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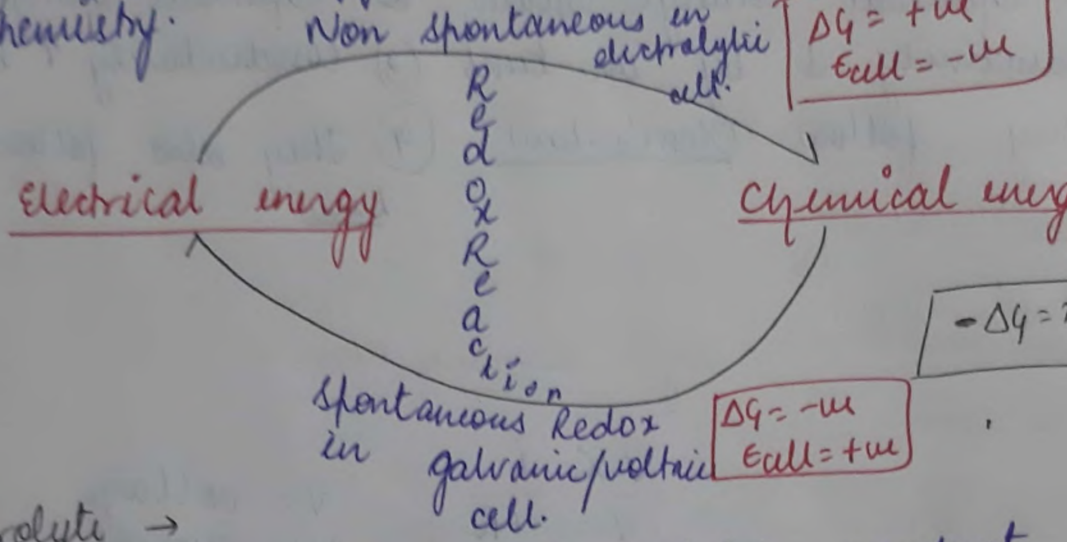
Electro- Chemistry →

NET { Part B = 4, Part C = 8 } CSIR — 12

GATE = 2 marks = 1, 1 mag = 1 } 3 marks

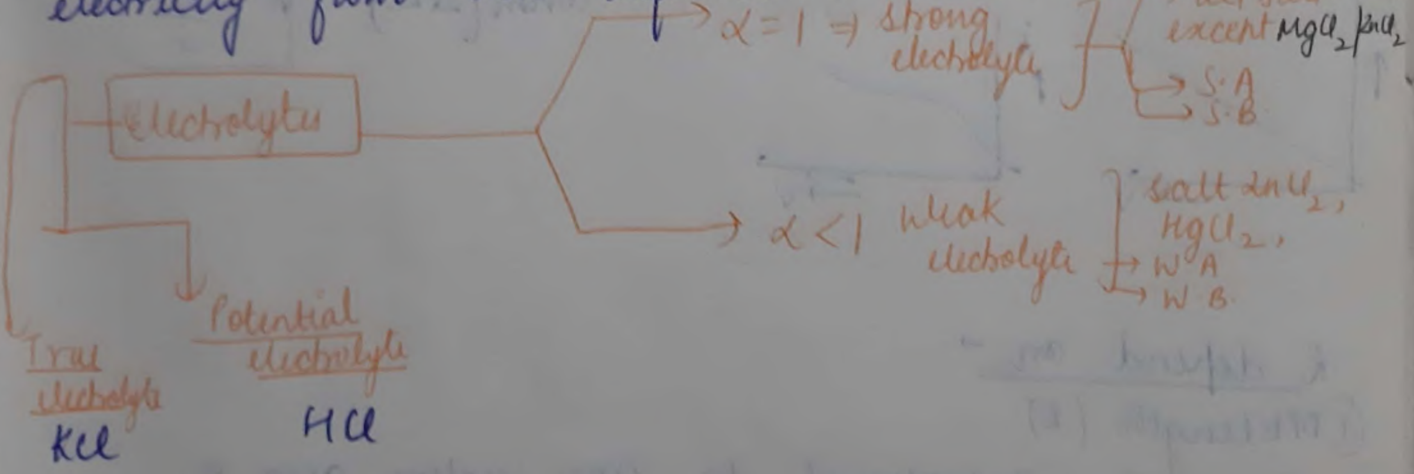
A study of interconversion of electrical energy into chemical energy and vice versa called electrochemistry.



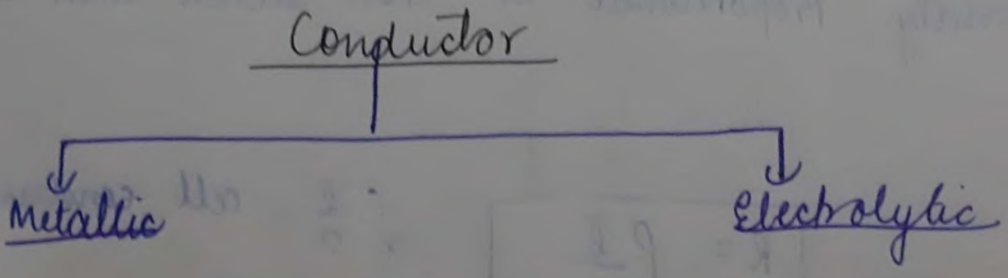
$$\boxed{-\Delta G = nFE_{cell}}$$

Electrolyte →

Those material which conduct electricity from their aqueous or molten state



Conductor



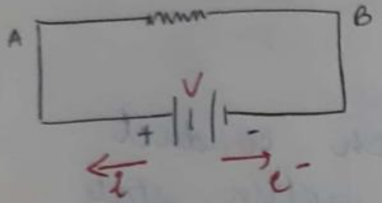
Conductor

Metallic	Electrolytic
① They conduct electricity due to presence of free electrons	① They conduct electricity due to the presence of free ions
② No chemical change obtain	② Chemical change occur.
③ Conductivity ↓ by inc temp	③ conductivity ↑ by ↑ temp.
④ They follow Ohm's Law	④ They also follow Ohm's Law

Resistance →

Ohm's Law :-

By Simonn Ohm →



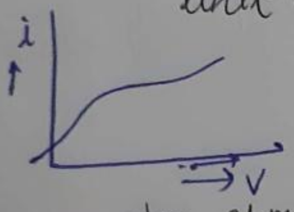
$V \propto i$

$$\boxed{V = iR}$$

V = voltage
i = current
R = resistance.

Unit of R → Ohm (Ω) $\boxed{R = \frac{V}{i}}$

Ohmic



Non ohmic

R depend on →

① DP to length (l)

② Inversaly Proportional to cross section area a.

$$\boxed{R \propto \frac{l}{a}}$$

$$\boxed{R = \rho \frac{l}{a}}$$ $\left\{ \frac{l}{a} = \text{all constant} = \rho \right\}$

ρ is called resistivity / specific resistance and it is material property.

$$\boxed{\rho = \frac{Ra}{l} = \frac{\text{Ohm } m^2}{m} = \text{Ohm-m}}$$

* **Conductance** $\{G/C\}\{\lambda^{-1}\}$

It is Reciprocal of Resistance..

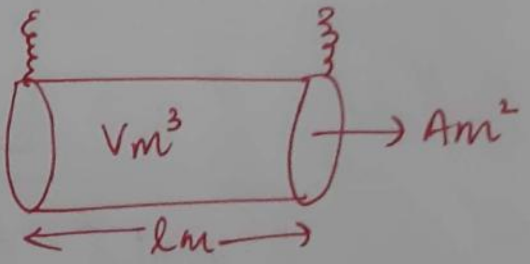
$\boxed{G = \frac{1}{R}}$ Unit of $G = (\text{Ohm}^{-1})$ / Sieman / mho
$\downarrow$ MKS

Specific conductance/ conductivity → K (Kappa)
Reciprocal of resisitivity/ specific resistance.

$\boxed{K = \frac{1}{\rho}}$ Unit of K = (~~ohm~~ Sieman - m)$^{-1}$ = $(S\text{-}cm^{-1})$

NOTE

On inc. dilution, conductance ~~inc~~ increase while K decreases. $\boxed{G = K \times V}$



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

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

$$G = K \cdot \frac{A}{l} \quad \left\{ \text{if } \begin{matrix} l = 1 \\ A = V \end{matrix} \right\}$$

$$\boxed{G = K \times V}$$

If $A = 1 cm^2$, $l = 1 cm$

then $\boxed{G = K}$

We have,

$$\lambda = K \times \frac{V}{l^2}$$

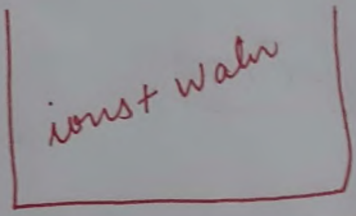
$$\Rightarrow \lambda = K \times \frac{V}{l^2} \times \frac{mole}{mole}$$

$$\boxed{\lambda = K \times V_m \times \frac{mole}{l^2}}$$

$V_m \rightarrow$ molar volume

Defination of $\lambda \rightarrow$ It is defined as total conductance produced by adding fixed amount of electrolyte in V volume of the solution. It increases by increasing volume.

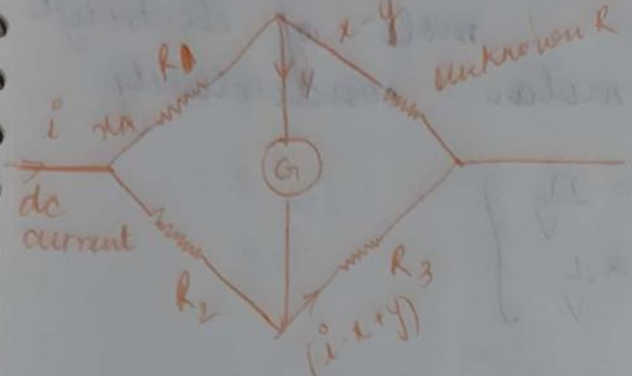
Conductance is an extensive quantity due to this for any solution.



$$\boxed{C_{total} = \Sigma C_i^{\circ} + water}$$

$$\boxed{K_{AgCl} = \underbrace{K_{AgCl\,(\text{saturated in water})}}_{\text{Total}} - K_{water}}$$

• How to calculate R, λ, K →

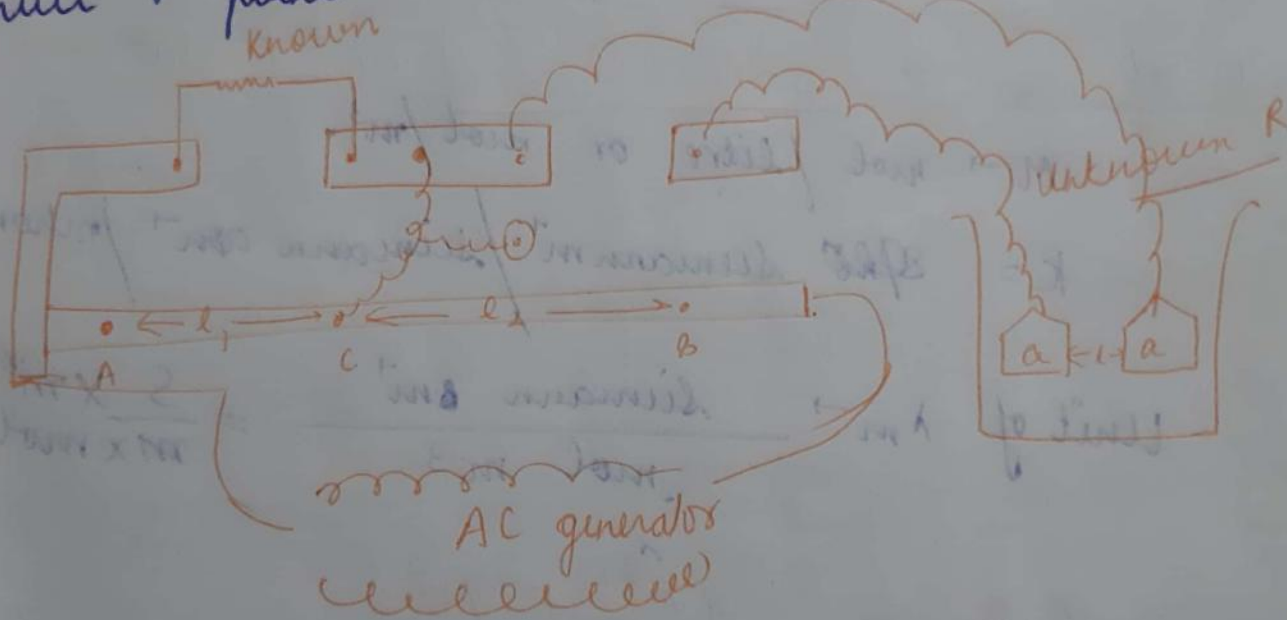


At null point →

$$\frac{R_1}{R_2} = \frac{R}{R_3}$$

$$\boxed{R = \frac{R_1}{R_2} \times R_3}$$

In case of conductivity cell we use A.C. instead of dc because d.c. create polarisation and due to use of A.C. we used Radio jockey for determining null point.



At null point →

$$\frac{R_1}{l_1} = \frac{R}{l_2}$$

$$\Rightarrow \boxed{R = \frac{R_1}{l_1} \times l_2}$$

★ λ_m [molar conductivity] →

Conductivity produced by 1 mole of electrolyte present in solⁿ called molar conductivity

$$\lambda = K \times V \qquad \left[\begin{matrix} C = \frac{n}{V} \\ C \propto \frac{1}{V} \end{matrix}\right]$$

$$\lambda = \frac{K \times 1000}{C}$$

If 1 mole ions present then C=M →

$$\boxed{\lambda_m = \frac{K \times 1000}{M}} \qquad M = \frac{mole \times 1000}{V(ml)}$$

Unit of λ_m → $\boxed{S\text{-}m^2\,mol^{-1}}$ or $\boxed{S\text{-}cm^2\,(mol^{-1})}$

M → mol / litre or mol / m^3.

K = siemann m^{-1} / siemann cm^{-1} / mhom^{-1}.

$$\text{Unit of } \lambda_m \rightarrow \frac{\text{siemann } m^{-1}}{mol\ m^{-3}} = \frac{S}{m} \times \frac{m^3}{mol}$$

$$* \quad A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

z factor/n factor $x \times y$

$$\# \quad \boxed{\lambda_m A_xB_y = x\lambda_m A^{y+} + y\lambda_m B^{x-}} \quad *$$

$$\rightarrow \quad HCl \longrightarrow H^+ + Cl^-$$

$$\begin{matrix} H_2SO_4 & \longrightarrow & 2H^+ & + & SO_4^{2-} \\ xM & & 2xM & & xM \end{matrix}$$

$$\# * \quad \boxed{\lambda_m H_2SO_4 = 2\lambda_m H^+ + \lambda_m SO_4^{-2}}$$

Q If molar conductivity of Cl^- is $x\ S\,cm^2\,mol^{-1}$ and λ_m of Ba^+ is $y\ S\,cm^2\,mol^{-1}$. find λ_m of $BaCl_2$.

$$BaCl_2 \rightleftharpoons Ba^{+2} + 2Cl^-$$
$$xM \qquad xM \qquad 2x\,M$$

$$= ~~x\lambda_{BaCl}~~ \quad \lambda Ba^{2+} + 2\lambda Cl^-$$

$$\boxed{\lambda_{m_{BaCl_2}} = y + 2x}$$

★ **λequivalent →**

Equivalent weight = $\frac{M.W}{n\ factor}$

For element

$\boxed{n\ factor = valency}$

Eq. weight = $\frac{Atomic\ weight}{valency}$

$E_H = \frac{1}{1} = 1$

$E_O = \frac{16}{2} = 8$

$E_{Cl} = \frac{35.5}{1} = 35.5$

$E_C = \frac{12}{4} = 3$

$E_N = \frac{14}{3}$

For ions

$\boxed{n\ factor = charge}$

Eq weight = $\frac{M.W}{|Charge|}$

$E_{OH^-} = \frac{17}{1}$

$E_{SO_4^{2-}} = \frac{96}{2} = 48$

$E_{CO_3^{-2}} = \frac{60}{2} = 30$

For salt

$\boxed{n\ factor = total +ve / negative\ charge}$

Eq. Weight = $\frac{MW\ or\ formula\ mass}{total\ +ve\ or\ negative\ charge}$

$E_{NaCl} = \frac{58.5}{1}$

$E_{Na_2CO_3} = \frac{106}{2}$

$E_{Al_2(SO_4)_3} = \frac{Mw}{6}$

GATE $E_{K_2SO_4Al_2(SO_4)_3 24H_2O} = \frac{Mw}{8}$

Equivalent weight

↓ For base

Acidity = no. of OH^- / n factor

$NaOH \rightarrow 1$

$Ba(OH)_2 \rightarrow 2$

$Al(OH)_3 \rightarrow 3$

For acid

Eq. weight of acid = $\frac{Mw}{\text{basicity of acid}}$ = no. of replicable H-atom / those H which attached with electronegative element (O/F/C/N)]

Monobasic acid →

$HClO_4$

HCl

HNO_3

HBr

HI

*H_3PO_2 → Arrhenius acid (Khud ka H atom deta Hai)

*H_3BO_3 → weak monobasic Lewis acid (Dusre ka H atom deta Hai)

Eqwt = $\frac{Mw}{1}$

Dibasic acid →

H_2SO_4

H_2SO_3

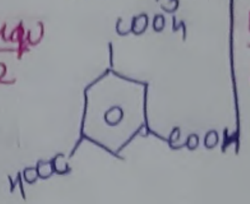
COOH
|
COOH
|
COOH

Eqwt = $\frac{Mw}{2}$

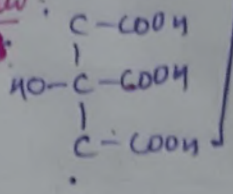
Tribasic acid →

H_3PO_4

$(COOH)_3$



$\frac{Mw}{3}$



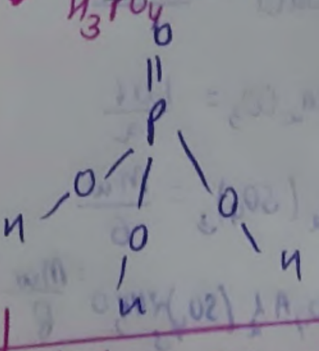
Tetrabasic acid

$H_4P_2O_7$ (Pyrophosphoric acid)

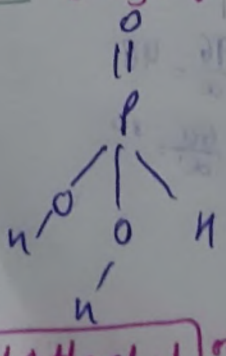
$\frac{Mw}{4}$

Determination of Monobasic acid, Di, Tri-basic acid →

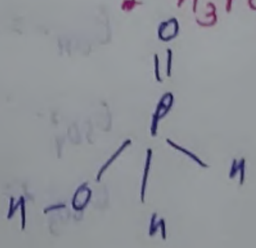
• H_3PO_4



• H_3PO_3



• H_3PO_2



$\boxed{\text{n factor = no. of OH/O attached HC/HN}}$ or no of electronegative atom attached with H.

↓

n factor = 3 2 1

Note :- In any reaction, polyprotic acid may be mono / di / tri - - .

* $\underbrace{H_3PO_4} + NaOH \longrightarrow \underbrace{NaH_2PO_4}$ -

$$\boxed{n\text{ factor} = \text{no of H in}_{\text{Reactant}} - \text{no of H in}_{\text{Product}}}$$

$= 3 - 2 = 1$

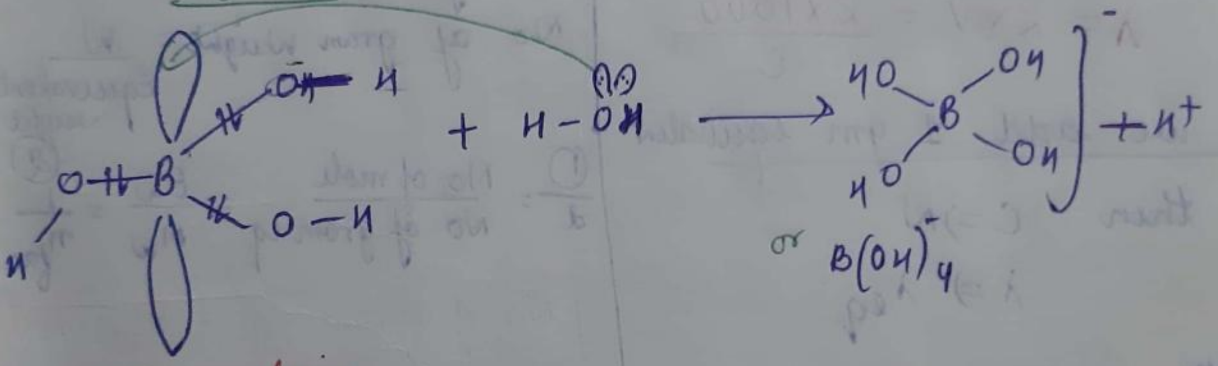
$\boxed{n\text{ factor} = 1}$

* $H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4$

$\boxed{n\text{ factor} = 2}$ $3-1=2$

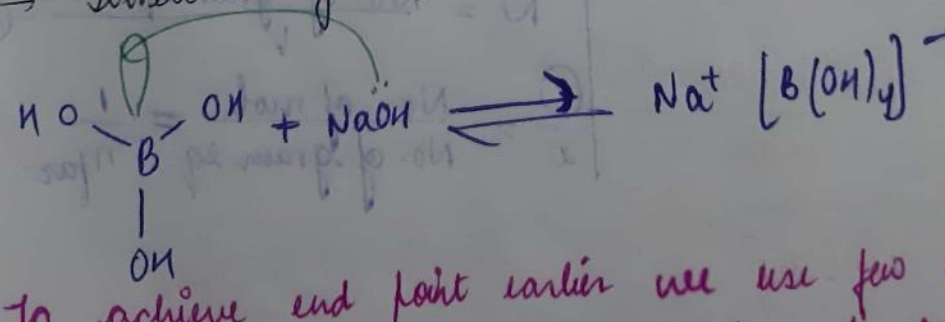
Imp

* H_3BO_3 Orthoboric acid



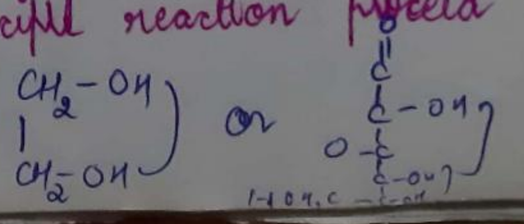
Weak monobasic
Lewis acid

→ Titration of H_3BO_3 with NaOH ??

