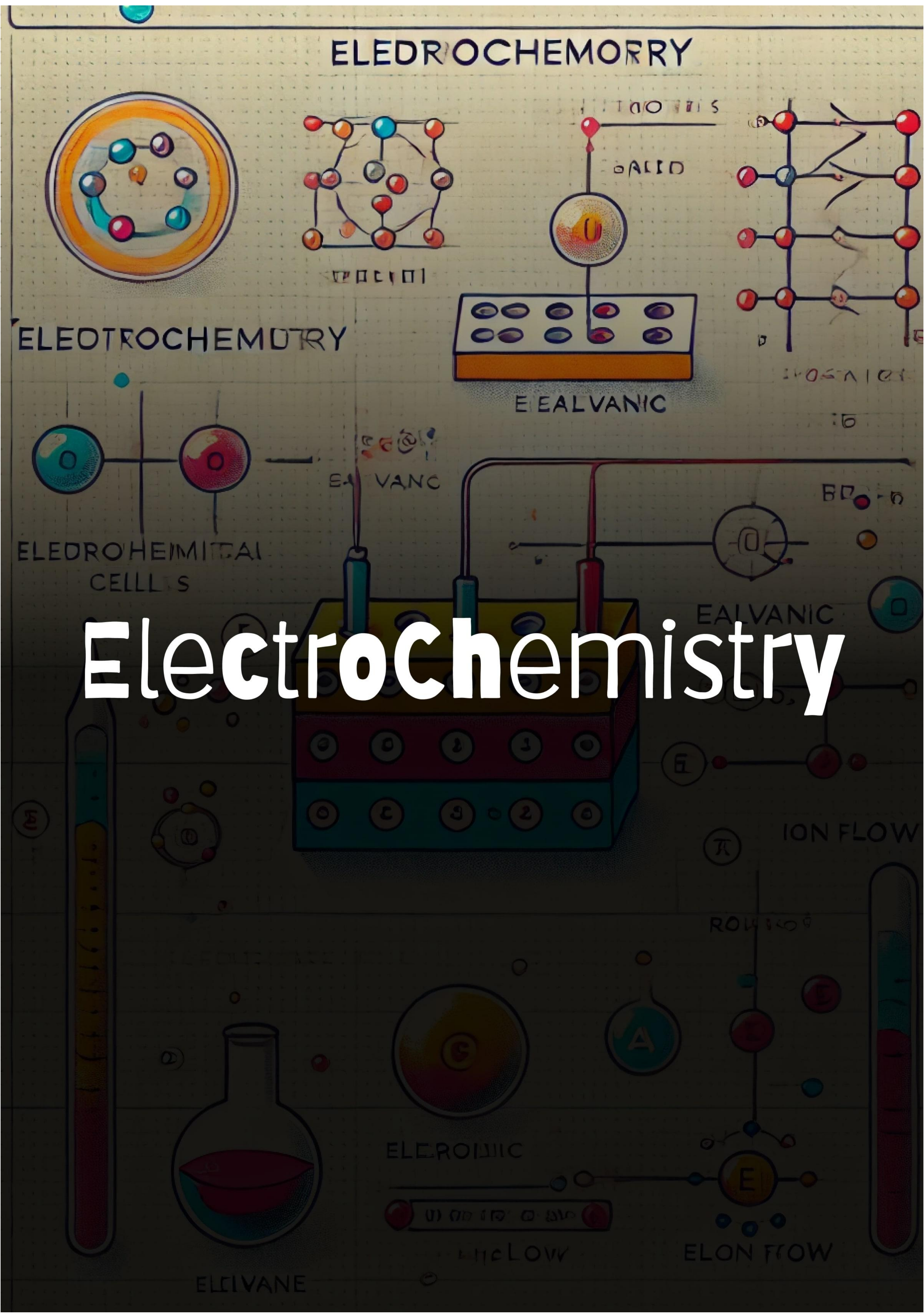
Electrochemistry



ELECTRO CHEMISTRY

ELECTRO CHEMISTRY

- Electro-chemical Cell
- Electro-lysis
- Chemical Conduction

Electro Chemical Cell A device which can convert chemical energy into electrical energy.

When a metal rod is placed in contact with its solution there may be two cases possible —

Solution Pressure
Electro-nation

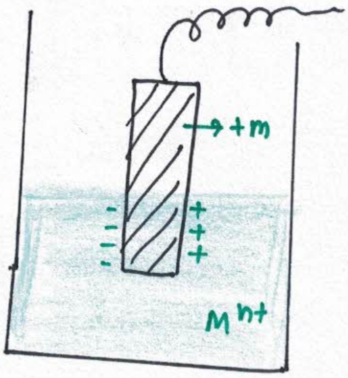
Osmatic Pressure
De-electronation

Osmatic Pressure

for some metals, the atom from neutral rod will move into solution in form of ions leaving behind the electron on the the rod. This tendency is called solution pressure.

In solution, concentration of $[M^{+n}]$ will increase. On the rod negative charge will increase. This process will take place till short time and some time sufficient negative charge will develop on the rod.

Example Zn rod is placed in contact with $ZnSO_4$ soluth
Because of change sepration three will be potential
difference b/w metal rod and its solution which is called
electrode potential and the metal rod in contact with
its salt solution is called electrode. [anode]



$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne$

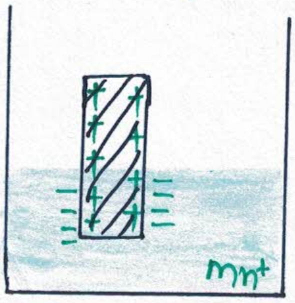
for anode

- Osmatic pressure > solution press.
- Always oxidation will occure at anode $M \longrightarrow M^{n+} + ne$
- Anode is used as source of solution.
- Solution polarity will be negative

Solution Pressure

Tendency of metal ion to get deposited on the rod.

This type of electrode is called Cathod.



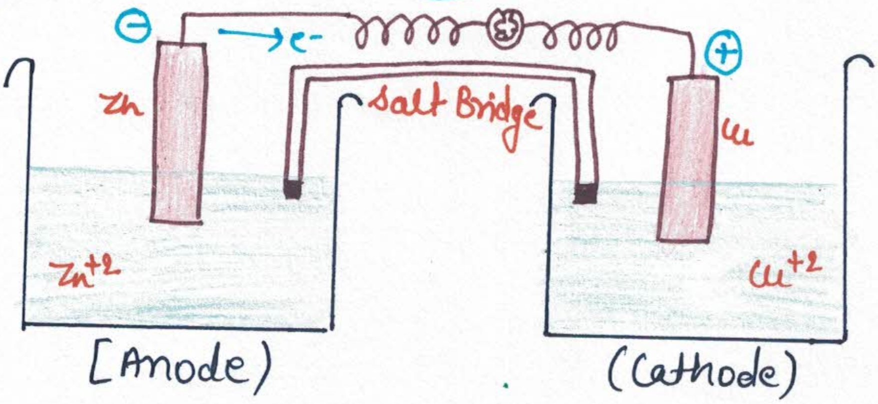
for Cathode

- solution pressure > Osmatic Press.
- Always reduction will occure at Cathode $M + ne \longrightarrow M$
- $[m]^{+n}$ conc^n will decrease.
- solution polarity will be negative
Ex:- Cu Metal.

for electrodes if we have osmatic pressure equal to solution pressure, then electrode is called Inert or null electrode. Ex:- Platinum electrode

Direction of e⁻ → anode to cathode
Direction of current → Cathode to anode

Construction of electrochemical Cell :-



LOAN

Anode ⇒ L ⇒ Left

O ⇒ oxidation

A ⇒ Anode

N ⇒ Negative

Salt Bridge

A 'U'-shaped glass tube is fitted with a paste of any electrode [generally KCl] with agar. agar solution and dried.

① It will form net like structure or porous structure. through which ion can move.

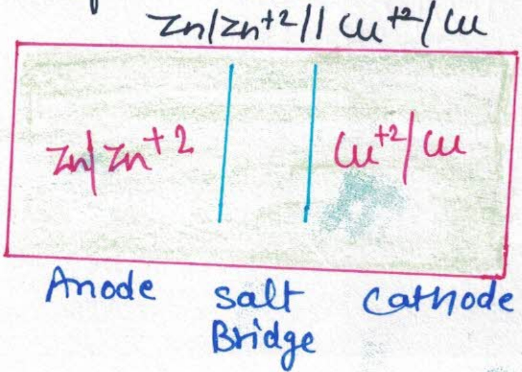
② Electrolyte to be used in salt bridge should be such as that its cation speed will be equal to speed of anion i.e Molarity of cation is equal to molarity of Anion.

③ If in any compartment there are silver ion [Ag^+] or murcurous ion [Hg_2^+ Hg^{+2}] or thallium ion [Tl^{+4}] then KCl should not be used. Otherwise there will be precipitation of $AgCl$, Hg_2Cl_2, $HgCl_2$ $TlCl$ respectively on opening of salt bridge and salt bridge will stop working.

④ In the case KNO_3 and NH_4NO_3 are used (sped are diff. but we have to use because of no other option) salt bridge complete the Internal circuit of the cell as well as maintain neutrility.

Construction of electro-chemical cell

NOTE Always ion must be on the side of salt Bridge.



Cell reaction:- $M \longrightarrow M^{n+} + ne \Rightarrow$ [Anode]

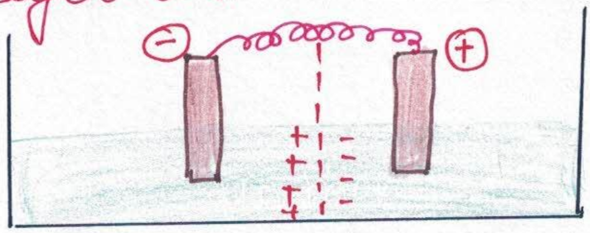
$ne + N^{+n} \longrightarrow N \Rightarrow$ [Cathode]

$M_{(s)} + M^{+n}_{(aq.)} \longrightarrow M^{+n}_{(aq.)} + M_{(s)}$

$$\boxed{Q_c = \frac{[M]^{n+}}{[N]^{+n}}}$$

In the reaction, M^{+n} keeps on increasing as it is at anode & N^{+n} keeps on decreasing as it is at cathode. Genrally Q_c keeps on ↑ing.

