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 donot 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.

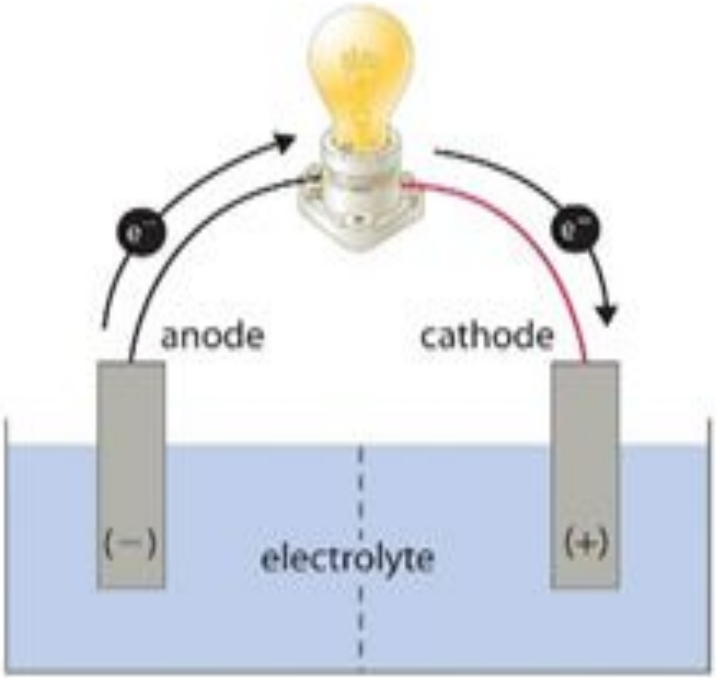
9. **Cell:** Device consisting of two half cell. The two half cells are connected through one wire.

10. **Salt bridge:** Contains solutions of a salt (KNO3 or NH4NO3) 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

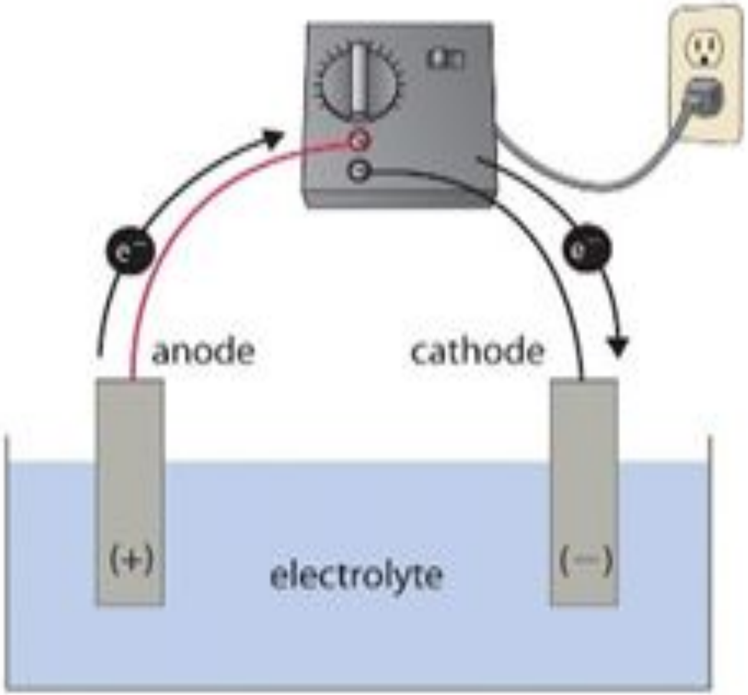
A cell is a device consisting of two half cells. Each half cell consists of an electrode dipped in an electrolyte solution. The two half cells are connected through one wire.

S.No	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

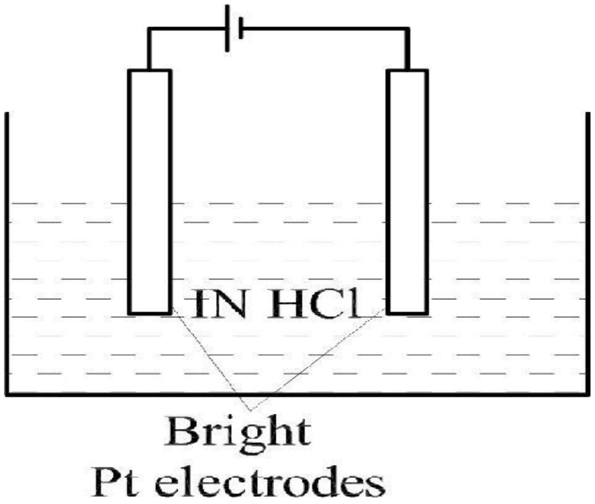
Energy released by spontaneous redox reaction is converted to electrical energy.



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

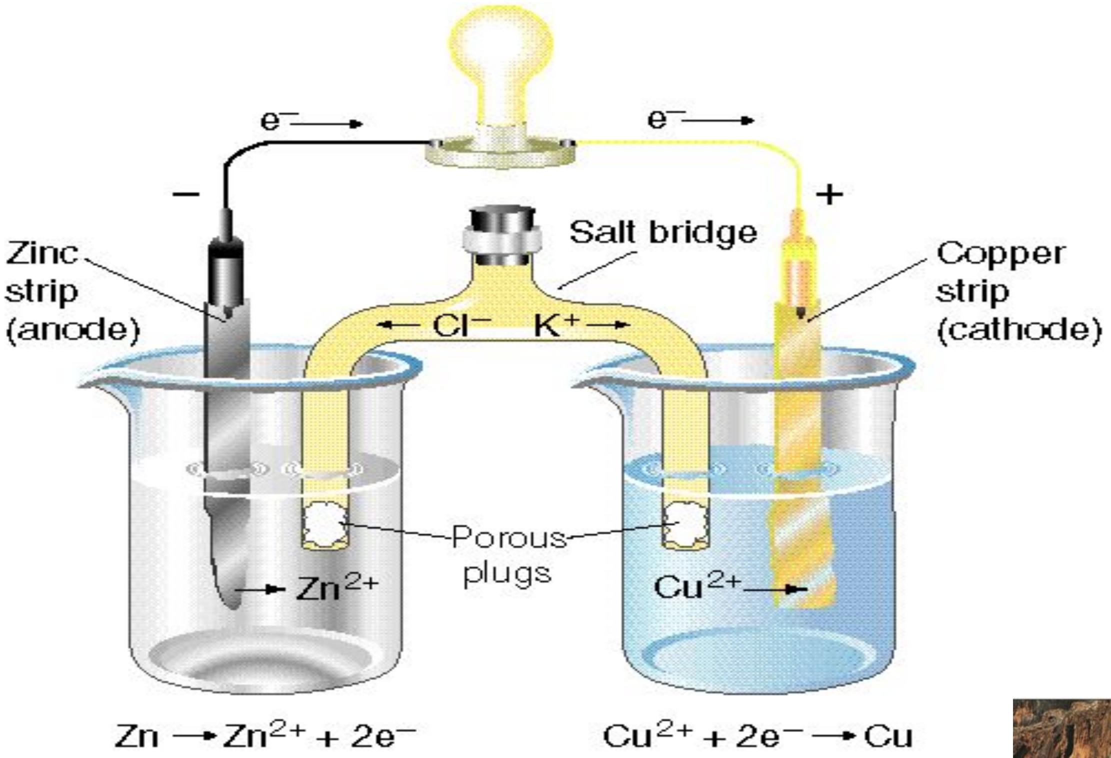
Electrolytic cell - ***Example :*** *Electrolysis of HCl.*



At anode : $2Cl^- \rightarrow Cl_2 + 2e$ **(oxidation)**

At cathode : $2H^+ + 2e^- \rightarrow H_2$ **(reduction)**

Electrochemical cell - *Example : Daniel cell*



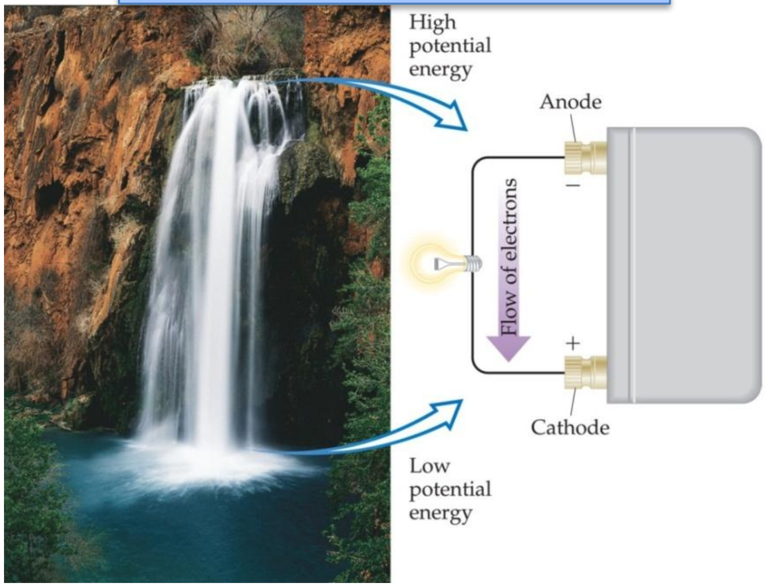
$Zn \rightarrow Zn^{2+} + 2e^-$ **(at anode)**

$Cu^{2+} + 2e^- \rightarrow Cu$ **(at cathode)**

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

(net cell reaction)

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 $(NH_4)_2NO_3$ 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 $Zn/ZnSO_4$ (1M) //) $CuSO_4$ (1M) /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

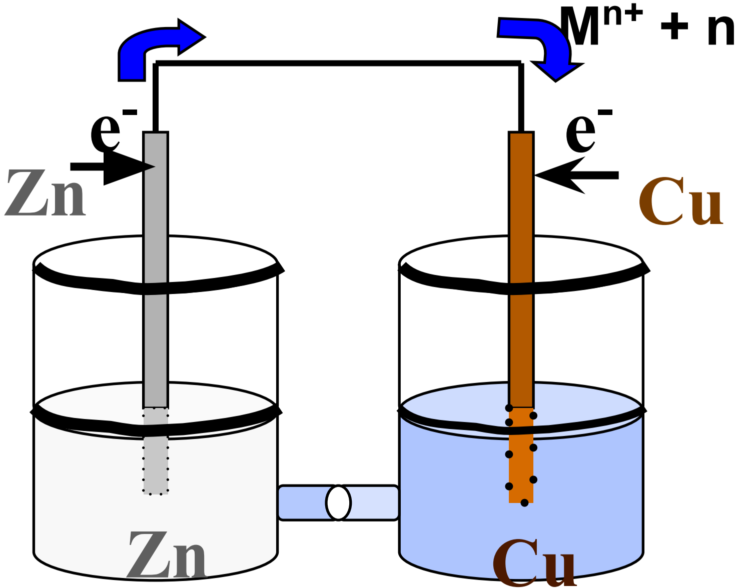
(i) Metal atoms go into solution in the form of ions.

$M \rightarrow M^{n+} + ne^-$ (Oxidation)

Example :

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

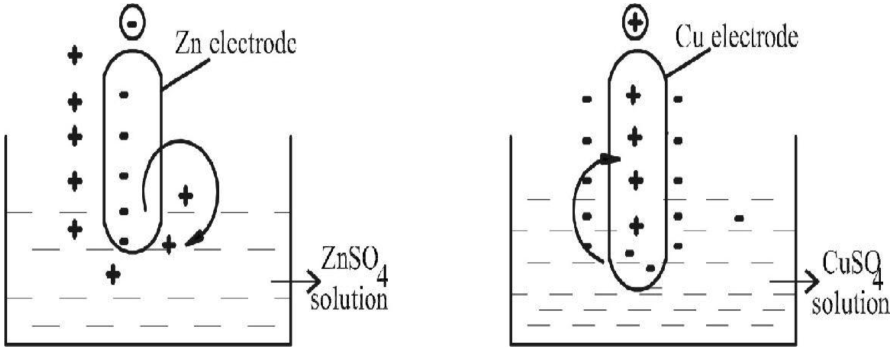
$M^{n+} + ne^- \rightarrow M$ (reduction)



$Zn \rightarrow Zn^{2+} + 2e^-$

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

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^oC.

Types of Electrodes

Reference Electrode:

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

e.g. Saturated calomel electrode (E_{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

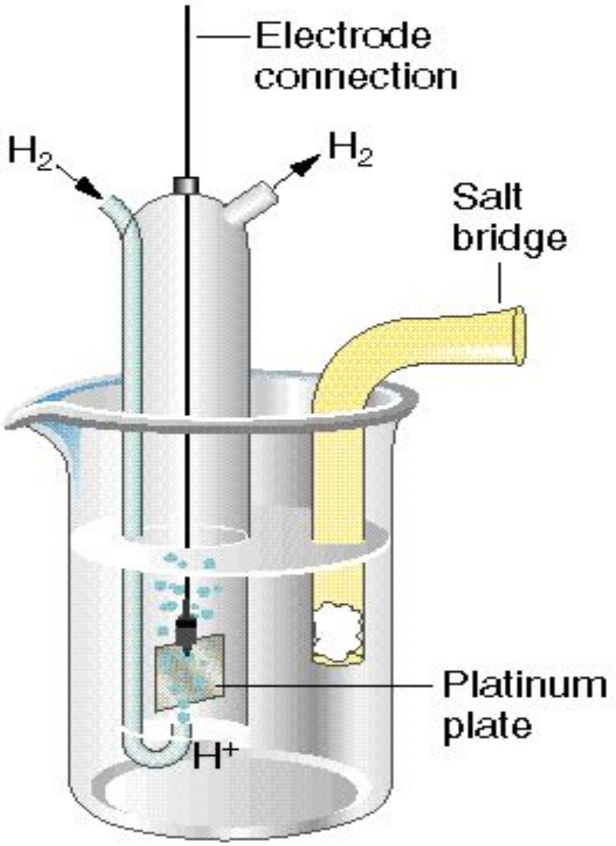
Construction

- 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.

$$\mathbf{H_2 (g) \rightarrow 2H + 2e}$$

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

$$\mathbf{Pt , H_2 (1atm) / H^+(1M) ; E^0 = 0V}$$



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)

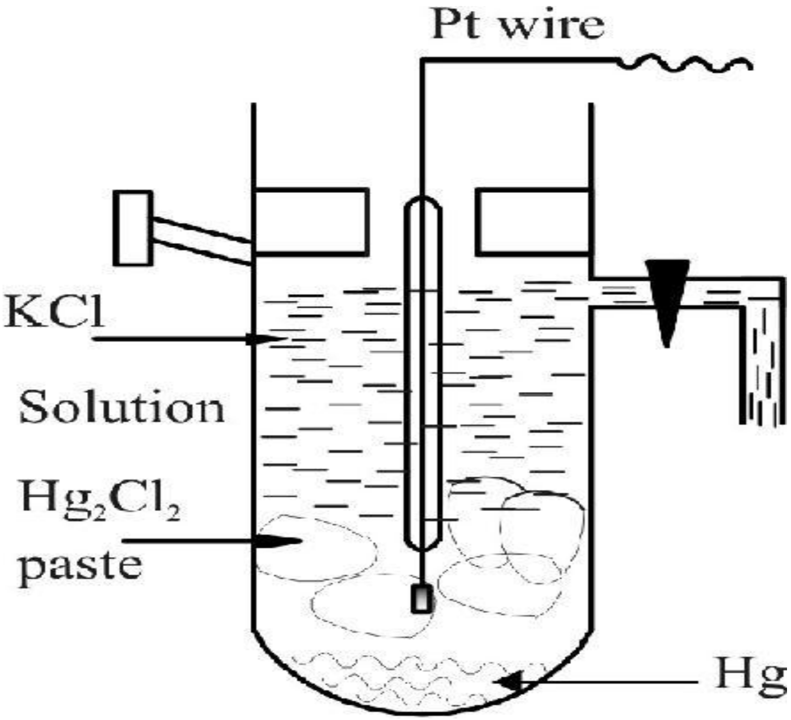
- Glass tube containing pure Hg at the bottom over which mercurous chloride is placed. The remaining portion of the tube is filled with saturated solution of KCl.

- The bottom of the tube is sealed with a platinum wire. The side tube is used for making electrical contact with a salt bridge.

Hg | Hg$_2$ Cl$_2$(s) | KCl (Saturated, Solution) E° = 0.2422V

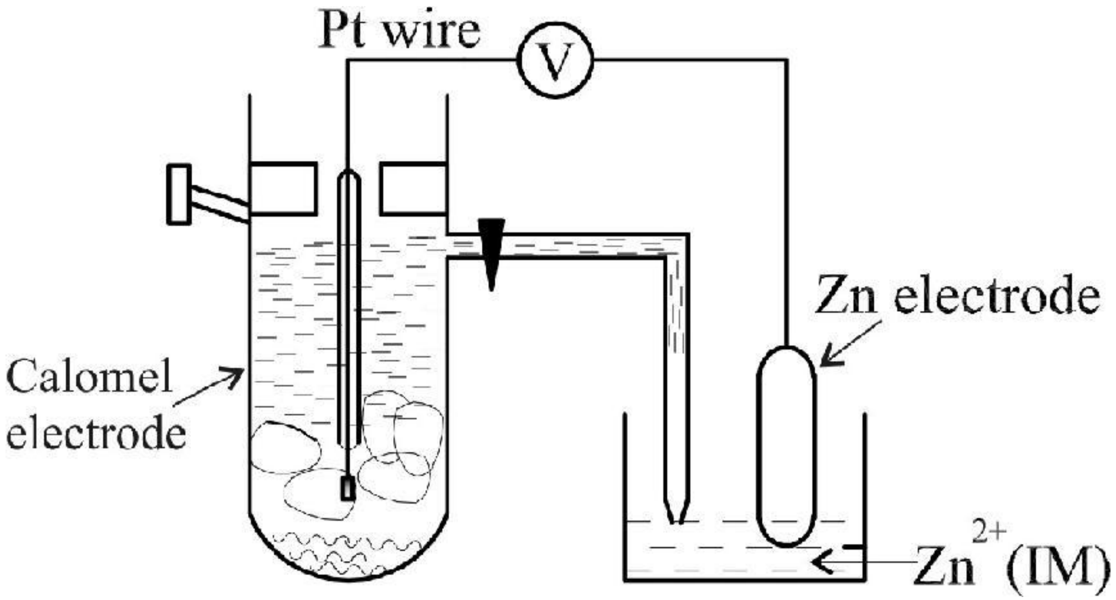
$$2\mathrm{Hg}(l) + 2\mathrm{Cl} \rightarrow \mathrm{Hg}_2\mathrm{Cl}_2(s) + 2e$$

$$\mathrm{HgCl}_2 + 2e \rightarrow 2\,\mathrm{Hg} + \mathrm{Cl}$$



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)



$Hg_2Cl_2(s) \rightarrow 2Hg_{(\;)} \quad 2Cl$

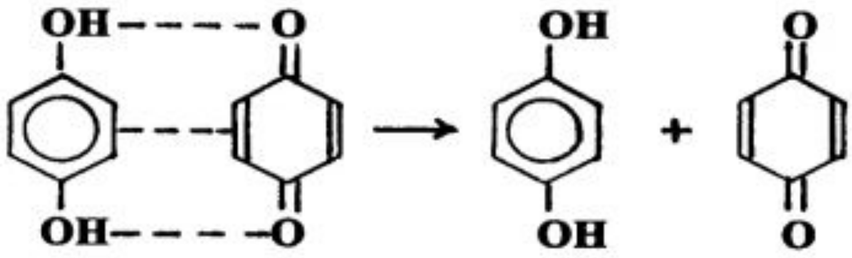
The emf of the cell is measured using a potentiometer.
The value of E_{cell} = 1.0025 volt.

$$E \quad = E^{o}_{right}\text{-----}\ E^{o}_{left}$$
$$E \quad = E^{o}_{cal}\ \text{---}\ E^{o}_{Zn}$$
$$E^{o}_{Zn} = E^{o}_{cal}\ \text{----}\ E^{o}_{cell}$$
$$= +0.2422 - 1.0025 = -0.7603\ V$$

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. Quinone + $2H^+$ $+2e^-$ ⇆ Hydroquinone

The electrode reaction is:

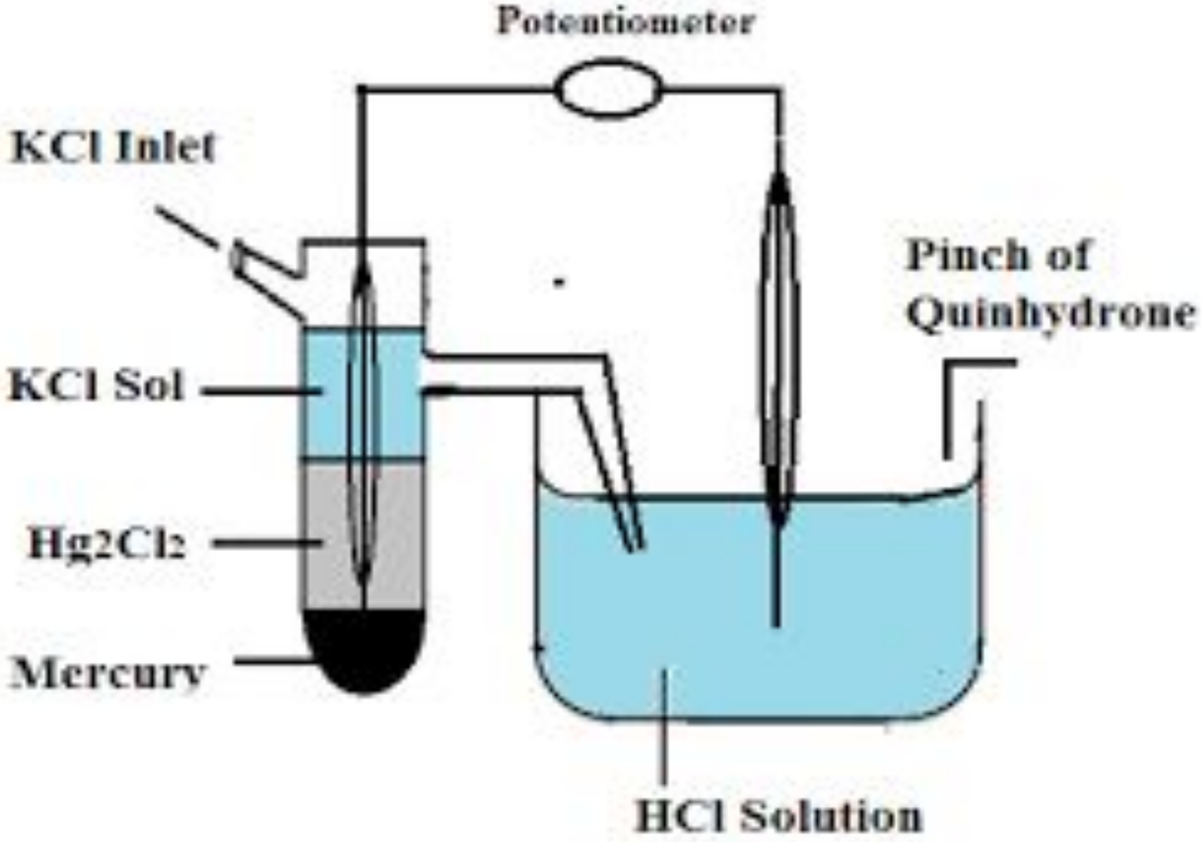


HQ H_2Q Q

$$C_6H_4O_2 + 2H^+ + 2e^- \Leftrightarrow C_6H_4(OH)_2$$

Quinone (Q) Hydroquinone (H_2Q)

Quinhydrone electrode in a cell.



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

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

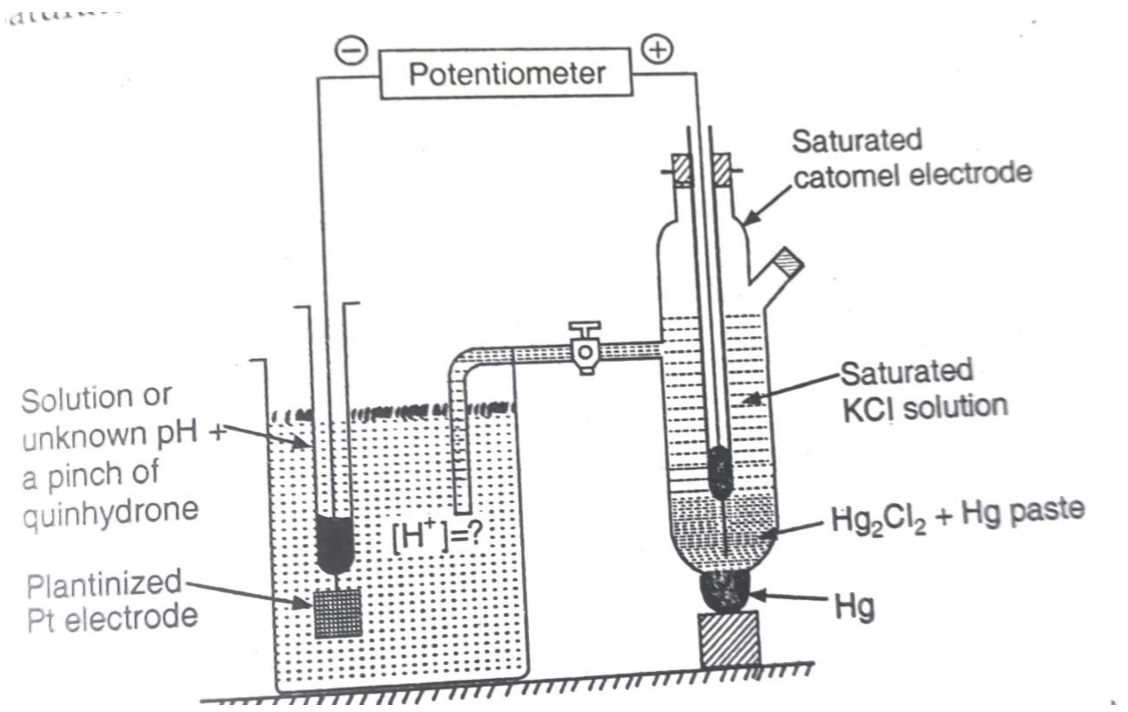
If quinone and hydroquinone are taken in equimolar concentrations, then $[Q] = [QH_2]$ then the above reaction reduces to

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

$$\mathbf{EQ = E^0 - 0.0592v\ pH = 0.6994v - 0.0592v\ pH}$$

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^+(unknown) | | KCl(sat), Hg_2Cl_2(s) | Hg^+

Ecell = E calomel – E QH
Ecell = 0.2422v – 0.6994v - 0.0592v pH

$$\mathbf{pH = \frac{0.6994v - 0.2422v + Ecell}{0.0592v}}$$

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

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

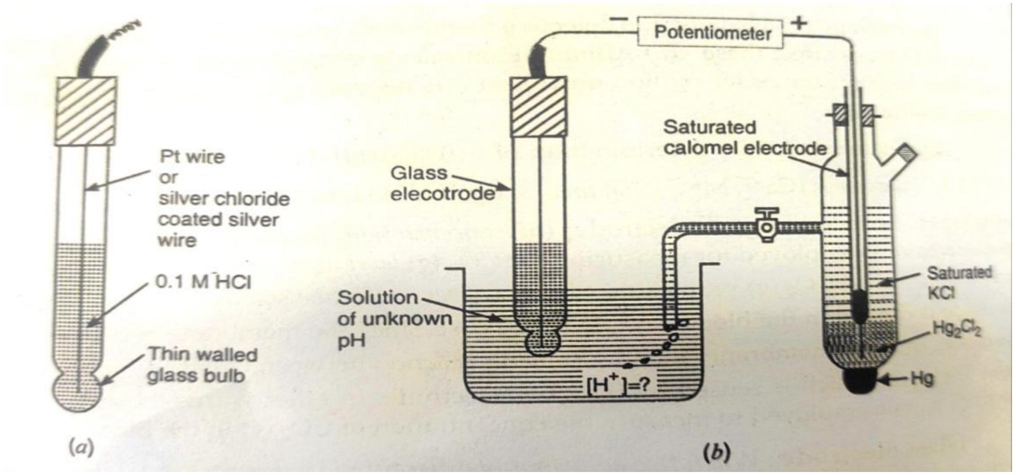
Glass electrode.