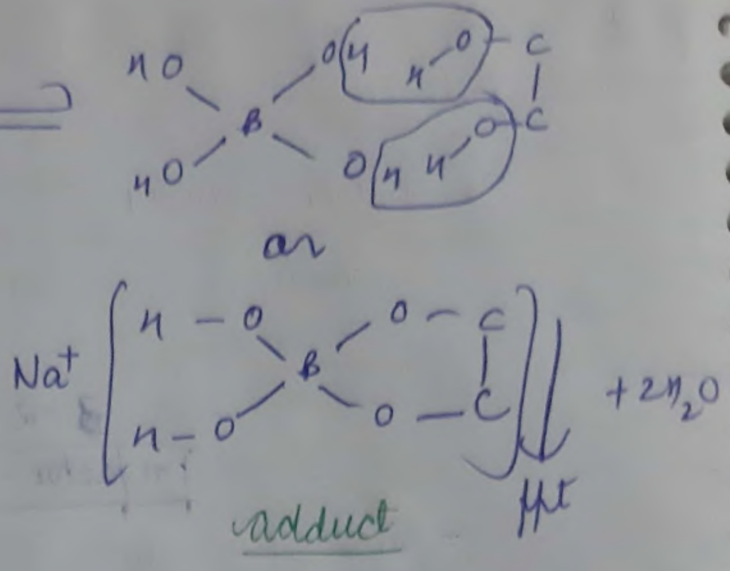


To achieve end point earlier we use few drops of cis-diol which form cyclic adduct and according to Le-Chatlier principle reaction proceed in forward dirⁿ.

* cis-diol



$H_3BO_3 + NaOH \rightleftharpoons$



$\lambda_{equivalent}$ [equivalent conductivity]

$$\lambda = K \times V = \frac{K \times 1000}{C}$$

If we add 1 gm equivalent →

then C ⇒ N

$\lambda \Rightarrow \lambda_{eq}$

then $\boxed{\lambda_{eq} = \frac{K \times 1000}{N}}$

Unit of $\lambda_{eq} = \frac{S(m^{-1}) \times m^3}{(eq)}$

$$\boxed{\begin{gathered}(S\,m^2\,eq^{-1})\\ (S\,cm^2\,eq^{-1})\end{gathered}}$$

No. of mole $= \frac{W}{MW}$ —①

No. of gram Weight $= \frac{W}{\text{Equivalent weight}}$ —②

$\frac{①}{②} = \frac{\text{No. of mole}}{\text{No. of gram eq}} = \frac{Ew}{Mw} = \frac{1}{n_{fac}}$

$$\boxed{\text{No. of gram eq.} = n_{fac} \times \text{mole}}$$

$M = \frac{\text{no. of mole} \times 1000}{V}$ —①

$N = \frac{\text{No. of gram eq} \times 100}{V}$ —②

$\frac{①}{②} = \frac{\text{No. of mole}}{\text{No. of gram eq}} = \frac{1}{n_{fac}}$

$$\boxed{N = M \times n_{fac}}$$

Relation b/w λ_m & λ_{eq} →

$$\lambda_m = \frac{K\times 1000}{M} \quad , \quad \lambda_{eq} = \frac{K\times 1000}{N}$$

or

$$\boxed{\frac{\lambda_m}{\lambda_{eq}} = \frac{N}{M} = n\ \text{factor}}$$

$$\boxed{\lambda_{eq} = \frac{\lambda_m}{n_{\text{factor}}}}$$

Q $A_x B_y$

$\lambda_m A_x B_y = X\ \text{Scm}^2(\text{mol}^{-1})$, $\lambda_{eq} A_x B_y = ?$

ⓐ $\frac{X}{x}$ ⓑ $\frac{X}{y}$ [✓ ⓒ $\frac{X}{xy}$] ⓓ $\frac{X}{x-y}$

Trick: $\boxed{\text{n factor is also multiply of } xy}$

→ $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$\lambda_m A_xB_y = x\lambda_m(A^{y+}) + y\lambda_m(B^{x-})$

$\lambda_{eq} = A_xB_y = \lambda_{eq}(A^{y+}) + \lambda_{eq}(B^{x-})$

Q If $\lambda_m Al^{+3} = x$, & $\lambda_m Cl^- = y$ for $AlCl_3$, then find $\lambda_m AlCl_3$ & $\lambda_{eq} AlCl_3$.

$\lambda_m AlCl_3 = 1\times\lambda_m Al^{+3} + 3\times\lambda_m Cl^-$

$= x + 3y$

$\lambda_{eq} AlCl_3 = \lambda_{eq} Al^{+3} + \lambda_{eq} Cl^-$

$= \frac{\lambda_m Al}{3} + \frac{\lambda_m Cl}{1} \Rightarrow \frac{x}{3} + \frac{y}{1} \Rightarrow \frac{x}{3} + y$

or $\lambda_{eq}\, AlCl_3 = \frac{\lambda_m\, AlCl_3}{x \times y} = \frac{x \cdot 1 \cdot y}{3 \times 1} = \frac{x \cdot y}{3}$

Q Calculate λ_{eq} for $AlCl_3$, when λ_m for it is 105 $S\,cm^2\,mol^{-1}$.

$$\lambda_{eq} = \frac{\lambda_m}{n\ factor} = \frac{105}{3 \times 1} = \frac{105}{3}$$

$$= 35\ S\,cm^2\,eq^{-1}$$

Q The equivalent conductivity of 0.05 M sol^n of $MgCl_2$ sol^n is 400 $S\,cm^2\,eq^{-1}$. A cell with electrode that are 1.5 cm^2 Area and 0.5 cm apart is fill with 0.05 molar $MgCl_2$ sol^n. How much current will flow when potential diff two electrodes is 5 Volt.

$\lambda_{eq} = 400\ S\,cm^2\,eq^{-1}$. $A = 1.5\ cm^2$, $l = 0.5$ cm.

$M = 0.05\ MgCl_2$. $I = ?$ $V = 5$ Volt.

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

$$\frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \Rightarrow \lambda = K \frac{A}{l}$$

$M = N \times n$ factor
$N = M \times n$ factor

$$\lambda_{eq} = \frac{K \times 1000}{N} \Rightarrow \frac{K \times 1000 \times \cancel{n\ factor}}{M \times m\ factor}$$

$$K = \frac{M \times \lambda_{eq} \times n\ factor}{1000 \times \cancel{n\ factor}}$$

$$\Rightarrow \frac{0.05 \times \cancel{400} \times 10^{-2}}{\cancel{1000} \times \cancel{2}}$$

$$= 10^{-2}$$

$\frac{0.05 \times 400 \times 2}{1000 \times 10^{-2}} = 40 \times 10^{-3}$. $\rho = \frac{1}{40 \times 10^{-3}}$

$V = IR$

$\frac{V}{R}$

$R = \rho \frac{l}{A} \Rightarrow \frac{1}{40 \times 10^{-3}} \times \frac{0.5}{1.5_3} = \frac{1000}{40 \times 3} = \frac{100}{12}$

$I = \frac{V}{R} \Rightarrow \frac{5 \times 12}{100} = \frac{60}{100} = 0.6$ Ampere

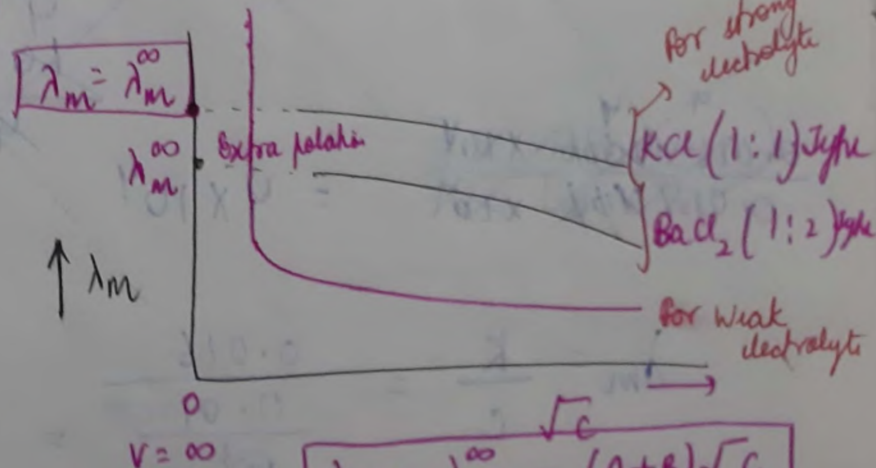
~~Effect of dilution on conductivity →~~

Effect of dilution on conductivity →

On increasing dilution, degree of dissociation increases for weak electrolyte and in case of strong electrolyte, ionic mobility increases.

On continuous increase in dilution concentration approaches to volume. At this point on extrapolation limiting value of molar conductivity achieve. This is called limiting conductivity or conductivity at infinite dilution.

$$\boxed{\lim_{c \to 0} \lambda_m = \lambda_m^{\infty}}$$



For strong electrolyte → $\boxed{\lambda_m = \lambda_m^{\infty} - (A+B)\sqrt{c}}$

where A+B → Debye Huckel constant, They depend on the nature of electrolyte.

For weak electrolyte →

$$\boxed{\alpha = \frac{\lambda_m}{\lambda_m^{\infty}}}$$

λ_m at infinite dilution for weak electrolyte are calculated by the help of famous Kohlrausch Law

Q The conductivity of 0.01 M solⁿ of acetic acid was found to be 0.016 S m⁻¹ Calculate α of acid

given $\lambda_m^\infty = 400\times10^{-4}\ S\,m^2\,mol^{-1}$

Sol $K = 0.016\ S\,cm^{-1}$, $\lambda_m^\infty = 400\times10^{-4}\ S\,m^2\,mol^{-1}$

$M = 0.01 M$

~~$\alpha = \frac{\lambda_m}{\lambda_m^\infty}$~~ , ~~$\lambda_m = \frac{K\times1000}{M} = \frac{0.016\times10^3}{0.010} = 16\times10^2$~~

~~$\alpha = \frac{K\times1000}{M\times\lambda_m^\infty}$~~ ~~$= \frac{0.016\times1000\times10^2}{0.01\times400\times10^{-4}\times10^3} = \frac{16\times1000\times10^{(2+1)}}{400\times}$~~

~~$\frac{0.016\times1000\times10^4}{0.010\times400\times10^4}$~~ $= 4\times10^4$

$$\lambda_m = \frac{K}{c} = \frac{0.016}{0.01\times10^{-3}} = \frac{0.016\times10^{-3}}{0.01}$$

$$= 16\times10^{-4}.$$

$$\lambda_m^\infty = 400\times10^{-4}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^\infty} = \frac{16\times10^{-4}}{400\times10^{-4}} = \underline{\underline{0.04}}$$

Q The specific conductivity of a saturated solⁿ of AgCl at 25°C is 3.41×10^{-6} S cm^{-1} and that of water is 1.6×10^{-6} S cm^{-1}. The molar conductivity at infinite is 138.3 S cm^2 mol^{-1}. Which is solubility of AgCl in water in mol/litre [solubility = molarity)

$\lambda_m^\infty = 138.3$ S cm^2 mol^{-1}, M : ?

$$K_{AgCl} = K_{AgCl}(\text{saturated}) - K_{water}$$

$$= 3.41 \times 10^{-6} - 1.6 \times 10^{-6}$$

$$= 1.81 \times 10^{-6} \text{ S cm}^{-1}.$$

$$\begin{array}{r} \overset{2}{\cancel{3}}.\overset{14}{\cancel{4}}1 \\ 1.60 \\ \hline 1.81 \end{array}$$

~~$\lambda_m^\infty = \frac{K \times 1000}{}$~~

AgCl is sparingly soluble salt so, $\lambda_m = \lambda_m^\infty$.

$$\lambda_m = \frac{K \times 1000}{M} \Rightarrow M = \frac{K \times 1000}{\lambda_m} \frac{\text{S-cm}^{-1}}{\text{S-cm}^2\text{mol}^{-1}}$$

$$= \frac{1.81 \times 10^{-6} \times 10^3}{138.3} \text{ [illegible]}$$

$$= 0.01308 \times 10^{-3} \frac{\text{mol}}{\text{cm}^3}$$

$$\boxed{M = 1.308 \times 10^{-5} \text{ mol/litre}}$$

~~$M = 1.308 \times 10^{-8}$ mol/litre~~

1m = 100cm

$(1m^3) = 10^6 cm^3$

$1L = 10^{-3} m^3 = 10^{-3}(10^6 cm^3)$

$= 10^3 cm^3 = 10^3$ ml $= 1000$ ml

For weak electrolyte →

From Ostwald Dilution law →

$$\begin{array}{lccc} HA & \longrightarrow & H^+ & + A^- \\ c & & 0 & 0 \\ c(1-\alpha) & & c\alpha & c\alpha \end{array}$$

$$\boxed{K_a = \frac{c\alpha^2}{(1-\alpha)}} \Rightarrow \# \boxed{K_a = \frac{c\left(\frac{\lambda_m}{\lambda_m^\infty}\right)^2}{1-\frac{\lambda_m}{\lambda_m^\infty}}}$$

Case I → if $1-\alpha \simeq 1$ for very weak

$$\boxed{K_a = c\alpha^2}$$ We know that $\alpha = \frac{\lambda_m}{\lambda_m^\infty}$

$$\# \boxed{K_a = c\left(\frac{\lambda_m}{\lambda_m^\infty}\right)^2}$$

Case II → $K_a = \frac{c\alpha^2}{1-\alpha}$

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

$$\frac{1}{\alpha} - 1 = \frac{c\alpha}{K_a}$$

$$\frac{1}{\alpha} = 1 + \frac{c\alpha}{K_a}$$

$$\frac{\lambda_m^\infty}{\lambda_m} = 1 + \frac{c\frac{\lambda_m}{\lambda_m^\infty}}{K_a}$$

Divide by λ_m^∞

$$\# \boxed{\frac{1}{\lambda_m} = \frac{1}{\lambda_m^\infty} + \frac{1}{K_a}\frac{c\lambda_m}{(\lambda_m^\infty)^2}}$$

Kohlrausch Law of Independent Migration

This law stated that at infinite dilution when dissociation of all the electrolyte are complete and where all the inter ionic effect disappear because of longer distance b/w the ions. Each ion migrate independently of its co ion and contribute to the total molar conductivity of an electrolyte of definite contribution which depend only on its own nature & not at all on the ion with which it is connected.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$\lambda^{\infty}_{m} A_xB_y = x\lambda^{\infty}_{m} A^{y+} + y\lambda^{\infty}_{m} B^{x-}$$

$$\lambda^{\infty}_{eq} A_xB_y = \lambda^{\infty}_{eq} A^{y+} + \cdot \lambda^{\infty}_{eq} B^{x-}$$

$$\boxed{\lambda^{\infty}_{eq} A_xB_y = \frac{\lambda^{\infty}_{m} A_xB_y}{xy}}$$

λ^{∞}_{eq} of some ions →

$H^+ \longrightarrow 349.84$

$OH^- \longrightarrow 197.6$

$Br^- \longrightarrow 78.4$

$I^- = SO_4^{--} \longrightarrow 76.8$

$Cl^- \longrightarrow 76.3$

$K^+ \longrightarrow 73.52$

$NH_4^+ \longrightarrow 73.40$

$Cu^{++} \longrightarrow 59.50$

$Mg^{+2} \longrightarrow 53.10$

$Na^+ \longrightarrow 50.11$ 0 - 8 - 1

$CH_3COO^- \longrightarrow 40.9$

Pair of electrolyte with same anions	λ_∞ (in mho)	Difference
KBr	151.92	23.41
NaBr	128.51	
KCl	149.61	23.41
NaCl	126.45	
KNO_3	144.96	23.41
$NaNO_3$	121.55	

Pair of electrolyte with same cations

	λ_∞ (mho)	(Difference)
NaBr	128.51	2.06
NaCl	126.45	
KBr	151.92	2.06
KCl	149.89	
LiBr	117.06	2.06
LiCl	115.03	

→ Application :→

$\lambda_m^\infty CH_3COONa = x$ $\lambda_m^\infty NaCl = y$ $\lambda_m^\infty HCl = z$

$$\boxed{\lambda_m^\infty CH_3COOH = \lambda_m^\infty CH_3COONa + \lambda_m^\infty HCl - \lambda_m^\infty NaCl}$$

$\boxed{\lambda_m^\infty CH_3COOH = x + z - y}$

Q Given that λ_m^∞ for $NH_4Cl = 120$, λ_m^∞ for $KOH = 140$ for λ_m^∞ for $KCl = 100$. Calculate λ_m^∞ for NH_4OH

$$\lambda_m^\infty NH_4OH = \lambda_m^\infty NH_4Cl + \lambda_m^\infty KOH - \lambda_m^\infty KCl$$

$$= 120 + 140 - 100$$

$$\boxed{\lambda_m^\infty NH_4OH = 160}$$

Q Given that λ_m^∞ for $Ca(OH)_2 = x_1$

$NH_4Cl = x_2$

$CaCl_2 = x_3$

Calculate λ_m^∞ for NH_4OH

$$Ca(OH)_2 + 2NH_4Cl - CaCl_2 = 2NH_4OH$$

$$2NH_4OH = x_1 + 2x_2 - x_3$$

$$\boxed{NH_4OH = \frac{x_1 + 2x_2 - x_3}{2}}$$

Q Given the following molar conductivity at 25°C

λ_m^∞ for $HCl \rightarrow 426\ S\,cm^2\,mol^{-1}$.

$NaCl \rightarrow 126\ S\,cm^2\,mol^{-1}$.

~~Na~~

Sodium Protonate $\rightarrow 83\ S\,cm^2\,mol^{-1}$.

What is the ionisation constant (K_a) for Protonic acid. If conductivity of 0.001 M Krotonic acid is $3.83 \times 10^{-5}\ S\,cm^{-1}$.

$$\lambda^\infty_{Krotonic\ acid} = \lambda^\infty_{Sodium\ Protonate} + \lambda^\infty_{HCl} - \lambda^\infty_{NaCl}$$

$$= 83 + 426 - 126$$

$$= 383\ S\,cm^2\,mol^{-1}$$

Galatron angel kew

$$\lambda_m = \frac{K \times 1000}{M} = \frac{385 \times 10^{-5} \times 10^{3}}{10^{-3}}$$

$$\lambda_m = 3.85 \times 10$$

~~$K_a \approx C\alpha^2$~~

$$\alpha = \frac{\lambda_m}{\lambda_m^{\infty}} = \frac{\cancel{3}\cancel{83} \times 10}{383 \times 10\cancel{0}}$$

$$\boxed{\alpha = 0.1}$$

$$K_a = C\alpha^2$$

$$= 0.001 \times 0.1 \times 0.1$$

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

$$\boxed{K_a = 10^{-5}}$$

Q A solⁿ having resistance 100 Ω are mixed with another solⁿ of equal volume having resistance 100 Ω. Then find the total resistance of the mixture.

Trick → $\frac{n}{R_{total}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \cdots$ → no. of solⁿ

$$\frac{2}{R} = \frac{1}{100} + \frac{1}{100} \qquad \frac{\cancel{2}}{R} = \frac{\cancel{2}}{100}$$

$$\boxed{R = 100\ \Omega}$$

~~Q Molar~~

Q Molar conductivity of aqueous solⁿ of HA is 200 S-cm² mol⁻¹, pH of solⁿ is 4 then find pK_a value of HA at 25°C. given - $\lambda^{\infty}_{m_{NaA}} = 100\ S\,cm^2\,mol^{-1}$, $\lambda^{\infty}_{m_{HCl}} = 425\ S\,cm^2\,mol^{-1}$, $\lambda^{\infty}_{m_{NaCl}} = 125\ S\,cm^2\,mol^{-1}$.

$\lambda_{m_{HA}} = 200\ S\ cm^2/mol$, $pH = 4$, $pK_a = ?$

$\lambda^{\infty}_{m\,NaA} = 100\ S\ cm^2/mol$, $\lambda^{\infty}_{m\,HCl} = 425\ S\ cm^2\ mol^{-1}$.

