^\infty} \times 100\%$

(iii) To calculate dissociation constant for weak electrolytes.

$\left[K_a = \frac{c\alpha^2}{1-\alpha}\right]$ when $\alpha \ll\ll 1$ then, $K_a = c\alpha^2$

Dissociation const.

Degree of Dissociation. $\left[\alpha = \sqrt{\frac{K_a}{c}}\right]$

Q. The resistance of 1N solution are 50 Ω and there length of electrode are 2.1 cm & area of vessel is 4.2 cm^2 So cal. equivalent conductivity & specific conductanee.

Sol: Given = $R = 50\ \Omega$

$l = 2.1\ cm$

$A = 4.2\ cm^2$

$N = 1N$

$$K = \frac{1}{R}\frac{l}{A}$$

$$= \frac{1}{50} \times \frac{2.1}{4.2_2} = \frac{1}{100}\ \Omega^{-1} cm^{-1}$$

$$\therefore \lambda_{eq} = \frac{K \times 1000}{N} = \frac{1}{100} \times 1000 = 10\ \Omega^{-1} cm^2\ g\ eq^{-1}.$$

Q for 0.08 M solution with specific conductance $2 \times 10^{-2}\ \Omega$ whereas for 0.1 M soln with resisty of 50 Ω cm, which have more molar conductivity?

Sol:

(i) $\lambda_m = \frac{K \times 1000}{M}$

$= \frac{2 \times 10^{-2} \times 1000}{0.08}$

$= 250\ \Omega^{-1}\ cm^2\ mol^{-1}$

(ii) $\lambda_m = \frac{K \times 1000}{M}$

$= \frac{1}{\rho} = K = \frac{1}{50}$

$= \frac{1 \times 1000}{50 \times 0.1} = 200\ \Omega^{-1}\ cm^2\ mol^{-1}$

Q. A solution of 0.5 mol l^{-1} have a conductance 0.0001 Ω^{-1} and cell const. of 0.1 cm^{-1} so calculate molar conductivity:-

Sol: Given, $M = 0.5\ M$

$G = 0.0001\ \Omega^{-1}$

$G^* = 0.1\ cm^{-1}$

$K = G \times G^*$

$K = 10^{-4} \times 10^{-1}$

$= 10^{-5}\ cm^{-1}\ \Omega^{-1}$

$\therefore \lambda_m = \frac{K \times 1000}{M} = \frac{10^{-5} \times 1000 \times 10^{2}}{5}$

$= 2 \times 10^{-2}\ \Omega^{-1}\ cm^2\ mol^{-1}$

Q. λ^{∞}_{eq} = of $H_4C_2O_4$ find?
(oxalic acid)

Given, $\lambda^{\infty}_{eq}\ Na_2C_2O_4 = 400\ S\ cm^2\ geq^{-1}$

$\lambda^{\infty}_{eq}\ H_2SO_4 = 700\ S\ cm^2\ geq^{-1}$

$\lambda^{\infty}_{eq}\ Na_2SO_4 = 450\ S\ cm^2\ geq^{-1}$

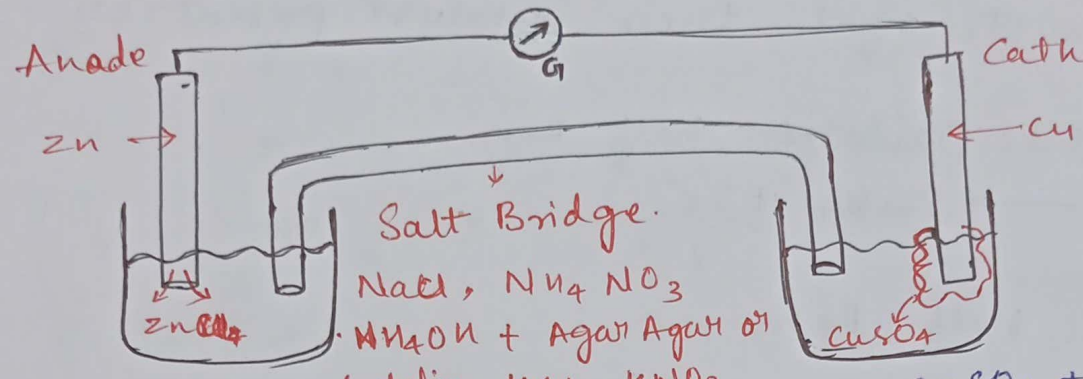
Sol: $\lambda^{\infty}_{eq}(H_2SO_4) + \lambda^{\infty}_{eq}(N_2C_2O_4) = \lambda^{\infty}_{eq}(Na_2SO_4) = \lambda^{\infty}_{CH_3COOH}$.

