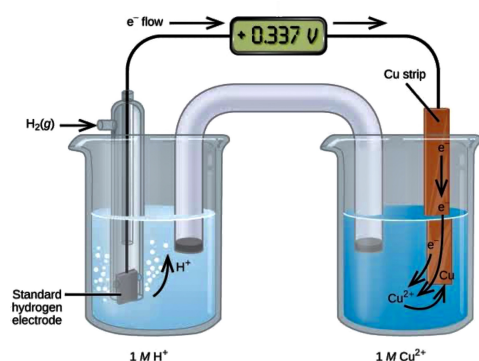


Flow Chart Of Complete Chapter : NCERT

Nernst Equation

- Emf of Cell
- Gibbs free energy
- Equilibrium



Cell

Galvanic Cell

Electrolytic Cell

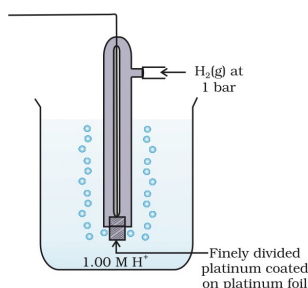
Electrolysis

Faraday's Law

Electrochemical Series

Electrochemistry

Standard Hydrogen Electrode



Conductance in solution

Batteries

Corrosion

Resistance

Resistivity

Conductance

Conductivity

Kohlrausch Law

Molar Conductivity

Electrochemistry

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

→ There are two types of cells. (i) Electrochemical Cells (ii) Electrolytic Cells.
[Galvanic cell]

Some Basic Definitions -:

Oxidation -: Loss of electron $\text{Zn} \rightarrow \text{Zn}^{+2} + 2e^-$

Reduction -: Gain of electron $\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$

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

Electrode -: Surface at which oxidation or reduction takes place.

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



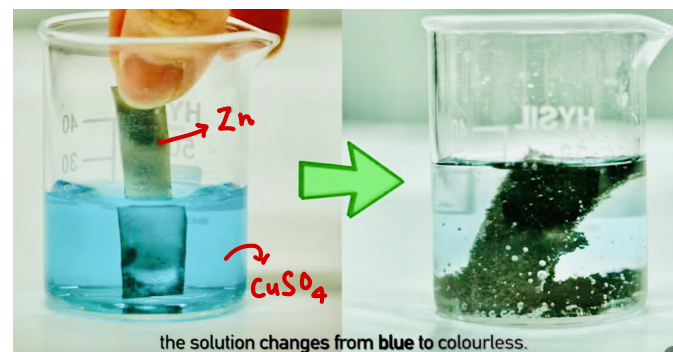
Placing a Zn rod in CuSO_4 solution -:

→ CuSO_4 solution is blue in colour. But if we place a Zn rod in CuSO_4 solution, colour fades out.

This is because of reduction of $\text{Cu}^{+2} \rightarrow \text{Cu}$.



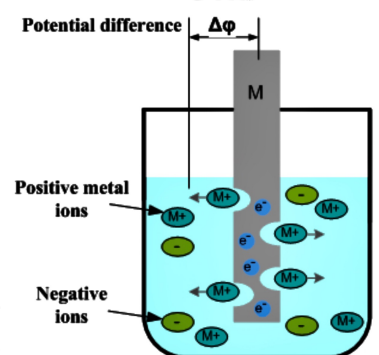
→ Above is a spontaneous reaction. It does not require any external work.



Electrode Potential -: Potential difference between metal and metal ion in which electrode is dipped is called electrode potential.

→ Electrode potential of Zn $\rightarrow \text{Zn} | \text{ZnSO}_4$

Electrode potential of Cu $\rightarrow \text{Cu} | \text{CuSO}_4$

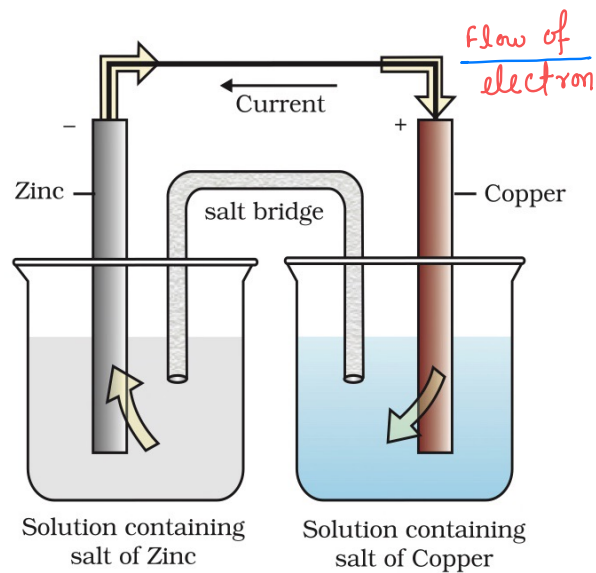


Galvanic or Voltaic Cell :- A galvanic

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

→ Spontaneous then $\Delta G = \text{ve}$.

→ In this device ΔG of spontaneous redox reaction is converted into electrical work (which may be used for running a motor, fan, heater etc.)



Construction :- It consist of two mettalic electrodes dipping in electrolytic solutions. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCl , KNO_3 etc. This tube is called salt bridge.

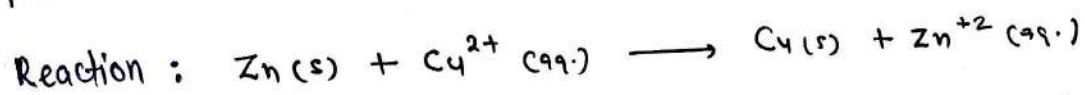
→ Salt bridge is necessary because

- (i) It connects the solution of two half cells, thus completes the cell circuit. [Delhi 2011] (1M)
- (ii) It prevents diffusion of solutions from one compartment to other.

→ In representation of cell, salt bridge is represented by $\parallel$.

→ In galvanic cell : oxidation at anode [negative plate]
reduction at cathode [positive plate]

Daniell Cell :- Among the galvanic cells 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 cell is called Daniell cell.



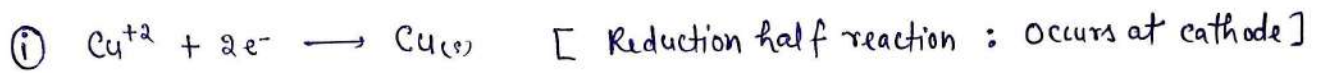
Cell Representation : $\text{Zn} \mid \text{Zn}^{2+}(\text{aq.}) \parallel \text{Cu}^{2+}(\text{aq.}) \mid \text{Cu}$ → phase boundary.

[Delhi 2013] (1M)

: Anode half cell $\parallel$ Cathode half cell
↕ salt bridge

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

→ The two half cell reactions are



Electrochemical Cell

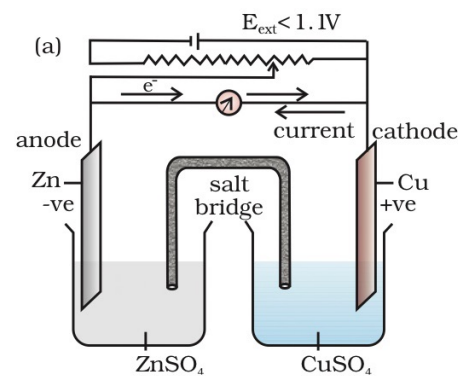
(i) Galvanic Cell

→ Chemical Energy → Electrical Energy

→ $\Delta G = \ominus \text{ve}$ Spontaneous Reaction

→ Power is produced.