$\lambda^{\infty}_{m\,NaCl} = 125\ S\ cm^2 mol^{-1}$

$$\Rightarrow \alpha = \frac{\lambda_{m_{HA}}}{\lambda^{\infty}_{m\,HA}} = \frac{200}{}$$

$$\lambda^{\infty}_{m\,HA} = \lambda^{\infty}_{m\,HCl} + \lambda^{\infty}_{m\,NaA} - \lambda^{\infty}_{m\,NaCl}$$

$$= 425 + 100 - 125$$

$$= 400\ S\ cm^2/mol$$

$$\alpha = \frac{200}{400}\ S\ cm^2/mol = 0.5$$

We have

$$\boxed{pH = pK_a + \log \alpha}$$

$$4 = pK_a + \log 1 - \log 2$$

$$4 + 0.3010 = pK_a$$

$$= \boxed{pK_a = 4.3010}$$

OR

$pH = 4$ $[H^+] = 10^{-pH} = 10^{-4} = C\alpha$

$$K_a = C\alpha^2 = C\alpha \cdot \alpha$$

$$= 10^{-4} \times 0.5$$

$$pK_a = -\log[K_a] = -\log[5 \times 10^{-5}] = 5 - \log 5$$

$$\boxed{= 4.30}$$

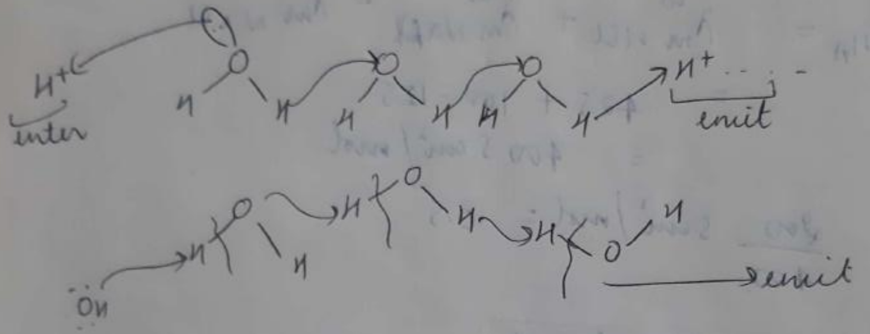
Scanned with CamScanner

Galat sugg

Abnormally high conductance of H^+ & OH^- ion →

Grothus Jumping Mechanism :-

In water, H^+ and OH^- have very high values of molar conductivity and it is explained ~~by~~ on the basis of Proton jumping Mechanism & explain by Grothus



Transport Number :-

Reaction of current carried by a particular ion wrt total current called transport number.

$$\boxed{I_{total} = I^+ + I^-}$$

Then Transport number of cation → $\boxed{t^+ = \frac{I^+}{I^- + I^+}}$

Transport number of anion → $\boxed{t^- = \frac{I^-}{I^- + I^+}}$

$\boxed{t^+ + t^- = 01}$

→ HCl $\boxed{t_{H^+} + t_{Cl^-} = 1}$ $\boxed{t_{H^+} >> t_{Cl^-}}$

NaCl $\boxed{t_{Na^+} + t_{Cl^-} = 1}$ $t_{Na^+} >> t$

Galat sugg

Abnormally high conductance of H^+ & OH^- ion →

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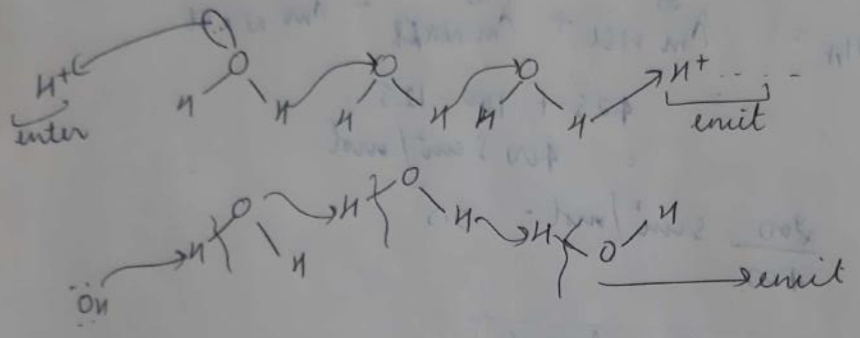

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Transport number of anion → $\boxed{t^- = \frac{I^-}{I^- + I^+}}$

$\boxed{t^+ + t^- = 1}$

→ HCl $\boxed{t_{H^+} + t_{Cl^-} = 1}$ $\boxed{t_{H^+} >> t_{Cl^-}}$

NaCl $\boxed{t_{Na^+} + t_{Cl^-} = 1}$ $t_{H^+} >> t_{Na^+}$

Effect of temp on Transport Number

On increasing temp, Transport number of those ion increase which have transport no. less than 0.5 and transport no of those ion decreases which have transport no. more than 0.5

Ionic Mobility →

$$\boxed{\text{Ionic mobility} = \frac{\text{Velocity}}{\text{Pot. gradient}}}$$

Gradient = $\frac{d(\text{Quantity})}{dx}$

Pot gradient → $\frac{dV}{dx}$

$$u^+ = \frac{V^+}{\frac{dV}{dx}} \quad \text{if } \frac{dV}{dx} = 1 \quad \boxed{u^+ = V^+}$$

$$u^- = \frac{V^-}{\frac{dV}{dx}} \quad \text{if } \frac{dV}{dx} = 1 \quad \boxed{u^- = V^-}$$

and $i \propto \text{velocity} \propto u$

$$\boxed{t_{\oplus} = \frac{u^{\oplus}}{u^{\oplus} + u^{\ominus}} \qquad t^{\ominus} = \frac{u^{\ominus}}{u^{\oplus} + u^{\ominus}}}$$

#

$$\boxed{\lambda_+ \propto u_+}$$

$$\boxed{\lambda_+ = nFu_+}$$

$$\boxed{\lambda_- = nFu_-}$$

Sol
Ans

Q A dilute sol^n of KCl is placed b/w two Pt electrode 10 cm apart across which a pot difference of 10V was applied. Which is correct statement. Given that $\lambda_{\oplus} = 96.5\ S\,cm^2\,mol^{-1}$.

ⓐ Ionic mobility of K^+ is $10^{-3}\ cm^2\,sec^{-1}\,voltage^{-1}$.

ⓑ Speed of K^+ ion is 10^{-4} cm/sec

ⓒ distance travelled by K^+ ion in 5×10^{4} sec is 5cm.

ⓓ Pot gradient is $^1/_{10}$ volt/cm.

$x = 10cm, \quad V = 10V. \quad \lambda_+ = 96.5\ S\,cm^2/mol.$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$\boxed{n=1}$$

$$\lambda_+ = nF\mu_+$$

$$96.5 = 1 \times 96500\ \mu_+$$

$$= \frac{965 \times 10^{-1}}{96500} = 10^{-3}. \qquad \boxed{\mu_+ = 10^{-3}}$$

Relation between Transport no & Ionic mobility & molar conductance

$$t^+ = \frac{\mu^+}{\mu^+ + \mu^-} \qquad t^- = \frac{\mu^-}{\mu^+ + \mu^-}$$

Let us assume →

$$A_xB_y \longrightarrow \underbrace{x}_{x = n^{\oplus}}A^{y+} + \underbrace{y}_{y = n^{\ominus}}B^{x-}$$

$$\boxed{x\lambda_m^{\infty} A^{y+} = n^+ \lambda_m^{\infty} A^{y+}}$$

$$y\lambda_m^\infty B^{x-} = n^\ominus \lambda_m^\infty B^{x-}$$

where

$$\boxed{\begin{aligned} u^+ &= n^\oplus \lambda^\oplus \\ u^\ominus &= n^\ominus \lambda^\ominus \end{aligned}}$$

$$t^\oplus = \frac{n^\oplus \lambda^\ominus}{n^\oplus\lambda^\oplus + n^\ominus\lambda^\ominus} = \frac{n^\oplus \lambda^\oplus}{\lambda_{salt}} = \frac{n^\oplus \lambda^\oplus}{\lambda_{A_xB_y}}$$

for A_xB_y

\# $\boxed{t_{A^{y+}} = \frac{x\lambda_{A^{y+}}}{\lambda_{A_xB_y}}} \rightarrow \frac{\text{Cation}}{\text{salt}}$

Relation b/w Specific conductance & K_ω (ionic product of water)

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$k = \frac{[H^+][OH^-]}{[H_2O]} \Rightarrow [H^+][OH^-] = k[H_2O]$$

$$= \underbrace{k[55.55]}_{} \rightarrow K_\omega$$

$$[H^+][OH^-] = K_\omega$$

$$[H^+] = \sqrt{K_\omega} \ \& \ [OH^-] = \sqrt{K_\omega} \quad — ①$$

$$\& \ K_{H_2O} = K_{H^+} + K_{OH^-}$$

$$K_{H_2O} = \lambda_{H^\oplus}[H^+] + \lambda_{OH^\ominus}[OH^-]$$

$$= \lambda_{H^+}\sqrt{K_\omega} + \lambda_{OH^-}\sqrt{K_\omega}$$

$$K_{H_2O} = [\lambda_{H^+} + \lambda_{OH^-}]\sqrt{K_\omega}$$

$$\sqrt{K_\omega} = \frac{K_{H_2O}}{\lambda_{H^+} + \lambda_{OH^-}} \Rightarrow \boxed{K_\omega = \left[\frac{K_{H_2O}}{\lambda_{H^+} + \lambda_{OH^-}}\right]^2}$$

at 25°C

$[H_2O] = 55.5 \frac{mol}{litre}$

and $[H^+] = [OH^-] = 10^{-7}$

$K_\omega = 10^{-7} \times 10^{-7} = 10^{-14}$

T ↑ K_ω ↑

$$\boxed{\lambda^\oplus = \frac{k^\oplus}{c}}$$

$$\boxed{\lambda^\ominus = \frac{k^\ominus}{c}}$$

Q The conductivity of water at 298 kelvin is 0.554×10^{-7} $S cm^{-1}$. Calculate the degree of dissociation & ionic product of water (K_w)

Given that $\lambda_{H^+} = 349.85$ $S cm^2 mol^{-1}$

$\lambda_{OH^-} = 197.8$ $S cm^2 mol^{-1}$.

$K = 0.554 \times 10^{-7}$.

$$K_w = \left[\frac{K_{H_2O}}{\lambda_{H^+} + \lambda_{OH^-}}\right]^2 = \left[\frac{0.554 \times 10^{-7}}{349.85 + 197.8}\right]^2$$

$$\frac{(0.554 \times 10^{-7})^2 \, S^2 cm^{-2}}{(547.65)^2 \, S^2 cm^4 mol^{-2}}$$

$$\frac{(5.54 \times 10^{-8})^2}{} = \frac{~~30.6916~~}{}$$

$mol^2 cm^{-6}$

$$\frac{30.6916 \times 10^{-16}}{29.9920 \times 10^4}$$

$$\boxed{K_w = 1.02 \times 10^{-20}} \; mol^2/ml^2$$

$$\boxed{K_w = 1.02 \times 10^{-14} \, mol^2/litre^2}$$

$K_w = C\alpha^2$

$$\alpha^2 = \frac{1.02 \times 10^{-14}}{55.55} = 0.018 \times 10^{-14}$$

$\alpha^2 = 1.8 \times 10^{-16}$

$$\boxed{\alpha = 1.34 \times 10^{-8}}$$

$$\boxed{K_w = c^2\alpha^2}$$

$\alpha^2 = \frac{K_w}{c^2} \Rightarrow \alpha = \frac{(1 \times 10^{-14})^{1/2}}{c}$ $\qquad \alpha = \frac{10^{-7}}{55.55}$

~~1400×10^{-7}~~ $\qquad \alpha = \frac{10000}{5555} \times 10^{-9}$

$$\boxed{\alpha = 1.799 \times 10^{-9}}$$

Solubility of sparingly soluble Salt :-

Soluble → Hydration energy > lattice energy

Insoluble → H.E < L.E

Sparingly soluble → HE ≃ LE

[S ≤ 0.001M] → very solubility
AgCl, AgBr, $BaSO_4$

We know that,

$$\lambda_m = \frac{K \times 1000}{M}$$

$$\lambda_m^{\infty} = \frac{K \times 1000}{S}$$

for sparingly soluble salt →

$V \sim V^{\infty}$ & $\lambda_m \sim \lambda_m^{\infty}$

then $\boxed{M = \text{solubility}}$

$\boxed{S = \frac{K \times 1000}{\lambda_m^{\infty}}}$ — ①

S
- mol/litre → Molar
- gm/lt → M×MW
- Eq/lt → Normality

We know that →

$$\boxed{K_{AgCl} = K_{AgCl\,(sat)} - K_{water}}$$

$$\boxed{K_{AgCl\,(sat)} = K_{AgCl} + K_{water}}$$

Put in ①

$$\# \quad \boxed{S = \frac{(\kappa_{AgCl_{sat}} - \kappa_{water}) \times 1000}{\lambda^{\infty}_{m(AgCl)}}}$$

$$\# \quad \boxed{S = \frac{(\kappa_{AgCl} + \kappa_{\omega}) \times 1000}{\lambda^{\infty}_{m}(AgCl)_{sat}}}$$

Q At 25°C, the specific conductance of saturated sol^n AgCl is 2.68×10^{-4} $S m^{-1}$ and that of water is 0.86×10^{-4} $S m^{-1}$. If the molar conductance at infinite dilution of $AgNO_3$, HCl, HNO_3 are 133×10^{-4} $S m^2 mol^{-1}$, 426×10^{-4} $S m^2 mol^{-1}$ & 421×10^{-4}.

$$\frac{\kappa_{AgCl_{sat}} - \kappa_{water} \times}{\lambda^{\infty}_{m} AgCl} \quad \frac{\cancel{S} m^{-1}}{\cancel{S} m^2 mol^{-1}}$$

$$\frac{(2.68 - 0.86) \times \cancel{10^{-4}} \times}{138 \times \cancel{10^{-4}} \times}$$

$$= \frac{1.82 \times}{138 \times} \quad \frac{mol}{litre}$$

$$\boxed{\text{~~13.188 mol/litre~~}}$$

16
2.68
0.86
1.82

133
426
559
421
138

$$\frac{1.82 \times 10^{-4} \times 1000}{138 \times \cancel{10^{-4}}}$$

$$\frac{1820}{138}$$

0.0131

In g/l → 0.0131×143.5

$= 1.89$

Q Equivalent conductivity of $BaCl_2$, H_2SO_4 & HCl are x_1, x_2, x_3 at infinite dilution. If the conductivity of saturated sol^n of $BaSO_4$ is x. Find K_{sp} of $BaSO_4$.

$BaCl_2 + H_2SO_4 - 2HCl$

$BaCl_2 \rightarrow x_1$, $H_2SO_4 \rightarrow x_2$, $HCl \rightarrow x_3$

$$\lambda^{\infty}_{BaSO_4} = \lambda^{\infty}_{BaCl_2} + \lambda^{\infty}_{H_2SO_4} - 2\lambda^{\infty}_{HCl}$$

$$\lambda^{\infty}_{BaSO_4} = x_1 + x_2 - 2x_3$$

$$S = \frac{K}{\lambda^{\infty}_m} = \frac{x}{x_1 + x_2 - 2x_3}$$

For Ba

Factors Affecting Conductance :-

① **Temperature** → On increasing temp conductance inc because ionic mobility of an ion increase

② **Viscosity** → On viscocity inc , ionic mobility decrease and conductance ↓ is.

③ **Nature of electrolyte** → In case of strong electrolyte, conductance is high and in case of weak electrolyte conductance is low.

④ **Dilution** → On increase dilution , conductance of [illegible] ↑ while ~~condu~~ specific conductance ↓

⑤ **Nature of curre** In DC current, conductance obtain is high compare to AC.

⑥ **Transport Number** → As TN ↑ conductance ↑

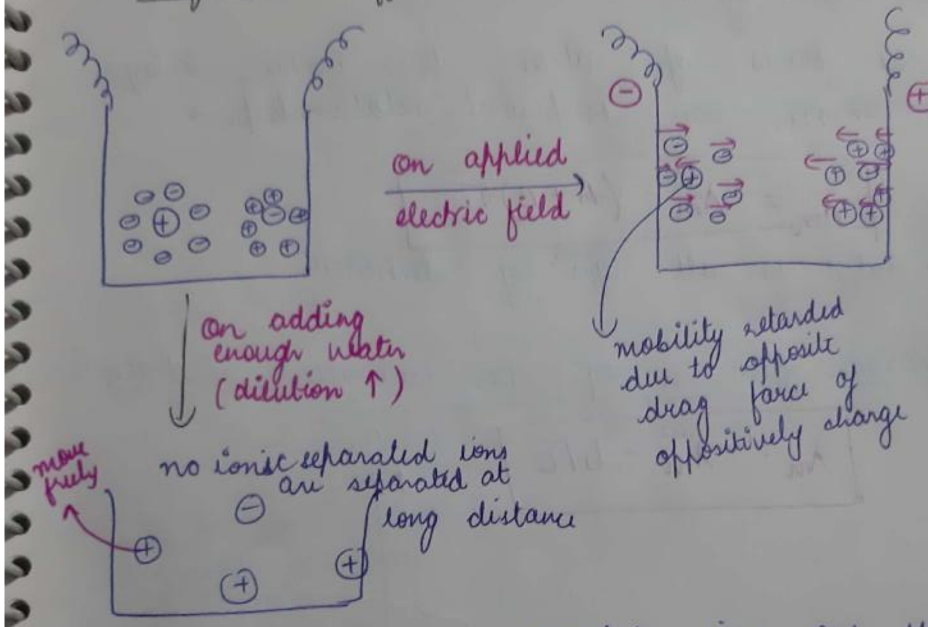
⑦ **Ionic mobility** → Ionic mobility ↑ conductance ↑

Debye Huckel Theory for strong electrolyte.

In case of strong electrolyte, two effect arises →

① Asymmetric effect
② Electrophoretic effect / Relaxation effect.

① Asymmetric Effect →

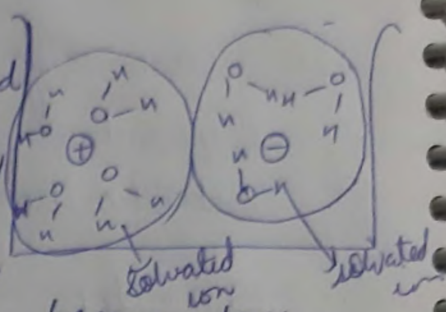


In case of strong electrolytes ions are surrounded by the oppositevely charge ions forming a ionic sphere. On applying electric field, ions and their environment moves in opposite direction and they provide a drag force which minimise the ionic mobility of ion-. This is called **Asymmetric effect**.

On inc. dilution ions are separated and due to this drag force become negligible and ionic mobility ↑.

② Electrophoretic / Relavation effect →

Due to the solvation, movement of ions opposed by viscous force or drug force applied by solvent molecule. They slow down the motion of ions this is called Relaxation/ electrophoretic



On increasing dilution, viscocity ~~of~~ of ion ↓ and ions became free.

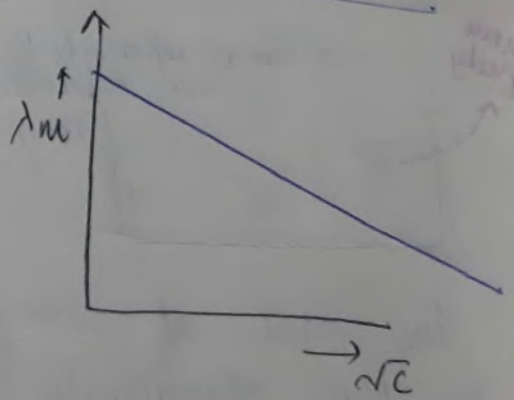
On the basis of above two factor, Debye-Huckel - Onsagar an empirical relationship →

$$\boxed{\lambda_m = \lambda_m^{\infty} - (A+B)\sqrt{C}}$$

This is valid for all type of electrolyte.

And Onsagar give a eqⁿ for univalent electrolyte →

$$\boxed{\lambda_m = \lambda_m^{\infty} - b\sqrt{C}}$$



Some other effect also arises →

① Wein effect → As E.F ↑ conductance ↑.

② Stoke's effect → As viscocity ↑ conductance ↓

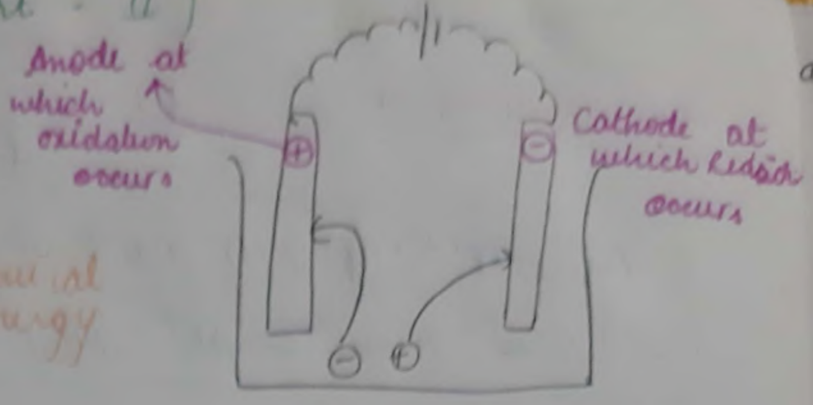
③ Falkin effect → As frequency of current ↑ conductance ↑.

Electrolysis → [Part - II]

Eletric energy $\xrightarrow[\text{Redox process}]{\text{Non-spontaneous}}$ Chemical energy

$\Delta G = +ve$

$E_{cell} = -ve$



Electrolytic cell

Decomposition of any electrolyte by passing electric current called electrolysis and container in which this process proceed called Electrolytic cell.

Study of electrolysis

↓ Qualitative [if in electrolytic cell one type of cation & anion present. Then cation goes to cathode & anion goes to anode]

↓ Quantitative

Qualitative
↓
which type of ion go at particular electrode } → when more than one type of ions present
↓

Tool → Discharge Potential

Potential required to deposit an ion from solⁿ to electrode

$$\boxed{\text{discharge potential} \propto \frac{1}{\text{discharge tendency}}}$$

Discharge Potential →

For cations →

$$\boxed{dt \propto \frac{1}{dP} \propto E^\circ_{R.P.}}$$

$Au^{+3} > Pt^{+2} > Ag^{+} > Hg^{+2} > Cu^{2+} > H^{\oplus} > Pb^{+2} > Sn^{2+} > Ni^{2+} > Co^{3+} > Cd^{2+} > Fe^{+3} >$
$Cr^{+3} > Zn^{2+} > Mn^{2+} > Al^{+3} > Mg^{+2} > Na^{+} > Ca > Ba^{+} > K^{+} > Li^{+}$

For anions →

$F^{\ominus} < SO_4^{-2} < NO_3^{-} < OH^{-} < Cl^{-} < Br^{-} < I^{-}$

It also depend on nature of electrode and concⁿ.

