

Unit – I

ELECTROCHEMISTRY

Unit Syllabus

Electrodes and electrochemical cells.

Electrode potential, standard electrode potential, single electrode potential and its determination.

Types of electrodes – calomel, quinhydrone and glass electrode.

Nernst equation - determination of pH of a solution by using quinhydrone and glass electrode.

Electrochemical series and its applications.

Batteries – Primary (dry battery) and secondary batteries (Lead – acid storage battery and Lithium ion battery) and next generation batteries

Electrochemical cells and its types. Electrode potential –origin – oxidation and reduction potent

INTRODUCTION

- Electrochemistry is a branch of chemistry.
- It deals with the chemical reactions produced by passing electric current through an electrolyte or production of electric current through a chemical reaction

Conductors

Conductor is a material which allows free flow of electricity.

Example: All metals, graphite, fused salts, solution of electrolytes

Non-conductors (Insulators)

Insulators are materials which do not conduct electrical current

Example: Wood, plastics, most of non metals.

Types of conductors

(i) Metallic conductors : The solid material, which conduct electric current due to the movement of electron from one end to the other end without producing chemical reaction.

Examples : *All metals & graphite.*

(ii) Electrolytic conductors : They conduct electric current due to the movement of ions from one electrode to another electrode in solution or in fused state. This process is accompanied by a chemical reaction.

Examples : *Metal ions dissolved solvent*

Cell Terminology

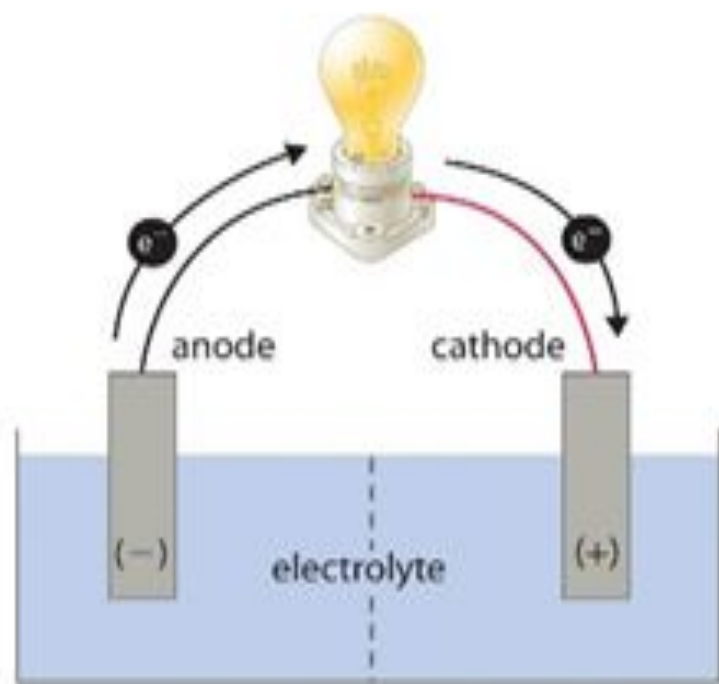
1. **Current:** Flow of electrons through a conductor.
2. **Electrode:** Electrode is a material (rod, bar, strip) which conducts electrons.
3. **Anode:** Electrode at which oxidation occurs.
4. **Cathode:** Electrode at which reduction occurs.
5. **Electrolyte:** Water soluble substance forming ions in solution and conducts electric current

- 6. Anode compartment:** Compartment of the cell in which the oxidation half reaction occurs. It contains the anode
- 7. Cathode compartment:** Compartment of the cell in which the reduction half reaction occurs. It contains the cathode
- 8. Half-cell:** It is the part of a cell, which contains an electrode dipped in an electrolyte. If oxidation occurs in this half-cell, then it is called the oxidation half cell. If reduction occurs at the cell, it is called the reduction half-cell.
- 9. Cell:** Device consisting of two half cell. The two half cells are connected through one wire.
- 10. Salt bridge:** Contains solutions of a salt (KNO_3 or NH_4NO_3) that literally serve as a bridge to completed the circuit, maintain electro neutrality of electrolyte and minimize. For precise measurement of potential a salt bridge is used.

TYPES OF CELLS

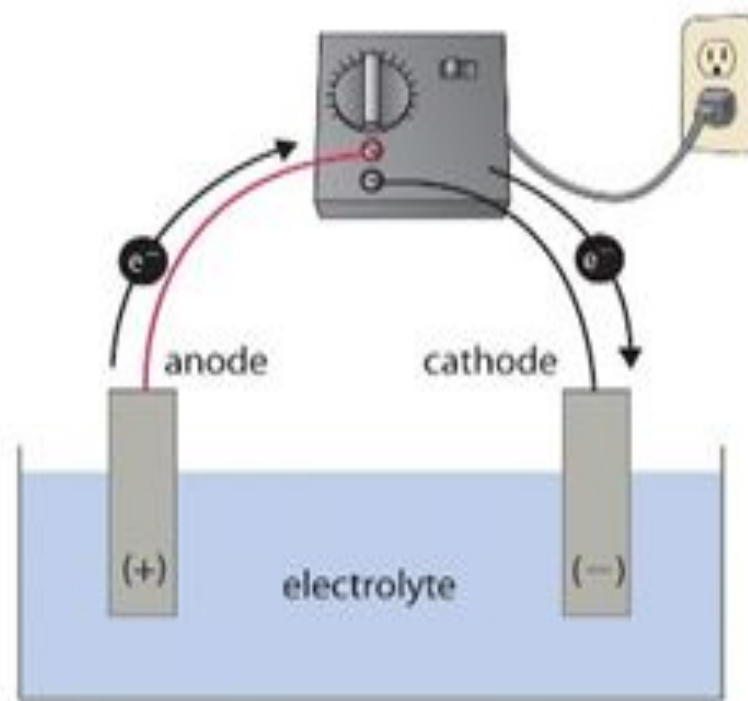
A cell is a device consisting of two half cells. Each half cell consists of an electrode dipped in an electrolyte solution. The two half cells are connected through one wire.

S.N o	Electrolytic cell	Electrochemical cell
1	Electrical energy converted to chemical energy. Example: Electrolysis, electroplating.	Chemical energy converted to electrical energy. Example: Daniel Cell
2	Anode carries +ve charge.	Anode carries –ve charge
3	Cathode carries – ve charge.	Cathode carries +ve charge.
4	Electrons are supplied to the cell from an external source.	Electrons are drawn from the cell
5	Amount of electricity is measured by coulometer	Emf produced is measured by potentiometer
6	Extent of chemical change is governed by Faraday's laws.	Emf of the cell depends on the concentration of the electrolyte and the nature of the electrode.



GALVANIC CELL

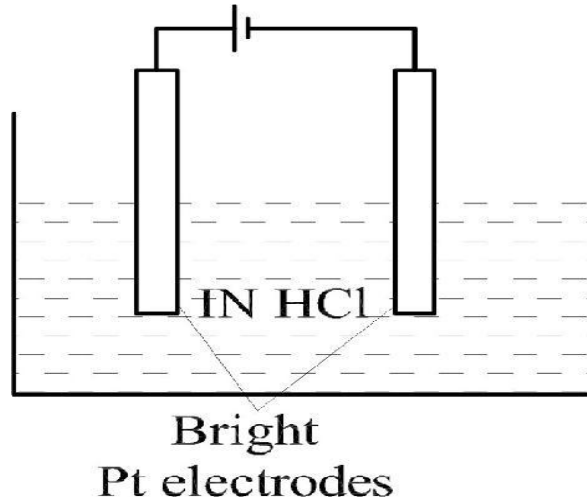
Energy released by spontaneous redox reaction is converted to electrical energy.



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

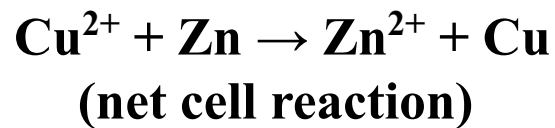
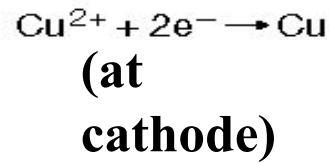
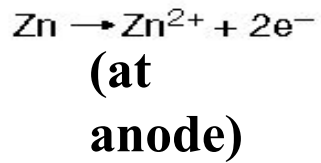
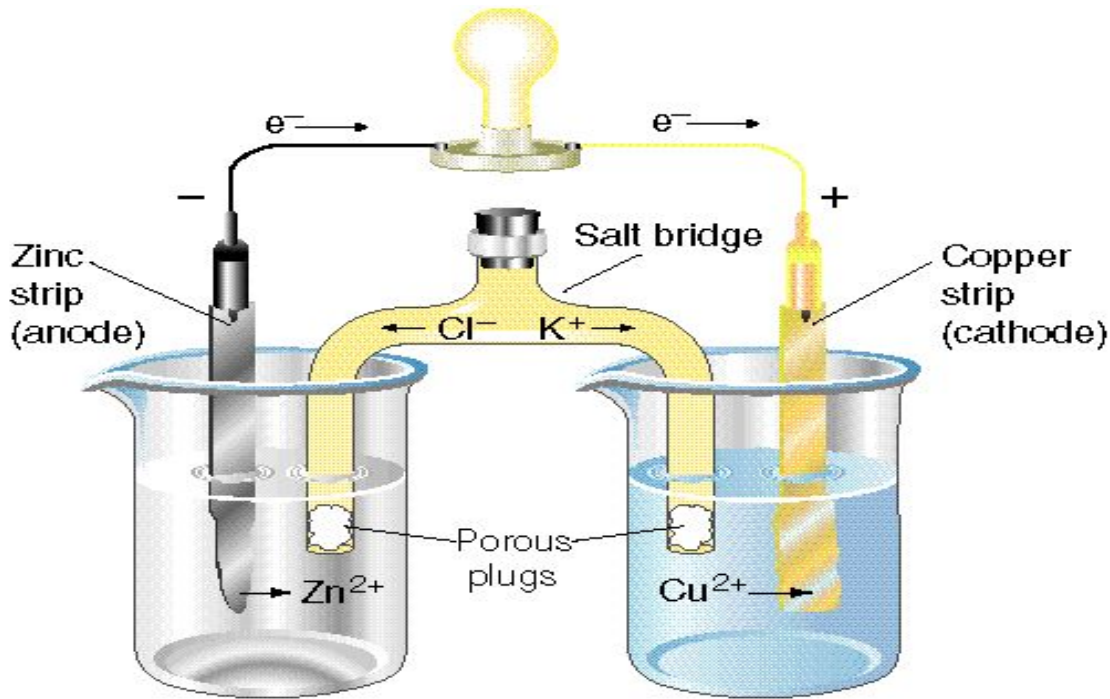
Electrolytic cell - *Example* : *Electrolysis of HCl.*



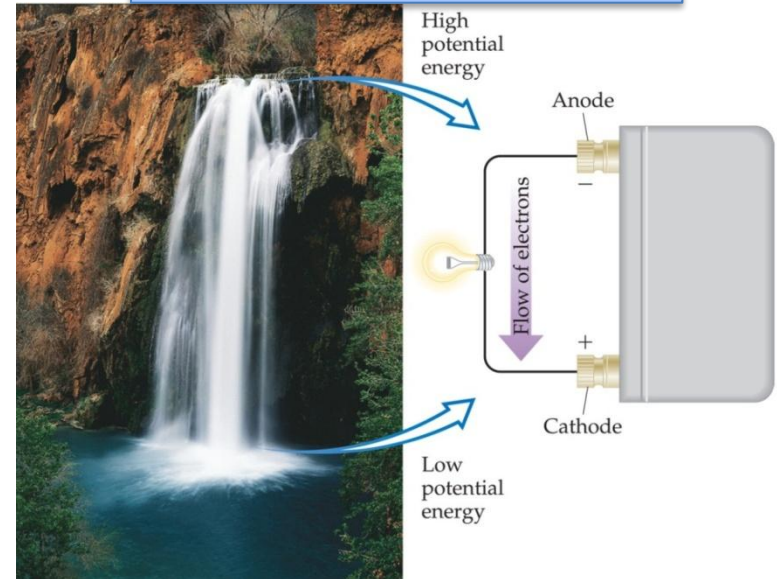
At anode : $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ (oxidation)

At cathode : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (reduction)

Electrochemical cell - Example : Daniel cell



Electromotive Force (emf)



Components of a Cell

- **At anode** : Oxidation of Zn to Zn^{2+} place with the liberation of electrons.
- **At cathode** : Reduction of Cu^{2+} to Cu place by the acceptance of electrons. The electrons liberated in oxidation reaction flow through external wire and are consumed by the copper ions at the cathode.
- **Salt bridge** : It consists of a U-tube containing a saturated solution of KCl or $(\text{NH}_4)_2\text{NO}_3$ agar-agar gel. It connects the two half cells.

Functions

- i. It eliminates liquid junction potential.
- ii. It provides a path for the flow of electrons between two half cells.

Representation (Cell diagram)

1. Galvanic cell consists of two electrodes, anode and cathode
2. Anode is written on the LHS and cathode on RHS
3. The anode is written with the metal first and then the electrolyte which are separated by a vertical line
Examples : Zn/Zn^{2+} (or) Zn/ZnSO_4
4. The cathode is written with the electrolyte first and then the metal.

Examples : Cu^{2+}/Cu (or) CuSO_4/Cu

5. The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

Cell is represented as $\text{Zn}/\text{ZnSO}_4 (1\text{M}) //) \text{CuSO}_4 (1\text{M}) / \text{Cu}$

ELECTRODE POTENTIAL ORIGIN OF ELECTRODE POTENTIAL

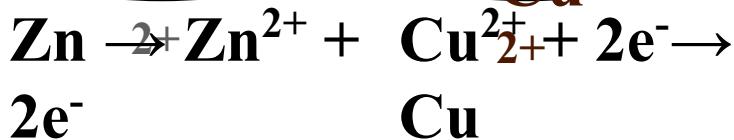
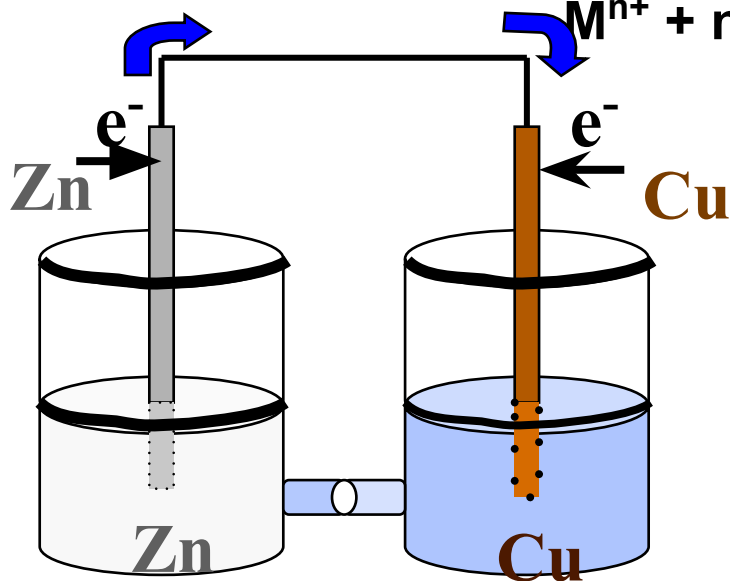
When a metal (M) is placed in a solution of its own salt (M^{n+}) one of the two processes are possible

(i) Metal atoms go into solution in the form of ions.

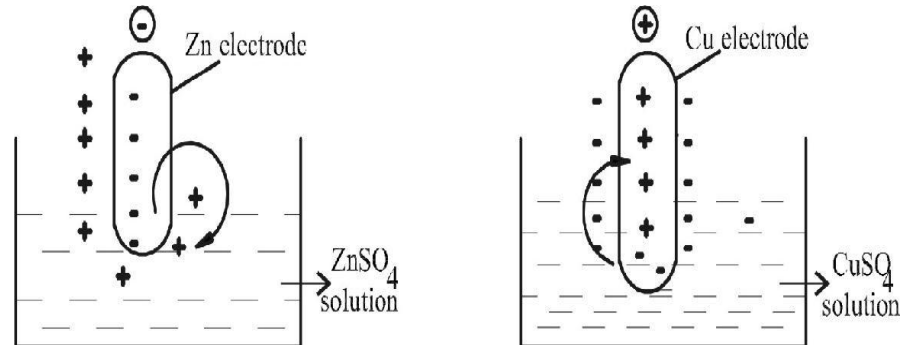


Example :

(ii) Metal ions from solution may deposit on the metal



Electrode Potential



At equilibrium, the potential difference becomes a constant value *which is known as the electrode potential of the metal. Thus the tendency of the electrode to lose electrons is called Oxidation potential and tendency of an electrode to gain electrons is called reduction potential.*

Single electrode potential (E) : It is the tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt.

Standard electrode potential (E°) : It is the tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt of 1M concentration at 25°C.

Types of Electrodes

Reference Electrode:

A reference electrode is that electrode whose potential is known and remain constant.

e.g. Saturated calomel electrode ($E_{\text{SCE}} = 0.242$)

Indicator Electrode:

An indicator electrode is that electrode whose potential depends on the activity of ions being titrated or estimated.

e.g. To carry out acid-base potentiometric titration Hydrogen gas.

Quinhydrone electrode and glass electrodes are used as indicator electrode.

Measurement Of Single Electrode Potential and its applications.

MEASUREMENT OF SINGLE ELECTRODE POTENTIAL

It is impossible to evaluate the absolute value of a single electrode potential. *Using reference electrode.*

Reference (or) Standard electrode

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose electrode potential is already known.

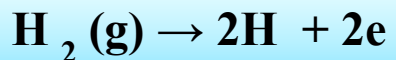
Examples : *Standard hydrogen electrode, Standard calomel electrodes.*

Standard hydrogen electrode (SHE)

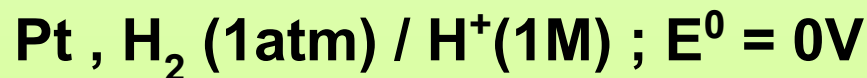
It is also called as Primary reference electrode because. The potential developed by this electrode is arbitrarily fixed as zero

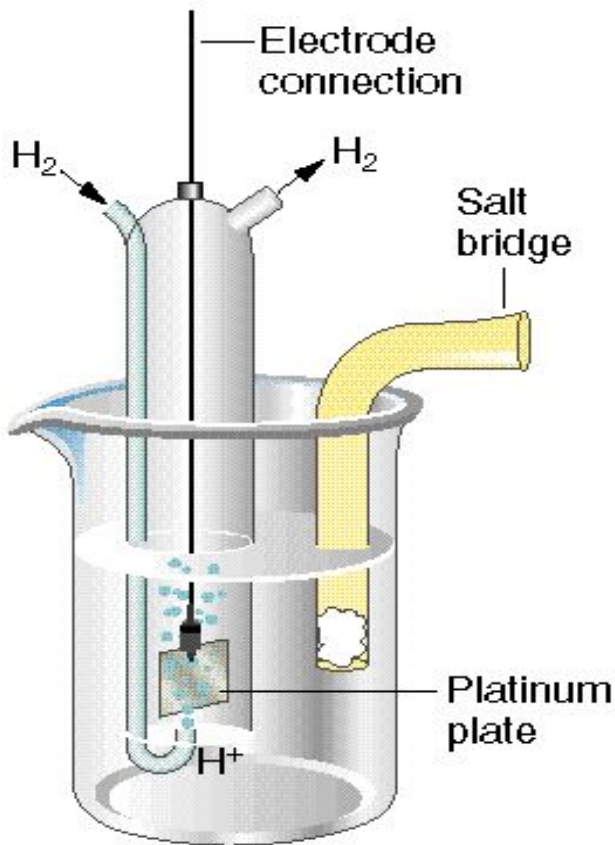
Construction

- It consists of a platinum foil that is connected to a platinum wire sealed in a glass tube.
- The Pt foil is dipped in 1M HCl. H_2 gas of 1 atm pressure is passed through the side of glass tube.



- The standard electrode potential of SHE is arbitrarily fix as zero





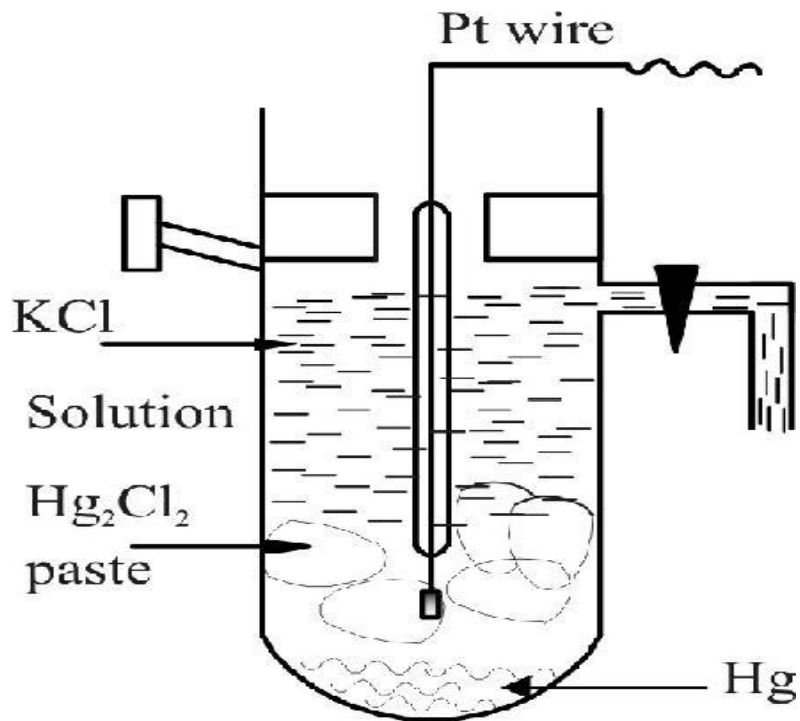
Limitations (or) drawbacks of SHE

- It is difficult to get pure hydrogen gas.
- The pressure of hydrogen is to be kept 1 atm all the time.
- It is difficult to set up and transport.
- Hydrogen gas reduces many ions like Ag^+ and affects compounds of Hg, Ag etc
- A large volume of test solution is required.
- It cannot be used in solutions of redox systems, the solution may poison platinum surface.

Saturated calomel electrode (SCE) (Secondary reference electrode)

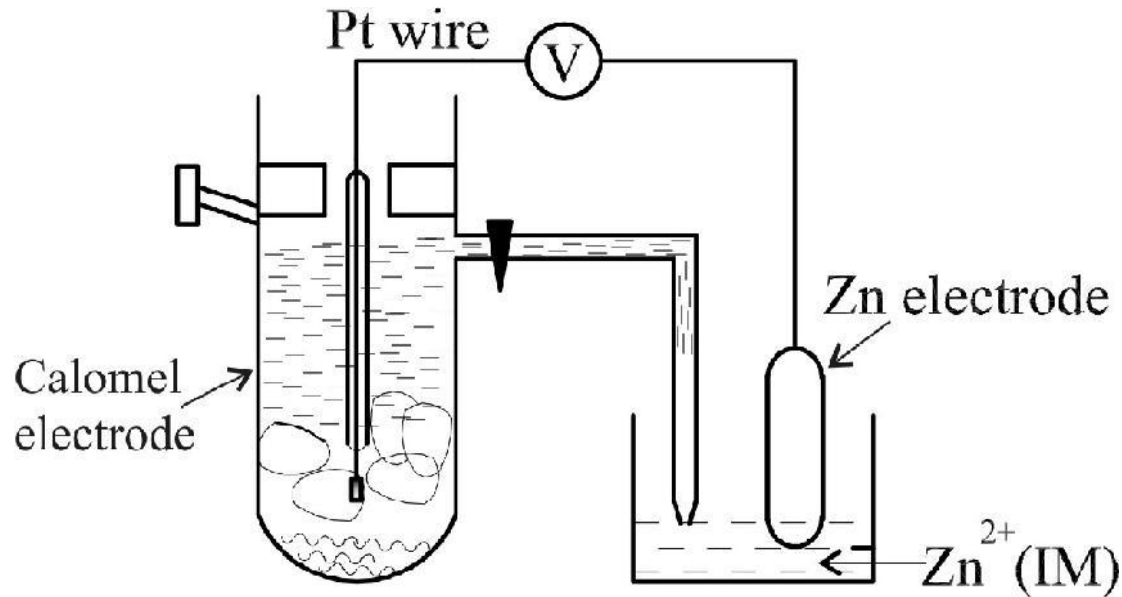
- Glass tube containing pure Hg at the bottom over which mercurous chloride is placed. The remaining portion of the tube is filled with saturated solution of KCl.
- The bottom of the tube is sealed with a platinum wire. The side tube is used for making electrical contact with a salt bridge.





KCl	(v)
0.1N	0.3335 V
1 N	0.281 V
Saturated	0.2422 V

Measurement of single electrode potential using a reference electrode (saturated calomel electrode)



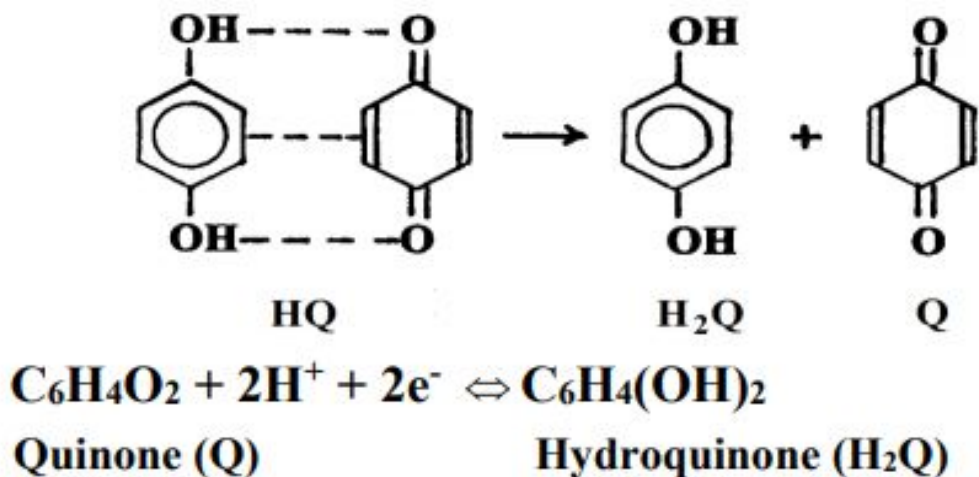
The emf of the cell is measured using a potentiometer.
The value of $E_{\text{cell}} = 1.0025$ volt.

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \\
 E_{\text{cell}} &= E_{\text{cal}}^{\circ} - E_{\text{Zn}}^{\circ} \\
 E_{\text{Zn}}^{\circ} &= E_{\text{cal}}^{\circ} - E_{\text{cell}}^{\circ} \\
 &= +0.2422 - 1.0025 = -0.7603 \text{ V}
 \end{aligned}$$

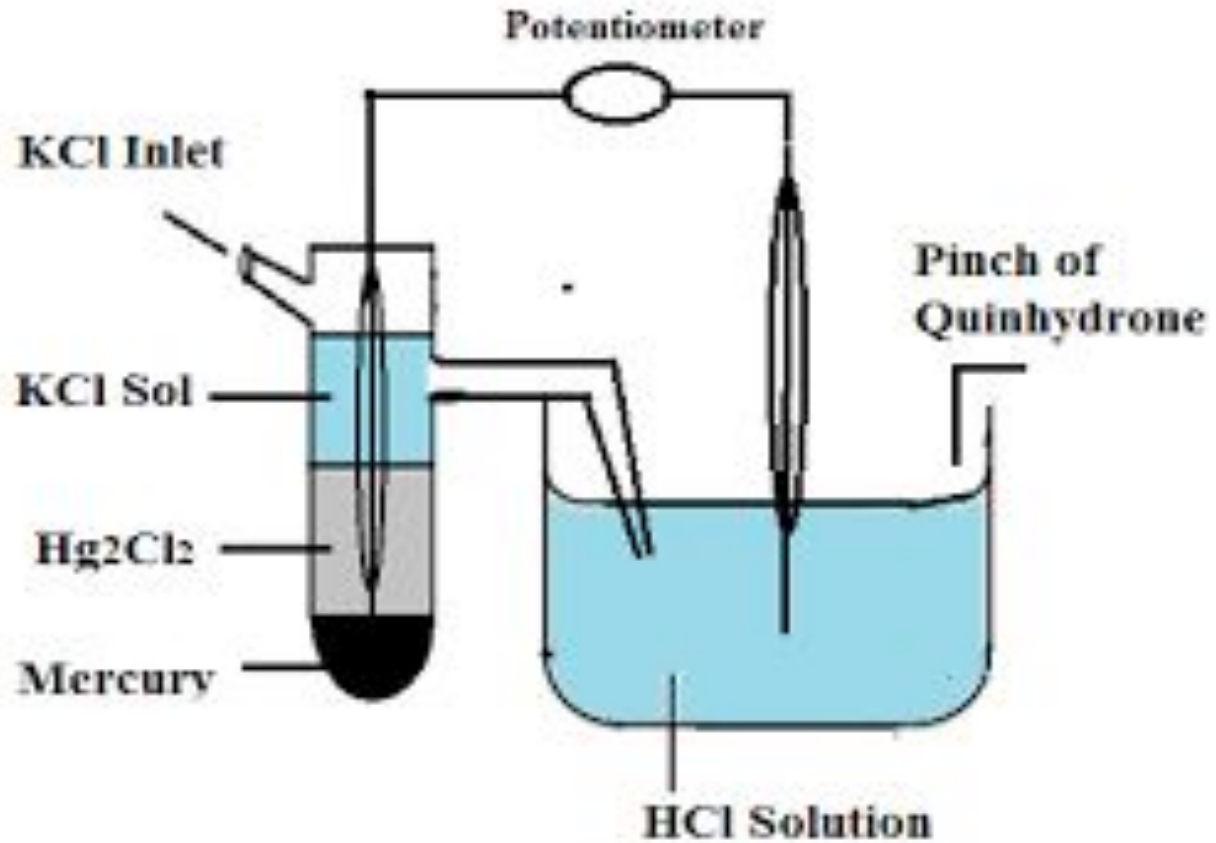
Quinhydrone electrode

- The quinhydrone electrode is a **type of redox electrode** which can be used to **measure the hydrogen ion concentration (pH)** of a solution.
- The electrode consists of an **inert metal electrode (usually a platinum wire) in contact with quinhydrone crystals** and a water-based solution.
- Quinhydrone is slightly soluble in water, dissolving to **form a mixture of two substances, quinone and hydroquinone**
- Each one of the two substances **can easily be oxidised or reduced to the other**. The potential at the inert electrode depends on the ratio of the activity of two substances. $\text{Quinone} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Hydroquinone}$

The electrode reaction is:



Quinhydrone electrode in a cell.



From the Nernst equation: $E = E^{\circ} + \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]}$ (or)

$$E = E^{\circ} - \frac{2.303RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2}$$

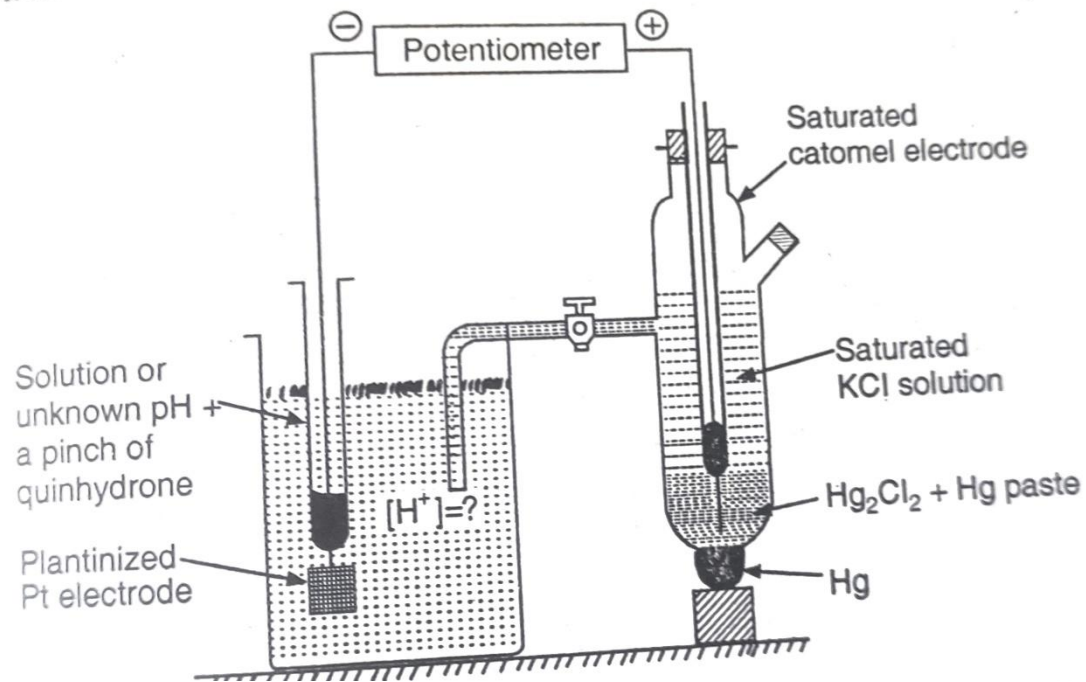
If quinone and hydroquinone are **taken in equimolar concentrations**, then $[Q] = [QH_2]$ then the above reaction reduces to

$$E = E^{\circ} - \frac{2.303RT}{2F} \log \frac{1}{[H^+]^2} = E^{\circ} - \frac{2.303RT}{F} \log \frac{1}{[H^+]}$$

$$E_Q = E^{\circ} - 0.0592v \text{ pH} = 0.6994v - 0.0592v \text{ pH}$$

Construction and working

QH electrode can very easily be set up by **adding a pinch of quinhydrone powder to the experimental solution** with stirring until the solution is saturated. Then **indicator electrode usually a bright platinum** is inserted in it. For determining the pH value, **this half cell is combined with saturated calomel electrode** and the emf of the cell is determine potentiometrically.



The complete cell may be represented as
 $Pt | H_2Q, Q, H^+(\text{unknown}) || KCl(\text{sat}), Hg_2Cl_2(s) | Hg^+$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{QH}}$$

$$E_{\text{cell}} = 0.2422\text{v} - 0.6994\text{v} - 0.0592\text{v pH}$$

$$pH = \frac{0.6994\text{v} - 0.2422\text{v} + E_{\text{cell}}}{0.0592\text{v}}$$

Merits and Demerits of the electrode:

Merits:

- i. Electrode is easy to set up.
- ii. It is also easy to handle.
- iii. It can be functioning satisfactorily also in highly acidic solution.
- iv. It is used to measure the pH of aqueous and non-aqueous solution.

Demerits:

- i. This electrode is functioning only in the pH range of 1 to 8
- ii. With the solution of pH greater than 8, the activity ratio is no longer remain equal to 1.
- iii. It cannot be functioning in presence of oxidising and reducing agents that can react rapidly with either hydroquinone or quinone.

Glass electrode

When two solutions of **different pH values** are separated by a thin glass membrane, there **develops a difference of potential** between the surfaces of the membrane. The potential value developed is **proportional to the difference in pH** of the test solution.

The **glass membrane functions as an ion exchange resin** and an equilibrium is set up between the **Na⁺ ions of the glass and H⁺ ions in the solution**.

For a particular type of glass the potential difference varies with H⁺ ion concentration, and is given by the expression

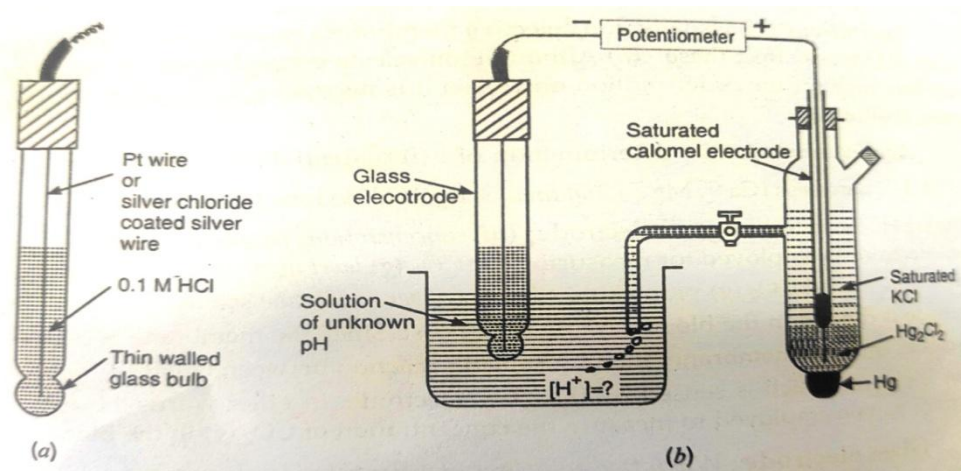
- $E_G = E_G^0 + 0.0591 \log [H^+]$
- $E_G = E_G^0 - 0.0591 \text{ pH}$

Glass electrode.