- 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

$^{-}$Ag | AgCl(s) | 0.1 M HCl | glass. Or Pt.0.1MHCl|Glass^{+}



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;

SCE ││Ag, AgCl │ HCl (0.1 N) │ Glass

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

$$pH = \frac{0.2422v - Ecell - E^{0}G}{0.0592v}$$

The E^0_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:

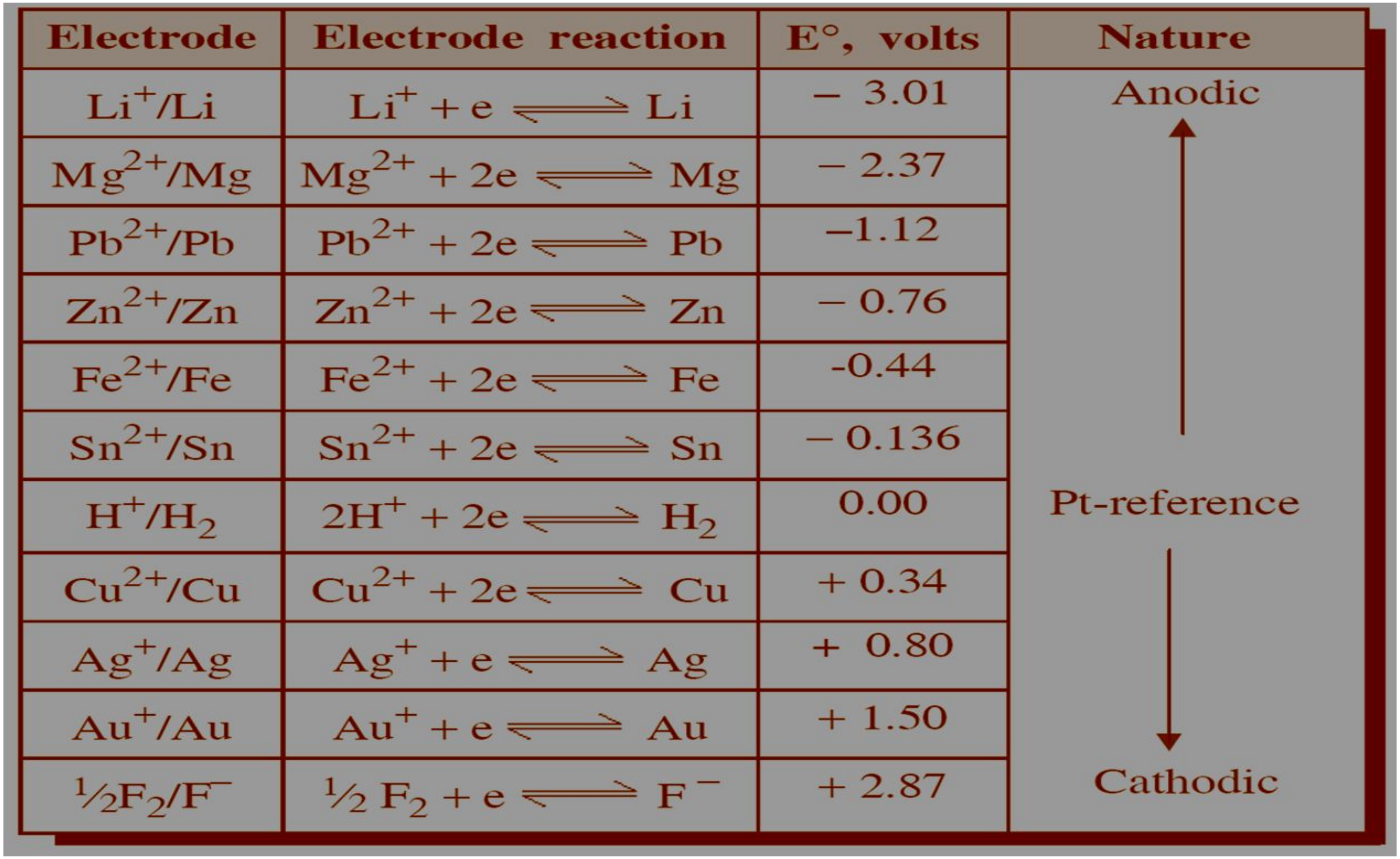
i. It provides a measure of pH in the pH range of 1 – 9.
ii. Using a pH meter, pH of the solution can be directly read.
iii. The electrode can be used in all aqueous solutions.
iv. Electrode is not affected by oxidizing and reducing agents or by any organic compound.
v. pH can be determined even for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

Demerits:

i. The electrode cannot function in highly acidic or alkaline medium
ii. It cannot produce proper response with 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	$Li^+ + e \rightleftharpoons Li$	– 3.01	Anodic ↑
Mg^{2+}/Mg	$Mg^{2+} + 2e \rightleftharpoons Mg$	– 2.37	
Pb^{2+}/Pb	$Pb^{2+} + 2e \rightleftharpoons Pb$	–1.12	
Zn^{2+}/Zn	$Zn^{2+} + 2e \rightleftharpoons Zn$	– 0.76	
Fe^{2+}/Fe	$Fe^{2+} + 2e \rightleftharpoons Fe$	-0.44	
Sn^{2+}/Sn	$Sn^{2+} + 2e \rightleftharpoons Sn$	– 0.136	
H^+/H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00	Pt-reference
Cu^{2+}/Cu	$Cu^{2+} + 2e \rightleftharpoons Cu$	+ 0.34	
Ag^+/Ag	$Ag^+ + e \rightleftharpoons Ag$	+ 0.80	
Au^+/Au	$Au^+ + e \rightleftharpoons Au$	+ 1.50	
$\frac{1}{2}F_2/F^-$	$\frac{1}{2} F_2 + e \rightleftharpoons F^-$	+ 2.87	↓ Cathodic

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 **($E_{cell} = E_{RHE} - E_{LHE}$)**

- ***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

  $Zn + CuSO_4 \rightarrow ZnSO_4 \quad + Cu$

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

  Standard electrode potentials are used to determine the equilibrium constants as follows: **G^o = In K 2.303 RT log K**

$$\log K = \frac{G^0}{2.303\ RT} = \frac{nFE^0}{2.303\ RT}\,[G^0 nFE^0]$$

- ***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

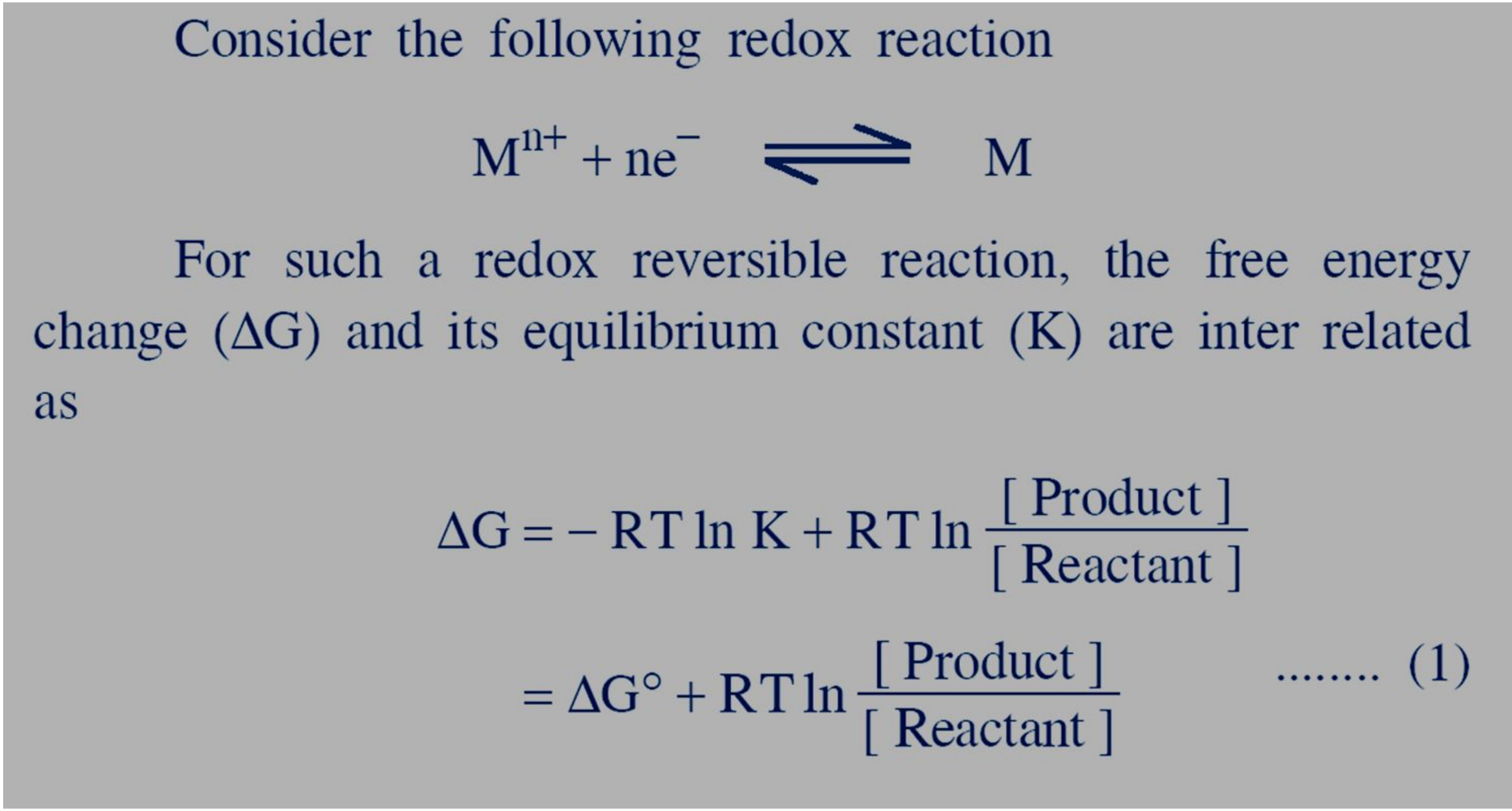
- **$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$**
- **$Ag + H_2SO_4 \rightarrow$ No reaction**

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

If E^o of a cell is positive the reaction is spontaneous.

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

NERNST EQUATION FOR ELECTRODE POTENTIAL



Consider the following redox reaction

$$M^{n+} + ne^{-} \rightleftharpoons M$$

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

$$\Delta G = -RT \ln K + RT \ln \frac{[\,\text{Product}\,]}{[\,\text{Reactant}\,]}$$

$$= \Delta G^\circ + RT \ln \frac{[\,\text{Product}\,]}{[\,\text{Reactant}\,]} \qquad \ldots\ldots\ldots \quad (1)$$

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

$$-\Delta G = nEF$$

(or)

$$-\Delta G^\circ = nE^\circ F \qquad \text{........ (2)}$$

where,

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

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

Comparing equation 1 and 2, it becomes

$$-\,nEF = -\,nE^\circ F + RT \ln \frac{[\,M\,]}{[\,M^{n+}\,]}. \qquad \text{.......(3)}$$

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

$[\because$ the activity of solid metal $[M] = 1\ ]$

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

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

(or)

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

When, R = 8.314 J/K/mole; F = 96500 coulombs ; T = 298 K (25°C), the above equation becomes

$$\mathbf{E = E^{\circ}_{red} + \frac{0.0591}{n} \log [\, M^{n+} \,]} \qquad \text{........(5)}$$

In general, $E = E^{\circ}_{red} + \dfrac{0.0591}{n} \log C$

Similarly for oxidation potential

$$\mathbf{E = E^{o}_{oxi} - \frac{0.0591}{n} \log [M^{n+}]} \qquad \text{........ (6)}$$

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

BATTERIES

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- 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

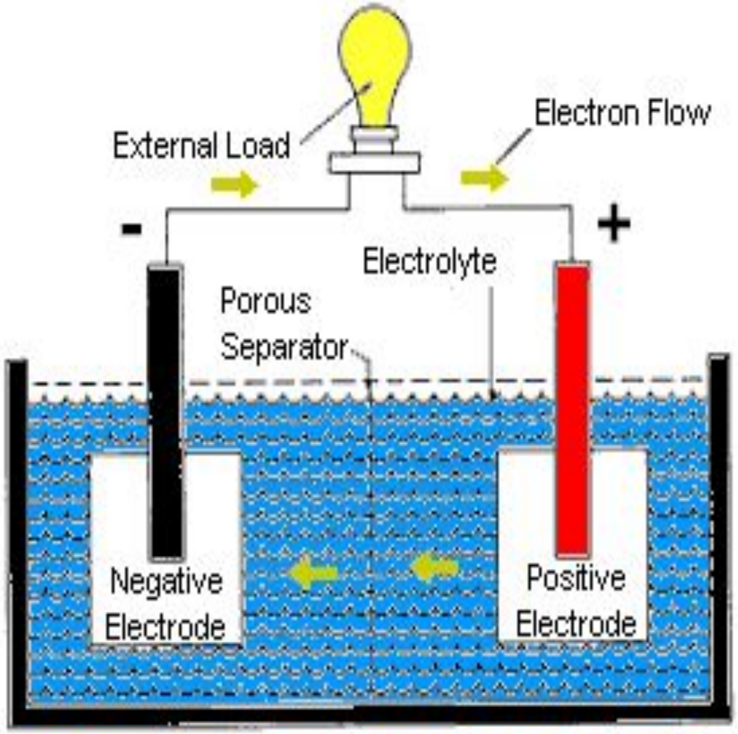
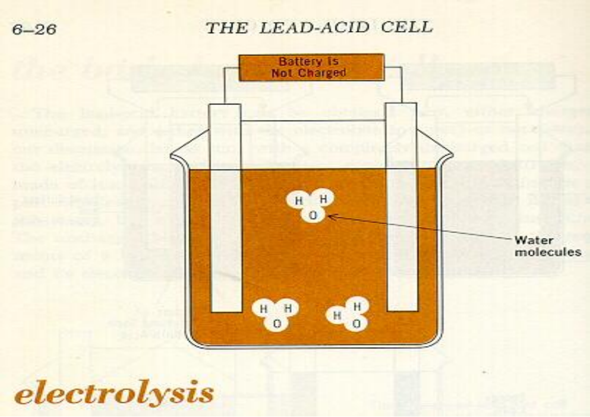
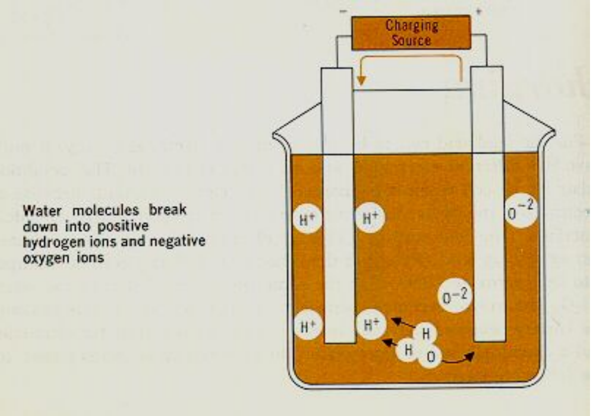


Figure 1 - Components of a Battery Cell (Discharge Circuit)

- 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.

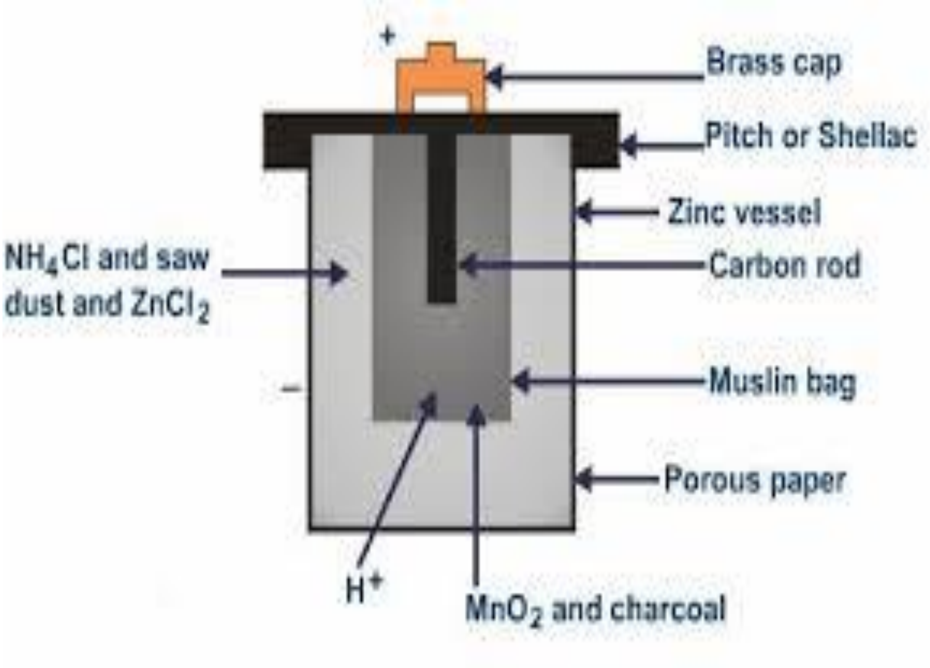
- Secondary batteries - the cell reaction can be made to proceed in either direction by withdrawing or supplying current to the battery system.

- 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.



Dry cell

Standard Zinc Carbon Batteries

- Chemistry

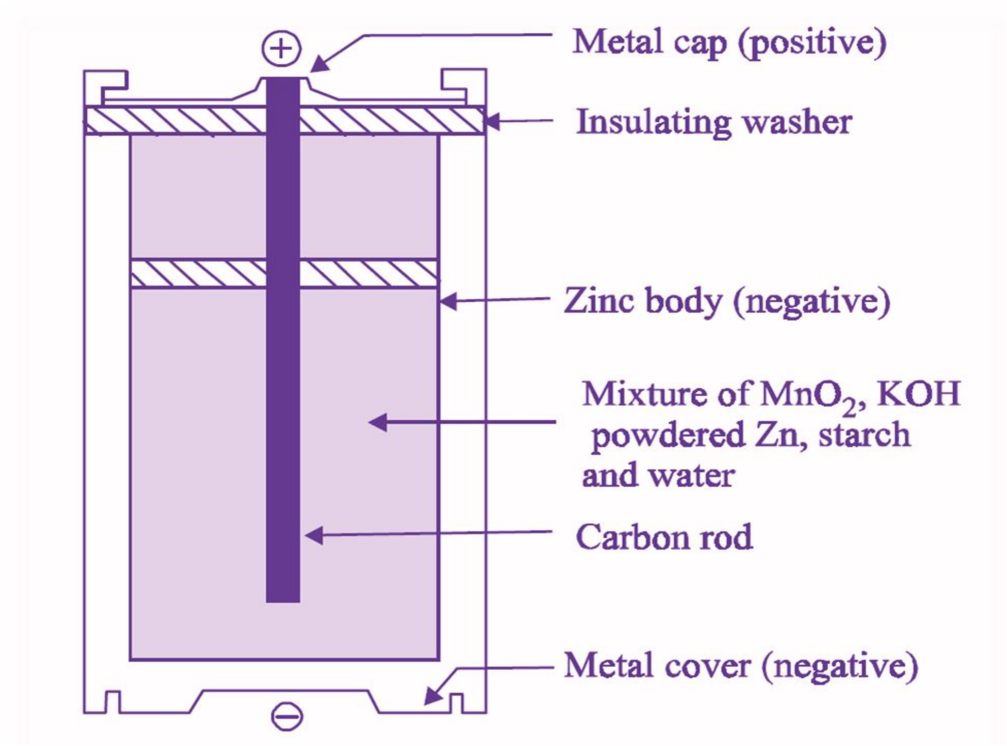
  Zinc (-), manganese dioxide (+)

  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:**

$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

- **Cathode:**

$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH\text{-}(aq)$

- **Net reaction:**

$Zn(s) + 2MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$

- --

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.

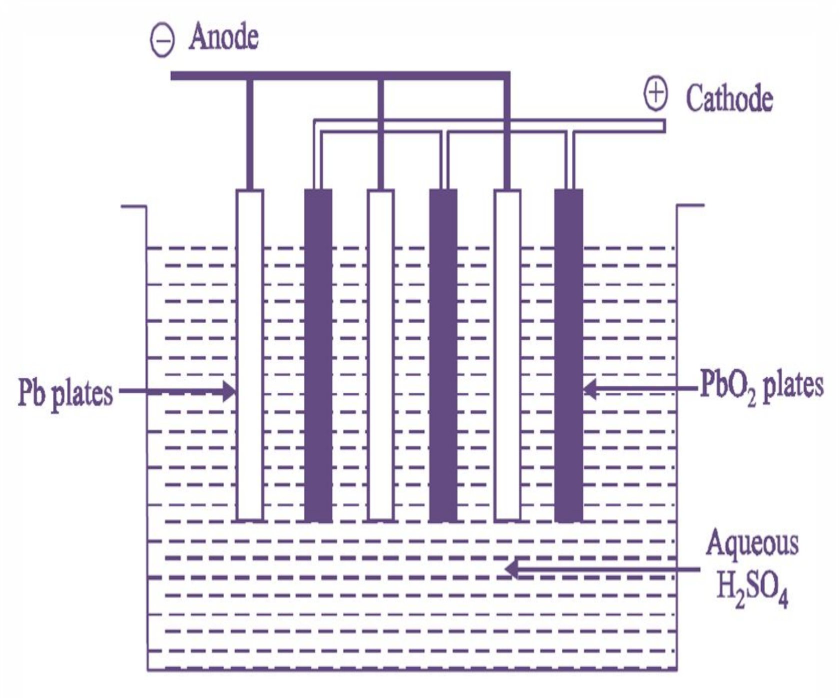
Uses of alkaline battery.

