

## Electro Chemistry

### Electro Chemistry :-

Electro chemistry is a branch of science that deals with conversion of chemical energy into Electrical energy, vice versa.

### Some Basic terminology :-

1] Electrolyte:- A substance which decomposes as a result of passage of Electric current is called Electrolyte.

This phenomenon is called Electrolysis.

2] Conductor:- A substance which allows the passage of an electric current through it is called Conductor.

Eg:- All metals, Graphite, fused salts, aqueous solution of acids and bases, salts.

3] Non Conductor (or) Insulator:- A substance which does not allow the passage of electric current through it is called non-conductor.

Eg:- All non-metals (except Graphite), wood, rubber, paper, glass.

### Types of Conductors :-

Conductors are divided into two types on the basis of conducting elements.

1] Electronic conductors.

2] Electrolytic conductors.

1] **Electronic Conductors**:- The conductors which conduct the electric currents without decomposition & conductivity is due to flow of free electrons are called Electronic conductors.

Ex:- Metals like Fe, Cu, Ag.

2] **Electrolytic Conductors**:- The conductors which conduct the electric current with decomposition and conductivity is due to flow of free ions/electrons

Ex:- Aqueous salts, acids, bases.

**Types of cells:-**

1] Electrolytic cells.

2] Galvanic cells (Electro Chemical cell)

**Electrolytic cells**:- Electrolytic cells that convert electrical energy into chemical energy.

**Galvanic cells**:- Electrochemical cells that convert chemical energy into electrical energy of spontaneous redox reaction is called Galvanic cell.

Ex:  $Zn | Zn^{2+} || Cu^{2+} | Cu$ .

**Structure and working of Galvanic cell:-**

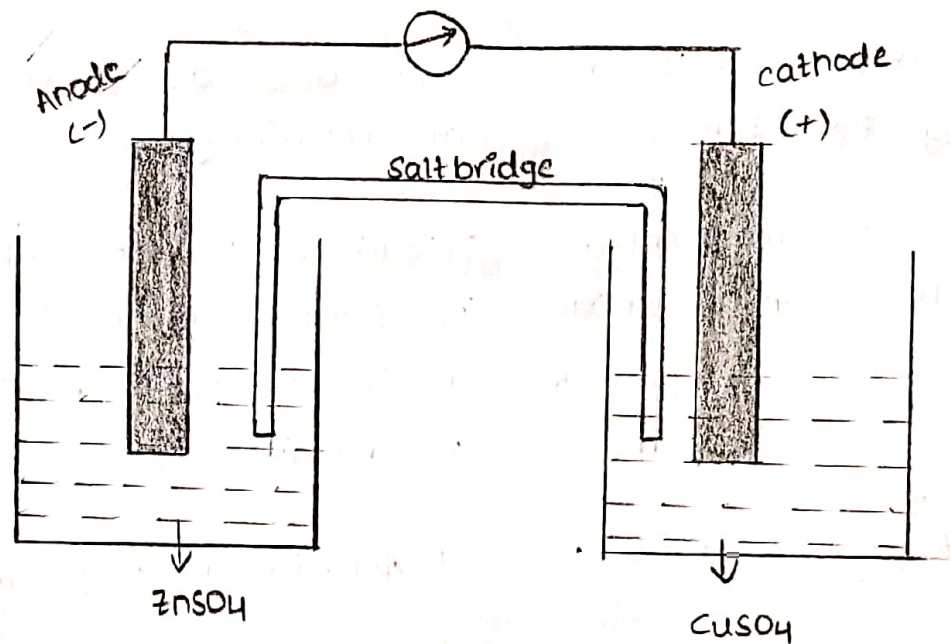
1] Zinc Anode immersed in  $ZnSO_4$ , it acts as anodic half cell.

2] Cu cathode immersed in  $CuSO_4$  solution acts as cathodic half cell.

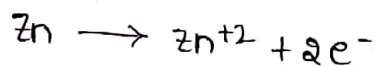
3] The two half cells are connected by inverted U-shaped tube called salt-bridge. It contains  $KCl$ ,  $KNO_3$  (or)  $NH_4NO_3$ .

## Functions of Salt Bridge:-

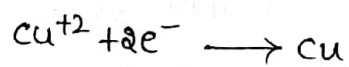
1. To prevent mixing of two solutions.
2. To prevent accumulation of
3. To made electrical contact between two half cells.



1] At anode :- oxidation takes place



2] At cathode :- Reduction takes place



Electrolytic cell	Galvanic Cell
1] It converts electrical energy into chemical energy.	1] It converts chemical energy into electrical energy.
2] It requires sources of electricity like battery.	2] It acts as a source of electricity.
3] Cathode is represented by negative sign & anode is represented by positive sign.	3] Cathode is represented by positive sign & anode is represented by negative sign.
4] Salt Bridge is absent	4] Salt Bridge is present
5] Two electrodes are present in same electrolyte	5] Two electrodes are present in separate electrolyte.
6] Electric current flows from anode to cathode	6] Electric current flows from cathode to anode.

In Daniel cell



The electrode potential of the right hand electrode (half cell) is written as

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + \frac{RT}{2F} \ln [\text{Cu}^{2+}(\text{aq})]$$

The left hand electrode is written as

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + \frac{RT}{2F} \ln [\text{Zn}^{2+}(\text{aq})]$$

$\therefore$  The cell potential  $E_{\text{cell}} =$  Electrode potential of the right electrode - Electrode potential of left electrode.

$$\therefore E_{\text{cell}} = \left[ E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + \frac{RT}{2F} \ln [\text{Cu}^{2+}(\text{aq})] \right] - \left[ E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + \frac{RT}{2F} \ln [\text{Zn}^{2+}(\text{aq})] \right]$$

$$\Rightarrow \left( E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} \right) + \frac{RT}{2F} \ln \left[ \frac{\text{Cu}^{2+}(\text{aq})}{\text{Zn}^{2+}(\text{aq})} \right]$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{RT}{2F} \ln \left[ \frac{\text{Cu}^{2+}(\text{aq})}{\text{Zn}^{2+}(\text{aq})} \right] \quad (\because E_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}})$$

$E^{\circ}_{\text{cell}}$  is cell potential in standard state.

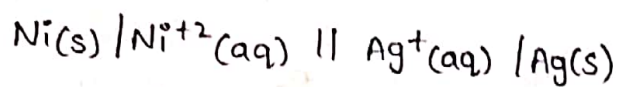
By converting natural logarithm to the base log & substituting the values  $R, T (298\text{K})$  &  $F$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0592}{2} \log \left[ \frac{\text{Cu}^{2+}(\text{aq})}{\text{Zn}^{2+}(\text{aq})} \right]$$

This equation is also written as

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

For a reaction which involves monovalent & bivalent ions, let us consider the cell



The expression for e.m.f of cell is written as

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{RT}{2F} \ln \frac{[\text{Ag}^+(\text{aq})]^2}{[\text{Ni}^{+2}(\text{aq})]}$$

The Nernst equation can be written as

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303}{RT} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Reference Electrodes:-

Reference electrode is an electrode of standard potential, with which we can compare with potentials of another electrodes.

