BY MRIDUL BHAIYA

ELECTRO CHEMISTRY

This book will guide you step by step
to get out of your problems

ELECTROCHEMISTRY

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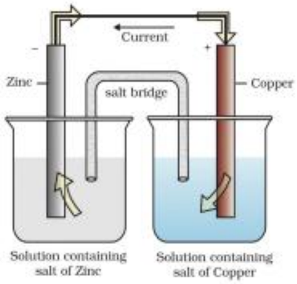
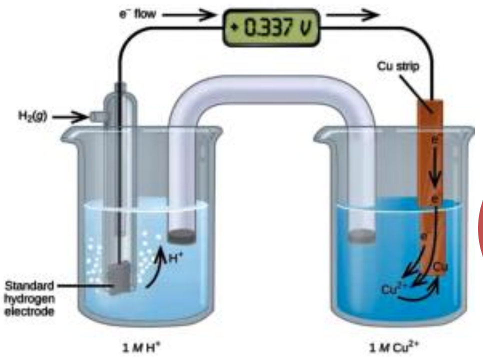
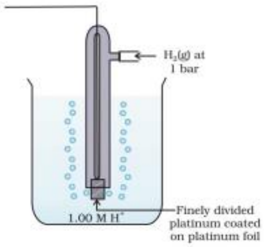
- **Nernst Equation**
  - EMF of Cell
  - Gibbs Free Energy
  - Equilibrium
- **Cell**
  - Galvanic Cell
  - Electrolytic Cell
    - Electrolysis
      - Faraday's Law





- **Electrochemical Series**
- **Batteries**
- **Corrosion**
- **Standard Hydrogen Electrode**



- **Conductance in Solution**
  - Resistance
  - Resistivity
  - Conductance
  - Conductivity
    - Molar Conductivity
      - Kohlrousch Law

INTRODUCTION

It is the study of production of electricity from energy which is released during spontaneous chemical reaction and the use of electrical energy to bring about non – spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

There are two types of cells

1. Electrochemical Cells [Galvanic Cell]
2. Electrolytic Cells

SOME BASIC DEFINITION

Oxidation : Loss of electrons $Zn \longrightarrow Zn^{+2} + 2e^-$

Reduction : Gain of electrons $Cu^{+2} + 2e^- \longrightarrow Cu$

Electrolyte : A solution that contains ions is called electrolyte. Electrolyte is an ionic conductor.

Electrode : Surface at which oxidation or reduction takes place.

- **Active Electrode:** Surface at which oxidation or reduction takes place and also involve in reaction.
  Ex: Copper, Zinc Electrode
- **Inert Electrode:** Metals like Platinum or Gold are used as inert electrode. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for conduction of electrons.

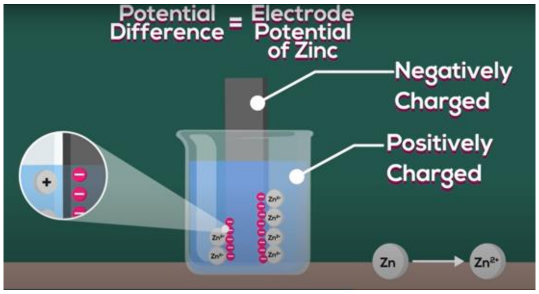
Work on Electrode:

1. Conduction of electrons
2. Oxidation
3. Reduction

Redox Reaction : An oxidation – reduction (redox) reaction.

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

Electrode Potential : Potential difference between metal and electrolyte is called electrode potential.



ELECTROCHEMISTRY : 3 BASIC EXPERIMENT

EXPERIMENT - 1

Placing a Zn Rod in $CuSO_4$ solution :

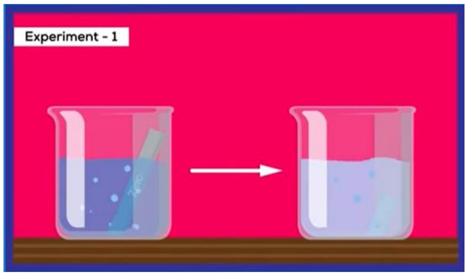
$CuSO_4$ solution is blue in colour because of Cu^{2+} ions. But if we place a Zn rod in $CuSO_4$ solutions, colour fades out.

This is because of reduction of $Cu^{+2} \longrightarrow Cu$

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

the solution changes from blue to colourless.

Above is a spontaneous reaction. It does not require any external work.

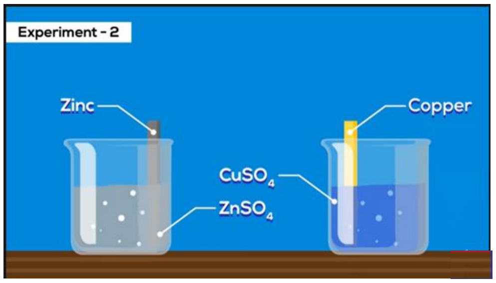


EXPERIMENT – 2

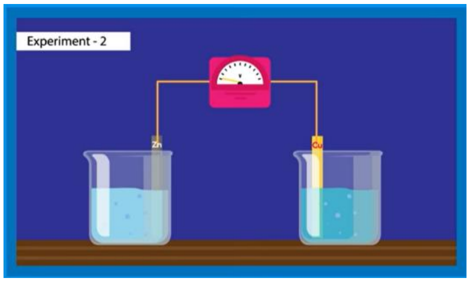
We will take two beakers in one beaker we take $ZnSO_4$ and we dip Zinc rod in it.

Second beaker we take $CuSO_4$ and dip copper rod.

When we take readings in voltmeter we find that there is little deflection in it which means a little amount of current must be flown in our setup.

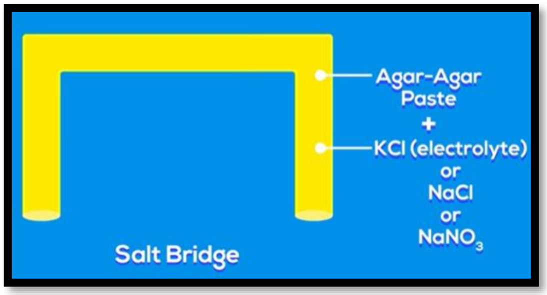


But after a small interval of time the current flowing will stop.



EXPERIMENT – 3

Now to keep the current flowing we will use a SALT BRIDGE



SALT BRIDGE is a U- shaped brigde which is filled by Agar-Agar Paste (A paste of polysachride like Gelatin, Albumin etc.) and an electrolyte like KCl, KNO_3 etc

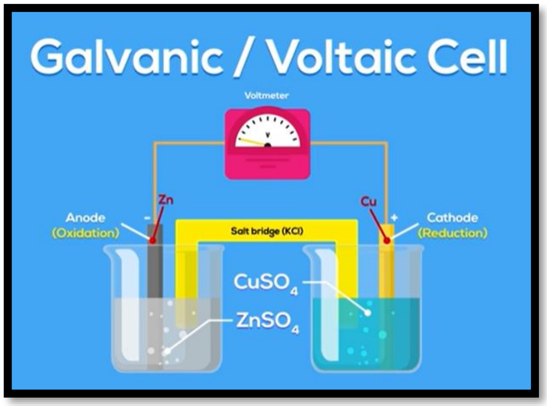
 # ELECTRONEUTRALITY PRINCIPLE

GALVANIC CELL OR VOLTAIC CELL

A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.

Converts the chemical energy of a spontaneous redox reaction into chemical energy.

- Spontaneous then ΔG = -ve
- In this devide ΔG of spontaneous redox reaction is converted into electrical work. (which may be used for running a motor, fan etc)



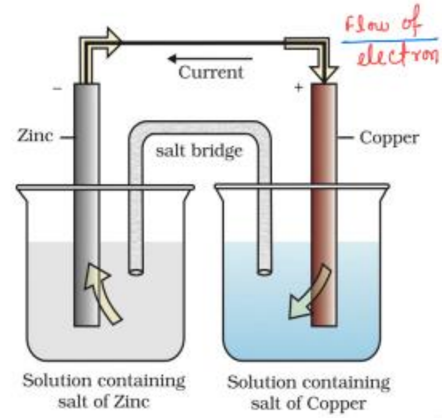
Construction:

It consists of two metallic electrodes dipping in electrolytic solution. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jell and an electrolyte like KCl, KNO_3 etc

This Tube is called **SALT BRIGDE**

Salt Bridge is necessary because – **[Delhi 2011]**

i. It connects the solution of two half cells. Thus completes the cell circuit.
ii. It maintains electrical neutrality within the internal circuit.
iii. It prevents diffusion of solutions from one compartment to another.



REPRESENTATION OF CELL :

- Salt brigde is represented by ||
- Anode half cell || Cathode half cell
- | represents phase boundary

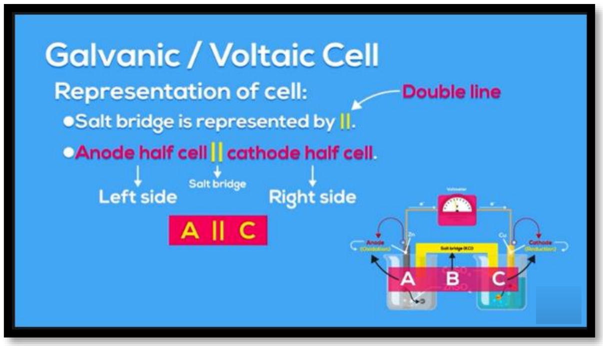
NOTE : Learn through A B C

Where A is anode

B is Bridge

C is Cathode

➢ **In Galvanic Cell** :
  - Oxidation at anode [Negative plate]
  - Reduction at cathode [Positive Plate]



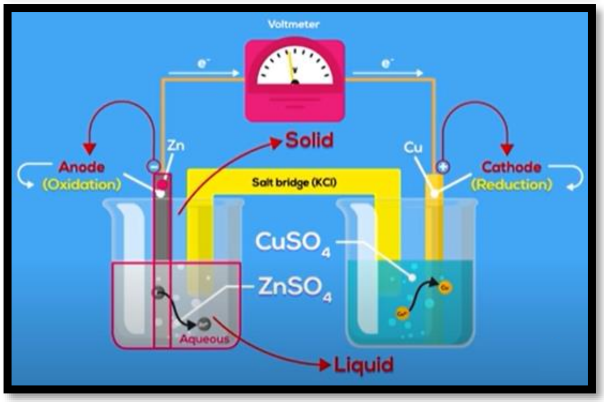
Galvanic / Voltaic Cell

Representation of cell:

- Salt bridge is represented by ||.
- Anode half cell || cathode half cell.

Left side — Salt bridge — Right side

A || C



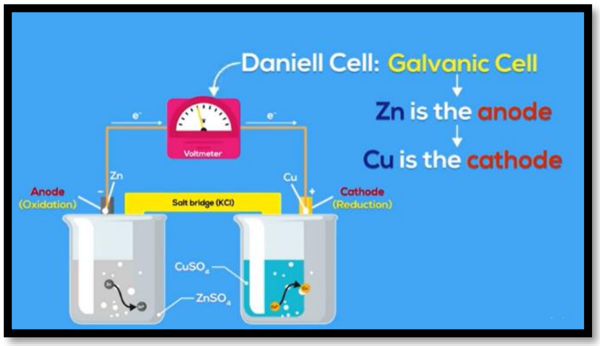
DANIELL CELL:

Among the galvanic cell when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ion to produce an electric current

That is Daniell cell

Reaction :

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



Daniell Cell: Galvanic Cell

Zn is the anode

Cu is the cathode

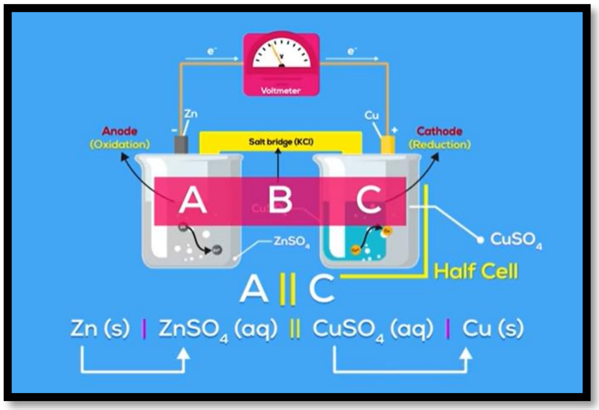
Cell Representation: **[Delhi 2013C]**

$$\underbrace{Zn_{(s)} | Zn^{+2}_{(aq.)}}_{\downarrow} \; || \; \underbrace{Cu^{+2}_{(aq.)} \overset{\curvearrowright}{|} Cu_{(s)}}_{\downarrow}$$

Phase Difference

: Anode Half cell || Cathode half cell

Salt Bridge

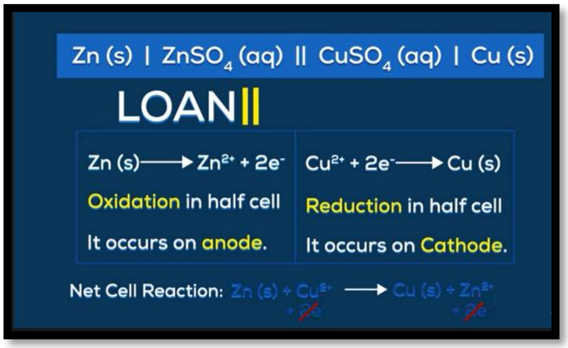


Zn : Anode (oxidation) and Cu : Cathode (reduction)

The two half cell reaction are

i. $Zn \longrightarrow Zn^{+2} + 2e^-$ [Reduction half reaction : occurs at cathode]

ii. $Cu^{+2} + 2e^- \longrightarrow Cu$ [Oxidation half reaction : occurs at anode]

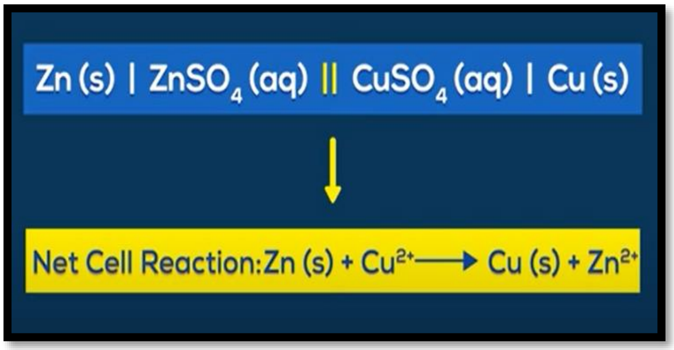


Zn (s) | $ZnSO_4$ (aq) || $CuSO_4$ (aq) | Cu (s)

LOAN||

$Zn(s) \longrightarrow Zn^{2+} + 2e^-$	$Cu^{2+} + 2e^- \longrightarrow Cu(s)$
Oxidation in half cell	Reduction in half cell
It occurs on anode.	It occurs on Cathode.