- Construction

The glass electrode assembly consists of a **thin glass bulb filled with 0.1 N HCl** and a **silver wire coated with silver chloride** immersed in it.

The Ag/AgCl electrode here acts as the internal reference electrode. The glass electrode is represented as



To carry out the **determination of pH** of a solution, **the glass electrode is connected with a saturated calomel electrode**. The emf of the cell is

Glass electrode.

The cell is therefore represented as;



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

$$\text{pH} = \frac{0.2422\text{v} - E_{\text{cell}} - E^{\circ}\text{G}}{0.0592\text{v}}$$

The E°_{G} value of a glass electrode can be determined by using a solution of known pH

Advantages of Glass electrode

- i) To determine pH of any solution
- ii) Small quantity of solution is sufficient for determination
- iii) Used even in the presence of metallic ions and poisons
- iv) Equilibrium is easily reached

Merits and Demerits of the electrode:

Merits:


- i. It provides a measure of pH in the pH range of 1 – 9.
- ii. Using a pH meter, pH of the solution can be directly read.
- iii. The electrode can be used in all aqueous solutions.
- iv. Electrode is not affected by oxidizing and reducing agents or by any organic compound.
- v. pH can be determined even for small volume of solution.

Demerits:

- i. The electrode cannot function in highly acidic or alkaline medium
- ii. It cannot produce proper response with $\text{pH} > 9$ or < 0.5 .
- iii. It cannot function in non-aqueous medium.
- iv. It needs standardisation every time before the use.

ELECTROCHEMICAL SERIES (OR) EMF SERIES

Various metals (electrodes) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale.

Electrode	Electrode reaction	E° , volts	Nature
Li^+/Li	$\text{Li}^+ + e \rightleftharpoons \text{Li}$	- 3.01	
Mg^{2+}/Mg	$\text{Mg}^{2+} + 2e \rightleftharpoons \text{Mg}$	- 2.37	
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2e \rightleftharpoons \text{Pb}$	-1.12	
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$	- 0.76	
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$	-0.44	
Sn^{2+}/Sn	$\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$	- 0.136	
H^+/H_2	$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$	0.00	
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	+ 0.34	
Ag^+/Ag	$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$	+ 0.80	
Au^+/Au	$\text{Au}^+ + e \rightleftharpoons \text{Au}$	+ 1.50	
$\frac{1}{2}\text{F}_2/\text{F}^-$	$\frac{1}{2} \text{F}_2 + e \rightleftharpoons \text{F}^-$	+ 2.87	

Significance of emf series (or) Application of electrochemical series

- ***Calculation of Standard emf of a Cell :***

We can calculate the standard emf of a cell, if the standard electrode potential values are known ($E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}}$)

- ***Relative ease of oxidation or reduction***

(a) Fluorine has higher +ve value of standard reduction potential (+2.87V) and shows higher tendency for reduction.

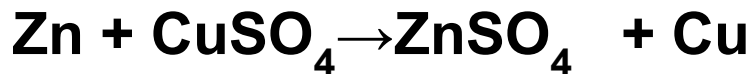
(b) Lithium has highest – ve value (–3.02V) and shows higher tendency towards oxidation.

- ***Displacement of one element by the other***

Metals with a lower reduction potential will displace metals with a higher reduction potential from their salt solution (Copper will displace silver from its solution).

Example :

Zn(-0.76V) will displace copper (+0.34V) from its solution



- ***Determination of equilibrium constant (K) for a reaction***

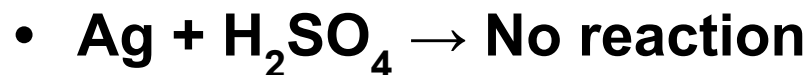
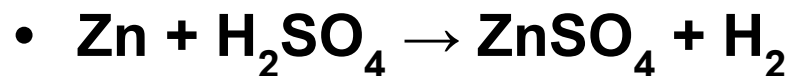
Standard electrode potentials are used to determine the equilibrium constants as follows: **$G^\circ = -2.303 RT \log K$**

$$\log K = \frac{G^\circ}{-2.303 RT} = \frac{nFE^\circ}{2.303 RT} \quad [G^\circ = -nFE^\circ]$$

- ***Hydrogen displacement behavior***

Metals with negative reduction potential (metals placed above H_2) in emf series will displace hydrogen from dilute acids solutions.

Example: Zn (-0.76 V) will displace H_2 from dilute acids whereas, silver (0.8) cannot



- ***Predicting the spontaneity of redox reactions***

If E° of a cell is positive the reaction is spontaneous.

If E° of a cell is negative the reaction is not feasible.

NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following redox reaction



For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter related as

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^{\circ} + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{..... (1)}\end{aligned}$$

where,

ΔG° = Standard free energy change

The above equation (1) is known as *Van't Hoff isotherm*.

The decrease in free energy ($-\Delta G$) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then 'n' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$\begin{aligned} -\Delta G &= nEF \\ \text{(or)} \\ -\Delta G^\circ &= nE^\circ F \end{aligned} \quad \text{..... (2)}$$

where,

$-\Delta G$ = decrease in free energy change.

(or) $-\Delta G^\circ$ = decrease in standard free energy change.

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \quad \dots\dots(3)$$

Dividing the above equation (3) by $-nF$

[∵ the activity of solid metal $[M] = 1$]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

In general, $E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

When, $R = 8.314 \text{ J/K/mole}$; $F = 96500 \text{ coulombs}$;
 $T = 298 \text{ K (25}^\circ\text{C)}$, the above equation becomes

$$E = E^\circ_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{.....(5)}$$

In general, $E = E^\circ_{\text{red}} + \frac{0.0591}{n} \log C$

Similarly for oxidation potential

$$E = E^\circ_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \quad \text{..... (6)}$$

The above equation 5&6 are known as “Nernst equation for single electrode potential”.



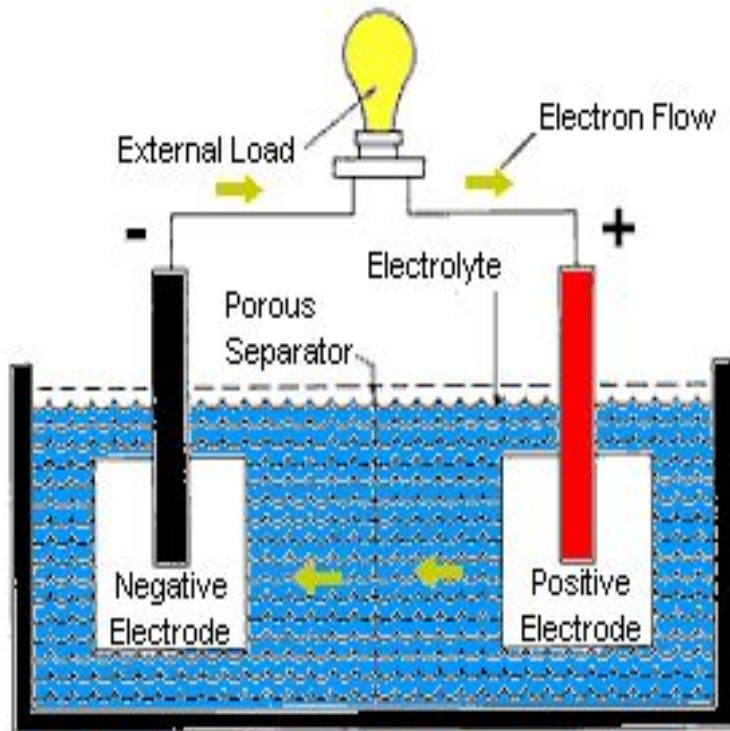
BATTERIES





- Battery is an array of cells connected in series and / or parallel to produce the desired voltage / current output.
- A cell is made up of two electrodes- anode and cathode.
- Each cell / electrode is associated with some charge transfer process called cell / electrode reaction.
- A cell is a device, which converts chemical energy into electrical energy and vice versa.
- Galvanic cell is a device that produces electrical energy from chemical energy
- Electrolytic cells convert electrical energy to chemical energy.

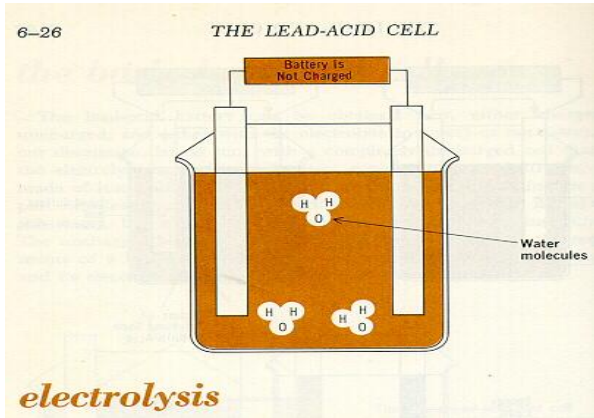
Cells



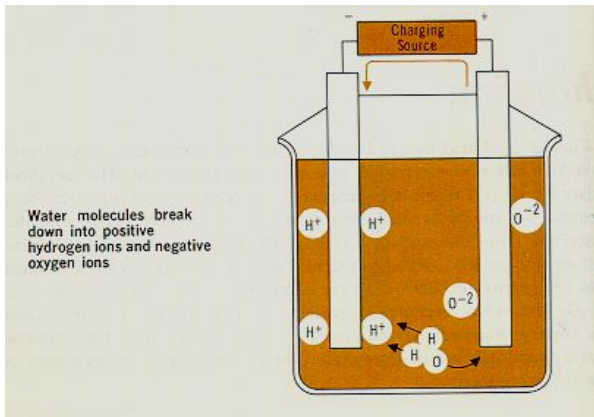
*Figure 1 - Components of a Battery Cell
(Discharge Circuit)*

- Positive electrode
- Negative electrode
- Electrolyte
- Separator

Electrolysis



- The producing of chemical changes by passage of an electric current through an electrolyte.



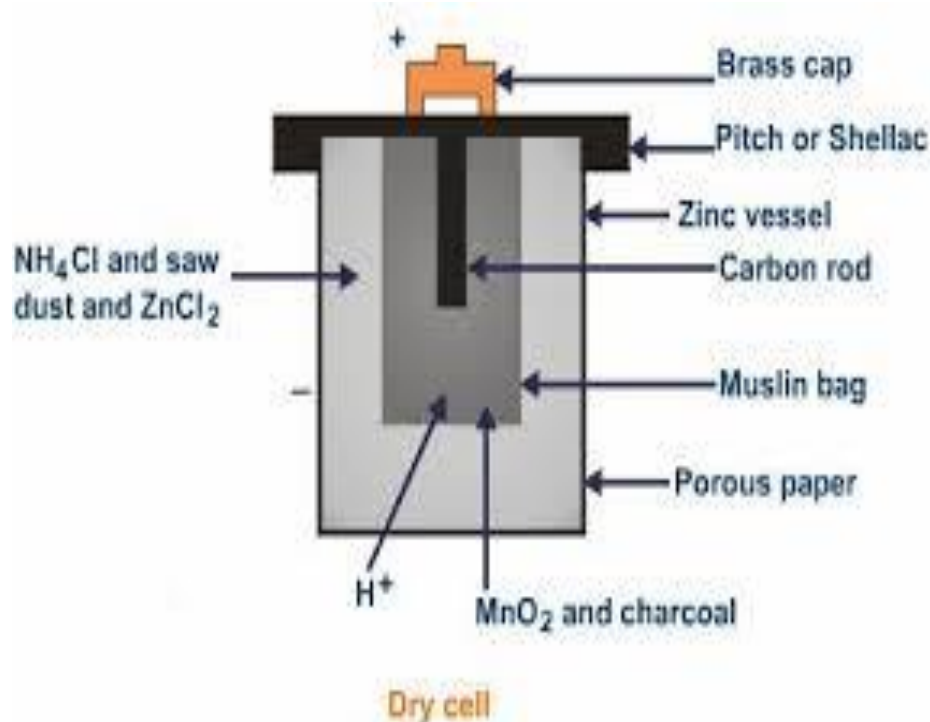
Types of Batteries

1. Primary or non-rechargeable.
 2. Secondary or rechargeable batteries.
 3. Flow battery
- The cell reactions for secondary batteries are somewhat **reversible** in nature while that of a primary battery is irreversible.
 - Every battery system is characteristic of its anode and cathode active materials.
 - Secondary batteries - the cell reaction can be made to proceed in either direction by withdrawing or supplying current to the battery system.
 - The current withdrawing process constitutes the discharging process and the current supplying process, as charging process.

DRY CELL

Uses of an electrolytic paste.

- The electrolytic paste reacts with the electrodes to produce a negative charge on one electrode and a positive charge on the other.
- The difference of potential between the two electrodes is the output voltage.



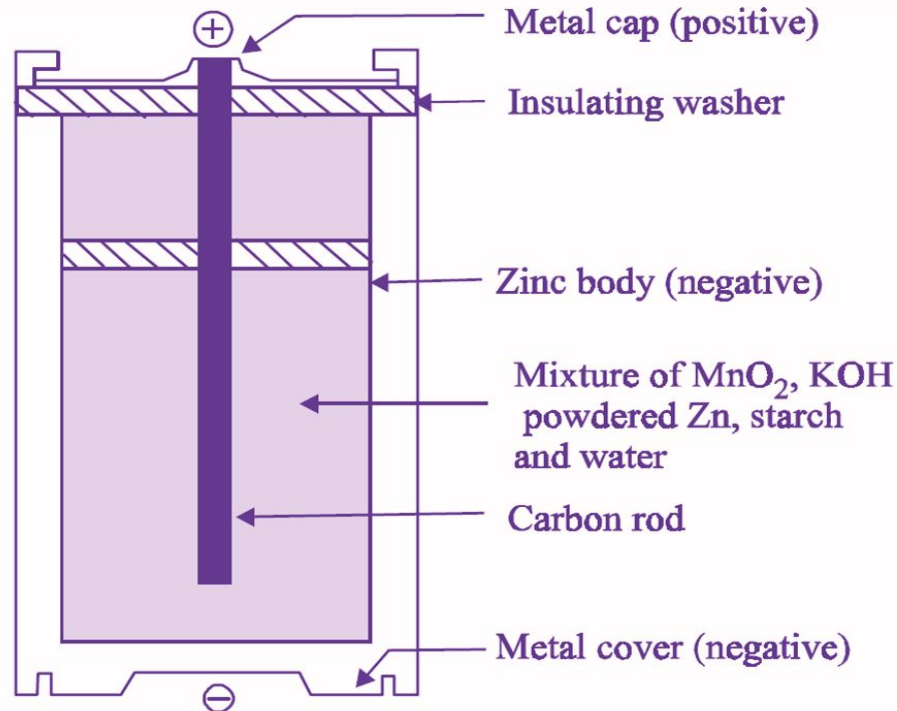
Standard Zinc Carbon Batteries

- Chemistry
 - Zinc (-), manganese dioxide (+)
 - Zinc, ammonium chloride aqueous electrolyte

- Features
 - + Inexpensive, widely available
 - Inefficient at high current drain
 - Poor discharge curve (sloping)
 - Poor performance at low temperatures

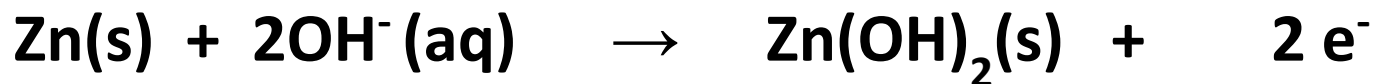
Alkaline batteries

- Improved form of dry cell.
- In this battery, zinc in powdered form is mixed with KOH to get a gel.
- Graphite rod is surrounded by a paste containing MnO_2 .
- The outside body is made of zinc.

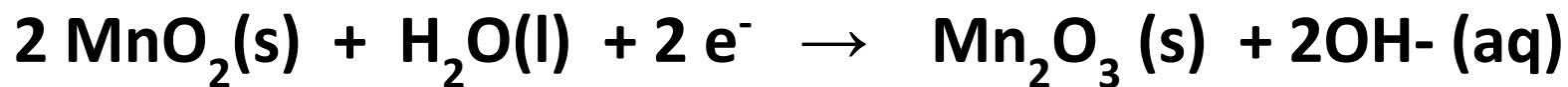


The cell reactions

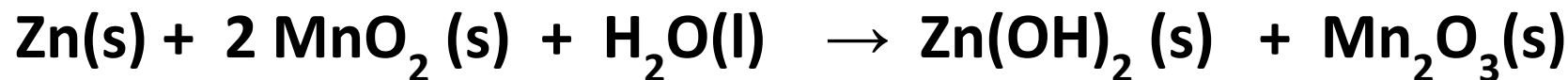
- Anode:



- Cathode:



- Net reaction:



-

Advantages of alkaline battery over dry battery

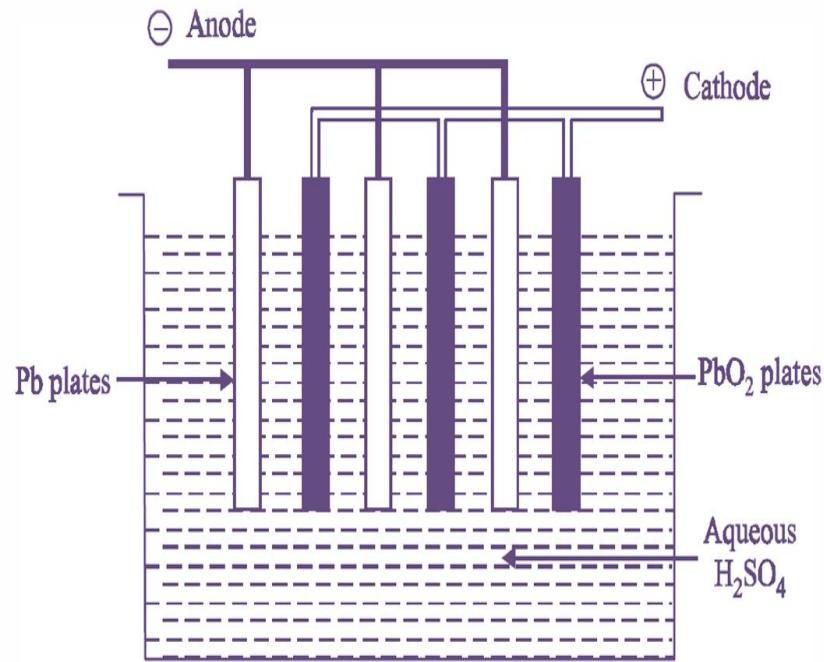
1. Zinc does not dissolve as readily in a basic medium
2. The alkaline battery maintains better its voltage as the current is drawn from it
3. The life a alkaline battery is longer than dry cell, since there is no corrosion of Zn.

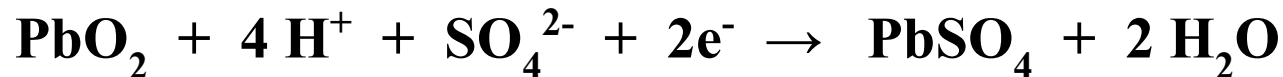
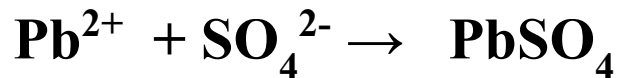
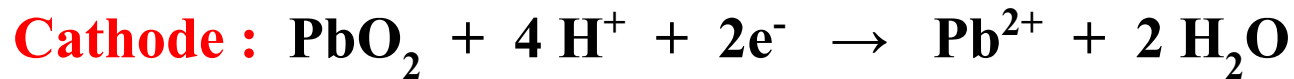
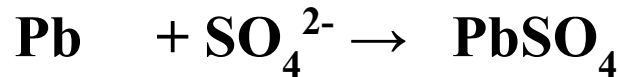
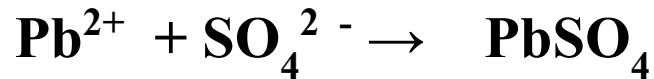
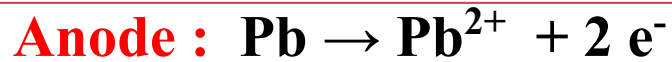
Uses of alkaline battery.

Alkaline batteries find used in camera exposure controls, calculators, watches etc.

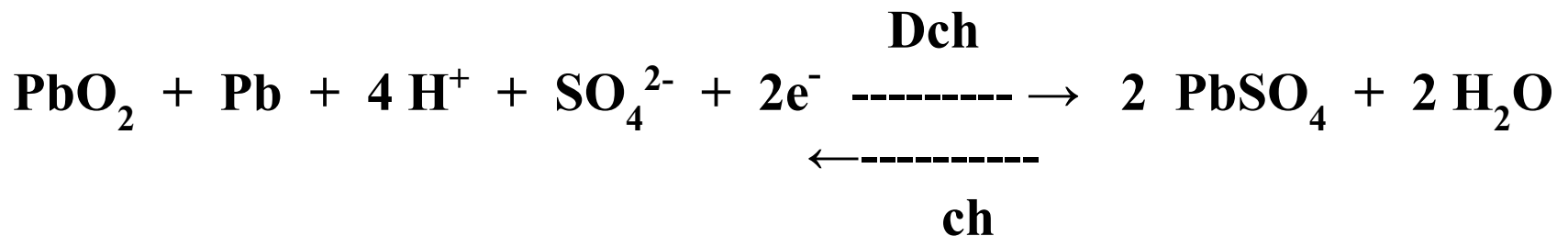
Lead-Acid Battery

- Positive terminal or cathode –
grid of lead-antimony alloy coated with lead dioxide.
- Negative terminal or anode -spongy lead
- Electrolyte- sulphuric acid



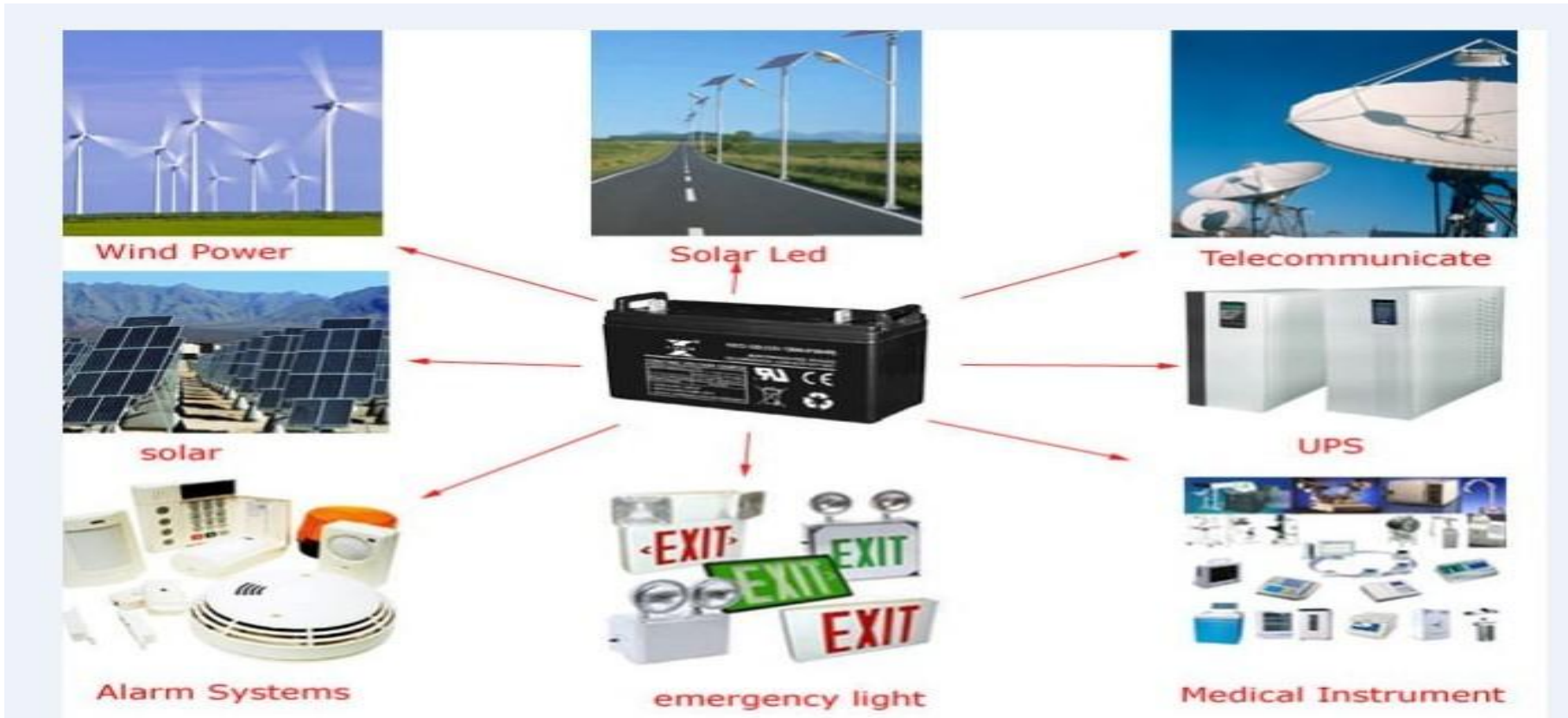


Overall cell reaction:



Uses:

1. SLI (Starting, lighting and ignition purposes) battery
2. Potable power source for remote areas, mountain regions etc.
3. Standby power source / Uninterrupted Power Supply (UPS)



Secondary Alkaline storage batteries:

These batteries use 20-25 % KOH as electrolyte.

• *Examples of this type of batteries are*

1. Nickel-iron (Edison cells),
2. Nickel-cadmium, nickel-hydrogen,
3. Nickel-metal hydride,
4. Silver-zinc etc.

Nickel-Cadmium(NICAD) battery

Example for rechargeable alkaline battery

- *They are more versatile than lead-acid batteries in various aspects.*
- *During charging and discharging, no loss of products and no gas evolution occur at the active electrodes.*
- *They possess low internal resistance, long shelf life without and good cycle life.*

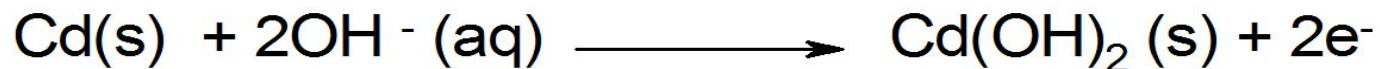
Construction

Anode : *Cadmium as a mixture of metal oxide and /or hydroxide*

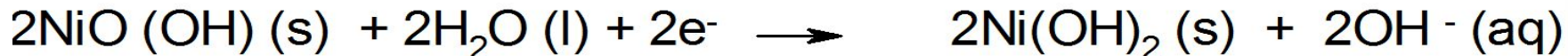
Cathode: *Nickel(III) oxide hydroxide (NiO(OH))*

Electrolyte: *KOH*

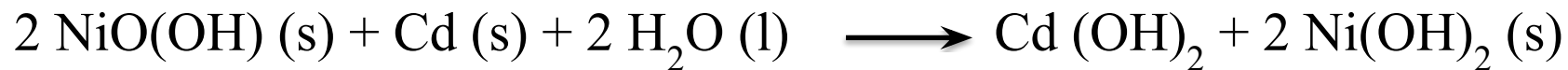
Anode



Cathode



Cell reaction



Cell representation:



Cell Voltage : 1.4 V

Advantages and uses of NiCad battery

1. Used in the sealed version for high current applications such as power tools and applications requiring high cycle life, such as computer power supply.
2. Large, sealed Ni - Cd cells are used in space applications, which require excellent system reliability and high cycle life.
3. Sintered Ni - Cd cells are used for standby power and for starting aircrafts.
4. Pocket type Ni - Cd cells are used for starting diesel engines and for emergency lighting.

LITHIUM BATTERIES

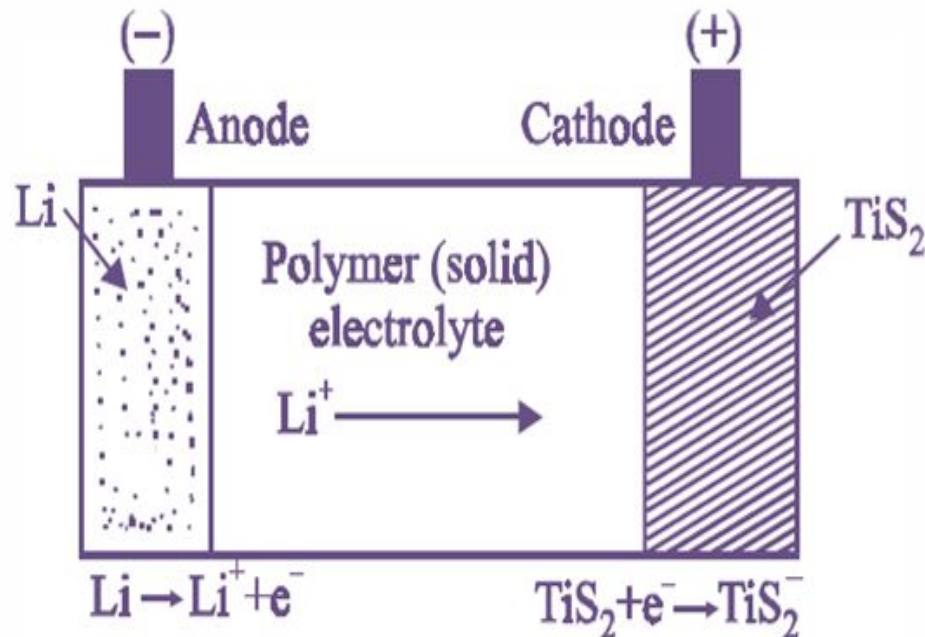
- Cells with lithium anodes are called Lithium batteries.
- Lithium primary cells can be broadly classified into
 - 1.Primary cells with solid cathodes: Ex: Li / MnO₂ Cell and
 - 2.Primary cells with liquid cathode: Ex: Li -SO₂ , Lithium-Thionyl chloride Cell

(Secondary) Rechargeable Lithium batteries:

- *Lithium batteries are characterized by high specific energy and high cycle life.*
- *These batteries have either lithium foils as anodes (negatives) or lithiated transition metal oxides as cathodes (positives) with solid polymer electrode.*
- *Electrolyte is immobilized polymer electrolyte with polymer separators.*
- *Examples for lithium batteries : Li- TiS_2 ,*
- *Li – sulphur ,Li – MnO_2 , Li – V_2O_5 batteries.*

Li- TiS₂ Battery

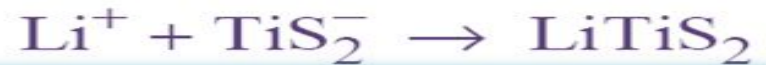
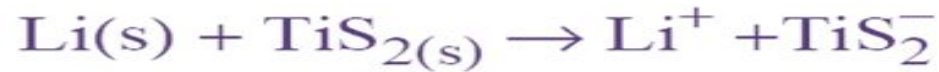
- *The electrode and cell reactions of this cell are given below:*
- *Anode: Lithium*
- *Cathode: TiS₂*
- *Electrolyte: A solid electrolyte (Polymer packed between the electrodes which permits the passage of ions but not electrons)*
- **CELL VOLTAGE - 3V**



Cell reactions

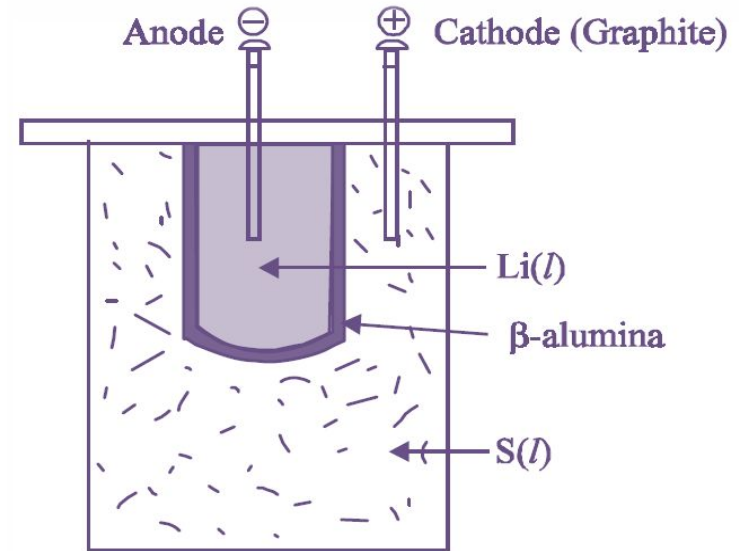


Overall reaction:



Lithium-Sulphur battery

- *Rechargeable battery.*
- *Anode is made of Li.*
- *Sulphur is the electron acceptor,*
- *The electron from Li is conducted to S by a graphite cathode.*
- *β -Alumina ($\text{NaAl}_{11}\text{O}_{17}$) is used as the solid electrolyte.*



- β -Alumina ($\text{NaAl}_{11}\text{O}_{17}$) allows the Li^+ ions to migrate to equalize the charge, but will not allow the big poly sulphide product ions.
- This battery is operated at high temperatures as Li and S should be in their molten states
- The direct reaction between lithium and sulphur is prevented by alumina present in the cell.

Cell Reactions



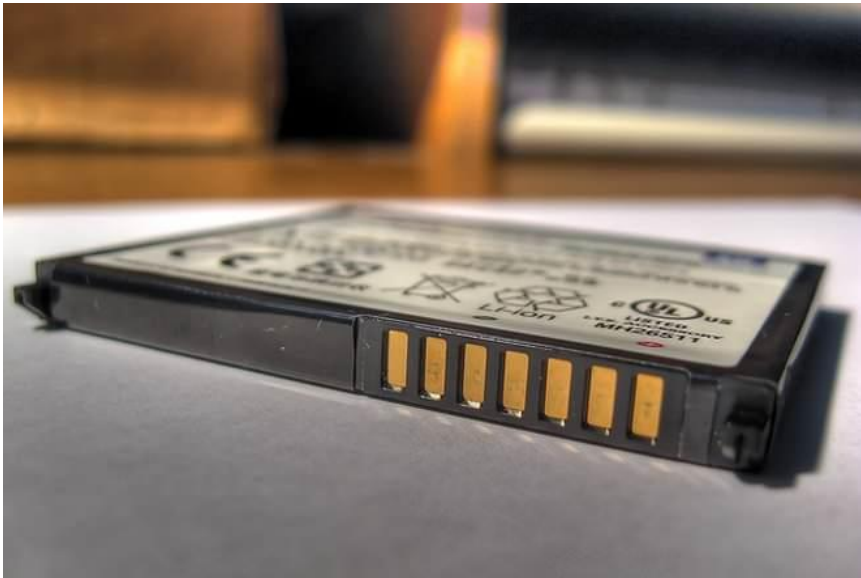
Advantages of lithium battery

1. Electrode potential (E°) of Li / Li^+ is most electronegative, So lithium battery generates a high voltage (3.0) than all other batteries
2. Only 7 g(1mol) of Li metal is needed to produce 1 mol of electrons during discharging
3. Lithium batteries can be made in different shapes and sizes.
4. There is no risk of leakage from the lithium battery, since all its constituents are solid

Applications

1. Lithium batteries are used in portable telephones, computers, and camcorders.
2. Lithium battery research is under progress for use in electric vehicle propulsion and as energy storage devices.
3. Example of such a battery system is FeS_2 (positive)– Li Al (negative) cell with molten chloride electrolyte. These batteries are operated at 400°C .
4. Lithium sulphur battery is used in electric cars.





NEXT GENERATION BATTERIES.