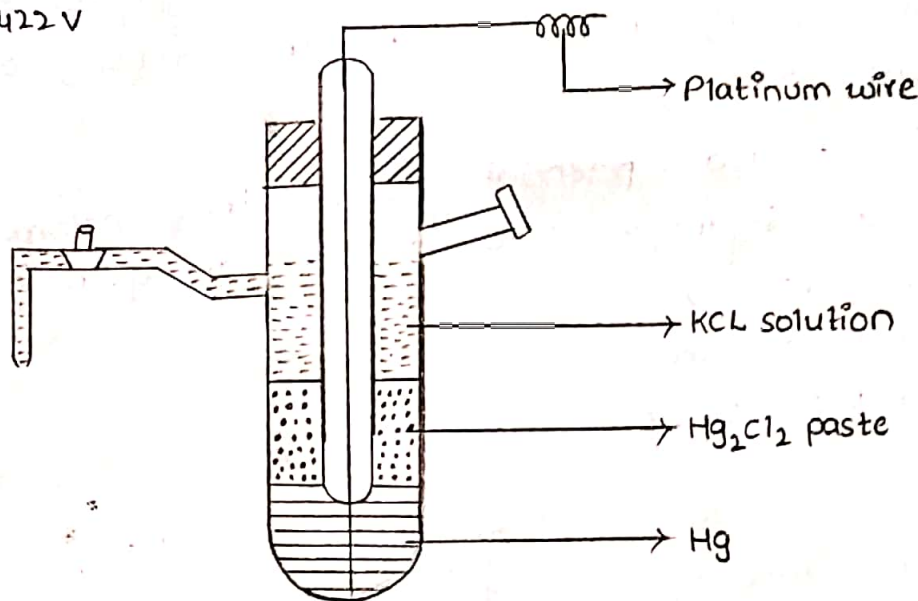
Secondary Reference Electrodes:-

Calomel Electrode :-

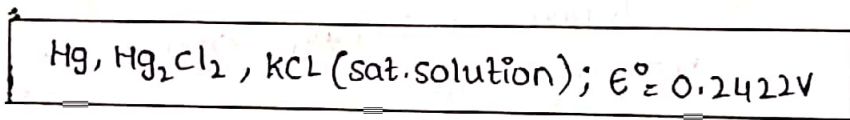
Construction:-

- Calomel electrode consists of a tube at the bottom of which a small amount of Hg is placed. It is covered with a paste of solid  $\text{Hg}_2\text{Cl}_2$  (calomel)
- A solution of KCl is then placed over the paste.
- A platinum wire, dipping into the mercury layer, is used for making electrical contact.
- The side tube is used for making electrical contact with a salt bridge.

→ The electrode potential of the calomel electrode is +0.2422 V

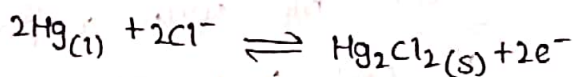
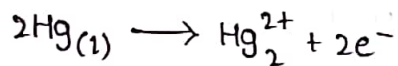


It is represented as

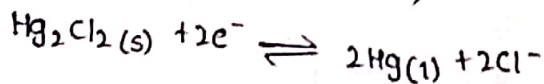
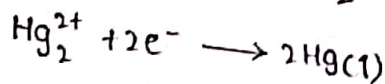
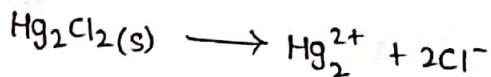


Working:-

If the electrode acts as anode the reaction is



If the electrode acts as cathode the reaction is



The electrode potential is given by (for example cathode)

$$E_{(\text{calomel})} = E^\circ_{(\text{calomel})} - \frac{RT}{2F} \ln a_{\text{Cl}^-}$$

The electrode potential depends on the activity of the chloride ions & it decreases as the activity of the chloride ions increases.

The single electrode potential of the three calomel electrodes on the hydrogen scale at 298K are given as

$$0.1 \text{ N KCl} = 0.3338 \text{ V}$$

$$1.0 \text{ N KCl} = 0.2800 \text{ V}$$

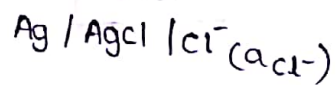
$$\text{Saturated KCl} = 0.2422 \text{ V}$$

Silver-Silver Chloride Electrode:-

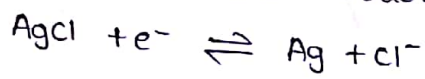
Construction and working:-

It is prepared by depositing a thin layer of AgCl electrolytically on a silver or platinum wire & it is then immersed in a solution containing chloride ions.

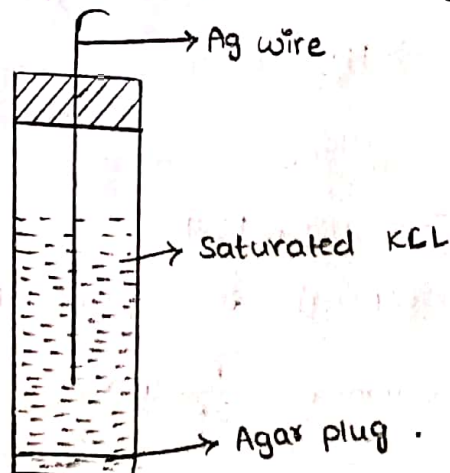
This electrode is represented as



and the electrode reaction is



The Ag-AgCl electrode is reversible with respect to the  $\text{Cl}^-$  ions. Its potential at 298K with saturated KCl is 0.290V & that with 0.1N KCl is 0.199V with respect to SHE.



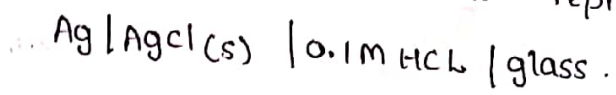


Glass electrode :-

Glass electrode is the universally employed for pH measurements.

Construction:- The glass electrode is made up of a special glass of relatively low melting point & high electrical conductivity. The assembly of glass electrodes consists of a thin glass bulb filled with 0.1N HCl and a silver wire coated with silver chloride is immersed in it. Here Ag/AgCl acts as an internal reference electrode.

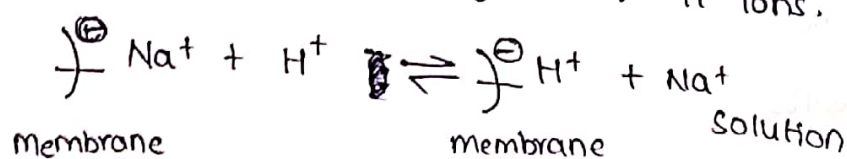
The glass electrode is represented as.



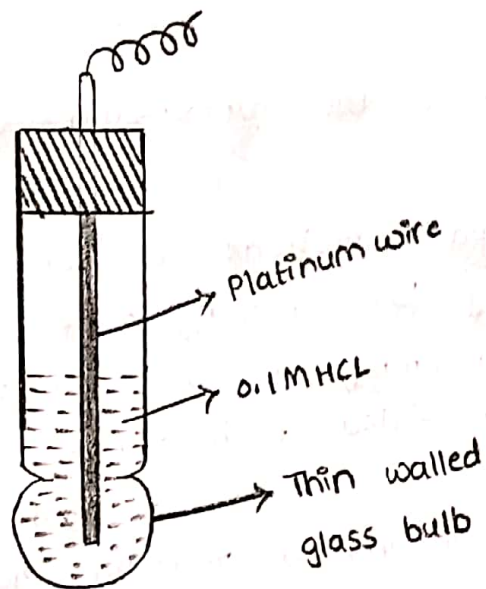
Principle:- When the glass electrode is immersed in another solution, whose pH value is to be determined there develops a potential b/w the two surfaces of the membrane.

→ The potential difference developed is proportional to the difference in pH value.