$400 + 700 - 450$

$= 650\ gcm^2\ geq^{-1}$ $= \lambda^{\infty}_{eq}(CH_4C_2O_4)$

DANIEL CELLS

ALONE
A - Anode
L - Left
O - Oxida.
N - -ve.
E



$Zn \longrightarrow ZnSO_2 + 2e^-$
Oxidation.

$CuSO_4 + 2e^- \longleftrightarrow Cu$
Red

It is also called Galvanic Cell two half cells are seperated by eachother by SALT BRIDGE.

SALT BRIDGE :- Inverted U-Tube contain solution of Salt Bridge is inverted u-tube containing electrolytes like KCl, KNO_3, NH_4NO_3 etc. The speed of cation and anion are nearly equal for both electrolytics Functions of Salt Bridge.

↳ It connect both two half cell and complete their circuit. It helps to maintain electrically neutral system if the salt Bridge removed the voltage drop to zero.

Cell Representation / Iupac / No. of e^- calculations / Over all Rxn / Half Rxn :-

Two Half Cell are seperated by Double seash line which is denoted as salt Bridge left side we write oxidation half Rxn. and right side we write reduction half Rxn. each half cell must be written in the form of there phase and their half cell must right their catalyst present etc.

1) Daniel Cell Oxidation half Rxn.

$$Zn \longrightarrow ZnSO_4 + 2e^-$$

Reduction Half Rxn.

$$CuSO_4 + 2e^- \longrightarrow Cu.$$

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$$

Oxi || Red.

$$Zn_{(s)} \,|\, ZnSO_{4(aq)} \,||\, CuSO_{4(aq)} \,|\, Cu_{(s)}$$

no. of $e^- \longrightarrow 2e^-$

Q. $Ti_{(s)} \,|\, Ti^{+}_{(aq)} \,||\, Sn^{+2}_{(aq)} \,|\, Sn_{(s)}$

(OHR) $(Ti \longrightarrow Ti^{+} + 1e^-) \times 2.$

(RHR) $Sn^{+2} + 2e^- \longrightarrow Sn$

Overall Rxn.

$$2Ti + Sn^{+2} \longrightarrow 2Ti^{+} + Sn.$$

no. of $e^- \longrightarrow 2e^-$

* $Al + Cu^{+2} \longrightarrow Al^{+3} + Cu$.

Cell Representation.

$Al | Al^{+3} || Cu^{+2} | Cu$.

(OHR) $(Al \longrightarrow Al^{+3} + 3e^-) \times 2$.

(RHR) $(Cu^{2+} + 2e^- \longrightarrow Cu) \times 3$.

Overall Rxn.

$2Al + 3Cu^{2+} \longrightarrow 2Al^{+3} + 3Cu$.

no of $e^- \longrightarrow 6e^-$

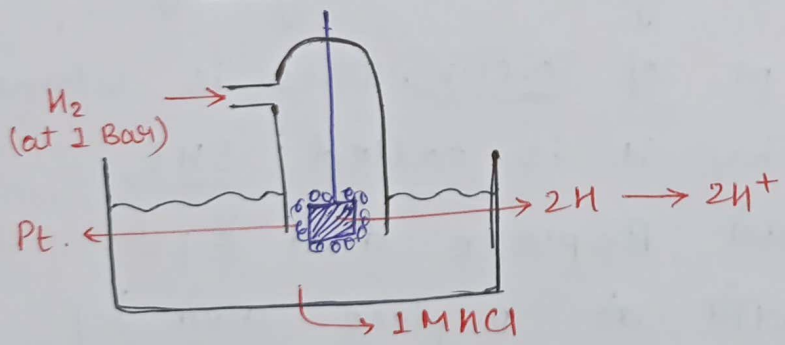
* $NaCl + H_2 \longrightarrow 2HCl + 2Na$.

Overall Rxn.

$Pt(s) | H_2(g)$ 1 bar | HCl || NaCl (aq.) / Na(s)

SHE [Standard Hydrogen Electrode Pt.]

Temp – 298 K / 25°C.



→ when standard hydrogen consists of a platinum electrode which is an anode electrode, which is dipped in acidic solution of 1M and temp 298 K and 1 atm pressure.

→ When oxidation of Hydrogen takes place this standard condition is called standard Hydrogen electrode potential.

→ This setup is completed kept at left side of Daniel cell, then we get a pt. i.e called Standard Reduction pt.

→ Now, we take different - diff. element with different - different solution, then we generate different - different pt. this pt kept in a table we got a . with respect to SHE. this is called ELECTROCHEMICAL SERIES.