If we will not use salt bridge then there will be a liquid liquid junction potential due to formation of electrical layer and it will decrease potential of cell.



Potential of all → $\boxed{E_{anode} + E_{cathode}}$

$Zn \longrightarrow Zn^{+2} + 2e \rightarrow$ Anode $\rightarrow E_{oxi}$

$2e + Zn^{+2} \longrightarrow Zn \longrightarrow$ Cathode $\rightarrow E_{red}$

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

Notation →

$$\boxed{\begin{aligned} E_{oxi} &= E_{Zn|Zn^{+2}} \\ E_{red} &= E_{Zn^{+2}|Zn} \end{aligned}}$$

$$\boxed{\begin{aligned} E_{cell} &= (E_{oxi})_{anode} + (E_{red})_{cathod} \\ &= (E_{red})_{cathode} - (E_{red})_{Anode} \end{aligned}}$$

Standered condition → It is one atmosphere pressure, Temprature in 25°C and concn of ion is considered 1 molar.

At standered condition ⇒ $E^{\circ}_{oxi} = -E^{\circ}_{red}$

$$E^{\circ}_{cell} = (E^{\circ}_{oxi})_{anode} - (E^{\circ}_{red})_{cathode}$$

$$\boxed{E^{\circ}_{cell} = (E^{\circ}_{red})_{cathod} - (E^{\circ}_{red})_{anode}}$$ standered potential of cell.

Example

$E^{\circ}_{Zn^{+2}/Zn} = -0.76\,V$; $E^{\circ}_{Cu^{+2}/Cu} = 0.34\,V$

$E^{\circ}_{cell} = 0.34 - (-0.76) = 1.1\,V$

Example $E^0_{Zn|Zn^{+2}} = 0.76$; $E^0_{Cu|Cu^{+2}} = -0.34V$

$E^0_{cell} = 0.76 + 0.34 = \boxed{1.1V}$

Example $E^0_{Zn|Zn^{+2}} = 0.76V$; $E^0_{Cu|Cu^{+2}} = 0.34V$

$E^0_{cell} = 0.76 + 0.34 = \boxed{1.1V}$

Example $E^0_{Cu|Cu^{+2}} = -0.34V$; $E^0_{Zn^{+2}|Zn} = -0.76V$

$E^0_{cell} = 0.76 + 0.34 = \boxed{1.1V}$

Standered Hydrogen electrode

Anode ; $H_2 \longrightarrow 2H^+ + 2e$ at anode ; $Pt_{(s)}|H_2|H^+||$

Cathode ; $2H^+ + 2e \longrightarrow H_2$ at cathode ; $||H^+|H_2|Pt_{(s)}$

$\boxed{E_{H_2|H^+} \longrightarrow 0}$ $\boxed{E_{H^+/H_2} = 0}$

concept

$E^0_{Fe^{+2}|Fe} = 0.41V$; $E_{Ag^+|Ag} = 0.85V$

Fe should be used as anode & Ag should be used as cathode. $E^0_{Li^+|Li} = -3.05V$ → best reducing agent (to be used as anode)

$E^0_{F_2|F^\ominus} = 2.87V$ → best oxidising agent (to be used as cathode)

In electrode potential series $E^0_{Li^+/Li} = -3.05V$; $E^0_{F_2|F} = 2.87V$

If we want to make feasible reaction then;

$\boxed{\Delta G < 0}$ free energy $G = -nFe$

n = no. of e⁻ in half cell rxn.
F = charge on faraday.
e = electrode Potential.

$$1F = 6.023 \times 10^{23} \times 1.6 \times 10^{-19} C$$
$$= 9.638 \times 10^4 = 96368\ C \simeq \boxed{96500\ 0}$$

for feasible $\Delta G < 0$; so for any feasible reaction $\boxed{E > 0}$

E → Inetensive property → independent of mass.

ΔG → Extensive Property → dependent on Mass.

Ques $E^\circ_{Cu^{+2}/Cu} = 0.34$; $E_{Li^+/Li} = -3.05\,V$; $E_{Cu^{+2}/Cu} = -0.74\,V$

$E^\circ_{Ag^+/Ag} = 0.85\,V$, find the reaction is feasible or not?

$3Ag + Cu \longrightarrow 3Ag^+ + Cu$

Soln $E^\circ = (E_{anode})_{oxi} + (E_{cathode})_{red.}$

$-0.85 - 0.74 < 0$

Not feasible

Solutn $2Li + Cu^{+2} \longrightarrow 2Li + Cu$

$\Rightarrow 3.05 + 0.34 > 0$

feasible

Soln $Cu + 2HCl \longrightarrow ?$

$Cu + 2HCl \longrightarrow Cu^{+2} + H_2$

$E^\circ = -0.34 + 0 < 0$

Not feasible

solutn $Li + HCl \longrightarrow ?$

$Li + 2HCl \longrightarrow Li^+ + H_2$

$E^\circ = 3.05 - 0 > 0$

feasible

NOTE If metal will react with acid, then it will envolve hydrogen gas if metal is present above Hydrogen in electrode potential series.

- As the electrode potential of electrode will decrease Its reducing nature will decrease.
- As the reduction potential of electrode will increase Its reducing nature will decrease.

Reduction Potential Order

Li K Ba Sr Ca Na Mg Al Zn Cr Fe Cd Co Ni Sn

लिक बसरका नाम गाल जिंकफी कुडकोनी Sn Pb H कुरंग

PbH Cu Hg Ag Pt Au

आग परायु

$F_2 > Cl_2 > Br_2 > I_2$

NERNST EQUATION

$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$

where ΔG = free energy of electrode
ΔG° = free energy at standered cond
Q = reaction quotient.

$\boxed{\Delta G = -nfE}$

$\Rightarrow -nfE = -nfE^\circ + RT\ln Q$

$\Rightarrow -nf(E^\circ - E) = RT\ln Q$

$\Rightarrow (E^\circ - E) = \frac{-RT\ln Q}{nf}$

$\Rightarrow E = E^\circ - \frac{RT\ln Q}{nf}$

$$\boxed{E = E^\circ - \frac{0.0591}{n}\log_{10} Q}$$ → Nersnt Equation

This equation can be used for cell potential as well as for electrode potential.

$$\frac{RT\ln Q}{nf} = \frac{8.314 \times 298}{2.303 \times n}\log_{10} Q$$
$$= \frac{0.0591}{n}\log_{10} Q$$

Example Zn|Zn⁺²||Cu⁺²|Cu

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

$\cancel{2}e^- + Cu^{+2}_{(aq)} \longrightarrow Cu_{(s)}$

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

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

$\boxed{E_{cell} = 1.1 - \frac{0.0591}{n}\log\frac{[Zn^{+2}]}{[Cu^{+2}]}}$

When $\frac{0.0591}{n}\log\frac{[Zn^{+2}]}{[Cu^{+2}]}$ is equal to 1.1, the cell will will stop working.

E_{cell} can't be zero or negative $E_{cell} \nleq 0$

If we get $E_{cell} = 0$ in calculation, then it means reaction is not complete; it is at equillibrium $\boxed{Q_c = K_c}$

$\Delta G = \Delta G^\circ + RT\ln K$ $\because \Delta G = 0$

$\Delta G^\circ = -RT\ln K$

$\ln K = \frac{-\Delta G^\circ}{RT}$

$$\boxed{K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{+nFE^\circ}{RT}}}$$

CONCENTRTON CELL

When anode and cathode are of same metal electrode It is called concentration cell.

The value of $E^\circ_{cell} = 0$ because $\boxed{E^\circ_{cell} = E_{cathode} + E_{anode} = 0}$

Example $Ag | \underset{xm}{Ag^+} || \underset{ym}{Ag^+} / Ag$

$$Ag \longrightarrow Ag^+ + e^-$$
$$Ag + e^- \longrightarrow Ag$$
$$\underset{(anode)}{Ag^+} + Ag \longrightarrow \underset{(cathode)}{Ag^+} + Ag$$

↳ $Q = \dfrac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$

↳ $E_{cell} = 0 - \dfrac{0.0591}{n} \log \dfrac{[Ag^+]}{[Ag^+]}$ ⇒ $\boxed{-\dfrac{0.0591}{n} \log \dfrac{x}{y} = E_{cell}}$

Quest Calculate E°_{cell} for the cell made of electrodes.

$E^\circ_{Ag | Ag^+} = -0.80V$ $\quad E^\circ_{MnO_4^- / Mn^{+2}} = 1.51V$

Ans. $E^\circ_{cell} = (E^\circ_{oxi}) + (E^\circ_{red}) \Rightarrow -0.80 + 1.51$

Cathode = MnO_4^- $\quad \Rightarrow \boxed{0.71V}$

Anode = Ag

Quest Check wheather following cell is feasible or not?

$\underbrace{Ag_{(s)} | Ag^+_{(aq.)}}_{-0.84V} || \underbrace{Cu^{+2}_{(aq)} / Cu_{(s)}}_{0.34V}$

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

Ans. $E^\circ_{cell} = -.84 + 0.34$

$= \boxed{-0.50V}$ Not feasible

Calculation of SRP → We will calculate SRP of an electrod from SRP of other electrode

SRP - Standered reduction Potential

Ex: $E^\circ_{Cu^{+2}|Cu} = 0.337$ $E^\circ_{Cu^{+2}/Cu^+} = 0.153V$ $E^\circ_{Cu^+/Cu} = ?$

$Cu^{+2} + 2e \longrightarrow Cu$ $\Delta G_1 = -2FE^\circ_1$ $-E^\circ = -2\times 0.337 + 0.153$

$Cu^{+2} + 2e \longrightarrow Cu^+$ $\Delta G_2 = -FE^\circ_2$ $E^\circ = 2\times 0.337 - 0.153$

$Cu^+ + e \longrightarrow Cu$ $\Delta G_3 = -FE_3$ $E^\circ = 0.674 - 0.154$

$\boxed{\Delta G_3 = G_1 - G_2}$ $\boxed{0.521V}$

Example Calculate $E^\circ_{MnO_4^-|MnO_2}$; $E^\circ_{MnO_4^-|Mn^{+2}} = 1.51V$

$E_{MnO_2|Mn^{+2}} = 1.23V$

$MnO_4^- + 5e \longrightarrow Mn^{+2}$ $\Delta G_1 = -5FE_1$

$MnO_2 + 2e \longrightarrow Mn^{+2}$ $\Delta G_2 = -2FE_2$

$MnO_4 + 3e \longrightarrow MnO_2$ $\Delta G_3 = -3FE_3$

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

$-3FE^\circ_3 = +2FE_2 - 5FE_1$

$3E_3 = -2\times 1.23 + 5\times 1.51$

$3E^\circ = -2.46 + 7.55$

$\boxed{E_3 = 1.69V}$

ΔG° is an extensive property while E° is an intensive. Therefore we can add and subtract according ΔG equation.