Theory:- The glass membrane of the glass electrodes undergoes an ion exchange reaction, the  $\text{Na}^+$  ions on the glass are exchanged for  $\text{H}^+$  ions.



The potential difference or the boundary potential ( $E_B$ ) at the interface is the result of the difference in potential ( $E_1 - E_2$ ) developed across the gel layer of the glass membrane between two liquids.



Advantages:-

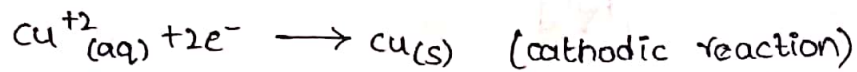
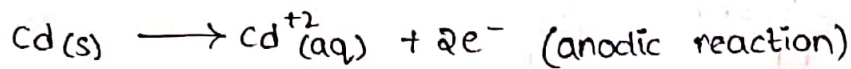
- 1] Glass electrode is the most convenient & simple to use
- 2] Equilibrium is rapidly achieved.
- 3] The results are accurate.
- 4] It can be used in turbid, colour & colloidal solutions.

Standard reduction potential values.

- ①  $\text{Ag}^+ : \text{Ag} \Rightarrow 0.80 \text{ volts}$
- ②  $\text{Cu}^{+2} : \text{Cu} \Rightarrow 0.34 \text{ volts}$
- ③  $2\text{H}^+ : \text{H}_2 \Rightarrow \pm 0.00 \text{ volt}$
- ④  $\text{Pb}^{+2} : \text{Pb} \Rightarrow -0.13 \text{ volts}$
- ⑤  $\text{Sn}^{+2} : \text{Sn} \Rightarrow -0.14 \text{ volts}$
- ⑥  $\text{Ni}^{+2} : \text{Ni} \Rightarrow -0.24 \text{ volts}$
- ⑦  $\text{Cd}^{+2} : \text{Cd} \Rightarrow -0.40 \text{ volts}$
- ⑧  $\text{Fe}^{+2} : \text{Fe} \Rightarrow -0.44 \text{ volts}$
- ⑨  $\text{Zn}^{+2} : \text{Zn} \Rightarrow -0.76 \text{ volts}$

Problems on calculation of the emf values.

- 1) To calculate the standard emf of the cell cadmium & copper & determine the cell reaction also

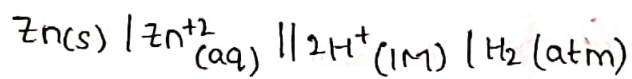


$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$\Rightarrow 0.34 + 0.40$$

$$\Rightarrow 0.74 \text{ volts.}$$

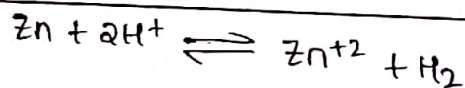
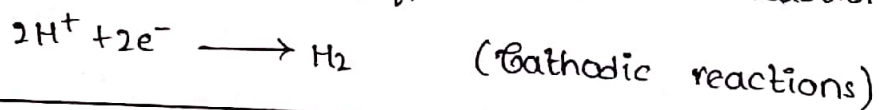
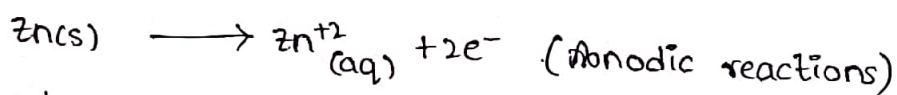
- 2) Calculate the emf of the cell represented as



$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$= 0.00 + 0.76$$

$$= 0.76 \text{ volts.}$$



- 3) Calculate the emf of the Zn-Ag cell at 25°C when concentration of  $\text{Zn}^{2+} = 0.10$  & concentration of  $\text{Ag}^+ = 10.0$  ( $E_0$  cell at 25°C = 1.56V)

Sol<sup>n</sup>

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \log \frac{[\text{Zn}^{+2}]}{[\text{Ag}^{+}]^2}$$

$$= E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{+2}]}{[\text{Ag}^{+}]^2}$$

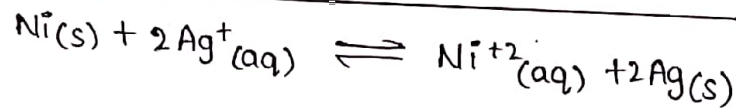
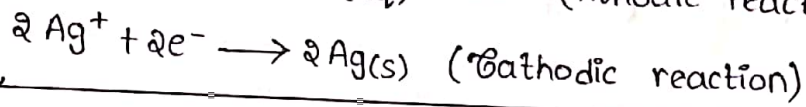
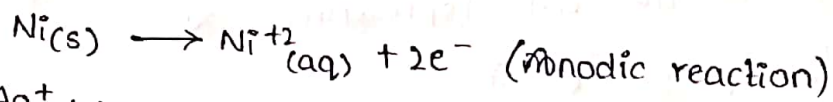
$$\Rightarrow 1.56 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{[0.10]}{[10]^2}$$

$$\Rightarrow 2.75 \text{ volts.}$$

4] Calculate the standard emf of Ni-Ag cell

Sol<sup>n</sup>

Cell reaction:-



$$\text{Emf} = E_{\text{R}} - E_{\text{L}}$$

$$\Rightarrow 0.80 + 0.24$$

$$\Rightarrow 1.04 \text{ volts.}$$

Conductometric titration:-

Principle :- Conductometric titration is a volumetric method based on the measurement of conductance of the solution during titration.

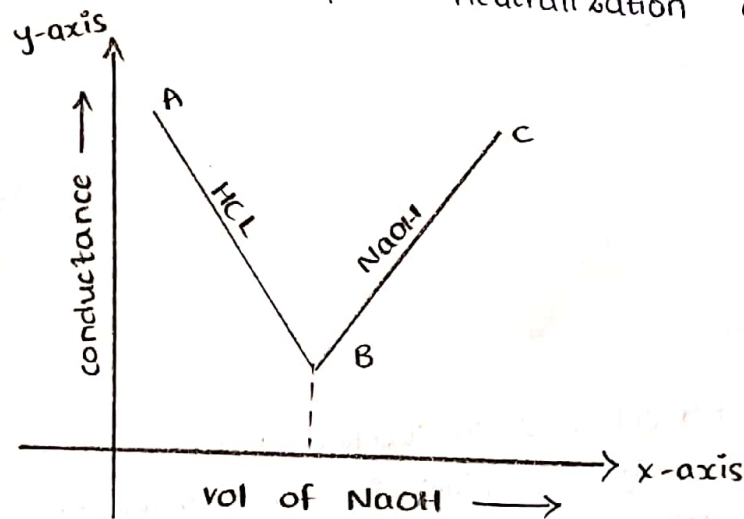
The conductance of a solution depends on

- (i) the number and charge on the free ions &
- (ii) the mobility of the ions.

## Acid-Base titrations:-

### 1) Strong acid vs strong base (HCL vs NaOH)

Known amount of acid (HCL) is taken in the conductivity cell & the alkali (NaOH) in the burette. Initially the conductivity of the HCL is high, this is due to the presence of fast moving  $H^+$  ions. As the NaOH is added gradually, conductance will be going on decreasing until the acid has been completely neutralized. This is due to the replacement of fast moving  $H^+$  ions by slow moving  $Na^+$  ions. The point 'B' indicates complete neutralization of all  $H^+$  ions.