Net Cell Reaction: $Zn(s) + Cu^{2+} + \cancel{2e^-} \longrightarrow Cu(s) + Zn^{2+} + \cancel{2e^-}$



Zn (s) | $ZnSO_4$ (aq) || $CuSO_4$ (aq) | Cu (s)

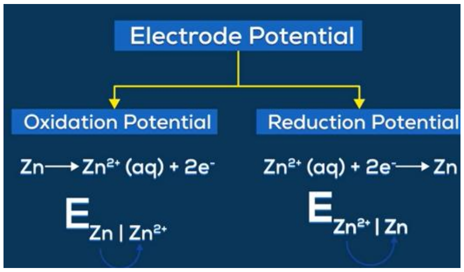
$\downarrow$

Net Cell Reaction: $Zn(s) + Cu^{2+} \longrightarrow Cu(s) + Zn^{2+}$

ELECTRODE POTENTIAL

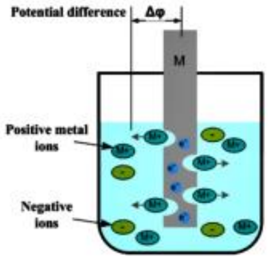
ELECTRODE POTENTIAL : Potential difference between metal and metal ion in which electrode is dipped is called ELECTRODE POTENTIAL.

- ➔ Electrode potential of Zn ⟶ Zn | $ZnSO_4$
- ➔ Electrode potential of Cu ⟶ Cu | $CuSO_4$



Electrode Potential

Oxidation Potential	Reduction Potential
$Zn \longrightarrow Zn^{2+}(aq) + 2e^-$	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn$
$E_{Zn \mid Zn^{2+}}$	$E_{Zn^{2+} \mid Zn}$



NOTE :

(i.) When the concentration of all the species involved in a half cell is unity then the electrode potential is known as **Standard Eelectrode potential**

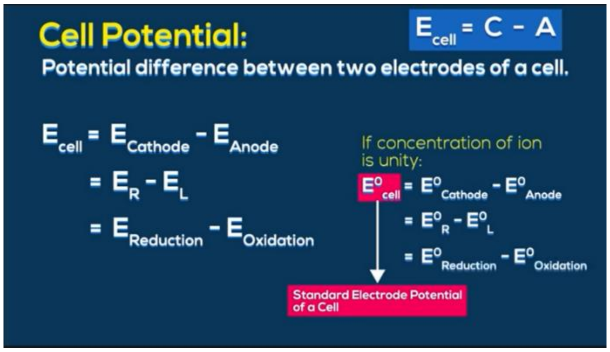
(ii.) **IUPAC Convention** : Standard Reduction Potential (SRP) is SEP.

E^0 : Standard Electode Potential

E : Electode Potential

CELL POTENTIAL

CELL POTENTIAL : The Potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.



Cell Potential: $E_{cell} = C - A$

Potential difference between two electrodes of a cell.

$E_{cell} = E_{Cathode} - E_{Anode}$

$= E_R - E_L$

$= E_{Reduction} - E_{Oxidation}$

If concentration of ion is unity:

$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$

$= E^0_R - E^0_L$

$= E^0_{Reduction} - E^0_{Oxidation}$

Standard Electrode Potential of a Cell

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

$= E_R - E_L$

$= E_{Reduction} - E_{oxidation}$

[**Cell** : **Anode Half cell || Cathode half cell**]

a. **For a reaction**

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

Cell : $Zn_{(s)} | Zn^{+2}_{(aq.)} || Cu^{+2}_{(aq.)} | Cu_{(s}$

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

b. **For a reaction**

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

Half cell reaction: Cathode (reduction) : $2Ag^+ + 2e^- \longrightarrow 2Ag$

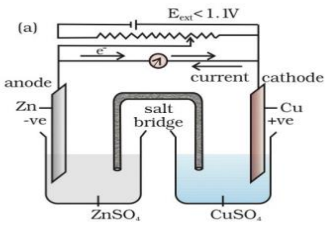
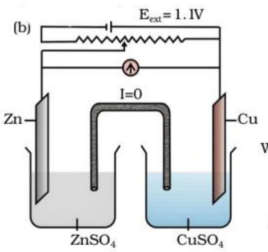
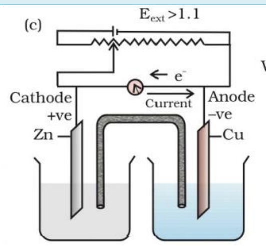
Anode (oxidation) : $Cu \longrightarrow Cu^{+2} + 2e^-$

Cell reprsentation : $Cu \mid Cu^{+2} \mid\mid Ag^+ \mid Ag$

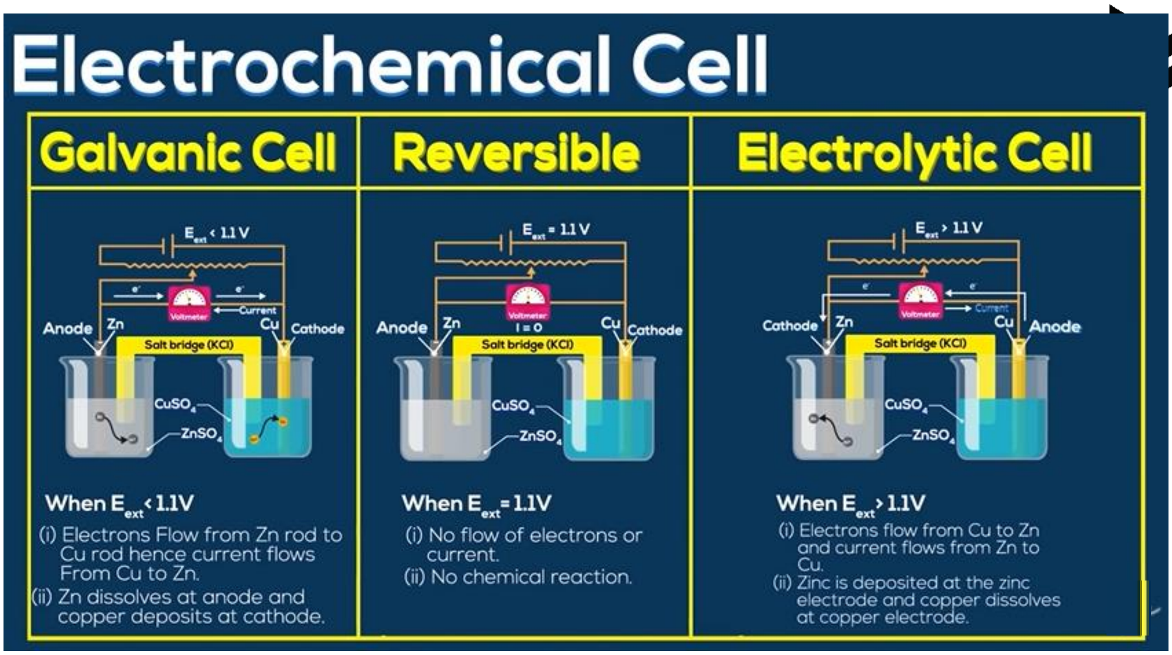
$$E_{cell} = E_{right} - E_{left}$$

$$= E_{Ag^+/Ag} - E_{Cu^{+2}/Cu}$$

ELECTROCHEMICAL CELL

Galvanic Cell	Reversible	Electrolytic Cell
Chemical Energy $\longrightarrow$ Electrical Energy	No net reaction	Electrical Energy $\longrightarrow$ Chemical Energy
ΔG = -ve (Spontaneous Reaction)		ΔG = +ve (Non-Spontaneous Reaction)
Power is produced		Power is consumed
 When $E_{ext} < 1.1$ V (i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn. (ii) Zn dissolves at anode and copper deposits at cathode.	 When $E_{ext} = 1.1$ V (i) No flow of electrons or current. (ii) No chemical reaction.	 When $E_{ext} > 1.1$ V (i) Electrons flow from Cu to Zn and current flows from Zn to Cu. (ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

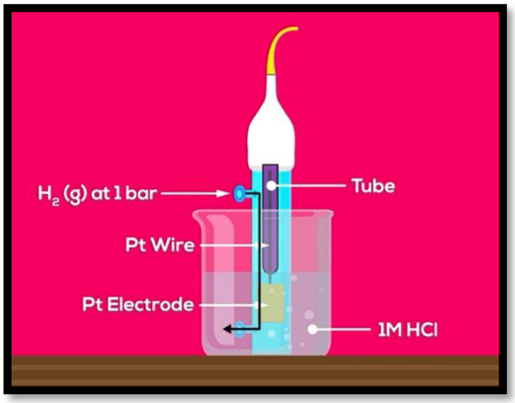
Functioning of Daniell cell when external voltage (E_{ext}) opposing the cell potential is applied.



Electrochemical Cell

Galvanic Cell	Reversible	Electrolytic Cell
When $E_{ext} < 1.1V$ (i) Electrons Flow from Zn rod to Cu rod hence current flows From Cu to Zn. (ii) Zn dissolves at anode and copper deposits at cathode.	When $E_{ext} = 1.1V$ (i) No flow of electrons or current. (ii) No chemical reaction.	When $E_{ext} > 1.1V$ (i) Electrons flow from Cu to Zn and current flows from Zn to Cu. (ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

STANDARD HYDROGEN ELECTRODE



a) Oxidation : $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$

b) Reduction : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

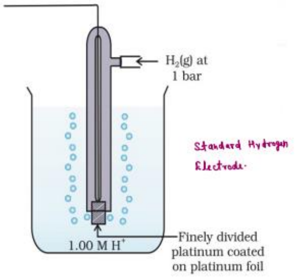
Representation of half cell:

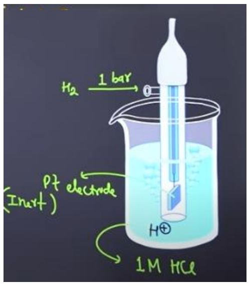
a) $Pt_{(s)} \mid H_{2(g)} (\text{ 1 bar }) \mid H^+_{(aq)}$
b) $Pt_{(s)} \mid H^+_{(aq)} \mid H_{2(g)} (\text{ 1 bar })$

SRP $\longrightarrow E^0_{H^+|H_2}$
SOP $\longrightarrow E^0_{H_2|H^+}$

IUPAC $E^0_{H^+|H_2} = 0$

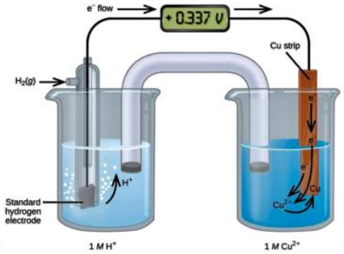
$E^0_{H_2|H^+} = 0$





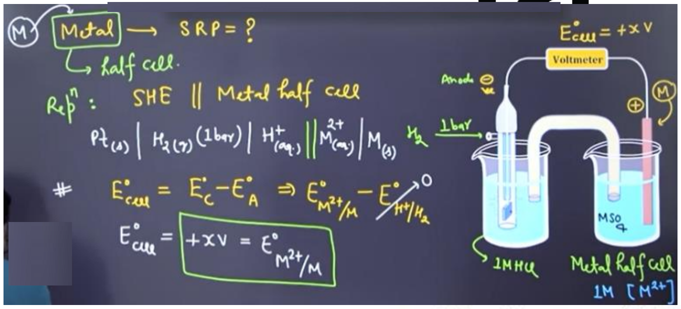
According to convention, a half cell called standard hydrogen electrode is assigned a zero potential at all temperatures corresponding to the reaction.

$$H^+ (aq) + e^- \longrightarrow \frac{1}{2} H_2(g)$$



Measurement of Electrode Potential

- Construct a cell by taking standard hydrogen electrode as anode (reference half cell) and other half cell as cathode, gives the reduction potential of other half cell.



Ⓜ Metal → SRP = ?
↳ half cell.

Repⁿ : SHE || Metal half cell

$Pt_{(s)} | H_{2(g)}(1bar) | H^+_{(aq.)} || M^{2+}_{(aq.)} | M_{(s)}$

$E^\circ_{cell} = E^\circ_C - E^\circ_A \Rightarrow E^\circ_{M^{2+}/M} - \cancelto{0}{E^\circ_{H^+/H_2}}$

$E^\circ_{cell} = \boxed{+xV = E^\circ_{M^{2+}/M}}$

Standard Hydrogen Electrode [$Pt(s) | H_2(g)(1 bar) | H^+_{(aq.)}(1M)$] || other half cell.

