

Water

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Introduction

- 1). Like air, water is one of the few basic materials which is of prime importance for the preservation of life on this earth.**
- 2). All are aware of the uses of water for drinking, cooking, cooking, bathing & for farming etc.**
- 3). But few know the importance of water as an engineering material.**
- 4). As an engineering material water is used for producing steam, in boilers to generate hydro-electric power, furnishing steam for engines, for construction of concrete structures for manufacturing purposes & as a solvent in chemical process.**

Sources of Water:

The Main Sources Of Water Are:

- 1). Rain water
- 2). River water
- 3). Spring or well water
- 4). Sea water

Types of impurities in water:

The impurities present in water are classified as:

1). Dissolved impurities: dissolved impurities may organic or inorganic.

Inorganic impurities: the carbonates, bicarbonates, sulphates, chlorides of calcium, magnesium, iron potassium and aluminium.

Organic impurities: Organic water products, amino acids, proteins, etc. Gases: O_2 , CO_2 , Oxides of nitrogen and sulphur, H_2S etc.

2). Suspended impurities: It is of two types:

- 1. Inorganic-** sand & clay;
- 2. Organic-** vegetable and animal matter.

3) Biological Impurities: Micro-organisms like pathogenic bacteria, fungi, algae, etc.

DISADVANTAGES OF HARDWATER/ CAUSES OF HARDNESS:

The following are the disadvantages when hard water is used for various purpose:

(i) DOMESTIC USE:

(a) Washing and Bathing: Hard water does not form lather easily with soap, so soap is wasted

(b) Drinking: Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys

(c) Cooking: The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.

(ii) **INDUSTRIAL USE:**

(a) Textile Industry: Hard water causes wastage of soap. Precipitates of calcium and magnesium soap adhere to the fabrics and cause problem such difference in color shades, dull shades, patches, etc.

(b) Paper Industry: Calcium and Magnesium salts in water may affect the quality of paper.

(c) Sugar Industry: Water containing sulphates, carbonates, nitrates affects the crystallisation of sugar.

(d) Pharmaceutical Industry: Hard water may form some undesirable products while preparation of pharmaceutical products.

(iii) STEAM GENERATION IN BOILERS: For steam generation, boilers are employed. If hard water is used in boilers, It may lead to the following troubles-

- (a) Boiler Corrosion
- (b) Scale and Sludge formation.
- (c) Priming and Foaming
- (d) Caustic embrittlement Pharmaceutical industry

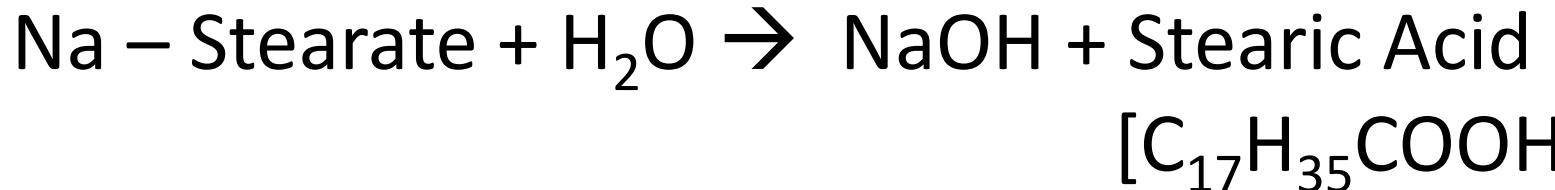
HARDNESS OF WATER (OR) HARDWATER AND SOFT WATER:

Hard Water: The water which does not produce lather (or) very little lather with soap is called Hard Water.

Soft Water: Soft water readily produces a lot of lather when mixed with little soap.

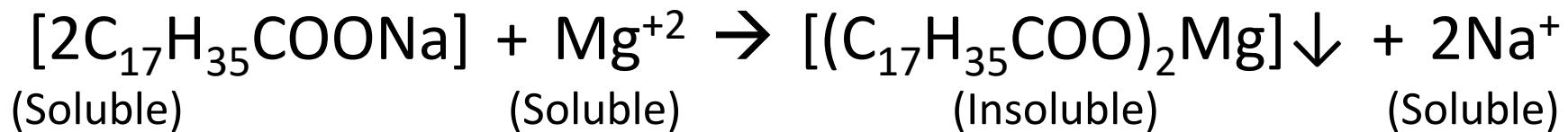
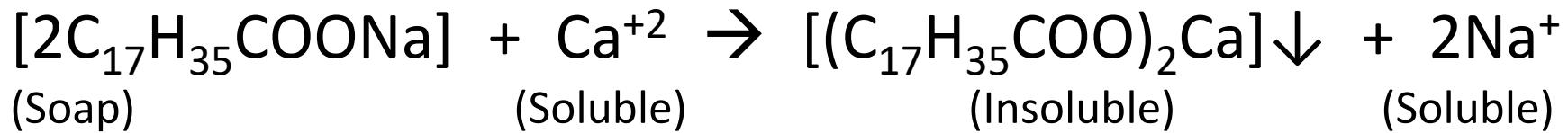
The Hardness of water is caused by the presence of dissolved salts such as Bicarbonates, Sulphates, Chlorides and Nitrates of bivalent metal ions like Ca^{+2} & Mg^{+2} .

Soap is sodium/ potassium salt of higher fatty acids like stearic, oleic and palmetic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.



Stearic Acid + Na-Stearate \rightarrow Formation of lather.

When soap comes in contact with HARD WATER, Sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.

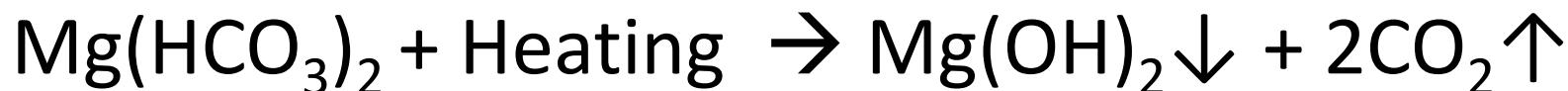
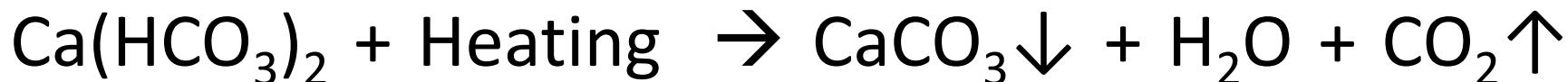


TYPES OF HARDNESS

The hardness of water is of two types-

- (1) Temporary hardness (or) Carbonate hardness
- (2) Permanent hardness (or) Non-Carbonate hardness

(1) Temporary Hardness: Temporary hardness is caused by two dissolved bicarbonate salts $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. The hardness is called “Temporary Hardness” because it can be removed easily by means of **boiling**.



(2) **Permanent Hardness:** Permanent hardness of water is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are CaCl_2 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$, MgCl_2 , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$. These hardness cannot be removed easily by boiling. Hence it is called “Permanent Hardness”. Only **chemical treatment** can remove this hardness.

Total Hardness Of Water = Temporary Hardness + Permanent Hardness

DEGREE OF HARDNESS:

- The Concentration of hardness as well as non-hardness constituting ions are, usually expressed in the term of “**Equivalent amount of CaCO_3** ”
- Since this mode permits the multiplication and division concentration, when required.
- The choice of CaCO_3 in particular is due to its molecular weight (m.wt.) is “100” (Equivalent wt. = 50), and
- Moreover, it is insoluble salt that can be precipitated in water treatment.

Therefore, 100 parts by weight of CaCO_3 hardness must be equivalent to-

- 162 parts by weight of $\text{Ca}(\text{HCO}_3)_2$ hardness
- 146 parts by weight of $\text{Mg}(\text{HCO}_3)_2$ hardness
- 136 parts by weight of CaSO_4 hardness
- 111 parts by weight of CaCl_2 hardness
- 164 parts by weight of $\text{Ca}(\text{NO}_3)_2$ hardness
- 120 parts by weight of MgSO_4 hardness
- 95 parts by weight of MgCl_2 hardness
- 148 parts by weight of $\text{Mg}(\text{NO}_3)_2$ hardness

Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
$\text{Ca}(\text{HCO}_3)_2$	162	81	100/ 162
$\text{Mg}(\text{HCO}_3)_2$	142	73	100/ 142
CaSO_4	136	68	100/ 136
FeCl_2	127	63.5	100/ 127
CaCl_2	111	55.5	100/ 111
MgSO_4	120	60	100/ 120
MgCl_2	95	47.5	100/ 95
CaCO_3	100	50	100/ 100
MgCO_3	84	42	100/ 84
CO_2	44	22	100/ 44
$\text{Ca}(\text{NO}_3)_2$	164	82	100/164
$\text{Mg}(\text{NO}_3)_2$	148	74	100/ 148
HCO_3^-	61	61	100/ 122
OH^-	17	17	100/ 34
CO_3^{2-}	60	30	100/ 60

Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
NaAlO ₂	82	82	100/ 164
Al ₂ (SO ₄) ₃	342	57	100/ 114
FeSO ₄ .7H ₂ O	278	139	100/ 278
H ⁺	1	1	100/ 2
HCl	36.5	36.5	100/ 73

The method of calculating degree of hardness is given by the following formula

- **Hardness causing salt in terms of equivalent of CaCO₃= (Amount (Mass) of the hardness causing salt x 100)/ Molecular weight of hardness causing salt**

UNITS OF HARDNESS:

The 5 different units in which the hardness of water is expressed as given below-

(1) **Parts per million (PPM)**: PPM is the number of parts of CaCO_3 equivalent hardness per 10^6 parts of water.

i.e., 1 PPM = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

(2) Milli grams Per Litre (mg/litre): mg/L is the number of milligrams of CaCO_3 equivalent hardness present per litre of water.

i.e., 1 mg/L = 1 mg of CaCO_3 equivalent hardness in 1L of water.

But 1 L water weighs = 1 kg of water

$$1 \text{ kg} = 1000 \text{ gms} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg}$$

$\therefore 1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water}$
 $= 1 \text{ part of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of water}$

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

(3) **Degree Of Clarke ($^{\circ}\text{Cl}$)**: It is number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water.

(or) It is defined as the number of parts of CaCO_3 equivalent hardness per 70,000 parts of water.

$\therefore 1 \ ^{\circ}\text{Cl} = 1 \text{ grain of } \text{CaCO}_3 \text{ eq. hardness per gallon of water.}$

(or) $1 \ ^{\circ}\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ eq. hardness per 70,000 parts of water}$

$\therefore 1 \text{ ppm} = 0.07 \ ^{\circ}\text{Cl}$

(4) Degree Of French ($^{\circ}\text{Fr}$): It is the number of parts of CaCO_3 equivalent hardness per 10^5 parts of water.

$1 \ ^{\circ}\text{Fr} = 1$ part of CaCO_3 equivalent hardness per 10^5 parts of water

$$\therefore 0.1 \ ^{\circ}\text{Fr} = 1 \text{ ppm}$$

Note: The hardness of water can be converted into all the four units by making use of the following interconversion formula-

$$1 \text{ ppm} = 1\text{mg/L} = 0.07^{\circ}\text{Cl} = 0.1^{\circ}\text{Fr}$$

$$1^{\circ}\text{Cl} = 1.43^{\circ}\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L}$$

(5) Milliequivalent per Litre (meq/L): It is the number of milliequivalent of hardness present per litre of water.

1 meq/L = 1 meq of CaCO_3 per litre of water
= $10^{-3} \times 50$ g of CaCO_3 eq. of hardness per litre of water
= 50 mg of CaCO_3 eq. of hardness per litre of water
= 50 mg/L of CaCO_3 eq.
= 50 ppm
 $\therefore 1 \text{ meq/L} = 50 \text{ ppm}$

PROBLEM:

(1) A sample of water gives an analysis 13.6 mg/L of CaSO_4 , 7.3 mg/L of $\text{Mg}(\text{HCO}_3)_2$. Calculate the total hardness and permanent hardness.

Sol:

Salt	Quantity (mg/L)	M. Wt.	Multiplication Factor	Eq. of CaCO_3	Hardness
CaSO_4	13.6	136	100/ 136	$13.6 \times (100/ 136) = 10$	P
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	100/ 146	$7.3 \times (100/ 146) = 5$	T

Total hardness= Temporary hardness + Permanent

$$\text{Hardness} = 5 + 10 = 15 \text{ mg/L} = 15 \text{ ppm}$$

$$\text{Permanent hardness} = 10 \text{ ppm}$$

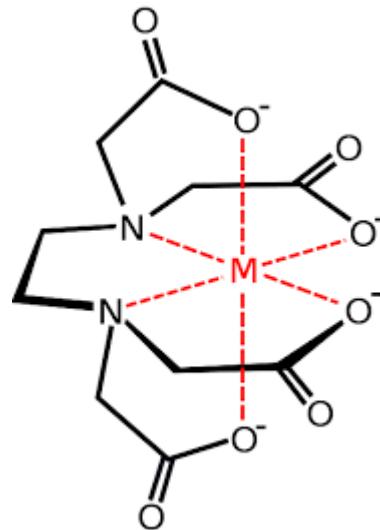
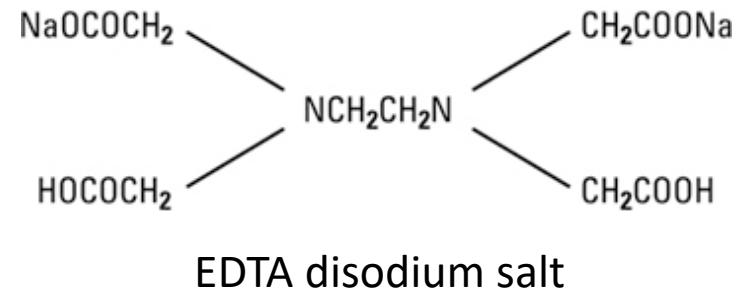
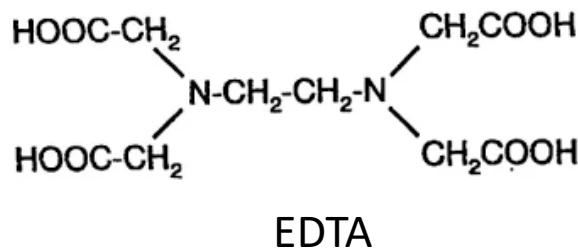
$$\text{Temporary hardness} = 5 \text{ ppm}$$

DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD:-

1. This is a Complexometric titration method where Ethylenediamine tetraacetic acid (EDTA) is used.
2. EDTA forms complexes with different metal ions at different pH.
3. Calcium & Magnesium ions form complexes with EDTA at pH 9- 10.

To maintain the pH 9- 10 NH_4Cl , NH_4OH buffer solution is used.

4. The disodium salt of EDTA is used for complexation.
5. An alcoholic solution of Eriochrome Black-T (EBT) is used as an indicator.



Metal-EDTA complex

BASIC PRINCIPLE:

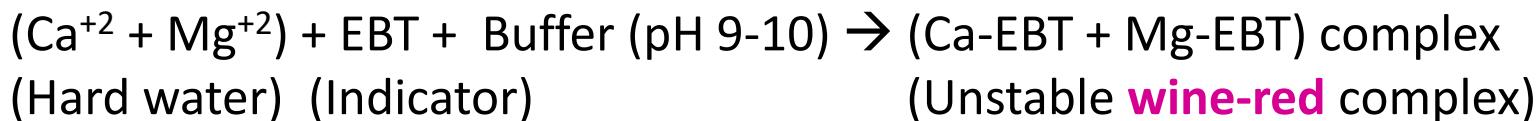
When hard water comes in contact with EDTA, at pH 9- 10, the Ca^{+2} & Mg^{+2} forms stable, colourless complex with EDTA.



Working:-

To the hard water sample, the alcoholic blue coloured EBT indicator is added along with the $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ buffer (pH 9-10) solution.

EBT forms an unstable wine-red complex with Ca^{+2} & Mg^{+2} .



This wine-red coloured [Ca-EBT & Mg-EBT] complex is then titrated against EDTA; when EDTA replaces EBT from Ca-EBT & Mg-EBT complex and forms stable colourless [Ca-EDTA] & [Mg-EDTA] complex releasing the blue coloured indicator EBT into H_2O .



Hence the colour change at the end point is wine-red to blue colour.

The titration is carried out in the following steps

1. **PREPARATION OF STANDARD HARD WATER:**

Dissolve 1gm of pure, dry CaCO_3 in minimum quantity of dilute HCl and evaporate the solution to dryness on a water-bath. Dissolve the residue in distilled water to make 1 litre in a standard flask and shake well.

Molarity of standard hard water solution =

$$\frac{\text{wt. of } \text{CaCO}_3}{\text{M.wt. of } \text{CaCO}_3} = \frac{1}{100} = 0.01\text{M}$$

(2) PREPARATION OF EDTA SOLUTION:

Dissolve 4 gms of pure EDTA-disodium salt crystals along with 0.1 gm of $MgCl_2$ in one litre of distilled water.

(3) PREPARATION OF INDICATOR (EBT):

Dissolve 0.5 gms of Erichrome Black-T in 100 ml of alcohol.

(4) PREPARATION OF BUFFER SOLUTION:

Add 67.5 gm of NH_4Cl to 570 ml of concentrated ammonia solution and dilute with distilled water to one litre

(5) STANDARDISATION OF EDTA SOLUTION:

Pipette out 20 ml of standard hard water solution into a conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured complex with EDTA taken in a burette after rinsing it with EDTA solution till the wine red colour changes to clear blue.

Note the burette reading and let the volume be “x”ml. Repeat the titration to get concurrent values.

(6) TITRATION OF SAMPLE HARD WATER (Total) :

Pipette out 20 ml of the water sample into a 250ml conical flask, add 2- 3 ml of buffer (pH 9-10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured solution with EDTA taken in the burette till a clear blue coloured end point is obtained.

Let the volume of EDTA be “y” ml. Repeat the titration to get concurrent values

(7) TITRATION FOR PERMANENT HARDNESS:

Pipette out 100 ml of hard water sample in a beaker and boil till the volume reduces to 20 ml. All the bicarbonates of Ca^{++} and Mg^{++} decomposes to CaCO_3 and Mg(OH)_2 . Cool the solution and filter the water into a flask, wash the beaker and precipitate with distilled water and add the washing to conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator and titrate with EDTA solution taken in the burette till a clear blue colour end point is obtained.

Note the burette reading. Let the volume be “z” ml.

CALCULATIONS:

Molarity of standard hard water solution = 0.01 M.

(Calculated in the preparation of standard hard water)

Molarity of EDTA solution (M₂): $\frac{V_1 M_1}{n_1} = \frac{V_2 M_2}{n_2}$

n₁ & n₂ are no. of moles of Ca⁺² and EDTA = 1 each
i.e., n₁=1, n₂=1

V₁ = volume of standard hard water

M₁= Molarity of standard hard water

V₂= volume of EDTA

M₂= molarity of EDTA

$$M_2 = \frac{V_1 M_1}{V_2} = \frac{20 \times 0.01}{x \text{ (titre value)}}$$

Molarity of sample hard water (M_3):

$$\frac{V_2 M_2}{n_2} = \frac{V_3 M_3}{n_3}$$

V_2 = volume of EDTA

M_2 = molarity of EDTA

V_3 = volume of sample hard water

M_3 = Molarity of sample hard water

$$M_3 = \frac{V_2 M_2}{V_3} = \frac{M_2 \times y \text{ (titre value)}}{20} = \frac{y \times 0.01}{x}$$

Total Hardness Of Water

= $M_3 \times 100$ gms/litre

= $M_3 \times 100 \times 1000$ mg/L or ppm = $(y/x) \times 1000$ ppm

Permanent Hardness Of Water:

$$\frac{V_2 M_2}{n_2} = \frac{V_4 M_4}{n_4} \quad M_4 = \frac{V_2 M_2}{V_4} = \frac{z M_2}{20} = z \times 0.01$$

V_2 = volume of EDTA

M_2 = molarity of EDTA

V_4 = volume of water sample containing permanent hardness (100 ml)

M_4 = Molarity of water sample containing permanent hardness

Permanent Hardness Of The Water Sample

$$= M_4 \times 100 \times 1000 \text{ ppm}$$

$$= z / x \times 1000 \text{ ppm}$$

Temporary Hardness Of The Water Sample

$$= (\text{Total Hardness} - \text{Permanent Hardness})$$

$$= (M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000) \text{ ppm}$$

$$= (M_3 - M_4) \times 100 \times 1000 \text{ ppm}$$

$$= \underline{(y-z)} \times 1000 \text{ ppm}$$

x

Problem:

1 gm of CaCO_3 was dissolved in HCl and the solution was made upto 1 Lit with distilled water. 50 ml of the above solution required 30 ml of EDTA solution for titration. 50 ml of hard water sample required 40 ml of the same solution of EDTA for titration. 50 ml of the hard water after boiling, filtering, etc. required 30 ml of the same EDTA solution for titration. Calculate the temporary hardness of the water.

Soln:

Molarity of CaCO_3 (SHW) solution (M_1) = $1/100 = 0.01 \text{ M}$

Molarity of EDTA solution (M_2) = $V_1 M_1 / V_2$

V_1 = volume of CaCO_3 solution = 50 ml

M_1 = Molarity of CaCO_3 solution = 0.01 M

V_2 = volume of EDTA = 30 ml

$M_2 = 50 \times 0.01 / 30 = 0.016 \text{ M}$

Molarity of Hard Water Sample Sol. (M_3) = $V_2 M_2 / V_3$

V_2 = volume of EDTA = 40 ml

M_2 = Molarity of EDTA = 0.016 M

V_3 = volume of hard water sample = 50 ml

$M_3 = 40 \times 0.016 / 50 = 0.0128 \text{ M}$

Total Hardness of water

$$= 0.0128 \times 100 \times 1000$$

$$= 1280 \text{ ppm}$$

Permanent hardness of water: $\frac{V_4 M_4}{n_4} = \frac{V_2 M_2}{n_2}$

$$M_4 = V_2 M_2 / V_4$$

$$n_4 = 1; V_2 = \text{volume of EDTA} = 30 \text{ ml}$$

$$n_2 = 1; M_2 = \text{molarity of EDTA} = 0.016$$

V_4 = volume of permanent hardness containing water = 50

$$M_4 = 30 \times 0.016 / 50 = 0.0096 \text{ M}$$

Permanent hardness of water

$$= 0.0096 \times 100 \times 1000 = 960 \text{ ppm}$$

Temporary hardness

$$= \text{Total hardness} - \text{Permanent hardness}$$

$$= 1280 - 960 = 320 \text{ ppm}$$

20ml of SHW containing 1.2gm CaCO₃ per litre required 35ml of EDTA. 50ml of hard water sample required 30ml of same EDTA. 100ml of hard water sample after boiling, cooling required 25ml of same EDTA. Calculate the hardness.

Solution: Strength of SHW= 1.2gm/ lit = 1200mg/ 1000ml = **1.2mg/ ml**

Volume of SHW= 20ml = $20 \times 1.2 = 24\text{mg of CaCO}_3$ eq hardness

Now, 20ml SHW = 35ml EDTA; i.e. 35ml EDTA = 24mg of CaCO₃ eq hardness

So, **1 ml EDTA= 24/35 mg CaCO₃ hardness**

50ml WS = 30ml EDTA = $30 \times 24/35 \text{ mg CaCO}_3$ hardness= 20.57mg

Thus, 1 lit WS= 1000ml = $1000 \times 20.57/50 = 411.4\text{mg}$

So, **Total hardness = 411.40ppm**

100ml of boiled sample= 25ml EDTA = $25 \times 24/35 = 17.14\text{mg CaCO}_3$ hardness

Thus, 1 lit BWS= 1000ml = $1000 \times 17.14/100 = 171.4\text{mg}$

So, **Permanent hardness = 171.40ppm**

Temporary Hardness = Total hardness – Permanent hardness

411.40 – 171.40 = 240.00ppm

BOILER TROUBLES:

Water finds a great use in various industries for generation of steam in boilers. When water is continuously evaporated to generate steam, the concentration of the dissolved salts increase progressively causing bad effects for steam boilers. The following are the boiler troubles that arise:

- (1) Priming and foaming
- (2) Caustic embrittlement
- (3) Boiler corrosion
- (4) Scale and sludge formation

PRIMING & FOAMING:

Priming: When a boiler is steaming rapidly, some particles of the liquid water are carried along with the steam. This process of “WET STEAM” formation is called ‘PRIMING’. Priming is caused by:

- (1) Presence of large amount of dissolved solids
- (2) High steam velocities
- (3) Sudden boiling
- (4) Improper boiler design
- (5) Sudden increase in steam production rate

It can be avoided by: (Preventions)

- (1) Maintaining low water level
- (2) Using softened water
- (3) Fitting mechanical steam purifiers
- (4) Using a well-designed boiler
- (5) Avoiding rapid change in steam rate
- (6) Blow-down of the boiler

Figure 3.12

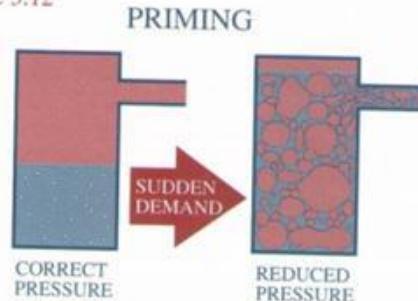
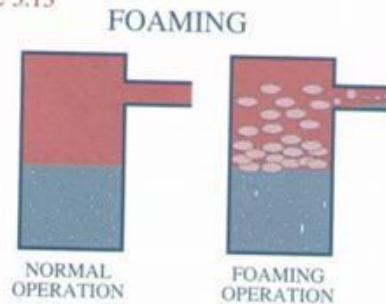


Figure 3.13



FOAMING:

Foaming is phenomenon of formation of foam or bubbles on the surface of water inside the boiler with the result that the foam may pass along with the steam.

Causes: The presence of large quantity of suspended impurities and oils lowers the surface tension producing foam.

Preventions: Foaming can be avoided by-

- (1) Adding anti foaming chemicals like castor oil
- (2) Removing oil from boiler water by adding compounds like “ NaAlO_2 ”
- (3) Blow down of the boiler can prevent the foaming

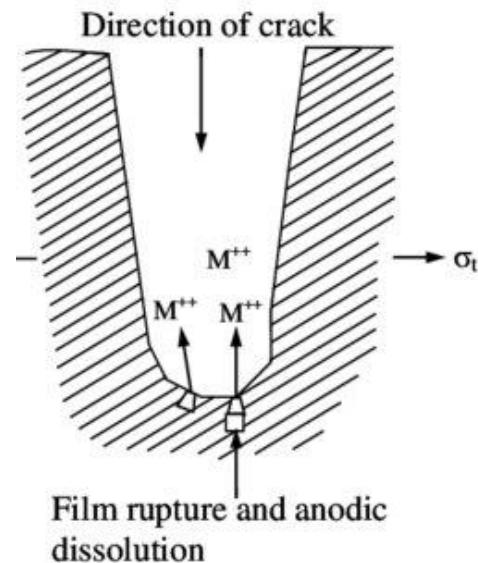
Disadvantages Of Priming & Foaming:

Priming & Foaming may cause the following boiler troubles:-

- (1) The actual height of the water in boiler is not judged
- (2) Wastage of heat with the result that it becomes difficult to keep up steam pressure and efficiency of the boiler is lowered

CAUSTIC EMBRITTLEMENT:

Caustic embrittlement is a term used for the appearance of cracks inside the boiler particularly at those places which are under stress such as rivetted joints due to the high concentration of alkali leading to the failure of the boiler. The cracks have appearance of brittle fracture. Hence, the failure is called “Caustic Embrittlement”



Reasons for the formation of Caustic Embrittlement:

The boiler feed water containing carbonates and bicarbonates of alkali metals, sodium hydroxide (NaOH) and a small quantity of silica or sodium silicate; it is purified by Lime-Soda Process.

During the softening process by lime soda process, free Na_2CO_3 is usually present in small portion in the soft water which decomposes to give NaOH and CO_2 at high pressure of the boilers.



The precipitation of NaOH makes the boiler water "**Caustic**"

The NaOH containing water flows into the small pits and minute haircracks present on the inner walls of the boiler.

As the water evaporates, the concentration of caustic soda (NaOH) increases progressively, creating a "**Concentration Cell**"

Thus, dissolving the iron of the boiler as Sodium Ferrate.



The cracking of the boiler occurs particularly at stressed parts like bends, joints, rivets, etc. causing the failure of the boiler.

The **iron** at plane surfaces **surrounded by dilute NaOH** becomes **Cathodic**; while the **Iron** at bends, rivets and joints is surrounded by **highly concentrated NaOH** becomes **Anodic** which consequently decayed or corroded

(Anodic site) Conc NaOH || dil NaOH (Cathodic site)
Iron at Joints & bends Iron at Plane surface

Prevention Of Caustic Embrittlement:

- (1) By adding Na_2SO_4 , tannin, etc. to the boiler water which blocks hair cracks. There by preventing infiltration of caustic soda solution
- (2) By using sodium phosphate as the softening agent instead of sodium carbonate

DISADVANTAGES OF CAUSTIC EMBRITTLLEMENT:

The cracking or weakening of the boiler metal causes failure of the boiler

(3) **BOILER CORROSION:** The decay of boiler material by chemical/ electro- chemical attack by its environment is called “Boiler Corrosion”.

Reasons for boiler corrosion are: (a) Dissolved oxygen (b) Dissolved CO_2 (c) Acids from dissolved salts.

(a) Dissolved Oxygen: Water usually contains about 8 mg/L of dissolved oxygen at room temperature. Dissolved O₂ at high temperature attacks boiler material.



Removal of dissolved O₂:

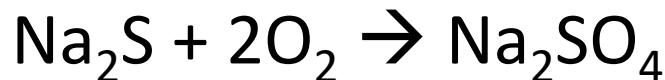
By adding calculated quantity of sodium sulphate (or) hydrazine (or) sodium sulphide



Sodium Sulphite



Hydrazine



(b) Dissolved CO₂:

Dissolved CO₂ has slow corrosive effect on the materials of boiler plate. Source of CO₂ into water is the boiler feed water which contains bicarbonates. Under the high temperature and pressure, maintained in the boiler the bicarbonates decompose to produce CO₂.

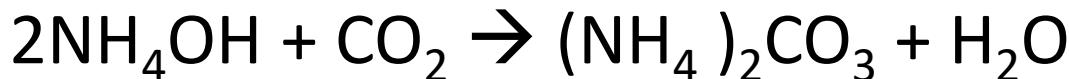


The disadvantage of the CO₂ is slow corrosive effect on boiler plates by producing **carbonic acid**



Removal of CO₂:

By the addition of calculated quantity of ammonia.



(c) Acids from dissolved salts:

Water containing dissolved Mg-salts liberate acids on hydrolysis



Disadvantages of the acid production is that the acids react with Iron of the boiler plate in a chain reaction to produce decay of the metal.



Consequently even a small amount of $MgCl_2$ can cause corrosion to a large extent.

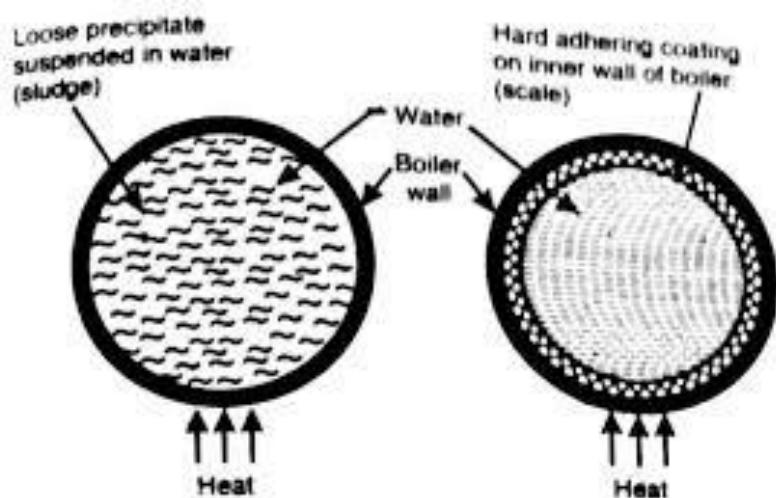
Preventions:

- (1) Softening of boiler water to remove $MgCl_2$ from the water
- (2) Addition of corrosion inhibitors like sodium silicates, sodium phosphate & sodium chromate
- (3) By frequent **blow-down operation** i.e., removal of water, concentrated with dissolved salts and feeding the boiler with fresh soft water.
- (4) Sludges and Scales formation: In boiler, water evaporates continuously and the concentration reaches saturation point, they form precipitates (scale or sludge) on the inner wall of the boiler

SLUDGE: “Sludge is a soft, loose and slimy precipitate formed within the boiler”. Sludge are formed by substances which have greater solubility in hot water than in cold water. Salts like $MgCO_3$, $MgSO_4$, $MgCl_2$, $CaCl_2$ etc., are responsible for sludge formation in boilers.

Disadvantages:

- (a) Sludge is a bad conductor of heat, hence it wastes a portion of heat generated.
- (b) Excessive sludge formation reduces the efficiency of the boiler.



Prevention:

- (a) Frequent blow-down operation should be carried out.
- (b) Use well-softened water.

SCALES: “Scales are the hard, adhering ppt formed on the inner wall of the boiler”. Very difficult to remove once they are deposited on Inner wall of the boiler.

They formed due to decomposition of Calcium bicarbonate, Calcium sulphate etc.,



REMOVAL OF SCALES:

- (1) Frequent blow-down operation can remove the scales which are loosely adhering.
- (2) By chemical treatment eg: CaCO_3 scale removed by washing with 5-10% of HCl.
- (3) By giving thermal shocks.

Prevention: Use soft water.

SOFTENING OF WATER:

The removal of hardness causing salts from water is called “Softening of water”.

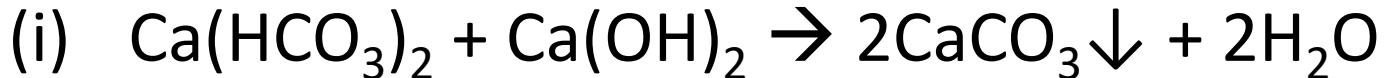
The 3 Industrial methods employed for softening of water are:

- (1) Lime-Soda Process
- (2) Zeolite (or) Permutite Process
- (3) Ion-Exchange (or) Demineralization process

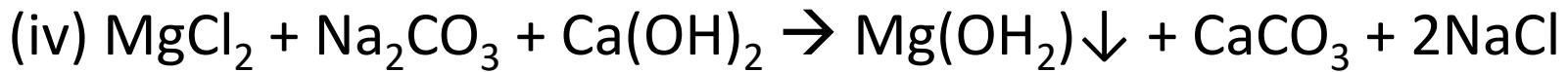
(1) LIME-SODA PROCESS:

This process is based on converting the soluble calcium and magnesium salts into Insoluble calcium carbonate and magnesium hydroxide precipitates by addition of calculated amount of lime (Ca(OH)_2) and Soda (Na_2CO_3). The precipitate are removed by filtration. Any free dissolved CO_2 and acids are also removed by this process. The various chemical reactions involved in this process are:

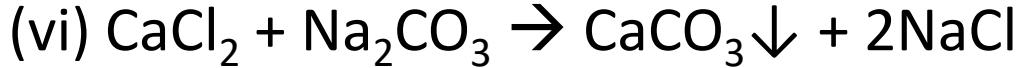
(a) For Calcium and Magnesium bicarbonates, only lime is required



(b) For MgSO_4 & MgCl_2 , both lime & soda are required



(c) For CaSO_4 & CaCl_2 , only Soda is required



(d) Other Reactions: Free acids, CO₂, H₂S dissolved iron and aluminium salts etc are also removed in this process



Constituent	Reaction	Requirement
Ca ⁺² (Permanent)	(i) $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$ (ii) $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	S
Mg ⁺² (Permanent)	(iii) $\text{MgSO}_4 + \text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$ (iv) $\text{MgCl}_2 + \text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCO}_3 + 2\text{NaCl}$	L + S
HCO ₃ ⁻	(v) $2\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L - S
Ca(HCO ₃) ₂ (Temporary)	(vi) $\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	L
Mg(HCO ₃) ₂ (Temporary)	(vii) $\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 \downarrow + 2\text{H}_2\text{O}$	2L
CO ₂	(viii) $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
H ⁺	(ix) $2\text{HCl} + \text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl} + \text{H}_2\text{O}$	L + S
Coagulants FeSO ₄	(x) $\text{FeSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{CaSO}_4$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	L + S
Al ₂ (SO ₄) ₃	(xi) $\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3 \downarrow + 3\text{CaSO}_4 + \text{H}_2\text{O}$ $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 3\text{Na}_2\text{SO}_4$	L + S
NaAlO ₂	(xii) $\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$	-L

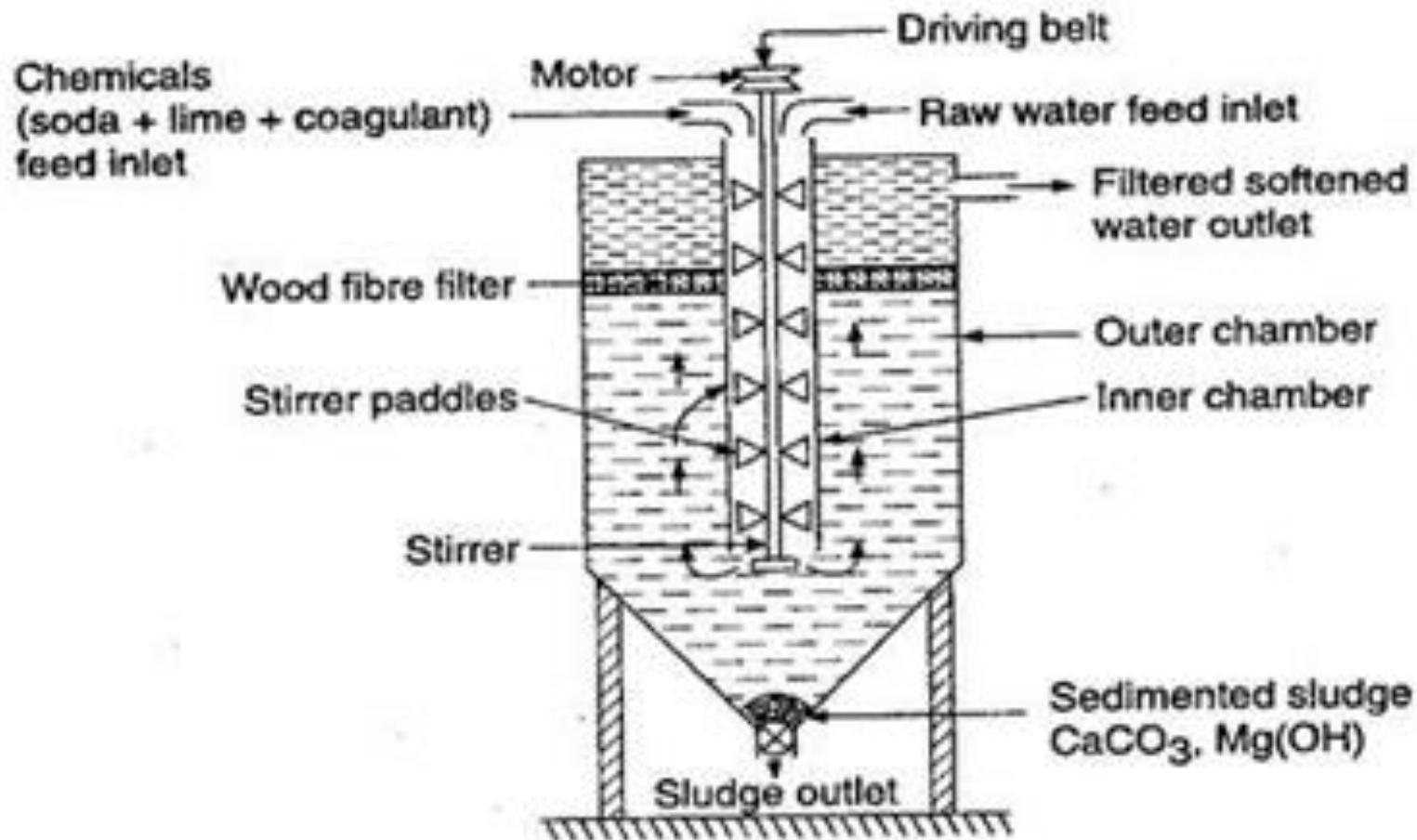
Calculation:

100 parts by mass of CaCO_3 are equivalent to 74 parts of $\text{Ca}(\text{OH})_2$ and 106 parts of Na_2CO_3 .

(a) Amount of **lime** required for softening =
74/100 (Temp Ca^{2+} + 2 x Temp. Mg^{2+} + Perm.
 $(\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+$ ($\text{HCl}/\text{H}_2\text{SO}_4$) +
 HCO_3^- - all in terms of CaCO_3 equivalent)

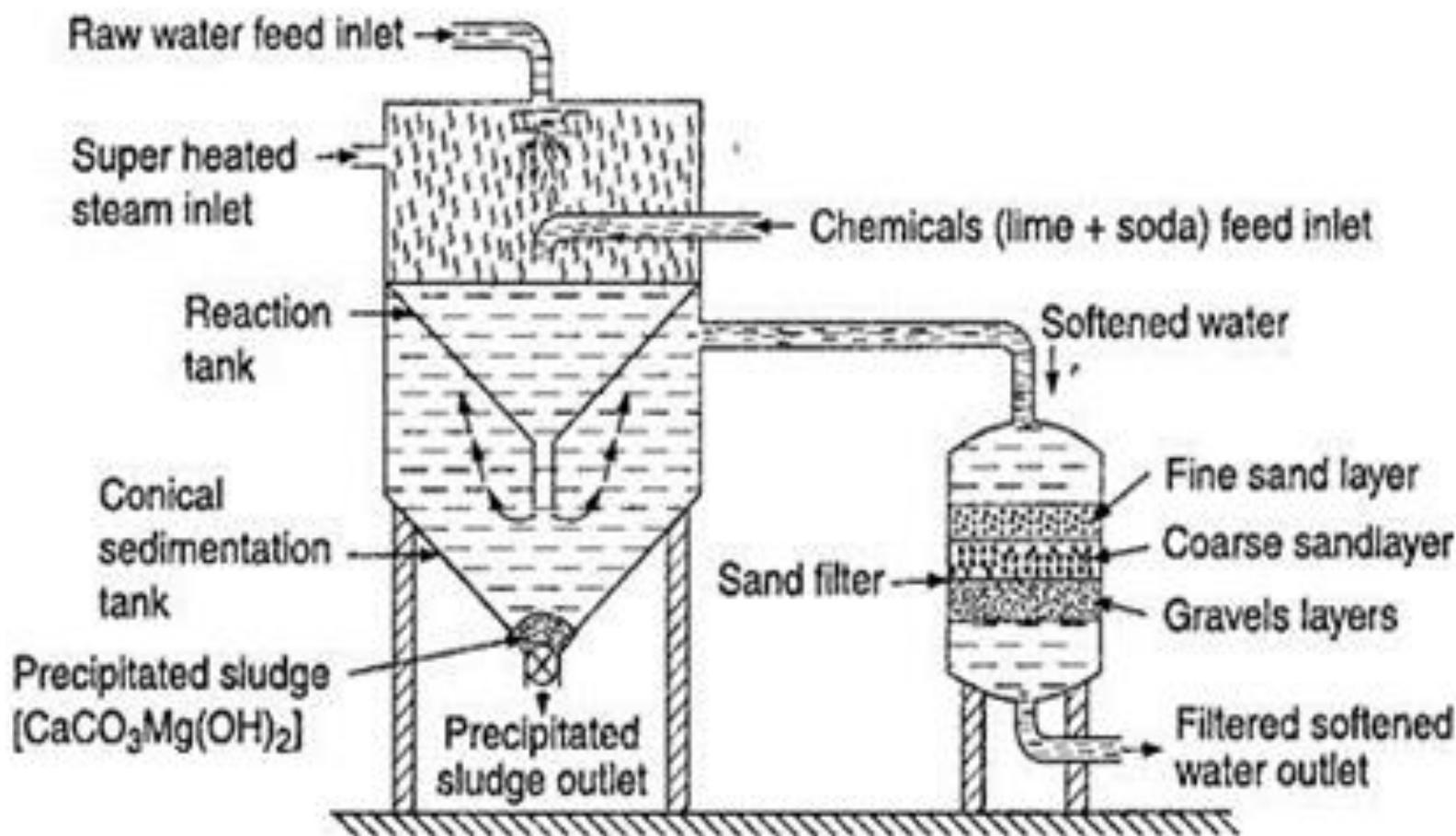
(b) Amount of **soda** required for softening =
106/100 (Perm. $(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{H}^+$
($\text{HCl}/\text{H}_2\text{SO}_4$) + HCO_3^- - all in terms of CaCO_3 eq.)

COLD-LIME-SODA PROCESS:



- In this method the lime & soda are mixed with hard water at room temperature with constant stirring.
- Generally the precipitates formed by this process are finely divided and in order to settle the precipitates, coagulants like alum, ferrous sulphate, etc. are added.
- The hard water to be softened is mixed with calculated quantity of chemicals (Lime + Soda + Coagulant) from the top into the inner chamber on vigorous stirring. The chemical reactions takes place and the hardness producing salts get converted into insoluble precipitates.
- The sludge is removed from the bottom of the outer chamber while the softened water passes through a wood fibre filter to ensure the complete removal of any residual sludge particles.
- The clear softened water is withdrawn from the top of the outer chamber.
- The softened water from this process contains a residual hardness of 50-60ppm

HOT-LIME-SODA PROCESS:



- This process is similar to the cold lime-soda process, but no coagulant is needed.
- Here the process is carried at a temperature of 80° to 150°C . Since the reaction carried out at high temperature.
 - (a) The reaction takes place faster
 - (b) The sludge settles rapidly
 - (c) Viscosity of soft water is lower, hence filtered easily
 - (d) The dissolved gases such as CO_2 , air, etc. driven out of the water
 - (e) The residual hardness is low, compared to cold lime- soda process.

Hot lime soda process consists of three parts-

- “REACTION TANK” in which complete mixing of water, chemicals and steam takes place and water gets softened.
- “Conical Sedimentation Vessel” where the sludge settle down.
- “SAND FILTER” where sludge is completely removed.

The softened water from this process contains a residual hardness of 15-30 ppm.

ADVANTAGES OF LIME-SODA PROCESS:

- I. This process is economical.
- II. Mineral content of the water is reduced.
- III. The process increases the pH value of water, which reduces the content of pathogenic bacteria.
- IV. Manganese and Iron salts are also removed by this process.
- V. The process improves the corrosion resistance of the water.

DISADVANTAGES OF LIME-SODA PROCESS:

- 1) Due to residual hardness, water is not useful for high pressure boilers.
- 2) Large amount of sludge is formed which creates disposal problem.

PROBLEMS:

- 1) Calculate the quantities of Lime & Soda required to soften 5000 litres of water containing the following salts: $MgCl_2 = 15.5$ ppm; $Ca(HCO_3)_2 = 32.5$ ppm, $CaSO_4 = 22.4$ ppm; $Mg(HCO_3)_2 = 14.6$ ppm; $NaCl = 50$ ppm

Soln: Calculation of Calcium Carbonate Equivalents:

Impurity mg/L	M. Wt.	CaCO ₃ eq.	Requirement
$MgCl_2 = 15.5$	95	$15.5 \times 100 \div 95 = 16.31$	L + S
$Ca(HCO_3)_2 = 32.5$	162	$32.5 \times 100 \div 162 = 20.06$	L
$CaSO_4 = 22.4$	136	$22.4 \times 100 \div 136 = 16.47$	S
$Mg(HCO_3)_2 = 14.6$	146	$14.6 \times 100 \div 146 = 10$	2L
$NaCl = 50$	-		

Lime = $74/100$ (Temp Ca^{2+} + 2 x Temp. Mg^{2+} + Perm.
 $(\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+$ ($\text{HCl}/\text{H}_2\text{SO}_4$) + HCO_3^- - all
in terms of CaCO_3 equivalent) \times (Vol of water/ 1000) \times
(100/ %P)

Lime required for litre of water:

$$= 74/100 (\text{Ca}(\text{HCO}_3)_2 + 2 \times \text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2) \text{ as } \text{CaCO}_3 \text{ eq.}$$

$$= 74/100 (20.06 + 2 \times 10 + 16.31)$$

$$= 74/100 \times 56.37$$

$$= 41.71 \text{ mg}$$

Lime req'd for 5000 litres of water

$$= 41.71 \times 5000 \div 1000 = 208.55 \text{ g} = 0.208 \text{ kg}$$

Soda = $106/100$ (Perm. $(Ca^{2+} + Mg^{2+} + Fe^{+2} + Al^{3+})$
+ H^+ (HCl/H_2SO_4) + HCO_3^- - all in terms of $CaCO_3$
eq.) \times (Vol of water/ 1000) \times (100/ %P)

Soda req'd for litre of water

$$= 106/100 [MgCl_2 + CaSO_4] \text{ as } CaCO_3 \text{ eq.}$$

$$= 106/100 [16.31 + 16.47]$$

$$= 106/100 [32.78]$$

$$= 34.74 \text{ mg}$$

Soda req'd for 5000 litres of water:

$$= 34.74 \times 5000 \div 1000 = 173.70 \text{ gm} = 0.173 \text{ kg}$$

Problem 1.20.37: Calculate amount of lime (90% pure) and soda (98% pure) for the treatment of 1 million litres of water containing $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$, $\text{CaCl}_2 = 33.3 \text{ ppm}$, $\text{HCO}_3^- = 91.5 \text{ ppm}$, $\text{MgCl}_2 = 38 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$. The coagulant $\text{Al}_2(\text{SO}_4)_3$ was added at the rate of 17.1 ppm.

Dec. 2012, 6 Marks

Solution :

$$L = \frac{74}{100} \left[\text{Temporary } \text{Ca}^{+2} + 2 \times \text{Temporary } \text{Mg}^{+2} + \text{Permanent } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4)) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \right] \times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg}$$

all in terms of their CaCO_3 equivalents

➤ Calculation of CaCO_3 equivalents for impurities.

Salt/impurity	Quantity ppm	Multiplication factor	CaCO_3 equivalents ppm	Requirement of Lime (L) and / or Soda (S)
$\text{Ca}(\text{HCO}_3)_2$	8.1	$\frac{100}{162}$	5	L
CaCl_2	33.3	$\frac{100}{111}$	30	S
HCO_3^-	91.5	$\frac{100}{61 \times 2}$	75	Add in lime Subtract in soda + L - S
MgCl_2	38	$\frac{100}{95}$	40	L + S

Salt/ impurity	Quantity ppm	Multiplication factor	CaCO ₃ equivalents ppm	Requirement of Lime (L) and / or Soda (S)
Mg (HCO ₃) ₂	14.6	$\frac{100}{146}$	10	2L
Al ₂ (SO ₄) ₃	17.1	$\frac{100}{114}$	15	+ L + S

➤ Calculation of quantity of Lime in kg required for softening water.

Quantity of lime,

$$\begin{aligned}
 L &= \frac{74}{100} \left[\text{Temporary Ca}^{+2} + 2 \times \text{Temporary Mg}^{+2} + \right. \\
 &\quad \left. \text{Permanent (Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) \right) + \text{CO}_2 + \text{HCO}_3^- - \text{NaAlO}_2 \\
 &\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg} \quad \text{all in terms of their CaCO}_3 \text{ equivalents.} \\
 &= \frac{74}{100} [5 + 2 \times 10 + 40 + 30 + 15 + 75] \times \frac{10^6}{10^6} \times \frac{100}{90} \text{ kg} \\
 &= \frac{74}{100} [185] \times \frac{100}{90} \text{ kg} = 152 \text{ kg}
 \end{aligned}$$

➤ Calculation of Qunatity of soda in kilogram required for softening water :

Qunatity of soda

$$\begin{aligned}
 S &= \frac{106}{100} \left[\text{Permanent (Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) \right) - \text{HCO}_3^- \right] \\
 &\times \frac{\text{Vol. of Water}}{10^6} \times \frac{100}{\% \text{ of purity}} \text{ kg all in terms of their CaCO}_3 \text{ equivalents.} \\
 &= \frac{106}{100} [30 + 40 + 15 - 75] \times \frac{10^6}{10^6} \times \frac{100}{98} \text{ kg} \\
 &= \frac{106}{100} [10] \times \frac{100}{98} \text{ kg} \\
 &= 10.8 \text{ kg}
 \end{aligned}$$

Quantity lime = 152 kg ...Ans.

Quantity of soda = 10.8 kg ...Ans.

Zeolite or Permutit Process:

Zeolite is “Hydrated sodium alumino silicate”. Its general formula is: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$; x= 2-10 y= 2- 6. Eg: Natrolite: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Natural zeolites are generally non-porous.

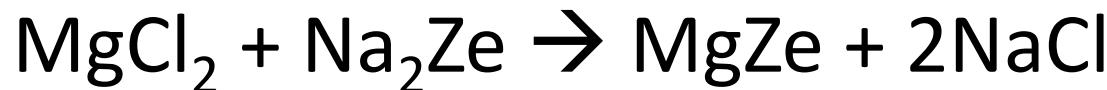
The artificial zeolite is called **Permutit**. These are prepared by heating together with chain clay, feldspar and soda ash. These are porous and have greater softening capacity than natural zeolite.

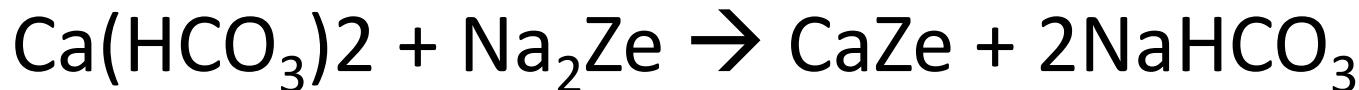
Working:

They exchange Na^+ ions with the hardness, producing ions (Ca^{2+} , Mg^{2+} , etc.) in water.

Sodium Zeolite is denoted as Na_2Ze .

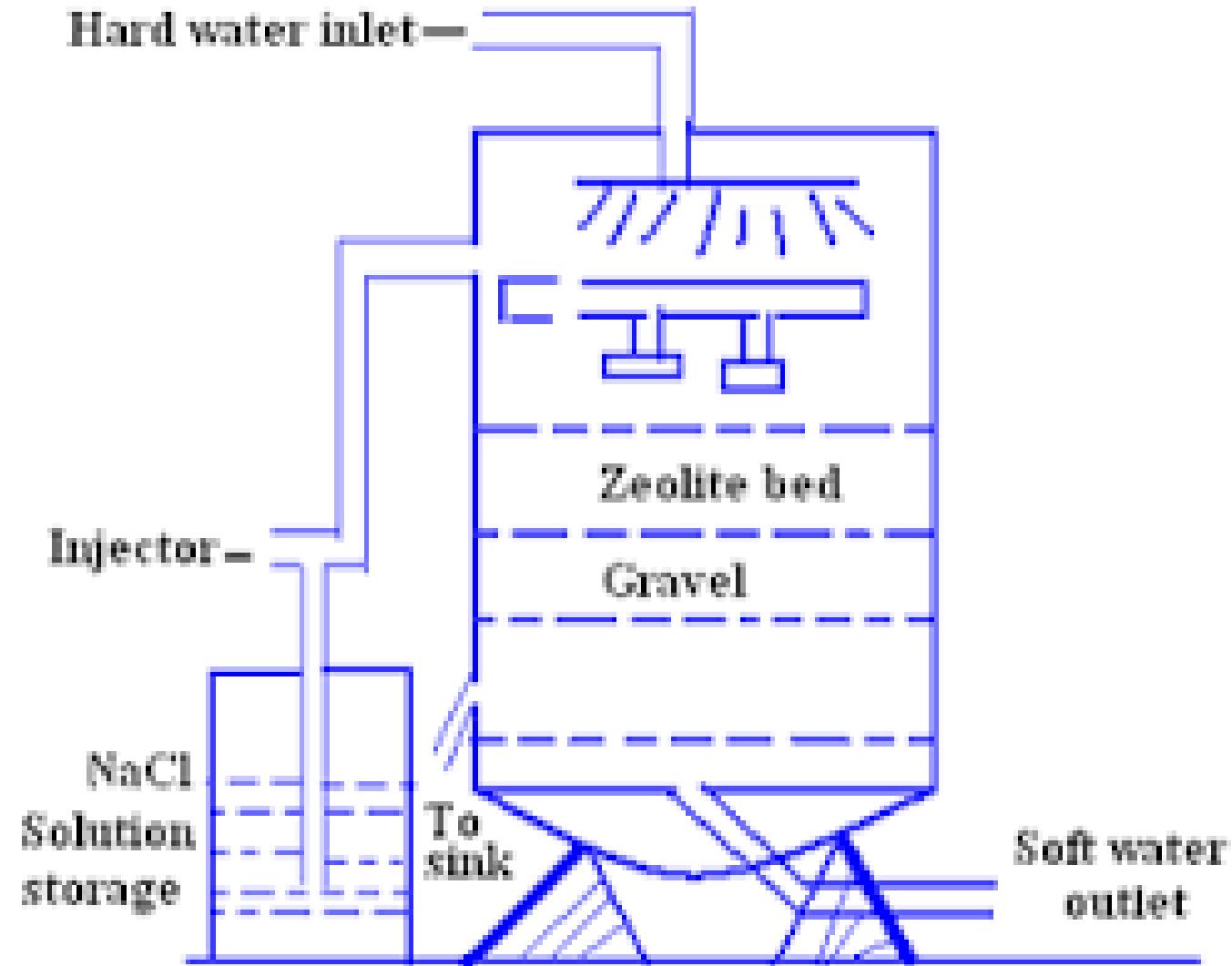
PROCESS: In this process hard water is passed through a bed of zeolite at ordinary temperature. The hard water percolates (filtered), Ca^{2+} , Mg^{2+} present in hard water are exchanged with Na^+ ions. The following reactions taking place:





Regeneration Of Zeolite: On continuous passing of hard water through sodium zeolite bed it is converted to calcium and magnesium zeolite which is known as 'Exhausted Bed'. Hence, it must be regenerated. This can be done by washing zeolite bed with **10% sodium chloride solution.**





ADVANTAGES:

- 1) The equipment is small and easy to handle.
- 2) It requires less time for softening.
- 3) Water obtained from this process contains a residual hardness upto 10 ppm.
- 4) Easy to regenerate.
- 5) No sludge is formed in this process.

DISADVANTAGES:

- 1) Highly turbid water cannot be treated by this process.
- 2) The process exchanges only Ca^{+2} & Mg^{2+} ions by sodium ions and hence the softened water contains more sodium salts.
- 3) All the acidic ions like HCO_3^- , CO_3^{2-} , etc. are not removed by this process.
- 4) Sodium bicarbonate decomposes in the boiler releasing CO_2 which leads to corrosion.
- 5) While Na_2CO_3 is hydrolysed to NaOH which creates caustic embrittlement of boiler.

