ELECTRO CHEMISTRY

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- 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

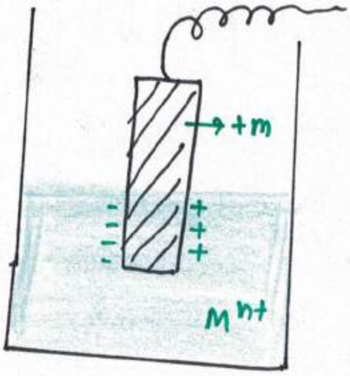
Osmatic Pressure
De-electronation

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 ite solution which is called electrode potential and the metal rod in contact with its salt solution is called electrode. [anode]



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

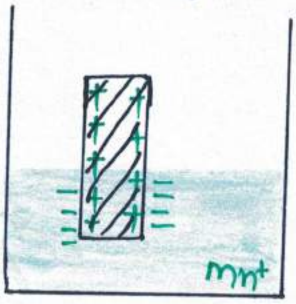
for anode

- 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.



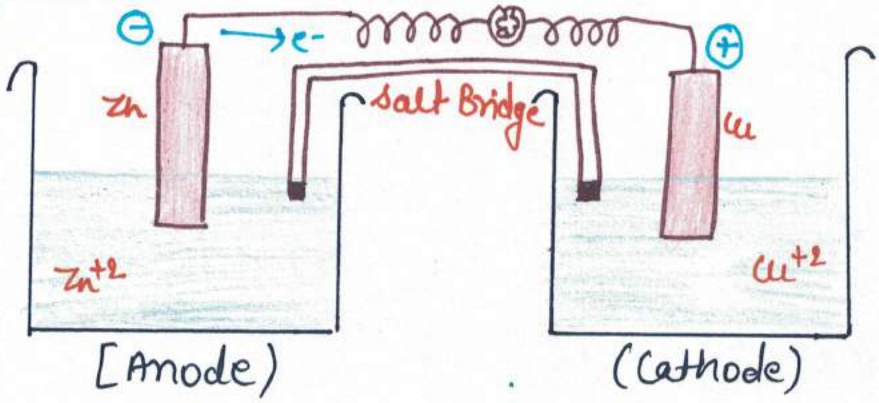
for Cathode

- Solution pressure > Osmatic Press.
- Always reduction will occure at Cathode $M + ne \longrightarrow M$
- $[m]^{+n}$ concn 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 electrochemicalCell :-



LOAN

Anode ⇒ L ⇒ Left

O ⇒ oxidatn

A ⇒ Anode

N ⇒ Negative

Salt Bridge A 'U'-shaped glass tube in fitted with a paste of any electrode [genrally KCl] with agar. agar solution and dried.

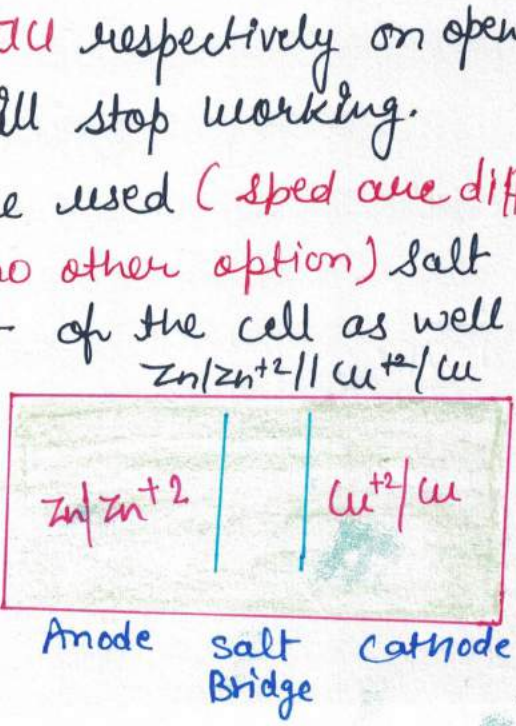
① It will form net like structure or porous structure. through which ion can move.

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.

$Zn|Zn^{+2}||Cu^{+2}|Cu$



Construction of electro-chemical cell

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

NOTE

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

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

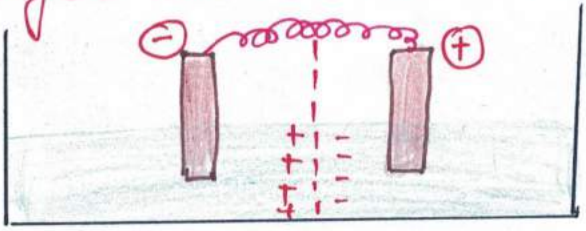
$$M_{(s)} + M^{+n}_{(aq.)} \longrightarrow m^{+n}_{(aq.)} + M_{(s)}$$

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

In the reaction, M^{+n} keeps on increasing as it is at anode & N^{+n} keeps on decreaseing 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 → $\boxed{\begin{array}{l} E_{oxi} = E_{Zn|Zn^{+2}} \\ E_{red} = E_{Zn^{+2}|Zn} \end{array}}$

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

Standered condition → It is one atmosphere pressure, Temprature in 25°c and conc^n 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

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

$E^\circ_{cell} = 0.34 - (-0.76) = 1.1V$

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.