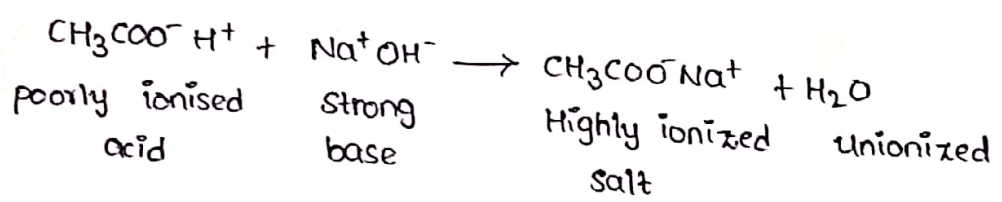
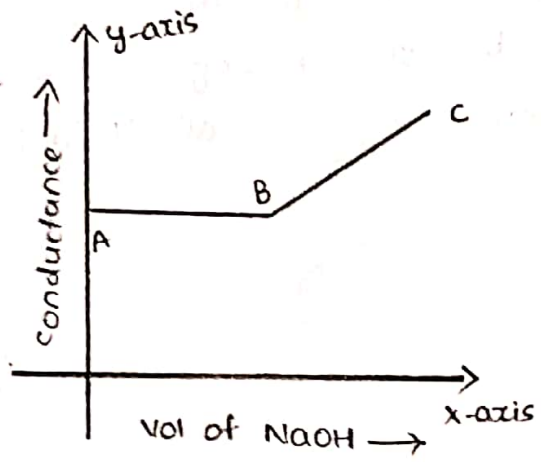


Further addition of NaOH will introduce the fast moving  $OH^-$  ions. Therefore the conductance, after reaching a certain minimum value, will begin to increase.

On plotting the conductance against the volume of alkali added, the two lines intersect at a point 'B' gives the end point. This corresponds to the volume of NaOH required for neutralization.

2) Weak acid vs strong base ( $\text{CH}_3\text{COOH}$  vs  $\text{NaOH}$ )

known amount of weak acid ( $\text{CH}_3\text{COOH}$ ) is taken in the conductivity cell and the alkali ( $\text{NaOH}$ ) in the burette. Initially the conductivity of  $\text{CH}_3\text{COOH}$  is low, this is due to the poor dissociation of  $\text{CH}_3\text{COOH}$ . As  $\text{NaOH}$  is added gradually, conductance will be going on slowly increasing. This is due to the formation of highly ionised  $\text{CH}_3\text{COONa}$ .



The point 'B' indicates complete neutralization of  $\text{CH}_3\text{COOH}$ . Further addition of  $\text{NaOH}$  introduces excess of fast moving  $\text{OH}^-$  ions. Therefore the conductance of the solution begins to increase even more sharply than before.

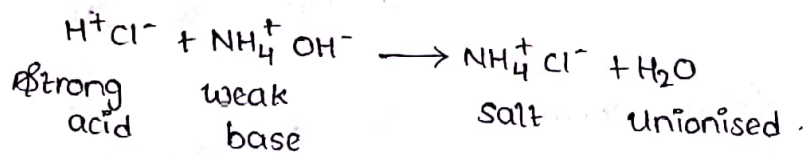
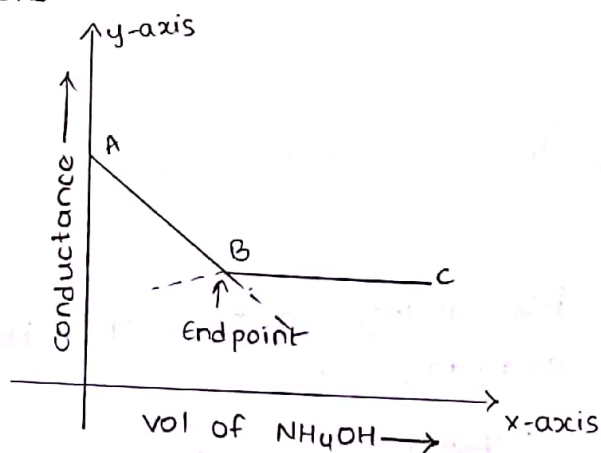
On plotting the conductance against the volume of alkali added, the two lines intersect at point 'B' gives the end point.

3) Strong acid vs weak base (HCl vs  $\text{NH}_4\text{OH}$ )

Known amount of HCl is taken in the conductivity cell &  $\text{NH}_4\text{OH}$  is added gradually from the burette.

Initially the conductivity of HCl is high. As the  $\text{NH}_4\text{OH}$  is added gradually the conductance will be going on decreasing until all the acids been completely neutralised.

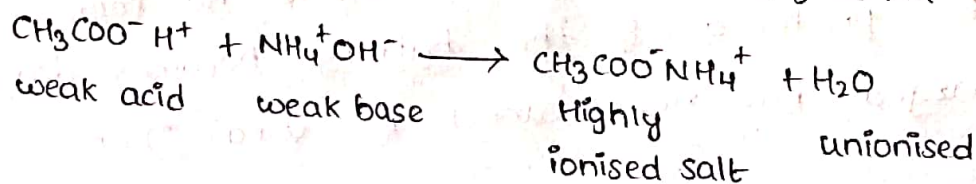
This is due to the replacement of  $\text{H}^+$  ions by slow moving  $\text{NH}_4^+$  ions.



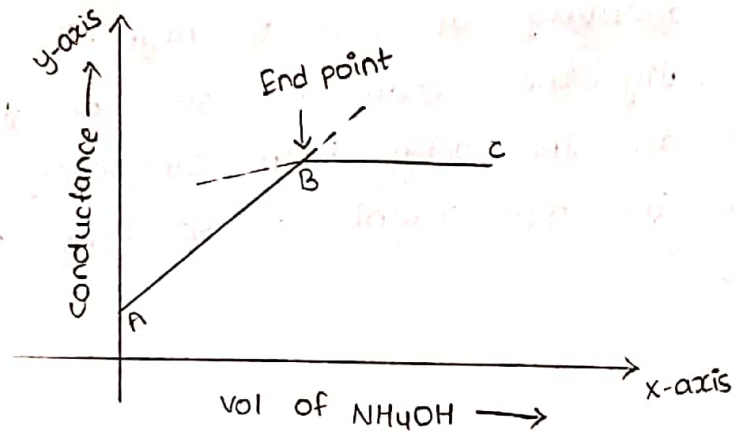
Further addition of poorly ionized  $\text{NH}_4\text{OH}$  does not cause any appreciable change in the conductance. The point of intersection B is the end point.

4) Weak acid vs weak base ( $\text{CH}_3\text{COOH}$  vs  $\text{NH}_4\text{OH}$ )

When  $\text{CH}_3\text{COOH}$  is titrated against  $\text{NH}_4\text{OH}$ , conductivity is going on increasing. This is due to the formation of highly ionised salt  $\text{CH}_3\text{COO}^-\text{NH}_4^+$ .



After the neutralisation of  $\text{CH}_3\text{COOH}$ , further addition of poor ionized  $\text{NH}_4\text{OH}$  does not cause any appreciable change in the conductance. The point of intersection 'B' is the end point.



### Batteries:-

- Electro chemistry has many applications both in science & in our everyday lives
- One of the most popular uses of galvanic cells are batteries.
- A battery is an electro chemical cell of several electro chemical cells connected in series. Batteries are classified into three types

1] Primary cell (or) Battery

2] Secondary cell (or) Battery

3] Fuel cell

- 1] Primary cell :- These cells are not recharged or cell reaction is not reversible. When the reactants have almost been converted to products further no more electricity is produced & the battery becomes dead. Hence, discharged batteries cannot be used again.