Problem-1:

The hardness of 10,000 Lit of hard water was completely removed by passing it through a zeolite softner. The zeolite softner required 5000Lit of NaCl solution containing 1170mg/Lit. Determine the hardness of water sample.

Solution: 5000L of NaCl solution= $5000 \times 1170\text{mg/Lit}$

$$= 5850000\text{mg}$$

$$= 5850000 \times \frac{50}{58.5} \text{ mg CaCO}_3 \text{ eq.}$$

$$= 5000000\text{mg}$$

Hardness of 10000Lit water= 5000000mg

Thus, hardness for 1Lit= $5000000 / 10000 = 500\text{mg CaCO}_3 \text{ eq}$

Hence, **Hardness = 500ppm**

Problem-2:

An exhausted zeolite softner was regenerated by passing 75Lit of NaCl solution having strength 75g/Lit. If hardness of water is 300ppm, then calculate the total volume that can be softened by the zeolite.

Solution: Amount of NaCl in 75Lit= $75 \times 75 = 5625$ gm of NaCl

$$\text{Quantity of NaCl} = 5625 \times \frac{100}{117} = 4807.69\text{gm} = 4.81 \times 10^6\text{mg CaCO}_3 \text{ eq.}$$

Hardness= 300ppm

So, 4.81×10^6 ppm is present in 4.81×10^6 Lit of water

$$\begin{aligned} & \frac{300}{4.81 \times 10^6} \\ & = 1.6 \times 10^4 \text{ Lit} \end{aligned}$$

Thus, Zeolite can soften 1.6×10^4 Lit of water

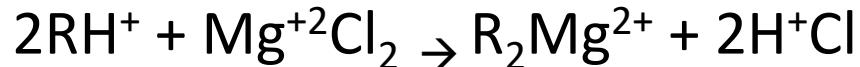
ION EXCHANGE PROCESS/ DEMINERALISATION PROCESS:

Ion exchange resins are insoluble, cross-linked, long chain organic polymers.

The functional groups attached to the chains can exchange hardness producing cations and anions present in the water.

PROCESS: The process involves the following steps:

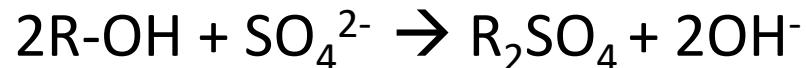
1) The first chamber is packed with cation exchange resin (RH^+). When the hard water is passed through a bed of cation exchange resin it exchanges H^+ with Ca^{+2} , Mg^{+2} , K^+ , Na^+ etc. of hard water.



Thus, the hardness producing cations (Ca^{+2} , Mg^{+2} etc) are removed

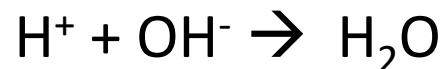
1) The second chamber is packed with anion exchange resin. The water coming out of the first chamber contains H^+ , Cl^- , SO_4^{2-} and HCO_3^- ions.

It is now passed through anion exchange resin bed which can exchange OH^- ions with anions like Cl^- , SO_4^{2-} and HCO_3^-



Thus, hardness producing anions like Cl^- , SO_4^{2-} and HCO_3^- are removed.

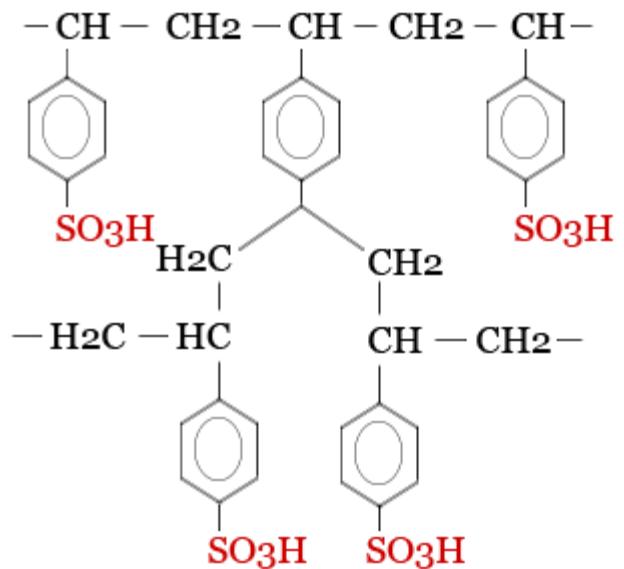
3) Thus, H^+ ions produced from first chamber combine with OH^- ions produced from second chamber to form water.



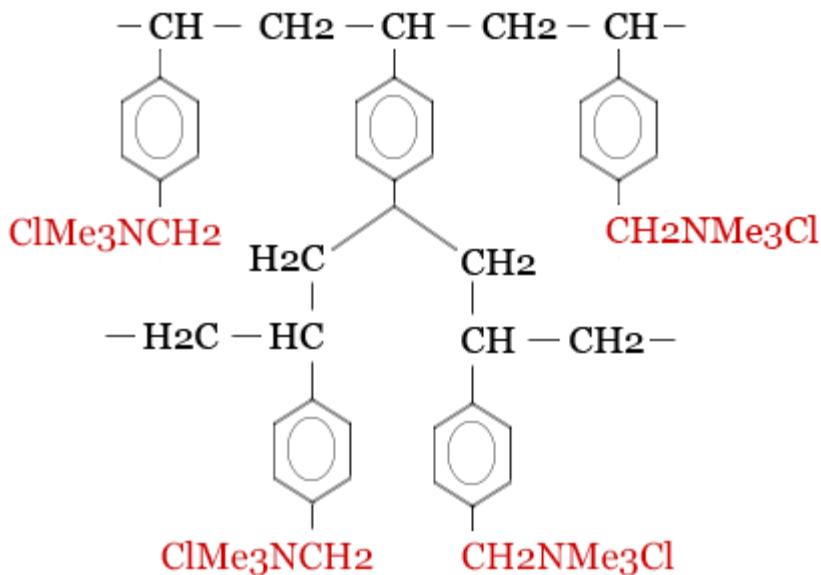
Hence, the water produced from ion-exchange process is completely free from all cations and anions of salts.

ION EXCHANGE RESIN

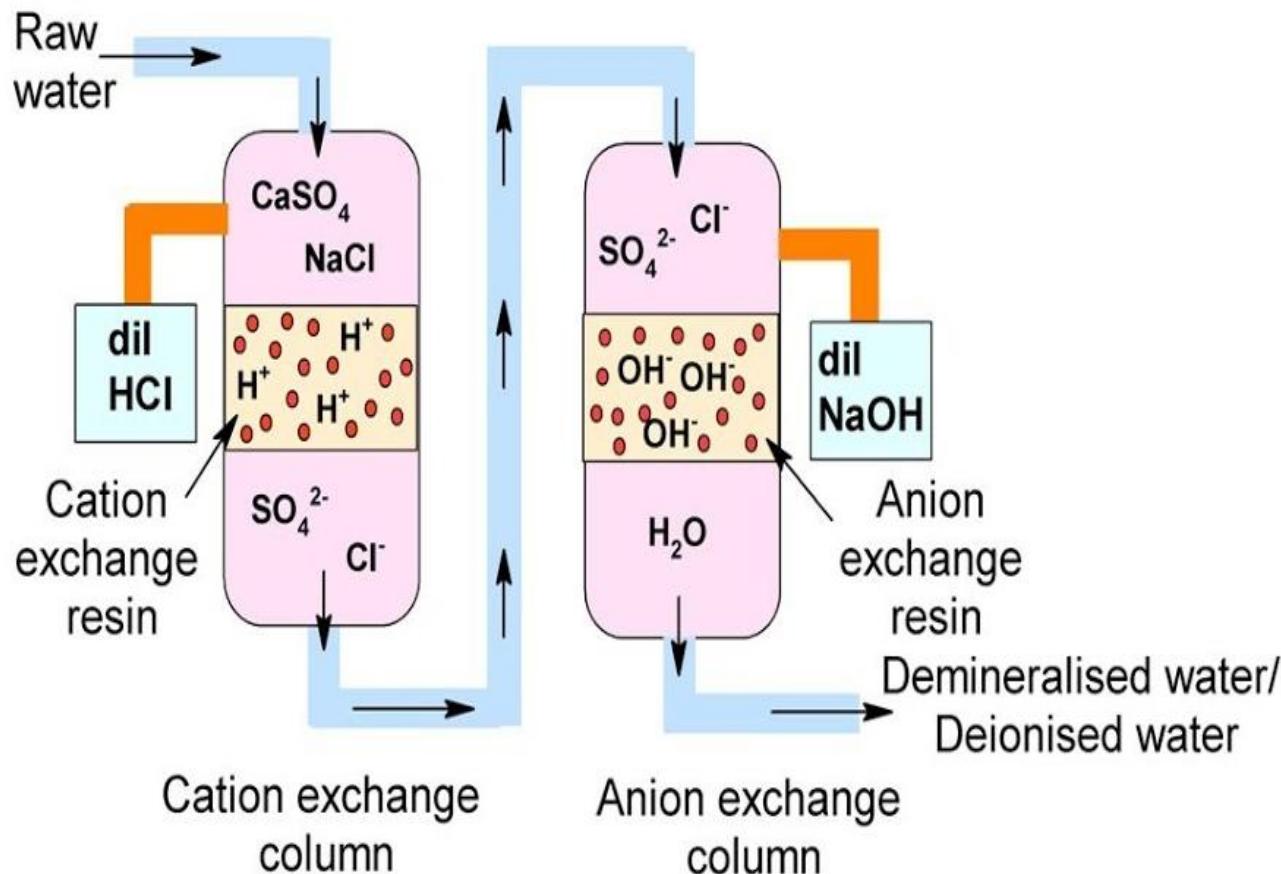
CATION EXCHANGE RESIN



ANION EXCHANGE RESIN



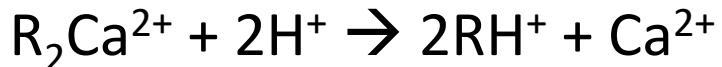
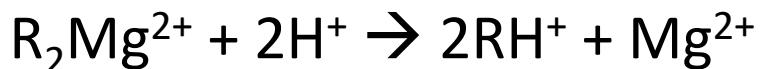
DEMINERALISATION PROCESS/ ION-EXCHANGE PROCESS



REGENERATION OF RESINS:

The resin bed gets exhausted, when used for a long period and can be regenerated:

(a) The exhausted cation exchange resin can be regenerated by passing **dil. HCl** (H^+)



(b) The exhausted anion exchange resin can be regenerated by passing **dil. NaOH** (OH^-)



ADVANTAGES:

- 1) The softened water by this method is completely free from all salts and fit for use in boilers.
- 2) It produces very low hardness nearly **2 ppm**.
- 3) Highly acidic or alkaline water can be treated by this process.

DISADVANTAGES:

- 1) The equipment is costly.
- 2) More expensive chemicals are required for regeneration.
- 3) Turbid water cannot be treated by this method.

Numerical

After treating 10^4 litres of water by ion-exchange, the cationic resin required 200 litres of 0.1N HCl and the anionic resin required 200 litres of 0.1N NaOH solutions for regeneration. Find the hardness of water.

Solution: Hardness of 10^4 litres of water = 200 lit of 0.1N HCl
= 200×0.1 Lit x 1 N CaCO_3 eq.
= 20 lit of 1N CaCO_3 eq.
= 20×50 g of CaCO_3 eq.
= 1000 g of CaCO_3 eq.

So, Hardness in 1lit water = $1000 / 10^4$ g of CaCO_3 eq.
= 100 mg of CaCO_3 eq.

Thus, hardness of water sample = 100 ppm

DESALINATION OF BRACKISH WATER:

Water containing high concentrations of dissolved solids with a peculiar salty or brackish taste is called ‘brackish water’.

Sea water is an example of brackish water containing about 3.5% of dissolved salts. This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

Commonly used methods are: 1) Electrodialysis
2) Reverse Osmosis

Electrodialysis:

Electrodialysis is based on the **principle** that the ions present in saline water migrate towards their respective electrodes through ion selective membranes under the influence of applied e.m.f.

The unit consists of a chamber with two electrodes, the cathode and anode.

The chamber is divided to 3-compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion.

The anode is placed near anion selective membrane while the cathode placed near cation selective membrane.

The anion selective membrane is containing positively charged functional groups such as R_4N^+ and is permeable to anions only.

The cation selective membrane consists of negatively charged functional groups such as RSO_3^- and is permeable to cations only.

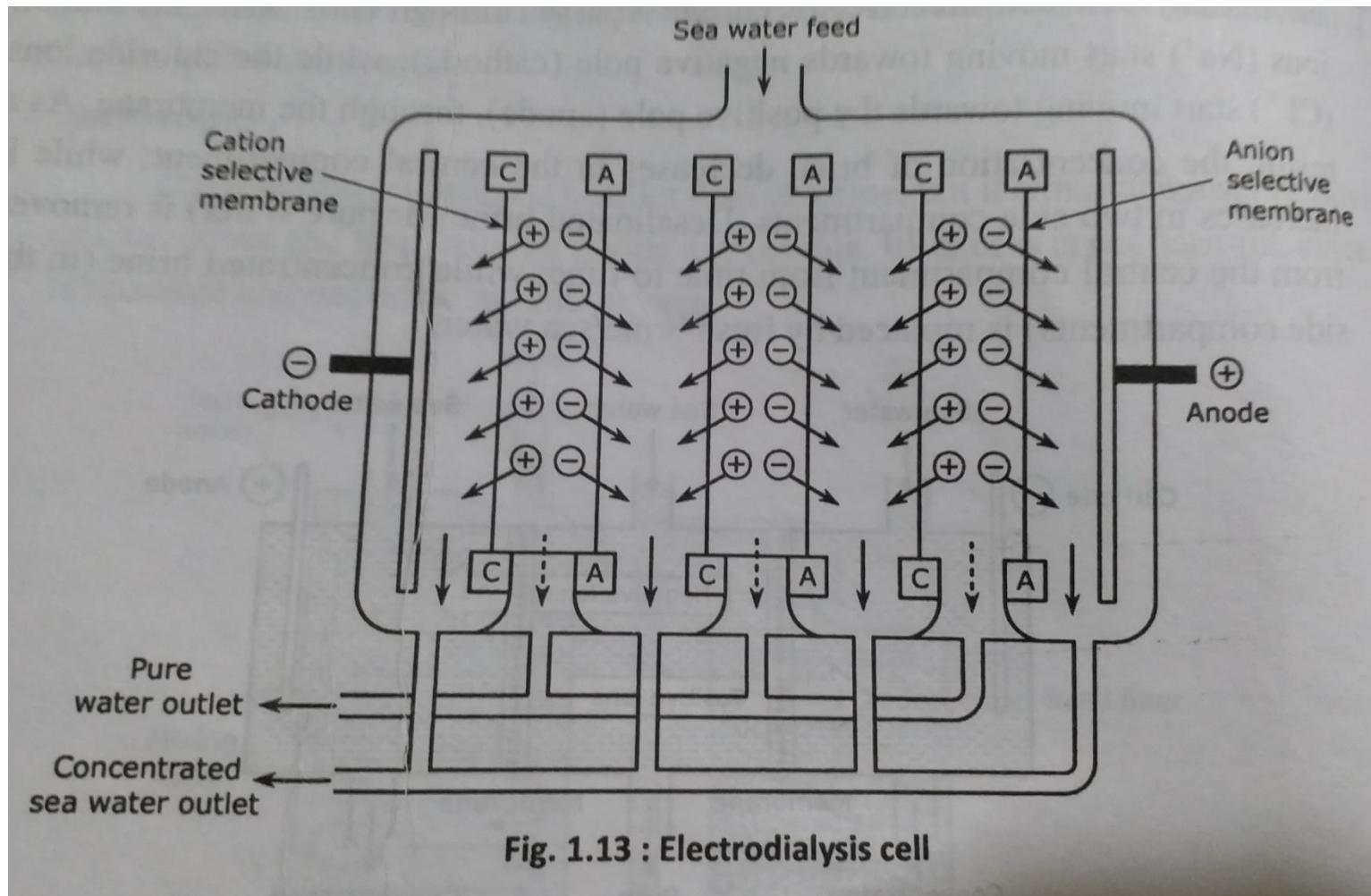


Fig. 1.13 : Electrodialysis cell

Under the influence of applied e.m.f. across the electrodes the cations move towards cathode through the membrane and the anions move towards anode through the membrane.

The net result is depletion of ions in the central compartment, while it increases in the cathodic and anodic compartments.

Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.

ADVANTAGES OF ELECTRODIALYSIS:

The unit is compact.

The process is economical as far as capital cost and operational expenses are concerned.

REVERSE OSMOSIS:

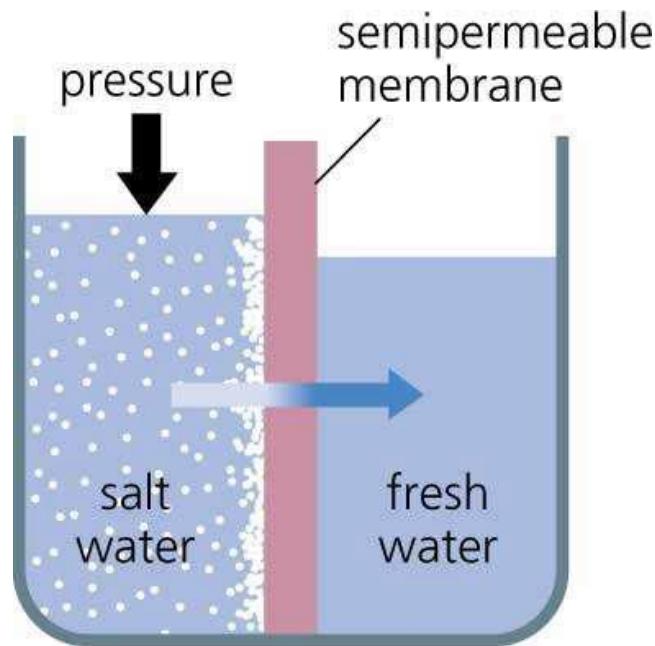
When two solutions of unequal concentration are separated by a semi-permeable membrane which does not permit the passage of dissolved solute particles, i.e., molecules and ions, flow of solvent takes place from the dilute solution to concentrated solution this is called as “OSMOSIS”.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side the solvent is forced to move from higher concentration to lower concentrated side across. Thus, solvent flow is reversed hence this method is called “Reverse Osmosis”

Thus, in reverse osmosis pure water is separated from the contaminated water. This membrane filtration is also called “Super Filtration” or “Hyper-Filtration”.

METHOD OF PURIFICATION:

The reverse osmosis cell consists of a chamber fitted with a semi-permeable membrane, above which sea water/ impure water is taken and a pressure of **15 to 40 kg/cm²** is applied on the sea water/ impure water. The pure water is forced through the semi permeable membrane which is made of very thin films of **cellulose acetate**. However superior membrane made of **Polymethacrylate and Polyamide** polymers have come to use.



ADVANTAGES:

Both ionic and non-ionic colloidal and high molecule weight organic matter is removed from the water sample

Cost of purification of water is less and maintenance cost is less.

This water can be used for high pressure boilers.

BOD and COD

BOD (Biological Oxygen Demand)

- It is a measure of amount of oxygen required for the **biological oxidation** of organic matter under aerobic conditions at 20°C for a period of 5 days.



- BOD is the direct measurement of extent of pollution in waste water & industrial effluent.
- Only applicable for bio-degradable pollutants.**
- Higher the BOD, higher will be the level of pollutants in water.
- Drinking water should have BOD less than 1 ppm.**

Principle

- Dissolved oxygen content of diluted waste-water is determined at the beginning of the reaction by Winkler's method or by DO meter.
- Same sample of water is kept for incubation in the presence of micro-organisms for 5 days at 20°C and decrease in the dissolved oxygen content is determined by Winkler's method or by DO meter.

$$\text{BOD} = [(\text{DO})_{\text{Blank}} - (\text{DO})_{\text{Incubated}}] \times \text{Dilution Factor}$$

$(\text{DO})_{\text{Blank}}$ = Dissolved oxygen of diluted sample in the beginning of the reaction

$(\text{DO})_{\text{Incubated}}$ = Dissolved oxygen of diluted sample after incubation for 5 days at 20 °C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} = \text{Vol taken for titration/ Total vol to which it is diluted}$$

Significance of BOD

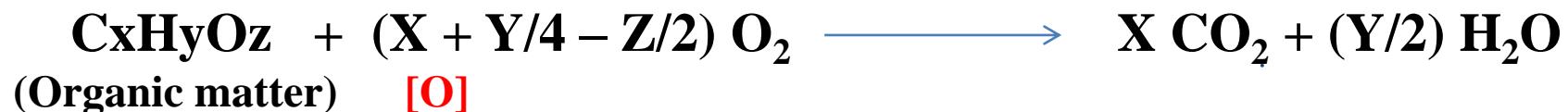
1. BOD gives the extent of bio-degradable pollutants in wastewater sample
2. It also helps in pollution control in water
3. It also express self-purification capacity of any water body.

BOD Meter



COD (Chemical Oxygen Demand)

- It is a measure of amount of oxygen required for the **chemical oxidation** of organic matter when refluxed in acidified potassium **dichromate** in the presence of Ag_2SO_4 or HgSO_4 catalyst for 3 hours.

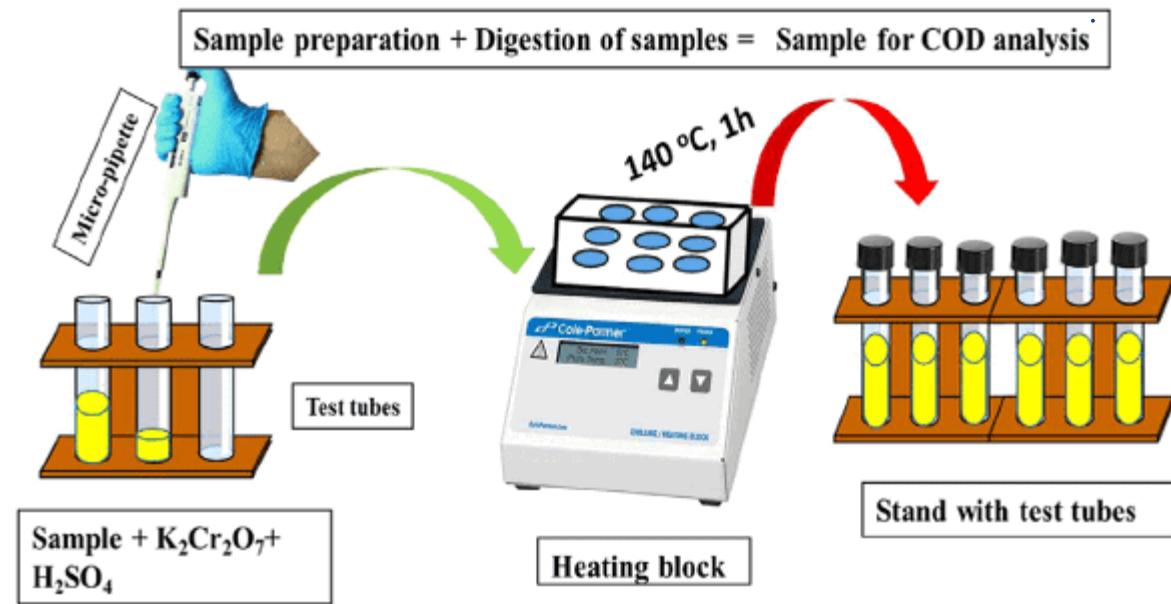


- COD is the direct measurement of extent of pollution in waste water & industrial effluent.
- Applicable for both **bio-degradable** and **non bio-degradable** pollutants.
- Higher the COD, higher will be the level of pollutants in water.
- Drinking water should have COD less than 1 ppm.**

Principle

- A known volume of waste water sample (say 250 ml) is refluxed with a known excess of standard potassium dichromate (1 N) and dilute/conc. sulfuric acid mixture in the presence of silver sulphate catalyst for about 3 hours.
- This oxidases organic matter to CO_2 , NH_3 and H_2O .
- The unreacted potassium dichromate is titrated against Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is (V_t).
- This gives the amount of potassium dichromate consumed (in terms of equivalent oxygen) required for degradation of organic pollutants.
- Blank titration is performed initially with known volume of distilled water sample and added acidified standard potassium dichromate titrated against Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is (V_b) (zero minute reading)

COD Meter



Principle

$$\text{COD} = \frac{(V_b - V_t) \times N_{FAS} \times 8 \times 1000}{Y} \text{ mg/L or ppm}$$

V_b = Volume of FAS required for blank titration

V_t = Volume of FAS required for reaction mass after time

Y = Volume of waste water sample taken

Significance of COD

1. COD gives the extent of pollution caused by bio-degradable and non bio-degradable pollutants in wastewater sample

2. It helps in rapid determination of pollutants level in water compared to BOD

3. It is taken as a basis for calculation of efficiency and designing of water treatment plants.

Comparison between BOD and COD

BOD	COD
It measures oxygen demand of biodegradable organic pollutants only	It measures oxygen demand of biodegradable and non biodegradable organic pollutants
Less stable measurement technique as micro-organisms are susceptible to variables such as pH and temperature	More stable measurement technique as no micro-organisms are used and potassium dichromate oxidizes any type of organic pollutants in water
Slow process, takes 5 days	Fast process , takes 3 hours
BOD values are generally less than COD values	COD values are generally greater than BOD values

Formulae

1. BOD = [(DO)_{Blank} – (DO)_{Incubated}] x Dilution Factor

(DO)_{Blank} = Dissolved oxygen of diluted sample in the beginning of the reaction

(DO)_{Incubated} = Dissolved oxygen of diluted sample after incubation for 5 days at 20⁰ C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}} = \text{Vol taken for titration/ Total vol to which it is diluted}$$

2. $\text{COD} = \frac{(V_b - V_t) \times N_{FAS} \times 8 \times 1000}{Y} \text{ mg/L or ppm}$

V_b = Volume of FAS required for blank titration

V_t = Volume of FAS required for reaction mass after time

Y = Volume of waste water sample taken

Problem 1.20.58: Two BOD bottles contained each of 5 ml of sewage sample and water diluted with distilled water to 300 ml. One 100 ml portion of the blank consumed 6.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen while 100 ml of the second bottle incubated at 20 °C for the five days required 1.6 ml of the same thiosulphate solution. Calculate the BOD content of the sample.

Solution : Difference in the volume of thiosulphate solution required for blank and the sample solution.

$$= 6.4 - 1.6 = 4.8 \text{ ml of } 0.05 \text{ N thiosulphate solution}$$

Since 1 litre of 1 N thiosulphate solution = 8 g oxygen

$$\begin{aligned}4.8 \text{ ml of } 0.05 \text{ N thiosulphate solution} &= [(8 \times 4.8 \times 0.05)/1000] * 100/300 \\&= 3.4 \times 10^{-4} \text{ g oxygen for 5 ml of sewage sample}\end{aligned}$$

Oxygen required for 1000 ml of sewage sample = 0.128 g

BOD for sample = 1285 mg/lit

...Ans.

A 50 ml of sample contains 840 ppm dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

problem 1.20.60 : A 10 ml of sample of waste water was refluxed with 20 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 26.2 ml of 0.1 M FAS solution. A blank of 10 ml of distilled water on refluxing with 20 ml of dichromate solution required 36 ml of 0.1 M FAS solution. Calculate the COD value of the wastewater.

Solution :

Difference in the volumes of the FAS required for the blank and sample solution = $36 - 26.2 = 9.8 \text{ ml}$

Since 1 litre of 1 M FAS = 8 g of oxygen

$$\begin{aligned} 9.8 \text{ ml of } 0.1 \text{ M FAS} &= 8 * 9.8 * 0.1 / 1000 \\ &= 7.84 * 10^{-3} \text{ of oxygen for } 10 \text{ ml of sample} \end{aligned}$$

Oxygen required for 1000 ml of waste water = 0.784 g

COD for waste water sample = 784 mg/lit

...Ans.

A 25 ml of Sewage water sample was refluxed with 10 ml of 0.25 N $K_2Cr_2O_7$ solution of dil. H_2SO_4 , Ag_2SO_4 & $HgSO_4$. The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same $K_2Cr_2O_7$ solution and 25 ml of distilled water under the same conditions

as the sample required 27 ml of 0.1 N FAS. Calculate the COD of sewage sample.

WATER FOR DOMESTIC USE & TREATMENT OF WATER FOR MUNICIPAL SUPPLY:

The following are the specification of water drinking purpose:

This water should be clear, colourless and odourless.

The water must be free from pathogenic bacteria and dissolved gases like H₂S.

The optimum hardness of water must be **125 ppm** and
pH must be 7.0 to 8.5

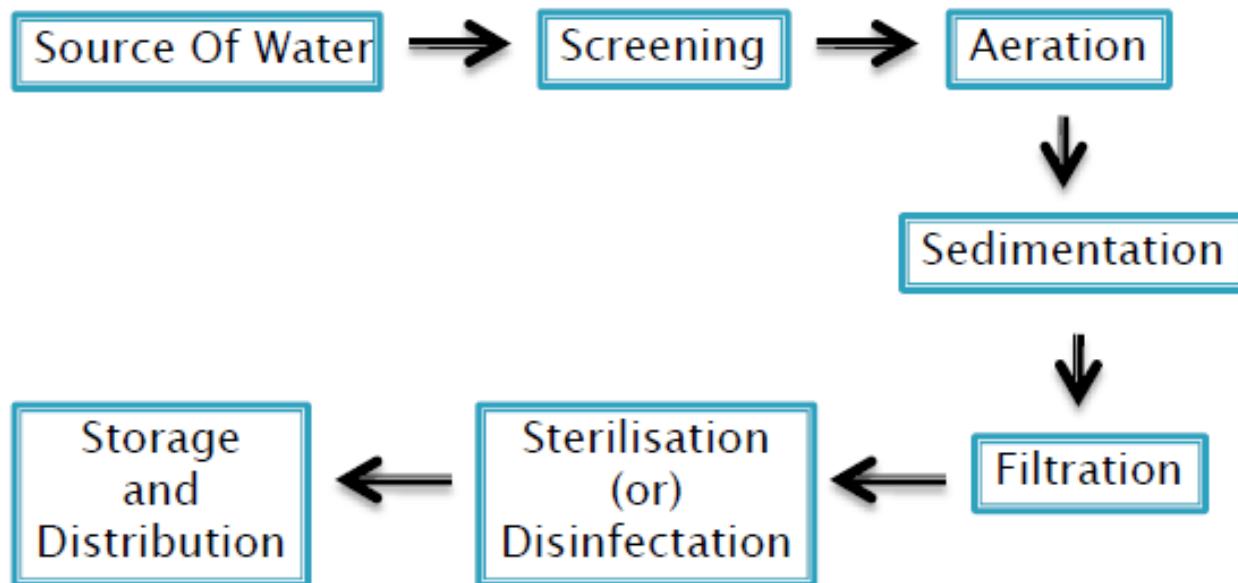
The turbidity in drinking water should not exceed **25ppm**

The recommended maximum concentration of total dissolved solids in potable water must not exceed **500ppm**

TREATMENT OF WATER FOR MUNICIPAL SUPPLY:

The treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria.

Various stages involved in purification of water for Municipal Supply:



- 1) SCREENING: The process of removing floating matter from water is known as “Screening”. In this process, water is passed through a screen (mesh/ sieve). The floating matter is arrested by the screen and the water is free from the floating matter.
- 2) AERATION: The water is then subjected to aeration which
 - i) Helps in exchange of gases between water and air.
 - ii) Increases the oxygen content of water
 - iii) Removes the impurities like ‘Fe’ and ‘Mn’ by precipitating as their hydroxides.
- 3) SEDIMENTATION:
 - i) Plain Sedimentation: The process of removing big sized suspended solid particles from water is called ‘Plain Sedimentation’. In this process, water is stored in big tanks for several hours. 70% of the solid particles settle down due to the force of gravity.

ii) Sedimentation By Coagulation:

This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum, ferrous sulphate and sodium aluminate.

When coagulant is added to water, “Floc Formation” takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

4) FILTRATION: This process of passing a liquid containing suspended impurities through a suitable porous materials so as to effectively remove suspended impurities and some micro-organisms is called “Filtration”.

It is mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

5) DISINFECTION OR STERILISATION: The process of killing pathogenic bacteria and other micro-organisms is called ‘Disinfection or Sterilisation’. The water which is free from pathogenic bacteria and safe for drinking is called Potable water. The chemicals used for killing bacteria are called ‘DISINFECTANTS’.

a) By adding Bleaching Powder: Water is mixed with required amount of bleaching powder, and the mixture is allowed to stand for several hours



(Hypo Chlorous Acid)

Germs + HOCl \rightarrow Germs are killed

The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which acts as a powerful germicide (disinfectant).

b) CHLORINATION: Chlorine is mixed with water in a chlorinator, which is a high tower having a number of baffle plates. Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and then sterilised water is taken out from the bottom.

ADVANTAGES:

- i) Storage required less space
- ii) Effective and economical
- iii) Stable and does not deteriorate
- iv) Produces no salts
- v) Ideal disinfectant

DISADVANTAGES:

- i) Excess of chlorine causes unpleasant taste and odour.
- ii) More effective at below pH 6.5 and less effective at higher pH values.

c) OZONATION: Ozone (O_3) is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.



This nascent oxygen kills bacteria as well as oxidizes the organic matter present in water.

ADVANTAGES:

Removes colour, odour and taste

DISADVANTAGES:

The method is costly.

Sewage treatment/ Activated sludge process

16 WASTE WATER TREATMENT

The main objectives of waste water treatment are :

- (i) To make sewage inoffensive so that it causes no odour,
- (ii) To prevent the destruction of aquatic life in rivers, canals, etc. into which waste water is generally discharged.
- (iii) To reduce or eliminate danger to the public health by possible contamination of water supplies.

Artificial treatment methods are generally used for waste water treatment. The main features of this method are :

- (a) To reduce the solid contents of the waste water,
- (b) To remove all nuisance-causing elements, and
- (c) To change the character of the waste water so that it safely be discharged in river, sea or applied on land.

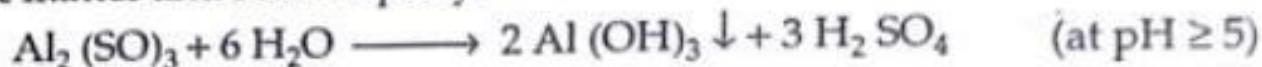
The following steps are generally employed in the artificial sewage treatment :

(A) Preliminary Process

The preliminary processes cause removal of large and coarse solids and inorganic matter suspended in waste water. The waste water is passed through mesh screens to remove gravels, coarse solids, silt, etc. Moreover, for the removal of large suspended floating matter, the waste water is passed through bar screens.

(B) Settling Process

The suspended inorganic and organic solids from the waste water are largely removed by settling process. In settling process, continuous flow type sedimentation tanks are employed. Sometimes, prior to sedimentation, chemical treatment is given to waste water. This helps in more rapid and complete removal of suspended matter. Alum, ferrous sulphate etc. are chemicals which are used for chemical treatment. These chemicals can produce large gelatinous flocs, which entrap finely divided organic matter and settle rapidly.

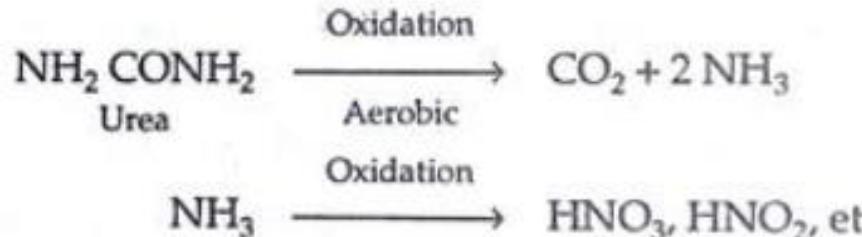


It is important to note that chemical coagulants have the ability to remove colloidal materials.

(C) Biological Treatment Process

It is essentially a aeration process in which aerobic chemical oxidation takes place. In this process, aerobic conditions are maintained all the times by filtering waste water through specially designed sprinkling filters. During this process, the carbon of the organic matter is converted into CO_2 ; the nitrogen into NH_3 and finally into nitrites and nitrates. The dissolved bases, present in the waste water, then form nitrite and nitrate of ammonium, and calcium nitrate etc.

Thus :



In the bottom of bed, the underdrain system is provided to collect effluent. Rotating arm distributions are used for delivering waste water to the filters. As the micro organism present in the waste water grow on surface of aggregates, using the organic material of sewage as food. Aerobic conditions are maintained and purified water is removed from the bottom. About 90% of BOD is removed by normal trickling filters.

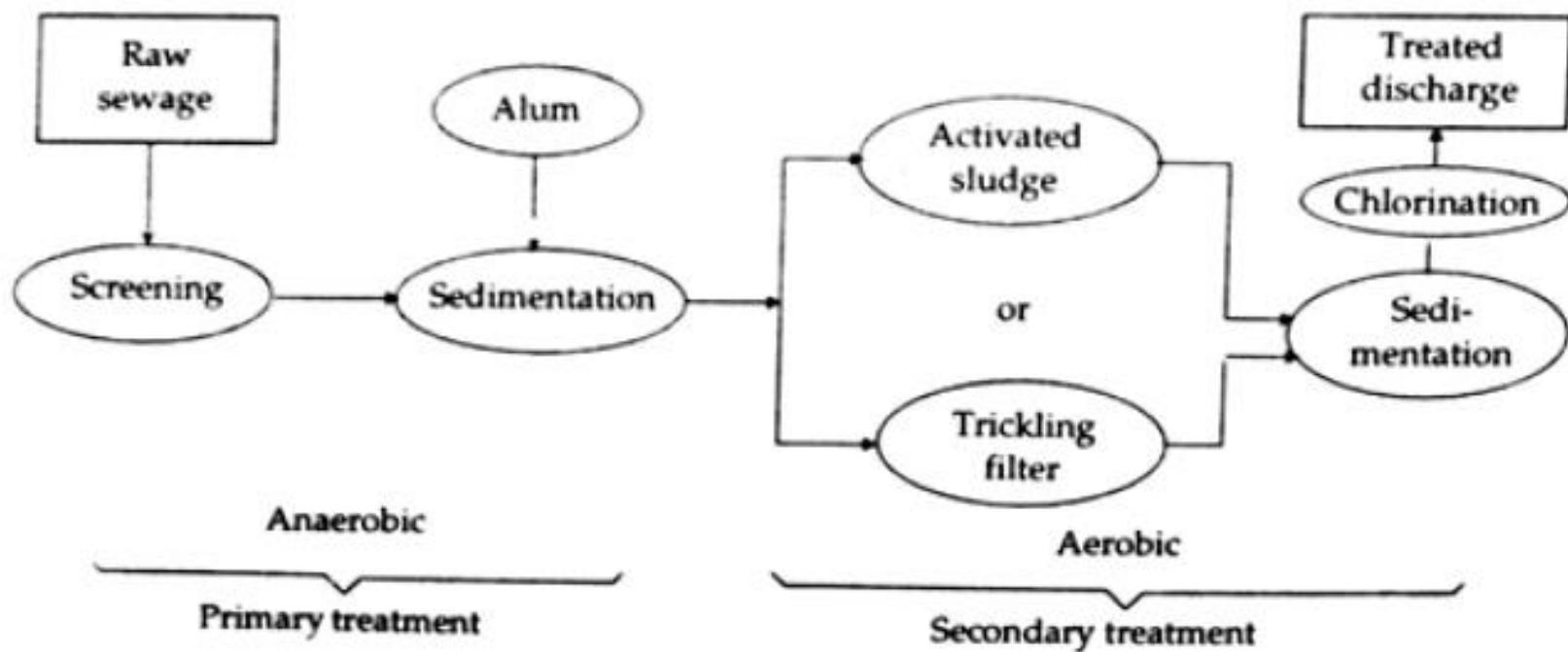
Activated Sludge Process

This process is based on the principle that if enough oxygen or air is passed through waste water containing aerobes, slow but complete aerobic oxidation occurs. This oxidation process can be quickened, if this aeration is carried out in the presence of a part of sludge from the previous oxidation process. This sludge is known as *activated sludge* since it contains organic matters inhabited by numerous bacterias, etc.

The activated sludge process consists in mixing the sedimented waste water with proper quantity of activate sludge. This mixture is then sent to the aeration tank, in which the mixed liquor is simultaneously aerated and agitated for 4 to 6 hours. Oxidation of the suspended organic matter takes place during this aeration process. The affluent, after aeration is sent to sedimentation tank. In this tank, sludge is deposited and clean and non-putrefying liquid (*i.e.*, a liquid which is free from bacteria) is drawn off. For seeding fresh batch of sewage, a part of the settled sludge is sent back while the remainder is disposed off by either dumping in sea or spreading uniformly over soil, followed by ploughing in or digestion process.

In this digestion process, the sludge is kept in the absence of air for a prolonged period of about 30 days in a closed tank. The sludge under these conditions suffers anaerobic decomposition yielding gases like methane, hydrogen sulphide, ammonium sulphide and phosphine.

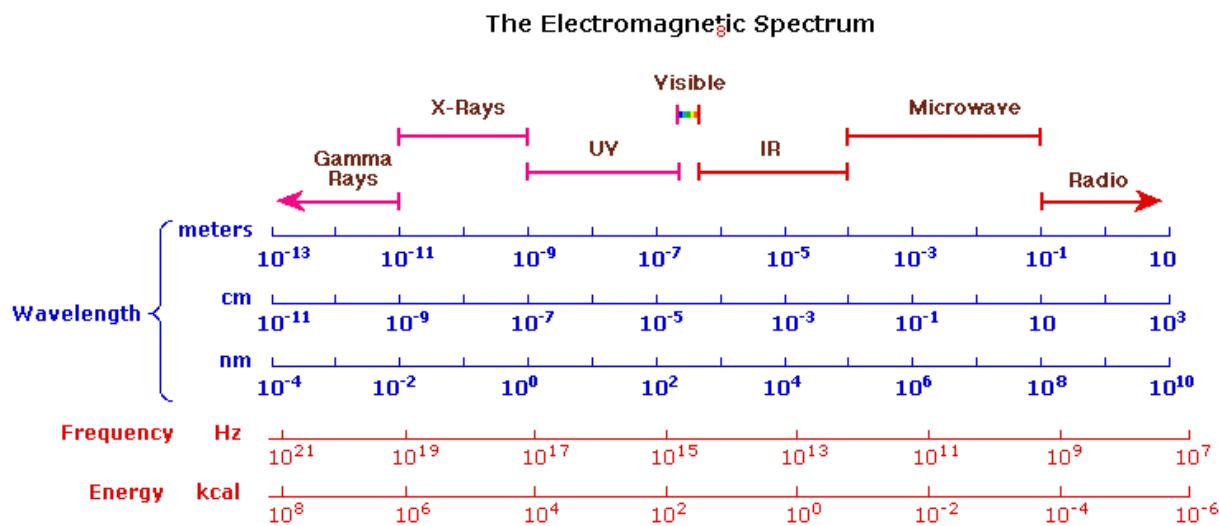
The waste water treatment process is schematically summarized below in Fig. 24.



1. UV-Visible spectroscopy

The Electromagnetic Spectrum

The visible spectrum constitutes a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This electromagnetic spectrum ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).



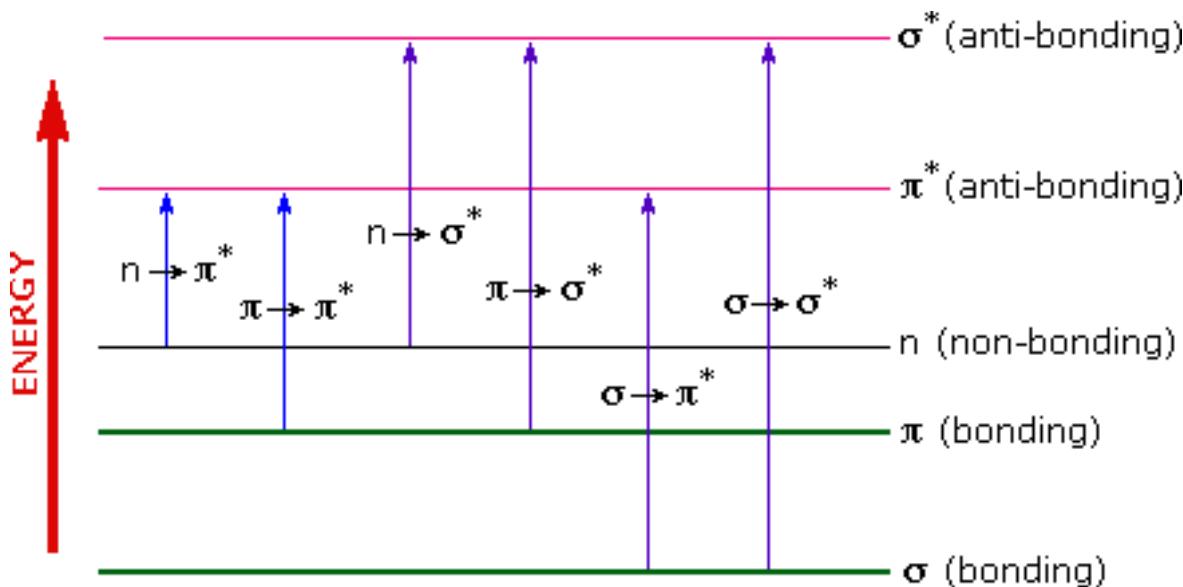
The energy associated with a given segment of the spectrum is proportional to its frequency. The equation below describes this relationship, which provides the energy carried by a photon of a given wavelength of radiation.

$$\nu = c/\lambda \quad \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light} (c = 3 \cdot 10^{10} \text{ cm/sec})$$
$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant} (h = 6.6 \cdot 10^{-27} \text{ erg sec})$$

Electronic Transition: (Self Study)

The visible region of the spectrum comprises photon energies of 36 to 72 kcal / mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal / mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy".



A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown above. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. Absorbance usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

When a beam of light passes through an absorbing medium, for example a solution, a part of the light is absorbed and the rest is transmitted. The amount of light absorbed depends on the concentration of the solution and the length traversed by the light through the solution. The quantitative relation between the amount of light absorbed, concentration and the length of the absorbing medium is governed by the laws- the Lambert's Law, the Beer's Law.

Lambert's Law:

The law states that “Equal fractions of the incident light are absorbed by successive layers of equal thickness of the absorbing medium”.

If a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of medium is proportional to intensity of the incident light i.e.

$$-\frac{dI}{I} \propto dx$$

$$\frac{dI}{I} = -k_1 dx \quad \text{---(i)}$$

Where I is intensity of the incident light of wavelength λ , x is the thickness of the medium and k_1 is proportionality factor. The negative sign indicates that due to absorption, the intensity of light decreases as it passes through the absorbing medium.

If I_0 is the initial intensity of incident light on the absorbing medium of length l and I_t is the intensity of transmitted beam, then the integration of eqn.(i) becomes

$$\ln(I_t/I_0) = -k_1 \cdot l$$

$$\ln(I_0/I_t) = k_1 \cdot l$$

$$\log_{10}(I_0/I_t) = \frac{-k_1 \cdot l}{2.303} \quad \text{---(ii)}$$

Beer's Law:

The law states that “Equal fractions of the incident light are absorbed by successive layers having equal concentration of the absorbing medium”.

The intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. i.e.

$$-\frac{dI}{I} \propto dc$$

$$\frac{dI}{I} = -k_2 dc \quad \text{---(iii)}$$

If I_0 is the initial intensity of incident light on the absorbing medium of concentration c and I_t is the intensity of transmitted beam, then the integration of eqn.(iii) becomes

$$\ln(I_t/I_0) = -k_2 \cdot c$$

$$\ln(I_0/I_t) = k_2 \cdot c$$

$$\log_{10}(I_0/I_t) = \frac{-k_2 \cdot c}{2.303} \quad \text{---(iv)}$$

Beer-Lambert's law:

A combination of Lambert's Law and Beer's Law results in Beer-Lambert's Law, it states that “Equal fractions of the incident light are absorbed by successive layers of equal thickness and equal concentration of the absorbing medium.”

Combining (ii) and (iv),

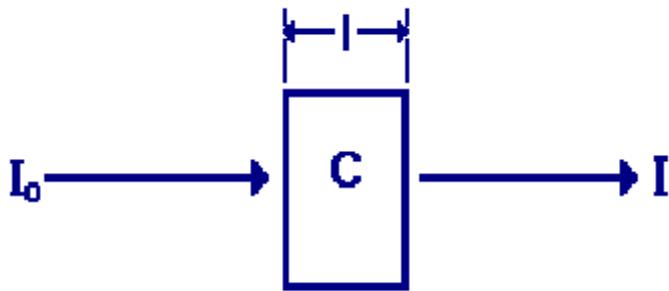
$$\log_{10}(I_0/I_t) = \frac{-k_2}{2.303} \times c \times l$$

$$\log_{10}(I_0/I_t) = \epsilon c l$$

$\log(I_0/I_t)$ is called as absorbance, if c is expressed in mol dm^{-3} and l in cm then ϵ is called as molar absorptivity or absorption coefficient.

Hence, $A = \epsilon c l = \log(I_0/I_t) = \log(1/T) = -\log(T)$ where T is transmittance.

Conditions: The law is only true for monochromatic light, which is light of a single wavelength or narrow band of wavelengths, and provided that the physical or chemical state of the substance does not change with concentration.

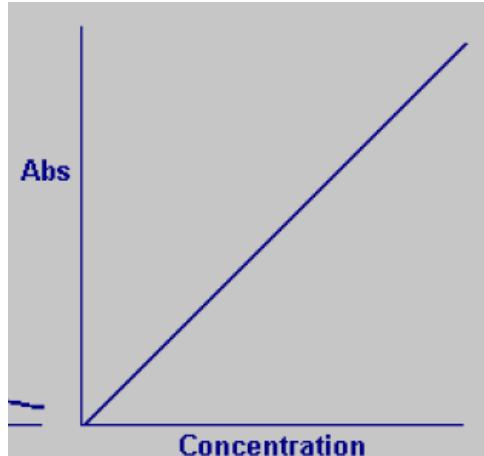


I_0 is the intensity of the incident radiation and I is the intensity of the transmitted radiation. The ratio I/I_0 is called transmittance. This is sometimes expressed as a percentage and referred to as %transmittance.

Mathematically, absorbance is related to percentage transmittance T by the expression:

$$A = \log_{10}(I_0/I) = \log_{10}(100/T) = \epsilon \times c \times L$$

Where, L is the length of the radiation path through the sample, c is the concentration of absorbing molecules in that path, and ϵ is the molar extinction coefficient - a constant dependent only on the nature of the molecule and the wavelength of the radiation. If concentration is expressed in mol/dm³ and L is expressed in dm then unit for ϵ is dm²/mol.



Absorbance vs concentration

Limitations of the Beer-Lambert law

1. The linear relationship between absorbance and concentration of solution is not observed at concentration above 10^{-2} M, hence concentrated solution do not obey Beer-Lambert's Law.
2. The law does not obeyed if the absorbing species reacts with the solvent, dissociates or associates in solution. The molecules of the absorbing species should remain as simple molecules and should not undergo any change in molecular condition.
3. The light incident on the absorbing medium should be monochromatic otherwise minor deviations from Beer-Lambert's Law are observed. Hence monochromators have to be used to produce monochromatic beams.

4. The molar absorptivity depends on the refractive index of the absorbing medium. The refractive index changes with the concentration of the absorbing medium. At high concentration these changes are considerable but at concentrations below 10^{-2} M, these changes can be neglected.
5. Temperature fluctuations and entry of stray light into the absorbing system also lead to deviations from Beer-Lambert's law.
6. The Fluorescence or phosphorescence can cause a positive deviation in % T and negative deviation for A in the system.
7. Non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band.

Ultraviolet-visible spectrophotometer

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The ratio I/I_0 is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

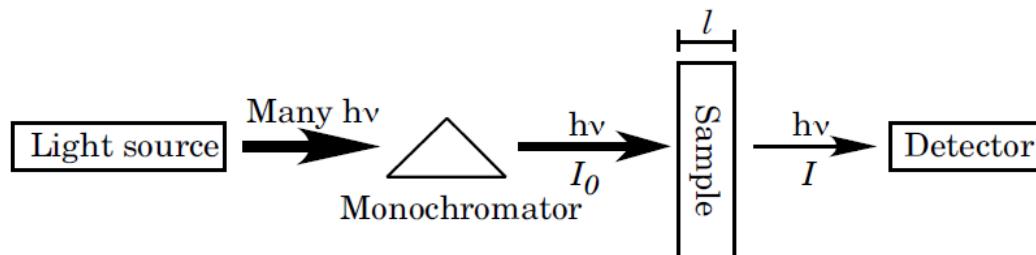
$$A = -\log(\%T/100\%)$$

The UV-visible spectrophotometer can also be configured to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_0) (such as a white tile). The ratio I/I_0 is called the reflectance, and is usually expressed as a percentage (%R).

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector.

Single beam spectrophotometer

A single beam spectrophotometer is comprised of a light source, a monochromator, a sample holder, and a detector. An ideal instrument has a light source that emits with equal intensity at all wavelengths, a monochromator that is equally efficient in splitting light into narrow groups of wavelength for all wavelengths, and a detector that is sensitive and responds equally to all wavelengths.



Light sources

Because no single light source with the appropriate characteristics exists, most spectrophotometers use two lamps, with one for the ultraviolet region and one for the visible region. The visible lamp is usually a tungsten lamp (300-2500 nm), while the ultraviolet lamp is a deuterium lamp (190-400 nm). An alternative, relatively rarely used spectrophotometers, although commonly used in other types of spectroscopic instruments, is a xenon arc lamp (160-2,000 nm).

Monochromators

Although prisms can be used as monochromators, most instruments use diffraction gratings. Light shining on the closely spaced grooves of a diffraction grating at an angle is separated into different wavelengths in a consistent manner, assuming that the grooves are consistently produced.

Detector

The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

The most commonly used detector is a photomultiplier tube (PMT). An incoming photon hits a thin metal film inside a vacuum tube. The metal film is maintained at a large negative potential, and emits electrons. These collide with a series of dynodes maintained at progressively lower potentials; each dynode emits several electrons in response to each incoming electron, resulting in a large amplification of the signal. Because the initial photon is required to initiate the process, most PMTs have very little dark current ("dark current" is signal without light). Proper functioning of a PMT requires a constant voltage across the PMT; maintaining a constant voltage in the face of a high signal requires a well-designed instrument. PMTs are wavelength dependent, with the degree of dependence being related to the metal used in the thin film; most PMTs exhibit the greatest sensitivity at ~400 nm.

An alternative type of detector uses photodiodes. Photodiodes are inexpensive but not very sensitive. Their low cost has allowed arrays of photodiodes to be set up to allow simultaneous detection of many wavelengths. In this type of spectrophotometer, the monochromator is located after the sample, so that it splits the multiwavelength light leaving the sample.

A charge coupled device (CCD) is a sensitive array detector. CCDs store charges released in response to photon impacts. Because the stored charges are stable for prolonged periods, a CCD can collect data for considerable time prior to readout of the signal. They are therefore potentially extremely sensitive. They will probably displace PMTs from some uses as their price

decreases. CCDs are used in digital cameras and other consumer products and are rapidly becoming less expensive as a result of both economies of scale and the development of improved production techniques.

Cuvettes (Sample Holder)

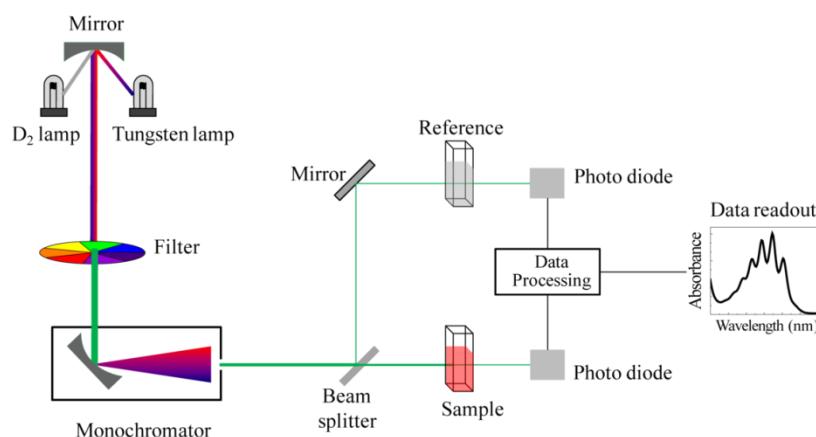
Most samples studied using visible and ultraviolet spectroscopy is liquid. The sample must therefore be placed in a transparent container to allow measurement. These containers are called cuvettes. Cuvettes are generally made from transparent plastic, glass, or quartz. Different cuvettes have different optical properties.

Working: The sample holder is filled with the solvent (blank). The absorbance value of the solvent is adjusted to zero for a particular wavelength, obtained by the rotation of the monochromator. The sample is then taken in the sample holder and its absorbance value is determined for the same wavelength. The procedure is repeated for different wavelengths obtained by the rotation of the monochromator. The absorbance values can be read either on a dial or a digital display. The λ_{max} values for the sample can be thus found.

Double Beam Spectrophotometer

A beam of visible light from an incandescent tungsten lamp passes through a colour filter which selects a narrow band of wavelengths. A mirror splits this narrow band into two beams—one passing through the sample and the other passing through the solvent (blank) hence the name Double beam Spectrophotometer.

The sample absorbs a part of beam whereas the solvent transmits it completely. The two beams then fall on the respective photocells, where photoelectrons are emitted and recorded.



Working: The solvent is first taken in both cuvettes, and zero level adjusted. The sample is then placed in the sample cuvette. It absorbs a part of the light and the transmitted beam emerging from it falls on the photodiode. This beam has less intensity than when only solvent was present in the sample cuvette. Hence there will be proportionate decrease in the electric current produced in photodiode and recorded.

Advantages of Double beam spectrophotometer over single beam spectrophotometer:

- Changes in the intensity of incident light due to voltage fluctuations in the power supply are compensated by splitting the incident beam into identical beams by the use of a mirror and two balanced photodiodes. Any error due to solvent or impurity is balanced out as identical beams pass through the blank and sample as the absorbance of blank is initially adjusted to zero.
- The readings are not affected by changes in sensitivity of photodiodes as the zero method is used.
- The scale of instrument is linear with the concentration of the sample solution.