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

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

E → Inetensive property → independant of mass.

ΔG → Extensive Property → dependent on Mass.

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

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

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

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

$-0.85 - 0.74 < 0$

Not feasible

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

$\Rightarrow 3.05 + 0.34 > 0$

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 कुहंग

PbH Cu Hg Ag

आग पयायु Pt

Au

$F_2 > Cl_2 > Br_2 > I_2$

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.

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

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

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

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

$$\boxed{E = E^\circ - \frac{0.0591}{n}\log_{10} Q} \longrightarrow \text{Nernst Equation}$$

Example $Zn|Zn^{+2}||Cu^{+2}|Cu$

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

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

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

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 $\boxed{Q_c = K_c}$

$$\Delta G = \Delta G^\circ + RT\ln K \quad \because \Delta G = 0$$
$$\Delta G^\circ = -RT\ln K$$
$$\ln K = \frac{-\Delta G^\circ}{RT}$$

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

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

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

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

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

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^-

Anode = Ag

$\Rightarrow \boxed{0.71V}$

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

$Cu^{+2} + 2e \longrightarrow Cu \quad \Delta G_1 = -2FE^\circ_1$

$Cu^{+2} + 2e \longrightarrow Cu^{+} \quad \Delta G_2 = -FE^\circ_2$

$Cu^{+} + e \longrightarrow Cu \quad \Delta G_3 = -FE_3$

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

$-E^\circ = -2 \times 0.337 + 0.153$

$E^\circ = 2 \times 0.337 - 0.153$

$E^\circ = 0.674 - 0.154$

$\boxed{0.521V}$

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

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

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

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

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

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

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

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

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

$\boxed{E_3 = 1.69V}$

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 sol^n.

In both cases conc^n of species are equal.

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

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

$$E_a = E^\circ + \frac{0.0591}{5} \times 8 \log [H^+]$$

$$(E_{RP})_a = E^\circ + \frac{0.0591}{5} 8 \log(2 \times 10^{-2})$$

$$(E_{RP})_a = E^\circ + \frac{0.0591}{5} \times 8 \times -2 \times 0.3010$$

$$= E^\circ - \frac{0.0591 \times 8 \times 2.7}{5}$$

$$(E_{RP})_b = E^\circ - \frac{0.0591 \times 8 \times 2.7}{5}$$

$\log(2 \times 10^{-2})$

$-2 \times \log 2$

-2×0.3010

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

oxidising power of a > b

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

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

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

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

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

$$= \boxed{-0.22V}$$

Ques for conc^n 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 $p^H=0$ $\quad p^{OH}=14$ $\quad [OH^-]=10^{-14}$ $\quad [H^+]_i = 1$ intial

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

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

$$= 0$$

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

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

$$E_{change} = E^\circ_{final} - E_{initial} \qquad = \frac{-0.0591}{2} \times \log 10^{14}$$

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

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 $E^\circ_{cell} = ?$

Ques.

$$H_2 \longrightarrow 2H^+ + 2e^- \text{ (anode)} \qquad \underset{(C_1 - x)}{HCOOH} \longrightarrow \underset{x}{HCOO^-} + \underset{x}{H^+}$$

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

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

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

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

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

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

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

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

$x = 0.09$

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

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

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

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

Ans.

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

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

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

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

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

$$E = 0.76$$

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

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

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

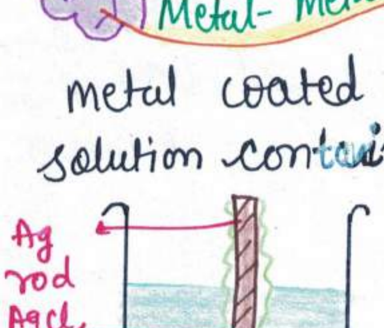
$$E^\circ = \frac{74.79 \times 298}{2 \times 96500} = \boxed{E = 0.77V}$$

Type of electrodes

Metal-Metal soluble salt electrode → Metal rod clipped 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 all 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.

$Ag|AgI_{(s)}|\underset{0.05}{KI}||\underset{0.05}{AgNO_3}|Ag_{(s)}$ $E_{cell} = 0.7884V$ at 298K.

Ans.