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



Anode : $Pb \rightarrow Pb^{2+} + 2\,e^-$

$$\begin{array}{l} Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \\ \hline Pb + SO_4^{2-} \rightarrow PbSO_4 \\ \hline \end{array}$$

Cathode : $PbO_2 + 4\,H^+ + 2e^- \rightarrow Pb^{2+} + 2\,H_2O$

$$\begin{array}{l} Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \\ \hline PbO_2 + 4\,H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2\,H_2O \end{array}$$

Overall cell reaction:

$$PbO_2 + Pb + 4\,H^+ + SO_4^{2-} + 2e^- \underset{\xleftarrow[\text{ch}]{\qquad}}{\xrightarrow{\text{Dch}}} 2\,PbSO_4 + 2\,H_2O$$

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 posses low internal resistance , long shelf life without and good cycle life.*

Construction

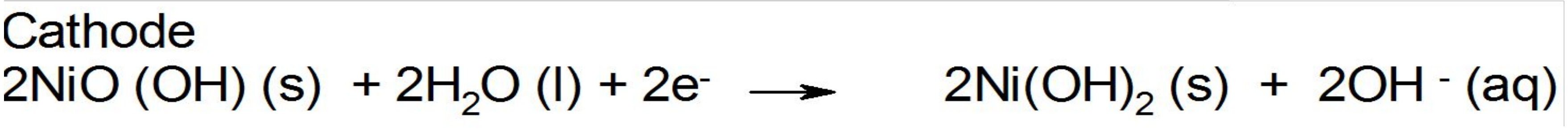
Anode : *Cadmium as a mixture of metal oxide and /or hydroxide*

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

Electrolyte: *KOH*

Anode

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$



Cathode

$$2NiO(OH)(s) + 2H_2O(l) + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

Cell reaction

$$2\ \mathrm{NiO(OH)}\ (s) + \mathrm{Cd}\ (s) + 2\ \mathrm{H_2O}\ (l) \longrightarrow \mathrm{Cd\ (OH)_2} + 2\ \mathrm{Ni(OH)_2}\ (s)$$

Cell representation:

$\mathrm{Cd\ /\ Cd\ (OH)_2\ //\ KOH\ /\ NiO(OH)\ /\ Ni}$

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 / MnO_2 Cell and

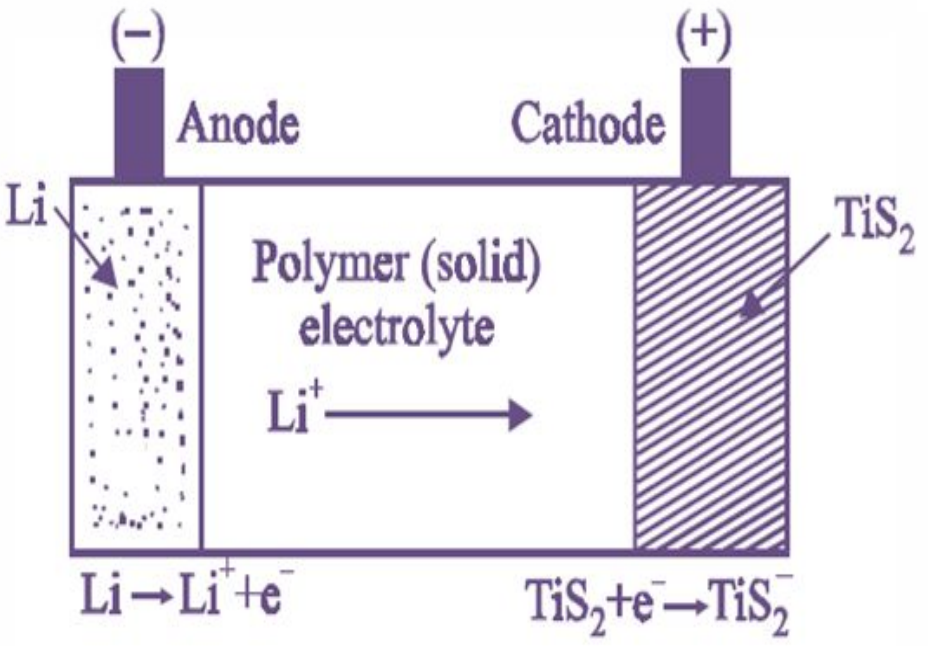
2.Primary cells with liquid cathode: Ex: Li –SO_2 , Lithium-Thionyl chloride Cell

(Secondary) Rechargeable Lithium batteries:

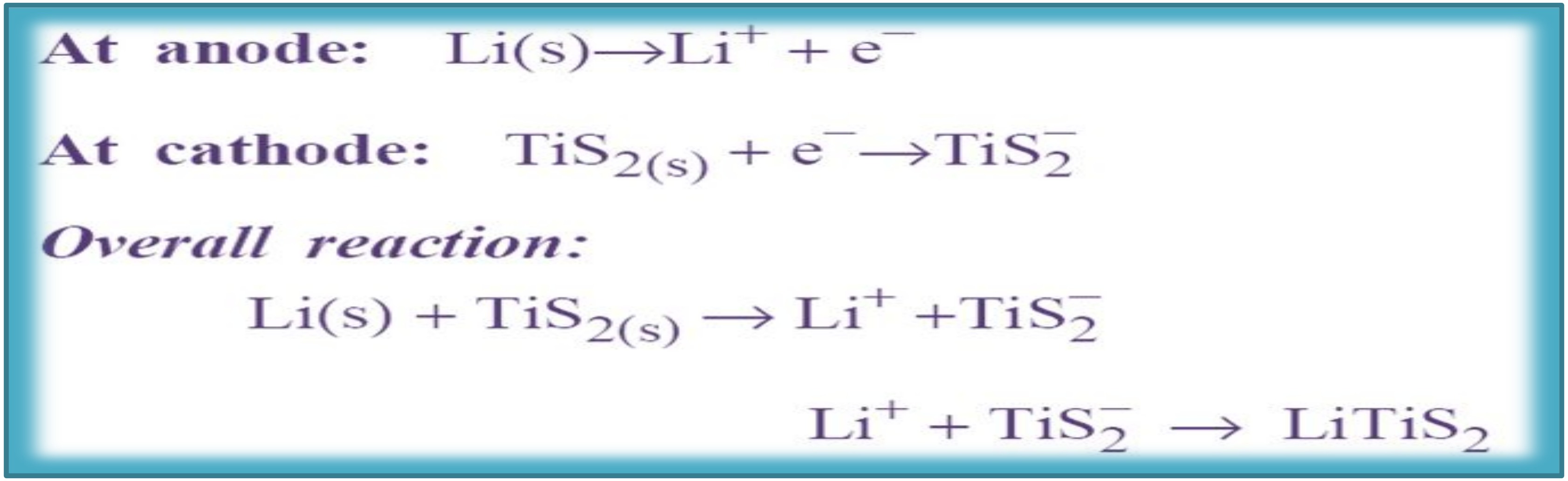
- *Lithium batteries are characterized by high specific energy and high cycle life.*
- *These batteries have either lithium foils as anodes (negatives) or lithiated transition metal oxides as cathodes (positives) with solid polymer electrode.*
- *Electrolyte is immobilized polymer electrolyte with polymer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

Li- TiS_2 Battery

- *The electrode and cell reactions of this cell are given below:*
- *Anode: Lithium*
- *Cathode: TiS_2*
- *Electrolyte: A solid electrolyte (Polymer packed between the electrodes which permits the passage of ions but not electrons)*
- ***CELL VOLTAGE - 3V***



Cell reactions



At anode: $Li(s) \longrightarrow Li^+ + e^-$

At cathode: $TiS_{2(s)} + e^- \longrightarrow TiS_2^-$

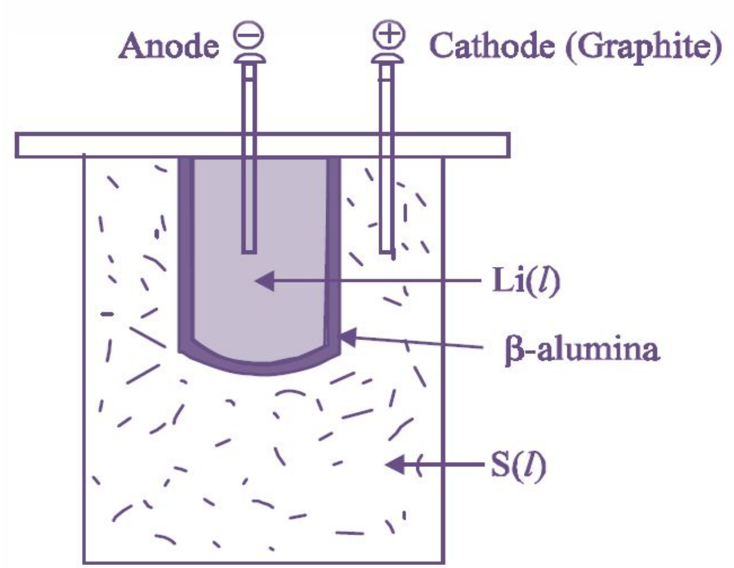
Overall reaction:

$$Li(s) + TiS_{2(s)} \longrightarrow Li^+ + TiS_2^-$$

$$Li^+ + TiS_2^- \longrightarrow LiTiS_2$$

$$LiTiS_2 \dashrightarrow Li^+ + TiS_2^-$$

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* ($NaAl_{11}O_{17}$) *is used as the solid electrolyte.*

- *β–Alumina ($NaAl_{11}O_{17}$) 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

At Anode: $2\,Li \rightarrow 2Li^+ + e^-$

At Cathode : $S + 2e^- \rightarrow S^{2-}$

Net reaction: $2\,Li + S \rightarrow 2Li^+ + S^{2-}$

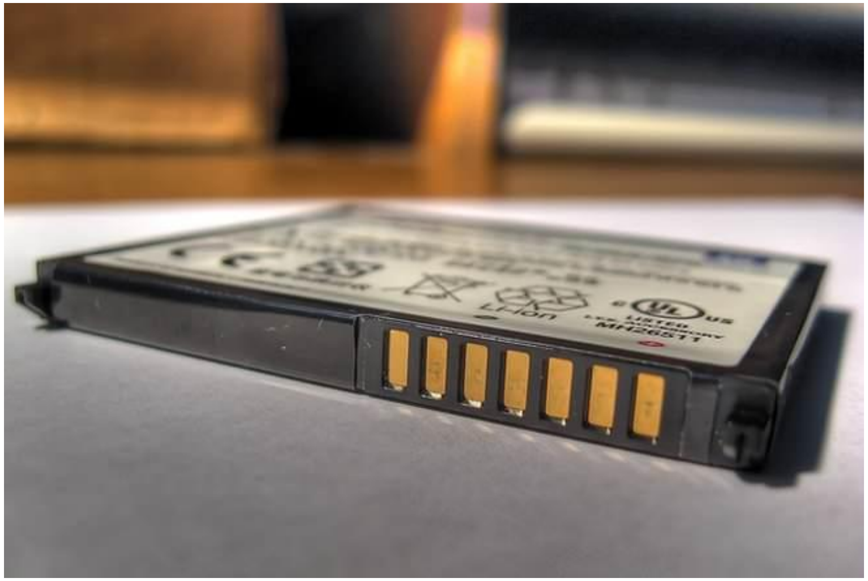
Advantages of lithium battery

1. Electrode potential (E^o) 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 potable 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 FeS2 (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.


UPS
Medical Device
Power Tool
Robot Vacuum Cleaner
e-Bike
Gardening Tool
Smart phone
Portable PC
e-Scooter
Mobile Phone
Tablet


LI-ION
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NEXT GENERATION BATERRIES.

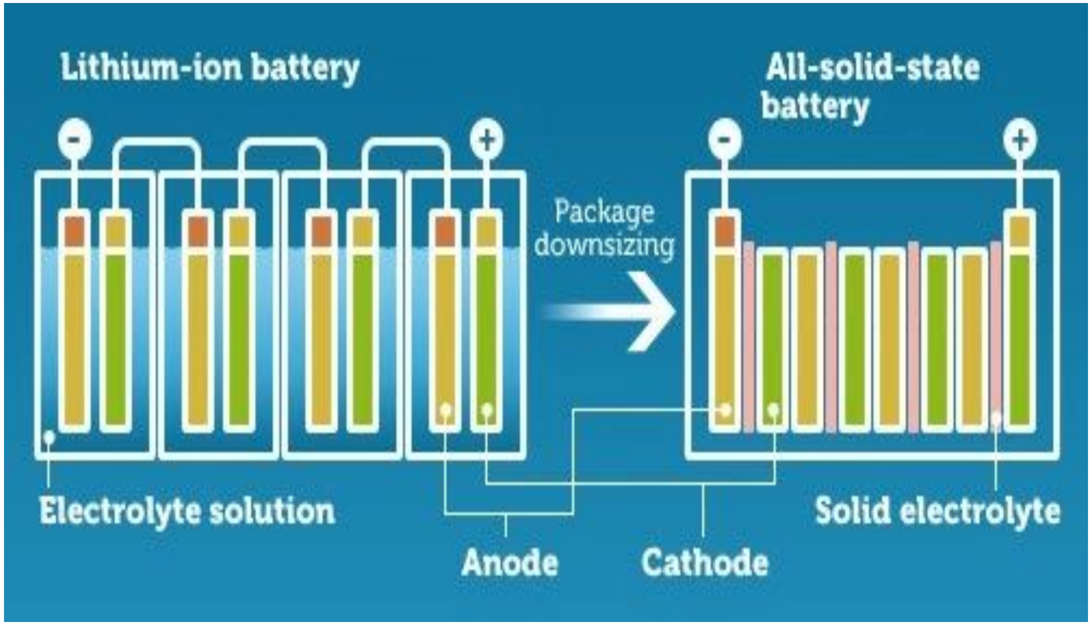
Lithium Solid-state Batteries

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 ($Li_2S–P_2S_5$).

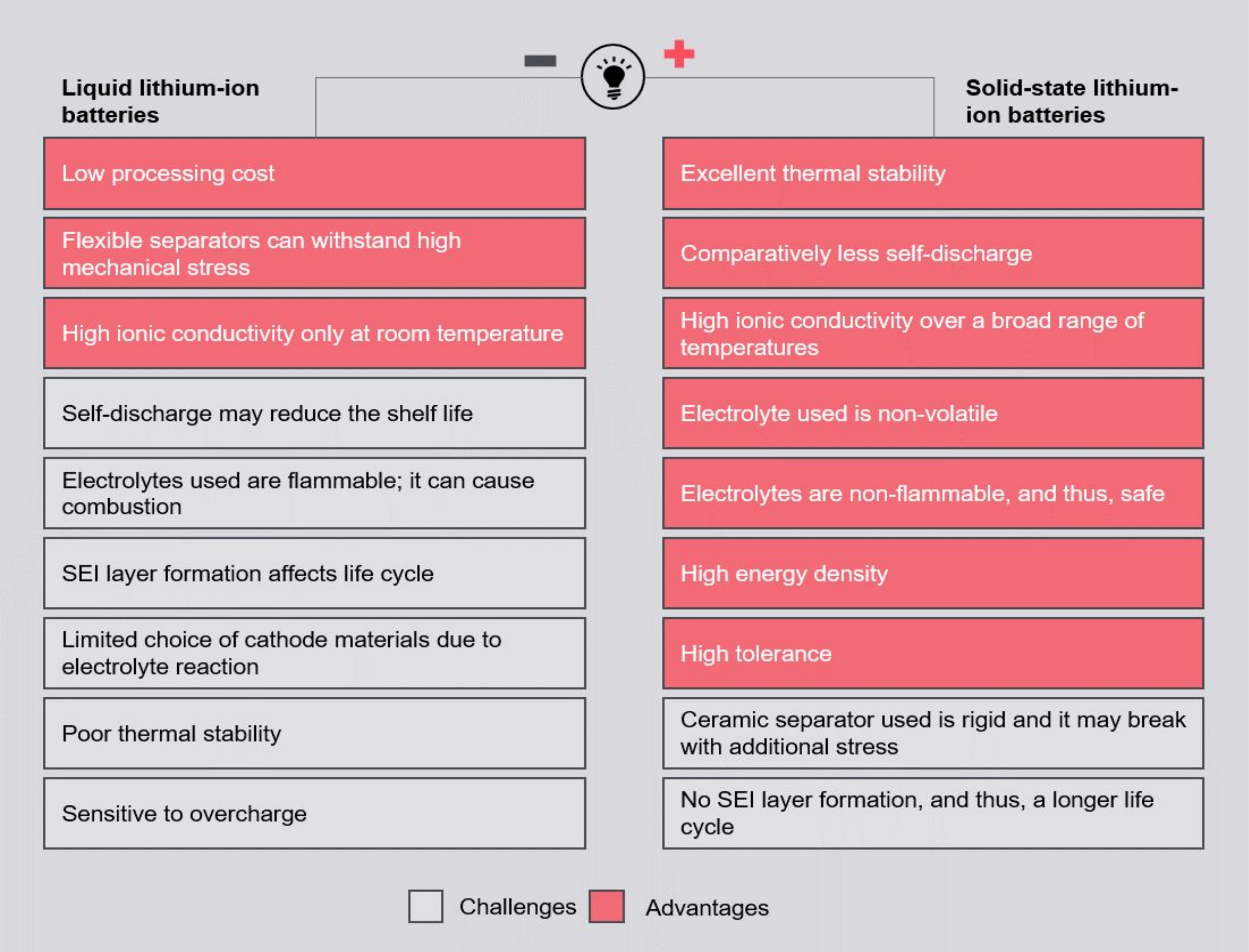


- Solid-state batteries can provide solutions for many problems of liquid Li-ion batteries, such as flammability, limited voltage, unstable solid-electrolyte interphase formation, poor cycling performance and strength.

- 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

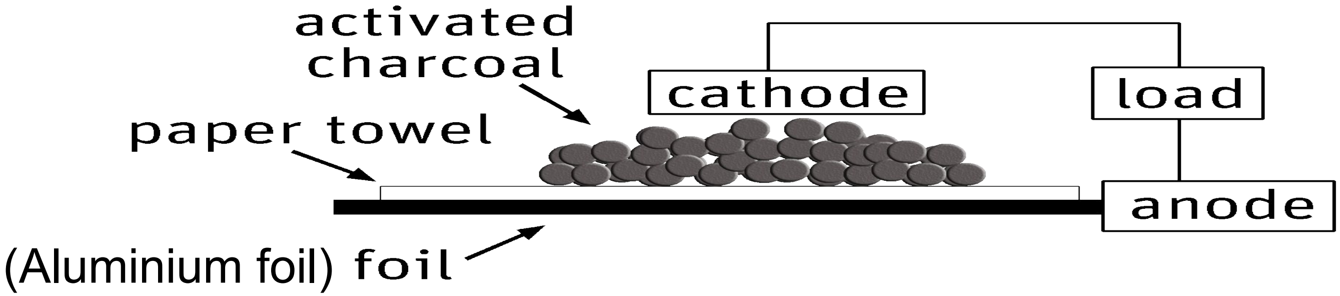


Liquid lithium-ion batteries	Solid-state lithium-ion batteries
🟥 Low processing cost	🟥 Excellent thermal stability
🟥 Flexible separators can withstand high mechanical stress	🟥 Comparatively less self-discharge
🟥 High ionic conductivity only at room temperature	🟥 High ionic conductivity over a broad range of temperatures
☐ Self-discharge may reduce the shelf life	🟥 Electrolyte used is non-volatile
☐ Electrolytes used are flammable; it can cause combustion	🟥 Electrolytes are non-flammable, and thus, safe
☐ SEI layer formation affects life cycle	🟥 High energy density
☐ Limited choice of cathode materials due to electrolyte reaction	🟥 High tolerance
☐ Poor thermal stability	☐ Ceramic separator used is rigid and it may break with additional stress
☐ Sensitive to overcharge	☐ 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:

- **Anode:** $Al(s) + 3OH-(aq) \rightarrow Al(OH)3(s) + 3e-$
  Cathode: $O2(g) + 2H2O(l) + 4e- \rightarrow 4OH-(aq)$
  Overall: $4Al(s) + 3O2(g) + 6H2O(l) \rightarrow 4Al(OH)3(s)$

- 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**

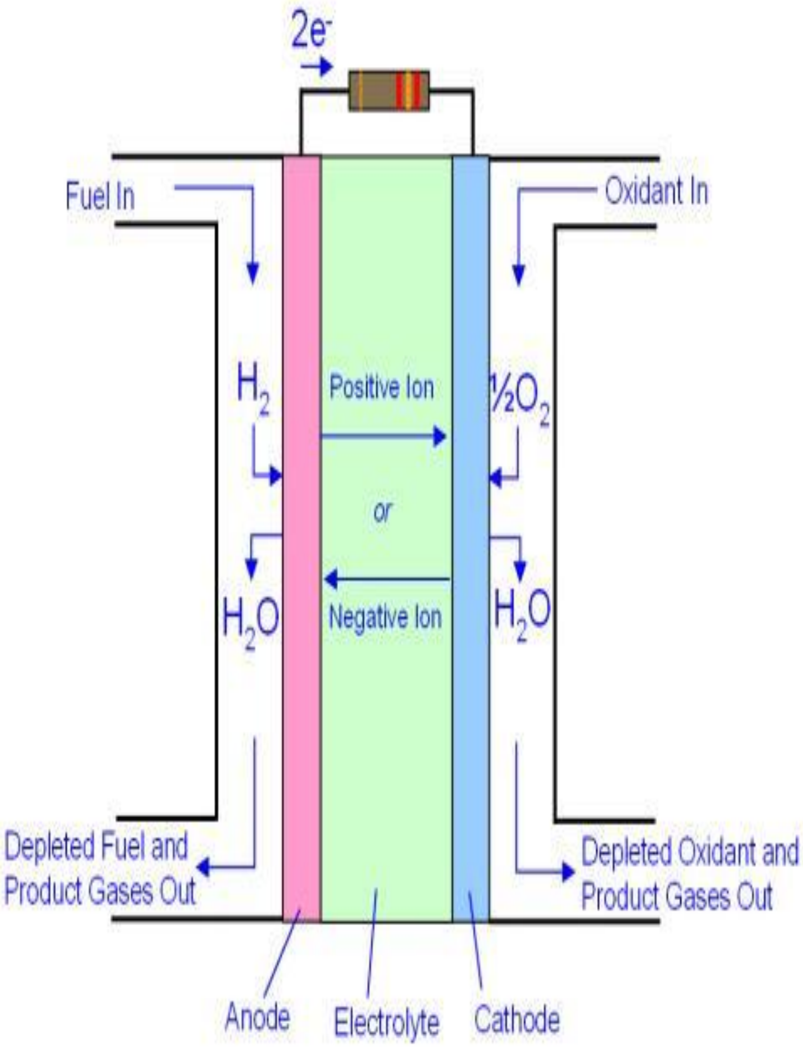
- Fuel undergoes oxidation at the anode liberating electron and the oxidation products of the fuel. The electron so liberated from the oxidation process reduce the oxidant at the cathode.

- 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.

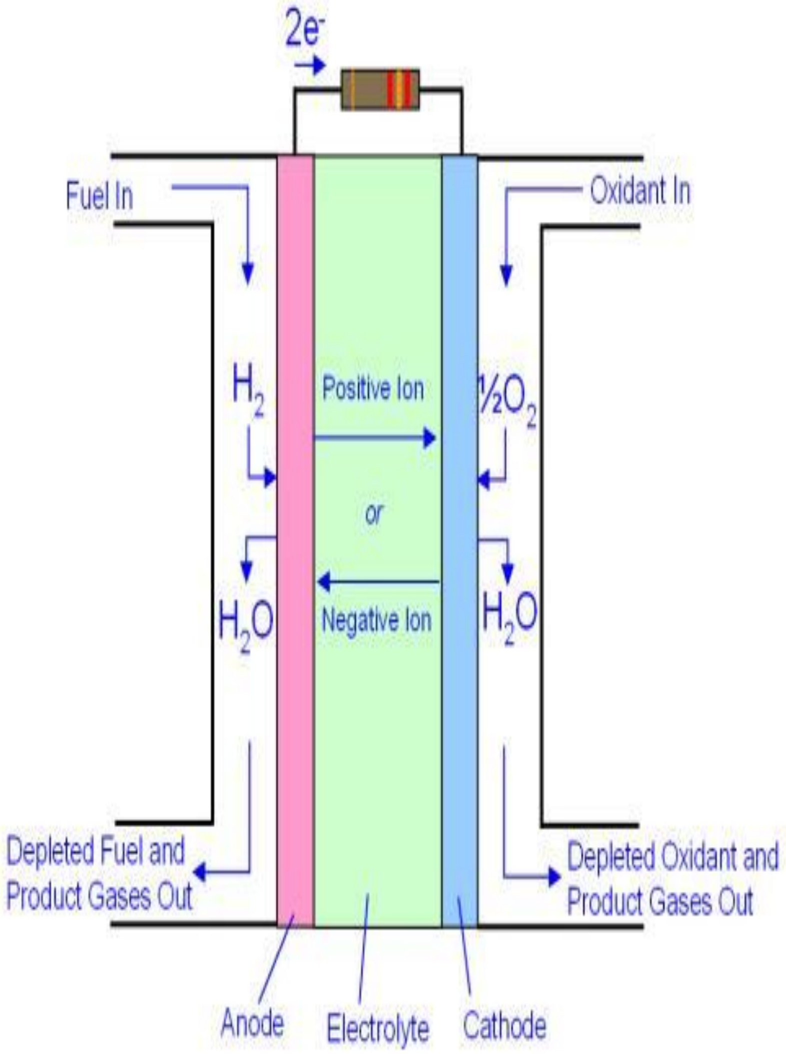


Anode :

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

Anodic reaction

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



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

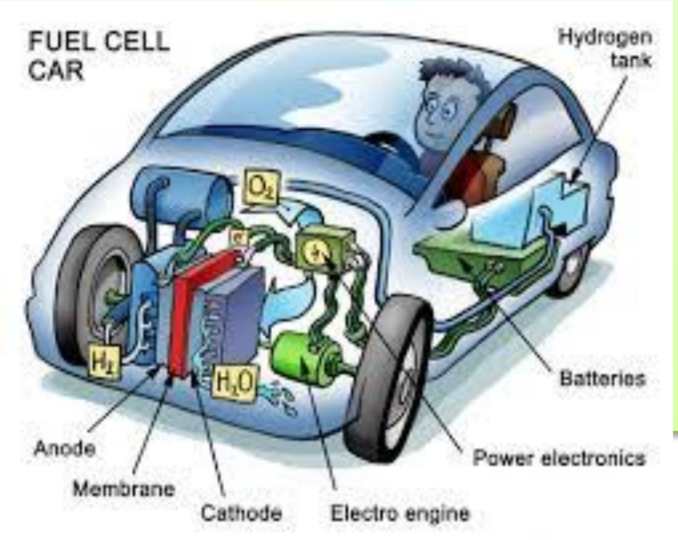
$$O_2 + 2\ H_2O + 4\ e- \rightarrow 4\ OH^-$$

Overall cell reaction

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

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:

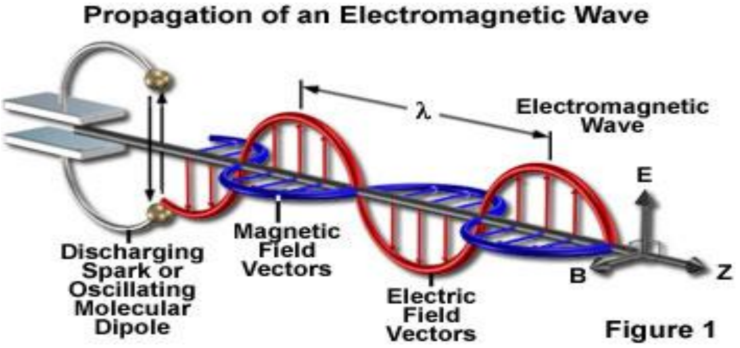
Electromagnetic radiation

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, $c = \nu\lambda$, (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 3×10^8 ms^{-1}.

Wavenumber ($\underline{\nu}$) - 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,

$$\nu = c/\lambda = c\underline{\nu}$$

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

$$E = h\nu = hc/\lambda = h\underline{\nu}$$

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

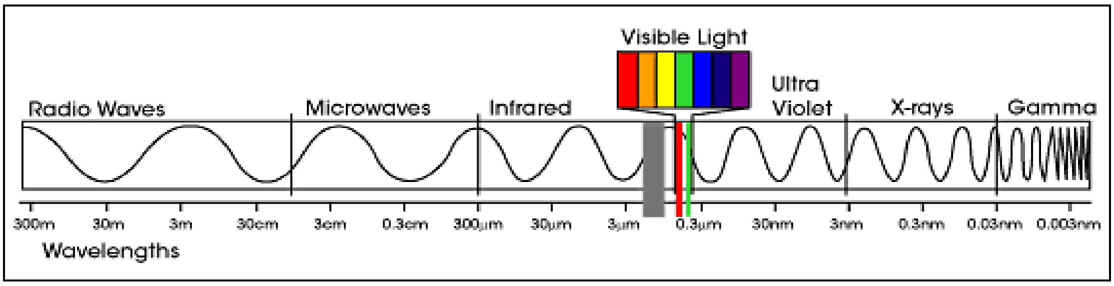
- EMR - a vast spectrum of frequencies and wavelengths.