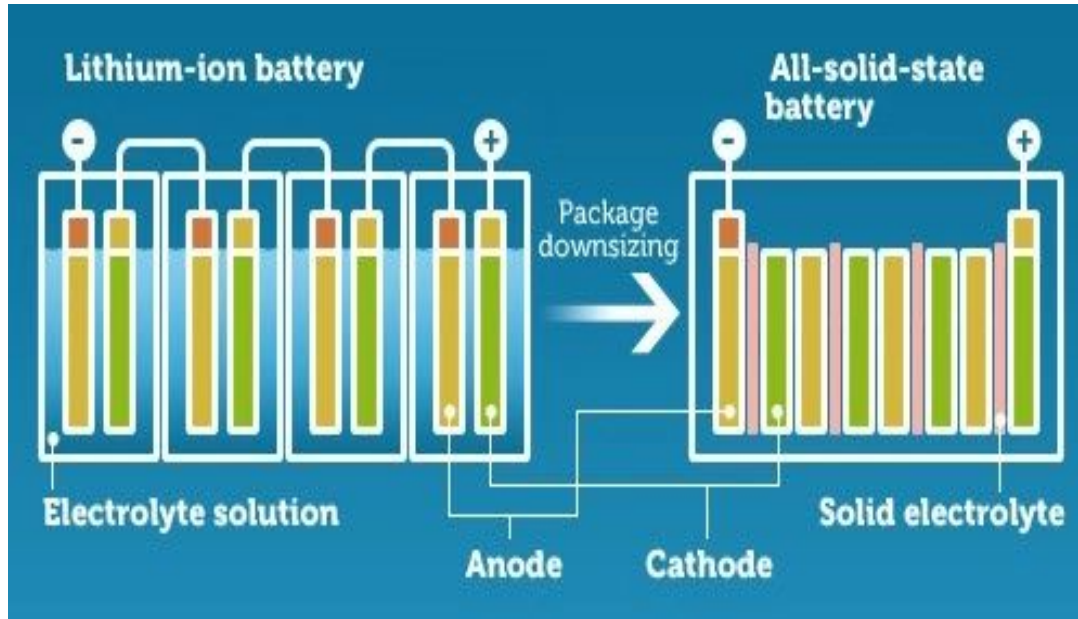
Lithium Solid-state Batteries

These batteries use solid electrodes and a solid electrolyte, instead of the liquid or polymer gel electrolytes found in lithium-ion or lithium polymer batteries.

Anode: Lithium, Graphite

Cathode: Cobalt, Manganese.

Solid electrolyte: Lithium phosphorus oxynitride (LIPON) and the lithium thiophosphates ($\text{Li}_2\text{S}-\text{P}_2\text{S}_5$).



- Solid-state batteries can provide solutions for many problems of liquid Li-ion batteries, such as flammability, limited voltage, unstable solid-electrolyte interphase formation, poor cycling performance and strength.
- In the charging & discharging cycle, ions transfer to and fro between the anode (negative electrode generally made of graphite) and cathode (positive electrode made of lithium).

Advantages of the solid-state battery technology

1. Higher cell energy density (by eliminating the carbon anode)
2. Lower charge time (by eliminating the need to have lithium diffuse into the carbon particles in conventional lithium-ion cells)
3. Ability to undertake more charging cycles and longer life.
4. Improved safety and Lower cost.
5. Increase capacity of EV batteries

Liquid lithium-ion batteries

Low processing cost

Flexible separators can withstand high mechanical stress

High ionic conductivity only at room temperature

Self-discharge may reduce the shelf life

Electrolytes used are flammable; it can cause combustion

SEI layer formation affects life cycle

Limited choice of cathode materials due to electrolyte reaction

Poor thermal stability

Sensitive to overcharge



Solid-state lithium-ion batteries

Excellent thermal stability

Comparatively less self-discharge

High ionic conductivity over a broad range of temperatures

Electrolyte used is non-volatile

Electrolytes are non-flammable, and thus, safe

High energy density

High tolerance

Ceramic separator used is rigid and it may break with additional stress

No SEI layer formation, and thus, a longer life cycle



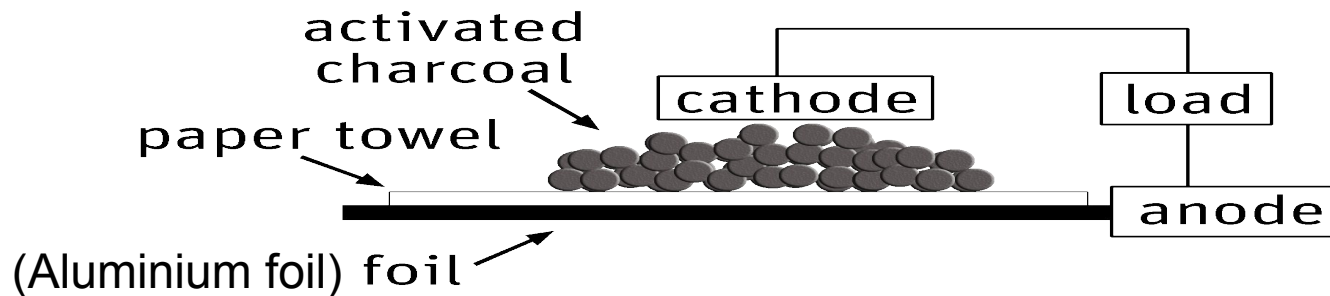
Challenges



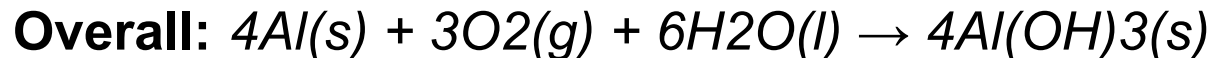
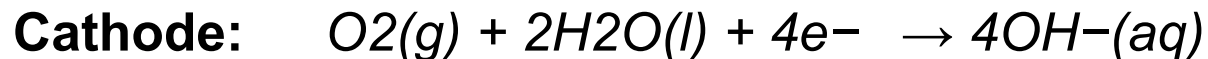
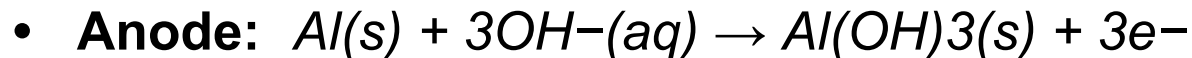
Advantages

Aluminium- Air battery

- To generate electrical energy, this battery relies on oxidation of aluminum at the anode, which releases electrons, and a reduction of oxygen at the cathode, which uses electrons. The movement of electrons through an external circuit generates an electric current that can be used to power simple devices. A diagram of the battery and equations for the half and overall reactions are given below:
- **Anode:** Aluminium
- **Cathode:** Oxygen(air)
- **Electrolyte:** KOH or NaOH.



Equations for the half and overall reactions:



- Aluminum foil provides an affordable supply of aluminum.
- Activated charcoal, which is mostly made of carbon, can conduct electricity and is non-reactive.
- It provides a highly porous surface that is exposed to oxygen in the air. One gram of activated charcoal can have more internal surface area than an entire basketball court!
- This surface provides a large number of sites to which oxygen can bind and participate in the cathode reaction.
- This large reaction area makes it possible for the simple aluminum–air battery to generate 1 volt (1 V) and 100 milliamps (100 mA).
- This is enough power to run a small electrical device and provides a safe and easy way to make a powerful battery at home or industry.

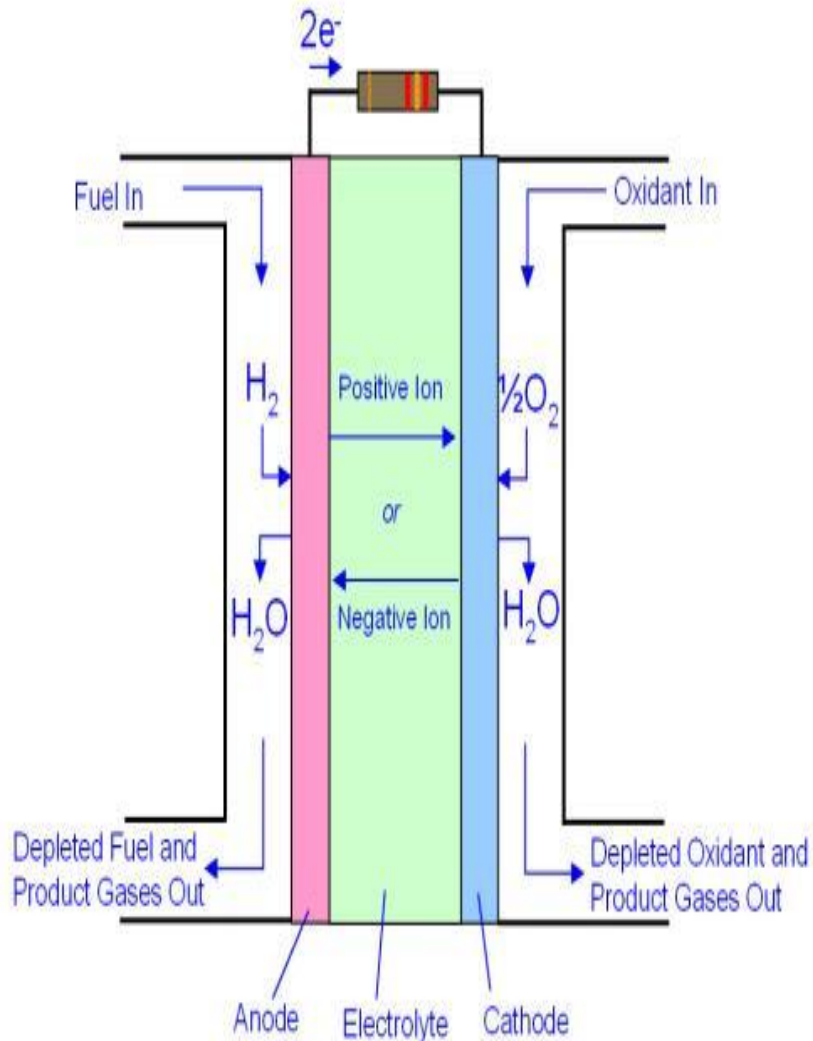
Fuel cell

- Electrochemical cell which converts the chemical energy of fuel into electrical energy by an electrochemical process in which fuel materials are oxidized.
- A fuel cell differs from a conventional battery that it requires continuous replenishment of the fuel electrode, unlike recharging.
- The basic arrangement in a fuel cell can be represented as follows.
- **Fuel/ electrode/electrolyte/electrode/oxidant**

- Fuel undergoes oxidation at the **anode** liberating electron and the oxidation products of the fuel. The electron so liberated from the oxidation process reduce the oxidant at the **cathode**.
- Thus movement of electrons constitute electric current.
- Varieties of fuel cells are in use. The important types of fuel cells are **hydrogen-oxygen fuel cell, methanol-air fuel cell, phosphoric acid fuel cell** etc.

Hydrogen-oxygen fuel cell:

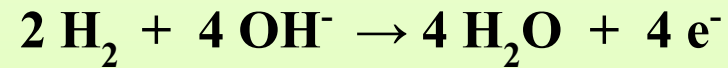
- The electrodes of a fuel cell are referred to as fuel electrode and oxidant electrode. The working of a hydrogen-oxygen fuel cell is based upon the reaction of hydrogen – fuel and oxygen – oxidant to form water.
- **Construction:** At the cathode, oxygen is diffused through a porous carbon electrode, impregnated with cobalt oxide, platinum or silver as catalyst. The two electrodes are separated by electrolyte such as KOH solution.

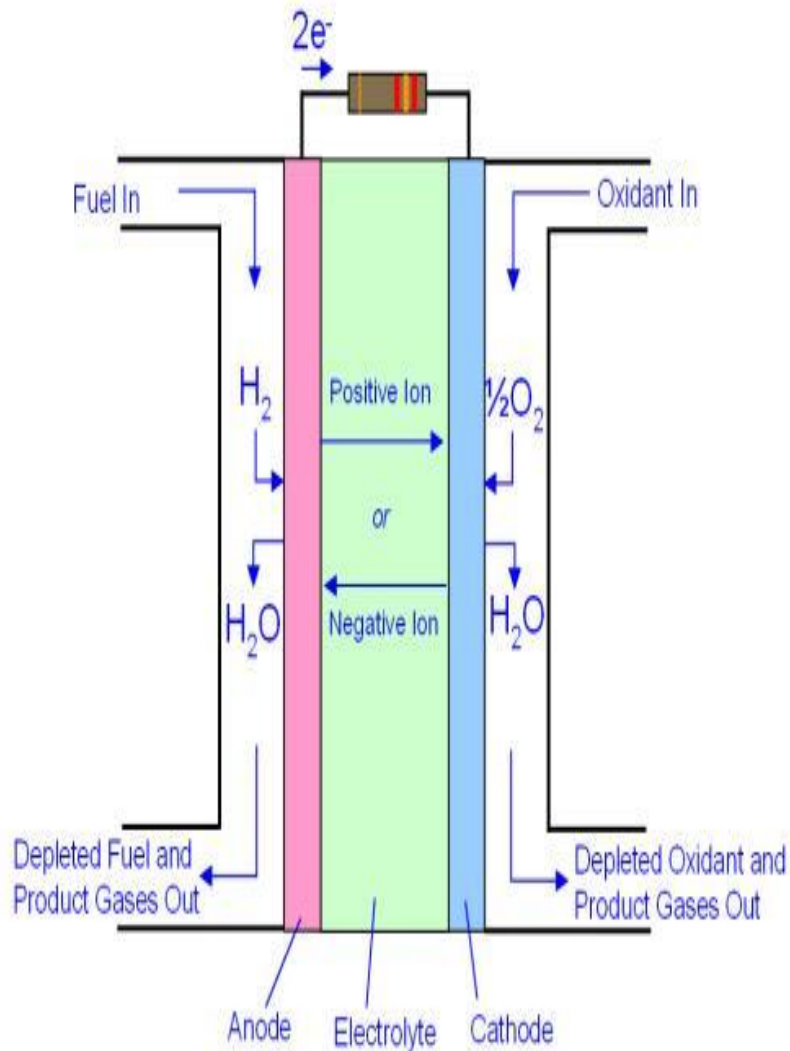


Anode :

- Porous carbon electrode embedded with a catalyst such as finely divided platinum or palladium.
- hydrogen gas is diffused through the electrode

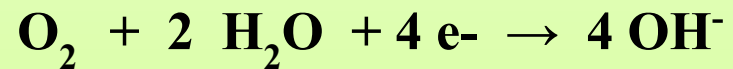
Anodic reaction





Cathode:

- porous carbon electrode, impregnated with cobalt oxide, platinum or silver as catalyst.
- oxygen is diffused through cathode.
- The two electrodes are separated by electrolyte such as KOH solution.
- **Cathodic reaction**

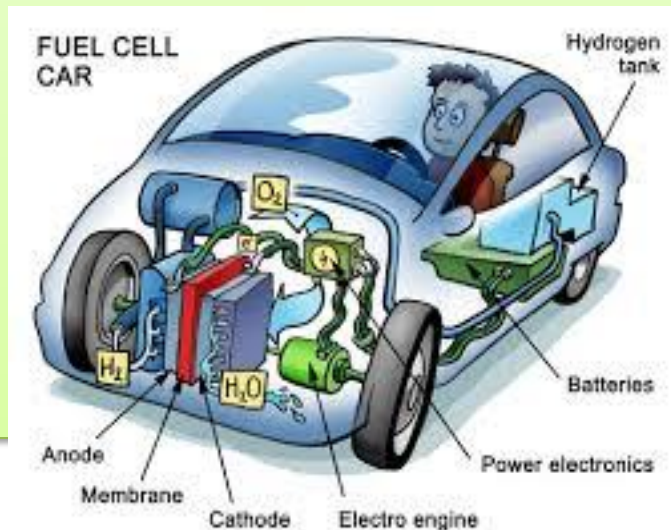


Overall cell reaction



Advantages

1. high efficiency
2. ability to operate on a variety of hydrocarbon fuels
3. no objectionable emissions
4. lesser land requirement compared to conventional power plants
5. direct energy conversion
6. without intermediate wastage as heat.



UNIT II: PHOTOCHEMISTRY AND SPECTROSCOPY

Lecture session 10: Introduction to electromagnetic radiation and its properties

INTRODUCTION:

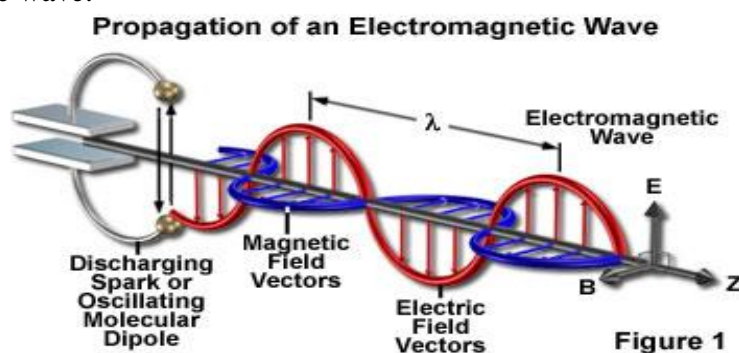
Electromagnetic radiation

Electromagnetic radiation is a form of energy that propagates in free space or through a medium at enormous velocities, which have a dual nature. Light consists of EMRs, which travels in the form of waves. In such a wave, time-varying electric and magnetic fields are mutually linked with each other at right angles and perpendicular to the direction of motion.

General Properties of Electromagnetic Radiation (EMR)

- **EMR** - looked at as sinusoidal waves - composed of a combination of two fields
- **Electric field** - to explain absorption and emission of radiation by analytes
- **Magnetic field at right angle to the electric field** - to explain phenomena - nuclear magnetic resonance in the course of special topics in analytical chemistry.
- **Wavelength (λ) of EMR wave** – inversely related to its energy
- It is defined as a distance between two consecutive maxima or two consecutive minima on the wave. Unit– cm, mm, μm , nm and Angstrom
- **Amplitude (A)** - length of the vector at a maximum or minimum in the wave.

In Fig.1, amplitude - length of any of the vertical arrows perpendicular to the direction of propagation of the wave.



Maxwell (1864) found that the electromagnetic radiation is made up of two mutually perpendicular oscillating electric and magnetic fields in planes at right angles to each other as shown in figure 1.

Frequency of EMR wave - directly proportional to the energy of the wave.

- Defined as the number of wavelengths passing a fixed point in space in one second. unit – s^{-1} or Hz (number of waves per unit time of EMR)

- Period of EMR wave - time in seconds required for one wavelength to pass a fixed point in space
- Frequency of the wave - a constant - a property of the source,
- Decrease in velocity of electromagnetic radiation in media other than vacuum - Attributed to a decrease in the wavelength of radiation upon passage through that medium.

Velocity (c) of EMR wave - The distance travelled by the wave in one second. It is denoted by c , where, $c = v\lambda$, (Velocity (c) = 18600 miles per second). Velocity of light in vacuum - greater than its velocity in any other medium. The velocity in light in vacuum is $3 \times 10^8 \text{ ms}^{-1}$.

Wavenumber (ν) - The number of waves per unit length (cm). it is equal to the reciprocal of wavelength in cm. Unit - cm^{-1} .

The three main wave properties such as wavelength, frequency and wave number are correlated by the equation,

$$v = c/\lambda = c\nu$$

According to Planck's Quantum theory, EMR propagates in a space not in continuous manner but in discrete energy packets called quanta.

The energy associated with one packet, i.e one quanta is

$$E = h\nu = hc/\lambda = h\nu$$

Hence, the emission or absorption of energy also takes place in discrete instalments of energy i.e quanta

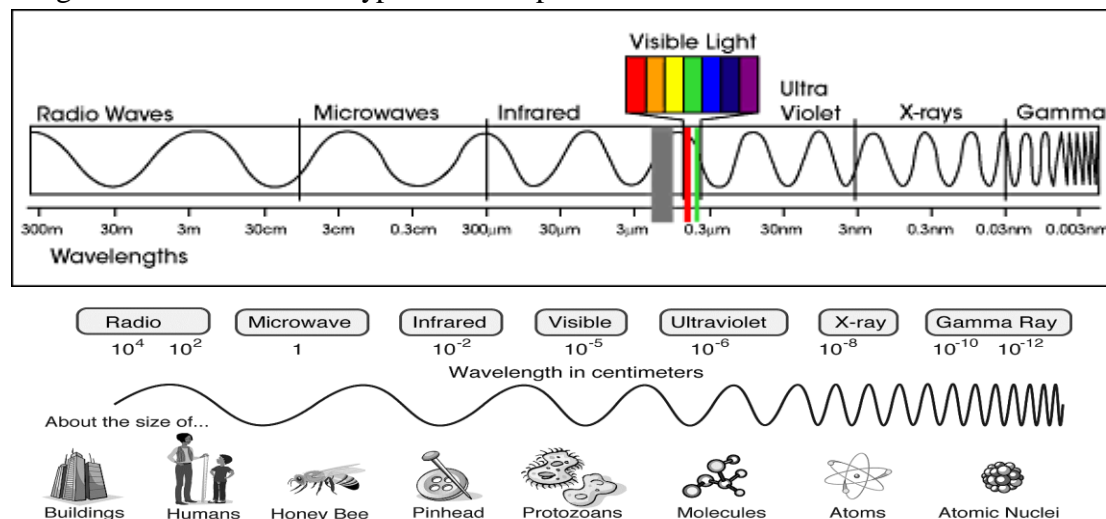
Electromagnetic Spectrum

The arrangement of all types of EMRs in order of their increasing wavelengths or decreasing frequencies

rays, X-rays, Far UV, UV, Visible, Near IR, IR, Far IR, Microwave, Radio frequency

- EMR - a vast spectrum of frequencies and wavelengths.
- EMR spectrum includes the very energetic gamma-rays radiation with a wavelength range from $0.005 - 1.4 \text{ \AA}$ to radio waves (RW) in the wavelength range up to meters (exceedingly low energy).
- Region of interest - very limited range from 180-780 nm.
- This limited range covers both ultraviolet and visible radiation.

Diagram below shows the typical EMR spectrum



Lecture session 11: Photochemistry– Photochemical reactions with examples – difference between photochemical and thermal reaction

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions. The visible and UV radiations (2000-8000Å wavelength) are mainly used in photochemical reactions.

Thermochemical reactions (dark reactions) are brought about by molecular collisions. These reactions are spontaneous and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy.

Example: Chemical reactions, which take place by the absorption of heat are called thermal reactions.

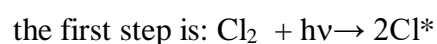


Dark Reactions

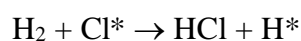
The chemical reactions, which take place in the absence of light, are called dark reactions.

Example: plant metabolism, Protein activity and cellular metabolism

All **photochemical reactions** take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change. For example, in the combination of hydrogen and chlorine,



The activated chlorine atoms (Cl^*) then undergoes chemical reaction

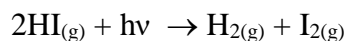


It is evident from the above reaction that the second step can occur in absence of light.

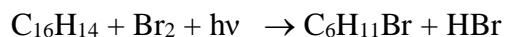
Simple reactions involving combination, decomposition, polymerization, oxidation and reduction can be brought about by exposure to such radiations (lower energy).

Examples:

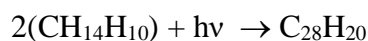
1. Dissociation reaction



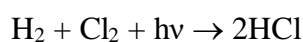
2. Double decomposition reaction



3. Polymerization reaction



4. Chain reaction



Characteristics of photochemical reaction:

1. Photochemical reactions take place by absorption of light.
2. When a light composing number of colours are used, the photochemical reaction may not be initiated by all colours.
3. The free energy change (ΔG) of a photochemical reaction may be either negative or positive.

Differences between photochemical and thermal reactions:

S. No.	Photochemical reactions	Thermochemical reactions
1.	These involve the absorption of light.	These involve either absorption or evolution of heat.
2.	Take place in presence of light.	Take place in dark or in presence of light.
3.	They are independent of temperature.	They are dependent of temperature. Rate of reactions is not affected by the intensity of light.
4.	Rate of reactions is dependent on the intensity of the light absorbed.	The free energy change is always negative
5.	The free energy change is negative or positive.	

Lecture session 12: Laws of Photochemistry - Grotthus – Draper law, Stark–Einstein law and Beer-Lambert Law – Applications and Limitations

LAWS OF PHOTOCHEMISTRY:

Grotthus-Draper Law (or) The Principle of Photochemical Activation:

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change.

However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be re-emitted as heat or light or it remains unused.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon).

When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Some important relations:

Photons	≡	quanta
One molecule absorbs	≡	one photon
One mole of a substance		one mole of quanta (or)
Containing 6.023×10^{23}	≡	6.023×10^{23} quanta of
(Avogadro number)		light (or) one Einstein
Molecules absorbs		

$$\begin{aligned}\text{One Einstein} &= N h \nu \\ &= N h c / \lambda [\because \nu = c / \lambda]\end{aligned}$$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation $E = h \nu = h c / \lambda$, where, h – Planck's constant (6.625×10^{-34} Js; c – velocity of light = 3.0×10^8 ms⁻¹; λ – wavelength of light.

The energy of an Einstein E, is an Avogadro number (N) of photons. It is given as $E = N h c / \lambda$. On substituting the values in the above equation it becomes

$$E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-34}) \times (3 \times 10^8) / \lambda \text{ J mol}^{-1} = 0.1196 / \lambda \text{ J mol}^{-1} \text{ in SI units}$$

In CGS units: $c = 3 \times 10^{10} \text{ cm s}^{-1}$; $h = 6.625 \times 10^{-27} \text{ erg s}^{-1}$

$$\therefore E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/\lambda \text{ erg mol}^{-1} = 1.196 \times 10^{16}/\lambda \text{ (in } \text{Å}) \text{ erg mol}^{-1}$$

$$1 \text{ cal} = 4.184 \times 10^7 \text{ ergs}$$

$$\therefore E = 1.196 \times 10^8/4.184 \times 10^7/\lambda \text{ cal mol}^{-1} \\ = 2.859/\lambda \text{ cal mol}^{-1}$$

If l is expressed in Å , then $E = 2.859 \times 10^8/\lambda \text{ (in } \text{Å}) \text{ cal mol}^{-1}$
 $= 2.859 \times 10^5/\lambda \text{ (in } \text{Å}) \text{ kcal mol}^{-1}$

LAMBERT's LAW: When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically, it may be stated as follows

$$-dI/dl \propto I \text{ (or)} \quad -dI/dl = kI \text{ ----- (1)}$$

Where I = the intensity of incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating equation 1 and putting $I = I_0$ when $l = 0$, we get

$$\ln I_0/I = kl \text{ (or)} \quad I = I_0 e^{-kl} \text{ ----- (2)}$$

BEER's LAW: The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0 e^{-kc} \text{ ----- (3)}$$

On combining both laws, we get $\log I_0/I = \epsilon cl$ ----- (4)

The equation 4 is termed as mathematical statement of Beer-Lambert's law. In the above equation ϵ = the molar absorption coefficient

$A = \log I_0/I$ is the absorbance (or) optical density (OD)

APPLICATION OF BEER-LAMBERT'S LAW

Determination of unknown concentration

First absorbance A_s of a standard solution of known concentration C_s is measured, then according to Beer-Lambert's law

$$A_s = \epsilon C_s x$$
$$A_s/C_s = \epsilon x \dots\dots\dots 1$$

Now, absorbance A_u of a solution of unknown concentration C_u is measured. Now we have

$$A_u = \epsilon C_u x$$
$$A_u/C_u = \epsilon x \dots\dots\dots 2$$

From equation 1 and 2, we get

$$A_s/C_s = A_u/C_u$$
$$\therefore C_u = A_u/A_s \times C_s \dots\dots\dots 3$$

Since the values of A_u and A_s are experimentally determined and C_s is known. The value C_u (unknown concentration) can be calculated from the equation 3

Limitations of Beer-Lambert's law:

The law is not valid

- ✓ Beer-Lambert's law is not obeyed if the radiation used is not monochromatic.
- ✓ It is applicable only for dilute solutions.
- ✓ The temperature of the system should not be allowed to vary to a large extent.
- ✓ It is not applied to suspensions.
- ✓ Deviation may occur, if the solution contains impurities.
- ✓ Deviation also occurs if the solution undergoes polymerization (or) dissociation.

Lecture session 13: Beer-Lambert Law – problems; determination iron by spectrophotometer

Problems:

1. A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, given $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Solution:

Transmittance, $I/I_0 = 0.4$ or $I_0/I = 2.5$; $\epsilon = 6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; l or $x = 2 \text{ cm}$

$$\text{Log } I_0/I = \text{Log } 2.5 = 0.3980 = \epsilon Cl$$

$$C = (0.3980/6000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times 2 \text{ cm}$$
$$= 3.316 \times 10^{-5} \text{ mol dm}^{-3}.$$

2. Calculate the optical density, if 10 % of incident light is transmitted

Solution:

$$\text{Optical density, } A = \text{Log } (I_0/I) = \text{Log } (100/10) = \text{log } (10) = 1.0$$

3. Calculate the molar absorptivity of a $1 \times 10^{-4} \text{ M}$ solution, which has an absorbance of 0.2, when the path length is 2.5 cm

Solution:

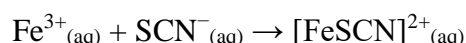
Here $A = 0.20$; $l = 2.5 \text{ cm}$; $C = 1 \times 10^{-4} \text{ mol dm}^{-3}$

Therefore absorptivity,

$$\epsilon = A/Cl = 0.20/(1 \times 10^{-4} \text{ mol.dm}^{-3} \times 2.4 \text{ cm}) = 8000 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$$

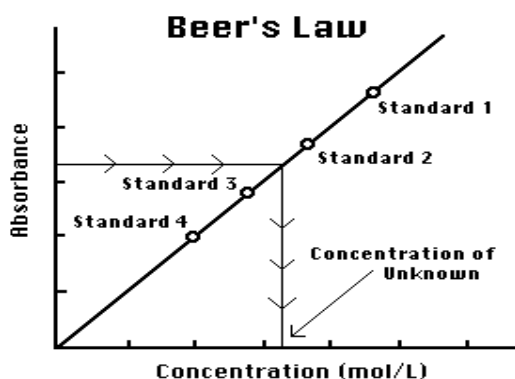
Estimation of Iron by colorimetry

In this analysis the iron present in a sample, form a solution containing Fe^{3+} (ferric) ions. To make the presence of these ions in solution visible, thiocyanate ions (SCN^-) are added. These react with the Fe^{3+} ions to form a blood-red coloured complex:



By comparing the intensity of the colour of this solution with the colours of a series of standard solutions, with known Fe^{3+} concentrations, the concentration of iron in solution may be determined. This technique is called colorimetry.

1. Using only the absorbance results obtained for your Fe^{3+} standard solutions (not your unknown iron sample), prepare a graph with $[\text{Fe}^{3+}]$ (in mol L^{-1}) as the horizontal axis and absorbance (at 490 nm) as the vertical axis. Before doing experiment, the colorimeter is set to be zero absorbance for blank solution.
2. Draw a line of best fit for your data points that go through the origin (because absorbance must be zero when Fe^{3+} concentration is zero). This is called as calibration curve, which obeys Beers-Lamberts Law.
3. Now identify the point on your line of best fit which corresponds to the absorbance measured for your unknown iron sample. By drawing a vertical line to the horizontal axis you will be able to determine the concentration of Fe^{3+} in your unknown solution.
4. Use this concentration to calculate the mass of iron (in mg) in your original sample
5. If the absorbance value you measured for your unknown iron sample is greater than the absorbance value for your highest concentration Fe^{3+} standard you will need to modify the above procedure. In the case of an iron tablet, you should repeat the analysis with a more dilute solution of iron samples.



Lecture session 14: Quantum efficiency (Φ) - classification of reactions based on quantum yield – Reason for high and low quantum yield

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency (ϕ) is introduced.

Quantum yield is defined as “the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in \AA ; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

$$\text{Number of Einstein's absorbed} = q/(Nhc/\lambda) = q\lambda/Nhc$$

$$\therefore \text{Quantum yield, } \phi = n/(q\lambda/Nhc) = nNhc/q\lambda$$

$$\text{In CGS units, } \phi = n/q \times [1.196 \times 10^{16}/\lambda \text{ (in } \text{\AA})]$$

Classification of photochemical reaction based on quantum yield:

Based on quantum yield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1, 2.
Examples: a) Dissociation of HI & HBr; b) Combination of $\text{SO}_2 + \text{Cl}_2$ and c) Ozonisation of O_2 .
2. The reaction in which the quantum yield is less than 1.
Examples: a) Dissociation of NH_3 , CH_3COCH_3 & NO_2 ; b) Transformation of maleic acid into fumaric acid.
3. The reaction in which the quantum yield is extremely high.
Examples: a) Combination of $\text{CO} + \text{Cl}_2$; b) Combination of $\text{H}_2 + \text{Cl}_2$.

High (or) Low Quantum Yield:

The quantum efficiency varies from zero to 10^6 . If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield $\phi = 1$.

High Quantum Yield: When two or more molecules are decomposed per photon, the quantum yield $\phi > 1$ and the reaction has a high quantum yield.

Low Quantum Yield: When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfill the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.
2. The reactivity of the molecules should be temperature independent.
3. The molecules in the activated state should be largely unstable and decompose to form the products.

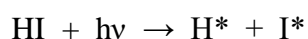
Causes (or) Reasons for high quantum yield:

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
2. Formation of intermediate products will act as a catalyst.
3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

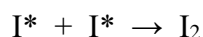
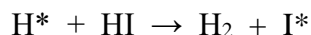
Examples:

1. Decomposition of HI: In the primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

Primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I.



secondary reaction



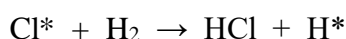
The overall reaction shows that the two HI are decomposed for one photon ($h\nu$).

Thus, the quantum yield (ϕ) = $2/1=2$

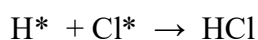
2. Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon and dissociates into two Cl atoms. This is followed by the secondary reaction as shown below:



Secondary reaction:



The Cl atom consumed in step 2 is regenerated in step 3..... this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.



Thus the quantum yield varies from 10^4 to 10^6

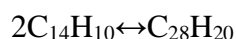
Causes (or) Reasons for low quantum yield:

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to enable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene



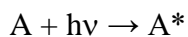
The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.



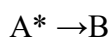
Processes of photochemical reactions: The overall photochemical reaction consists of

i) *Primary reaction* and ii) *Secondary reaction*.

i. In the primary reaction, the quantum of light is absorbed by a molecule 'A' resulting in the formation of an excited molecule A*.



ii. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.



Photochemical Decomposition of HI: It takes place in the radiation of wave length between 2070 Å - 2820 Å. The quantum yield of the reaction is found to be closer to 2.0.

**Lecture session 15: Jablonski Diagram - Internal conversion - Inter-system crossing
Fluorescence & Phosphorescence**

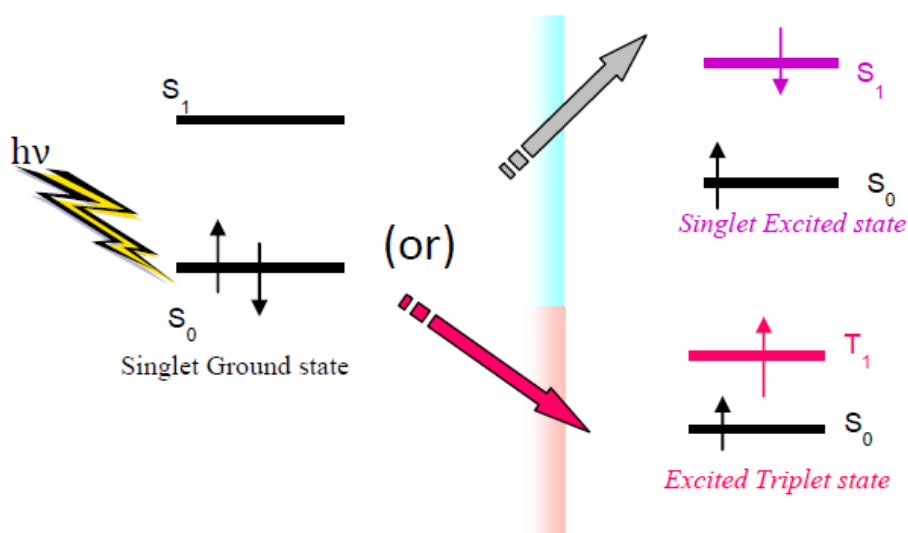
Mechanism of Photophysical Processes (or) Mechanism of Fluorescence and Phosphorescence (or) Jablonski Diagram

Most molecules possess an even number of electrons and all the electrons are paired in ground state. The spin multiplicity of a state is given by $2S + 1$, where S is the total electronic spin.

i) When the spins are paired ($\uparrow\downarrow$), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$$S = s_1 + s_2 = (1/2) - (1/2) = 0$$

$\therefore 2S + 1 = 1$, ie., spin multiplicity is 1. The molecule is in the singlet ground state.



ii) On absorption of a suitable energy, one of the paired electrons goes to a higher energy level. The spin orientation of the two electrons may be either

a) parallel ($\uparrow\uparrow$), then $S = s_1 + s_2 = (1/2) + (1/2) = 1$, $\therefore 2S + 1 = 3$, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

b) or anti-parallel ($\uparrow\downarrow$), then $S = s_1 + s_2 = (1/2) - (1/2) = 0$, $\therefore 2S + 1 = 1$, ie., spin multiplicity is 1. The molecule is in the singlet (S) excited state.