Ex:- 1] Voltaic cell (copper and zinc plates dipping in dil H<sub>2</sub>SO<sub>4</sub>)

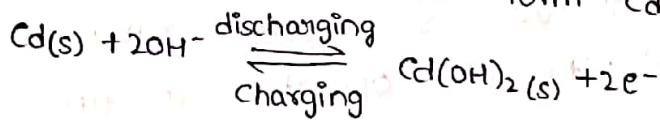
2] Daniel cell (Zn electrode in ZnSO<sub>4</sub> & Cu in CuSO<sub>4</sub>)

2] Secondary cell or Battery:- The chemical reactions are reversed by passing direct electric current in opposite direction. The cells are designed for repeated use & they are able to rechargeable

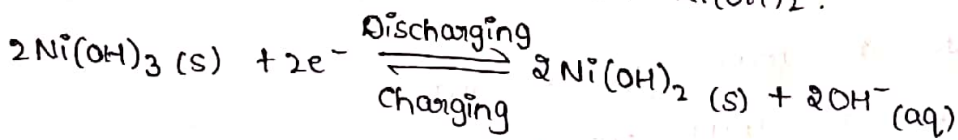
Eq:- Ni-cd storage cell, Mercury battery

Ni-cadmium cell :- It consists of cadmium Anode & a cathode is a paste of Ni(OH)<sub>2</sub>

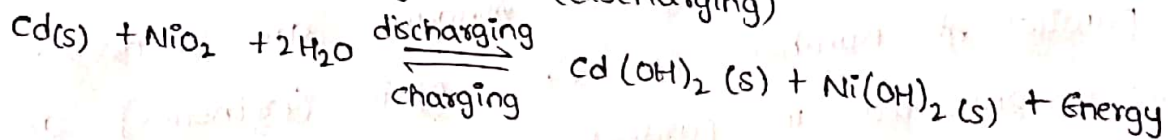
At anode:- Cadmium is oxidised to Cd<sup>2+</sup> & further it combines with OH<sup>-</sup> ions to form Cd(OH)<sub>2</sub>



At cathode:- NiO<sub>2</sub> is reduced to Ni<sup>2+</sup> ions which further combine with OH<sup>-</sup> ions to form Ni(OH)<sub>2</sub>.



Overall reaction during use (discharging)

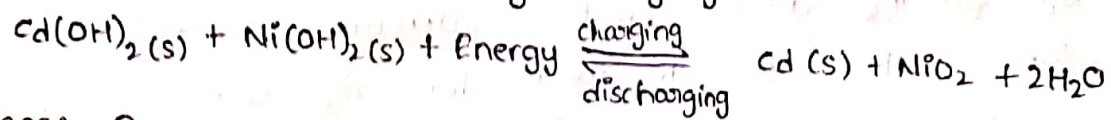


For the above cell. Reactions, it is clear that there is no formation of gaseous products. The products of Cd(OH)<sub>2</sub> & Ni(OH)<sub>2</sub> adhere well to the surfaces. This can be reconverted by recharging the cell

### Recharging the Battery:-

When the current is passed in the opposite direction, the electrode reaction gets reversed. As a result Cd gets deposited on anode &  $\text{NiO}_2$  on the cathode.

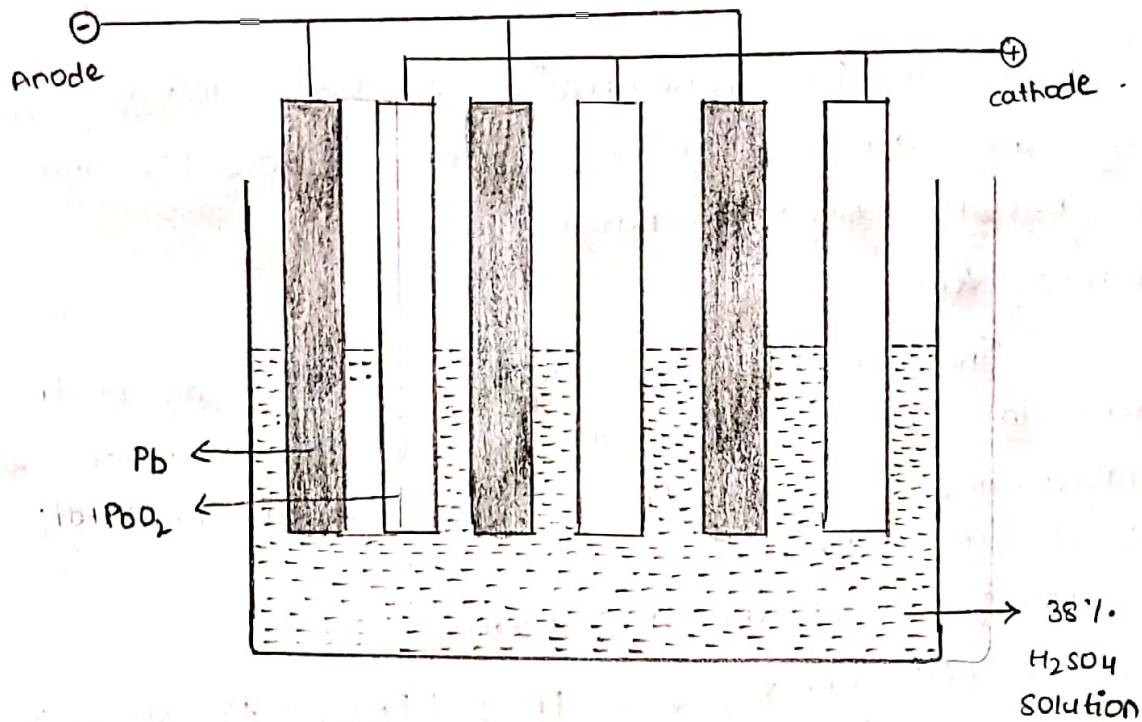
The net reaction during charging is



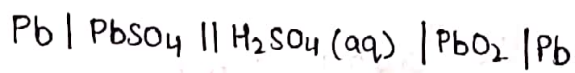
Uses:- It is used in calculator, electronic flash lights, transistors & cordless appliances.

**Lead-Acid Storage cell:-** This is a secondary type of battery which can operate both as a voltaic cell & as an electrolytic cell. When it acts as a voltaic cell it supplies electrical energy & becomes run down. When it is recharged, the cell operates as an electrolytic cell.

- The lead-acid storage battery consists of a number of 3 to 6 voltaic cells.
- The anode is made up of lead.
- The cathode is made up of lead dioxide ( $\text{PbO}_2$ )
- A number of lead plates anodes are connected in parallel. A number of  $\text{PbO}_2$  plates (cathodes) are also connected in parallel.
- Various plates are separated from the adjacent one by insulators, like rubber (or) glass (or) fiber.
- The entire combination is then immersed in dil  $\text{H}_2\text{SO}_4$  (38% by mass) having density of 1.309.