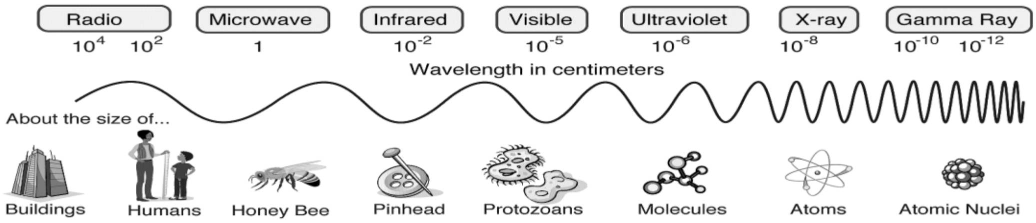
- EMR spectrum includes the very energetic gamma-rays radiation with a wavelength range from 0.005 – 1.4 Å to radio waves (RW) in the wavelength range up to meters (exceedingly low energy).

- 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 (2000-8000Ǻ 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.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

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 first step is: $Cl_2 + h\nu \rightarrow 2Cl^*$

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

$$H_2 + Cl^* \rightarrow HCl + H^*$$

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

   $2HI_{(g)} + h\nu \rightarrow H_{2(g)} + I_{2(g)}$

2. Double decomposition reaction

   $C_{16}H_{14} + Br_2 + h\nu \rightarrow C_6H_{11}Br + HBr$

3. Polymerization reaction

   $2(CH_{14}H_{10}) + h\nu \rightarrow C_{28}H_{20}$

4. Chain reaction

   $H_2 + Cl_2 + h\nu \rightarrow 2HCl$

***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.
4.	Rate of reactions is dependent on the intensity of the light absorbed.	Rate of reactions is not affected by the intensity of light.
5.	The free energy change is negative or positive.	The free energy change is always negative

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 Containing 6.023 x 1023 (Avogadro number) Molecules absorbs	≡	one mole of quanta (or) 6.023 x 1023 quanta of light (or) one Einstein

$$\text{One Einstein} = Nh\nu$$
$$= Nhc/\lambda \, [\therefore \nu = c/\lambda]$$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation $E = h\nu = hc/\lambda$, 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 $E = Nhc/\lambda$ 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: $c = 3 \times 10^{10}$ cm s^{-1}; $h = 6.625 \times 10^{-27}$ erg s^{-1}
$\therefore E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/\lambda$ erg mol^{-1} = $1.196 \times 10^{16}/\lambda$ (in Ǻ) erg mol^{-1}

1 cal = 4.184×10^{7} ergs

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

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

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

Where I = the intensity if 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

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

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

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

On combining both laws, we get $\log I_0/I = \varepsilon cl$ ————(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 As of a standard solution of known concentration C is measured, then according to Beer-Lambert;s law

$$A_s = \varepsilon C_s x$$

$$As/Cs = \varepsilon x \text{ ………………………}1$$

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

$$A_u = \varepsilon C_u x$$

$$A_u/C_u = \varepsilon x\text{………………………}2$$

From equation 1 and 2, we get

$$A_s/C_s = A_u/C_u$$

$$\therefore\ C_u = A_u/A_s \text{ x } C_s\text{………………}3$$

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

***<u>Limitations of Beer-Lambert’s law</u>*:**

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 ε = 6000 dm³ mol⁻¹cm⁻¹.***

   Solution:

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

   $\text{Log } I_o/I = \text{Log } 2.5 = 0.3980 = \varepsilon Cl$

   $C = (0.3980/6000\ dm^3\ mol^{-1}cm^{-1}) \text{ x } 2\ cm$

   $= 3.316 \text{ x } 10\text{-}5\ mol\ dm^{-3}$.

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

   Solution:

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

3. **Calculate the molar absorptivity of a 1 x 10-4 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 cm; C= 1 X 10-4 M/ mol dm-3
Therefore absorptivity,
$\varepsilon = A/Cl = 0.20/(1 \times 10^{-4}\ mol.dm^{-3} \times 2.4\ cm) = 8000\ dm^{3}mol^{-1}cm^{-1}$

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:

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow [FeSCN]^{2+}_{(aq)}$$

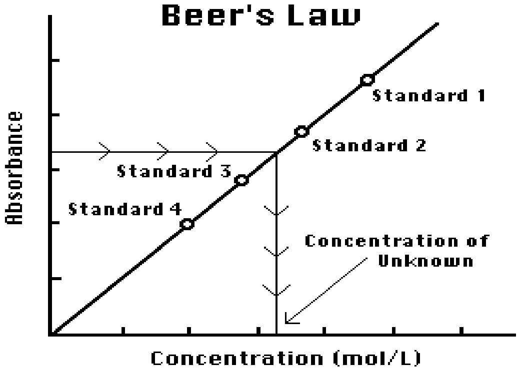
By comparing the intensity of the colour of this solution with the colours of a series of standard solutions, with known Fe^{3+} concentrations, the concentration of iron in solution may be determined. This technique is called colorimetry.

1. Using only the absorbance results obtained for your Fe3+ standard solutions (not your unknown iron sample), prepare a graph with $[Fe^{3+}]$ (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 Å; 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

Number of Einstein’s absorbed = $q/(Nhc/\lambda) = q\lambda/Nhc$

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

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

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 SO_2 + Cl_2 and c) Ozonisation of O_2.

2. The reaction in which the quantum yield is less than 1.
   Eaxmples: 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 CO + Cl_2; b) Combination of H_2 + 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.

$$HI + h\nu \rightarrow H^* + I^*$$

secondary reaction

$$H^* + HI \rightarrow H_2 + I^*$$

$$I^* + I^* \rightarrow I_2$$

Overall reaction: $2HI + h\nu \rightarrow H_2 + I_2$

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 discussed into two Cl atoms. This is followed by the secondary reaction as shown below:

Primary reaction: $Cl_2 + h\nu \rightarrow 2\,Cl^*$
Secondary reaction:

$$Cl^* + H_2 \rightarrow HCl + H^*$$

$$H^* + Cl_2 \rightarrow HCl + Cl^* \text{ (step 3)}$$

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.

$$H^* + Cl^* \rightarrow HCl$$

$$Cl^* + Cl^* \rightarrow Cl_2$$

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 anable 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

$$2C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$

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

$$2C_{14}H_{10} \leftrightarrow C_{28}H_{20}$$

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*.

$$A + h\nu \rightarrow A^*$$

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

$$A^* \rightarrow B$$

Photochemical Decomposition of HI: It takes place in the radiation of wave length between 2070 Ǻ - 2820 Ǻ. 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

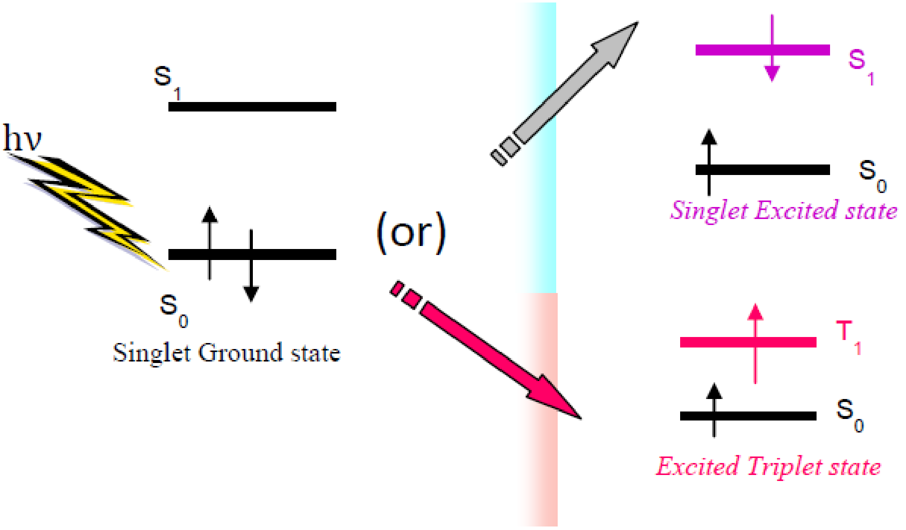
Mechanism of Photophysical Processes (or) Mechanism of Fluorescence and Phosphorescence (or) Jablonski Diagram

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 (↑↓), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$$S = s_1 + s_2 = (1/2) – (1/2) = 0$$

∴ 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 (↑↑), then $S = s_1 + s_2 = (1/2) + (1/2) = 1$, ∴ $2S + 1 = 3$, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

   b) or anti-parallel (↑↓), then $S = s_1 + s_2 = (1/2) - (1/2) = 0$, ∴ $2S + 1 = 1$, 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.

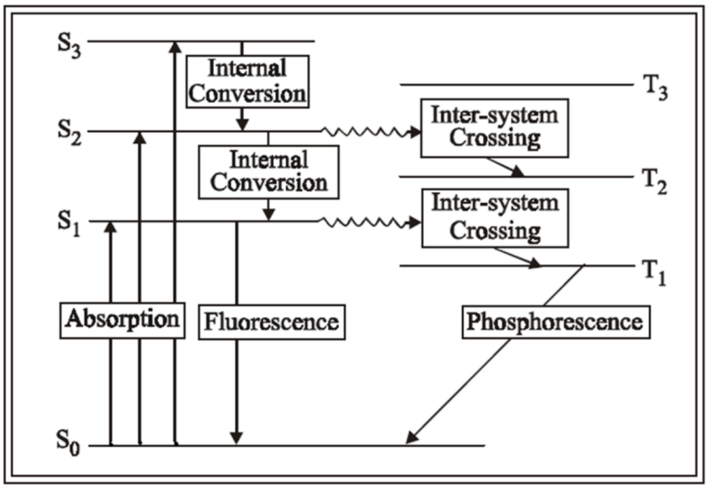


Fig. 3.5 Jablonski diagram of various photophysical processes

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 theses 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.

   $$S_3 \rightarrow S_1;\ S_2 \rightarrow S_1 \text{ (or) } T_3 \rightarrow T_1;\ T_2 \rightarrow T_1$$

   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.

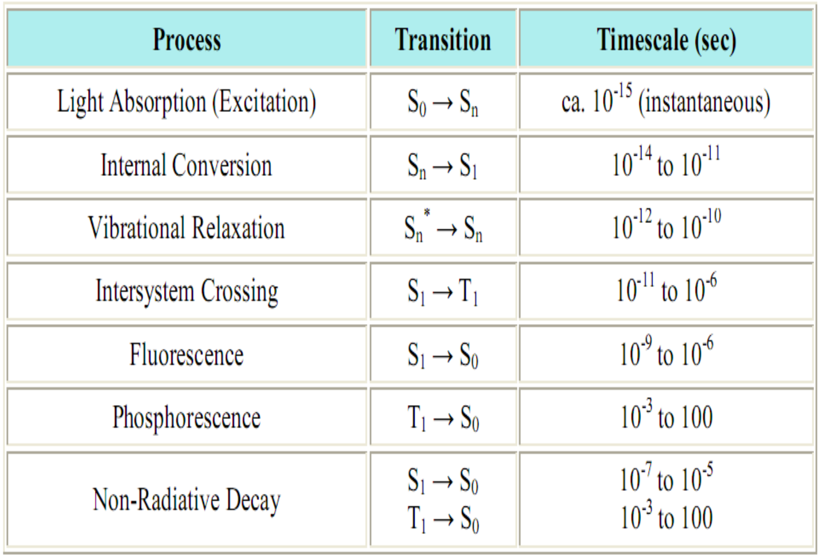
b. ***Phosphorescence***: The emission of radiation due to the transition from the triplet excited state T_1 to the ground state S_0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition.

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)	$S_0 \to S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \to S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \to S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \to T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \to S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \to S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \to S_0$ $T_1 \to S_0$	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:

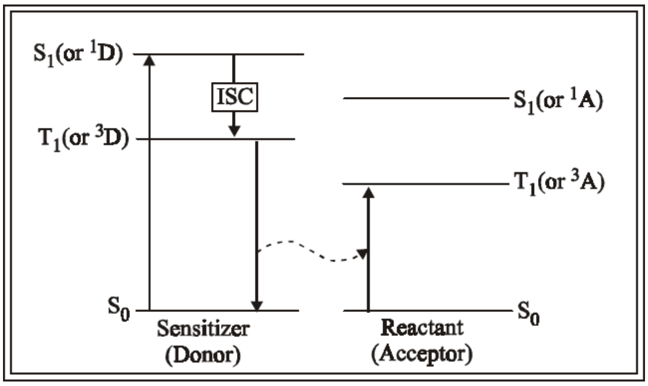
Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer 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:

$D + h\nu \rightarrow {}^1D$
${}^1D \rightarrow {}^3D$
${}^3D + A \rightarrow D + {}^3A$
${}^3A \rightarrow$ Products (photosensitization)
${}^3D \rightarrow$ Products (quenching)

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.

$Hg + h\nu \rightarrow Hg^*$
$Hr^* + H_2 \rightarrow H_2^* + Hg$
$H_2^* \rightarrow 2H$

2. ***Photosynthesis in plants***: During photosynthesis of carbohydrates in plants from CO_2 and H_2O, 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 CO_2 and H_2O molecules, which then react to form glucose.

$$\text{Photosynthesis:}\quad \text{Chll} + h\nu \rightarrow {}^{*}\text{Chll}\ \text{(excited)}$$

$$6\,H_2O + 6\,CO_2 + {}^{*}\text{Chll} \rightarrow C_6H_{12}O_6 + 6\,O_2 + \text{Chll}\ ,\qquad \Delta G = -\text{Ve}$$

In the presence of light and chlorophyll ΔG^o becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG^o for this reaction is +2875 kJ. Since ΔG^o 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 photo physical 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**:** CaF_2, uranium, petroleum, organic dyes like eosin, fluorescein), chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.

Types of fluorescence:

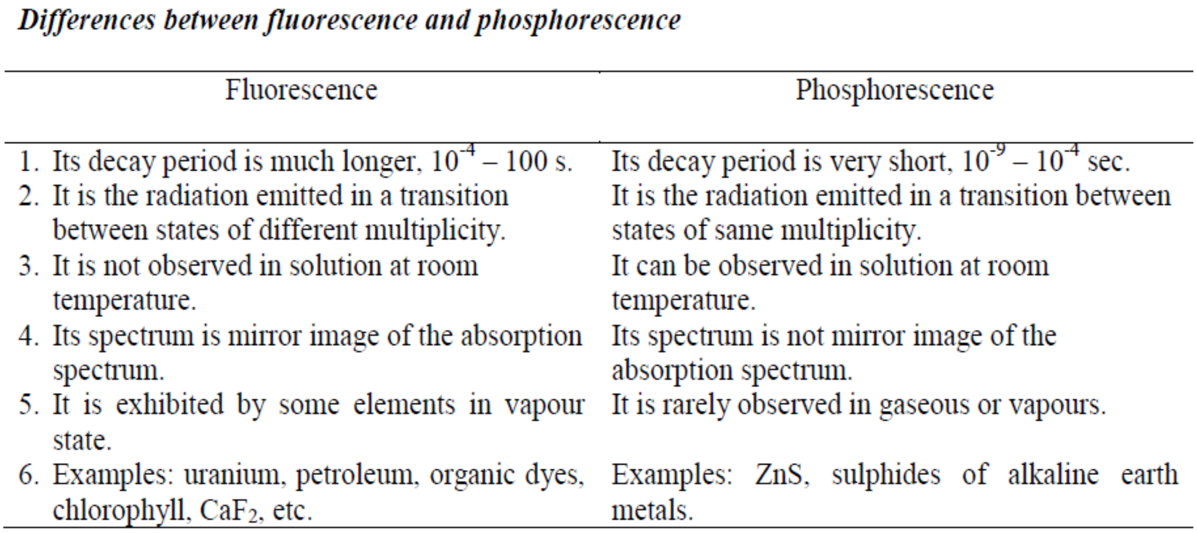
a) ***Resonance fluorescence***: If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence.

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

$$\text{Reactants} \quad \underset{\text{Dark}}{\overset{\text{light}}{\longleftrightarrow}} \quad \text{Products}$$

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

$$A \quad \underset{k_{-1},\ \text{Dark}}{\overset{k_1,\ \text{light}}{\longleftrightarrow}} \quad B$$

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 quatum yield ranging from 10^4 -10^6 in the light of wavelength 4800Å. Nernst gave a chain mechanism, which is universally accepted now-a-days

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

$$Cl_2 + hv \overset{k_1}{\leftrightarrow} 2Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

The other stages are

$$Cl + H_2 \overset{k_2}{\leftrightarrow} HCl + H\ (exothermic) \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$H + Cl_2 \overset{k_3}{\leftrightarrow} HCl + Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

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.,

$$Cl + walls \overset{k_4}{\leftrightarrow} \frac{1}{2} Cl_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

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:

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

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

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

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

$$k_2\,[Cl]\,[H_2] = k_3\,[H]\,[Cl_2] \ldots\ldots\ldots..7$$

Eq.6 + eq.7 gives:

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

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

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

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

$$[H] = \frac{k_2\,[H_2]}{k_3\,[Cl_2]}.\frac{k_1 I_{abs}}{k_4} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 9 \quad \text{or}$$

Now Substituting the values of [Cl] and [H_2] from eq. 8 and 9 in eq. 5, we get

$$\frac{d[HCl]}{dt} = k_2\,[H_2]\frac{k_1 I_{abs}}{k_4} + k_3\,[Cl_2].\frac{k_2}{k_3}.\frac{k_1}{k_4}\,\frac{[H_2].I_{abs}}{[Cl_2]}$$

$$= k_1\,k_2\frac{[H_2].I_{abs}}{k_4} + k_1\,k_2\,\frac{[H_2].I_{abs}}{k_4}$$

Or

$$\frac{d[HCl]}{dt} = 2.k_1\,k_2\frac{[H_2].I_{abs}}{k_4} \ldots\ldots\ldots\ldots\ldots 10$$

Or

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

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 became 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 :

$$
\begin{aligned}
&A + h\nu \rightarrow A^{*} \qquad (activation)\\
&A^{*} \overset{k1}{\rightarrow} A + h\nu \qquad (fluorescence)\\
&A^{*} \overset{k2}{\rightarrow} A \quad (internal\ quenching)\\
&A^{*} + Q \overset{k3}{\rightarrow} A + Q' \quad (external\ quenching)
\end{aligned}
$$

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

Φ_f or $\phi_q = I_f/Ia = k_1[A^*] / (k_1[A^*] + k_2[A^*] + k_3[A^*][Q])$

$=k_1 / (k_1 + k_2 + k_3 [Q])$

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

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

Put $1/k_2+k_2 = \tau$

$\varphi_0/\varphi_Q=1+k_3 \tau[Q]$

or

$\varphi_0/\varphi_Q=1+k_{sv}[Q]$

where, $K_{sv} = k_3\tau$ 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.

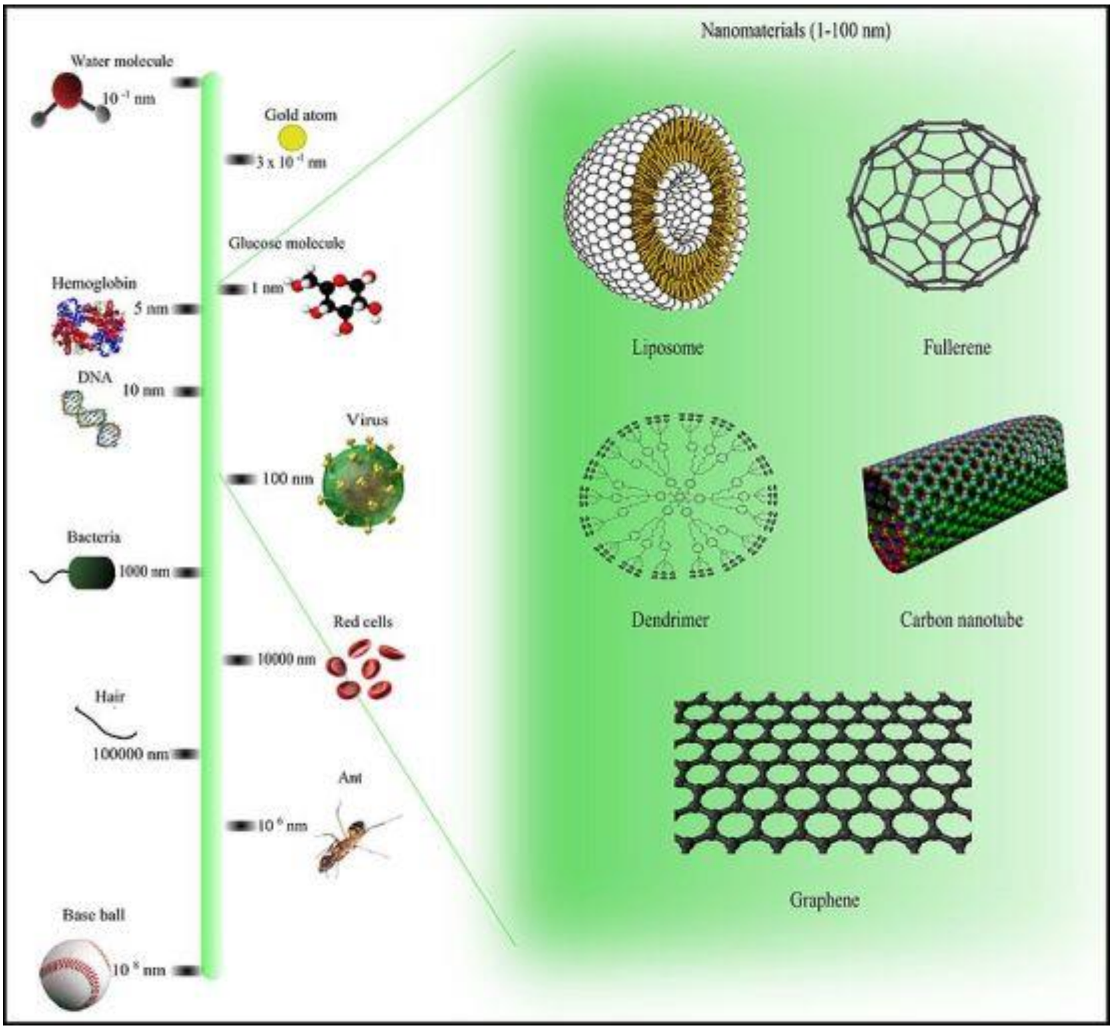


Figure 01: Comparison between Nanomaterials and Bulk Materials

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?

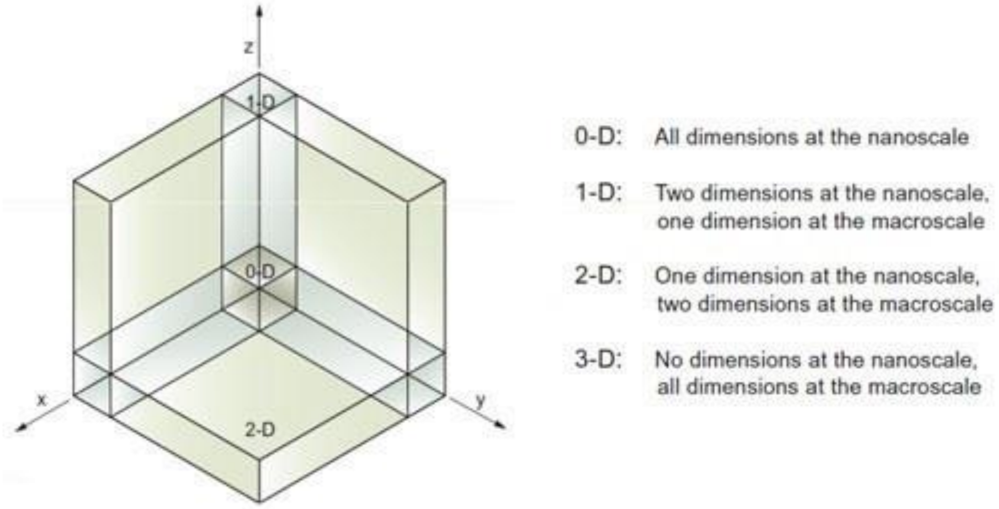
Bulk materials are particles that have their size above 100 nm in all dimensions. Most of the times, we use this term in order to name a substance that is granular or lumpy and exists in free-flowing form. we use the grain size and grain distribution in characterizing these materials. Moreover, we can 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:

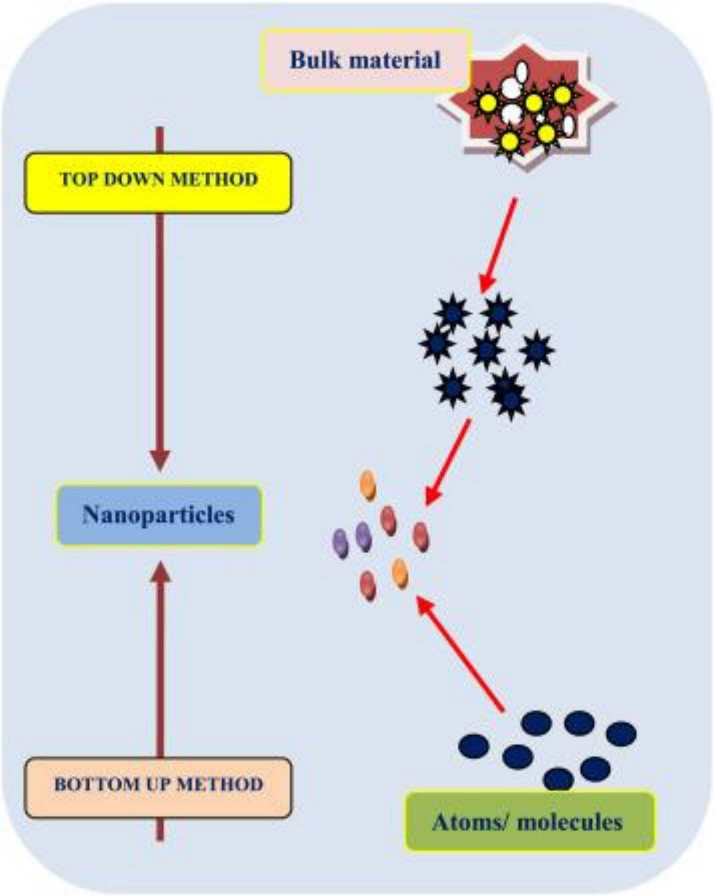
- Gold nanoparticles are red in color, while bulk gold is yellow.
- Carbon nanotubes are stronger than steel, but they are also much lighter.
- Silver nanoparticles are more antimicrobial than bulk silver.
- Zinc oxide nanoparticles are more effective at absorbing UV light than bulk zinc oxide.