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

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

$Ag^+_c = 0.05 M$

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

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

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

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

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

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

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

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.① 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 $Zn|\underset{0.1}{Zn^{+2}}||\underset{0.01M}{Cu^{+2}}|Cu$

Ans

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

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

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

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

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

Quest① Astandered 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^0_{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

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

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

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

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

$$E = 0.46 - \frac{0.0591}{2}\log\frac{3\times10^{-2}}{3\times10^{-6}} = 0.46 - \frac{0.0591}{2}\times 4$$

$$= 0.46 - 0.1182 = \boxed{0.34}$$

Ques: The Emf of all $Pt_{(s)}|\underset{1atm}{H_2}|\underset{1.3\times10^{-3}}{HOCN}||\underset{0.8M}{Ag^{+}}|Ag_{(s)}$ is 0.982 V. Calculate Ka for HOCN if E°_{red} of electrode = 0.8 V.

Ans.

$$\underset{1.3\times10^{-3}-x}{HOCN} \longrightarrow \underset{x}{H^{+}} + \underset{x}{OCN^{-}}$$

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

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

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

$$\frac{x^2}{1.3\times10^{-3}-x} = Ka$$

↳ $x^2 = Ka\times1.3\times10^{-3} - Ka\,x$ ↳ $x^2 + x\,Ka - 1.3\times10^{-3}\,Ka = 0$

↳ $Ka = \dfrac{x^2}{1.3\times10^{-3}-x}$ ↳ $0.982 = 0.8 - \dfrac{0.0591}{2}\log\dfrac{[H^{+}]^2}{[Ag^{+}]^2 H_2}$

↳ $\dfrac{-0.364}{0.064} = \log\dfrac{[H^{+}]^2}{Ag^{+}}$ ↳ $\dfrac{[H^{+}]^2}{[Ag^{+}]^2} = 10^{-6}$

↳ $[H^{+}]^2 = 10^{-6}\times 64\times10^{-2}$ ↳ $[H^{+}] = 8\times10^{-4}$

↳ $Ka = \dfrac{64\times10^{-8}}{1.3\times10^{-3} - 8\times10^{-4}} = \dfrac{64\times10^{-8}}{5\times10^{-4}} = \boxed{1.28\times10^{-3} = Ka}$

THERMODYNAMICS OF CELL

$G = H - T\Delta S$ — ⓘ ↳ $dG = dH - TdS - SdT$

$H = U + PV$ — (ii) ↳ $dH = \underbrace{dU + PdV}_{dQ} + VdP$

$dQ = dU + PdV$ (iii) ↳ $dH = dQ + VdP$

$dS = \dfrac{dQ}{T}$ (iv) ↳ $dG = dQ + VdP - TdS - SdT$

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

$$\boxed{dG = VdP - SdT}$$

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

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

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

$$\boxed{\Delta H = -nFE_{cell} + \frac{nFTdE_{cell}}{dt}} \qquad \boxed{\Delta S = \frac{nF\,dE_{cell}}{dt}}$$

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

Remember only —

$\Delta S = nF\left[\frac{dE_{cell}}{dT}\right]$

$\Delta G = nFE$ By using we can find —

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

$\Delta C_P = nFTd^2$

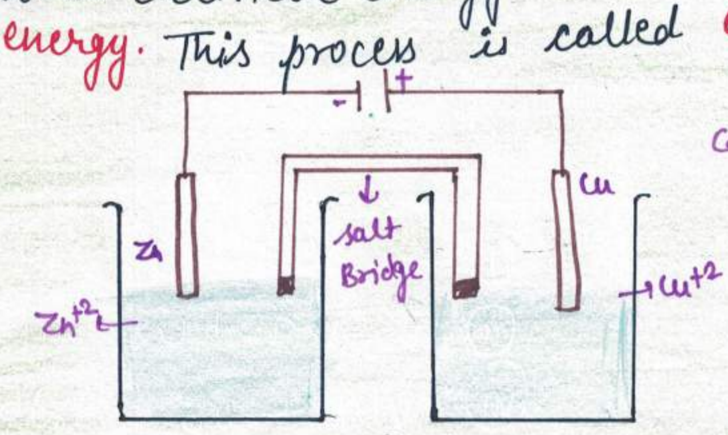
HEAT CAPACITY

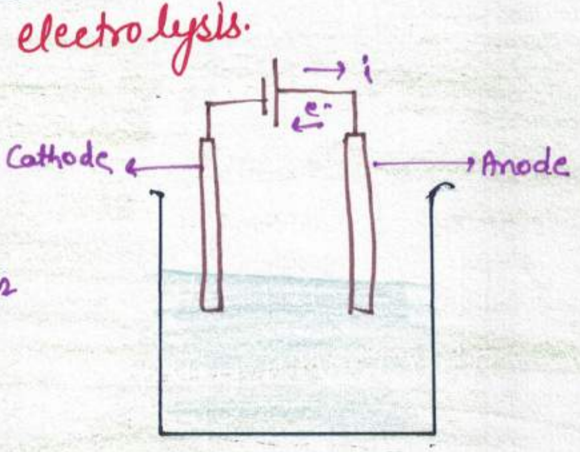
$$\boxed{C_P = \frac{d(\Delta H)}{dT}} \qquad \boxed{C_P = \frac{TnF\,dE}{dT^2}}$$