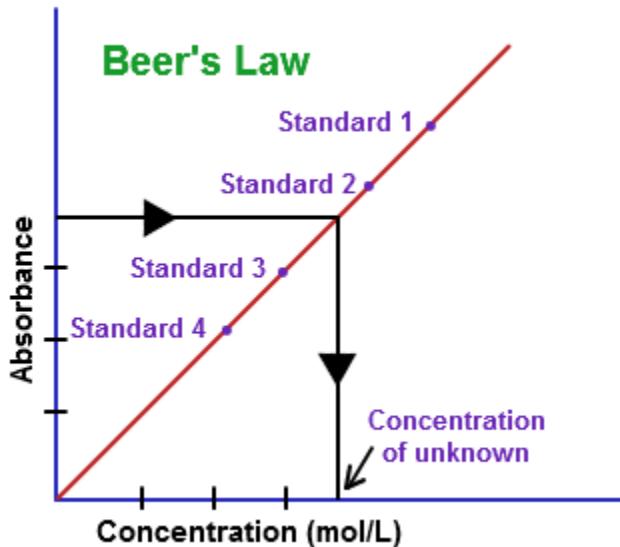
Applications:

- Determination of λ_{max} and identifying the functional groups:** It is possible to identify a particular group in a molecule by determining its λ_{max} value. In spectrophotometers, the beams of characteristic wavelength are produced, these are absorbed by sample, which are indicative of functional groups as different functional groups in the molecule absorb their own λ_{max} values.

Function group	Example	λ_{max} in nm	Solvent
-COOH	Acetic acid	208	Ethyl alcohol
-COCl	Acetyl chloride	220	Hexane
-CONH ₂	Acetamide	178	Hexane
-NO ₂	Nitromethane	201	Methyl alcohol

- Quantitative Analysis (Calibration curve method):** UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

In this, a series of solutions of different concentrations of the compound is prepared. Usually the concentrations vary from 10^{-3} M to 10^{-2} M. The absorbance is then determined for these standard solutions at the wavelength which absorbed maximally by the coloured compound (λ_{max}). A graph of absorbance versus the concentration is then plotted.



From the calibration curve the concentration of the unknown solution can be found out as shown.

- 3) **Photometric titrations:** Spectrophotometric measurements can be employed to advantage in locating the equivalence point of a titration, provided the analyte, reagent or titration product absorbs radiation. Alternatively absorbing indicator can provide the absorbance change necessary for the location of equivalence point.
- 4) A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.
- 5) UV-Vis spectroscopy is also used in the semiconductor industry to measure the thickness and optical properties of thin films on a wafer. UV-Vis spectrometers are used to measure the reflectance of light, and can be analyzed via the Forouhi-Bloemberg dispersion equations to determine the Index of Refraction (n) and the Extinction Coefficient (k) of a given film across the measured spectral range.

2. pH Metry

Definition of pH

pH is an abbreviation of “pondus hydrogenii” and was proposed by the Danish scientist S.P.L. Sørensen in 1909 in order to express the very small concentrations of hydrogen ions.

In 1909, pH was defined as the negative base 10 logarithm of the hydrogenion concentration. However, as most chemical and biological reactions are governed by the hydrogen ion activity, the definition was quickly changed. As a matter of fact, the first potentiometric methods used actually resulted in measurements of ion activity.

The definition based on hydrogen ion activity is the definition we use today:

$$\text{pH} = -\log_{10} a_{\text{H}^+}$$

pH Theory:

pH is measured using a setup with two electrodes: the indicator electrode and the reference electrode. These two electrodes are often combined into one - a combined electrode. When the two electrodes are immersed in a solution, a small galvanic cell is established. The potential developed is dependent on both electrodes. Ideal measuring conditions exist when only the potential of the indicator electrode changes in response to varying pH, while the potential of the reference electrode remains constant.

The measured voltage can be expressed by the Nernst equation in the following way:

$$E = E_{\text{ind}} - E_{\text{ref}} = E'_T - R \cdot T/F \cdot \ln a_{\text{H}^+}$$

where

E = Measured voltage (mV)

E_{ind} = Voltage of indicator electrode (mV)

E_{ref} = Voltage of reference electrode (mV)

E'_T = Temperature dependent constant (mV)

R = Gas Constant (8.3144 J/K)

T = Absolute Temperature (K)

F = Faraday's constant (96485 C)

By using the base ten logarithm, the formula can be written as:

$$E = E'_T - 2.303 \cdot R \cdot T/F \cdot \log a_{\text{H}^+}$$

By introducing the pH definition as $\text{pH} = -\log a_{\text{H}^+}$, pH can be expressed at the temperature T as follows:

$$\text{pH}_T = \text{pH}_{T^\circ} - \frac{E}{R' \cdot S \cdot T}$$

where

R' = constant = 0.1984 mV/K

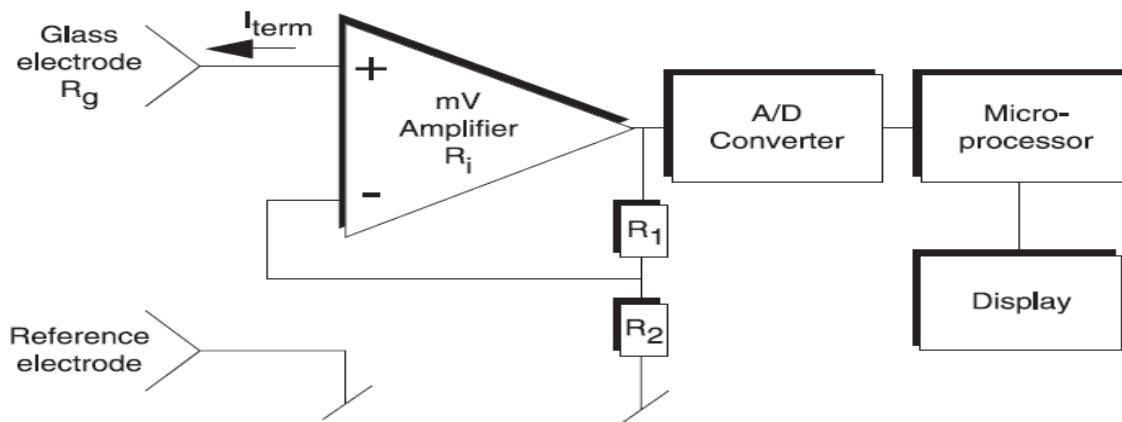
S = sensitivity, a correction factor which takes into account that the electrode response may differ from the theoretical value.

pH° = zero pH which is defined as the pH value at which the measured potential is zero. Figure 2 illustrates that the pH° will change with temperature and that another slope will be observed.

Working of pH- meter

A pH meter measures the potential difference (in mV) between the electrodes and converts it to a display of pH.

In order to obtain a correct measurement, the input amplifier and the converting circuit must meet certain requirements. The principal construction of a pH meter can be seen in the simplified diagram below.



The potential difference between the reference electrode and the glass electrode is amplified in the mV amplifier before the A/D converter feeds the signal to the microprocessor for result calculation. To attain reliable and consistent results, the amplifier and other circuits must have a small temperature coefficient, i.e. the influence of temperature variations must be under control.

Normally, the result is displayed in numeric form although a few pH meters with pointers are still available. The term analog or digital pH meter is often used to distinguish between these two forms of display. However, it is also used to differentiate between control convert circuitry in analog or digital form.

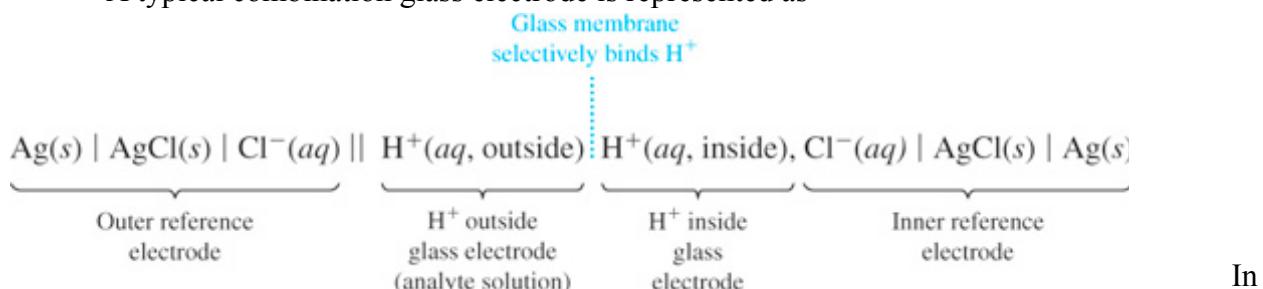
In an analog pH meter, the adjustment of zero pH and sensitivity is carried out using adjustable resistances (dials) and the amplification factor is under direct manual control. The signal is then sent through an A/D converter. The output is a digital signal for the numeric display.

In a digital pH meter, the amplifier works under the same conditions all the time and is directly connected to an A/D converter. The converter's output is then manipulated by digital circuitry (microprocessor-based) and the calculated pH is then displayed. Use of a temperature sensor provides both temperature correction and a temperature display.

To Measure pH of solution i.e. Measurement of pH:

A pH measurement system consists of a pH probe, reference probe, temperature sensor, pH meter and the sample to be measured. In most cases the three probes are combined in one electrode. When the pH probe is in contact with a solution a potential forms between the pH probe and the reference probe. The meter measures the potential and converts it, using the calibration curve parameters, into a pH value.

A typical combination glass electrode is represented as



In order to measure the pH of a sample first the standardization of pH meter is required to be done before analyzing the sample.

a) Standardization of pH meter:

A two point standardization method is used to standardize the pH meter, it involves immersing the pH assembly i.e. glass electrode into a standard reference pH buffer ($\text{pH} = 4.0$) and recording the reading, if the meter reading is more or less than the expected value (4.0) then it is adjusted to pH 4.0 using a crew nob.

Standardization at only one pH value does not assure the validity of reading at other pH values considerably. Hence a second standard reference buffer $\text{pH} = 9.2$ is used. The pH meter reading is recorded using this second buffer solution and the reading is adjusted to pH 9.2 using a crew nob.

During both the steps, the glass electrode is rinsed with distilled water. Immerse the glass electrode previously in water for several hours. Start the measurement more than 5 minutes after switching on. Rinse well the detecting unit with water, and blot the water gently with a piece of filter paper very time.

b) To measure pH of solution:

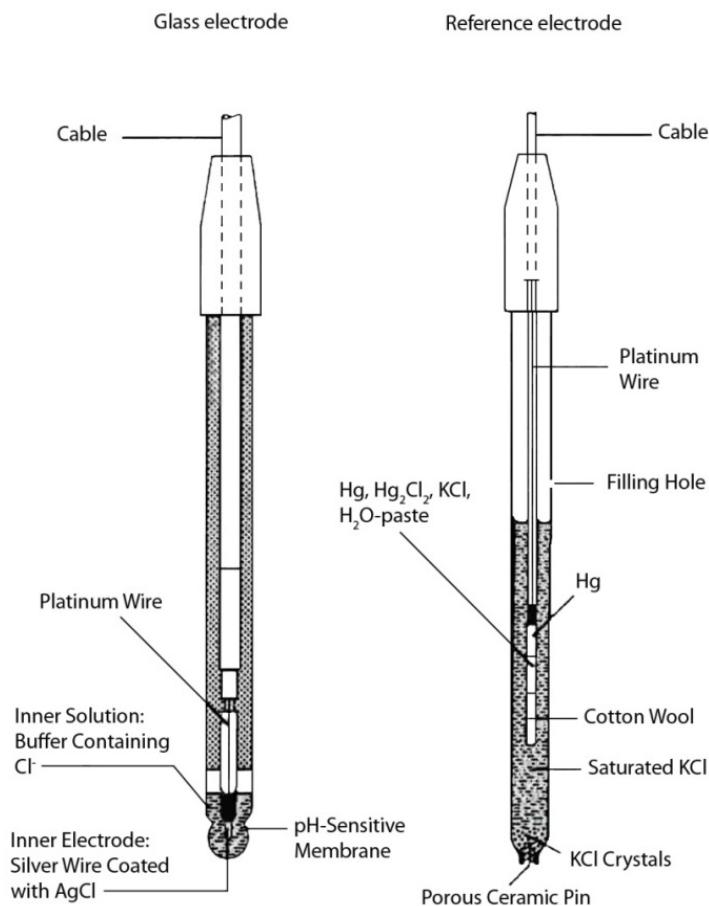
Wash well the detecting unit with water, and blot the water gently with a piece of filter paper. Place glass electrode in solution you wish to measure pH. Be sure that it is stirring slowly during measure and pH adjustment and take readings.

c) Precautions:

When analysis is complete, put pH meter in stand-by mode. Remove electrode from solution and rinse thoroughly with water. Blot dry and put back in yellow pH storage buffer. Place parafilm over the hole and around the bottle to minimize evaporation.

Glass Electrode:

Construction: It consists of a glass bulb membrane, which gives it its name and an electrically insulating tubular body, which separates an internal solution and a silver/silver chloride electrode from the studied solution. The Ag/AgCl electrode is connected to a lead cable terminated with some connector that can hook up to a special voltmeter, the pH meter. It is represented as $\text{Ag/AgCl} \mid \text{HCl} \mid \text{glass} \parallel \text{probed solution} \mid \text{reference electrode}$



Working: The pH meter measures the potential difference and its changes across the glass membrane. The potential difference must be obtained between two points; one is the electrode contacting the internal solution. A second point is obtained by connecting to a reference electrode, immersed in the studied solution.

The potential difference relevant to pH measurement builds up across the outside glass/solution interface.

$$E_{\text{glass wall/solution}} = E_o - RT/2.303F \log a(\text{H}_3\text{O}^+)$$

Where R is the molar gas constant 8.314 J mol⁻¹ K⁻¹, T is the temperature in kelvins, F is the Faraday constant 96,485.3 C

$$E_{\text{glass}} = E_0 - 0.59 \times \log[H^+]$$

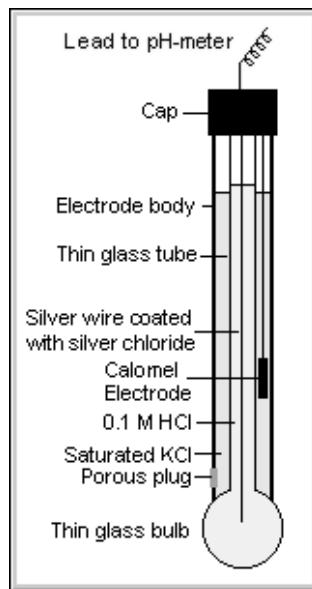
Reference Electrode:

The reference electrode is a silver wire coated with silver chloride in contact with a defined electrolyte solution, see above figure. In many reference electrodes a gel is used instead of a liquid as the internal filling. These gels also contain KCl to maintain the reference potential and add sufficient conductivity. As described in 2.2 the reference potential is constant as long as the internal electrolyte is constant. The reference potential also varies slightly with temperature.

The tube containing all the reference elements and solutions/gel is in contact with the sample to measure through a junction (diaphragm). It is essential to maintain a free flow of ions through the junction. Otherwise the reference electrode will not respond properly to pH changes in the sample.

$$E_{\text{ref}} = E_0 - 0.59 \times \log[\text{Cl}^-]$$

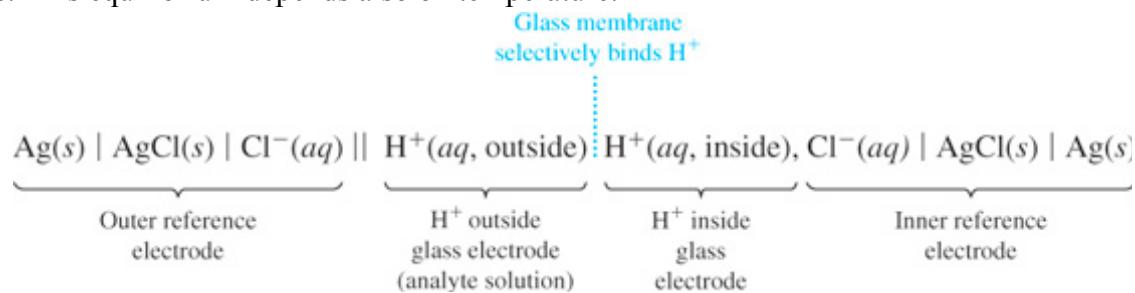
Combination Electrode:



Construction: The fig. shows the internal components of the pH electrode. The heart of the electrode is a thin bulb of pH-sensitive glass, which is blown onto the end of a length of glass tubing. The pH-sensitive glass (glass membrane) is sealed to the electrode and contains a solution of potassium chloride at pH 7. A silver wire plated with silver chloride contacts the solution. The Ag/AgCl combination in contact with the filling solution sets an internal reference potential. This potential depends on the chloride concentration in the filling solution and as long as this electrolyte concentration is maintained, the electrode potential is constant.

Working: The outside surface of the glass membrane is in contact with sample being measured and the inside surface contacts the filling solution. A complex mechanism at each glass liquid interface defines the potential the pH glass electrode, while the inner pH glass/ filling

solution potential is constant, the outside potential varies based on the H^+ ions concentration in sample. This equilibrium depends also on temperature.



3. Conductometry

Conductometry is general method, where two electrode systems are used for simultaneous measurement of all electroactive compounds in a solution. It is a measurement of electrolytic conductivity to monitor a progress of chemical reaction.

Conductometric Titration:

Conductance is a property of solutions of electrolytes. It is the measure of the number of ions present in the solution, as well as the current carrying capacity of the ions. When the solution contains one single electrolyte, the measured conductance of the solution can be related to concentration of the electrolyte.

Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added. The equivalence point is the point at which the conductivity undergoes a sudden change. Marked increase or decrease in conductance is associated with the changing concentrations of the two most highly conducting ions, viz. the hydrogen and hydroxyl ions. The method can be used for titrating coloured solutions or homogeneous suspension e.g.: wood pulp suspension, which cannot be used with normal indicators.

Principle:

When solution of one electrolyte is added to another electrolyte without appreciable volume change, the conductance of the solution will alter, if an ionic reaction occurs. If no ionic reaction takes place then the conductance of the solution will simply increase. On the other hand, if an ionic reaction occurs, the ion added may replace another ion and hence bring about change in the conductance.

Let A^+B^- be the ions of titrand and C^+D^- be ions of the titrant, the ionic reaction in the titration is combination of A^+ and D^- , AD formed may be insoluble or weakly ionized.



Thus as the titration proceeds, A^+ are replaced by C^+ . The conductance of the solution increases or decreases depending on whether conductance of C^+ is greater than or less than that of A^+ . After equivalence point the ionic reaction does not occur and hence, the conductance of the solution will raise due the excess addition of titrant C^+D^- .

The principle of conductometric titration is changes in the conductance of the solution due to difference in the ionic conductance or due to production of more number of ions in the solution. Both factors permit, location of the equivalence point by conductance measurements.

Procedure:

A definite volume of the solution to be estimated is pipetted out in a beaker. A dip type conductivity cell is place in a beaker. Addition of distilled water may be necessary if the cell does not dip completely in the solution. The cell is connected to a conductometer and the conductance of the solution is measured. The titrant is filled in the burette. The titrant is added in the small portions, generally 0.5 mL at a time. The solution is stirred after each addition. The

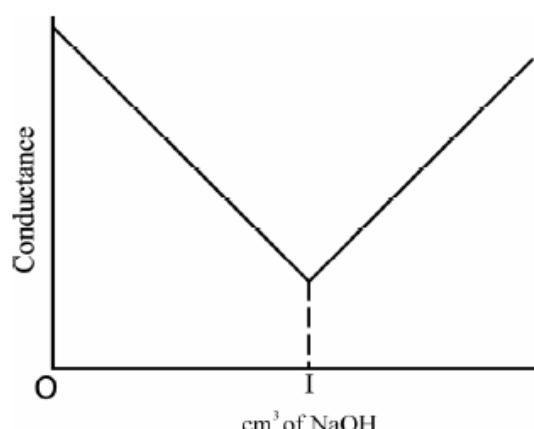
solution is allowed to stand for a minute or two after stirring before conductance is measured. Addition of titrant is continued till about seven to eight readings beyond the equivalence point are obtained. The plot of conductance against volume of the titrant added is used to locate the equivalence point.

Titration Curves:

Some Typical Conductometric Titration Curves are:

1) Strong Acid with a Strong Base, [HCl Vs NaOH]

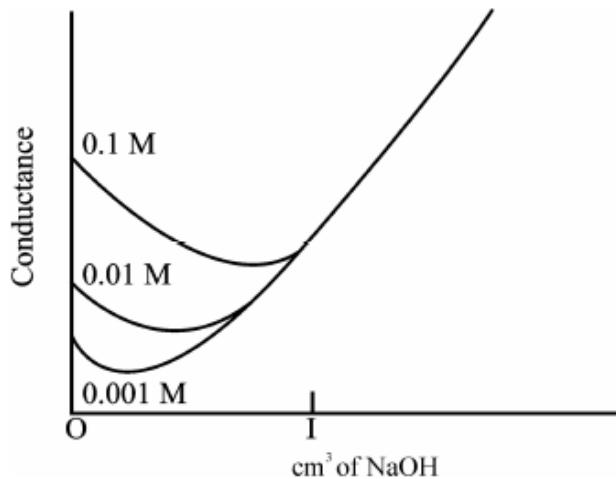
Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH^- ions



Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

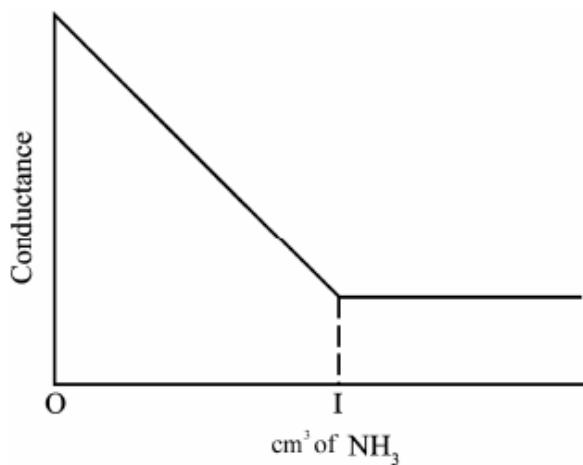
2) Weak Acid with a Strong Base, [CH₃COOH Vs NaOH]

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH₃COOH to CH₃COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH₃COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH-ions.



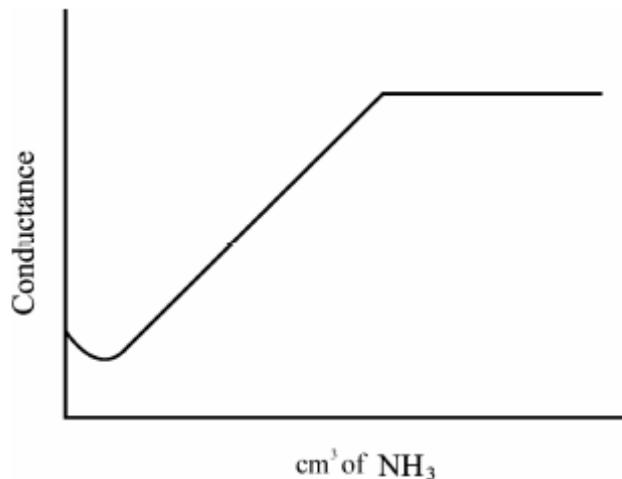
Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

- 3) Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia:** Initially the conductance is high and then it decreases due to the replacement of H+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.



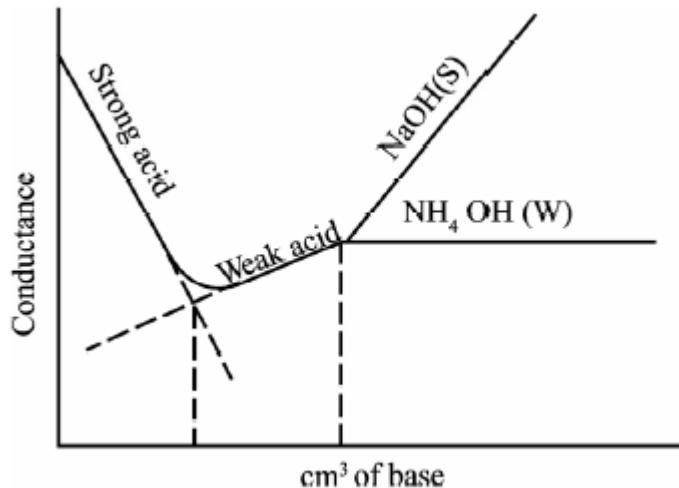
Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_3OH)

- 4) Weak Acid with a Weak Base:** The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting.



Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH₄OH)

- 5) **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base:** In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH⁻ ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to Fig.



Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH₃COOH) vs. a strong base (NaOH) or a weak base (NH₄OH)

Advantages of Conductometric titrations:

Conductometric titration are found to possess several advantages over normal titrimetry namely,

1. Coloured solutions can be titrated.
2. The method works equally well for dilute solutions also, as it is based on the changes in the conductance, rather than the absolute value of the conductance.
3. In conductometric titrations, it is not necessary to make observations around the equivalence point, with small increments of the titrant added. The observations, far away from the equivalence point, on either side are of importance.
4. An extremely weak acid or a weak base can be titrated conductometrically, which may not be possible in normal titrimetry.
5. A mixture of weak and strong acids, can also be titrated with relative ease. Thus, making the simultaneous determination possible.

Limitations:

1. In dilute solutions, obtuse curves are obtained. With obtuse curves it is difficult to locate the equivalence point accurately.
2. The overall accuracy of the conductometric titrations is limited as the technique does not permit addition of small increments of the titrant.

4. IR spectroscopy

In contrast to ultraviolet spectroscopy IR spectrum provides a rich array of absorption bands which can provide accurate structural information about a molecule. It provides the methods for studying materials in all three physical states i.e. solid, liquid and gas. Analytically useful IR spectrum covers the following range of electromagnetic spectrum.

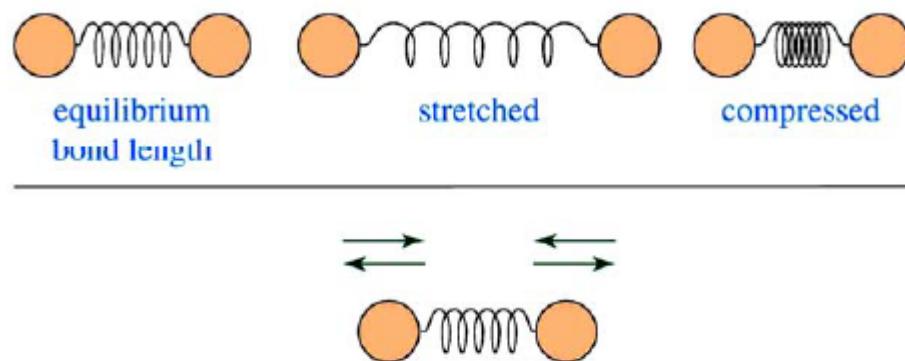
Near IR 15000 cm^{-1} to 3000 cm^{-1}

Mid IR 4000 cm^{-1} to 400 cm^{-1}

Far IR 200 cm^{-1} to 10 cm^{-1}

Most used 4000 cm^{-1} to 670 cm^{-1}

Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms. Specific bonds respond to (absorb) specific frequencies.

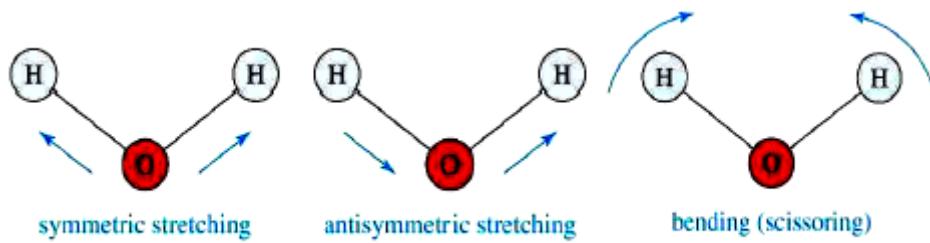


VIBRATIONAL MODES:

The information contained in IR spectrum originates from molecular vibrations. These are either fundamental vibrational modes that are associated with the vibrations of specific functional group, or molecule, vibrational overtones or summational modes of fundamental vibrations.

A molecule resembles a system of balls of varying masses corresponding to atoms of a molecule and spring of varying lengths corresponding to various chemical bonds. There are two fundamental vibrational modes.

1. **Stretching:** in which the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.
2. **Bending:** in which the position of the atom changes relative to the bond axis. Covalent bonds can vibrate in several modes, including stretching, rocking, and scissoring.



The various stretching and bending vibrations occur at certain frequencies. When an IR radiation of same frequency is incident on the molecule, the energy is absorbed and the amplitude of that vibration increases correspondingly. When the molecule returns to ground state the absorbed energy is released as heat.

A nonlinear molecule containing n atoms has $3n-6$ possible vibrational modes through which IR radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule.

Which substances give a signal in IR spectrum?

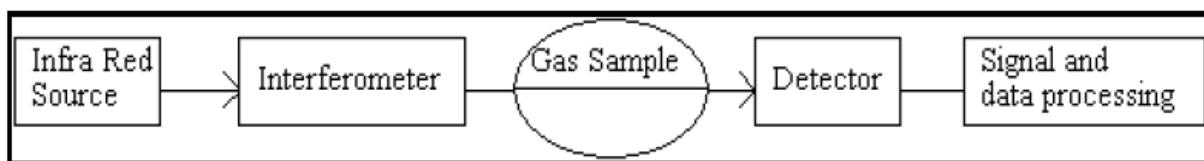
Ans: The molecules that contain polar bonds i.e. molecules composed of atoms of different elements, organic compounds and inorganic compounds (H_2O , CO_2 , NO_2 , HCl , salts...) can give a signal in IR spectrum. Whereas pure chemical elements in molecular or crystal state e.g. Ar , O_2 , O_3 , N_2 , Cl_2 , S_8 , silicon, graphite, Diamond etc cannot give a signal in IR spectrum.

Basic Principle:

When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called infrared spectrum of the material. Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorption it is possible to determine whether various chemical groups are present or absent in a chemical structure.

Instrumentation of FTIR:

The basic components of an FTIR are shown schematically in fig.



1. **The Source:-** Infrared energy is emitted from a glowing black body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. **The Interferometer:-** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. **The Sample:-** The gaseous sample can be directly analysed. Liquid can also be used directly but in diluted form in NaCl plates. Solid compound can be mixed with KBr and formed a pallet and used.

The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. **The Detector:-** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

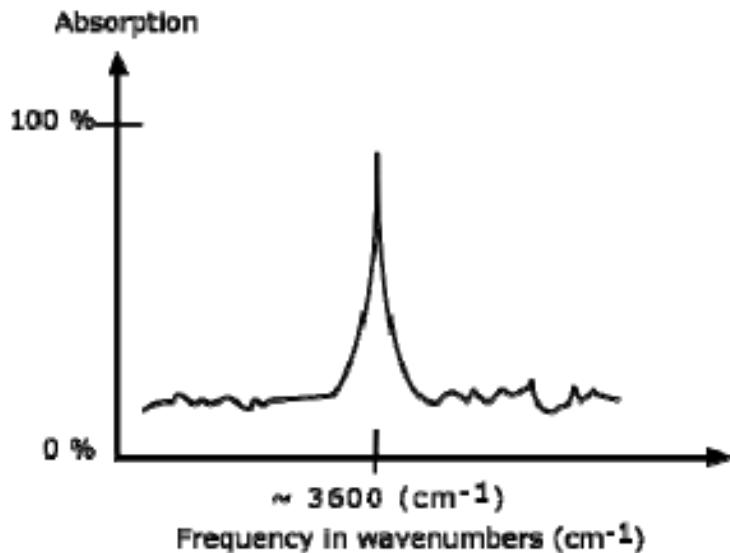
5. **The Computer:-** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Working:

The infrared source emits a broad band of different wavelength of infrared radiation. The IR source used is a SiC ceramic at a temperature of 1550 K. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse Fourier transform on entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally, the intensity of the IR beam is detected by a detector, which is a liquid nitrogen cooled MCT (Mercury–Cadmium–Telluride) detector. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

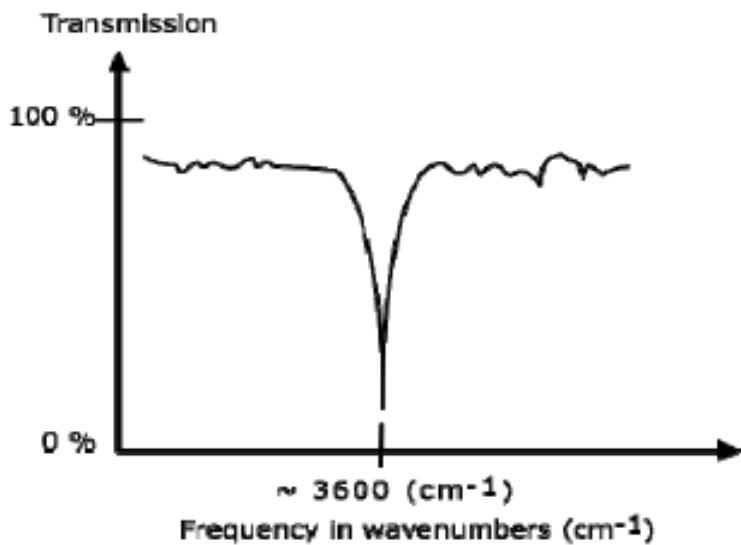
AN IR SPECTRUM IN ABSORPTION MODE:

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs intensity of the transmission (or absorption). Frequencies appear in the x-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the y-axis in percentage units.



The graph above shows a spectrum in absorption mode.

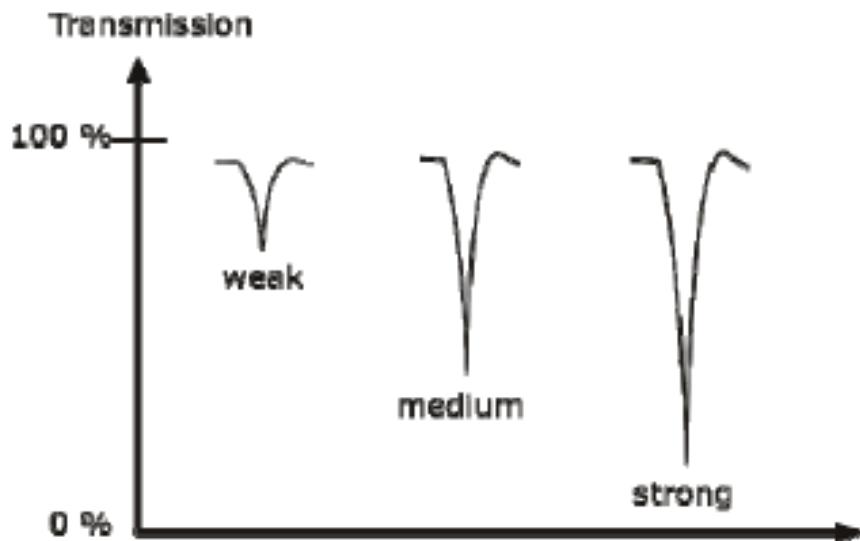
AN IR SPECTRUM IN TRANSMISSION MODE:



The graph above shows a spectrum in transmission mode. This is the most commonly used representation and the one found in most chemistry and spectroscopy books.

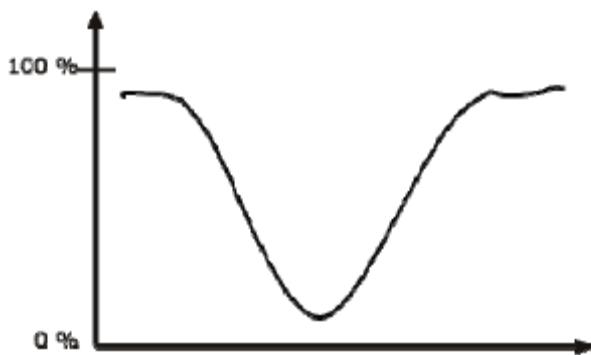
CLASSIFICATION OF IR BANDS

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.



Infrared band shapes come in various forms. Two of the most common are narrow and broad. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



INFORMATION OBTAINED FROM IR SPECTRA

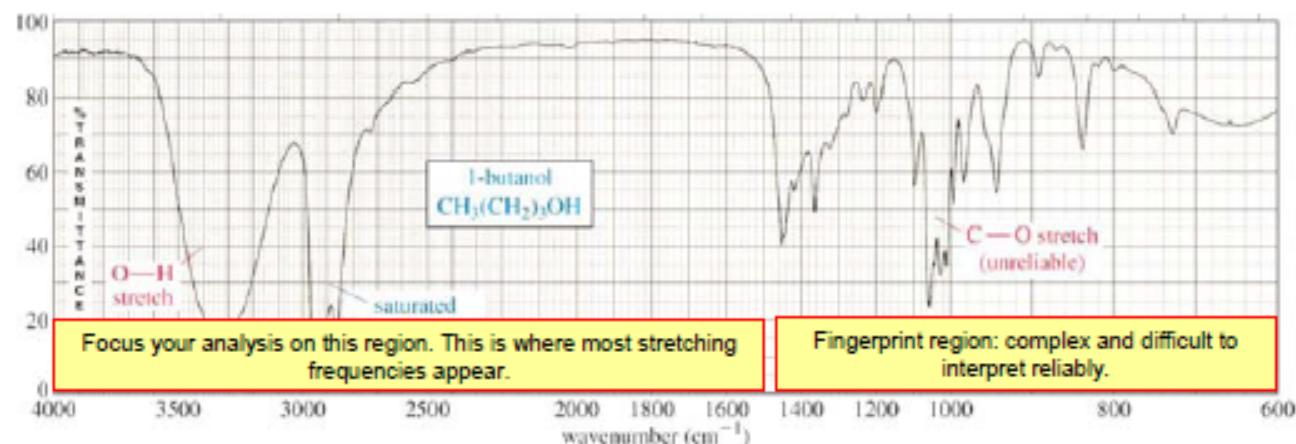
- IR is most useful in providing information about the presence or absence of specific functional groups.
- IR can provide a molecular fingerprint that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR does not provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the $600 - 1400 \text{ cm}^{-1}$ range is called the fingerprint region.

This is normally a complex area showing many bands, frequently overlapping each other.

It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.



FUNCTIONAL GROUPS AND IR TABLES:

Characteristic IR Absorption Frequencies of Organic Functional Groups

Functional Group	Type of Vibration	Characteristic Absorptions (cm^{-1})	Intensity
Alcohol			
O-H	(stretch, H-bonded)	3200-3600	strong, broad
O-H	(stretch, free)	3500-3700	strong, sharp
C-O	(stretch)	1050-1150	strong
Alkane			
C-H	stretch	2850-3000	strong
-C-H	bending	1350-1480	variable
Alkene			
=C-H	stretch	3010-3100	medium
=C-H	bending	675-1000	strong
C=C	stretch	1620-1680	variable
Alkyl Halide			
C-F	stretch	1000-1400	strong

C-Cl	stretch	600-800	strong
C-Br	stretch	500-600	strong
C-I	stretch	500	strong
Alkyne			
C-H	stretch	3300	strong, sharp
-C≡C-	stretch	2100-2260	variable, not present in symmetrical alkynes
Amine			
N-H	stretch	3300-3500	medium (primary amines have two bands; secondary have one band, often very weak)
C-N	stretch	1080-1360	medium-weak
N-H	bending	1600	medium
Aromatic			
C-H	stretch	3000-3100	medium
C=C	stretch	1400-1600	medium-weak, multiple bands
Analysis of C-H out-of-plane bending can often distinguish substitution patterns			
Carbonyl	Detailed Information on Carbonyl IR		
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Ether			
C-O	stretch	1000-1300 (1070-1150)	strong
Nitrile			
CN	stretch	2210-2260	medium
Nitro			
N-O	stretch	1515-1560 & 1345-1385	strong, two bands

IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)

Functional Group	Type of Vibration	Characteristic Absorptions (cm ⁻¹)	Intensity
------------------	-------------------	--	-----------

Carbonyl			
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Acid			
C=O	stretch	1700-1725	strong
O-H	stretch	2500-3300	strong, very broad
C-O	stretch	1210-1320	strong
Aldehyde			
C=O	stretch	1740-1720	strong
=C-H	stretch	2820-2850 & 2720-2750	medium, two peaks
Amide			
C=O	stretch	1640-1690	strong
N-H	stretch	3100-3500	unsubstituted have two bands
N-H	bending	1550-1640	
Anhydride			
C=O	stretch	1800-1830 & 1740-1775	two bands
Ester			
C=O	stretch	1735-1750	strong
C-O	stretch	1000-1300	two bands or more
Ketone			
acyclic	stretch	1705-1725	strong
cyclic	Stretch	3-membered - 1850 4-membered - 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705	strong
, -unsaturated	Stretch	1665-1685	strong
aryl ketone	Stretch	1680-1700	strong

How to analyse the IR spectrum?

When analysing the IR spectrum of an unknown molecule, first efforts on determining the presence or absence of a few major functional groups. The C=O, O-H, N-H, C-O, C=C, $\text{C}\equiv\text{C}$, -CN, and NO₂ peaks. These peaks are most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C-H absorption near 3000cm⁻¹, almost all the compounds have these absorptions.

Follow the steps

1. **Is carbonyl group is present?** The C=O group give rise to a strong absorption in the region 1820-1660 cm⁻¹. The peak is often strongest in the spectrum and of medium width.

2. **If C=O is present**, then check the following types

3.

Acids	Is O-H also present? Broad absorption near 3400-2400cm ⁻¹ usually overlaps with C-H
Amides	Is N-H also present? Medium absorption near 3400cm ⁻¹ , sometimes double peaks with same size.
Esters	Is C-O present? Strong intensity absorption near 1300-1000cm ⁻¹
Anhydrides	Two C=O absorption near 1810 and 1760cm ⁻¹
Aldehydes	Is aldehyde C-H present? Two weak absorption near 2850 and 2750 cm ⁻¹
Ketones	The preceding five choices have been eliminated

4. **If C=O absent**, then check the following options

Alcohols, Phenols	Check for O-H, broad absorption near 3400-3300cm ⁻¹ , confirm this by finding C-O near 1300-1000cm ⁻¹
Amines	Check for N-H, Medium absorptions near 3400cm ⁻¹
Ethers	Check for C-O near 1300-1000cm ⁻¹ and absence of O-H near 3400cm ⁻¹

5. **Double bonds and/or aromatic rings**

1. C=C is weak absorption near 1650cm ⁻¹
2. Medium strong absorption in the region 1600-1450cm ⁻¹ , these often imply on aromatic ring
3. Confirm the double bond or aromatic ring by consulting the C-H region; aromatic and vinyl C-H occurs to left of 3000cm ⁻¹ , aliphatic C-H occurs to right of this value.

4. **Triple bonds**

1) C≡N is medium sharp absorption near 2250cm ⁻¹
2) C≡C is e weak, sharp absorption near 2150cm ⁻¹
3) Check also for acetylenic C-H near 3300cm ⁻¹

5. **Nitro groups**

Two strong absorption at $1600\text{-}1530\text{cm}^{-1}$ and $1390\text{-}1300\text{cm}^{-1}$

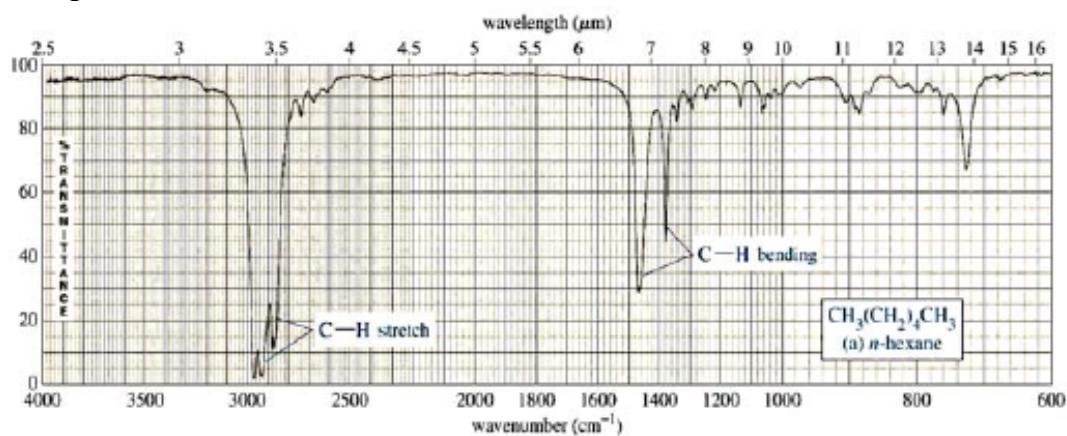
6. Hydrocarbons

None of the preceding found.

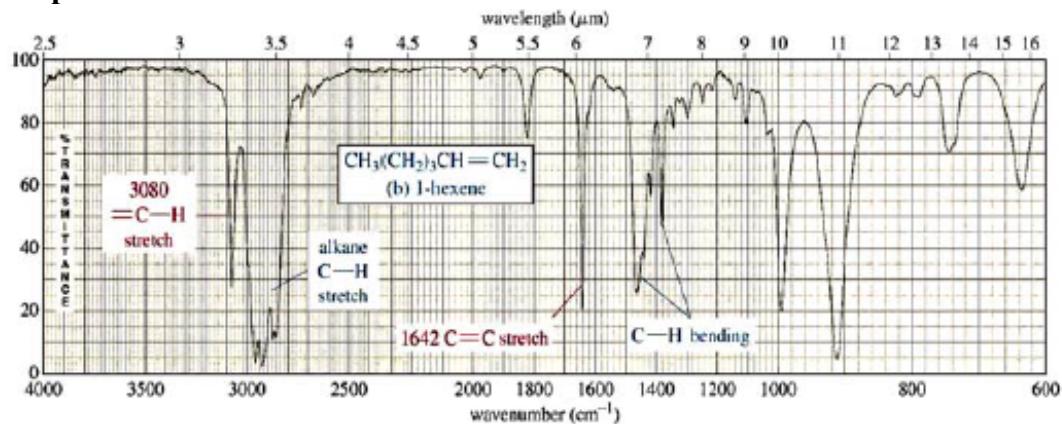
Major absorptions are in C-H region near 3000cm^{-1}

Very simple structure the only another absorption appear near 1460 and 1375cm^{-1}

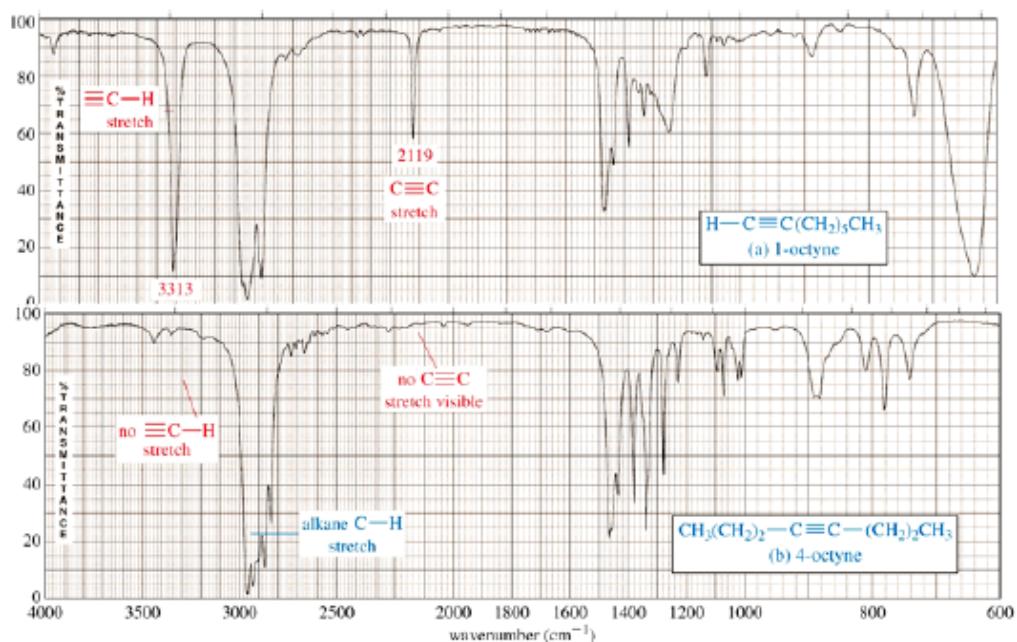
IR spectrum of n-Hexane



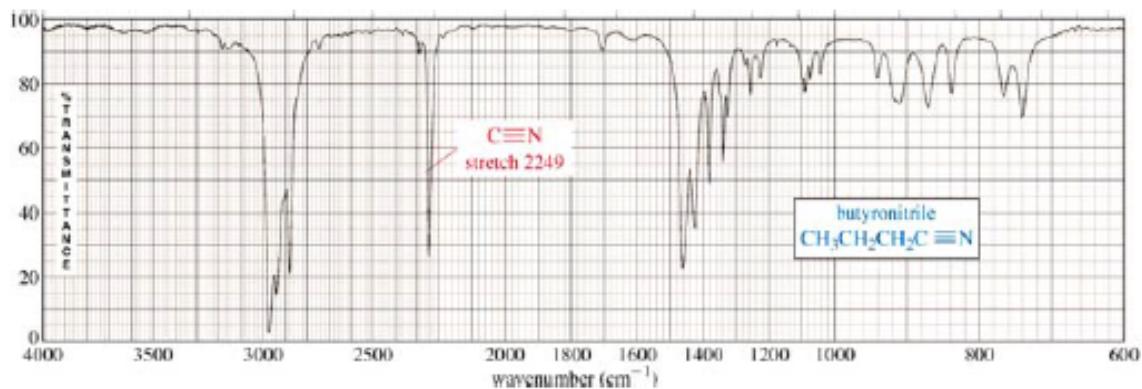
IR spectrum of 1-Hexene



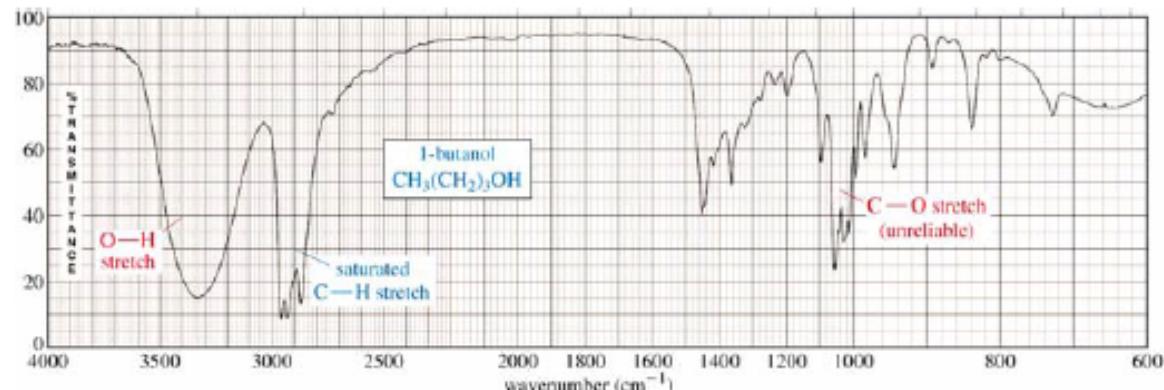
IR spectrum of 1-Octyne and 4-Octyne



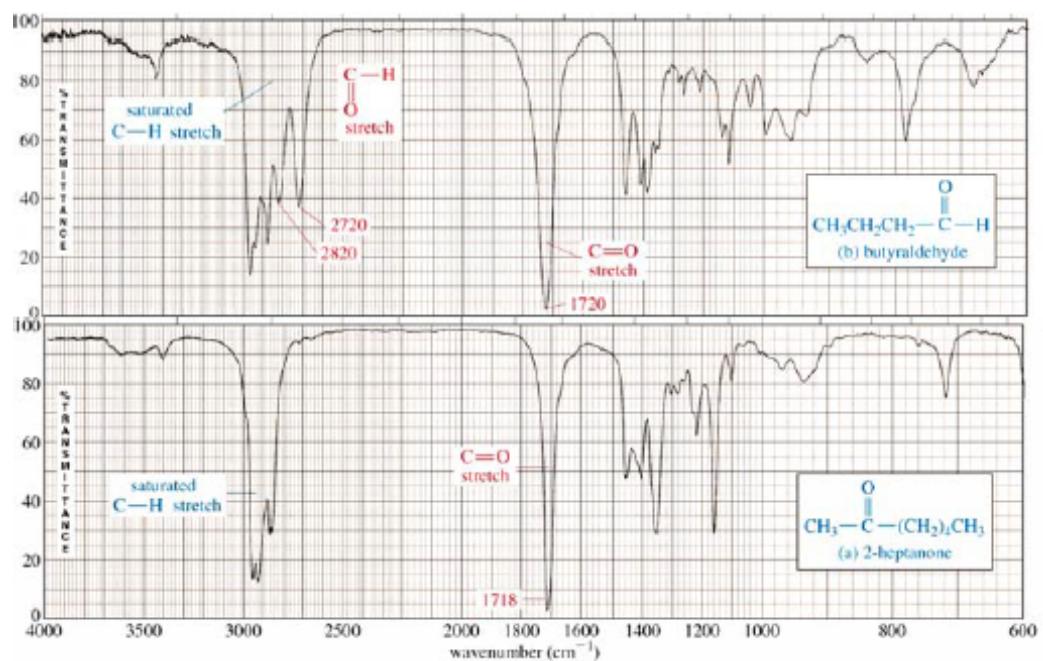
IR spectrum of Butyronitrile



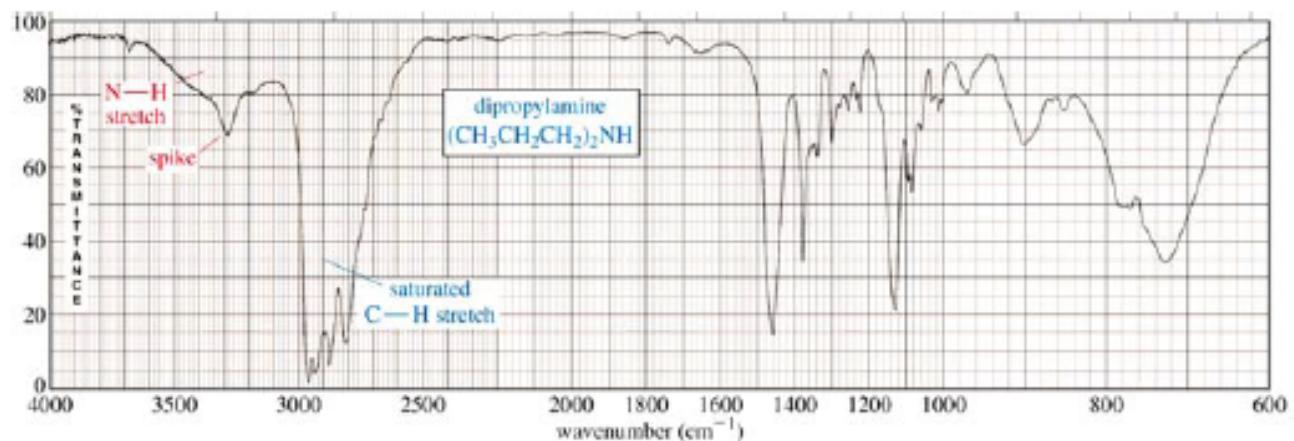
IR spectrum of 1-Butanol



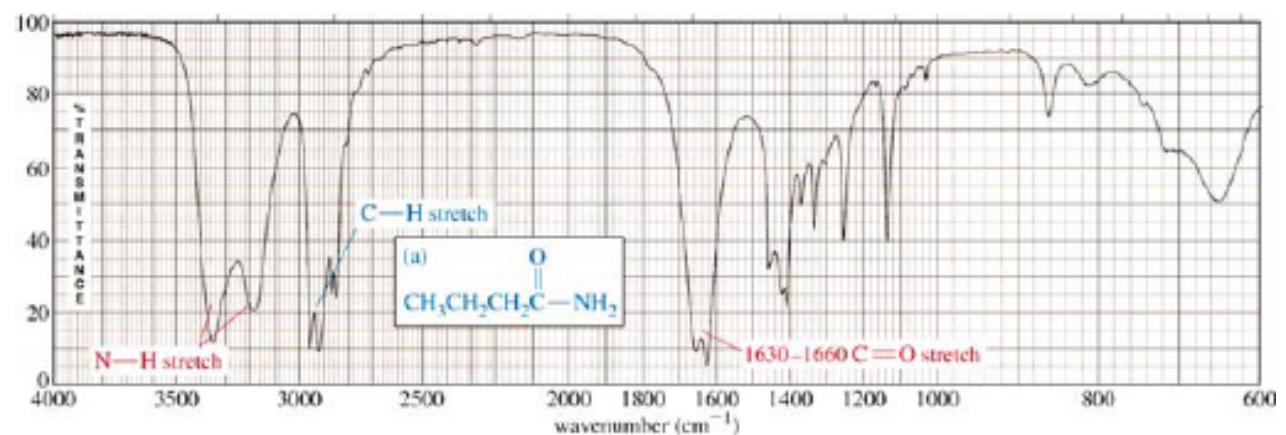
IR spectrum of 1-Butanal and 2-Heptanone



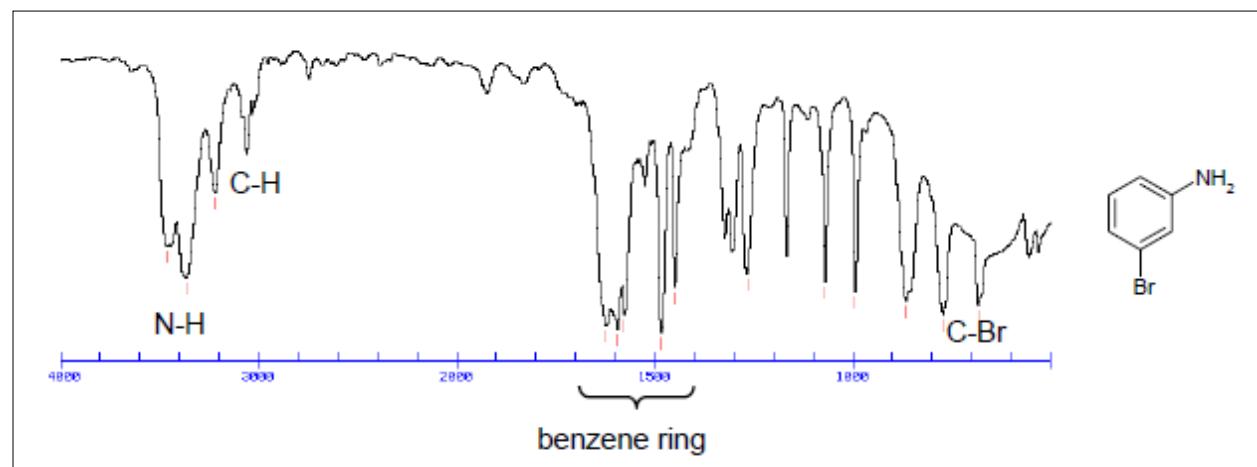
IR spectrum of n-Hexanoic acid



IR spectrum of 1-Butanamide



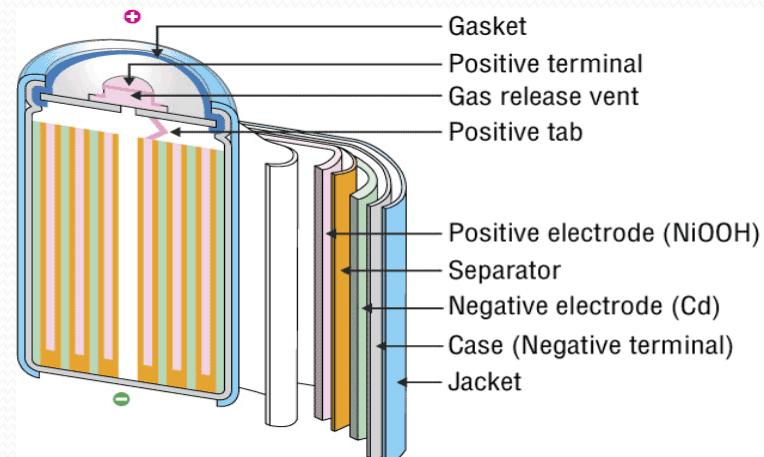
IR spectrum of 3-Bromoaniline



NICKEL-CADMIUM AND Li-ion BATTERY

INTRODUCTION

- The nickel–cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. Ni-Cd batteries are made in a wide range of sizes and capacities.
- Nickel(hydroxide)-cadmium systems are the most common small rechargeable battery type for portable appliances. The sealed cells are equipped with “jelly roll” electrodes, which allow high current to be delivered in an efficient way. These batteries are capable of delivering exceptionally high currents, can be rapidly recharged hundreds of times, and are tolerant of abuse such as over discharging or overcharging.
- It produces a voltage of about 1.4 V



INVENTIONS AND SCOPE

- Nickel-cadmium (NiCd)
- Invented by Waldemar Jungner in 1899. Developments were slow, but in 1932, advancements were made to deposit the active materials inside a porous nickel-plated electrode. Further improvements occurred in 1947 by absorbing the gases generated during charge, which led to the modern sealed NiCd battery.
- For many years, NiCd was the preferred battery choice for two-way radios, emergency medical equipment, professional video cameras and power tools. In the late 1980s, the ultra-high capacity NiCd rocked the world with capacities that were up to 60 percent higher than the standard NiCd.
- Since the disposal of battery is hazardous to environment alternative cells are being used such as paper battery

RECENT TRENDS

The primary trade-off with Ni-Cd batteries is their higher cost and the use of cadmium. This heavy metal is an environmental hazard, and is highly toxic to all higher forms of batteries.

