

ELECTROCHEMISTRY AND BATTERY CHEMISTRY

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ELECTRO CHEMISTRY

Definition: Electrochemistry is the study of process involving the interconversion of electrical energy and chemical energy.

Chemical reactions can be used to produce electrical energy, conversely, electrical energy can be used to carry out chemical reactions that do not proceed spontaneously.

⇒ Electrochemistry serves as an interface between chemistry and everyday life. When we ~~turn~~ switch on a calculator, a computer, use digital watch and so on depending upon the electrochemical reactions occurring in cells or batteries

conductors: A substance that allow electric current

to pass through it is called a conductor.
eg All metals, graphite, aqueous solution of acids and bases

Electrode: — Electrode is a material which conducts electrons

Anode: — Anode is the electrode at which oxidation occurs.



Cathode: — Cathode is the electrode at which reduction occur.



ELECTROCHEMICAL CELL: It is device which can interconvert chemical and electrical energy.

⇒ Systems utilizing a redox reaction to produce or use electrical energy

Redox reactions: electron transfer process

Oxidation: loss of 1 or more e^-

Reduction: gain of 1 or more e^-

TYPES OF CELLS

Galvanic cell

① The chemical energy of a spontaneous redox reaction is converted to electrical work

② A device in which chemical energy is changed to electrical energy

③ Cathode (-ve)
Anode is (-ve)

④ The energy generated by a spontaneous reaction is converted into electrical energy

Electrolytic cell

① The electrical energy used to carry out a non spontaneous redox reaction

② A device in which electrical energy is changed to chemical energy.

③ Cathode (-ve)
Anode (+ve)

④ A non spontaneous reaction is carried out using electrical energy



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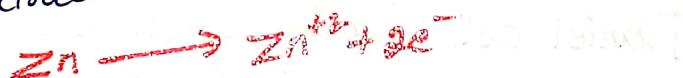
GALVANIC CELL : DANIEL CELL

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Definition: Galvanic cell is a electrochemical cell used for converting chemical energy into electrical energy.
→ A redox reaction is utilized to get electrical energy and the emf of such a cell is directly proportional to the intensity of chemical reaction taking place in it.
⇒ Galvanic cell is combination of two half cell and it is connected by salt bridge. The electrode where oxidation occurs is called "Anode" while the electrode where reduction occurs is called "cathode".

⇒ In Daniel cell consist of Zn electrode dipped in ZnSO_4 solution where oxidation occurs. A copper electrode dipped in CuSO_4 solution where reduction takes place.

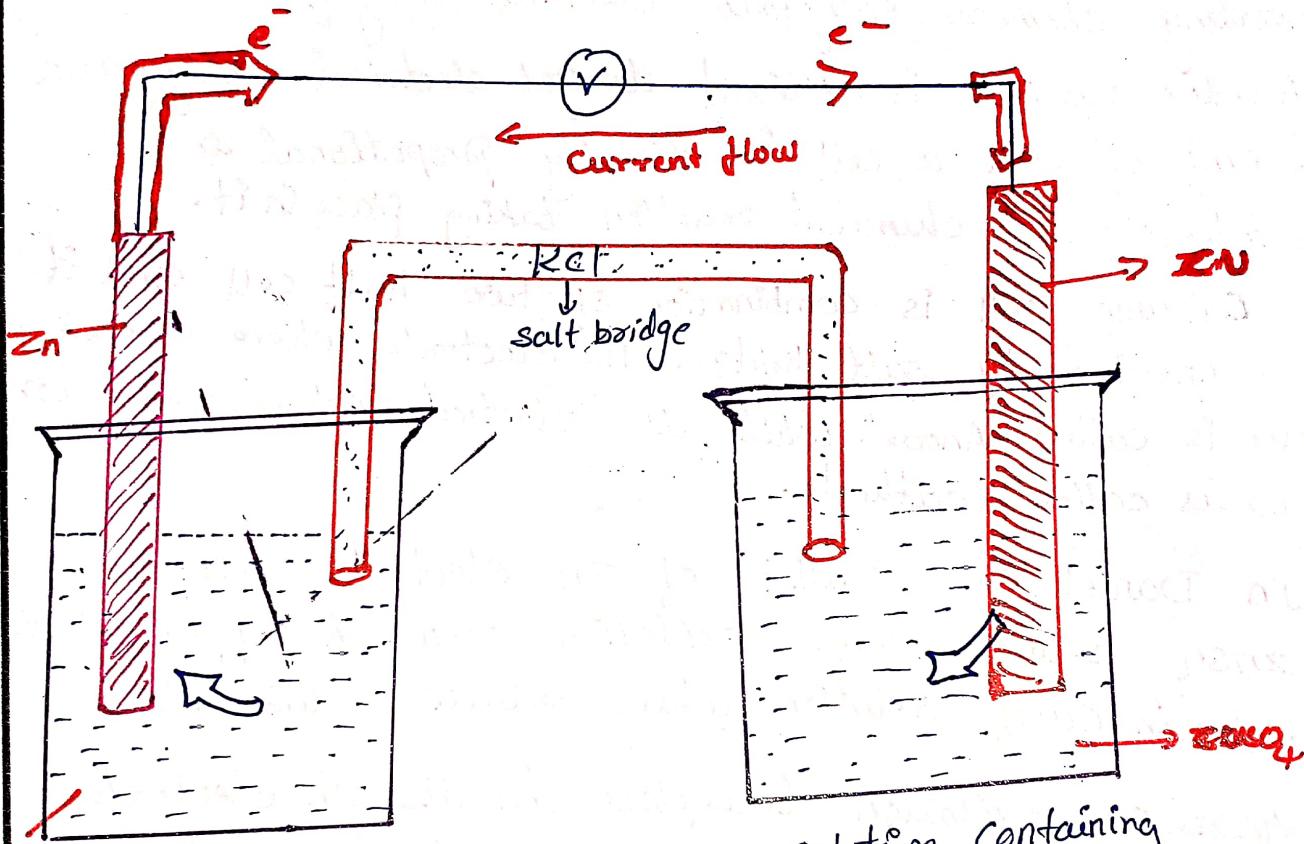
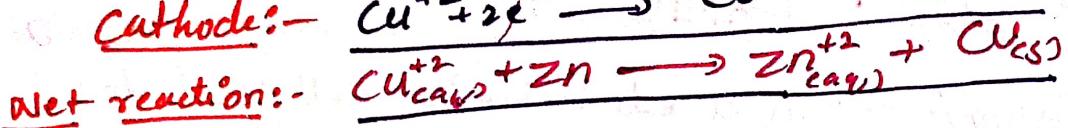
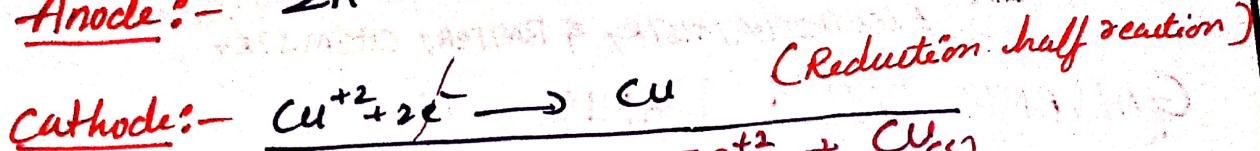
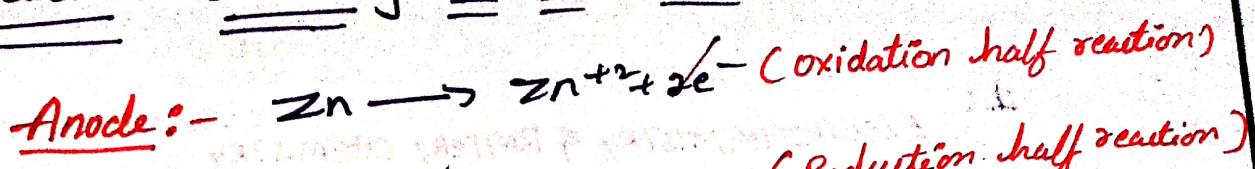
At Anode:— Oxidation takes place in the Zn electrode by loss of electrons so this electrode is called negative electrode or Anode.



At cathode: Reduction takes place in the copper electrode by acceptance of electrons. So this electrode is called the positive electrode (or) cathode



Reaction Occuring in the Cell



$ZnSO_4$
solution containing
salt of Zn

solution containing
salt of Copper

Daniel cell having electrodes of
Zn and Cu dipped in the solution
of their respective salts



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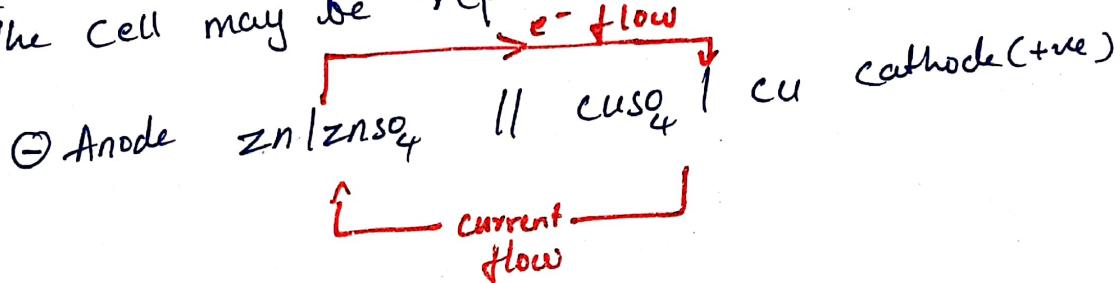
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Electron flow from anode to cathode thus electrical energy is produced and the current flow is due to difference in electrode potentials of both electrodes from cathode to anode.

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The cell may be represented as



Functions of salt bridge:

- It completes the inner circuit of the cell
- It maintains electrical neutrality in both compartments by providing oppositely charged ions
- It prevents the two electrolytic solutions from mixing

Inert electrolyte

- Does not participate in the cell reaction
- For an electrolyte to be used in salt bridge speed of cations and anions should be same
- eg KCl , KNO_3 , NaNO_3 , NaCl etc.

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Galvanic cell - cell notation / cell Representation

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The following representation is used for writing galvanic cell.

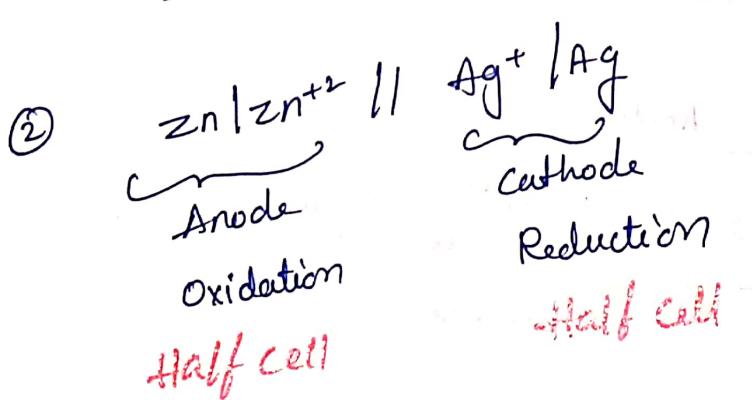
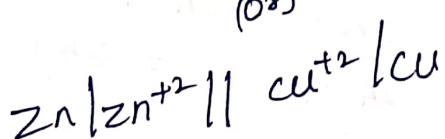
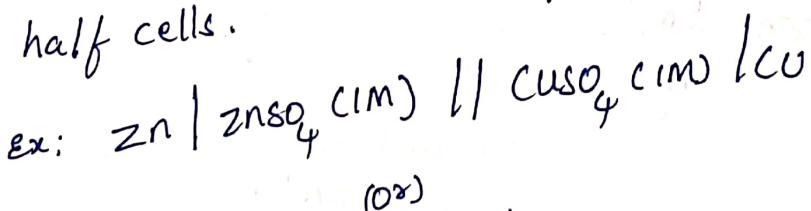
→ Galvanic cell has two electrodes anode and cathode

Anode is always written on left hand side while Cathode on right hand side.

→ The negative electrode is at the extreme left and the positive electrode on the extreme right.

The double vertical lines between two liquids signifies the salt bridge or semipermeable membrane separating

two half cells.

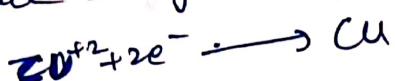


CELL REACTION:-

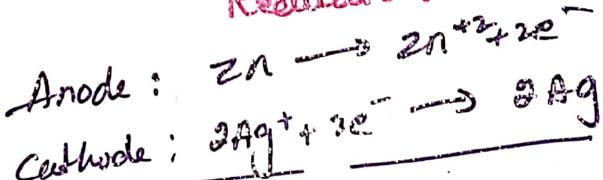
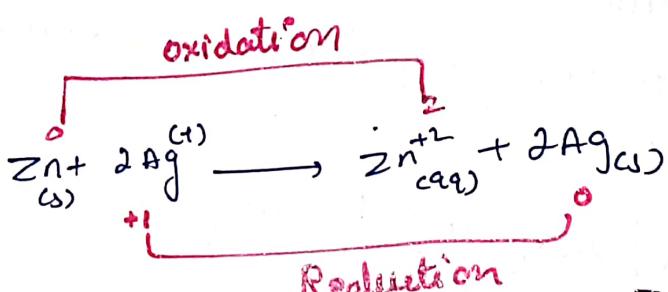
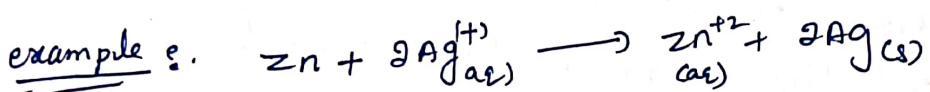
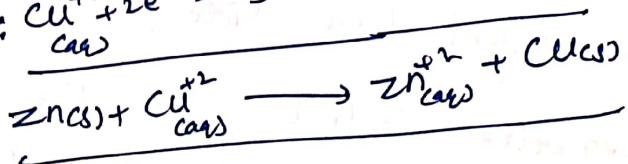
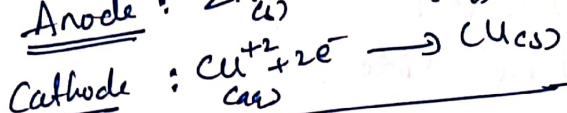
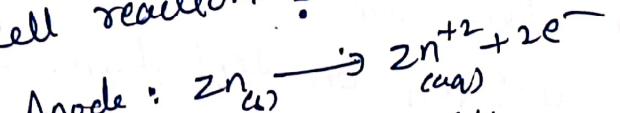
The cell reaction of the electrode where oxidation takes place is given below



The cell reaction of the electrode where reduction takes place is given by



The total cell reaction :-



CELL REACTION :-

Anode

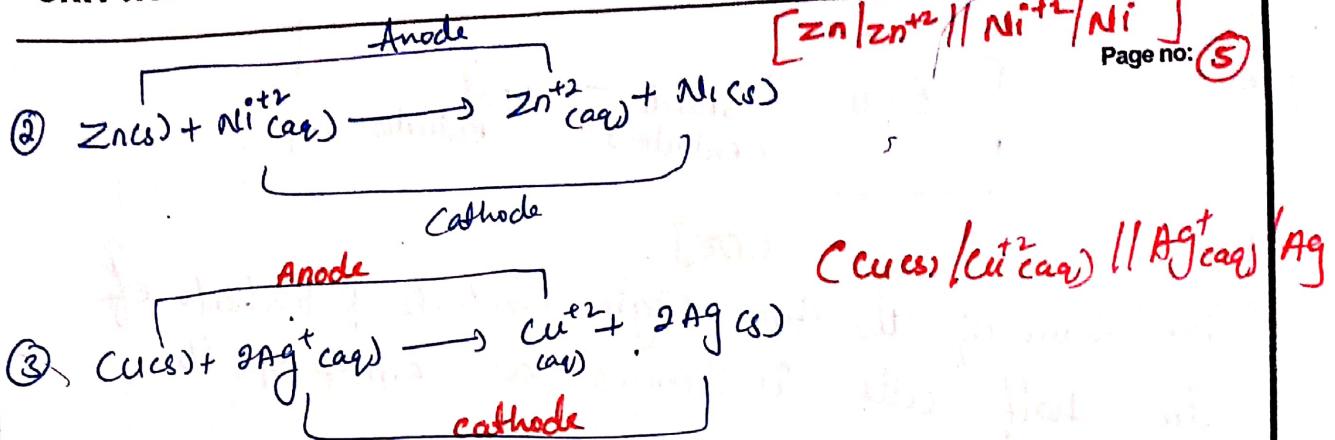




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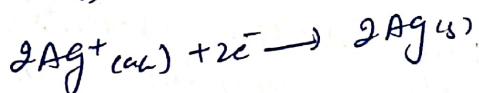
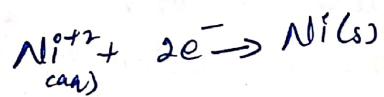
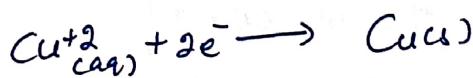
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The half cell reactions are:-

Cathodic (reduction) reactions



CELL POTENTIAL :- [EMF of the cell]

CELL POTENTIAL :- [V] In an electrochemical cell the potential difference across the electrodes operates as a driving force for the flow of electrons and thereby current and is known as cell potential / electromotive force. It is defined as "difference of electrode potentials".