→ (a)



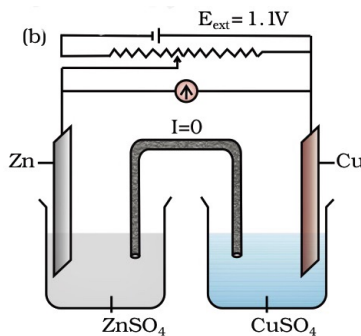
When $E_{\text{ext}} < 1.1 \text{ V}$

- (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.

(ii) Reversible

→ No Net reaction

(b)



When $E_{\text{ext}} = 1.1 \text{ V}$

- (i) No flow of electrons or current.
- (ii) No chemical reaction.

$$E_{\text{cell}} = 1.1 \text{ V}$$

(iii) Electrolytic cell

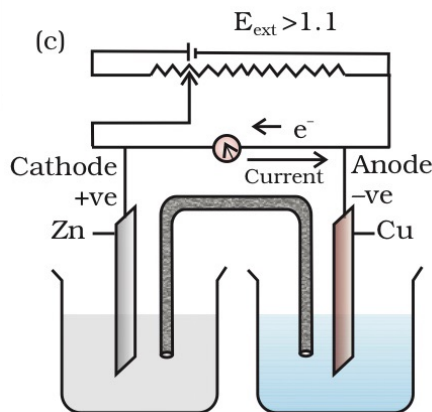
→ Electrical energy → Chemical energy

→ Non spontaneous Reaction

[$\Delta G = +\text{ve}$]

→ Power is consumed.

(c)



When $E_{\text{ext}} > 1.1 \text{ V}$

- (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.

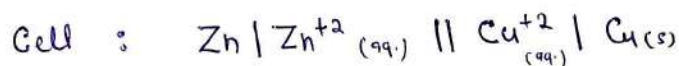
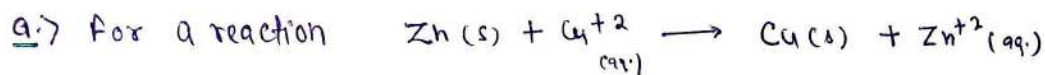
→ Functioning of Daniell cell when external voltage (E_{ext}) opposing the cell potential is applied.

NOTE:- (i) When the concentration of all the species involved in a half cell is unity then the electrode potential is known as Standard Electrode Potential.

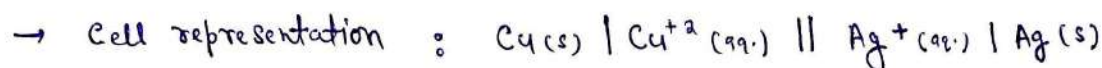
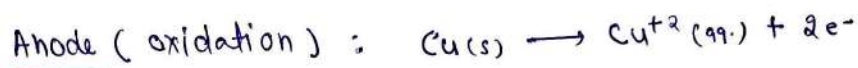
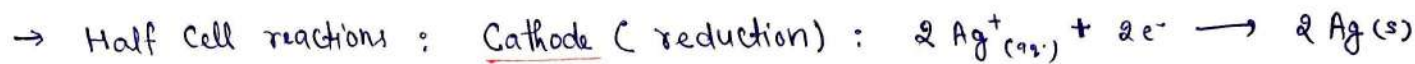
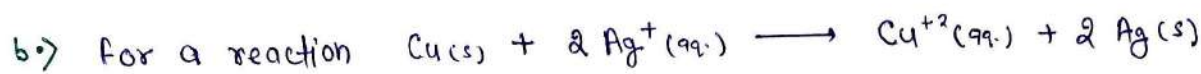
(ii) IUPAC Convention : Standard Reduction Potential (SRP) is SEP.

(iii) Cell Potential :- The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.

→ $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}}$ [cell : Anode half || Cathode half cell]



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



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

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

Standard Hydrogen Electrode :-

→ Representation of half cell for standard hydrogen electrode : $\text{Pt(s)} | \text{H}_2(\text{g}) (1\text{ bar}) | \text{H}^{+}_{(\text{aq})}$

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

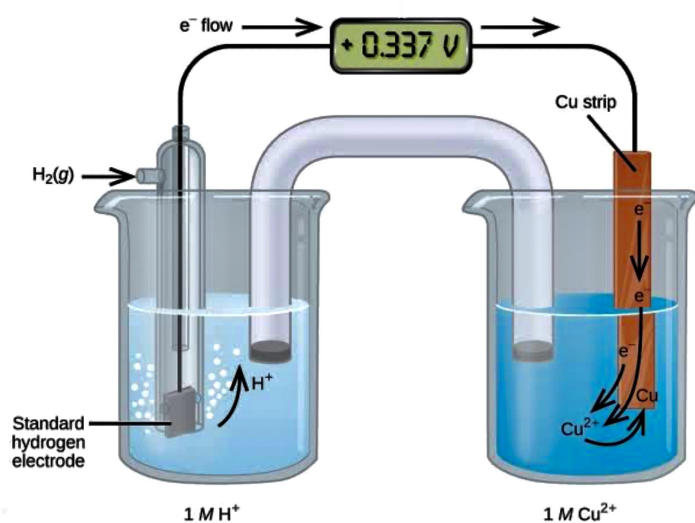
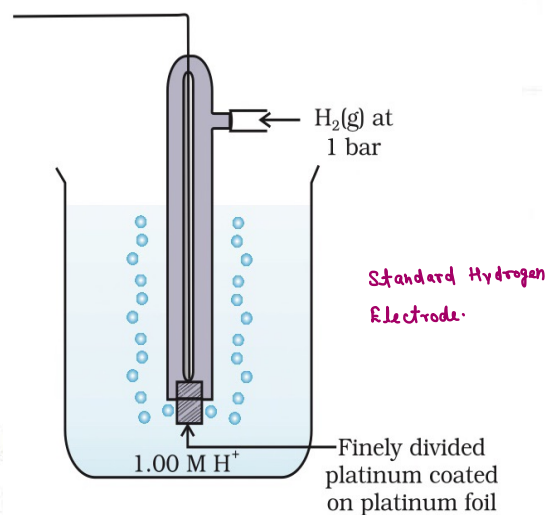


→ Measurement of electrode potential :-

→ 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.