- If the concentration of the oxidised and the reduced forms of species in the right hand half cell are unity. Then the cell potential is equal to standard electrode potential (E^0_R) of the given half cell.

$$E^\circ = E^\circ_R - E_L = E^\circ_R - 0 = E^\circ_R$$

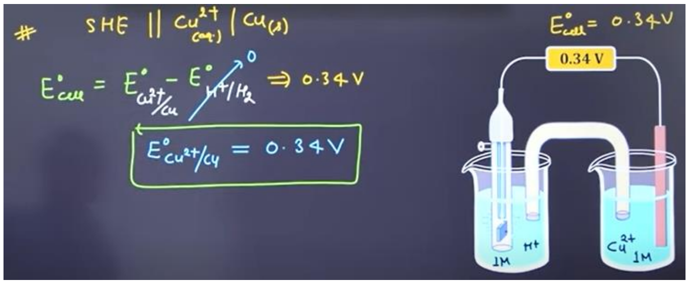
Measurement of SRP of Copper

→ ⓘ To calculate $E^\circ_{Cu^{+2}/Cu}$, make a cell $Pt(s) | H_2(g)(1bar) | H^+(aq.)\ 1M || Cu^{+2}(aq.)\ 1M | Cu$

→ EMF of this cell = 0.34V

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

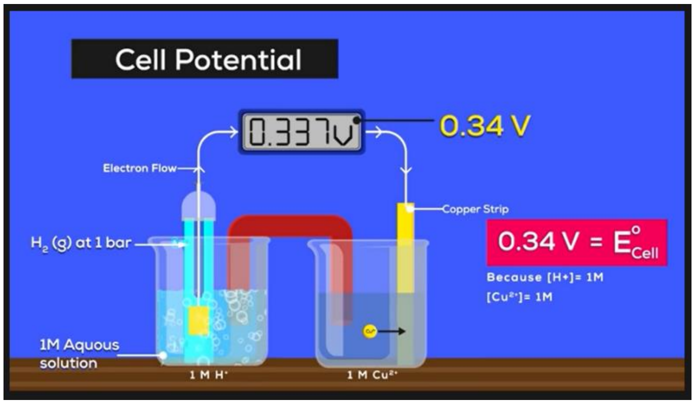
$0.34V = E^\circ_{Cu^{+2}/Cu} - 0$ then $\boxed{E^\circ_{Cu^{+2}/Cu} = 0.34V}$



SHE || $Cu^{2+}_{(aq.)} | Cu_{(s)}$

$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - \cancelto{0}{E^\circ_{H^+/H_2}} \Rightarrow 0.34V$

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



Measurement of SRP of Zinc

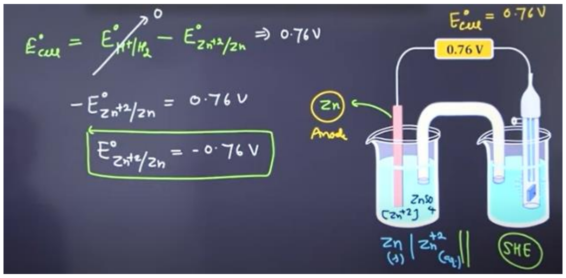
Similarly ; $E^\circ_{Zn^{+2}/Zn}$ can be calculated by following cell.
(ii)

$Pt(s) | H_2(g)(1 bar) | H^+(aq.)\ 1M || Zn^{+2}_{(aq.)}(1M) | Zn$

→ $E^\circ_{cell} = -0.76V$

$E^\circ_{cell} = E^\circ_{Zn^{+2}/Zn} - E^\circ_{SHE} = E^\circ_{Zn^{+2}/Zn} - 0$

then $\boxed{E^\circ_{Zn^{+2}/Zn} = -0.76V}$



$E^\circ_{cell} = \cancelto{0}{E^\circ_{H^+/H_2}} - E^\circ_{Zn^{+2}/Zn} \Rightarrow 0.76V$

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

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

- In first case, +ve value of SEP indicates that Cu^{+2} get reduced more easily than H^+, means we can say that H_2 gas can reduce Cu^{+2} ion,
- In second case, -ve value of SEP indicates that Zn get oxidised by H^+ ion.

EMF of Daniell Cell

Cell : $Zn_{(s)} \mid Zn^{+2}_{(aq)} (1M) \parallel Cu^{+2}_{(aq.)} (1M) \mid Cu_{(s)}$

$$E^\circ_{cell} = E^\circ_{Cu^{+2}|Cu} - E^\circ_{Zn^{+2}|Zn} = 0.34\,V - (-0.76V) = 1.10\,V$$

Inert Electrode : Metals like platinum gold are used as inert electrode. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for conduction of electrons.

For Ex: Hydrogen Electrode : $Pt_{(s)} \mid H_{2(g)} \mid H^+_{(aq.)}$

Bromine Electrode : $Pt_{(s)} \mid Br_{2(aq.)} \mid Br^-_{(aq.)}$

NERNST EQUATION

It gives relation between electrode potential, temperature and concentration of metal ions.

Half cell reaction : $M^{n+}_{(aq.)} + ne^- \longrightarrow M_{(s)}$

$n \rightarrow$ No. of electrons

$$\rightarrow E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\rightarrow \boxed{E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}}$$

$\leftarrow$ R = Gas constant = $8.314\ J\,K^{-1}\,mol^{-1}$

F = Faraday's constant = $96\,487\ C\,mol^{-1}$

T = 298 K and $[M] = 1 = [\text{Solid}]$

In Daniell Cell : Electrode potential for any concentration of Cu^{+2}/Zn^{+2}.

For Cathode : $E_{Cu^{+2}|Cu} = E^\circ_{Cu^{+2}|Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{+2}_{(aq.)}]}$

For Anode : $E_{Zn^{+2}|Zn} = E^\circ_{Zn^{+2}|Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{+2}_{(aq.)}]}$

NERNST EQUATION : DANIELL CELL

Cell reaction : $Zn_{(s)} + Cu^{+2}_{(aq.)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq.)}$

Cell Potential $E_{cell} = E_{Cu^{+2}/Cu} - E_{Zn^{+2}/Zn}$

$$= \left[E^\circ_{Cu^{+2}/Cu} - E^\circ_{Zn^{+2}/Zn}\right] - \frac{0.059}{2} \log \frac{[Zn^{+2}_{(aq.)}]}{[Cu^{+2}_{(aq.)}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{+2}_{(aq.)}]}{[Cu^{+2}_{(aq.)}]} \quad — [\#]$$

Q. For the cell $Zn_{(s)} | Zn^{+2} (2M) || Cu^{+2} (0.5M) | Cu_{(s)}$ **[Delhi 2011 C]**

i. Write the equation for each half cell

ii. Calculate cell potential at 25°C.

Given : $E^\circ_{Zn^{+2}/Zn} = -0.76V$

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

Ans. ⓘ Anode : $Zn_{(s)} \longrightarrow \underset{[2M]}{Zn^{+2}_{(aq.)}} + 2e^-$

Cathode : $\underset{(0.5M)}{Cu^{+2}_{(aq.)}} \xrightarrow{+2e^-} Cu_{(s)}$

ⓘⓘ $E^\circ_{cell} = E^\circ_{Cu^{+2}/Cu} - E^\circ_{Zn^{+2}/Zn} = 0.34V - (-0.76V) = 1.10V$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \Rightarrow 1.10V - \frac{0.059}{2} \log \frac{2}{0.5}$$

$$E_{cell} = 1.10V - \frac{0.059}{2} \times 0.602V = 1.10V - 0.0178V = 1.0822V$$

Q. A Zn rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at its dilution at 298 K. Caluculate the electrode potential ? **[Delhi 2012 C]**

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

Answer :- Reaction $Zn^{+2} + 2e^- \longrightarrow Zn$ $\quad \underline{n=2}$

By using nernst equation, we get $E_{Zn^{+2}|Zn} = E^\circ_{Zn^{+2}|Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{+2}]}$

$\rightarrow [Zn^{+2}] = \frac{95}{100} \times 0.1 = 0.095\,M$; $\quad E_{Zn^{+2}|Zn} = -0.76V - \frac{0.059}{2} \log \frac{1}{0.095} = \underline{-0.7901V}$

Question :- Calculate the emf of the following cell at 298 K.

$2Cr(s) + 3Fe^{+2}(0.1M) \longrightarrow 2Cr^{+3}(0.01M) + 3Fe(s)$ (3M)

Given : $E^\circ_{Cr^{+3}/Cr} = -0.74V$ $\quad E^\circ_{Fe^{+2}|Fe} = -0.44V$ [Delhi 2016]

Answer :- Half cell reactions ÷ At anode : $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

At cathode : $[Fe^{+2} + 2e^- \longrightarrow Fe] \times 3$

$\rightarrow E^\circ_{cell} = E^\circ_{Fe^{+2}|Fe} - E^\circ_{Cr^{+3}|Cr}$ $\quad$ then $\boxed{n=6}$

$= -0.44V - (-0.74V)$ $\quad \rightarrow E = E^\circ - \frac{0.059}{n} \log \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$

$= 0.3\,V$

$$E_{cell} = 0.3V - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3}$$

$\boxed{E_{cell} = 0.31V}$

Question :- Calculate the emf of the following cell at 25°C (3M)

$Ag(s) \mid Ag^+(10^{-3}M) \parallel Cu^{2+}(10^{-1}M) \mid Cu(s)$ [CBSE 2013]

Given → $E^\circ_{cell} = +0.46\,V$ and $\log 10^n = n$

ⓘ $[Ag(s) \longrightarrow Ag^+_{(aq.)} + e^-] \times 2$

(ii) $Cu^{+2}_{(aq.)} \xrightarrow{+2e^-} Cu(s)$

$2Ag_{(s)} + Cu^{+2} \longrightarrow Cu + 2Ag^+$

$\boxed{n=2}$

Answer -: $E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Cu^{+2}]}$

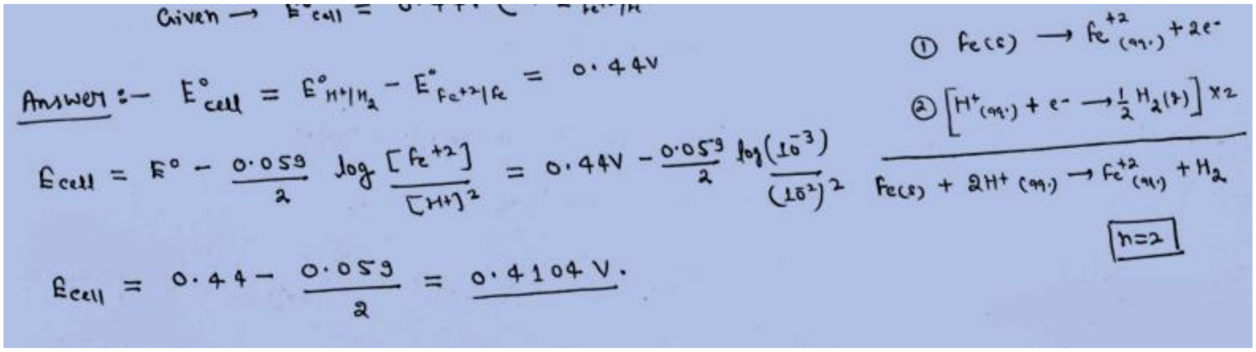
$E_{cell} = 0.46V - \frac{0.059}{2} \log \frac{(10^{-3})^2}{(10^{-1})}$

$\underline{E_{cell} = 0.608\,V}$

Question -: Calculate the emf of the following cell at 298 K (25°C) (3M)

$Fe(s) \mid Fe^{2+}(0.001M) \parallel H^+(.01M) \mid H_2(g)(1\,bar) \mid Pt(s)$ [Delhi 2013|2015]

Given → $E^\circ_{cell} = 0.44V$ (or $E^\circ_{Fe^{+2}/Fe} = -0.44V$ and $E^\circ_{H^+/H_2} = 0V$)



Given → E°_{cell} =

Answer :- $E^\circ_{cell} = E^\circ_{H^+|H_2} - E^\circ_{Fe^{+2}|Fe} = 0.44V$

① $Fe_{(s)} \longrightarrow Fe^{+2}_{(aq.)} + 2e^-$

② $\left[H^+_{(aq.)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}\right] \times 2$

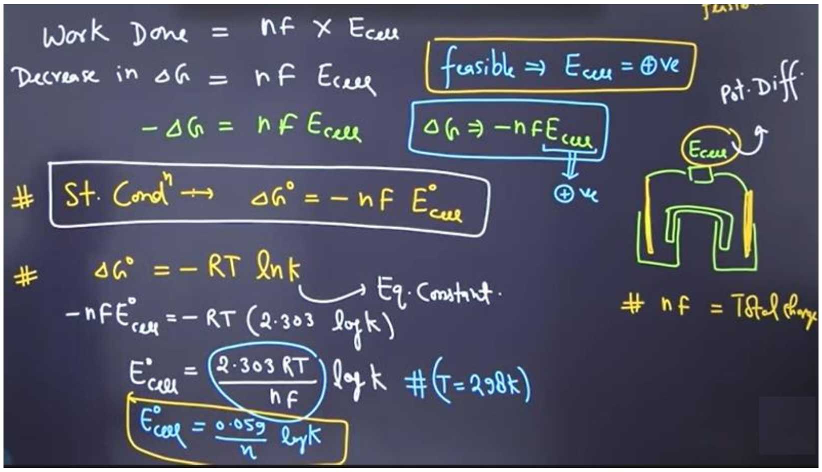
$Fe_{(s)} + 2H^+_{(aq.)} \longrightarrow Fe^{+2}_{(aq.)} + H_2$

$\boxed{n=2}$

$$E_{cell} = E^\circ - \frac{0.059}{2}\log\frac{[Fe^{+2}]}{[H^+]^2} = 0.44V - \frac{0.059}{2}\log\frac{(10^{-3})}{(10^{-2})^2}$$

$$E_{cell} = 0.44 - \frac{0.059}{2} = \underline{0.4104\ V.}$$

Relation Between E$_{cell}$ and ∆G



Work Done = nF × E_{cell}

Decrease in ΔG = nF E_{cell}

$-\Delta G = nFE_{cell}$

$\boxed{\text{feasible} \Rightarrow E_{cell} = \oplus ve}$

$\boxed{\Delta G \Rightarrow -nFE_{cell}}$ ⇓ ⊕ve

$\boxed{\text{St. Cond}^n \longleftrightarrow \Delta G^\circ = -nFE^\circ_{cell}}$

$\Delta G^\circ = -RT\ \ln K$ → Eq. Constant.