Recently, nickel-metal hydride and lithium-ion batteries have become commercially available and cheaper, the former type now rivaling Ni-Cd batteries in cost..

The batteries are more difficult to damage than other batteries, tolerating deep discharge for long periods.

Ni-Cd batteries typically last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries such as lead/acid batteries.

Compared to lead-acid batteries, Ni-Cd batteries have a much higher energy density.

In consumer applications, Ni-Cd batteries compete directly with alkaline batteries. A Ni-Cd cell has a lower capacity than that of an equivalent alkaline cell, and costs more.

The capacity of a Ni-Cd battery is not significantly affected by very high discharge currents.

CELL REPRESENTATION AND CELL REACTION

A typical Ni-Cd battery is represented as



Cell reaction while discharging

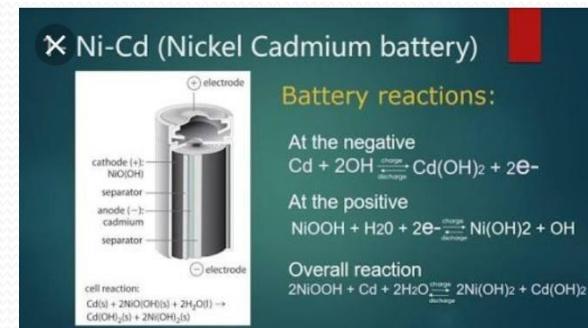
At Anode: oxidation of Cd metal



At cathode: reduction of NiO(OH)



Net Cell reaction:



ADVANTAGES

- Fast and simple charging process
- It is compact and lighter than traditional batteries
- It has a longer life than lead storage batteries
- Available in a wide range of sizes and performance options
- Good low-temperature performance
- Only battery that can be ultra-fast charged with little stress

LIMITATIONS

- It is rather more expensive than a lead storage battery
- It has a lower energy density value
- Cadmium is a toxic metal. Cannot be disposed of in landfills
- Memory effect; needs periodic full discharges
- High self-discharge; needs recharging after storage

APPLICATIONS

- Ni-Cd cells are popularly used in many appliances because they are available in variety of sizes and capacities.
- Few examples are:
 - ❖ Calculators
 - ❖ Electronic flash units
 - ❖ Transistors
 - ❖ Cordless appliances



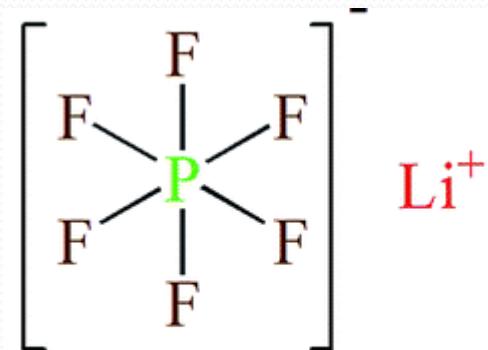
LI-ION BATTERY DESCRIPTION



- A lithium-ion battery or Li-ion battery (abbreviated as LIB) is a type of rechargeable battery in which lithium ions move from the **negative electrode to the positive electrode during discharge** and back when charging.
- The electrolyte, which allows for ionic movement, and the two electrodes are the constituent components of a lithium-ion battery cell.

ELECTROLYTES

- Role-
 1. Ion conduction between cathode and anode.
 2. They are generally, Lithium salts dissolved in organic solvent.
- Commercial electrolytes: in Carbonate solvent.



ANODE MATERIALS

- Requirements:
 1. Large capabilites of adsorption.
 2. High efficency of charge/discharge.
 3. Low reactivity against electrolyte.
 4. Fast reaction rate.
 5. Low cost
 6. Environment friendly
- Commercial anode materials:

Hard Carbon, Graphite

CATHODE MATERIALS

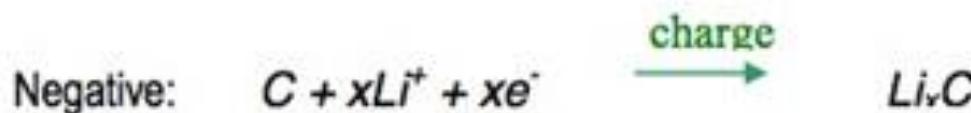
- Requirements:
 1. A high discharge voltage
 2. A high energy capacity
 3. A high power density
 4. Light weight
 5. Low self discharge
 6. Environment friendly
- Commercial cathode materials:
LiCoO₂, LiFePO₄ etc.

CHEMICAL REACTIONS

- Main essential components...
- Anode: Graphite [carbon] - C(s)
- Cathode: Lithium Cobalt Oxide - LiCoO₂
- Electrolyte: Typically a combination of lithium salts - LiPF₆, LiBF₄, or LiClO₄, in an organic solvent, such as either.
- Separator: The separator is a very thin sheet of micro perforated plastic. - CH₂=CHCl

REACTIONS WHILE CHARGING

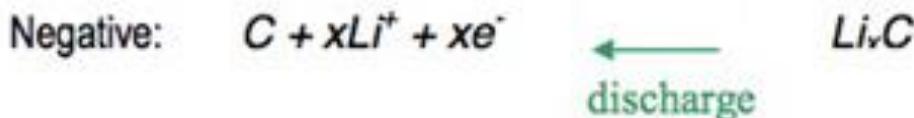
- On charge the positive electrode, cathode, material is oxidized, Li^+ ions are de-intercalated from the layered lithium LiCoO_2 , pass across the electrolyte and are intercalated between the graphite layers in graphite by an electrochemical reduction reaction proceeding at the negative electrode.



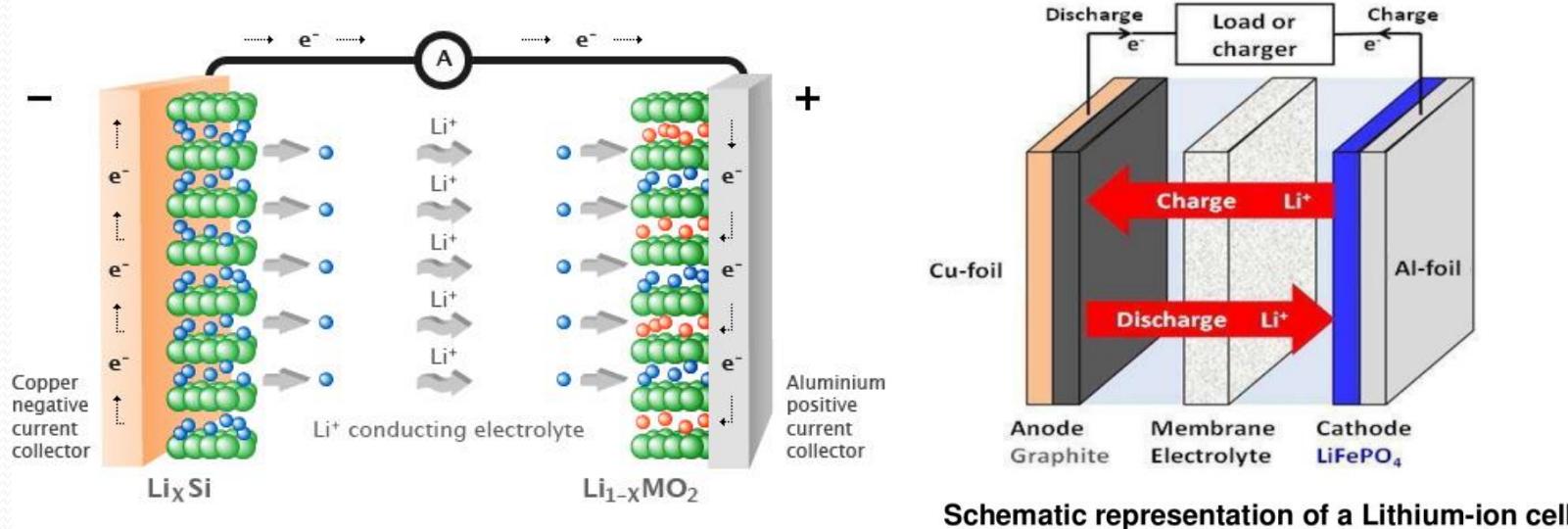
XX= Various Combining elements including Cobalt and Manganese

REACTIONS WHILE DISCHARGING

- When the cell is discharged, an oxidation reaction occurs at the negative electrode, Li⁺ ions are de-intercalated from the anode and migrate across the electrolyte to be re-intercalated into the cathode material, due to charge balance the equivalent number of electrons travel through the external circuit. A simultaneous electrochemical reduction reaction proceeds at the positive electrode and accepts electrons from the external circuit, Li⁺ ions from the electrolyte, to reform the starting material. A change from electronic current to ionic current occurs at the electrode



XX= Various Combining elements including Cobalt and Manganese



Schematic representation of a Lithium-ion cell



XX= Various Combining elements including Cobalt and Manganese

Lithium-ion Battery

Advantages

Light-weight

Have higher energy density than other rechargeable batteries

Rate of charge loss is less

Have a greater number of charge and discharge cycles

Need not be discharged completely (due to absence of memory effect)

Operates at higher voltage than other rechargeable batteries (approx. 3.7 volt)

Disadvantages

Involves risk of bursting

Costly, compared to other batteries

Complete discharge damage the battery

Extremely sensitive to high temperatures (degrades very quickly, if exposed to heat)

Very short lifespan (2 to 3 years from the date of manufacturing, even if not in use)

Not available in standard cells sizes (AA, C, and D) like others

APPLICATIONS

- Emergency Power Backup Or UPS
- Dependable Electric And Recreational Vehicle Power
- Solar Power Storage
- Reliable And Lightweight Marine Performance
- Solar Power Storage
- Surveillance Or Alarm Systems In Remote Locations
- Personal Freedom With Mobility Equipment
- Portable Power Packs That Eliminate Downtime



Mining



Space Applications



Consumer Electronics



Power Invertors



Energy Storage System



Lithium Ion Batteries



Electric Vehicles
(EV, HEV, PHEV)



Defence /Military Applications



Marines and Submarines



Telecom Towers



Solar and Wind Energy Storage



Railways

INTRODUCTION

Any physical activity in this world, whether carried out by human beings or by nature, is cause due to flow of energy in one form or the other. The word ‘energy’ itself is derived from the Greek word ‘en-ergon’, which means ‘in-work’ or ‘work content’. The work output depends on the energy input. Thus in all industrial operation, the input of energy is must to obtain the output from in the form of work. Over the years due to rapid industrialization and population growth the requirements of energy has increased manifolds. It is also known that usage of Fossils fuels as compared to other energy sources is maximum, which is unsustainable. Moreover, during their uses the environmental issues have also been encountered. Overall view of this situation has made man to look for other sustainable sources of energy like green fuels, solar energy and battery technology.

Classification

Energy sources are classified into following two category

1. Conventional or Non-Renewable Sources

Conventional energy resources which are being traditionally used for many decades and were in common use around oil crisis of 1973 are called conventional energy resources, e.g., fossil fuel, Coal

2. Non-Conventional or Renewable Sources

Non-conventional energy resources which are considered for large scale use after oil crisis of 1973, are called non-conventional energy sources, e.g., solar, wind, Hydro, Tidal

Solar Energy:

The electromagnetic radiation from sun is commonly known as solar energy. These radiations are resulted from thermo nuclear fusion reaction on the surface of sun. All the radiation from the sun is not in the same wavelength range. Almost 92% lie in the range of 315 nm to 1400nm. The estimated amount of solar flux reaching the atmosphere of earth is approximately $1400\text{W/m}^2\text{min}$.and that of heat equivalent is $2.68 \times 10^{24}\text{J/Year}$. The eco system of earth utilizes about 0.2-0.5 % of total amount of solar energy received. It indicates clearly that large amount solar energy get wasted, which otherwise can be immense use for satisfying needs of humans.

Advantage of solar energy:

1. It is non-polluting and non-depleting source of energy.
2. It is renewable source of energy.
3. It is available abundantly.

In spite of this advantage, the use of solar energy in large scale is still not in practice, due to following reasons,

1. Non availability of intense light in all areas throughout year
2. Difficulties faced in economic collection and conversion of solar energy into other forms of energy such as electricity.

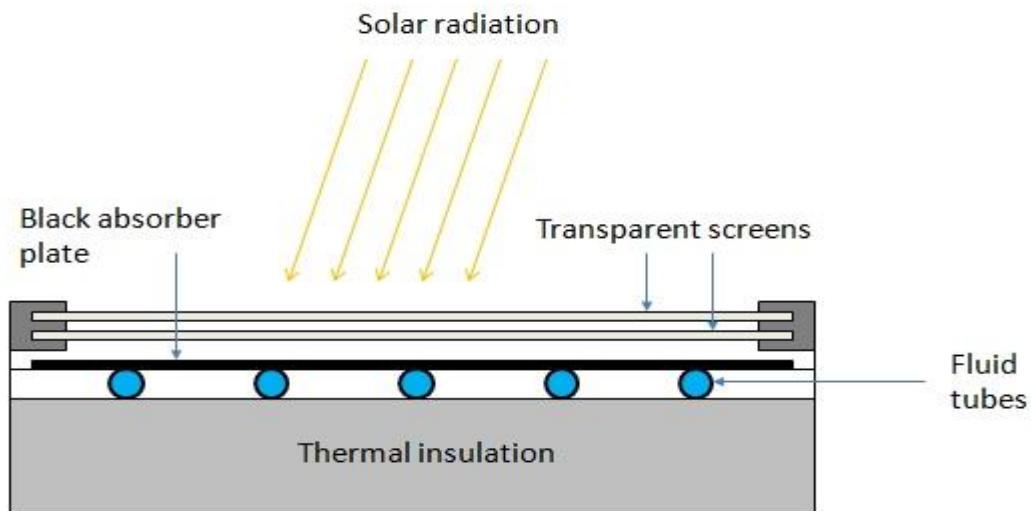
The solar energy has been successfully used in following purpose

- i) Heating: Used for water and space heating in colder countries.
- ii) Electricity: Using solar energy electric energy can be generated.

Flat Plate Collector:

The device works on the principle of black body in which heat absorbing capacity and tendency of a black surface is utilized to achieve benefits for human.

Diagram:



Construction:

These are the main components of a typical flat-plate solar collector:

- Black surface - absorbent of the incident solar energy
- Glazing cover - a transparent layer that transmits radiation to the absorber, but prevents radiative and convective heat loss from the surface
- Tubes containing heating fluid to transfer the heat from the collector
- Support structure to protect the components and hold them in place
- Insulation covering sides and bottom of the collector to reduce heat losses

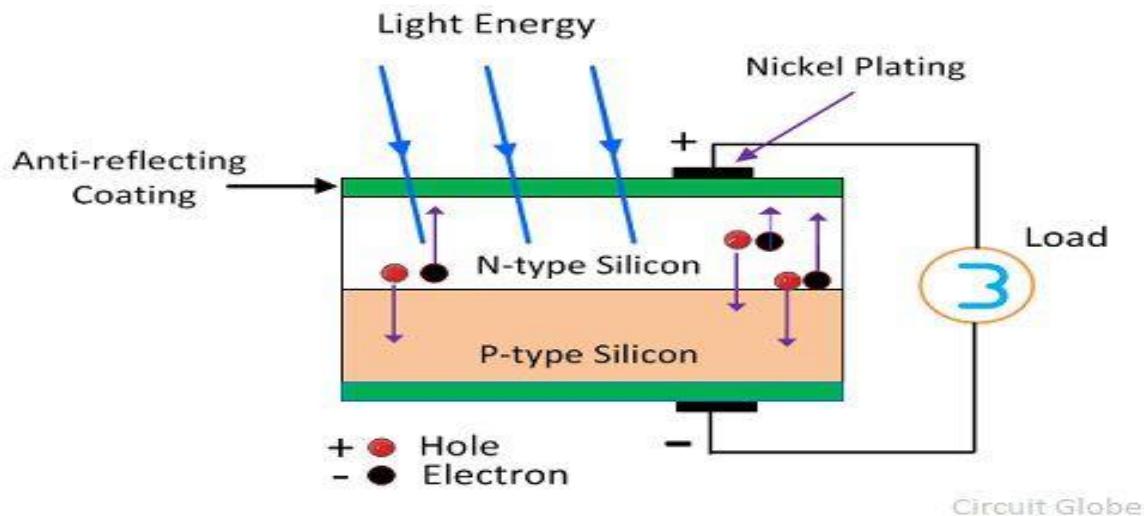
Application

Some advantages of the flat-plate collectors are that they are: Easy to manufacture

- Low cost, Collect both beam and diffuse radiation
- Permanently fixed (no sophisticated positioning or tracking equipment is required)
- Little maintenance

PHOTO VOTAIC CELL (SOLAR CELL)

A conventional solar cell structure is shown in figure:



Semiconductors like silicon has the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and hole). Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

Construction: A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon. Hence these two layers form p-n junction. A metallic grid is the electrical contact of the diode and allows light to fall on the semiconductor between the grid lines. An anti-reflective layer between the grid lines increases the amount of light transmitted to semiconductor.

Working: of tiny energy packets called photon. When light radiation falls on the p-n junction diode, photon is absorbed and electron-hole pairs are generated. The electrons are diffused and collected at the n-type end and holes are diffused and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use. The current output of a cell depends on its efficiency and size and is proportional to the intensity of sun light striking the surface of the cell. Therefore, photovoltaic cells are connected electrically in series or parallel circuits to produce higher voltages, currents and power levels. A number of solar cells electrically connected to each other and mounted in a support structure or frame is called a photovoltaic module. A photovoltaic array is the complete power generating unit, consisting of any number of photovoltaic modules and panels.

Advantage	Disadvantage
1. Fuel source is vast and essentially infinite.	1. Sun light is diffuse or relatively low density energy.
2. Does not contribute to global change or pollution.	2. Poor reliability of auxiliary elements including storage.
3. No moving parts and so no wear and tear and low operating cost	3. Sun light is a diffuse, i.e., it is relatively low density energy.
4. High reliability in modules.	4. Energy can be produced only during the day time.

BATTERY TECHNOLOGY:

Battery is a combination of two or more electrochemical cells. These electrochemical cells store energy in the form of chemical energy, and this is converted into electrical energy when connected to an electrical circuit in which an electrical current can flow. A cell consists of two electrodes with an electrolyte placed between them. The negative electrode is known as the cathode, while the positive electrode is known as the anode. The electrolyte between them can either be a liquid or a solid. Today many cells are enclosed in a special container, and there is an element known as a separator placed between the anode and cathode. This is porous to the electrolyte and prevents the two electrodes from coming into contact with each other.

Batteries are becoming more widely used. As the use of portable and mobile equipment increases, so does the use of battery technology. The increasing demands being placed on batteries has meant that the technology has developed considerably in the past few years, and more development can be expected in the future. With the huge demand for batteries, there is a wide variety of different battery and cell technologies available. These range from the established non-rechargeable technologies such as zinc-carbon and alkaline batteries to rechargeable batteries that have moved from NiCd through NiMH cells to the newer lithium ion rechargeable batteries. Another area of battery technology that is becoming more important is the green or environmental aspects. Some of the old battery technologies contain chemicals which can be considered as toxic. Now new designs are seeking to use more environmentally friendly chemicals. Nickel cadmium cells are now considered as being environmentally unfriendly and are not as widely used as they were previously. Other batteries also contain harmful chemicals and this is likely to have a significant impact on the direction of future developments.

Primary and secondary cells

Although there are many different types of battery, there are two main categories of cell or battery that can be used to provide electrical power. Each type has its own advantages and disadvantages and therefore each type of battery is used in different applications, although they can often be interchanged:

- **Primary batteries:** Primary batteries are essentially batteries that cannot be recharged. They irreversibly transform chemical energy to electrical energy. When the chemicals within the battery have all reacted to produce electrical energy and they are exhausted, the battery or cell cannot be readily restored by electrical means.
- **Secondary batteries:** Secondary batteries or secondary cells are different to primary ones in that they can be recharged. The chemical reactions within the cell or battery can be reversed by supplying electrical energy to the cell, restoring their original composition.

BATTERY TYPES & THEIR PROPERTIES		
CELL TYPE	NOMINAL VOLTAGE V	CHARACTERISTICS
Primary cells and batteries		
Alkaline manganese dioxide	1.5	Widely available, providing high capacity. Shelf life normally up to about five years. Capable of providing moderate current.
Lithium thionyl chloride	3.6	Good for low to medium currents. High energy density and long shelf life.
Lithium manganese dioxide	3.0	Long shelf life combined with high energy density and moderate current capability.
Mercury oxide	1.35	Used for button cells but are virtually phased out now because of the mercury they contain.
Silver oxide	1.5	Good energy density. Mainly used for button cells.
Zinc carbon	1.5	Widely used for consumer applications. Low cost, moderate capacity. Operate best under intermittent use conditions.
Zinc air	1.4	Mostly used for button cells. Have a limited life once opened and low current capability but a high energy density.
Secondary cells and batteries		
Nickel cadmium NiCd	1.2	Were in very common use, but now giving way to NiMH cells and batteries in view of environmental impacts. Low internal resistance and can supply large currents. Long life if used with care.
Nickel metal hydride NiMH	1.2	Higher capacity but more expensive than NiCads. Charging must be carefully controlled. Being used in many applications where NiCads were previously used.
Lithium ion		Highest capacity and they are now widely used in many laptops, mobile phones, cameras. . etc. Charging must be carefully controlled and often have a limited life ~ typically 300 charge discharge cycles.
Lead acid	2.0	Widely used for automotive applications. Relatively cheap, but life expectancy often short.

Battery definitions, terms, & terminology

- Anode:** The definition for the anode is the electrode at which an oxidation reaction occurs. This means that the anode electrode is a supplier of electrons. However the electron flow reverses between charge and discharge activities. As a result, the positive electrode is the anode during charging and the negative electrode is the anode during discharging.

In order to prevent confusion, the anode is normally defined for its activity during the discharge cycle. In this way the term anode is used for the negative electrode in a cell or battery.

- Battery:** A battery is the generic name for a unit that creates electrical energy from stored chemical energy. Strictly it consists of two or more cells connected in an appropriate series / parallel arrangement to provide the required operating voltage and capacity to meet its operating requirements. The term battery is also frequently used to refer to a unit consisting of a single cell, especially when it contains battery management circuitry.

- Cathode:** The definition of a cathode is the electrode in a battery or other system at which a reduction reaction occurs. The electrode takes up electrons from an external circuit. Accordingly, the negative electrode of the battery or cell is the cathode during charging and the positive electrode is the cathode during

discharging.

To prevent confusion the cathode is normally specified for the discharge cycle. As a result, the name cathode is commonly used for the positive electrode of the cell or battery.

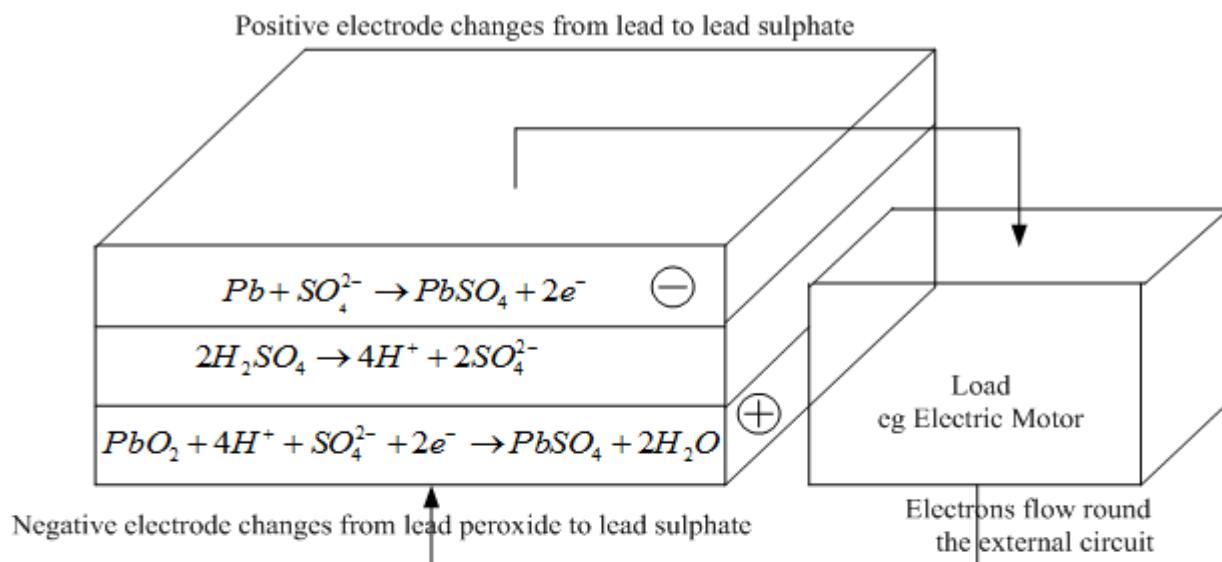
- **Capacity:** The capacity of a battery or cell is defined as the amount of energy that it can deliver in a single discharge. Battery capacity is normally specified in amp-hours (or milli-amp-hours) or as watt-hours.
- **Charge rate or C-rate:** The definition of the charge rate or C-rate of a battery or cell is the charge or discharge current in Amperes as a proportion of the rated capacity in Ah. For example, in the case of a 500 mAh battery, a C/2 rate is 250 mA and a 2C rate would be 1 A.
- **Constant-Current Charge:** This refers to a charging process where the level of current is maintained at a constant level regardless of the voltage of the battery or cell.
- **Constant-Voltage Charge:** - This definition refers to a charging process in which the voltage applied to a battery is held at a constant value over the charge cycle regardless of the current drawn.
- **Cycle Life:** The capacity of a rechargeable cell or battery changes over its life. The definition of the battery life or cycle life of a battery is number of cycles that a cell or battery can be charged and discharged under specific conditions, before the available capacity falls to a specific performance criteria - normally 80% of the rated capacity.
- **Cut-off voltage:** As a battery or cell is discharged it has a voltage curve that it follows - the voltage generally falling over the discharge cycle. The definition for a cell or battery of the cut-off voltage cell or battery is the voltage at which the discharge is terminated by any battery management system. This point may also be referred to as the End-of-Discharge voltage.
- **Deep Cycle:** A charge discharge cycle in which the discharge is continued until the battery is fully discharged. This is normally taken to be the point at which it reaches its cut-off voltage, typically 80% of discharge.
- **Energy Density:** The volumetric energy storage density of a battery, expressed in Watt-hours per litre (Wh/l).
- **Power Density:** The volumetric power density of a battery, expressed in Watts per litre (W/l).
- **Rated Capacity:** The capacity of a battery is expressed in Ampere-hours, Ah and it is the total charge that can be obtained from a fully charged battery under specified discharge conditions
- **Self-Discharge:** It is found that batteries and cells will lose their charge over a period of time, and need re-charging. This self-discharge is normal, but varies according to a number of variables including the technology used and the conditions. Self-discharge is defined as the recoverable loss of capacity of a cell or battery. The figure is normally expressed in a percentage of the rated capacity lost per month and at a given temperature. The self-discharge rate of a battery or cell is very dependent upon the temperature.
- **Separator:** This battery terminology is used to define the membrane that is required within a cell to prevent the anode and cathode shorting together. With cells being made more compact, the space between the anode and cathode becomes much smaller and as a result the two electrodes could short together causing a catastrophic and possibly explosive reaction. The separator is an ion-permeable, electronically non-conductive material or spacer that is placed between the anode and cathode.

Lead acid battery

- **Positive plate:** This is covered with a paste of lead dioxide.
 - **Negative plate:** This is made of sponge lead.
 - **Separator:** This is an insulating material between the two plates, but it allows the electrolyte and the ions into it to enable conduction without the two plates touching.
 - **Electrolyte:** This consists of water and sulphuric acid
- These constituents are all contained within a plastic container which acts to keep the electrolyte in and the battery together.

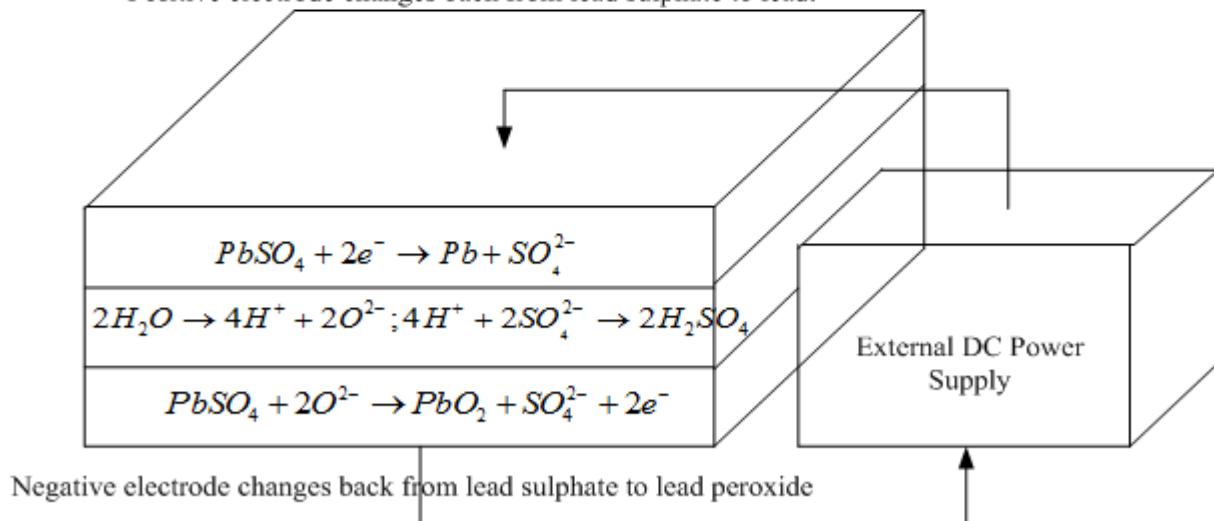
The overall battery will normally consist of several cells placed in series to give the required voltage as each cell is capable of providing an EMF of 2.1 volts.

ENERGY



Reactions during the discharge of the lead acid battery.
Note that the electrolyte loses sulphuric acid and gains water.

Positive electrode changes back from lead sulphate to lead.



Reaction during the charging of the lead acid battery.
Note that the electrolyte sulphuric acid concentration increases.

In order to enable the basic lead acid cell to produce a voltage, it must first receive charge. The voltage applied to provide this must be greater than the 2.1 volts to enable current to flow into the cell. If it were less than this, charge would actually flow out of it.

Once charged, the cell or battery will be able to provide charge to external circuits, often operating over several hours dependent upon the drain on the cell or battery.

Lead Acid Battery Advantages

- Mature technology
- Relatively cheap to manufacture and buy (they provide the lowest cost per unit capacity for rechargeable cells)
- Large current capability
- Can be made for a variety of applications
- Tolerant to abuse
- Tolerant of overcharging
- Wide range of sizes and specifications available
- Many producers worldwide

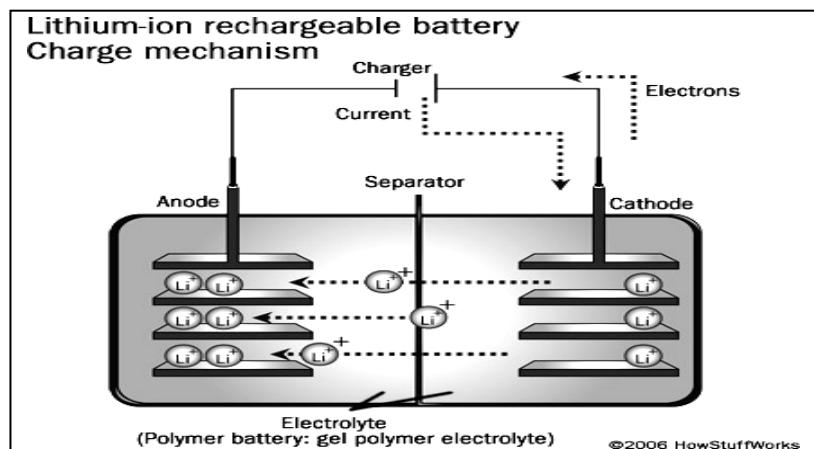
Lead Acid Battery Disadvantages

- Fails after a few years use lifespan typically 300 - 500 cycles
- Cannot always be used in a variety of orientations
- Corrosive electrolyte (can cause burns to people and corrosion on metalwork)
- Lead is not environmentally friendly
- Acid needs disposing of with care
- Not suitable for fast charging
- Must be stored in charged state once electrolyte introduced
- Typical charging efficiency only around 70%

Lithium Ion Battery

Since the late 1980s rechargeable lithium cells have come onto the market. They offer greatly increased energy density in comparison with other rechargeable batteries, though at greatly increased cost. It is a well-established feature of the most expensive laptop computers and mobile phones that lithium rechargeable batteries are specified, rather than the lower cost NiCad or NiHM cells that we have been considering earlier. The battery consists of an anode of Lithium, dissolved as ions, into a carbon. The cathode material is made up from Lithium liberating compounds, typically the three electro-active oxide materials,

- i. Lithium Cobalt-oxide (LiCoO_2)
- ii. Lithium Manganese-oxide (LiMn_2O_4)
- iii. Lithium Nickel-oxide (LiNiO_2)



Construction:

1. A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil – cathode.
2. A negative electrode made with specialty carbon has a current collector of thin copper foil – anode.
3. A separator is a fine porous polymer film.
4. An electrolyte made with lithium salt in an organic solvent.
5. The electrolytes are selected in such a way that there should be an effective transport of Li-ion to the cathode during discharge.
6. The type of conductivity of electrolyte is ionic in nature rather than electronic

Working:

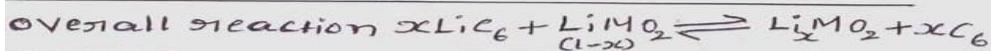
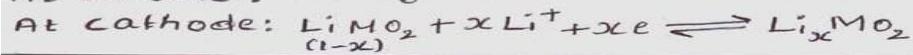
1. The traditional batteries are based on galvanic action but Lithium ion secondary battery depends on an "intercalation" mechanism.
 2. This involves the insertion of lithium ions into the crystalline lattice of the host electrode
- Intercalation:** The process where the lithium ions in the lithium ion battery are inserted into the electrode is called intercalation.

without changing its crystal structure.

3. These electrodes have two key properties. One is the open crystal structure, which allow the insertion or extraction of lithium ions and the second is the ability to accept compensating electrons at the same time. Such electrodes are called intercalation hosts.
4. The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:
5. The lithium ion is inserted and exerted into the lattice structure of anode and cathode during charging and discharging
6. During discharge current flows through external circuit and light glows
7. During charging, no the electrons flows in the opposite direction.
8. During charging, lithium in positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.

During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode

Reactions:



where, M = Co, Ni, Mn

Advantages

1. They have high energy density than other rechargeable batteries
2. They are less weight
3. They produce high voltage out about 4 V as compared with other batteries.
4. No liquid electrolyte means they are immune from leaking.
5. Fast charge and discharge rate
6. Long cycle life, tolerate microcycles.
7. Very low self-discharge rate

Disadvantage:

1. They are expensive.
2. Internal impedance is higher than equivalent
3. Degrades at higher temperature
4. It does sustain overcharging
5. Long term implication is not yet clear
6. They are not available in standard cell types.
7. It requires to charge regularly

Applications

1. The Li-ion batteries are used in cameras, calculators.
2. They are used in cardiac pacemakers and other implantable device.
3. They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.
4. They are used to operate laptop computers and mobile phones and aerospace application.
5. Lithium ion rechargeable battery used as main power supply for mobile phone , PCs, digital camera replacing Nickel metal hydride cell
6. Up to 1000MAh capacity and more available for use in traction application as well as stand by power.

ENERGY

Prepared by Dr. Pushpendra rai

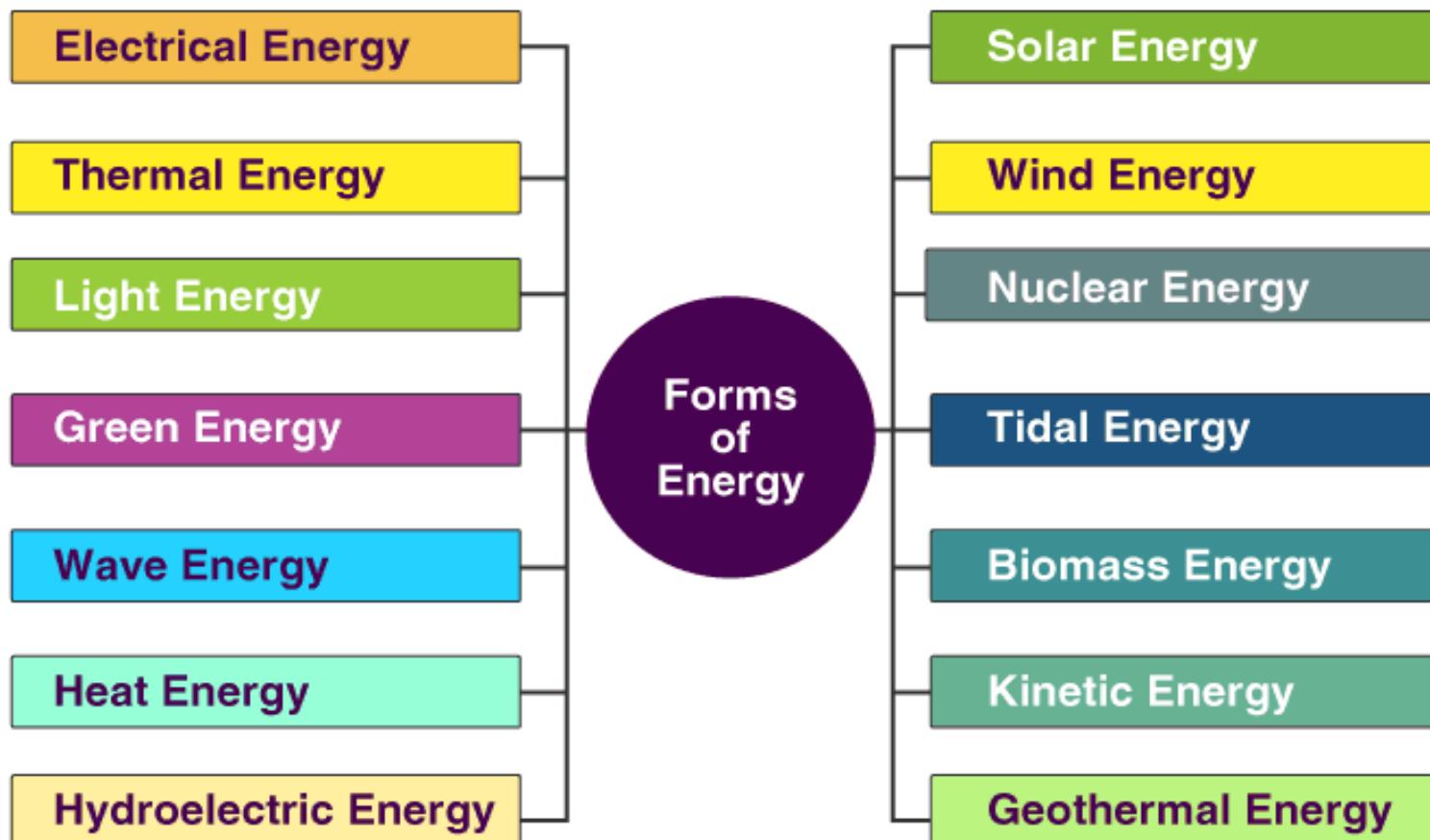
Modified by Dr. Druman Utekar

Energy

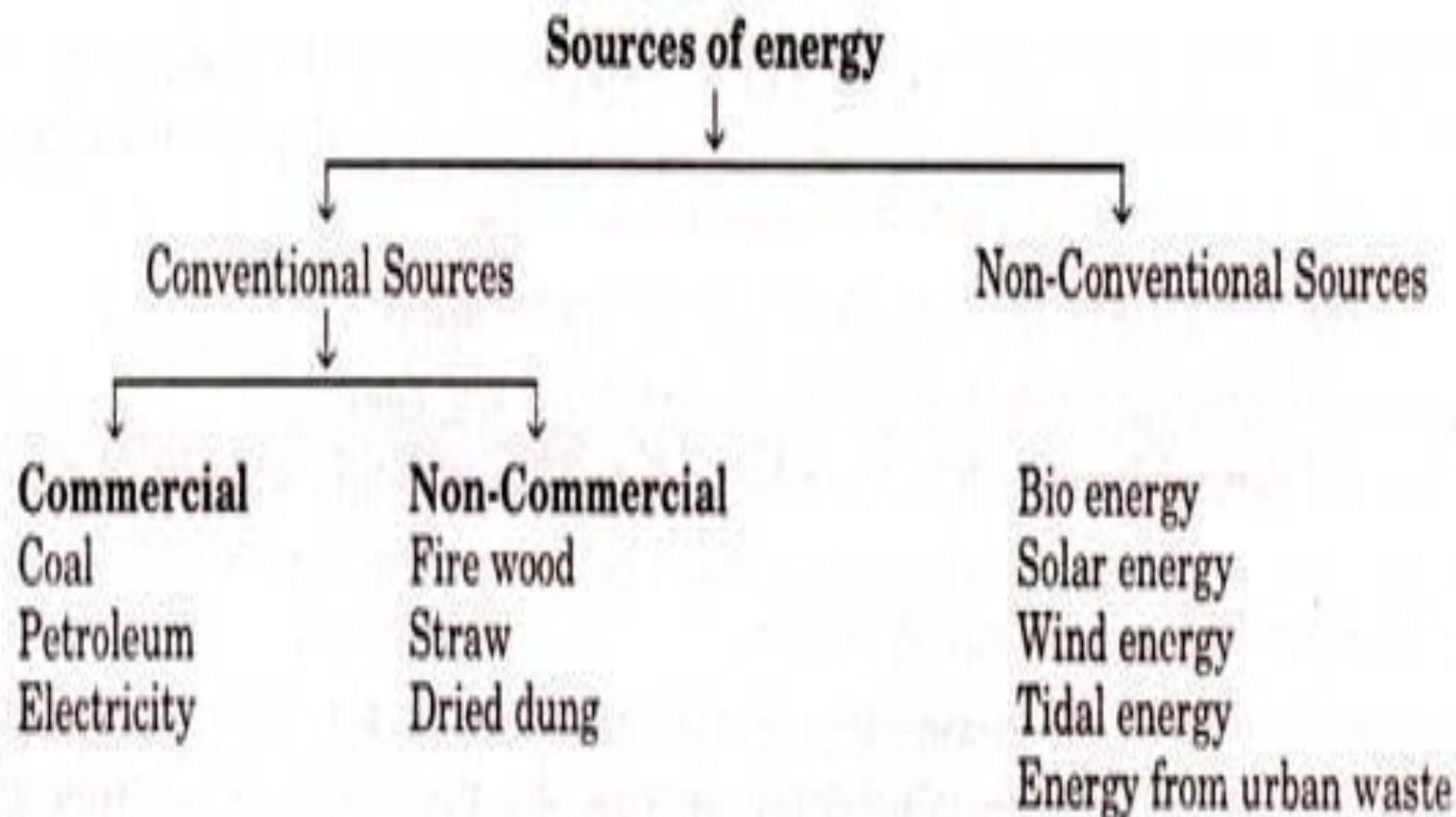
The sun, directly or indirectly, is the source of all the energy available on Earth. Energy is essential to life and all living organisms.

Energy is a conserved quantity and the law of conservation of energy states that energy can neither be created nor destroyed but can only be converted from one form to another. The SI unit of energy is Joule.

Types of Energy



Classification of Energy



Distinction: Conventional (non-renewable) and nonconventional energy (renewable) sources.

Renewable resources	Non-renewable resources
Resources which can be renewed or can be reused are renewable resources.	Resources which cannot be renewed or reused once utilized are called non-renewable resources.
These include components like air, water, wind, sunlight etc.	These include components like fossil fuels, LPG gases.
They are sustainable resources.	They are exhaustible resources.
Their rate of renewal is greater than the rate of getting exhausted.	Their rate of renewal is slower than the rate of getting exhausted.
They are mostly environmental friendly and does not cause pollution.	They are the main cause of pollution.

Solar Energy

The electromagnetic radiation from sun is commonly known as solar energy. These radiations are resulted from thermo nuclear fusion reaction on the surface of sun. All the radiation from the sun is not in the same wavelength range. Almost 92% lie in the range of 315 nm to 1400nm. The estimated amount of solar flux reaching the atmosphere of earth is approximately 1400W/m²min. and that of heat equivalent is 2.68×10^{24} J/Year. The eco system of earth utilizes about 0.2-0.5 % of total amount of solar energy received. It indicates clearly that large amount solar energy get wasted, which otherwise can be immense use for satisfying needs of humans.

Advantage of solar energy:

1. It is non-polluting and non-depleting source of energy.
2. It is renewable source of energy.
3. It is available abundantly.

In spite of these advantages, the use of solar energy in large scale is still not in practice, due to following reasons,

1. Non availability of intense light in all areas throughout year
2. Difficulties faced in economic collection and conversion of solar energy into other forms of energy such as electricity.

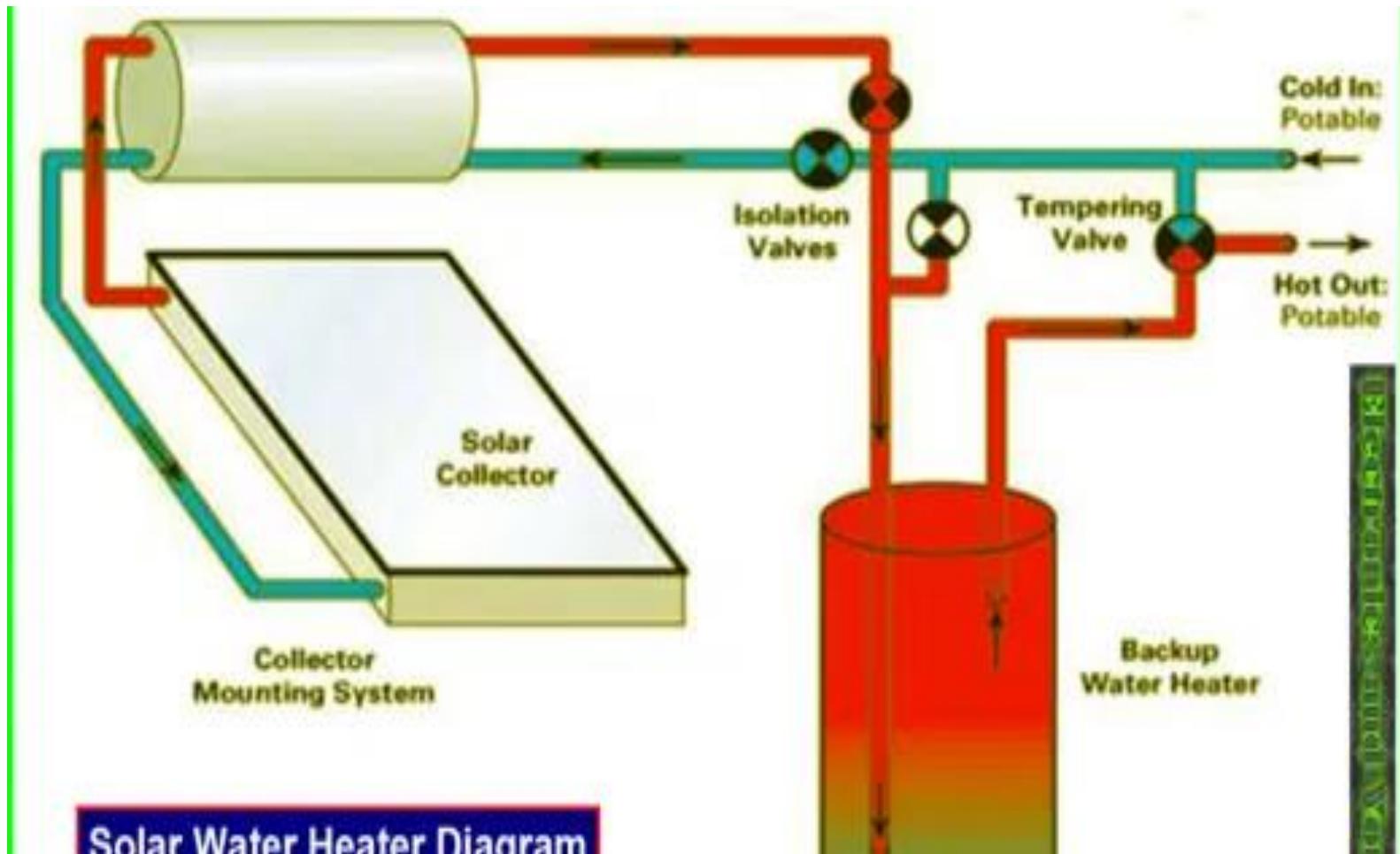
The solar energy has been successfully used in following purpose

- i) Heating: Used for water and space heating in colder countries.
- ii) Electricity: Using solar energy electric energy can be generated.

Advantages and Disadvantages

Advantages	Disadvantages
Reduces consumption of fossil fuels.*	Currently, electricity from PV systems is more expensive than electricity produced from fossil fuel or nuclear power plants.
Reduces production of greenhouse gases.*	Expensive to buy.
Reduces production of various pollutants.*	Requires engineering expertise to design and install systems.
Good for remote applications: satellites, rural hospital equipment in developing countries, telecommunication equipment, etc.	Production of PV systems from single silicon crystals is technically challenging, and energy- and time-consuming.
Reduces the loss of electricity due to power line resistance (distribution losses) because it can be sited where the electricity is used.	Sunlight is not constant, so must get electricity from other sources at night or on cloudy days or store it (such as batteries, etc.)
Reduces water consumed in electrical generation processes by displacing electrical demand.	Sunlight is diffuse; PV would take much space to produce enough electricity to meet our current needs (an area ~one sixth the size of Arizona)
Does not contribute to thermal pollution of waterways.	* Once manufactured, PV systems produce no waste products. Manufacturing of almost any device uses some nonrenewable resources, consumes energy and produces waste products.
No hidden costs.	PV systems consume some nonrenewable resources if a system component needs repair or maintenance (such as batteries, inverter, etc.).
Can provide energy independence.	
PV cells last ~ 30 years.	
Uses a renewable energy source.	

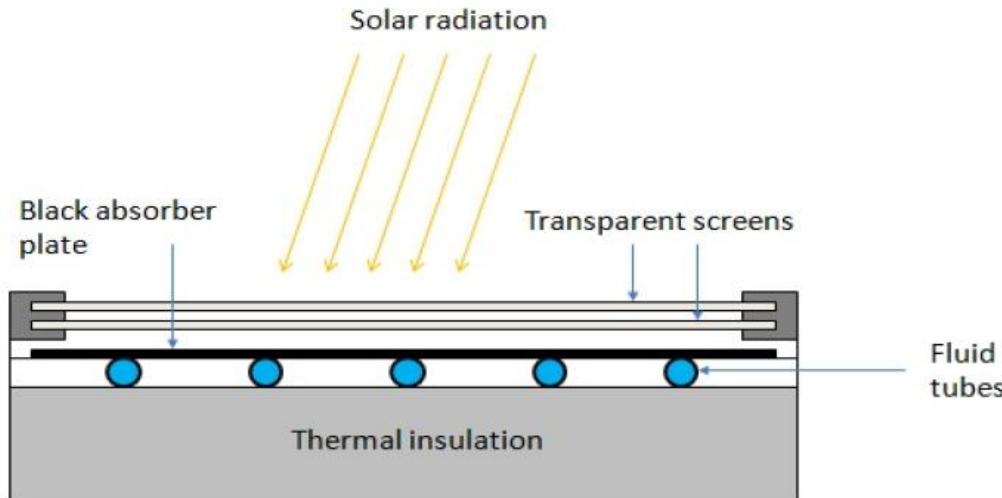
Solar Water Heater



Flat Plate Collector:

The device works on the principle of black body in which heat absorbing capacity and tendency of a black surface is utilized to achieve benefits for human.

Diagram:



Construction:

These are the main components of a typical flat-plate solar collector:

- ❑ Black surface - absorbent of the incident solar energy
- ❑ Glazing cover - a transparent layer that transmits radiation to the absorber, but prevents radiative and convective heat loss from the surface
- ❑ Tubes containing heating fluid to transfer the heat from the collector
- ❑ Support structure to protect the components and hold them in place
- ❑ Insulation covering sides and bottom of the collector to reduce heat losses

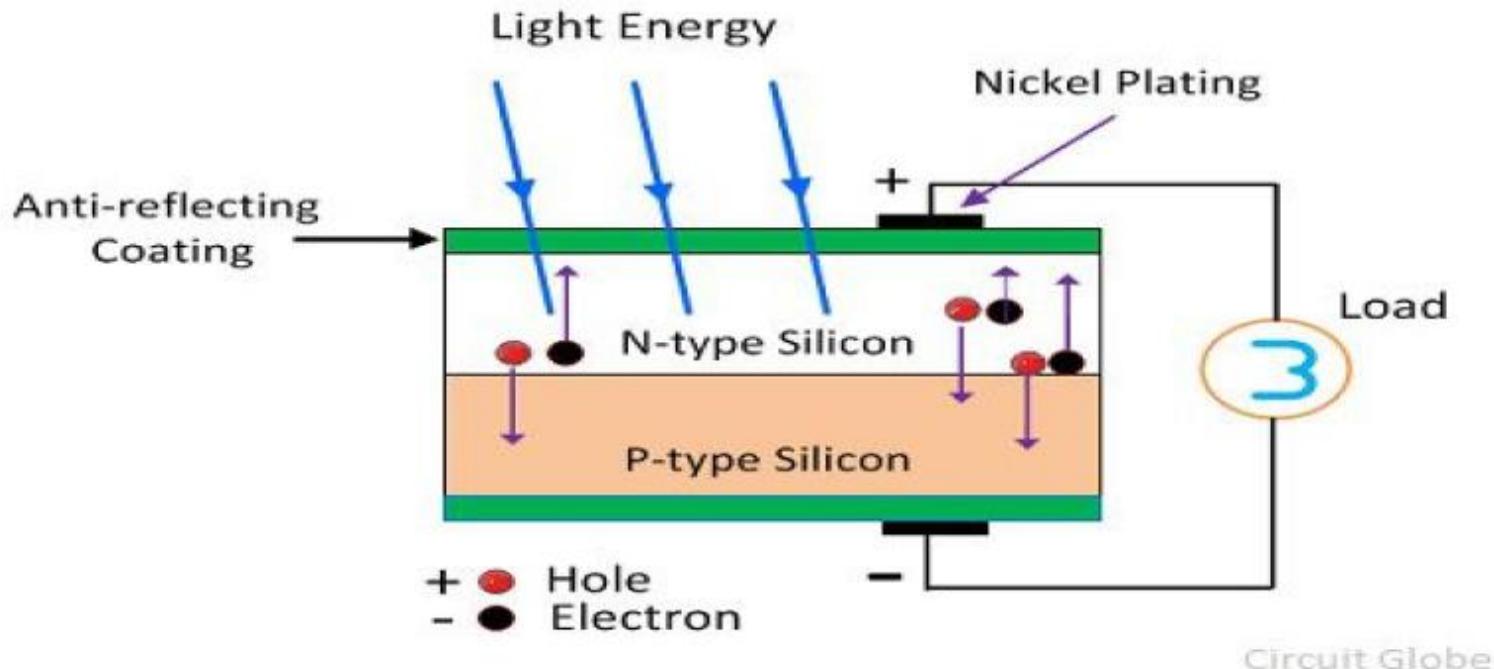
Application

Some advantages of the flat-plate collectors are that they are:Easy to manufacture

- ❑ Low cost, Collect both beam and diffuse radiation
- ❑ Permanently fixed (no sophisticated positioning or tracking equipment is required)
- ❑ Little maintenance

PHOTO VOTAIC CELL (SOLAR CELL)

A conventional solar cell structure is shown in figure:



Semiconductors like silicon has the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and hole). Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

Construction: A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon. Hence these two layers form p-n junction. A metallic grid is the electrical contact of the diode and allows light to fall on the semiconductor between the grid lines. An anti-reflective layer between the grid lines increases the amount of light transmitted to semiconductor.