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 (Na2CO3) and chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) 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 Al_2O_3 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 nanaoparticles 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.

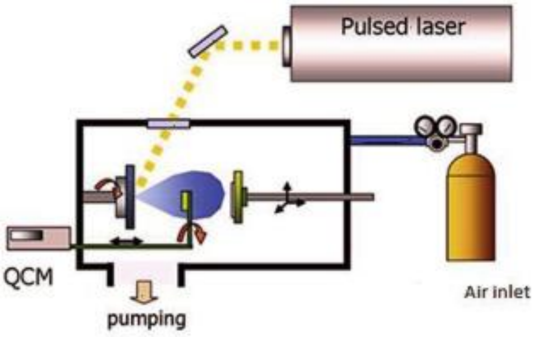


Fig. Pulsed laser deposition of ablated species.

Application

- Preparation of thin film of tungsten selenides.
- Preparation of platinum-ruthenium (Pt–Ru) nanoparticles.
- Formation of Yttria-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 H_2O 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:

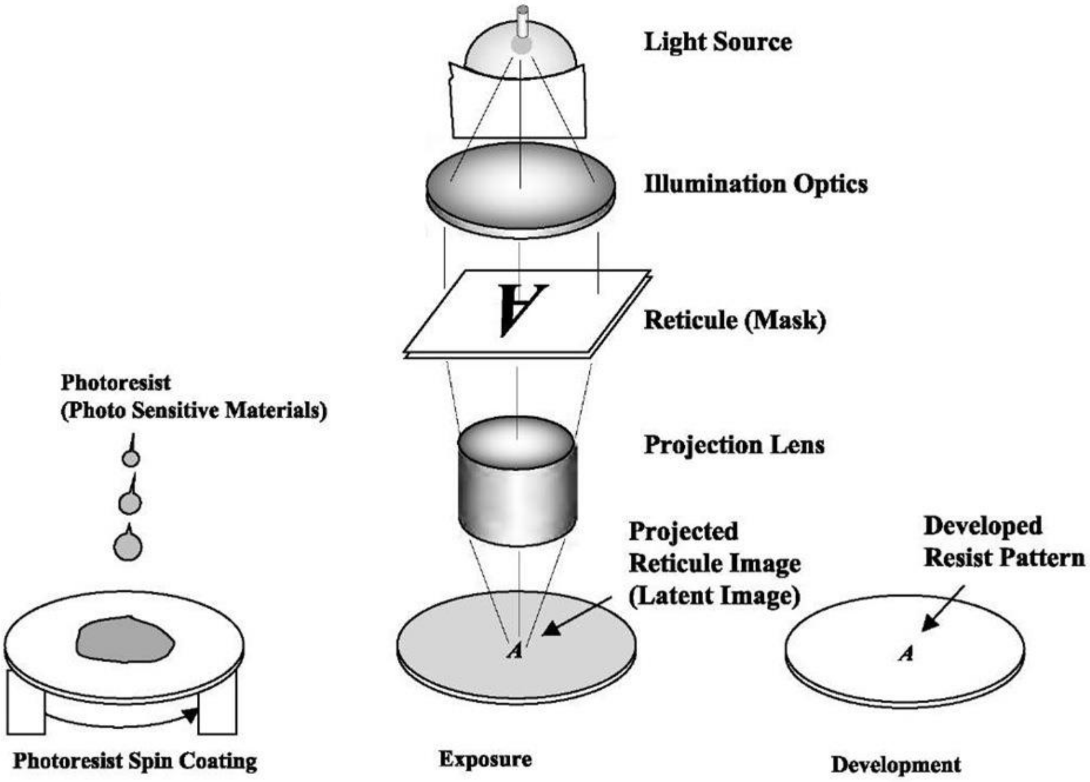
Electron beam lithography uses a focused beam of electrons to expose the photoresist. This technique can create smaller features than optical beam lithography, but it is slower and more expensive.

Example:

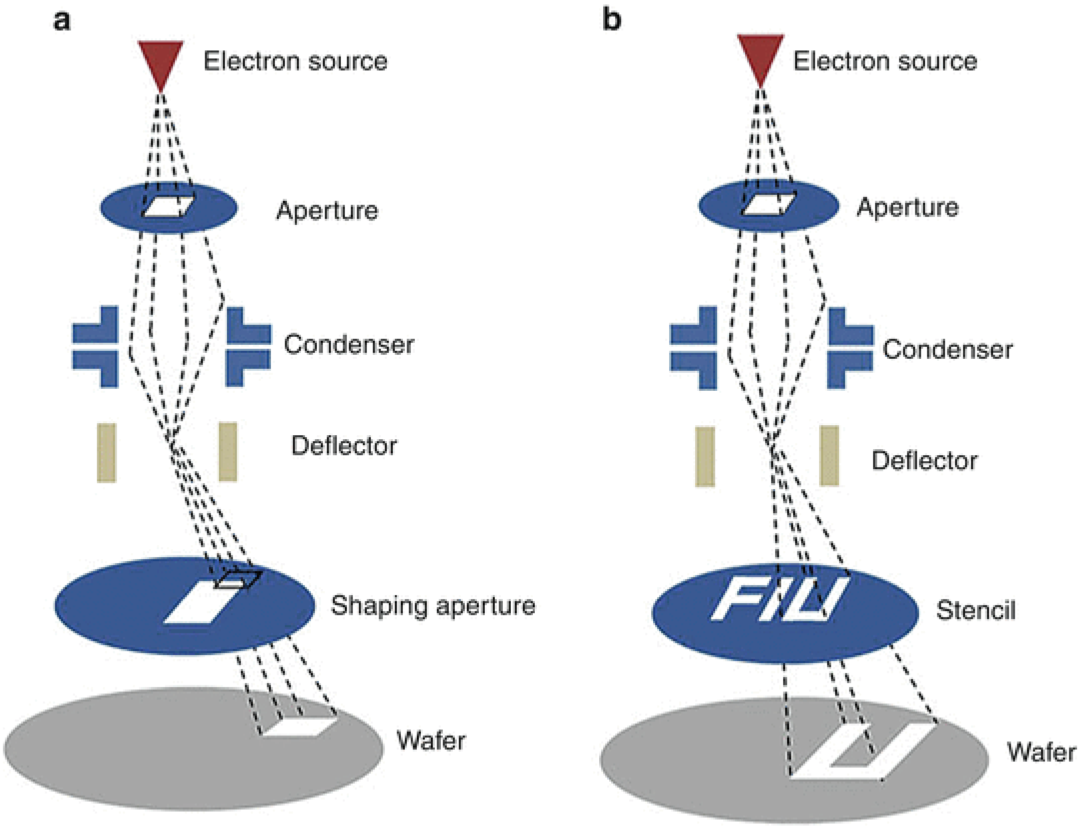
To create a transistor, the following steps would be taken:

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.

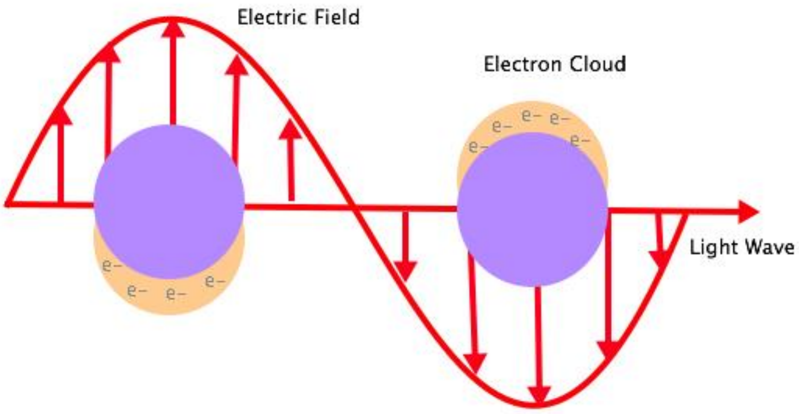


Figure - Shows how as a light wave passes through a material, the induced electric field creates a charge separation in the atoms, creating an electron cloud that then allows for electrons to move freely.

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.

Engineering Materials

Abrasives

Abrasives are very hard substances used for grinding, shaping and polishing other materials

Properties of Abrasives

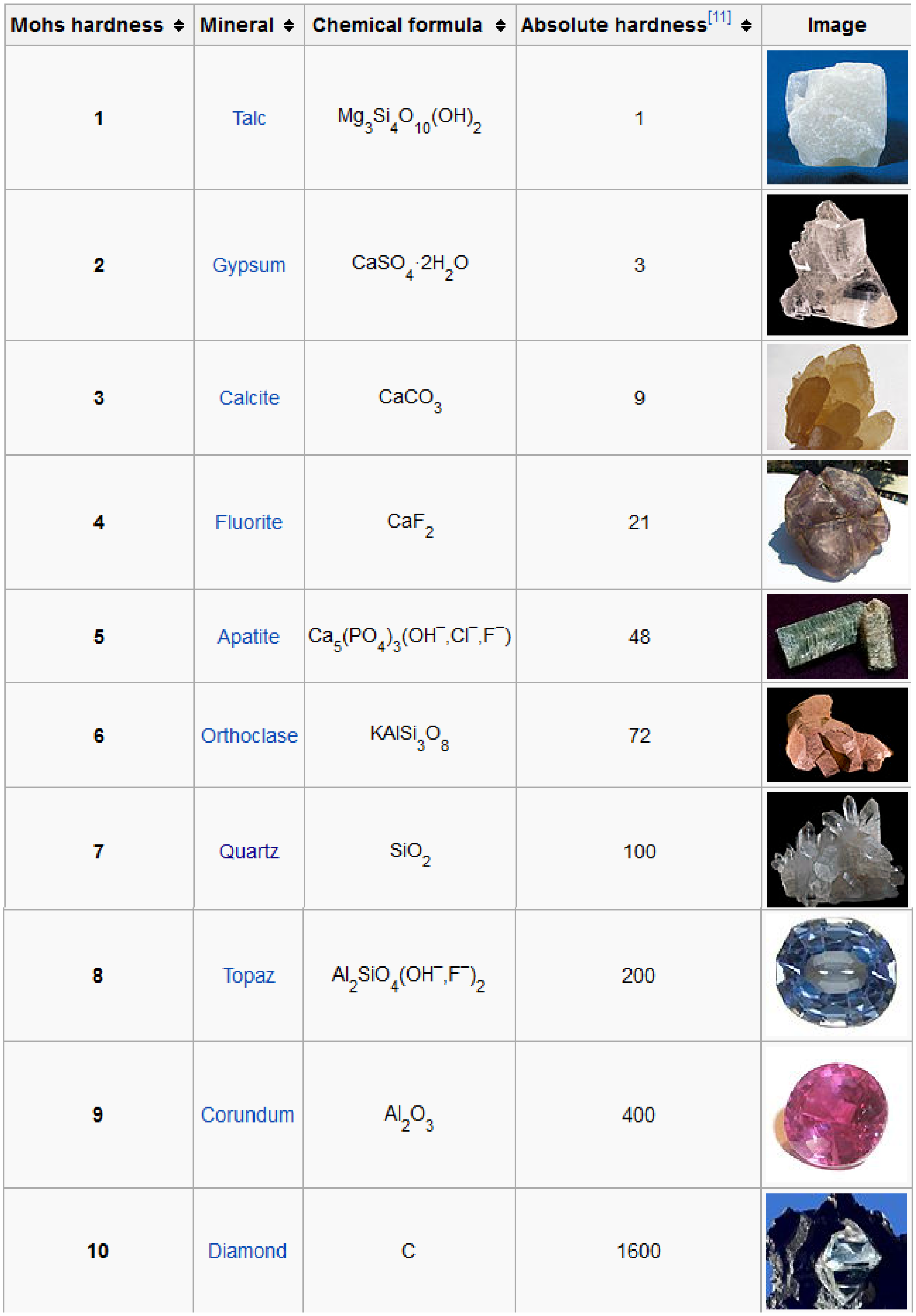
- Have very high melting point
- Chemically inert
- High abrasive power (ability to scratch away or sharp other materials)
- Sometimes hard and brittle or soft and flexible

Hardness of Abrasives

The Moh’s scale of mineral hardness is a qualitative ordinal scale which characterizes the scratch resistance of various minerals through the ability of a harder material to scratch a softer material. The hardness of an abrasive material is measured by Moh’s scale

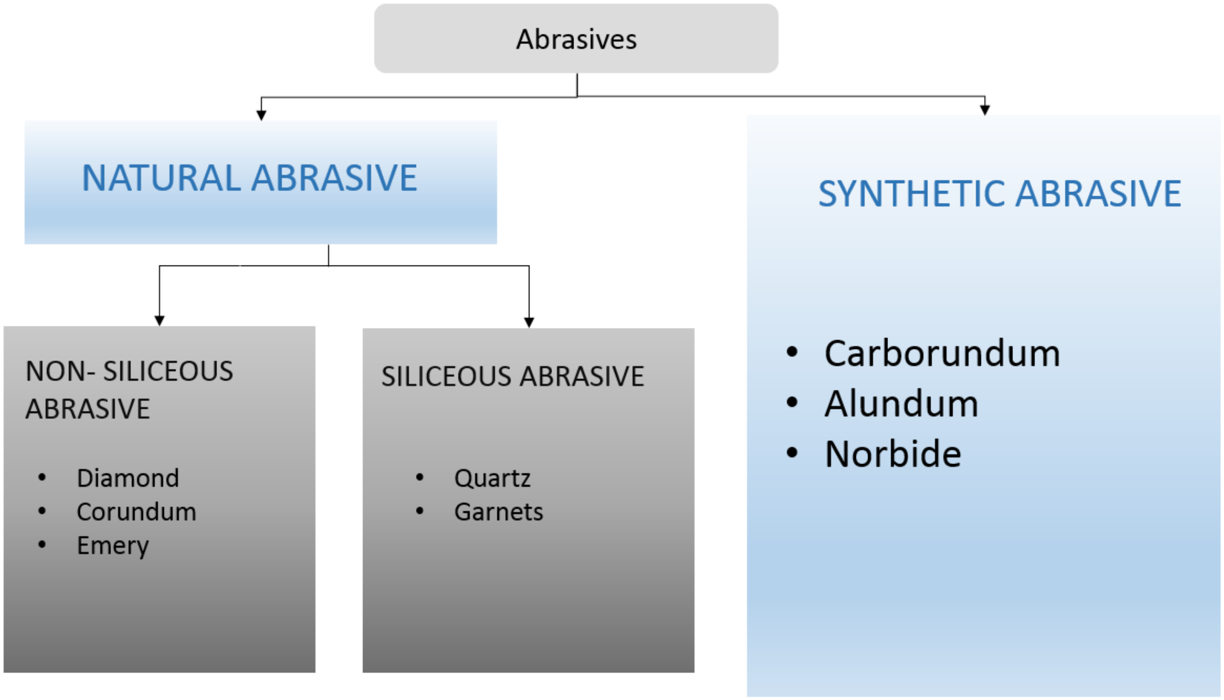
Characteristics of Abrasives

- Hard
- Resist abrading action
- Chemically inactive
- High refractoriness
- High Melting Point
- Not affected by frictional heat



Mohs hardness	Mineral	Chemical formula	Absolute hardness[11]	Image
1	Talc	$Mg_3Si_4O_{10}(OH)_2$	1	
2	Gypsum	$CaSO_4 \cdot 2H_2O$	3	
3	Calcite	$CaCO_3$	9	
4	Fluorite	CaF_2	21	
5	Apatite	$Ca_5(PO_4)_3(OH^-,Cl^-,F^-)$	48	
6	Orthoclase	$KAlSi_3O_8$	72	
7	Quartz	SiO_2	100	
8	Topaz	$Al_2SiO_4(OH^-,F^-)_2$	200	
9	Corundum	Al_2O_3	400	
10	Diamond	C	1600	

Types of Abrasives



Natural Abrasives

Diamond

Properties

- Crystalline Carbon, hardest substance
- Ranks first in Moh’s scale (Hardness 10)
- Chemically insert
- Not affected by Acids & Alkalis
- **Borts** – Off Color Diamond

  Carbando – Black color diamond

Uses:

- Drilling points
- Cutting stones, rocks

- Grinding wheels

Corundum

Properties

- Pure Crystalline Alumina (Al_2O_3)
- Transparent material, but can have different color based on the presence of impurities in it. (If red , its called Ruby)
- Ranks second in Moh’s scale (Hardness 9)

Uses:

Grinding

- Glass
- Gems
- Metals

Emery

Properties

- Fine grained , opaque, black color material
- Aggregate of 55- 75 % crystalline alumina, 20-40 % magnetite, 12 % other materials (tourmaline)
- Ranks third in Moh’s scale (Hardness 8)
- Grinding depends on proportion of alumina

Uses:

- Tips of cutting and drilling tools
- Making abrasive papers & cloth

Garnet

Properties

- Trisilicates of alumina, magnesia and ferrous oxide.
- General formula : $X_3Y_2(SiO_4)_3$

- Major varieties:
    - Grossular : $Ca_3Al_2Si_3O_{12}$
    - Andradite : $Ca_3Fe_2Si_3O_{12}$
    - Spessartine : $Mn_3Fe_2Si_3O_{12}$
- Hardness : 6.5 to 7.5 in Moh's scale

Uses:

- Along with glue to make paper or cloth as it is soft in nature
- Bearing pivots, watches, glass grinding and polishing metal

Quartz

Properties

- Pure Crystalline Silica
- General Formula : SiO_2
- Ranks fourth in Moh's scale (Hardness 7)

Uses:

- Grinding pigments in paint industry
- Granules in grinding machines
- Hydrated form used in sand paper

Synthetic Abrasives

Caborundum or Silicon Carbide

Manufacturing process

- $SiO_2 + 3C \xrightarrow{1500^oC} SiC + 2CO$
- Addition of saw dust while burning increases the porosity
- Addition of salt removes iron and other impurities as volatile chlorides, which too increases porosity
- Binded with clay or silicon nitrate

Properties

- High thermal conductivity, intermediate between metals and ceramics
- Low expansion
- High resistance to abrasion and spalling
- Withstands load upto 1650 ^oC
- Intermediate between conductors and insulators
- Strength , Density , Abrasion-resistance , Chemical resistance, softening temperature

  Of Self bonded product **>** Silicon nitrite bonded product **>** Clay bonded product

Uses:

- ✓ Heating elements in furnaces as rods and bars
- ✓ Partial walls of chamber klins, coke ovens, muffle furnace
- ✓ When bonded with tar are excellent for making high conductivity crucibles

Norbide or Boron Carbide

Manufacturing process

- $2B_2O_3 + 7C \xrightarrow{2700^oC} B_4C + 6CO\uparrow$

Properties

- Hardness is 9 on Moh's scale
- Light weight and black in color
- Resistance to chemical and erosion
- Better than diamond in resisting oxidation

Uses

- Grinding dyes
- Cutting and sharpening of hard high speed tools
- Used to prepare scratch and wear resistance coatings

Alundum

Manufacturing process

- $\text{Bauxite (Al)} + 3O_2 \xrightarrow[C]{\triangle} 2Al_2O_3$

Properties

- Hardness is 9 on Moh's scale
- Resistance to acids
- Stable at high temperature
- Not as hard as carborundum, but less brittle and tougher

Uses

- Grinding hard steel and high tensile strength materials
- Manufacturing of abrasive wheels

Applications of abrasives

- ✓ As loose powder
    - **Example :** Quartz and Garnet
- ✓ As abrasive paper or cloth
    - **Example :** Alumina and Silicon carbide
- ✓ Grinding wheels

Manufacturing of abrasive paper or cloth

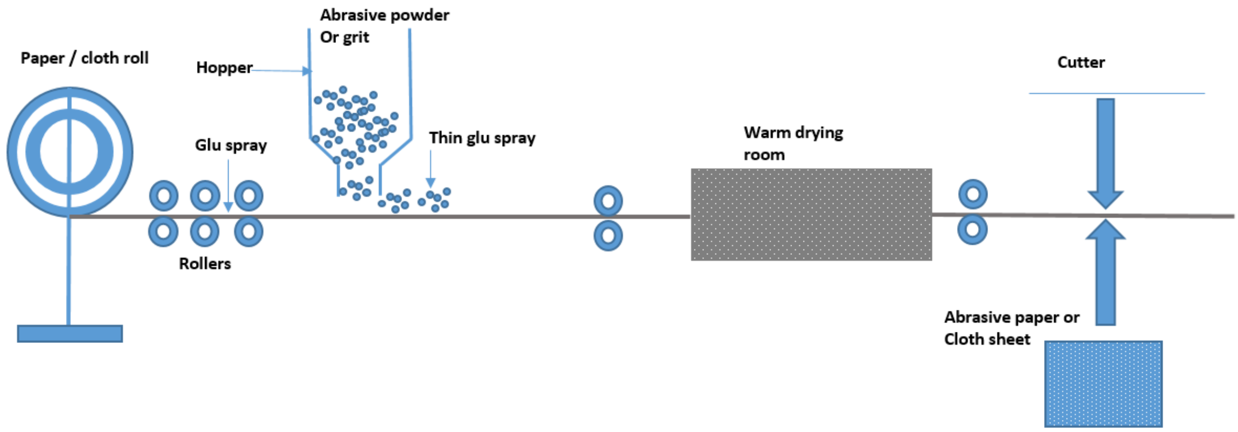


Figure showing manufacturing process of abrasive paper or cloth

The roller paper or cloth is made to pass through series of rollers and thin coating glues applied on it on its upper side. Its then passed on a hopper from which the grit of abrasive is allowed to fall and spread evenly on the glued paper or cloth.

The paper or cloth is again applied with a thin coating of glue and dried in a warm room. The dried abrasive paper is then cut into sheets of desired size. Finally they are allowed to age for few days so that the glu sets firmly. Depending upon hardness, grain size, chemical composition and purity, different number of abrasive papers or cloth are sold in the market.

Grinding Wheels

Grinding wheels are expandable wheels, composed of an abrasive compound

Characteristics

- ✓ Abrasive Grain

    Actual abrasive is selected according to the intended purpose of the grinding wheel and hardness of the material being cut

- ✓ Grain Size

    Grain size vary from 8 (coarsest) to 1200 (finest) determines the physical size of the abrasive grains

- ✓ Wheel grade

    Grade from A (soft) to Z (hard), determines how tightly the bond holds the abrasive

- ✓ Grain spacing

    Varies from 1 (densest) to 16 (least dense)

- ✓ Wheel bond

    It determines how the wheel holds the abrasive

Uses:

- ✓ Removal of scales from the iron surfaces
- ✓ Sharpening cutting tools
- ✓ Sharpen the knives, tools etc.,

……………………………………………………

Refractories

- Materials that can withstand high temp without softening and deformation in their shape.
- Used for the construction of furnaces, converters, kilns, crucibles, ladles etc.

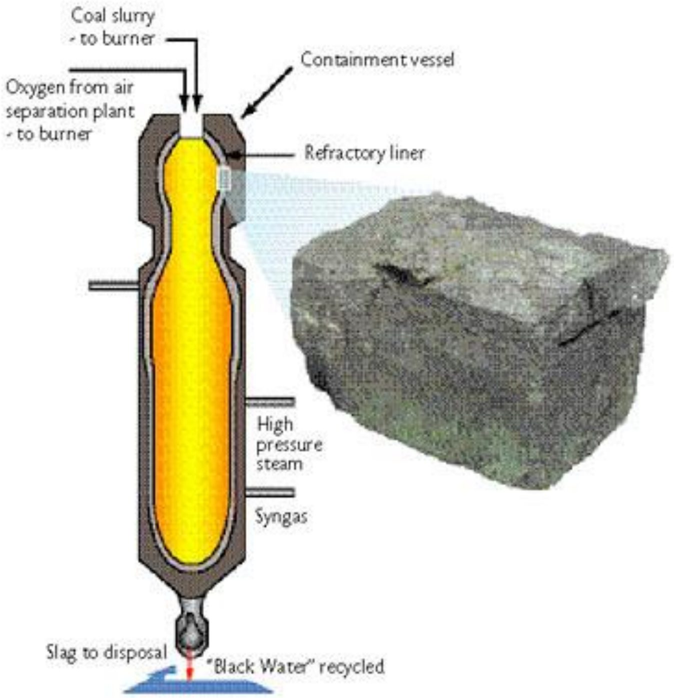


Fig (1) : Schematic of gasifier cross section showing the location of the spent refractory brick

Characteristics of refractories

1. Infusible at operating temperature
2. Chemically inert towards corrosive gases, liquids etc.
3. Should not suffer change in size at operating temp
4. Should have high refractoriness
5. Should have high load bearing capacity at operating temp.