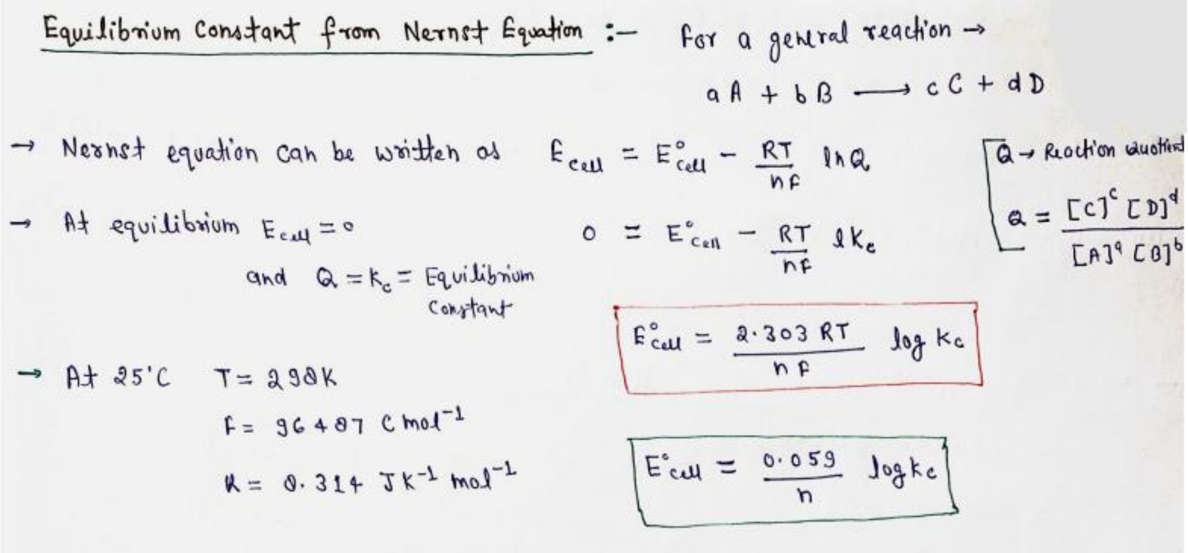
$-nFE^\circ_{cell} = -RT\ (2.303\ \log K)$

$E^\circ_{cell} = \left(\frac{2.303\ RT}{nF}\right)\log K$ # (T = 298K)

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

nF = Total charge

Equilibrium constant for Nernst Equation



Equilibrium Constant from Nernst Equation :- For a general reaction →

$$aA + bB \longrightarrow cC + dD$$

→ Nernst equation can be written as $E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q$

Q → Reaction Quotient

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

→ At equilibrium $E_{cell} = 0$ and $Q = K_c$ = Equilibrium Constant

$$0 = E^\circ_{cell} - \frac{RT}{nF}\ln K_c$$

$$\boxed{E^\circ_{cell} = \frac{2.303\ RT}{nF}\log K_c}$$

→ At 25°C T = 298K

F = 96487 C mol^{-1}

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

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

Example —: for Daniell cell $E^\circ_{cell} = 1.1V$ then → $1.1V = \frac{0.059}{2} \log K_c$

$Cu^{2+} + Zn \longrightarrow Cu + Zn^{+2}$ $n = 2$ = No. of electron tranfered

$\log K_c = 37.288$

$K_c = 2 \times 10^{37}$

Relation between E_{cell} and Gibbs energy of reaction :-

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

[Electrical work done in one second is equal to electrical potential multiplied by total charge ($E_{cell} \times nF$)]

→ Work done by galvanic cell is equal to decrease in Gibbs energy.

→ If concentration of all the reacting species is unity then $E_{cell} = E^\circ_{cell}$.

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

→ By measuring E°_{cell}, we can calculate ΔG° and equilibrium constant ($\Delta G^\circ = -RT\ln K$)

Example -: for Daniell cell $E^\circ_{cell} = 1.1V$ then value of $\Delta G^\circ = ?$ If $F = 96500\ C\ mol^{-1}$

[CBSE 2013 Delhi 2013C]

$\hookrightarrow \boxed{n=2}$ $\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.1$

(2M)

$\Delta G^\circ = -212300\ J\ mol^{-1}$

Question :- Calculate ΔG° and $\log K_c$ for the following reaction :

$$Cd^{2+}(aq.) + Zn(s) \longrightarrow Zn^{2+}(aq.) + Cd(s)$$

(CBSE 2019) (3M)

Given : $E^\circ_{Cd^{2+}/Cd} = -0.403V$, $E^\circ_{Zn^{+2}/Zn} = -0.763V$

Answer -: $E^\circ_{cell} = E^\circ_{Cd^{2+}/Cd} - E^\circ_{Zn^{+2}/Zn} = (-0.403) - (-0.763) = 0.36V$

$n = 2$ = No. of moles of electron used , $F = 96500\ C\ mol^{-1}$

① → $\Delta G^\circ = -nE^\circ F = -2 \times 96500 \times 0.36V = \underline{69480\ J\ mol^{-1}}$

② → $E^\circ_{cell} = \frac{0.059}{n} \log K_c$ then $\log K_c = \frac{nE^\circ_{cell}}{0.059} = \frac{2 \times 0.36}{0.059} = \underline{12.18}$

Question :- A copper - silver cell is set up. The copper ion concentration is 0.10M. The concentration of silver ion is not known. The cell potential when measured was 0.422V. Determine the concentration of silver ions in the cell. (3M)

[Delhi 2010]

Given : $E^\circ_{Ag^+/Ag} = 0.80V$, $E^\circ_{Cu^{+2}/Cu} = 0.34V$

Answer -: Cell Reaction : $Cu_{(s)} + 2Ag^+_{(aq.)} \longrightarrow Cu^{2+}_{(aq.)} + 2Ag_{(s)}$

$$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{+2}/Cu} = 0.80V - 0.34V = 0.46V$$

By using Nernst equation : $E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$ n = 2 = No. of electron taking part

$(E_{cell} = 0.422V)$

$([Cu^{+2}] = 0.1M)$

$$0.422V = 0.46V - \frac{0.059}{2} \log \frac{0.1}{[Ag^+]^2}$$

$$\log \frac{0.1}{[Ag^+]^2} = 1.288 \Rightarrow \frac{0.1}{[Ag^+]^2} = \text{antilog } 1.288 = 19.41$$

$$\rightarrow \frac{0.1}{19.41} = [Ag^+]^2 = 0.00515$$

$$\rightarrow [Ag^+] = 0.0717 = \underline{7.17 \times 10^{-2} M}$$

Question :- (i) Write the formulation for the galvanic cell in which the reaction takes place. Identify the cathode and the anode reactions in it.

[CBSE 2011C] (5M)

$$Cu_{(s)} + 2Ag^+_{(aq.)} \longrightarrow Cu^{+2}_{(aq.)} + 2Ag_{(s)}$$

Answer -:

At anode : $Cu_{(s)} \longrightarrow Cu^{+2}_{(aq.)} + 2e^-$

At cathode : $2Ag^+_{(aq.)} + 2e^- \longrightarrow 2Ag_{(s)}$

→ [Delhi 2010C] (1M)

(ii) Write the Nernst equation and calculate the emf of the following cell.

$Sn_{(s)} | Sn^{2+} (0.04M) || H^+ (0.02M) | H_{2(g)} | Pt_{(s)}$ (1 bar) Given: $E^\circ_{Sn^{+2}/Sn} = -0.14V$

→ At anode : $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq.)} + 2e^-$ $\boxed{n=2}$

At cathode : $2H^+_{(aq.)} + 2e^- \longrightarrow H_{2(g)}$

Net Reaction : $Sn_{(s)} + 2H^+_{(aq.)} \longrightarrow Sn^{2+}_{(aq.)} + H_{2(g)}$

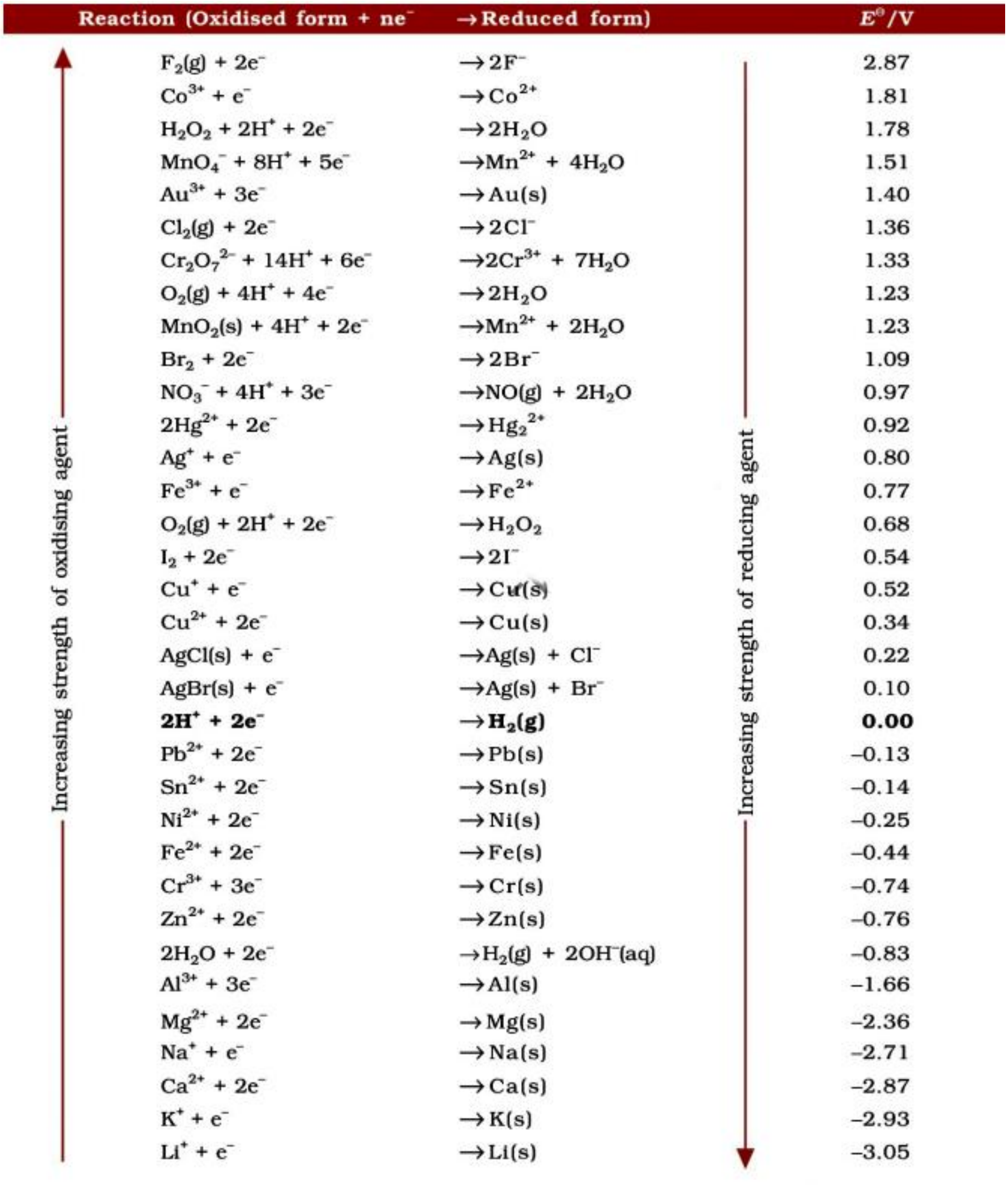
$$\rightarrow E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Sn^{+2}/Sn} = 0V - (-0.14V) = 0.14V$$

$$\rightarrow E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Sn^{+2}]}{[H^+]^2}$$

$$= 0.14V - \frac{0.059}{2} \log \frac{0.04}{(0.02)^2} = 0.14V - \frac{0.059}{2} \log \left(\frac{4}{100}\right)\left(\frac{100}{2}\right)^2$$

$E_{cell} = 0.0809V$

Table of SEP at 298K



Reaction (Oxidised form + ne$^-$	→Reduced form)	$E^\ominus$/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$\mathbf{2H^+ + 2e^-}$	$\mathbf{\rightarrow H_2(g)}$	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

➔ For F_2 gas SEP is highest in table indicating that F_2 has maximum tendency to get reduced to F^- : F_2 is the strongest oxidising agent.

➔ Li has lowest SEP indicating that Li^{+2} is a weakest oxidising agent and Li metal is the most powerful reducing agent.

➔ As value of SRP decreases for metal ion -> Reducing power of metal increases.

Example : Arrange following metals in an increasing order of their reducing power

SEP of metals are –

i. $K^+ \mid K = -2.93V$
ii. $Ag^+ \mid Ag = 0.80V$
iii. $Cu^{2+} \mid Cu = 0.34V$
iv. $Mg^{2+} \mid Mg = -2.37V$
v. $Cr^+ \mid Cr = -0.74V$
vi. $Fe^{+2} \mid Fe = -0.44V$

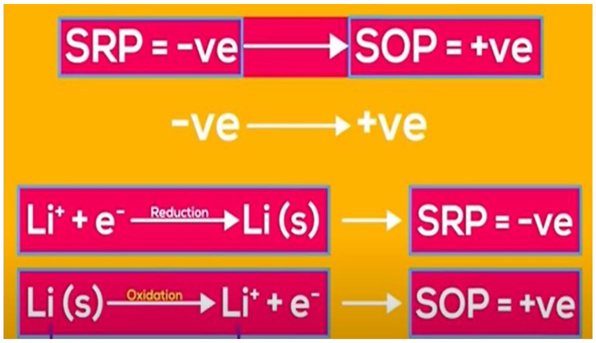
Reducing power of mertal $\propto \frac{1}{\text{Reduction Potential}}$ **[CBSE 2010]**

Order of Reducing power : Ag < Cu < Fe < Cr < Mg < K

Note: **SRP↑ ⟶ More Oxidising Power**


Oxidising Power ∝ SRP ⟶ OP ∝ RP


Reducing Power $\propto \frac{1}{SRP}$


SRP = -ve ⟶ SOP = +ve

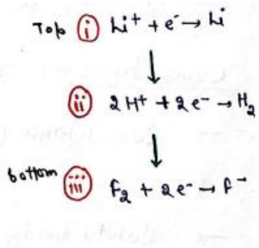
-ve ⟶ +ve

$Li^+ + e^- \xrightarrow{\text{Reduction}} Li(s)$ ⟶ SRP = -ve

$Li(s) \xrightarrow{\text{Oxidation}} Li^+ + e^-$ ⟶ SOP = +ve

ELECTROCHEMICAL SERIES

ELECTROCHEMICAL SERIES : If SRP values of different electrodes are arranged in a series order, then series is called Electrochemical Series.