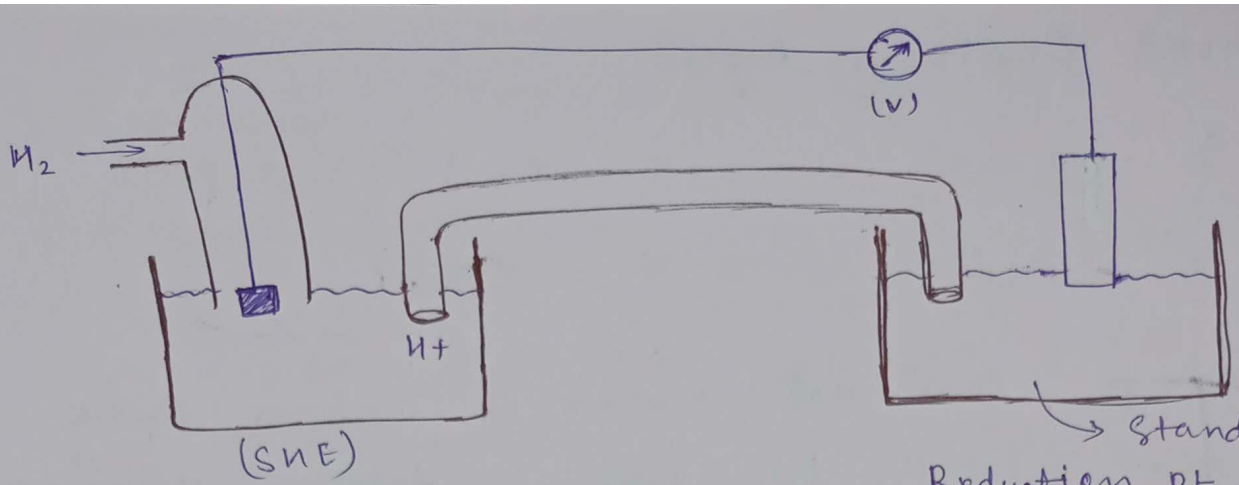
PROPERTIES OF SERIES :-

- Top Elements in Series are Eletropositive and down are Electronegative.
- Top of the series are good reducing agent & down of the series are good oxidizing agent.
- Hydrogen has a pt. of 0.00V, this is standard condition that's why it is called SHE.

★ ऊपर वाले नीचे को Replace करते हैं। (For metals)

★ नीचे वाले ऊपर वाले को Replace करते हैं।

(For non-metals)



$Mg^{+2} + 2e^- \longrightarrow Mg$

$Cu^{+2} + 2e^- \longrightarrow Cu$

$K^+ + 1e^- \longrightarrow K$

- Top elements Series are more active than lower (metal)
- Feasible $\Rightarrow$ $+E^\circ_{cell} = E_{cathode} - E_{anode}$ (+ve) (+ve) (−ve)

↳ $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

↳ $Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$

↳ $CuSO_4 + Ag \longrightarrow$ No Rxn

↳ $KBr + Cl_2 \longrightarrow KCl + Br$

↳ $KBr + I_2 \longrightarrow$ No Rxn.

Good Reducing Agent

$A^{+2} + 2e^- \longrightarrow A \quad = -2.4$

$B^{+2} + 2e^- \longrightarrow B \quad = -1.6$

→ More -ve (Right part)

Good Oxidising Agent

$X^{+2} + 2e^- \longrightarrow X = +2.3$

$Y^{+2} + 2e^- \longrightarrow Y = +3.3$

} → more +ve (left part)

Like (Li) kings (K) can (Ca) not (Na) make (Mg) a (Al) zebra (Zn) caze (Cr)
In (Fe) cold (Cd) night (Ni) to (Sn) pop (Pb) hydrogen (H) cuckoo. (Cu)
I (I) feinted (Fe^{3+}) As (Ag) He (Hg) Brought (Br) chlorinated (Cl) Gold (Au)
for (F) me.

$E°cell = E_{cathode} - E_{Anode}$

$= E_{right} - E_{left}$

$= E_{red} - E_{oxi}$

$E°cell$ → Daniel

$Zn / Zn^{2+} \,||\, Cu^{2+} / Cu$

$E°cell = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$

$= 0.337 + (0.763)$

$E°cell = 1.10$ volts

Nernst Eq:

↓

$E_{cell} = E°cell = \frac{2.303\,RT}{nF} \log_{10}\left[\frac{[P]}{[R]}\right]$ → Ionic form.