Working: of tiny energy packets called photon. When light radiation falls on the p-n junction diode, photons are absorbed and electron-hole pairs are generated. The electrons are diffused and collected at the n-type end and holes are diffused and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use. The current output of a cell depends on its efficiency and size and is proportional to the intensity of sun light striking the surface of the cell. Therefore, photovoltaic cells are connected electrically in series or parallel circuits to produce higher voltages, currents and power levels. A number of solar cells electrically connected to each other and mounted in a support structure or frame is called a photovoltaic module. A photovoltaic array is the complete power generating unit, consisting of any number of photovoltaic modules and panels.

Advantages & Disadvantages

Photovoltaic solar energy

Advantages:

- environmentally friendly
- no noise, no moving parts
- no emissions
- no use of fuels and water
- minimal maintenance requirements
- long lifetime, up to 30 years
- electricity is generated wherever there is light, solar or artificial
- PV operates even in cloudy weather conditions
- modular “custom-made” energy can be sized for any application from watch to a multi-megawatt power plant

Limitations:

- PV cannot operate without light
- high initial costs that overshadow the low maintenance costs and lack of fuel costs
- large area needed for large scale applications
- PV generates direct current special DC appliances or an inverter are needed
- in off-grid applications energy storage is needed

Fuel cells

- H₂-O₂ fuel cells-Self Study

Fuels

- Fuels can be defined as substances which undergo combustion in the presence of air to produce a large amount of heat that can be used economically for domestic and industrial purpose.
- Examples, Wood, Coal, Kerosene, Petrol

Classification of chemical fuels

- A) Based on the origin:
 - i) Primary or natural fuels
 - ii) Secondary or artificial or derived fuels
- B) Based on Physical State:
 - i) Solid Fuels
 - ii) Liquid Fuels
 - iii) Gaseous Fuels
- C) Based on Chemical Nature
 - i) Organic eg. Vegetable fuel, coal
 - ii) Inorganic eg. Iron Pyrites
 - iii) Nuclear Fuels eg. Uranium oxide

Characteristic Properties of Fuels

- Fuels are characterized by testing certain physical and chemical properties.
 - i) Calorific Value should be as high as possible.
 - ii) Ignition temperature-Moderate
 - iii) Flame temperature should be as high as possible.
 - iv) Flash and Fire point should be as high as possible.
 - v) Aniline point should be low.
 - vi) Cloud and Pour point should be as low as possible.
 - vii) Viscosity should be adequate.
 - viii) Coke number should be as high as possible.
 - ix) Moisture content-as low as possible.
 - x) Volatile matter as low as possible.
 - xi) Ash content should be absent.
 - xii) Easy risk free transport should be possible.
 - xiii) Storage space-ideally fuel should occupy small space.
 - xiv) Air requirement- adequate
 - xv) Harmless products should be produced on combustion.

Calorific Value

- Calorific value is defined as the number of parts of water which gets heated through 1°C by the heat evolved by the complete combustion of one unit weight of fuel(unit volume of gaseous fuels) under the conditions such as
 - i) Whole of heat evolved is absorbed by water.
 - ii) The products formed leave the system at atmospheric temperature and pressure.
- It is the most important property of fuel.

Units of calorific value

1) B.T.U. (British Thermal Unit)

A British thermal unit may be defined as the heat required to raise the temperature of one pound of water from 60°F to 61°F.

2) K.C.U. (Kilogram Centigrade Unit)

The calorie, a unit of heat may be defined as, the heat required to raise the temperature of one Kg of water from 15°C to 16°C.

Correlation between BTU and KCU:

$$1\text{BTU} = 0.252\text{KCal} = 252\text{Cal}$$

$$1\text{KCal} = 3.968 \text{ BTU}$$

3) C.H.U. (Centigrade Heat Unit)

The calorific value can also be expressed as centigrade heat unit (C.H.U.), which is the amount of heat required to raise temperature of one pound of water through one degree centigrade.

1) High Calorific value (HCV) or Gross Calorific value (GCV):

High calorific value may be defined as the total amount of heat produced when one unit of the fuel has been burnt completely and the products of combustion have been cooled to 16°C or 60°F.

2) Low calorific value(LCV) or Net Calorific value (NCV)

Low calorific value may be defined as the net heat produced when unit mass or volume of fuel is completely burnt and products are allowed to escape.

$$\begin{aligned} \text{NCV or LCV} &= \text{GCV (HCV)} - \text{Latent Heat of water formed} \\ &= \text{GCV(HCV)} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam} \\ &= \text{GCV(HCV)} - 0.09 \times \%H \times 587 \end{aligned}$$

Because 1 part by weight of hydrogen produces 9 parts (1+8) by mass of water.

Dulong Formula

- The calorific value of fuels is determined theoretically by Dulong formula or I.A. Davies formula.
- It is expressed as

$$Q = 1/100 [8080 \times C + 34500 \times (H - O/8) + 2240 \times S]$$

Where, Q = Calorific value in KCU/Kg

C = % of carbon

H = % of hydrogen

O = % of oxygen

S = % of sulphur

Dulong formula for HCV & LCV

$$HCV = 1/100 [8080 \times C + 34500 \times (H - O/8) + 2240 \times S]$$

$$LCV = HCV - [9/100 \times \%H \times 587]$$

Experimentally calorific value of solid and liquid fuel is determined using Bomb Calorimeter.

- Numerical 1: A sample of coal contains C = 55%, O = 28%, H = 7%, S = 0.7%, N = 0.2%, Ash = 0.2%. Calculate the GCV and NCV.

Soln:

$$\begin{aligned} \text{GCV} &= 1/100[8080C + 34500(H-O/8) + 2240S] \\ &= 1/100 [8080 \times 55 + 34500(7-28/8) + 2240 \times 0.7] \\ &= 5667 \text{ Kcal/Kg} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{HCV} - 0.09 \times \% \text{ H} \times 587 \\ &= 5667 - 0.09 \times 7 \times 587 \\ &= 5297.19 \text{ Kcal/Kg} \end{aligned}$$

- Numerical 2: A sample of coal has following composition C = 70%, O = 8%, H = 10%, N = 3%, S = 2%, Ash = 7%. Calculate HCV and GCV.

- Numerical 3: A sample of coal contains C = 61%, O = 32%, S = 0.5%, N = 0.2% and Ash = 0.3%. If NCV of coal is 5313.02KCal/Kg. Calculate % H and GCV.

$$\text{GCV} = 1/100[8080C + 34500(H-O/8) + 2240S] \text{---i)}$$

$$\text{NCV} = \text{GCV} - 0.09 \times \% \text{ H} \times 587$$

$$\text{GCV} = \text{NCV} + 0.09 \times \% \text{ H} \times 587 \text{-----ii)}$$

$$1/100[8080C + 34500(H-O/8) + 2240S] = \text{NCV} + 0.09 \times \% \text{ H} \times 587$$

Numerical 3: A sample of coal contains C = 61% , O = 32%, S = 0.5%, N = 0.2% and Ash = 0.3%. If NCV of coal is 5313.02KCal/Kg. Calculate % H and GCV.

$$GCV = \frac{1}{100}[8080C + 34500(H-O/8) + 2240S] \text{----i)}$$

$$NCV = GCV - 0.09 \times \%H \times 587$$

$$GCV = NCV + 0.09 \times \%H \times 587 \text{-----ii)}$$

$$\frac{1}{100}[8080C + 34500(H-O/8) + 2240S] = NCV + 0.09 \times \%H \times 587$$

Numerical 3: A sample of coal contains C = 70% , O = 25%, S = 1%, N = 1% and Ash = 0.5%. If NCV of coal is 5200KCal/Kg. Calculate % H and GCV.

$$GCV = 80.80 \times 70 + 345(H - 25/8) + 22.40 \times 1 \text{----i)}$$

$$= 5656 + 345H - 1078.125 + 22.4$$

$$= 4600 + 345H$$

$$NCV = GCV - 0.09 \times \%H \times 587$$

$$GCV = 5200 + 0.09 \times \%H \times 587$$

$$= 5200 + 52.83H \text{-----ii)}$$

$$4600.275 + 345H = 5200 + 52.83H$$

$$345H - 52.83H = 5200 - 4600.275$$

$$292.17H = 599.725$$

$$H = 2.05\%$$

$$GCV = 5308.44 \text{Kcal/Kg}$$

Coal

Purpose of Analysis of Coal

- To decide price of coal
- To determine quality
- To specify use of coal for a particular purpose.
- To calculate theoretical calorific value of coal.
- To calculate air requirement for complete combustion of coal and design the furnace fire box suitably.

- Types of Analysis of Coal

- A) Proximate Analysis

- i) % Moisture
 - ii) % Volatile Matter
 - iii) % Ash
 - iv) Fixed Carbon

- B) Ultimate Analysis

- i) % Carbon and % Hydrogen
 - ii) % Nitrogen
 - iii) % Sulphur
 - iv) % Ash

Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which

- a) % Moisture b) % VM c) % Ash d) % Fixed Carbon are found out.

a) % Moisture

A known weight of powdered and air dried coal sample is taken in a crucible and it is placed in an oven for 1hr at 110°C. Then the coal is cooled in a desiccator and weighed out. If the initial weight of the coal is W gms and final weight is W1 gms.

Then the loss in weight (W-W1) corresponds to moisture in coal.

$$\% \text{ Moisture} = \frac{\text{Loss in weight} \times 100}{\text{Weight of coal sample}} = \frac{(W-W_1) \times 100}{W}$$

b) % Volatile Matter

Moisture free coal left in the crucible in first experiment W1 is covered with a lid loosely. Then it is heated at 925°C in a muffle furnace for 7min.

The crucible is taken out and cooled in a desiccator. Then it is weighed (W2 gms) .

$$\% \text{ Volatile matter} = \frac{\text{weight of volatile matter} \times 100}{\text{Weight of coal sample}} = \frac{(W1-W2) \times 100}{W}$$

c) % Ash

The residual coal in the above experiments is heated and burnt in an open crucible at above 750°C for half hour.

The coal gets burnt. The ash left in crucible is cooled in a desiccator and weighed W3 gms.

$$\% \text{ Ash} = \frac{\text{weight of ash} \times 100}{\text{Weight of coal}} = \frac{W3 \times 100}{W}$$

d) % Fixed Carbon:

It is found by calculations

$$\% \text{FC} = 100 - (\% \text{ moisture} + \% \text{ VM} + \% \text{ Ash})$$

Significance or Importance of proximate analysis

a) Moisture

It decreases calorific value of coal largely as it does not burn and takes away heat in the form of latent heat.

It increases ignition point of coal.

Hence a coal with lower moisture % is better quality.

b) Volatile matter

It decreases calorific value of coal.

It elongates flame and decreases flame temperature.

It form smoke and pollute air.

However the coals containing 15-25% of VM on carbonization gives coke oven gas which is source of various organic aromatic chemicals.

Such coal have good coaking property and coke can be obtained from the coals.

Overall regarding burning of coal the coal with lesser VM is better quality coal.

c) Ash

It reduces calorific value of coal as ash is non-burning part in coal.

Ash disposal is a problem.

Ash fuses to form clinker at high temperature obstructing the air supply of coal burning furnace.

Hence lesser the % ash better is the quality of coal.

d) Fixed carbon

Carbon is the burning part in coal and higher the fixed carbon higher is calorific value.

Hence a good quality coal contains high fixed carbon percentage.

Numerical 1: A sample of coal was analysed for content of moisture, volatile matter & ash. From the following data, calculate the percentage of the above quantities.

- i) weight of coal taken = 2.5g
- ii) weight of coal after heating at 110°C = 2.365g
- iii) weight of coal after heating at covered crucible at 950°C = 1.165g
- iv) constant weight obtained at the end of the experiment = 0.460g

Soln:

a) % Moisture = $\frac{(W-W_1) \times 100}{W} = \frac{(2.5-2.365) \times 100}{2.5} = 5.4\%$

b) % volatile Matter = $\frac{(W_1-W_2) \times 100}{W} = \frac{(2.365-1.165) \times 100}{2.5} = 48\%$

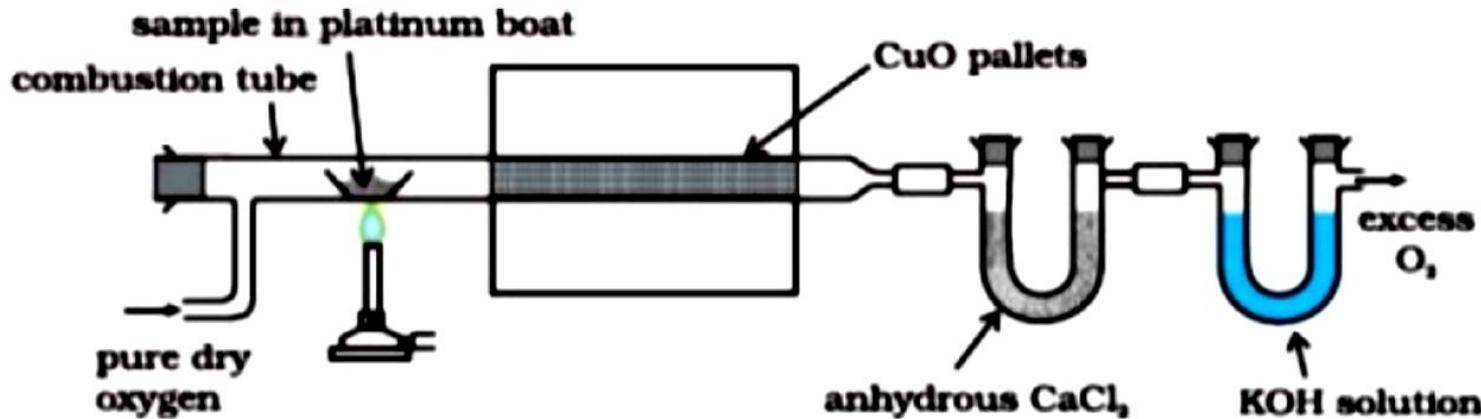
c) % Ash = $\frac{W_3 \times 100}{W} = \frac{0.460 \times 100}{2.5} = 18.4\%$

d) % Fixed Carbon = $100 - [\% \text{ moisture} + \% \text{ VM} + \% \text{ Ash}]$
= $100 - [5.4 + 48 + 18.4] = 28.2\%$

Ultimate Analysis

1) Carbon and 2) hydrogen:

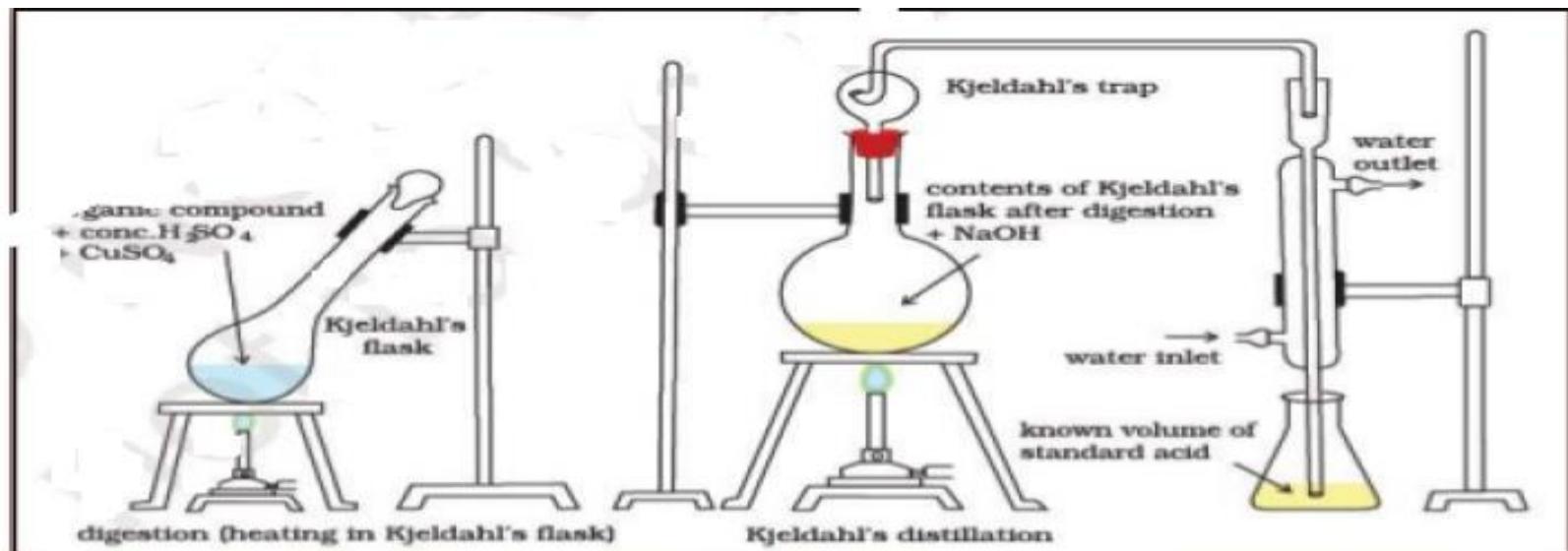
- About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO₂ and H₂O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl₂ tubes of known weights.
- The increase in weights of these are then determined.
- C + O₂ ---->CO₂
- 2H₂ + O₂-----> 2H₂O
- KOH + CO₂-----> K₂CO₃ + H₂O
- CaCl₂ + 7 H₂O-----> CaCl₂.7 H₂O



$$C = \frac{\text{Increase in mass of KOH} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

$$H = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

3) Nitrogen by Kjeldahl's Method: About 1 g of accurately weighed powdered 'coal is heated with concentrated H₂SO₄ along-with K₂SO₄(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 KOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as:



$$\text{Percentage of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

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 sulphatThe washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of S} = \frac{\text{Weight of BaS0}_4 \text{ residue obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

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 constituent 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 (SO_2 and SO_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.

Numerical 1: 0.2g of Coal Sample is accurately weighed and is burnt in a combustion apparatus. The gaseous products of combustion are absorbed in potash bulb and calcium chloride tubes of known weights. The increase in weight of potash bulb and CaCl_2 tube are 0.66g and 0.08g respectively. Calculate the % C and % H in coal sample.

Numerical 2: 3g of coal was heated in Kjeldahls flask and NH_3 gas evolved was absorbed in 40mL of 0.5N HCl. After absorption the excess acid required 18.5mL of 0.5N KOH for exact neutralization. 2.3g of coal sample in quantitative analysis gave 0.35g BaSO_4 . Calculate % of N and S in coal sample.

Soln: Volume of NH_3 consumed by 0.5N HCl is in terms of 0.5N KOH

40ml of 0.5N HCl = 40mL of 0.5N KOH---assumed---V1 _____ blank

Unreacted acid = 18.5ml of 0.5N KOH----V2 _____ back titration

Vol of acid reacted with absorbed NH_3 in term of 0.5N KOH = $40 - 18.5\text{ml} = 21.5\text{mL}$

% N = volume of acid consumed(V1-V2) x N KOH x 1.4
weight of coal sample

% S = Wt of BaSO_4 formed x 32x 100
wt of coal sample x 233

Numerical 3: 2.5 g of coal was heated in Kjeldahls flask and NH_3 gas evolved was absorbed in 40mL of 0.5 N HCl. After absorption the excess acid required 8.5mL of 0.25N KOH for exact neutralization.

Soln:

Blank titration = 40mL of 0.5N HCl = 40mL of 0.5N KOH

Back titration = 8.5mL of 0.25N KOH = 4.25 ml of 0.5N KOH---- $n_1v_1=n_2v_2$

Liquid Fuels These are naturally found under the sea surface. Liquid fuels find extensive use in domestic and industrial fields. 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, O and S. The average composition of crude oil is C = 80 - 87 %, H = 11-15%, S = 0.1 - 3.5%, (N + O) = 0.1- 2.5%. 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 $\text{C}_{35}\text{H}_{72}$ 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.

SECONDARY BATTERIES

INTRODUCTION

- Rechargeable batteries (also known as secondary cells) are batteries that potentially consist of reversible cell reactions that allow them to recharge, or regain their cell potential, through the work done by passing currents of electricity.

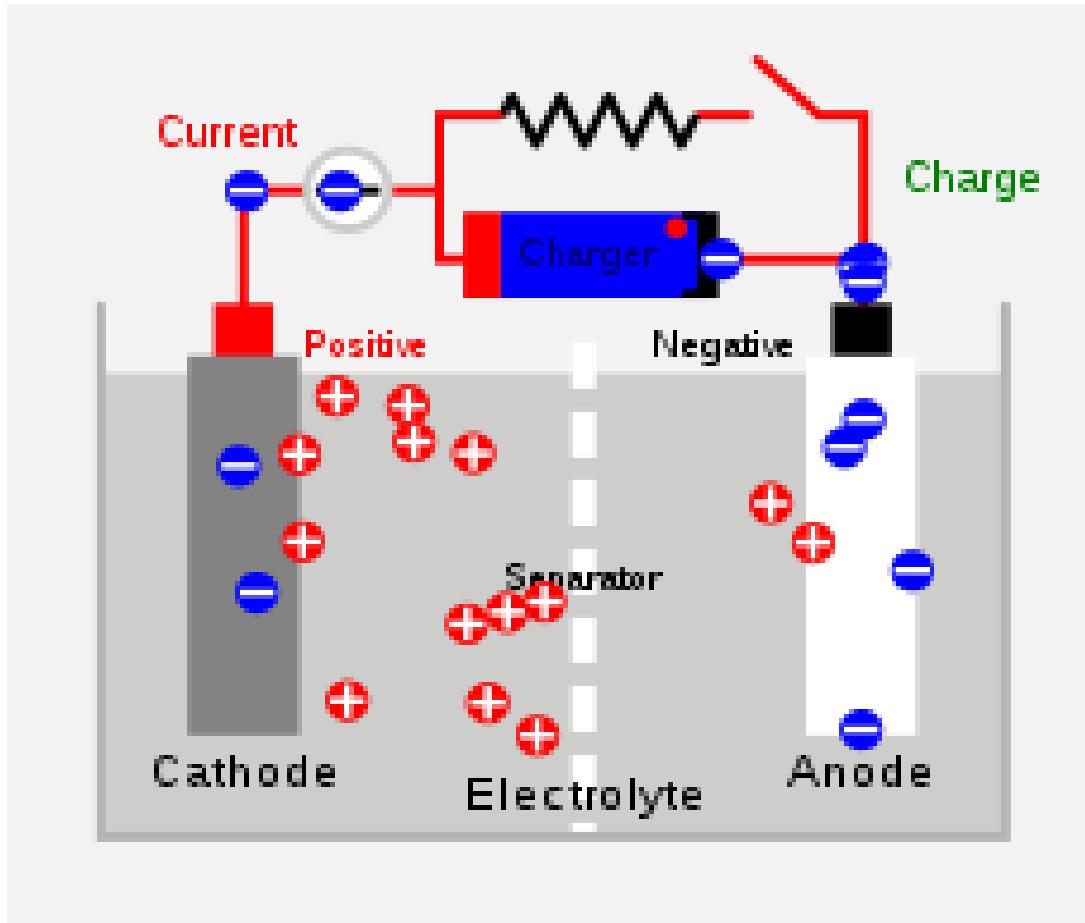
WORKING

- Rechargeable (or secondary) batteries contain active materials that can be regenerated by charging. All batteries have positive and negative terminals, marked (+) and (-) respectively, and two corresponding electrodes. The electrodes must not touch each other, and are separated by the electrolyte, which facilitates the flow of electric charge between the electrodes. A collector conducts the charge to the battery's exterior and through the load.

- When a battery is inserted into an electrical device, the device completes the circuit between the two terminals and triggers electrochemical reactions within the battery. The anode undergoes an oxidation reaction with the electrolyte and releases electrons, while the cathode undergoes a reduction reaction and absorbs the free electrons. The product of these two reactions is electricity, which is channeled out of the battery and into the device.

- When a secondary battery is recharged, its electrodes undergo an opposite process to the discharging action described above. As the battery charger passes electricity through the battery, its cathode is oxidized and produces electrons which are then absorbed by the anode. When the battery is fully charged, it can be connected to a load and discharged again.

WORKING(CHARGING)



**nickel–
cadmium
battery**

**lead–acid
battery**

Types Of Secondary Batteries

**lithium-ion
battery**

1. LEAD ACID BATTERIES

1 Chemistry of a Lead Acid Battery

2 Composition of a Lead Acid Battery

Positive Plate: Lead Oxide (PbO)

Negative Plate: Lead (Pb)

Electrolyte: sulphuric acid (H_2SO_4)

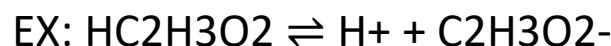
3 Review of Acid Terminology

Strong vs. Weak Acids

Strong acids completely ionize in water



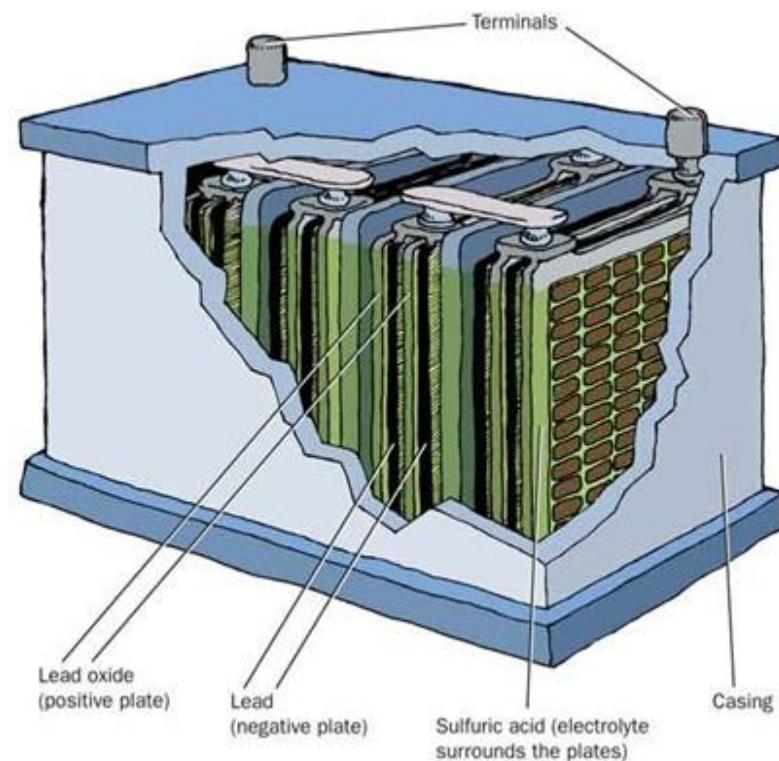
Weak acids partially ionize in water



(note \rightleftharpoons versus \rightarrow) Monoprotic vs. Diprotic Acids

Monoprotic acid has one H^+ (EX: HCl)

Diprotic acid has two H^+ (EX: H_2SO_4)



4 The Electrolyte: H₂SO₄

H₂SO₄ is classified as a strong acid (completely ionizes) but that is not exactly true. The first ionization of H₂SO₄ is complete and occurs instantly when in water.



But! The second ionization is extremely partial.



This is very important in understanding the chemistry of a lead acid battery!

5 for understanding

In general, is sulfuric acid considered a strong or weak acid?

Strong- Why is sulfuric acid considered to be strong?

It completely ionizes

What ion related to sulfuric acid is weak?

HSO₄⁻ Why is the bisulfate ion, HSO₄⁻ considered weak?

It partially ionizes

6 Lead Acid Batteries are rechargeable

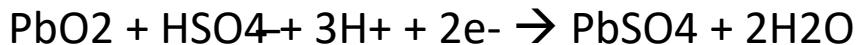
This leads to two different sets of redox reactions.
The discharging phase. The charging phase.

7 Chemistry of Discharge Phase

Negative plate reaction (oxidation):



Positive plate reaction (reduction):



Overall discharge redox reaction:



Note: states are removed for simplicity

Pb, PbO₂, and PbSO₄ are always solids

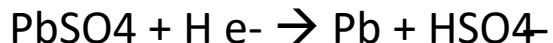
HSO₄⁻, H⁺, and H₂SO₄ are always aqueous

H₂O is always a liquid

8 The flow of electrons = ELECTRICITY!

9 Chemistry of Charge Phase

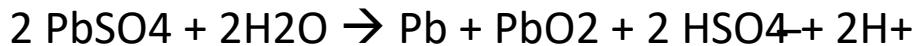
Negative plate reaction (reduction):



Positive plate reaction (oxidation):



Overall charge redox reaction:



10 for understanding

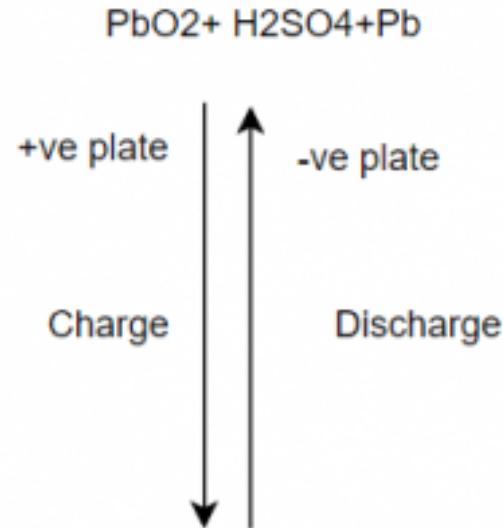
What metal is always at the negative plate? Pb

What compound is always at the positive plate? PbO₂

What is the electrolyte in a battery? H₂SO₄ or HSO₄⁻

What compound is the “waste” product of discharge and has to be removed in the charging process? (think!) PbSO₄

The combined equation for both the processes is represented as



11 Why do batteries “die”?

Dead Battery



New Battery

When the battery discharges solid PbSO_4 is formed.

In a new battery, the PbSO_4 is in a spongy form which can easily be converted back to Pb and PbO_2 .

Over time the PbSO_4 will tend to crystallize.

The crystallized PbSO_4 cannot be converted back to Pb and PbO_2 so there is not only less reactant material but it also coats the surface of the Pb and PbO_2 .

New Battery

Dead Battery

Life

The optimum functional temperature for lead acid battery is 25°C which means 77°F . The increase in the range of temperature shortens longevity. A per the rule, for every 80°C increase in temperature, it reduces the half-life of the battery. While a value regulated battery that functions at 25°C has a **lead acid battery life** of 10 years. And when this is operated at 33°C , it has a life period of 5 years only.

Lead Acid Battery Applications

These are employed in emergency lightening to provide power for sump pumps.

Used in electric motors

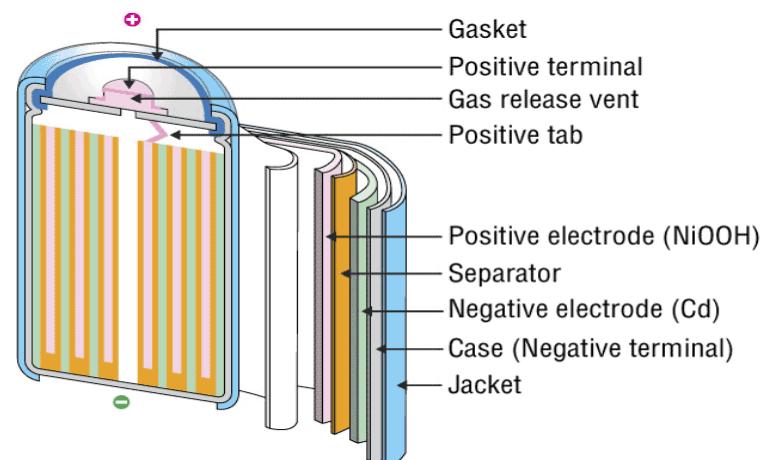
Submarines

Nuclear submarines

2. NICKEL-CADMIUM BATTERY

INTRODUCTION

- The nickel–cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. Ni–Cd batteries are made in a wide range of sizes and capacities.
- Nickel(hydroxide)–cadmium systems are the most common small rechargeable battery type for portable appliances. The sealed cells are equipped with “jelly roll” electrodes, which allow high current to be delivered in an efficient way. These batteries are capable of delivering exceptionally high currents, can be rapidly recharged hundreds of times, and are tolerant of abuse such as over discharging or overcharging.
- It produces a voltage of about 1.4 V



INVENTIONS AND SCOPE

- Nickel-cadmium (NiCd)
- Invented by Waldemar Jungner in 1899. Developments were slow, but in 1932, advancements were made to deposit the active materials inside a porous nickel-plated electrode. Further improvements occurred in 1947 by absorbing the gases generated during charge, which led to the modern sealed NiCd battery.
- For many years, NiCd was the preferred battery choice for two-way radios, emergency medical equipment, professional video cameras and power tools. In the late 1980s, the ultra-high capacity NiCd rocked the world with capacities that were up to 60 percent higher than the standard NiCd.
- Since the disposal of battery is hazardous to environment alternative cells are being used such as paper battery

RECENT TRENDS

The primary trade-off with Ni–Cd batteries is their higher cost and the use of cadmium. This heavy metal is an environmental hazard, and is highly toxic to all higher forms of batteries.

Recently, nickel–metal hydride and lithium-ion batteries have become commercially available and cheaper, the former type now rivaling Ni–Cd batteries in cost..

The batteries are more difficult to damage than other batteries, tolerating deep discharge for long periods.

Ni–Cd batteries typically last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries such as lead/acid batteries.

Compared to lead–acid batteries, Ni–Cd batteries have a much higher energy density.

In consumer applications, Ni–Cd batteries compete directly with alkaline batteries. A Ni–Cd cell has a lower capacity than that of an equivalent alkaline cell, and costs more.

The capacity of a Ni–Cd battery is not significantly affected by very high discharge currents.

CELL REPRESENTATION AND CELL REACTION

A typical Ni-Cd battery is represented as

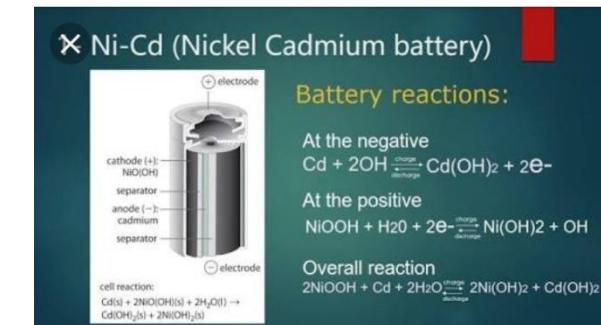


Cell reaction while discharging

At Anode: oxidation of Cd metal



At cathode: reduction of NiO(OH)



Net Cell reaction:



ADVANTAGES

- Fast and simple charging process
- It is compact and lighter than traditional batteries
- It has a longer life than lead storage batteries
- Available in a wide range of sizes and performance options
- Good low-temperature performance
- Only battery that can be ultra-fast charged with little stress

LIMITATIONS

- It is rather more expensive than a lead storage battery
- It has a lower energy density value
- Cadmium is a toxic metal. Cannot be disposed of in landfills
- Memory effect; needs periodic full discharges
- High self-discharge; needs recharging after storage

APPLICATIONS

- Ni-Cd cells are popularly used in many appliances because they are available in variety of sizes and capacities.
- Few examples are:
 - ❖ Calculators
 - ❖ Electronic flash units
 - ❖ Transistors
 - ❖ Cordless appliances



3.

RECHARGEABLE
LITHIUM
BATTERIES

DESCRIPTION

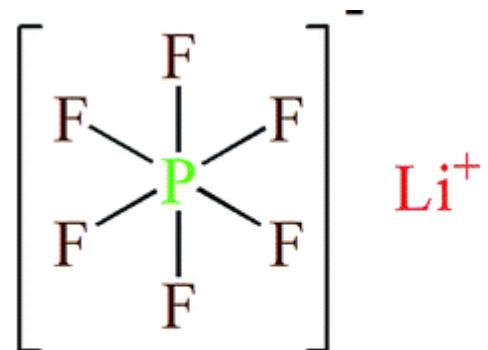


Lithium-ion battery or Li-ion battery (abbreviated as LIB) is a type of rechargeable battery in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging.

- The electrolyte, which allows for ionic movement, and the two electrodes are the constituent components of a lithium-ion battery cell.

ELECTROLYTES

- Role-
 1. Ion conduction between cathode and anode.
 2. They are generally, Lithium salts dissolved in organic solvent.
- Commercial electrolytes: LiPF_6 in Carbonate solvent.



ANODE MATERIALS

- Requirements:
 1. Large capabilites of adsorption.
 2. High efficency of charge/discharge.
 3. Low reactivity against electrolyte.
 4. Fast reaction rate.
 5. Low cost
 6. Environment friendly
- Commercial anode materials:
Hard Carbon, Graphite

CATHODE MATERIALS

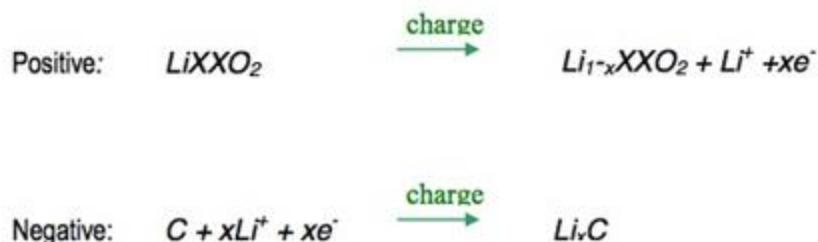
- Requirements:
 1. A high discharge voltage
 2. A high energy capacity
 3. A high power density
 4. Light weight
 5. Low self discharge
 6. Environment friendly
- Commercial cathode materials:
LiCoO₂, LiFePO₄ etc.

CHEMICAL REACTIONS

- Main essential components...
- Anode: Graphite [carbon] - C(s)
- Cathode: Lithium Cobalt Oxide - LiCoO₂
- Electrolyte: Typically a combination of lithium salts - LiPF₆, LiBF₄, or LiClO₄, in an organic solvent, such as either.
- Separator: The separator is a very thin sheet of micro perforated plastic. - CH₂=CHCl

REACTIONS WHILE CHARGING

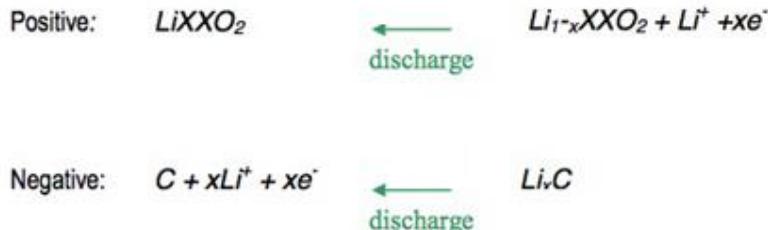
- On charge the positive electrode, cathode, material is oxidized, Li⁺ ions are de-intercalated from the layered lithium LiCoO₂, pass across the electrolyte and are intercalated between the graphite layers in graphite by an electrochemical reduction reaction proceeding at the negative electrode.



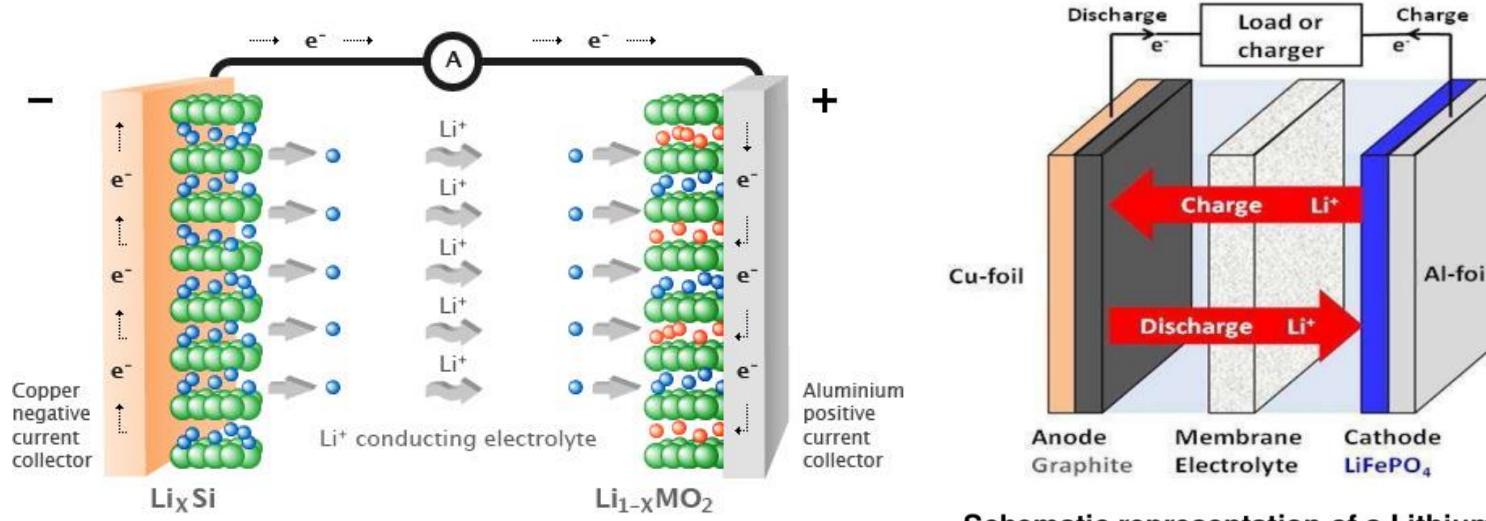
XX= Various Combining elements including Cobalt and Manganese

REACTIONS WHILE DISCHARGING

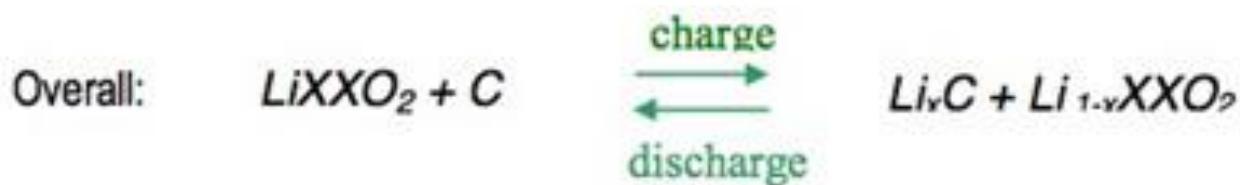
- When the cell is discharged, an oxidation reaction occurs at the negative electrode, Li^+ ions are de-intercalated from the anode and migrate across the electrolyte to be re-intercalated into the cathode material, due to charge balance the equivalent number of electrons travel through the external circuit. A simultaneous electrochemical reduction reaction proceeds at the positive electrode and accepts electrons from the external circuit, Li^+ ions from the electrolyte, to reform the starting material. A change from electronic current to ionic current occurs at the electrode/electrolyte interface.



XX= Various Combining elements including Cobalt and Manganese



Schematic representation of a Lithium-ion cell



XX= Various Combining elements including Cobalt and Manganese

APPLICATIONS

- Emergency Power Backup Or UPS
- Dependable Electric And Recreational Vehicle Power
- Solar Power Storage
- Reliable And Lightweight Marine Performance
- Solar Power Storage
- Surveillance Or Alarm Systems In Remote Locations
- Personal Freedom With Mobility Equipment
- Portable Power Packs That Eliminate Downtime



Mining



Space Applications



Consumer Electronics



Power Invertors



Energy Storage System



Lithium Ion Batteries



Electric Vehicles
(EV, HEV, PHEV)



Defence /Military Applications



Marines and Submarines



Telecom Towers



Solar and Wind Energy Storage



Railways

Waste to energy conversion

Waste to Energy

- The increasing industrialization, urbanization and changes in the pattern of life give rise to generation of increasing quantities of wastes.
- Scarcity of fossil fuels particularly petroleum crude is forcing us to develop some clean technology for the utilization of the fossil fuels as well as to utilize renewal resources.
- In recent years, technologies have been developed that not only help in generating substantial quantity of decentralized energy but also in reducing the quantity of waste for its safe disposal.



Types of waste

- There are different types of waste which are generated from our daily or industrial activities such as organic waste, e-waste, hazardous waste, inert waste etc.
- Organic waste refers to waste which degrades or broken down by microorganisms over time. All organic wastes are essentially carbon based compounds.
- Organic waste has significant portion in overall waste generation in industrial/urban/ agricultural sector and therefore it can be used for energy generation.

waste

hazardous waste

radioactive waste

industrial waste,
electronic waste, medical
waste, etc.

non-hazardous waste

municipal waste

other non-
hazardous
(industrial)
waste

organic waste

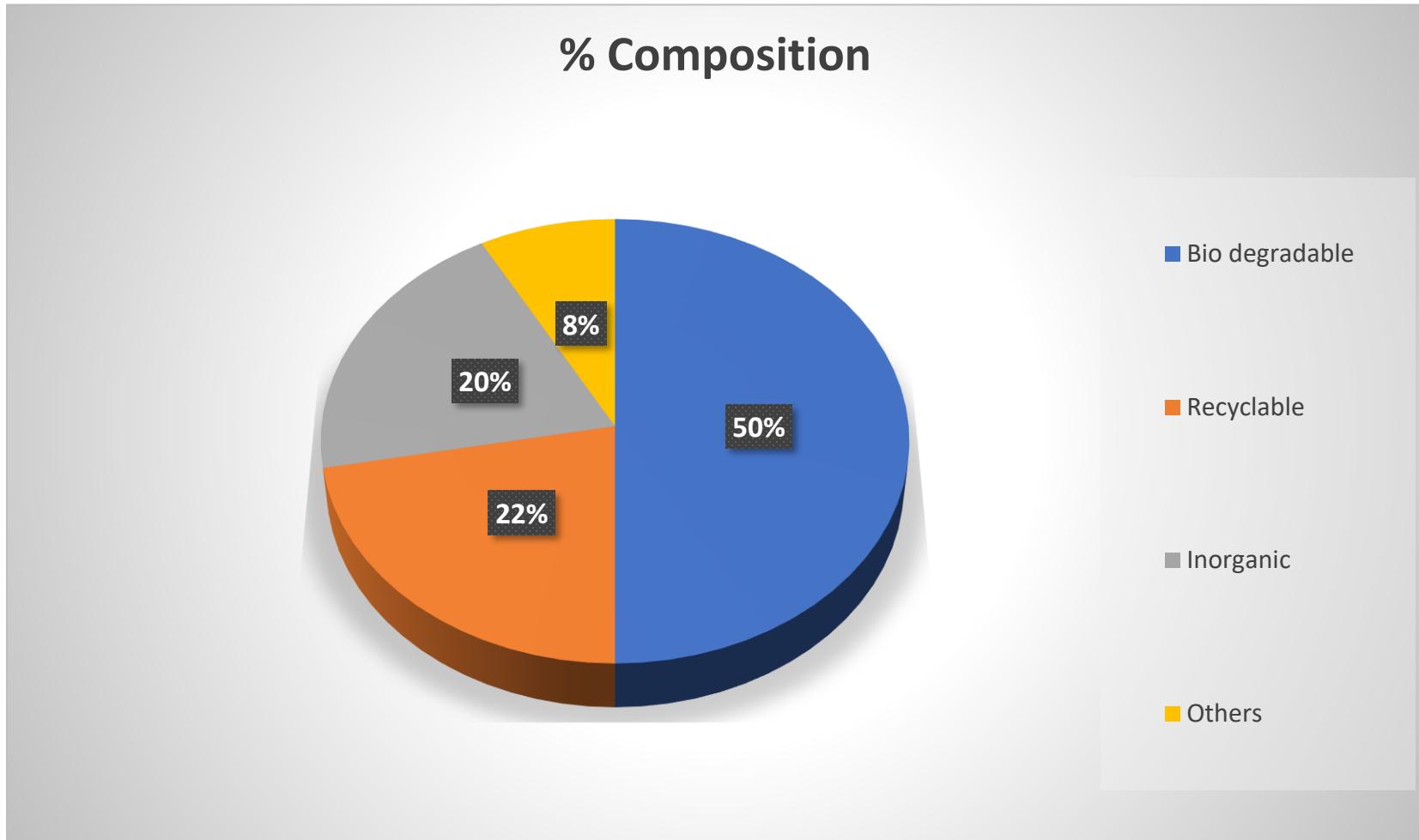
packaging waste

other materials:
glass, plastic,
metal, etc.

Important Parameters of different types of waste

Solid Waste	Waste Water	Waste Gas
Elemental Composition C, H, N, O & S	BOD & TOC	Particulate Matter
Moisture, Volatile & Ash content	pH,	Nox, Sox and CO
Bulk Density,	TDS and TSS	Heavy metal ions
Heating Value	Cations and anions	Hydrocarbon and other fuel
Hence the factors like Carbon content of solid waste , BOD and sludge content of liquid fuels and Combustible gas content of gaseous waste are important parameters for converting waste in to energy.		

Composition of Municipal Waste



Need for energy production from waste

- Waste to energy conversion gives the following advantages
- 1) It meets some energy demand, on the other way it gives some a systematic solid waste management system.
- 2) It helps us to achieve the sustainability goal of the society,
- 3) Decrease in production of green house gases
- 4) Reduction of dependance on fossils fuels
- 5) Waste to energy technology converts municipal waste into electric, heat and fuels
- 6) Reduction of waste going to land fills

Methods of production of energy from waste

- 1. Incineration: incineration is a waste treatment process that involves the combustion of organic substances content in waste materials
- 2. Gasification: gasification is a process that converts carbonaceous feedstocks into combustible gasses including H₂ and CO mainly carbon monoxide and hydrogen dioxide gas.
- 3. Pyrolysis: pyro means fire, lysis means cutting. So, this is the process that is thermal decomposition process which decomposes carbonaceous material by the application of heat in absence of oxygen.
- 4. Anerobic Digestion: In an oxygen-free tank, this material is broken down to biogas and fertilizer.
- In incineration we used excess amount of oxygen in gasification we use controlled amount of oxygen and in pyrolysis we use no oxygen theoretically.

E-waste

- Electronic waste or E-waste describes the discarded electrical or electronic devices.
- Sources of e-waste
- Waste produced due to data generating & processing devices like computers, monitors, speakers, keyboards, printers etc.
- Electronic devices used in TV, DVDs and CDs.
- Equipment's used in communication like phones, landlines phones, mobiles etc.
- Household equipment like vacuum cleaner, microwave ovens, washing machines, air conditioners etc

Effect of e-waste on environment

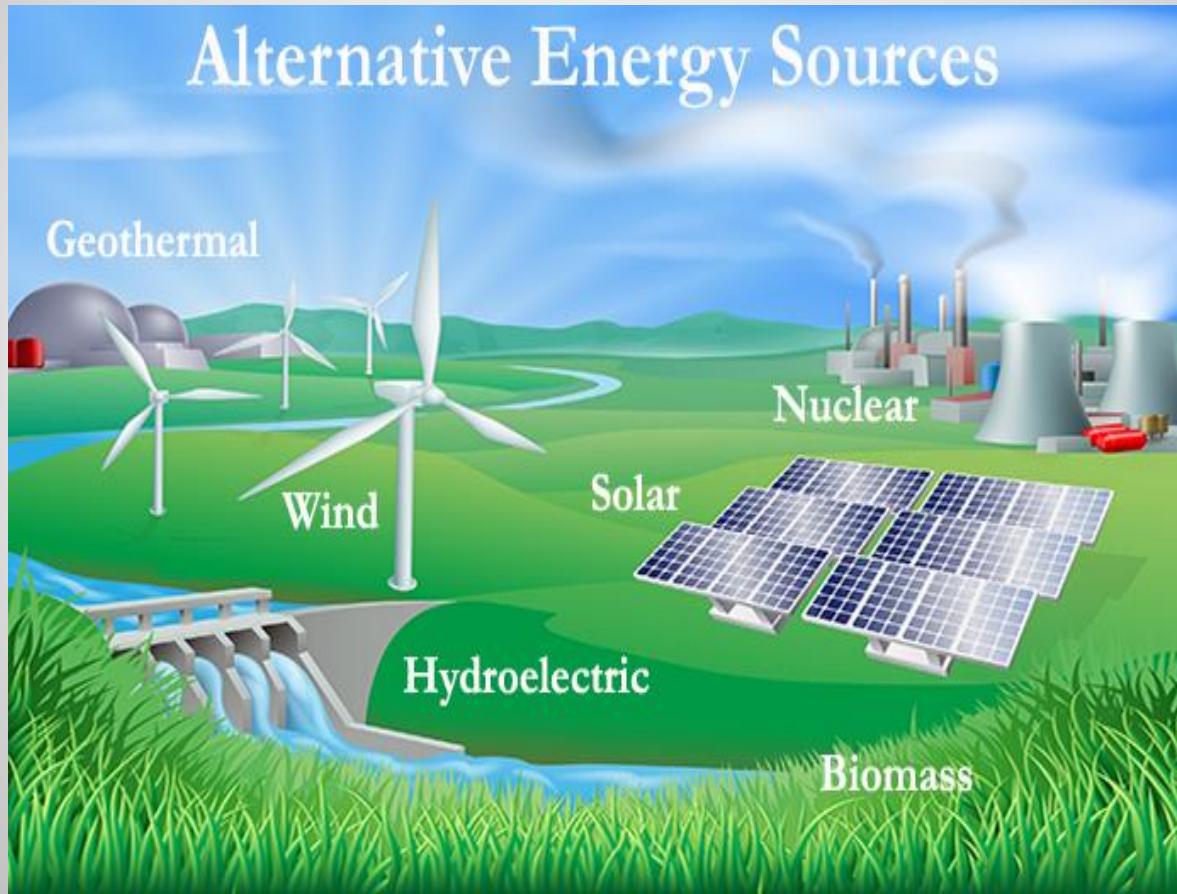
- Emission from e-waste create environmental damage
- Toxic chemicals from e-waste enter into soil-crop-food pathway.
- They are non-biodegradable causing pollution of soil
- E-waste dumping yards causes pollution and health hazards.
- It cause health hazards due to lead, mercury, cadmium poisoning

E-waste management

- Common methods
- Landfill disposal
- Incineration
- Acid treatment
- Advanced method
- Recycling
- It involves
- Disassembling-carefully separating various components
- Upgrading-involves mechanical or chemical or metallurgical methods to recover the metals
- Glass, plastic, metals can be recovered and then mixed with other ingredients to produced many valuable recycled products.

- Thank you

RENEWABLE ENERGY



RENEWABLE SOURCES:-

- SOLAR ENERGY
- WIND ENERGY
- TIDAL ENERGY
- GEOTHERMAL ENERGY
- WAVE ENERGY
- OCEAN THERMAL ENERGY
- BIOGAS

NON-RENEWABLE SOURCES:-

- COAL, COKE
- PETROLEUM AND ITS DERIVATIVES
- NUCLEAR FUEL
- NUCLEAR GAS

Need for Renewable Resources

- In the current scenario, the demand of fossil fuels is ever increasing. The globe is being affected very badly because of the emission of harmful gases by these fuels.
- Recent statistics state that if global warming continues at the same rate, then there would be 4 degree Celsius rise in the global temperature by 2100. Also India has overtaken America which was then the second largest producer of sulphur dioxide. This is very alarming and so we have tried our best to give a small contribution to save the nature.

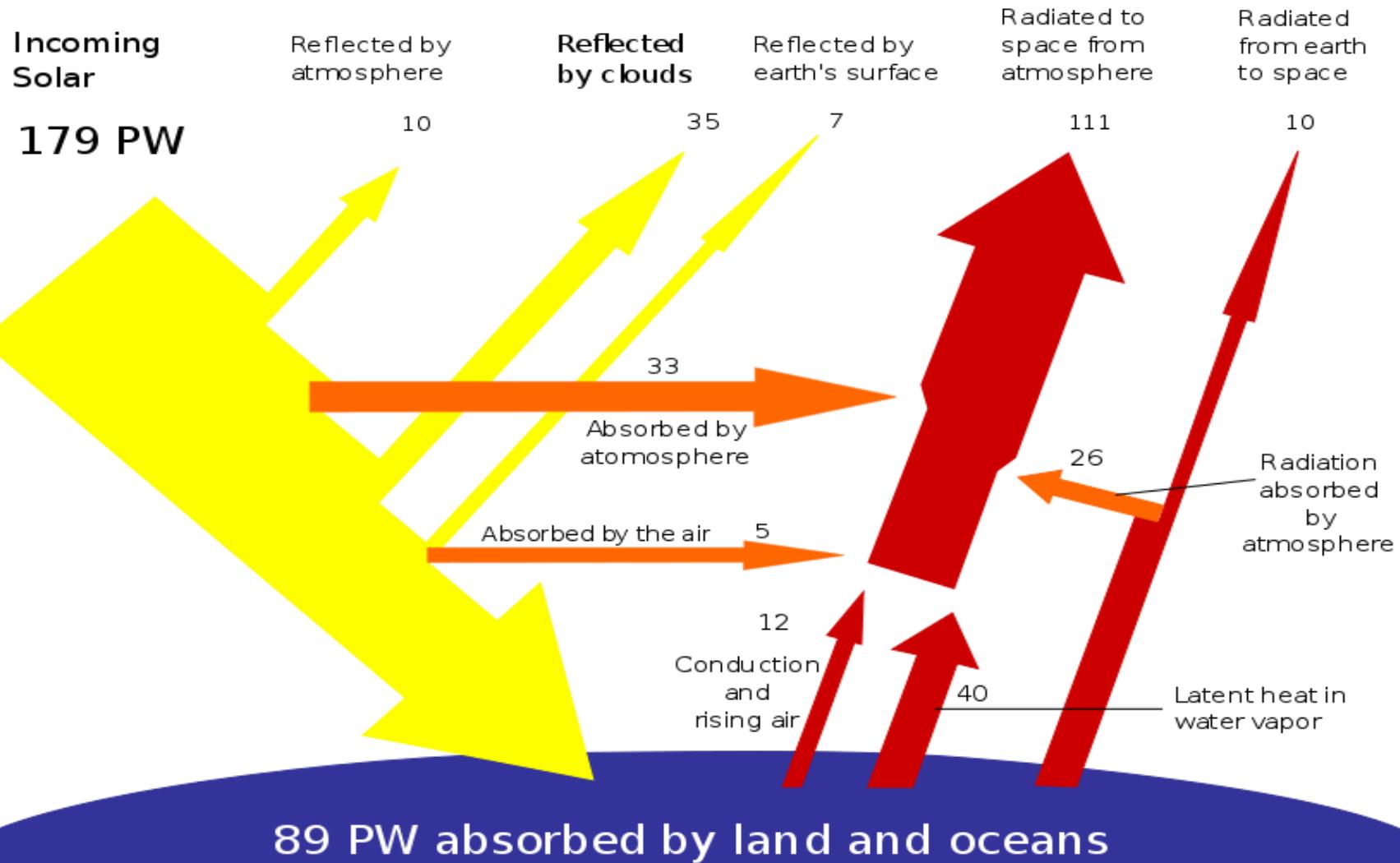
ADVANTAGES AND DISADVANTAGES OF RENEWABLE SOURCES OF ENERGY:-

ADVANTAGES:-	DISADVANTAGES:-
1. They have minimal impact on the environment.	1. They contain energy in diluted form.
2. They are widely available.	2. But, availability is uncertain or periodic.
4. Renewable energy facilities generally require less maintenance than traditional generators.	3. It is difficult to generate the quantities of electricity that are as large as those produced by traditional fossil fuel generators.
4. They are non polluting.	4. Their collection is expensive.