Example Pridict whether the following equation will take place or not ?

$Cu_{(s)} + 2H_{(aq.)} \longrightarrow Cu^{+2}_{(aq)} + H_{2(g)}$ $E^\circ_{Cu^{+2}/Cu} = 0.34$

$E_{H^+/H_2} = 0$

$E^\circ_{cell} = (E^\circ_{anode}) + (E^\circ_{cath.})$ $\Rightarrow -0.34 + 0$

$\Rightarrow \boxed{-0.34}$ Not feasible

Example Pridict feasibility of reaction

$E^\circ_{Fe^{+3}/Fe^{+2}} = 0.77V$ $E_{I_2/I^\ominus} = 0.54V$

$2Fe^{+3} + 2I \longrightarrow 2Fe^{+3} + I_2$

$E^\circ_{cell} = 0.77 - 0.54$

$= 0.23V$

does not depands on the stoichiometric cofficient.

Ques In which of the following solution oxidising power of $KMnO_4$ will be greater.

[A] 0.01 M H_2SO_4 sol   [B] 0.001 M H_2SO_4 soln.

In both cases concn of species are equal.

Ans. $E_a = E^\circ - \frac{0.0591}{5}\log\frac{[\cancel{Mn^{+2}}]}{[\cancel{MnO_4^-}][H^+]^8}$

$MnO_4^- + 8H + 5e^- \longrightarrow Mn^{+2} + 4H_2O$

$\log(2\times10^{-2})$

$-2\times\log 2$

-2×0.3010

$E_a = E^\circ + \frac{0.0591}{5}\times8\log[H^+]$

$(E_{RP})_a = E^\circ + \frac{0.0591}{5}8\log(2\times10^{-2})$

$(E_{RP})_a = E^\circ + \frac{0.0591}{5}\times8\times-2\times0.3010$

$= E^\circ - \frac{0.0591\times8\times1.7}{5}$

$\boxed{(E_{RP})_a > (E_{RP})_b}$

$(E_{RP})_b = E^\circ - \frac{0.0591\times8\times2.7}{5}$

oxidising power of a>b

Ques Caclutae $E_{Cu^{+2}/Cu}$ at pH=14. Given that K_{sp} of $Cu(OH)_2 = 10^{-19}$ and $E_{Cu^{+2}/Cu} = 0.34$ at 298K.

Ans. pH = 14 $[H^+] = 10^{-14}$; $[OH] = 1$; $Cu^{+2} = 10^{-19}$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{1}{Cu^{+2}}$ $Cu^{+2} + 2e^- \longrightarrow Cu$

$E_{cell} = 0.34 - \frac{0.0591}{2}\log\frac{1}{10^{-19}} \Rightarrow 0.34 - 0.0295\times19$

$= \boxed{-0.22V}$

Ques for concn cell ; $E_{cell} = 0.029$ V at 298 K Calculate n=?

$X_{(s)} | X^{n+}_{aq} \,||\, X^{n+}_{(aq)}\,)\, X_{(s)}$

$(\frac{1}{20}M)$ $(\frac{1}{2}M)$

$X \longrightarrow X^{n+} + e^-$

$X^{n+} + e^- \longrightarrow X$

$X^{n+} + Y \longrightarrow X^{n+} + X$

Ans. $0.029 = E^\circ - \frac{0.0591}{n}\log\left(\frac{1}{10}\right)$

$0.029 = E^\circ + \frac{0.0591}{n}$ $\boxed{E^\circ_{cell} = 0}$

$n = \frac{0.0591}{0.029} = \boxed{2 \text{ Ans}}$

Quest ① A Hydrogen electrode is immersed in a solution $p^H = 0$ (HCl). By How much will the the reduction potential change if an equivalent amount of NaOH is added to this solution so that solution become neutral. ($P_{H_2} = 1$ atm)

Ans. $p^H = 0$ $p^{OH} = 14$ $[OH^-] = 10^{-14}$ $[H^+]_i = 1$ initial

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

$$(E_{cell})_i = 0 - \frac{0.0591}{2} \times 0$$

$$= 0$$

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

$$Q = \frac{[H_2]}{[H^+]^2} \Rightarrow (E_{cell})_f = 0 - \frac{0.0591}{2} \times \log \frac{[H_2]}{[H^{+2}]}$$

$$= \frac{-0.0591}{2} \times \log 10^{-14}$$

$$E_{change} = E^\circ_{final} - E_{initial}$$

$$= \boxed{0.4137\,V}$$

$$= \boxed{0.4137}$$

Quest ① E_{cell} of $Pt_{(s)} | \underset{1atm}{H_2} | \underset{Ka_1}{HCOOH} || \underset{Ka_2}{CH_3COOH} | H_2 | Pt_{(s)}$; Calculate $E^\circ_{cell} = ?$

Ans.

$$H_2 \longrightarrow 2H^+ + 2e^- \text{ (anode)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (cathode)}$$

$$\underset{(C_1 - x)}{HCOOH} \longrightarrow \underset{x}{HCOO^-} + \underset{x}{H^+}$$

$$\hookrightarrow E_{cell} = 0 - \frac{0.0591}{2} \log \frac{1 \times (\sqrt{C_1 Ka_1})^2}{1 \times (\sqrt{C_2 Ka_2})^2}$$

$$\hookrightarrow E_{cell} = \frac{-0.0591}{2} \log \frac{C_1 Ka_1}{C_2 Ka_2}$$

$$\boxed{E_{cell} = \frac{0.0591}{2} \log \frac{C_2 Ka_2}{C_1 Ka_1}}$$

Ques.① Calculate E_{cell} for $Pt | H_{2(g)} | \underset{\alpha = 75\%}{1N\ KOH} | \underset{\alpha = 90\%}{\frac{N}{10}\ HCl} | H_{2(g)} | Pt_{(s)}|$

Solⁿ

$$\underset{1-x}{KOH} \longrightarrow \underset{x}{K^+} + \underset{x}{OH^-}$$

$x = 0.75$ $[OH^-] = 0.75$

$[H^+] = 1.3 \times 10^{-14}$

$$\underset{\frac{1}{10} - x}{HCl} \longrightarrow \underset{x}{H^+} + \underset{x}{Cl^-}$$

$x = 0.09$

$x = 9 \times 10^{-2}$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \left[\frac{(\frac{4}{3} \times 10^{-14})^2}{(9 \times 10^{-2})^2} \right] \Rightarrow -\frac{0.0591}{2} \times 2 \log \left[\frac{4}{7} \times 10^{-12} \right]$$

$$\Rightarrow -0.0591 \left[\log \frac{4}{27} - 12 \right] \Rightarrow 12.48 \times 0.0591 \Rightarrow \boxed{0.737V}$$

Ques At 298 K, the equillibrium constant for reaction $Zn + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{+2}$ is 10^9. If $E^\circ_{Zn^{+2}/(Zn+4NH_3)} = -1.03\,V$ then value of $E_{Zn|Zn^{+2}} = ?$

Ans.

$$10^9 = \frac{[Zn(NH_3)_4]^{+2}}{[Zn^{+2}]}$$

$$E = E^\circ - \frac{0.0591}{2}\log 10^9$$

$$E = 1.03 - \frac{0.06}{2} \times 9$$

$$E = 0.76$$

$$Zn \longrightarrow Zn^{+2} + 2e^- = -2FE^\circ$$

$$Zn^{+2} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{+2} = 1.09\,V$$

$\Delta G = \Delta G^\circ + RT\ln Q$ At equlibrium $\Delta G = 0$

$$0 = \Delta G^\circ + RT\ln Q$$

$$-2FE^\circ + 8.31 \times 298 \times 9$$

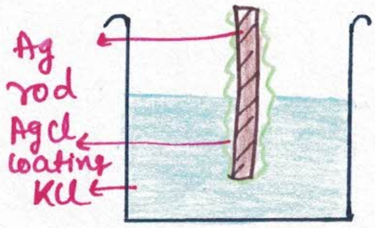
$$E^\circ = \frac{74.79 \times 298}{2 \times 96500} = \boxed{E = 0.77\,V}$$

Type of electrodes

Metal-Metal soluble salt electrode → Metal rod dipped in its own solution $Ag|AgNO_3$, $Cu|CuSO_4$.

Gas-electrode → $Pt|H_2|H^+$ ⇝ Hydrogen electrode

Metal- metal Insoluble salt electrode → In this half cell a metal coated with its insoluble salt in contact with a solution containing the anion of Insoluble salt.



This electrode can be used as cathode or anode, the solution have $Cl^\ominus$ ion that will give priciptation of AgCl.

At anode ⇐

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

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

$$Ag_{(s)} + Cl^-_{(aq.)} \longrightarrow AgCl + e^-$$

$$\boxed{Ag_{(s)}/AgCl_{(s)}/Cl^\ominus||}$$

at cathode

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

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

$$AgCl_{(s)} + e \longrightarrow Ag_{(s)} + Cl^-_{(aq.)}$$

$$\boxed{||Cl^\ominus/AgCl_{(s)}|Ag_{(s)}}$$

Quest. ① Calculate Ksp of AgI with the help of following cell.

$Ag | AgI_{(s)} | \underset{0.05}{KI} || \underset{0.05}{AgNO_3} | Ag_{(s)}$

Ecell = 0.7884 V at 298K.

Ans.