Enthaphy $\Delta H = \Delta G + T\Delta S = -nFE + TnF\left(\frac{dE}{dT}\right)_P$

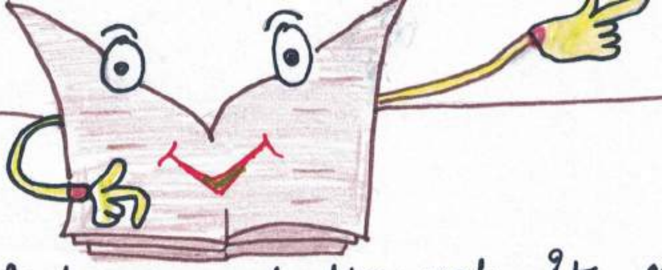
ELECTROLYSIS

It is reverse process of eleoro-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 towards anode and will get neutrilised after releasing extra charge

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

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

- In case two or more type of potential (positive and negative) ions +nt in solution during electrolysis, certain ions are discharged and librated at the electrode in preference to other.

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 general such competition, the ion which are stronger oxidising agent is discharged first at cathode (high reduction potential)

Order of Decomposit^n Similarly ion which is stronger reducing agent will get deposit first at anode [low reduction potential]

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

Increasing order of Decomposition →

Increasing order of deposition :- 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. $CuSO_4$

(Cu^{+2} ✓, H_2O) ⇓ cathode

(SO_4^{-2}, H_2O ✓) ⇓ 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^+, H_2O ✓)

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

Anode ⇒ Br^-, H_2O

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

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

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

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.

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

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

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

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

$W_1 = Z_1 \times F$

$E_1 = Z_1 \times F$

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

$W_2 = Z_2 \times F$

$E_2 = Z_2 \times F$

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

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

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.

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

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

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

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

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

2 mole e^- required i. e

$2 \times 96500 = 193000C$

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

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

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 released 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 cm² by passing a current of 0.2 A for 3 Hours. Calculate the thick mass of silver deposited (density of silver is deposited is 9.67 g/cm³

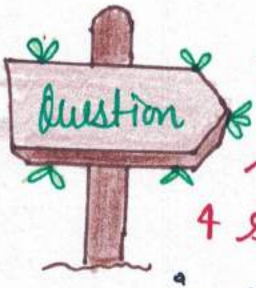
$$W = \frac{Eit}{F} = \frac{108 \times 0.2 \times 3 \times 60 \times 60}{1 \times 96500} \Rightarrow \frac{7776 \times 3}{9650} =$$

$\boxed{2.41g}$

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

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

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



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

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

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

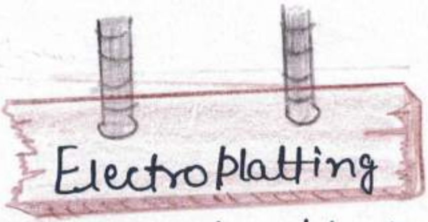
$$q_1 = \int i\,dt \Rightarrow 2\int_0^2 t\,dt \Rightarrow 2\left[\frac{t^2}{2}\right]_0^2 = 4C$$

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

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

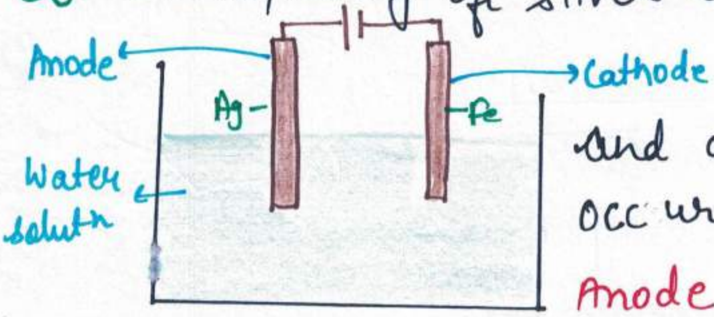
$$W = W_1 + W_2 \Rightarrow \frac{108}{96500}(4 + 49.2) \Rightarrow \frac{5745.6}{96500}$$

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



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.