Classification of refractories

Refractories

CHEMICAL NATURE

- Acidic Refractories
  - Silica , Alumina
- Basic Refractories
  - Magnesite, Dolomite
- Neutral Refractories
  - Graphite, Carborundun

REFRACTORINESS

- Low Heat Duty
- Intermediate Heat Duty
- High Heat Duty
- Super Heat Duty

Properties of refractoriness

- **Refractoriness:** “It is the ability to withstand very high temp. without softening or deformation under particular service condition.”
- Most of the refractories are mixtures of several metallic oxides and they don’t have a sharp melting point
- Refractoriness of a refractory is generally measured as the softening temperature and is expressed in terms of Pyrometric Cone equivalent (PCE)
- **Pyrometric Cone :** **“**Is a refractory specimen of standard dimension (38mm height and 19mm triangular base) and composition. “

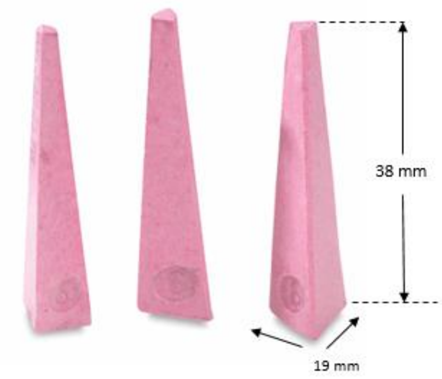
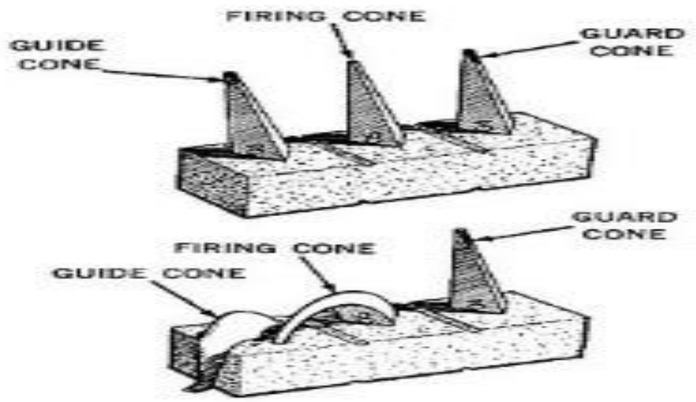


Figure showing Pyrometric Cones

Objectives of PCE Test

- To determine the softening temperature of a test refractory material.
- To classify the refractories
- To determine the purity of the refractories
- To check whether the refractory can be used at particular servicing temperature.



Guiding cone is one cone number cooler than firing cone

Firing cone is the desired cone for ware being tested

Guard cone is one cone hotter than firing cone

- **Seger Cone:** “Are pyramid shaped standard refractory of definite composition and dimensions and hence it has a definite softening temperature.”
- Refractoriness is determined by comparing the softening temperature of a test cone with that of a series of seger cones
- A test cone is prepared from a refractory for which the softening temperature to be determined, as the same dimensions of seger cones

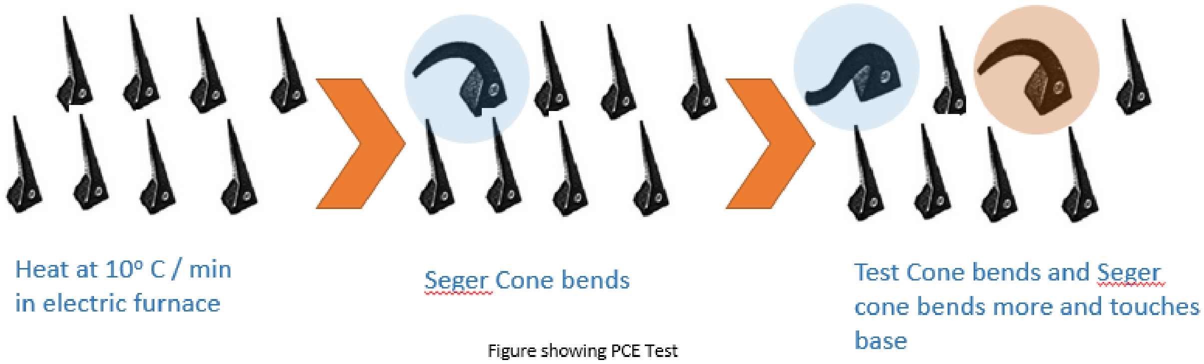
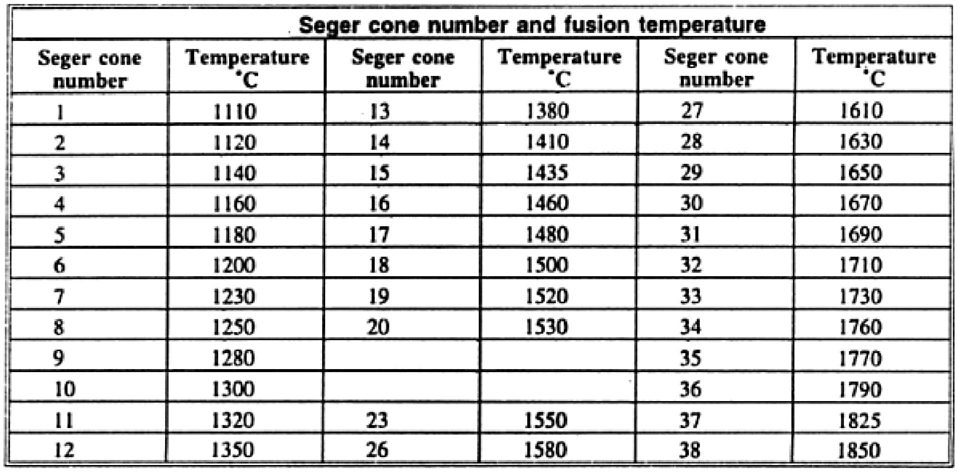


Figure showing PCE Test

Pyrometric Cone Equivalent (PCE) Number

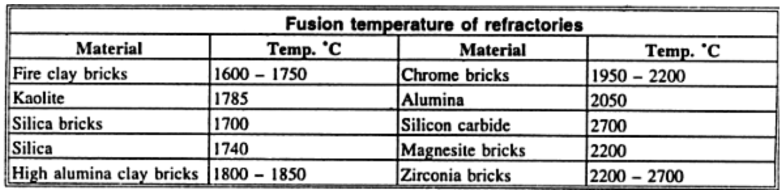
PCE Number is the value representing the number of standard cones which also fuses with test cone for a given refractory



Seger cone number and fusion temperature

Seger cone number	Temperature °C	Seger cone number	Temperature °C	Seger cone number	Temperature °C
1	1110	13	1380	27	1610
2	1120	14	1410	28	1630
3	1140	15	1435	29	1650
4	1160	16	1460	30	1670
5	1180	17	1480	31	1690
6	1200	18	1500	32	1710
7	1230	19	1520	33	1730
8	1250	20	1530	34	1760
9	1280			35	1770
10	1300			36	1790
11	1320	23	1550	37	1825
12	1350	26	1580	38	1850

Figure showing Seger Cone Number and fusion temperature



Fusion temperature of refractories

Material	Temp. °C	Material	Temp. °C
Fire clay bricks	1600 – 1750	Chrome bricks	1950 – 2200
Kaolite	1785	Alumina	2050
Silica bricks	1700	Silicon carbide	2700
Silica	1740	Magnesite bricks	2200
High alumina clay bricks	1800 – 1850	Zirconia bricks	2200 – 2700

Figure showing fusion temperature of various refractories

Refractories Under Load (RUL) Test

The temperature at which the refractory deforms by 10^{o} is called refractoriness under load.

Refractories used in industries and metallurgical operations should bear varying loads hence it should have high mechanical strength at operating temperature. The load bearing capacity is measured by RUL test. It is conducted by applying a constant load of 3.5 or 1.75 Kg / cm^3 to the test specimen of 5 cm^2 base and 75 cm height , heated in a furnace at 10 ^{o}C / min.

Porosity

- All refractories contain pores, either due to manufacturing methods or deliberately made(by incorporating saw-dust or cork during manufacture).
- Porosity is the ratio of its pore’s volume to the bulk volume.

$$P = \left(\frac{W - D}{W - A} \right) X\ 100$$

W = Weight of saturated specimen in air

D = Weight of dry specimen

A = Saturated speciment in water

- An important property of refractory bricks as it affects many other refractory characteristics
- In a porous refractory, molten charge, slags, gases etc. are likely to enter more easily to a greater depth and may react and reduces the life of the refractory material
- Porosity Decreases strength, resistance to abrasion , resistance to corrosion, penetration by slag / gases etc.,

Dimensional Stability

Resistance of a material to any volume changes, which may occur on its exposure to high temperature, over a prolonged time

- Dimensional changes can be permanent or reversible
- Irreversible changes may result either in the contraction or expansion of a refractory

Thermal Spalling

Property of breaking, cracking or peeling of refractory material under high temp

Thermal spalling is mainly due to

a. **Rapid Change in temperature**

This causes uneven expansion and contraction within the mass of a refractory, and leads to development of uneven stresses and strain

a. **Slag penetration**

This causes variation in the co-efficient of expansion and leads to spalling

Thermal spalling can be decreased by

(i) Using high porosity , low co-efficient of expansion and good thermal conductivity refractory.
(ii) A voiding sudden temperature changes.
(iii) By modifying the furnace design

Thermal Expansion

Expansion of a refractory material, when exposed to heat for a longer duration

- Refractory expansion has an impact on the capacity of the furnace lifetime
- Repeated expansion and contraction of refractory materials due to thermal impact causes wear & tear, breakdown etc.,

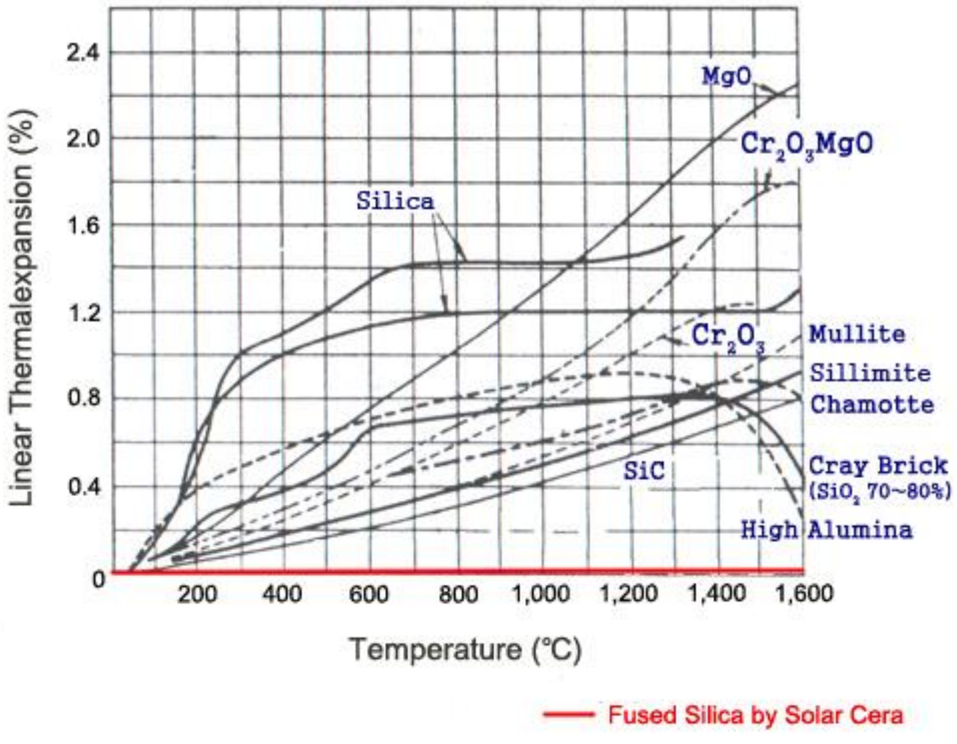
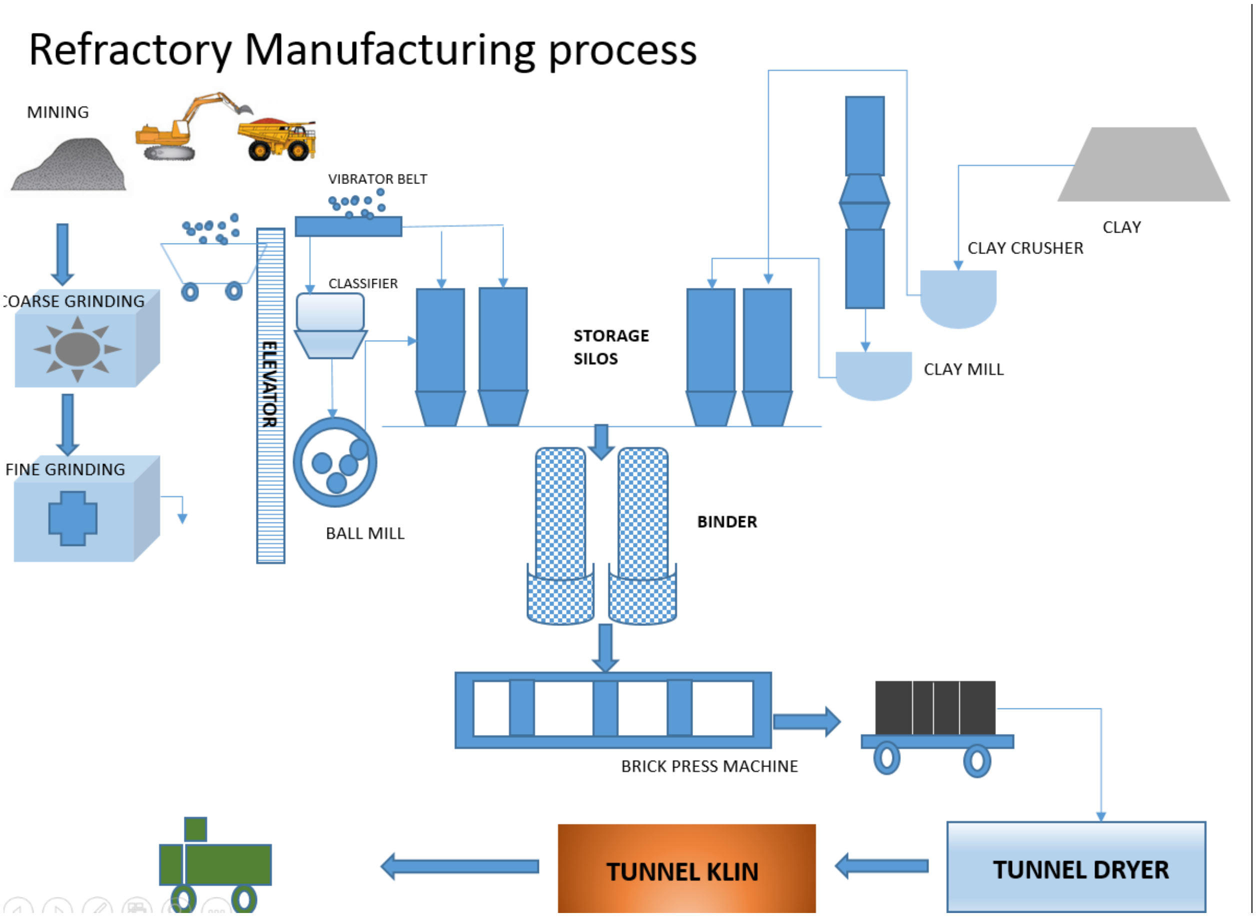


Figure showing thermal expansion % of various refractories

Characteristics of good refractory material

A good refractory material should have high refractoriness, high RUL, high dimensional stability and low porosity, thermal spalling, thermal expansion.

Manufacturing of refractories


Refractory Manufacturing process

1. **Grinding**

   Raw materials are crushed and ground to powder using crushers and ball mills

2. **Mixing**

   Two or more powdered raw materials are mixed with suitable binding material which makes moulding easier

3. **Moulding**

   Moulding can be done either mechanically or manually by applying pressure

4. **Drying**

   Drying is carried out slowly to remove moisture

5. **Firing**

   It is done at temperature as high as or higher than their operating temperature in klins

The refractories are fired

i. To stabilize and strengthen

ii. to remove water of hydration

iii. Facilitate development stable mineral to form the finished products

Examples of refractory bricks

Alumina Bricks or fire clay bricks (Acidic)

Composition: 50 % or more of Calcium Bauxite Al_2O_3 . They are manufactured by calcined bauxite with clay.

Manufacture: The raw materials and clay are ground to fine powder with required amount of water and converted into a paste. The pasty material is converted into brick by machine crushing or slip casting. The bricks after moulding is dried slowly and then fired in kiln to about 1200 – 1400^oC for 6 to 8 days.

Properties:

- Low coefficient of expansion
- High porosity
- Little tendency to thermal spalling
- Resistance to slag
- Stable and wear resistance
- High temperature load bearing capacity
- Inert to gases lik COl_2 , H_2 and natural gas

Uses:

- **Medium Duty Bricks :** 50 – 60 % of Al_2O_3
  - Cement rotary klins
  - Soaking pits
  - Reheating furnace
  - Hearths & walls
- **High Duty Bricks** : 75 % of Al_2O_3
  - Hottest zones of cement rotary klins

    - Brass melting reverberatories
    - Aluminium melting furnaces

Magnesite bricks (Basic)

Composition: It contains mainly MgO and manufactured by calcined Magnesite with caustic magnesia or iron oxide or sulphite lye as binding material

Manufacture: The raw materials and binding materials are ground to fine powder and mixed with water which forms a pasty material. Moulding of pasty material is done by machine pressing to required shape. The moisture is removed by drying at room temperature and firing is done at 1500 °C for 8 hours.

Properties:

- Withstands 2000 °C without load and upto 1500 °C under load of 3.5Kg / cm^2
- Good resistance to basic slags
- Little shrinkage and more of spalling
- Poor resistance to abrasion
- Easily combines with Carbon dioxide and water
- Highly sensitive to sudden change to temperature

Uses :

- Steel Industry for lining of
    - Basic Convertors
    - Open – hearth furnace
- Copper Convertors
- Reverberatory furnaces
- Refining furnaces for Gold, silver and platinum etc.,
- Hot mixture linings

Caborundum or Silicon Carbide (SiC) Bricks (Neutral)

Composition: Sand 60 % and Coke 40 %

Manufacture : SiC is manufactured by mixed 60 % sand and 40 % of coke along with salt and saw dust in an electrical furnace at 1500°C . Saw dust increases the porosity and salt converts iron and impurities as volatile chloride. The silicon carbide is mixed with bonding agents like clay, silicon nitride etc., and moulded, dried and fired at 2000°C

Properties:

- High thermal conductivity
- Low thermal expansion
- ‘Clay bonded’ can be used upto **1750°C**
- ‘Silicon nitrate bonded’ poses high strength and thermal shock resistance
- ‘Self bonded’ has high refractoriness, strength , density, abrasion resistance and chemical resistance
- Oxidizes when heated at **900°C -1000°C** , which can be prevented by coating with zirconium

Uses:

- **Partial Walls of**
    - Chamber klins, coke ovens, muffle furnace
- **Floor for**
    - Heat treatment furnace
- **Heating elements in forms of**
    - Rods and Bars (globars)

LUBRICANTS

In machine, the friction between metal to metal parts arises due to moving surfaces and machine experienced a resistance which retards their movement.

Due to friction large amount of energy is liberated in the form of heat which reduces the efficiency of machine.

Lubricants - substances which apply between two moving and sliding surface to reduce friction between them.

Lubrication - the process by which friction between sliding surface is reduce, known as Lubrication.

Liquid Lubricants

It includes animal oils, vegetable oils, petroleum oils, synthetic lubricants.

Animal oils: tallow oil, whale oil etc.

Vegetable oils: castor oil, palm oil etc

Petroleum oils: petroleum fractions

Synthetic lubricants: polyglycol, silicones etc.

Semi-solid Lubricants (Grease)

Semi-solid Lubricants are formed by emulsifying oil and fat with thickening agents like soap of sodium, calcium, lithium, aluminum at higher temperature.

Classification

Soda based: In this case sodium soaps are used as a thickening agent in mineral or petroleum oil. They are slightly soluble in water. They can be used up to 175^{o}C.

Lithium based: In this case lithium soaps are emulsifying with petroleum oil. They are water resistance and used up to 15^{o}C.

Calcium based - In this case calcium soaps are emulsifying with petroleum oil. They are also water resistant and used up to 80^{o}C. At higher temperature soap and petroleum oil are separate from each other.

Solid Lubricants

Graphite, molybdenum disulphide (MoS_2), boron nitride $(BN)_x$ are predominantly used as a solid lubricants. They are used under high temperature and high load (pressure).

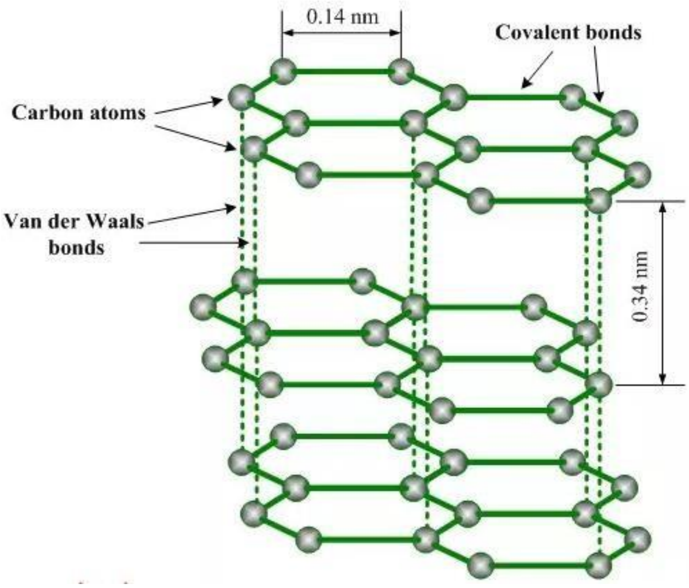
Graphite

It is most widely used as a solid lubricant.

Graphite has layer structure; layers are held together with the help of weak Vander Waals' forces which facilitate the easy sliding of one layer on the other layer.

It is very soapy to touch, non-inflammable. It is used at higher temperature (around 450^{o}C) condition.

They are either used as powder form or mixed with oil or water.



Molybdenum disulphide (MoS_2)

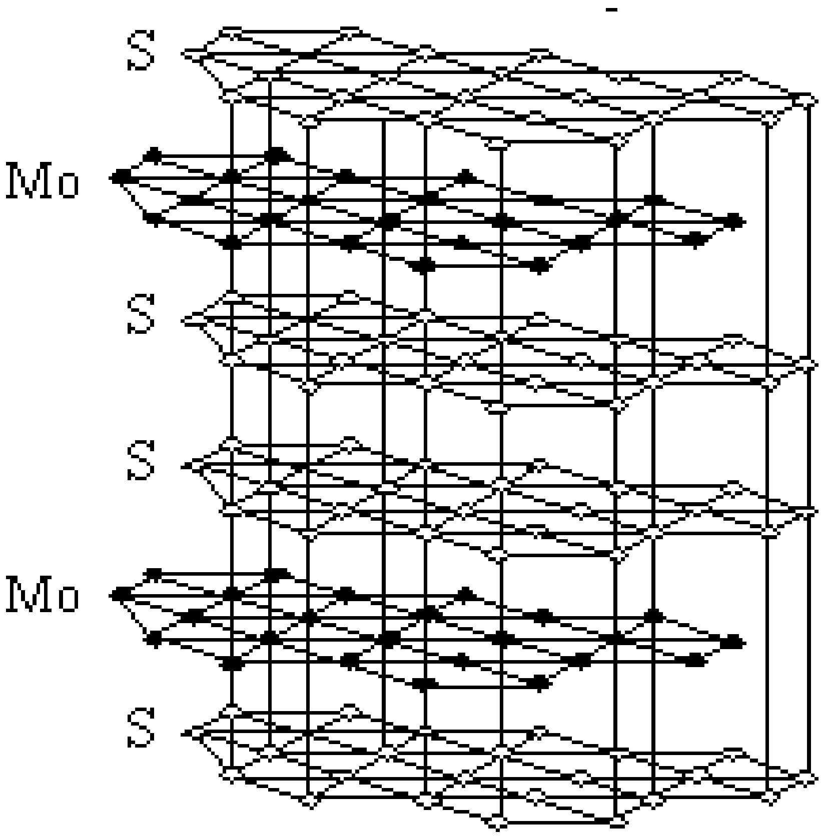
It is sandwich like structure in which hexagonal layer of molybdenum (Mo) lies between two hexagonal layers of sulfur (S) atom.

Like graphite each layers are held together with weak Vander Waals' forces.

It is stable up to 400°C.

It is differ from graphite because it is used in high vacuum unlike graphite (graphite is mixed with water or oil).

It adheres even more strongly to the metal or other surface.



Properties of Lubricants

Cloud Point - the temperature at which lubricating oil becomes cloudy in appearance.

Pour Point - the lowest temperature at which the lubricant oil become semi-solid and ceases to flow.

It indicates the suitability of lubricants used in cold condition.

Good lubricant should possess low pour point.

Flash point - the lowest temperature at which vapors of the material will ignite for a moment when an ignition source brought near to it.

The lubricating oil should have flash point reasonably above its working temperature.

Fire point - the lowest temperature at which the vapour of that fuel will continue to burn for at least 5 seconds when an ignition source brought near to it.

Fire point is around 10^{o}C higher than flash point.

Viscosity - the property of a fluid that determines its resistance to flow.

It is an indicator of flow ability of lubricating oil.

The lower viscosity greater will be the flow ability.

If temperature increases viscosity of the lubricating oil decreases and pressure increases viscosity of lubricating oil increases.

In short we can say that good lubricating oil is that whose viscosity does not change with temperature.

Viscosity Index - the variation of viscosity of a liquid with temperature is called viscosity index.

A relatively small change in viscosity with temperature is indicated by high viscosity index whereas, a low viscosity index shows, a relatively large change in viscosity with temperature.

Mechanism of Lubrication

Thick Film or Fluid Film or Hydrodynamic Lubrication

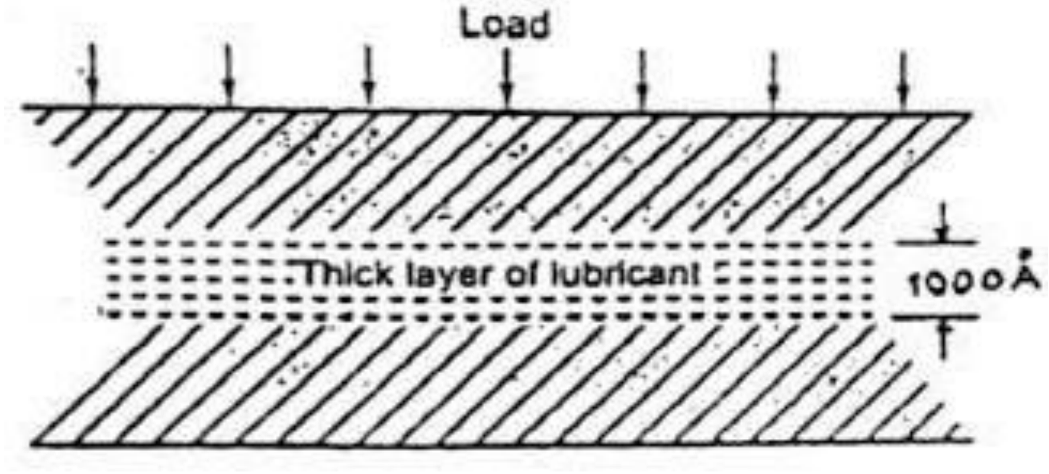
It is carried out with the help of liquid lubricants.