Standard Hydrogen Electrode $[\text{Pt(s)} | \text{H}_2(\text{g}) (1\text{ bar}) | \text{H}^{+}_{(\text{aq})} (1\text{ M})] || \text{other half cell}$

→ If the concentrations 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°_R) of the given half cell. $E^{\circ} = E^{\circ}_R - E_L = E^{\circ}_R - 0 = E^{\circ}_R$



→ To calculate $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$, make a cell $\text{Pt}(s) | \text{H}_2(g) (1 \text{ bar}) | \text{H}^+(aq.) 1 \text{ M} || \text{Cu}^{2+}(aq.) 1 \text{ M} | \text{Cu}$

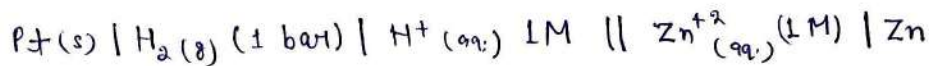
→ EMF of this cell = 0.34 V

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

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

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

(ii)



→ $E^\circ_{\text{cell}} = -0.76 \text{ V}$

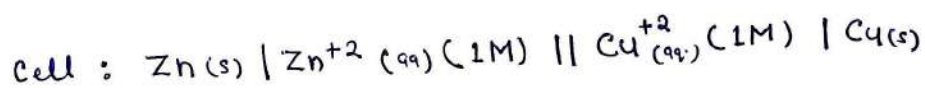
$$E^\circ_{\text{cell}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - E^\circ_{\text{HSE}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - 0$$

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

→ 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 :-



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

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.

For example - : Hydrogen Electrode : $\text{Pt}(s) | \text{H}_2(g) | \text{H}^+(aq.)$

Bromine Electrode : $\text{Pt}(s) | \text{Br}_2(aq.) | \text{Br}^-(aq.)$

Nernst Equation :- It gives relation between electrode potential, temperature and concentration of metal ions.

For reaction $\text{M}^{n+}(aq.) + n e^- \longrightarrow \text{M}(s)$

$n \rightarrow$ No. of electrons

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

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

$$\left\{ \begin{array}{l} R = \text{Gas constant} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ F = \text{Faraday's constant} = 96487 \text{ C mol}^{-1} \\ T = 298 \text{ K} \quad \text{and} \quad [\text{M}] = 1 = [\text{solid}] \end{array} \right.$$

→ In Daniell cell : Electrode Potential for any given concentration of $\text{Cu}^{2+}/\text{Zn}^{2+}$

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

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

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

$$= [E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}] - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}_{(\text{aq})}]}{[\text{Cu}^{2+}_{(\text{aq})}]}$$

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

Question:- For the cell $\text{Zn(s)} | \text{Zn}^{2+}(2\text{M}) || \text{Cu}^{2+}(0.5\text{M}) | \text{Cu(s)}$ (3M) [Delhi 2011C]

(i) Write the equation for each half cell.

(ii) calculate cell potential at 25°C .

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

$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$

Answer:- (i) Anode: $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-}$
[2M]

Cathode: $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \longrightarrow \text{Cu(s)}$
(0.5M)

(ii) $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = 0.34\text{V} - (-0.76\text{V}) = 1.10\text{V}$

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

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

Question:- A Zn rod is dipped in 0.1M solution of ZnSO_4 . The salt is 95% dissociated at its dilution at 298K. Calculate the electrode potential. [Delhi 2012C] (2M)

$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$

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

By using Nernst equation, we get $E_{\text{Zn}^{2+}/\text{Zn}} = E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$

→ $[\text{Zn}^{2+}] = \frac{95}{100} \times 0.1 = 0.095\text{M}$; $E_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V} - \frac{0.059}{2} \log \frac{1}{0.095} = -0.7901\text{V}$

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



(3M)

[Delhi 2016]

Given: $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$

$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$

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

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

$\rightarrow E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{2+}/\text{Fe}} - E^\circ_{\text{Cr}^{3+}/\text{Cr}}$

$= -0.44\text{V} - (-0.74\text{V})$

$= 0.3\text{V}$

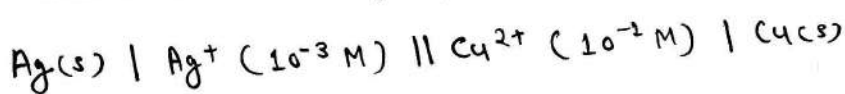
then $n = 6$

$\rightarrow E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$

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

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

Question:- Calculate the emf of the following cell at 25°C



(3M)

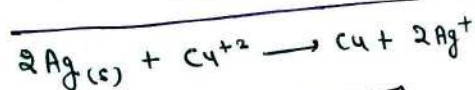
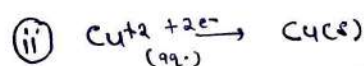
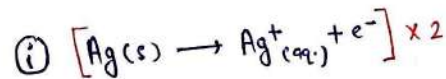
[CBSE 2013]

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

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

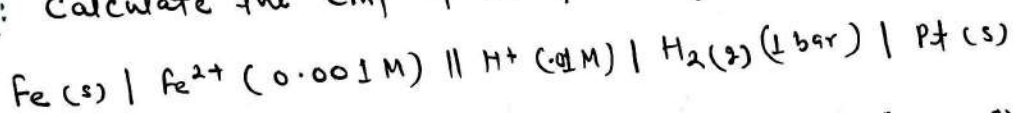
$E_{\text{cell}} = 0.46\text{V} - \frac{0.059}{2} \log \frac{(10^{-3})^2}{(10^{-2})}$

$E_{\text{cell}} = 0.60\text{V}$



$n = 2$

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



(3M)

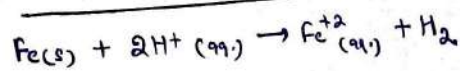
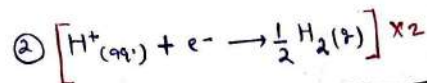
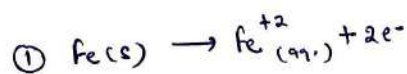
[Delhi 2013/2015]

Given $\rightarrow E^\circ_{\text{cell}} = 0.44\text{V}$ (or $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$ and $E^\circ_{\text{H}^+/\text{H}_2} = 0\text{V}$)

Answer:- $E^\circ_{\text{cell}} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = 0.44\text{V}$

$E_{\text{cell}} = E^\circ - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} = 0.44\text{V} - \frac{0.059}{2} \log \frac{(10^{-3})}{(10^0)^2}$

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



$n = 2$

Equilibrium constant from Nernst Equation :- For a general reaction $\rightarrow$



$\rightarrow$ Nernst equation can be written as $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$

$\rightarrow$ At equilibrium $E_{\text{cell}} = 0$

and $Q = K_c = \text{Equilibrium constant}$

$$0 = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K_c$$

$$Q \rightarrow \text{Reaction quotient}$$

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

$$E_{\text{cell}}^{\circ} = \frac{2.303 RT}{nF} \log K_c$$

$\rightarrow$ At 25°C $T = 298K$

$$F = 96487 \text{ C mol}^{-1}$$

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

$$E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log K_c$$

Example - : For Daniell cell $E_{\text{cell}}^{\circ} = 1.1V$ then $\rightarrow 1.1V = \frac{0.059}{2} \log K_c$



$n = 2 = \text{No. of electron transferred.}$

$$\log K_c = 37.288$$

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

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

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

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

$\rightarrow$ Work done by galvanic cell is equal to decrease in Gibbs energy.

$\rightarrow$ If concentration of all the reacting species is unity then $E_{\text{cell}} = E_{\text{cell}}^{\circ}$.