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

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

$Ag + Ag^+ \qquad Ag + Ag^+$

$E_{cell} = 0.7884 \quad E^0_{cell} = 0$

$Ag^+_c = 0.05\ M$

$\Rightarrow E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{Ag^+_a}{Ag^+_c}$

$\Rightarrow 0.7884 = 0 - \frac{0.0591}{1} \log \frac{Ksp}{[25 \times 10^{-4}]}$

$[Ag^+][I^-] = Ksp$

$[Ag^+] \times 0.05 = Ksp$

$[Ag^+]_a = \frac{Ksp}{0.05}$

$\Rightarrow \frac{-0.7884}{0.06} = \log \frac{Ksp}{25 \times 10^{-4}} \quad \Rightarrow \log \frac{K_{sp}}{25 \times 10^{-4}} = 1.3$

$\Rightarrow K_{sp} = 25 \times 10^{-4} \times 10^{-13} \quad \Rightarrow \boxed{Ksp = 2.5 \times 10^{-16}}$

To find Ksp of Ag|AgCl insoluble salt electrode use;

$$\boxed{E^0_{Cl|AgCl|Ag} = E^0_{Ag|Ag} + 0.059 \log [Ksp(AgCl)]}$$

Ques ② A graph is plotted b/w Ecell and $\log \frac{[Zn^{+2}]}{[Cu^{+2}]}$ the curve was linear with Interact on cell axis equal to 1.1 V. Calculate Ecell for $Zn | \underset{0.1}{Zn^{+2}} || \underset{0.01 M}{Cu^{+2}} | Cu$

Ans

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

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

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

$Zn^{+2} = 0.1 = 10^{-1}$

$Cu^{+2} = 0.01 = 10^{-2}$

$\Rightarrow E_{cell} = 1.1 - \frac{0.0591}{2} \log \frac{[10^{-1}]}{[10^{-2}]} \Rightarrow 1.1 - \frac{0.0591}{2}$

$\Rightarrow 1.1 - 0.029 \quad \Rightarrow \boxed{1.07 V}$

Quest ③ A standered Reduction potential of copper and silver are 0.34 V and 0.8V. A galvanic cell is constructed using Cu and Ag. Determine anode and cathode of cell, E°cell, cell potential when concn of Cu^{+2} and Ag^+ are 3×10^{-2} M and 1.73×10^{-3} M.

Ans. Ag ⟶ Cathode

Cu ⟶ Anode

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

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

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

$$E^{\circ}_{cell} = 0.8 - 0.34 = \boxed{0.46}$$

$$E = 0.46 - \frac{0.0591}{2} \log \frac{3 \times 10^{-2}}{3 \times 10^{-6}} = 0.46 - \frac{0.0591}{2} \times 4$$

$$= 0.46 - 0.1182 = \boxed{0.37}$$

Ques. The Emf of all $Pt_{(s)} | \underset{1atm}{H_2} | \underset{1.3 \times 10^{-3}}{HOCN} || \underset{0.8M}{Ag^{+}} | Ag_{(s)}$ is 0.982 V. Calculate Ka for HOCN if E°_{red} of electrode = 0.8 V.

Ans.

$$\underset{1.3 \times 10^{-3} - x}{HOCN} \longrightarrow \underset{x}{H^{+}} + \underset{x}{OCN^{-}}$$

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

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

$$2Ag^{+} + H_2 \longrightarrow 2H^{+} + 2Ag$$

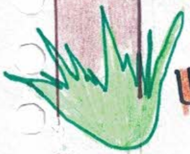
$$\frac{x^2}{1.3 \times 10^{-3} - x} = Ka$$

$$\Rightarrow x^2 = Ka \times 1.3 \times 10^{-3} - Ka\,x \qquad \Rightarrow x^2 + x\,Ka - 1.3 \times 10^{-3} Ka = 0$$

$$\Rightarrow Ka = \frac{x^2}{1.3 \times 10^{-3} - x} \qquad \Rightarrow 0.982 = 0.8 - \frac{0.0591}{2} \log \frac{[H^{+}]^2}{[Ag^{+}]^2 H_2}$$

$$\Rightarrow \frac{-0.364}{0.064} = \log \frac{[H^{+}]^2}{Ag^{+}} \qquad \Rightarrow \frac{[H^{+}]^2}{[Ag^{+}]^2} = 10^{-6}$$

$$\Rightarrow [H^{+}]^2 = 10^{-6} \times 64 \times 10^{-2} \qquad \Rightarrow [H^{+}] = 8 \times 10^{-4}$$



$$\Rightarrow Ka = \frac{64 \times 10^{-8}}{1.3 \times 10^{-3} - 8 \times 10^{-4}} = \frac{64 \times 10^{-8}}{5 \times 10^{-4}} = \boxed{1.28 \times 10^{-3} = Ka}$$

THERMODYNAMICS OF CELL

$$G = H - T\Delta S \quad \text{— (i)}$$

$$H = U + PV \quad \text{— (ii)}$$

$$dQ = dU + PdV \quad \text{(iii)}$$

$$dS = \frac{dQ}{T} \quad \text{(iv)}$$

$$\Rightarrow dG = dH - TdS - SdT$$

$$\Rightarrow dH = \underbrace{dU + PdV}_{dQ} + VdP$$

$$\Rightarrow dH = dQ + VdP$$

$$\Rightarrow dG = dQ + VdP - TdS - SdT$$

$dG = T\cancel{dS} + VdP - T\cancel{dS} - SdT$

$\boxed{dG = VdP - SdT}$

at constant P $(dP=0)$ = $dG = -SdT$

$S = -\dfrac{dG}{dT}$ $\Delta S = -\dfrac{d\Delta G}{dT}$

$\Delta H = \Delta G + T\Delta S$

$$\boxed{\Delta H = -nfE_{cell} + \frac{nfT\,dE_{cell}}{dt}}$$

$$\boxed{\Delta S = \frac{nf\,dE_{cell}}{dt}}$$

$$\boxed{\frac{dE_{cell}}{dt} \Rightarrow \text{Temprature Cofficient}}$$

Remember only –

$\Delta S = nf\left[\dfrac{dE_{cell}}{dT}\right]$

$\Delta G = nfE$ By using we can find –

$\Delta H = \Delta G + T\Delta S$

$\Delta C_P = nfTd^2$

HEAT CAPACITY

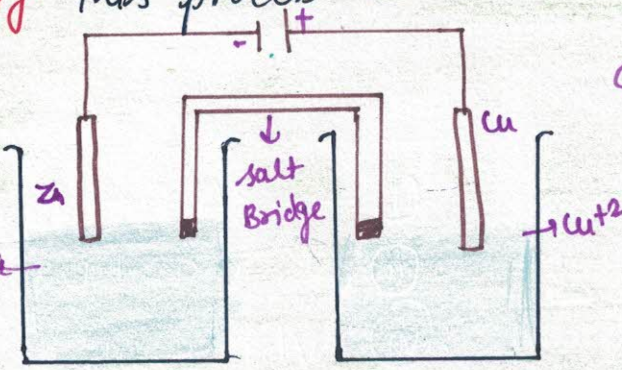
$$\boxed{C_P = \frac{d(\Delta H)}{dT}}$$

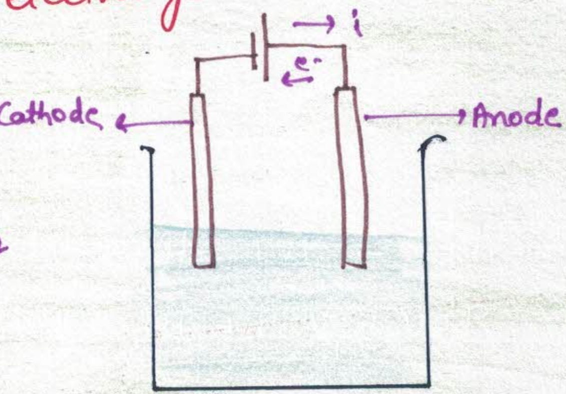
$$\boxed{C_P = \frac{TnF\,dE}{dT^2}}$$

Enthaphy $\Delta H = \Delta G + T\Delta S = -nfE + Tnf\left(\dfrac{dE}{dT}\right)_P$

ELECTROLYSIS

It is reverse process of elecoro-chemical cell. If we will apply external potential that is more than potential of electrochemical cell. then process will reverse and electrical energy will be converted into chemical energy. This process is called electrolysis.





electrolysis is process of decomposition of an electrolytes.

on passing electrical current through its aquous solution in its molten state. The cell used for this process is called electrolysis cell. In this anode will be electrode connected with positive terminal of battery and cathode will be electrode connected with negative terminal of the battery.

- During electrolysis, cation will be attracted towards cathode and will get neutrilised after accepting e^- from cathode.
- Anions will be ~~attracted~~ attracted towards anode and will get neutrilised after releasing extra charge

At cathode :- $A + e^- \longrightarrow A$

At anode :- $B^- \longrightarrow B + e$

Oxidation and reduction of water

Reduction :—

$H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH$

oxidation :—

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

- In case two or more type of potential (positive and negative) ions prnt in solution during electrolysis, certain ions are discharged and libirated at the electrode in preference to other.
- In genral such competition, the ion which are stronger oxidising agent is discharged first at cathode (high reduction potential)

Similarly ion which is stronger reducing agent will get deposit first at anode [low reduction potential]

Order of Decomposit^n

Li^+, K^+, Na^+, Mg^+, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}

Increasing order of Decomposition

Increasing order of depasition :- SO_4^{-2}, NO_3^-, OH^- Cl^-, Br^-, I

Electrolysis of Molten $PbBr_2$

$PbBr_2 \longrightarrow Pb^{+2} + 2Br^-$

At Anode :- $Pb^{+2} + 2e^- \longrightarrow Pb_{(s)}$

at Cathode :- $2Br^- \longrightarrow Br_2 + 2e^-$

$$\boxed{Pb^{+2} + 2Br^- \longrightarrow Pb_{(s)} + Br_{2(g)}}$$

Electrolysis of NaCl & $PbBr_2$

At anode :- $2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

At cathode :- $Pb^{+2} + 2e^- \longrightarrow Pb_{(s)}$

$$\boxed{Pb^{+2} + 2Cl^- \longrightarrow Pb_{(s)} + Cl_{2(g)}}$$

Electrolysis of aq. $CuSO_4$

$(\overset{\checkmark}{Cu^{+2}}, H_2O)$ $\Downarrow$ cathode

$(SO_4^{-2}, \overset{\checkmark}{H_2O})$ $\Downarrow$ anode

At anode :- $Cu^{+2} + 2e^- \longrightarrow Cu$

At cathode :- $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Electrolysis of NaCl (Molten

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

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

$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$

$$\boxed{2Na^+ + 2Cl^- \quad 2Na + Cl_{2(g)}}$$

Electrolysis of aq. NaBr

$H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Cathode $= (Na^+, \overset{\checkmark}{H_2O})$

$(H_2O_{R.P} > Na^+_{R.P})$

Anode $\Rightarrow$ Br^-, H_2O

$(\overset{\checkmark}{H_2O}_{R.P}) > (Br^-_{R.P})$

NOTE

- During electrolysis of aquous solution of electrolyte same time water will involve in electrode reaction rather than ion derived from solute

At anode :- $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ $E^\circ_{red} = -1.23V$

At cathode :- $2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$ $E^\circ_{red} = 0.83V$

- In electrolysis of aquous NaCl oxidation of H_2O at anode is not kinetically favoured (as activation energy of oxidation of H_2O is high) because of Over potential
- On electrolysis of aq. NaCl, the solution becom Basic

FARADAY LAW

The weight or amount of any substance during electrolysis will be propostional to amount of charge passed during electrolysis.