At high concⁿ of H_2SO_4 → dt $\boxed{SO_4^{2-} > OH^{-}}$

For dilute solution → dt $\boxed{OH^{-} > Cl^{-}}$

only two
Pt, graphite
Inert
They provide only path not participate in reacⁿ

electrode

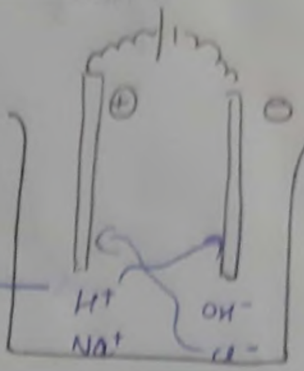
Active
They participate in reacⁿ

Electrolysis of Aq NaCl using Pt electrode →

At cathode →

Reduction

$$\boxed{H^+ + e^- \longrightarrow \frac{1}{2} H_2}$$



left → NaOH

pH of electrode ↑

At anode Oxidation

$$\boxed{Cl^- \longrightarrow 1/2\, Cl_2 + e^-}$$

At cation →

$H^+ > Na^+$

At anion →

$Cl^- > OH^-$

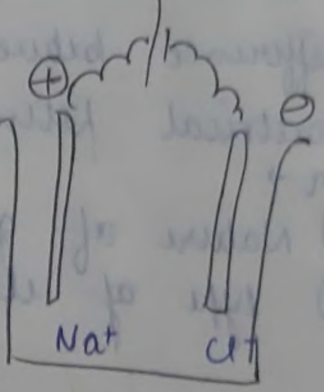
Electrolysis of Molten NaCl →

At cathode →

$$Na^+ + e^- \longrightarrow Na$$

At anode →

$$Cl^- \longrightarrow 1/2\, Cl_2 + e^-$$



Q At 291 K, the ionic velocity of Ag^+ ion is 0.00057 cm^{-1} and that of NO_3^- ion is 0.00063 cm^{-1}. What is the values of $\lambda^\infty_{AgNO_3}$ at 290 K. If the Specific conductivity of 0.1 N is 0.0097 $\Omega^{-1} cm^{-1}$. Find degree of dissociation at this dilution

$$\lambda_{AgNO_3} = \cancel{\frac{K \times 10^3}{N}} \qquad \boxed{\lambda^\infty = \mu \times n \times F}$$

$$\lambda^\infty_{Ag^+} = 0.00057 \times 1 \times 96500 = 55.005$$

$$\lambda^\infty_{Cl^-} = 0.00063 \times 1 \times 96500 = 60.795$$

$$\lambda^\infty_{AgCl} = 55.005 + 60.795$$

$$= 115.8000\ S\,cm^2\,mol^{-1}$$

$$\lambda_{AgNO_3} = \frac{\kappa \times 1000}{N \cdot m} = \frac{0.000947 \times 1000 \times 10}{0.1 \times 10^6}$$

$$= 9.47$$

$$\boxed{\alpha = \frac{\lambda}{\lambda^\infty}} = \frac{9.47}{115.800} = 0.817$$

$$\boxed{\alpha = 0.817}$$

→ Over - Voltage →

Difference between the actually applied potential and theoretrical potential called over voltage. It is depend on→

① Nature of gas evolved
② type of electrode

$$\boxed{V_{\text{over voltage}} = V_{\text{actual applied voltage}} - V_{\text{theoretrically applied voltage}}}$$

for eg →

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad E^\circ_{\text{oxidation}} = -1.36 \text{ volt}$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad E^\circ_{\text{oxidation}} = -1.23 \text{ volt}$$

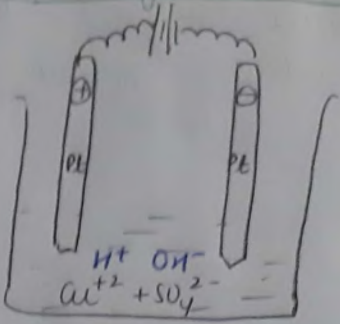
or (it should takes place)

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

At anode, acc. to thermodynamics oxidation of water should takes place instead of Cl^- ion but the rate of reacⁿ of water is very slow & to make it fast some extra potential difference is applied during the electrolysis of aqueous NaCl. At this extra or greater potential [over voltage] the rate of oxidation of Cl^- dominates over the oxidation of H_2O.

Q Write the product of aqueous NaCl in presence of active mercury electrode.

Electrolysis of aqueous $CuSO_4$ using Platinum electro



discharge tendency of cation →

$\boxed{Cu^{+2} > H^+}$

discharge tendency of anion →

$\boxed{SO_4^{--} < OH^-}$

At anode

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

or

$$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

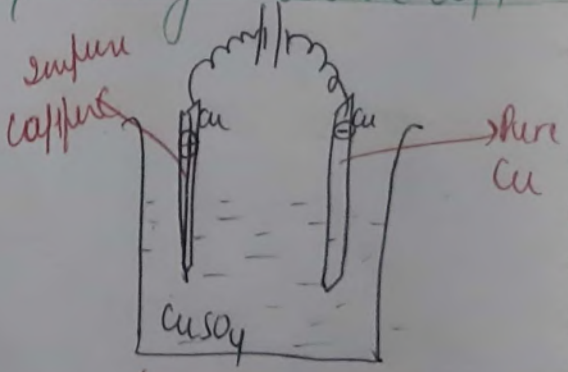
At cathode

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

$\boxed{\text{Left} = H_2SO_4}$

pH (decrease)

Electrolysis of aqueous $CuSO_4$ using active Copper electrode



When Cu electrode used →

At anode → [slim] ()

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

$\boxed{E^\circ_{oxi} = -0.34\ \text{Volt}}$

Anode Mud → World's expensive mud

At cathode [fat ]

Reduction → $Cu^{2+} + 2e^- \rightarrow Cu$

$\boxed{E^\circ_{Red} = +0.34\ \text{Volt}}$

(98% Pure Cu contains 2%. gold & Silver is present

Electrolysis of H_2SO_4 →

dt = $\boxed{OH^- > SO_4^-}$

dil H_2SO_4

cation → H^+ $C_{OH^-} >> C_{SO_4^{2-}}$

Case I → If H_2SO_4 is dilute.

At cathode →
↳ always reduction

$2H^+ + 2e^- \longrightarrow H_2$

At ~~cathode~~ anode →
↳ always oxidation

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

Case II → If H_2SO_4 is concentrate →

At cathode →

$2H^+ + 2e^- \longrightarrow H_2$.

At anode →

d.t. $SO_4^{--} > OH^-$

$2SO_4^{--} \longrightarrow S_2O_8^{--} + 2e^-$

$\downarrow H_2O$

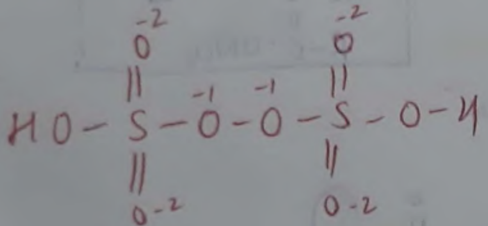
$H_2S_2O_8$ Peroxy sulphuric acid

$\downarrow H_2O$

$\boxed{H_2O_2 + H_2SO_4}$

Imp

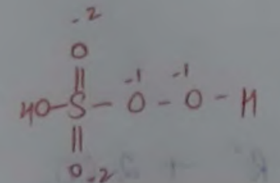
2.2 $\frac{400}{18}$



$HO-\overset{\overset{-2}{O}}{\underset{\underset{O^{-2}}{\|}}{\overset{\|}{S}}}-\overset{-1}{O}-\overset{-1}{O}-\overset{\overset{-2}{O}}{\underset{\underset{O^{-2}}{\|}}{\overset{\|}{S}}}-O-H$

$\frac{\text{Theoretrical } 0.5 - \text{group no}}{2} = n$ = Peroxy linkage

= fraction + 0.5 ⇒ Peroxy linkage

→  → H_2SO_5 → Caros acid

$HO-\overset{\overset{-2}{O}}{\underset{\underset{O^{-2}}{\|}}{\overset{\|}{S}}}-\overset{-1}{O}-\overset{-1}{O}-H$

$\% \, SO_3 = \left(\frac{\% \text{ oleum} - 100}{18}\right) \times 80$

→ 105% Oleum, $\frac{5}{18} \times 80 = 22.2\%$.

→ 109% Oleum, $\frac{9}{18} \times 100 = 40\%$.

Electrolysis of $CaSO_4$ using inert electrode

Here, no electrolysis of $CaSO_4$ in aqueous medium.
Molarity & Normality increase.

$Ca^{+2} < H^+$ $SO_4^{-2} < OH^-$

At cathode

$H^+ + e^- \rightarrow H$

At anode →

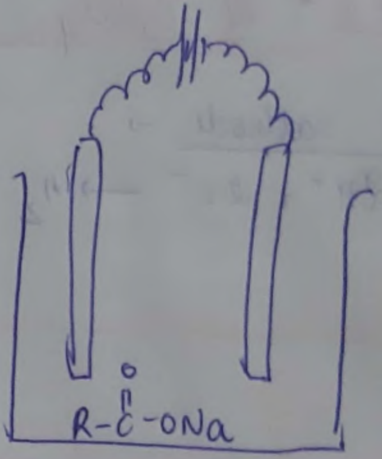
$4OH^- \longrightarrow 2H_2O + 4e^- + O_2$.

→ Kolbe Electrolysis →

At cathode →

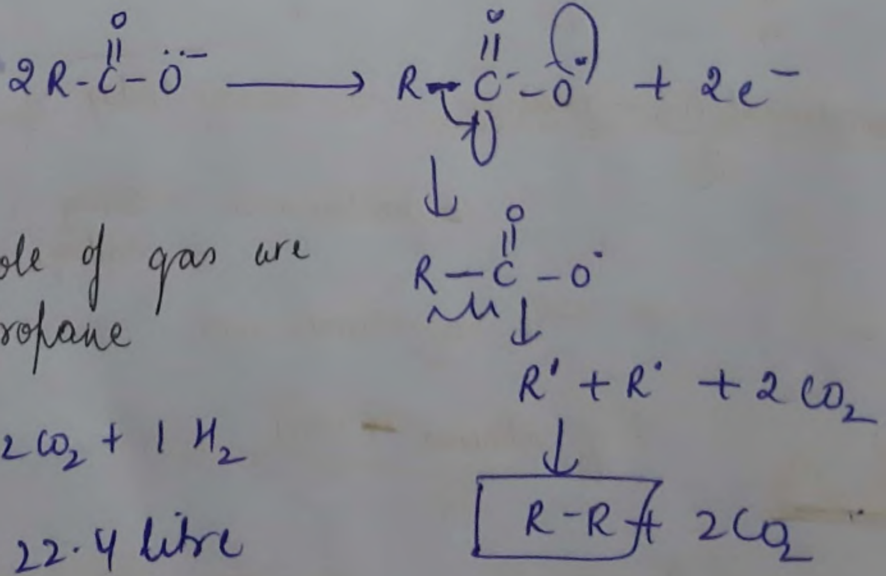
dt $Na^{\oplus} < H^{\oplus}$

$2H^+ + 2e^- \longrightarrow H_2\uparrow$



At anode → **DT** $R-\overset{O}{\overset{\|}{C}}-O^- > OH^-$

Oxidation →



$$2R-\overset{O}{\overset{\|}{C}}-\ddot{O}^{-} \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\cdot} + 2e^-$$

$$\downarrow$$

$$R-\overset{O}{\overset{\|}{C}}-O^{\cdot}$$

$$\downarrow$$

$$R^{\cdot} + R^{\cdot} + 2CO_2$$

$$\downarrow$$

$$\boxed{R-R} + 2CO_2$$

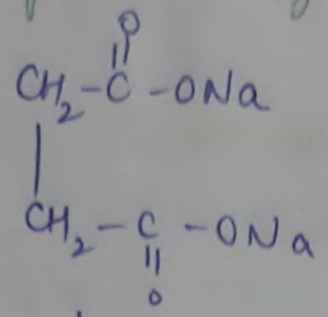
Q How many mole of gas are formed when R=Propane

3 mole → $2CO_2 + 1H_2$

Volume at STP 3 × 22.4 litre

$\boxed{67.2 \text{ litre}}$

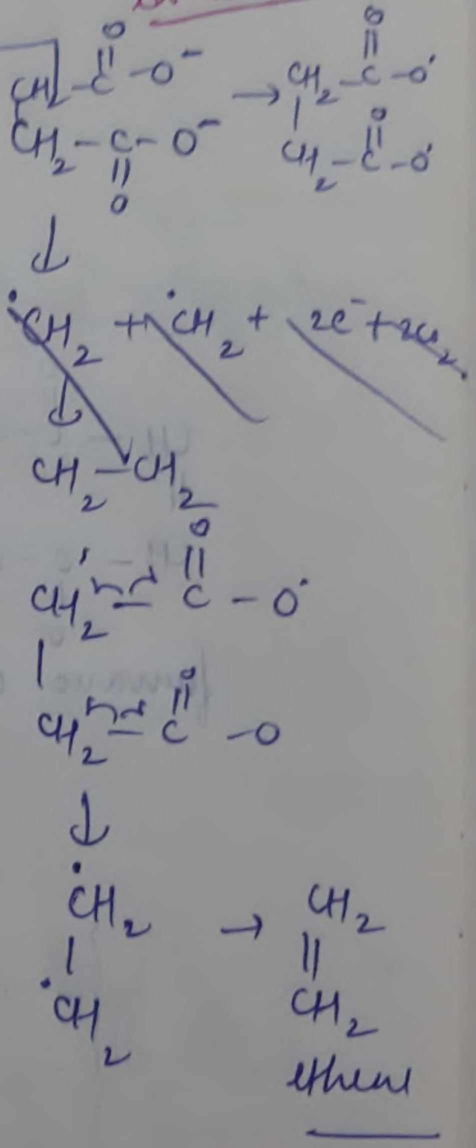
Electrolysis of Saturated dicarboxylate →



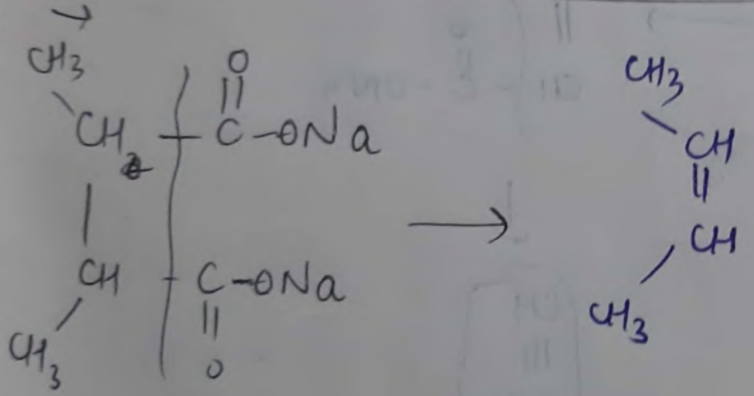
At cathode

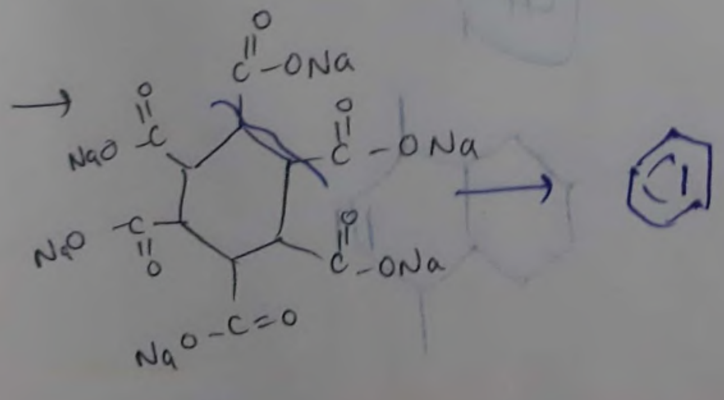
$2H^+ + 2e^- \rightarrow H_2\uparrow$

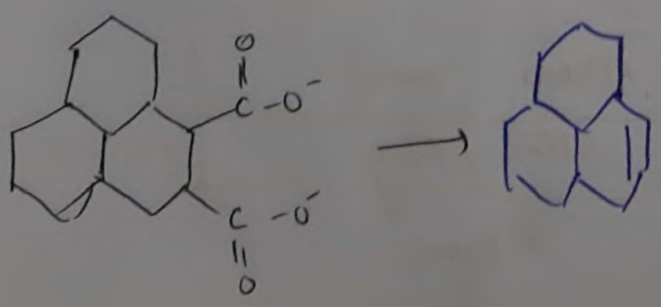
At anode



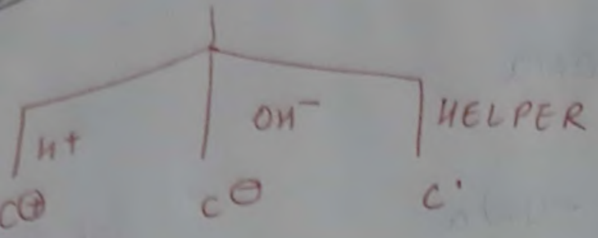
$+ 2CO_2 + 2e^-$







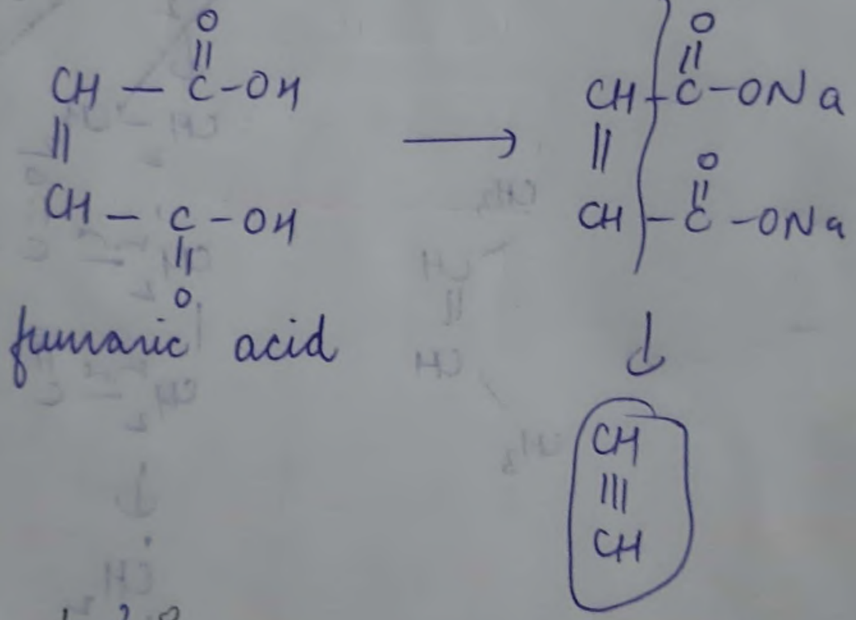
Imp for Reaction Mechanism



Heat > 500°C
Electricity
Light
Peroxide
E
Radical

→ free-Radical
↓
intermediate

Electrolysis of unsaturated Dicarboxylate →



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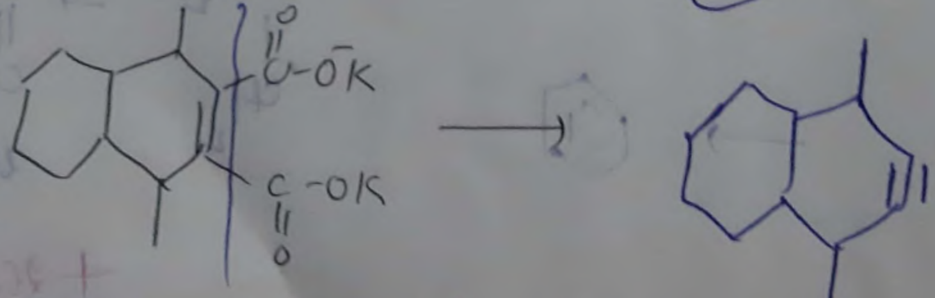
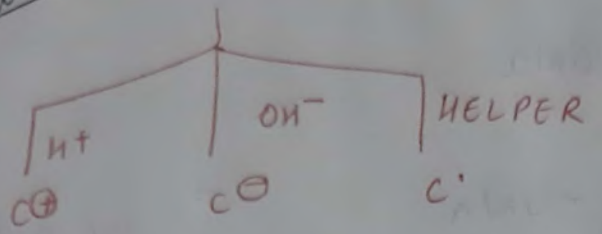


Hydrocarbon	Product of electrolysis
Monocarboxylate	Alkane (even)
Saturated dicarboxylate	Alkene / Ring
Unsaturated dicarboxy	Alkyne

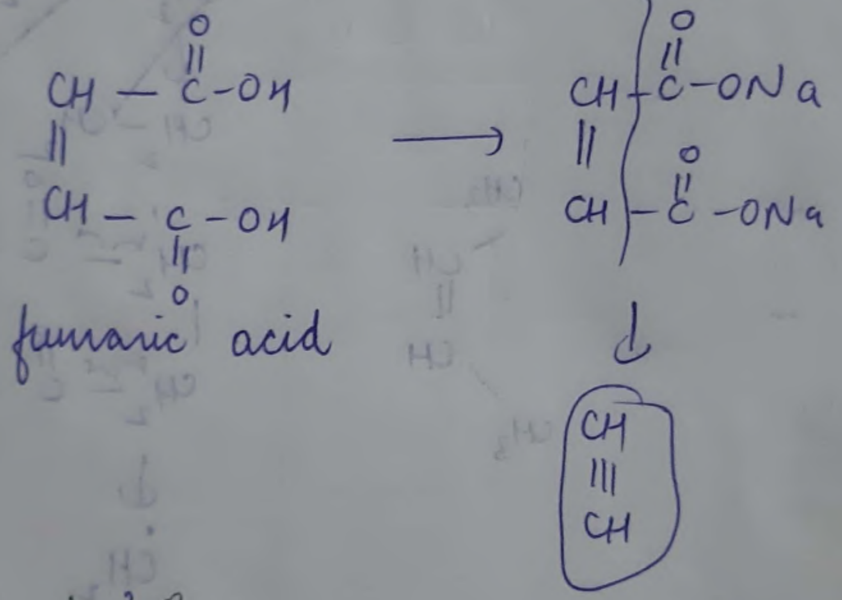
Imp for Reaction Mechanism



Heat > 500°C
Electricity
Light
Peroxide
E
Radical

→ free-Radical
↓
intermediate

Electrolysis of unsaturated Dicarboxylate →



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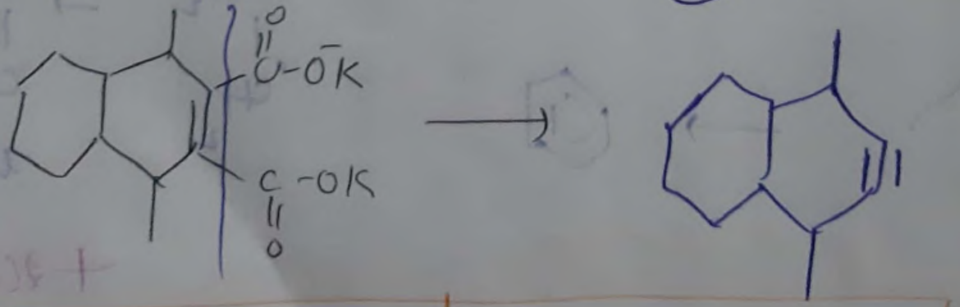


Hydrocarbon	Product of electrolysis
Monocarboxylate	Alkane (even)
Saturated dicarboxylate	Alkene / Ring
Unsaturated dicarboxylate	Alkyne

Hydrocarbon P500

Faraday Law of Electrolysis :-

Faraday First Law :- Acc. to Faraday first law, amount of material deposited or liberated at a particular electrode is dirctly proptional to charge supply in electrolytic cell.

$$w \propto q \qquad \left[i = \frac{q}{t},\ q = it \right]$$

$$w \propto it$$

$$\boxed{w = zit} \text{ — ①}$$

where, z is called electrochemical equivalence.

w = mass deposited or liberated

i = current

t = time.