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

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

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

$$\hookrightarrow n = 2$$

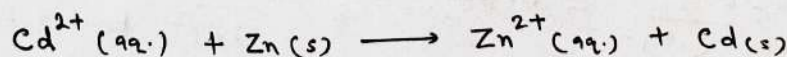
$$\Delta G^{\circ} = -nFE^{\circ} = -2 \times 96500 \times 1.1$$

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

[CBSE 2013
Delhi 2013c]

2M

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



CBSE 2019

3M

Given : $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.403V$, $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.763V$

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

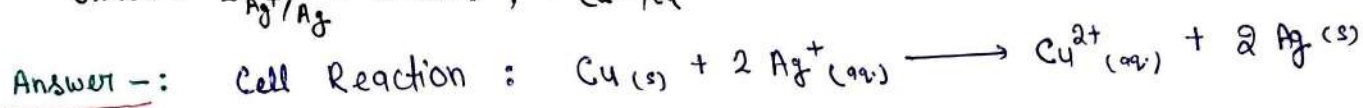
$n = 2 = \text{No. of molar of electron used}, F = 96500 \text{ C mol}^{-1}$

① $\Delta G^\circ = -nF E^\circ = -2 \times 96500 \times 0.36 \text{ V} = \underline{69480 \text{ J mol}^{-1}}$

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

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

Given : $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}, E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$ [Delhi 2010]



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

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

($E_{\text{cell}} = 0.422 \text{ V}$)

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

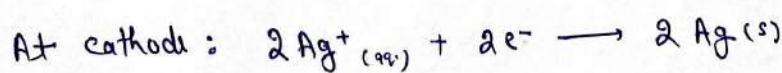
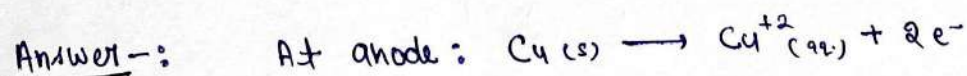
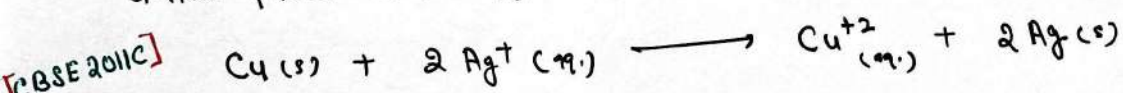
$0.422 \text{ V} = 0.46 \text{ V} - \frac{0.059}{2} \log \frac{0.1}{[\text{Ag}^+]^2}$

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

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

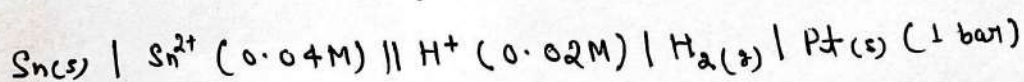
$\rightarrow [\text{Ag}^+] = 0.0717 = \underline{7.17 \times 10^{-2} \text{ M}}$

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

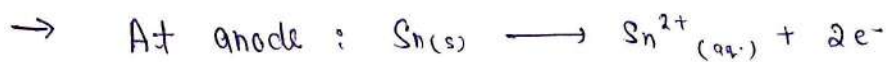


} [Delhi 2010C] (1M)

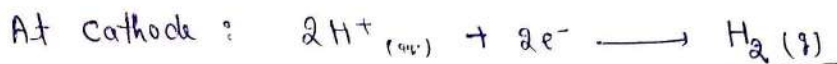
(ii) Write the Nernst equation and calculate the emf of the following cell.



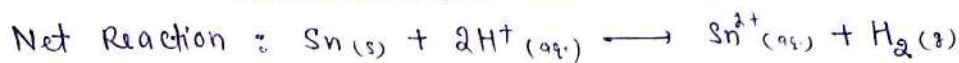
Given : $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$



$$\boxed{n=2}$$



$$\begin{aligned} \rightarrow E_{\text{cell}}^{\circ} &= E_{\text{H}^+/\text{H}_2}^{\circ} - E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} \\ &= 0\text{V} - (-0.14\text{V}) \\ &= 0.14\text{V} \end{aligned}$$



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

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

$$\rightarrow E_{\text{cell}} = 0.0009\text{V}$$

Table of SE P at 298K

Reaction (Oxidised form + ne ⁻)	→ Reduced form)	E°/V
F ₂ (g) + 2e ⁻	→ 2F ⁻	2.87
Co ³⁺ + e ⁻	→ Co ²⁺	1.81
H ₂ O ₂ + 2H ⁺ + 2e ⁻	→ 2H ₂ O	1.78
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻	→ Mn ²⁺ + 4H ₂ O	1.51
Au ³⁺ + 3e ⁻	→ Au(s)	1.40
Cl ₂ (g) + 2e ⁻	→ 2Cl ⁻	1.36
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻	→ 2Cr ³⁺ + 7H ₂ O	1.33
O ₂ (g) + 4H ⁺ + 4e ⁻	→ 2H ₂ O	1.23
MnO ₂ (s) + 4H ⁺ + 2e ⁻	→ Mn ²⁺ + 2H ₂ O	1.23
Br ₂ + 2e ⁻	→ 2Br ⁻	1.09
NO ₃ ⁻ + 4H ⁺ + 3e ⁻	→ NO(g) + 2H ₂ O	0.97
2Hg ²⁺ + 2e ⁻	→ Hg ₂ ²⁺	0.92
Ag ⁺ + e ⁻	→ Ag(s)	0.80
Fe ³⁺ + e ⁻	→ Fe ²⁺	0.77
O ₂ (g) + 2H ⁺ + 2e ⁻	→ H ₂ O ₂	0.68
I ₂ + 2e ⁻	→ 2I ⁻	0.54
Cu ⁺ + e ⁻	→ Cu(s)	0.52
Cu ²⁺ + 2e ⁻	→ Cu(s)	0.34
AgCl(s) + e ⁻	→ Ag(s) + Cl ⁻	0.22
AgBr(s) + e ⁻	→ Ag(s) + Br ⁻	0.10
2H⁺ + 2e⁻	→ H₂(g)	0.00
Pb ²⁺ + 2e ⁻	→ Pb(s)	-0.13
Sn ²⁺ + 2e ⁻	→ Sn(s)	-0.14
Ni ²⁺ + 2e ⁻	→ Ni(s)	-0.25
Fe ²⁺ + 2e ⁻	→ Fe(s)	-0.44
Cr ³⁺ + 3e ⁻	→ Cr(s)	-0.74
Zn ²⁺ + 2e ⁻	→ Zn(s)	-0.76
2H ₂ O + 2e ⁻	→ H ₂ (g) + 2OH ⁻ (aq)	-0.83
Al ³⁺ + 3e ⁻	→ Al(s)	-1.66
Mg ²⁺ + 2e ⁻	→ Mg(s)	-2.36
Na ⁺ + e ⁻	→ Na(s)	-2.71
Ca ²⁺ + 2e ⁻	→ Ca(s)	-2.87
K ⁺ + e ⁻	→ K(s)	-2.93
Li ⁺ + e ⁻	→ Li(s)	-3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

→ For F_2 gas SRP 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 SRP indicating that Li^+ is a weakest oxidising agent and Li metal is the most powerful reducing agent.