$R = 8.314\ K^{-1} mol^{-1} J$

$T = 298\ K / 25°C$

$F = 96500$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log_{10} \frac{[P]}{[R]}$$

For Daniel cell:

$$Zn + Cu^{+2} \longrightarrow Cu + Zn^{+2}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

"[ ]" → Concentration, Molarity.

eg: $Cu | Cu^{2+} \,||\, Ag^{+}(0.01) | Ag$

$E^\circ_{cell}\ Cu^{2+}/Cu = 0.34$

$E^\circ_{cell}\ Ag^{+}/Ag = 0.77$

[O.H.R] $Cu \longrightarrow Cu^{2+} + 2e^-$

[R.H.R] $(Ag^{+} + 1e^- \longrightarrow Ag) \times 2$

$$Cu + 2Ag \longrightarrow Cu^{2+} + 2Ag$$

$n = 2$

$P = Cu^{+2} = 10^{-3}$ $\quad R = 2Ag^{+2} = 10^{-2}$

$$E^\circ_{cell} = E_{cat} - E_{An}$$

$$= E_{Ag} - E_{Cu}$$

$$= 0.77 - 0.34$$

$$= (+0.43) \text{ volts.}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log_{10} \frac{[P]}{[R]}$$

$$= 0.43 - \frac{0.0591}{2} \log_{10} \frac{[Cu^{+2}]}{[Ag^{+}]^2}$$

$$= 0.43 - \frac{0.06}{2} \log_{10} \frac{(10^{-3})}{(10^{-2})^2}$$

$$= 0.43 - 0.03 \frac{\log_{10} 10}{1}$$

$$[E_{cell} = 0.40 \text{ volts}]$$

Calc Of Log :-

log → log = $\log_{10}$

→ ln = ln → $\log_e$ (natural log)

$[2.303 \times \log_{10} x = \ln x]$

* $\log(x.y) = \log x + \log y$.

* $\log(x/y) = \log x - \log y$.

* $\log x^y = y \log x$

- $\log_{10}(1) = 0$
- $\log 2 = 0.3010$
- $\log 4 = \log(2)^2 = 2 \cdot \log 2 = 2 \times 0.3010 = 0.6020$
- $\log 5 = 0.69$
- $\log 6 = \log(2 \cdot 3) = \log 2 + \log 3 = 0.7780$
- $\log 3 = 0.477$
- $\log 7 = 0.84$
- $\log 8 = 3 \log 2 = 3 \times 0.3010 = 0.9030$
- $\log 9 = 2 \log 3 = 2 \times \overline{0}.477 = 0.954$
- $\log 10 = 1$

Q. $Zn \mid Zn^{+2}(0.01) \parallel Fe^{+3}(0.01) \mid Fe.$

$E^\circ_{cell} = Zn^{+2} \mid Zn = (0.76)$

$E^\circ_{cell} = Fe^{+3} \mid Fe = (-0.036)$

Sol: $E^\circ_{cell} = 0.036 + 0.76$

$= 0.724$ volts.

[O.H.R]

$(Zn \longrightarrow Zn^{+2} + 2e^-) \times 3$

[R.H.R]

$(Fe^{+3} + 3e^- \longrightarrow Fe) \times 2$

$3Zn + 2Fe^{3+} \longrightarrow 3Zn^{+2} + 2Fe$

[n = 6]

$$E_{cell} = E^\circ_{cell} - \frac{2.303}{nF} RT \log_{10} \frac{P}{R}$$

$$E_{cell} = 0.724 - \frac{0.0591}{6} \cdot \log_{10} \frac{[Zn^{2+}]^3}{[Fe^{+3}]^2}$$

$$E_{cell} = 0.724 - \frac{0.06}{6} \log_{10} \frac{[0.01]^3}{[0.01]^2}$$

$$E_{cell} = 0.724 - 0.01 \log_{10} \frac{[10^{-2}]^3}{[10^{-2}]^2}$$

$$= 0.724 - 0.01 \log_{10} 10^{-2}$$

$$= 0.724 + 0.02 \log_{10} 10^{1}$$

$$E_{cell} = 0.724 \text{ volts.}$$

Relationships of E°_{cell} / E_{cell} / ΔG / ΔG° / K_c

ΔG → +ve : non-spontaneous

ΔG → −ve : spontaneous

ΔG → 0 : Equilibrium.

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

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

For Equilibrium:

$$\Delta G = 0 = -nFE_{cell}$$

$$= -nF\left(E^\circ_{cell} - \frac{2.303}{nF} RT \log_{10} K_c\right)$$

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$0 = -nF E^\circ_{cell} + \cancel{nF} \times \frac{2.303RT}{\cancel{nF}} \log_{10} K_c.$$

$$nF E^\circ_{cell} = -2.303 RT \log_{10} K_c$$

$$\Delta G^\circ = -2.303 RT \log_{10} K_c$$

$$E^\circ_{cell} = \frac{2.303RT}{nf} \log_{10} K_C$$

$$\therefore E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K_c$$

$$E_{cell} = (-0.059) \log_{10} 10^{pH}.$$