SOLAR ENERGY

iNTRODUCTION

- 'Solar' is a Latin word for the sun and Energy is the ability to do work.
So, we can define solar energy as energy obtained from the sun.
- Nuclear fusion reactions taking place in the sun giving rise to electromagnetic radiations. 45% of these radiations, are absorbed by the earth.
- One of the basic and natural use of solar energy is photosynthesis.
- Solar energy is radiant light and heat energy from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture, molten salt power plants and artificial photosynthesis.



Reasons for using Solar energy:-

Solar energy is a major renewable energy source with the potential to meet many of the challenges facing the world.

- 1) Solar Power Is Good for the Environment**
- 2) Combats Climate change**
- 3) Solar Power Causes Less Electricity Loss**



Advantages of Using Solar Energy

- Renewable energy source available free of cost
- Clean and pollution free
- The source does not deplete with use
- Available naturally in every consumer's premises



PAY LESS IN ENERGY BILLS



BE A PART OF CLEAN ENERGY EFFORTS



PROTECT AGAINST EVER-RISING ELECTRIC RATES



INCREASE THE VALUE OF YOUR HOME

LIMITATIONS OF USING SOLAR ENERGY:-

- 1) Uneconomical
- 2) Weather Dependent
- 3) Solar Energy Storage Is Expensive
- 4) Uses a Lot of Space
- 5) Still in developmental stage



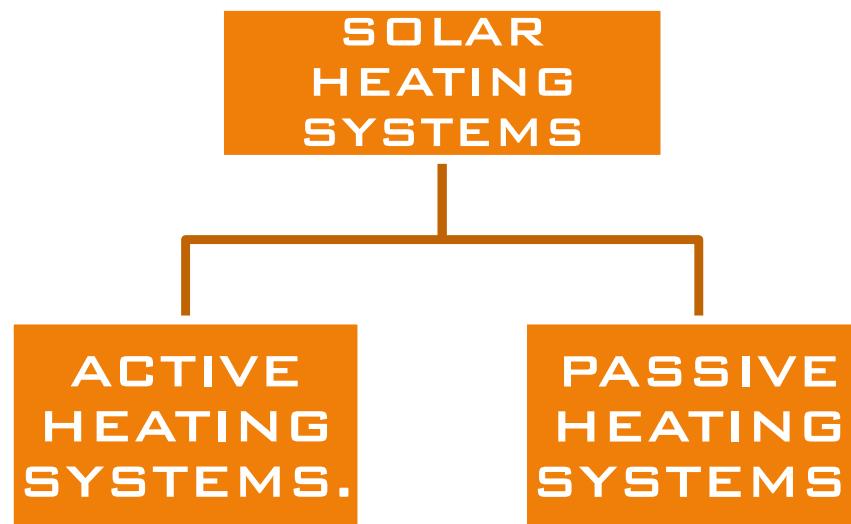
APPLICATIONS OF SOLAR ENERGY:-

- 1) Solar domestic heating purposes.
- 2) Solar cooking.
- 3) Electricity generation.
- 4) Solar thermal power production.
- 5) Solar furnaces.
- 6) Solar green houses.
- 7) Driving force for batteries

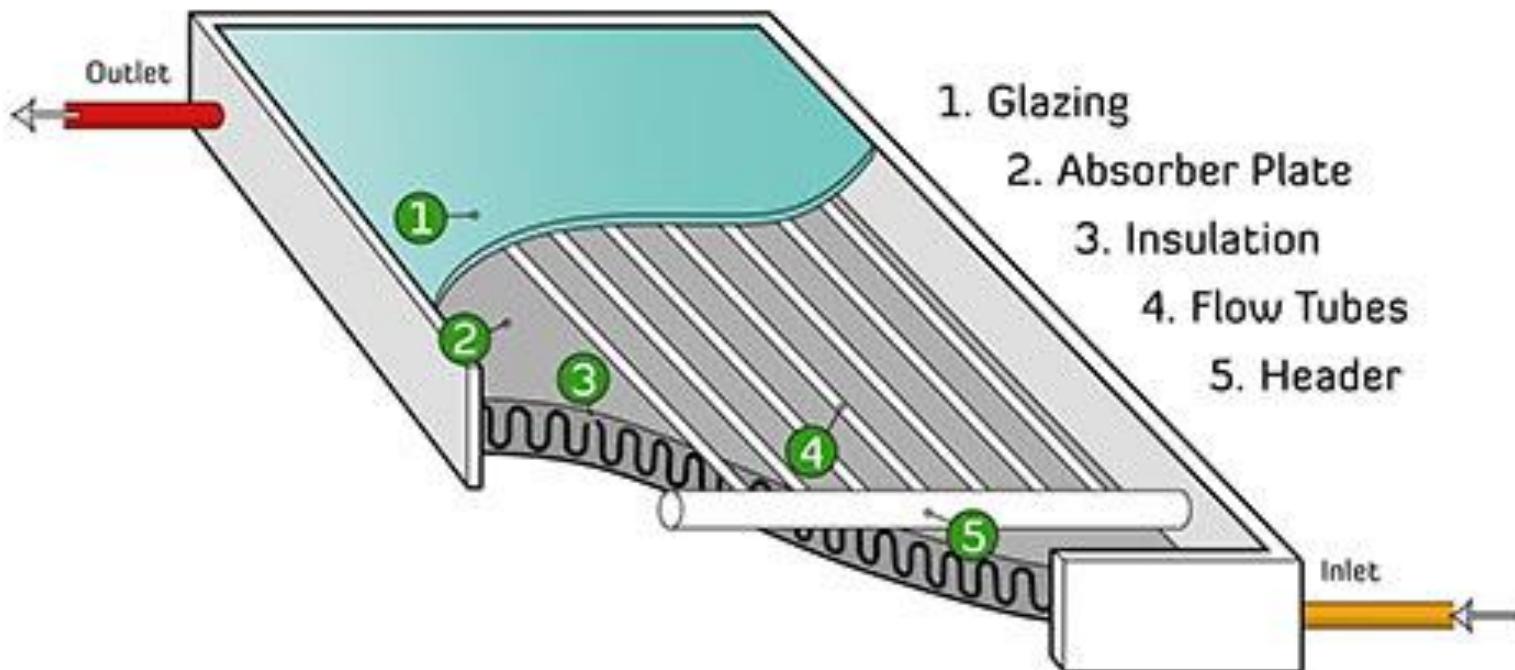


Solar Heating

- No conversion equipment or complex collection required for domestic heating
- Simple principle of black body principle (solar panels), flat plate collectors are used.



FLAT PLATE COLLECTOR:-



- It is a common type of solar “panel” is one that is used strictly for heat production, usually for heating water
- Consists of a black (or dark) surface behind glass that gets super-hot in the sun
- Upper limit on temperature achieved is set by the power density from the sun
 - dry air may yield 1000 W/m^2 in direct sun
 - using σT^4 , this equates to a temperature of $364 \text{ }^\circ\text{K}$ for a perfect absorber in radiative equilibrium (boiling is $373 \text{ }^\circ\text{K}$)
- Trick is to minimize paths for thermal losses

- You want to channel as much of the solar energy into the water as you can
 - this means suppressing other channels of heat flow
- Double-pane glass
 - cuts conduction of heat (from hot air behind) in half
 - provides a buffer against radiative losses (the pane heats up by absorbing IR radiation from the collector)
 - If space between is thin, inhibits convection of air between the panes (making air a good insulator)
- Insulate behind absorber so heat doesn't escape
- Heat has few options but to go into circulating fluid

- Glass is transparent to visible radiation (aside from 8% reflection loss), but opaque to infrared radiation from 8-24 microns in wavelength
 - collector at 350 °K has peak emission at about 8.3 microns
 - inner glass absorbs collector emission, and heats up
 - glass re-radiates thermal radiation: half inward and half outward: cuts thermal radiation in half
 - actually does more than this, because outer pane also sends back some radiation: so 2/3 ends up being returned to collector

Efficiency-

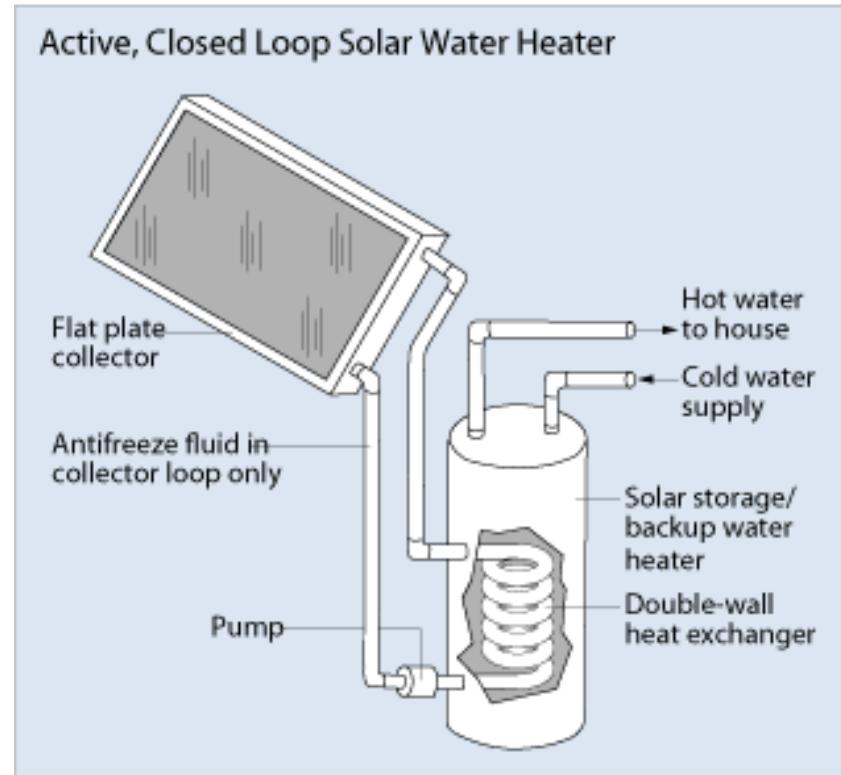
- Two-pane design only transmits about 85% of incident light, due to surface reflections
- Collector is not a *perfect* absorber, and maybe bags 95% of incident light (guess)
- Radiative losses total maybe 1/3 of incident power
- Convective/Conductive losses are another 5–10%
- Bottom line is approximately 50% efficiency at converting incident solar energy into stored heat
 - $0.85 \times 0.95 \times 0.67 \times 0.90 = 0.49$

Domestic use-

- Typical showers are about 10 minutes at 2 gallons per minute, or 20 gallons.
- Assume four showers, and increase by 50% for other uses (dishes, laundry) and storage inefficiencies:
 - $20 \times 4 \times 1.5 = 120$ gallons ≈ 450 liters
- To heat 450 l from 15 °C to 50 °C requires:
$$(4184 \text{ J/kg/}^{\circ}\text{C}) \times (450 \text{ kg}) \times (35 \text{ }^{\circ}\text{C}) = 66 \text{ MJ}$$
 of energy
- Over 24-hour day, this averages to 762 W
- At average insolation of 200 W/m² at 50% efficiency, this requires 7.6 m² of collection area
 - about 9-feet by 9-feet, costing perhaps \$6–8,000

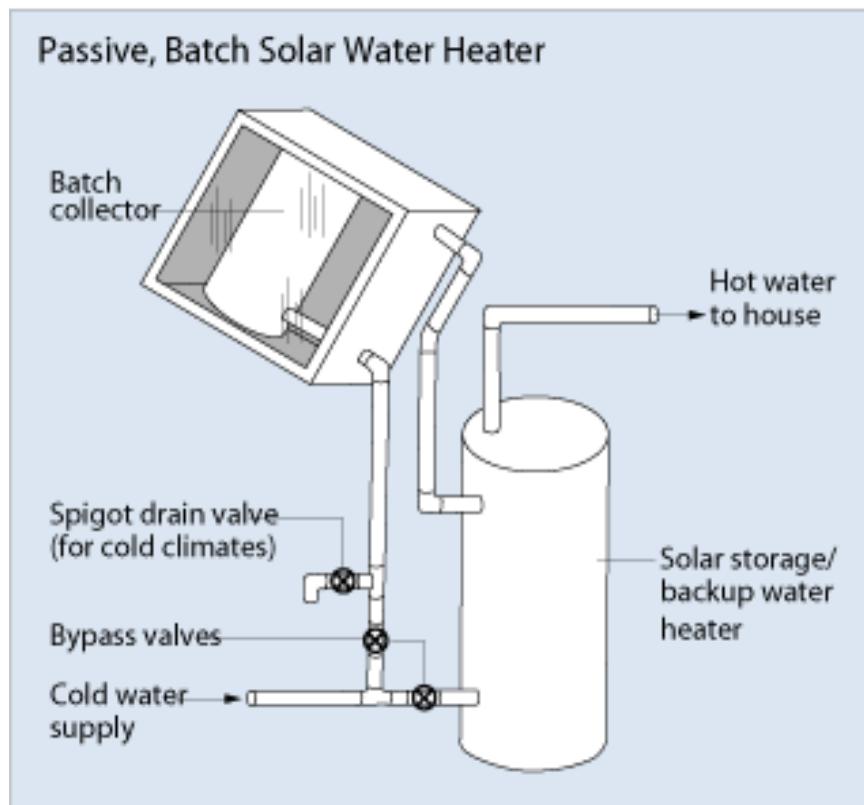
Active heating system

- a) Active systems use one or more pumps to circulate water and/or heating fluid. This permits a much wider range of system configurations.
- b) Easily controlled and higher efficiency
- c) Features like safety functions, remote access ,informative displays, backup, etc make it expensive



Passive heating system:-

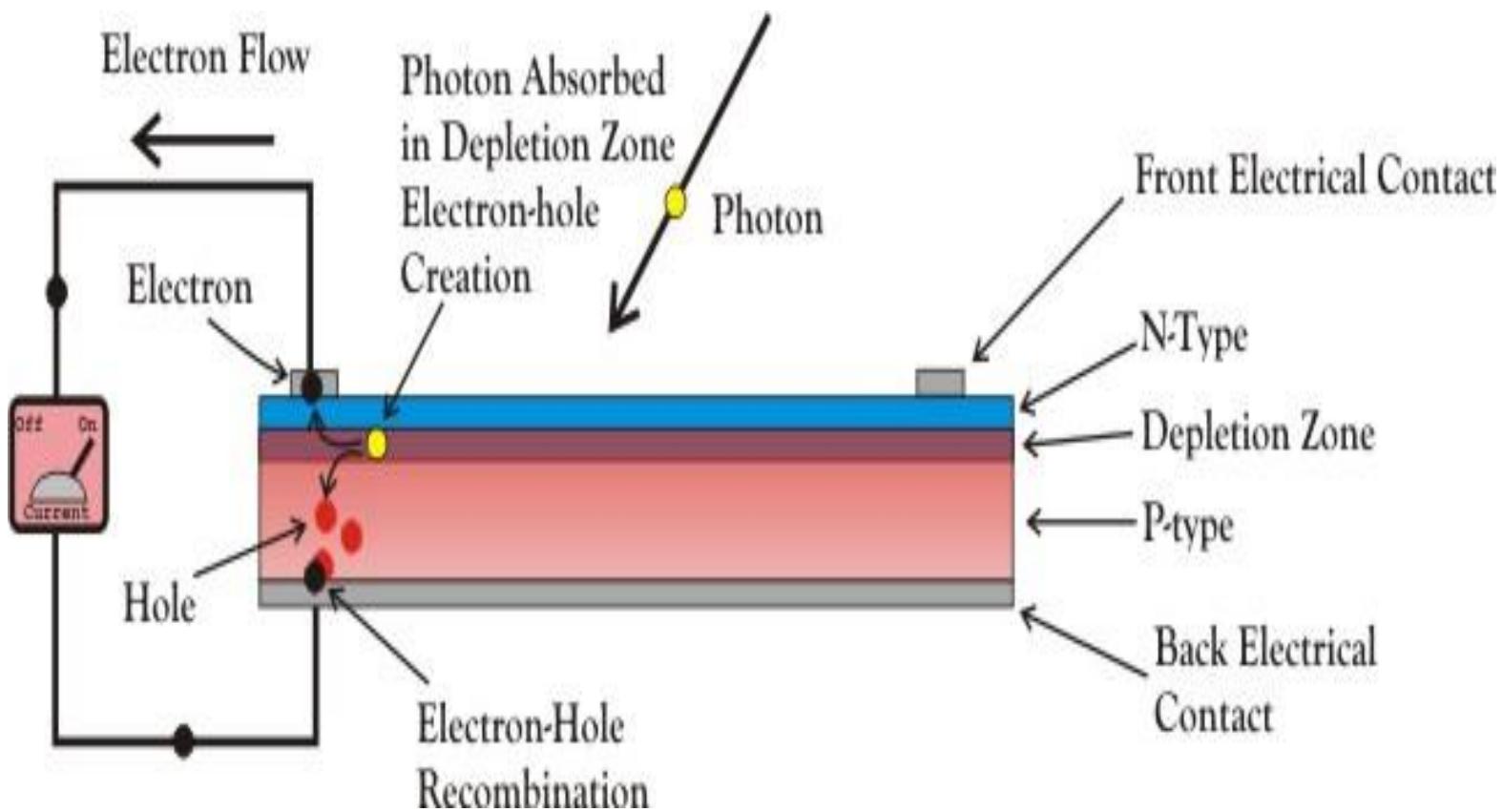
- a) Relies on natural convection for circulation
- b) Less expensive than active systems
- c) More reliable and may last longer



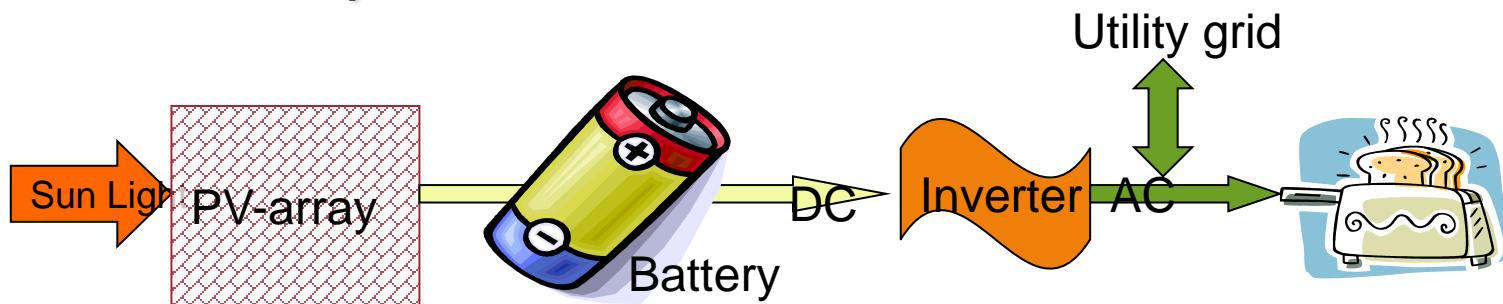
Production Of Electricity

- Photovoltaic cell
- Solar trough collector

Photovoltaic Cells:-



- Sunlight impinges on silicon crystal
- Photon liberates electron
- Electron drifts aimlessly in p-region
- If it encounters junction, electron is swept across, constituting current
- Electron collected at grid, flows through circuit (opposite current lines)



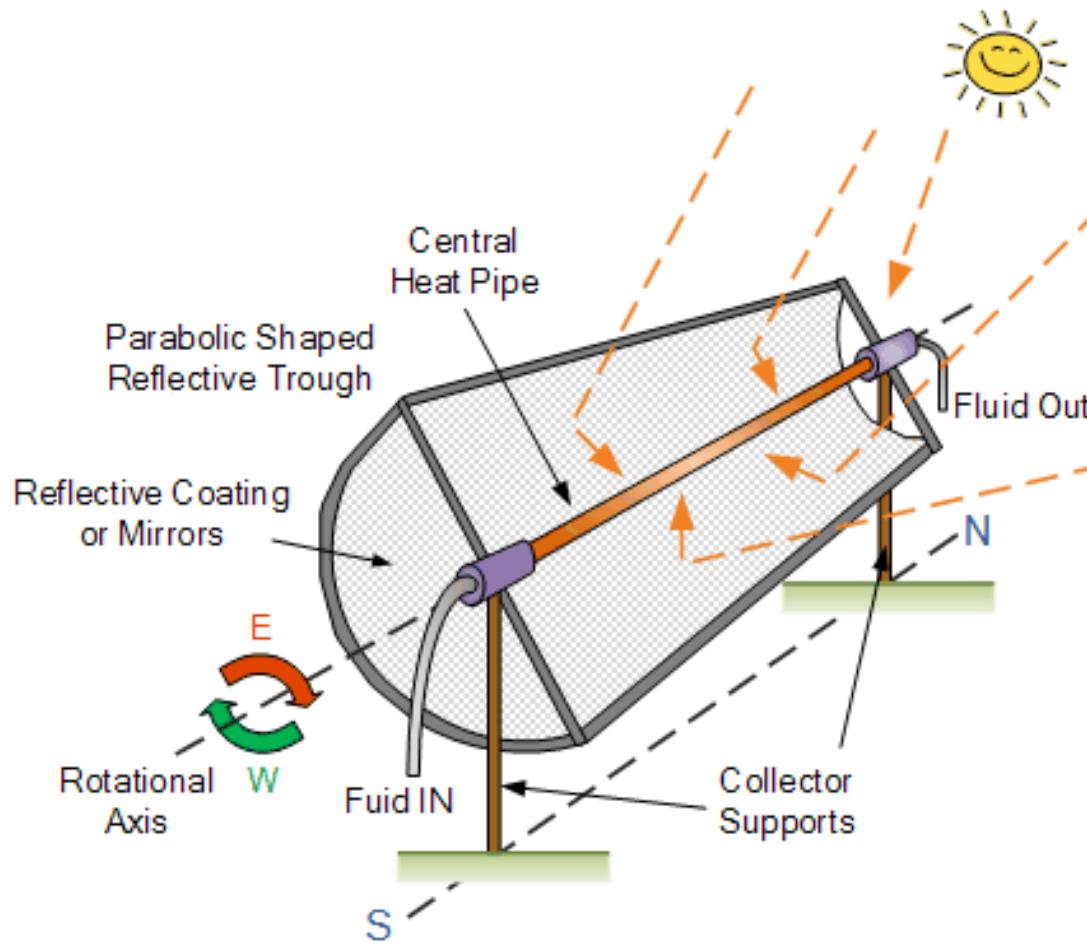
- Sunlight is turned into DC voltage/current by PV
- Can charge battery (optional)
- Inverted into AC
- Optionally connect to existing utility grid
- AC powers household appliances

- A solar cell, or photovoltaic cell , is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon
- Solar cells are described as being photovoltaic, irrespective of whether the source is sunlight or an artificial light. They are used as a photodetector for detecting light or other electromagnetic radiation near the visible range, or measuring light intensity.

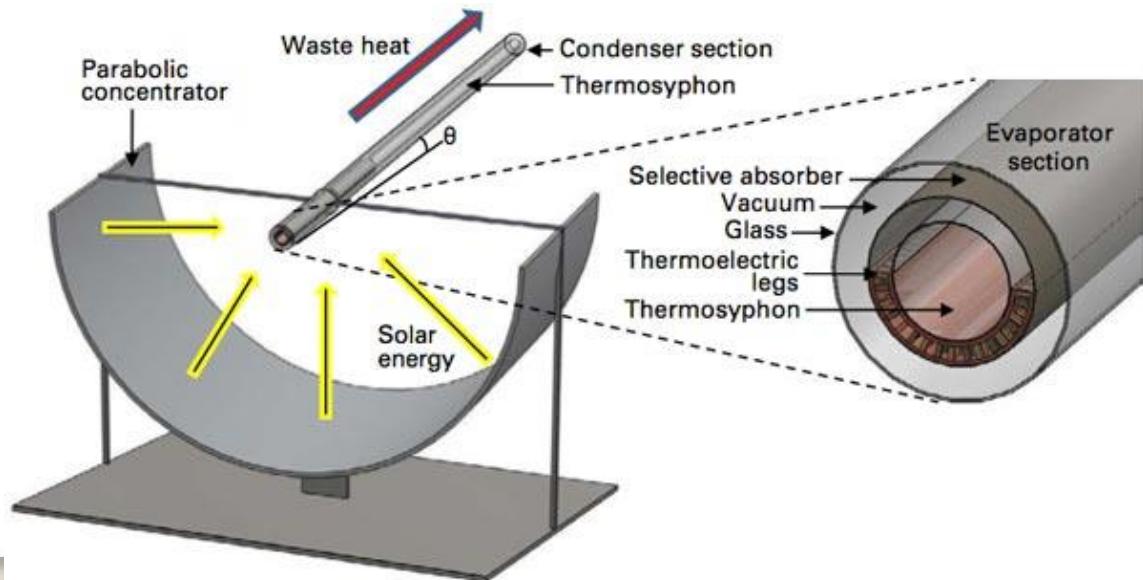
The operation of a photovoltaic (PV) cell requires three basic attributes:

- I. The absorption of light, generating either electron-hole pairs or excitons.
- II. The separation of charge carriers of opposite types.
- III. The separate extraction of those carriers to an external circuit.

Solar Trough Collector



A **parabolic trough** is a type of solar thermal collector that is straight in one dimension and curved as a parabola in the other two, lined with a polished metal mirror. The energy of sunlight which enters the mirror parallel to its plane of symmetry is focused along the focal line, where objects are positioned that are intended to be heated.



SOLAR PLANTS IN INDIA

- KAMUTHI SOLAR POWER PROJECT, TAMIL NADU: ONE OF THE LARGEST IN INDIA. OUTPUT: **648 MW**
- CHARANKA SOLAR PARK, GUJARAT: **LARGEST** IN ASIA AND SECOND LARGEST IN THE **WORLD**.
- HYBRID PLANT, LEH, JAMMU & KASHMIR.
- SINGLE AXIS TRACKER SOLAR PLANT, VELLAKOIL,TN.



Panda Solar farm Datong, China 250Acre, 100MW Mega Project

Advanced Technologies in Solar Energy Harnessing

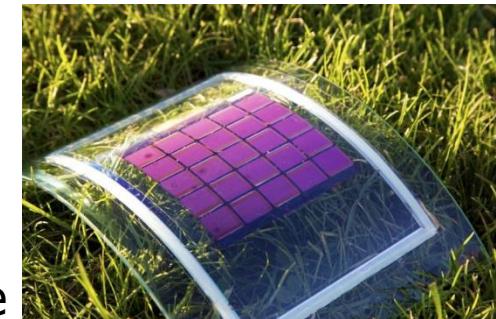
AORA Solar came with this new concept of harnessing the solar energy. It has begun the construction of this solar-biogas power plant in Ethiopia. The concept is inspired by the Sunflower, by creating the Solar Panel that faces the Sun



Innovation in Solar Cells

Organic solar cells:-

- i. Made of titanium dioxide instead of silicon.
- ii. Silicon is a limited resource while TiO₂ is available in plenty.
- iii. TiO₂ is cheaper than silicon.
- iv. Organic solar cells can be made in normal conditions of temperature and pressure while normal solar cells require vacuum conditions for manufacturing.
- v. Efficiency is greater.



COULD THE WORLD BE



100% SOLAR?



All known fossil fuel reserves could be totally spent within
the next 100 years, according to recent estimates.

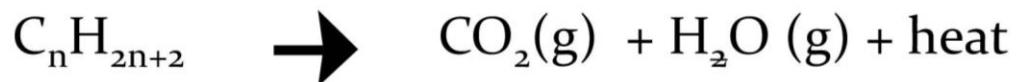
Fuels

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives a large amount of heat that can be used economically.

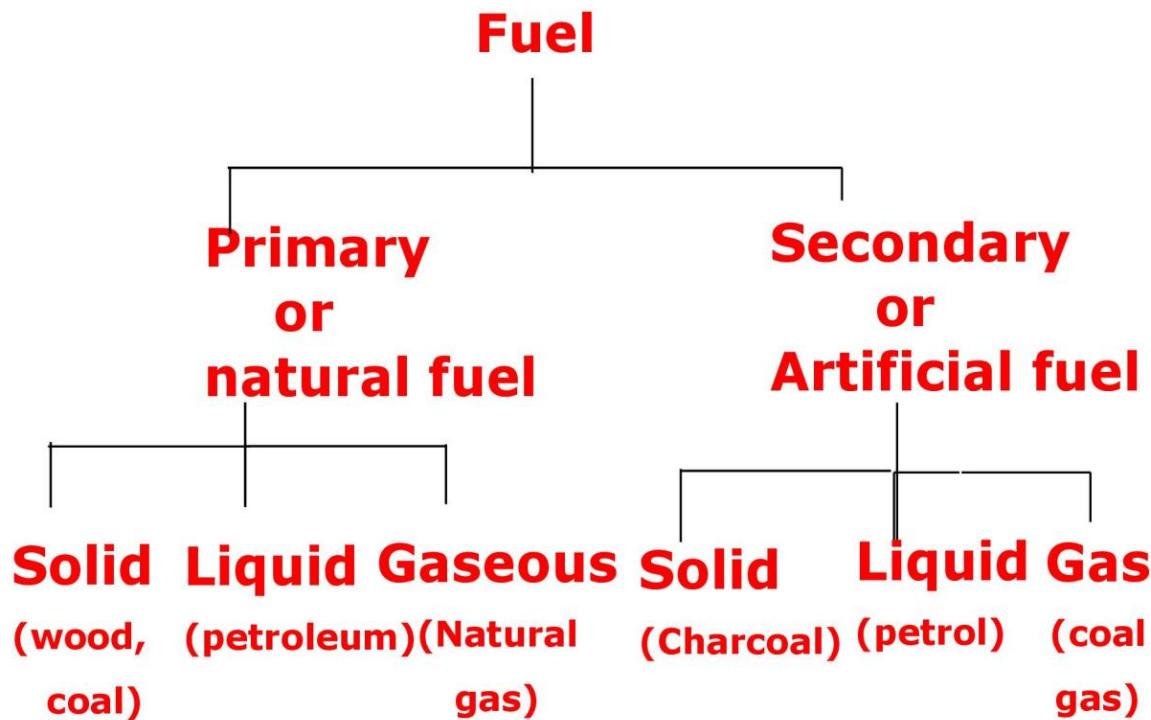
For example, wood, coal, kerosene, petrol, diesel and water gas.

Combustion is a chemical reaction in which a substance combines with oxygen producing heat, light and flame.

Combustion reaction of a fuel can be represented as follows



Classification of Fuels



Primary fuels are found in nature whereas

Secondary fuel are prepared from primary fuel by processing them in a number of ways.

Characteristics of Good Fuel

A good fuel should have

- high calorific value
- moderate ignition temperature
- low moisture content
- low non combustible matter content
- low cost and easy availability
- easy to transport and storage cost should be low
- products of combustion should not be harmful.
- burn in air without much smoke
- combustion should be easily controllable.

Calorific Value

Calorific value of a fuel is the total quantity of heat liberated when one unit of fuel is burnt completely.

Gross or Higher calorific value (G.C.V or H.C.V): It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been cooled to room temperature.

Net or Lower calorific value (N.C.V or L.C.V) : It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been permitted to escape.

L.C.V= H.C.V – Latent heat of water vapour formed

Theoretical calculation of Calorific value using Dulong's Formula

$$H.C.V = [8080C + 34500(H-O/8) + 2240 S]/100 \text{ kcal/kg}$$

Where,

C= % of carbon in the fuel

H= % of hydrogen in the fuel

O= % of oxygen in the fuel

S= % of sulphur in the fuel

And

Calorific value of carbon= 8080 kcal/kg

Calorific value of hydrogen= 34500 kcal/kg

Calorific value of sulphur= 2240 kcal/kg

L.C.V= H.C.V – Latent heat of water vapour formed

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

Units of Calorific Value

Units of calorific value	Solid fuel	Liquid fuel	Gaseous fuel
CGS method	cal/g	cal/g	cal/cm ³
MKS method	Kcal/Kg	Kcal/Kg	Kcal/m ³
FPS method	B.Th.U/lb	B.Th.U/lb	BTU/ft ³
SI method	Joule/Kg	Joule/Kg	Joule/m ³

$$1 \text{ Kcal/kg} = 1.8 \text{ B.Th.U/lb}$$

$$1 \text{ Kcal/m}^3 = 0.1077 \text{ B.Th.U/ft}^3$$

The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of **1kg of water from 15°C to 16°C**.

A British Thermal Unit may be defined as, the heat required to raise the temperature of **one pound of water from 60°F to 61°F**.

$$1\text{BTU} = 2.252\text{Kcal} = 2252\text{cal}$$

$$1\text{kcal} = 1000\text{cal}$$

$$1\text{kcal} = 3.968\text{BTU}$$

Centigrade Heat unit is the heat required to raise the temperature of **1pound water through 1 degree centigrade**.

$$1\text{kcal} = 2.2\text{CHU} = 3.968\text{BTU}$$

$$1\text{kcal/kg} = 1.8\text{BTU/lb}$$

$$1\text{kcal/m}^3 = 0.1077\text{BTU/ft}^3$$

$$1\text{BTU/ft}^3 = 9.3\text{kcal/m}^3$$

Numerical:

1. Convert 450cal/gm into- a. kcal/kg b. BTU/lb c. kcal/m³ d. BTU/ft³ e. CHU/lb.

Solution: a. 450kcal/kg b. 810BTU/lb c. d. e. 449.09CHU/lb

2. Calculate the gross and net calorific values of a coal sample having the following composition C = 80%; H = 7%; O = 3%; S = 3.5%; N = 2.5% and ash 4.4%

Solution

$$(I) \text{ G.C.V} = 1/100[8080*\%C + 34500(\%H - O/8) + 2240*\%S] \text{ kcal/kg}$$

$$= 1/100[8080*80 + 34500(7 - 3/8) + 2240*3.5] \text{ kcal/kg}$$

$$= 8828.0 \text{ kcal/kg}$$

$$(II) \text{ N.C.V} = \text{G.C.V} - [0.09H*587] \text{ kcal/kg}$$

$$= 8828 - [0.09*7*587] \text{ kcal/kg}$$

$$= 8458.2 \text{ k cal/kg}$$

Numerical:

3. A sample of coal contains: C= 60%, O= 33%, H= 6%, S= 0.5%, N= 0.3%, Ash= 0.2%. Calculate GCV and NCV.

Solution: GCV= 5506.075Kcal/kg, NCV= 5216.095Kcal/kg

4. A sample of coal contains C= 70%, O= 8%, N= 3%, S= 2%, Ash= 7%. If LCV is 8277.50Kcal/kg, find HCV and %H.

Solution: %H= 9.84 HCV= 8750.60 Kcal/kg

5. A sample of coal contains C= 61%, H= 6%, S= 0.5%, N= 0.2%, Ash= 0.3%. Calculate GCV and NCV.

Solution: %O= 32 GCV= 4250 Kcal/kg NCV= 3933.02 Kcal/kg

Comparison of Solid, Liquid and Gaseous Fuels

Solid fuel	Liquid fuel	Gaseous fuel
1. Calorific value: Their calorific value is low.	Their calorific value is high	Their calorific value is highest.
2. Pollution: Their ash content is high and they produces lot of smoke on burning.	Their ash content is low and they burn without smoke.	They are almost pollution free; they burn without smoke and ash less.
3. Ignition temp and fire hazard: They possess moderate ignition temperature	Their ignition temp is low so there is a chance of fire hazard.	They have a very low ignition temp so they are highly inflammable and chances of fire hazard is highest.
4. Cost: Their production cost is low.	Cost is relatively higher than solid fuel.	They are more costly compare to solid and liquid fuel.

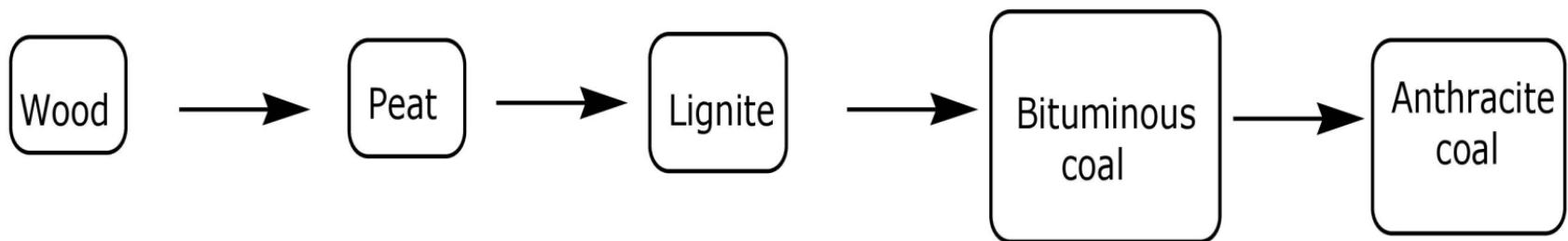
Solid fuel	Liquid fuel	Gaseous fuel
<p>5. Transportation: They are easy to transport through normal carriage so cost is low.</p>	<p>They can be transported through pipelines hence it is more costly.</p>	<p>They can be conveyed through pipelines hence costly.</p>
<p>6. Storage Their storage needs lot of space but there is no risk.</p>	<p>Costly special storage tank is required for storing and safety precaution has to be taken to prevent fire hazard as most of them are highly inflammable and volatile</p>	<p>They can be compressed in cylinder so storage does not need lot of space. Safety precaution has to be taken to prevent fire hazard as they are highly inflammable and volatile.</p>
<p>3. Mode of operation during combustion: Their thermal efficiency is low and ignition temperature is high so large proportion of heat is wasted during combustion. They require a large excess of air for complete combustion. But the combustion operation cannot be controlled easily.</p>	<p>Their ignition temp is low so firing is easier and fire can be extinguished by stopping liquid fuel supply. The flame produced by burning can be easily controlled by adjusting fuel supply.</p>	<p>Their ignition temp is lowest so firing is very easy. The flame produced by burning can be easily controlled by adjusting fuel supply.</p>

Solid Fuel

Classification of Coal

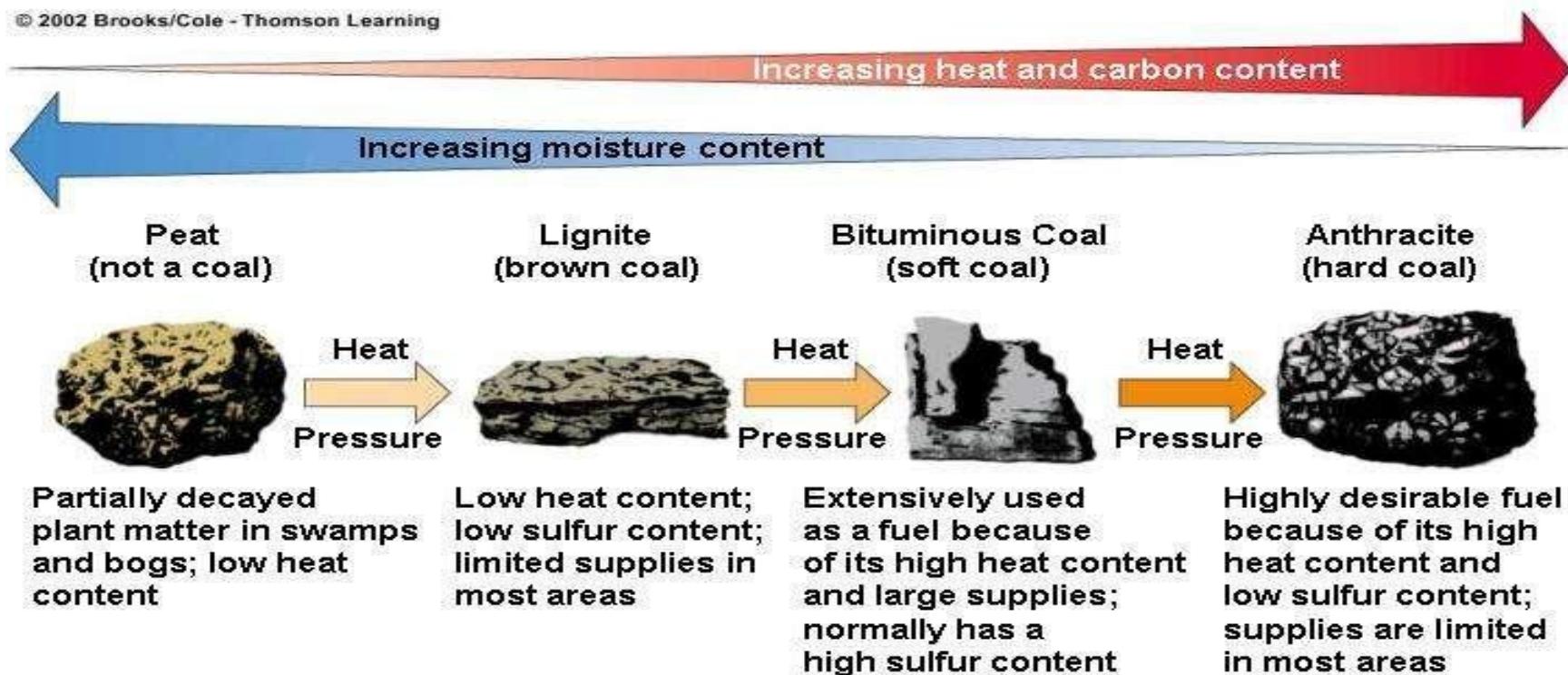
Coal is a primary solid fuel which occurs in nature in very impure form of carbon. It is a fossil fuel.

Wood, peat, lignite, bituminous and anthracite are the different stages in the conversion of wood to coal. Carbon content is highest in anthracite coal.



Coal formation process

© 2002 Brooks/Cole - Thomson Learning



Classification of Coal

	Wood	Peat	Lignite	Bituminous coal	Anthracite coal
% of Moisture content	25	25	20	4	1.5
% of Carbon content	50	57	60-80	83	93.3
% of Hydrogen content	6	5.7	5	5	3
Calorific value (Kcal/kg)	4000- 4500	4500- 5000	6500- 7000	8100- 8600	8650- 8700

Analysis of coal:

The purpose is to-

1. To decide the price of coal.
2. To determine the quality of coal.
3. To specify the use of coal for a particular purpose.
4. To calculate the theoretical calorific value of coal.
5. To calculate the air requirement for complete combustion of coal and design the furnace fir box suitably.

Analysis of coal sample is required to access the quality of coal.

(A) Proximate analysis (PA): It is the process of determination of moisture, volatile matter, ash and fixed carbon content.

(B) Ultimate analysis (UA): It is the process of determination of composition of various components of coal which includes the determination of % of C, H, S, N, O and ash content. It is necessary for utilization of coal for industrial purpose.

The **significance** of various parameters of proximate coal analysis:

Moisture :

Moisture increases transportation, handling, storage cost

Moisture decreases the heat content per kg of power plant coal

Moisture increases heat loss due to evaporation and superheating of vapor

Moisture helps in binding the fines

Moisture helps in radiation heat transfer

Volatile matter:

Volatile matter also contributes to the heating value of coal

Increase in percentage of volatile matter in coal proportionately increases flame length (smoky flame) and helps in easier ignition of coal

Sets minimum limit of furnace height and volume

Influences secondary oil support

Ash:

Ash is an impurity which will not burn

Ash content is important in design of furnace grate, combustion volume, pollution control equipment (ESP) and Ash handling plant

Ash increases transportation, handling, storage cost

Ash affects combustion efficiency and boiler efficiency

Ash causes clinkering and slagging problems in boiler

Fix carbon:

Fix carbon acts as a main heat generator during burning.

Fix carbon gives a rough estimate of heating value of coal

PROXIMATE ANALYSIS OF COAL :

Procedure:

Determination of Inherent Moisture: Transfer about 1g (W_{coal}) of powdered air-dried coal sample into a previously weighed silica crucible. Place the open crucible with sample in an ***electric oven*** and heat it at about ***105 - 110°C*** for an **hour**. Take out the crucible after one hour from the oven and cool it in a **desiccator** (containing moisture absorbing anhydrous calcium chloride). Then weigh the crucible with sample. Calculate the loss in weight.

$$\text{Weight before heating} - \text{Weight after heating} = \text{Loss in weight of coal}$$

$$\% \text{Moisture} = \frac{\text{Loss in weight}}{\text{Weight of Coal}} \times 100$$

ii) Volatile matter: The dried sample of coal left in the crucible in step (i) is then covered with a lid and placed in a muffle furnace, maintained at 950°C . The crucible is taken out after 7 minutes of heating. It is cooled first in air then in a desiccator and finally weighed.

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

Determination of ash

- Coal sample of accurate weight in a crucible is heated in muffle furnace at **700+50 degree Celsius** for $\frac{1}{2}$ an hour. Crucible is taken out and cooled first in air and then in **desiccators** and **weighed**.
- **% of ash** =
$$\frac{\text{weight of ash left} * 100}{\text{weight of coal taken}}$$

(2) Fixed carbon content: It is determined indirectly by deducting the sum of total moisture, volatile matter and ash content from 100.

$$\%FC = 100 - (\%M + \%VM + \%Ash)$$

Numerical:

A sample of coal is analyzed as follows: Exactly 2.5 g was weighted into silica crucible. After heating for an hour at 110°C, the residue weighed 2.415g. The crucible next was covered with a vented lid and strongly heated for exactly seven minutes at 950°C. The residue weighed 1.528g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245g. calculate the percentage result of above analysis.

Significance of Ultimate Analysis

1. 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 to.
2. Nitrogen has no calorific value and hence its presence in coal is undesirable. Thus, a good quality coal has very little nitrogen content.
3. Sulphur is usually present to the extent of 0.5–3.0% and is derived from ores like iron pyrite and gypsum, etc., mines along with the coal. Sulphur, although contributes to the heating value of coal, on combustion it produces acids which have harmful effects of corroding the equipment and also causes atmospheric pollution.
4. Oxygen content decreases the calorific value of coal. High oxygen content coals are characterized by high inherent moisture content, 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 actually present.

Ultimate Analysis

i) Carbon and Hydrogen (Combustion Method):

An accurately weighed coal sample (1-2g) is burnt in a current of oxygen in combustion apparatus. As a result C and H of the coal are converted into CO_2 and H_2O respectively. These are absorbed respectively in KOH and CaCl_2 tubes of known weights. The increase in the weights of KOH and CaCl_2 tubes corresponds to the amount of CO_2 and H_2O formed respectively.

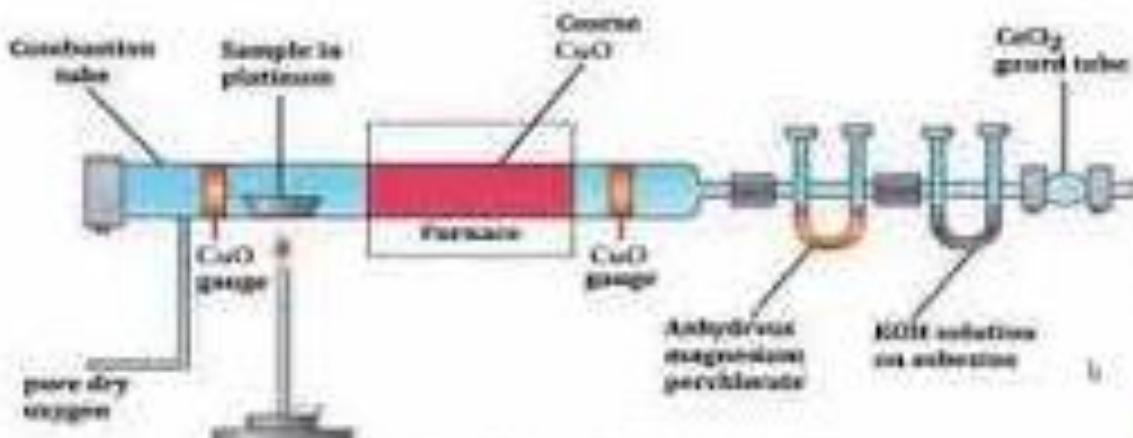
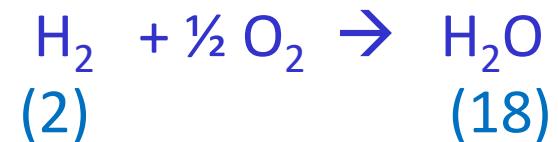
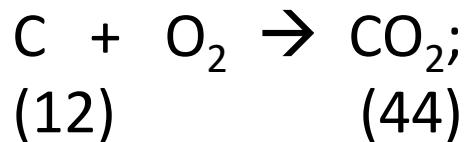


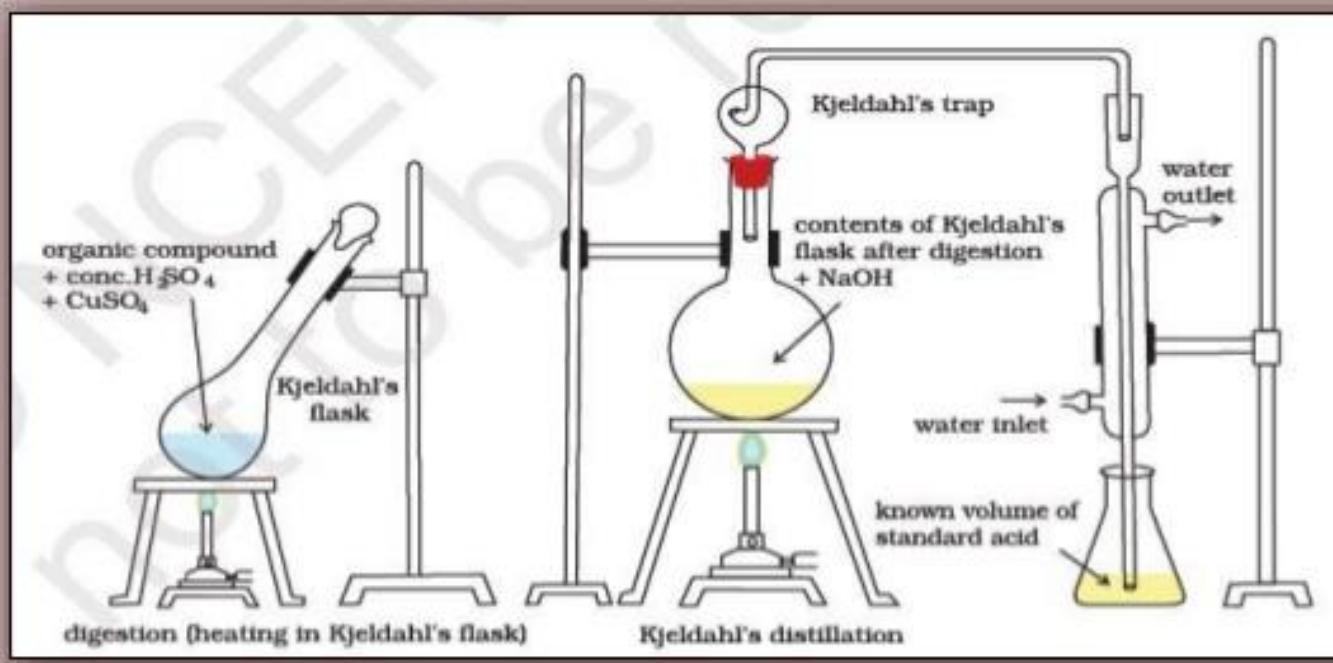
Fig 11.2 Estimation of Carbon and Hydrogen



$$\text{So, \%C} = \frac{\text{Increase in wt. of KOH tube} \times 12 \times 100}{\text{Wt. of coal sample} \times 44}$$

$$\text{\%H} = \frac{\text{Increase in wt. of CaCl}_2\text{ tube} \times 2 \times 100}{\text{Wt. of coal sample} \times 18}$$

Determination of Nitrogen



- 1g of accurately weighed powdered coal is heated with conc. H_2SO_4 in kjeldahl flask.
- It is treated with excess KOH.

- Liberated ammonia is distilled over and absorbed in a known **volume of standard** solution of acid.
- Unused acid is determined by back titration with standard **NaOH**.

% of N is
volume of acid used*normality*1.4
weight of coal sample taken

$$\% \text{ of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{weight of coal taken}}$$



Let weight of coal taken = W gm.

Vol of N/10 NaOH required for blank Rdg = Y ml.

Vol. of N/10 NaOH required = x ml (to titrate unreacted acid)

Vol. of N/10 acid reacted with ammonia = (y-x) ml.

Vol. of N/10 ammonia = (y-x) ml.

1000 ml of 1N ammonia solution = 17 gm of NH₃

1000 ml of 1N NH₃ Solution = 14 gm of N.

1000 ml of 0.1N NH₃ solution = 1.4 gm of N.

$$\therefore (\text{y}-\text{x}) \text{ ml of } 0.1\text{N NH}_3 \text{ solution} = \frac{1.4(\text{y}-\text{x})}{1000} \text{ gm of N}$$

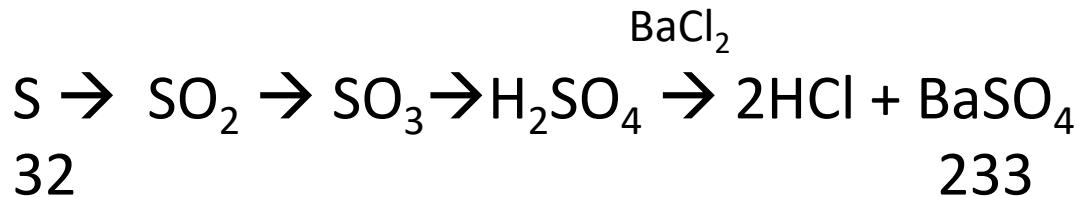
$$\text{W gm of coal contains } \frac{1.4(\text{y}-\text{x})}{1000} \text{ gm of N.}$$

$$\therefore 100 \text{ gm of coal contains} = \frac{1.4(\text{y}-\text{x})}{1000} \times \frac{100}{\text{w}} = \% \text{ N} = \frac{1.4(\text{y}-\text{x})}{10 \times \text{w}}$$

$$\text{OR } \% \text{ of N} = \frac{\text{vol. of acid used} \times \text{normality} \times 1.4}{\text{weight of coal taken}}$$

Determination of Sulphur:

Take 10ml of distilled water in a bomb calorimeter. Burn the known weight of powdered and air dried coal sample in it. Collect the washings in a beaker and add barium chloride solution to it. Filter the precipitate of barium sulphate formed. Dry it and weigh it. Calculate the %S as-



$$\% \text{S} = \frac{\text{Weight of BaSO}_4 \text{ ppt}}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$$

Determination of ash and oxygen

- Coal sample of accurate weight in a crucible is heated in muffle furnace at **700+50 degree Celsius** for $\frac{1}{2}$ an hour. Crucible is taken out and cooled first in air and then in **desiccators** and **weighed**.
 - **% of ash** = $\frac{\text{weight of ash left} * 100}{\text{weight of coal taken}}$
 - **% of oxygen** is
100-percentage of (**C+H+S+N+Ash**)

Numerical:

1. 0.2g of coal sample is burnt. The gaseous products are absorbed in potash bulb and calcium chloride tube of known weight. The increase in weight of potash bulb and calcium chloride tube are 0.66gm and 0.08gm respectively. Calculate %C and %H. (Solution: C= 90%; H= 4.44%)
2. 3gm of coal was heated in Kjeldahl's flask and ammonia formed was absorbed in 40ml of 0.5N acid. After absorption, the excess acid required 18.5ml of 0.5N KOH for neutralization. 2.3gm of same coal sample gave 0.35gm BaSO_4 ppt. Calculate %N and %S. (N= 5.01%; S= 2.089%)

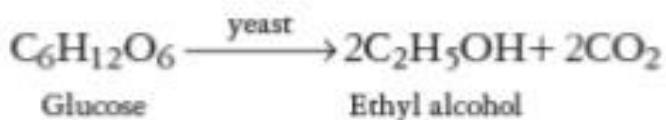
Power Alcohol and Synthetic Petrol

Power Alcohol

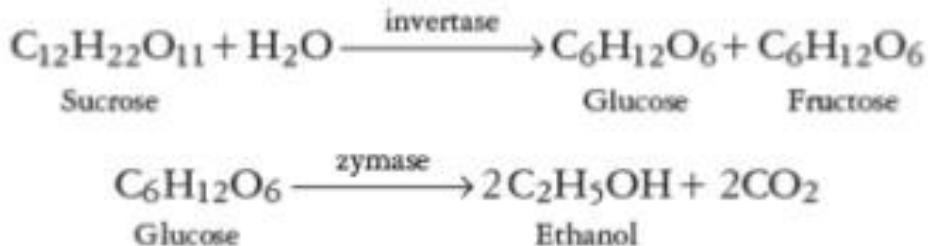
Ethyl alcohol is used as additive to motor fuels. When blended with petrol at concentrations of 5–10%, it is called power alcohol. The addition of alcohol to petrol increases its octane number.

Manufacture of Ethanol

1. By fermentation



2. Using Molasses as raw material



The advantages of power alcohol are as follows:

1. Ethyl alcohol is a good antiknocking agent and power alcohol has octane number 90, while that of petrol is 65.
2. Any moisture content present is absorbed by alcohol.
3. Ethyl alcohol contains oxygen atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are largely reduced.
4. Power alcohol is cheaper than petrol.

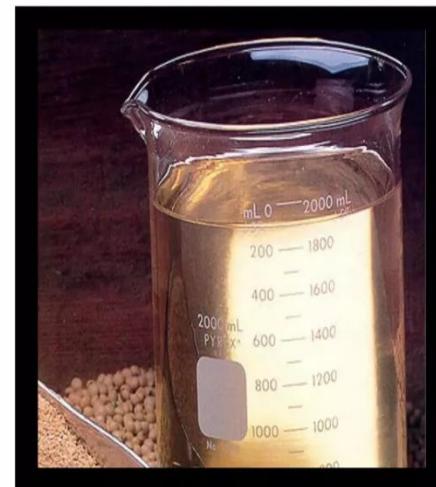
The disadvantages of power alcohol are as follows:

1. Ethyl alcohol has calorific value 7000 cal/g much lower than that of petrol which has 11500 cal/g. However, this problem could be overcome by using a specially designed engine with higher compression ratio.
2. The output of the power generated is reduced up to 35%.
3. It has high surface tension and its atomization is difficult, especially at lower temperature, thereby causing starting trouble.
4. It may undergo oxidation reaction to form acetic acid, which corrodes engine parts.
5. As it contains oxygen atoms, the amount of air required for complete combustion is less, therefore, the carburetor and engine need to be modified.

Bio-Diesel

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by Transesterification of vegetable oil or animal fat , which can be used (alone, or blended with conventional petro-diesel) in unmodified diesel-engine vehicles.