Electromotive force
→ Electromotive force is defined as "difference of potential which cause flow of current from one electrode of higher potential to the other electrode of lower potential".

FACULTY NAME: ANJUM BEGUM

SUBJECT:CHEMISTRY(BS105CH)

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

(Reduction potential
of right hand side) (Reduction potential
of left hand side)

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

(Reduction) (Reduction)

(OR)

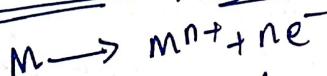
The sum of the two single electrode potentials of two half cells is termed as e.m.f of the cell

$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$$

(Red.) (Red.)

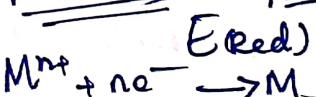
Electrode potential : [E] : It is the measure of tendency of metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt. In this process, there develops a potential between the metal atom and its corresponding ion called electrode potential

Oxidation potential [E_{Ox}]

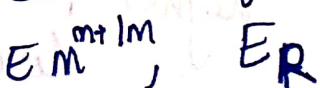


→ potential developed when metal lose e⁻ when it is come in contact with salt solution of its own e.g. $E_M | M^{n+}, E_L$

Reduction potential



⇒ potential developed when metal gain e⁻. When it is come in contact with salt solution of its own



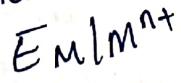
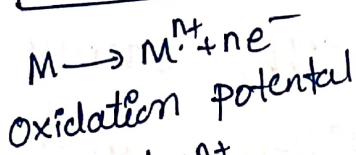
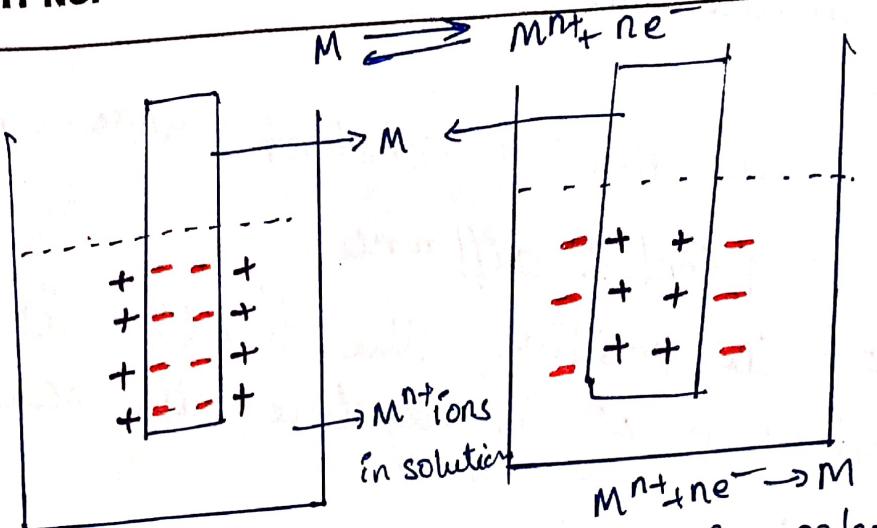


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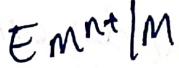
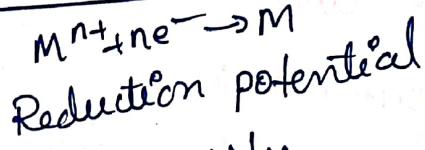
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E_{left, Boxd}

E_{Anode}



E_{right, Ered}

E_{Cathode}

Standard Electrode Potential :-

It is the measure of tendency of metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt of 1 molar concentration

at 25°C.

→ It is represented as E°

NERNST EQUATION :-

The Nernst equation is derived from the Gibbs Free energy under standard conditions

ΔG is also related to E under general conditions. $\Delta G = -nFE$

Where n is the number of electrons transferred in the reaction

$\Rightarrow F$ is the Faraday constant (96,500 C/mol)

$\Rightarrow E$ is potential difference.

Hence, when E° is positive, the reaction is spontaneous and when E° is negative, the reaction is non-spontaneous.

From thermodynamics, the Gibbs energy change under non-saturated conditions can be related to the Gibbs energy change under standard equations. $\Delta G = \Delta G^\circ + \frac{2.303RT}{nF} \log Q$

$$\text{where } \Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

$$Q = \frac{\text{[product]}}{\text{[Reactant]}}$$

$$\Delta G = \Delta G^\circ + \frac{2.303RT}{nF} \log \left[\frac{P}{P^\circ} \right]$$

$$-nFE = -nFE^\circ + 2.303RT \log \left[\frac{P}{P^\circ} \right]$$

divide both sides by $-nF$

$$E = E^\circ - \frac{2.303RT}{nF} \log \left[\frac{P}{P^\circ} \right]$$



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Where E = Electrode potential

E° = Standard electrode potential

R = gas constant 8.314 J/mol

T = absolute temperature $- 298 \text{ K}$

F = Faraday constant $- 96500 \text{ coulomb}$

n = valency of the ion

Substituting all the values we get the potential of the electrode at 25°C as

$$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[P]}{[R]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

General Nernst equation

Nernst equation for oxidation potential :-

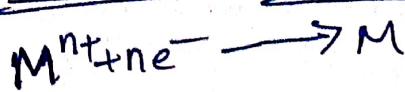


$$E_{\text{ox}} = E_{\text{ox}}^\circ - \frac{0.0591}{n} \log \frac{[M^{n+}]}{[M]}$$

[$\because M = \text{unity}$]

$$E_{\text{ox}} = E_{\text{oxd}}^\circ - \frac{0.0591}{n} \log [M^{n+}]$$

For Reduction potential



$$E_{\text{cell}} = E_{\text{Red}}^{\circ} - \frac{0.0591}{n} \log \left[\frac{M}{M^{n+}} \right]$$

$$E_{\text{Red}} = E_{\text{Red}}^{\circ} - \frac{0.0591}{n} \log \left[\frac{1}{[M^{n+}]} \right]$$

$$E_{\text{Red}} = E_{\text{Red}}^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

Cell potential

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Red}]}{[\text{Oxid}]}$$

Applications:-

- ⇒ To find the electrode and cell potential. electrode and cell potentials can be calculated under the given set of conditions by using Nernst equation.
- ⇒ It is used to determine ion concentration
- ⇒ It is also used to in pH measurements

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TYPES OF ELECTRODES

REFERENCE ELECTRODE :- A reference electrode is an electrode with standard potential. Reference electrodes are of two types (1) primary reference electrode - eg standard hydrogen Electrode [SHE]
(2) secondary reference electrode - Standard calomel electrode [SCE]

STANDARD CALOMEL ELECTRODE: (SCE)

SECONDARY REFERENCE ELECTRODE :- Looking into the difficulties encountered with SHE, in regular practice the use of secondary reference electrode is promoted.
The potential of these electrode is obtained with respect to primary reference electrode.
and hence the name is secondary reference eg calomel electrode
Silver - silver chloride electrode -

Calomel electrode

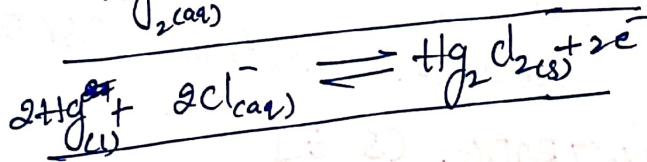
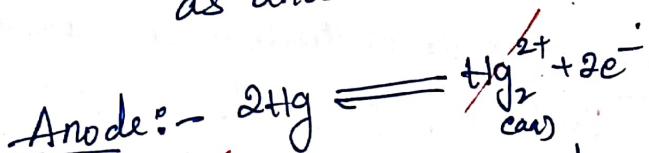
It consists of Mercury in contact with KCl solution Saturated with mercurous chloride,
 Hg_2Cl_2

The potential of the electrode depends on the concentration of the electrolyte KCl.

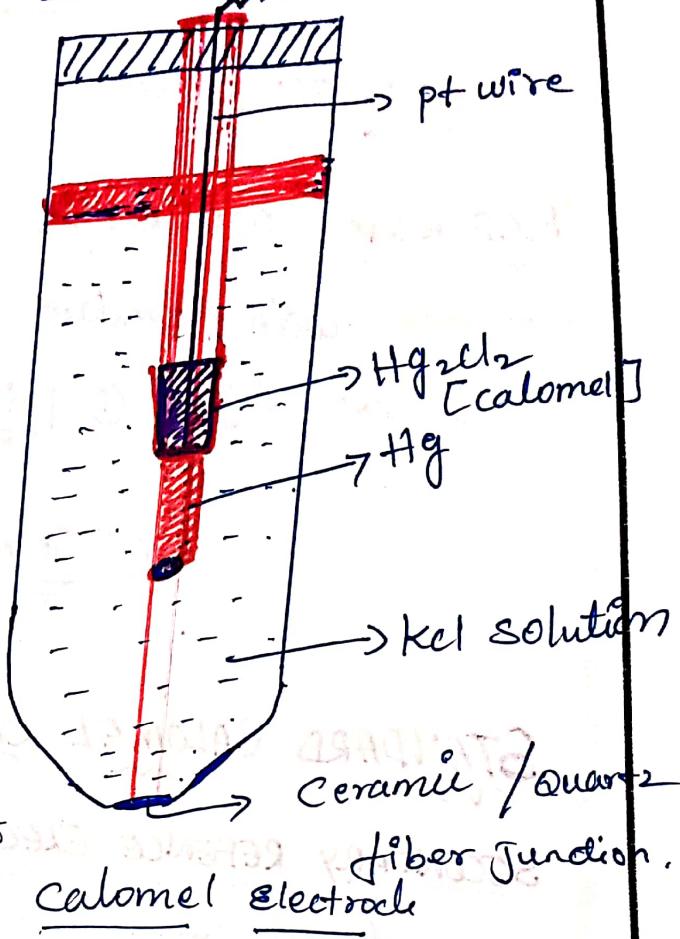
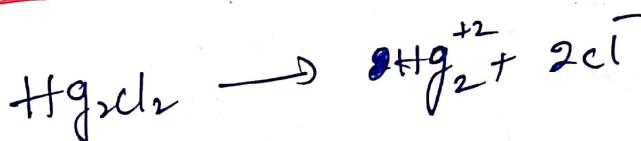
Cell representation $Hg, Hg_2Cl_2 | KCl \text{ conc}$

Anode :- $Hg, Hg_2Cl_2 | KCl$

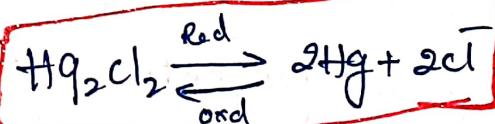
When electrode is used for
as anode



Cathode :- $KCl \text{ conc} | Hg, Hg_2Cl_2, pt$



Redox Reaction



$$E^\circ = 0.2422 V$$

In calomel electrode, the concentration of Cl^- ions plays an important role in deciding the potential.

→ generally Saturated KCl is used when the corresponding name of the electrode is Saturated Calomel electrode with $E^\circ = 0.2422$ at $25^\circ C$.



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→ The other forms being normal electrode

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$$1N \text{ KCl} - E^{\circ} = 0.2810$$

$$\text{and deca-normal } 0.1N \text{ KCl} \rightarrow E^{\circ} = 0.3335V$$

Advantages :-

- It is simple to construct.
- Result of cell potential measurements are reproducible and stable over a long period & does not vary with temperature.

Quinhydrone electrode :-

It is a type of redox electrode which can be used to measure the H^{+} ion concentration of a solution. The electrode consists of an inert metal electrode (Platinum wire) in contact with quinhydrone crystals and a water based solution.

→ Quinhydrone is slightly soluble in water, formed by equi-molar mixture of hydroquinone and quinone.

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The reduction potential of quinhydrone electrode is 0.699V

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Advantages:-

- ⇒ The electrode is very easy to set up.
- ⇒ The pH value obtained is very accurate.
- ⇒ very small quantities of solution is sufficient for the measurement.

Disadvantages:-

- ⇒ The electrode cannot be used in more alkaline solution ($\text{pH} > 8.5$) and also with solution that react with quinone or hydroquinone.

Note:-

Quinhydrone electrode doesn't give satisfactory results in strongly alkaline solutions where $\text{pH} > 8.5$. This is due to the fact that hydroquinone $\text{pH} > 8.5$. This is due to the fact that hydroquinone ionizes as an acid and gets oxidized by atmospheric oxygen after normal equilibrium between hydroquinone and quinone.

Determination of pH using Quinhydrone electrode

In acidic medium

$$E_Q^2 E_Q^0 - 0.059194$$

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

$$E_{\text{cell}} = E_{\text{Q}} - 0.0591 \cdot \text{pH.} - E_{\text{SCE}}$$

$$E_{SCE} = 0.2422 \text{ V}$$

$$E_Q^o = 0.699 \text{ V}$$

$$E_{\text{cell}} = 0.699 - 0.0891 \text{ pH} - 0.2422$$

$$0.0591 \text{ pH} = 0.457 - E_{\text{cell}}$$

$$pH = \frac{0.457 - E_{cell}}{0.0591}$$

GLASS ELECTRODE

GLASS ELECTRODE

Construction:-

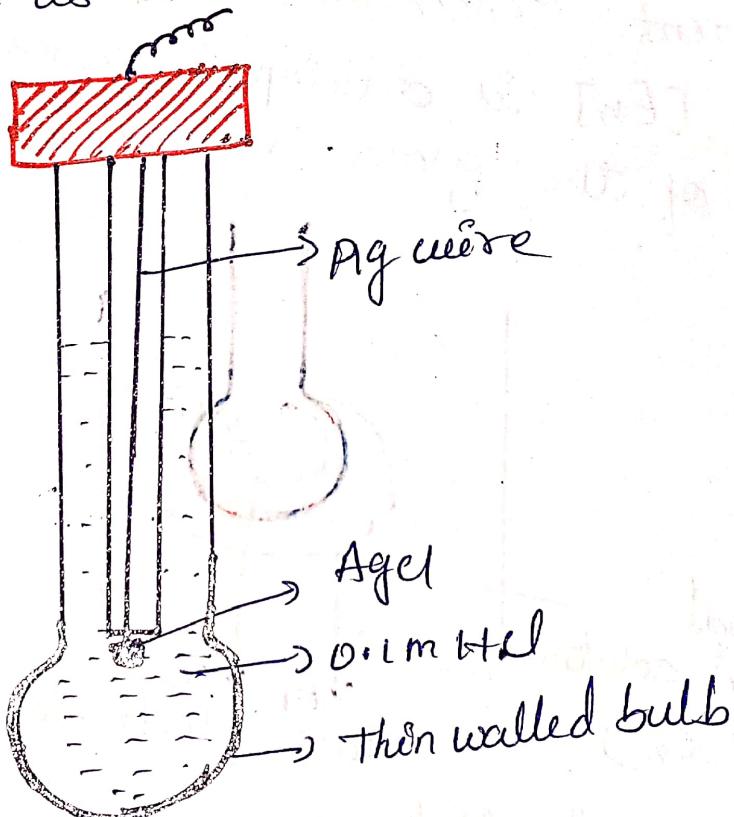
Construction:- Glass electrode consist of a thin walled glass bulb, made from low melting point glass having electrical conductivity, blown at the end of glass tube.