Since the electron can jump from the ground state to any of the higher electronic states depending upon the energy of the photon absorbed we get a series of

a) singlet excited states ie., S_1, S_2, S_3 , etc., (first singlet excited state, second singlet excited state, third singlet excited state, etc.) and

b) triplet excited states ie., T_1, T_2, T_3 , etc., (first triplet excited state, second triplet excited state, third triplet excited state, etc.).

Generally singlet excited state has higher energy than the corresponding triplet excited state. Thus, the energy sequence is as follows: $E_{S1} > E_{T1} > E_{S2} > E_{T2} > E_{S3} > E_{T3}$ and so on.

When a molecule absorbs light radiation, the electron may jump from S_0 to S_1, S_2 (or) S_3 singlet excited state depending upon the energy of the light radiation as shown in Jablonski diagram. For each singlet excited state there is a corresponding triplet excited state, ie. $S_1 \rightarrow T_1; S_2 \rightarrow T_2; S_3 \rightarrow T_3$, etc.

The molecule, whether it is in singlet or triplet excited state, is said to be activated. Thus,

$A_0 + h\nu \rightarrow A^*$ where A_0 – ground state molecule and A^* - excited state molecule.

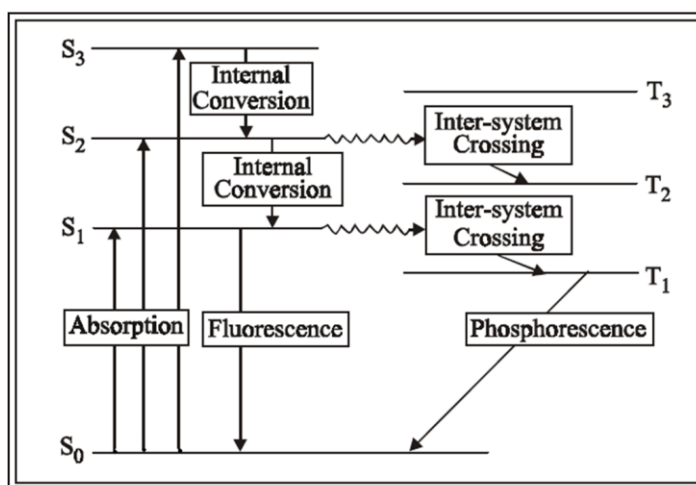
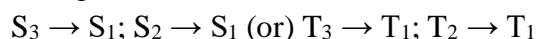


Fig. 3.5 Jablonski diagram of various photophysical processes

Types of transitions: The activated molecules returns to the ground state by emitting its energy through the following general types of transitions.

1. **Non-radiative transitions** do not involve the emission of any radiations, so these are also known as non-radiative or radiationless transitions. Non-radiative transitions involve the following two transitions.

a. **Internal conversion (IC):** These transitions involve the return of the activated molecule from the higher excited states to the first excited states, ie.



The energy of the activated molecule is given out in the form of heat through molecular collisions. This process is called internal conversion (IC) and occurs in less than about 10^{-11} second.

b. **Inter system crossing (ISC):** The molecule may also lose energy by another process called inter system crossing (ISC). These transitions involve the return of the activated molecules from the states of different spins ie. Different multiplicity ie., $S_2 \rightarrow T_2$; $S_1 \rightarrow T_1$. These transitions are forbidden, occurs relatively at slow rates.

2. **Radiative transitions** involve the return of activated molecules from the singlet excited state S_1 and triplet state T_1 to the ground state S_0 . These transitions are accompanied by the emission of radiations. Thus, radiative transitions involve the following two radiations.

a. **Fluorescence:** The emission of radiation due to the transition from singlet excited state S_1 to ground state S_0 is called fluorescence ($S_1 \rightarrow S_0$). This transition is allowed transition and occurs in about 10^{-8} second.

b. **Phosphorescence:** The emission of radiation due to the transition from the triplet excited state T_1 to the ground state S_0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition.

3. **Quenching of fluorescence:** The fluorescence may be quenched, when the excited molecule collides with a normal molecule before it fluoresces. During quenching, the energy of the excited molecule gets transferred to the molecule with which it collides. Quenching occurs in two ways.

a. **Internal quenching:** Quenching may also occur, when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching.

b. **External quenching:** Quenching may also occur from the addition of an external substance, which absorbs energy from the excited molecule. This phenomenon is called external quenching.

Time scale for different photo physical process is given below

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Lecture session 16: Photosensitization – Mechanism and examples - quenching Difference between Fluorescence and Phosphorescence

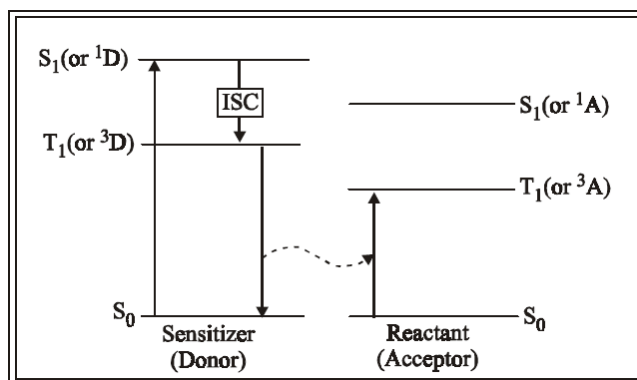
ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS:

Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction.

1. **Photosensitization:** The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,
 - i) Atomic photosensitizers : mercury, cadmium, zinc and
 - ii) Molecular photosensitizers: benzophenone, sulphur dioxide.
2. **Quenching:** When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

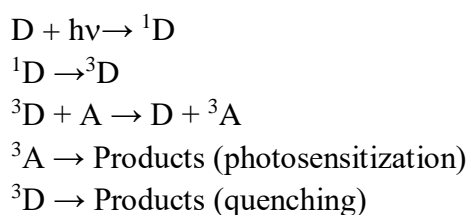
Mechanism of Photosensitization and Quenching can be explained by considering a general donor (D) and acceptor (A) system. In a donor-acceptor system, the donor D (sensitizer)

absorbs the incident photon and gets excited from ground state (S_0) to singlet state (S_1). Then the donor attains the triplet excited state (T_1 or 3D). The triplet state of the donor is higher than the triplet state of the acceptor (A). This triplet excited state of the donor collides with the acceptor produces the triplet excited state of the acceptor (3A) and returns to the ground state (S_0). If the triplet excited state of the acceptor (3A) gives the desired products, the mechanism is called photosensitization. If the products are resulted directly from the excited state of the donor (3D), then A is called quencher and the process is called quenching.



Mechanism of photosensitization:

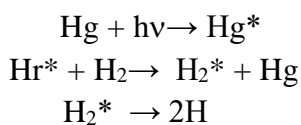
The sequence of photosensitization and quenching may be represented as follows:



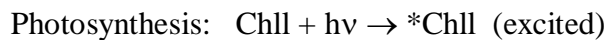
It is necessary that the energy of the triplet excited state of the donor (sensitizer) must be higher than the triplet excited state of the acceptor (reactant). Thus the energy available is enough to excite the reactant molecule to its excited state. The dotted line indicates the transfer of energy from the sensitizer to reactant.

Examples for photosensitized reactions:

1. **Dissociation of hydrogen molecule:** UV light does not dissociate H_2 molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.



2. **Photosynthesis in plants:** During photosynthesis of carbohydrates in plants from CO₂ and H₂O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO₂ and H₂O molecules, which then react to form glucose.



In the presence of light and chlorophyll ΔG° becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG° for this reaction is +2875 kJ. Since ΔG° is positive, the above reaction is not possible.

PHOTOPHYSICAL PROCESS: Generally atoms or molecules go to excited state by the absorption of suitable radiation. If the absorbed radiation is not used to cause a chemical reaction, it will be re-emitted as light of longer wavelength. This process is called as photophysical process.

Types of photophysical process:

Photophysical process is of two types,

- i) Fluorescence and
- ii) Phosphorescence.

i) **Fluorescence:**

When a molecule or atom absorbs radiation of higher frequency (shorter wavelength), it gets excited. Then the excited atom or molecule re-emits the radiation of the same frequency or lower frequency within short time (about 10^{-8} sec.). This process is called fluorescence, stops as soon as the incident radiation is cut off. The substance which exhibits fluorescence is called fluorescent substance.

Examples: CaF₂, uranium, petroleum, organic dyes like eosin, fluorescein), chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.

Types of fluorescence:

a) **Resonance fluorescence:** If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence.

Example, when mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited. Subsequently, when it returns to its ground state, it emits radiation of the same frequency, which it absorbed.

b) **Sensitized fluorescence:** If the molecule is excited, due to the transfer of part of excitation energy from the foreign substance, it emits the radiation of lower frequency, the process is known as sensitized fluorescence.

Example, if the mercury vapour is mixed with the vapours of silver, thalium, lead or zinc, which do not absorb radiation at 253.7 nm and then exposed to the radiation, a part of the excitation energy from mercury is transferred and gets excited to higher energy state. When it returns to its ground state, it emits radiation of lower frequency.

- ii) **Phosphorescence:** When a substance absorbs radiation of higher frequency, the emission of radiation is continuous for some time even after the incident light is cut off. This process is called phosphorescence (or) delayed fluorescence. The substance which shows phosphorescence is called phosphorescent substance.

Differences between fluorescence and phosphorescence

Fluorescence	Phosphorescence
1. Its decay period is much longer, $10^{-4} - 100$ s.	Its decay period is very short, $10^{-9} - 10^{-4}$ sec.
2. It is the radiation emitted in a transition between states of different multiplicity.	It is the radiation emitted in a transition between states of same multiplicity.
3. It is not observed in solution at room temperature.	It can be observed in solution at room temperature.
4. Its spectrum is mirror image of the absorption spectrum.	Its spectrum is not mirror image of the absorption spectrum.
5. It is exhibited by some elements in vapour state.	It is rarely observed in gaseous or vapours.
6. Examples: uranium, petroleum, organic dyes, chlorophyll, CaF_2 , etc.	Examples: ZnS , sulphides of alkaline earth metals.

Lecture session 17: Photochemical reaction kinetics with example

Photochemical equilibrium

In some photochemical reactions, equilibrium is maintained in the reactants and the product of the decomposition. The forward reaction in most cases is indicated by light, while the backward reaction by dark

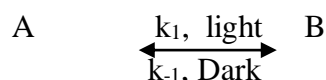


The quantum yields of the two processes in some case are different. This is known as photochemical equilibrium or photostationary state.

Photochemical equilibrium is different from the normal thermal equilibrium, since the energy in case of photochemical equilibrium is provided through the absorbed radiation

Equilibrium constant

Consider the reaction which is light in forward direction and dark/thermal sensitive in reverse direction



Rate of the forward reaction = $k_1 I_{abs}$

Rate of the reverse reaction = $k_{-1} C_B$

At equilibrium: $k_1 I_{abs} = k_{-1} C_B$

$$K = \frac{k_{-1}}{k_1} = \frac{I_{abs}}{C_B}$$

Hence, photochemical equilibrium constant K, is directly proportional to the intensity of the light absorbed.

Example

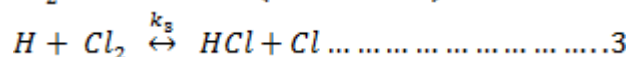
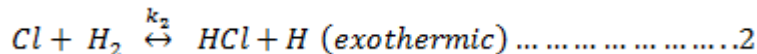
Kinetics of photochemical synthesis of HCl

This reaction is accompanied by exceptionally high quantum yield ranging from $10^4 - 10^6$ in the light of wavelength 4800\AA . Nernst gave a chain mechanism, which is universally accepted now-a-days

When exposed to the light of wavelength 4785\AA , the primary step I photochemical dissociation of Cl molecule

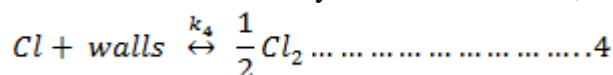


The other stages are



The Cl atom is generated in Eq. 3 again reacts with hydrogen molecule to follow the reaction as in eq. 2 and 3 to occur again and the chain is propagated in this way. Therefore, the quantum yield of the reaction is high as compared to hydrogen-bromine reaction, which is characterized by an endothermic process.

It was found that in absence of oxygen, the rate of the reaction is proportional to the intensity of the light absorbed. The chain is terminated by the reaction vessel, i.e.,



The rate of formation of HCl may be calculated by the fact that is formed in eq. 2 and 3. Thus k_1, k_2, k_3 and k_4 be the rate constants, then:

$$\frac{d[HCl]}{dt} = k_2 [Cl] [H_2] + k_3 [H] [Cl_2] \dots \dots \dots 5$$

For Cl atom: Considering the stationary state, the Cl atom is formed in eq. 1 and 3 and removed in eq 2 and 4, so it follows

$$k_1 I_{abs} + k_3 [H][Cl_2] = k_2 [Cl][H_2] + k_4 [Cl] \dots \dots \dots 6$$

For Hydrogen atom: Similarly, hydrogen atoms are formed in eq.2 and removed by eq.3. For the stationary state, we have:

$$k_2 [Cl] [H_2] = k_3 [H] [Cl_2] \dots \dots \dots 7$$

Eq.6 + eq.7 gives:

$$k_1 I_{abs} = k_4 [Cl]$$

$$[Cl] = \frac{k_1 I_{abs}}{k_4} \dots \dots \dots 8 \text{ or}$$

Substituting the value of [Cl] in eq. 7, we get

$$k_2 [H_2] \frac{k_1 I_{abs}}{k_4} = k_3 [H] [Cl_2]$$

$$[H] = \frac{k_2 [H_2]}{k_3 [Cl_2]} \cdot \frac{k_1 I_{abs}}{k_4} \dots \dots \dots 9 \text{ or}$$

Now Substituting the values of [Cl] and [H₂] from eq. 8 and 9 in eq. 5, we get

$$\begin{aligned} \frac{d[HCl]}{dt} &= k_2 [H_2] \frac{k_1 I_{abs}}{k_4} + k_3 [Cl_2] \cdot \frac{k_2}{k_3} \cdot \frac{k_1 [H_2] \cdot I_{abs}}{k_4 [Cl_2]} \\ &= k_1 k_2 \frac{[H_2] \cdot I_{abs}}{k_4} + k_1 k_2 \frac{[H_2] \cdot I_{abs}}{k_4} \end{aligned}$$

Or

$$\frac{d[HCl]}{dt} = 2 \cdot k_1 k_2 \frac{[H_2] \cdot I_{abs}}{k_4} \dots \dots \dots 10$$

Or

$$\frac{d[HCl]}{dt} = k [H_2] \cdot I_{abs}$$

Where, $k = \frac{k_1 k_2}{k_4}$

i.e., the rate of the formation of HCl is directly proportional to the intensity of light absorbed

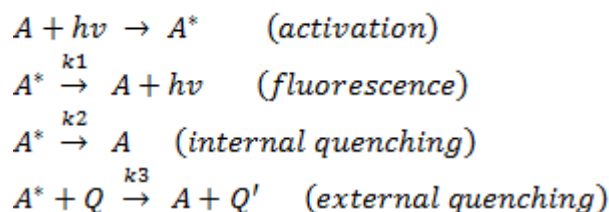
Lecture session 17: Stern-Volmer relationship and Applications of photochemistry

Stern-Volmer relationship

Fluorescence may be quenched (i.e., stopped) when the excited state species undergoes collision with a normal molecule before it has the chance to fluoresce. The quenching of fluorescence occurs because of the energy transfer from the excited state species to the molecule with which it collides.

Quenching may also occur when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching. Quenching may also result from the presence of an externally added species which takes up energy from the

excited state molecule. This phenomenon is called external quenching. If Q is the quencher, we may then write :



By applying s.s.a to A^* , we have

$$I_a = k_1[A^*] + k_2[A^*] + k_3[A^*][Q]$$

Where I_a is the intensity of light absorbed

If I_f represents the intensity of fluorescence, the quantum yield for the fluorescence is given by

$$\begin{aligned}
 \Phi_f \text{ or } \phi_q &= I_f/I_a = k_1[A^*] / (k_1[A^*] + k_2[A^*] + k_3[A^*][Q]) \\
 &= k_1 / (k_1 + k_2 + k_3 [Q])
 \end{aligned}$$

In the absence of the quencher, i.e., when $[Q]=0$, the quantum yield

$$\phi_0 = k_1/(k_1+k_2)$$

Hence, the ratio of the two quantum yields

$$\phi_0/\phi_q = (k_1+k_2+k_3[Q]) / (k_1+k_2) = 1 + (k_3 [Q] / k_1+k_2)$$

$$\text{Put } 1/k_2+k_2 = \tau$$

$$\phi_0/\phi_q = 1 + k_3 \tau [Q]$$

or

$$\phi_0/\phi_q = 1 + k_{sv}[Q]$$

$$\text{where, } K_{sv} = k_3\tau \text{ and } \tau = 1/(k_1+k_2)$$

This is known as a Stern-Volmer equation in which K_{sv} is called the Stern- Volmer constant, τ is lifetime of A^* in the absence of external quenching.

From stern-Volmer equation we see that ϕ_0/ϕ_q depends linearly on $[Q]$. The slop of the line gives $k_3\tau$ from which τ can be determined.

Applications of photochemistry

Photochemistry has many practical applications. One of the main branches in photochemistry is concerned with investigating different types of chemical reactions that occur when molecules are exposed to light.

In particular, photochemical studies have been used extensively for research on new drug development as well as solar energy conversion technology. Applications of photochemistry in everyday life include decontamination of drinking water, production of hydrogen fuel, and food processing, etc.

Decontamination of drinking water

When it comes to the treatment of drinking water, photochemistry is a very important part. It can be used in many different ways including purification and decontamination.

The first example of using the process for decontamination would be UV light being used on bacteria or viruses present in water tanks where no chemicals are able to dissolve properly yet. After this step has been completed, other steps involving filters that remove chemical particles could then take place.

Production of hydrogen fuel

Hydrogen is used in all types of gas turbines. Gas turbine technology is also being developed for vehicles, and these engines are the most efficient type so far available.

Splitting of water through photo catalyst is available now –a-days for the production of Hydrogen and Oxygen. The hydrogen fuel cells that power electric cars are another example of photochemistry.

The water molecules needed during this process can be provided by splitting them into their components with additional electricity from solar panels on the vehicle roof or other renewable sources plugged in when parked at home overnight.

Food processing

Photochemistry, the use of light for chemical reactions, is common in food processing. This can be used to either reduce or increase production time or potentially improve quality. The uses of photochemistry include:

- Draining liquid from brined foods; helps remove any excess salt after curing.
- Sterilization – exposure to ultraviolet radiation kills pathogens present on surfaces such as equipment that comes into contact with ready-to-eat food like salads. It does not interfere with the taste, smell, or texture of the product which makes it an efficient way to keep products safe once they are packed
- Slow down ripening processes by blocking certain wavelengths of light. This is a popular technique for extending the shelf life and improving the quality of foodstuffs such as tomatoes

- Increase shelf life by reducing the amount of oxygen in packaging which prevents oxidative rancidity.

Medicine

One of the most important uses for photochemistry in medicine is to create a photosensitizer. Photosensitizers are drugs that respond to light by becoming activated and killing cells, sometimes only cancerous cells. This can be used to kill bacteria or viruses, destroy diseased tissues such as tumors, treat skin conditions like psoriasis and eczema, or even combat arthritis.

Another medical application where photochemistry plays an important role is laser eye surgery. Lasers use light energy at high intensities so that it focuses on very specific parts of your cornea without damaging surrounding tissue. The lasers cut away sections of the cornea using heat generated from photo-acoustic waves caused when photons interact with water molecules.

Environment protection

There are several ways photochemistry is used to protect the environment. One way is used to detect and identify pollutants in water. Water molecules that contain impurities absorb ultraviolet (UV) radiation, which results in a change of wavelength for the emitted fluorescent photons. This can be measured by instruments called fluorometers, which output an electronic signal indicating the presence of certain materials such as sewage or oil spills. The more intense this fluorescence, the higher level of contamination present.

Photography

Silver halide photographic film uses a chemical reaction involving light to create an image on the film. In modern photography, there are three types of films: black and white negative (neg), color reversal camera negative (reversal) and color print paper positive (print). Photography is also found in printing processes such as digital photo printers which use lasers to expose photosensitive materials before developing them into prints that can be viewed under visible light or projected onto screens with slide projectors.

Because photochemistry has been around for so long it has become a fundamental process involved in most aspects of everyday life from how we produce food through refrigeration all the way up to advanced scientific research.

NANOCHEMISTRY

INTRODUCTION

Nanochemistry is the study of chemistry at the nanoscale. One nanometer (nm) is one billionth of a meter, so nanochemistry deals with materials and structures that are between 1 and 100 nanometers in size. This is the size range where materials exhibit unique properties that are different from their bulk counterparts.

For example, gold nanoparticles are much more catalytically active than bulk gold. This is because the small size of the nanoparticles gives them a high surface area to volume ratio, which means that there are more atoms on the surface of the nanoparticles that can react with other molecules.

Nanochemistry is a rapidly growing field with applications in a wide range of areas, including electronics, energy, medicine, and environmental science. For example, nanomaterials are being used to develop new types of solar cells, batteries, and drug delivery systems.

Here is a summary of the introduction to nanochemistry that you provided:

- **The prefix "nano" means one billionth.**
- **Atoms are very small, with diameters ranging from 0.1 to 0.5 nanometers.**
- **Nanochemistry deals with structures of matter that are between 1 and 100 nanometers in size.**
- **Materials at the nanoscale exhibit unique properties that are different from their bulk counterparts.**
- **Nanochemistry is a rapidly growing field with applications in a wide range of areas.**

Nanoparticles

Nanoparticles are particles with a size of 1-100 nanometers (nm). They are often obtained as colloids, which are suspensions of particles in a liquid. Colloidal nanoparticles have a tendency to remain single crystals, and hence are called nanocrystals. A large percentage of atoms in nanocrystals are present on the surface, which gives them unique electronic, magnetic, and optical properties. Nanoparticles can also be called quantum dots, because they exhibit electronic behavior governed by quantum physics.

Nanomaterials

Nanomaterials are materials having components with a size less than 100 nm in at least one dimension. They can be categorized into one-dimensional (layers), two-dimensional (tubes), and three-dimensional (particles) nanomaterials. Some examples of nanomaterials include:

- **Inorganic nanomaterials:** metal nanomaterials (Ag, Au, Al, Cd, Cu, Fe, Zn, Pb), metal oxide nanomaterials (ZnO, CuO, MgAl₂O₄, TiO₂, CeO₂, Fe₂O₃, SiO₂, Fe₃O₄)
- **Carbon-based nanomaterials:** graphene, fullerene, single-walled carbon nanotube, multiwalled carbon nanotube, carbon fiber, activated carbon, carbon black
- **Organic nanomaterials:** dendrimers, cyclodextrin, liposome, micelle
- **Composite nanomaterials:** any combination of metal, metal oxide, carbon, and/or organic nanomaterials

Nanochemistry

Nanochemistry is the study of chemistry at the nanoscale. It is a highly interdisciplinary field, drawing on concepts from chemistry, physics, materials science, and biology. Nanochemistry is concerned with the synthesis, characterization, and properties of nanomaterials. It also investigates the unique chemical and physical interactions that occur at the nanoscale.

Nanotechnology

Nanotechnology is the application of nanochemistry to the design and construction of devices, materials, and systems at the nanoscale. It is a rapidly developing field with a wide range of potential applications in areas such as electronics, medicine, energy, and environmental science.

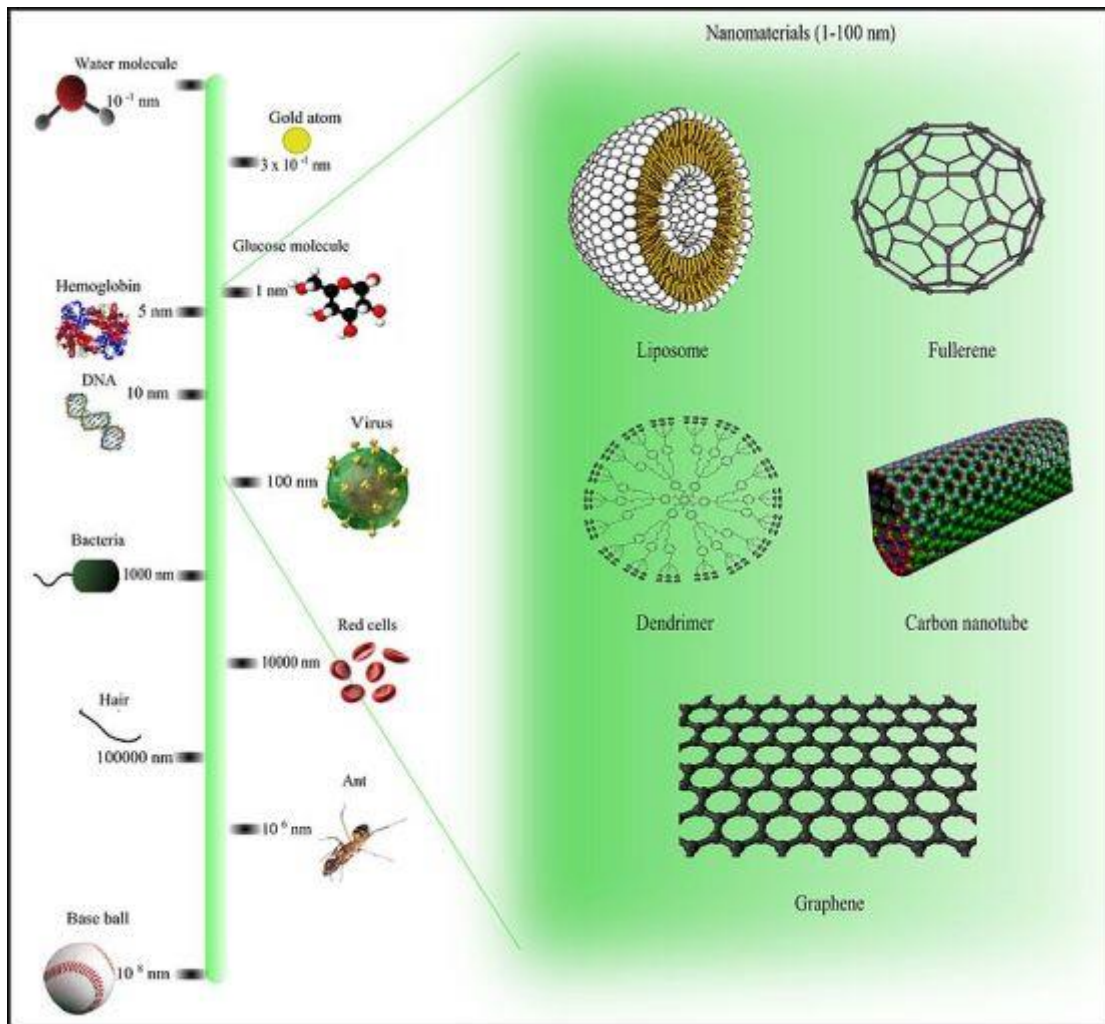


Figure 01: Comparison between Nanomaterials and Bulk Materials

There are many applications of these materials in various manufacturing processes, healthcare applications, various products including paints, filters, lubricant additives, etc. For example, nanozymes are substances that are nanoparticles, and they have enzyme-like characteristics.

What are Bulk Materials?

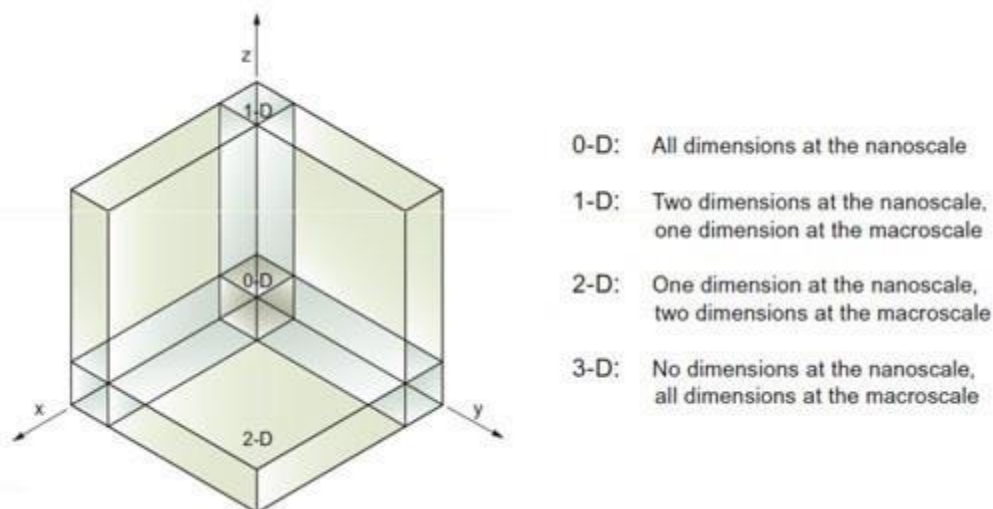
Bulk materials are particles that have their size above 100 nm in all dimensions. Most of the times, we use this term in order to name a substance that is granular or lumpy and exists in free-flowing form. We use the grain size and grain distribution in characterizing these materials. Moreover, we can explain their properties using the bulk density, moisture content, temperature, etc. There are two forms of these materials as follows:

1. Cohesionless, free-flowing bulk materials
2. Cohesive bulk materials

Bulk materials include the material we use in the construction field; plaster, sand, gravel, cement, etc. Moreover, it includes raw materials that we use for various industries such as ore, slag, salts, etc. In addition to that, this includes powdery materials such as pigments, fillers, granules, pellets, etc.

What is the Difference Between Nanomaterials and Bulk Materials?

Nanomaterials are materials with at least one dimension that is less than 100 nanometers (nm). **Bulk materials** are materials with all dimensions greater than 100 nm.



Nanomaterials have different properties than bulk materials due to their small size and high surface area to volume ratio. The following are some of the key differences in properties between nanomaterials and bulk materials:

- **Optical properties:** Nanomaterials can have different optical properties than bulk materials, such as different colors, absorption spectra, and scattering properties. This is because the size and shape of nanoparticles can affect the way they interact with light.
- **Electrical properties:** Nanomaterials can also have different electrical properties than bulk materials. For example, nanoparticles can be more conductive or semiconducting than bulk materials. This is because the surface of nanoparticles can have different electronic properties than the interior.

- **Mechanical properties:** Nanomaterials can also have different mechanical properties than bulk materials, such as increased strength and hardness. This is because the small size of nanoparticles allows them to resist deformation and fracture.
- **Chemical properties:** Nanomaterials can also have different chemical properties than bulk materials. For example, nanoparticles can be more reactive than bulk materials. This is because the high surface area to volume ratio of nanoparticles gives them more atoms that are exposed to the environment.

The following table summarizes some of the key differences in properties between nanomaterials and bulk materials:

Property	Nanomaterials	Bulk materials
Size	At least one dimension less than 100 nm	All dimensions greater than 100 nm
Surface area to volume ratio	High	Low
Optical properties	Can be different from bulk materials	Similar to bulk materials
Electrical properties	Can be different from bulk materials	Similar to bulk materials
Mechanical properties	Can be different from bulk materials, such as increased strength and hardness	Similar to bulk materials
Chemical properties	Can be different from bulk materials, such as increased reactivity	Similar to bulk materials

Due to their different properties, nanomaterials have a wide range of applications in areas such as medicine, energy, electronics, and environmental engineering. For example, nanoparticles are used in drug delivery systems, solar cells, and water purification filters.

Here are some specific examples of how the properties of nanomaterials are different from those of bulk materials:

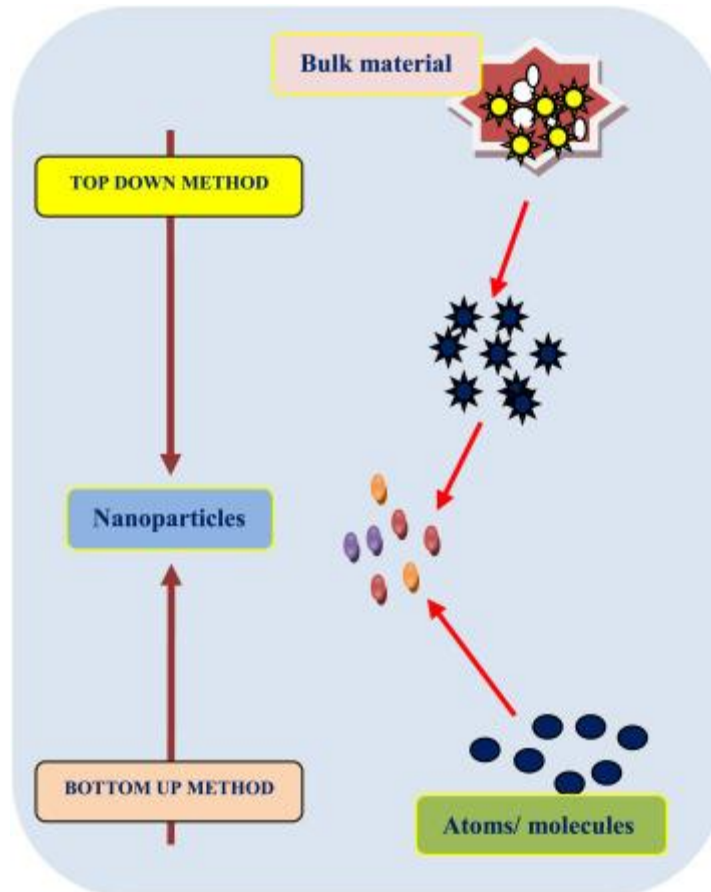
- Gold nanoparticles are red in color, while bulk gold is yellow.
- Carbon nanotubes are stronger than steel, but they are also much lighter.
- Silver nanoparticles are more antimicrobial than bulk silver.
- Zinc oxide nanoparticles are more effective at absorbing UV light than bulk zinc oxide.

Researchers are still actively studying the properties of nanomaterials and developing new applications for them.

SYNTHESIS OF NANO –MATERIALS

For the preparation of metallic nanoparticles, various methods are used, which are classified into two types: bottom-up methods and top-down methods, and are listed in Table. The preparation of nanoparticles' starting material is where both processes diverge most. While atoms or molecules are the starting materials in bottom-up approaches, top-down methods start with bulk material and use various physical, chemical, and mechanical processes to reduce particle size to nanoparticles. (Fig.)

Sr. No.	Top down methods		Bottom up methods	
	Methods	Examples	Methods	Examples
1	Mechanical milling	Ball milling Mechanochemical method	Solid state methods	Physical vapor deposition Chemical vapor deposition
2	Laser ablation		Liquid state synthesis methods	Sol gel methods Chemical reduction Hydrothermal method Solvothermal method
3	Sputtering		Gas phase methods	Spray pyrolysis Laser ablation Flame pyrolysis
4			Biological methods	Bacteria Fungus Yeast Algae Plant extract
5			Other methods	Electrodeposition process Microwave technique Supercritical fluid precipitation process Ultra sound technique



Top down methods

1. Mechanical milling

Ball milling

The working principal of mechanical milling is reduction in the particle size with high energy ball milling. In 1970, John Benjamin has developed this method of particle size reduction. This intern is responsible for modification of surface properties. The success of mechanical milling is affected by process variable and properties of milling powder. It is categorized into low energy and high energy milling that depend on induced mechanical energy to powder mixture. Nanosized particles are generally produced using high energy ball milling process. This method is widely preferred for intermetallic nanoparticles synthesis.

Step 1: Add the material to be milled and grinding balls to a cylindrical container.

Step 2: Rotate the container around its axis at high speed.

Step 3: The grinding balls collide with each other and with the material, reducing its particle size.

Step 4: Continue milling until the desired particle size is achieved.

Advantages

- Uses for large scale production of high purity nanoparticles with superior physical properties such as enhanced solubility of the drug components which

are poorly water soluble in a cost-effective manner.

- *It gives rise to some new and improved properties for the components based on their grain size and material composition.*

Disadvantages

- High energy required.
- Extensive long period of milling time.
- Contamination of powder due to steel balls.
- Very sensitive microstructure can be grinded.

Applications

- This method is preferred to blend aluminium with magnesium and carbon in order to alter its chemical properties and combustion behavior.
- Preparation of elemental powder of aluminium (Al) and beta-silicon carbide (β -SiC).
- Recently the ceramic nanoparticles WC-14% magnesium oxide (MgO) has been prepared.
- It is widely used method for mechanical alloying to produce amorphous alloys such as metal-metal, transition metal-metalloid, and metal-carbon systems for various purposes.