→ As value of SRP decreases for metal ion $\Rightarrow$ Reducing power of metal increases

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

SRP of metals are $\rightarrow$ (i) $K^+|K = -2.93V$

(ii) $Ag^+|Ag = 0.80V$

(iii) $Cu^{2+}|Cu = 0.34V$

(iv) $Mg^{2+}|Mg = -2.37V$

(v) $Cr^{3+}|Cr = -0.74V$

(vi) $Fe^{2+}|Fe = -0.44V$

Reducing Power of metal $\propto \frac{1}{\text{Reduction Potential}}$

[CSE 2010]

2M

Order of reducing power : $Ag < Cu < Fe < Cr < Mg < K$

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

Application of Series -:

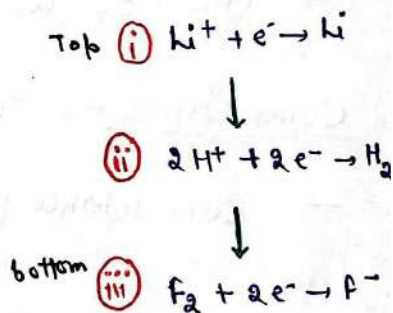
(i) SRP $\downarrow \Rightarrow$ Reducing Power $\uparrow$

$\Rightarrow$ Oxidising Power $\downarrow$

(ii) Anode : Oxidation $\rightarrow$ Electrode higher up in series.

Cathode : Reduction $\rightarrow$ 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.



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

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

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



Conductance of electrolytic solutions and its measurement :-

Resistance - Resistance is the hindrance provided by a conductor in the passage of current.
(R)

→ $R \propto \text{length of conductor (l)}$
 $\propto \frac{1}{\text{Cross sectional area (A)}}$

$$R \propto \frac{l}{A} \Rightarrow \boxed{R = \rho \frac{l}{A}}$$

$$\rightarrow \rho = R \frac{A}{l} = \text{Resistivity}$$

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

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

→ Unit of resistivity [Specific Resistance] = ohm-metre [$\Omega \text{ m}$]

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

$$\rightarrow \text{Conductance [G]} = \frac{1}{R} = \frac{A}{\rho l} = k \frac{A}{l} = \text{Conductivity} \times \frac{1}{\text{Cell constant}}$$

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

$$\rightarrow \text{Cell constant} = \frac{l}{A} \quad (G^*)$$

$$\text{Unit of cell constant} = \text{m}^{-1}$$

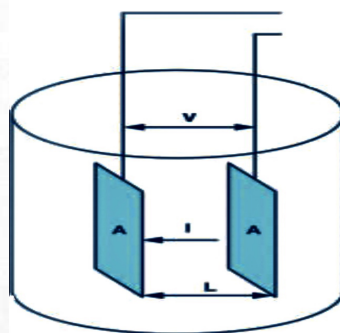
$$\text{Unit of conductance} = \text{ohm}^{-1} = \text{Siemens} \quad (S)$$

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

In case of conductance of a solution -:

l → length between the electrodes

A → Cross sectional area of electrodes.



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 accomodate sufficient volume of the solution that contains 1 mole of electrolyte.

→ If V volume of solution contains 1 mole of electrolyte, then

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

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

→ Molar conductivity $\uparrow$ with $\downarrow$ 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 $\Lambda_m = \text{S m}^2 \text{ mol}^{-1}$ or $\text{S cm}^2 \text{ mol}^{-1}$

Limiting Molar Conductivity :- When concentration $\rightarrow 0$ Then $\Lambda_m = \Lambda_m^\circ$

→ When concentration approaches zero, the molar conductivity reaches a limiting value known as limiting molar conductivity (Λ_m°). [CBSE 2017] (1M)

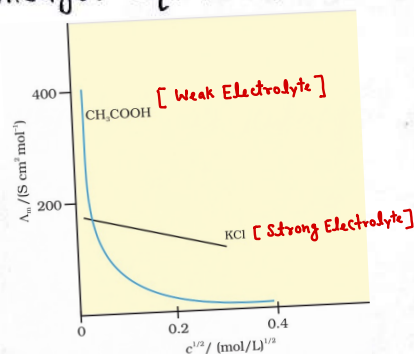
→ For strong electrolytes [KCl], Λ increases slowly with dilution and can be represented by DHO Equation (Debye - Huckle - Onsager Equation).

$$\boxed{\Lambda_m = \Lambda_m^\circ - A c^{1/2}}$$

$c \rightarrow$ concentration of electrolyte.

$A \rightarrow$ constant

[CBSE 2019] (2M)



Question :- Λ_m of a 1.5 M solution of an electrolyte is found to be $130.9 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity of this solution. [CBSE 2010/2012] (2M)

Answer :- $M = 1.5 \text{ mol/L}$

$$\text{We know that } \rightarrow \Lambda_m = \frac{k \times 1000}{M} \text{ then } k = \frac{M \cdot \Lambda_m}{1000} = \frac{(1.5)(130.9)}{1000} = 0.208 \text{ S cm}^{-1}$$

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

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

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

→ Molar Conductivity $\Lambda_m = \frac{k \times 1000}{M}$ $k = \frac{1}{200}\ \Omega^{-1}\text{ cm}^{-1}$

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

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 its molar conductivity, Conductivity and resistivity? [CBSE 2012] (3M)

Answer:- Molarity of NaOH solution = 0.05 M

Diameter = 1 cm , Radius = 0.5 cm , Area $A = \pi r^2 = (3.14)(0.5)^2$
 $A = 0.785\text{ cm}^2$

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

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

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

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

$$\Lambda_m = 229.6\ \text{S cm}^2\text{ mol}^{-1}$$

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

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

$$\boxed{\text{Cell Constant } G^* = k \cdot R} = 0.146 \times 10^{-3} \times 1500\text{ cm}^{-1} = 0.219\text{ cm}^{-1}$$

Kohlrausch Law —: "Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

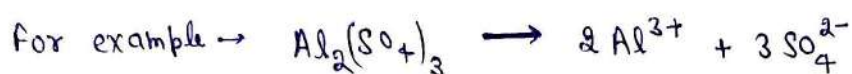
For Strong Electrolyte

→ For NaCl : $\Lambda_{\text{NaCl}}^{\circ} = \Lambda_{\text{Na}^+}^{\circ} + \Lambda_{\text{Cl}^-}^{\circ}$

→ CH_3COOH at infinite dilution ($c \rightarrow 0$) : $\Lambda_{\text{CH}_3\text{COOH}}^{\circ} = \Lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \Lambda_{\text{H}^+}^{\circ}$
[Delhi 2010, CBSE 2010C]

2M

→ If an electrolyte on dissociation gives n_1 cations and n_2 anions then its limiting molar conductivity $\Lambda_m^{\circ} = n_1 \Lambda_+^{\circ} + n_2 \Lambda_-^{\circ}$



$$\Lambda_m^{\circ} [\text{Al}_2(\text{SO}_4)_3] = 2 \Lambda_m^{\circ} (\text{Al}^{3+}) + 3 \Lambda_m^{\circ} (\text{SO}_4^{2-})$$

Question :- The value of Λ_m° of $\text{Al}_2(\text{SO}_4)_3$ is $858 \text{ S cm}^2 \text{ mol}^{-1}$, while $\Lambda_m^{\circ} (\text{SO}_4^{2-})$ is $160 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the limiting ionic conductivity of Al^{3+} .