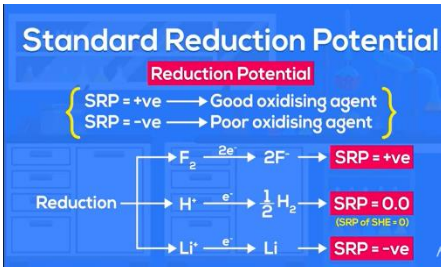

Top ⓘ $Li^+ + e^- \rightarrow Li$

↓

ⓘⓘ $2H^+ + 2e^- \rightarrow H_2$

↓

bottom ⓘⓘⓘ $F_2 + 2e^- \rightarrow F^-$

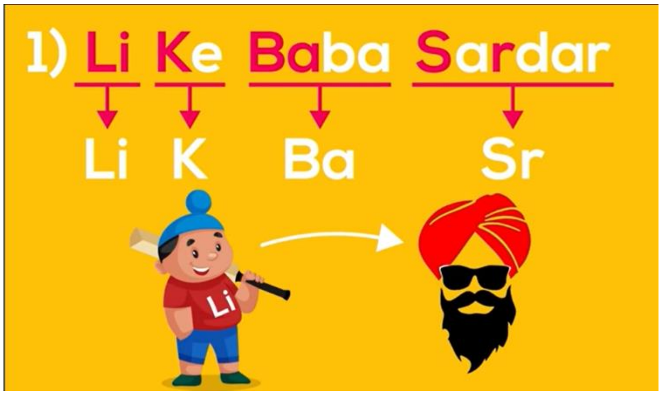

Standard Reduction Potential

Reduction Potential

SRP = +ve ⟶ Good oxidising agent
SRP = -ve ⟶ Poor oxidising agent

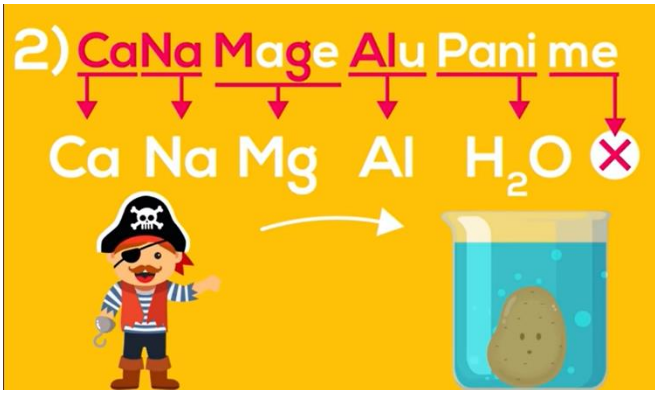
Reduction ⟶ $F_2 \xrightarrow{2e^-} 2F^-$ ⟶ SRP = +ve
$H^+ \xrightarrow{e^-} \frac{1}{2}H_2$ ⟶ SRP = 0.0 (SRP of SHE = 0)
$Li^+ \xrightarrow{e^-} Li$ ⟶ SRP = -ve

MNEMONICS



1) Li Ke Baba Sardar

Li K Ba Sr

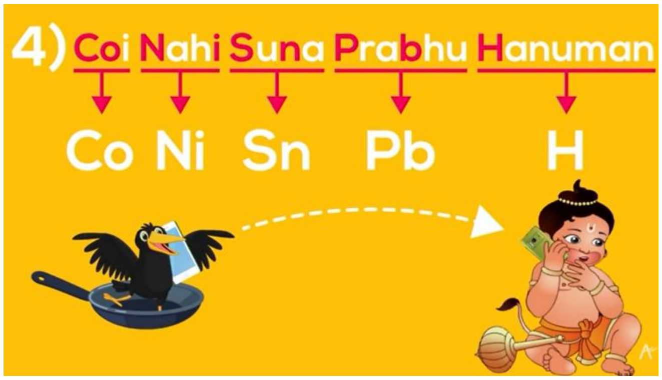


2) CaNa Mage Alu Pani me

Ca Na Mg Al H_2O ✕

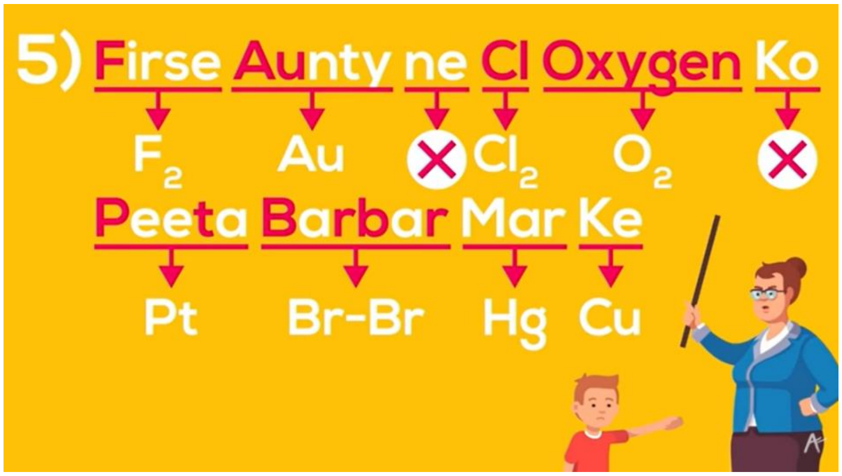
3) Maine Zinda Crow Fry Crdiya

Mn Zn Cr Fe Cd



4) Coi Nahi Suna Prabhu Hanuman

Co Ni Sn Pb H



5) Firse Aunty ne Cl Oxygen Ko

F_2 Au ✕ Cl_2 O_2 ✕

Peeta Barbar Mar Ke

Pt Br-Br Hg Cu

Application of Series -:

i. Prediction of reducing/oxidising power

SRP ↓ ⇒ Reducing Power ↑

⇒ oxidising Power ↓

ii.

Anode : Oxidation → Electrode higher up in series.
Cathode : Reduction → Lower in series with respect to anode.

For Daniell cell
→ Anode : Zn
→ Cathode : Cu

iii. Metals which are higher up in series can displace metals in lower in series from their salt solution.

$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$ $E^\circ_{Zn^{+2}/Zn} = -0.76V$

$ZnSO_4 + Cu \longrightarrow$ No reaction. $E^\circ_{Cu^{+2}|Cu} = 0.34V$

iv. Metals placed above than hydrogen can release H_2 gas on reaction with dilute acid solution.

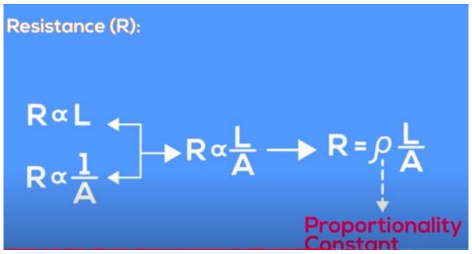
$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

$Cu + HCl \longrightarrow$ No reaction.

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS AND ITS MEASUREMENT

Some Basic Terms

1. **Resistance (R) :** It is the hindrance provided by the conductor in the passage of current



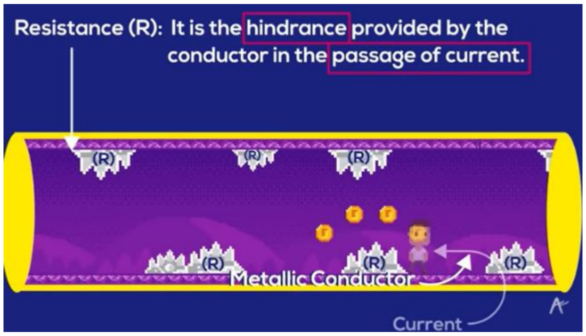
Resistance (R):

$R \propto L$

$R \propto \frac{1}{A}$

$\rightarrow R \propto \frac{L}{A} \rightarrow R = \rho \frac{L}{A}$

Proportionality Constant



Resistance (R): It is the hindrance provided by the conductor in the passage of current.

Unit of Resistance : **Ω ohm**

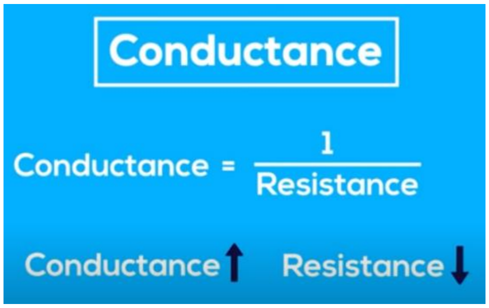
Definition of Resistivity

It is defined as the resistance offered by a conductor of unit length and unit cross-sectional area.

[If $A = 1\ m^2$ and $l = 1\ m$ then $\rho = R$.]

Unit of Resistivity : **Ω-m ohm-meter**

Conductance : The ease with which current flows through a conductor.



Conductance

Conductance = $\frac{1}{\text{Resistance}}$

Conductance ↑ Resistance ↓

G = 1/R => A/ρl => (1/ρ)A/l => κ A/l

Unit : Ω^{-1} : Siemen (S)

Conductivity : **κ = 1/ρ = l/RA**

Unit: Ω^{-1}-m^{-1} S m^{-1} or Ω^{-1}-cm^{-1} S cm^{-1}

→ Conductance [G] $= \frac{1}{R} = \frac{A}{\rho l} = K\frac{A}{l}$ = Conductivity × $\frac{1}{\text{Cell constant}}$

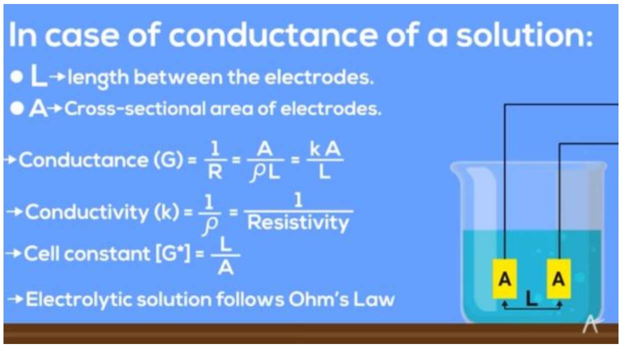
→ Conductivity (K) $= \frac{1}{\rho} = \frac{1}{\text{Resistivity}}$

→ Cell constant (G*) $= \frac{l}{A}$

Unit of cell constant = m^{-1}

Unit of conductance = ohm^{-1} = Siem (S)

Unit of conductivity = $S\ m^{-1}$
= $ohm^{-1}\ m^{-1}$



In case of conductance of a solution:

- L → length between the electrodes.
- A → Cross-sectional area of electrodes.

→ Conductance (G) = $\frac{1}{R} = \frac{A}{\rho L} = \frac{kA}{L}$

→ Conductivity (k) = $\frac{1}{\rho} = \frac{1}{\text{Resistivity}}$

→ Cell constant [G*] = $\frac{L}{A}$

→ Electrolytic solution follows Ohm's Law

MOLAR CONDUCTIVITY [Λ_m or λ_m] :

The conductance of solution kept between the electrodes at unit distance apart and having area of cross section large enough to accommodate sufficient volume of the solution that contains 1 mole of electrode.

- ➔ If V volume of solution contains 1 mole of electrolyte, then
  Molar conductivity **Λ_m = κ A/l = κ . V**

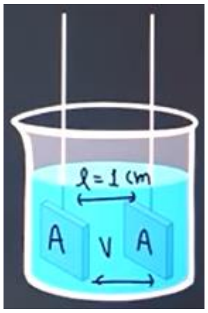
molar conductivity $\Lambda_m = k\frac{A}{l} = \boxed{k \cdot V = \Lambda_m}$

[Since $l = 1$ then $V = l \times A = A$]

- ➔ Molar Conductivity ↑ with ↓ in concentration (means dilution). This is because the total volume V of solution containing 1 mole of electrolyte increases on dilution.
- ➔ Relation between Λ_m and Molarity (M) :-

$$\boxed{\Lambda_m = \frac{k \times 1000}{M}}$$

- ➔ Unit of Λ_m = $Sm^2\ mol^{-1}$ or $Scm^2\ mol^{-1}$



Limiting Molar conductivity [Λ^0_m]

When the concentration -> 0

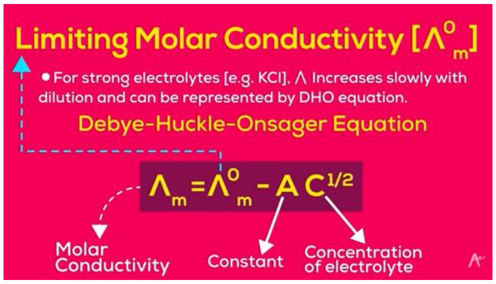
When the concentration approaches to 0, the molar conductivity reaches limiting value known as limiting molar conductivity.

For strong electrolye [KCl]. Λ increases slowly with dilution and can be represented by DHO Equation (Debye – Huckle – Onsager Equation).

$$\boxed{\Lambda_m = \Lambda^0_m - A\, c^{1/2}}$$

C = concentration of electrolyte.