2. Mechanochemical synthesis

Procedure for mechanochemical synthesis of nanoparticles:

1. Mix the starting materials (reactants) stoichiometrically.
2. Mill the reactants using a ball mill at low temperatures without any external heating.
3. During milling, the reactants will undergo deformation, fracture, and welding.
4. Chemical reactions will occur at the surface interface between the reactants.
5. The nanoparticles produced will be surrounded by the byproduct material, which is dispersed in a soluble salt matrix.
6. Remove the byproduct by washing with a suitable solvent.
7. Dry the nanoparticles at 105°C for 12 hours.

Example:

To synthesize Fe_3O_2 nanoparticles using the mechanochemical method, mix sodium carbonate (Na_2CO_3) and chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) stoichiometrically and mill them using a ball mill at low temperatures without any external heating. During milling, the reactants will undergo deformation, fracture, and welding. Chemical reactions will occur at the surface interface between the reactants, resulting in the formation of Fe_3O_2 nanoparticles. The nanoparticles produced will be surrounded by the byproduct material, which is sodium chloride (NaCl). Remove the NaCl by washing with water. Dry the Fe_3O_2 nanoparticles at 105°C for 12 hours.

Disadvantages

The microstructures (nanostructures/nanoparticles) formed are highly sensitive to grinding condition and may get affected from unwanted contamination from milling media and atmosphere.

For the preparation of smaller particles (smaller than 20 nm) long term milling is required.

Applications

- Simple and efficient method of nanoparticle preparation.
- Can be performed at low temperatures without the use of external heating.
- Can be used to synthesize a wide range of nanoparticles.
- Environmentally friendly, as it does not require the use of organic solvents.

8. Laser ablation

Procedure of laser ablation method

1. Place solid target material under a thin layer of liquid.
2. Expose the target to pulsed laser irradiation.
3. Laser irradiation fragments the target material into nanoparticles.
4. Nanoparticles remain in liquid, forming a colloidal solution.

Key parameters:

- Laser type (e.g., Nd:YAG, Ti:Sapphire, copper vapor)
- Laser pulse duration and energy
- Liquid type and volume
- Presence or absence of surfactant

Example:

To produce gold nanoparticles, a gold target would be placed under a thin layer of water. The target would then be exposed to pulsed Nd:YAG laser irradiation. Laser irradiation would fragment the gold target into nanoparticles. Nanoparticles would remain in water, forming a colloidal solution. The size and distribution of the gold nanoparticles could be controlled by adjusting the laser parameters.

Advantages

- Can produce nanoparticles of a wide variety of materials
- Precise control over particle size and distribution
- High-purity nanoparticles
- Scalable process

Disadvantage

Prolong time laser ablation leads to formation of high amount of nanoparticles in the colloidal solution which block the laser path and also laser energy is get absorbed by already formed nanoparticles instead of target surface. This overall leads to reduction in ablation rate.

Application

- Preparation of Al₂O₃ nanoparticles coating.
- Preparation of silicon nanoparticles.

9. Ion sputtering

Ion sputtering method includes vaporization of a solid through sputtering with a beam of inert gas ions. Recently this method was used for the preparation of nanoparticles from several metals using magnetron sputtering of metal targets. In this method collimated beams of the nanoparticles is formed and the mass nanostructured films are deposited on the silicon substrates. The entire process is performed at relatively low pressures (1 mTorr).

Sputter deposition is done in evacuated vacuum chamber where sputtering gas is admitted and working pressure (eg. 0.05 and 0.1 mbar) is maintained. A very high voltage is introduced in to the target (cathode) and free electrons are moved in spiral path using magnetic system where they collide with sputtering gas (argon) atoms and leads to ionization of gas. This continuous process produces a glow discharge (plasma) to ignite. The positively charged gas ions attracted towards target where they continuously impinge. This event repeated occurs and approaches the surface of target with energy above the surface binding energy, an atom can be expelled. The collisions occur between metal atoms and gas molecules continuously in vacuum chamber that leads to scattering of atoms forming a diffuse cloud.

Advantages

- The composition of sputtered material is not altered and remains same as that of the target material.
- Method of choice for refractory metals and intermetallic compounds than other methods like evaporation and laser ablation.
- Economical method as the sputtering equipment is less expensive than electron-beam lithography systems.
- Less impurities are generated than those created by chemical methods.
- Alloy nanoparticles can be produced with easier control on composition than other chemical reduction methods.
- This method is a versatile technique to synthesize ionic nanoparticles with spacious sizes and compositions that are not obtainable in solution.
- Slow deposition of heavier ions or mass-selected ions gives unparalleled control of different parameters such as size, composition and charges of ions deposited onto surfaces.

Disadvantages

The nature sputtering gas (He, Ne, Ar, Kr, and Xe) can produce effect on surface morphology, composition, texture, and the optical properties of the nanocrystalline metal oxide films.

Application

- Synthesis of variety of nanomaterials on surface that employed for catalysis process, photovoltaics, magnetism, memory, cluster-surface interactions, hydrophobic coatings, and “nanoportals” for hydrogen storage.
- For preparation of core-satellite Si–Ag and stable Pd-core MgO-shell nanoparticles for the catalytic methanol oxidation reaction.
- Heavy and complex ions such as peptides, proteins, protein assemblies, organometallic complexes, metal clusters, and nanoparticles can be easily placed on the substrates without altering their basic properties.

- This method allows deposition of large molecules like large non-volatile species that are not easy to deposit by traditional atomic and molecular layer deposition techniques.

Bottom up methods

Nanoparticle synthesis using bottom up approach is based on formation nanoparticles from smaller molecules like joining of atoms, molecules or small particles. In this method, nanostructured building blocks of the nanoparticles first formed and then assembled to produce final nanoparticle.

Solid state methods

1. Physical vapor deposition method

Procedure for physical vapor deposition (PVD)

1. Place the substrate in a vacuum chamber.
2. Vaporize the material to be deposited using a thermal or sputtering process.
3. Condense the vaporized material on the substrate to form a thin film or nanoparticles.

Pulsed laser deposition (PLD) is a type of PVD that uses a laser to vaporize the material to be deposited. This method is often used to deposit thin films of lanthanum strontium cobalt and metal nanoparticles on carbon nanotubes.

PLD procedure:

1. Place the substrate in a vacuum chamber.
2. Focus a laser on a solid target of the material to be deposited.
3. The laser ablates (vaporizes) the target, forming a plasma of ablated species.
4. The ablated species are deposited on the substrate to form a film.

Example:

To deposit a thin film of lanthanum strontium cobalt on a carbon nanotube substrate using PLD, you would:

1. Place the carbon nanotube substrate in a vacuum chamber.
2. Focus a laser on a solid target of lanthanum strontium cobalt.
3. The laser ablates the target, forming a plasma of ablated lanthanum strontium cobalt species.
4. The ablated species are deposited on the carbon nanotube substrate to form a thin film of lanthanum strontium cobalt.

Advantages of PVD:

- PVD can be used to deposit a wide variety of materials, including metals, ceramics, and polymers.
- PVD films can be very thin and uniform.
- PVD films can be deposited on a variety of substrates.

Disadvantages of PVD:

- PVD can be a complex and expensive process.
- PVD films can be susceptible to defects.

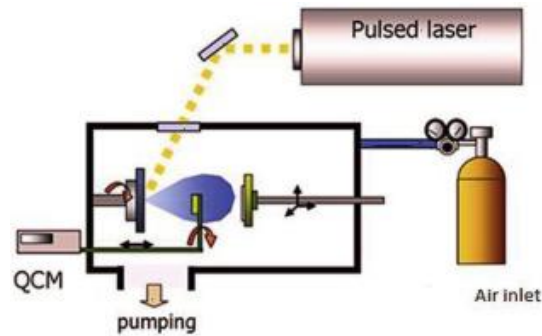


Fig. Pulsed laser deposition of ablated species.

Application

- Preparation of thin film of tungsten selenides.
- Preparation of platinum-ruthenium (Pt–Ru) nanoparticles.
- Formation of Ytria-stabilized zirconia.
- This method is used for the formation of most efficient thin-film solar cells, Cu (In,Ga) Se₂ thin film using pulsed laser deposition (PLD). The femtosecond (fs)-pulsed laser deposition (Fs-PLD) derived copper indium gallium selenide (CIGS) thin films shows prominent antireflection and excellent crystalline structure.

2. Chemical vapor deposition method

CVD is a process of depositing a thin film of a material on a substrate surface through a chemical reaction of gaseous molecules containing the desired material.

Steps involved:

1. Place the substrate in a vacuum chamber.
2. Introduce a precursor gas into the chamber.
3. Heat the chamber to a high temperature.
4. The precursor gas reacts on the substrate surface to form a thin film of the desired material.
5. Remove the substrate from the chamber.

Types of CVD:

- **Thermally activated CVD (TACVD):** The precursor gas is decomposed by heat.
- **Plasma enhanced CVD (PECVD):** The precursor gas is decomposed by plasma.
- **Photo-initiated CVD (PICVD):** The precursor gas is decomposed by light.

Advantages of CVD:

- Can be used to deposit a wide variety of materials.
- Can be used to produce thin films with precise thickness and composition.

- Can be used to deposit films on a variety of substrates.

Disadvantages of CVD:

- Requires expensive equipment.
- Can be a complex process to control.
- Can produce hazardous byproducts.

Applications of CVD:

- Manufacturing semiconductors and other electronic devices.
- Coating optical components.
- Depositing protective coatings on metals and other materials.

Example:

To deposit a thin film of silicon dioxide (SiO_2) on a silicon substrate using CVD, the following steps would be taken:

1. Place the silicon substrate in a vacuum chamber.
2. Introduce a precursor gas, such as silane (SiH_4), into the chamber.
3. Heat the chamber to a temperature of about 400 degrees Celsius.
4. The silane gas reacts on the silicon substrate surface to form a thin film of silicon dioxide.
5. Remove the silicon substrate from the chamber.

The thickness and composition of the silicon dioxide film can be controlled by varying the process parameters, such as the temperature, pressure, and flow rate of the precursor gas.

Liquid state synthesis methods

1. Sol gel method

Procedure of sol-gel method for nanoparticles synthesis:

1. Mix a metal alkoxide (precursor) with a solvent (usually alcohol).
2. Add a catalyst to initiate the reaction.
3. The reaction undergoes hydrolysis and condensation, forming a sol (colloidal suspension of nanoparticles).
4. The sol is then dried to form a gel.
5. The gel can be heated to form a ceramic or thin film.

Advantages:

- Simple and versatile method for synthesizing a wide range of nanoparticles.
- Good control over particle size and morphology.

Applications:

- Synthesis of a variety of metal oxide nanoparticles, such as ZnO₂, NiO₂, and TiO₂.
- Preparation of thin metal films.
- Production of catalysts, sensors, and other nanomaterials.

Simplified example:

To synthesize ZnO₂ nanoparticles using the sol-gel method:

1. Mix zinc acetate (precursor) with ethanol (solvent).
2. Add a few drops of nitric acid (catalyst).
3. Stir the mixture until a clear sol is formed.
4. Pour the sol into a Petri dish and allow it to dry.
5. Heat the dried gel at 500°C to form ZnO₂ nanoparticles.

The ZnO₂ nanoparticles can then be used for a variety of applications, such as catalysis, gas sensing, and UV light detection.

2. Chemical reduction method

Procedure for chemical reduction method of metal nanoparticle synthesis:

1. Dissolve the ionic salt in an appropriate medium.
2. Add a surfactant to the solution.
3. Add a reducing agent to the solution.
4. Reduce the ionic salt to metal nanoparticles.
5. Cap the metal nanoparticles with a stabilizer.

Advantages:

- Simple
- Versatile

Disadvantages:

- Reducing agents may be toxic, expensive, or have poor reducing ability.

Applications:

- Preparation of a variety of metal nanoparticles, including copper, silver, and gold nanoparticles.

Example:

To prepare copper nanoparticles using potassium borohydride as a reducing agent:

1. Dissolve copper sulfate pentahydrate in water.
2. Add sodium dodecyl sulfate (SDS) to the solution.
3. Add potassium borohydride to the solution.
4. The copper sulfate will be reduced to copper nanoparticles.
5. The copper nanoparticles will be capped by the SDS molecules.

The resulting copper nanoparticle dispersion can be used for a variety of applications, such as catalysis and sensing.

3. Hydrothermal method

Hydrothermal Synthesis Procedure:

1. Mix aqueous solutions of metal salts in a sealed vessel.
2. Heat the vessel to high pressure and temperature.
3. Nanoparticles of metal oxides will form inside the vessel.
4. Cool the vessel and recover the nanoparticles.

Advantages:

- Can produce nanoparticles of desired size and shape
- Can produce well-crystallized nanoparticles
- Can produce nanoparticles with high crystallinity

Disadvantages:

- Processes are difficult to control
- Limited reliability and reproducibility

Applications:

- Suitable for preparation of powders in the form of nanoparticles or even single crystals

Example:

To synthesize titanium dioxide (TiO₂) nanoparticles using the hydrothermal method, you would mix aqueous solutions of titanium chloride (TiCl₄) and sodium hydroxide (NaOH) in a sealed vessel. You would then heat the vessel to a temperature of 180 degrees Celsius and a pressure of 20 MPa for 12 hours. After cooling the vessel, you would recover the TiO₂ nanoparticles using filtration.

Note: The hydrothermal method is a versatile technique that can be used to synthesize a wide variety of nanoparticles, including metal oxides, semiconductors, and ceramics.

4. Solvothermal method

Procedure for solvothermal method:

1. **Prepare a solution of precursor chemicals in a solvent.** The solvent can be water, methanol, ethanol, or polyol.
2. **Place the solution in a pressure vessel and seal it.**
3. **Heat the vessel to a temperature above the boiling point of the solvent.** This will create high pressure and temperature inside the vessel.
4. **Maintain the high pressure and temperature for a period of time.** This will allow the precursors to react and form nanocrystals.
5. **Cool the vessel and remove the nanocrystals.**

Advantages of solvothermal method:

- Produces high quality crystallized monodispersed nanocrystals.
- Preferred over conventional oil bath heating for preparing nanocrystallites with narrow size distribution and high degree of crystallization.

Applications of solvothermal method:

- Synthesis of silver nanoparticles.
- Rapid synthesis of nanostructures of Pt, Pd, Ag, and Au using polyethylene glycol or methanol as reducing agent under microwave assisted condition.
- Preparation of high quality crystallized monodispersed nanocrystals of nitrites, metal oxides, and new semiconductor materials.

Gas phase methods

Pyrolysis procedure for nanoparticle preparation:

1. **Prepare a precursor solution.** This can be done by dissolving a suitable metal salt (e.g., acetate, nitrate, chloride) in a solvent (e.g., water, ethanol).
2. **Atomize the precursor solution.** This can be done using a nebulizer, ultrasonic atomizer, or other atomization technique.

3. **Introduce the atomized precursor solution into a hot reactor.** The reactor temperature should be high enough to decompose the precursor and vaporize the solvent.
4. **Collect the nanoparticles.** This can be done using a filter, electrostatic precipitator, or other collection technique.

Advantages of spray pyrolysis:

- Relatively simple and low-cost method.
- The particle size can be controlled and reproducible.

Applications of spray pyrolysis:

- Synthesis of nano-metal oxides and mixed metal oxides.
- Preparation of nanoparticles for various applications, such as catalysis, sensors, and solar cells.

Simplified example:

To synthesize zinc oxide nanoparticles by spray pyrolysis:

1. Prepare a precursor solution by dissolving zinc acetate in water.
2. Atomize the precursor solution using a nebulizer.
3. Introduce the atomized precursor solution into a hot reactor at a temperature of around 500 degrees Celsius.
4. Collect the zinc oxide nanoparticles using a filter.

The resulting zinc oxide nanoparticles can be used for a variety of applications, such as catalysis, sensors, and solar cells.

Biological method/biomimetic method/green synthesis method

Procedure

1. **Choose a biological source:** This could be bacteria, fungi, plants, or plant extracts.
2. **Prepare the biological source:** This may involve growing the microorganisms, extracting the plant compounds, or purifying the enzymes.
3. **Mix the biological source with a solution of metal ions:** This is the solution that you want to synthesize nanoparticles from.
4. **Incubate the mixture:** This will allow the biological source to reduce the metal ions and form nanoparticles.
5. **Purify the nanoparticles:** This may involve washing the nanoparticles with water or another solvent, or using centrifugation to separate the nanoparticles from the rest of the mixture.

Advantages of biological nanoparticle synthesis

- Cost-effective
- Eco-friendly

- Easy to scale up for large-scale production
- Does not involve the use of high pressure, energy, temperature, or toxic chemicals

Examples of biological nanoparticle synthesis

- **Bacteria:** Silver nanoparticles can be synthesized using bacteria such as *Lactobacillus* species and *Klebsiella pneumoniae*.
- **Fungi:** Gold nanoparticles can be synthesized using fungi such as *Fusarium oxysporum* and *Aspergillus fumigatus*.
- **Plants:** Copper nanoparticles can be synthesized using plants such as *Brassica juncea* and *Ilex crenata*.

Applications of biological nanoparticles

- **Medicine:** Nanoparticles can be used to deliver drugs to specific cells in the body, or to kill cancer cells.
- **Agriculture:** Nanoparticles can be used to improve the growth of plants or to protect them from pests and diseases.
- **Environment:** Nanoparticles can be used to clean up pollution or to generate renewable energy.

Overall, biological nanoparticle synthesis is a simple, cost-effective, and eco-friendly way to produce nanoparticles with a wide range of applications.

Other methods of nanoparticle synthesis

1. Electrochemical deposition

Procedure:

1. Prepare an electrolytic bath containing metal salts. The baths are either acidic or basic and use a three terminal potentiostat.
2. Attach the cathode electrode to the substrate where the metal nanoparticles are to be deposited.
3. Apply a slight voltage for a suitable time.
4. Rinse the substrate and dry it.

Example:

Synthesis of gold nanoparticles (AuNPs) using ED:

1. Prepare an electrolytic bath containing gold chloride (HAuCl₄).
2. Attach the cathode electrode to a glassy carbon electrode.
3. Apply a voltage of -0.3 V for 10 minutes.
4. Rinse the glassy carbon electrode with water and dry it.

This will produce a thin film of AuNPs on the surface of the glassy carbon electrode.

- .

Applications

- Synthesis of nanoparticles, nanowire, and nanorods.
- Nanomaterial production such as nanowires of Au, Co, Ni, and Pt.

2. Microwave assisted nanoparticles preparation

Nowadays microwave techniques are more proffered over thermal heating for the preparation nanoparticles. Microwave frequency of range 300 MHz to 300 GHz is applied that leads to orientation of polar molecule such as H₂O with the electric field. The re-orientation of dipolar molecules with an alternating electric field causes molecular friction and loss of energy in the form of heat. Recently this technique was successfully implemented for the preparation of silver nanoparticles where silver nitrate solution is irradiated with carboxymethyl chitosan, which acts as reducing agent and a stabilizer.

Advantages

- Highly effective technology for nanoparticle preparation.
- Simple, rapid volumetric heating and the consequent dramatic increase in reaction rate.
- Homogenous heating throughout the process can speed up the reaction rate by the orders of magnitude compared with conventional heating.

Disadvantages

Shorter crystallization time and homogeneous nucleation because of uniform heat of microwave oven.

Applications

- Useful technique in various fields of chemistry and materials science.
- Widely used for several plant-based extracts to prepare various metal nanoparticles.

Ultra sound technique

The following is a simplified procedure for the sonochemistry method of ultrasound-assisted material synthesis:

1. Prepare a solution containing the precursor materials for the desired nanostructure.
2. Place the solution in a sonochemical reactor, such as an ultrasonic cleaning bath, direct-immersion ultrasonic horn, or flow reactor.
3. Apply high-intensity ultrasound to the solution.
4. The ultrasound will induce acoustic cavitation, which will generate high temperatures and pressures in the vicinity of the collapsing bubbles.
5. These extreme conditions will promote the chemical reactions necessary to produce the desired nanostructure.
6. Once the synthesis is complete, the nanostructures can be collected from the solution.

Advantages of the sonochemistry method:

- Eco-friendly and green
- Fast and easy
- Can be used to synthesize a wide variety of nanostructures from different materials
- Does not require reducing agents for the synthesis of noble metal nanostructures

Disadvantages of the sonochemistry method:

- The rate of the reaction depends on the ultrasonic frequency

Applications of the sonochemistry method:

- Synthesis of unusual nanostructured inorganic materials
- Synthesis of nanostructured materials from volatile organometallic compounds

Examples of sonochemical synthesis:

- Synthesis of gold nanoparticles from gold chloride solution

- Synthesis of silver nanoparticles from silver nitrate solution
- Synthesis of zinc oxide nanoparticles from zinc acetate solution
- Synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution
- Synthesis of carbon nanotubes from methane gas

The sonochemistry method is a powerful tool for the synthesis of nanostructured materials with a variety of potential applications in catalysis, electronics, energy storage, and environmental remediation.

Nanolithography

Nanolithography is a process used to create structures on the nanometer scale. It is used in a variety of industries, including semiconductor manufacturing, MEMS/NEMS devices, and drug delivery.

Simplified procedure:

1. A photoresist is applied to a substrate.
2. A mask is placed over the photoresist and exposed to light or electrons.
3. The photoresist is developed, removing the exposed areas.
4. The substrate is etched, transferring the pattern from the photoresist to the substrate.
5. The remaining photoresist is removed.

Optical beam lithography:

Optical beam lithography uses light to expose the photoresist. The wavelength of the light determines the minimum feature size that can be created.

Electron beam lithography:

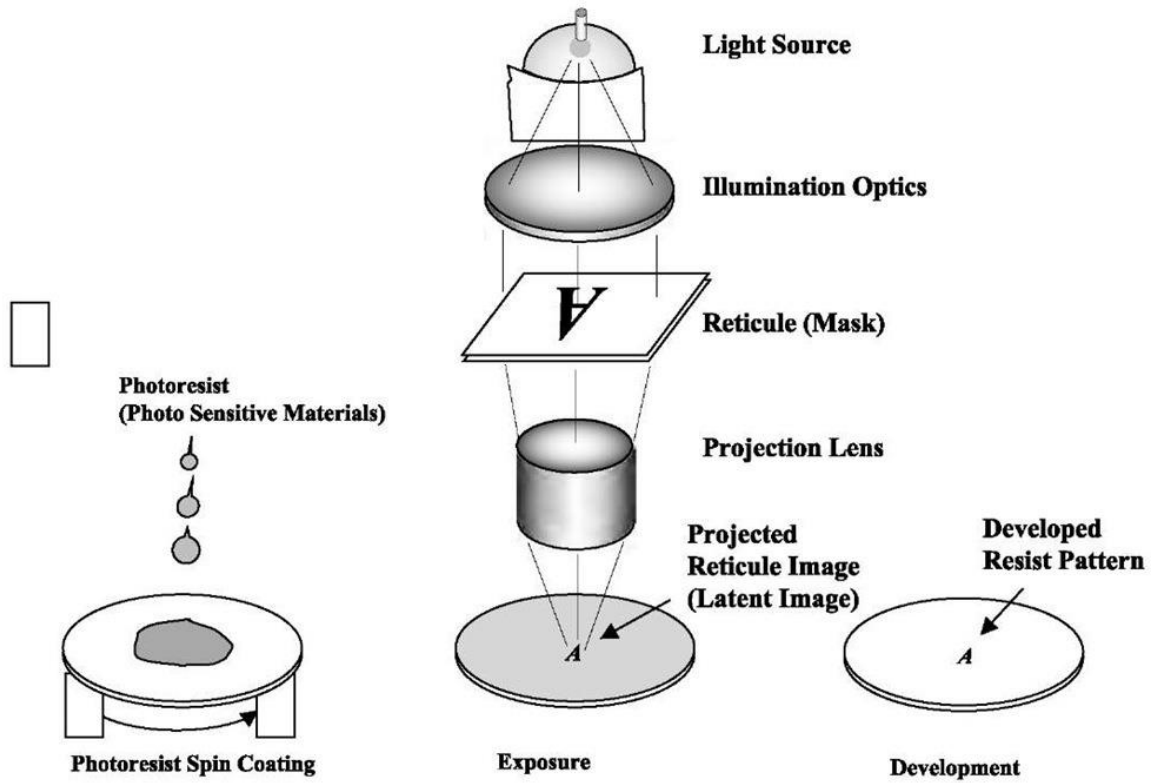
Electron beam lithography uses a focused beam of electrons to expose the photoresist. This technique can create smaller features than optical beam lithography, but it is slower and more expensive.

Example:

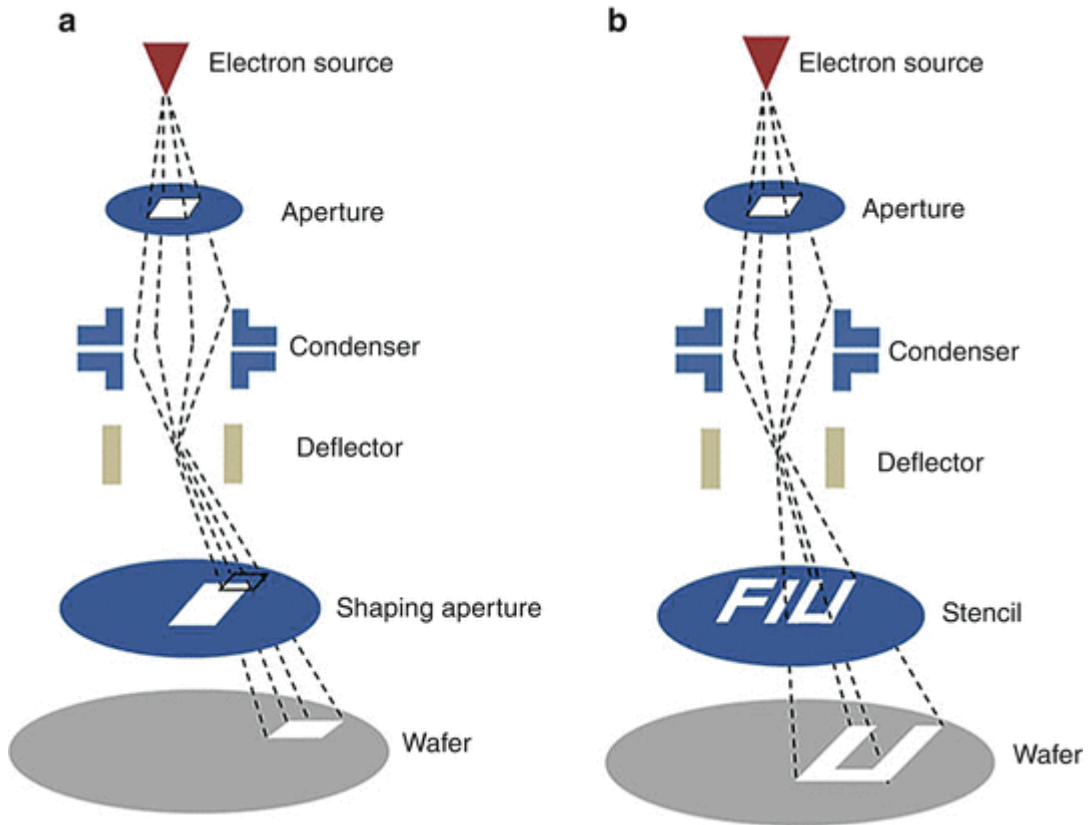
To create a transistor, the following steps would be taken:

1. A photoresist is applied to a silicon wafer.
2. A mask with the pattern of the transistor is placed over the photoresist and exposed to UV light.
3. The photoresist is developed, removing the exposed areas.
4. The silicon wafer is etched, transferring the pattern of the transistor to the silicon.
5. The remaining photoresist is removed.

Nanolithography is a powerful tool that can be used to create a wide variety of nanostructures. It is essential for the manufacturing of many modern devices, including smartphones, computers, and medical devices.



Optical beam lithography



Electron Beam Lithography

Nanophotonics-Fundamentals, Challenges, Future Prospects and Applied Applications.

Nanophotonics is a rapidly growing field of science and technology that deals with the interaction of light with matter at the nanoscale. The nanoscale is typically defined as the range of dimensions from 1 to 100 nanometers, which is equivalent to one-billionth of a meter. At this scale, light and matter interact in ways that are different from what is observed at larger scales.

Fundamentals of nanophotonics

One of the key fundamentals of nanophotonics is the concept of **nanoconfinement**. Nanoconfinement occurs when light is confined to a region that is smaller than its wavelength. This can be achieved using a variety of nanostructures, such as waveguides, resonators, and antennas. Nanoconfinement can lead to a number of interesting effects, such as enhanced light-matter interactions, slow light, and subwavelength imaging.

Another key fundamental of nanophotonics is the concept of **quantum confinement**. Quantum confinement occurs when the dimensions of a material are comparable to the de Broglie wavelength of its charge carriers. This can lead to a number of interesting optical effects, such as bandgap engineering and quantum well lasers.

Challenges in nanophotonics

One of the main challenges in nanophotonics is the fabrication of nanostructures with the desired optical properties. This can be difficult because the tolerances for nanoscale structures are extremely small. Another challenge is the integration of nanophotonic devices into existing optical systems. This can be difficult because nanophotonic devices often operate at a different wavelength range than traditional optical components.

Future prospects of nanophotonics

The future prospects of nanophotonics are very bright. Nanophotonic devices have the potential to revolutionize a wide range of industries, including telecommunications, computing, and healthcare. For example, nanophotonic devices could be used to develop new types of optical communication systems that are faster and more efficient than current systems. Nanophotonic devices could also be used to develop new types of optical computing devices that are smaller and more powerful than current devices. Finally, nanophotonic devices could be used to develop new types of medical devices for imaging, diagnostics, and therapy.

Applied applications of nanophotonics

Nanophotonics is already being used in a number of applications, including:

- **Optical communications:** Nanophotonic devices are being used to develop new types of optical communication systems that are faster and more efficient

than current systems. For example, nanophotonic devices are being used to develop new types of optical amplifiers and optical switches.

- **Optical computing:** Nanophotonic devices are being used to develop new types of optical computing devices that are smaller and more powerful than current devices. For example, nanophotonic devices are being used to develop new types of optical interconnects and optical processors.
- **Healthcare:** Nanophotonic devices are being used to develop new types of medical devices for imaging, diagnostics, and therapy. For example, nanophotonic devices are being used to develop new types of optical microscopes, optical biosensors, and optical imaging agents.
- **Energy:** Nanophotonic devices are being used to develop new ways to generate, store, and transmit energy. For example, nanophotonic devices are being used to develop new types of solar cells, batteries, and fuel cells.

Quantum confined materials-Size effect, (surface plasmon resonance (SPR)- principle, application).

Quantum confined materials are materials whose electronic properties are altered due to their small size. This size effect is caused by the confinement of electrons to a small region of space, which changes their energy levels and wavefunctions. Quantum confined materials can have a variety of unique properties, such as tunable bandgaps, enhanced optical absorption, and increased electrical conductivity.

One important property of quantum confined materials is **surface plasmon resonance (SPR)**. SPR is a phenomenon that occurs when light interacts with the collective oscillations of free electrons on the surface of a metal. SPR is highly sensitive to the size, shape, and composition of the metal nanoparticles, and it can be used to detect and monitor a wide range of molecules and biological systems.

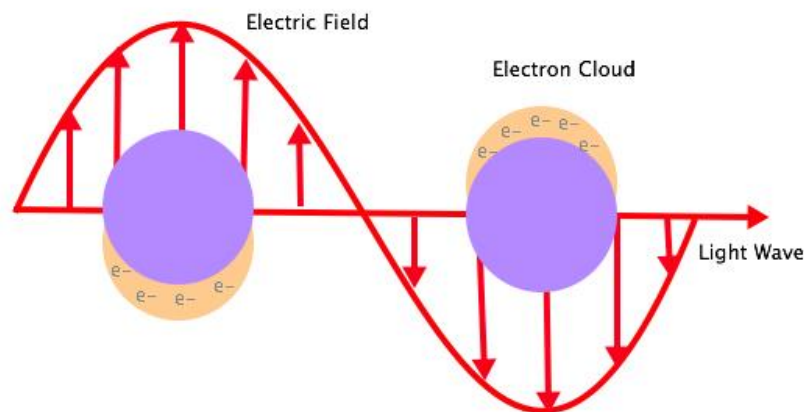


Figure - Shows how as a light wave passes through a material, the induced electric field creates a charge separation in the atoms, creating an electron cloud that then allows for electrons to move freely.

Size effect

The size effect in quantum confined materials is caused by the confinement of electrons to a small region of space. This confinement changes the energy levels and wavefunctions of the electrons, which in turn can have a significant impact on the optical and electrical properties of the material.

For example, the bandgap of a quantum confined semiconductor can be tuned by changing the size of the semiconductor nanocrystals. This is because the energy

levels of the electrons and holes in the semiconductor are quantized, meaning that they can only take on certain values. By changing the size of the nanocrystals, it is possible to change the energy of the bandgap, which can be useful for applications such as solar cells and light-emitting diodes.

Surface plasmon resonance (SPR)

Surface plasmon resonance (SPR) is a phenomenon that occurs when light interacts with the collective oscillations of free electrons on the surface of a metal. SPR is highly sensitive to the size, shape, and composition of the metal nanoparticles, and it can be used to detect and monitor a wide range of molecules and biological systems.

When light interacts with a metal nanoparticle, it can excite the free electrons in the nanoparticle to oscillate. These oscillating electrons create a surface plasmon wave, which is a wave of electromagnetic radiation that propagates along the surface of the nanoparticle. The frequency of the surface plasmon wave is determined by the size, shape, and composition of the metal nanoparticle, as well as the refractive index of the surrounding medium.

Applications

Quantum confined materials and SPR have a wide range of potential applications in a variety of fields, including:

- **Electronics:** Quantum confined materials can be used to create new types of electronic devices, such as transistors, solar cells, and light-emitting diodes.
- **Photonics:** Quantum confined materials can be used to develop new types of optical devices, such as lasers and waveguides.
- **Biomedicine:** SPR can be used to develop new types of biosensors to detect and monitor diseases.
- **Food safety:** SPR can be used to develop new methods to detect and monitor foodborne pathogens.
- **Environmental monitoring:** SPR can be used to develop new methods to detect and monitor environmental pollutants.

UNIT-IV WATER TECHNOLOGY

Lecture session 28: Topics: Sources of water, impurities in water and their effects. WHO guideline and BIS guideline for drinking water.

Water plays an important role in our daily life. 70% of the earth is covered by water, out of which 97% is in oceans and hence saline (not usable) 2% is locked as polar ice caps (not available for use) only 1% is available as surface and ground water (Usable) Though the ground water is clear, it contains dissolved salts, hence not pure. Surface water contains dissolved salts, dissolved gases and suspended impurities. Water is an essential commodity for any engineering industry. The sources for water are of stationary or of flowing type. Depending on the source, water may consist of impurities in soluble or dispersed or suspended form. The impurities in water impart some undesirable properties to water and hence render water ineffective for the particular engineering application.

Sources of water

1. Surface water

Rain water is the most pure form of water because it is obtained due to precipitation of surface water. When it flows it dissolves considerable amount of gases and suspended solid particles which are both organic and inorganic.

Eg. River water, lake water etc.

2. Sea water

It is the most impure form of water. The continuous evaporation of water from the surface of sea makes it richer in dissolved impurities.

3. Underground water

A part of the rain water which percolates into the earth and comes in contact with a number of minerals and dissolves some of them.

Eg. Shallow and deep springs and wells

Impurities of water

1. Physical Impurities

These impurities impart the color, odour, taste of water and also makes it turbid.

Eg. Clay, sand oil globules, vegetable and animal matter

2. Chemical Impurities

These impurities pollute the water and produces harmful effects on human beings.

➤ Dissolved Inorganic salts: Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} etc.

➤ Dissolved Gases: CO_2 , O_2 , N_2 , Oxides of nitrogen.

3. Biological impurities

These impurities are due to the discharge of domestic and sewage waste into water which causes diseases.

Eg. Microorganisms like bacteria, fungi etc.

Drinking water quality standards

- Planet needs drinking water to survive and that water may contain many harmful constituents, there are no universally recognized and accepted international standards for drinking water.
- Even where standards do exist, and are applied, the permitted concentration of individual constituents may vary by as much as ten times from one set of standards to another (World Health Organization (**WHO**) and **BIS**).

Access to safe drinking-water is essential to health, a basic human right and a component of effective policy for health protection.

The importance of water, sanitation and hygiene for health and development has been reflected in the outcomes of a series of international policy forums.

WHO published four editions of the Guidelines for drinking-water quality (in 1983–1984, 1993–1997, 2004, and 2011).