Mathematically, $W \propto Q$ $\quad W = ZQ \quad [Q = i \times t)$

$\boxed{W = Zit}$ where z is proportionality constant. z = electrochemical equivalent.

$i = \frac{dq}{dt} \Rightarrow dq = i\,dt$ $\quad \boxed{Q = \int i\,dt}$

Faraday's Second Law

On applying same charge in different electrodes, then amount of deposited metal or substance will be proportional to its equivalent weight

For this we should connect the electrode in series as they should have charge

When 1 mole of charge applied.

$Na + e^- \longrightarrow Na$ $\quad$ Na formed = 1 mole (M = 23)

$Cu^{+2} + 2e^- \longrightarrow Cu$ $\quad$ Cu formed = 1/2 mole (M = 63.5/2)

$Al^{+3} + 3e^- \longrightarrow Al$ $\quad$ Al formed = $\frac{1}{3}$ mole (M = 27/3)

$$\boxed{\text{Eq. Wt} = \frac{\text{Molar Mass}}{n\text{-factor}}}$$

$W_1 = Z_1 \times F$

$E_1 = Z_1 \times F$

$Z_1 = \frac{E_1}{96500}$

$W_2 = Z_2 \times F$

$E_2 = Z_2 \times F$

$Z_2 = \frac{E_2}{96500}$

In this example with one mole e- charge we are getting 23g Na 31.7g Cu, 9gm Al i.e equivalent mass of each metal.

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

According to Faraday's Ist Law $W = ZQ$

for two electrodes on applying 1 faraday charg i.e 96500 we get the equation derived before i.e

$$Z = \frac{E}{96500} \qquad W = Zit \qquad W = \frac{Eit}{96500}$$

Question How many colomb of charge required for following reactions:-

(i) $Cu^{+2} \longrightarrow Cu$ (1 mol) (2.) $MnO_4^- \longrightarrow Mn^{+2}$

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

2 mole e^- required i.e

$2 \times 96500 = 193000C$

$\boxed{1.93 \times 10^5 C}$

(2) $Mn^{+7} + 5e^- \longrightarrow Mn^{+2}$

5 mole e^- required

$5 \times 96500 =$

$\boxed{4.825 \times 10^5 C}$

Question How many gram of Cu will get deposited by passing 2A for 30 minutes in aquous $CuSO_4$ solution and what will be wt. of O_2 relased at anode?

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

$E = \frac{63.5}{2}$

$W = \frac{Eit}{F} = \frac{63.5 \times 2 \times 30 \times 60}{2 \times 96500}$

$\Rightarrow \boxed{1.18g}$

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

$E = \frac{32}{4} = 8gm.$

$W = \frac{Eit}{F} = \frac{8 \times 2 \times 30 \times 60}{96500}$

$\Rightarrow \boxed{0.29g}$

Question Silver is electro-deposited on a vessel of total surface area 800 cm^2 by passing a current of 0.2A for 3Hours. Calculate the thick mass of silver deposited (density of silver is deposited is 9.67 g/cm^3

$W = \frac{Eit}{F} = \frac{108 \times 0.2 \times 3 \times 60 \times 60}{1 \times 96500} \Rightarrow \frac{7776 \times 3}{9650} =$

$\boxed{2.41g}$

$$800 \times \text{Thickness} \times 9.67 = 2.41$$

$$\text{Thickness} = \frac{2.41}{800 \times 9.67} = \frac{1}{4 \times 800} = \frac{1}{3200} = 0.0312 \times 10^{-2}$$

$$\Rightarrow \boxed{3.12 \times 10^{-4}\,\text{cm}}$$

Question In an aquous solution of silver nitrate a variable current is passed for 4 second. Calculate of silver deposited.

$i = 2t \quad 0 \leq t \leq 2$

$i = 8.2t \quad 2 \leq t \leq 4$

$$q_1 = \int i\,dt \Rightarrow 2\int_0^2 t\,dt \Rightarrow 2\left[\frac{t^2}{2}\right]_0^2 = 4C$$

$$q_2 = i\int dt \Rightarrow 8.2\int t\,dt \Rightarrow 49.2C$$

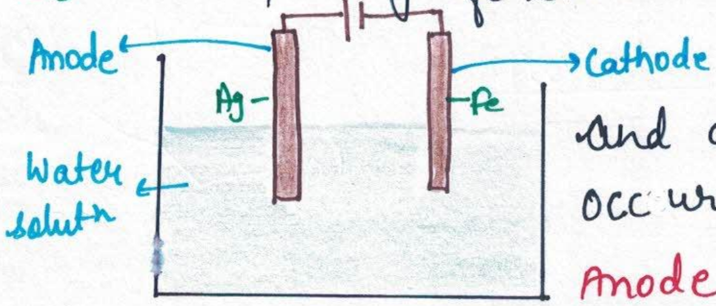
$$W_1 = \frac{108 \times 4}{96500} \qquad W_2 = \frac{108 \times 49.2}{96500}$$

$$W = W_1 + W_2 \Rightarrow \frac{108}{96500}(4 + 49.2) \Rightarrow \frac{5745.6}{96500}$$

$$\Rightarrow \boxed{0.0059\,g}$$

Electroplatting

Electroplatting of sliver and Gold on the rod :-



In this process, at anode and at cathode following reaction will occur:-

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

$2H_2O \longrightarrow O_2 + 4H^+ + 4e$

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

$H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Ag will deposit from anode to iron on the Cathode. Fe will not deposite as Ag is more preferable than Fe.

ELECTROLYTIC CONDUCTION

Conduction are two types —

1. Electronic conductor
2. Electrolytic Conductor

Electronic Conductor

In this type of conductor, flow will be due to electron.

- There will be no decomposition of any electrode
- On increase the Temprature resistance will increase.

Electrolytic Conductor

This conduction is due to ions. When current is passed, there will be decomposition of electrolytes (WA, SA, WB, SB, salt)

- On increase temprature resitance will decrease due to more production of charge carriers.

factor affecting electrolytic conductance

- Nature of electrolyte
- Nature of solvent
  - [Polar] ⇓ More conductance
  - [non-polar] ⇓ Less conductance
- Concentration :- $Conc^n$ ↑ conductance ↓
- Temprature on increasing Temprature conductivity will ↑e

Some Defination

Resistance (R)

- It is hindrance provide by conductor in passage of curren

  (R is expressed in ohm)
- Resistance symbol is Ω
- The resistance (R) of a conductor is directly proportional to its length and Inversly proportional to cross section Area (A)

$R \propto l$ —①

$R \propto \frac{1}{A}$ —②

from equation ① & ② $\Rightarrow R \propto \frac{l}{A} \Rightarrow \boxed{R = \frac{\rho l}{A}}$

ρ = constant [resistivity constant]

Ohm's Law The current carried out by a conductor is directly proportional to electrical potential difference b/w the two end of a conductor.

$V \propto I \Rightarrow \boxed{V = RI}$

Conductance (C & G) It is inverse of resistance. Its unit is Ω^{-1} or mho or ℧.

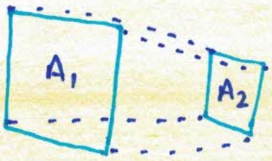
Conductivity It is also called specific conductance.

$$\boxed{\sigma = K = \frac{1}{\rho}}$$

$\sigma = K =$ conductivity.

$$R = \rho\frac{l}{A} \Rightarrow \frac{1}{R} = \frac{1}{\rho}\frac{A}{A} = \boxed{K = \underbrace{C}_{\text{conductance}}\frac{l}{A}}$$

Here, l is the distance b/w the two electrodes b/w the two electrodes. A is the Area of cross section of electrodes.



In such type of cells, the area we take is the common area. In this case area is A_2

$$\boxed{\frac{l}{a} = \text{cell constant}}$$

- Conductivity of conductor is reciprocal to its resistivity.
- l/a is known as cell constant in cm^{-1} and SI unit m^{-1}.
- Conductance is an additive property. e.g In aquous solution containing several electrolytes, the total conductance will be $\boxed{C_T = \Sigma c_i + C_{water}}$

Cwater is neglisible w.r.to Σc_i (3.5×10^{-5} S cm^{-1}) → Siemen.

[Σc_i = total conductance of all ion
Cwater = conductance of water.]

If electrodes are diffiault area of cross section, then common area of electrodes is taken as effective of cross section.

Question

Three different solution of same electrolyte & of same concn are prepared. find out which soln will have greater conductance and which has greater conductivity?

(i) Ist soln is prnt b/w two electrodes of area of cross section 5cm² & distance b/w electrodes is 2 cm.

(ii). IInd solution is prnt b/w two electrodes of area 4cm² & $l = 3$ cm.

(iii). IIIrd solution = $A = 2\text{ cm}^2$ $l = 1$ cm.