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- ⇒ The special type of glass used to contain Na_2O (22%) CaO (6%) and SiO_2 (72%).
- ⇒ The bulb contains 0.1M HCl solution, sealed into the glass tube is a Ag wire coated with AgCl at the lower end.
- the lower end of Ag wire dips into hydrochloric acid, forming Ag-AgCl electrode.
- Ag-AgCl act as an internal reference electrode.

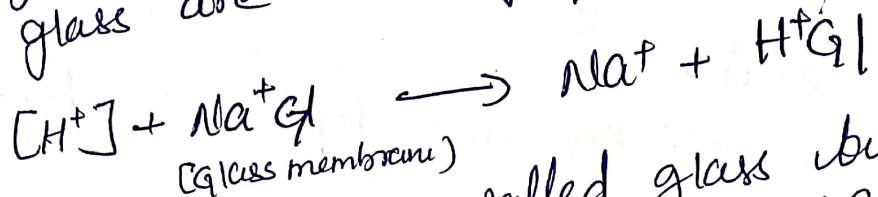


Cell Representation
 $\text{Ag}, \text{AgCl} | 0.1\text{M HCl} | \text{glass}$

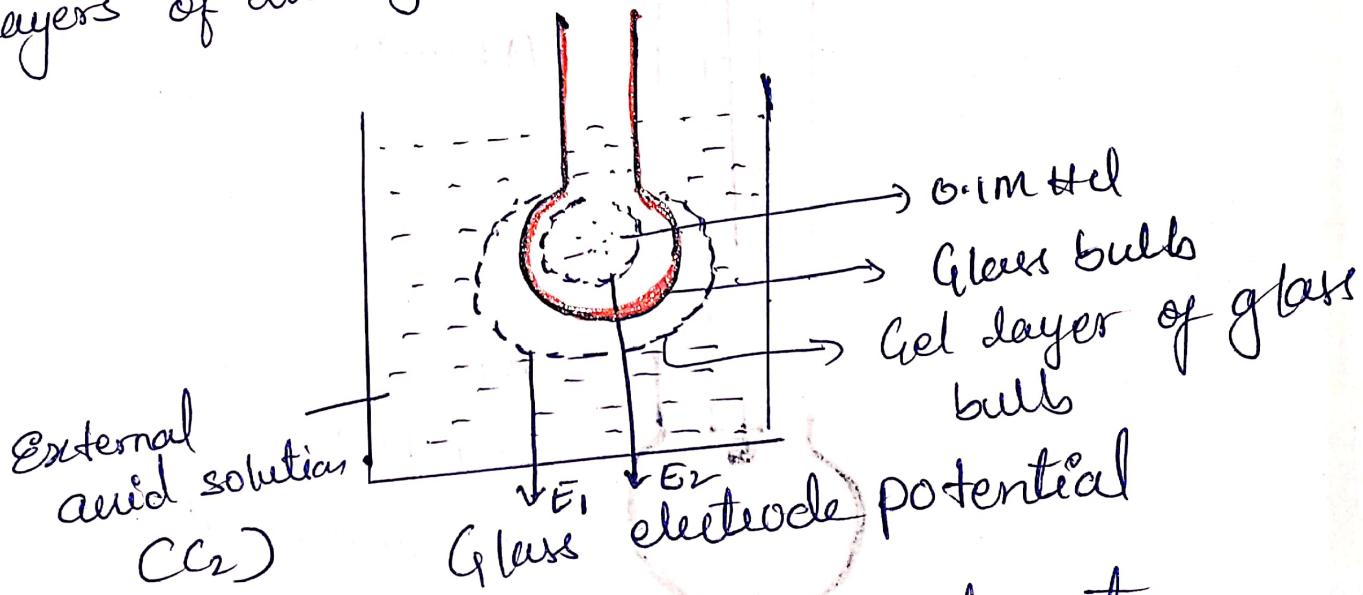
Glass electrode Potential

Glass electrode is dipped in solution whose pH is to be measured.

A glass membrane of silicate glass is sensitive to H^+ ions of the solution. In the membrane undergoes ion exchange reaction. The Na^+ ions of glass are exchanged with H^+ ions.



When this thin walled glass bulb containing 0.1M HCl (C_2) is dipped in acidic solution of different concentration (C_1) [$C_1 > C_2$], a boundary potential $[E_b]$ is developed across the gel layers of the glass membrane.



Boundary potential, E_b arises due to difference in H^+ ion concentration inside and outside the glass bulb.



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$$E_b = E_1 - E_2$$

$$\therefore E_b = \frac{2.303 RT}{NP} \log \frac{C_2}{C_1}$$

where C_1 is the concentration of H^+ inside the glass bulb. [is constant 0.1M HCl]

C_2 is the concentration of H^+ outside the glass bulb

the potential of glass electrode :-

$$E_g = E_g^\circ + 0.0591 \log [H^+]$$

$$E_g = E_g^\circ - 0.0591 \text{ pH}$$

Measurement of pH of solution using Glass electrode :-

$$E_{\text{cell}} = E_R - E_L$$

$$E_{\text{cell}} = E_g - E_{\text{SCE}}$$

$$E_{\text{cell}} = [E_g^\circ - 0.0591 \text{ pH}] - E_{\text{SCE}}$$

$$0.0591 \text{ pH} = E_g^\circ - E_{\text{SCE}} - E_{\text{cell}}$$

$$\text{pH} = \frac{E_g^\circ - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}$$

Advantages :-

- Glass electrode is easy to operate and simple. It does not get easily poisoned.
- ⇒ Equilibrium is easily reached
- ⇒ It gives accurate results

Disadvantages

- Glass electrode is made of delicate glass bulb therefore should be handled carefully
- ⇒ It can be used in solutions with pH range 0-10 only

Application:- Glass electrode is ion selective electrode, sensitive towards H^+ , extensively used to measure pH of the solution precisely

BATTERIES

Definition:- Battery is an arrangement of several electrochemical cells connected in series, that can be used as a source of direct electric current.

A cell :- contains only one anode and cathode

A battery :- contains several anodes and cathodes



Advantages of Batteries :-

- ⇒ Batteries act as a portable source of electrical energy
- ⇒ The portability of electronic equipment has been made possible in the form of handsets by batteries
- ⇒ A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better ~~shelf~~ cell life and tolerance to service.
- High capacity, which is very small variation of voltage during discharge.
- ⇒ High energy efficiency, which is calculated as
- $$\% \text{ of efficiency} = \frac{\text{energy released on discharge}}{\text{energy required for charge}} \times 100$$

TYPES OF BATTERIES

- ① Primary Battery → ~~Alkaline cell~~ → ~~Lithium cell~~
- ② Secondary Battery → ~~Lead-acid, Ni-Cd~~ → ~~Lithium ion~~
- ③ Flow or Fuel Battery → ~~H₂O₂ cells~~ → ~~CH₃OH - O₂ cells~~

① PRIMARY BATTERY (or) PRIMARY CELLS:-

In this cells, the electrode reaction cannot be reversed by passing an external electrical energy. The reactions occur only once and after use they become dead. Therefore, they are not chargeable.
eg Dry cell (Zinc - carbon cell)
Alkaline cells
Lithium cell.

② Secondary Battery (or) Secondary Cells:

In these cells, the electrode reactions can be reversed by passing an external electrical energy therefore, they can be recharged by passing electric current and used again and again.
eg Lead - acid
Ni - cd
Lithium ion battery

③ Flow Battery (or) Fuel Cells:-

In these cells, the reactants, products and electrolytes are continuously passing through the cell. In these chemical energy gets converted into electrical energy
① Hydrogen - oxygen ② Methanol - oxygen



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Dry cells (or) Leclanche's Cells:-

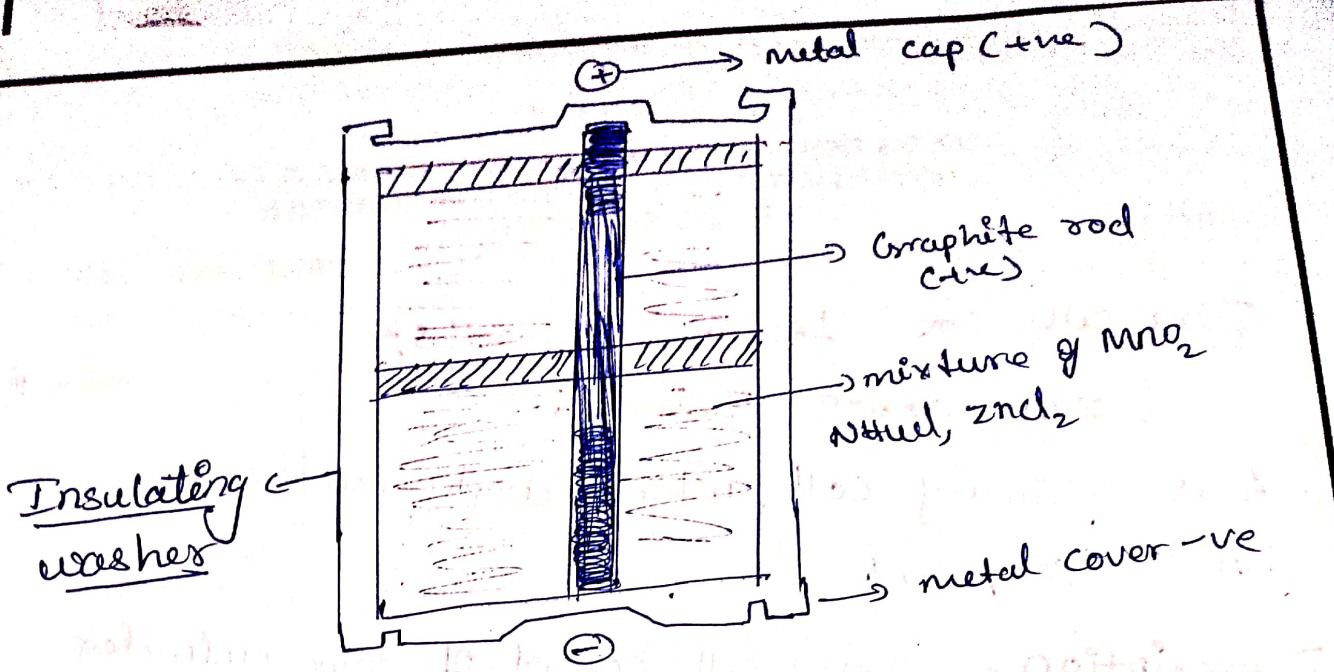
[Zn - Carbon] Battery:-

It is primary cell, which works without fluid component.

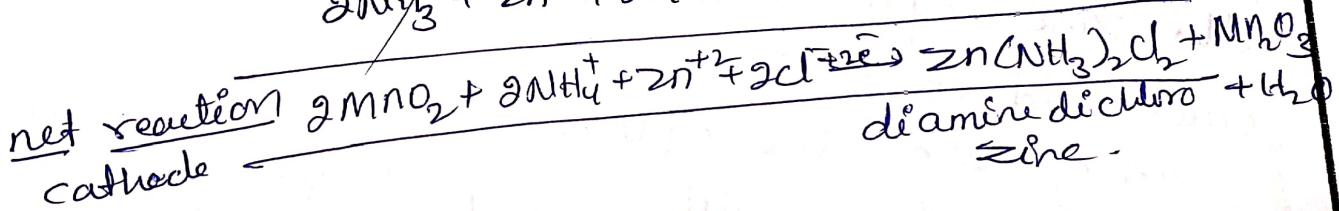
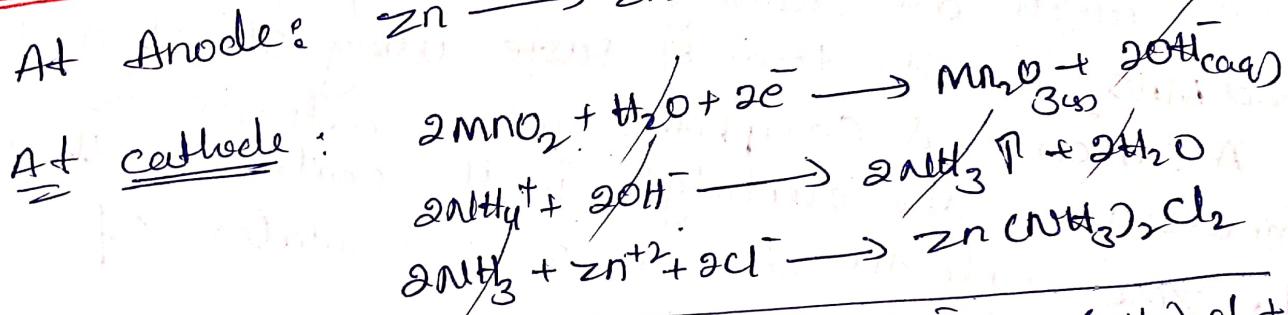
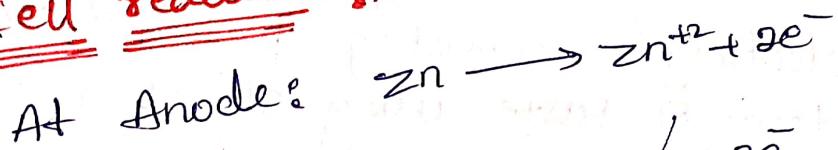
Description :- A dry cell consist of zinc cylinder which acts as anode. This zinc cylinder is filled with an electrolyte consisting of NH_4Cl , ZnCl_2 and MnO_2 in the form of paste using starch and the carbon rod (graphite) acts as cathode is immersed in the electrolyte in the centre of the cell. The zinc cylinder has an outer insulator of cardboard case.

During use the cylinder gets consumed and at the end it will develop holes which are responsible for leakage.

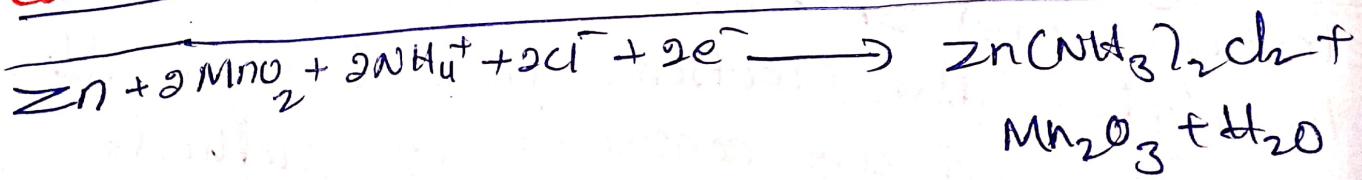
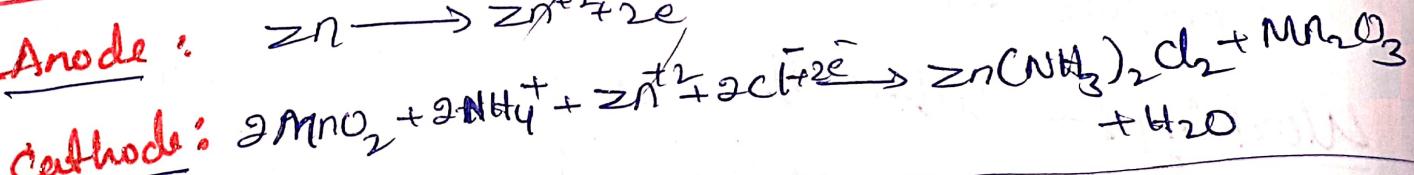
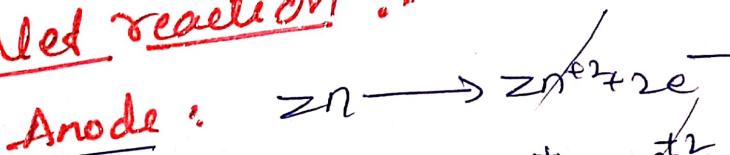
Working :- When the cell is working zinc loses electrons and Zn^{+2} ions get dissolved in the electrolyte. The electrons pass through the circuit and are consumed at cathode. This cause discharge of NH_4^+ ions from electrolyte.