"**Biodiesel**" is standardized as mono-alkyl ester.



Why biodiesel

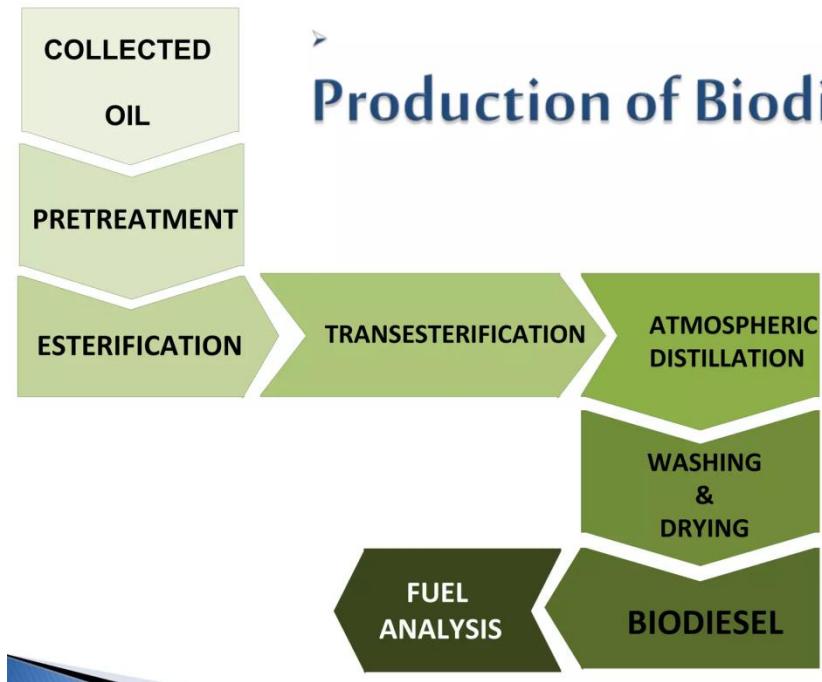
- Globally, transportation accounts for 25% of energy demand and nearly 62% of oil consumed.
- The generation of electricity is the single largest use of fuel in the world.
- More than 60 % of power generated comes from fossil fuels.

➤ Security Of Supply

➤ Reduction Of Green House Gas Emissions

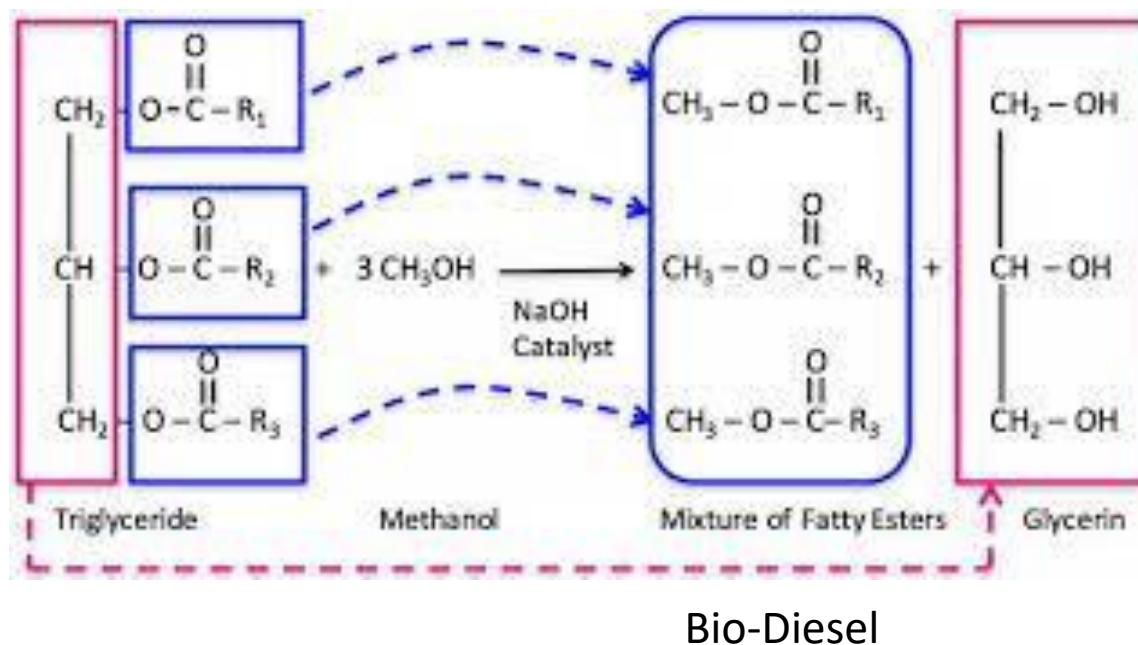
➤ Social Structure & Agriculture

Production of Biodiesel



- This is the process of separating the fatty acids from their glycerol backbone to form biodiesel and glycerine.

- Transesterification is the reversible reaction of oil with an alcohol (methanol or ethanol) to form fatty acid alkyl esters and glycerol.
- The vegetable oil molecules is reduced to about 1/3rd its original size, lowering its viscosity, making it similar to diesel.



Uses of Biodiesel

- Electricity production
- Transportation
 - Railways
 - Ships
 - Automobiles

Railway usage

- The British businessman Richard Branson's Virgin Voyager train number 220007 Thames Voyager, billed as the world's first "biodiesel train".



Indian Initiatives

- National Mission on Biodiesel has been launched by GOI
 - State Governments designated special authorities/bodies to manage
 - Ministry of Petroleum and Natural Gas notified biodiesel purchase policy
 - Government Institutes are working on technology and promotion
 - Public and private sectors are working on processing and end use
- The former President of India, **Late Dr. Abdul Kalam**, is one of the strong advocates of Jatropha cultivation for production of bio-diesel.

Biodiesel : First trial run on train

- First successful trial run of a superfast passenger train was conducted on Dec 31, 2009
- Delhi - Amritsar Shatabdi Express used 5% of biodiesel fuel.
- Railway annual fuel bill = Rs 3400 crore (for Diesel)
- 10% mixture with Diesel = reduced (Rs.300-400 crore / annum)
- 5% substitution is accepted.

- The **State Bank of India** provided a boost to the cultivation of Jatropha in India by signing a MoU with **D1 Mohan**, a joint venture of D1 Oils plc, to give loans to the tune of **1.3 billion rupees to local farmers** in India.

Interesting Practicalities States

- Andhra Pradesh has entered into a formal agreement with **Reliance Industries** for Jatropha planting.
- The company has selected 200 acres (0.81 km^2) of land at Kakinada to grow Jatropha for **high quality bio-diesel fuel**.
- Chhattisgarh has decided to plant 160 million saplings of Jatropha in all its 16 districts during 2006 with the aim of becoming **a bio-fuel self-reliant state by 2015**.

Maharashtra-

Major Issues

- Land Availability
- Certified High Yielding Varieties
- Plant Health
- Availability of labor
- Irrigation
- Costs

- On Nov 2005, the Maharashtra Government aimed to cultivate Jatropha on 600 km^2 in the state.
- September 2007-**Hindustan Petroleum Corporation Limited(HPCL)** joined hands with the **Maharashtra State Farming Corporation Ltd(MSFCL)** for a Jatropha seed-based bio-diesel venture.
- Jatropha plant would be grown on 500 acres (2 km^2) in Nashik and Aurangabad.

Advantages

- Bio diesel is environmental friendly.
- It can help reduce dependency on foreign oil.
- It helps to lubricate the engine itself, decreasing engine wear.
- It offers similar power to diesel fuel.
- It is safer than conventional diesel.
- It can be made from waste products.
- It can be made at home easily.

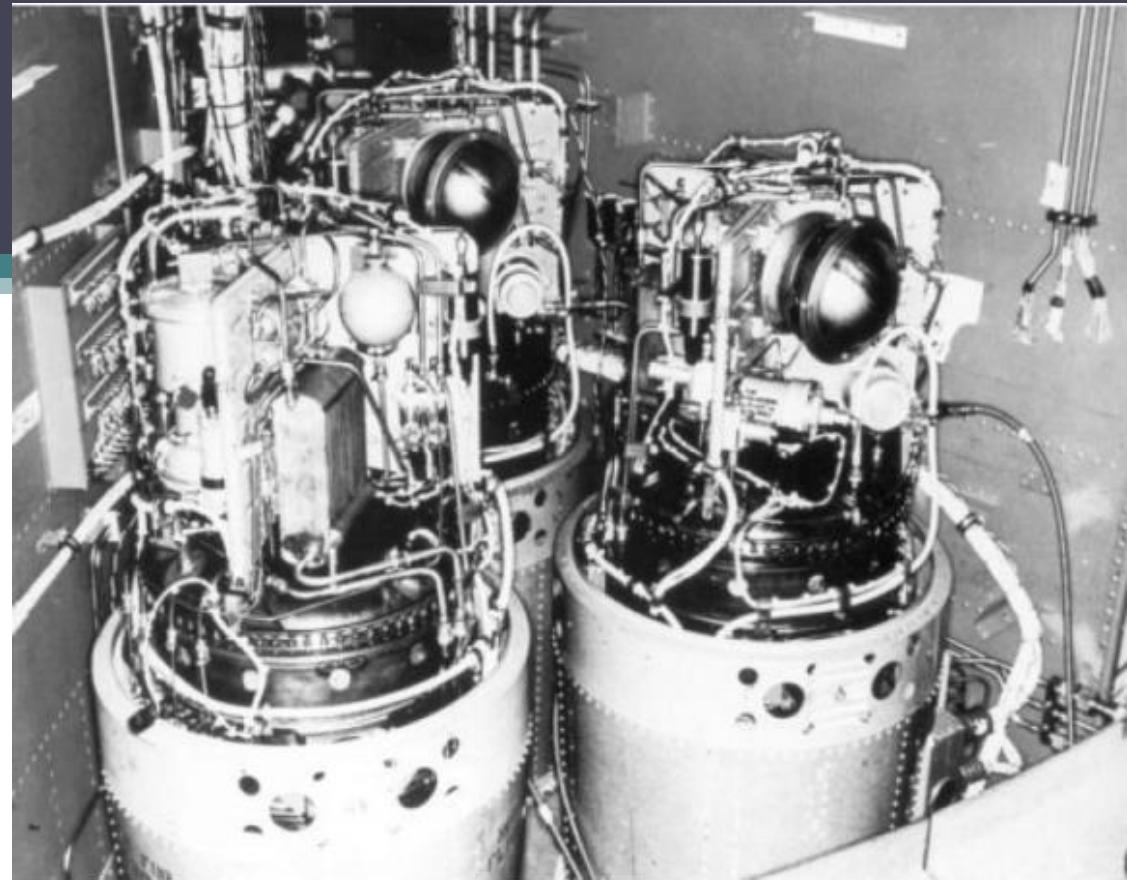
Disadvantages

- Its storage for long period is not suitable for engine operation.
- It becomes gel in cold weather.
- It has water content. (Hygroscopic)
- It has higher (10%) Nox emissions.
- It decreases horsepower. (25%)

Conclusion

- By mixing of 20 per cent biodiesel with diesel will help India to save 7.3×10^6 tones of diesel per year.
- In India about 33 million hectares of wasteland is available and can effectively be used for cultivation of jatropha plants.
- It offers business possibility to agricultural enterprises and rural employment.
- Biodiesel is least-cost-strategy to comply with state and federal regulations.
- Use of biodiesel does not require major engine modifications. The only thing that changes is air quality.
- Biodiesel has positive attributes such as increased cetane, high fuel lubricity & high oxygen content.
- Biodiesel reduces by as much as 65 % the emission of small particles of solid combustion products.
- The ozone (smog) forming potentials of hydrocarbons is less than diesel fuel.
- Sulfur emissions are essentially eliminated with pure biodiesel .
- Biodiesel contain no petroleum, but can be blended with conventional diesel fuel.
- These fuel can be used in any diesel engine without any modification.
- Biodiesel is degradable , non toxic and free from sulphur and lead.

FUEL CELLS



FUEL CELLS

- A fuel cell is an electrochemical device that produces electricity without combustion by combining hydrogen and oxygen to produce heat and water

History of Fuel Cells

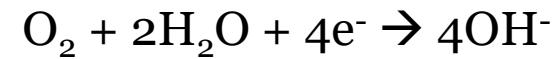
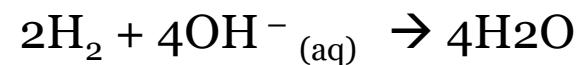
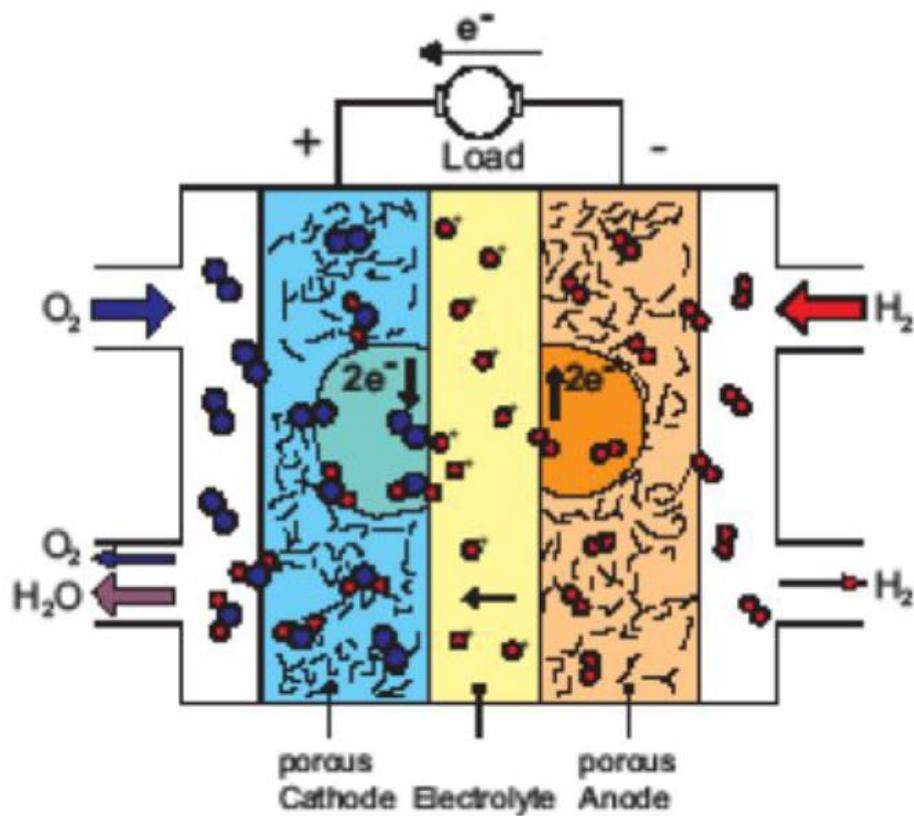
- Discovered by German scientist G.H.Shoenbein.
- First developed by William Grove.
- Developed by Grove while conducting research on electrolysis.
- Between 1930s to 1950s, British engineer Francis Thomas Bacon worked on developing alkaline fuel cells.
- He demonstrated a working stack in 1958
- The technology was licensed to Pratt and Whitney where it was utilized for Apollo spacecraft fuel cells

Advantages of Fuel Cells over conventional energy sources

- They produce zero or very low emissions, especially Green House Gases depending on the fuel used.
- Efficiency of fuel cells is more than efficiency of conventional heat engines.
- They have an excellent response time.
- They require minimal maintenance.
- No recharging is required.

Structure of Hydrogen fuel cell

Hydrogen Fuel Cell



Working Principle-

- A fuel cell is a device which uses Hydrogen (or a hydrogen rich fuel) and oxygen to create electricity by an electrochemical process.
- A single fuel cell consists of an electrolyte sandwiched between two electrodes (a porous anode and cathode.)
- Hydrogen or a hydrogen rich fuel is fed to the anode where a catalyst separates hydrogen's negatively charged electrodes from positively charged ions (protons).
- At the cathode, the oxygen combines with the electrons and, in some cases, with species like protons or water, resulting in water or hydroxide ions, respectively.

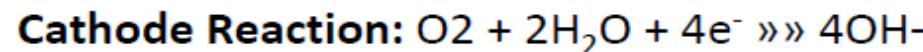
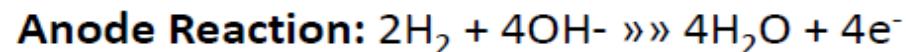
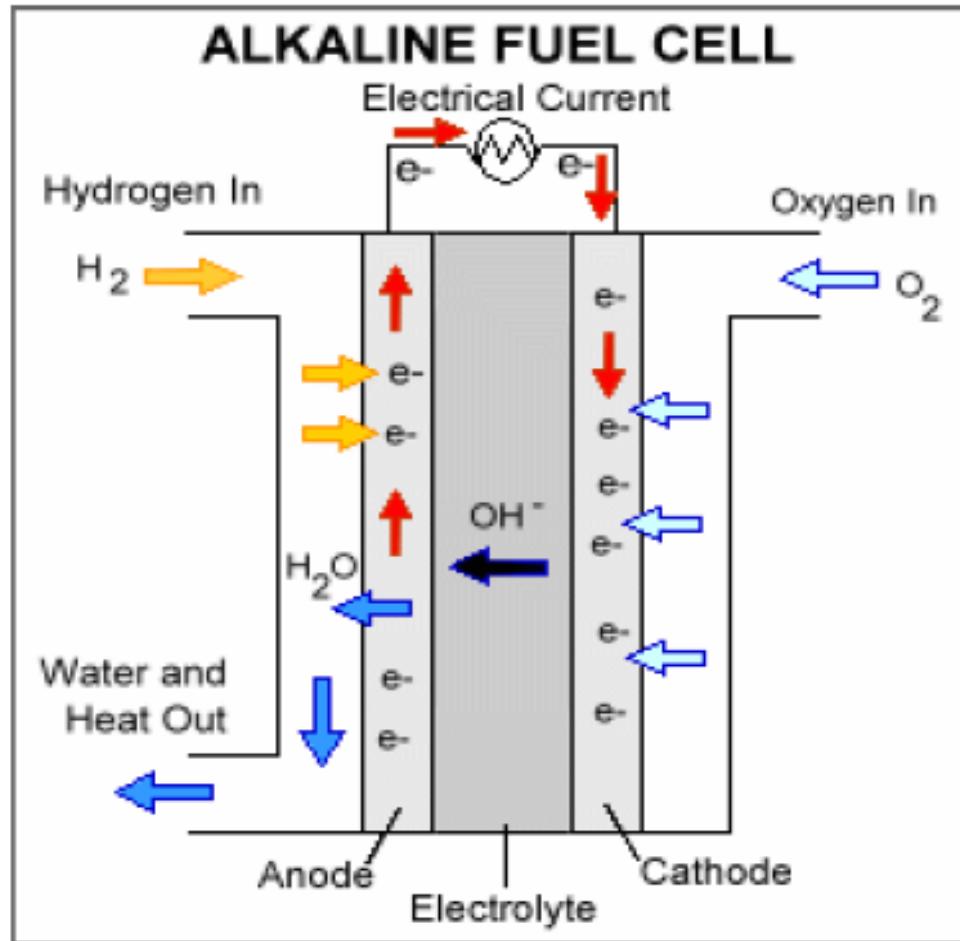
- The electrons from anode side of the cell cannot pass through the membrane to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell. The movement of the electrons is an electrical current
- This is how generation of electric current takes place via a fuel cell

Factors on which Power generated depends

The power generated by fuel cell depends on factors such as:

- Fuel cell type.
- Cell size.
- Temperature at which it operates.
- Pressure at which the gases are supplies to the cell.

Diagram of an alkaline fuel cell



Alkaline fuel cells

- Alkaline fuel cells use an alkaline electrolyte such as 40% aqueous potassium hydroxide.
- In alkaline fuel cells travel through the electrolyte to the anode where they combine with the anode to form water and electrolyte
- These fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non precious metals as a catalyst at the anode and cathode.
- High temperature AFCs operate between 373K-523K.
- However more recent AFCs operate at lower temperatures between 296K-343K.

Advantages

- The efficiency is as high as 60%
- Cathode reaction is faster in an alkaline electrolyte; thus leading to high performance.

Disadvantages

- This cell is easily poisoned by CO₂.
- Even the smallest amount of CO₂ in air can affect the performance of the cell's operation, making it necessary to purify both the hydrogen and oxygen used in the cell.
- Susceptibility to poisoning reduces cell's lifetime.

Applications of fuel cells

- Fuel cells are very useful in remote locations, such as spacecraft, remote weather stations, rural locations including research stations, and in certain military applications.
- As of 2015, two fuel cell vehicles have been introduced in commercial market in limited quantities: the Toyota Mirai and the Hyundai ix35 FCEV. Additional demonstration models include the Honda FCX Clarity, and Mercedes-Benz F-Cell

- As of August 2011, there were a total of approximately 100 fuel cell buses deployed around the world.
- In 2013 there were over 4,000 fuel cell forklifts used in material handling in the US.
- In 2005 a British manufacturer of hydrogen-powered fuel cells, Intelligent energy, produced the first working hydrogen run motorcycle called the Emission Neutral Vehicle. The motorcycle holds enough fuel to run for four hours, and to travel 160 km (100 mi) in an urban area, at a top speed of 80 km/h (50 mph)



Toyota Mirai



Hyundai Nexo

Advantages of fuel cells

- Hydrogen being the most abundant element in the universe, makes hydrogen fuel cells more viable
- Hydrogen has the highest energy content.
- Hydrogen is non polluting
- Reduces dependency on fossil fuels

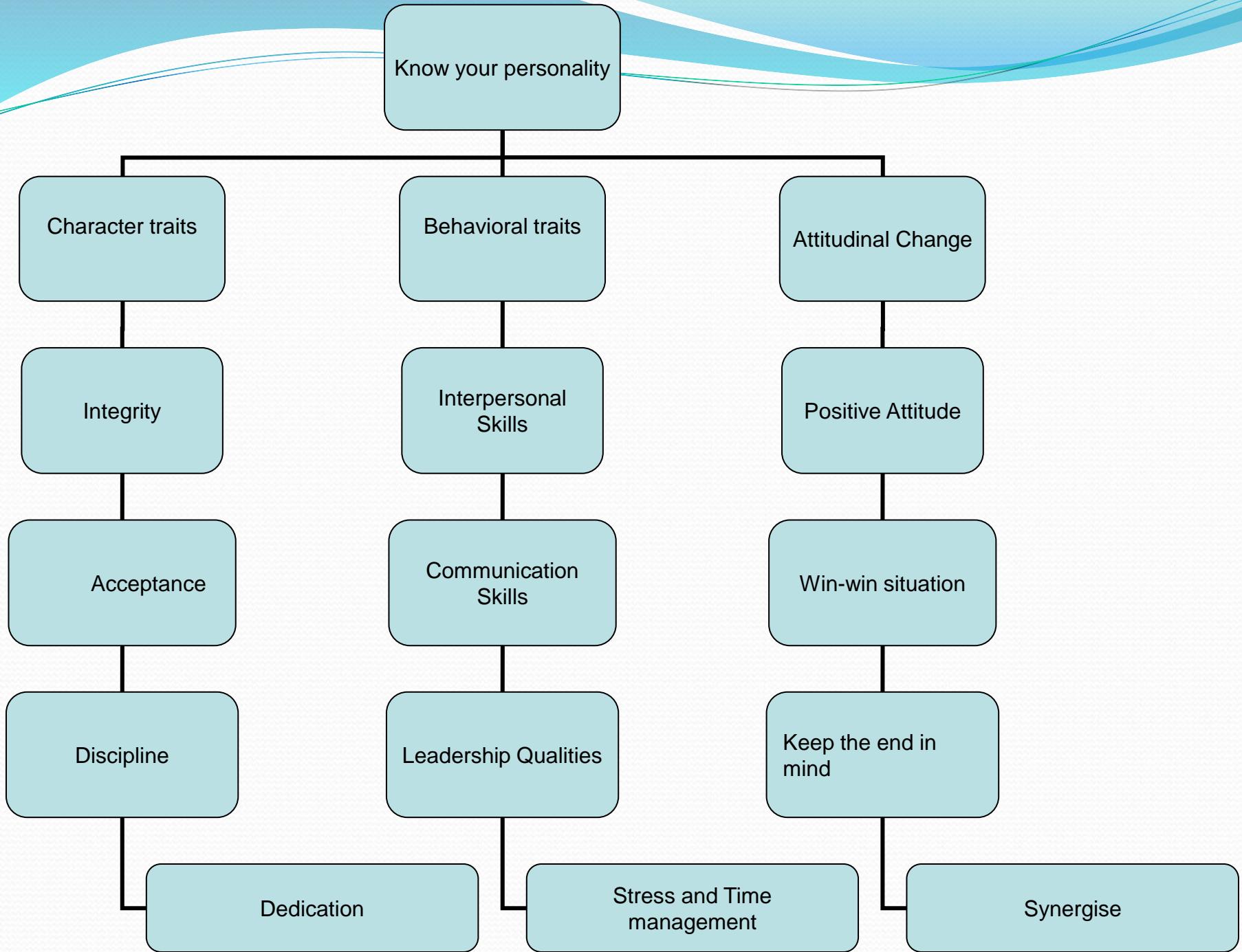
Disadvantages of fuel cells

- Hydrogen is very expensive, not because it is rare but because its difficult to generate, handle and store requiring bulky tanks like those for CNG.
- It can be stored at moderate temperatures and pressures in a tank containing a metal-hydride absorber or carbon absorber, but both of these are very expensive.
- Fuel cells are often very bulky and can not be used everywhere.
- The actual cells in which power generated is stored can store only a small amount of power. This reduces the reliability of the entire process

PERSONALITY DEVELOPMENT



- A man is identified by his personality – public image.
- It is the totality of the person and not merely external looks, but character, behavioral traits and attitude towards life.
- Personality development – is the improvement of behavioral traits such as communication skills, interpersonal relationships, attitude towards life and restoring our ethics.



TYPES OF PERSONALITY

Nine Types

- Perfectionists
- Helpers
- Romantics
- Achievers
- Asserters
- Questioners
- Adventurers
- Observers and
- Peacemakers.

Cont..

Perfectionists – are realistic, conscientious and principled
Ex: Narayan Murthy – Infosys.

Helpers – are warn, concerned, nurturing and sensitive to other people's needs
Ex: Mother Teresa.

Achievers – are energetic, optimistic, self assured and goal oriented
Ex: Sachin Tendulkar

Romantics – have sensitive feelings and are warm and perceptive
Ex: M. F. Hussain – great Indian Painter

Observers – have a need for knowledge and are introverted, curious, analytical and insightful.
Ex: Amartya Sen - Great economist

Cont..

Questioners – are responsible and trustworthy.

Ex: Shabana Azmi

Adventurers – are energetic, lively and optimistic. They want to contribute to the world

Ex: Vijay Mallya - NRI businessman.

Asserters – are direct, self-reliant, self confident and protective.

Ex: T. N. Seshan - Chief Election Commissioner.

Peacemakers – are receptive, good-natured and supportive.

They seek union with others and the world around them

Ex: Atal Bihari Vajpayee.

It can help in the following ways

- To learn the business etiquette of exchanging cards, wishing on first meeting, bowing when you are visiting Japan and the like.
- Voice modulation, diction, communication skills, phone etiquette, hygiene, empowerment skills, time management and positive thinking.
- To cultivate a friendly, interactive manner. Essentials like giving a speech, voice development and modulation of voice.
- It enhances the sense of confidence and self-worth.

PERSONALITY TEST

This can identify:

- Value system
- Emotional reaction to a critical situation
- Moods and characteristic behaviour traits.
- Maturity in handling a crisis.
- Ability to adjust himself to the stress of day-to-day executive lifestyle.
- Self-confidence, personal ambition, emotional control and sociability etc.
-

BODY LANGUAGE

Body language communicates much more than words. Body language signals are called ‘leakages’ because you may try to tell something, but the truth will leak out visually.

AVOID SUCH BODY LANGUAGE

- Crossed arms or legs
- Carrying books or papers across your chest
- Slumped posture
- Sitting perched on the edge of the chair
- Wringing hands
- Tapping foot
- Rocking legs
- Drumming fingers
- Biting nails

Cont..

- Fiddling with the jewelry or hair
- Covering your mouth with your hand while talking
- Rocking in your chair
- Scratching a lot
- Clearing your throat too much
- Straightening your tie
- Playing with watch or cufflinks
- Hands in the pocket

LOOKING AGGRESSIVE

- Arms folded across the chest
- Staring
- Pointing
- Making a fist
- Leaning over someone

BEHAVING RUDELY

- Working when someone is talking to you
- Puffing
- Tollerling
- Smirking
- Whispering
- Cracking knuckles
- Grooming yourself'
- Standing too close
- Packing up folders and papers well before the meeting is over
- Shaking hands too hard or limp handshakes

Cont..

- Yawning when the meeting is in progress
- Looking at your watch repeatedly
- Blinking a lot
- Fiddling with rings, watches, earrings and chains
- Tapping or clicking pens
- Playing with paper clips
- Jingling money in pocket
- Picking at fingernails
- Twiddling bits of hair
- Smoking

LEADERSHIP QUALITIES

- Courage
- Self-control
- A keen sense of justice and fairness
- Definiteness of plans
- The habit of doing more than being paid for
- A pleasing personality
- Sympathy and understanding
- Mastery of details
- Willingness to assume full responsibility
- Co-operation

PERSONAL QUALITIES

- accurate
- adaptable
- astute
- can work under pressure
- careful
- committed
- competent
- cooperative
- courteous

Cont..

- decisive
- dedicated
- energetic
- methodical
- meticulous
- orderly
- organized
- positive
- practical

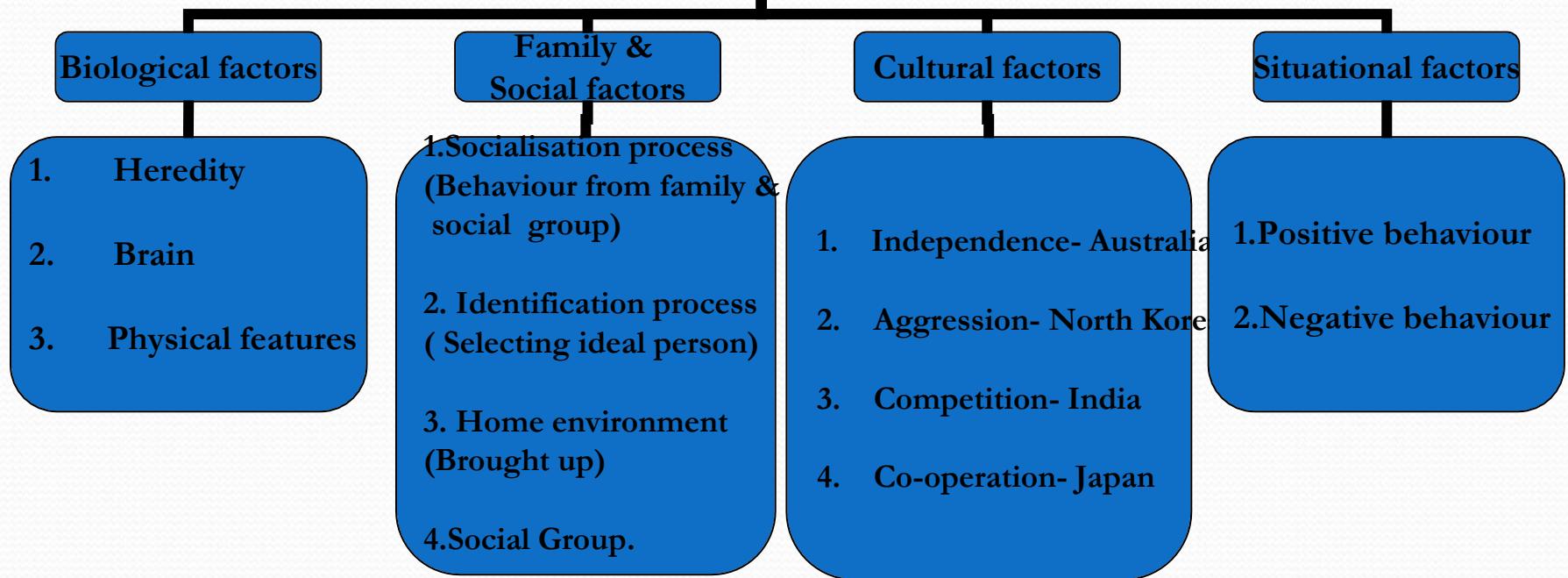
Cont..

- extrovert
- flexible
- friendly
- get on well with other people
- good communicator
- good sense of humour
- good time-keeper
- hard working
- imaginative

Cont..

- independent worker
- lively
- logical
- loyal
- self confident
- self motivated
- sensitive
- thorough
- thoughtful
- vigilant
- work well with others

Determinants of personality



Holland's Personality-Job Fit Theory

Type	Personality	Occupations
<i>Realistic</i>	Shy, Stable, Practical	Mechanic, Farmer, Assembly-Line Worker
<i>Investigative</i>	Analytical, Independent	Biologist, Economist, Mathematician
<i>Social</i>	Sociable, Cooperative	Social Worker, Teacher, Counselor
<i>Conventional</i>	Practical, Efficient	Accountant, Manager Bank Teller
<i>Enterprising</i>	Ambitious, Energetic	Lawyer, Salesperson
<i>Artistic</i>	Imaginative, Idealistic	Painter, Writer, Musician

Type A and B

Type A Personality

- Always moving, walking, and eating rapidly.
- Feel impatient with the rate at which most events take place.
- Strive to think or do two or more things at once.
- Cannot cope with leisure time.
- Are obsessed with numbers, measuring their success in terms of how many or how much of everything they acquire.

Type B Personality

- Never suffer from a sense of time urgency with its accompanying impatience.
- Feel no need to display or discuss either their achievements or accomplishments unless such exposure is demanded by the situation.
- Play for fun & relaxation, instead of exhibit their superiority at any cost.
- Can relax without guilt.

Big 5 in Short...

Personality Factors	Characters
1. Conscientiousness	Careful, dependable and self disciplined
2. Agreeableness	Courteous, good natured, empathic and caring.
3. Neuroticism	Poised, secure and calm.
4. Openness	Sensitive, flexible, creative and curious.
5. Extroversion	Outgoing and cautious.



THANK YOU

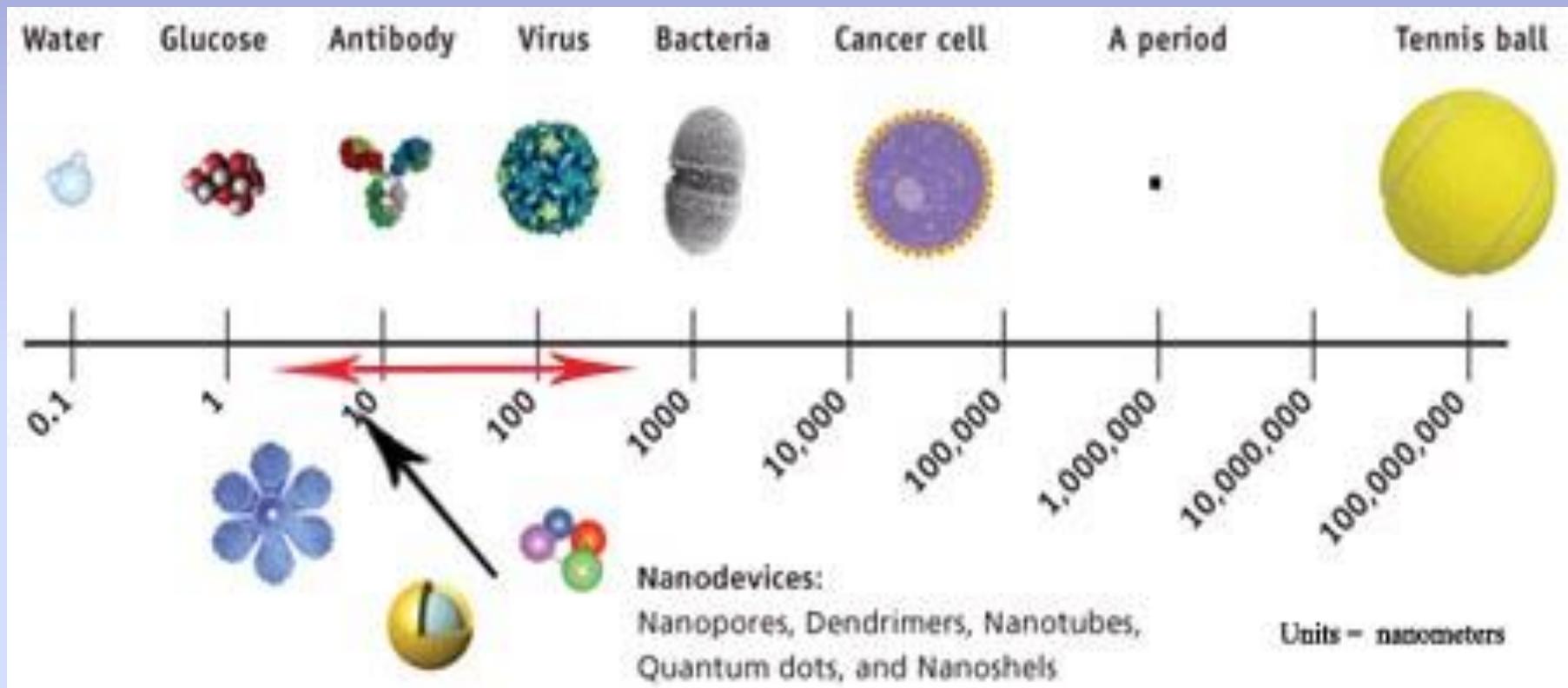
Nanomaterials

Nanotechnology

- is already making **today's** products:
 - Lighter
 - Stronger
 - Faster
 - Smaller
 - More Durable

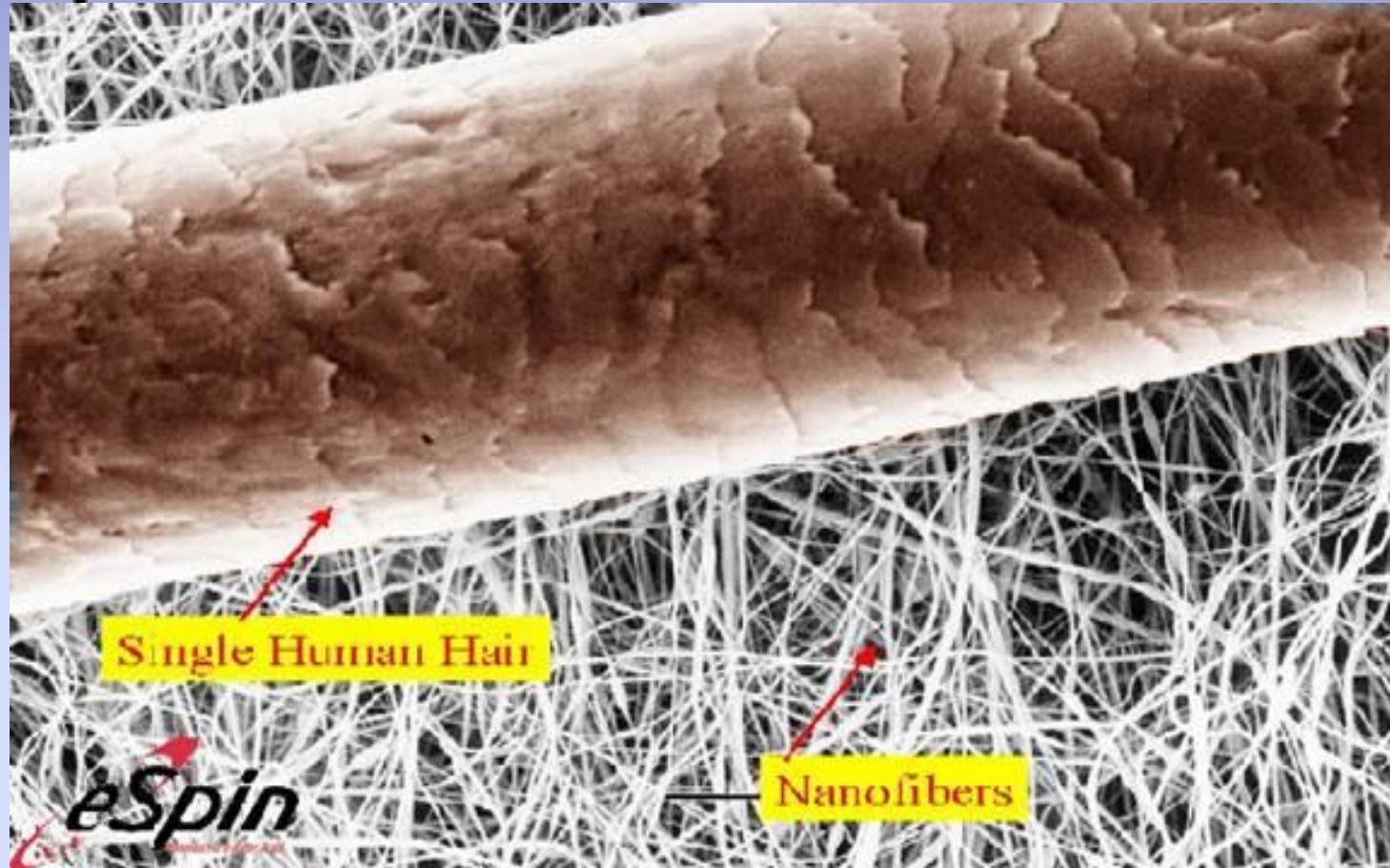


How small is Nano - small?



Units in nanometers (μm)

Compared to Human Hair



A Human Hair is about 100,000 μm wide

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.

A nanometer is one millionth of a millimeter- approximately 100,000 times smaller than the diameter of a human hair.

Properties of Nanomaterials-

- (i) large fraction of surface atoms;
- (ii) high surface energy;
- (iii) spatial confinement;
- (iv) reduced imperfections,

Two principle factor causing properties of nanomaterials to differ significantly from bulk materials.

- ❖ **Relative surface area**
- ❖ **Quantum effects**

These property can change or enhance property such as reactivity, strength, electric and magnetic behaviour.

Surface Effect

- As the size of particle decreases greater proportion of atom are found at the surface for e.g.

Size 30 nm- 5% of atom on its surface

Size 10 nm- 20% of atom on its surface

Size 3 nm- 50% of atom on its surface

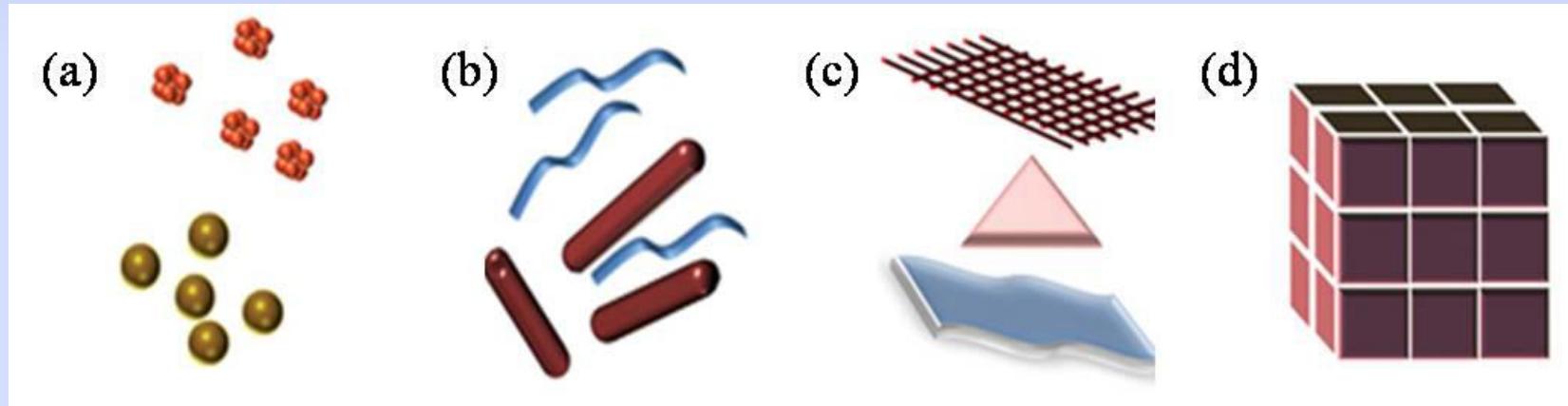
To understand the effect of particle size on surface area, consider an American Silver Eagle coin. This silver dollar contains 31 grams of coin silver and has a total surface area of approximately 3000 square millimeters. If the same amount of coin silver were divided into nanoparticles—say 10 nanometer in diameter—the total surface area of those particles would be 7000 square meters (which is equal to the size of a soccer field)

Quantum Effect

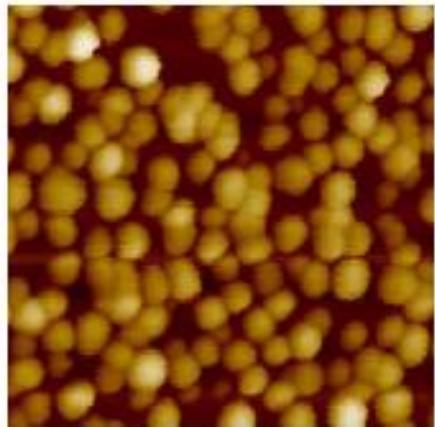
- The quantum confinement effect can be observed once the diameter of particle is of the same magnitude as the wavelength of electron
- Quantum confinement effect is responsible for increase of energy gap between energy state and band gap.
- When particles are small their electric, optical and magnetic properties differ significantly from bulk materials

Classification of Nano Materials

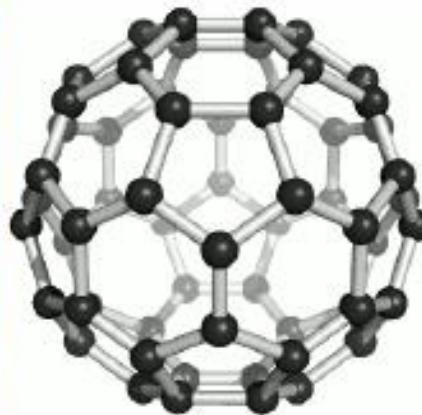
- Zero dimension (quantum dots)
- One dimension (quantum wires, rods)
- Two dimension (plates, network, quantum wells)
- Three dimension (fullerenes- C60, haekelites)



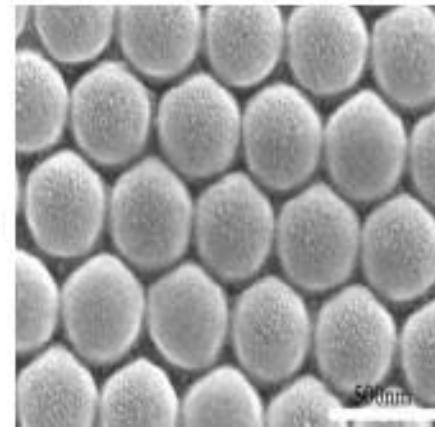
Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.



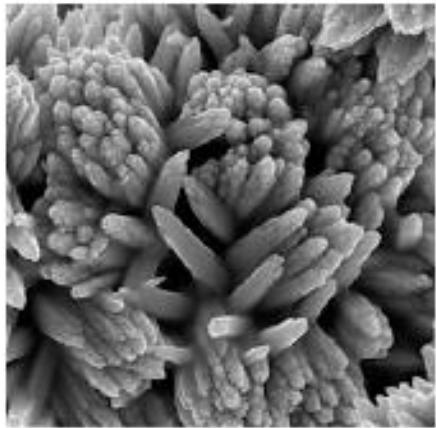
Au nanoparticle



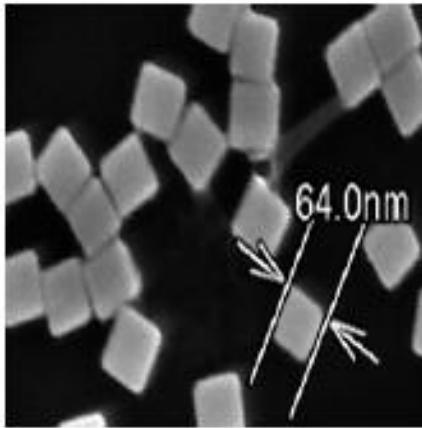
Buckminsterfullerene



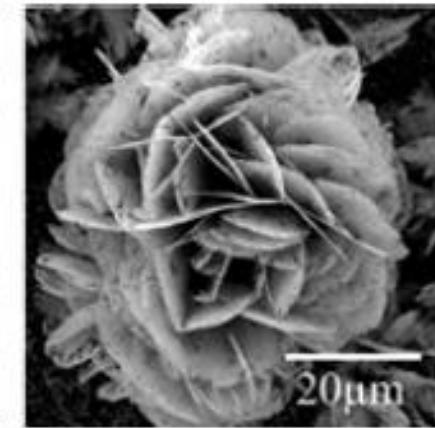
FePt nanosphere



Titanium nanoflower



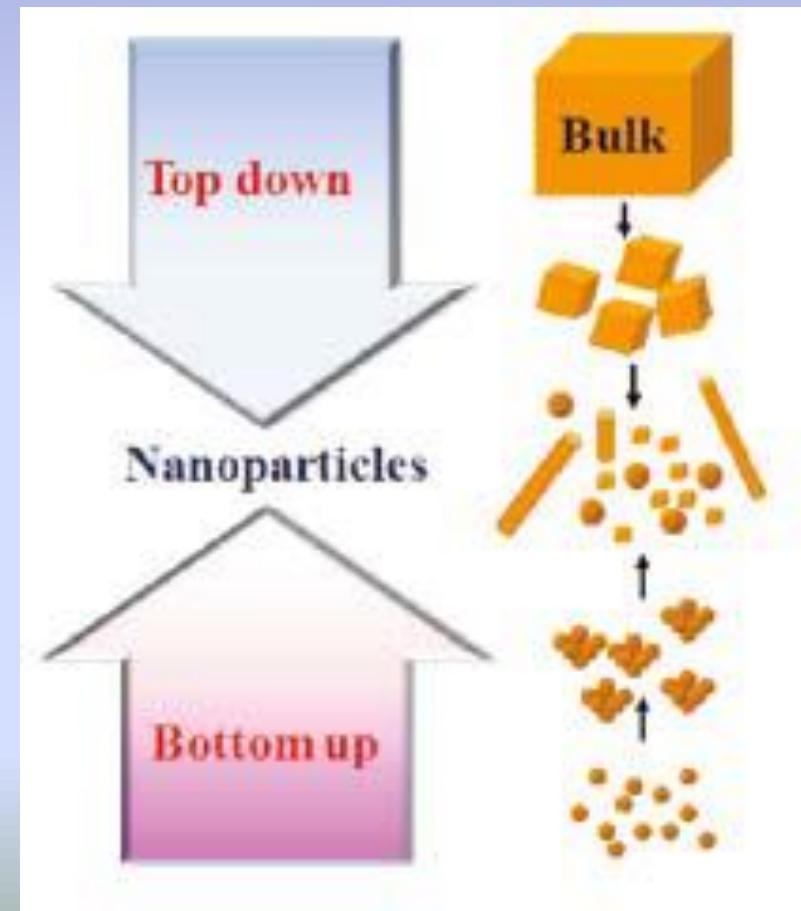
Silver nanocubes



SnO₂ nanoflower

- **Nanomaterial - synthesis and processing**
- Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ‘bottom up’ or the ‘top down’ approaches to synthesize nanomaterials.

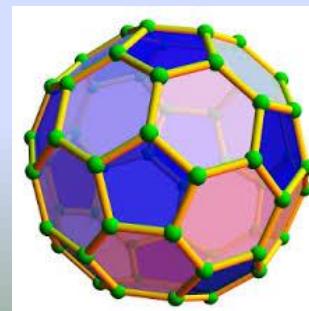
Schematic illustration of the preparative methods of nanoparticles.



- **Bottom up**
- assemble atoms (*sol-gel method, precipitation etc.*)
- *Example, synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures)*
- **Top down**
- dis-assemble
- *For example, the synthesis of porous silicon by electrochemical etching*
- This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

Fullerenes

- **Fullerenes** are spherical carbon-cage molecules with sixty (C₆₀) or more carbon atoms. The molecule was named after R. Buckminster Fuller, who confirmed structural formula . A hollow pure carbon molecule in which atom lies at the vertices of polyhedron with **12 pentagonal** faces and any number of hexagonal faces.
- Each carbon is bound to other three carbon in pseudo spherical arrangement of alternating pentagonal and hexagonal rings in the manner of soccer ball . Hence the nick name Bucky ball. They measure about **0.7-1.5 nm** in diameter. They are fascinating for scientists because they show unusual properties for carbon materials. Fullerenes are studied for potential medical use: they are strong antioxidants; one could also bind specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma. Heat resistance and superconductivity are some of the more heavily studied properties of fullerenes in mechanical engineering.

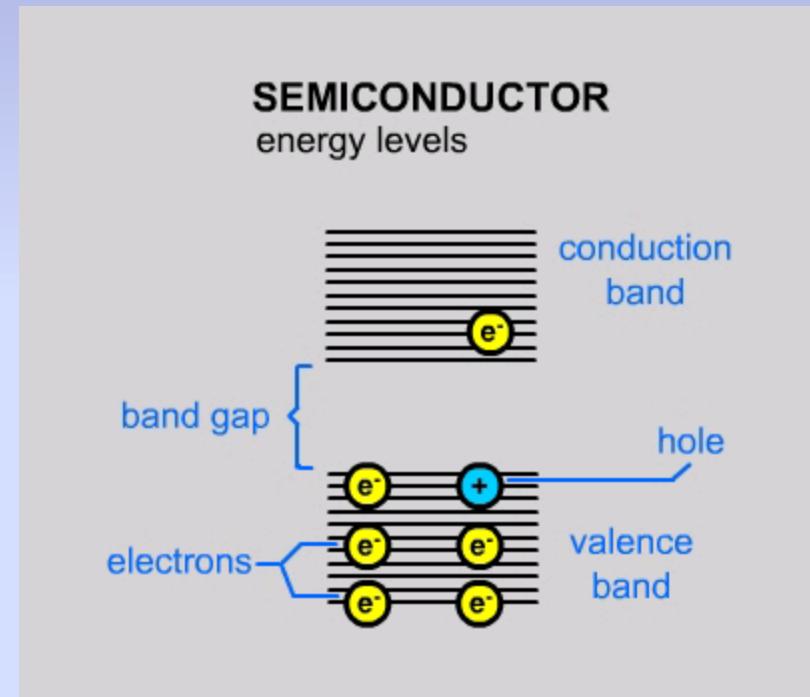


Quantum dot:

In two words, a **semiconductor nanocrystal.**

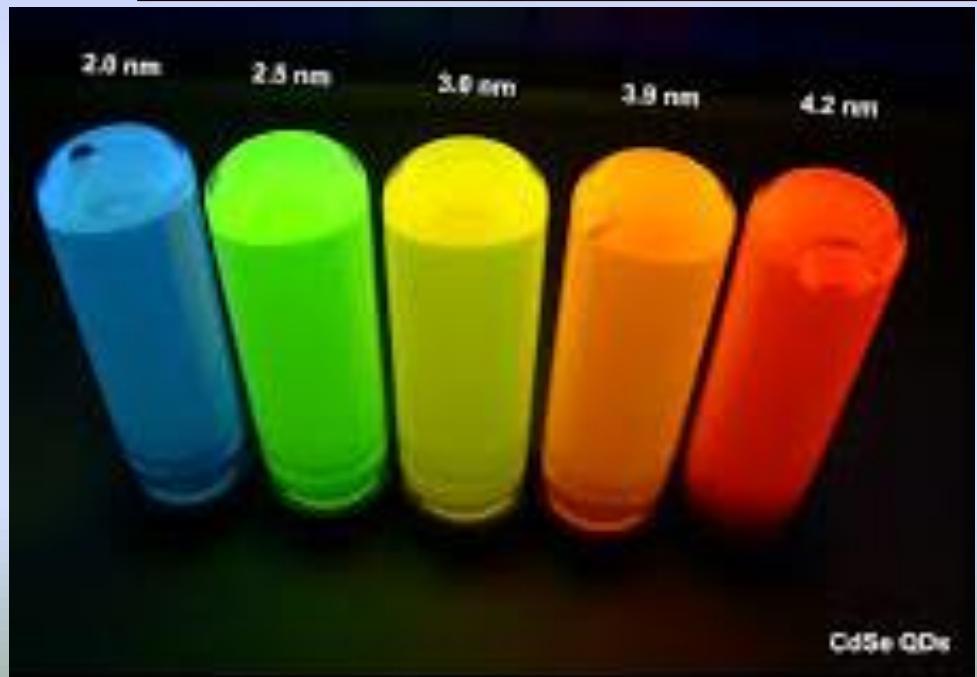
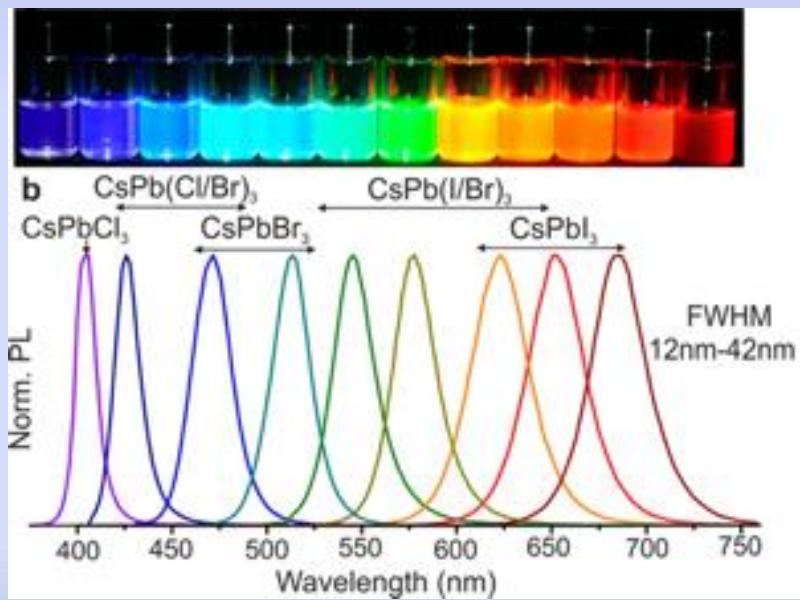
Easily tunable by changing the size and composition of the nanocrystal

- The average distance between an electron and a hole in a exciton is called the Excited Bohr Radius.
- When the size of the semiconductor falls below the Bohr Radius, the semiconductor is called a quantum dot.