If $i = 1$ amp, $t = 1$ sec, $q = 1C$ then $\boxed{w = z}$

* Charge on 1 mole e^- $= 6.022 \times 10^{23} \times (1.6 \times 10^{-19} C)$

$= 96450 \simeq 96500\,C$

$$\Downarrow$$

$$\boxed{1F = 96500\,C}$$

$Ag^+ + 1e^- \longrightarrow Ag$, 1F give 1 gm eq of Ag — Equivalent mass = 1 g equ

$Cu^{+2} + 2e^- \rightarrow Cu$, 1F give 1 gm Eq of Cu

$Al^{+3} + 3e^- \rightarrow Al$, 1F give 1 gm Eq of Al

~~96500 C g~~

$$96500\,C = E\ gm$$

$$\boxed{1C = \frac{E}{96500}}$$

$\frac{Cu}{2}$

Z is the mass deposited by applying 1 c charge →

$$Z = w = \frac{E}{96500}$$

from ①

$$W = \frac{E}{96500} \times i \cdot t$$

$$W = \frac{E}{F} \times it$$

$$\boxed{E = \frac{Mw}{n}}$$

$$\boxed{W = \frac{Mw \times it}{nF}} \text{ — ②}$$

$$\boxed{d \times V = \frac{Mw \times it}{nF}}$$

where $d = \frac{M}{V}$ or $\frac{W}{V}$

$$\boxed{W = dV}$$

$$\boxed{d \times a \times l = \frac{Mw \times it}{nF}}$$

l → length

a → area

from 2

$$\frac{W}{Mw} = \frac{i \times t}{n \times F}$$

we have

$\frac{W}{Mw}$ = mole = N

$$\boxed{N = \frac{it}{nF}}$$

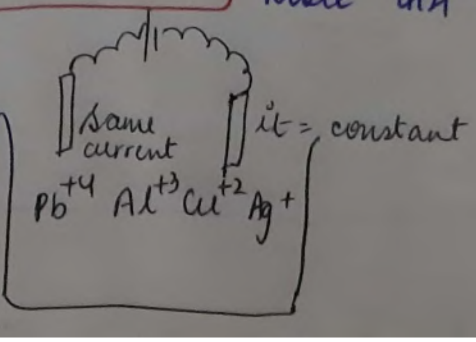
At constant current and time →

$$\boxed{N \propto \frac{1}{n\text{ factor}}}$$

जिसका n factor ज्यादा होगा उसके Mole कम मिलेंगे

Q Order of mole →

$$\boxed{Ag^+ > Cu^{2+} > Al^{+3} > Pb^{+4}}$$



We have

$$\boxed{\text{Mole} = N = \frac{W}{MW} = \frac{V}{22.4} = \frac{\text{No. of particle}}{6.022 \times 10^{23}}}$$

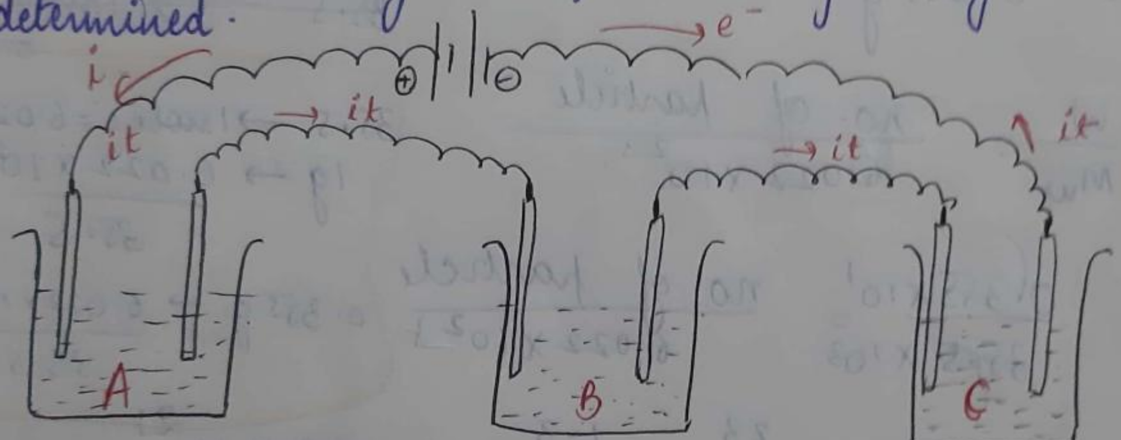
then

$$\boxed{N = \frac{it}{nF} = \frac{V \text{ at STP}}{22.4}}$$

Faraday Second Law of electrolysis :-

Acc. to Faraday second law. if we supply same amount of charge in different electrolytic cell connecting by series order to each other then gram equivalent (W/E) of substances in all connecting electrolytic cell are equal.

From Faraday law, values of Avagadro no (N_A) is determined.



We know that, $W = \frac{E}{F} it$

At constant it → $W \propto E$

$\Rightarrow \frac{W}{E} = \text{constant}$

$$\boxed{\frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C} = \text{constant}}$$

Q The total charge supplied in an electrolysis process for depositing Cu from $CuSO_4$ solⁿ is 1 Faraday. It will result in how much cathodic deposition of Cu.

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

[Mass of Cu = 63.5]

$$2F \longrightarrow 63.5$$

$$1F \longrightarrow \frac{63.5}{2} = \boxed{31.75\ gm}$$

Q How many no. of e^- are lost during the electrolysis of 0.355g of Cl^-.

$W =$ 0.355 g

$$Cl_2^- \longrightarrow \frac{1}{2}Cl_2 + e^-$$

~~35.5 → 1mole e^- = 6.022×10~~

$$35.5 \rightarrow 1mole\ e^- = 6.022\times10^{23}$$

$$1g \rightarrow \frac{6.022\times10^{23}}{35.5}$$

$$0.355g \rightarrow \frac{6.022\times10^{23}\times0.355}{35.5}$$

$$\frac{W}{M_W} = \frac{\text{no. of particle}}{6.022\times10^{23}}$$

$$\frac{\cancel{0.355}\times10^{1}}{\cancel{35.5}\times10^{3}} = \frac{\text{no. of particle}}{6.022\times10^{23}}$$

$$6.022\times10^{23}\times10^{1-3} = 6.022\times10^{21}$$

$$\boxed{\text{No. of particle} = \text{No. of } e^-}$$

$$\boxed{\text{No. of } e^- = 6.022\times10^{21}}$$

ω

$\boxed{\text{Current efficiency } (\eta) = \frac{\text{Output}}{\text{Input}} \times 100}$ in terms of mass $= \frac{W_{output}}{W_{input}} \times 100$

$$\boxed{\text{Fuel efficiency } (\eta) = \frac{\Delta G \times 100}{\Delta H}}$$

ΔG → useful energy
ΔH → total energy

Ques Electrolysis of solⁿ of $CuSO_4$ for 60 minutes using 10 A current result in 11.2 g of Cu metal on cathode. Thus give the efficiency of the electrolytic cell.

$$W = \frac{Mw \times it}{nF}$$

$$\cancel{i = \frac{W \times n \times F}{Mw \times t}}$$

$$W = \frac{\cancel{63.5} \times \cancel{10} \times \overset{30}{\cancel{60}} \times 60}{\cancel{2} \times 96500}$$

$$= \frac{635 \times 30 \times 60}{96500}$$

$$= \frac{1905 \times 10^{-1} \times 60}{965}$$

$$\frac{11430}{965}$$

$$\underline{W = 11.8445\ g}$$

% efficiency $= \frac{11.2000 \times 100}{11.8445} = \frac{112000}{118445} \times 100 = 0.9455 \times 100$

$$\boxed{\%\ \text{efficiency} = 94.56}$$

Q How many gm of Cu will be deposited on passing 2 amp current for 30 minutes in aqueous $CuSO_4$ and what will be weight of O_2 produced at anode.

Ans <u>At cathode</u> → $Cu^{+2} + 2e^- \to Cu$

<u>At anode</u> $2OH^- \longrightarrow H_2O + 2e^- + \frac{1}{2}O_2$

I = 2amp, t = 30min

$$W_{Cu} = \frac{Mw \times it}{nF} \Rightarrow \frac{63.5 \times \cancel{2} \times 3\cancel{0} \times 6\cancel{0}}{\cancel{2} \times 965\cancel{00}}$$

$$= \frac{1143}{965}$$

$$\boxed{W_{Cu} = 1.1845}$$

$$W_{O_2} = \frac{16 \times \cancel{2} \times 3\cancel{0} \times 6\cancel{0}}{\cancel{2} \times 965\cancel{00}} = \frac{8 \times 18}{965}$$

$$\boxed{W_{O_2} = 0.298\,g}$$

Q Silver is electro deposited on a vessel of total surface area $800cm^2$ by passing a current of 0.2 Ampere for 3 hours. Calculate the thickness of silver deposited given that density of silver is 9.67 gm/cm³

$A = 800cm^2$, $I = 0.2\,A$, $t = 3$ hours $= 3 \times 3600$ sec

$l = ?$ $d = 9.67\ gm/cm^3$.

$$l = \frac{Mw \times i \times t}{n \times F \times d \times a} = \frac{108 \times 0.2 \times 3 \times 36\cancel{00}}{1 \times 965\cancel{00} \times 9.67 \times 8\cancel{00}}$$

$$= \frac{108 \times 2 \times 3 \times 36}{965 \times 967 \times 8 \times 10}$$

$$\cancel{\frac{648 \times 10^{-6}}{7465240}} = \cancel{\boxed{8.68 \times 10^{-6}}}$$

$$= \frac{23328}{7465.240} \times 10^{-4} = \boxed{3.125 \times 10^{-4} \text{ cm}}$$

Q In an aqueous sol^n of silver nitrate ($AgNO_3$) a variable amount is passed for 4 sec. calculate amount of Ag deposited

when $i = 2t$ while $(0 \leq t \leq 2)$

$i = 0.2t$ while $(2 \leq t \leq 4)$

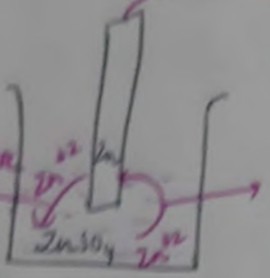
$i =$ ______ $(t > 4 \text{ sec})$

Part - 3 Electrode

When any metallic rod dipped into its electrolytic sol^n or any other electrolytic sol^n, then a system form called half cell and metal rod in this half cell called electrode.

→ anode → Oxidation

→ cathode → Reduction



Sol^n pressure
↓
electrolytic
↓
delectration
↓
oxidation

osmotic pressure
↓
electration
↓
Reduction

As anode → $Zn \longrightarrow Zn^{+2} + 2e^-$

$\boxed{S.P > O.P}$

$E^\circ_{Zn/Zn^{+2}} = +0.76$ Volt

As cathode → $Zn^{+2} + 2e^- \longrightarrow Zn$

$\boxed{O.P. > S.P}$

$E^\circ_{Zn/Zn^{+2}} = -0.76$ Volt

Reduction

Case I → $\boxed{S.P. > O.P}$

L O A N

Left oxidation anode negative

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

Case II^n → $\boxed{O.P > S.P}$

$Zn^{+2} + 2e^- \longrightarrow Zn(s)$ → Reduction

-ve sign indicate reac^n is not feasible & reverse reac^n is feasible.
+ve sign indicate reac^n is feasible

Anode → Oxidation
Cathode → Reduction

Electrode Potential →

Potential develop between the contact of metallic rod (electrode) and electrolytic sol^n called electrode Potential.

Electrode Potential is an ~~intrinsic~~ intensive property and it is non-additive in nature.

If in half cell, electrode is very pure and electrolytic sol^n is 1 molar and temperature ~~of~~ is 298 Kelvin then such electrode called Standard electrode and electrode potential developed b/w electrode & electrolyte is called Standard electrode potential.

Standard electrode are ~~standardly~~ experimentally determined with the help of ~~standard electrode~~ refrence electrode.

Important point regarding electrode potential →

① Electrode potential of any single electrode can not be determined independently.

② Electrode potential is an intensive property and it is not additive in nature. but ΔG is useful energy and all energy(ΔG) are extensive quantity and they are additive in nature.

$$E^\circ_{cell} = \frac{W^\circ}{nF}$$

Workdone = -ve

$\underline{\Delta G = -ve}$ $q_0 = nFC$

$$\boxed{E^\circ_{cell} = -\frac{\Delta G^\circ}{nF}}$$

Work done is taken as -ve bcoz work is done by the system.

$$\boxed{-\Delta G^\circ = nFE^\circ_{cell}} \quad \text{or} \quad \boxed{\Delta G^\circ = -nFE^\circ_{cell}}$$

Thermodynamically & Mathematically correct

Thermodynamically wrong & Mathematically correct

for spontaneous ΔG should be negative
& E° should be positive

*

$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{+2} + 2e^-, \quad E^\circ_{Fe/Fe^{2+}} = E_1 \text{ volt} \quad \boxed{\Delta G_1 = -2FE_1}$$

$$\mathrm{Fe}^{+2} \rightleftharpoons \mathrm{Fe}^{+3} + 1e^- \quad E^\circ_{Fe^{2+}/Fe^{3+}} = E_2 \text{ volt} \quad \boxed{\Delta G_2 = -1FE_2}$$

$$\underline{\mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{+3} + 3e^-} \quad E^\circ_{Fe/Fe^{3+}} = E_3 \text{ volt} \quad \boxed{\Delta G_3 = -3FE_3}$$

We know that,

$$\Delta G_3 = \Delta G_2 + \Delta G_1$$

$$-3FE_3 = -2FE_2 - 1FE_1$$

$$3E_3 = 2E_1 + E_2$$

$$\boxed{E_3 = \frac{2E_1 + E_2}{3}}$$

Trick याद करना है

\#

$$\boxed{E_3 = \frac{n_1E_1 + n_2E_2}{n_3}}$$

*

$$Cu^{+2} \xrightarrow[n_2=1]{E_2=x} Cu^{+} \xrightarrow[n_1=1]{E_1=y^0} Cu$$

$E_3 = ?$
$n_3 = 2$

$$E_3 = \frac{n_1E_1 + n_2E_2}{n_3} \Rightarrow \frac{y+x}{2}$$

Ans $\boxed{E_3 = \frac{x+y}{2}}$

Q The Reduction potential for Cu in acid solⁿ is →

$$Cu^{2+} \xrightarrow[n_1=1]{0.15V} Cu^{+} \xrightarrow[n_2=1]{0.50\,Volt} Cu$$

$E^\circ = x$ Volt, $n_3 = 2$

Calculate x, Does Cu^+ disproportionate in Solⁿ.

$Cu^{2+} + e^- \longrightarrow Cu^{+}$, $E_1^\circ = 0.15$ Volt, ΔG_1

$Cu^{+} + e^- \longrightarrow Cu$, $E_2^\circ = 0.5$ Volt, ΔG_2

$$E^\circ = \frac{n_1E_1 + n_2E_2}{n_3} \Rightarrow x = \frac{1\times 0.15 + 1\times 0.50}{2} = \frac{0.15+0.50}{2}$$

$$x = \frac{0.65}{2} = 0.325 \text{ volt}$$

$\boxed{x = 0.325 \text{ volt}}$

disproportion reaⁿ →

$Cu^+ \longrightarrow Cu^{+2} + e^-$ $E_{OP} = -0.15$

$Cu^+ + e^- \longrightarrow Cu$ $E_{RP} = 0.50$

red.

$2Cu^+ \longrightarrow Cu^{+2} + Cu^0$ $E^\circ = 0.50 - 0.15 = 0.35$ volt

oxidation

Positive ↓ Reaⁿ ↓ feasible

Q Cu^{2+} is more stable than Cu^{+}. Why ???

Because it has very high hydration energy and low Reduction potential.

$\boxed{Cu/Cu^{2+} \rightarrow 0.34 \text{ volt}}$ $\boxed{Cu/Cu^{+} \rightarrow 0.54 \text{ volt}}$

Q $Cu^{+} + e^{-} \longrightarrow Cu$, $\underset{n=1}{E_1^\circ} = x_1$ volt

$Cu^{+2} + 2e^{-} \longrightarrow Cu$, $E_2^\circ = x_2$ volt

for $Cu^{+2} + e^{-} \rightarrow \overset{n_2=2}{\underset{n_3=1}{Cu^{+}}}$, E°, will →

ⓐ $x_1 - 2x_2$ ⓑ $x_1 + 2x_2$ ⓒ $x_1 - x_2$ [✓ ⓓ $2x_2 - x_1$]

~~$E^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3} = x_1 + 2x_2$~~

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

$$\underbrace{Cu^{+2} + e^{-} \longrightarrow Cu^{+} + e^{-} \longrightarrow Cu}_{E_2^\circ = x_2 \text{ volt}}$$

$$Cu \longrightarrow Cu^{+} + e^{-} \quad = -x_1$$
$$Cu^{+2} + 2e^{-} \longrightarrow Cu \quad = x_2$$
$$Cu^{+2} + e^{-} \longrightarrow Cu^{+} \quad (2x_2 - x_1)$$

Q $$\underbrace{Mn^{+7} \xrightarrow[1\times E_1]{} Mn^{+6} \xrightarrow[1\times E_2]{} Mn^{+5} \xrightarrow[1\times E_3]{} Mn^{+4} \xrightarrow[3\times E_4]{} Mn^{+1}}_{E_5 \times 6 = E_1 + E_2 + E_3 + 3E_4}$$

$$\boxed{E_5 = \frac{E_1 + E_5 + E_3 + 3E_4}{6}}$$

Q Give the E° values for the following reac^n sequence →

$$Mn^{+6} \xrightarrow{1.28V} Mn^{+5} \xrightarrow{2.9V} Mn^{4+} \xrightarrow{0.96V} Mn^{3+} \xrightarrow{1.5V} Mn^{+2}$$

The complete voltae of E° for $Mn^{6+} \longrightarrow Mn^{2+}$ [in volt is]

$$\frac{1.28+2.9+0.96+1.5}{4} \Rightarrow \frac{6.64}{4} = 1.66 \text{ volt}$$

$$\begin{array}{r} {}^{2\ 1} \\ 1.28 \\ 2.9 \\ .96 \\ 1.5 \\ \hline 6.64 \end{array} \quad \frac{6.64}{4} = 1.66$$

NET DEC 2013

Q92 The limiting molar conductivities of NaCl, NaI and RbI are 12.7, 10.8 and 9.1 $mS\,m^2\,mol^{-1}$ respectively. The limiting molar conductivity of RbCl, would be →

ⓐ 32.6 $mS\,m^2\,mol^{-1}$

ⓑ 7.2 $mS\,m^2\,mol^{-1}$

ⓒ 14.4 $mS\,m^2\,mol^{-1}$

[✓ ⓓ 11.0 $mS\,m^2\,mol^{-1}$]

$$\begin{array}{r} 12.7 \\ 10.8 \\ 9.1 \\ \hline 32.6 \end{array}$$

For RbCl →

RbI + NaCl − NaI

= 9.1 + 12.7 − 10.8

= 11.0 $mS\,m^2\,mol^{-1}$.

③ Electrode Potential depend on following factor →

ⓐ Temperature

ⓑ Conc^n of electrolyte

ⓒ Nature of reac^n at electrode

These parameters are correlated by the great scientist Nernst

Let us consider a Redox Reacⁿ,

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

Direction Coefficient, $\boxed{Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}} = \frac{\text{Product}}{\text{Reactant}} = \frac{[P]}{[R]}$

At equilibrium, $\Delta G = 0$ and $Q =$

From thermodynamics, $\Delta G = \Delta G^\circ + 2.303RT\log Q.$

$$\boxed{\begin{aligned}\Delta G &= -nFE_{cell}\\ \Delta G^\circ &= -nFE^\circ_{cell}\end{aligned}}$$

$$-nFE_{cell} = -nFE^\circ_{cell} + 2.303RT\log Q$$

$$* \quad \boxed{E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log Q}$$

This is required Nernst eqⁿ

At S.T.P.