A = Constant

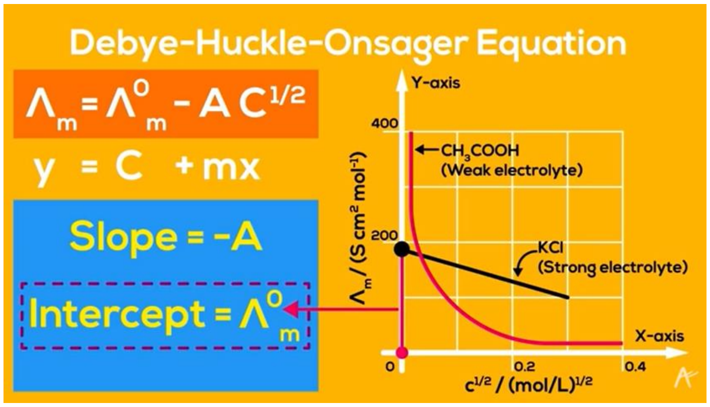


Limiting Molar Conductivity [Λ^0_m]

- For strong electrolytes [e.g. KCl], Λ increases slowly with dilution and can be represented by DHO equation.

Debye-Huckle-Onsager Equation

$\Lambda_m = \Lambda^0_m - A\,C^{1/2}$



Debye-Huckle-Onsager Equation

$\Lambda_m = \Lambda^0_m - A\,C^{1/2}$

$y = C + mx$

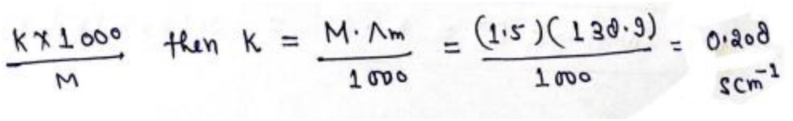
Slope = -A

Intercept = Λ^0_m

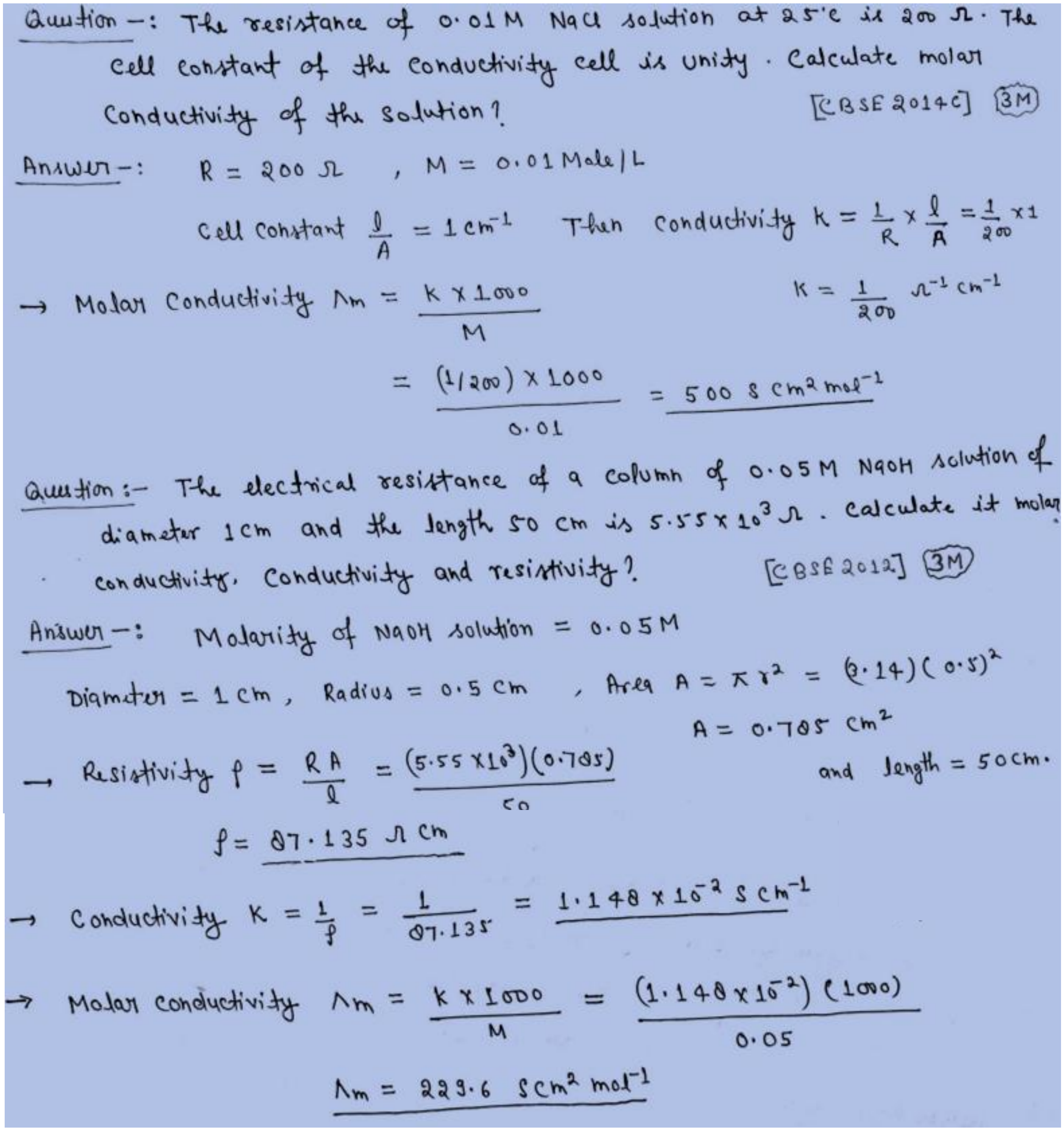
Q. Λ_m of a 1.5 M solution of an electrolyte is found to be 138.9 s cm^2 mol^{-1}. Calculate the conductivity of this solution.

Ans: M = 1.5 mol/L

We know that ->



$$\frac{K \times 1000}{M} \text{ then } K = \frac{M \cdot \Lambda_m}{1000} = \frac{(1.5)(138.9)}{1000} = 0.208 \; Scm^{-1}$$



Question -: The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell is unity. Calculate molar conductivity of the solution? [CBSE 2014C] (3M)

Answer -: $R = 200\ \Omega$, $M = 0.01$ Mole/L

Cell constant $\frac{l}{A} = 1\ cm^{-1}$ Then conductivity $K = \frac{1}{R} \times \frac{l}{A} = \frac{1}{200} \times 1$

$K = \frac{1}{200}\ \Omega^{-1} cm^{-1}$

→ Molar Conductivity $\Lambda_m = \frac{K \times 1000}{M}$

$$= \frac{(1/200) \times 1000}{0.01} = \underline{500\ S\ cm^2\ mol^{-1}}$$

Question :- The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and the length 50 cm is $5.55 \times 10^3\ \Omega$. Calculate it molar conductivity, conductivity and resistivity? [CBSE 2012] (3M)

Answer -: Molarity of NaOH solution = 0.05 M

Diameter = 1 cm , Radius = 0.5 cm , Area $A = \pi r^2 = (3.14)(0.5)^2$

$A = 0.785\ cm^2$

and length = 50 cm.

→ Resistivity $\rho = \frac{RA}{l} = \frac{(5.55 \times 10^3)(0.785)}{50}$

$\rho = \underline{87.135\ \Omega\ cm}$

→ Conductivity $K = \frac{1}{\rho} = \frac{1}{87.135} = \underline{1.148 \times 10^{-2}\ S\ cm^{-1}}$

→ Molar conductivity $\Lambda_m = \frac{K \times 1000}{M} = \frac{(1.148 \times 10^{-2})(1000)}{0.05}$

$\Lambda_m = \underline{229.6\ Scm^2\ mol^{-1}}$

→ **Question :-** The resistance of a conductivity cell containing 0.001 M KCl solution at 298K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298K is 0.146×10^{-3} S cm^{-1} ? [Delhi 2012] (3M)

Answer -: $K = 0.146 \times 10^{-3}\ S\,cm^{-1}$ and $R = 1500\ \Omega$

$$\boxed{\text{Cell Constant } G^* = K \cdot R} = 0.146 \times 10^{-3} \times 150\,cm^{-1} = 0.219\ cm^{-1}$$

KOHLRAUSCH LAW

It states that " *Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte*."

- ➔ For NaCl : $\Lambda^\circ_{NaCl} = \Lambda^\circ_{Na^+} + \Lambda^\circ_{Cl^-}$ $\boxed{\text{For Strong Electrolyte}}$
- ➔ CH_3COOH at infinite dilution ($C \longrightarrow 0$) : $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COO^-} + \Lambda^\circ_{H^+}$
- ➔ If an electrolyte on dissociation gives n_1 cations and n_2 anions then its limiting molar conductivity $\Lambda^\circ_m = n_1 \Lambda_+ + n_2 \Lambda_-$

For Example : $Al_2(SO_4) \longrightarrow 2\,Al^{3+} + 3\,SO_4^{2-}$

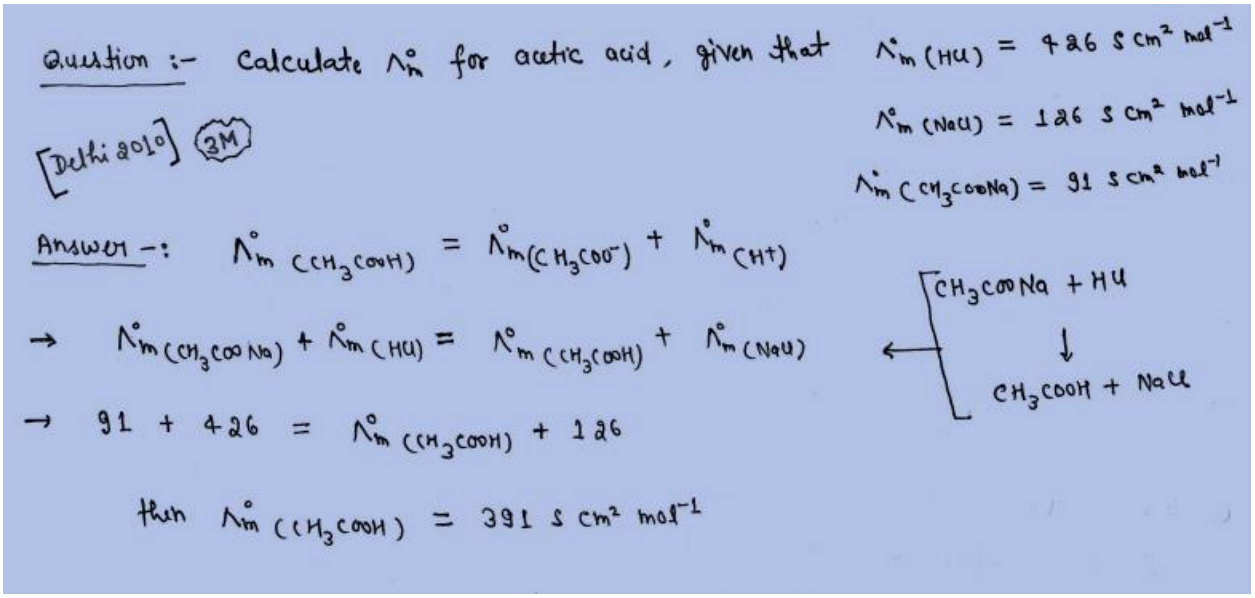
$$\Lambda^\circ_{m\,[Al_2(SO_4)_3]} = 2\,\Lambda^\circ_{m\,(Al^{+3})} + 3\,\Lambda^\circ_{m\,(SO_4^{2-})}$$

Q. The value of Λ^0_m of $Al_2(SO_4)_3$ is 258 S cm^2 mol^{-1}, while $\Lambda^0_{m(SO_4)}$ is 160 S cm^2 mol^{-1}. Calculate the limiting ionic conductivity of Al^{3+}.

Answer: $\Lambda^\circ_{m\,[Al_2(SO_4)_3]} = 2\,\Lambda^\circ_{m\,(Al^{+3})} + 3\,\Lambda^\circ_{m\,(SO_4^{2-})}$

$$\Lambda^\circ_{m\,(Al^{3+})} = \frac{\Lambda^\circ_{m\,(Al_2(SO_4)_3)} - 3\,\Lambda^\circ_{m\,(SO_4^{2-})}}{2} = \frac{258 - 3 \times 160}{2}$$

$$\Lambda^\circ_{m\,(Al^{3+})} = 189\ S\,cm^2\,mol^{-1}$$



Question :- Calculate Λ_m° for acetic acid, given that $\Lambda_m^\circ(HCl) = 426\ S\ cm^2\ mol^{-1}$

$\Lambda_m^\circ(NaCl) = 126\ S\ cm^2\ mol^{-1}$

$\Lambda_m^\circ(CH_3COONa) = 91\ S\ cm^2\ mol^{-1}$

[Delhi 2010] (3M)

Answer -: $\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(CH_3COO^-) + \Lambda_m^\circ(H^+)$

$\rightarrow \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) = \Lambda_m^\circ(CH_3COOH) + \Lambda_m^\circ(NaCl)$ $\leftarrow$ $CH_3COONa + HCl \downarrow CH_3COOH + NaCl$

$\rightarrow 91 + 426 = \Lambda_m^\circ(CH_3COOH) + 126$

then $\Lambda_m^\circ(CH_3COOH) = 391\ S\ cm^2\ mol^{-1}$

Degree of Dissociation [α]

The ratio of molar conductivity (Λ_m) at a specific contentration to the molar conductivity at infinite dilution ($\Lambda^0{}_m$) is known as degree of dissociation (α)

$$\boxed{\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}}$$

Question: Calculate the degree of dissociation of acetic acid at 298K, given that

$\Lambda_m(CH_3COOH) = 11.7\ S\ cm^2\ mol^{-1}$, $\Lambda_m^\circ(CH_3COO^-) = 40.9\ S\ cm^2\ mol^{-1}$

$\Lambda_m^\circ(H^+) = 349.1\ S\ cm^2\ mol^{-1}$

[Delhi 2011C] (3M)

Answer: Degree of dissociation = $\boxed{\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}}$

$\underset{(CH_3COOH)}{\Lambda_m^\circ} = \Lambda_m^\circ CH_3COO^- + \Lambda^\circ_{H^+}$