(1.) $K = C\frac{l}{A}$ $K_1 = C_1 \frac{2}{5}$

$K_1 = 0.4\ C_1$

$K_2 = 0.45 C_2$

$K_3 = 0.5\ C_3$

$K_1 = K_2 = K_3$

$\boxed{C_1 > C_3 > C_2}$

'Kappa' → K is constant than C will vary

NOTE
If conductivity is same for all the electrolytes then concn is also same for all electrolytes

Electrolytic Conductance

Specific conductance → conductance of a unit cube of soln is called its specific conductance.

Molar conductance → (Λ_m) The conductance of solution kept b/w the electrodes at unit distance apart and having area of cross section large enough to accomodate sufficient volume of solution that contain one mole of electrolyte

Equivalent conductance (λ_e):- It is defined as conductance of all the ions produced by one gram equivalent of electrolyte dissolved in V ml. of solution, when the distance b/w electrode is 1cm and area of electrode is so large that whole of the solution is contained b/w them.

$\boxed{\lambda_e = K \times V}$ ⇝ in ml. ⇒ equivalent of solute = 1.

In 100ml equivalent of solute = $\frac{1000}{V}$

$\frac{1000}{V} = N \Rightarrow \boxed{V = \frac{1000}{N}}$

$$\boxed{\lambda_e = \frac{1000K}{N}}$$

NOTE

Relation b/w K, λ_m, λ_e

$\lambda_m = V \times K$

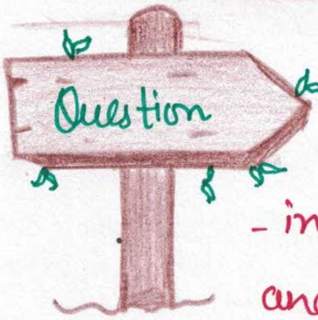
$\lambda_e = K \times V$

$m = \frac{1000}{V} = V = \frac{1000}{M}$

$\lambda_e = \frac{K \times 1000}{N}$

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

$\frac{\lambda_m}{\lambda_e} = \frac{N}{M} \Rightarrow \boxed{\lambda_e = \frac{\lambda_m}{n}}$



Specific conductivity of $\frac{1}{50}$ N KCl at 298 K is 0.001765 ohm^{-1} and resistance of cell containing the solution is 100 ohm. Calculate cell constant and find out λ_e of above solution.

$C = \frac{1}{100} \Rightarrow K = 0.001765$

↳ $K = C\frac{l}{A} \Rightarrow \frac{l}{A} = K \times C \Rightarrow 0.001765 \times 100$

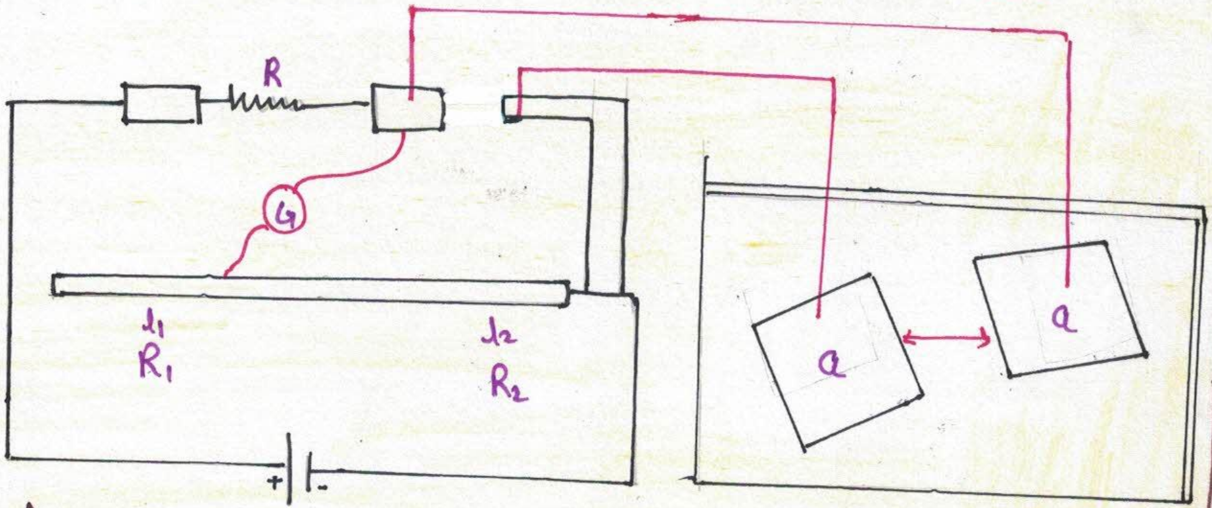
$\Rightarrow \boxed{0.176 \text{ cm}^{-1}}$

↳ $\lambda_m = K \times V$ $\qquad \lambda_E = \frac{1000K}{N}$

$\lambda_m = \frac{1000K}{V}$ $\qquad \lambda_E \Rightarrow \frac{1000 \times 0.001765 \times 50}{1}$

$\Rightarrow \boxed{88.250 \text{ mho}}$

Practical Measurement of K, C, $\wedge_m$, $\wedge_c$ of a soluth.



- It is based on balance wheat stone bridge.
- This Instrument is called meter bridge.
- In this we have one meter long bridge wire of known substance has resistance proportional to its length and one known resistance Ro. If bridge is balanced with this electrolytic cell, then we can apply —

$$\frac{R_1}{R_0} = \frac{R_2}{R'} \Rightarrow R' = \frac{R_0 R_2}{R_1} = \frac{R_0 R_2}{l_1}$$

where R' is the resistance of electrolytic cell. Its reciprocal is conductance.

- Electrolytic cell, we have its cell constant & concn of cell. $C = \frac{1}{R}$, $K = \frac{Cl}{A}$

$$\wedge_m = \frac{1000\,K}{M}$$

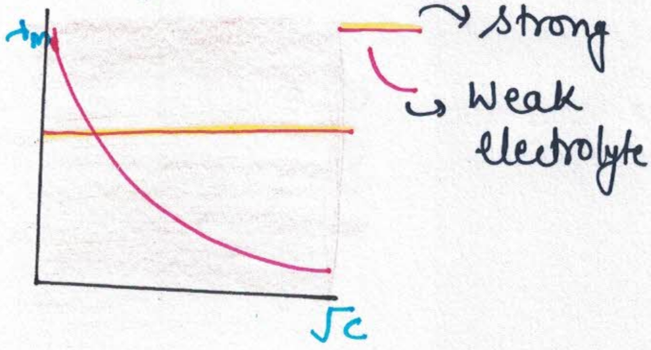
$$\wedge_e = \frac{1000\,K}{N}$$

Variation of conductivity with dilution we are interested in conductivity now with dilution.

Variation of conductivity On dilution, specific conductance of solution will ↓es.

Variation of λ_m / λ_E on dilution, equivalent conductivity / molar conductivity will ↑es.

Variation of λ_m / λ_E with conc^n from strong electrolyte $\boxed{\lambda_m = \lambda_m^\infty - b\sqrt{c}}$ where b is the constant. This equation is given by Debye & Huckle.



- For same conc^n weak electrolyte as of strong electrolyte, the λ_m or λ_e value are very (↓es) Low in compairision to strong electrolyte.
- At ∞ dilution weak electrolyte will be 100% dissociated. So they have high value of λ_m / λ_e.
- In the case of strong electrolyte we can calculate λ_m^∞ λ_m^0 by extrapolation. but in the case of weak electrolyte we can't calculate
- At infinite dilution when dissociation of electrolyte is 100%, then we can calculate molar conductivity of electrolyte w.r. to their ions. This Law is called "Kohlraush Law"

Kohlrausch Law on Dilution

Name	Λ°_m	Differance	Name	Difference
KCl	235	35	NaCl	40
NaCl	200		NaBr	
KBr	195	35	KCl	40
NaBr	160		KBr	
KI	155	35	RbCl	40
NaI	120		RbBr	

- At Infinte dilution, each ion makes a definate contribut towards equivalent conductance of electrolyte irrespective of nature of ion with which it is associated.

- The value of equivalent conductance at Infinite dilution for any electrolyte is sum of contribution of its ions.

$$AB \longrightarrow A^- + B^-$$

$$(\Lambda^\circ_E)_{AB} = (\Lambda^\circ_E)_{A^+} + (\Lambda^\circ_E)_{B^-}$$

$$MgCl_2 \longrightarrow Mg^{+2} + 2Cl^-$$

$$(\Lambda^\circ_E)_{MgCl_2} = (\Lambda^\circ_E)_{Mg^{+2}} + (\Lambda^\circ_E)_{Cl^-}$$

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

$$(\Lambda^\circ_E)_{NaCl} = (\Lambda^\circ_E)_{Na^+} + (\Lambda^\circ_E)_{Cl^-}$$

$$BaCl_2 \longrightarrow Ba^{+2} + 2Cl^-$$

$$(\Lambda^\circ_E)_{BaCl_2} = (\Lambda^\circ_E)_{Ba^{+2}} + (\Lambda^\circ_E)_{Cl^-}$$

$$AlCl_3 \longrightarrow Al^{+3} + 3Cl^-$$

$$(\Lambda^\circ_E)_{AlCl_3} = (\Lambda^\circ_E)_{Al^{+3}} + (\Lambda^\circ_E)_{Cl^-}$$

$$A_xB_y \longrightarrow xA^+ + yB^-$$

$$(\Lambda^\circ_m)_{A_xB_y} = x(\Lambda^\circ_m)_{A^+} + y(\Lambda^\circ_m)_{B^-}$$

$$(\Lambda^\circ_m)_{AlCl_3} = (\Lambda^\circ_m)_{Al^{+3}} + 3(\Lambda^\circ_m)_{Cl^-}$$

$$(\Lambda^\circ_m)_{BaCl_2} = (\Lambda^\circ_m)_{Ba^{+2}} + 2(\Lambda^\circ_m)_{Cl^-}$$

Ques $(\Lambda^\circ_E)_{CH_3COOH} = ?$ if $(\Lambda^\circ_E)_{CH_3COONa} = a$; $(\Lambda^\circ_E)_{HCl} = b$; $(\Lambda^\circ_E)_{NaCl} = c$

Ans. $a = (\Lambda^\circ_E)_{CH_3COO^-} + (\Lambda^\circ_E)_{Na^+}$ $\quad b = (\Lambda^\circ_E)_{H^+} + (\Lambda^\circ_E)_{Cl^-}$

$c = (\Lambda^\circ_E)_{Na^+} + (\Lambda^\circ_E)_{Cl^-}$

$$\boxed{\begin{aligned}(\Lambda^\circ_E)_{CH_3COOH} &= (\Lambda^\circ_{CH_3COO^-}) + (\Lambda^\circ_E)_{H^+} \\ &= a + b - c\end{aligned}}$$

Ques $(\Lambda^\circ_m)_{CH_3COONa} = 91.6$ $\quad (\Lambda^\circ_m)_{HCl} = 425$ $\quad (\Lambda^\circ_m)_{NaCl} = 128.1\ \Omega^{-1}\,cm^{+2}\,mol^{-1}$

$(\Lambda^\circ_M)_{CH_3COOH} = ?$

Ans. $\Lambda^\circ_m CH_3COOH = a + b - c \Rightarrow 91.6 + 42\ \ - 128.1$

$\Rightarrow 516.6 - 128.1$

$\boxed{388.5\ \Omega^{-1}\ cm^{+2}\ mol^{-1}}$

Ques $(\Lambda^\circ_m)_{Ba(OH)_2} = 523.28$ $\quad (\Lambda^\circ_m)_{NH_4Cl} = 129.8\ \Omega^{-1}\,cm^2\,mol^{-1}$

$(\Lambda^\circ_m)_{BaCl_2} = 280$ $\quad (\Lambda^\circ_m)_{NH_4OH} = ?$

Ans.