In this mechanism, two moving and sliding surfaces are separated by thick film of lubricant fluid of about 1000A°, consequently reduce wearing and tearing of metals.

Therefore it is known as thick film or fluid film lubrication or hydrodynamic (hydro meaning liquid and dynamic meaning relative motion) lubrication.

In this case fluid is formed by mixing of hydrocarbon oils and anti-oxidants with long chain polymer so as to maintain viscosity.

Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, scientific equipments.



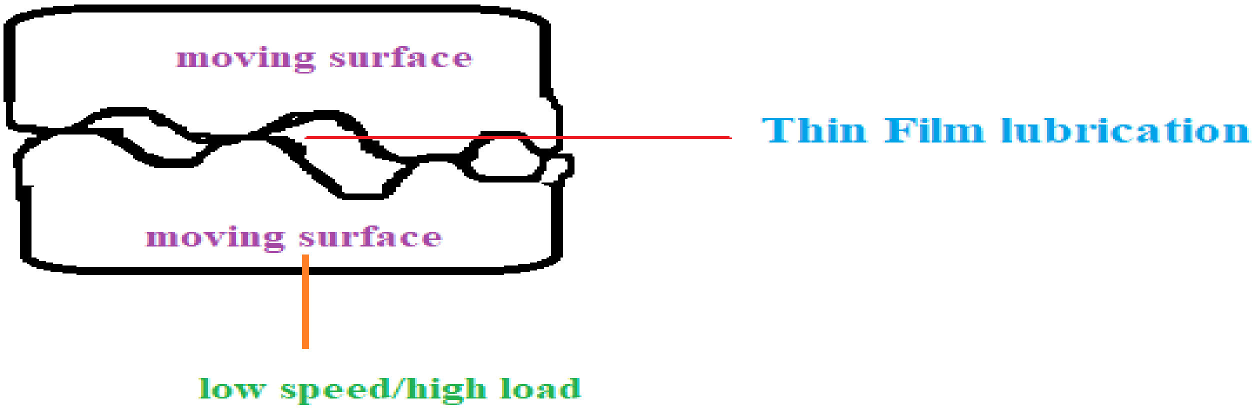
Thin Film or Boundary Lubrication

It is carried out with semi-solid (grease) and solid (graphite and molybdenum disulphide) lubricants.

Boundary lubrication is a condition in which the lubricant film becomes too thin to provide total separation.

In this type of lubrication a thin film of lubricant is adsorbed on the surface by weak Vander Waals forces.

Thin film lubrication is operating at relatively low speed and heavy loading (pressure).



Extreme Pressure (or Temperature) Lubrication

In this mechanism, moving or sliding surfaces are under high pressure and speed, therefore this is known as extreme pressure lubrication.

In such a case high temperatures generated due to friction, under these condition liquid lubricants are fail to stick and decompose or vaporize.

These problems are minimized by special additives are added to mineral oils.

These additives form durable films on metal surfaces which can withstand high loads and high temperatures.

Important additives are organic compound having group like chloride, sulphur, phosphorus etc.

They react with metallic surface to form metallic compound (possess high melting points and serve as good lubricants under extreme temperatures and pressures) like chlorides, sulphides, phosphate as more durable film.

Composite Materials

A material system consisting of a mixture of two or more macro-

constituents which are mutually insoluble, differing in form and

/ or composition and forming distinct phases.

The stiffness is increased without any brittleness.

Examples:

Wood – cellulose and lignin cementing materials.

Bone – strong protein callogen and hard material apatite).

Rain-proof cloth – cloth impregnated with water proof materials.

Insulating tape, reinforced concrete, etc.

Advantages over conventional materials

Higher specific strength.

Lower specific gravity.

Higher stiffness.

Better thermal shock resistance.

Cheaply and easily fabricable.

Lower electrical conductivity.

Lower thermal expansion.

Better corrosion and oxidation resistance.

Applications

In automobile industries, turbine engines, storage tanks, sport goods.

Marine applications – propellers, shafts, spars and other ship parts.

Aeronautical applications – components of rockets, aircrafts, missiles.

Communication antennae, electronic circuit board.

Safety equipments like ballistic protection.

Constituents of Composites

Matrix phase – the continuous body constituent and give bulk form.

It may be metal, ceramics or polymer.

Composites using these matrix – metal matrix composites (MMC)

- ceramic matrix composites (CMC)
- polymer matrix composites (PMC)

PMC – epoxy, polyamide, phenolics, silicons, polysulphones

Functions of matrix phase :

Binds the dispersed phase together.

Acts as a medium to transmit and distribute an applied load.

Protects the dispersed phase from chemical action and keep in proper position and orientation during the application of loads.

Prevents propagation of brittle cracks, due to its plasticity and softness.

Requirements of a good matrix phase:

It should be ductile and corrosion resistant and possess high bonding Strength between matrix and dispersed phase.

Dispersed Phase – the structural constituent which determines the internal structure of composite.

The important dispersed phases are :

Fibre – glass, carbon and aramid fibres.

Particulate – small pieces of hard solid material (metallic or non-metallic).

The distribution of particles in a matrix is usually random and resulting in isotropic composite.

Effect of particulates:

Increase in surface hardness.

Improving the performance at elevated temperature.

Abrasion elevated resistance is improved.

Shrinkage and friction is reduced.

Increase in the strength.

Thermal and electrical conductivities are modified.

Cost of composite is reduced.

Flakes – thin solids (eg. Mica flakes) having a two-dimensional geometry.

They impart equal strength in a plane compared to fibres.

Whiskers – thin strong filaments or fibres made by growing a crystal.

Eg. Graphite, SiC, sapphire, silicon nitride and aluminium oxide.

Role of interface: locus of chemical reaction, site for nucleation and

site for preferential adsorption.

Types of composites

Fibre-reinforced composites – involve three components (filament,

a polymer matrix and a bonding agent).

Glass fibre-reinforced polymer composites – employ glass fibres.

They posses lower densities, higher tensile strengths and impact

Resistance and excellent resistance to corrosion and chemicals.

Limitations –

They can be used upto limited temperature service conditions.

They cannot be used as structural components due to lack of stiffness.

Applications : Automobile parts, storage tanks, industrial floorings,

Plastic pipes, etc.

Carbon fibre-reinforced polymer composites – employed in situations requiring -

excellent resistance to corrosion, higher density and retention of

Desired properties even at elevated temperatures.

Applications : structural components of aircraft and helicopters,

Recreational equipments, sport materials, etc.

Aramid fibre-reinforced polymer composites –

Short fibre-reinforced composites – give effective reinforcement due to their high aspect ratio, high surface area, inherent toughness,

strength, heat stability and high wear strength.

Applications – automobile brakes and clutches.

Long fibre-reinforced composites – metal like ductile.

Applications – in commercial aircrafts, helicopter parts, etc.

Alumina and / or carbon fibre-reinforced metal composites – have improved specific strength, stiffness, abrasion resistance, creep resistance and dimensional stability.

Applications : components of engine in automobile and turbine.

Particulate composites – has very resistance to abrasion and corrosion, and finds application in valves, spray nozzles, pump parts, etc.

Layered composites – plywood, stainless steel cooling vessel, etc.

Lecture: 37

Fuels –Introduction, definition, classification, calorific value, Gross and Net, theoretical calculation.

INTRODUCTION

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives large amount of heat that can be used economically for domestic and industrial purposes. During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat. The calorific value of a fuel depends mainly on the two elements.

$$C + O_2 \longrightarrow CO_2 + 94 \text{ kcals.}$$
$$2H_2 + O_2 \longrightarrow 2H_2O + 68.5 \text{ kcals.}$$

So, carbon compounds have been used for many centuries as the source of heat and energy.
The main source of fuel is coal and petroleum. These are stored fuels available in earth's crust and are generally called fossil fuels because they were formed from the fossilised remains of plants and animals.

Classification of Fuels are classified as

1. **Primary fuels** which occur in nature as such, e.g. coal, petroleum and natural gas.
2. **Secondary fuels** which are **derived from the primary fuels**, e.g. coke, gasoline, coal gas, etc.

Both primary and secondary fuels may be further classified based upon their physical state as (i) solid fuels (ii) liquid fuels and (iii) gaseous fuels.

CALORIFIC VALUE

Calorific value of a fuel is "**the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely**."

Units of heat :

(1) **'Calorie'** is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).

(2) "**Kilocalorie**" is equal to 1,000 calories. It may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus**: 1 kcal = 1,000 cal**

(3) "**British Thermal unit" (B.T.U.)** is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.

1 B.T.U. = 252 cal = 0.252 kcal
1 kcal = 3.968 B.T.U.

Higher or gross calorific value (HCV)

Higher or gross calorific value: Usually, all fuels contain some hydrogen and when the calorific value of hydrogen-containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value". So, **gross or higher calorific value (HCV) is "the total amount of heat produced,**

when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"(i.e., 15°C or 60°F).

Lower or net calorific value (LCV)

Lower or net calorific value: In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along-with hot combustion gases. Hence, a lesser amount of heat is available. So, **net or lower calorific value (LCV) is "the net heat produced, when unit mass /volume of the fuel is burnt completely and the products are permitted to escape**".

Net calorific value = Gross calorific value - Latent heat of condensation of water vapour produced
= GCV - Mass of hydrogen per unit weight of the fuel burnt x 9 x Latent heat of condensation of water vapour

Dulong's formula for calorific value from the chemical composition of fuel is :

$$HCV = 1/100\ [8{,}080\ C + 34{,}500\ (H – O/8) + 2{,}240\ S]\ \text{kcal/kg}$$

where C, H, 0, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water, and

$$LCV = [\ HCV - 9H/100 \times 587]\ \text{kcal/kg} = [HCV - 0.09\ H \times 587]\ \text{kcal/kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of H_2O, and latent heat of steam is 587 kcal/kg.

Lecture :38

Solid fuel- Coal- classifications, Analysis- Proximate and ultimate

Solid Fuels

COAL

Coal is regarded as a fossil fuel produced from large accumulations of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years. Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions. It is chiefly composed of C, H, N, and 0, besides non-combustible inorganic matter.

Classification of Coal

Coals are classified on the basis of their rank. Rank is defined as the degree or extent of maturation and is therefore a qualitative measure of carbon contents. Peat, lignite and sub-bituminous coals are referred as low rank coals while bituminous coals and anthracites are classed as high rank. In European terminology, the lignite and sub-bituminous coals are called soft coals while bituminous coals and anthracite coals are termed as hard coals. In North American terminology, the coal series is written as

$$\textbf{Wood} \longrightarrow \textbf{peat} \longrightarrow \textbf{lignite} \longrightarrow \textbf{bituminous} \longrightarrow \textbf{anthracite.}$$

Analysis of Coal

In order to assess the quality of coal the following two types of analysis are made.

1. Proximate Analysis It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.

2. Ultimate Analysis It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. Since it is used
for the determination of elements present in the coal, it is also called elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

(1) Proximate analysis

(1) **Moisture**: About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).

.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

(2) **Volatile matter**: The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925°± 20°C. The crucible is taken out of the oven after 7 *minutes* of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Wt. of coal sample taken}} \times 100$$

(3) **Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700 ± 50°
C for 1/2 *hour*. The crucible is then taken out, cooled first in air, then in desiccator and weighed.
Heating, cooling and weighing is repeated, till a *constant weight* is obtained. The residue is reported as
ash on percentage-basis.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

(4) **Fixed carbon**: Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

Importance of proximate analysis*:*

Proximate analysis provides following valuable informations in assessing the *quality of coal:*

(1) Moisture: Moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".

(2) Volatile matter: A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal. Higher volatile content in coal is undesirable.

A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO_2 and N_2). Volatile matter content is of special significance in coal gas manufacture and in carbonization plants, particularly when by-product recovery is the main object. Thus, high-volatile matter containing coals do not cake well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

(3) Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes. trouble during firing by forming clinker), which block the inters paces of the grate. This in-turn causes obstruction to air supply; thereby the burning of coal becomes *irregular*. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. The presence of ash also causes early wear of furnace walls, burning of apparatus and *feeding* mechanism.

(4) Fixed carbon: Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of rued carbon is desirable.

(B) Ultimate analysis involves in the following determinations:

(1) Carbon and hydrogen: About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$$\begin{array}{llll} C + O_2 \longrightarrow & CO_2: & H_2 + \frac{1}{2} O_2 \longrightarrow & H_2O \\ 12 & 44 & 2 & 18 \end{array}$$

$$2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$CaCl_2 + 7\,H_2O \longrightarrow CaC1_2.7\,H_2O$$

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube x 12 x 100}}{\text{Weight of coal sample taken x 44}}$$

$$\text{and percentage of H} = \frac{\text{Increase in weight of } CaCl_2 \text{ tube x 2 x 100}}{\text{Weight of coal sample taken x 18}}$$

(2) Nitrogen: About 1 g of accurately weighed powdered 'coal is heated with concentrated H_2SO_4 along-with K_2S0_4(catalyst) in a long-necked flask(called *Kjeldahl's flask).* After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a *known volume of standard acid solution.* The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\underline{\text{Volume of acid used x Normality x 1.4}}$$

Percentage of N = . Weight of coal taken

(3) Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of S} = \frac{\text{Weight of BaS04 obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

(4) Ash determination is carried out as in proximate analysis.

(5) Oxygen: It is obtained by difference.
Percentage of O = 100 - Percentage of (C + H + S + N + ash)

Significance of ultimate analysis*:*

(1) Carbon and hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible consti1fent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.

(2) Nitrogen has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.

(3) Sulphur, although contributes to the heating value of coal, yet on combustion produces acids ($S0_2$ and $S0_3$), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal.
Presence of sulphur is highly undesirable in coal to be, used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.

(4) Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1. 7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Lecture: 39

Carbonization process-Metallurgical coke-Manufacture of coke by Otto Hoffmann process.

METALLURGICAL COKE

Good coke for metallurgy should possess the following *requisites:*

(**1) Purity**: It should have moisture, ash, sulphur and phosphorus contents as low as possible. A low percentage of moisture helps in keeping down the heating expenses. Excess of ash hinders the heating and also helps in slag formation, which is not desirable in fuels. According to Dr. Mott, 2% of excess coke is required for the removal of 1 % ash. Presence of S and P gives on burning, undesirable products like SO_2 P_20_3 and P_2O_5, which adversely affect the quality of the metal being produced. Moreover, presence of sulphur makes the coke brittle.

(2) Porosity : Coal should be porous, so that oxygen can easily come in contact with the carbon of coke, thereby helping in complete combustion at a high rate.

(3) Strength: The coke should be quite compact, hard, strong to withstand dropping abrasion as well as the pressure of the over-burden (ore + fuel + flux) in the furnaces. It would be useless to employ weak coke in blast furnaces, as the weight of ore, etc., would crush the coke to breeze and thus prevent the essential passage of gases up the furnace.

(4) Size: The size of metallurgical coke should be neither too big nor too small. In case the size is too big, the uniformity of heating is never maintained, but on the other hand, if the coke size is too small, choking will result.

(5) Cost: Coke should be cheap and easily available near the site of the metallurgical plant, so that the transportation cost is low.

(6) Combustibility: Coke should burn easily. The combustibility of coke depends upon the nature of the coal, carbonization temperature and reaction temperature. Cokes obtained from strongly coking coals are not as combustible as those derived from weakly caking and non-caking coals. At a given temperature, cokes obtained by high-temperature carbonization process are less combustible compared to those obtained by low-temperature carbonization. However, at high combustion temperatures (800° - 900°C), all cokes appears to be equally reactive. At about 1,000°C, it appears that the rate of combustion depends only on the rate of oxygen/air supply.

(7) Calorific value: The calorific value of coke should be high.

(8) Low ash, S and P contents to avoid the incorporation of these in the metal to be extracted.

(9) Reactivity to steam: Reactivity towards steam increases with the reaction temperature and varies inversely with carbonizing temperature at which the coke was produces. Moreover, coke derived from non-caking coals are more reactive to steam than those derived from taking coals.

Coal versus coke in metallurgical processes:

(1) Coal does not possess as much strength and porosity as coke.
(2) By coking, much of undesirable sulphur is removed.
(3) Coke burns with short flame, due to expulsion of much of its volatile matter during carbonization.

Because of these reasons, *"coke is preferred to coal for metallurgical purposes"*, particularly in blast furnaces. On the other hand, coal burns with a long flame, which is suitable only for reverberatory furnaces.

Coking quality: The coals which on heating, in the absence of air, becomes soft, plastic and {use together to large coherent masses, are called **caking coals**. Consequently, such coals are difficult to be oxidized. If the residue (i.e.: coke) obtained after heating is porous, hard, strong and usable for metallurgical purpose, the original coal, is known as coking coal

TYPES OF CARBONIZATION OF COAL

These are *two* types of carbonization of coal:

(1) **Low-temperature carbonization**: In this process, the heating of coal is carried our at 500 - 700°C. The yield of coke is about 75-80% and it contains about 5-15% volatile matter. *It is not mechanically strong, so it cannot be used as a metallurgical coke.* However, it burns easily giving practically a smokeless, hot and radiant fire. Hence, it is suitable for domestic purposes. The by-product gas produced (about 130-150 m3/tonne) by this process is richer in heating value (about 6,500-9,500 kcal/m3) and is, therefore, a more valuable gaseous fuel.

(2) **High-temperature carbonization** is carried out at 900 - 1,200°C with the object of producing coke of the right porosity, hardness, purity, strength, etc., so that it can be used in metallurgy. Nearly all the volatile matter of coal is driven off and the yield of coke is about 65-75%, containing only 1-3% volatile matter. The by-product gas produced is high in volume (about 300-390 m3/tonne), but its calorific value is low (about 5,400-6,000 kcal/m3).

MANUFACTURE OF METALLURGICAL COKE

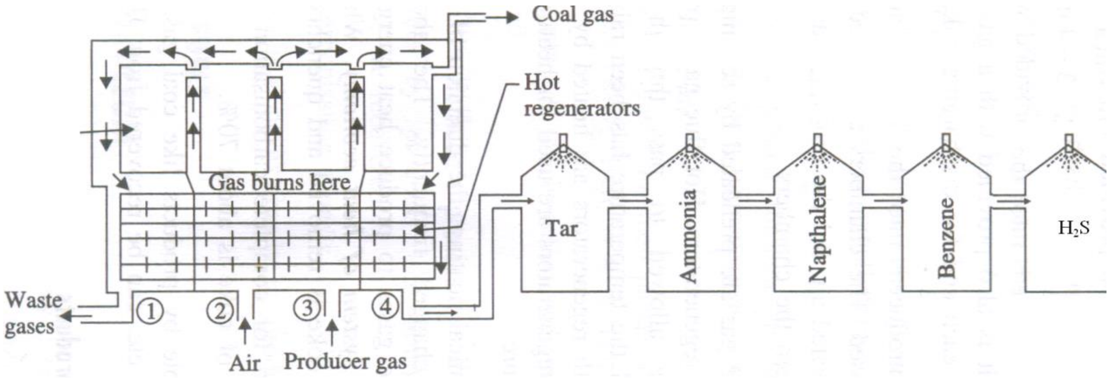
The coke, for *metallurgical purposes,* is obtained by either of the following processes:

Otto Hoffman's by-product oven:

In order to: (1) *increase the thermal efficiency* of the carbonization process, and (ii) *recover valuable by-product* (like coal gas, ammonia, benzol oil, tar, etc.), Otto Hoffman developed modern by-product coke oven which, unlike beehive oven, is *heated externally* by a portion of coal gas produced during the process itself or by producer gas or by blast furnace gas. Moreover, the heating is done on the basis of *"regenerative system of heat economy", i.e.,* utilizing the waste flue gases for heating the checker-work of bricks.

The by-product coke oven consists of number of narrow *silica chambers* (each about 10 to 12 m long, 3 to 4 m high and 0.40 to 0.45 m wide) erected side-by-side with *vertical flues* in-between them to form a sort of battery. Each chamber is provided with *a charging hole at the top, a gas off-take* and *a refractory-lined cast iron door* at each ends for discharging coke.

A charge consisting *of finely crushed coal* is introduced through the charging holes at the top of chambers, which are then closed tightly at both ends to prevent any access of air. The coke ovens are heated to 1,200°C by burning gaseous fuel (like producer gas) and usually employing a regenerative principle to achieve as economical heating as possible. The flue gases produced during combustion, before escaping to chimney, pass on their *sensible heat* to one of the two sets of checker brick-work, until this brick-work has been raised to a temperature of about 1,000°C. The flow of heating gases is then *reversed* and the inlet gases are



passed through the heated checker brick-work, which thus serves to preheat the inlet gases. The flue gases are then allowed to pass through the second set of checker bricks to heat it. This checker-work then serves to preheat the inlet gases. Thus, this cycle goes on. The heating is actually continued, till the evolution of volatile matter *ceases* completely. Carbonization of a charge of coal takes about between 11 to 18 hours. When carbonization is completed, a massive *ram* pushes the red hot coke into a truck. It is subsequently quenched by a water spray *('wet quenching')*. In place of wet quenching, "dry quenching" offers advantages, because the coke produced is more strong, dense, graphitized and non-reactive. In this method, the red hot coke is placed in a chamber and cooled by passing inert gases from boilers (like nitrogen). The heated inert gases are then circulated to boilers, where they generate steam. The coke produced by 'dry quenching' is cheaper, drier and contains lesser dust than 'wet-quenched' coke.

Recovery of by-products : The gas coming out from the oven is known as "coke oven gas" and is mainly composed of ammonia, H_2S, naphthalene, benzene, tar, moisture, etc.

(i)Recovery of tar : The gas is first passed through a tower in which liquor ammonia is sprayed. Here dust and tar get collected in a tank below, which is heated by steam coils to recover back ammonia sprayed. The ammonia is used again.

(ii) Recovery of ammonia: The gases from the chamber are then passed through a tower in which water is sprayed. Here ammonia goes into solution as NH_4OH.

(iii) Recovery of naphthalene: The gases are then passed through another tower in which water at very low temperature is sprayed. Here naphthalene gets condensed.

(iv) Recovery of benzene: The gases are then sprayed with petroleum, when benzene and its homologues are removed.

(v) Recovery of H_2S : The gases are then passed through a purifier, packed with moist Fe_2O_3. Here H_2S is retained.

$$Fe_2O_3 + 3\,H_2S \longrightarrow Fe_2O_3 + 3\,H_2O$$

After some time, when all Fe_2S_3 is changed into Fe_2O_3, the purifier is exposed to atmosphere, when Fe_2O_3 is regenerated,

$$Fe_2S_3 + 4\,O_2 \longrightarrow 2\,FeO + 3\,SO_2$$

$$4FeO + O_2 \longrightarrow 2\,Fe_2O_3$$

Lecture: 40

Liquid fuel-Petroleum processing and fractions-manufacture of synthetic petrol by Bergius process. Knocking in SI and CI engines. Octane and cetane number

Liquid Fuels

The important liquid fuels are petroleum, petroleum products, tar, alcohols. These are naturally found under the sea surface. Liquid fuels are also obtained synthetically from' hydrogenation of coat. Liquid fuels find extensive use in domestic and industrial fields.

Petroleum

Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, 0 and S. The average composition of crude oil is C =80 - 87 %, H =11-15%, S = 0.1 - *3.5%*, (N +O) =0.1- 0.5%.

a) Classification of petroleum

Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.

. i) Paraffinic-base type crude oil: It contains saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and little amount of naphthalenes and aromatics.

ii) Asphaltic-base type crude oil: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.

iii) Mixed-base type crude oil : It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.

Mining of Petroleum

Refining of Petroleum

The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally conveI1ed into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

Step -I: Separation of water (Cottrell's process)

The crude oil from the oil well is an extremely stable emulsion 0 f oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

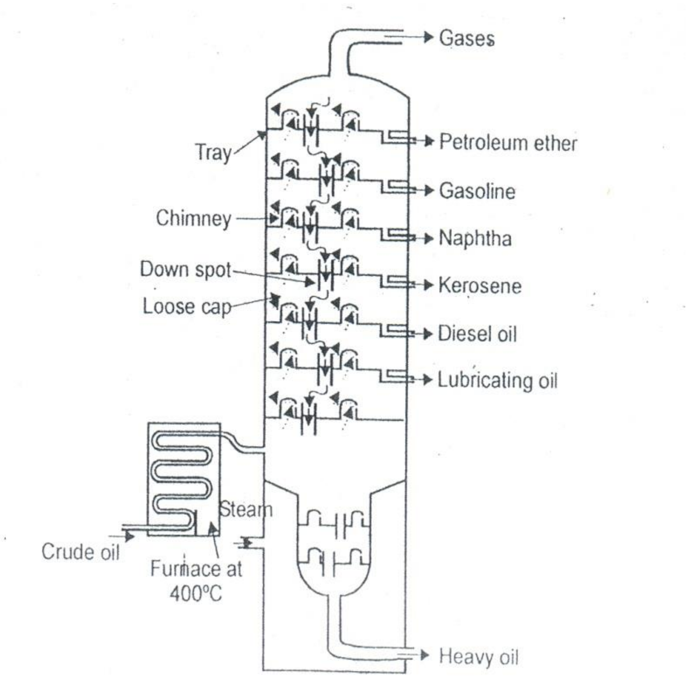
Step - II: Removal of harmful impurities

a) The presence of NaCI and MgCI in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.

b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

Step - III: Fractional distillation

The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)



Fractional distillation of Crude oil

When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.

Various fractions of crude oil and their compositions and uses

Sn.	**Name of the fractions**	**Boiling range (^{O}C)**	**Composition of Hydrocarbons .**	**Uses**
1.	Uncondensed gases	Below 30°C	C_1 to C_4	As domestic and industrial fuel under the name LPG
2.	Petroleum ether	30 70 °C	C_5 to C_7	As a solvent.
3.	Gasoline (or) petrol.	40 - 120 °C	C_5 to C_9	As motor fuel, solvent and in dry cleaning.
4.	Naphtha (or}solvent spirit .	120. - 180 °C	C_9 to C_{10}	As solvent and in dry cleaning.
5.	Kerosene oil.	180 - 250 °C	C_{10} to C_{I6}	As fuel for jet engines and an illuminant.