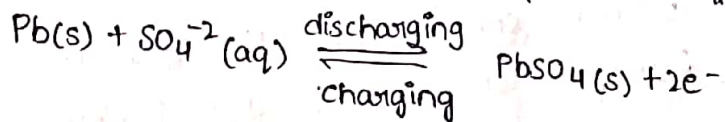


The cell may be represented as

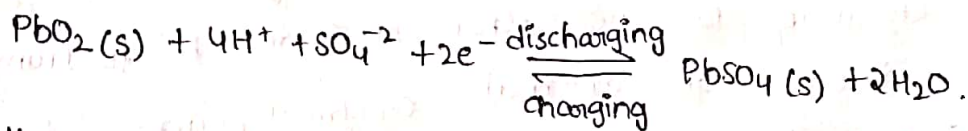
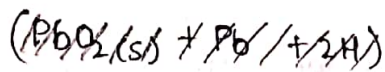


Working (Discharging)

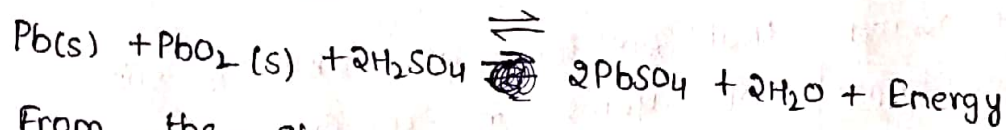
At anode :- lead is oxidised to  $\text{Pb}^{+2}$  ions, which further combines with  $\text{SO}_4^{-2}$  ions, insoluble  $\text{PbSO}_4$



At cathode:-  $\text{PbO}_2$  is reduced to  $\text{Pb}^{+2}$  ions which further combines with  $\text{SO}_4^{-2}$  ions forms insoluble  $\text{PbSO}_4$ .



Overall cell reaction



From the above cell reactions it is clear that  $\text{PbSO}_4$  is precipitate at both the electrodes &  $\text{H}_2\text{SO}_4$  is used up.

As a result, the concentration of  $H_2SO_4$  decrease & hence the density of  $H_2SO_4$  falls below  $1.20 \text{ g/ml}$ . So the battery needs recharging.

Recharging the battery:-

The cell can be charged by passing electric current in opposite direction. The electrode reactions gets reversed. As a result Pb is deposited at Anode &  $PbO_2$  at the cathode.

The density of  $H_2SO_4$  also increases.



Uses:-

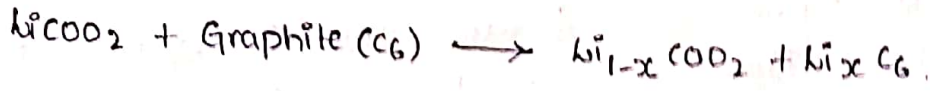
- ① Lead storage cell is used to supply current mainly in automobiles; such as cars, buses, trucks etc;
- ② It is also used in gas engine ignition, telephone exchanges, hospitals,

Lithium cells:- These cells do not contain metallic lithium. Hence they are called lithium ion cell & use lithium ions instead of lithium.

- In fact the cell's operation does not actually involve true oxidation & reduction.
- But it uses the pass of  $Li^+$  ions through the electrolyte from one electrode to the other electrode by the transfer of electrons through an external electrical circuit to maintain charge balance.
- It was discovered that  $Li^+$  ions are able to slip between two layers of atoms in certain crystals such as graphite &  $LiCO_2$ .

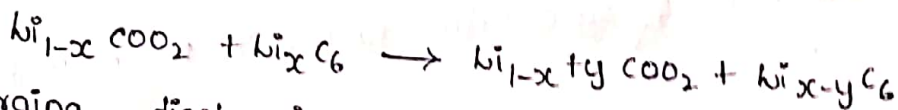
→ When the cell is discharged constructed, it is in its uncharged state with no  $Li^+$  ions between the layers of carbonates in the graphite

→ When the cell is discharged,  $Li^+$  ions have  $LiCoO_2$  & travel through the electrolyte to graphite ( $C_6$ )

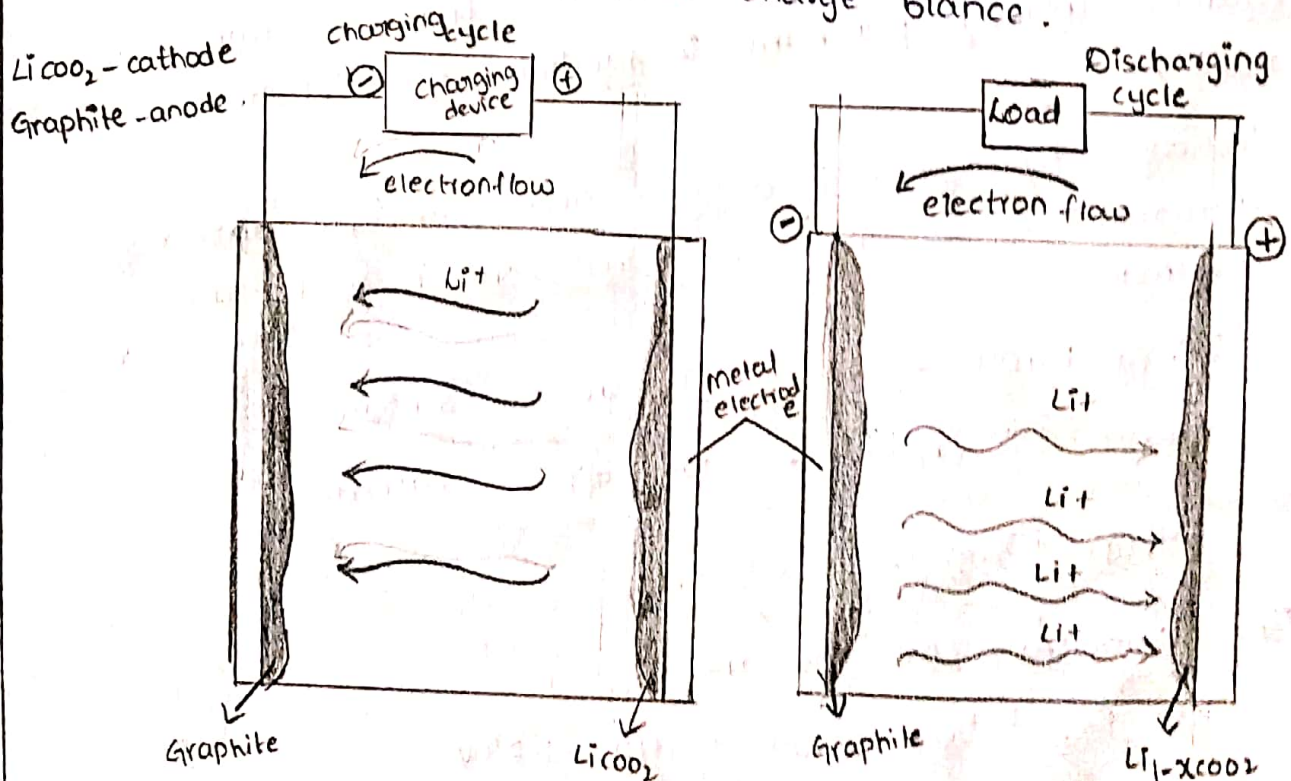


→ When the cell is spontaneously discharges to provide electrical power.  $Li^+$  ions move back through electrolyte to the cobalt oxide while the electrons move through the external electrical circuit from the graphite electrode to the cobalt oxide electrode.

Discharging:-



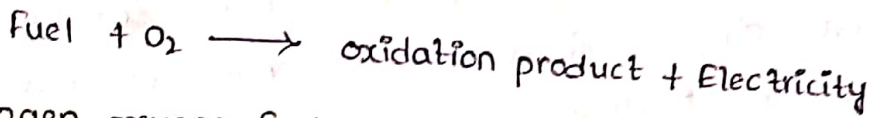
→ charging discharging cycles  $Li^+$  ions back & forth b/w two electrodes with electrons flowing through external circuit to keep the charge balance.