Cell reactions :-



Net reaction :-





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A voltage of dry cell is about 1.5V

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USES :- It is used in transistors radios, calculators, torches, Flash lights etc

Disadvantages:-

→ these cells do not have long life because the acidic medium corrodes the container. Then current rapidly rundown.

SECONDARY BATTERY

① Lead-acid cells (or) Lead-accumulator or storage cells

Lead-acid storage cell is a secondary battery which can be operated both as a voltaic cell and as an electrolytic cell.

When it is acts as voltaic cell, it supplies electrical energy and becomes rundown. When it is recharged, the cell operates as an electrolytic cell.

Description:-

A lead acid storage battery consists of number of (3 to 6) voltaic cells connected

in series to get 6 to 12v battery.

In each cell the anode is made of lead

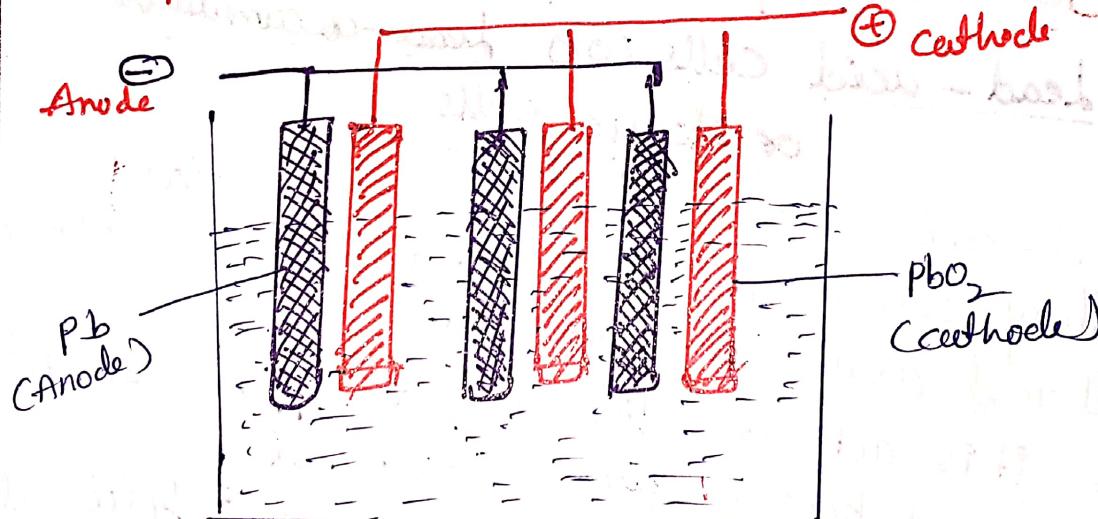
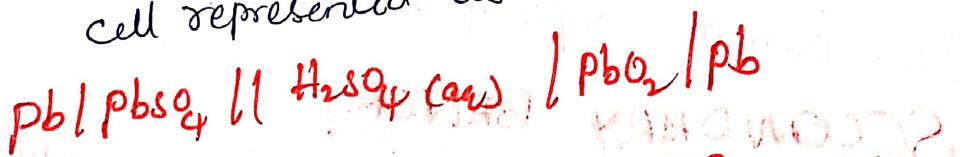
the cathode is made of lead dioxide PbO_2 (or)

a grid made of lead. packed with PbO_2

→ A number of PbO_2 plates (cathode) are also connected in parallel. various plates are separated by insulators like rubber (or) glass fibre.

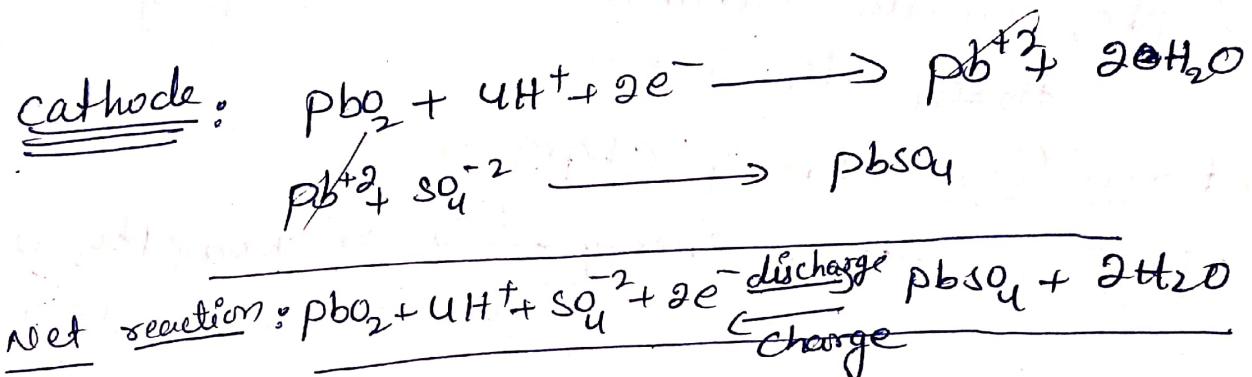
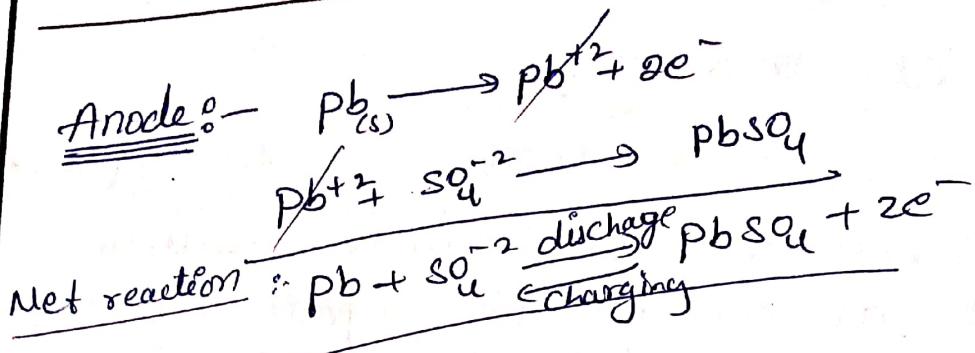
the entire combination is then dipped in dil H_2SO_4 (38% by mass) having density of 1.30 gm/ml.

cell represented as

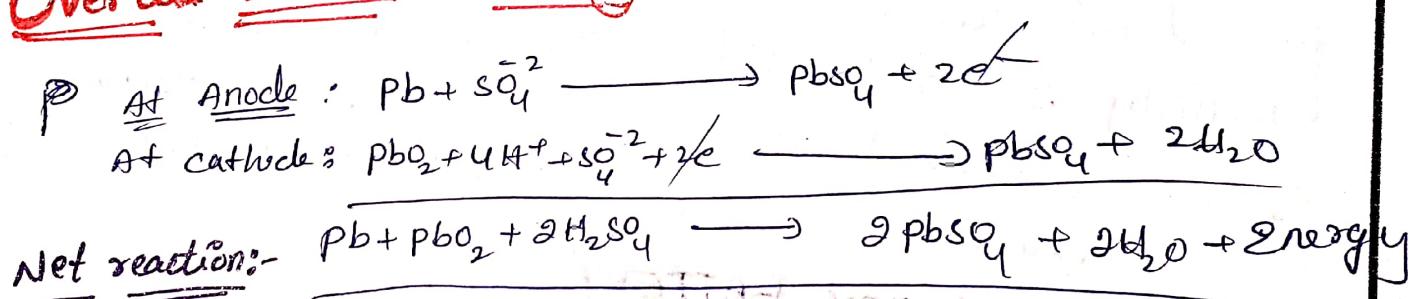


Lead - acid cell

Working :- When Pb is oxidized Pb^{+2} ions which further combine with SO_4^{-2} form insoluble PbSO_4



Overall reaction during Use (discharging)



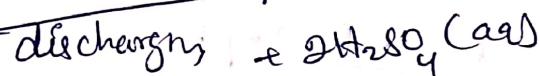
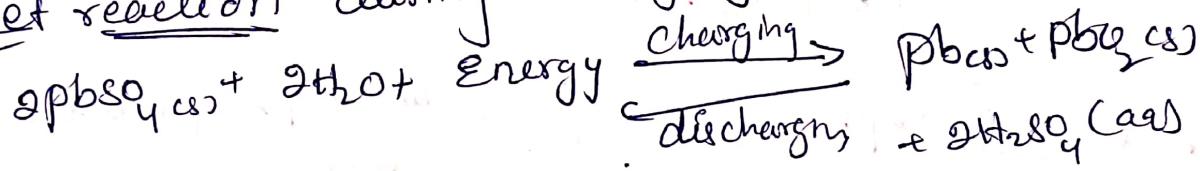
From the above reaction it clear that $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up.

As a result concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/lit so the battery needs recharging.

Recharging the Battery:

It can be charged by passing electric current in opposite directions. The electrode reaction gets reversed as a result Pb deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases.

Net reaction during charging



Applications

- Lead acid cells are used to supply current mainly in automobiles such as cars, buses, trucks etc.
- It is also used in gas engine ignition, telephone exchanges, hospitals, power stations etc.

2) LITHIUM ION BATTERY

Lithium ion batteries are the most popular rechargeable batteries and are used in many portable electronic devices.



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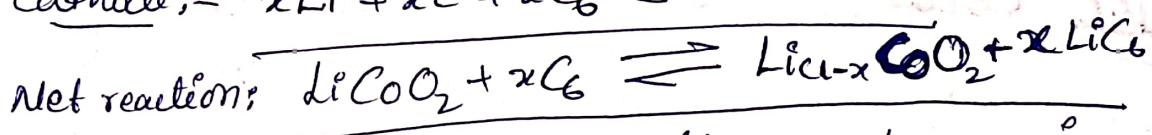
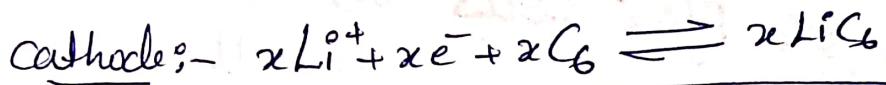
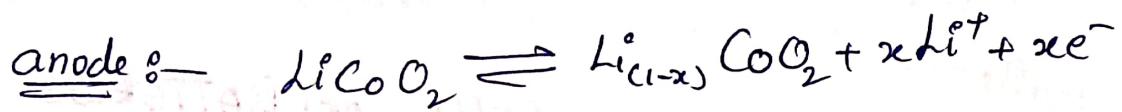
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The components of lithium ion battery are the negative electrode made from carbon (Graphite), positive electrode made from metal oxide like lithium cobalt oxide (LiCoO_2).

The reaction are:

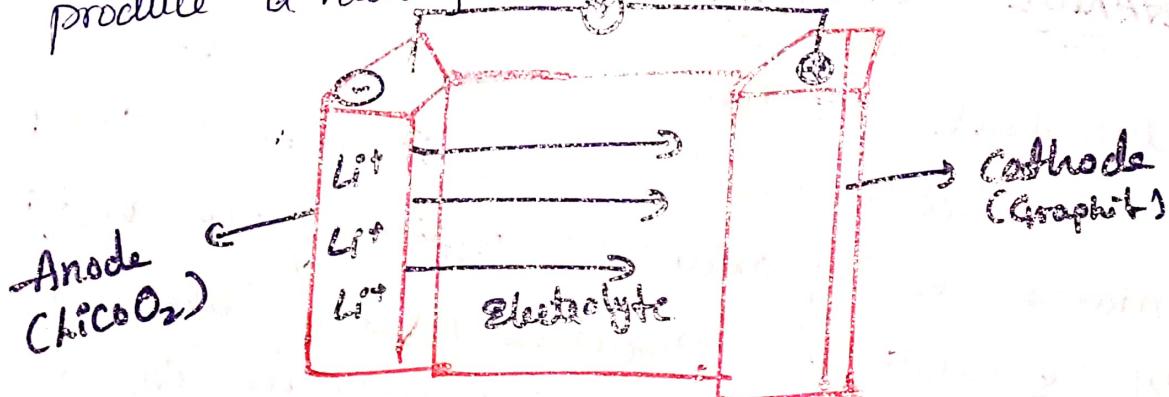


with the coefficients representing moles, x in

no more than about 0.5 moles.

→ the battery voltage is about 3.7V

→ lithium batteries are popular because they can provide a large amount of current, are lighter than comparable batteries of other types produce a nearly constant voltage as they discharge.

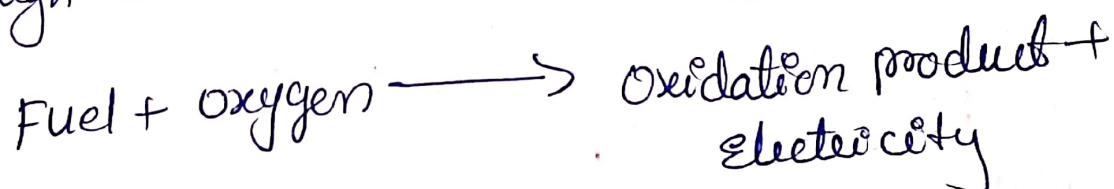


Advantages

- Li ion batteries are rechargeable and portable
- No thermal runaway due to overheating with these batteries
- Other safety measures like short circuit separator (for over heating), tear away tabs (for internal pressure), thermal interrupt (over charging) and vent (pressure relief) are provided
- Batteries less toxic and recycled.