↳ $523.28 = (\Lambda^\circ)_{Ba^{+2}} + 2(\Lambda^\circ)_{OH^-}$

↳ $129.8 = (\Lambda^\circ_m)_{NH_4^+} + (\Lambda^\circ_m)_{Cl^-}$

↳ $280 = (\Lambda^\circ_m)_{Ba^{+2}} + 2(\Lambda^\circ_m)_{Cl^-}$

$$\left[\begin{aligned} &2(\Lambda^\circ_m)_{NH_4^+} - (\Lambda^\circ_m)_{Ba^{+2}} = \\ &129.8 \times 2 - 280 \\ &\Rightarrow -20.4 \end{aligned}\right]$$

$2(\Lambda^\circ_m)_{NH_4^+} + (\Lambda^\circ_m)_{Ba^{+2}} = -20.4$

$2(\Lambda^\circ_m)_{NH_4^+} + (\Lambda^\circ_m)_{OH^-} = 523.28 - 20.4 \Rightarrow 502.88$

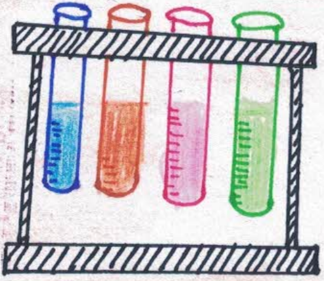
$(\Lambda^\circ_m)_{NH_4OH} = 251.44\ \Omega^{-1}\,cm^2\,mol^{-1}$

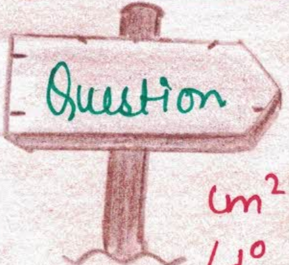
For calculation of degree of Dissociation for this we use Kohlrausch Law.

$$\boxed{\alpha = \frac{\Lambda_E}{\Lambda^\infty_E}}$$

$$K_{eq} = \frac{C\alpha^2}{1-\alpha}$$

$$\boxed{K_{eq} = \frac{c\left(\frac{\lambda_E}{\lambda_E^\infty}\right)^2}{1-\left(\frac{\lambda_E}{\lambda_E^\infty}\right)}}$$





Molar Conductivity of CH_3COOH at 298 K & conc^n of 0.1M & 0.01M are 5.28, 49.2 Ω^{-1} cm^2 mol^{-1}. Calculate α for conc^n given and $(\lambda^\circ_m)_{H^+} = 349.8$, $(\lambda^\circ_m)_{CH_3COO^-} = 40.9$

↳ $CH_3COOH \longrightarrow CH_3COO^- + H^+$

$\lambda^\infty = 40.9 + 349.8 \Rightarrow 370.17$

$\alpha = \frac{\lambda^\circ_H}{\lambda^\infty_H} =$ $\boxed{\alpha_1 = \frac{5.2}{390.7} = 0.013}$ $\boxed{(\alpha_2) = \frac{49.2}{390.7} = 0.125}$

Ionic Mobility

It is distance covered by ion per second under potential gradient of one volt /cm.

Potential Gradient ∘∘ It is ratio of potential difference across the electrode to distance b/w them.

Absolute Ionic Mobility ∘∘ It is mobility of ions at infinite dilution.

$$u = \frac{v}{V/L} = \frac{\text{speed}}{\text{potential gradient}} = \frac{\text{cm/s}}{\text{volt/cm}} = \boxed{\text{cm}^2\,\text{s}^{-1}\,\text{volt}^{-1}}$$

at infinite dilution, for any ion:—

$u_{C^+} \propto \lambda^\circ_{C^+} \Rightarrow$ $F\,u^\circ_{C^+} = \lambda^\circ_{C^+}$

$u_{A^-} \propto \lambda^\circ_{A^-} \Rightarrow$ $F\,u^\circ_{A^-} = \lambda^\circ_{A^-}$

Transport No.

for cation transport No. ⇒

$$\boxed{t_c = \frac{u_c}{u_c+u_a}}$$

for anion transport no. ⇒

$$\boxed{t_a = \frac{u_a}{N_c+u_a}}$$

Question

Molar conductivity at ∞ dilution for $K^+ = 64.34$ Ω^{-1} cm^2 mol^{-1}. In KCl solⁿ, what will be its ionic Molality for K^+ ion.

$$u^\circ_{K^+} = \frac{\lambda^\circ_{K^+}}{96500} = \frac{64.35}{96500} = \frac{6.6}{100\times100}$$ $$\boxed{6.6\times10^{-4}\ cm\ s^{-1}\ volt}$$

for sparingly soluble salt, molar conductivity,

$$\boxed{\Lambda_m = \frac{K\times1000}{s}}$$ → solubility of compound.

$$AgCl \longrightarrow \underset{s}{Ag} + \underset{s}{Cl^-}$$

Here s is solubility of AgCl, not Ag^+ & Cl^-

Ques. The conductivity of a standered solution of AgBr at 298 K is 8.5×10^{-7} $S\,cm^{-1}$. If $\lambda^\circ_{Ag^+}$ & $\lambda^\circ_{Br^-} = (62$ & $78)$ $S\,cm^2$ mol^{-1} find $S = ?$ $K_{sp} =$ AgBr

Ans. $\Lambda^\infty = 62+78 = 140\ S\,cm^2\,mol^{-1}$

$$\Lambda = \frac{1000K}{s} \Rightarrow s = \frac{1000K}{\Lambda} = \frac{1000\times8.5\times10^{-7}}{140}$$

$$K_{sp} = S^2 \Rightarrow \boxed{36\times10^{-12}} \qquad \Rightarrow S = \boxed{6\times10^{-6}}$$

Ques. Conductivity of a standered solution of $Co_2[Fe(CN)_6]$ is 2×10^{-6} $S\,cm^{-1}$. The conductivity of water used to prefer the solution is 8×10^{-7} $S\,cm^{-1}$. If ionic Molar conductivity of Co^{+2} and $[Fe(CN)_6]^{-4}$ are 80 and 440 $ohm^{-1}\,cm^2$ mol^{-1}. Calculate K_{sp} of $Co_2[Fe(CN)_6]$.

Ans.

$K_T = K_W + K_E \rightarrow$ electrolyte

$K_E = 2 \times 10^{-6} - 8 \times 10^{-7}$

$= (2 - 0.8) \times 10^{-6}$

$= 1.2 \times 10^{-6}$

$\Rightarrow \Lambda = \dfrac{1000K}{S} \Rightarrow S = \dfrac{1000K}{\Lambda}$

$\Rightarrow S = \dfrac{1000 \times 1.2 \times 10^{-6}}{600}$

$\Rightarrow \dfrac{1.2 \times 10^{-5}}{6} = \boxed{2 \times 10^{-6}}$

$K_{sp} = 4S^3$

$= 4 \times (2 \times 10^{-6})^3$

$= \boxed{32 \times 10^{-18}\ M^3}$

Ques. Calculate $(\Lambda_M^\infty)_{CaCl_2}$ & $(\Lambda_m^\infty)_{MgSO_4}$ if $\Lambda_{Ca^{+2}} = 119\ S\,cm^2\,mol^{-1}$

$\Lambda^\infty_{Cl^-} = 76.3\ S\,cm^2\,mol^{-1}$ $\Lambda^\infty_{Mg^{+2}} = 106\ S\,cm^2\,mol^{-1}$

$\Lambda^\infty_{SO_4^{-2}} = 160.5\ S\,cm^2\,mol^{-1}$

Ans.

$CaCl_2 \longrightarrow Ca^{+2} + 2Cl^-$

$\Lambda^\infty_{CaCl_2} = 119 \; 2 \times 76.3$

$= 119 + 152.6$

$\boxed{271.6\ S\,cm^2\,mol^{-1}}$

$\Lambda^\infty_{MgSO_4} = 106 + 160.5$

$\boxed{266.5\ S\,cm^2\,mol^{-1}}$

Ques. Λ°_m for NaCl, HCl, NaAc are 126.4, 425.9 & 91 $S\,cm^2\,mol^{-1}$ Λ°_m for HAc

Ans.

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

$HCl \longrightarrow H^+ + Cl$

$NaAc \longrightarrow Na^+ + Ac^-$

$HAc \longrightarrow H^+ + Ac^-$

$126.4 - 425.9 + \Lambda^\circ_{HAc} = 91$, $\Lambda_{HAc} = 91 + 425.9 \div 126.4$

$\boxed{390.5\ S\,cm^2\,mol^{-1}}$

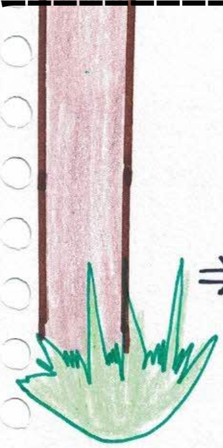
Ques. The Conductivity of 0.001028 M CH_3COOH is 4.95×10^{-5} $S\,cm^{-1}$ Calculate $K_a = ?$ if $(\Lambda^\circ_m)_{CH_3COOH} = 390.5\ S\,cm^2\,mol^{-1}$

Ans.