The primary goal of the Guidelines is to protect public health associated with drinking-water quality. The overall objectives of the Guidelines are to:

- provide an authoritative basis for the effective consideration of public health in setting national or regional drinking-water policies and actions;
- provide a comprehensive preventive risk management framework for health protection, from catchment to consumer, that covers policy formulation and standard setting, risk-based management approaches and surveillance;
- emphasize achievable practices and the formulation of sound regulations that are applicable to low-income, middle-income and industrialized countries alike;
- summarize the health implications associated with contaminants in drinking-water, and the role of risk assessment and risk management in disease prevention and control;
- summarize effective options for drinking-water management; and
- provide guidance on hazard identification and risk assessment.

Parameter	Table	World Health Organization	European Union	United States	China	Canada
1,2-dichloroethane		“	3.0 µg/l	5 µg/l	“	“
Acrylamide		“	0.10 µg/l	“	“	“
Aluminium	Al		0,2 mg/l			no limit listed
Antimony	Sb	ns	5.0 µg/l	6.0 µg/l	“	6.00 µg/l
Arsenic	As	10µg/l	10 µg/l	10µg/l	50µg/l	10.0 µg/l
Barium	Ba	700µg/l	ns	2 mg/L	“	1.00 mg/L
Benzene		10µg/l	1.0 µg/l	5 µg/l	“	“
Benzo(a)pyrene		“	0.010 µg/l	0.2 µg/l	0.0028 µg/l	“
Beryllium	Be					"
Boron	B	2.4 mg/l	1.0 mg/L	“	“	5.00 mg/L
Bromate		“	10 µg/l	10 µg/l	“	“
Cadmium	Cd	3 µg/l	5 µg/l	5 µg/l	5 µg/l	5.00 µg/l
Calcium	Ca					200 mg/L
Chromium	Cr	50µg/l	50 µg/l	0.1 mg/L	50 µg/l (Cr6)	0.050 mg/L
Cobalt	Co					"
Copper	Cu	“	2.0 mg/l	TT	1 mg/l	1.00 mg/L
Cyanide		“	50 µg/l	0.2 mg/L	50 µg/l	“
Epichlorohydrin		“	0.10 µg/l	“	“	“
Fluoride		1.5 mg/l	1.5 mg/l	4 mg/l	1 mg/l	“
Gold	Au					no limit listed
hardness	CaCO3					0–75 mg/L=soft
Iron	Fe		0,2 mg/l			0.300 mg/L
Lanthanum	La					no limit listed
Lead	Pb	“	10 µg/l	15 µg/l	10 µg/l	10.0 µg/l
Magnesium	Mg					50.0 mg/L
Manganese	Mn		0, 05 mg/l			0.050 mg/L
Mercury	Hg	6 µg/l	1 µg/l	2 µg/l	0.05 µg/l	1.00 µg/l
Molybdenum	Mo					no limit listed
Nickel	Ni	“	20 µg/l	“	“	no limit listed

Nitrate		50 mg/l	50 mg/l	10 mg/L (as N)	10 mg/L (as N)	“
Nitrite		“	0.50 mg/l	1 mg/L (as N)	“	“
Pesticides Total		“	0.50 µg/l	“	“	“
Pesticides (individual)		“	0.10 µg/l	“	“	“
pH						6.5 to 8.5
Phosphorus	P					no limit listed
Potassium	K					no limit listed
Scandium	Sc					no limit listed
Selenium	Se	40 µg/l	10 µg/l	50 µg/l	10 µg/l	10.0 µg/l
Silicon	Si					no limit listed
Silver	Ag					0.050 mg/L
Sodium	Na					200 mg/L
Strontium	Sr					no limit listed
Tin	Sn					no limit listed
Titanium	Ti					no limit listed
Tungsten	W					no limit listed
Uranium	U					0.10 mg/L
Vanadium	V					no limit listed
Zinc	Zn					5.00 mg/L
vinyl chloride			0,50 µg/l			
chlorides			250 mg/l			

For India these standards are set by the Bureau of Indian Standards - BIS, Indian Standards Institute – ISI. The relevant BIS standard is BIS: 10500 available from the BIS site www.bis.org.in

Parameters	USEPA	WHO	ISI	ICMR
pH (mg/l)	6.5-8.5	6.5-8.5	6.5-8.5	6.5-9.2
Turbidity NTU	-	-	10	25
Conductivity (mg/l)	-	-	-	-
Alkalinity (mg/l)	-	-	-	-
Total hardness (mg/l)	-	500	300	600
Iron *mg/l)	-	0.1	0.3	1.0
Chlorides (mg/l)	250	200	250	1000
Nitrate (mg/l)	-	-	45	100
Sulfate (mg/l)	-	-	150	400
Residual (mg/l) free Chlorine	-	-	0.2	-
Calcium (mg/l)	-	75	75	200
Magnesium (mg/l)	-	50	30	-
Copper (mg/l)	1.3	1.0	0.05	1.5
Fluoride (mg/l)	4.0	1.5	0.6-1.2	1.5
Mercury (mg/l)	0.002	0.001	0.001	0.001
Cadmium (mg/l)	0.005	0.005	0.01	0.01
Selenium (mg/l)	0.05	0.01	-	-
Arsenic (mg/l)	0.05	0.05	0.05	0.05
Lead (mg/l)	-	0.05	0.10	0.05
Zinc (mg/l)	-	5.0	5.0	0.10
Chromium (mg/l)	0.1	-	0.05	-
<i>E. coli</i> (MPN/100 ml)	-	-	-	-

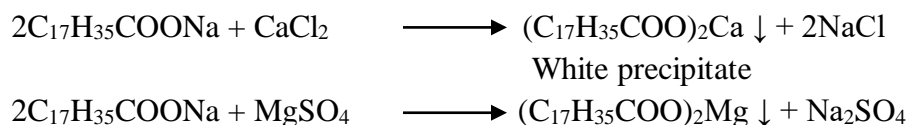
Lecture session 29: Topics: Water characteristics – Hardness – Types of hardness – Disadvantages of hard water in domestic and industry

Quality of water for different uses

Purpose	Quality requirements
Drinking	Palatable, clear and free from colour, odour, turbidity and pathogens.
Domestic washing	Soft water producing lather readily.
Textile dyeing	Free from colour, turbidity, organic matter, Fe and Mn.
Boiler feed water	Free from dissolved salts, suspended impurities, silica and dissolved gases.
Drugs and pharmaceuticals	Soft and clear. Free from pathogens, colour, odour and suspended impurities.
Construction	Not too hard, should contain less amount chlorides.
Paper industry	Free from colour, turbidity, organic matter, Fe, Mn, silica and alkalinity.

Hardness

The property of water which prevents it from lathering. Water which does not produce lather with soap solution but produces white precipitate is called hard water and which produces lather readily with soap solution are called soft water.



Types of Hardness

- Temporary Hardness or Carbonate Hardness (CH) or Alkaline Hardness (AH)
This is due to the presence of bicarbonates of calcium and magnesium. It can be removed by mere boiling. The bicarbonates are converted into insoluble carbonates and hydroxides, which can be removed by filtering.



- Permanent Hardness or Non-carbonate Hardness (NCH) or Non-alkaline Hardness (NAH)
This is caused by the presence of chlorides and sulphates of calcium and magnesium. It cannot be removed by boiling. It can be removed only by chemical or special treatment.

Units of Hardness

The concentration of hardness is expressed in terms of equivalent amount of CaCO_3 because it is the most insoluble salt obtained in water treatment and its molecular weight is 100 (Eq. Wt 50). The different units are

- ppm : 1 part of CaCO_3 equivalent hardness in 10^6 parts of water
 - mg/L : 1 mg of CaCO_3 equivalent hardness in 1 L of water
- Weight of 1 L of water = 1 Kg. = 1000 g = 1000000 mg = 10^6 mg

$$\text{Hence } 1\text{ppm} = 1\text{mg} / \text{L}$$

Disadvantages of Hard Water

- (a) In domestic uses. For washing and bathing, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap gets wasted also.

For cooking hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant. Drinking of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

- (b) In industrial uses. For textile industry and dyeing industry, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.
1. For sugar industry, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
 2. Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the paper industry. Iron salts interfere with the color of the paper.
 3. In laundry, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
 4. The hydration of cement and final hardening of cement are affected by use of hard water in concrete making.
 5. Hard water is not suitable for preparing drug solutions in pharmaceutical industry.
 6. For steam generation in boilers, hard water creates many problems like (i) scale formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.

Lecture session 30: Topics: Boiler feed water - requirements, disadvantages of hard water in boilers and heat exchangers - scale and sludges formation and their preventive methods.

BOILER FEED WATER

Water is largely used in boilers (as feed) for the production of steam. The presence of impurities in water sample renders it hard (and corrosive too in some cases) which cannot be used as boiler feed as it may pose the problems of corrosion, embrittlement of the boiler vessel etc. Water with some specifications, used in boilers for steam generation is called boiler feed water.

Requisites of boiler feed water

- (i) It should be free from suspended solids and dissolved corrosive gases such as CO_2 , SO_x , NO_x , halogens, hydrogen halide etc.

- (ii) Hardness should be less than 0.1 ppm
- (iii) Alkalinity (soda and caustic alkalinity values) should be in the range 0.1 – 1 ppm ; less than 0.5 ppm alkalinity is preferable
- (iv) It should be free from dissolved salts and oily / soapy matter that reduces the surface tension of water.
- (v) Boiler feed water should be free from hardness producing substances.

Disadvantages of using hard water in boiler:

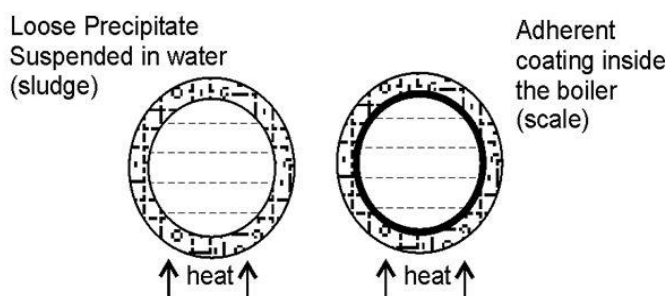
If hard water is fed directly into the boiler it leads to the following boiler troubles which reduce the efficiency of the boiler. The main destructive effects of using hard water in boilers are

- (i) Formation of scales and sludges
- (ii) Boiler corrosion
- (iii) Caustic embrittlement
- (iv) Priming and foaming.

BOILER TROUBLES

SCALES AND SLUDGES:

In boiler, water is converted to steam. During this process, when the volume of water decreases, a saturation point is reached and all the dissolved salts precipitate out. Depending on the physical and chemical nature of the impurity (salt) it may form a loose, slimy, non-adhering precipitate (Sludge) or hard strongly adhering precipitate (Scale)



Sludge

Loose, slimy and non adhering precipitate due to presence of salts like $MgCl_2$, $MgSO_4$, $CaCl_2$, $MgCO_3$. It forms in colder portions of boilers and the portion where water flow rate is low.

Disadvantages:

1. Sludges are poor conductor of heat.
2. Excess of sludge formation decreases the efficiency of boiler.

Prevention and removal

1. By using softened water
2. By performing frequent blow down operation

Scale

Hard, adherent coating due to presence of salts like $Mg(HCO_3)_2$, $Mg(OH)_2$, $Ca(HCO_3)_2$, $CaSO_4$

Disadvantages:

1. Wastage of fuel: Scales are poor conductors (almost insulators) of heat and result in a low heat transfer rates. To maintain steady heat supply to water, greater heat energy has to be supplied. This results in over-heating of the boiler and also increased fuel consumption. The extent of fuel wastage depends on the thickness and nature of the scale, as evidenced from the following table:

Scale thickness (mm)	0.325	0.625	1.5	2.5
Fuel wastage (%)	10	15	50	80

2. Decrease in efficiency: Scales, if deposited in the boiler components such as valves, condensers etc., choke in fluid paths and hence lead to decreased efficiency of the boiler.
3. Lowering of boiler safety: Scale formation demands over-heating of the boiler for maintaining a constant supply of steam. Boiler plates, initially maintained at a temperature of 180°C in the absence of scales has to be heated to a temperature of 370°C to maintain the steam supply, if covered with 12 mm thick scale. The over-heating of the boiler tubes renders the boiler material softer and weaker and hence the boiler becomes unsafe at high steam pressures.
4. Danger of explosion: when scales undergo cracking due to uneven expansion, water comes in contact with overheated boilerplates suddenly. This results in sudden formation of large amount of steam and hence the development of high pressure of steam, which may cause the boiler explosion.

Prevention and removal

- i) By dissolving in acids like HCl, H₂SO₄
- ii) By applying external and internal treatment.
- iii) Removed by scrapping, wire brushes etc.

Lecture session 31: Topics: Boiler troubles- Priming and Foaming, caustic embrittlement explanation with the elimination of these problems.

PRIMING & FOAMING

- ✓ During the production of steam in the boiler, due to rapid boiling, some droplets of liquid water are carried along with steam.
- ✓ Steam containing droplets of liquid water is called wet steam. These droplets of liquid water carry with them some dissolved salts and suspended impurities.
- ✓ This phenomenon is called carry over. This leads to priming and foaming.

Priming: When steam is produced rapidly in boilers the steam velocity suddenly increases and some droplets of liquid water are carried along with steam. Steam containing droplets of liquid water is called wet steam. The process of wet steam formation is called Priming.

Priming is caused by

- Presence of large amount of dissolved solids.
- High steam velocity.
- Sudden boiling.
- Improper boiler design.

Priming can be prevented by

- Using treated water.
- Controlling the velocity of steam.
- Fitting mechanical steam purifiers.
- Maintaining low water level.
- Good boiler design.

Foaming: Oil or any other polymeric substance present in boiler feed water, reduces surface tension of water forming bubbles which do not break easily in boilers giving a foam appearance. This process is called foaming.

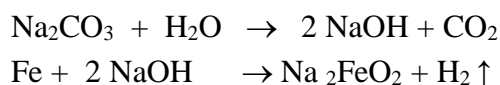
Foaming is caused by

- Presence of oil & grease.
- Presence of finely divided sludge particles.

Foaming can be prevented by adding coagulants like sodium aluminate, ferrous sulphate etc.

CAUSTIC EMBRITTLEMENT:

Caustic embrittlement means intercrystalline cracking of boiler metal. Boiler water usually contains a small proportion of Na_2CO_3 . In high pressure boilers this undergoes decomposition to give NaOH . This NaOH flows into the minute hair cracks and crevices, usually present on the boiler material, by capillary action and dissolves the surrounding area of iron as sodium ferroate. This causes brittleness of boiler parts, particularly stressed parts like bends, joints, rivets, etc., causing even failure of the boiler.



Caustic embrittlement can be prevented by

- i) using sodium phosphate as softening agent instead of sodium carbonate.
- ii) by adding tannin, lignin to the boiler water, which blocks the cracks.

Lecture session 32: Topics: Boiler corrosion due to various agents and its prevention, Softening of hard water (external)- zeolite process – advantages and limitations.

BOILER CORROSION:

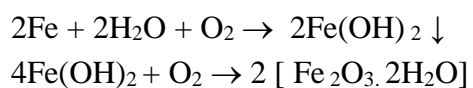
Boiler corrosion is decay of boiler material by chemical or electrochemical attack of its environment.

Boiler corrosion is due to presence of

- Dissolved oxygen
- Dissolved carbon dioxide
- Dissolved salts like magnesium chloride

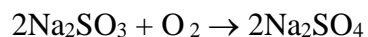
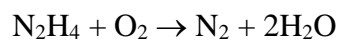
1. **Dissolved oxygen (DO):**

When water containing dissolved oxygen is fed into boilers the following reaction occurs corroding the boiler material (rust formation)

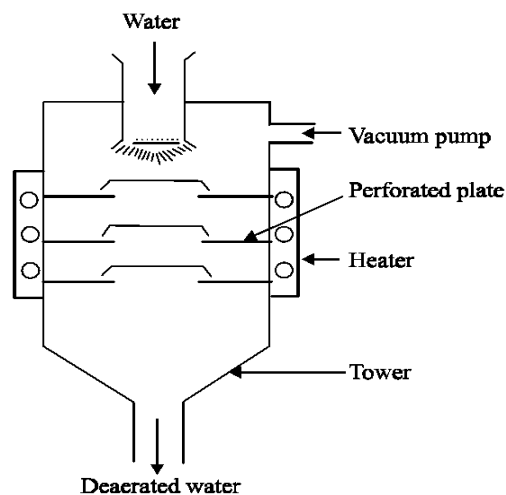


D. O. oxygen can be reduced

i) By adding hydrazine / sodium sulphite

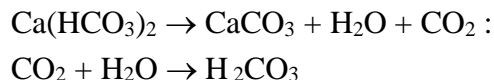


ii) By mechanical deaeration method.



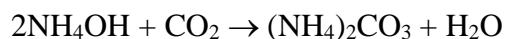
2. Dissolved carbon dioxide:

When water containing bicarbonates is heated, carbon dioxide is evolved which makes the water acidic. This is detrimental to the metal. It leads to corrosion called of boiler material.



Prevention methods for removing dissolved carbon dioxide:

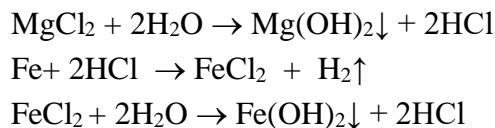
By treatment with ammonium hydroxide:



Can be removed by mechanical deaeration method along with oxygen.

3. Dissolved MgCl_2 :

Acids produced from salts that are dissolved in water are mainly responsible for the corrosion of boilers. Salts like magnesium and calcium chloride undergo hydrolysis at high temperature to give HCl, which corrodes the boiler. Presence of HCl is more damaging due to chain reaction.



MgCl_2 can be removed by i) internal conditioning and ii) external conditioning

INTERNAL CONDITIONING OR SEQUESTRATION

Internal conditioning is treating the water after feeding into the boiler. An internal treatment is accompanied by adding a appropriate chemical to the boiler water either (a)to precipitate the scale forming impurities in the form of sludges, which can be removed by blow down operation or (b) to convert them into compounds which will stay in dissolved form without causing harm to the boiler.

Internal treatment methods are, generally, followed by blow-down operation, so that accumulated sludge is removed. Important internal conditioning/treatment methods are

➤ **Carbonate conditioning:**

Scale forming salts like CaSO_4 present in the water adheres more strongly on the surface of the boiler. This can be prevented by precipitating Ca as CaCO_3 which gives rise to a loosely adhering scale, by adding Na_2CO_3 .



Disadvantage / Limitation:

1. Applicable only for low pressure boiler
2. Causes caustic embrittlement and corrosion in high pressure boilers as the un-reacted Na_2CO_3 will be converted in to NaOH and CO_2 .

➤ **Phosphate Conditioning:**

In high-pressure boilers, scale formation can be avoided by the addition of sodium phosphate to the water sample. Here, calcium (and also magnesium) ions (responsible for hardness) are precipitated as their phosphates (sludges) and can be removed easily by filtration. Three types of phosphates conditioning— mono, di and trisodium phosphates are employed in phosphate conditioning.

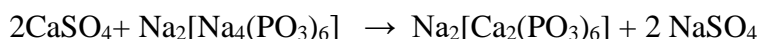
The advantages of phosphate conditioning over carbonate conditioning are (i) it can be applied to high-pressure boilers and (ii) it can be used for softening / conditioning acidic, neutral or alkaline water sample.



If acidic water is to be conditioned, trisodium phosphate can be used. For neutral and alkaline water samples disodium phosphate and monosodium phosphate can be used respectively.

➤ **Calgon conditioning:**

It is the process of addition of *calgon* or *sodium hexametaphosphate* to the boiler feed water. The calcium ions (responsible for scale / sludge formation) are complexed by calgon to form a soluble complex and hence prevented from their scale forming action.



This phenomenon of complexing of the ions is called sequestration. Calgon is the sequestering agent used. The other internal conditioning agents used are ethylenediamine

tetracetic acid (EDTA) and sodium aluminate (NaAlO_2). EDTA functions by sequestration phenomenon whereas sodium aluminate functions by precipitation phenomenon.

➤ **Colloidal conditioning:**

In low pressure boilers scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar etc. They get coated over the scale forming precipitates, converting into loose deposits which can be easily removed blow-down operations.

Lecture session 33: Topics: Softening of hard water (external) - Zeolite process,- advantages & limitations, Demineralization (Ion exchange) process – explanation with mechanisms, regeneration of resins

EXTERNAL CONDITIONING:

Three types of external conditioning methods in use are

- (i) Lime-soda process
- (ii) Permutit or zeolite process and
- (iii) Demineralization process.

The first process is based the precipitation of hardness causing ions by the addition of soda (Na_2CO_3) and lime ($\text{Ca}(\text{OH})_2$) whereas the second and third process is based ion exchange mechanism (ion exchange process).

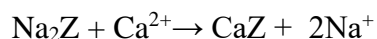
An ion exchange process may be defined as a reversible exchange of ions between a liquid phase and a solid phase. Materials capable of exchanging cations are called cation exchangers and those which are capable of exchanging anions are called anion exchangers. Both anion and cation exchangers are used in water treatment.

NATURAL AND SYNTHETIC ZEOLITE PROCESS.

- ✓ Zeolites are of two types - natural zeolites and Synthetic zeolites.
- ✓ Natural Zeolites are non porous materials Ex. Natrolite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$.
- ✓ Synthetic Zeolites also called permutits are porous and poses a gel structure. Ex- Sodium Zeolite. Synthetic Zeolites have higher exchange capacity per unit weight.
- ✓ Sodium Zeolites are used for water softening and they have general chemical structure as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y2\text{H}_2\text{O}$ wher $x= 2-10$: $y=2- 6$

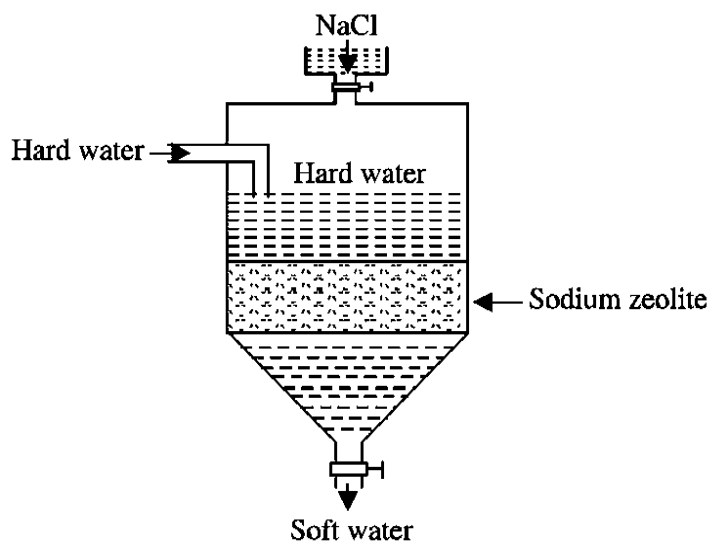
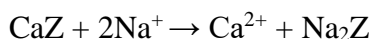
- ✓ They are considered as hydrated sodium aluminosilicates which are capable of exchanging their sodium ions for divalent ions of metals present in water
- ✓ Zeolites are represented as Na_2Z . Where Z is insoluble zeolite frame work.

Process: Hardwater is allowed to percolate through a bed of Zeolite kept in a cylinder. The hardness causing ions are taken up by the zeolite and simultaneously releasing the equivalent sodium ions in exchange for them.



Regeneration: When the zeolite bed is exhausted (i.e saturated with Ca^{2+} and Mg^{2+}) it cannot soften water further.

Exhausted Zeolites is reclaimed by treating the bed with a concentrated NaCl solution(10% brine)

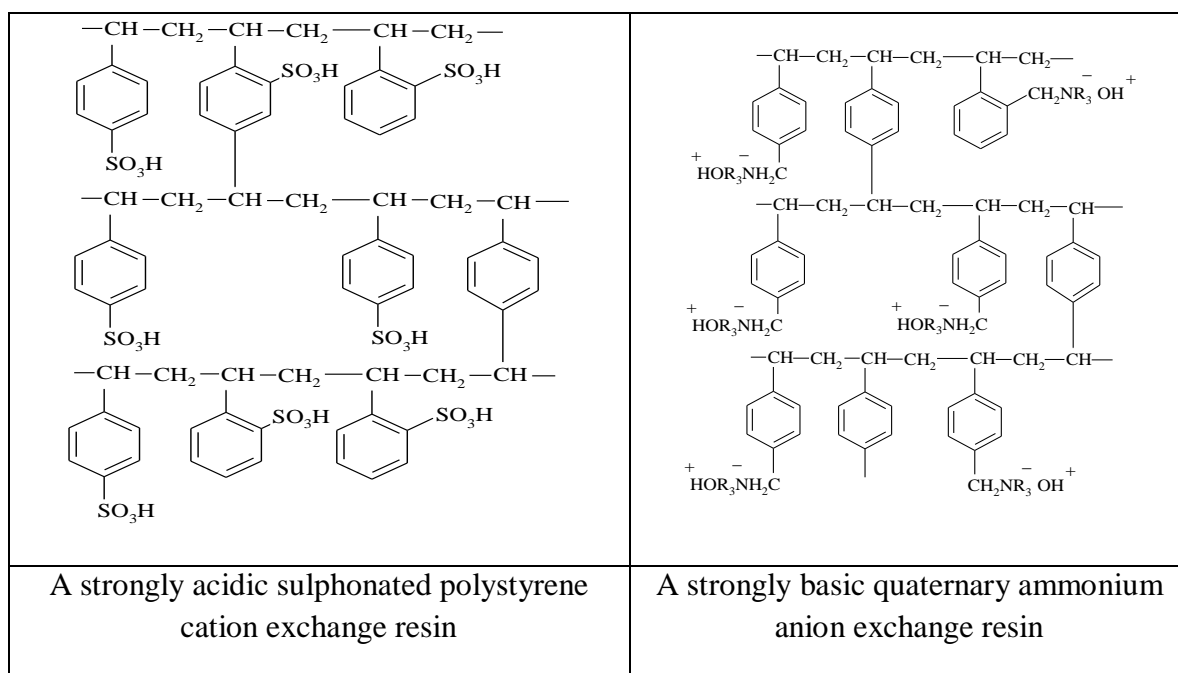


Lecture session 6 : Topics: Demineralization (Ion exchange) process – explanation with mechanisms – regeneration:

DIMINERALISATION USING ION EXCHANGE RESINS

Dimineralisation or Deionisation can be carried out using ion exchange resins (IER). IE resins are insoluble, cross-linked long chain organic polymers with micro-porous structure. The functional groups attached to the polymeric chain have the tendency to exchange the (hardness causing) ions. Acidic functional groups such as carboxyl (-COOH), sulphonic acid (-SO₃H) have the capacity to exchange cations whereas basic functional groups such as amines (-NH₂), hydroxyl (-OH) have the capacity to exchange anions. Ion exchange resins are generally synthesized such as styrene-divinyl benzene copolymers

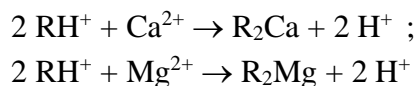
The copolymer has the structure of alternate styrene and divinyl benzene units with the aromatic rings bearing the substituents of acidic / basic functional groups such as sulphonic acid, carboxylic acid, (substituted) amines etc.



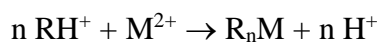
Process: It is the process of removal of any mineral (cation or anion) from the water sample. Water sample is first passed through a column called cation exchanger, which is packed with cation exchange resins. This causes the removal of cations by ion exchange process, but renders

the water sample acidic. The cation exchange resins are synthesized by the carboxylation or sulphonation of styrene-divinyl benzene copolymers. The structure of these resins is given below

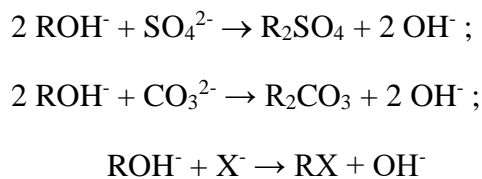
Cation exchange resin is generally represented as RH^+ ; the ion exchange process is represented as



The exchange of any metallic cation (M^{n+}) can be written as



The acidic water coming out of the cation exchanger is then fed to a column called anion exchanger, which is packed with anion exchange resins. This causes the removal of anions by ion exchange process and also neutralizes the acidity of the water sample, explained as follows. The anion exchange resins are synthesized by the hydroxylation or amination of styrene-divinyl benzene copolymers. Anion exchange resin is generally represented as ROH^- ; the ion exchange process is represented as

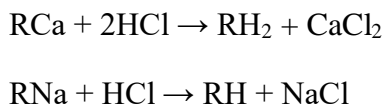


The ultimate reaction taking place on passing the water sample through the cation and anion exchanger systems is

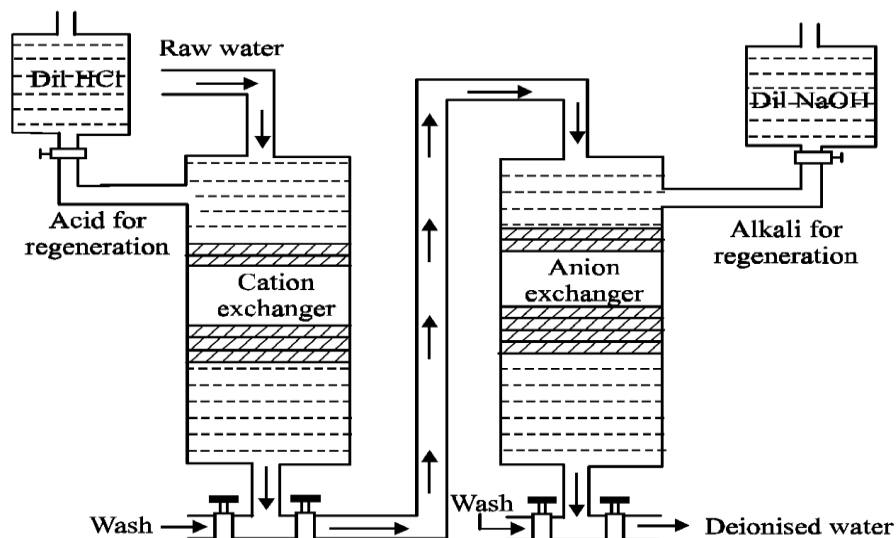
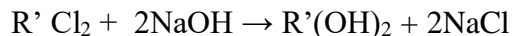


Regeneration

When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil HCl or dil H_2SO_4 .



Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil NaOH.



Lecture session 34: Topics: Domestic water treatment (Large-scale water treatment) - Removal of suspended particles, disinfection- Break point chlorination

Treatment of water for domestic supply:

Drinking or portable water, fit for human consumption, should satisfy the following essential requirements

1. It should be clear and odoursless
2. It should be pleasant in taste
3. Turbidity should not exceed 10 ppm
4. It should be free from dissolved gas like H₂S
5. It should be free from Cr, Pb Mn etc.,
6. TDS should be less than 500 ppm
7. It should free from disease-producing micro-organisms, etc.

Purification of water for domestic use

Removing various types of impurities the following treatment process are employed

Screening:

It is a process of removing the floating material like leaves, wood pieces, etc. from water.

Aeration:

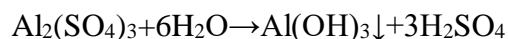
The process of mixing water with air is known as aeration. This leads to remove gases like CO_2 , H_2S .

Sedimentation:

It is a process of removing suspended impurities by allowing the water to stand undisturbed for 2-6 hours in a big tank.

Coagulation:

In this method certain chemicals called coagulants, like alum, added to the water. Coagulant, when added to water, forms an insoluble gelatinous, flocculant precipitate, which descends through the water, combine to form a bigger flocs, which settle down easily



Filtration:

It is the process of removing bacteria, colour, taste, odour by passing water through bed of fine sand and other proper sized granular materials. Filtration is carried out by using sand filter which is shown in Fig. 1.

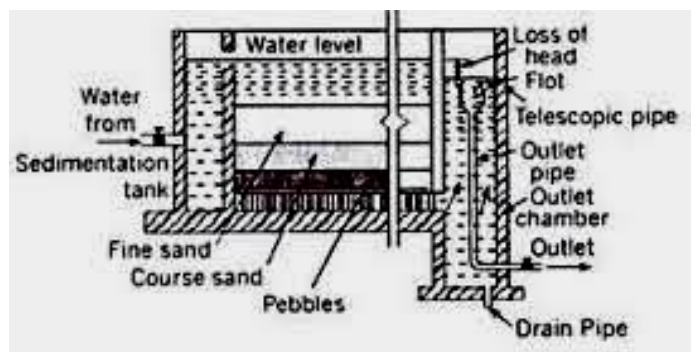


Fig. 1 Sand Filtration

Sterilization (or) disinfection:

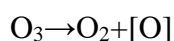
The process of destroying the harmful bacteria is known as sterilization.

1. By boiling:

Water boiled for 10-15 minutes, all the harmful bacteria are killed and the water becomes safe for use. However it is not practically possible to boil huge amounts of water. Moreover it cannot take care of future possible contaminations.

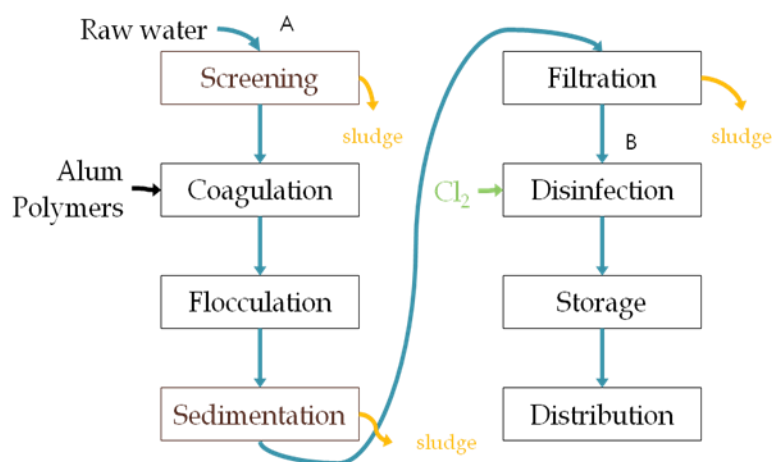
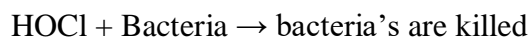
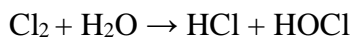
2. By Ozonation:

Ozone is a powerful disinfectant and is readily absorbed by water, which produce nascent oxygen. The nascent oxygen is very powerful oxidizing agent and kills all the bacteria's as well as oxidizes the organic matter present in water.



3. By Chlorination

Chlorine with water produces hypochlorous acid, which is powerful germicide. The germicidal action of chlorine is explained by the recent theory of Enzymatic hypothesis, according to which the chlorine enters the cell walls of bacteria and kill the enzymes which are essential for the metabolic processes of living organisms.



Flow chart of Water Treatment process

Break point chlorination:

It involves in addition of sufficient amount of chlorine to oxidises: (a) organic matter, (b) reducing substances (Fe^{2+} , H_2S etc) and (c) free ammonia in raw water; leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing bacteria's.

Chlorination, used at both household and large-scale levels, is one of the most effective and widely used methods for disinfecting water and making it safe to drink. Whatever the level, it is important that the correct quantity of chlorine is added to remove all impurities.

When the dosage of applied chlorine to the water rich in organic compounds or ammonia is gradually increased, the results obtained can be depicted in Fig. 2, which consists of four stages as follows

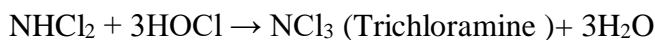
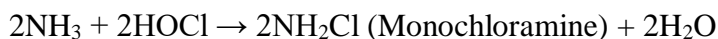
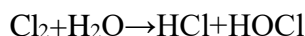
Between points 1 and 2

When you first add chlorine to water, it immediately begins to oxidize metals like iron and manganese, which reduce chlorine. This initial reaction wipes out a certain portion of chlorine, which is why nothing shows up on the graph until point (A).

The water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual.