6.	Diesel oil (or) gas oil	250 320 °C	C_{10} to C_{I8}	As Diesel engine fuel.
7.	Heavy oil.	320 - 400 °C	C_{17} to C_{30}	Production of gasoline by cracking process.

Various fractions recovered from Heavy Oil

Sn.	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons .	Uses
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
3.	Paraffin wax	-	C_{20} to C_{28}	Used in candles, wax paper, boot polish, etc
4.	Grease	-	-	Used as lubricants.
5.	Asphalt or bitumen	Above 400°C	C_{30} and above	Used for making roads, water proof roofing, etc

Synthesis of Gasoline

The gasoline obtained from the fractional distillation of crude petroleum oil is not enough to meet the requirement of the present community due to vast increase of automobiles. Hence an alternate source need of finding out to manufacture synthetic petrol.

Synthetic petrol can be manufactured by the process of hydrogenation of coal. The preparation of liquid fuels from solid coal is called hydrogenation of coal.

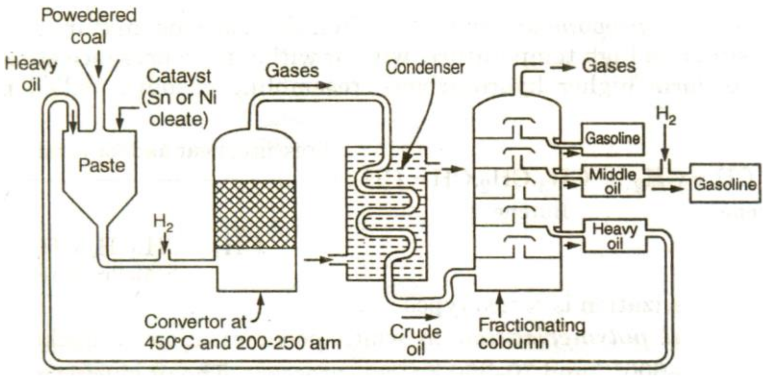
Gasoline is synthesised by the following methods.
1. Fischer- Tropsch process.
2. Bergius process.

Bergius process.

This method was developed by Bergius in Germany during the First World War. The low ash coal is *finely powdered* and made into a *paste* with *heavy oil* and then a *catalyst* (composed of tin or nickel oleate) is incorporated. The whole is heated with hydrogen at 450°C and under a pressure 200-250 atm for about 1.5 hours, during which hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons.

The issuing gases (from the reaction vessel) are led to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get: (i) gasoline, (ii) middle oil, and (iii) heavy oil. The latter is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yields more gasoline. The yields of gasoline in about 60% of the coal dust used.

Bergius process



Knocking

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine. Causes of knocking in S.I
Engine [Petrol engines]

In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking". Knocking property of the fuel reduces the efficiency of engine. So a good gasoline should resist knocking.

Chemical structure and knocking

The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.

Straight chain paraffins> Branched chain paraffins> Cycloparaffins > Olefins > Aromatics.

Improvement of antiknock characteristics

The octane number of fuel can be improved by

(i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.

(ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).

LEADED PETROL (ANTI-KNOCK AGENT)

The anti-knock properties of a gasoline can be improved by the addition of suitable additives. Tetraethyl lead (TEL) or $(C_2H_5)_4$ Pb is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

Disadvantages of using TEL

When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life. To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases.

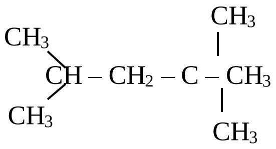
But this creates atmospheric pollution. So nowadays aromatic phosphates are used instead of TEL

(iii) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

OCTANE NUMBER (or) OCTANE RATING

Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100.

Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.'



Iso-octane (Octane number = 100)

$$CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – CH_2 - CH_3$$

n - heptane (Octane number = 0)

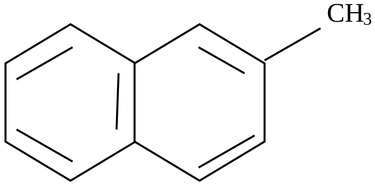
CETANE NUMBER (or) CETANE RATING

Cetane number is introduced to express the knocking characteristics of diesel. Cetane has a very short ignition lag and hence its cetane number is taken as 100. On the other hand 2-methyl naphthalene has a long ignition lag and hence its cetane number is taken as zero.

$CH_3 - (CH_2)_{14} - CH_3$

n-cetane (hexa decane)

cetane number = 100



2-methyl naphthalene (cetane number = 0)

Definition

Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl napthalene, which has the same ignition lag as the fuel under test".

The cetane number decreases in the following order.

n-alkanes > Cycloalkanes > alkenes >branched alkanes >aromatics

.

The cetane number of a diesel oil can be increased by adding additives called dopes.

Important dopes: *Ethyl nitrate, Iso-amyl nitrate.*

Lecture 41 Gaseous fuels - CNG, LPG, Water gas and a producer gas

COMPRESSED NATURAL GAS

Natural Gas is obtained from wells dug in the oil bearing regions. When natural gas occurs along with petroleum in oil wells, it is called as ‘wet gas’ and contains gaseous hydro carbons from C1 to C4. The wet gas is then suitably treated to remove propane, propene, butane and butane, which is used as LPG.When the natural gas is compressed, it is called Compressed Natural Gas (CNG). The primary component present in CNG is methane. It is mainly derived from natural gas.

The natural gas can either be stored in a tank of a vehicle as compressed natural gas (CNG) at 3,000 or 3,600 psi or as liquified natural gas (LNG) at typically 20-150 psi. A suitably designed natural gas engine may have a higher output compared with a petrol engine because the octane number of natural gas is higher than that of petrol.

Compressed natural gas vehicles require a greater amount of space for fuel storage than convention gasoline power vehicles. Since it is a compressed gas, rather than a liquid like gasoline, CNG takes up more space for each GGE (Gallon of Gas Equivalent). This makes it difficult to design smaller vehicles that look and operate like the vehicles that people are accustomed to.

CNG is often confused with liquefied natural gas (LNG). While both are stored forms of natural gas, the key difference is that CNG is in compressed form, while LNG is in liquefied form. CNG has a lower cost of production and storage compared to LNG as it does not require an expensive cooling process and cryogenic tanks. CNG requires a much larger volume to store the same mass of natural gas and the use of very high pressures (3000 to 4000 lbf/in², or 205 to 275 bar).

CNG has been made mandatory for all public transport in the Indian capital city of New Delhi.

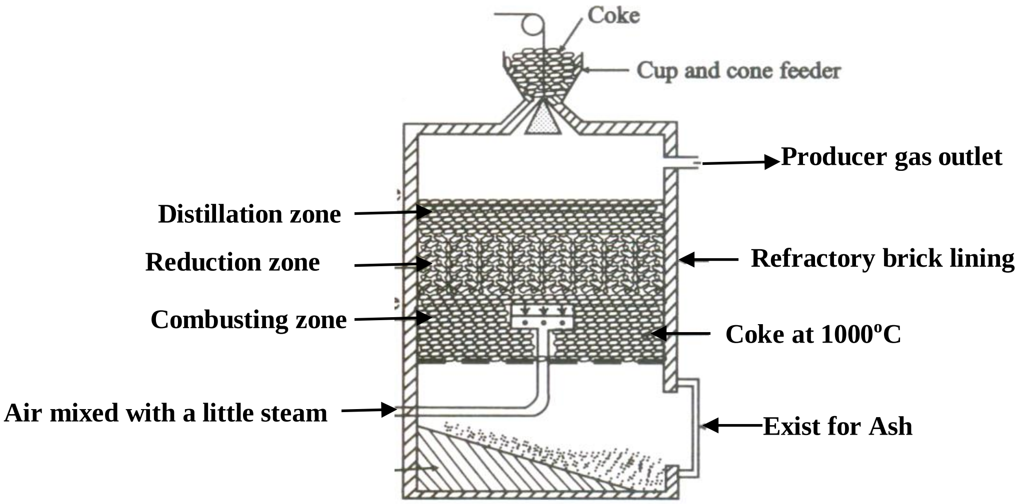
(CNG)

Properties
l. CNG is; the cheapest, cleanest and least environmentally impacting alternative fuel.
2. Vehicles powered by CNG produce less carbon monoxide and hydrocarbon (HC) emission.
3. It is less expensive than petrol and diesel.
4. The ignition temperature of CNG is about 550°C. CNG requires more air for ignition.

Producer Gas

Producer gas is a mixture of combustible gases, CO(30%) and H2(15%) with large amount of non combustible gases N2(56%) and CO2(3%). Its calorific value is 1300kcal/m3

It is prepared by passing air mixed with a little steam over a red hot coke maintained at about l100°C in a special reactor called gas producer. It consists of a steel vessel of (3 m in diameter, 4f m in height) inside lined with refractory bricks. It is provided with cup and cone feeder at the top and a side opening for produced gas exit. At the bottom, it has inlets for passing air and steam.



Manufacture of producer gas

Various Reactions

The reactions of producer gas production can be divided into four zones as follows.

(i) Ash Zone

This is the lowest zone consists mainly of ash. The incoming air and steam mixture is preheated in this zone.

(ii) Combustion or Oxidation Zone

This is the zone next to ash zone. Here the coke is oxidised to CO and CO2. Both the reactions are exothermic. Hence, the temperature of the bed reaches around 1,100°C.

$$C + O_2 \longrightarrow CO \qquad \text{exothermic } H + 95 \text{ k cal}$$
$$C + {}_{1/2}O_2 \longrightarrow CO_2 \qquad \text{exothermic } H + 29 \text{ k cal}$$

(iii) Reduction Zone

This is the middle zone. Here both CO_2 and steam combine with red hot coke and liberate H_2 and CO. The reduction reactions are endothermic and the temperature in the zone is about 1000°C. If no steam is supplied, the temperature of the producer raise and this may fuse the ash and refractory lining.

$$C + CO_2 \longrightarrow 2CO \qquad \text{endothermic} - 36 \text{ k cal}$$
$$C + H_2O \longrightarrow CO + H_2 \qquad \text{endothermic} - 29 \text{ k cal}$$

(iv) Distillation or Drying Zone

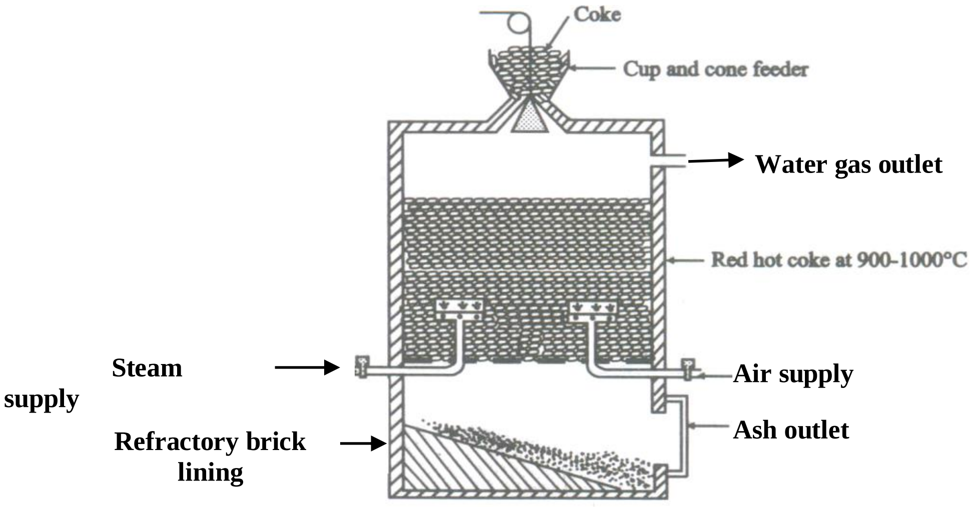
In this zone (400 - 800°C) the down coming coal is heated by the outgoing gases. The heat given by the gases and the heat coming out from the reduction zone will distill the fuel.

Uses

1. It is used as a reducing agent in metallurgical operations.
2. It is also used for heating muffle furnaces, open-hearth furnaces etc.

WATER GAS

It is a mixture of combustible gases, CO(41%) and H_2 (51%) with small amount of noncombustible gases, CO_2(4%) and N_2(4%). Its calorific value is about 2800 kcal/m3



Manufacture of water gas

Manufacture

The water gas producer consists of a tall steel vessel, lined inside with refractory bricks. It is provided with cup and cone feeder at the top and a side opening for water gas exit. At the bottom it is provided with two inlet pipes for passing air and steam

When steam and little air is passed alternatively over a red hot coke maintained at about 900 - l000°C in a reactor, water gas is produced.

Reactions

The reactions of water gas production involves the following two steps.

Step 1

In the first step, steam is passed through the red hot coke, where CO & H_2 gases are produced. The reaction is endothermic. Hence, the temperature of the coke bed falls.

$$C + H_2O \longrightarrow CO + H_2 \qquad \text{endothermic} – 29 \text{ k cal}$$

Step 2

In the second step, in order to raise the temperature of the coke bed to 1000 C , the steam supply is temporarily cut off and air is blown in. The reaction is exothermic.

$$C + O_2 \longrightarrow CO_2 \qquad \text{exothermic H} + 95 \text{ k cal}$$

$$2C + O_2 \longrightarrow 2CO \qquad \text{exothermic H} + 59 \text{ k cal}$$

Thus the steam – run and air blow are repeated alternatively to maintain proper temperature.

Uses.

It is used for the production of H_2 and in the synthesis of ammonia. It is also used as a source of and illuminating gas and fuel gas.

Lecture : 42

Catalytic converter – an exhaust emission control device that converts toxic gases and pollutants in exhaust gas from an internal combustion engine into less-toxic pollutants by catalyzing a redox reaction.

Each car on the road is a source of harmful carbon monoxide, hydrocarbons, and nitrogen oxides. With millions of cars being driven each day, this pollution and smog can create big problems. Exhaust emissions contribute to breathing illnesses, poor air quality, and environmental pollution.

Catalytic converter is located on the underside of your car, in the exhaust system between the exhaust manifold and muffler.

The part itself is either beaded or honeycomb shaped and coated in a metal catalyst, usually a combination of platinum, rhodium, and palladium.

Two catalytic events (chemical reactions) take place:

The reduction catalyst is the first of the two catalytic events to occur.

It uses the metal catalysts to reduce harmful nitrogen oxides by separating the molecules into nitrogen and oxygen.
The nitrogen is trapped within the converter, while the oxygen passes through.
The oxidation catalyst is the second catalytic event.
It reduces unburned hydrocarbons and carbon monoxide by burning (oxidizing) them over the metal catalyst.

Dark exhaust smoke and the smell of sulfur or rotten eggs from your exhaust are more noticeable signs of a bad catalytic converter.

Other car problems can also lead to a damaged catalytic converter:
Misfiring spark plugs or a failed oxygen sensor can cause a catalytic converter to overheat.
It can also be damaged by contaminants in the fuel; leaded fuel will destroy the catalyst metals, though it is rarely found in the United States.

Engine coolant can leak into the combustion system due to a faulty cylinder head gasket, eventually clogging the catalytic converter.
Fluid leaks of any kind should be fixed quickly; this will help prevent potential damage to the catalytic converter or other parts of your car.

Types

A 2-way (or "oxidation", sometimes called an "oxi-cat") catalytic converter has two simultaneous tasks: Oxidation of CO to CO_2 : $2\ CO + O_2 \rightarrow 2\ CO_2$
Oxidation of hydrocarbons (unburnt and partially burned fuel) to carbon dioxide and water : $C_xH_{2x+2} + [(3x+1)/2]\ O_2 \rightarrow x\ CO_2 + (x+1)\ H_2O$ (a combustion reaction)
This type of catalytic converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions.

They were also used on gasoline engines in American- and Canadian-market automobiles until 1981.
Because of their inability to control oxides of nitrogen, they were superseded by three-way converters.

Three-way : Three-way catalytic converters have the additional advantage of controlling the emission of nitric oxide (NO) and nitrogen dioxide (NO_2) species are precursors to acid rain and smog.

A three-way catalytic converter has three simultaneous tasks.

Reduction of oxides of nitrogen into N_2

$$C + 2NO_2 \longrightarrow CO_2 + 2NO$$

$$CO + NO \longrightarrow CO_2 + 1/2\,N_2$$

$$2CO + NO_2 \longrightarrow 2CO_2 + 1/2\,N_2$$

$$H_2 + NO \longrightarrow H_2O + 1/2\,N_2$$

Oxidation of carbon, hydrocarbons and CO to CO_2

$$C + O_2 \longrightarrow CO_2$$

$$CO + 1/2\,O_2 \longrightarrow CO_2$$

$$a\,C_xH_y + b\,O_2 \longrightarrow c\,CO_2 + d\,H_2O$$

These three reactions occur most efficiently when the catalytic converter receives exhaust from an engine running slightly above the stoichiometric point.

To maintain catalyst efficiency, the air : fuel ratio must stay close to stoichiometric and not remain rich or lean for too long.

Lecture :43 Combustion- Introduction and theoretical calculation of air.- Problems

Theoretical calculation of calorific value

1. Elements always combine in definite proportions to give. the products. For example 12 gm of carbon combines with 32 gm of oxygen to give 44 gm of CO_2

$$\begin{array}{ccc} C + O_2 & \longrightarrow & CO_2 \\ 12 \quad 32 & & 44 \end{array}$$

Similarly, 4gm of hydrogen combines with 32gm of oxygen to give 36gm of H_2O.

$$\begin{array}{ccc} 2\,H_{2(g)} + O_{(g)} & \longrightarrow & 2H_2O_{(g)} \\ 4 \quad 32 & & 36 \end{array}$$

2. At STP (273 K, l atm) one mole of all gases occupy a volume of 22.4litres. Hence at S.T.P. 22.4 liters of

CO_2 will have a weight of 44gm, its molecular weight.

3. Air contains 21 % of oxygen by volume and 23 % of oxygen by weight, Hence 1 m3 of oxygen will be supplied by

$$\frac{1 \times l00}{21} = 4.76m^3 \text{ of air}$$

Similarly 1 kg of oxygen will be supplied by $\frac{lxl00}{23}$ = 4.3 5 kg of air.

4. Molecular weight of air is $28.94mol^{-1.}$

5. Minimum oxygen required = (Theoretical O_2 required) - (O_2 present in fuels).

6. The mass of flue gas is calculated by balancing the carbon in the fuel and the carbon in the flue gas.

7. Minimum O_2 required is calculated on the basis of complete combustion of fuel. If as a result incomplete combustion or CO is formed then O_2 is calculated for the conversion of CO to CO_2.

8. If the fuel contains both O_2 and H_2, the amount of hydrogen and oxygen may be present in the form of as H_2O, which is a non-combustible substance. The remaining available hydrogen takes part in the combustion reaction.

$$2\ H_2(g) + O(g) \longrightarrow 2H_20$$

32 gm of oxygen combines with 4gm of hydrogen, Hence 1 part of hydrogen combines with 8 parts of oxygen.

$$\text{Available oxygen} = \text{Mass of hydrogen} - \left[\frac{\text{Mass of Hydrogen}}{8}\right]$$

Hence, theoretical amount of oxygen required for complete combustion of 1 kg of fuel is given by the equation,

$$\{32/12 \times C + 8[H - O/8] + S\}\ kg$$

C, Hand S are masses of carbon. Hydrogen and sulphur respectively per kg of the fuel. Since 1 kg of air-contains 23%of oxygen by weight, the amount of air required theoretically to burn 1 kg of fuel completely is given by equation.

$$100/23\ \{32/12 \times C + 8[H - O/8] + S\}\ Kg$$

According to Dulong's formula for the theoretical calculation of calorific value is, GCV (or)HCV = 1/100 [8080C + 34500 (H – O/8) + 2240S] Kcal/kg

Where C, H, O and S represent the % of the corresponding elements in the fuel. It is based on the assumption that the calorific value orc, Hand S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely.

However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio H:O as 1:8 by weight. So the surplus hydrogen available for combustion is' $H - \frac{0}{8}$.

NCV (or) LCV = [HCV – 9/100H x 587] kcal.kg

Theoretical calculation of minimum air requirement for combustion of a fuel

Combustion is the process of burning any combustible substance in the presence of oxygen, which liberates energy in the form of heat and light. For efficient combustion, it is essential that the fuel must be brought into intimate contact with sufficient quantity of air or oxygen.

The combustible substance usually present in fuels, which enter into the combustion, are mainly C, H, S and O. But N, CO_2 and ash are incombustible matters present in the fuel, .do not take any oxygen during combustion.

For the complete combustion of a given quantity of fuel can be calculated by considering the following point. Substances always combine in definite proportions, which are determined by the molecular weights of the substances.

i) Combustion of carbon

$$\underset{12}{C} + \underset{32}{O_2} \longrightarrow \underset{44}{CO_2} \text{ (by weight)}$$

12 parts by weight-of carbon requires 32 parts by weight of oxygen for complete combustion. 'C' parts by weight of carbon requires == 32 C /12 == 2.67 C

(H- 0/8) parts by weight of hydrogen requires = $\frac{(H - O/8) \times 32}{4}$

= 8 (H- O/8)

ii) Combustion of hydrogen

. When oxygen is present in the fuel, it always combines with hydrogen. The combined hydrogen does not take part in combustion reaction. Therefore, the quantity of combined hydrogen must be deduced from the total hydrogen in the fuel.

$$
\begin{array}{lcl}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
\;\;2 \quad\;\; 2 & & 36 \text{ (by weight)}
\end{array}
$$

4 parts by weight of H_2 requires 32 parts by weight O_2 (or) 2 parts by volume of H_2 require 1 part by volume of O_2

There fore 'H' parts by weight of hydrogen require $\frac{32 \text{x } H}{4}$ parts by weight of O_2.

iii) **Combustion of carbon monoxide**

$$
\begin{array}{llcl}
CO + \frac{1}{2} O & & \longrightarrow & CO_2 \\
28 & 16 & & \text{(by weight)} \\
1 & 0.5 & & \text{(by volume)}
\end{array}
$$

1 volume of CO requires 0.5 volume of oxygen.

iv) Combustion of sulphur

$$
\begin{array}{llcl}
S + & O_2 & \longrightarrow & SO_2 \\
32 & 32 & & \text{(by weight)} \\
1 & 1 & & \text{(by volume)}
\end{array}
$$

1 volume of 'S' requires 1 volume of oxygen.

v) Combustion of methane

$$
\begin{array}{llcl}
CH_4 + & 2O_2 & \longrightarrow & CO_2 + 2\, H_20 \\
16 & 64 & & \text{(by weight)} \\
1 & 2 & & \text{(by volume)}
\end{array}
$$

Lecture: 44

Ignition Temperature and explosive range.Flue gas analysis by Orsat method. Summarisation of topics in Unit V

Flue Gas Analysis (Orsat's method)

The mixture of gases such as CO_2, O_2, CO, etc., coming out from the combustion chamber is called flue gases. The analysis of a flue gas would give idea about the complete or incomplete combustion process. If the flue gases contain considerable amount of CO, it indicates that incomplete combustion and it contain a considerable amount of oxygen indicates, complete combustion. The analysis of flue gas is carried out by using Orsat's apparatus.

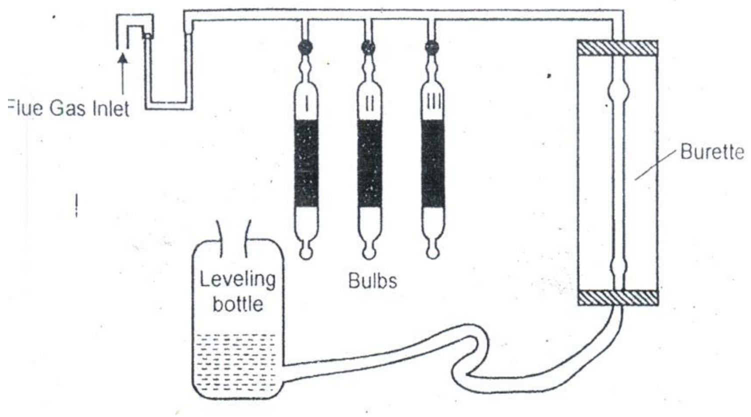
Description of Orsat's Apparatus

It consists of a horizontal tube, having 3 way stopcock. At one end of this tube, U-tube containing fused $CaCl_2$ is connected. The other end of this tube is connected with a graduated burette. The burette is surrounded by a water-jacket to keep the temperature of gas constant. The lower end of the burette is connected to a water reservoir by means of a rubber tube. The level of water in the burette can be raised or lowered by raising or lowering the reservoir. The horizontal tube is also connected with three different absorption bulbs I, II and III for absorbing CO_2, O_2 , CO.

Bulb- I : It contains 'potassium hydroxide' solution, and it absorbs only CO_2

Bulb - II: It contains 'alkaline pyrogallol' solution, and it absorbs only CO_2 and O_2

Bulb.:III : It contains 'ammoniacal cuprous chloride' solution, and it absorbs only CO_2, O_2 and CO.



Orsat's Apparatus

Working

The 3-way stopcock is opened to the atmosphere and the reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The 3-way stopcock is now connected to the flue gas supply, the flue gas is sucked into the burette, and the volume of flue gas is adjusted to 100 cc by raising and lowering the reservoir. Then the 3-way stop cock is closed.

a) Absorption of CO_2 .

The stopper of the bulb-1 containing KOH solution is opened and all the gas is passed into the bulb-1 by raising the level of water in the burette. The gas enters into the bulb-I, where CO_2 present in the flue gas is absorbed by KOH. The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of CO_2.The decrease in volume of the flue gas in the burette indicates the volume of CO_2 in 100 cc of the flue gas.

b) Absorption of O_2

Stopcock of bulb-I is closed and stopcock of bulb-II is opened. The gas is again sent into the absorption bulb-II, where O_2 present in the flue gas is absorbed by alkaline pyrogallol (925 g of pyrogallol + 200g of KOH in 500 ml distilled water). The decrease in volume of the flue gas in the burette indicates the volume of O_2.

c) Absorption of CO

.

Now stopcock of bulb-II is closed and stopcock of bulb-Ill is opened. The remaining gas is sent into the absorption bulb-III, where CO present in the flue gas is absorbed by ammoniacal cuprous chloride (100 g $CuCl_2$ + 125 mL liquor ammonia + 375 mL distilled water). The decrease in volume of the flue gas in the burette indicates the volume of CO. The remaining gas in the burette after the absorption of CO_2, O_2 and CO is taken as nitrogen.