FUEL CELLS (OR) FLOW CELLS (OR) BATTERIES

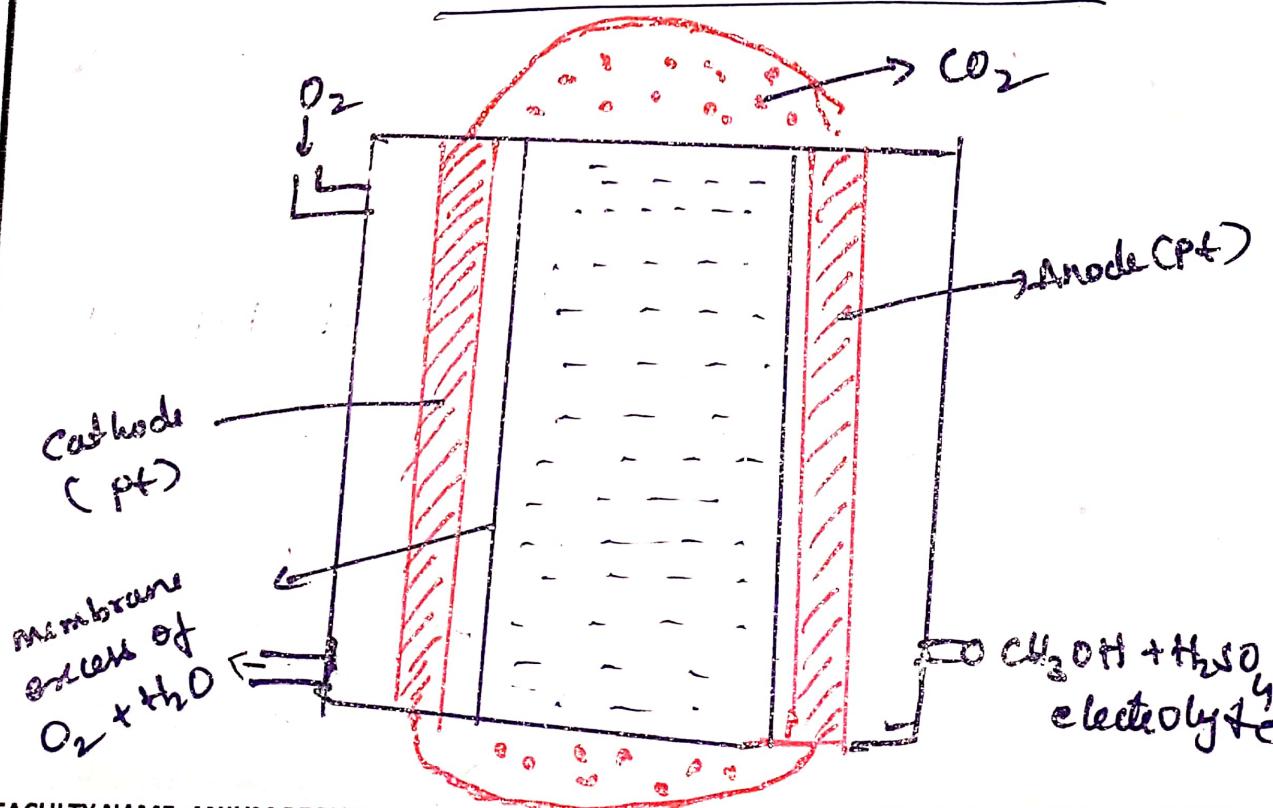
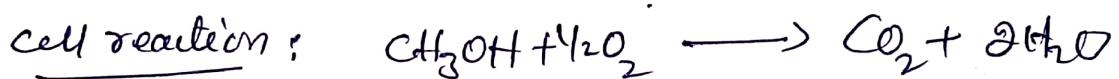
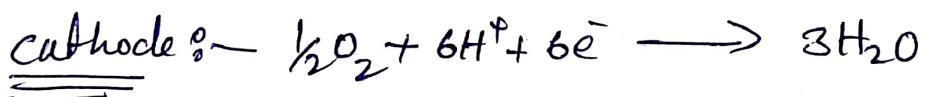
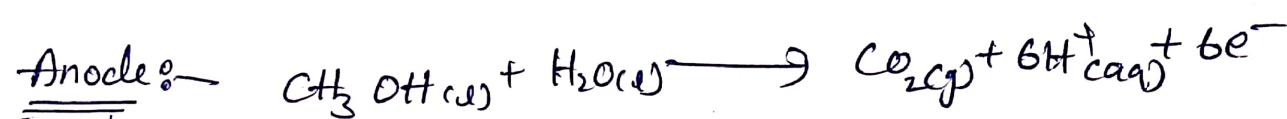
It is voltage cell which converts the chemical energy of the fuels directly into electricity without combustion. In these cells the reactant, product and electrolyte pass through the cells.



METHANOL - OXYGEN CELLS :-

In this fuel cell has many advantages because methanol readily available and it is very cheap. It contains easily oxidizable hydroxyl group and is highly soluble in aqueous medium like sulphuric acid. Also, the product of reaction is CO_2 which is non-toxic.

→ it contains two platinum electrodes kept
 in a chamber containing aqueous sulphuric acid
 ⇒ A polymeric membrane is inserted near the cathode.
 To prevent oxidation of methanol at cathode.
 ⇒ A mixture of methanol and sulphuric acid
 is passed through anode chamber and pure
 oxygen gas is pumped into cathode chamber.
 The reaction takes place to form carbon dioxide
 and water which is removed continuously



Uses :-

due to their high energy density, light weight
fast recharging ability, methanol-oxygen cells are
widely used.

- used in radio transitors
- the most important application of a fuel cell
is its use in space flight.
- it is hoped that fuel-cell technology will
bring a revolution in the area of energy production

Ques:- What are the applications of fuel cells?

A:- After the discussion about the working
of fuel cells, we can say that they have

the following applications:-

1. In space flights

2. In cars

3. In mobile phones

4. In portable devices

5. In power plants

6. In homes

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Problems Based on EMF

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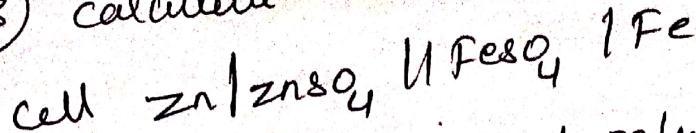
① Calculate the e.m.f. of the following reaction -
 at 25°C. $E_{Zn}^{\circ}(\text{ox}) = 0.763\text{V}$
 $E_{\text{Cath}}^{\circ}(\text{Red}) = 0.337\text{V}$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{R}} - E_{\text{L}} \\ &= E_{\text{Red}} - E_{\text{Ox}} \quad (\text{def. of } E^{\circ}) \quad E_{\text{cell}}^{\circ} = E_{\text{Cath}}^{\circ} - E_{\text{Anode}}^{\circ} \\ &= 0.337 - (-0.763) \\ &= 0.337 + 0.763 \\ &= 1.1\text{volts} \end{aligned}$$

② the Potential. of the cell $\text{Zn}^{(\text{red})} | \text{Zn}^{+2} / \text{Zn}^{+2} // \text{Ag}^{+} / \text{Ag}$
 at 25°C $1.54\text{V}_{\text{cell}}$. where $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.799\text{V}$
 $E_{\text{Zn}^{+2}/\text{Zn}^{+2}} = ?$
 $E_{\text{Ag}^{+}/\text{Ag}} = 0.799$

$$\begin{aligned} E_{\text{cell}} &= 1.54\text{V} \\ E_{\text{cell}} &= E_{\text{Anode}} + E_{\text{Cathode}} \\ &= E_{\text{Zn}^{+2}/\text{Zn}^{+2}} + E_{\text{Ag}^{+}/\text{Ag}} \\ E_{\text{Zn}^{+2}/\text{Zn}^{+2}} &\rightarrow E_{\text{cell}} - E_{\text{Ag}^{+}/\text{Ag}} \\ &= 1.54 - 0.799 \\ &= +0.744\text{V} \end{aligned}$$

(3) calculate the emf of the following



standard electrode potential
of $Zn^{2+}/Zn = -0.76 V$ (cathode)

$$E_{Fe^{2+}/Fe} = 0.44 V$$

$$E_{cell} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

$$= E_{Fe^{2+}/Fe} - E_{Zn^{2+}/Zn}$$

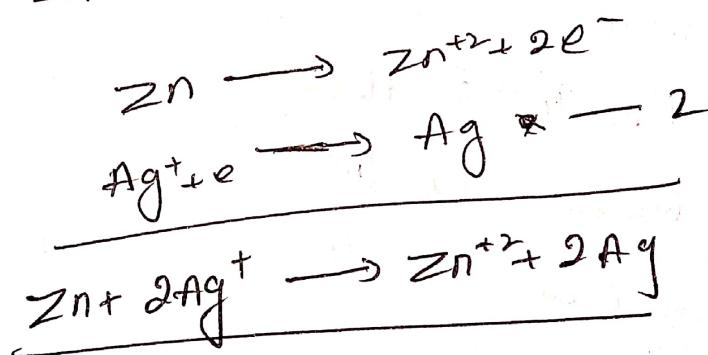
$$= 0.44 - (-0.76)$$

$$= 0.44 + 0.76$$

$$= \underline{\underline{1.20 V}}$$

Problems Based on Nernst equation:

① What is emf of following cell at $25^{\circ}C$
 $Zn|Zn^{2+}(0.1 M)||Ag^+(0.01 M)|Ag$.
 the standard emf of the cell is $1.054 V$.



Electrode potential for cell

$$E = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[Ag^+]^2}{[Zn]}$$



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$$E = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[0.01]^2}{[0.1]}$$

$$= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log 10^3$$

$$= E_{\text{cell}}^{\circ} + \frac{0.0591 \times 3}{2} \log 10$$

$$= 1.5V + 0.08865$$

$$= 1.62V$$

- ② The potential of the cell $\text{Zn}(\text{Zn}^{+2} \text{cm}) \parallel \text{Cu}^{+2}(\text{m}) \text{Cu}$ at 25°C is 1.01 volts. Calculate the potential of cell $\text{Zn}(\text{Zn}^{+2} \text{cm} \text{ (0.5 m)}) \parallel \text{Cu}^{+2}(\text{m}) \text{ Cu}$ at the same temperature.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \left[\frac{\text{Cu}^{+2}}{\text{Zn}^{2+}} \right]$$

$$E_{\text{cell}}^{\circ} = 1.01V$$

$$= 1.01 + \frac{0.0591}{2} \log_{10} \left[\frac{0.1}{0.5} \right]$$

$$= 1.01 + 0.0296 \log_{10} 0.2$$

$$= 1.01 + 0.0296 \times 0.69897$$

$$= 1.01 + 0.0207$$

$$= 1.1207V$$

① Calculate the standard electrode potential of Cu^{+2}/Cu , if the electrode potential at 25°C is 0.296V when $[\text{Cu}^{+2}]$ Concentration is 0.015M .

$$E = E^\circ + \frac{0.0591}{n} \log [\text{Cu}^{+2}]$$

$$\textcircled{a} \quad E = 0.296$$

$$n = 2$$

$$E^\circ = -E_{\text{cell}} + \frac{0.0591}{n} \log (\text{Cu}^{+2})$$

$$= 0.296 + \frac{0.0591}{2} \log (0.15)$$

$$= 0.296 + 0.0296 \times 1.824$$

$$= 0.296 + 0.054$$

$$= \underline{\underline{0.3499\text{V}}}$$

⑤ calculate the emf of Daniel cell at 25°C when the concentration of ZnSO_4 and CuSO_4 are 0.001M and 0.01M respectively. the standard potential of the cell is 1.1 volts.

$$E = E^\circ + \frac{0.0591}{n} \log \left[\frac{\text{Cu}^{+2}}{\text{Zn}^{+2}} \right]$$

$$= 1.1 + \frac{0.0591}{2} \log \left[\frac{0.01}{0.001} \right]$$

$$= 1.1 + 0.0296 \log 10$$

$$= \underline{\underline{1.1296\text{V}}}$$

Water Chemistry

Introduction :-

Water is one of the few basic materials which is prime importance for the preservation of life on this earth. The uses of water for drinking, bathing, farming etc. As an engineering material water is used for producing steam in boilers to generate hydro-electric power, furnishing steam for engines for refrigeration, air conditioning, for construction & for manufacturing purposes & as a solvent in chemical process.

Hence an engineer should possess knowledge regarding the composition, troubles that arise due to composition of water & prevention of these trouble.

Occurrence :-

Water is widely distributed in nature. It has been estimated that about 75% matter on the earth's surface, consist of water. Beside visible water on earth, there is a large amount of water under earth to an average depth of over kilometers. Air contain 12-15% of volume of water vapour. The body of human beings consist of about 60% of water, plants, fruits, vegetable contain 90-95% of water.

Sources of water:-

The main sources of natural water are:-

- Rain water
- River water
- Spring or well water
- Sea water

Impurities of Water:-

The various impurities present in natural water may be broadly categorised as :-

- 1) Suspended matter
- 2) Dissolved substances
- 3) Colloidal impurities
- 4) Organic impurities

Sources of Impurities:-

- a) Rain water carries floating impurities
- b) Gases like CO_2 , O_2 from atmosphere
- c) When water percolates through the layers of soil it dissolved salts in composition of water.
- d) The organic impurities are introduced into water due to decomposition of plant & animal remain in water due to contamination of water with sewage & waste.

Effect of Impurities present in Natural Water

Water :- Water containing impurities has number of bad effects when used for domestic & industrial purpose.

① Bad effect for domestic purposes :- ① The dissolved salts of calcium and magnesium in water does not give lather with soap.

② In cooking also dissolved impurities of water increases, boiling point of water.

③ The suspended impurities in water are harmful for drinking purposes as it contain pathogenic bacteria.

④ Paper Industry :- The dissolved impurities react with the chemical used to give paper a smooth glossy surface effecting the colour of paper.

⑤ Dyeing Industry :- The dissolved salts will react with dyes to form undesirable precipitation, which give improper shades.

⑥ Textile Industry :- When soap is used for washing yard, undesirable

precipitates produced will adhere to the fabric while dyeing and does not give exact colour.

④ Sugar Industry :— Water for sugar refineries must be free from sulphates, alkali carbonates, nitrates etc bacteria, in presence of impurities sugar may not crystallise well & may be decompose during storage.

⑤ Bakeries :— The presence of organic matter is harmful and it may affect the action of yeast.

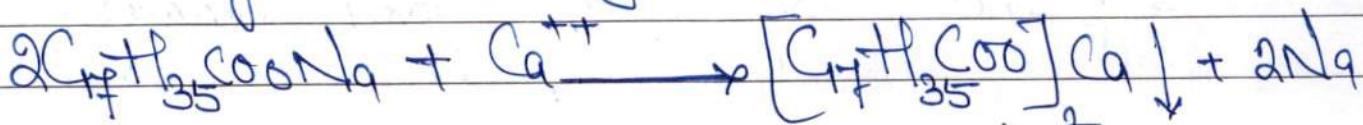
⑥ Boilers :— The dissolved salts in water produce scale, sludges, caustic embitterment etc during the steam generation in boilers.

Uses of water:

- 1 → Domestic purpose
- 2 → Industrial purposes
- 3 → Municipal purposes
- 4 → Agricultural purposes.

+ Hard water & Soft water:-

Hard water :- Water which does not produce lather with soap solⁿ, but produces white precipitate is called hard water.

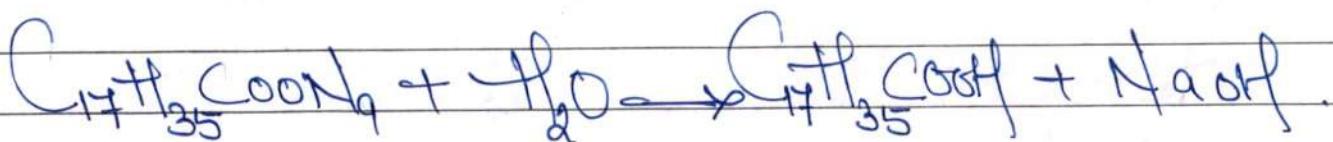


Sodium stearate hardness insoluble ppt
(Soap) causing (scum)
ion

Soft Water :-

~~Soft~~ water. Water, which produces lather readily with soap solution is called soft water.

Ca & Mg salts ~~eg~~ Distilled water, rainwater
This is due to absence of



Sodium Stearate

stearic acid (lather)

Types of Hazardous:-

Depending upon the type of dissolved salt present in water hardness of water can be classified into two types.

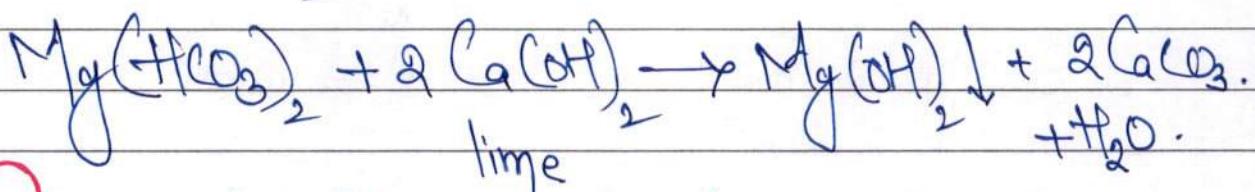
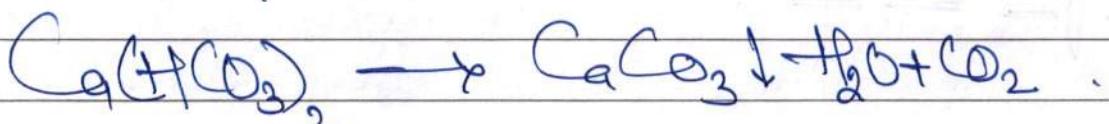
1. Temporary hardness.
2. Permanent hardness.