3M

[CBSE 2013C]

Answer :-

$$\Lambda_m^{\circ} (\text{Al}_2(\text{SO}_4)_3) = 2 \Lambda_m^{\circ} (\text{Al}^{3+}) + 3 \Lambda_m^{\circ} (\text{SO}_4^{2-})$$

$$\Lambda_m^{\circ} (\text{Al}^{3+}) = \frac{\Lambda_m^{\circ} (\text{Al}_2(\text{SO}_4)_3) - 3 \Lambda_m^{\circ} (\text{SO}_4^{2-})}{2} = \frac{858 - 3 \times 160}{2}$$

$$\Lambda_m^{\circ} (\text{Al}^{3+}) = 109 \text{ S cm}^2 \text{ mol}^{-1}$$

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

[Delhi 2010] 3M

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

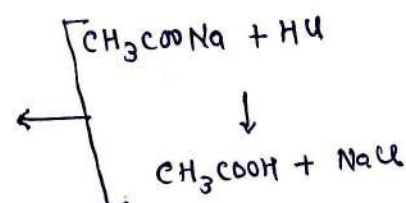
$$\Lambda_m^{\circ} (\text{CH}_3\text{COONa}) = 91 \text{ S cm}^2 \text{ mol}^{-1}$$

Answer :- $\Lambda_m^{\circ} (\text{CH}_3\text{COOH}) = \Lambda_m^{\circ} (\text{CH}_3\text{COO}^-) + \Lambda_m^{\circ} (\text{H}^+)$

→ $\Lambda_m^{\circ} (\text{CH}_3\text{COONa}) + \Lambda_m^{\circ} (\text{HCl}) = \Lambda_m^{\circ} (\text{CH}_3\text{COOH}) + \Lambda_m^{\circ} (\text{NaCl})$

→ $91 + 426 = \Lambda_m^{\circ} (\text{CH}_3\text{COOH}) + 126$

then $\Lambda_m^{\circ} (\text{CH}_3\text{COOH}) = 391 \text{ S cm}^2 \text{ mol}^{-1}$



→ At higher concentration, weak electrolyte (like CH_3COOH) have lower degree of dissociation. Hence for such electrolytes, the change in Λ_m with dilution is due to increase in degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mole of electrolyte.

→ Degree of dissociation :- The ratio of molar conductivity (Λ_m) at a specific concentration to the molar conductivity at infinite dilution (Λ_m°) is known as degree of dissociation (α). [Delhi 2015C] 2M

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

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

$$\Lambda_m(\text{CH}_3\text{COOH}) = 11.7 \text{ S cm}^2 \text{ mol}^{-1}, \quad \Lambda_m^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$$

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

[Delhi 2011C] 3M

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

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{COO}^-) + \Lambda_m^\circ(\text{H}^+)$$

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

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

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

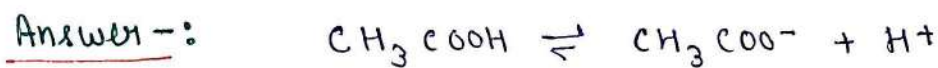
$$\text{Given: } \lambda_{(\text{H}^+)}^\circ = 349.5 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \lambda_{(\text{HCOO}^-)}^\circ = 50.5 \text{ S cm}^2 \text{ mol}^{-1}$$

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

$$\Lambda_m^\circ(\text{HCOOH}) = \lambda_{(\text{H}^+)}^\circ + \lambda_{(\text{HCOO}^-)}^\circ = 50.5 + 349.5 = 400 \text{ S cm}^2 \text{ mol}^{-1}$$

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

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



Initial concⁿ C 0 0

After time t, C - C α C α C α

$\alpha \rightarrow$ 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 $\rightarrow$

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

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

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

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

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

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

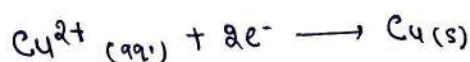
Electrolysis

$\rightarrow$ Electrolytic Cells:- When external potential applied becomes greater than E°_{cell} of electrochemical cell, electron flows from cathode to anode, means that electrochemical cell becomes electrolytic cell. [CBSE 2019 | 2016] 1M

$\rightarrow$ In electrolytic cells, electrical energy is used to carry out non-spontaneous chemical reactions and the process which takes place in an electrolytic cell is called electrolysis.

Purification of impure copper:-

$\rightarrow \text{Cu}^{2+}$ ion discharge at cathode

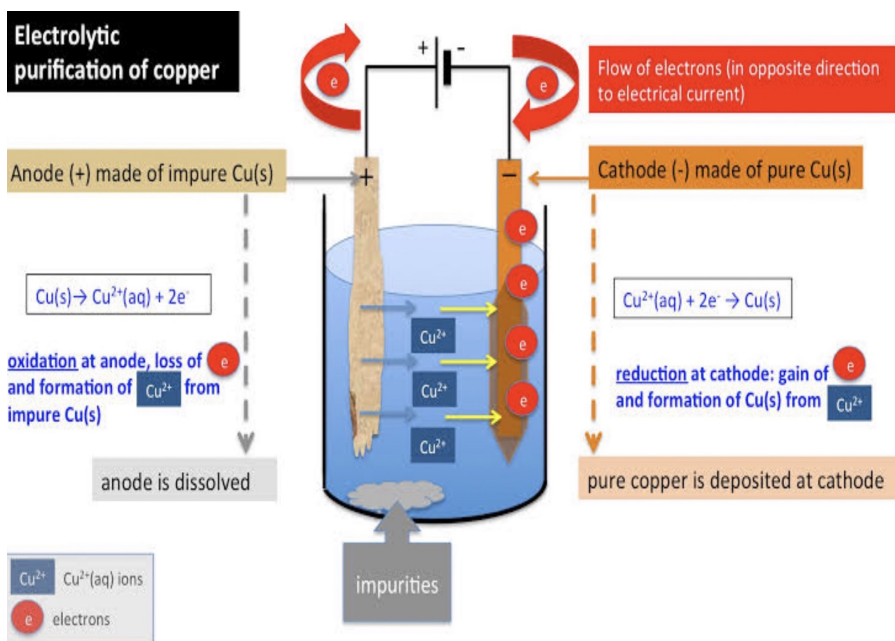


$\rightarrow$ Copper metal is deposited on the cathode.

$\rightarrow$ At anode, copper is dissolved (oxidised). $\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e^-$

$\rightarrow$ Impure copper : Anode

$\rightarrow$ pure copper : Cathode.



Faraday's laws of electrolysis [Quantitative aspects of electrolysis] -:

(i) 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 melt).

→ If w gram of substance gets deposit on passing Q Coulomb of electricity, Then

$$W \propto Q \quad \text{or} \quad W = Z Q$$

$$W = \text{Zeit}$$

$z \rightarrow$ electrochemical equivalent

$i \rightarrow$ current [Ampere]

$t \rightarrow$ time [second]

(ii) Second Law - : The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

→ Equivalent Weights [atomic mass of metal / no. of electrons required to reduce the cation]

$$\rightarrow \frac{W_1}{E_1} = \frac{W_2}{E_2}$$

$W \rightarrow$ mass of substance deposited.

$E \rightarrow$ equivalent weight.