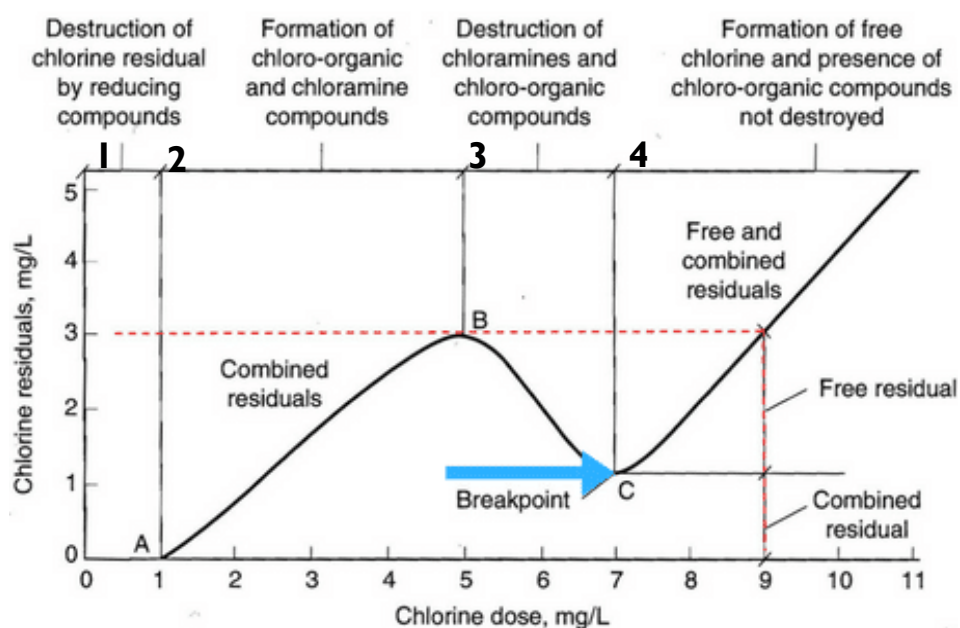
Between points 2 and 3

The chlorine reacts with organics and ammonia naturally found in the water. Some combined chlorine residual is formed - chloramines. Note that if chloramines were to be used as the disinfecting agent, more ammonia would be added to the water to react with the chlorine. The process would be stopped at point 3. Using chloramine as the disinfecting agent results in little trihalomethane production but causes taste and odor problems since chloramines typically give a "swimming pool" odor to water.



Between points 3 and 4

The chlorine will break down most of the chloramines in the water, actually lowering the chlorine residual. Finally, the water reaches the breakpoint, shown at point 4. The breakpoint is the point at which the chlorine demand has been totally satisfied - the chlorine has reacted with all reducing agents, organics, and ammonia in the water. When more chlorine is added past the breakpoint, the chlorine reacts with water and forms hypochlorous acid in direct proportion to the amount of chlorine added. This process, known as breakpoint chlorination, is the most common form of chlorination, in which enough chlorine is added to the water to bring it past the breakpoint and to create some free chlorine residual.



Chlorine residuals Vs Chlorine dose

At municipal level, various terms are used to describe the aspects of chlorination process. Chlorine dosage is the amount of chlorine added to the water system in milligrams per litre (mg/l). Chlorine demand is the amount of chlorine that combines with the impurities and therefore is no longer available as a disinfecting agent. The chlorine that remains in the water after the chlorine demand has been satisfied is called free chlorine residual. A certain amount of residual chlorine is a good idea because it protects against future recontamination.

The *benefits* of point-of-use chlorination include:

- Chlorine is proven to be effective in the reduction of bacteria and most viruses.

- The residual chlorine is effective in protection against recontamination.
- It is easy to use.
- Chlorine is easily available at low cost.

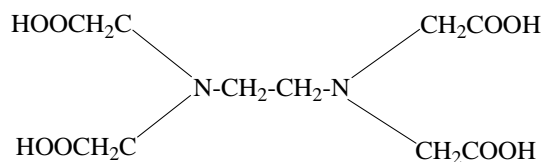
The *drawbacks* of chlorine treatment include:

- It provides relatively low protection against some viruses and parasites.
- Lower effectiveness in water contaminated with organic and certain inorganic compounds.
- Potential objections to taste and odour.
- Some people have concerns about the potential long-term carcinogenic effects of chlorination byproducts.

Lecture session 35: Water analysis: Hardness – determination by EDTA method- Alkalinity – determination by double indicator method

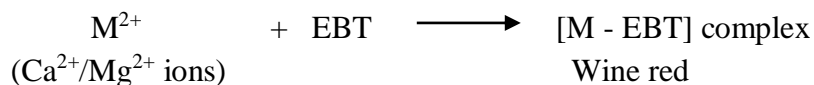
Determination of hardness of water by EDTA method

This is a complexometric method where ethylene diaminetetraacetic acid (EDTA) is used to determine the temporary and permanent hardness of water.

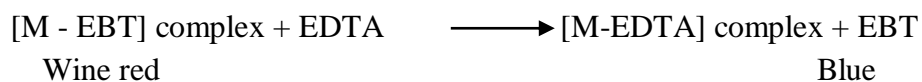


Principle

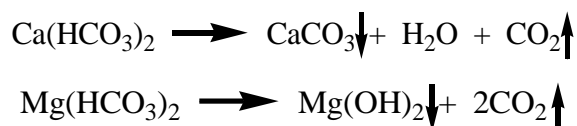
In order to obtain the equivalence point, EBT or eriochrome black – T (an alcoholic solution of blue dye) is employed as indicator which initially forms a stable complex with Ca^{2+} and Mg^{2+} ions and forms a wine-red color complex. This indicator is effective at a pH of about 10 and hence buffer ($\text{NH}_4\text{OH-NH}_4\text{Cl}$) is added in each titration.



During the course of the titration against EDTA solution, it forms a stable complex and releases free EBT, which instantaneously combines with M^{2+} ions still present in the solution, thereby wine red color is retained. When all metal ions have formed [M-EDTA] complex, then the next drop of EDTA added replaces the EBT indicator from the complex and makes it completely free. Then the color changes from wine red to steel blue. The change of color marks the end point of the titration.



Temporary hardness of water is caused by the presence of bicarbonates of Ca and Mg and permanent hardness is caused by chlorides and sulphates of Ca and Mg. Total hardness is estimated by titrating the sample water against disodium salt of EDTA using Eriochrome Black-T indicator. Temporary hardness is removed on boiling the water sample and hence temporary hardness is calculated as a difference of permanent hardness from the total hardness.



Procedure:

Titration I: Standardization of EDTA

Pipette out 20 mL of standard hard water (1 g CaCO_3 dissolved in HCl and evaporated to dryness, then diluted to 1 lit where 1 ml of this solution contains hardness equivalent to 1 mg of CaCO_3) into a clean conical flask. Add 10 mL of ammonical buffer solution, 2 drops/ a pinch of Eriochrome Black-T indicator and titrate against EDTA solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordancy. Note the concordant value as V_1 ml.

Volume of standard hard water = 20 mL

1 mL of std. hard water contains 1 mg of CaCO_3

20 mL of std. hard water contains 20 mg of CaCO_3

20 mL of std. hard water consumes V_1 mL of EDTA

V_1 mL of EDTA = 20 mg of CaCO_3

1 mL of EDTA = $20 / V_1$ mg of CaCO_3

Titration II: Estimation of total hardness

Pipette out 50 mL of given sample of hard water into a clean conical flask. Add 10 mL of ammonical buffer solution and 2 drops/a pinch of EBT indicator and titrate against EDTA

solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordancy. Note the concordant value as V_2 ml.

50 ml of water sample consumes V_2 mL EDTA

$$\text{Total Hardness in 1000 mL} \equiv \frac{20}{V_1} \times V_2 \times \frac{1000}{50} \text{ mg of CaCO}_3$$

Titration III: Estimation of permanent hardness

Pipette out 100 mL of water sample in a 250 mL beaker. Boil for 30-45 minutes, cool and filter. Wash the precipitate with distilled water. Collect the filtrate and washings in a 250 mL conical flask. Add 10 mL of ammonical buffer and 2 drops/a pinch of EBT indicator and titrate against EDTA solution taken in the burette. The end point is the change of color from wine red to steel blue. Repeat the titration for concordancy and note the concordant titre value as V_3 mL.

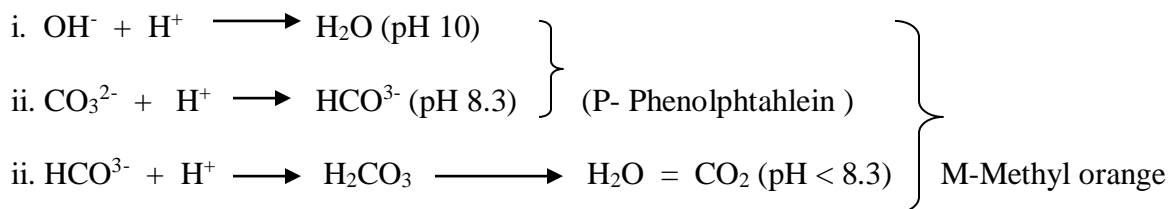
$$\text{Permanent Hardness in 1000 ml sample} \equiv \frac{20}{V_1} \times V_3 \times \frac{1000}{100} \text{ mg of CaCO}_3$$

$$\text{Temporary Hardness} = \text{Total Hardness} - \text{Permanent Hardness}$$

Estimation of Alkalinity in Water

Principle:

The alkalinity of any medium is a measure of its capacity to neutralize acids. The major anions contributing to alkalinity of water are hydroxides, carbonates and bicarbonates. If the pH of the water sample is (a) ≥ 10 , the alkalinity must be attributed to hydroxide and carbonate, (b) ≥ 8.3 but ≤ 10 generally due to carbonate and bicarbonate and (c) ≤ 8.3 , largely due to bicarbonate. When dilute sulphuric acid is added to the water sample, the following reactions are expected to be complete very rapidly.



Procedure:**Titration I: Standardization of sulphuric acid:**

Pipette out 20 ml of standard sodium carbonate solution into a clean conical flask. Add 2 drops of methyl orange indicator and titrate against sulphuric acid taken in the burette. The end point is the change of color from yellow to pink. Repeat the titration for concordancy. Note the concordant value as V1 ml. The strength of $\text{Na}_2\text{S}_2\text{O}_3$ can be calculated from the following equation

Titration II: Estimation of alkalinity of water:

Fill the burette with standardized sulphuric acid. out 20 ml of the water sample into a clean conical flask. Add a drop of Phenolphthalein indicator to it. Titrate it against sulphuric acid taken in the burette until the colour changes from pink to colourless. Note the value as [P] ml. To the same reaction mixture add a drop of methyl orange & continue the titration with H_2SO_4 taken in the burette. The end point is change of color from pale yellow to pink. Note the value as [M] ml. Repeat the titration for concordancy. Calculate the type of alkalinity in the given sample using table 1. Based on the P and M values, alkalinity causing ions of the water sample is determined.

Sl.No.	Relative titre values with	Alkalinity due to		
		OH-	CO_3^{2-}	HCO_3^-
1.	[P] = 0	0	0	[M]
2.	[P] = M	[M]	0	0
3.	[P] = $\frac{1}{2}$ [M]	0	2[P]	0
4.	[P] > $\frac{1}{2}$ [M]	2[P] – [M]	2[M] – 2[P]	0
5.	[P] < $\frac{1}{2}$ [M]	0	2[P]	[M] – 2[P]

Calculations:

$$(\text{VN})_{\text{Acid}} = (\text{VN})_{\text{Na}_2\text{CO}_3}$$

$$N_{\text{Acid}} = (\text{VN})_{\text{Na}_2\text{CO}_3} / V_{\text{Acid}}$$

If $[P] < \frac{1}{2} [M]$

$$(i) \text{ The strength of } \text{CO}_3^{2-} = \frac{2 [P] \times N_{\text{acid}} \times 50 \times 1000}{\text{Vol. of water}} = \dots\dots\dots \text{ ppm}$$

$$(ii) \text{ The strength of } \text{HCO}_3^- = \frac{[M] - 2 [P] \times N_{\text{acid}} \times 50 \times 1000}{\text{Vol. of water}} = \dots\dots\dots \text{ ppm}$$

If $[P] = [M]$,

$$(iii) \text{ The strength of } \text{OH}^- = \frac{[M] \times N_{\text{acid}} \times 50 \times 1000}{\text{Vol. of water}} = \dots\dots\dots \text{ ppm}$$

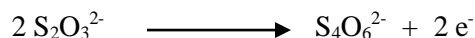
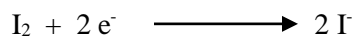
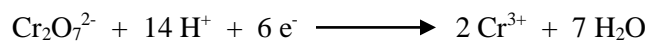
$$(iv) \text{ Total alkalinity} = \dots\dots\dots \text{ ppm}$$

Lecture session 36: Determination of dissolved oxygen by Winkler's method and Determination of chloride by Mohr's method

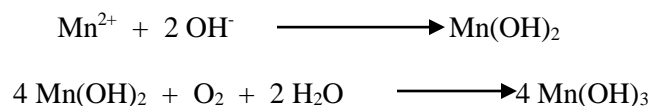
Estimation of dissolved oxygen in water

Principle:

In this method, a large excess of potassium iodide is added to acidified potassium dichromate solution. Iodine liberated is titrated against sodium thiosulphate solution.



DO in water sample is used to oxidize iodide in the presence of the catalyst MnSO_4 and interference-eradicating agent azide. Manganous ion (Mn^{2+}) produces $\text{Mn}(\text{OH})_2$ under alkaline condition, which is converted rapidly to $\text{Mn}(\text{OH})_3$ by the dissolved oxygen.



The brown precipitate of Mn(OH)_3 dissolves on acidification and oxidizes iodide ion to iodine. The DO content of the water sample can be calculated by titrating the liberated iodine against previously standardized sodium thiosulphate solution.

Procedure:

Titration I: Standardization of Sodium thiosulphate

Fill the burette with sodium thiosulphate solution. Pipette out 20 mL of standard potassium dichromate solution into a clean conical flask. Add about 10 ml of dilute sulphuric acid followed by 10 mL of potassium iodide and titrate against thio solution taken in the burette. When the solution becomes straw yellow, add 1 mL of freshly prepared starch, and observe the intense blue colour. Continue the titration with vigorous shaking until the blue colour disappears. Note down the titre value. Repeat the titration for concordancy and calculate the strength of thiosulphate.

$$\text{Strength of Na}_2\text{S}_2\text{O}_3, N_{\text{Na}_2\text{S}_2\text{O}_3} = (\text{VN})_{\text{K}_2\text{Cr}_2\text{O}_7} / V_{\text{Na}_2\text{S}_2\text{O}_3}$$

Titration II: Determination of dissolved oxygen

Fill the BOD bottle with sample water. Using a dropper, add 2 ml of manganese sulphate solution, 2 ml alkali iodide and sodium azide reagents, by placing the dropper just below the surface of the water sample in the BOD bottle. Replace stopper, to exclude the air bubbles and invert the bottle several times to mix thoroughly. Allow the floc to settle, then remove the stopper and add 2 ml of conc. H_2SO_4 down the neck of bottle. Re-stopper and mix by inversion until I_2 is uniformly distributed. Measure the volume of mixture in the BOD bottle and transfer the mixture into a clean conical flask and titrate it with standardized thio taken in the burette till the appearance of pale straw yellow. Add 1-2 ml of starch indicator and titrate it again until the blue colour disappears. Note the value and calculate the amount of dissolved oxygen using following formula

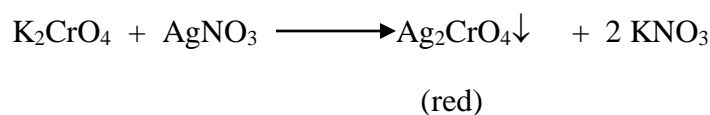
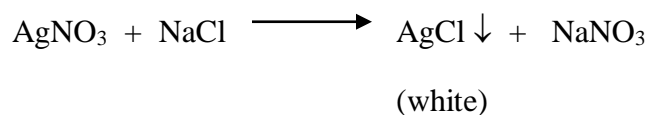
$$\text{The amount of DO} = \frac{8 \times (\text{VN})_{\text{Na}_2\text{S}_2\text{O}_3} \times 1000}{\text{Volume of water sample}} \text{ . mg/L or ppm}$$

Determination of chloride by Mohr's method

Principle:

The method is based on the formation of a sparingly soluble brick red precipitate of silver chromate at the end point when the sample is titrated against standard silver nitrate solution using potassium chromate as indicator.

The reaction involved are as follows:



Procedure:

Titration I : Standardization of silver nitrate

Pipette out 20 ml of standard sodium chloride in a conical flask. Add 5 drops of potassium chromate indicator and titrate against silver nitrate solution till the colour changes from yellow to brick red colour. Repeat the titration for concordant value.

$$\text{Strength of AgNO}_3 (N_{\text{AgNO}_3}) = (VN)_{\text{NaCl}} / V_{\text{AgNO}_3}$$

Titration II: Estimation of Chloride

Transfer the given water sample into 100 ml standard flask and make up to the mark with distilled water. Pipette out 20 ml of the made up solution in a conical flask. Add 5 drops of potassium chromate indicator and titrate against standardized silver nitrate solution till the colour changes from yellow to brick red colour. Repeat the titration for concordant value and calculate the chloride content using given formula.

$$\text{Chloride content} = \frac{(VN)_{\text{AgNO}_3} \times 35.45 \times 1000}{\text{Vol. of water sample}}$$

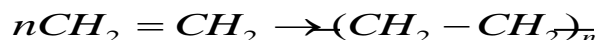
Unit 5- Materials Chemistry

Introduction – Polymers – Monomer; Classification of polymers – Natural and Synthetic (Inorganic and Organic) examples

Poly means many and mers means units.

Polymers are macromolecules formed by the repeated linking of large number of small molecules. This is called **polymer**.

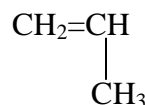
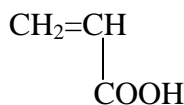
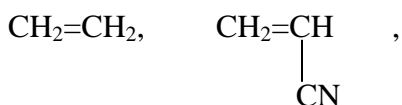
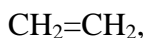
Example:



Monomer: (Repeating unit)

Monomer is a micro/small molecule which combines with each other to form a polymer.

Example:



Ethylene

acrylonitrile

acrylic acid

Propylene

POLYMERISATION:

Polymerisation is a process in which large number of small molecules combines to give big molecule with or without elimination of small molecules.

CLASSIFICATION OF POLYMERS:

Polymers are classified in to four main categories.

- 1. Based on the source / origin**
- 2. Based on the structure**
- 3. Based on the mode of synthesis**
- 4. Based on the intermolecular forces**

1. Based on Source / Origin

- a) Natural polymers
- b) Synthetic polymers

(a) Natural Polymers

The polymers which are isolated from the natural materials such as plant and animals are called as natural polymers.

- i. **Starch** – It is a polymer of α D- glucose. It is a food reserve of plants
- ii. **Cellulose** – It is a polymer of β –D glucose. It is a chief structural material of plant
- iii. **Proteins** – These are polymers of α amino acids. These are the building blocks of animal cells.

Generally they have 20 to 100 α amino acids, joined together in a highly organized arrangement.

- iv. **Nucleic acids** – RNA and DNA are the examples
- v. **Natural rubbers** – Substances obtained from latex is known as natural rubber.

(b) Synthetic polymer

- i. Polymers which are prepared artificially in the laboratories are referred as synthetic polymers or manmade polymers.

Eg. Polyethylene, teflon, nylon, bakelite PVC, polyester, terylene etc

ORGANIC AND INORGANIC POLYMERS:

If the polymer consisting of only carbon atom as the main chain, then the polymer is called **organic polymers**.

Example: Nylon, Teflon.

If the polymer consisting of atoms other than carbon atoms as the main chain, then the polymer is called **inorganic polymers**.

Example: Silicones.

2. Based on structure

- i. Linear polymers
- ii. Branched chain polymers
- iii. Cross-linked polymers

i. Linear Polymers

- Monomeric units are linked together to form a long straight chain.
- have repeat units joined end to end in single chains

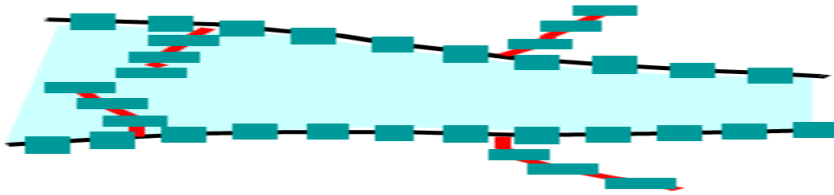
- may be extensive Van der Waals forces and hydrogen bonding between the chains.
Examples: polyethylene, PVC, nylon



ii. Branched chain polymers

Monomeric units are linked to constitute long chains (main chain) Eg. Glycogen and Amylopectin

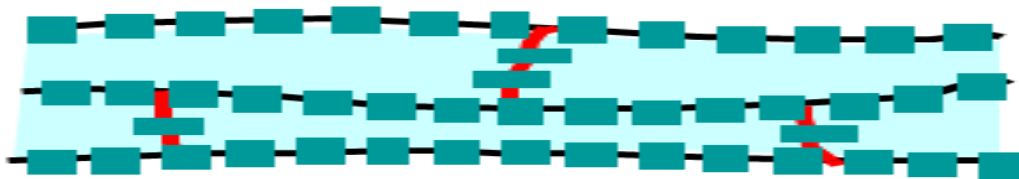
Where side-branch chains have connected to main chains



iii. Cross linked polymers

In cross-linked polymers, adjacent linear chains are joined to one another at various positions by covalent bonding of atoms to constitute a three dimensional network.

Examples: Bakelite, formaldehyde resin etc.



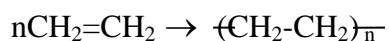
3. Based on Synthesis

- Addition polymers
- Condensation polymers
- Copolymers

Addition polymers

Monomeric units are repeatedly added to form long chains, with out elimination of any byproduct molecules.

Example: Polyethylene.

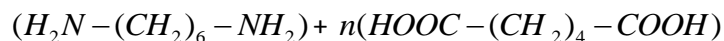


Condensation polymers

The monomers are repeatedly added to form products with the elimination of simple molecules like H_2O , NH_3 , ROH , etc, the products formed are called condensation polymers.

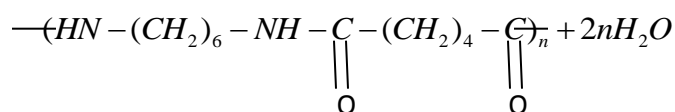
Example: Nylon 6:6

Hexamethylene diamine and adipic acid condense to form a polymer called **Nylon 6:6** (Polyamide).



Hexamethylene Diamine

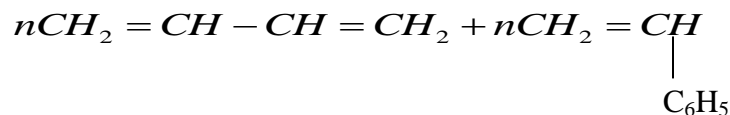
Adipic acid



Nylon 6:6

Copolymerisation:

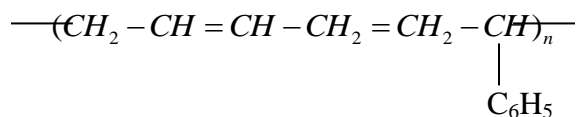
Two or more monomers combine to give polymer. High molecular weights polymers are obtained by copolymerization are called **Copolymers**.



Butadiene

Styrene

Co-polymerisation



Polybutadiene-Co- Styrene

(Styrene butadiene rubber, SBR)

DIFFERENCES BETWEEN ADDITION AND CONDENSATION POLYMERISATION:

S.NO	ADDITION POLYMERISATION	CONDENSATION POLYMERISATION
1	Monomer must have atleast one multiple bond.	Monomer must have atleast two identical or different functional groups.
2	Monomer adds to one another to give polymer.	Different monomers condense to give polymer.
3	No by product is formed.	By product is formed.
4	Thermoplastics are formed.	Thermosetting plastics are formed.
5	Homo chain polymer is obtained.	Hetero chain polymer is obtained.
6	Eg. Polyethylene	Eg. Bakelite

TYPES OF COPOLYMER:

It is subdivided into three types,

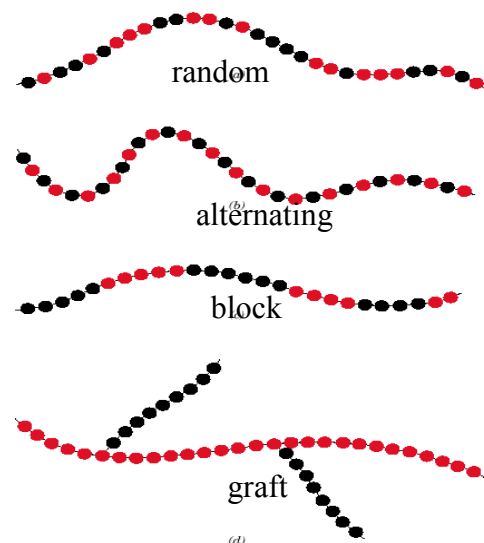
- (i) Random copolymer.
- (ii) Alternating
- (iii) Block copolymer.
- (iv) Graft copolymer.

random – A and B randomly positioned along chain

alternating – A and B alternate in polymer chain

block – large blocks of A units alternate with large blocks of B units

graft – chains of B units grafted onto A backbone



4. Based on Intermolecular Forces

On the basis of the magnitude of intermolecular forces like Van-der-waal's force and hydrogen bonds, the polymers are classified into four types

1. Elastomers - polymers have weak intermolecular forces. Eg. Rubber
2. Fibers - polymers which have strong intermolecular forces such as hydrogen bonds. These are thread like polymers Eg. Silk, Terylene
3. Thermoplastic polymers - polymers in which various chains are held together by weak Vanderwaal's force of attraction - Eg. Polyethylene, polystyrene
4. Thermosetting polymers - polymers in which the various chains are held together by strong covalent bonds or crosslinks. Eg. Bakelite

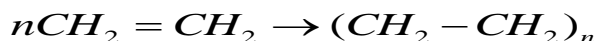
NOMENCLATURE OF POLYMERS:

1. HOMOPOLYMER:

Polymers containing same type of monomers (**A**) are known as **homopolymer**.

Example:

Polyethylene, PVC.



TYPES OF HOMOPOLYMER:

It is divided into 3 types based on the manner, in which monomers are arranged,

- (i) Linear homopolymer
- (ii) Branched homopolymer.
- (iii) Cross linked homopolymer.

2. HETEROPOLYMER OR COPOLYMER:

Polymer containing more than one type of monomer (**A & B**) is known as **copolymer** or heteropolymers.

Example:

Nylon (polyamide), Terylene (Polyester), SBR Rubber.

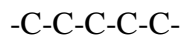


3. HOMOCHAIN POLYMER:

If the main chain of a polymer is made up of same species of atoms are called **homochain polymer**.

Example:

Polyethylene, PVC.



4. HETEROCHAIN POLYMER:

If the main chain of a polymer is made up of different atoms are called **heterochain polymer**.

Example:

Nylon, terylene.

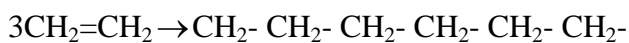


Lecture session 38: Degree of polymerization – Functionality- bi, mixed, poly functional monomers and its significance

DEGREE OF POLYMERISATION:

The number of repeating units in a polymer chain is known as degree of polymerization.

Example:



The degree of polymerization, $n=3$.

It is represented by the following relationship

Molecular weight of the polymer

Degree of Polymerisation= -----

Molecular weight of the repeating unit

(i) OLIGO POLYMERS:

Polymers with low degree of polymerization are known as oligo polymers, their molecular weight from 500-5000.

(ii) HIGH POLYMERS:

Polymers with high degree of polymerization are known as high polymers, their molecular weight from 10000-200000.

FUNCTIONALITY:

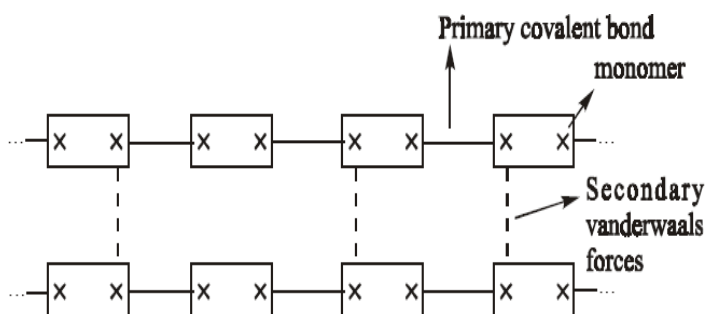
The number of bonding sites in a monomer is called **functionality**.

S.NO	EXAMPLE	FUNCTIONALITY
01	CH_3Cl	1 (It contains one functional group).
02	$n\text{CH}_2=\text{CH}_2$	2 (Two bonding sites are due to the presence of one double bond in the monomer. Therefore ethylene is a bifunctional monomer)
03	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	2 (This monomer contains two functional groups. Hence it is a bifunctional monomer)
04	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	3 (This monomer contains three reactive sites)

Significance

Bifunctional monomers

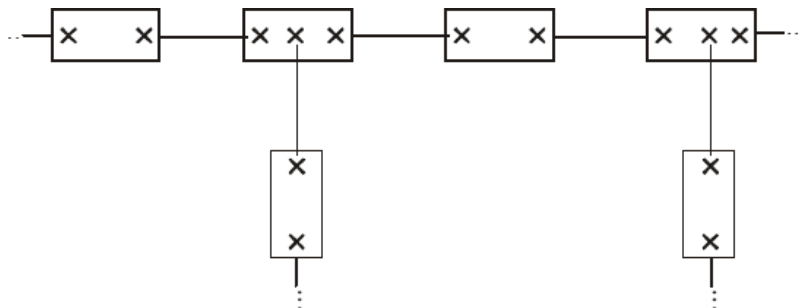
- ❖ Bifunctional monomers (i.e., functionality of the monomer is 2) mainly form linear (or) straight chain polymer.
- ❖ Each monomeric unit in the linear chain is linked by strong covalent bonds (primary bonds), but the different chains are held together by weak vander waal's forces of attraction (secondary bonds).
- ❖ Therefore, there is no restriction to movement of one chain over another.
- ❖ These types of polymers are soft and flexible, and possess less strength, low heat resistance.
- ❖ These are soluble in organic solvents



Trifunctional monomers

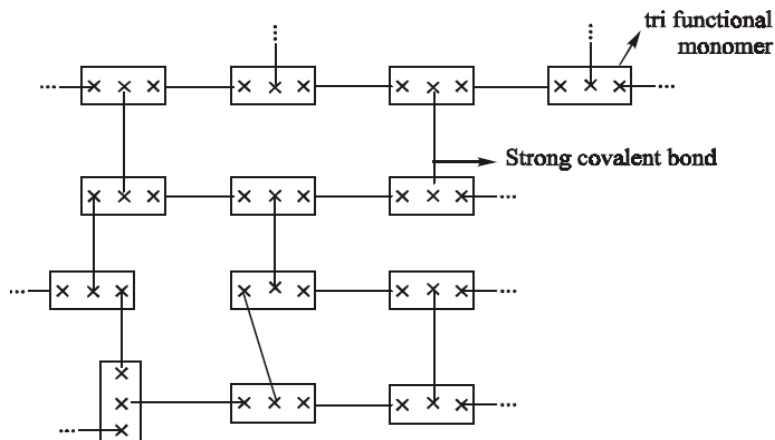
- ❖ When a trifunctional monomer (i.e., functionality of the monomer is 3) is mixed in small amounts with a bifunctional monomer, they form branched chain polymer.

- ❖ The movement of polymer chain in branched polymer is more restricted than that of straight chain polymers.



Poly functional monomers

- ❖ Poly functional monomers form cross-linked polymer (three-dimensional network polymer).
- ❖ All the monomers in the polymer are connected to each other by strong covalent bonds.
- ❖ Therefore the movement of polymer chain is totally restricted.
- ❖ These types of polymers are hard and brittle and possess very high strength and heat resistance.
- ❖ They are insoluble in almost all organic solvents.



Free radical polymerization mechanism of polymerization

MECHANISM OF ADDITION POLYMERISATION:

The mechanism of addition polymerization involves three types,

- (i) Free radical mechanism.
- (ii) Ionic mechanism.

(iii) Co-Ordination mechanism.

FREE RADICAL MECHANISM:

It involves three steps,

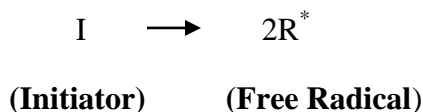
(i) Initiation

(ii) Propagation

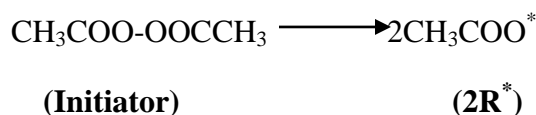
(iii) Termination.

1. INITIATION:

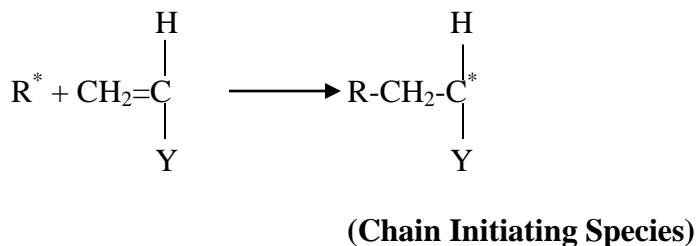
(a) Production of free radicals by homolytic dissociation of an initiator or catalyst.



Example:

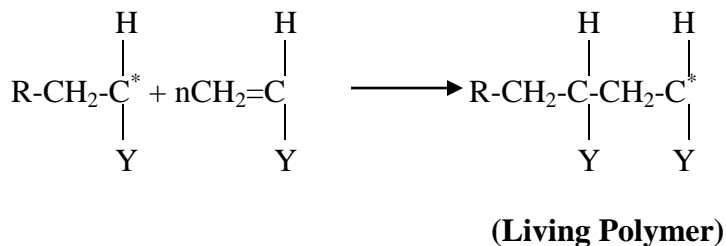


(b) Addition of free radical to the first monomer to produce chain initiating species.



2. PROPAGATION:

It means the growth of chain initiating species by successive addition of large number of monomers.



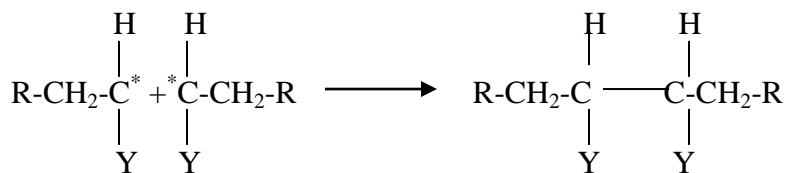
The growing chain of the polymer is known as **living polymer**.

3. TERMINATION:

Termination of the growing chain of polymer occurs by coupling or disproportionation reactions.

(a) COUPLING or COMBINATION:

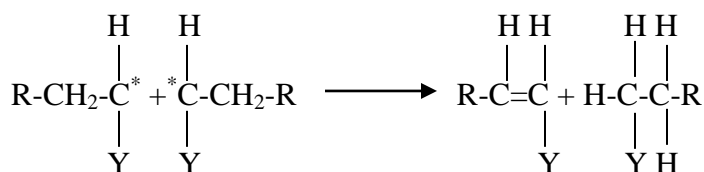
Coupling of free radical of one chain end with free radical of another chain.



Dead Polymer

(b) DISPROPORTIONATION:

Transfer of a hydrogen atom of one radical center to another radical center.



The product of addition polymerization is known as **dead polymer**.

PROPERTIES OF POLYMERS

1. Tacticity (Or) Stereo specific Polymer: (Related to order)

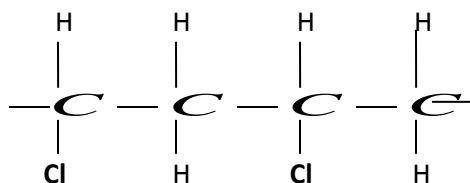
The orientation of monomeric unit or functional groups in a polymer molecule can takes place in orderly or disorderly with respect to main chain. This type of orientation is known as **tacticity**.

This orientation results in 3 types of stereo regular polymer are as follows,

(i) Isotactic Polymer:

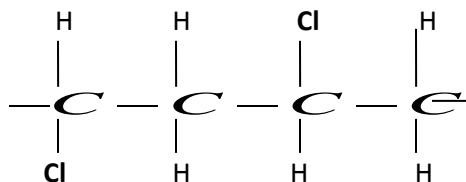
In isotactic polymer, all the functional groups are arranged on the same side of the main chain.

Example:



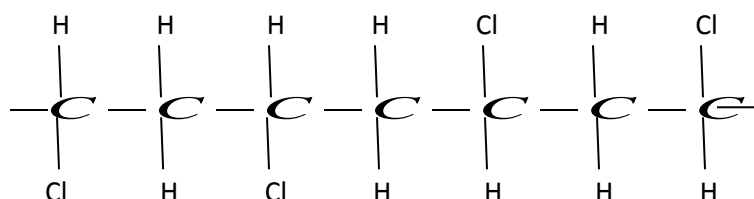
(ii) Syndiotactic polymer:

In syndiotactic polymer, all the functional groups are arranged in alternating position along the main chain.



(iii) Atactic polymer:

In atactic polymer, the functional groups are arranged in randomly along the main chain.