$M = 0.001028\ m$ $K = 4.95 \times 10^{-5}$

$\Lambda = \dfrac{1000K}{M} = \dfrac{1000 \times 4.95 \times 10^{-5}}{0.001028\ m} = \dfrac{4.95 \times 10^{-2}}{0.001028}$

$\alpha = \dfrac{\Lambda}{\Lambda^\circ_m} = \dfrac{4.95 \times 10^{-2}}{1.028 \times 10^{-3} \times 390.5}$

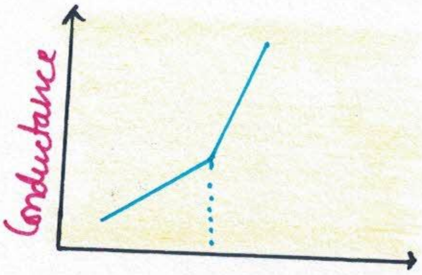


$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{1.028\times10^{-3} \times \left[\frac{4.95\times10^{-2}}{1.028\times10^{-3}\times390.5}\right]^2}{1-\left(\frac{4.95\times10^{-2}}{1.028\times10^{-3}\times390.5}\right)}$$

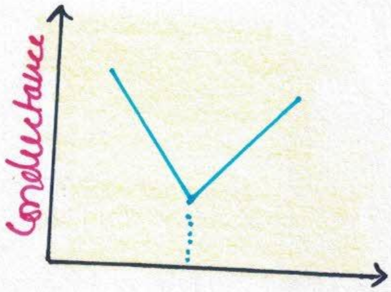
$$\Rightarrow \frac{\frac{22\times10^{-3}}{1528}}{1-\frac{48}{390.5}} = \frac{22\times10^{-3}\times390.5}{1528\times342.5} = \boxed{1.6\times10^{-5}\ Mol/L}$$

Graph

Weak acid + strong Base



Strong acid + Strong Base



In the case of electrolysis of aquous. NaCl at anode oxidation of water should occure but it is slow. If we apply high voltage then oxidation of chloride ion will occure and this potential is called over-voltage/ over potential.

$NaCl \longrightarrow Na^+ + Cl^-$ [concⁿ NaCl]

Cathode :- $2e^- + H_2O \longrightarrow H_2 + 2OH^-$

Anode :- $2Cl^- \longrightarrow Cl_2 + 2e^-$

$NaCl \longrightarrow Na^+ + Cl^-$ [dil NaCl]

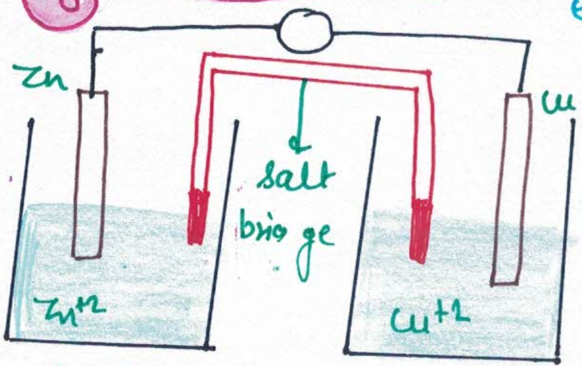
Cathode:- $2e + H_2O \longrightarrow H_2 + 2OH^-$

Anode:- $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Electro-chemistry Short Notes.

Electrochemical Cell

A device which can convert chemical energy to electrical energy.



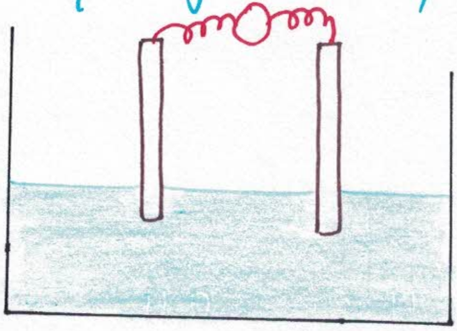
Direction of e⁻ ⇒ Anode to cathode

Direction of current ⇒ Cathode to anode

Salt-Bridge

A U-shape glass tube which is filled with a paste of any electrode (usually KCl) with agar-agar powder & dried.

There is No salt bridge used, then there is junction of liquid-liquid junction potential. → This decrease the potential of the cell.



$$\text{Potential of cell} = (E_{oxi})_{Anode} + (E_{red})_{cathode}$$

$$(E_{oxdi})_{Anode} = (-E_{red})_{Anode}$$

$$(E_{oxd})_{cathode} = (-E_{red})_{cathode}$$

Ex:- $\left[\begin{array}{l} E_{Zn|Zn^{+2}} = c \\ E_{Zn^{+2}|Zn} = -c \end{array}\right]$

At standered condition (1 atm, T=25°c) concⁿ of ion is taken to be 1 Molar.

Thus, at standered condition, E is written as E°.

Example $(E^\circ)_{Zn^{+2}/Zn} = -0.76\,V$ $\quad E^\circ_{Cu^{+2}/Cu} = 0.34\,V$

$$E^\circ_{cell} = [(E^\circ)_{oxid}]_{Anode} + [(E^\circ)_{red}]_{cathode}$$

$$0.76 + 0.34 = \boxed{1.1\,V}$$

At anode always oxidation occurs and vice-versa for cathode.

NOTE $E^\circ_{cell} > 0$ for the cell to work.

STANDERD HYDROGEN CELL ⇛

$H_2 \longrightarrow 2H^+ + 2e$ [Anode] $E^\circ_{oxi} = C$

$2H^+ + 2e^- \longrightarrow H_2$ [Cathode] $E^\circ_{red} = -C$

Thus $E^\circ_{cell} = (E_{oxi})_{Anode} + (E^\circ_{red})_{cathode}$

$C + (-C) = 0$

When cathode and anode is made up from one element then $E_{cell} = 0$

Gibbs free Energy ⇛

$\Delta G = -nFE$ $1F = 96500\,C$

$n \rightarrow$ no. of e^- tranffered

$\Delta G < 0$
$\Delta E > 0$ feasible

NOTE As reduction potential of electrode $\downarrow$es, reducing nature $\uparrow$es and vice versa.

Nerst Equation ⇛

$$E = E^\circ - \frac{0.0591}{n} \log_{10} Q$$

n = no. of e^- transfered
Q = Reaction Quotient

At equillibrium :- $Q = K_c$ $\Delta G = 0$

$\Delta G = \Delta G^\circ + RT\ln Q$

$$\boxed{-\Delta G = RT\ln K_c}$$

Faraday's Law of Electrolyte ⇛

$W = Zit$ $Z = \frac{E}{96500}$

W = amount of substance deposited during electrolytes

$Z = \frac{E}{96500}$, E = no. of equivalent i = current t = time

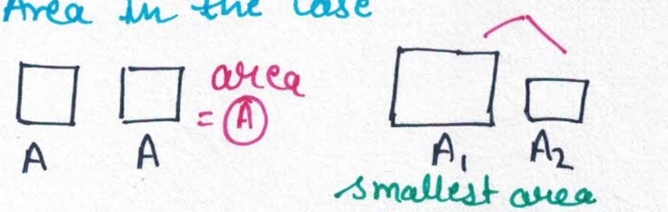
Electrolytic Conduction ⇛

$R = \rho \frac{l}{A}$ $\frac{1}{\rho} = \left(\frac{1}{R}\right)\frac{l}{A}$

$\frac{1}{\rho} = \sigma \rightarrow$ conductivity $\frac{1}{R} = C \rightarrow$ Conductance

$\left(\frac{l}{A}\right) =$ cell constant $\sigma = C\left(\frac{l}{A}\right)$

Area in the Case



smallest area prefered.

Molar Conductivity

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

M = Mobality
K = conductivity (σ)
Λ_m = Molar conductivity

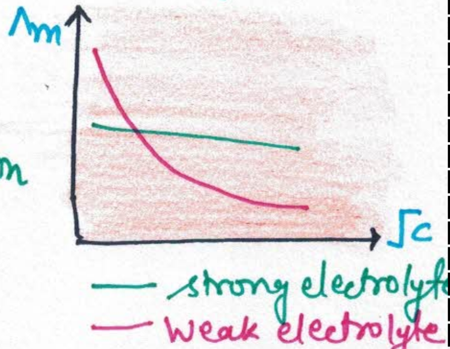
Equivalent Conductivity

$\lambda_e = \frac{1000K}{N}$

N = Normality

Debye Huckel Law

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



Λ_m^∞ is the molar conductivity at ∞ dilution
b = Constant
c = Consentration.

Kohlrauch Law

At ∞ dilution, when dissociation of electrolyte is 100%, then we can relate molar conductivity of electrolyte w.r.t. to its ions.

$$MgCl_2 \longrightarrow Mg^{+2} + 2Cl^-$$

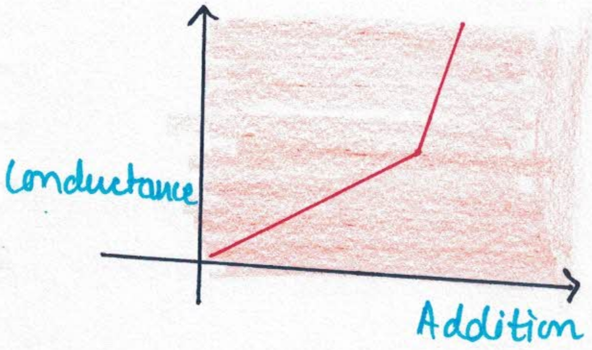
$$(\lambda^0_E)_{MgCl_2} = (\lambda^0_E)_{Mg^{+2}} + (\lambda^0_E)_{Cl}$$

$$(\lambda^0_M)_{MgCl_2} = (\lambda^0_m)_{Mg^{+2}} + \boxed{2}(\lambda^0_m)_{Cl}$$

In λ^0_m we need to take the cofficient too.

Graph

Weak acid + Strong Base



Strong acid + strong Base