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

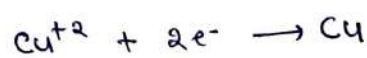
→ charge on 1 mole of electron = 1 faraday = $N_A \times (1.6021 \times 10^{-19} \text{ C})$

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

$$= 96487 \text{ C mol}^{-1} \approx 96500 \text{ C mol}^{-1}$$

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



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

$$\rightarrow \begin{array}{l} 2 \times 96500 \text{ C charge for } = 63 \text{ g of Cu} \\ 1 \text{ C} \quad \quad \quad \quad \quad \quad = \frac{63 \text{ g}}{2 \times 96500 \text{ C}} \end{array}$$
$$\text{then, } 9000 \text{ " " } = \frac{63 \times 900}{2 \times 96500} = 0.2930 \text{ g.}$$

$$[a = i \cdot t = 1.5 \times 600 = 900c]$$

Question:- How many electrons flow through a metallic wire if a current of 0.5 is passed for 2h? given $1F = 96500 \text{ C mol}^{-1}$ [CBSE 2017] 1.5M

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

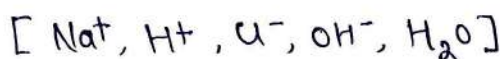
$$Q = 3600 \text{ C}$$

$$\rightarrow Q = n \cdot e^- \Rightarrow n = \frac{Q}{e^-} = \frac{3600 \text{ C}}{1.6 \times 10^{-19} \text{ C}} = 2250 \times 10^{19}$$

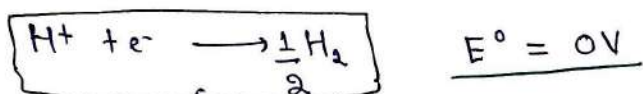
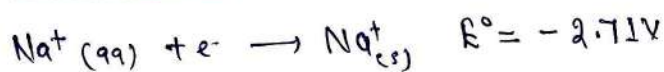
Products of electrolysis:-

Electrolysis of aqueous NaCl

$\rightarrow$ Ions in aqueous NaCl



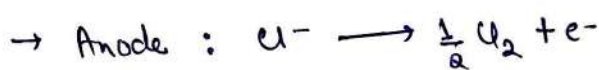
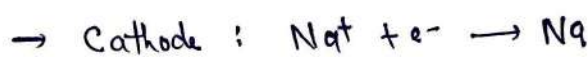
$\rightarrow$ At Cathode, Competition between H^+/Na^+



$\rightarrow$ More feasible than above reaction.

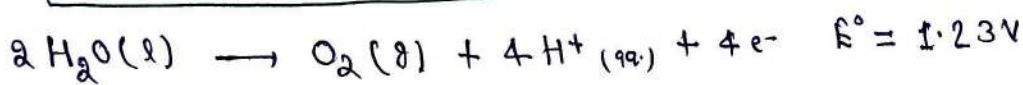
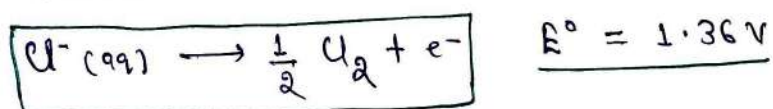
Electrolysis of molten NaCl

$\rightarrow$ Here we have only one cation (Na^+) and one anion (Cl^-)

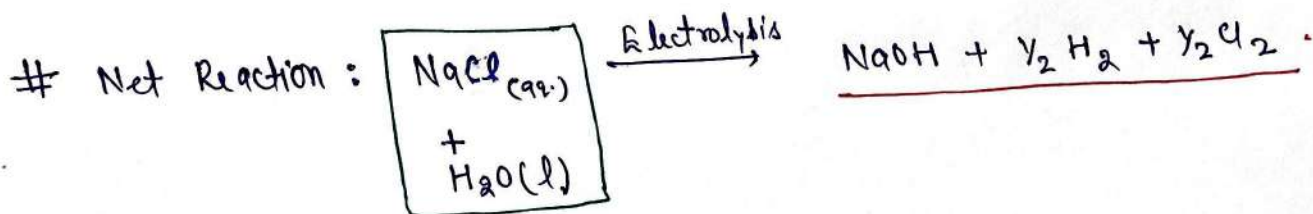


$\rightarrow$ So, we get Na metal and Cl_2 gas on electrolysis of molten NaCl.

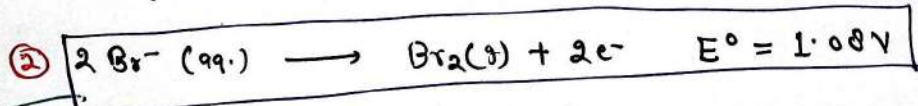
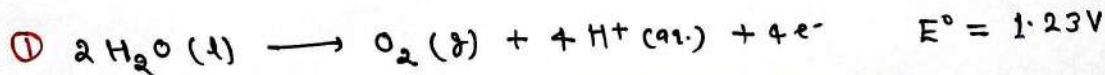
$\rightarrow$ At anode, Competition between Cl^- and $\text{H}_2\text{O}(\text{l})$



(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)



Question:- Which reaction occurs at anode and why?

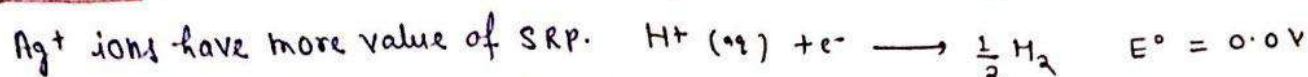
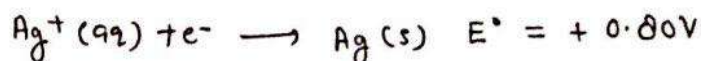


$\rightarrow$ This reaction is preferred because it has lower reduction potential.

2M
[CBSE 2011C]

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

Answer:-

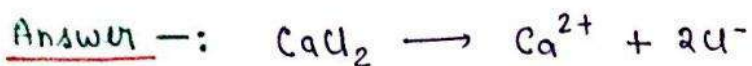


Therefore Ag^+ ions are discharged at cathode in preference of H^+ ions.

[Delhi 2015] (1M)

Question:- How much electricity in terms of Faradays is required to produce 20g of Ca from molten CaCl_2 ?

[Delhi 2013] (2M)



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 0.1207A for 50 min. [Given: Atomic mass of Cu = 63.5 g mol⁻¹]

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

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

$$= 0.1207 \times 50 \times 60$$

$$= 366.1\text{C}$$

(b) Mass of copper deposited at the cathode

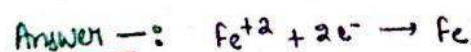
$$m = ZIt = Z \cdot Q = \left[\frac{\text{Equivalent Weight}}{96500} \right] \cdot Q$$

$$m = \frac{(63.5/2)}{96500} \times 366.1 = 0.127\text{g}$$

[Delhi 2011] (3M)

Question:- A steady current of 2A was passed through 2 electrolytic cells X and Y connected in series containing electrolytes FeSO_4 and ZnSO_4 until 2.0g of Fe 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)



→ 56g of Fe is deposited by $2 \times 96500\text{C}$

$$\rightarrow 20\text{g of Fe} \quad \text{---} : \quad \frac{96500 \times 2 \times 2.0}{56} \text{C}$$

$$= 9650\text{C}$$

$$\# \text{ Time } t = \frac{Q}{I} = \frac{9650}{2} = 4825\text{s}$$



$2 \times 96500\text{C}$ charge deposits Zn = 65.3g

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

$$= 3.27\text{g}$$

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.