Fuel cells:-

→ The galvanic cells can only produce electrical energy for a limited time because the electrode reactants are eventually depleted. Fuel cells are different. They are electrochemical cells in which electrode reactants are supplied continuously & are able to operate without theoretical limit as long as.

→ In a fuel cell an electrical energy is obtained without combustion from oxygen & a gas that can be oxidised.

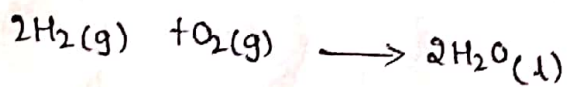
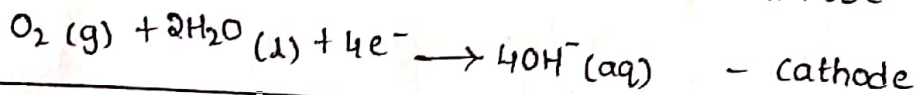
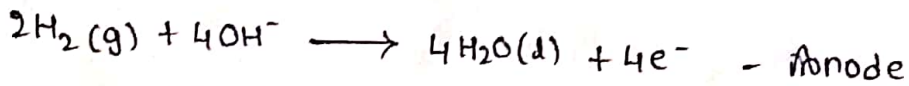


Hydrogen-oxygen fuel cell:-

→ One of the simplest & successful fuel cell is hydrogen oxygen fuel cell.

→ It consists of an electrolyte, a hot (200°C) concentrated solution of KOH in the centre compartment is in contact with two porous electrodes that contain catalyst (usually platinum) to facilitate the electrode reactions.

→ Gaseous hydrogen & oxygen under pressure are circulated so as to come in contact with the electrodes.

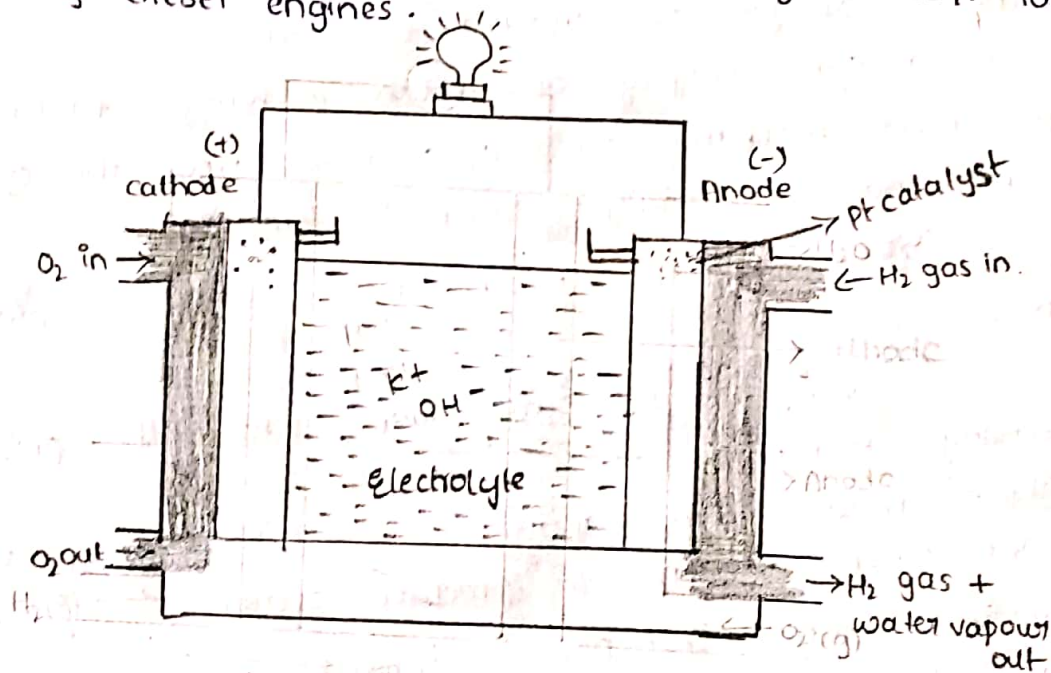


The standard emf of the cell is

$$E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = 0.83 + 0.40 = 1.23\text{V}.$$

In actual practice the EMF of cell is 0.8 to 1.0V

- Generally, large number of these cells are connected in series to make a battery called fuel cell battery
- $H_2 - O_2$  fuel cells are an attractive alternative to gasoline powered engine. particularly because they are pollution free & the only product of the reaction is harmless water.
- Fuel cells are also thermodynamically efficient, converting as much as 75% of available energy to useful work compared to approximately 25-30% for gasoline & diesel engines.



- The major problem associated with fuel cells are
  - (i) Energy cost of generating  $H_2$  fuels
  - (ii) problem in providing storage and distribution of highly flammable hydrogen
  - (iii) availability of alternative fuels

### Applications:-

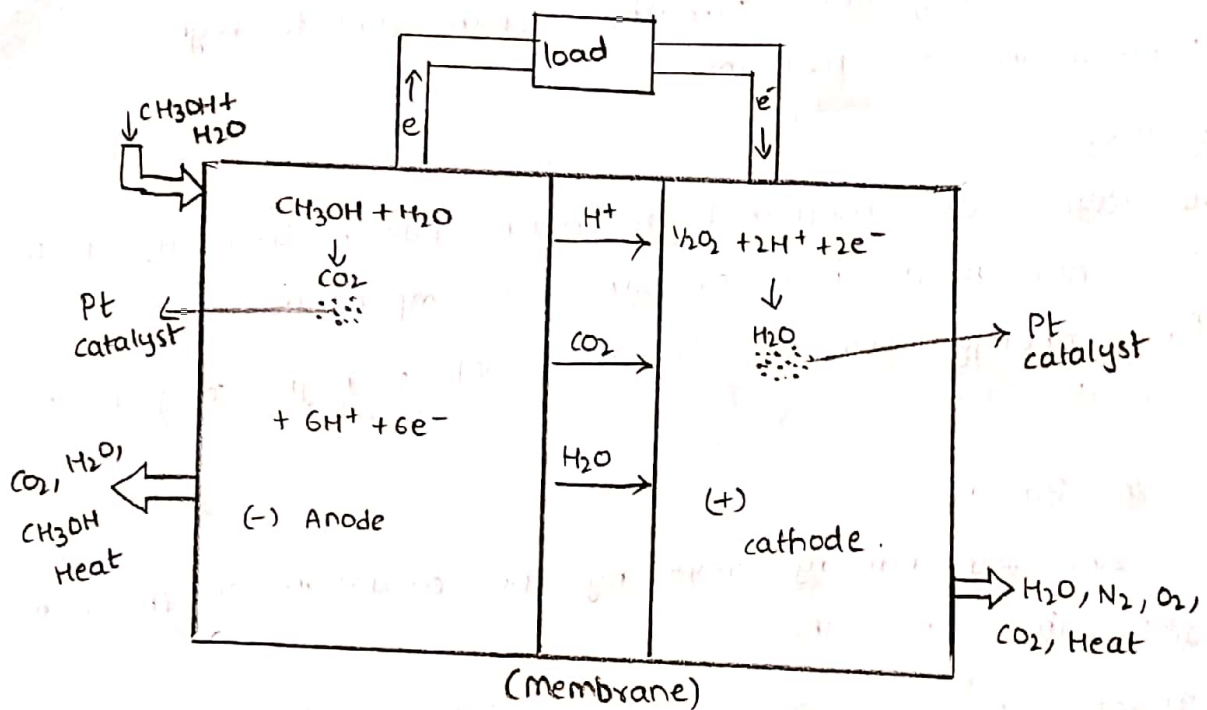
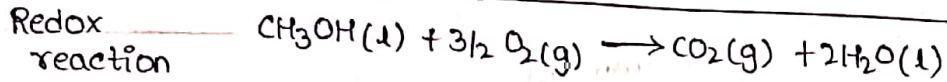
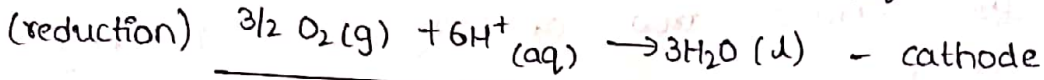
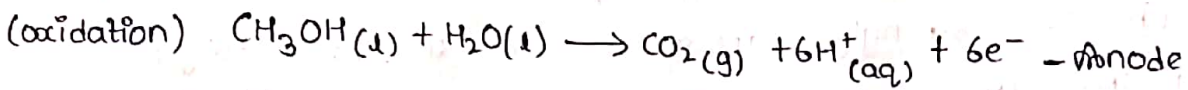
- 1]  $H_2-O_2$  fuel cells are used as auxiliary energy source in space vehicles, submarines or military vehicles.
- 2] The weight of fuel battery for 15 days space is about 250kg.
- 3] In case of  $H_2-O_2$  fuel cells, the product of water proves to be a valuable source of freshwater to the astro\_\_\_\_\_