Temporary Hardness or carbonate hardness
or alkaline hardness :-

This is due to the presence of bicarbonates of calcium and Mg. It can be removed by:

- ① boiling the water
- ② adding lime to water.

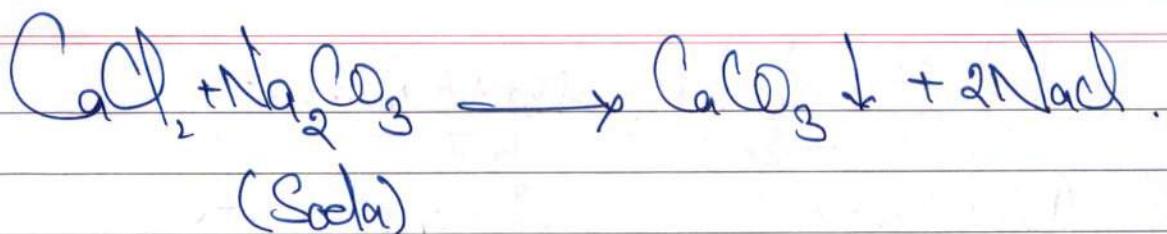
The above two process convert the bicarbonates into insoluble carbonates.



Permanent hardness (or) Non carbonate hardness (or) non-alkaline hardness :-

This is due to the presence of chlorides, sulphides of calcium and magnesium. It can't be removed by boiling the water but it can be removed by chemical reaction.

Eg - lime-soda process.
 Zeolite process.



Expression of hardness in terms of equivalent of CaCO_3 :

The concentration of hardness producing salts are usually expressed in terms of an equivalent amount of CaCO_3 . CaCO_3 is chosen as standard because

(1) Its molecular weight is 100 and equivalent weight (50) is a whole number so the calculation in water analysis can be simplified.

(2) It is the most insoluble salt, that can be precipitated in water treatment.

$$\frac{\text{Amount of equivalent to } \text{CaCO}_3}{\text{amount of hardness}} = \frac{\text{Causing salt}}{\text{mol wt of } \text{CaCO}_3} \times \frac{\text{mol wt of } \text{CaCO}_3}{\text{mol wt of hardness}}$$

$$\text{CaCO}_3 \text{ equivalent} = \frac{\text{wt of salt}}{\text{mol wt of salt}} \times 100 -$$

Units of hardness:-

① Parts per millions :- It is defined as the number of parts of CaCO_3 equivalent hardness per 10^6 parts of water.

$$1\text{ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^6 \text{ parts of water}$$

② Milligrams per litre :- It is defined as the number of milligrams of CaCO_3 equivalent hardness per one litre of water.

$$1\text{mg/lit} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in 1 lit of water}$$

③ Clark's Degree (cl) :- It is defined as the number of CaCO_3 equivalent hardness per 40000 parts of water.

$$1\text{cl} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 40,000 \text{ parts of water}$$

④ French Degree :- (fr) It is defined as the number of parts of CaCO_3 equivalent hardness per 10^5 parts of water.

$$1\text{fr} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 10^5 \text{ parts of water}$$

Relationship between Various Units :-

$$1 \text{ ppm} = 1 \text{ mg/lit} / = 0.1^\circ \text{F} = 0.07 \text{ d}^\circ.$$

$$1^\circ \text{C} = 1.43 \text{ Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/lit}.$$

Problem based on hardness :-

A sample of hard water contain the following dissolved salts per lit. $\text{CaCl}_2 = 11.1 \text{ mg/l}$, $\text{CaSO}_4 = 1.36 \text{ mg/l}$, $\text{Ca(HCO}_3\text{)}_2 = 16.2 \text{ mg/l}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg/l}$, turbidity = 10 mg/l. Calculate the temporary, permanent & total hardness of water in ppm.

Hardness causing salt HCs	Weight of HCs	Mol. wt of HCs	Equivalent of CaCO_3 $\frac{\text{wt}}{\text{mol.wt}} \times 100$
CaCl_2	11.1	111	$\frac{11.1}{111} \times 100 = 10$
CaSO_4	1.36	136	$\frac{1.36}{136} \times 100 = 1 \text{ mg}$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$\frac{16.2}{162} \times 100 = 10 \text{ mg}$
$\text{Mg}(\text{HCO}_3)_2$	14.6	146	$\frac{14.6}{146} \times 100 = 10 \text{ mg}$

Note :- Silica & turbidity must not be considered because they do not cause hardness to water.

Temporary hardness :- $\text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$

10 + 10

= 20 mg/l i.e. 20 ppm

Permanent hardness :- $\text{CaCl}_2 + \text{CaSO}_4$

10 + 1

11 mg/l i.e. 11 ppm

Total hardness :- Temporary + permanent hardness.

= 20 + 11

= 31 mg/l i.e. 31 ppm

Q) Calculate the amount of temporary & permanent hardness of a water which contains the following impurities - e.g.:

$$\text{Ca}(\text{HCO}_3)_2 = 121.5 \text{ ppm}$$

$$\text{Mg}(\text{HCO}_3)_2 = 116.8 \text{ ppm}$$

$$\text{MgCl}_2 = 79.2 \text{ ppm}$$

$$\text{CaSO}_4 = 102 \text{ ppm}$$

Sol? - Calculation of CaCO_3 equivalent :-

$$\text{CaCO}_3 \text{ equivalent} = \frac{\text{wt of hardness causing salt}}{\text{wt. wt. of hardness causing salt}} \times 100$$

Hardness causing salt	wt of HCl	Mol. wt of HCl	$\text{CaCO}_3 = \frac{\text{wt of HCl}}{\text{mol. wt.}} \times 100$
$\text{Ca}(\text{HCO}_3)_2$	121.5	162	$\frac{121.5}{162} \times 100 = 75$
$\text{Mg}(\text{HCO}_3)_2$	116.8	146	$\frac{116.8}{146} \times 100 = 80$
MgCl_2	92	95	$\frac{92}{95} \times 100 = 83.3\bar{3}$
CaSO_4	102	136	$\frac{102}{136} \times 100 = 75$

$$\begin{aligned}
 \text{Temporary hardness} &= \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 \\
 &= 75 + 80 \\
 &= 155 \text{ ppm}
 \end{aligned}$$

Permanent hardness = $MgCl_2 + CaSO_4$

$$83.37 + 75 \\ = 158.37 \text{ ppm}$$

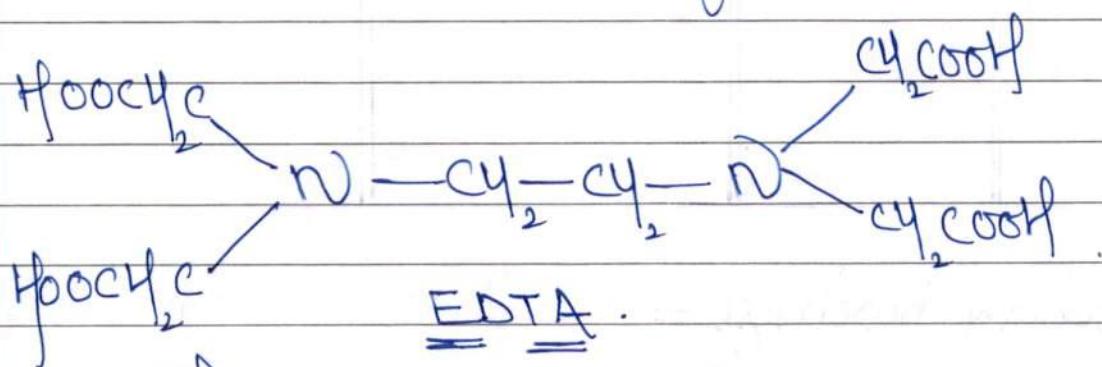
Total hardness :- Temporary + permanent.

$$= 155 + 158 \cdot 37 \\ = 313 \cdot 37 \text{ ppm}$$

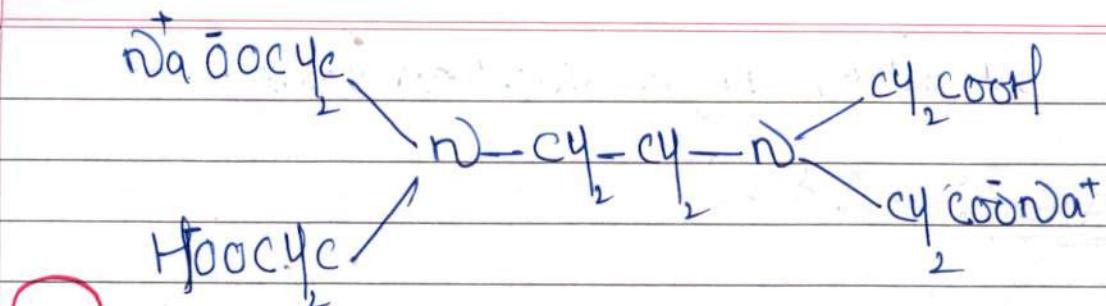
Estimation of hardness by EDTA method

Hardness of water is determined by the EDTA method, which involves complexometric titration.

EDTA is ethylene diamine tetra acetic acid, the structure of EDTA is.

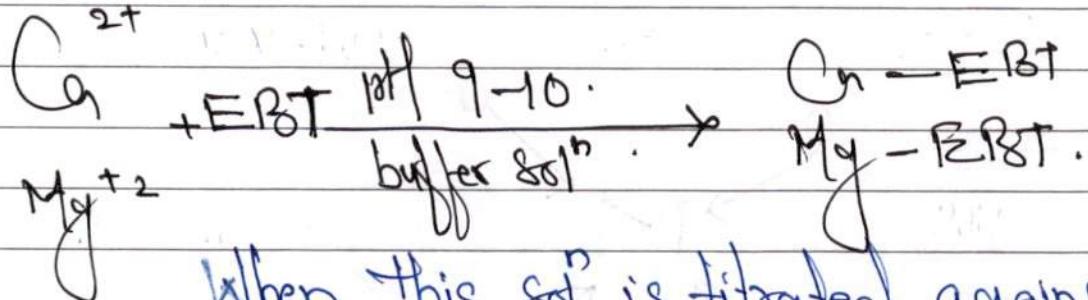


Since EDTA insoluble in water, its disodium salt is used as complexing agent.

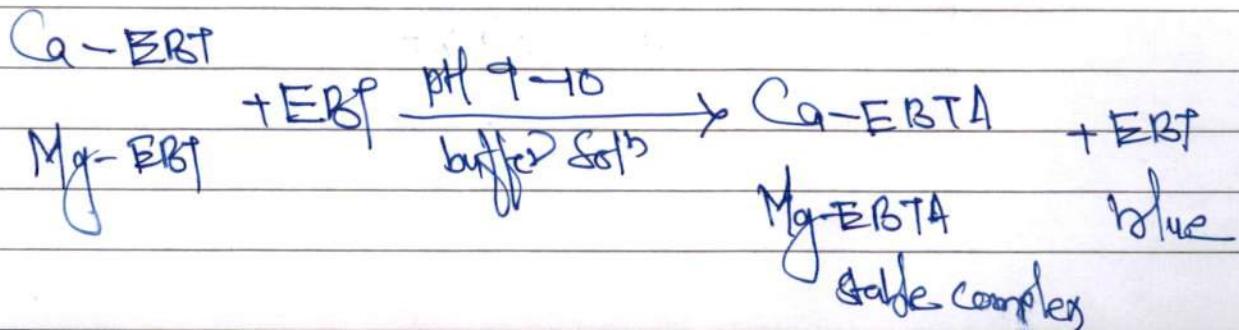


Principle - The amount of hardness causing ions (Ca^{2+} & Mg^{2+}) can be estimated by titrating the water sample against EDTA using Eriochrome black T (EBT) (Indicator) at pH 9-10 in order to maintain the pH, buffer solution (NH_4OH - NH_4Cl mixture) is added. Only at this pH such complexation is possible.

When the EBT indicator is added to the water sample, it forms wine red coloured weak complex with Ca^{2+} & Mg^{2+} ions.



When this sol' is titrated against EDTA the EBT free is colour steel blue. thus end point is Wine red to blue.



Chemicals Required :-

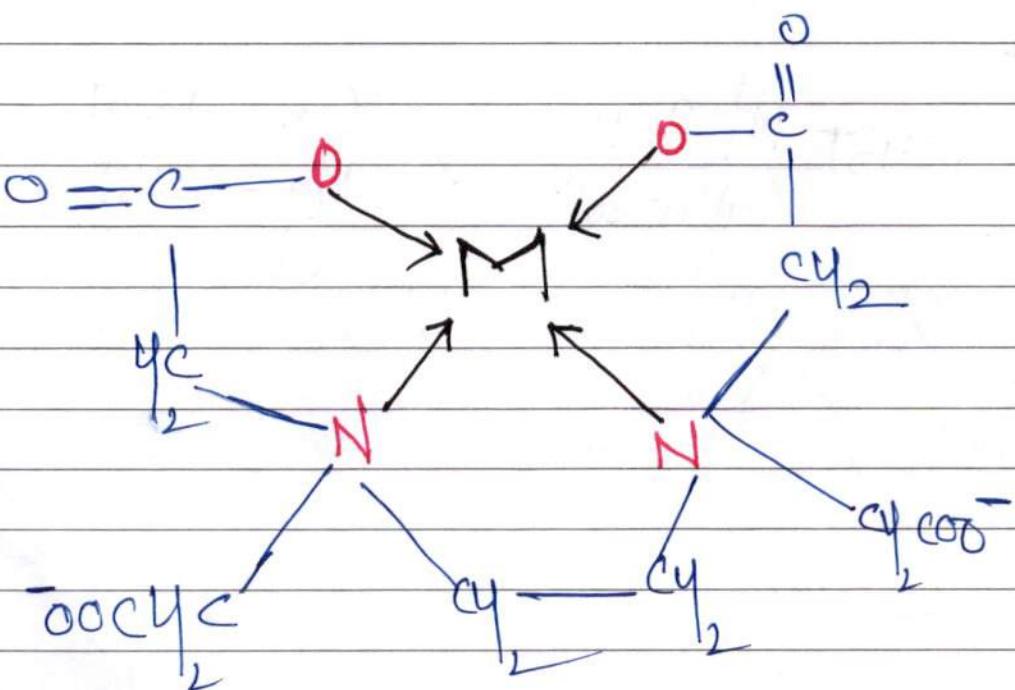
EDTA Soln :- Dissolve 8.72 gms of EDTA in 1000ml of distilled water.

Standard hard water :- 1 gm of CaCO₃ is dissolved in minimum quantity of HCl and then made upto 1000ml

EBT Indicator :- 0.5 gms of EBT in 100ml of alcohol.

Buffer solution :- 67.5 gms of NH₄Cl and 57 gms of NH₃ are dissolved and the soln is made up to 1000 ml using distilled water.

Metal EDTA complex :-



Experimental Procedure :-

Standardisation of EDTA :— Pipette out 20ml of standard hardness water into clean conical flask add 5ml of buffer soln and 2-3 drops of EBT Indicator. Now titrate it against EDTA soln taken in the burette, the end point is the change of colour from wine red to steel blue.

Let the volume of EDTA consumed be x ml

$$\text{molarity of standard} = \frac{\text{Weight of } \text{CaCO}_3}{\text{mol. wt. of } \text{CaCO}_3}$$

$$= \frac{1}{100} = 0.01 \text{ M}$$

Std Water v/s EDTA

$$\frac{M_1 V_1}{\eta_1} = \frac{M_2 V_2}{\eta_2} \quad (\eta_1 = \eta_2 = 1)$$

M_1 = molarity of std. water

V_1 = volume of std water

M_2 = molarity of EDTA

V_2 = volume of EDTA = x ml.