2. GLASS-TRANSITION TEMPERATURE (T_g):

Introduction:

If the non-crystalline polymer (amorphous powder) is melted and then cooled, the polymer becomes more viscous. If the temperature is reduced still, it becomes rubbery. At still lower temperature it becomes hard and elastic polymer glass.

Definition:

The temperature at which the polymer undergoes the transformation from a rubber to glass is known as **glass-transition temperature (T_g)**.

At glass-transition temperature, there is a change in the properties of the polymer.

Example:

For an amorphous polymer, the stiffness is increases below the T_g .

The T_g depends upon the chemical nature of the polymer.

- (i) The T_g is low for flexible chain polymers.
- (ii) The introduction of the groups which stiffen the polymer chain and increases in the value of T_g .
- (iii) If the polymer chain has bulky groups, then the T_g is high.

- (iv) The presence of polar groups like $-\text{CN}$, $-\text{Cl}$, $-\text{OH}$ tends to increase the T_g .

Conducting polymers – mechanism of conduction in polyacetylene and applications

Introduction

In general, polymers are insulators as they do not conduct electricity through them. Since long ago, the polymers were traditionally used as insulating material until the discovery of electrical conductivity in doped polyacetylene in 1970s by A.G. MacDiarmid, A.J. Heeger, Hideki Shirakawa.

Later, in year 2000, the pioneers were recognized and were awarded Noble Prize in Chemistry in recognition of their great contribution for the discovery and development of Conducting polymers.

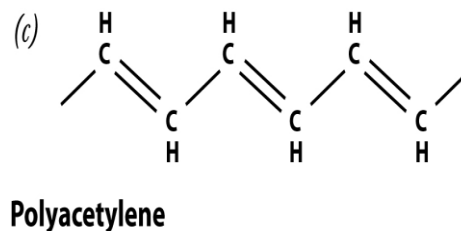
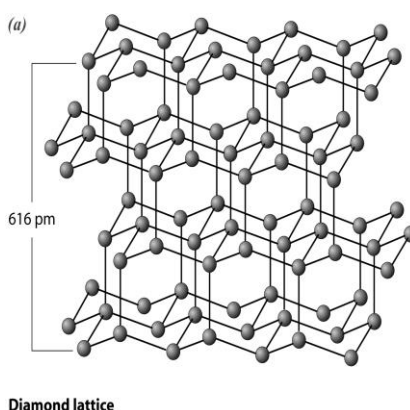
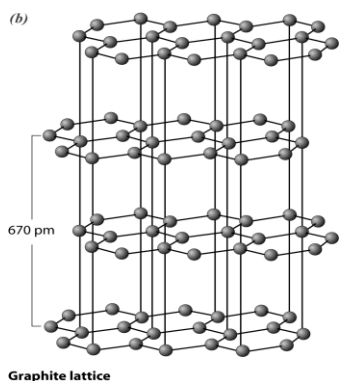
The electrical conductivity observed in the doped polyacetylene was of order 10^3 S/cm^2 . Later, many other conducting polymers like polyaniline, polypyrrole, polythiophene etc were discovered. Therefore, the polymers which allow electric current to pass through them are called as “electrically conducting polymers” or simply conducting polymers. As the electrical conductivity may be ionic or electronic in nature, the conducting polymers include both the electronically and ionically conducting polymers. The electronically conducting polymers include conjugated conducting polymer while the ionically conducting polymer are generally termed as polymer electrolytes.

The conductivity depends on the number of charge carriers (number of electrons) in the material and their mobility. In a metal it is assumed that all the outer electrons are free to carry charge and the impedance to flow of charge is mainly due to the electrons "bumping" in to each other.

Insulators however have tightly bound electrons so that nearly no electron flow occurs so they offer high resistance to charge flow. So for conductance free electrons are needed.

What makes the material conductive?

Three simple carbon compounds are diamond, graphite and polyacetylene. They may be regarded as three- two- and one-dimensional forms of carbon materials



Diamond, which contains only σ bonds, is an insulator and its high symmetry gives it isotropic properties. Graphite and acetylene both have mobile π electrons and are, when doped, highly anisotropic metallic conductors.

How can plastic become conductive?

Plastics are *polymers*, molecules that form long chains, repeating themselves. In becoming electrically conductive, a polymer has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. *Polyacetylene* is the simplest possible conjugated polymer. It is obtained by polymerisation of acetylene.

Two conditions to become conductive in polymers

- The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds.
- In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker.

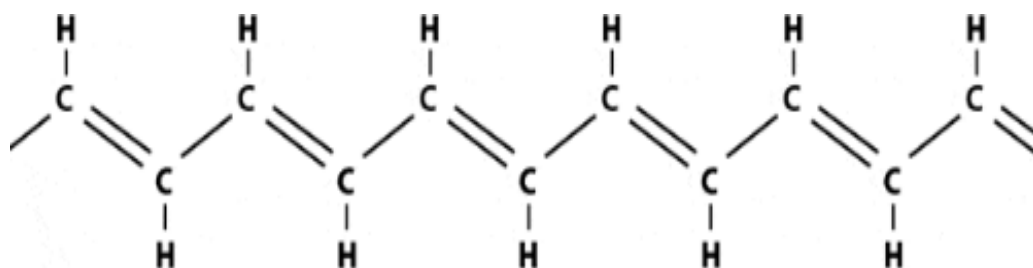


Figure 1

- The second condition is that the plastic has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as **Doping**.

There are two types of doping

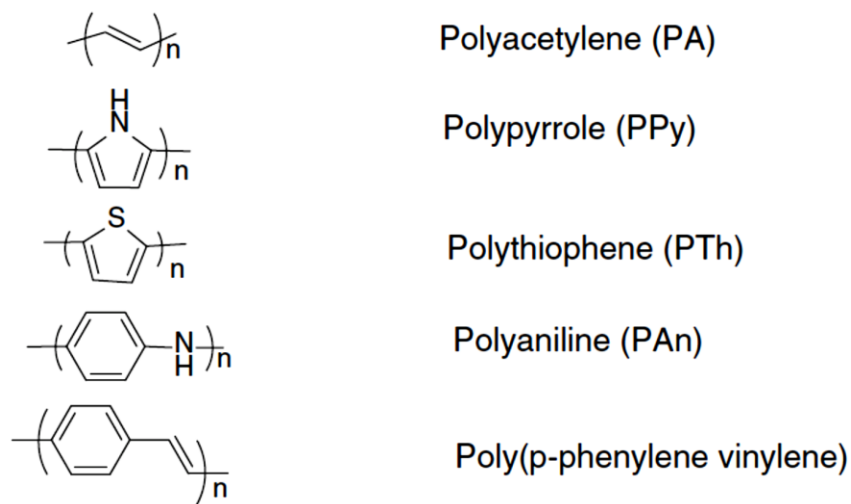
- oxidation with halogen (or *p*-doping).
- Reduction with alkali metal (called *n*-doping).

Structure of Conducting Polymers

Conducting polymers (CPs) have a very unusual structure compared to the insulating polymers. The conducting polymers have conjugated π -electron (alternate C-C and C=C) system in their polymeric backbone (Figure 1). Among the various CPs, the polyacetylene possesses simplest backbone structure which is mainly composed of alternate single and double bond carbon in the chain. This π -electron system is delocalized over the entire backbone of the polymer chain. The polyacetylene is of two types based on its hydrogen atoms locations i) trans-polyacetylene and ii)

cis-polyacetylene. The trans-polyacetylene possesses two hydrogen atoms on opposite sides while in cis-polyacetylene two hydrogen atoms are placed on the same side of the double bond. The trans-polyacetylene represents a degenerate conjugated polymer and possesses equivalent structures after exchanging its double bond and single bond whereas, the cis-polyacetylene and other CPs are non-degenerate conjugated polymers which have non-equivalent structures after exchanging their double and single bonds.

The most important property of the CPs is their redox nature, they can be easily oxidized and reduced provided suitable conditions and this process is called doping of CPs and it causes electrical conduction in the CPs. The electrical conductivity of most of the doped CPs lies in the range 10^{-3} - 10^3 S/cm².



Basic structure of some conjugated polymers.

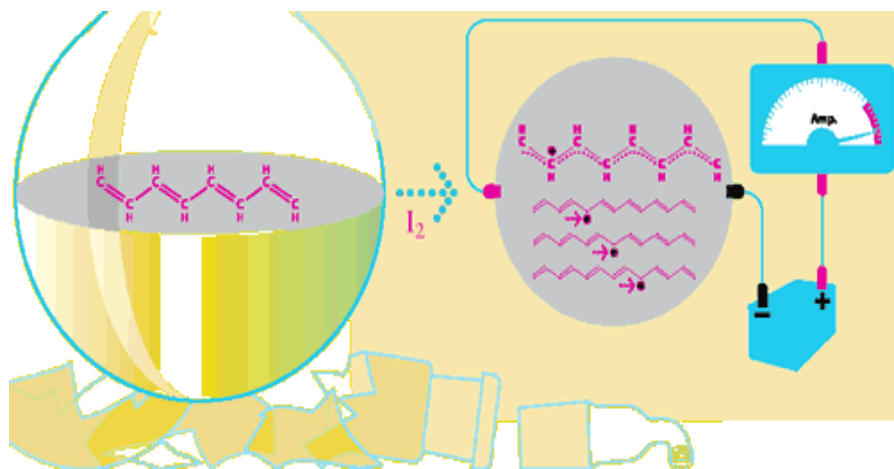
Doping of Conducting Polymers

The doping of the CPs generates charge carriers. The concept and process of doping in CPs are very different from that of inorganic semiconductors. In inorganic semiconductors some other metals are added/replaced as a part of doping while in case of doping of CPs, oxidation/reduction of the CPs backbone is accomplished with the help of some electron acceptor/donor as a result, charge carriers are generated in the CPs backbone. It is also to note that the degree of doping in CPs is much higher than that of inorganic semiconductors, for example, in case of CPs, the concentration of charge carrier generated may reach to the order of 10^{21} /cm³. It also causes volume change (expansion) and changes in morphology of the CPs due to counter ion doping.

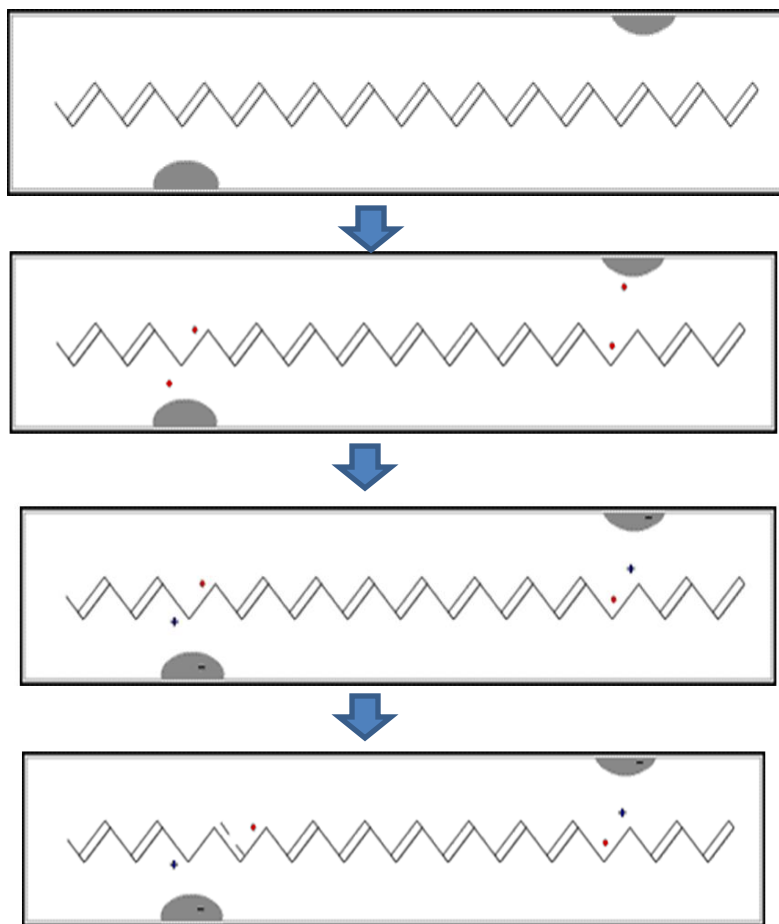
Doping process

- The halogen doping transforms polyacetylene to a good conductor.
- Oxidation with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain.

- The iodine molecule attracts an electron from the polyacetylene chain and becomes I_3^- . The polyacetylene molecule, now positively charged, is termed a radical cation, or *polaron*.



- The lonely electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond successively moves along the molecule.
- The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.



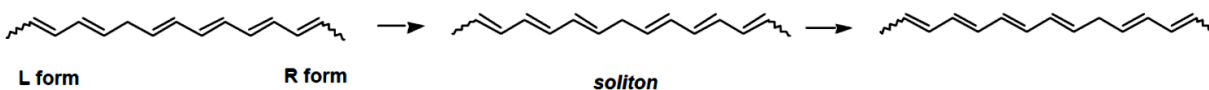
Charge Carriers in Conducting Polymers

We have seen how the doping of CPs generates charge carriers in them. For example, in case of trans-polyacetylene of degenerate state, the important charge carriers are solitons and polarons. While in case of nondegenerate CPs, like cis-polyacetylene, polyaniline, polypyrrole, polythiophene etc. the main charge carriers are polarons and bipolarons. The soliton is an unpaired π -electron species resembles the charge on free radicals and can be delocalized along the backbone of trans-polyacetylene. The soliton is mainly of three types neutral, positive and negative. The neutral soliton on oxidation forms a positive (+) soliton and on reduction forms a negative (-) soliton. The neutral soliton possesses a spin of $1/2$, whereas there is no spin for the positive and negative solitons.

Polarons are major charge-carriers which are present in CPs with degenerate and non-degenerate states. Similar to solitons, polarons are also positive and negative. Which are form by the oxidation and reduction of backbone chain of CPs. The bipolaron are produced on coupling of two polarons (+ or -) and possesses double charges compared to polarons. The bipolaron has no spin, and it can be formed when the concentration of polarons are high in the CPs main chains. The positive bipolaron and negative bipolaron correspond to the hole pair or the electron pair.

Mechanism of Charge Transport

The introduction of charge carriers in CPs because of its doping leads to local relaxation. The geometries in ionized and ground are different; the electronic structure is affected by the localized electron states in the gap which modify the π system. In order to understand the mechanism of conduction, let us see the case of polyacetylene (PA), The asymmetry of PA in its ground state, the two equivalent polyene chains marked L and R are inter-converted due to intervention of a soliton. It is a neutral defect or a “kink” in the PA chain that propagates down the chain and reduces the barrier of the inter-conversion.



Inter-conversion of degenerate state of polyacetylene.

The movement of the charge carriers can be explained hopping mechanism exhibited by bipolarons as in Figure 3.

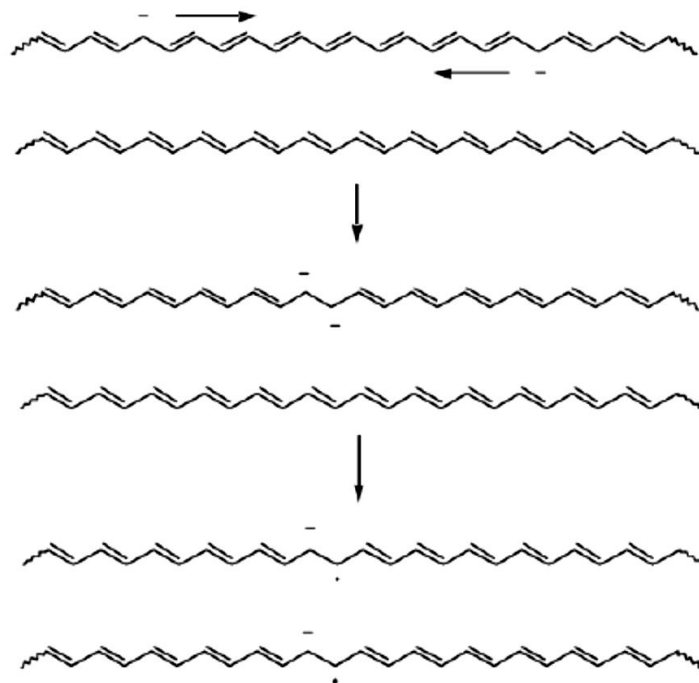
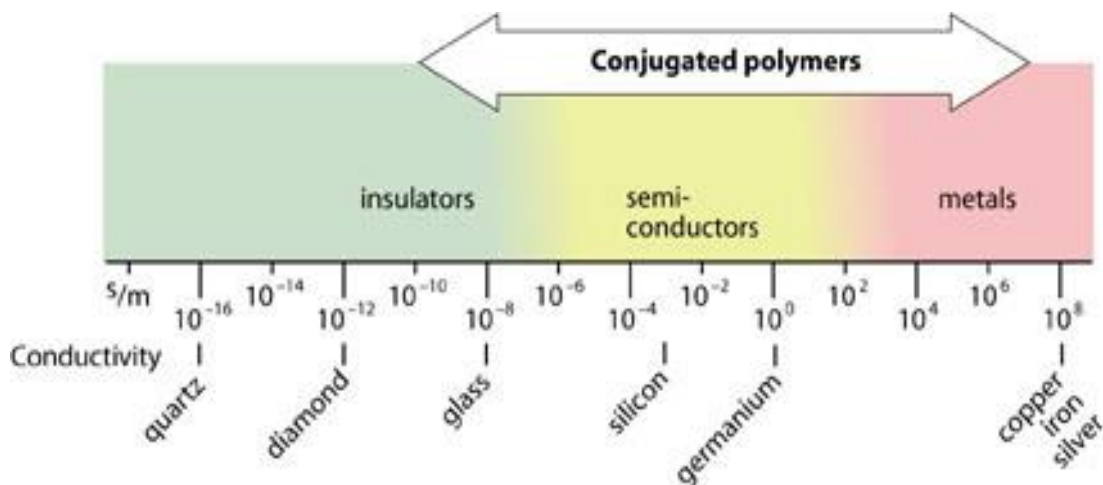


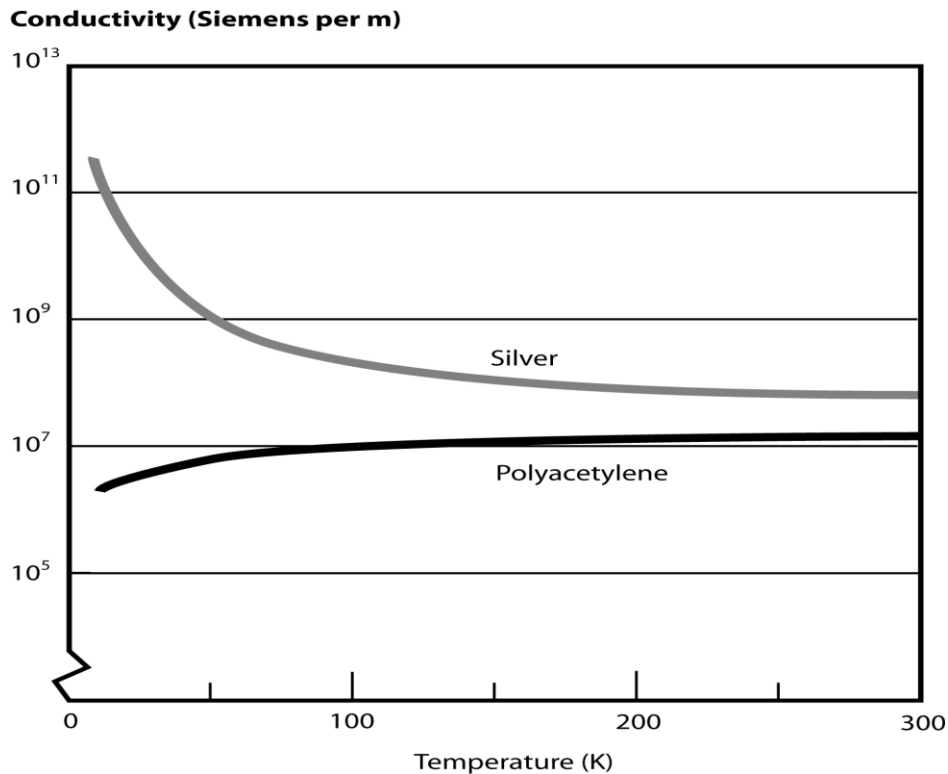
Figure 3. Movement of charge carriers in the backbone of CPs.

Doping - For Better Molecule Performance

- Doped polyacetylene is, e.g., comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.



- Conductivity of conductive polymers compared to those of other materials, from quartz (insulator) to copper (conductor). Polymers may also have conductivities corresponding to those of semiconductors.
- The conductivity of conductive polymers decreases with falling temperature in contrast to the conductivities of typical metals, e.g. silver, which increase with falling temperature.



Factors that affect the conductivity

- Density of charge carriers.
- Their mobility.
- The direction.
- presence of doping materials (additives that facilitate the polymer conductivity)
- Temperature.

Applications

Conducting polymers have many uses. The most documented are as follows:

- anti-static substances for photographic film
- Corrosion Inhibitors
- Compact Capacitors
- Anti Static Coating
- Electromagnetic shielding for computers "Smart Windows"

A second generation of conducting polymers have been developed these have industrial uses like:

- Transistors
- Light Emitting Diodes (LEDs)
- Lasers used in flat televisions
- Solar cells
- Displays in mobile telephones and mini-format television screens

Composites: Definition, need for composites and classification

COMPOSITE MATERIALS

Definition: A composite material may be defined as an artificially prepared or natural multiphase material that exhibits a significant properties of the both the constituent material such as high strength, stiffness and high coefficient of thermal expansion in which the chemically dissimilar phases are separated by distinct interface

(or)

A material which is composed of two or more materials at a microscopic scale and have chemically distinct phases. Heterogeneous at a microscopic scale but statically homogeneous at macroscopic scale.

Need for composite materials:

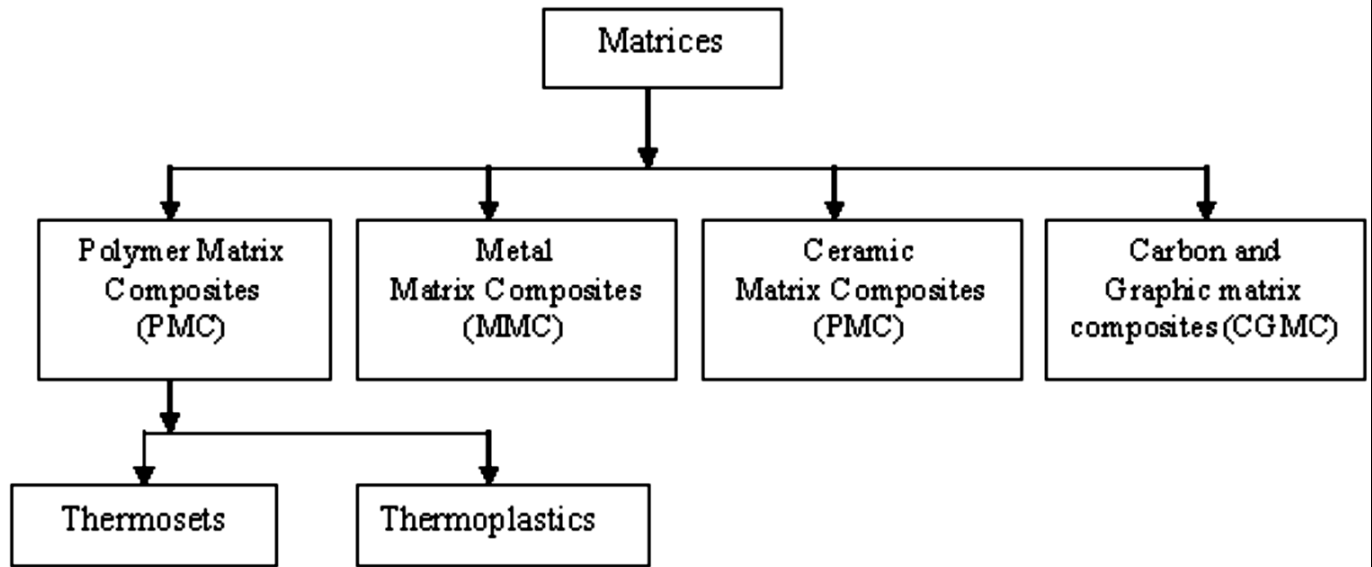
Composites are improving the design process and end products across industries, from aerospace to renewable energy. Each year, composites continue to replace traditional materials like steel and aluminum. As composite costs come down and design flexibility improves, fiber-reinforced composites like carbon fiber and fiberglass open up new design opportunities for engineers.

- ✓ Composites have a high strength-to-weight ratio.
- ✓ Composites are durable.
- ✓ Composites open up new design options.
- ✓ Composites are now easier to produce.
- ✓ Corrosion resistance
- ✓ Wear resistance
- ✓ Reduced weight
- ✓ Fatigue life. etc.,

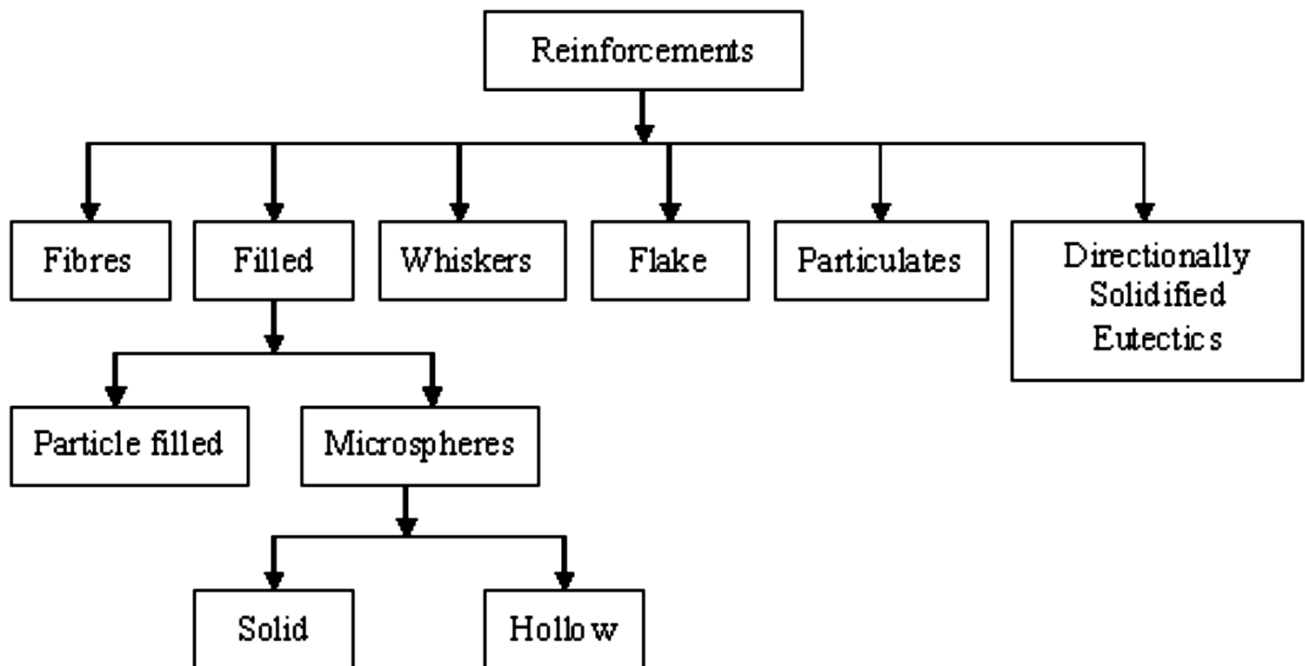
Classification

There are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic, polymer) and the second is based on the material structure:

Based on matrix material



Based on reinforcing material structure



Constitution – Matrix materials (Polymer matrix, metal matrix and ceramic matrix and Reinforcement (fiber, particulates, flakes and whiskers)

Constituents of Composites

Two essential constituents of composites are

- 1. Matrix phase:* It is the continuous body constituent (Dispersion phase) which encloses the composite and gives its bulk form. It may be polymer, metal or ceramic material.

Functions of matrix phase:

- i. binds the dispersed phase together**
- ii. acts as a medium to transmit and distribute an externally applied load to the dispersed phase**
- iii. protects the dispersed phase from chemical action and keep in proper position**
- iv. prevents propagation of brittle crack, due to its plasticity and softness**

Requirement of a good matrix phase: it should be ductile and corrosion resistance and possess high bonding strength between matrix and dispersed phase

- 2. Dispersed phase :** It is the Structural constituent (Dispersed phase) which determines internal structure of the composite and gives its bulk form. It may be Fiber, Particulate, Flakes or Whiskers

The important dispersed phases

- i. Fibers :** it is a long and thin filament of any polymer, metal or ceramic having high length to diameter ratio such as crystal size diameter.
Characteristics: high aspect ratio (length to diameter ratio), high tensile strength, high stiffness, causes lowering of overall density of composite
Eg. Glass fibers, carbon fibers, aramid fibers
- ii. Particulates:** it is as small pieces of hard solid materials (metallic or non-metallic). The distribution of particles in a given matrix is usually, random, thereby the resulting isotropic composites due to their inherent hardness, the particulates in a composite causes constraints on the plastic deformation on the matrix phase. In other words, the matrix transfers some of the applied stress, thereby the particles bear a fraction of applied load.
Effect of adding particulates to matrix materials: surface hardness increased, elevated temperature performance is increased, abrasion resistance is improved, friction is reduced, cost of composite is reduced thermal and electrical conductivity are modified, strength is increased
- iii. Flakes:** flakes are thin solids having a two dimensional geometry eg. Mica flakes which is having equal strength compared to fibers. Packing of flakes can be carried out more efficiently than that of fibers or spherical particulates. Mica flakes are used in electrical and thermal insulating appliances.
- iv. Whiskers:** whiskers are thin strong filaments or fibers made by growing a crystal. Eg graphite, silicon carbide, silicon nitride and aluminum oxide. They possess high elastic modulus, high degree of crystallinity and high strength.

Role of interface in composites:

1. The transmission of stress from the matrix to reinforcing dispersion phase is dependent on the interfacial bond strength, so composites have
 - a. Good interfacial bond, the failure mode is, usually, a sharp and well defined break

- b. Poor interfacial bond, the fracture progress one bond failure followed by matrix failure
2. The interface can serve as
 - a. Locus of chemical reaction
 - b. Site for nucleation
 - c. Site for preferential adsorption

The composite materials are commonly classified based on matrix constituent also. The major composite classes include Organic Matrix Composites (OMCs), Metal Matrix Composites (MMCs) and Ceramic Matrix Composites (CMCs). The term organic matrix composite is generally assumed to include two classes of composites, namely Polymer Matrix Composites (PMCs) and carbon matrix composites commonly referred to as carbon-carbon composites.

These three types of matrixes produce three common types of composites

Metal Matrix Composites (MMC)

Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase.

Metal matrix composites, at present though generating a wide interest in research fraternity, are not as widely in use as their plastic counterparts. High strength, fracture toughness and stiffness are offered by metal matrices than those offered by their polymer counterparts. They can withstand elevated temperature in corrosive environment than polymer composites. Most metals and alloys could be used as matrices and they require reinforcement materials which need to be stable over a range of temperature and non-reactive too.

Ceramic Matrix Composites (CMC)

Ceramic Matrix Composites are composed of a ceramic matrix and embedded fibers of other ceramic material (dispersed phase).

Ceramics can be described as solid materials which exhibit very strong ionic bonding in general and in few cases covalent bonding. High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favourite for applications requiring a structural material that doesn't give way at temperatures above 1500°C. Naturally, ceramic matrices are the obvious choice for high temperature applications.

Polymer Matrix Composites (PMC)

Polymer Matrix Composites are composed of a matrix from thermoset (Unsaturated Polyester (UP), Epoxy (EP)) or thermoplastic (Polycarbonate (PC), Polyvinylchloride, Nylon, Polystyrene) and embedded glass, carbon, steel or Kevlar fibers (dispersed phase).

Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. It follows, therefore, that high temperature resins are extensively used in aeronautical applications.

Two main kinds of polymers are thermosets and thermoplastics. Thermosets find wide ranging applications in the chopped fiber composites form particularly when a premixed or moulding compound with fibers of specific quality and aspect ratio happens to be starting material as in epoxy, polymer and phenolic polyamide resins.

Types of composites

Three main types of composites

A. Fiber reinforced Composite

- It is consist of dispersed phase fiber and a continuous or dispersion phase polymer or metal or metal alloy with a bonding agent. The fiber can be employed in the form of continuous length, staples or whiskers.
- Such composites possess high specific strength, specific modulus, stiffness, corrosion resistance and lowers density

Some important types of Fiber reinforced composites are

1. Glass fiber reinforced polymer composite

Fiber glass reinforced composites can be produced by properly incorporating the continuous or discontinuous glass fibers with in a plastic matrix. Polyesters are most commonly used matrix material. most recently nylons

It is the most popular fiber reinforcement material due to Easily available, easily fabricated, highly economical and which provides stiffness, strength, impact resistance and resistance to corrosion and chemicals.

limitations: they can fuse or melt at high temperatures

Applications: Automobile parts, storage tanks, floorings and plastic pipes etc

2. Carbon fiber reinforced polymer composites

Carbon fibers like (graphite, Graphenes or carbon nano tubes) dispersed in the polymer matrix.

They provide excellent resistance to corrosion, lighter density, retention of desired properties even at elevated temperatures.

limitations: High cost

Applications: Structural components of air craft like wings and bodies, sport equipment, fishing rods etc.

3. Alumina oxide/ carbon fiber reinforced metal composites:

Fibers of alumina or carbon dispersed in metal or metal alloy matrix which possess improved specific strength, stiffness, wear resistance, creep resistance and resistance to thermal distortion etc

Ex:1. Fiber Al_2O_3 / carbon in a matrix metal alloy find applications in the preparation of components of automobile engines.

2 . Fiber Al_2O_3 / W_2O_3 in a matrix of Ni or Co based alloy find applications in the preparation of components of turbine engines.

B. Particulate Composite

The solid particulates of metal oxides or carbides of varying size and form dispersed in metal, metal alloy, ceramic or polymer liquid matrix.

Particle reinforced composites are further classified into the following two types

1) Large -particulate composites 2) Dispersion strengthened composites

1) Large -particulate composites

Large particle composite used with all the three major types of materials, namely metals, polymer and ceramics.

Example : 1. concrete which is composed of cement matrix and particulates of sand and gravel.

2. Automobile tire in which Carbon black particles dispersed in rubber matrix

3. Ceramic - metal composites which are known as cermets. The most commonly used cermets are

Ex: 1. Al_2O_3 dispersed in Cr matrix possess good strength and good thermal shock resistance.

2. Tungsten carbide (WC) dispersed in Co matrix finds application in preparation of Valves, Spray nozzles and machine parts which require high surface hardness.

2) Dispersion strengthened composites

Very small particles of the range 10-100nm size are used in this which improve strength and hardness. Metals and Metal alloys may be hardened and strengthened by the uniform dispersion of high volume percent of very hard and inert materials, the strength is achieved due to interactions between particle and dislocations within the matrix. example Thoria-dispersed Nickel Precipitation hardening: The strength and hardness of some metal alloys may be improved by the formation of extremely small uniformly dispersed particles of a second phase within the original phase matrix with the help of appropriate heat treatment. This process called Precipitate hardening or Age hardening

C.Laminate Composites

When a fiber reinforced composite consists of several layers with different fiber orientations, it is called multilayer (angle-ply) composite.

A Laminar composite consists of two-dimensional sheets or panels that have preferred high strength direction, successive oriented fiber reinforced layers of these are stacked and then cemented together in such a way that the orientation of the high strength varies with each successive layer

Example: Plywood, Copper bottom steel articles

Properties of composite materials –mechanical, electrical and corrosive properties

In selecting a composite materials an optimum combination of properties is usually sought rather one particular property by selecting appropriate composite materials

It increases the

- strength,
- stiffness,
- maintain the strength in higher temperatures,
- better toughness,
- impact and thermal shock resistance,
- better creep and fatigue strength,
- lower the electrical conductivity,
- better corrosion resistance

Example: The wings of an aircraft must be light weight and strong, stiff and tough

Natural rubber is relatively weak –adding significant amount of carbon black to natural rubber improves the strength drastically

Applications of composite materials- in different sectors

- In automobile industries, Transportation industries, turbine engines, wire drawing dies stroge tanks, sports goods, high speed machinery etc.
- Marine applications like propellers, shafts, hulls and other ship parts
- Aeronautical applications like components of rockets, air crafts helicopters, missiles etc
- Communications antennae, electric circuit boards (PCB)
- Safety equipment's like ballistic protection