$T = 298K$, $R = 8.314$ J/mol-K, $F = 96500$

L-atm is biggest unit

$R = 8.314 \frac{\text{Joule}}{\text{mol K}} = 2 \frac{\text{Calorie}}{\text{mol K}} = \frac{0.08\ \text{L-atm}}{\text{mol K}}$

$\boxed{1\ \text{L atm} = 101.31\ \text{Joule}}$

$\boxed{1\ \text{Cal} = 4.2\ \text{Jou}}$

$$\frac{2.303RT}{nF} = \frac{0.059}{n} = \frac{0.6}{n}$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q} \text{ — } ①$$

At equilibrium,

$$\Delta G = 0, \quad Q = K_{eq}$$

$$\boxed{E^\circ_{cell} = \frac{0.059}{n}\log K_{eq}}$$

$$\boxed{\log K_{eq} = \frac{nE^\circ_{cell}}{0.059}}$$

$$\boxed{K_{eq} = 10^{\left(\frac{nE^{\circ}_{cell}}{0.059}\right)}}$$

For anode Reaction →

$$\cancel{M(s) \rightleftharpoons M^{n+}}$$

$$M(s) \rightleftharpoons M^{n+} + ne^{-} \qquad Q = \frac{[M^{n+}]}{[M(s)]} = [M^{n+}]$$

$$E_{M/M^{n+}} = E^{\circ}_{M/M^{n+}} - \frac{0.059}{n} \log [M^{n+}]$$

$\left\{ [S] = [L] = 1 \right.$ conc^{n} of solid & liquid is alwz 1 $\}$

or $$\boxed{E_{O.P} = E^{\circ}_{O.P} - \frac{0.059}{n} \log [M^{n+}]} \text{ --- ①}$$

For cathode

$$M^{n+} + ne^{-} \longrightarrow M \ , \quad Q = \frac{1}{[M^{+n}]}$$

$$E_{R.P} = E^{\circ}_{R.P.} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

$$\boxed{E_{R.P} = E^{\circ}_{R.P} + \frac{0.059}{n} \log [M^{n+}]} \text{ --- ②}$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$\boxed{= E_{(R.P)cathode} - E_{(R.P)anode}} \qquad \boxed{E_{RP} = -E^{\circ}_{OP}}$$

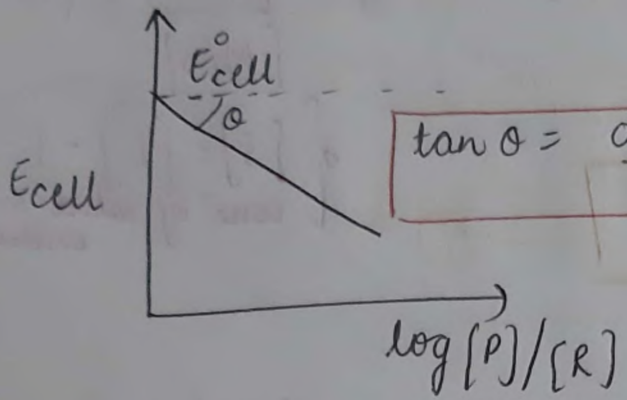
$$\left.\begin{aligned} &= E_{(R.P.)cathode} + E_{(O.P)anode} \\ &E_{(O.P)anode} - E_{(R.P)cathode} \end{aligned}\right\} \text{Use less}$$

EMF = Electro motive force
↓
(when cell is not in any circuit or working mode)

Graph b/w E_{cell} and concⁿ →

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[P]}{[R]}$$

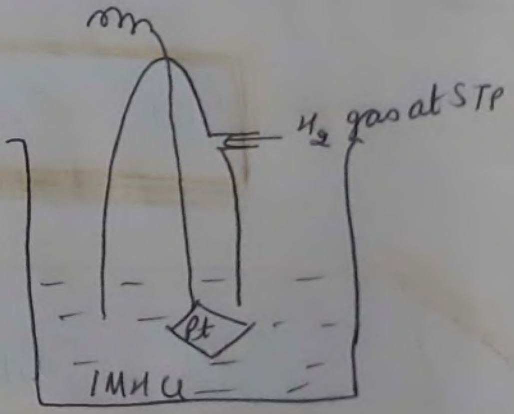
[P] = concⁿ of Product
[R] = concⁿ of Reactant



$$\boxed{\tan\theta = \frac{0.059}{n}}$$

Standard Hydrogen Electrode [SHE]

Electrode → Inert electrode of Pt block
Electrolyte → 1 M HCl



Reactions :-

At cathode, Pt, HCl/H_2 - - -

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2 \ , E_{H^+/H_2}$$

At anode Pt, $\frac{1}{2}H_2(g)$/HCl

$$\frac{1}{2}H_2 \longrightarrow H^+ + e^- \ , E_{1/2 H_2/H^+}$$

By IUPAC

$$E^{\circ}_{SHE} = 0 \text{ Volt}$$

Applying Nernst eq^n →

for cathode → $H^+ + e^- \rightarrow \frac{1}{2} H_2$

$P_{H_2} = 1$ atm

$Q = \frac{(P_{H_2})^{1/2}}{[H^+]}$

and $n = 1$

$$E_{cathode} = E^\circ_{cathode} - \frac{0.059}{1} \log \frac{(1\,atm)^{1/2}}{[H^+]}$$

$$\underset{(R.P)}{E_{cathode}} = -0.0591\left[-\log[H^+]\right]$$

$$= -0.059\,(pH_{cathode})$$

for anode → $\frac{1}{2} H_2 \rightarrow H^+ + e^-$

$$\underset{(O.P)}{E_{anode}} = E^\circ_{anode} - 0.059 \log \frac{[H^+]}{1}$$

$$\underset{(OP)}{E_{anode}} = 0.0591\,[pH_{anode}]$$

$$E_{cell} = \underset{RP}{E_{cathode}} - \underset{OP}{E_{anode}}$$

$$= -0.059\,pH_{cathode} - (-0.059\,pH_{anode})$$

$$\boxed{E_{cell} = 0.059(pH_{anode} - pH_{cathode})}$$

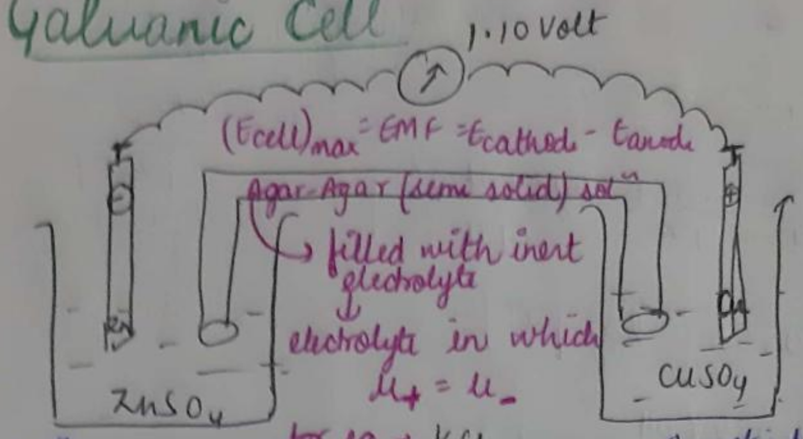
Q How much will potential of a Hydrogen electrode change when its sol^n initially at $pH = 0$ is neutralised to $pH = 7$?

Initially, $E_{cathode} = -0.059 \times 0 = 0$

$(E_{cathode})_{final}$ $-0.059 \times 7 = -0.413$

⇒ Decreased by 0.413 volt

Galvanic Cell



for eg → KCl

Sol^n pressure > osmotic pressure

$E_{R.P.}$ (low)

Osmotic pressure > sol^n pressure

$E_{R.P.}$ (high)

When electrodes are Hg / Ag / Tl
than NH_4NO_3, KNO_3

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

$$\boxed{E^\circ_{RP} = -0.76 \text{ volt}}$$

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

$$\boxed{E^\circ_{RP} = 0.34 \text{ volt}}$$

Functions of salt Bridge →

① It complete the internal circuit
② It maintains electrical neutrality.
③ It help to remove LJP (liquid junction potential

Representation of cell →

$$Zn(s)/\underset{c_1}{Zn^{+2}(aq)} \,//\, \underset{c_2}{Cu^{+2}(aq)}/Cu(s)$$

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

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

$$Q = \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}}$$

For favourable working or high E_{cell} →

$[Cu^{2+}] > [Zn^{2+}]$

$\boxed{c_2 > c_1}$

Calculation of E°_{RP} of Zn electrode :-

0.76V

$$Zn/\underset{E^\circ_{RP} = x \text{ volt}}{Zn^{+2}(aq)} \,//\, H^+/\underset{E^\circ_{RP} = 0.0 \text{ volt}}{\tfrac{1}{2}H_2(g)}, Pt$$

$\Rightarrow 0.76V = E^\circ_{cathode} - E^\circ_{anode}$
$= 0 - x$

$\boxed{x = -0.76 \text{ volt}}$

Calculation of E°_{RP} of Cu electrode →

$$\overset{\ominus}{Pt(s), \frac{1}{2}H_2} \Big| \underset{0}{H^+(aq)} \Big|\Big| \underset{x}{Cu^{+2}} \Big| \overset{\oplus}{Cu(s)}$$

$$\Rightarrow 0.34\ V = x - 0 \Rightarrow \boxed{x = 0.34\ V}$$

From above method, we can find the electrode potential of any metallic and non-metallic electrode.

~~Electro-Chemical Series→~~

~~When standard reduction potential of different metallic & non-metallic electrode are arranged in increasing or decreasing order of their reduction potential, then a series obtained is calle~~

From above method, we can find the electrode potential of any metallic and non-metallic electrode.

Imp

→ Electrochemical series :-

When standard reduction potential of different metallic and non-metallic electrode are arrange in increasing or decreasing order of their standard reduction potential then a series obtain called electrochemical series.

It is also called activity series.

Electrochemical Series

Trick → upar wala deta hain → e^-
neeche wala leta hain → e^-

Anode

↑ Reducing power

↓ Oxidising Power

* ~~Bas~~ most reactive metals and they can replace H_2 gas from cold water & mineral acid/base

ले $Li^+ + e^- \rightleftharpoons Li$ $E^\circ_{RP} = -3.07$ volt
के K^+
बारह Ba^{+2}
सरदार Sr^{+2}
का Ca^{+2}
नाम Na^+

Moderately Reactive metals they can replace H_2 from mineral acid & hot water

मांगे $Mg^{+2} + 2e^- \rightleftharpoons$ $E^\circ_{R.P.} = -2.00$ volt
अल्लादीन Al^{+3}
महान Mn^{+2}
जा $Zn^{+2} + 2e^- \rightleftharpoons Zn$ $E^\circ_{RP} = -0.76$ volt
कर Cr^{+2}
फेंके Fe^{+2}
कलम दवात Cd^{+2}
कोई Co^{+2}
नही Ni^{+2}
सुनो Sn^{+2}
प्रभात Pb^{+2}

है $H^+ + e^- \longrightarrow \frac{1}{2} H_2$ $E^\circ_{RP} = 0$
क्यों $Cu^{+2} + 2e^- \longrightarrow Cu$ $E^\circ_{R.P} = +0.34$ volt
आरु $I_2 + 2e^- \longrightarrow 2I^\ominus$
होगी $Hg^{+2} + 2e^- \longrightarrow Hg$
आज $Ag^+ + e^- \longrightarrow Ag$
ब्राह्मण $Br_2 + 2e^- \longrightarrow 2Br^-$
पण्डित $Pt^{+2} + 2e^- \longrightarrow Pt$
कलावती $Cl_2 + 2e^- \rightarrow Cl_2$
लूई गोल्ड $Au^{+3} + 3e^- \rightarrow Au$
फिर $F_2 + 2e^- \rightarrow 2F^-$ $E^\circ_{RP} = +2.08$ volt

Cathode

Hg
Ag
Pt
Au

H
A
P
A

$\text{oxide} \xrightarrow{\Delta} O_2\uparrow$.

$PtO_2 \xrightarrow{\Delta} O_2$
$HgO \xrightarrow{\Delta} O_2$
$Au_2O_3 \xrightarrow{\Delta} O_2$

They are not react in water (cold/hot) & acids (except few)

Cu
Hg
Ag
Pt
Au

> Nobel metal they are do not react with any acid it dissolve only in aqua regia ($HNO_3 + HCl$)
$\boxed{1 : 3}$

Application of Electro-Chemical series:-

① Reactivity of Metals $\propto \frac{1}{E^0_{R.P.}} \propto$ Reducing Power

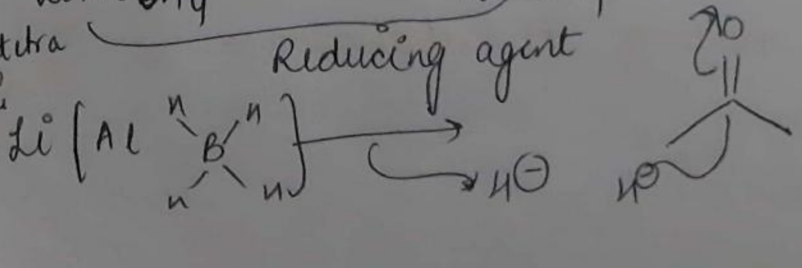
$Li > K > Ba > \cdots > Au$

In non-aqueous state Cesium is most reactive metals.

* $\overset{+1}{Li}\overset{+3}{Al}BH_4$ $NaBH_4$

Lithium tetra hydride aluminate

Reducing agent



①a → More reactive metal can replace less reactive metal

$$\underset{\text{Blue}}{Zn + CuSO_4} \longrightarrow \underset{\text{white}}{ZnSO_4} + Cu$$

$$ZnSO_4 + Cu \longrightarrow \text{No Reac}^n$$

Ques $A + BX \longrightarrow AX + B$

which is correct →

① $E_{RP}A > E_{RP}B$

② $E_{RP}B > E_{RP}A$

③ $E_{RP}B = E_{RP}A$

④ none of these

$$\boxed{E_{RP} \propto \frac{1}{\text{Reactivity}}}$$

①b → If two metal electrodes are given, then electrode having lower values of E°_{RP} behave as a anode & electrode having relatively high values of E°_{RP} as a cathode

Ques $E^\circ_{RP}A = -2.78$, $E^\circ_{RP}B = -1.08$, $E^\circ_{RP} = +1.18$ $E^\circ_{RP} =$

for cell having maximum E_{cell} which is correct

ⓐ anode of D & cathode of B

ⓑ anode of D & cathode of A

ⓒ Cathode of D & Anode of A

ⓓ Anode of B & Cathode of C

high diff and low value of E_{RP} as anode & high behave as cathode

①c → Metal having lower E°_{RP} cannot restored in having high E°_{RP}

NOTE → In container of zinc, sol^n of $CuSO_4$ salt cannot stored

①d → Discharge tendency of metallic ion $\propto E^\circ_{RP} \propto \frac{1}{\text{discharge potential}}$

$$\xleftarrow{\text{discharge tendency}}$$

$$Au^{+3} > Pt^{+2} > Ag^{+} > \ldots > Li^{+}$$

(8) Jor

2 a

2 b Me

non n

Therm

fre

② For non-metals →

2-a $\boxed{\text{Reactivity} \propto \text{oxidising power} \propto E^\circ_{RP}}$

$\boxed{F_2 > Cl_2 > Br_2 > I_2}$

Superhalogen

$\boxed{I_2 > Br_2 > Cl_2 > F_2}$ → discharge tendency

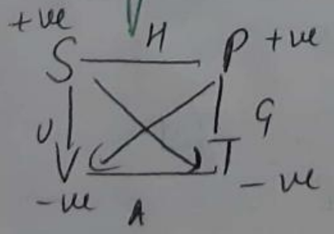
2-b More reactive non-metal can replace less reactive non metal from their salt.

set Ist
$$\begin{cases} F_2 + 2KCl \rightarrow 2KF + Cl_2 \\ F_2 + 2KBr \rightarrow 2KF + Br_2 \\ F_2 + 2KI \rightarrow 2F + I_2 \end{cases}$$

set II
$$\begin{cases} Cl_2 + 2KF \rightarrow \times \ \{\text{No Reac}^n\} \\ Cl_2 + 2KBr \rightarrow KCl + Br_2 \\ Cl_2 + 2KI \rightarrow KCl + I_2 \end{cases}$$

set III Cl_2
$$\begin{cases} Br_2 + 2KF \rightarrow \times \\ Br_2 + 2KCl \rightarrow \times \\ Br_2 + 2KI \rightarrow 2KBr + I_2 \end{cases}$$

Thermodynamics of Electrochemistry →



$$\boxed{dG = VdP - SdT} \quad - ①$$

from eqⁿ ① at constant Pressure →

$$(dG)_P = -SdT$$

$$\boxed{\left(\frac{dG}{dT}\right)_P = -S} \text{ — } ② \qquad -\Delta S = \left(\frac{d\Delta G}{dT}\right)_P$$

We also know →

$$dG = dH - TdS$$

From above eq^n →

$$\boxed{dG = dH + T\left(\frac{d(\Delta G)}{dT}\right)_P} \longrightarrow ③$$

→ Gibbs Helmholtz equation

We know that

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

from eq^n ③

$$\Delta G\ \cancel{-nFE_{cell}} = \Delta H + T\left[\frac{d}{dT}(-nFE_{cell})\right]_P$$

$$\boxed{\Delta G = \Delta H - nFT\left(\frac{dE_{cell}}{dT}\right)_P} \longrightarrow ④$$

here $\left(\frac{dE_{cell}}{dT}\right)_P$ = called Temp coefficient of electrochemical cell.

For high performance $\left(\frac{dE_{cell}}{dT}\right)_P$ should be low.

From eq^n ④ →

$$nFT\left(\frac{dE_{cell}}{dT}\right)_P = \Delta H - \Delta G$$

$$nF\cancel{T}\left(\frac{dE_{cell}}{dT}\right)_P = \cancel{T}dS$$

$\left\{\begin{array}{l} \Delta G = \Delta H - \\ T\Delta S = \Delta H \end{array}\right.$

$\boxed{\left(\frac{dE_{cell}}{dT}\right)_P = \frac{dS}{nF}}$ → in form of entro

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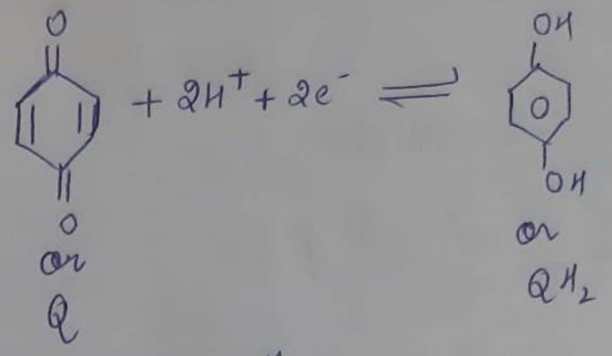
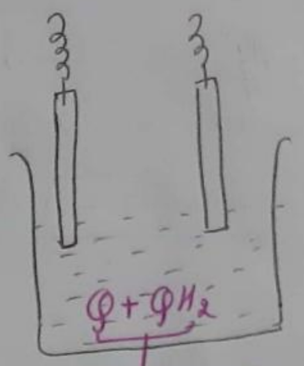
$$\boxed{dS = nF\left(\frac{dE_{cell}}{dT}\right)}$$

Different types of electrode :-

① Quinhydrone - electrode →





equimolar solⁿ
it means
$[Q] = [QH_2]$

Apply Nernst eqⁿ →

$$E_{Q/QH_2} = E^\circ_{Q/QH_2} - \frac{0.059}{2}\log\frac{\cancel{[QH_2]}}{\cancel{[Q]}[H^+]^2}$$

$$= E^\circ_{Q/QH_2} - \frac{0.059}{2}\log[H^+]^{-2}$$

$$= E^\circ_{Q/QH_2} + 0.059\log[H^+]$$

$$= E^\circ_{Q/QH_2} - 0.059[-\log H^+]$$

$$E_{Q/QH_2} = E^\circ_{Q/QH_2} - 0.059\,pH$$

$$\boxed{pH = \frac{E^\circ_{Q/QH_2} - E_{Q/QH_2}}{0.059}}$$

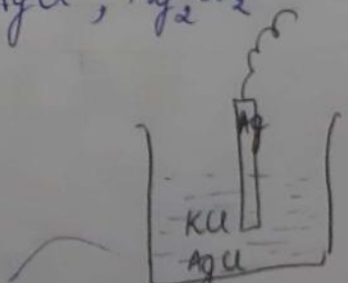
② Metal / metal insoluble salt electrode :-

sparingly soluble salt like $AgCl$, Hg_2Cl_2

$$AgCl\,(s) \rightleftharpoons \underset{(s)}{Ag^+} + \underset{(s)}{Cl^-}$$

$$K = \frac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$$

$$K[AgCl] = [Ag^+][Cl^-]$$



Metal = Ag
insoluble salt = AgCl

$$\boxed{K_{sp} = [Ag^+][Cl^-] = s \times s}$$

At cathode →

$Ag^+ + e^- \longrightarrow Ag$

$AgCl \longrightarrow Ag^+ + Cl^-$ } Reduction

cathode reacⁿ $AgCl + e^- \longrightarrow Ag + Cl^-$ $E^\circ_{AgCl/Ag/Cl^-}$

as anode $Ag \longrightarrow Ag^+ + e^-$ E°_{Ag/Ag^+}

$AgCl_{(s)} \longrightarrow Ag^+_{(aq)} + Cl^-$

$$\boxed{Q = [Ag^+][Cl^-] = K_{sp}} \quad -①$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$\underset{(R.P.)}{E^\circ_{AgCl/Ag/Cl^-}} - \underset{(R.P.)}{E^\circ_{Ag/Ag^+}}$$

From Nernst eqⁿ →

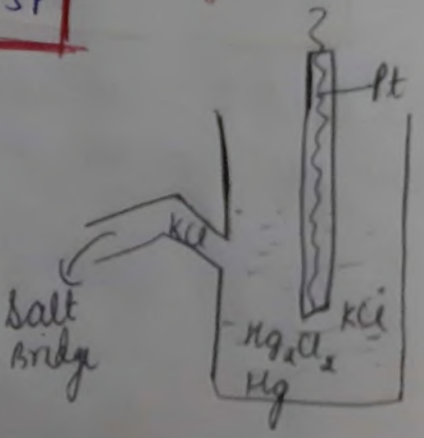
$$E_{cell} = E^\circ_{cell} - \underline{0.059} \log [Ag^+][Cl^-]$$

$$\boxed{E_{cell} = E^\circ_{cell} - 0.059 \log K_{sp}}$$ from ①

③ Calomel electrode →

Hg → Hg_2^{2+} → mercurous, Hg_2Cl_2 → Calomel

Hg → Hg^{2+} → mercuric, $HgCl_2$ → Carrosive Sublimate



* E_{cell} depend on Normality of KCl.