$\rightarrow$ Then $\alpha = \frac{11.7}{390} = 3 \times 10^{-2}$

= 40.9 + 349.1 = 390 S cm^2 mol $^{-1}$

Question -: Conductivity of 2.5×10^{-4} M methanoic acid is 5.25×10^{-5} S cm^{-1}. Calculat its molar conductivity and degree of dissociation. [C BSE 2015] ③M

Given : $\lambda^{\circ}_{(H^+)} = 349.5$ S cm^2 mol^{-1} and $\lambda^{\circ}_{(HCOO^-)} = 50.5$ S cm^2 mol^{-1}

Answer -:

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} = 210 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^{\circ}_m (HCOOH) = \lambda^{\circ}_{(H^+)} + \lambda^{\circ}_{(HCOO^-)} = 50.5 + 349.5 = 400 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{210}{400} = 0.525$$

Question -: The conductivity of 0.001 M acetic acid is 4×10^{-5} S cm^{-1}. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2 mol^{-1}. [Delhi 2013C] ②M

Answer -:

$$\begin{array}{lccc} & CH_3COOH & \rightleftharpoons & CH_3COO^- + H^+ \\ \text{Initial Con}^n & C & & 0 \quad\quad 0 \\ \text{After time } t, & C - C\alpha & & C\alpha \quad\quad C\alpha \end{array}$$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} \quad \# \ \Lambda^{\circ}_m = 390 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \Lambda_m = \frac{K \times 1000}{M} = \frac{(4 \times 10^{-5})(1000)}{(0.001)}$$

$$\Lambda_m = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\rightarrow \alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{40}{390} = 0.103$$

$\alpha \rightarrow$ Degree of dissociation

Then, Dissociation constant

$$K = \frac{C\alpha \cdot C\alpha}{C - C\alpha}$$

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

Put value of α in above equation →

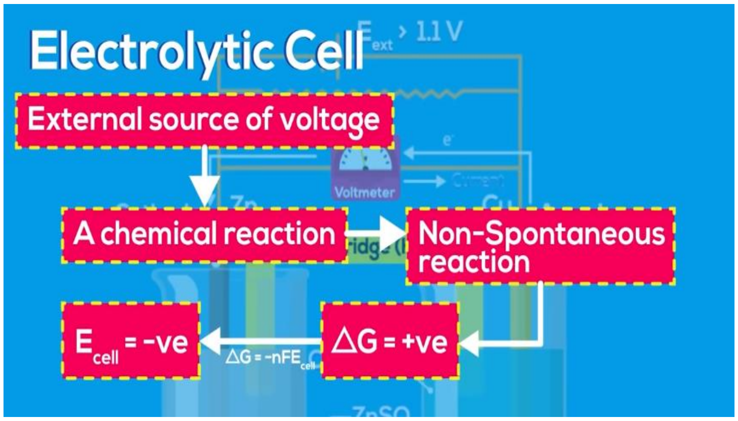
$$K = \frac{(0.001)(0.103)^2}{(1 - 0.103)}$$

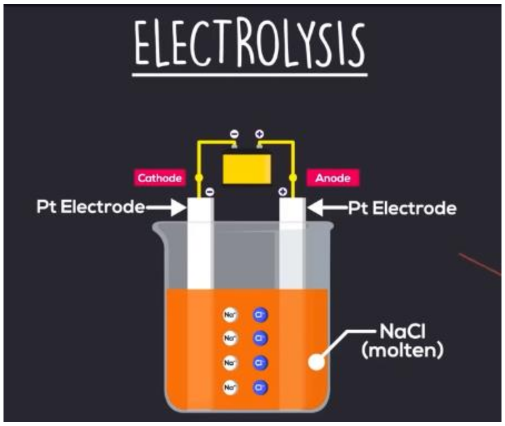
$$\boxed{K = 1.18 \times 10^{-5}}$$

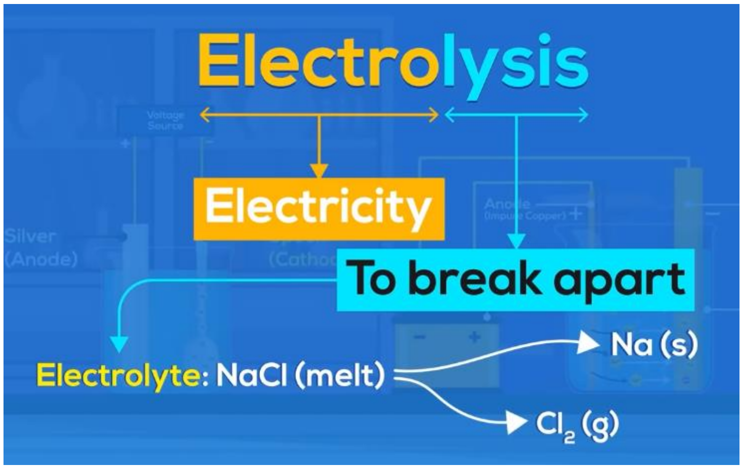
ELEECTROLYSIS

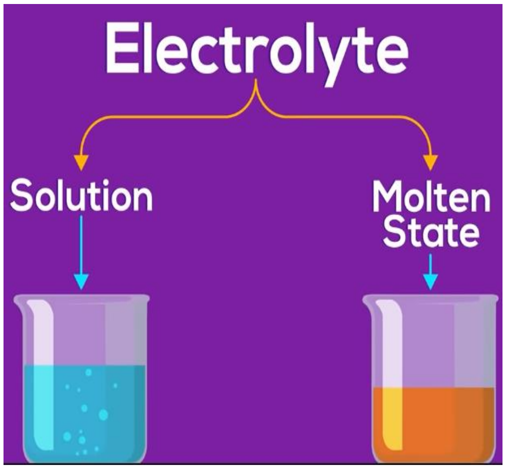
ELECTROLYTIC CELLS :

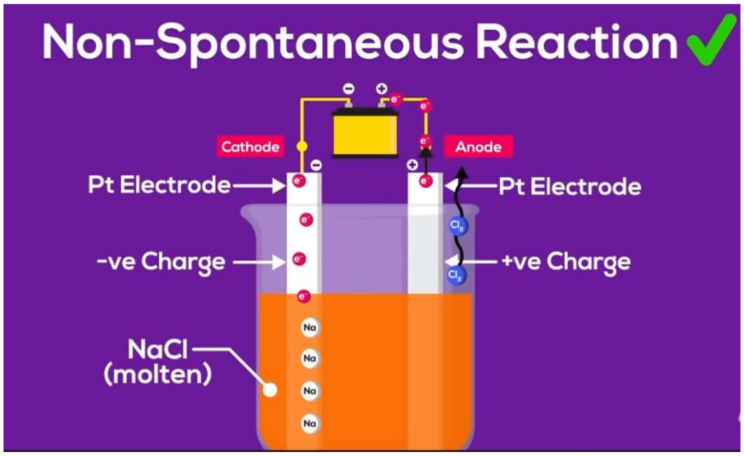
When external potential applied becomes greater than E^0_{cell} of electrochemical cell, electron flows from cathode to anode, means that electrochemical cell becomes electrolytic cell.

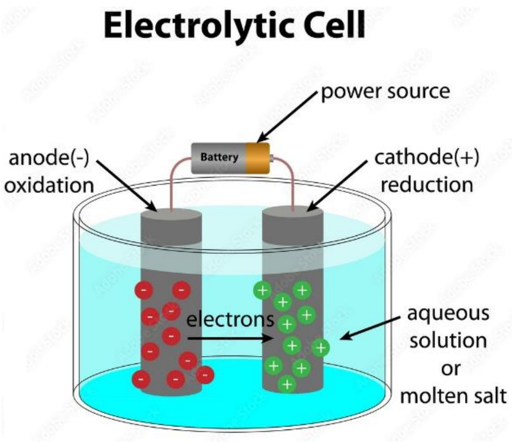




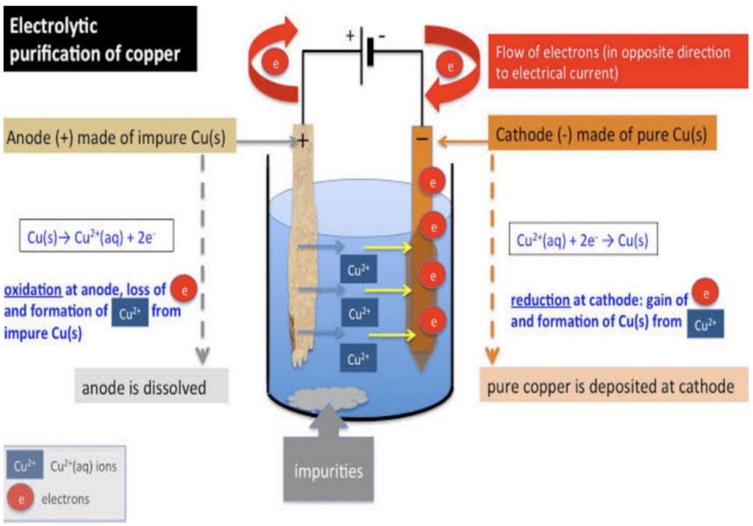








In electrolytic cell, electrical energy is used to carry out non-spontaneius chemical reactions and the process which takes place in an electrolytic cell is called electrolysis



Purification of Impure Copper :-

→ Cu^{2+} ion discharge at cathode

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

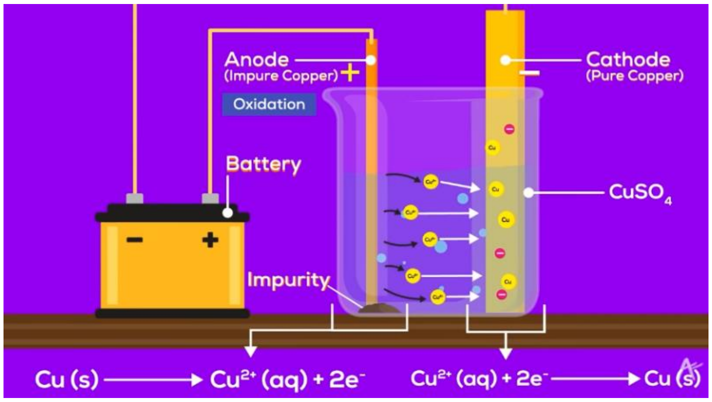
→ Copper metal is deposited on the cathode.

→ At anode, Copper is dissolved (oxidised)

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

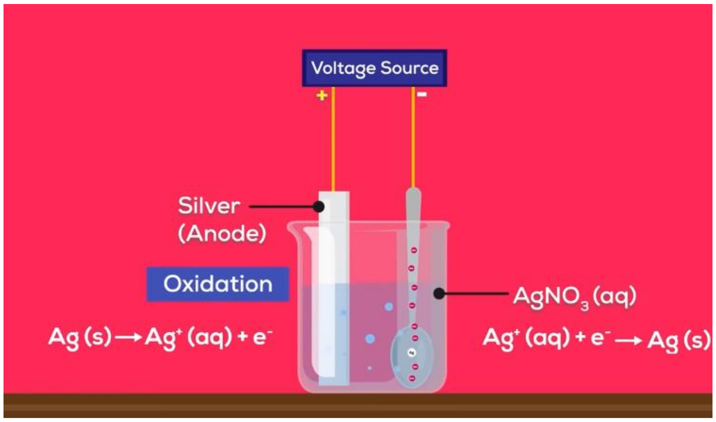
→ **Impure Copper** : Anode

→ Pure Copper : Cathode



Making of Silver Spoon

In electroplating practice, the current is usually introduced from an external source and the anode is the positive electrode and cathode is a negative electrode. The cathode is the electrode where the electrochemical reduction reaction occurs. The anode is that where the electrochemical oxidation reaction occurs.

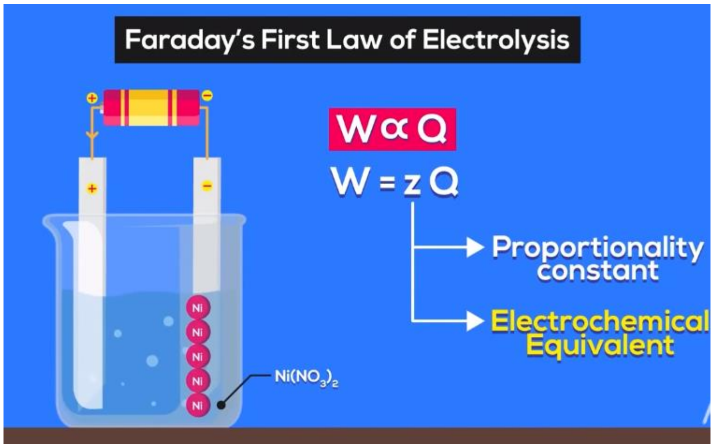


The electroplating process uses an anode and a cathode. In electroplating, the metal dissolved from the anode can be plated onto the cathode. The anode is provided with direct current, oxidizing, and dissolving its metal atoms in the electrolyte solution. At the cathode, the dissolved metal ions are decreased, and the metal is placed on the product.

FARADAY LAWS OF ELECTROLYSIS

IMPORTANT

Quantitative Aspects of Electrolysis



FIRST LAW: "The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or molten)."

→ If W gram of substance gets deposited on passing Q coulomb of electricity. Then

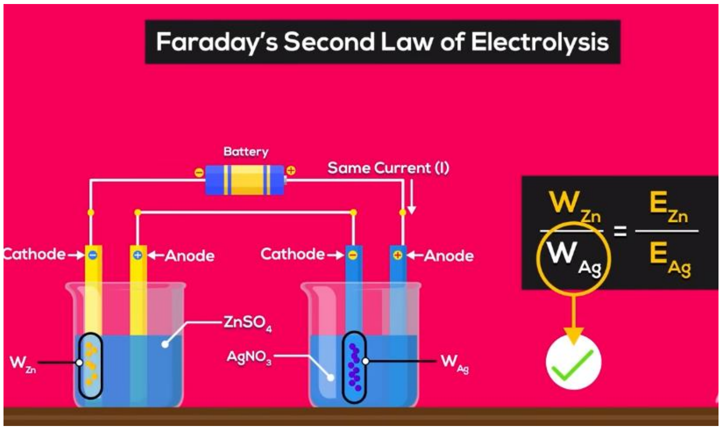
$W \propto Q$ or $W = Z\,Q$

$$\boxed{W = Z\,I\,t}$$

Where Z → Electrochemical equivalent

I → Current [Ampere]

T → Time [Second]



SECOND LAW: "The amount of different substance liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights."