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{20 \times 0.01}{x \text{ ml}}$$

Estimation of Total hardness of Water Sample:

Pipette out 20ml of the given hard water sample into clean conical flask and titrated it against EDTA as before.

Let the volume of EDTA consumed by EDTA $\sqrt{3}$ s hard water sample.

$$M_2 V_2 = M_3 V_3$$

M_2 = molarity of EDTA

V_2 = Volume of EDTA = y ml

M_3 = molarity of hard water - ?

V_3 = Volume of hard water = 20 ml.

$$M_3 = \frac{M_2 V_2}{V_3} = \frac{M_2 \times y \text{ ml}}{20}$$

Total hardness = $M_3 \times 100 \times 1000$ ppm

Estimation of permanent hardness of Water Sample:

Take 100ml of the same water sample in a 250 ml beaker. Boil it for 15 min. During boiling temporary hardness gets removed.

cool and filter the sol' and make upto 100ml in standard flask by adding distilled water.

Tipette out 20ml of the made up solution into clear conical flask and titrate it against EDTA as before.

EDTA v/s permanent hard water sample.

$$M_2 V_2 = M_4 V_4$$

M_2 = molarity of EDTA

V_2 = Volume of EDTA - "2" ml (burette reading)

M_4 = molarity of EDTA hard water - ?

V_4 = Volume of hard water - 20ml.

$$M_4 = \frac{M_2 V_2}{V_4} = \frac{M_2 \times 2}{20}$$

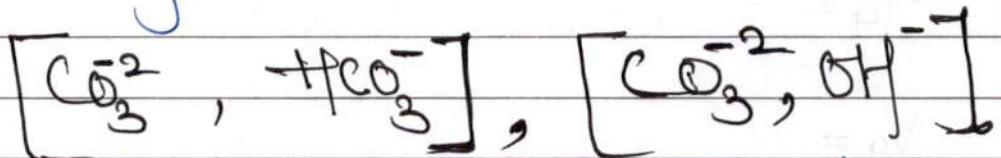
Permanent hardness = $M_4 \times 100 \times 1000$ ppm

Temporary hardness = Total hardness - Permanent hardness.

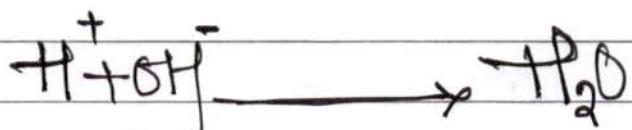
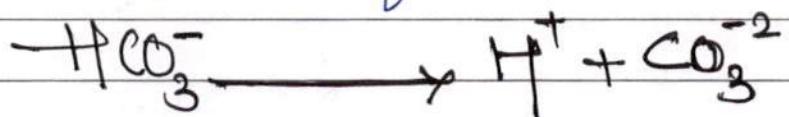
Alkalinity of Water & its determination

(The presence of anions such as CO_3^{2-} , HCO_3^- and OH^- results in alkalinity of water. The estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators. In this titrations, two indicators are used as different anions give end points at different pH values.

Out of the three anions CO_3^{2-} , OH^- and HCO_3^- any two of them can exist in water together.



HCO_3^- and OH^- cannot be present together because H^+ ion of HCO_3^- neutralises OH^- .

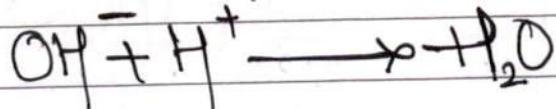
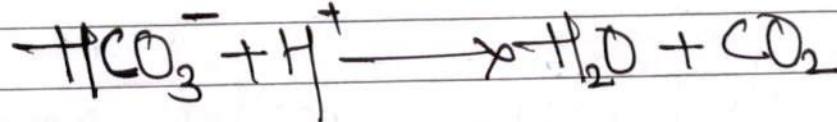


Experimental Procedure :-

100 ml of water sample is taken in flask & two drops of phenolphthalein is added to it. The colour become pink, due to $\text{pH} > 10$. The water sample of pink coloured is titrated against N/50 HCl . At the end point, pink colour disappears. This endpoint is termed as 'P'-end point.

Now add two drops of methyl orange indicator to the same water (pH falls below 4). At the end point pink colour reappears. This end point is 'M' end point (methyl orange end point).

Reactions:-



Calculations:- At the endpoint - phenolphthalein (i.e. 'P' point) ml.

alkalinity calculated in terms of CaCO_3 .

CO_3^{2-} vs HCl titration

$$N_1 V_1 = N_2 V_2$$

N_1 = normality of CO_3^{2-} ?

V_1 = volume of water sample - 100ml.

N_2 = normality of HCl - $N/50 = 0.02N$

V_2 = volume of HCl (burette reading) 'P' ml.

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{0.02 \times P}{100}$$

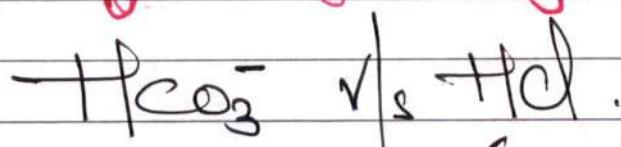
Alkalinity in terms of CaCO_3 :-

$$= N_1 \times 50 \times 1000$$

$$= \frac{0.02 \times P \times 50 \times 1000}{100}$$

(10⁻³) ppm.

Alkalinity using methyl Orange :-



$$N_1 V_1 = N_2 V_2$$

N_1 = normality of HCO_3^- - ?

V_1 = volume of HCO_3^- - 100ml.

N_2 = normality of HCl $N/50 = 0.02N$.

$V_2 = \text{Volume of HCl (burette reading)}$
 $- V_1 \text{ ml.}$

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{0.02 \text{ M}}{100}$$

alkalinity in terms of $\text{CaCO}_3 = \frac{0.02 \text{ M}}{100}$

alkalinity in terms of $\text{CaCO}_3 = \frac{0.02 \text{ M} \times 50 \times 1000}{100}$
 10 M ppm

Conclusion :-

$P = M$, only OH^- ions present

$P = \frac{1}{2} M$, only CO_3^{2-} ions present

$P < \frac{1}{2} M$, CO_3^{2-} & HCO_3^- ions present

$P > \frac{1}{2} M$, CO_3^{2-} & OH^- ions present

$P = 0$, HCO_3^- ions present

Problem based on EDTA method :-

100 ml of a sample of water requires 18 ml of an EDTA solⁿ for titration. 22 ml of the same solⁿ of EDTA required for titration of 100 ml of standard hard water containing 1 gm of CaCO_3 per litre. Calculate hardness of water sample in ppm.

$$\text{Standard hard water molarity} = \frac{\text{wt CaCO}_3}{\text{mol wt of CaCO}_3}$$

$$= \frac{1}{100} = 0.01 \text{ M}$$

Calculation of molarity of EDTA (ox)
Standard titration of EDTA

Std. Water \sqrt{s} EDTA.

$$M_1 V_1 = M_2 V_2$$

$$M_1 = \text{molarity of std. water} = 0.01 \text{ M}$$

$$V_1 = \text{Volume of std. water} = 100 \text{ ml}$$

$$M_2 = \text{molarity of EDTA} = ?$$

$$V_2 = \text{Volume of EDTA} = 22 \text{ ml}$$

Estimation of total hardness:-

EDTA $\sqrt{\frac{V_2}{V_3}}$ Water sample

$$M_2 \sqrt{V_2} = M_3 \sqrt{V_3}$$

M_2 = molarity of EDTA = 0.045 M.

V_2 = Volume of EDTA = 18 ml.

M_3 = molarity of water sample - ?

V_3 = Volume of water sample = 100 ml.

$$M_3 = \frac{M_2 \sqrt{V_2}}{\sqrt{V_3}} = \frac{0.045 \times 18}{100}$$

$$= 0.08181 M$$

Total hardness: — $M_3 \times 100 \times 1000$

$$= 0.0818 \times 100 \times 1000$$

Potable Water: — = 8181 mg/lit.

Access to good quality drinking water is essential to human health. The world health organisation (WHO) estimated that nearly quarter of

of the World's six billion people currently lack access to good quality of drinking water.

Water, free from contaminants or water that is safe for human consumption is called potable water.

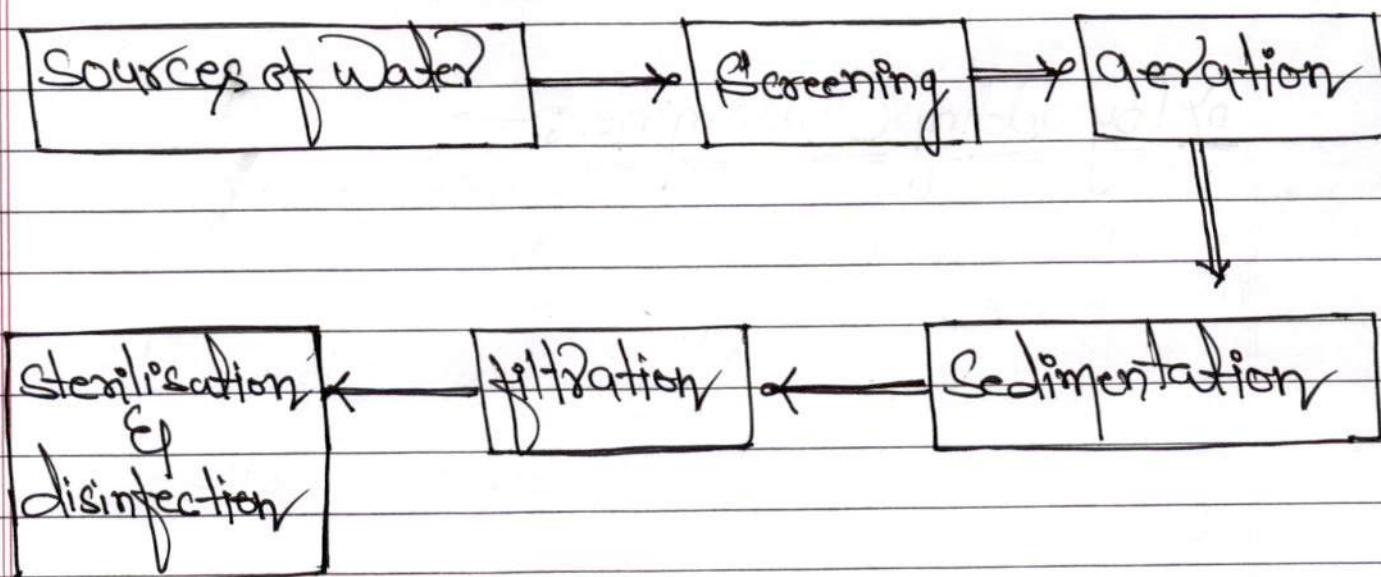
Specification of potable Water :-

- The water should be clear, colourless & clean.
- The water should be clear free from pathogenic bacteria & dissolved gases like this.
- Optimum hardness of water must be 125 ppm and pH must be 7.0 to 8.5
- The turbidity in drinking water should not exceed 20 ppm.
- The recommended maximum concentration of total dissolved solids in potable water must not exceed 500 ppm.
- The water must be free from heavy metals like lead, Arsenic, chromium & manganese.

- The chloride content must be 250 ppm & total hardness must not exceed 300 ppm.

Treatment of Water (3) Steps involved in potable water purification :- The treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities & harmful pathogenic bacteria.

The following flow diagrams of the water treatment for domestic purpose & various steps involved in purification are given as.



sterilisation or disinfection:- The process of destroying the harmful bacteria is known as sterilisation or disinfection.

Method of Sterilisation :-

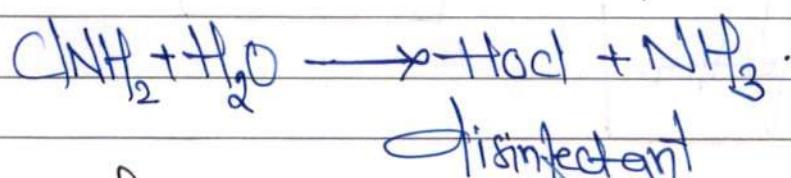
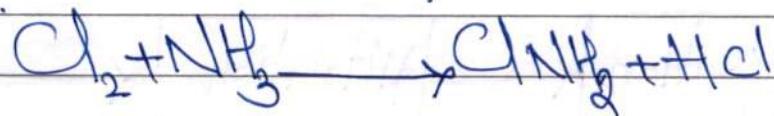
① Disinfection by chlorination :- By using sufficient quantity of chlorine disinfection will complete otherwise it will not. Chlorination can be done by following methods.

By adding chlorine gas :- Chlorine gas can be bubbled in the water as a very good disinfectant.

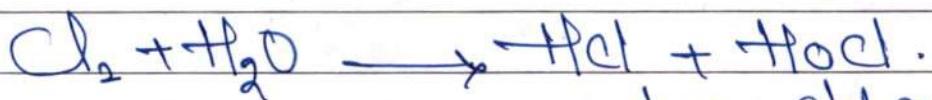
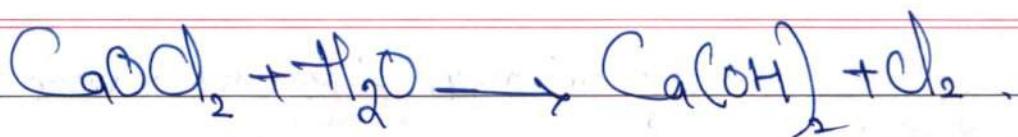


$HOCl + \text{Bacteria} \rightarrow \text{killed bacteria}$

By adding chloramine :- When chlorine & ammonia are mixed in the ratio 2:1 a compound chloramine is formed.



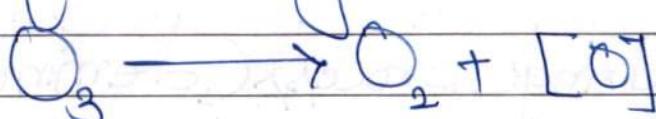
By adding bleaching powder :- When bleaching powder is added to water it produces hydrochlorous acid ($HOCl$). $HOCl$ is powerful germicide.



hypochlorous acid

II Ozonation :- (using Ozone)

Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks to give nascent oxygen.



The nascent oxygen is powerful oxidising agent and kills the bacteria.

Break point chlorination :-

Chlorine may be added to water directly as gas or in the form of bleaching powder. At one point on further chlorination the oxidation of chloramines and other impurities starts and there is fall in the combined chlorine content. Thus the residual chlorine decreases to a minimum point.

At which oxidation of chloramine & other impurities complete and free residual chlorine begins to appear this minimum point is known as break point chlorination.

External treatment of Hard Water :-

The treatment given to water for removal of hardness causing salts before it is taken into the boiler is called "external treatment of water".

The external treatment can be done by the following process.