At cathode :-

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$$

$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$$

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

At anode

$$2Hg \longrightarrow Hg_2^{2+} + 2e^-$$

$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$$

$$\boxed{Q = [Hg_2^{2+}][Cl^-]^2 = K_{sp}}$$

From Nernst eq^n →

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log [Hg_2^{2+}][Cl^-]^2$$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log K_{sp}}$$

④ Redox electrode :-

For Fe^{+2}/Fe^{+3} →

$n_2 > n_1$

Cathode $Fe^{+3}_{(a)} + \cancel{1e^-} \longrightarrow Fe^{+2}$

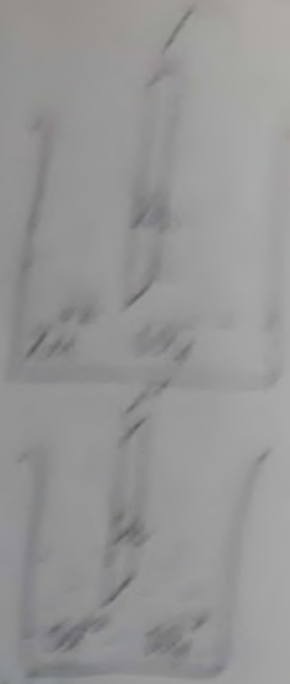
anode $Fe^{+2} \longrightarrow \underset{(b\ conc^n)}{Fe^{+3}} + \cancel{1e^-}$

conc^n of Fe^{+3} (a) & (b) are charge.

Fe^{+2}/Fe^{+3}
Sn^{+2}/Sn^{+4}
Ce^{+2}/Ce^{+4}
} anyone among these three

5) Metal metal ion electrode

M/M^{n+}



6) Standard hydrogen electrode

7) Standard chlorine electrode

GATE
Ques

From the data of the two half cell rxn:-

$AgCl + e^- \longrightarrow Ag + Cl^-$, $E^0_{red} = 0.22$ volt

$Ag \longrightarrow Ag^+ + e^-$ $E^0_{ox} = -0.80$ volt

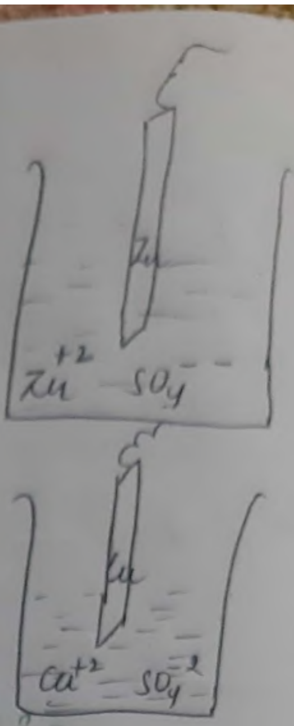
Calculate the solubility product (K_{sp}) of AgCl at 298 kelvin

We have

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log [Ag^+] \ldots$$

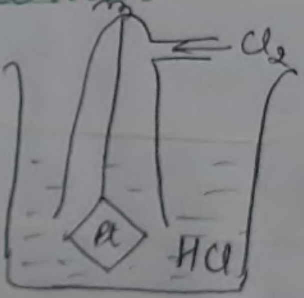
⑤ Metal-Metal ions electrode :-

M/M^{+n}



⑥ Standard hydrogen electrode :-

⑦ Standard Chlorine electrode :-



GATE Ques

From the data of the two half cell Reac^n

$AgCl + e^- \longrightarrow Ag + Cl^-$, $E^0_{R.P} = 0.22$ volt.

$Ag \longrightarrow Ag^+ + e^-$ $E^0_{O.P} = -0.84$ volt , $E_{RP} = +0.$

Calculate the solubility Product (K_{SP}) of AgCl at 298 kelvin.

We have

$$E_{cell} = E^0_{cell} - \frac{0.059}{1} \log [Ag^+][Cl^-]$$

$0 = E^\circ_{cell} - 0.059 \log K_{SP}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.22 - (+0.84)$

$\begin{array}{r} 0.84 \\ 0.22 \\ \hline 62 \end{array}$

$E^\circ_{cell} = -0.58$

$\log K_{sp} = \dfrac{E^\circ cell}{0.059} = \cancel{\dfrac{1.06 \times 10}{0.059}} = \cancel{\dfrac{1060}{59}}$

~~$\log K_s = 17.96$~~

~~$K_s = 10^{17.96}$~~

$\begin{array}{r} 84 \\ 22 \\ \hline \end{array}$

$= \dfrac{-0.580}{0.059} = \dfrac{-580}{59} = -9.83$

$$\boxed{K_{SP} = 10^{-9.831}}$$

Q The solubility product of AgBr is 5×10^{-13} at 298K. If standard Reduction potential of half cell E° AgBr/Ag/Br⁻ is 0.07 volt. Calculate standard Reduction of E_{Ag/Ag^+}

$E^\circ_{cathode} = 0.07$ volt

$E^\circ_{anode} = ?$

84

$K_{SP} = 5 \times 10^{-13}$

$E_{cell} = E_{cathode} - E_{anode}$

$0.72629 = 0.07 - E_{an}$

$E_{anode} = 0.07 + 0.7262$

$= 0.77629$ volt

$E^\circ_{cell} = \dfrac{+0.059}{1} \log K_{SP} = \dfrac{+0.059}{1} \log(5 \times 10^{-13}$

$= +0.059[\log 5 - 13]$

$+0.059[0.69 - 13] = +0.059 \times -12.31$

$= -0.72629$

We have

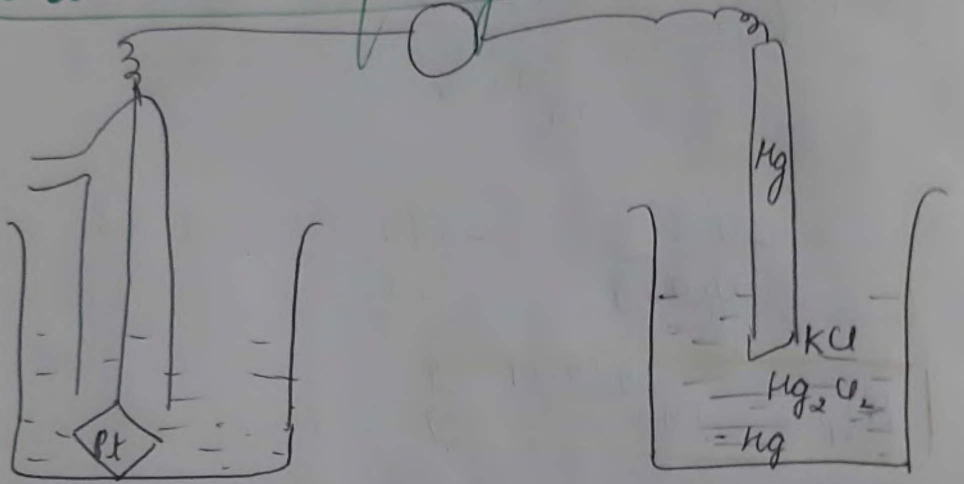
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{anode} = E^\circ_{cathode} - E^\circ_{cell}$$

$$= -0.7269 - 0.07$$

$$\boxed{E^\circ_{anode} = 0.7769 \text{ Volt}}$$

Calculation of pH →



Standard hydrogen electrode
(SHE)

Calomel Standard electrode
(CSE)
Reference cell

We know that →

$$E^\circ_{cell} = E^\circ_{CSE} - E^\circ_{SHE} \quad - ①$$

and

$$E_{cell} = E_{CSE} - E_{SHE} \quad - ②$$

$$\frac{1}{2}H_2 \longrightarrow H^+ + e^-$$

$$Q = \frac{[H^+]}{[PH_2]^{1/2}}$$

then $$E_{H_2/H^+} = 0 - \frac{0.059}{1} \log \frac{[H^+]}{[PH_2]^{1/2}}$$

$$(E_{H_2}/H^+)_{O.P.} = 0.059pH + \frac{1}{2}\log P_{H_2} \times 0.059$$

$$(E_{H_2}/H^+)_{R.P} = -0.059pH - \frac{1}{2}\log P_{H_2} \times 0.059 \quad ③$$

$P_{H_2} \rightarrow$ Pressure of H_2

then put in ②

$$\boxed{E_{cell} = E_{CSE} + 0.059(pH) + \frac{1}{2}0.059\log P_{H_2}}$$

If $P_{H_2} = 1$ atm

then $E_{cell} = \underset{\text{Referen}}{E_{CSE}} + 0.059pH$

$$\boxed{pH = \frac{E_{cell} - E_{CSE}}{0.059}}$$

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Q28 At 298 K, the emf of the cell

$Pt/H_2(1\,bar)/H^+ sol^n // Cl^-/Hg_2Cl_2/Hg$

is 0.7530 volt the standard potential of Calomel electrode is 0.2802 volt. If the liquid junction pot is zero the pH of sol^n is

(a) 4.7 (b) 7.4 [✓ (c) 8.0] (d) 12.7

$E_{cell} = 0.7530$

$E_{cathode} = 0.2802$ volt.

$$\boxed{E_{cell} = E_{CSE} + 0.059\,pH}$$

$0.7530 - 0.2802 = 0.059pH$

$\Rightarrow \boxed{pH = 8.01}$

6 13
0 7530
2802
4728

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Q For the following reacⁿ →

$$\overset{+7}{2MnO_4^-} + 5H_2\overset{+3}{C_2}O_4 + 6H^+ \longrightarrow \overset{+2}{2Mn^{+2}} + 8H_2O + 10\overset{+4}{CO_2}$$

anode $E^\circ_{(CO_2/H_2CO_3)}$ = −0.49 volt at 298 K. E_{Red} = −0.

~~Reduction → cathode~~

oxidation → anode

cathode $E^\circ_{MnO_4^-/Mn^{+2}}$ → +1.51 volt E°_{Red} = +1.51 volt

Q Calculate eq constant

ⓐ 10^{500} ⓑ 10^{338} ⓒ 10^{38} ⓓ 10^{833}

$E_{cell} = E_{cathode} - E_{anode}$

= ~~−0.49 + 1.51 volt~~ = 1.51 − (−0.49)

= 2.0

E_{cell} = ~~1.02 volt~~

$$\log k_c = \frac{n \times E^\circ_{cell}}{0.059} = \cancel{\frac{\times 1.02}{0.059}}$$

$$\frac{10 \times 2 \times 1000}{0.059} = 0.338 \times 1000$$

$$\log k_c = 338$$

$$\boxed{K_c = 10^{338}}$$

Q The emf of Hydrogen electrode to be zero. What should be pressure of hydrogen required in neutral pH if $E^\circ_{(H^+/H_2)} = 0$.

$E_{H^+/H_2} = -0.059\left[\frac{1}{2}\log pH_2 + pH\right]$

$0 = -0.059\left[\frac{1}{2}\log pH_2 + 7\right]$

$\frac{1}{2}\log pH_2 = -7$

$\boxed{pH_2 = 10^{-14}}$

Q For the reacⁿ

~~$Hg_2Cl_2(s) + H_2(g)$~~ $\longrightarrow$

$\overset{+1}{Hg_2}Cl_2(s) + \overset{0}{H_2}(g) \longrightarrow 2\overset{0}{Hg}(l) + 2\overset{+1}{H}Cl(aq)$

Correct representation of cell & calculate ΔG, ΔH, ΔS at 298 kelvin if $E_{cell} = 0.2684$ Volt and Temp coefficient $\left(\frac{dE}{dT}\right)_P$ is -3×10^{-4} Volt/kelvin.

$Hg_2Cl_2/2Hg // H_2/2HCl$

$\Delta G = -nFE_{cell}$

$\Delta G = -2 \times 96500 \times 0.2684$

$\boxed{\Delta G = \text{[illegible]}}$ = [illegible]

$dS = nF\left(\frac{dE}{dT}\right)_P$

$= 2 \times 96500 \times -3 \times 10^{-4}$

-2895×10^{-6}

$\boxed{dS = 2 \times 2.895 \times 10^{-3}} = 5.79 \times 10^{-3}$

We have $\Delta G = \Delta H - nFT\left(\frac{dE_{cell}}{dT}\right)$

~~ΔG~~ = ~~nRT~~ -

$\Delta H = \Delta G + nFT\left(\frac{dE_{cell}}{dT}\right)$

$= 25900.6 + 2 \times 96500 \times 298 \times -3 \times 10^{-4}$

$= 25900.6 - 17254.20 \quad 25900.6 - 8627.12 \times 10^{-4+4}$

$= 17273.5$

electrode cell also work when E_{cell} = +

Concentration cell →

In these conc^n cell, flow of current is due to the difference in ~~of~~ conc^n of two similar electrode in electrolytic solution because if the two concentration became same then $\boxed{E^\circ_{cell}=0}$ E°_{cell} became ~~&~~ zero because here no redox reac^n occurs.

It is of two types →

1. Electrode concentration cell
2. Electrolyte concentration cell

① Electrode conc^n cell →

If two same electrode having diff conc^n are dipped in similar electrolyte then electrode conc^n cell will be formed.

same →

$$Pt(s)\ H_2(P_1) / H^+_{C_1} \,||\, H^+_{C_1} / H_2(P_2) / Pt(s)$$

different

At cathode →

$$\cancel{2H^+ + 2e^-} \longrightarrow H_2(P_2)$$

At anode →

$$H_2(P_1) \longrightarrow \cancel{2H^+ + 2e^-}$$

Overall reac^n

$$H_2(P_1) \longrightarrow H_2(P_2)$$

$$Q = \frac{P_2}{P_1}$$

From Nernst eq^n →

$$E_{cell} = 0 - \frac{0.059}{2}\log\frac{P_2}{P_1}$$

$$E_{cell} = \frac{0.059}{2}\log\frac{P_1}{P_2}$$

for working must be positive

$\boxed{\text{Then } P_1 > P_2}$

→ $Pt, \underset{(c)}{HCl}(aq) / \underset{(aq)}{Cl_2}(P_1) // \underset{(c)}{HCl} / Cl_2(P_2)\ Pt/s)$

At ~~cathode~~ anode →

$$2Cl^- \longrightarrow \underset{(P_1)}{Cl_2} + 2e^-$$

At cathode $\underset{(P_2)}{Cl_2} + 2e^- \longrightarrow 2Cl^-$

$$2Cl \longrightarrow 2Cl^-$$

Working if $\Delta G = -ve$
$E_{cell} = +ve$
then $\boxed{P_2 > P_1}$

From Nernst eqⁿ →

$$E_{cell} = 0 - \frac{0.059}{2} \log \frac{P_1}{P_2}$$

$$\boxed{E_{cell} = \frac{0.059}{2} \log \frac{P_2}{P_1}}$$

② **Electrolyte concentration cell →**

Those concⁿ cell in which two electrode are dipped in electrolyte ~~[illegible]~~ having diff concⁿ with help of salt bridge.

$$Cd / \underset{c_1}{CdCl_2}(aq) // \underset{c_2}{CdCl_2} / Cd$$

Anode $Cd \longrightarrow \underset{(c_1)}{Cd^{2+}} + \cancel{2e^-}$

Cathode $\underset{(c_2)}{Cd^{+2}} + \cancel{2e^-} \longrightarrow Cd$

$$\underset{(c_2)}{Cd} \longrightarrow \underset{(c_1)}{Cd}$$

Applying Nernst eqⁿ

$$E^\circ_{cell} = 0$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{c_1}{c_2}$$

$$\boxed{E_{cell} = \frac{0.059}{2} \log \frac{c_2}{c_1}}$$

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* If H_2 Concentration cell is neither electrode nor electrolyte concⁿ cell then cell notation.

Anode Bridge Cathode

$Pt, H_2(P_1) / HCl(c_1) // HCl(c_2) / H_2(P_2), Pt$

<u>Anode</u> → $\frac{1}{2}H_2(P_1) \longrightarrow H^+(c_1) + 1e^-$

<u>Cathode</u> $H^+_{(c_2)} + 1e^- \longrightarrow \frac{1}{2}H_2(P_2)$

<u>Net</u> $\frac{1}{2}H_2(P_1) + H^+(c_2) \longrightarrow H^+(c_1) + \frac{1}{2}H_2(P_2)$

$$Q = \frac{c_1 P_2^{1/2}}{c_2 P_1^{1/2}} = \frac{c_1}{c_2}\left(\frac{P_2}{P_1}\right)^{1/2}$$

<u>Applying Nernst eqⁿ</u> →

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q$$

<u>We have $E^\circ_{cell} = 0$ for concⁿ cell</u>,

~~Ecell~~

$$E_{cell} = -\frac{0.059}{n}\log\frac{c_1}{c_2}\left(\frac{P_2}{P_1}\right)^{1/2}$$

for working E_{cell} = +ve

$$\boxed{E_{cell} = \frac{0.059}{1}\log\frac{c_2}{c_1}\left(\frac{P_1}{P_2}\right)^{1/2}}$$

$$\boxed{c_2(P_1)^{1/2} > c_1(P_2)^{1/2}}$$

Thermodynamic Activity →

In chemical thermodynamics, activity (a) measure effective conc of the solution. Effective conc of species in a mixture in the sense that the species chemical potential depend on the activity of the real sol. In the same way, conc used for the ideal sol.

Activity (a) → Real sol
Concentration [m, M, N] → ideal sol

Activity is an dimensionless quantity and activity of pure substance in condensed phase [solid and liquid] taken as unity.

$$a \propto \frac{c}{c^\circ} \quad , \text{where } c^\circ = 1\,M$$

$$a = \gamma \frac{c}{c^\circ}$$

$\boxed{a = \gamma c}$ where γ is coefficient of activity and for dilute sol $\gamma = 1$

$\boxed{a = c}$ → activity is consider as conc for dilute sol

For gases, activity of gases is effective partial pressure called **fugacity**.

$$\boxed{(a)_g = f = \frac{P}{P^\circ}}$$

~~chemical eqb~~

Chemical potential and Activity →

$$\boxed{\mu_i = \mu_i^\circ + RT \ln a_i} \quad \text{(for Real)}$$

$$\boxed{\mu_i = \mu_i^\circ + RT \ln c_i} \quad \text{(for ideal)}$$

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E) Mean Activity Coefficient :

It is not possible to have only one kind of ion in a solⁿ there are cation and anion both present in the solⁿ to make it electrically neutral. The activity of electrolyte solⁿ having electrolyte A_xB_y is given as

$$\underset{M}{A_xB_y} \longrightarrow \underset{xM = M_+}{xA^{y+}} + \underset{yM = M_-}{yB^{x-}}$$

Then, activity of salt = activity of cation × activity of anion

$$a = a_+^x a_-^y \quad -①$$

Mean activity is defined as → $a_+^x \cdot a_-^y = (a_\pm)^{x+y}$

$$a_+ = \gamma_+ M_+ \quad , \quad a_- = \gamma_- M^-$$

Put in ① $a = (\gamma_+ M_+)^x (\gamma_- M_-)^y$

$$(\gamma_+ xM)^x (\gamma_- yM)^y$$

$$= (\gamma_+)^x (\gamma_-)^y x^x y^y (M)^{x+y}$$

$$\begin{array}{lll} H_2SO_4 \rightarrow & 2H^+ & + SO_4^- \\ 2M & 4 \times M & 2M \end{array}$$

$$\boxed{a_{salt} = (\gamma_\pm)^{x+y} x^x y^y (M)^{x+y}}$$

here, $(\gamma_\pm)$ is called mean ionic activity coefficient

$$\boxed{\underset{\text{mean ionic activity}}{\boxed{(a_\pm)}}^{x+y} = (\gamma_\pm)^{x+y} x^x y^y (M)^{x+y}}$$

Q Calculate mean ionic activity of $CaCl_2$ having molality $2M$ and mean ionic activity coefficient $(\gamma_\pm)$ is $\gamma_\pm$.

$$CaCl_2 \longrightarrow \underset{x=1}{Ca^{+2}} + \underset{2}{2Cl^-}$$

$$(a_\pm)^{2+1} = (\gamma_\pm)^{2+1} \cdot 1^1 \times 2^2 \cdot (2M)^3$$

$$= (\gamma_\pm)^3 32 M^3 \Rightarrow \boxed{(a_\pm) = \gamma_\pm M 2 \sqrt[3]{4}}$$

0.5 M of $Al_2(SO_4)_3$
and mean ionic activity coefficient

$$Al_2(SO_4)_3 \longrightarrow 2Al^{+3} + 3SO_4^{2-}$$

$$(a_\pm)^{x+y} = (\gamma_\pm)^{x+y} x^x y^y (M)^{x+y}$$

$$= (\gamma_\pm)^5 \, 2^2 \, 3^3 (0.5M)^{3+2}$$

$$(a_\pm)^5 = (\gamma_\pm)^5 \times 108 \times (0.5M)^5$$

2 | 108
2 | 54
3 | 27
3 | 9

$$\boxed{(a_\pm) = (108)^{1/5} \times 0.5M \times (\gamma_\pm)}$$

Ionic Strength →

Ionic strength of a solⁿ is a measure of electrical intensity due to the presence of ions in the solution

$$\boxed{I = \frac{1}{2} \Sigma c_i z_i^2}$$ ~~$\frac{mole}{litre}$~~ coulomb^2 $\frac{mole}{litre}$

where c_i = concⁿ of ith ion
z_i = charge of ith ion

→ $CaCl_2 \rightarrow Ca^{+2} + 2Cl^-$
2M   2M   4M

$$I = 1/2 \left[2M(+2)^2 + 4M(-1)^2 \right]$$

$$= \frac{1}{2}[2 \times 4 + 4 \times 1] = \frac{1}{2}[8+4] = \frac{12}{2} = 6 \text{ mol/L}$$

Q Calculate mean ionic activity of $Al_2(SO_4)_3$ having molality 0.5 M and mean ionic activity coeffici

$$Al_2(SO_4)_3 \longrightarrow 2Al^{+3} + 3SO_4^{2-}$$

$$(a_\pm)^{x+y} = (\gamma_\pm)^{x+y} x^x y^y (M)^{x+y}$$

$$= (\gamma_\pm)^5 2^2 3^3 (0.5M)^{3+2}$$

$$(a_\pm)^5 = (\gamma_\pm)^5 \times 108 \times (0.5M)^5$$

2 | 108
2 | 54
3 | 27
1 | 9

$$\boxed{(a_\pm) = (108)^{1/5} \times 0.5M \times (\gamma_\pm)}$$

Ionic Strength →

Ionic strength of a solⁿ is a measure of electrical intensity due to the presence of ions in the solution

$$\boxed{I = \frac{1}{2} \sum c_i z_i^2} \quad \frac{mole}{litre} \quad ~~coulomb~~ \frac{mole}{litre}$$

where c_i = concⁿ of ith ion
z_i = charge of ith ion

→ $CaCl_2 \longrightarrow Ca^{+2} + 2Cl^-$
$\quad 2M \qquad\quad 2M \qquad 4M$

$$I = \frac{1}{2}\left[2M(+2)^2 + 4M(-1)^2\right]$$

$$= \frac{1}{2}\left[2\times4 + 4\times1\right] = \frac{1}{2}\left[8+4\right] = \frac{12}{2} = 6\,mol/L$$

Q Calculate ionic strength of 0.1 M NaCl →

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

$\;\;0.1 \qquad\quad 0.1 \quad 0.1$

$$\frac{1}{2}\left[0.1 + 0.1\right] = \frac{0.2}{2} = \boxed{0.1\,mol/L}$$

Q Calculate ionic strength of 0.1 M $CaCl_2$ →

$CaCl_2 \longrightarrow Ca^{+2} + 2Cl^-$

$\;\;0.1 \qquad\quad 0.1 \qquad 2 \times 0.1$

$\cancel{\frac{1}{2}}\ \Sigma cz^2$

$$\frac{1}{2}\left[0.1 \times (+2)^2 + 0.2 \times [-1]^2\right]$$

$$\frac{1}{2}\left[0.1 \times 4 + 0.2 \times 1\right]$$

$$= \frac{[0.4 + 0.2]}{2} = \frac{0.6}{2} = \boxed{0.3\,mol/L}$$

Q Find ionic strength of solⁿ containing 0.2 M NaCl of 100 ml and 0.2 M $CaCl_2$ of 100 ml.