① 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.

Lecclanche Cell :- [Dry cell]

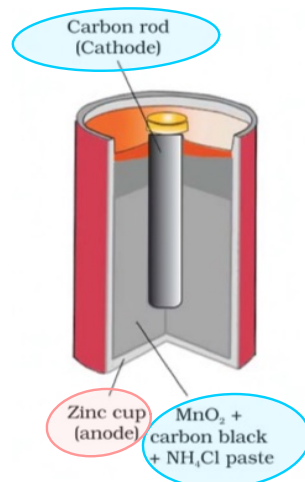
Anode :- Zinc container

Cathode :- Carbon rod [surrounded by MnO_2 + Carbon]

→ The space between electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 .

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

Cathode Reaction :- $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$



Overall Reaction :- $\text{Zn(s)} + 2\text{NH}_4^+ + 2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + \text{H}_2\text{O(l)} + [\text{Zn(NH}_3)_2]^{2+}$

→ By using Nernst equation $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Zn(NH}_3)_2]^{2+}}{[\text{NH}_4^+]^2}$

Due to the presence of ions $[\text{Zn(NH}_3)_2]^{2+}$ in the overall reaction, its voltage decreases with time. [CBSE 2014 C] (2M)

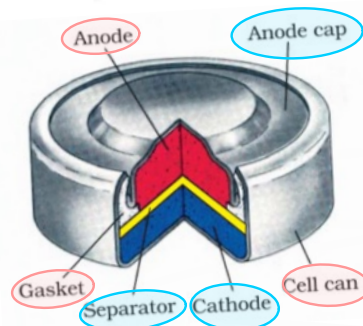
→ Use : Commonly used in transistors and clocks.

Mercury cell :-
Anode : Zn-Hg amalgam
Cathode : Paste of HgO and carbon
Electrolyte : Paste of $\text{ZnO} + \text{KOH}$

Anode Reaction : $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$

Cathode Reaction : $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$

Overall Reaction : $\text{Zn(Hg)} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + \text{Hg(l)}$



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

[Delhi 2011] (2M)

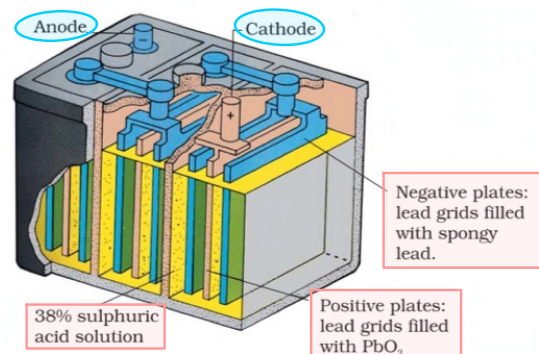
(b) Secondary Batteries :- A secondary cell after use can be recharged by passing current through it in opposite direction so that it can be used again. A secondary cell can undergo a large no. of discharging and charging cycles. [Delhi 2015C] (1M)

Lead Storage Battery :- It is a most important secondary cell, commonly used in automobiles and invertors.

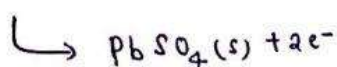
Anode : Lead [Pb]

Cathode : A grid of lead with PbO_2 .

Electrolyte : 38% H_2SO_4 solution (by mass)



Anode Reaction : $Pb(s) + SO_4^{2-}(aq.)$



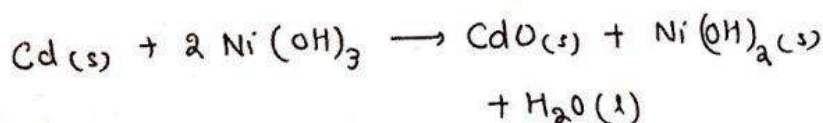
Cathode Reaction :- $PbO_2(s) + SO_4^{2-}(aq.) + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall Reaction :- $Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \rightarrow 2PbSO_4 + 2H_2O(l)$

[Delhi 2012 / 2011 / CBSE 2012C] (2M)

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 :-



[CBSE 2011C / 2010C] (2M)



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

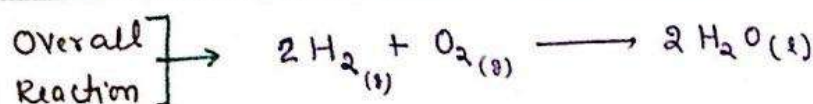
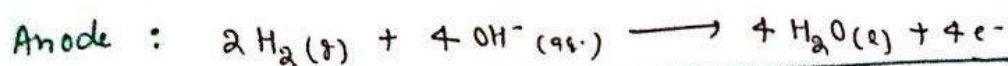
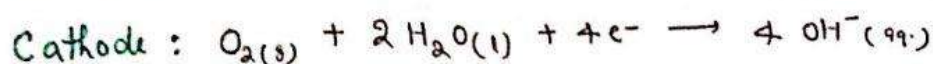
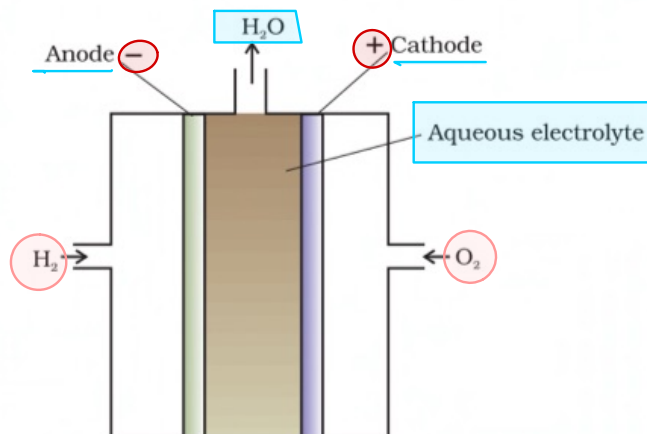
Fuel Cells :- Galvanic cells that are designed to convert the energy of combustion of fuels [like H_2 , CH_4 , CH_3OH] directly into electrical energy are called fuel cells.

H₂-O₂ Fuel Cell :- It is an important fuel cell which uses the reaction of H₂ with O₂ to form H₂O.

→ 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. [Delhi 2016] (1/2)

→ In the cell H₂ and O₂ 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.



[CASE 2011C] (2M)

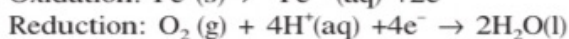
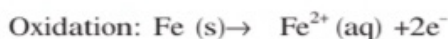
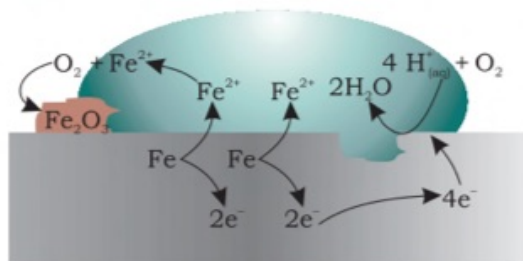
Advantages of H₂-O₂ cell :- Fuel cell do not cause any pollution unlike thermal plant (coal, oil burning produces CO₂ gas). Efficiency of fuel cell is high than thermal plants.

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.

[Delhi 2011]

(2M)



Atmospheric