→ Equivalent Weight

$$\left[\frac{\text{atomic mass of metal}}{no.of\ electrons\ required\ to\ reduce\ the\ cation}\right]$$

→ $$\boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2}}$$

W → mass of substance deposited

E → Equivalent weight

NOTE :- $Ag^+(aq) + e^- \longrightarrow Ag$ [one mole of the electron is required for the reduction of one mole of Ag^+ ion.]

→ charge on 1 mole of electron = 1 faraday $= N_A \times (1.6021 \times 10^{-19}\ C)$

$= (6.02 \times 10^{23}\ mol^{-1})\ (1.6021 \times 10^{-19}\ C)$

$= 96487\ C\,mol^{-1} \cong 96500\ C\,mol^{-1}$

Question :- A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Answer -: $t = 10 \times 60 = 600$ second

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

2F charge is required for $\underset{63\text{ g of Cu.}}{\underline{1\text{ mol Cu}}}$

→ $2 \times 96500\,C$ charge for $= 63$ g of Cu

$1C$ " " $= \dfrac{63\,g}{2 \times 96500\,C}$

then, $900C$ " " $= \dfrac{63 \times 900}{2 \times 96500} = 0.2938\,g.$

$\left[\begin{array}{l} Q = i \cdot t \\ \quad = 1.5 \times 600 = 900C \end{array} \right]$

Question :- How many electrons flow through a metallic wire if a current of 0.5 is passed for 2h? given $1F = 96500\,C\,mol^{-1}$

[CBSE 2017] (1.5M)

Answer -: charge $Q = i \cdot t = (0.5)(2 \times 60 \times 60)$

$Q = 3600C$

→ $Q = n \cdot e^- \Rightarrow n = \dfrac{Q}{e^-} = \dfrac{3600C}{1.6 \times 10^{-19}C} = 2250 \times 10^{19}$

Products of electrolysis :-

→ **Electrolysis of aqueous NaCl**

→ Ions in aqueous NaCl

$[Na^+, H^+, Cl^-, OH^-, H_2O]$

→ At cathode, Competition between H^+/Na^+

$Na^+(aq) + e^- \longrightarrow Na_{(s)}$ $E^\circ = -2.71V$

$\boxed{H^+ + e^- \longrightarrow \frac{1}{2}H_2}$ $\underline{E^\circ = 0V}$

↳ More feasible than above reaction.

→ At anode, competition between Cl^- and $H_2O(l)$

$\boxed{Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2 + e^-}$ $\underline{E^\circ = 1.36V}$

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^\circ = 1.23V$

(The reaction at anode with lower value of E° is preferred but due to overpotential requirement of oxygen, above reaction is preferred although it has more E° value)

→ **Electrolysis of molten NaCl**

→ Here we have only one cation (Na^+) and one anion (Cl^-)

→ Cathode : $Na^+ + e^- \longrightarrow Na$

→ Anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

→ So, we get Na metal and Cl_2 gas on electrolysis of molten NaCl.

Question :- Which reaction occur at anode and why? (2M) [CBSE 2011C]

① $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$ $E^\circ = 1.23V$

② $\boxed{2Br^-(aq.) \longrightarrow Br_2(g) + 2e^- \quad E^\circ = 1.08V}$

→ This reaction is preferred because it has lower reduction potential.

Question :- Which reaction is feasible at cathode and why?

Answer -: $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E^\circ = +0.80V$

Ag^+ ions have more value of SRP. $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2$ $E^\circ = 0.0V$

Therefore Ag^+ ions are discharged at cathode in preference of H^+ ions. [Delhi 2015] (1M)

Question -: How much electricity in terms of faradays is required to produce 20g of Ca from molten $CaCl_2$? [Delhi 2013C] (2M)

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

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

$2F \longrightarrow 40g$

Then (1F) $\longleftarrow$ 20g # 1F is required to produce 20g of Ca.

Question :- An aqueous solution of $CuSO_4$ was electrolysed between Pt electrodes using a current of 0.1287 A for 50 min. [Given : Atomic mass of Cu = $63.5\ g\,mol^{-1}$

(i) Write the cathodic Reaction -: $Cu^{+2} + 2e^- \longrightarrow Cu$

(ii) Calculate ⓐ Electric charge passing through solution $Q = It$

$= 0.1287 \times 50 \times 60$

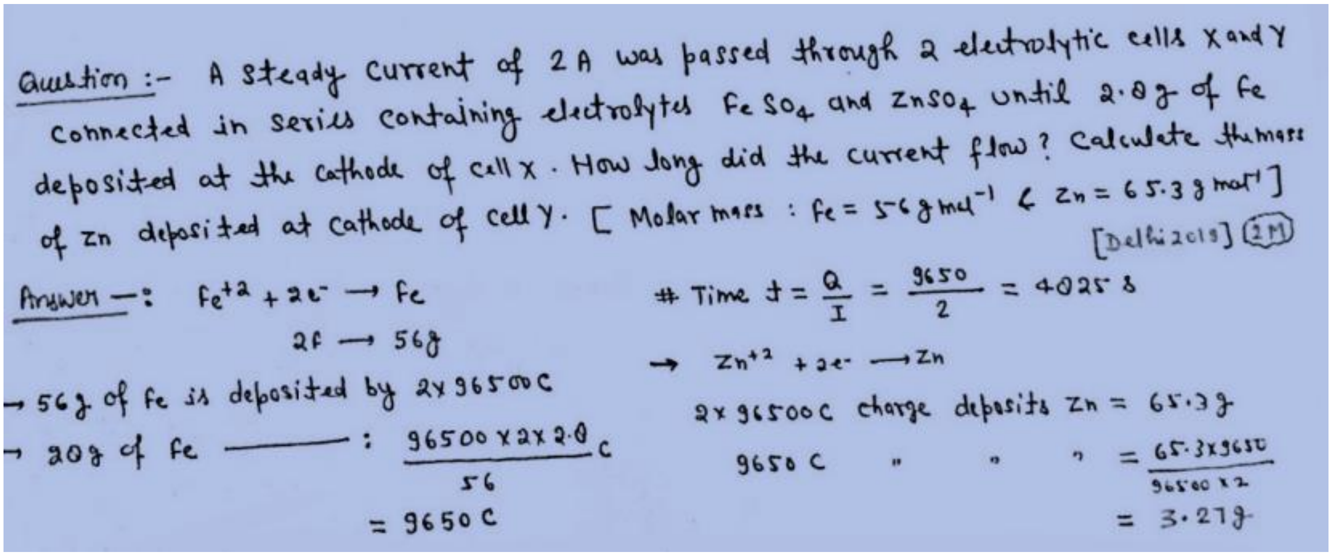
$= 386.1\,C$

ⓑ Mass of copper deposited at the cathode

$$m = ZIt = Z \cdot Q = \left[\frac{\text{Equivalent Weight}}{96500}\right] \cdot Q$$

$$m = \frac{(63.5/2)}{96500} \times 386.1 = 0.127g$$

[Delhi 2011C] (3M)



Question :- A steady current of 2 A was passed through 2 electrolytic cells X and Y until 2.0 g of Fe connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at cathode of cell Y. [Molar mass : Fe = 56 g mol⁻¹ & Zn = 65.3 g mol⁻¹]

[Delhi 2019] ②M

Answer —: $Fe^{+2} + 2e^- \rightarrow Fe$

$2F \rightarrow 56g$

→ 56g of Fe is deposited by 2 × 96500 C

→ 20g of Fe ——— : $\frac{96500 \times 2 \times 2.0}{56}$ C

$= 9650$ C

Time $t = \frac{Q}{I} = \frac{9650}{2} = 4025$ s

→ $Zn^{+2} + 2e^- \rightarrow Zn$

2 × 96500 C charge deposits Zn = 65.3 g

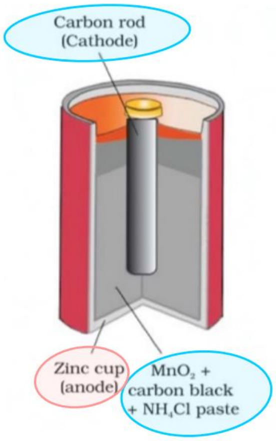
9650 C " " " $= \frac{65.3 \times 9650}{96500 \times 2}$

$= 3.27g$

Batteries : A battery contains one or more than one cell connected in series. It is basically a galvanic cell where the chemical energy of redox reaction is converted into electrical energy. There are mainly 2 types of batteries.

A.) Primary Batteries – In primary batteries the reaction occurs only once and after use over a time period battery becomes dead and can not be reused again.

Leclanche Cell : [Dry Cell]



Anode : Zinc Container

Cathode : Carbon rod [Surrounded by MnO_2 + Carbon]

→ The space between elecrtrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$

Anode reaction :- $Zn_{(s)} \rightarrow Zn^{+2} + 2e^-$

Cathode reaction :- $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

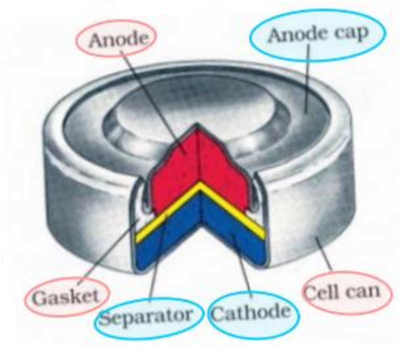
Overall Reaction :- $Zn_{(s)} + 2NH_4^+ + 2MnO_2 \rightarrow Mn_2O_3 + H_2O + [Zn(NH_3)_2]^{2+}$

→ By using Nerst Equation

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[Zn(NH_3)_2]^{2+}}{[NH_4^+]^2}$$

Due to the pressuer of ions ($[Zn(NH_3)_2]^{2+}$) in the overall reaction, its voltage decreases with time

→ Use : Commonly used in transistors and clocks

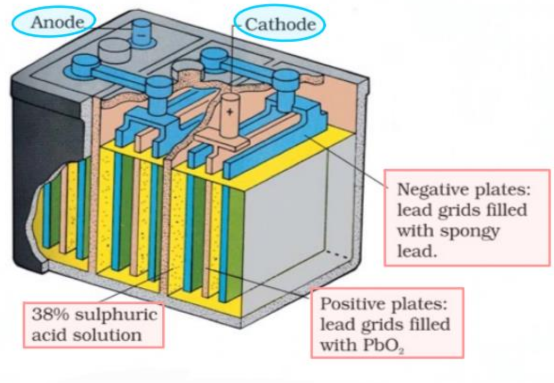


Mercury Cell :- Anode : Zn-Hg amalgam
Cathode : Paste of HgO and Carbon
Electrolyte : Paste of ZnO + KOH
Anode reaction : $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$
Cathode reaction : $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$
Overall Reaction : $Zn(Hg) + HgO \rightarrow ZnO + Hg$

→ The voltage of a mercury cell remains constant during it's life as the overall reaction does not involve any ion in solution whose concentration can change during it's life time.

B.) Secondary Batteries :- A secondary cell after use can be recharged by passing current through it in opposite direction so that it can be used again. A secondary cell can undergo a large no. of discharging and charging cycles.

Lead Storage Battery :- It is a most important secondary cell, commonly used in automobiles and invertors.
Anode : lead [Pb]
Cathode : A grid of lead with PbO_2
Electrolyte : 38% H_2SO_4 solution (by mass)



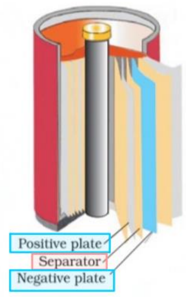
Anode Reaction : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_4 + 2e^-$

Cathode Reaction : $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} \xrightarrow{+4H^+ + 2e^-} PbSO_4 + 2H_2O$
Overall Reaction : $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Nickel – Cadmium Cell :- Ni-Cd cell is a secondary cell. It has longer life than lead storage cell but more expensive to manufacture.

The overall reaction during discharging is :-

$Cd + 2Ni(OH)_3 \rightarrow CdO + Ni(OH)_2 + H_2O$



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Fuel Cells :- Galvanic cells that are designed to convert the energy of combustion of fuels [Like H_2, CH_4, CH_3OH] directly into electrical energy are called fuel cells.

H_2 – O_2 Fuel Cell :- It is an important fuel cell which uses the reaction of H_2 with O_2 to form H_2O.

→ The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the Astronauts.

→ In the cell H_2 and O_2 are bubbled through porous carbon electrodes into concentrated aq. NaOH solution.

→ The catalysts like Pt or Pd are incorporated into the electrodes for increasing the rate of electrode reactions.

Cathode : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

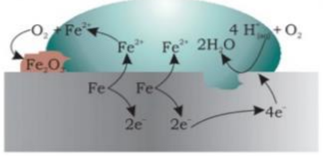
Anode : $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Overall Reaction : $2H_2 + O_2 \rightarrow 2H_2O$

Advantages of H_2-O_2 cell :- Fuel cell do not cause any pollution unlike thermal plant (Coal, oil burning produces CO_2 gas). Efficiency of fuel cell is high than thermal plants.

Corrosion :- It is basically an electrochemical phenomenon in which a metal oxide or other salt of metal forms a coating on the metal surface

For example :- Rusting of iron



→ Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

→ Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Atomospheric
oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

This Chapter Ends here !! But not your work

Go to Practice Questions, Solve Dpps attend MCQs and revise the notes after some 2nd 4th and 7th day

To get 95+ you have to keep on revising what you studied.

[Remember Consistency and HardWork Gives Great Result]

NOTES MADE BY

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