If solⁿ is separated molarity also half then $NaCl \to 0.1$, $CaCl_2 \to 0.1$

$I_{NaCl} = 0.1$

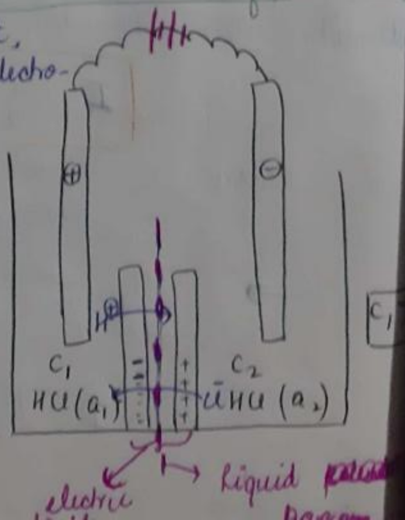
$$I_{CaCl_2} = \frac{1}{2}\left\{0.1 \times (2)^2 + 0.2 \times (-1)^2\right\} = 0.3$$

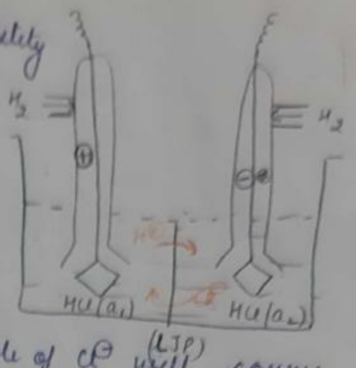
$$\boxed{\underbrace{I_{NaCl} + I_{CaCl_2}}_{I_{sol^n}} = 0.4\ mol/L}$$

5.18 Electrolytic concentration Cell with transference

In this cell, no salt bridge is present, so there is transfer of ion from one electrolytic solⁿ to other. In a cell if two electrolytic solⁿ of different concⁿ or activity in contact with each other then a potential difference developed across the boundary of two solⁿ. This is called liquid junction potential or diffusion potential.

$$\boxed{E_{LJP} = E_{\text{with transference}} - E_{\text{without Transference}}}$$





It arises because of difference
rate of diffusion (ionic mobility
transport no) of positive and
gative ion from one solⁿ
another solⁿ.

ell in which electrode are
versible with respect to cation
hen if 1 F of electricity is
ithdrawn from the cell
So, $t_{\oplus}$ mole of H^+ and $t_{\ominus}$ mole of $Cl^{\ominus}$ will carry
e electricity at particular time.

At anode → $\frac{1}{2}H_2(P) \rightarrow H^+_{(a_1)} + e^-$ — ①

At cathode → $H^+_{(a_2)} + e^- \rightarrow \frac{1}{2}H_2(P)$ — ②

$$\boxed{\begin{array}{l} H^+ + Cl^- = 1F \\ \text{or} \quad t^{\oplus} + t^{\ominus} = 1 \end{array}}$$

Transfer of $t^{\oplus}$ mole of $H^{\oplus}$ from left to Right

$$t^{\oplus} H^{\oplus}(a_1) \longrightarrow t^{\oplus} H^{\oplus}(a_2) \quad — ③$$

Transfer of $t^{\ominus}$ mole of Cl^- from right to left →

$$t^{\ominus} Cl^{\ominus}(a_2) \rightarrow t^{\ominus} Cl^{\ominus}(a_1) \quad — ④$$

Then net change in the cell is obtained by adding the above four changes, thus we have →

$$\cancel{\frac{1}{2}H_2(P)} + H^+_{(a_2)} + t^{\oplus}H^{\oplus}_{(a_1)} + t^{\ominus}Cl^-_{(a_2)} \longrightarrow H^+_{(a_1)} + \cancel{\frac{1}{2}H_2(P)} + t^{\oplus}H^+_{(a_2)} + t^{\ominus}Cl^{\ominus}_{(a_1)}$$

On cancelling common term →

$$H^{\oplus}_{(a_2)} + t^{\oplus}H^{\oplus}_{(a_1)} + t^{\ominus}Cl^{\ominus}_{(a_2)} \rightarrow H^+_{(a_1)} + t^{\oplus}H^+_{(a_2)} + t^{\ominus}Cl^-_{(a_1)}$$

$$H^+_{(a_2)} - t^{\oplus}H^{\oplus}_{(a_2)} + t^{\ominus}Cl^-_{(a_2)} \rightarrow H^+_{(a_1)} + t^{\ominus}Cl^{\ominus}_{(a_1)} - t^{\oplus}H^+_{(a_1)}$$

$$(1-t^{\oplus})H^{\oplus}_{(a_2)} + t^{\ominus}Cl^{\ominus}_{(a_2)} \rightarrow (1-t^{\oplus})H^+_{(a_1)} + t^{\ominus}Cl^{\ominus}_{(a_1)}$$

$$t^{\ominus}H^{\oplus}_{(a_2)} + t^{\ominus}Cl^{\ominus}_{(a_2)} \longrightarrow t^{\ominus}H^{\oplus}_{(a_1)} + t^{\ominus}Cl^{\ominus}_{(a_1)}$$

$$\boxed{t^{\ominus}_{HCl}(a_2) \longrightarrow t^{\ominus}\, HCl(a_1)}$$

From the above second eq^n →

$$Q = \frac{(a_1)^{t-}\,(a_1)^{t-}}{(a_2)^{t-}\,(a_2)^{t-}} = \left(\frac{a_1}{a_2}\right)^{2t\ominus}$$

$$\boxed{Q = \left(\frac{a_1}{a_2}\right)^{2t\ominus}}$$

Then from Nernst's eq^n →

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

$$E_{cell} = 0 - \frac{0.059}{1}\log\left(\frac{a_1}{a_2}\right)^{2t\ominus}$$

$$\# \boxed{E_{cell} = 2t_{\ominus} \times 0.059 \log\left(\frac{a_2}{a_1}\right)}$$

$$\Rightarrow \boxed{E_{cell\ with\ LJP} = 2t_{\ominus}\, 0.059 \log\left(\frac{a_2}{a_1}\right)} \rightarrow \text{with LJP}$$

$$\boxed{E_{cell\ without\ LJP} = 0.059 \log\left(\frac{a_2}{a_1}\right)} \rightarrow \text{without LJP}$$

$$E_{LJP} = E_{with} - E_{without}$$

$$\boxed{E_{LJP} = (2t_{\ominus} - 1)\, 0.059 \log\left(\frac{a_2}{a_1}\right)} \rightarrow E_{LJP}$$

$$t_{\ominus} + (t_{\ominus} - 1)\, 0.059 \log\left(\frac{a_2}{a_1}\right)$$

$$\left[\begin{array}{l} t_{\ominus} = 1 - t \\ t_{\ominus} - 1 = t_{+} \end{array}\right.$$

Or $$\boxed{E_{LJP} = (1 - t_{\oplus})\, t_{\oplus}\, 0.059 \log \frac{a_2}{a_1}}$$

or $$\boxed{E_{LJP} = (t_{\ominus} + t_{\oplus})\, 0.059 \log \frac{a_2}{a_1}}$$

Q For 1 Molar aqueous NaCl sol^n, the mean ionic activity coefficient is equal to →

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

I = 1 Mol/litre

$$\log \gamma_{\pm} = -0.059\,|1\times1|\,1$$

$$\gamma_{\pm} = 10^{-0.059} = \underline{0.87297}$$

Note :-

Activity coefficient calculated using Debye-Huckel is less than 1.

Analytical Electrochemistry →

① Conductometric titration
② Potentiometric titration
③ Spectrophotometric titration
④ Polorography
⑤ Amperiometry

① Conductomeric Titration →

In a electrolytic solution, each ion have different conductance due to this when ion having high conductance when replaced by ion having low conductance then conductance of the solution decreases. by this technique we can find end point by plotting conductance against the volume of titrant. This phenomenon is called conductometric titration.

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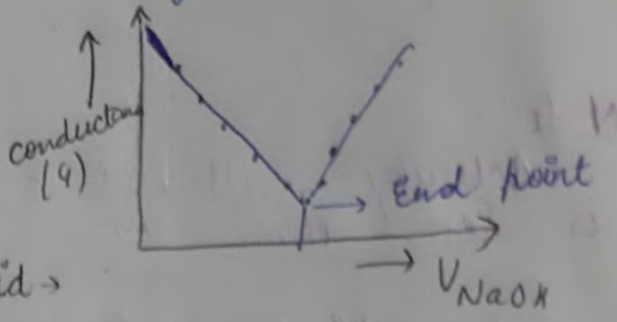
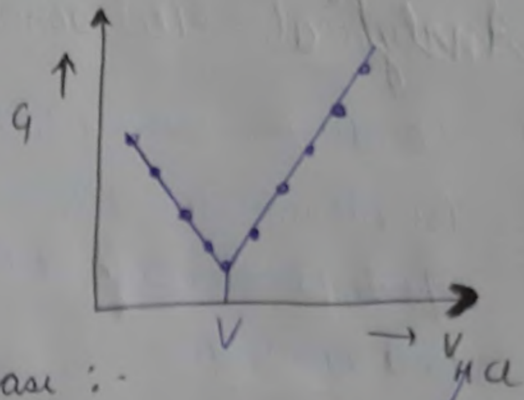
① Strong Acid v/s Strong base →

$H^{\oplus}$ have high conductance as we add NaOH $H^{\oplus}$ neutrali and conductance decrease very rapidly. when all the $H^{\oplus}$ neutralised by OH^- then adding few drop of NaOH, conductance increase. suddenly at this stage End point achieved.

$NaOH + HCl \rightarrow NaCl + H_2O$

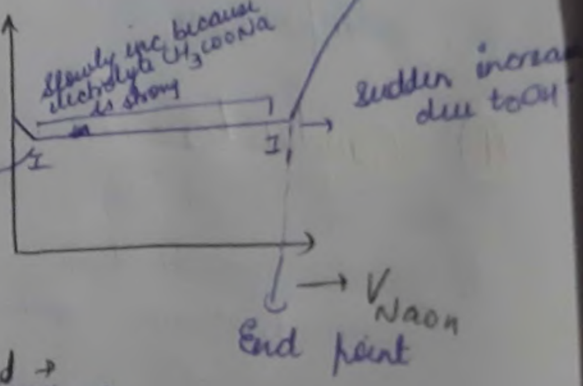


② Strong Base v/s Strong Acid →



③ Weak acid v/s Strong base :-

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$



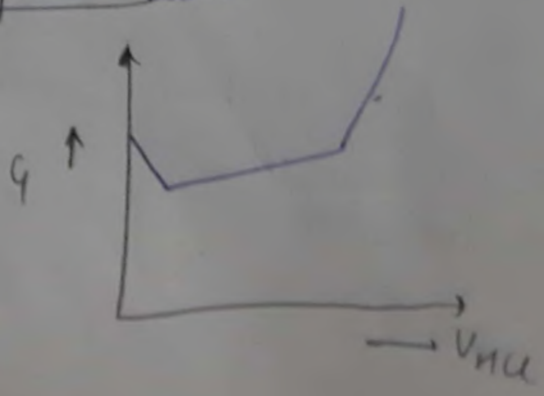
drop in conductance because of consumption G of H^+ present due to CH_3COOH

Slowly inc because electrolyte CH_3COONa is strong

sudden increase due to OH

④ Weak base v/s Strong acid → Titrant

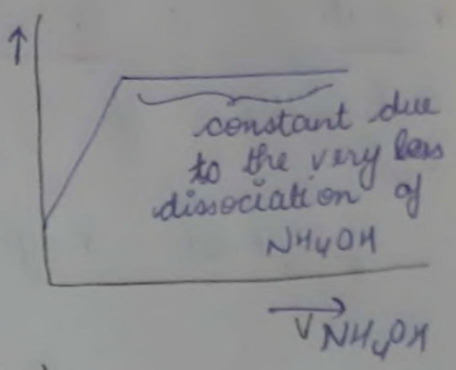
$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$



⑤ Weak acid v/s Weak base →

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

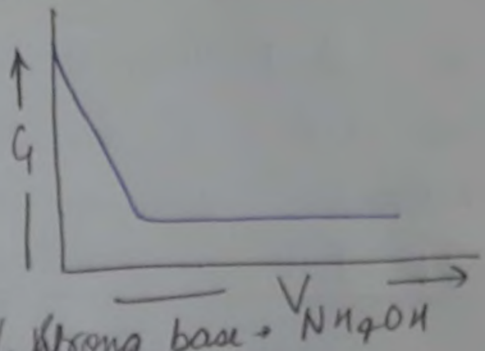
Reacⁿ of weak acid and weak base result in buffer



⑥ Strong acid v/s Weak base →

$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$

Akansha

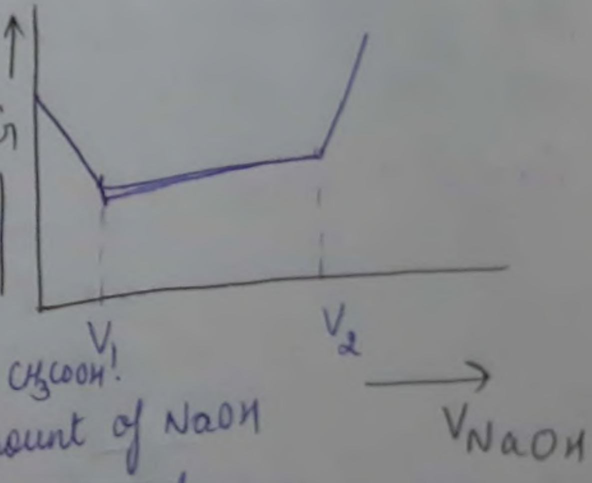


Imp

⑦ (Strong acid + Weak acid) v/s Strong base →

$CH_3COOH + HCl$ v/s $NaOH$

Volume V_1 represent amount of NaOH require to neutralise HCl only. Volume V_2 represent the amount of NaOH require to neutralise HCl as well as CH_3COOH and volume $\boxed{V_2 - V_1}$ amount of NaOH required to neutralise CH_3COOH only.



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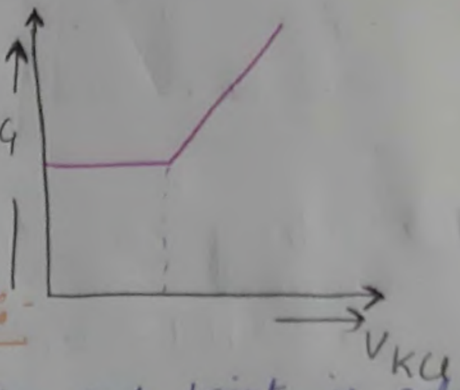
② Precipitation Reac^n →

⇒ Titration of $AgNO_3$ v/s KCl

Conductance of Ag^+ is near to conductance to K^+.

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$



③ Spectrophotometric titration :-

In spectrophotometric titration, the end point is calculated from data of the absorbance of sol^n. since spectrophotometric titration are carried in vessel for which light path is constant.

The absorbance is proportional to conc thus in a titration where the titrant/reactant/product absorb radiation. The plot of absorbance v/s volume is plotted and by which we can calculate end point.

Case I → When only reactant absorb light

$$\underbrace{S}_{\text{Reactant}} + \underbrace{T \longrightarrow \text{Product}}_{\text{do not show absorbance}}$$

Reactant: shows absorbance

The fall in graph indicate that as reac^n proceed the reactant consume. So absorbance decrease

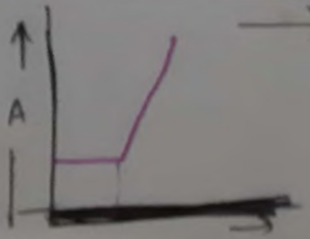
Case II → When only titrant absorb

$$S + T \rightarrow \text{Product}$$

S ↓ do not absorb [A = 0]

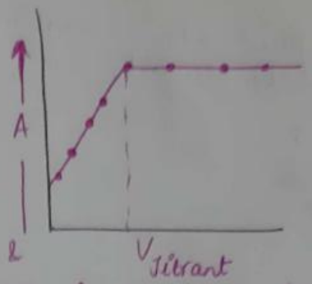
T ↓ absorb

Product ↓ do not absorb [A = 0]



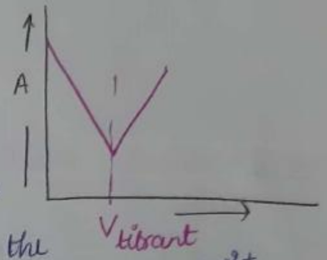
Case III → When only product absorb

$$\underbrace{S}_{A=0} + \underbrace{T}_{A=0} \rightarrow \underbrace{P}_{A\neq 0}$$



Case IV → When both substrate & titrant give absorbance & product does not give absorbance

$$\underset{\substack{\text{coloured}\\ A\neq 0}}{S} + \underset{\substack{\text{coloured}\\ A\neq 0}}{T} \longrightarrow \underset{\substack{\text{colourless}\\ A=0}}{P}$$



The most important titrantions are complexometric titration of Fe^{3+} and Cu^{2+} against EDTA. In this titration the complex form by the Fe^{3+} is more stable than complex form by Cu^{2+}.

So, whenever we take reading the first reading is related is Fe^{+3} concentration and second reading is related to Cu^{2+} concentration.

④ Amp~~he~~rometry →

It is also proportional to dropping Mercury electrode. Here, diffuse current is proportional to electro-active material in the sol^n. If some of the electro-active material is removed by interaction by reagent. The diffuse current will decrease. This is the fundamental principle of Amperometry titration. Generally use for the precipitation titration.

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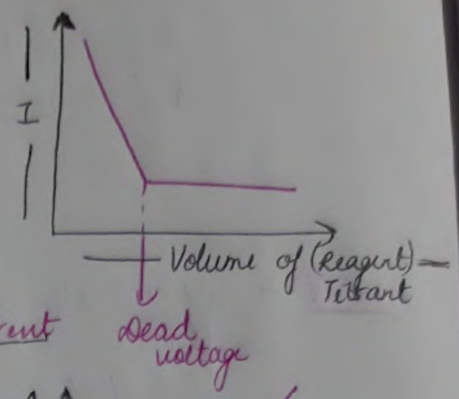
Case I → When Reactant is carrying current

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$

(Reactant) (Reagent)

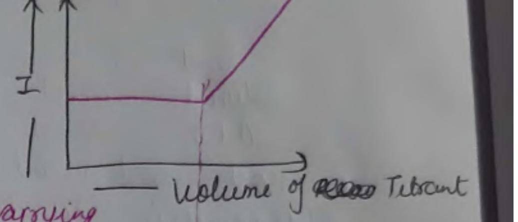
substrate ↓ on which attack takes place

↓ which attack first



Case II → When Reagent is carrying current

$R + T \longrightarrow P.$



Case III → When Reactant & Reagent carrying current :-

$R + T \longrightarrow P$