- Ion Exchange process (Demineralisation)
- Zeolite process
- Lime Soda process

Ion Exchange (or) Demineralisation :-

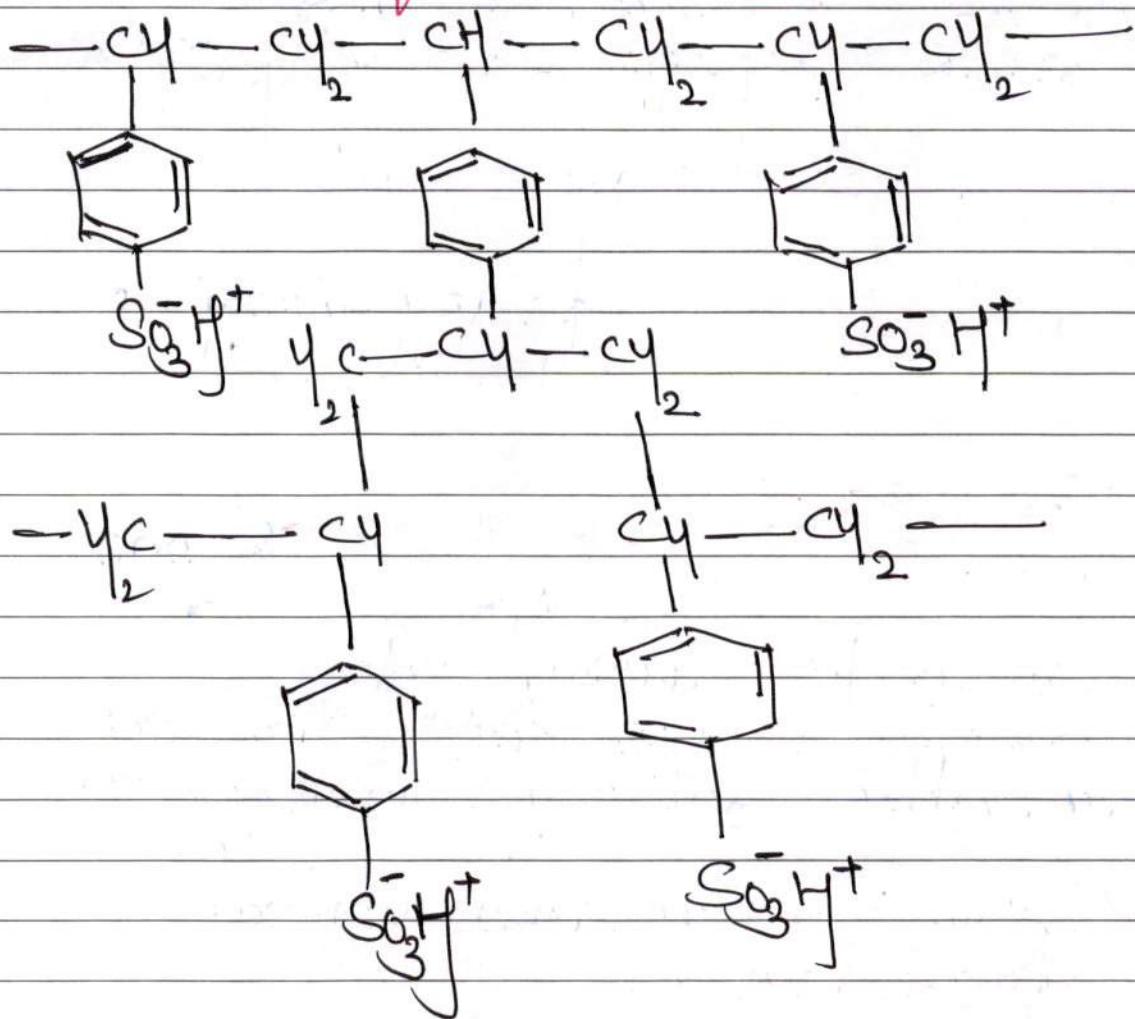
This process removes almost all the ions both this process removes almost all (Cations & anions) present in hard water.

Ion exchangers are of two types anionic and cationic they are copolymer of styrene & divinyl benzene. The polymers have two types of functional group the first group has SO_3H (or) COO^- which H^+ are replaced with cations such as $\text{Ca}^{2+}/\text{Mg}^{2+}$.

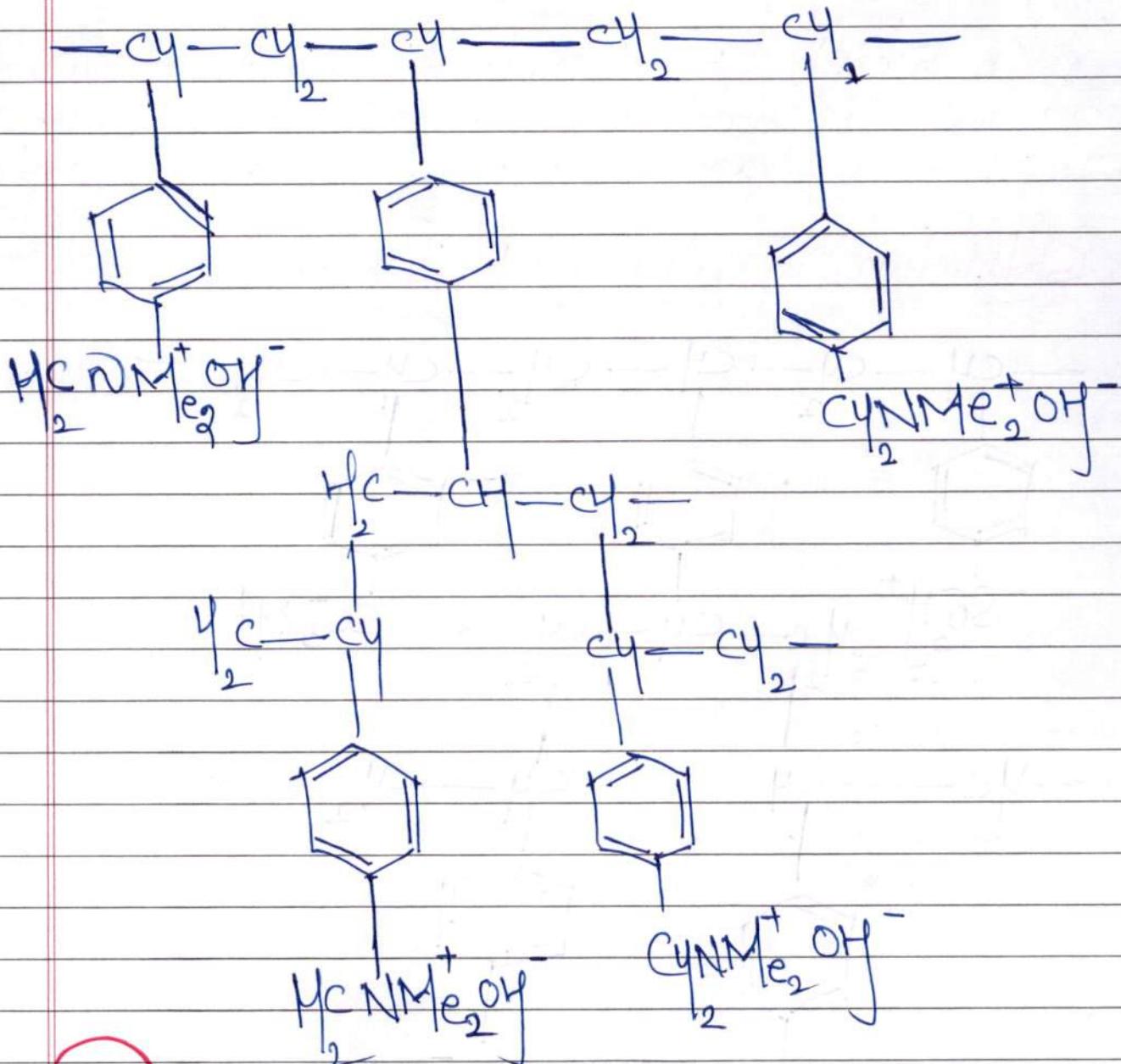
The 2nd group contains 4-substituted amino-groups such as $\text{NH}_2^+ \text{OH}^- > \text{NH}_3^+ \text{OH}^- > \text{N}^+ \text{OH}^-$

In which OH is replaced by anion in water
general representation of cations and anions
(exchanged) are H-R and ROH respectively

Structure of cation exchanger Resin:-

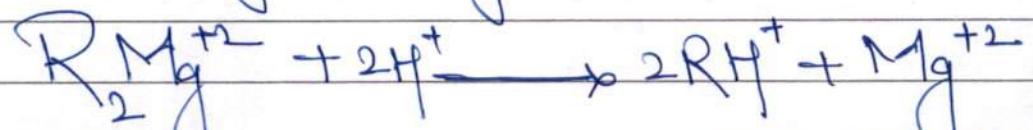


Structure of Anion Exchange Resin :-

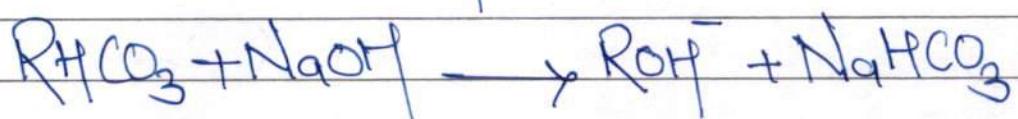
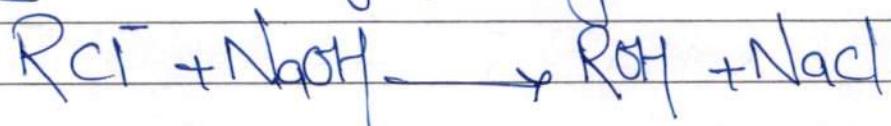


Process :- The raw water is first passed through cation exchanger and the removal of cations takes place in the following ways.

The exhausted cation exchanger resin can be regenerated by passing dilute HCl.



The exhausted anion exchanger resin can be regenerated by passing dilute NaOH

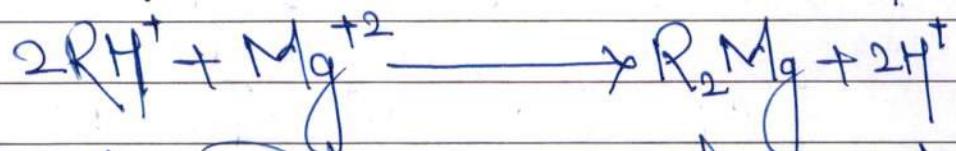


Advantages:-

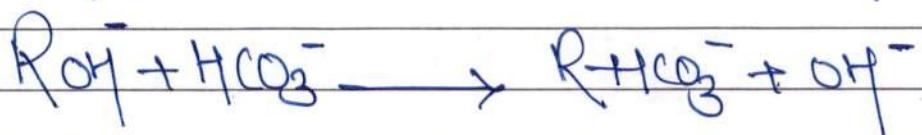
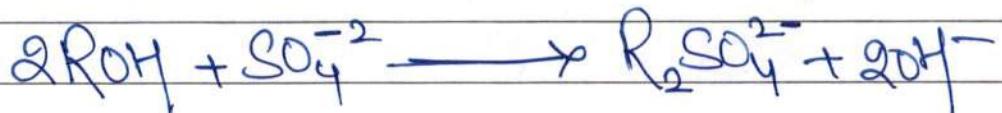
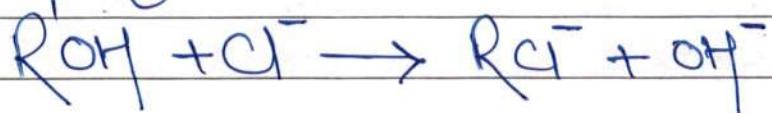
- The softened water by this method is completely free from all salts & it is used in boilers.
- It provides very low hardness nearly 2 ppm
- Highly acidic or alkaline water can be treated by this process.

Disadvantages:-

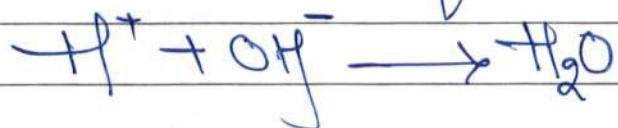
- The equipment is costly



When the water is passed through the anion exchanger and the removal of anions takes place in the



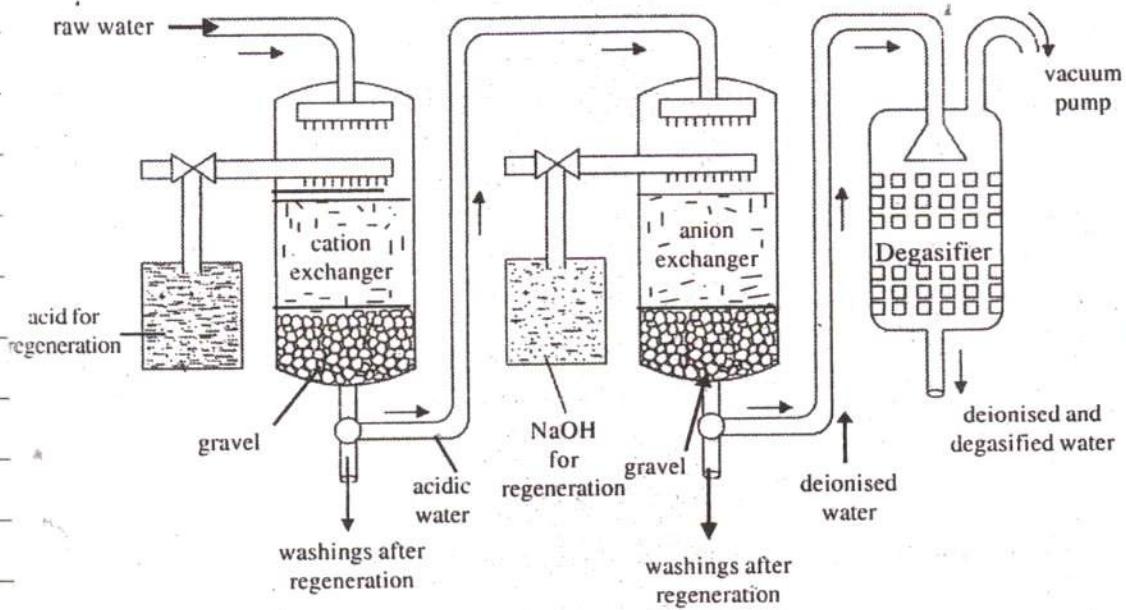
The H^+ ions produced from first chamber combines with OH^- ions produced from second chamber to form water.



Thus the water coming from the exchanger is free from all ions known as "de-ionisation or de-mineralisation" of water.

Regeneration of Resins:

The continuous passing of hard water through cation and anion exchange resin, the resins loose their exchanging capacities i.e. exchangers exhausted.



• More expensive chemicals required for regeneration

- Turbid water can not be treated by this method

Desalination of Water :- The process carried out to remove the common salt (NaCl) from the water body is known as "Desalination".

The water containing dissolved salts with a peculiar salty or brackish taste is called "brackish water".

- Brackish water is totally unfit for human

consumption & important method employed for desalination are

- ① Distillation
- ② Freezing
- ③ Reverse Osmosis
- ④ Electro-dialysis.

Osmosis:- The process in which the flow of solvent takes place from low concentration solⁿ to high concentration solⁿ through semipermeable membrane is called "Osmosis".

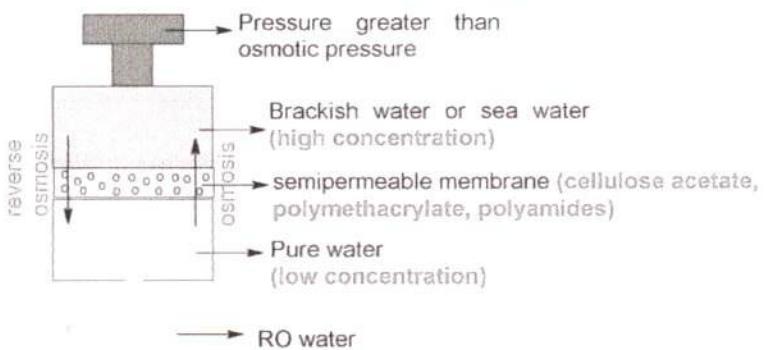
Osmotic pressure:- In Osmosis, only solvent can flow but not solute which produces a pressure called "Osmotic pressure".

Reverse Osmosis:- On applying external pressure (more than osmotic pressure), the flow of solvent takes place from high concentrated solⁿ to low concentrated solⁿ through a semipermeable membrane is called as "Reverse Osmosis".

Reverse Osmosis is also called as hyperfiltration or Super filtration.

Method:- In this process sea water is kept in contact with fresh water through semipermeable membrane (cellulose or poly methyl acrylate)

REVERSE OSMOSIS PROCESS



A pressure of 15-40 kg/cm² applied to the side of fresh water through semipermeable membrane i.e. reverse osmosis takes place.

Significance:- • The process removes ionic as well as non ionic dissolved salt easily.

- The process removes colloidal & high molecular weight compounds.
- The process is economical & convenient.

- The process is carried out at room temperature.
- It is suitable for converting sea water into drinking water.
- The membrane can be replaced easily.