### Methanol fuel cell:-

- Methanol oxygen is another fuel cell
- It is a sub-category of proton exchange fuel cell
- The direct methanol fuel cells relies upon the oxidation of methanol on catalyst layer to form  $CO_2$ .
- Water is consumed at the anode which is produced at cathode
- The positive ions are transferred across the proton exchange membrane.
- Often made from anode to cathode where they react with oxygen to produce water.
- Electrons are transported through as an external electrical circuit from Anode to cathode providing power to a connected devices. currently platinum is used as catalyst in both half reactions.
- Methanol & water are absorbed on a catalyst usually of platinum particles & lose protons,  $CO_2$  is formed



→ Methanol or water mixture is circulated through an anode of cell while O<sub>2</sub> or air is circulated at cathode of the cell



→ From the cell reaction it is observed that for the forming final product as CO<sub>2</sub>, water has to be added

→ The six electrons pass the load resistance of the outer circuit & are consumed at the cathode together with six protons

→ For the reaction of one molecule of methanol, 3/2 O<sub>2</sub> molecules will be reduced to 3H<sub>2</sub>O & at a stationary anode. part of this water is introduced at the fuel compartment again. For a six electron

Charge transfer.

Limitations:-

- 1] During the methanol oxidation reaction CO is formed which is strongly absorbed on to Pt catalyst, reducing the surface area of catalyst & lowering the performance.
- 2] Methanol is toxic & flammable.
- 3] Limited in the power they produce.
- 4] The efficiency of current is low due to high permeation of methanol.

Advantages:-

- 1] Storage of methanol is much easier than  $H_2$  as it does not need high pressure or temperature.
- 2] The energy density of methanol is high comparison of  $H_2$ .

Zinc - Air Battery :-

Zinc - Air battery work by the oxidation of Zn with oxygen from the air.

Construction:- A \_\_\_\_\_ of loose granulated Zn particles mixed with an electrolyte such as KOH to form a porous anode. The zinc plates, in the other side acts as cathode.

Working :-

- Oxygen from the air, at the cathode forms hydroxide ions which migrate into the zinc paste & form zincate.
- $[Zn(OH)_4]^{-2}$  releasing electrons to travel to the cathode.
- This zincate decays into zinc oxide & water.
- The water & hydroxide ions from the electrodes are

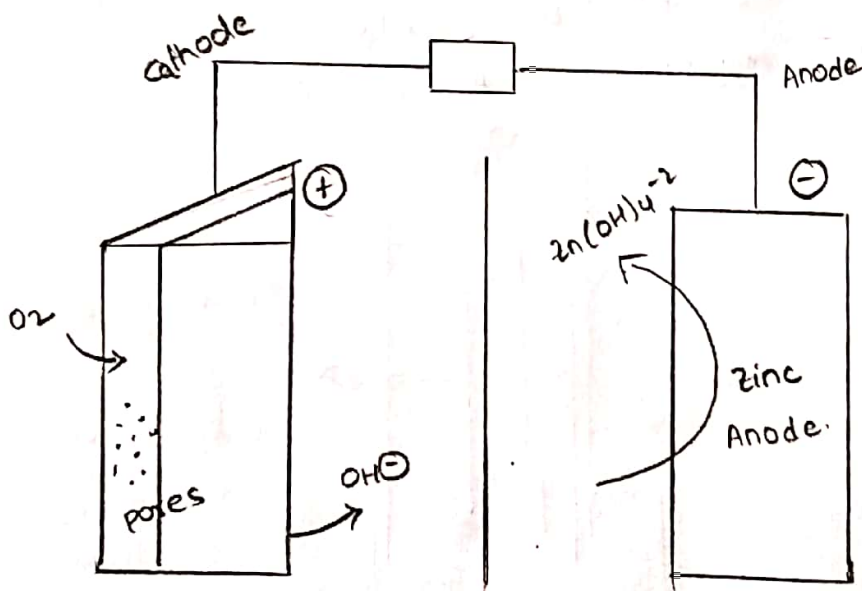
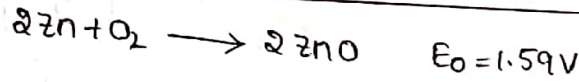
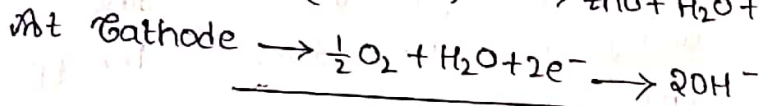
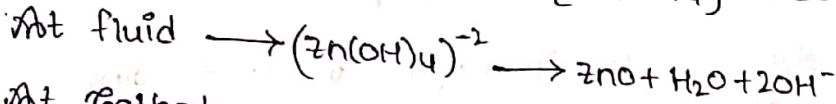
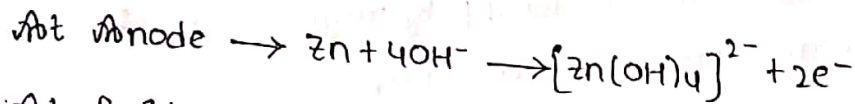
recycled. So the water is not consumed. This battery produces 1.65V

Factors affecting the reaction:-

- The rate of reaction can be controlled by varying the oxygen flow
- The rate of reaction can be increased by replacing oxidized zinc/electrolyte paste by fresh paste

cell : Granulated Zn | 6M KOH | Air | c

Chemical reactions:-



Electrochemical sensors :-

Eg:- oxygen sensor :-

- The cell consists of a Pt disk cathodic working electrode embedded in a centrally located cylindrical insulator, surrounding the lower end of this insulator is a ring shaped silver anode.
- The tubular insulator and electrodes are mounted inside a second cylinder that contains a buffered solution of KCl.
- Membrane is made up of teflon / polyethylene is held in place at the bottom end of the ring.
- When the oxygen sensor is immersed in a flowing stirred solution of the analyte, oxygen diffuses through the membrane into the thin layer of electrolyte immediately.

Cathodic reaction :-  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anodic reaction :-  $Ag + Cl^- \rightarrow AgCl(s) + e^-$