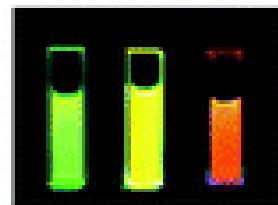


Tuning Quantum Dots

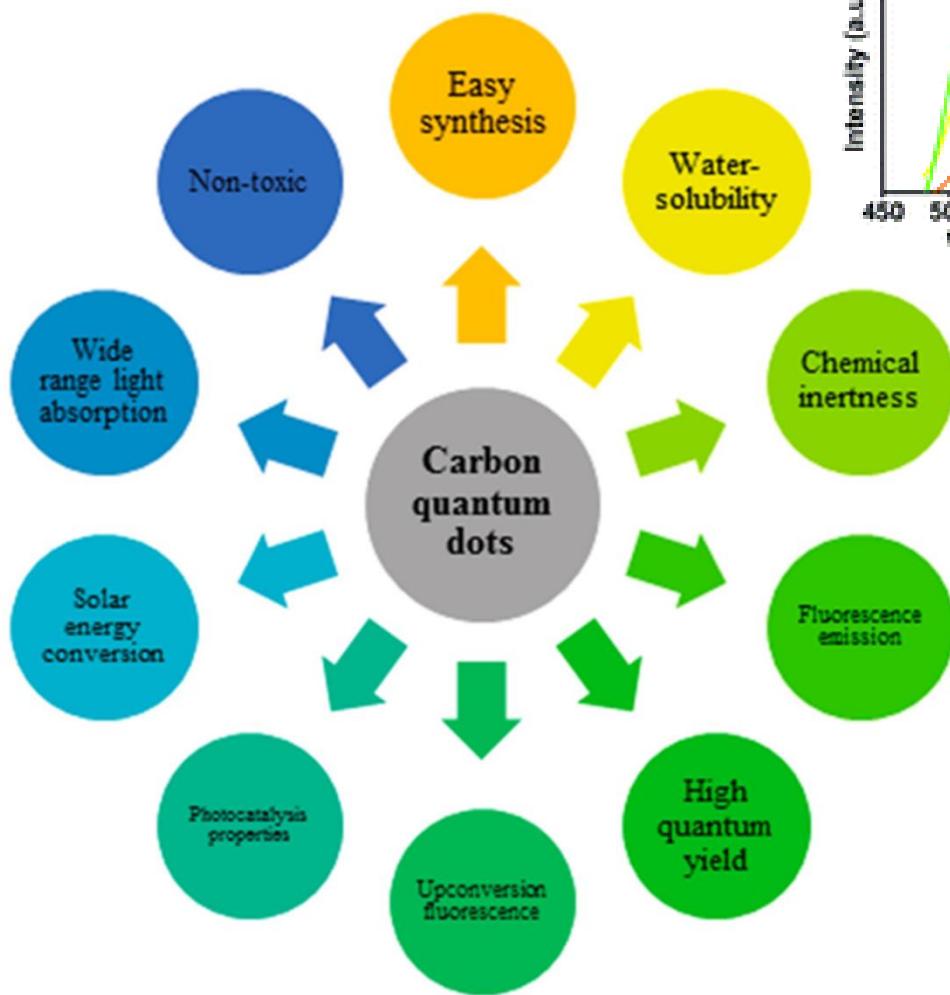
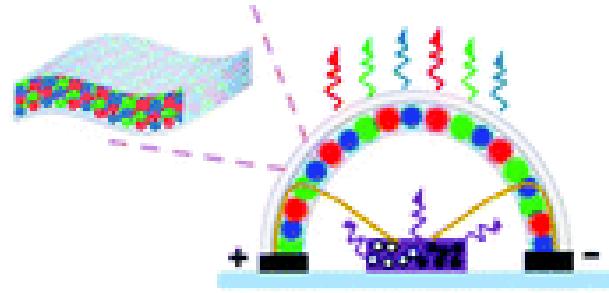
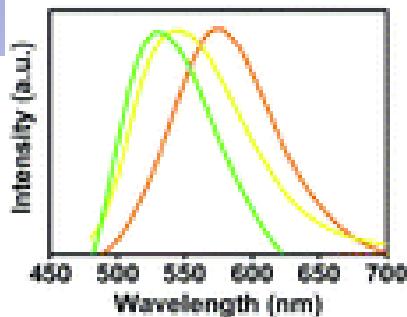
- By changing size, shape, and composition, quantum dots can change their absorptive and emissive properties dramatically



Multicolor Fluorescent Carbon Quantum Dots



White Light Emitting Diodes



Applications:

- Medicine-
 - Can be set to any arbitrary emission spectra to allow labeling and observation of detailed **biological processes**.
 - Quantum Dots can be useful tool for monitoring **cancerous cells** and providing a means to better understand its evolution.
 - In the future, Qdots could also be armed with tumor-fighting toxic therapies to provide the **diagnosis and treatment** of cancer.
 - Qdots are much more resistant to degradation than other optical imaging probes such as organic dyes, allowing them to **track cell processes** for longer periods of time.
 - Quantum dots offer a wide **broadband absorption** spectrum while maintaining a distinct, static emission wavelength.
- LED-
 - Used to produce inexpensive, industrial quality **white light**.
 - Marked improvement over traditional LED–phosphor integration by dot's ability to absorb and emit at **any desired wavelength**.
 - Produce white light by **intermixing** red, green, and blue emitting dots homogenously within the phosphor difficult to accomplish with the traditional LED-phosphor set up.

Solar Cells and Photovoltaics

- Traditional solar cells are made of semi-conductors and expensive to produce. Theoretical upper limit is 33% efficiency for conversion of sunlight to electricity for these cells.
- Utilizing quantum dots allows realization of third-generation solar cells at ~60% efficiency in electricity production while being \$100 or less per square meter of paneling necessary.
- Effective due to quantum dots' ability to preferentially absorb and emit radiation that results in optimal generation of electric current and voltage.

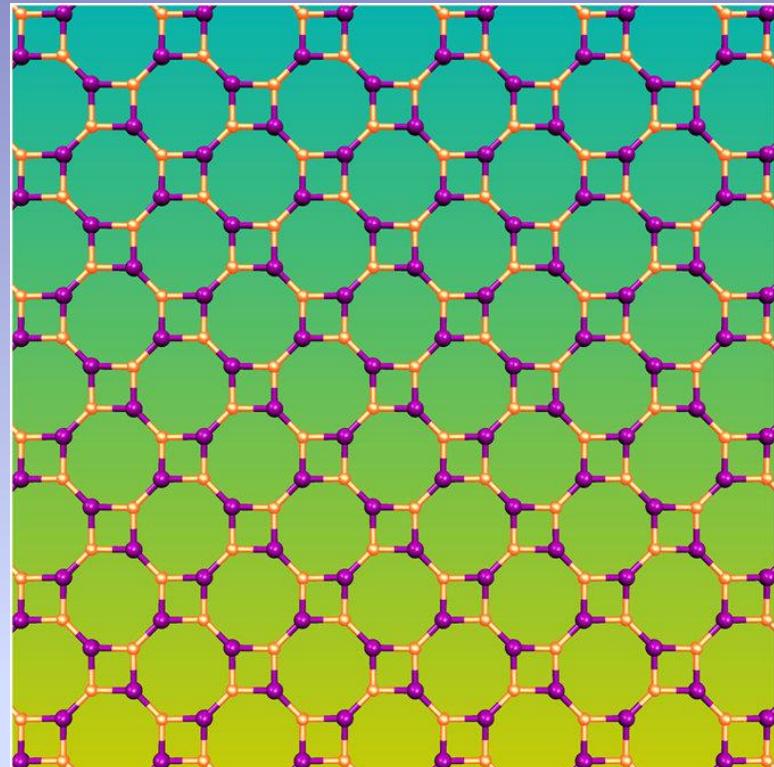
• Other Future Quantum Dot Applications...

- **Anti-counterfeiting capabilities:** inject dots into liquid mixtures, fabrics, polymer matrices, etc. Ability to specifically control absorption and emission spectra to produce unique validation signatures. Almost impossible to mimic with traditional semi-conductors.
- **Counter-espionage / Defense applications:** Integrate quantum dots into dust that tracks enemies. Protection against friendly-fire events.
- Research continues. The possibilities seem endless...

The name ‘Hacekelite’ has been proposed to designate a three-fold coordinated network generated by a periodic arrangement of pentagons, hexagons and heptagons

Starting from a planar Haeckelite array, tubular structures are obtained by applying the same wrapping procedure as for the usual nanotubes, which are rolled up sheets of graphene.

The Haeckelite nanotubes may adopt various shapes, among which coiled structures, doublescrew molecules, corrugated cylinders, and pearl-necklace-like nanotubes are the most spectacular.



GaN Hacekelite 8-4

- A planar structure containing square and octagonal rings which is called Haeckelites 8-4

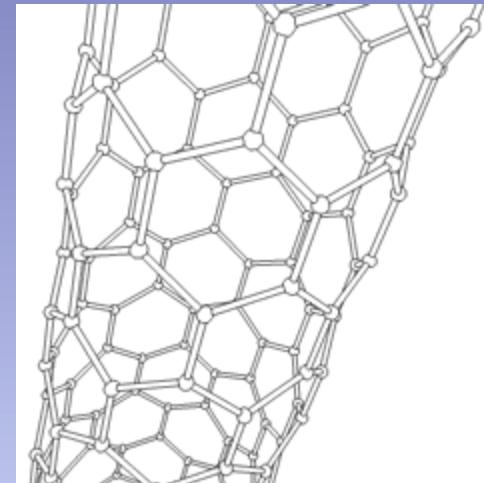
Properties:

- * Regular coiled nanotubes exhibit exceptional mechanical, electrical, and magnetic properties due to the combination of their peculiar helical morphology and the fascinating properties of nanotubes.
- * For straight nanotubes with small diameter, it has been demonstrated that they exhibit either metallic or semiconducting electrical conduction depending on their chiral vectors and independent of the presence of dopant or defects.
- * Coiled nanotubes can show even semimetallic characteristics, in addition to the metallic and semiconducting behaviors, which could not be manifested in straight nanotubes.
- * Straight carbon nanotubes as discontinuous reinforcement for polymer matrices is regarded as the ultimate carbon fiber with break strengths as high as 200 GPa and elastic moduli in the 1 TPa range.
- * Carbon nanotubes also have aspect ratios of around 103, w500 times more surface area per gram, and possess extraordinary capability of returning to their original, straight structure following deformation

Applications of haeckelites:

- * Potential to be incorporated in various nano-technology devices as mechanical components in the form of **resonating elements or nano-springs** and in novel **reinforcement composites**.
- * carbon-based material that can be used as **carbon fillers** in reinforcement composites.
- * **tactile sensors** incorporating carbon micro-coils had better discrimination abilities when compared to conventional sensors, making haeckelites novel tactile sensors.
- * ability to **inhibit the breeding of keloid fibroblast**, i.e., cancer cells associated with leukaemia of the uterus.
- * useful as **electromagnetic nano-transformers or nano-switches**.
- * useful as a tool to **detect mass change** as small as a few tens of attograms.

Carbon nanotubes(CNT)

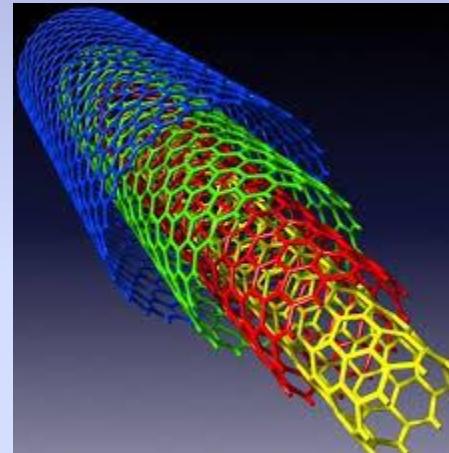
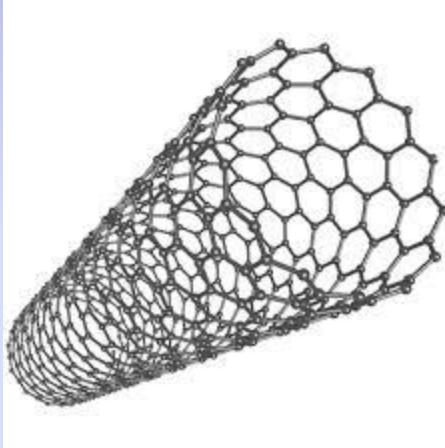


- Their name is derived from long hollow structure with wall formed by one atom thick sheets of carbon called graphene. These sheets are rolled at specific and discrete (chiral) angle. The combination of rolling angle and radius decides the nano tubes properties For e.g. Whether nano tube shell is metal or semi conductor.
- They have outstanding mechanical and electronic properties and are good thermal conductors. The tensile strength, or breaking strain of CNTs is 6-7 times that of steel. They are among the stiffest and strongest fibers known. CNTs can be metallic or semiconducting depending on their structure. Some CNTs are the most efficient electrical conductors ever made, while others behave more like silicon. These properties, coupled with the lightness of carbon nanotubes, give them great potential for use in reinforced composites, nanoelectronics, sensors and nanomechanical devices.

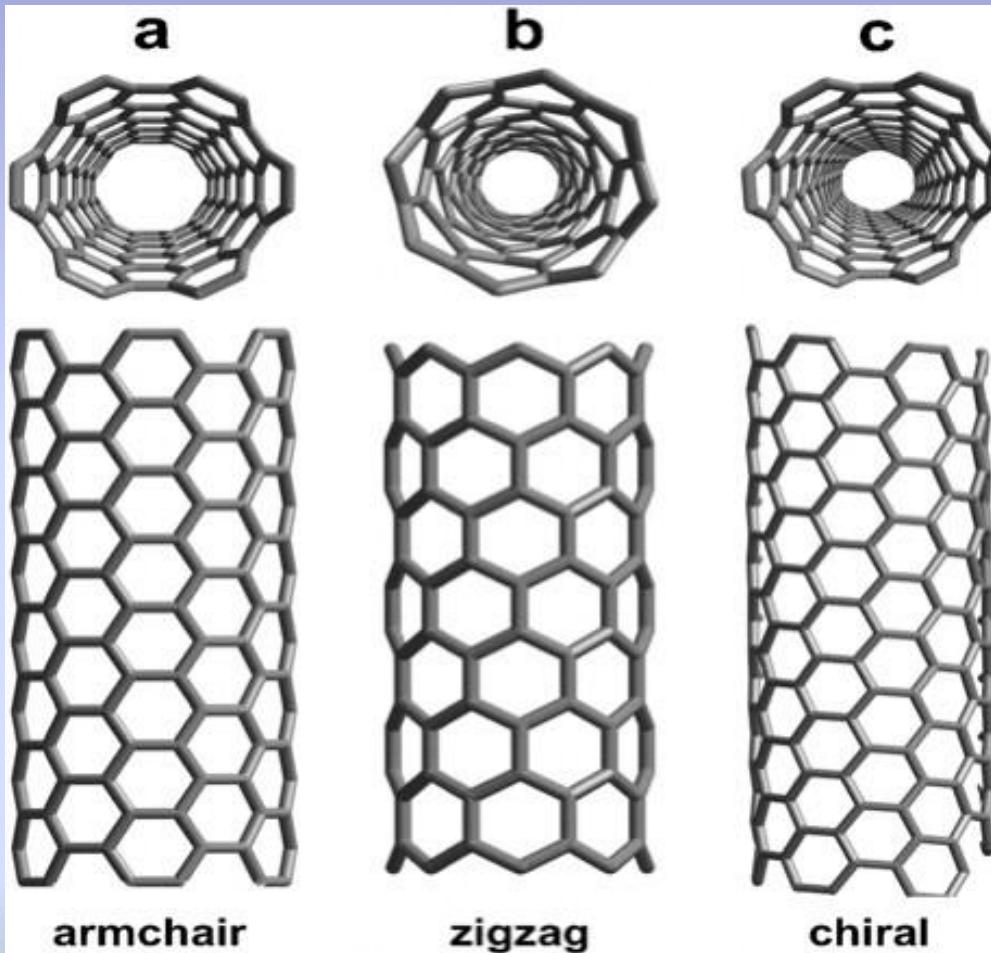
Classification of Carbon nanotubes

- Carbon nano tubes are categorized as,

Single walled nano tubes (**SWNT**) Multi walled nano tubes (**MWNT**)



Nanotubes have been constructed with length-to-diameter ratio of up to **132,000,000 : 1** significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology



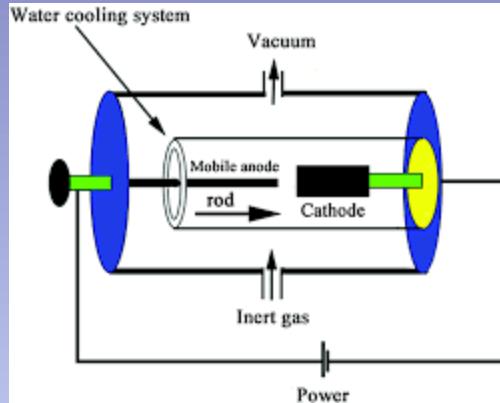
Single-walled
carbon nanotubes:

- armchair - metallic
- zigzag - semiconducting
- chiral - semiconducting
- multi-walled - metallic

Method of Preparation

- Arc Method
- Laser Method
- Chemical deposition method

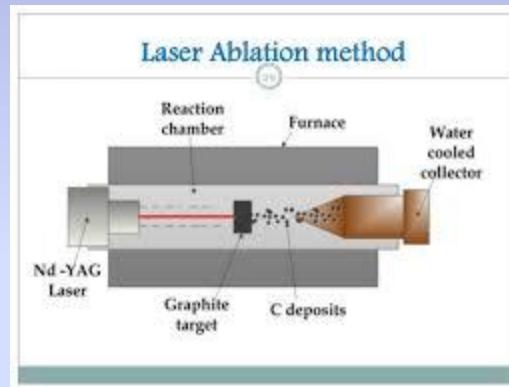
Arc Method



- The carbon arc discharge method, initially used for producing C₆₀ fullerenes, is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and requires further **purification**- to separate the CNTs from the soot and the residual catalytic metals present in the crude product. This method creates CNTs through arc-vaporization of **two carbon rods placed end to end**, separated by approximately **1mm**, in an enclosure that is usually filled with **inert** gas at low pressure. Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of **50 to 100A**, driven by a potential difference of approximately **20V**, creates a **high temperature discharge** between the two electrodes. The discharge **vaporizes the surface** of one of the carbon electrodes, and forms a small **rod-shaped deposit** on the other electrode. Producing CNTs in **high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode.**

Laser Method

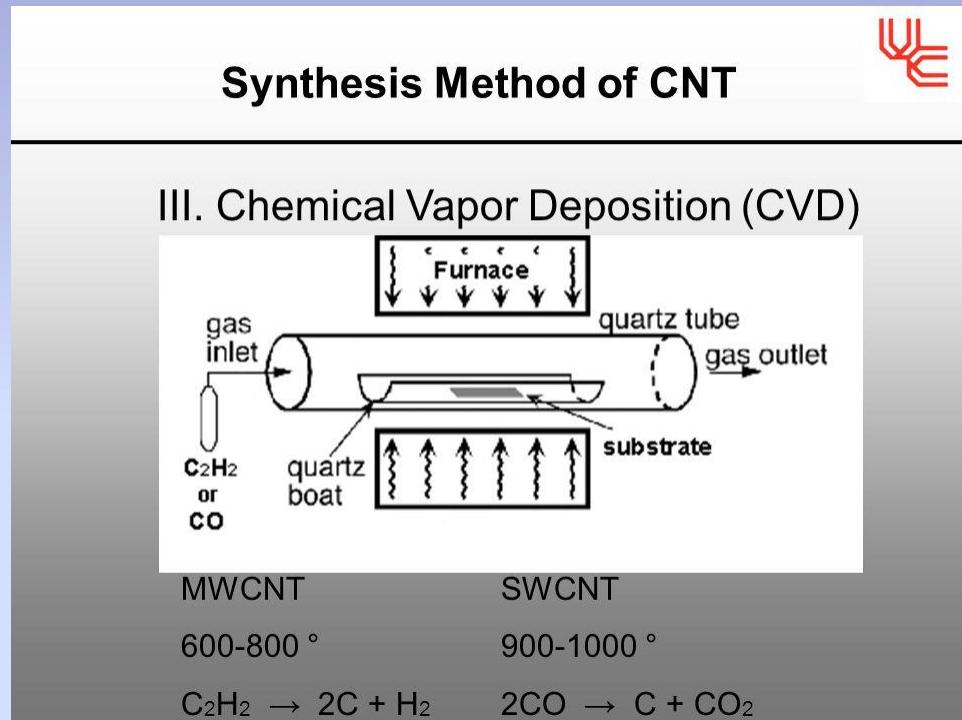
- In 1996 CNTs were first synthesized using a **dual-pulsed laser**. Samples were prepared by laser vaporization of **graphite rods** with a **50:50 catalyst mixture of Cobalt and Nickel** at **1200°C** in **flowing argon**, followed by **heat treatment** in a **vacuum** at **1000°C** to remove the C₆₀ and other fullerenes. The **initial laser vaporization pulse** was followed by a **second pulse**, to vaporize the target more uniformly. The use of **two successive laser pulses minimizes** the amount of carbon deposited as **soot**.



- The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The material produced by this method appears as a **mat of "ropes"**, **10-20nm in diameter** and up to **100µm or more in length**. Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis. By **varying the growth temperature**, the **catalyst composition**, and other process **parameters**, the average nanotube diameter and size distribution can be varied.

Chemical Vapor Deposition

- The simplest method to produce nanoparticles is by heating the desired material in a furnace containing the desired material.
- Large amounts of CNTs can be formed by **catalytic CVD** of **acetylene over Cobalt and iron catalysts supported on silica or zeolite**. In this method gases like CH_4 and C_2H_6 are cracked under the pressure of **10^4 Pa** in presence of catalyst like Fe, Co, Ni, Pt .
- Catalyst plays very important role in formation of carbon nanotubes.
- Both **MWNT** and **SWNT** can be obtained by this method. **SWNT** can be produced at **$600-1150^\circ\text{C}$** and **MWNT** are produced at low temperature of **$300-800^\circ\text{C}$** .



Main properties of carbon nanotubes

- Electrical Conductivity
- Strength and Elasticity
- Thermal Conductivity
- High aspect ratio and Field emission

Electrical Conductivity

- The conductivity of CNT have been found to be function of their **chirality**, degree of **twist** as well as **diameter**. CNTs can be either metallic or semi conductor. The **resistivity** of single walled nanotubes ropes was of the order of 10^{-4} ohm-cm at 27°C. This means they are the most **conductive** carbon fiber known. The current **density** that was possible to achieve was 10^9 A/cm² (while copper burn at 10^6 A/cm²) It has been reported that SWNT may contain some defects. These defects allow the SWNT to act as **transistors, rectifying diodes**. It has also been reported that single wall nanotubes can route **electrical speed up to 10 GHz.**

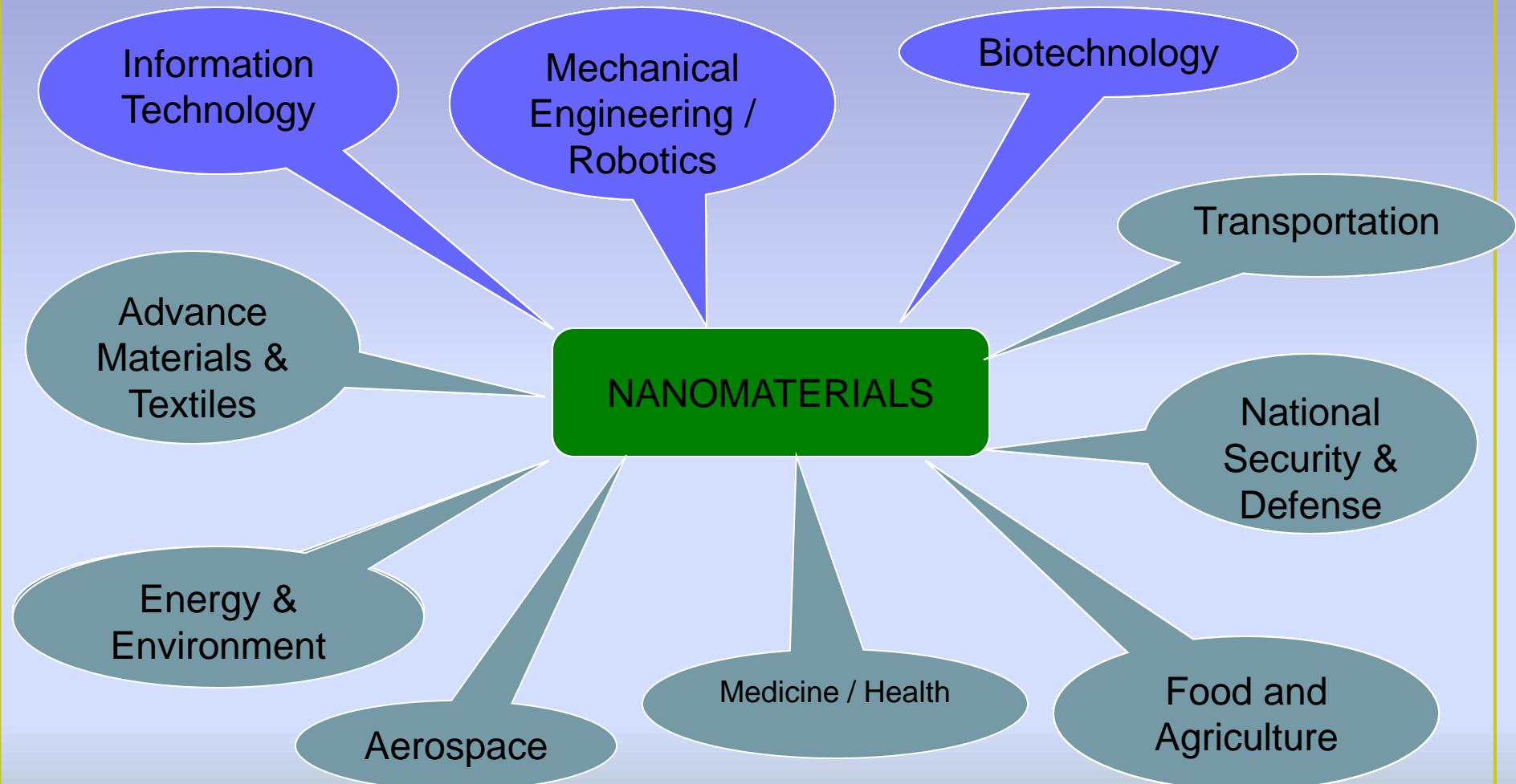
Strength and Elasticity

- CNTs are expected to be ultimate **high strength** fiber. Single walled nanotubes are **stiffer than steel** and are **resistant** to damage from physical forces. Pressing on the tip of nanotubes will cause it to **bend without damage** to the tip. This property make CNTs very useful as probe tip for **high resolution scanning** probe microscopy. The current **Young's modulus** value for single walled nanotubes is about 1 teraPascal but this value is highly disputed and a value as **high** as 1.8 TPa(tera Pascal). Young modulus depend on **size and chirality** of single walled nano tube.

Thermal conductivity and High aspect ratio

- CNTs have been shown to exhibit **superconductivity** below 20°K. Preliminary experiments and simulation studies on thermal property of CNT show very **high thermal conductivity**. It is expected therefore nanotube **reinforcement** in polymeric materials may also significantly improve the **thermal and thermo mechanical properties** of composites. CNTs represent **very high aspect ratio**. The high aspect ratio means that **lower loading** of CNTs is needed than to other conductive material. CNTs have proven to be **excellent additives** to impart electric conductivity in plastics.

Application of nanomaterials



Nano mechanics and lubricants

Carbon nanotubes are **stiff** and hard like diamond but **flexible** due to this they find several **mechanical application**. Cutting tools made up of Nano crystalline materials such as tungsten carbide titanium carbide are more **wear resistant** than convectional counter parts. They find application in **drill, helmets, bullet proof cloth, etc.** At present fastest known **oscillators** are made up of nanotubes. Nanotubes develop material which are **slicker** than Teflon and also **waterproof**. Membrane made up of CNTs allow **liquid flow** up to five times faster than conventional membrane.

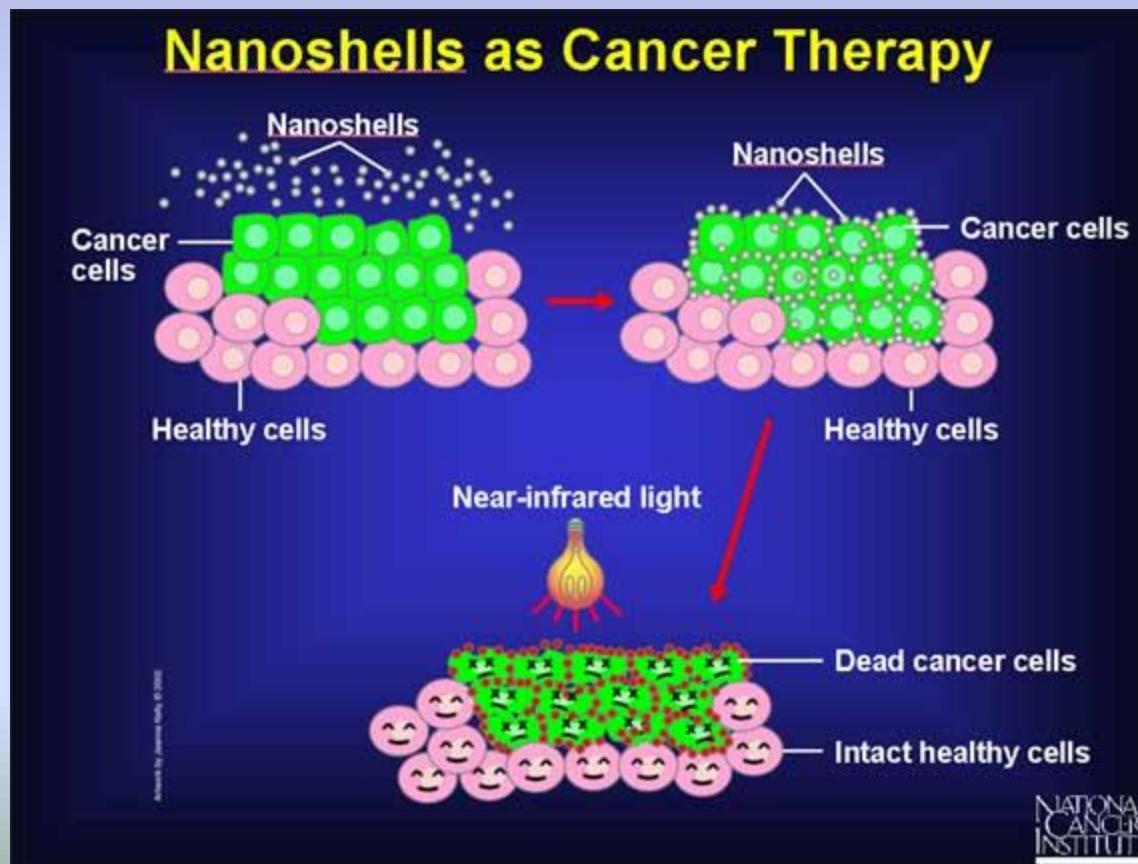
Nano sphere of inorganic material can act as **nano sized ball bearing**. They also find application in **high performance engine and drivers**.

Medicine

- Nanomaterials are of the size 10^{-9} . Hence they are smaller or comparable than **single cell, virus, protein**. Thus materials can freely **move through tissue or bind to biological system**. Endothelium layers are porous thus nano particle can **penetrate** through them and can be used as medicine or **carrier**. Many of magnetic nano particles have been used in **cancer therapy** like hyperthermia. Magnetic particles are also used for **tagging** cancer cells, bacteria red blood cells. They are also used in **contrast enhancing** agent in MRI. Thus they can be used to **detect** brain tumor liver tumor and lymph nodes.

Nano shells as Cancer Therapy

Nano shells are injected into cancer area and they recognize cancer cells. Then by applying near-infrared light, the heat generated by the light-absorbing Nano shells has successfully killed tumor cells while leaving neighboring cells intact.



Environment & Catalyst

- With nano technology it is possible to synthesize metal nano particles of highly ordered mono dispersed film. These nano catalyst **greater activity and specific in action**. It is possible to achieve **specific or selective activity**. This will reduce huge requirement of all **rare earth metal** in the production of catalyst
- Nano porous aluminum silicates(zeolites) are used in **water treatment**. Nano porous membrane with definite and desired pore are used as **nano filters** for dust and impurities from air and water. Gold nano particles are used for **degradation of toilet odor**. Nano ZnO is used for **degradation of chlorinated phenol**. Nano photo catalyst are used for **degradation of pollutant** present in waste water. Nanomaterials are used as
- catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in **automobile catalytic converters** and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

Electronics

- Traditional electronic circuits are built by etching individual components into silicon wafers. Rapid technological progress was first predicted in 1965 by Gordon Moore who stated that integrated circuit(IC) **density and performance** would double every 18 months. **Electronic miniaturization** has been the true driving force for nanotechnology research and applications. Nano electronics can help us to improve the **capabilities** of electronics devices while we **reduce their weight and power consumption**. Nanotechnologies are therefore expected to enable the production of smaller, cheaper devices with **increasing efficiency**. CNTs are being used for **low voltage** field emission displays. Nano crystalline nickel and metal hydrides are envisioned to require **less frequent recharging and last longer**. Nano scale fabricated magnetic material find application in **data storage**. Nanowires for junctionless transistors.

Importance of Nanomaterials-

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

- (i) Nano-phase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
- (ii) Nano-structured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.
- (iii) Nano-sized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.
- (iv) Single nano-sized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

(v) Nano-structured metal clusters and colloids of mono- or plurimetallic composition

have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electro-catalysis (fuel cells). Enantioselective catalysis was also

achieved using chiral modifiers on the surface of nanoscale metal particles.

(vi) Nano-structured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NO_x , CO , CO_2 , CH_4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars or consumer goods. Nano-crystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

(vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

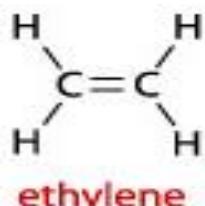
- Nano-Aluminium is used as solid fuel in rocket propulsion.
- Sun-screen lotions containing nano-TiO₂ provide enhanced sun protection factor (SPF) by blocking UV radiation while eliminating stickiness.

POLYMERS

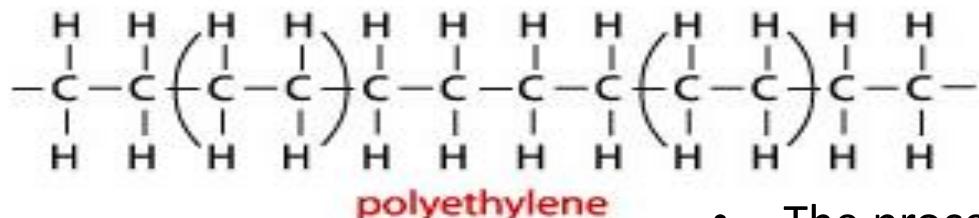
Carbon-based compounds

**Polymers ARE CHAINS OF
Monomers joined together.**

- A polymer is a macromolecule with high molecular mass ranging from 5000 to one million, which are formed by combination of one or more low molecular weight compound/ s. The unit substance from which polymer is obtained is called monomer.

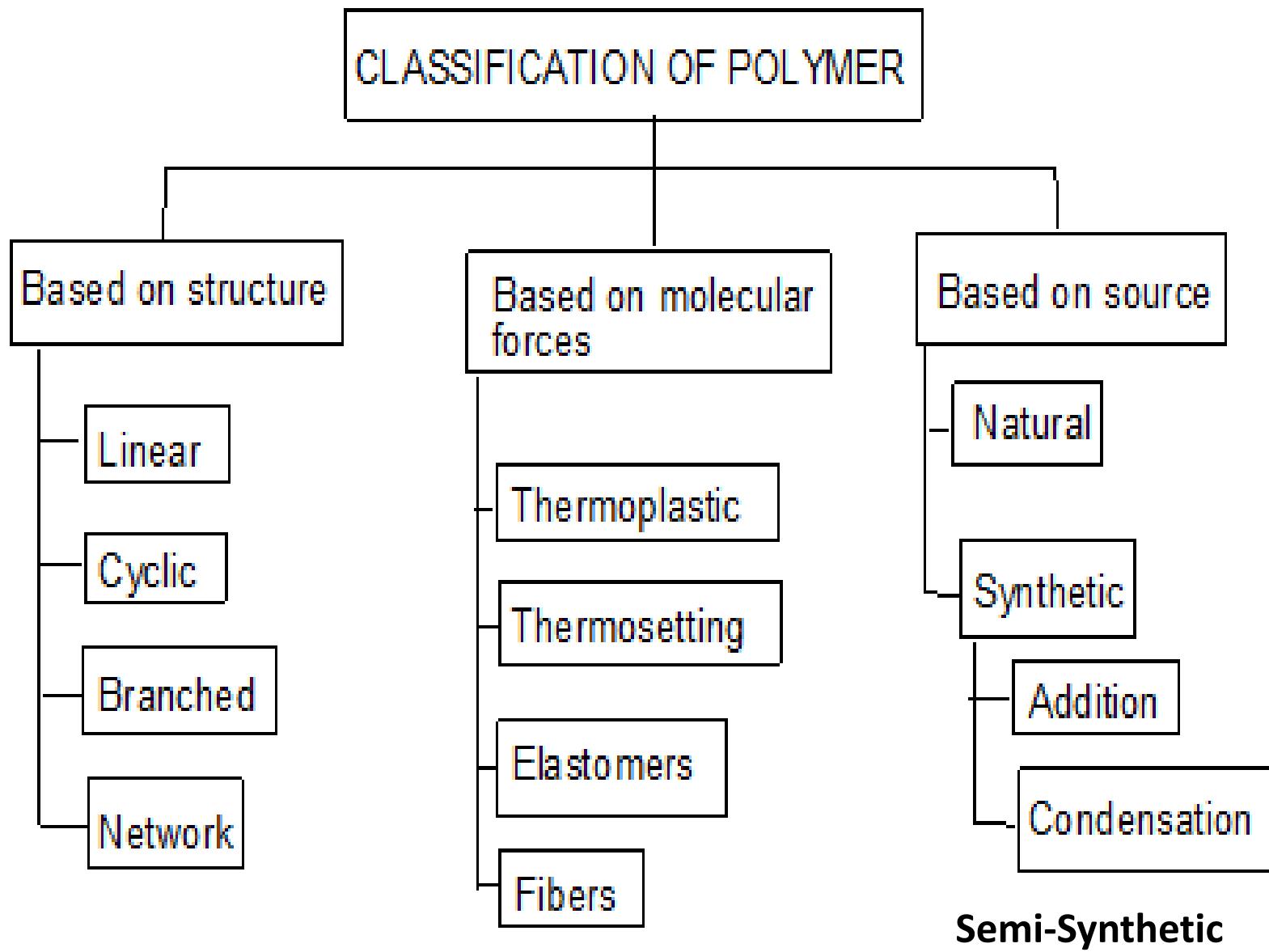


polymerization



- The process by which polymers are obtained is called polymerization
- For e.g. polyethylene is obtained by repeating ethylene unit as a result of polymerization.

Classification of Polymers



- Polymers can be separated into **plastics** and **rubbers** (**fibres not included here**)
- As engineering materials, it is appropriate to divide them into the following three categories:
 1. **Thermoplastic polymers**
 2. **Thermosetting polymers**
 3. **Elastomers** where (1) and (2) are plastics and (3) are rubbers

Thermoplastic Polymers - Thermoplastics (TP)

- Solid materials at room temperature but viscous liquids when heated to temperatures of only a few hundred degrees
- This characteristic allows them to be easily and economically shaped into products
- They can be subjected to heating and cooling cycles repeatedly without significant degradation

Thermosetting Polymers - Thermosets (TS)

- Cannot tolerate repeated heating cycles as thermoplastics can

When initially heated, they soften and flow for molding

But elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid

If reheated, thermosets degrade and char rather than soften

Elastomers: Polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress

- Also known as rubber
- Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape
- Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastics

Examples of Polymers

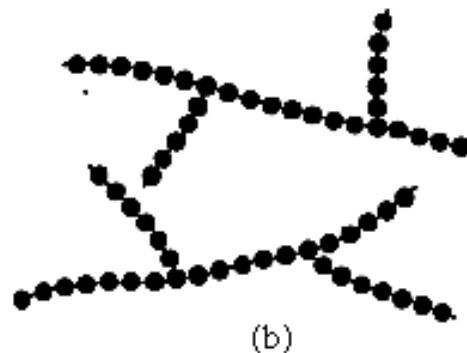
- **Thermoplastics:** Polyethylene, polyvinylchloride, polypropylene, polystyrene, etc.
- **Thermosets:** Phenolics, epoxides, and certain polyesters
- **Elastomers:** Natural rubber, (vulcanized) Synthetic rubbers, which exceed the tonnage of natural rubber

Linear, Branched, and Cross-linked Polymers

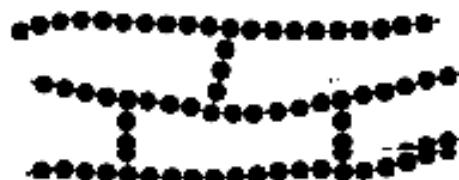
- **Linear structure** –chain-like structure Characteristic of thermoplastic polymers
- **Branched structure** –chain-like but with side branches Also found in thermoplastic polymers
- **Cross-linked structure** -Loosely cross-linked, as in an elastomer
Tightly cross-linked, as in a thermoset



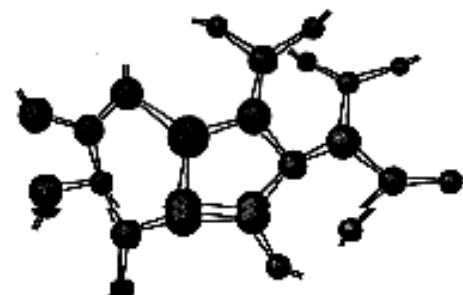
(a)



(b)



(c)



(d)

ii) On the basis of nature of monomer

- Homopolymers (comprise of monomers of the same type)
 - Linear (homochain or heterochain)
 - Branched
 - Cross-linked
- Heteropolymers/ Copolymers (Different repeating units)
 - Linear; Branched; Graft (regular/irregular); Block (regular/irregular)

iii) On the basis of chemical nature

- Organic (polymer backbone chain made up of carbon atom)
- Inorganic (No carbon atoms in the backbone chain, eg., Silicone rubbers)

a) Homopolymer



(a) Simple polymer

b) Copolymer



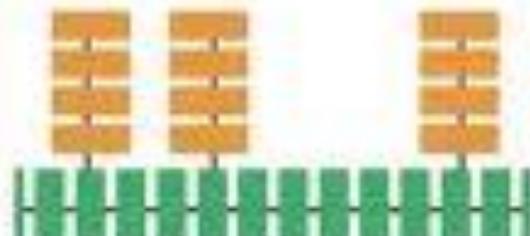
(b) Alternating copolymer

c) Block copolymer



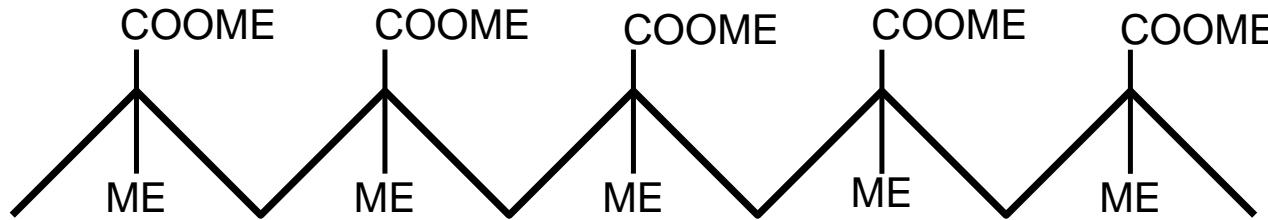
(c) Block copolymer

d) Graft copolymer

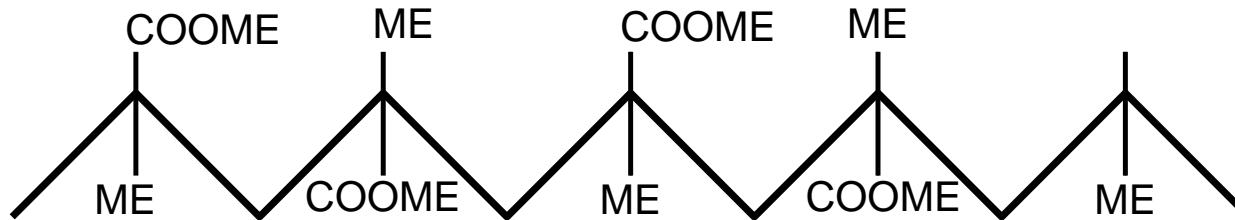


(d) Graft copolymer

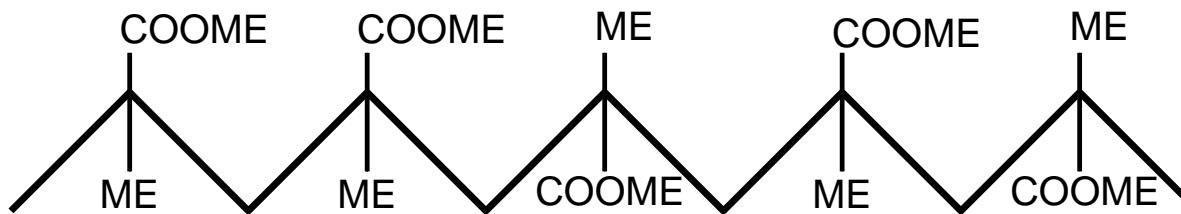
- **Depending on tacticity:**
- Isotactic – similar groups on same side of chain



- Syndiotactic – two groups alternate



- Atactic – displays no regular pattern



❖ Every other carbon in the chain is a stereocenter

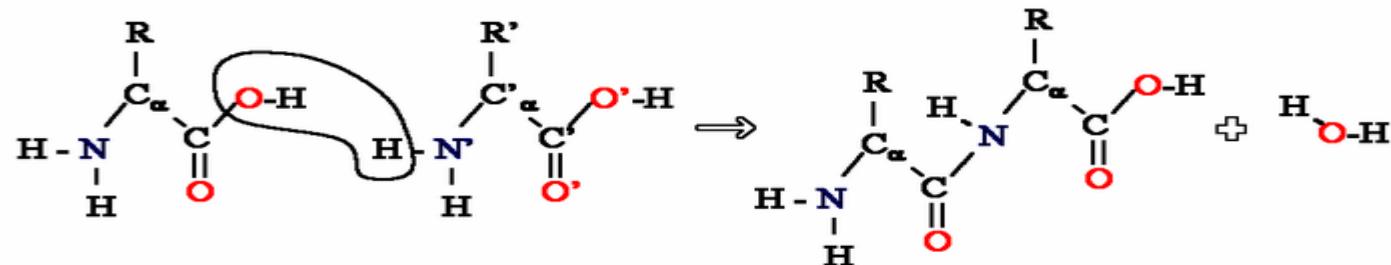
Classification based Polymerization

- **Addition Polymerization:** A polymer formed by direct repeated addition of monomers is called addition polymerization. In this type of polymers monomers are unsaturated compounds or derivatives of alkenes.



Fig 1: The polymerisation of ethene into poly(ethene)

- **Condensation Polymerization:** Condensation polymerization involves condensation of two different monomers which are normally bi functional group. During the process there is loss of small molecule such as water



- **Effect of Branching on Properties**
 - Thermoplastic polymers always possess linear or branched structures, or a mixture of the two
 - Branches increase entanglement among the molecules, which makes the polymer:
Stronger in the solid state. More viscous at a given temperature in the plastic or liquid state

- **Effect of Cross-Linking on Properties**
- Thermosets possess a high degree of cross-linking, while elastomers possess a low degree of cross-linking
- Thermosets are hard and brittle, while elastomers are elastic and resilient
- Cross-linking causes the polymer to become chemically set. The reaction cannot be reversed. The polymer structure is permanently changed; if heated, it degrades or burns rather than melt

- Mechanical Properties of Thermoplastics
- Low modulus of elasticity (stiffness) E is two or three orders of magnitude lower than metals and ceramics
- Low tensile strength TS is about 10% of the metal
- Much lower hardness than metals or ceramics
- Greater ductility on average Tremendous range of values, from 1% elongation for polystyrene to 500% or more for polypropylene

- **Physical Properties of Thermoplastics**
- Lower densities than metals or ceramics Typical specific gravity for polymers are 1.2 Ceramics specific gravity = 2.5 Metals specific gravity = 7.0
- Much higher coefficient of thermal expansion Roughly five times the value for metals and 10 times the value for ceramics
- Much lower melting temperatures
- Specific heats two to four times those of metals and ceramics
- Thermal conductivities about three orders of magnitude lower than those of metals
- Insulating electrical properties

- General Properties and Characteristics of Thermosets
 - Rigid - modulus of elasticity is two to three times greater than TP
 - Brittle, virtually no ductility
 - Less soluble than TP in common solvents
 - Capable of higher service temperatures than TP
 - Cannot be remelted - instead they degrade or burn

CHARACTERISTICS OF IDEAL POLYMER

- Should be *inert and compatible with the environment.*
- Should be *non-toxic.*
- Should be *easily administered.*
- Should be *easy and inexpensive to fabricate.*
- Should have *good mechanical strength.*

Why are polymers/ plastics extensively used-

- Plastics are strong, light weight, flexible and durable.
- Plastics show superior optical properties (clarity, gloss and color).
- Plastics can be easily moulded into a variety of shapes and sizes.
- Plastics have excellent mechanical strength (tensile properties, tear resistance and impact resistance).

- Plastics are relatively cheap compared to tin, glass and steel.
- Plastics are reusable and recyclable.
- Plastics have long use life.

- Plastics are good electrical / heat insulators.
- Plastics do not corrode or decay.
- Plastics are cheap and disposable.
- Plastics are resistant to chemicals, water or grease.

- **Compounding of polymer**
- Polymer and Additives
- Usually, polymers are mixed with added ingredients (serve a variety of purposes)
 - Properties of a polymer can often be beneficially changed by combining it with additives
- 2 types of additives
 - Modifying additives
 - Protective additives
- **Fillers**
 - Reinforcing fillers- to toughen polymers. e.g. carbon black added to rubber; improvement in abrasion resistance
 - Non-reinforcing fillers- are in powder, added to cheapen the mix (usually these additives do not enhance the properties). e.g. calcium carbonate.
- **Plasticizer**- usually non-volatile liquids, desired to increase the flexibility. e.g. flexible plasticized PVC, eg. Tricresyl phosphate, triphenyl phosphate, etc.
- **Binders**- Hold the constituents together. Eg. Cellulose derivatives. Influence properties of plastics.

- **Types of Additives by Function**
- Resin- main constituent.
- **Fillers** –to strengthen polymer or reduce cost
- **Plasticizers** –to soften polymer and improve flow
- **Colorants** –pigments or dyes
- **Lubricants** –to reduce friction and improve flow, eg. Vegetable oil, soaps, etc.
- **Flame retardents** –to reduce flammability of plastic
- **Cross-linking agents** –for thermosets
- **Stabilizers**- Ultraviolet light absorbers –to reduce degradation from sunlight, Antioxidants –to reduce oxidation damage
- **Pigments**- used to colour the product, eg. Titanium oxide- white color, iron oxide red color, etc.
- **Catalyst**- accelearate polymerisation, eg. H₂O₂, benzoyl peroxide, etc.

Fabrication/ Moulding

Molding or **moulding** is the process of manufacturing by shaping liquid or pliable raw material using a rigid frame called a mold or matrix. This itself may have been made using a pattern or model of the final object.

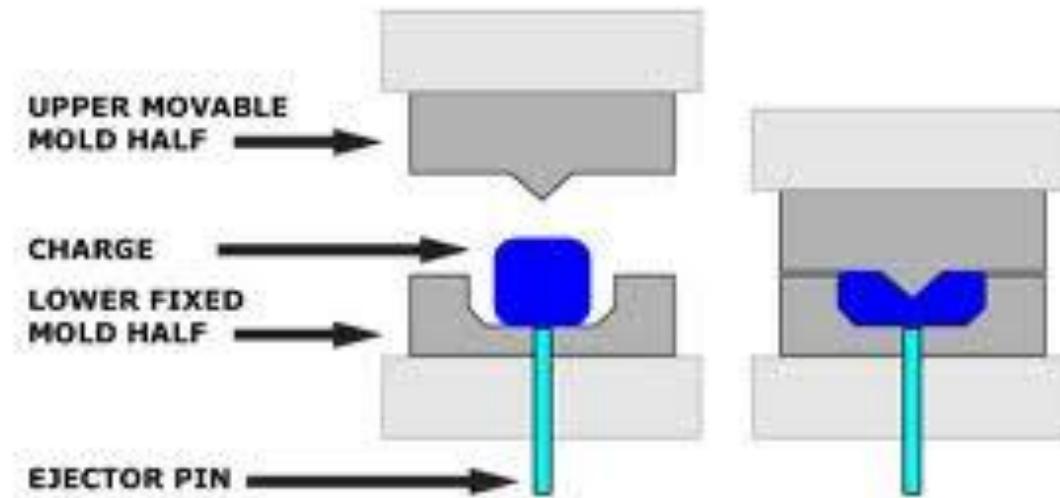
A **mold** or **mould** is a hollowed-out block that is filled with a liquid or pliable material like plastic, glass, metal, or ceramic raw materials. The liquid hardens or sets inside the mold, adopting its shape. A mold is the counterpart to a cast. The very common bi-valve molding process uses two molds, one for each half of the object.

Compression Molding is a process in which a molding polymer is squeezed into a preheated mold taking a shape of the mold cavity and performing curing due to heat and pressure applied to the material.

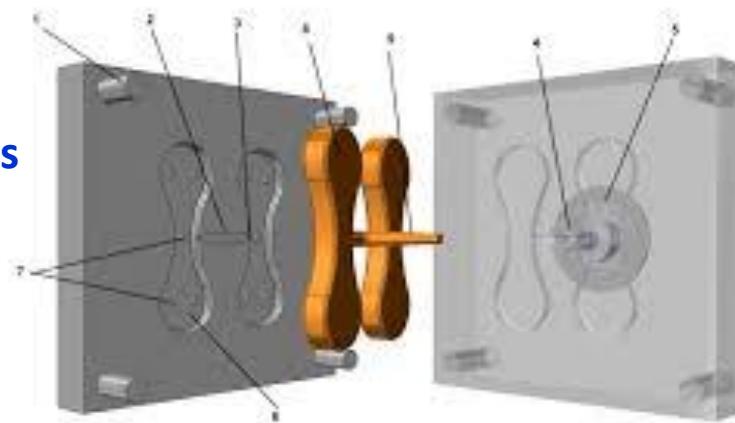
The method is used mostly for molding **thermosetting resins (thermosets)**, but some thermoplastic parts may also be produced by Compression Molding.

The method uses a split mold mounted in a hydraulic press

COMPRESSION MOLDING



Thermoplastic and thermosets



https://www.youtube.com/watch?v=GqE93pbV_9I

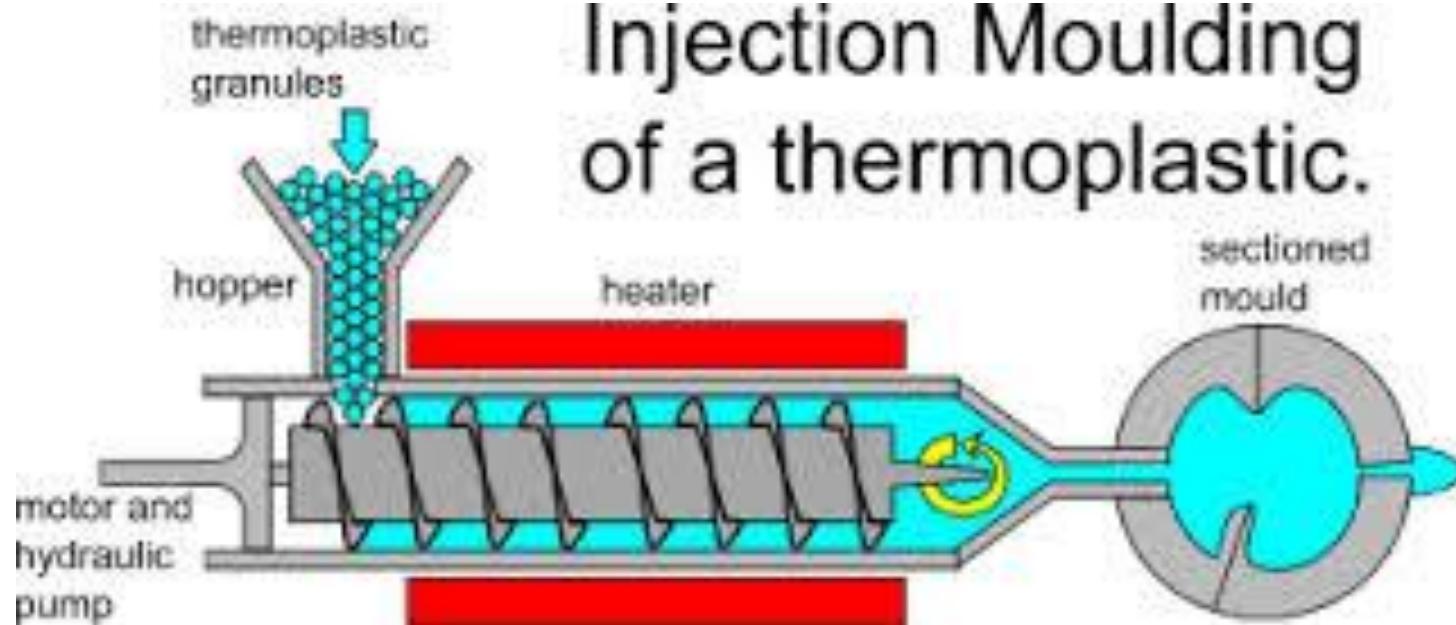
Injection molding

- Injection molding is a method to obtain molded products by injecting plastic materials molten by heat into a mold, and then cooling and solidifying them.
The method is suitable for the mass production of products with complicated shapes, and takes a large part in the area of plastic processing.

Advantages of Injection Molding

- High production rates
- Wide range of materials can be used
- Low labor costs
- Minimal scrap losses

Injection Moulding of a thermoplastic.



Thermoplastic

<https://www.youtube.com/watch?v=b1U9W4iNDiQ>

Transfer Molding

The method is used primarily for molding thermosetting resins (thermosets), but some thermoplastic parts may also be produced by Transfer Molding

The method combines features of both Compression Molding (hydraulic pressing and the same molding materials - thermosets) and Injection Molding (ram-plunger and filling the mold through a sprue).

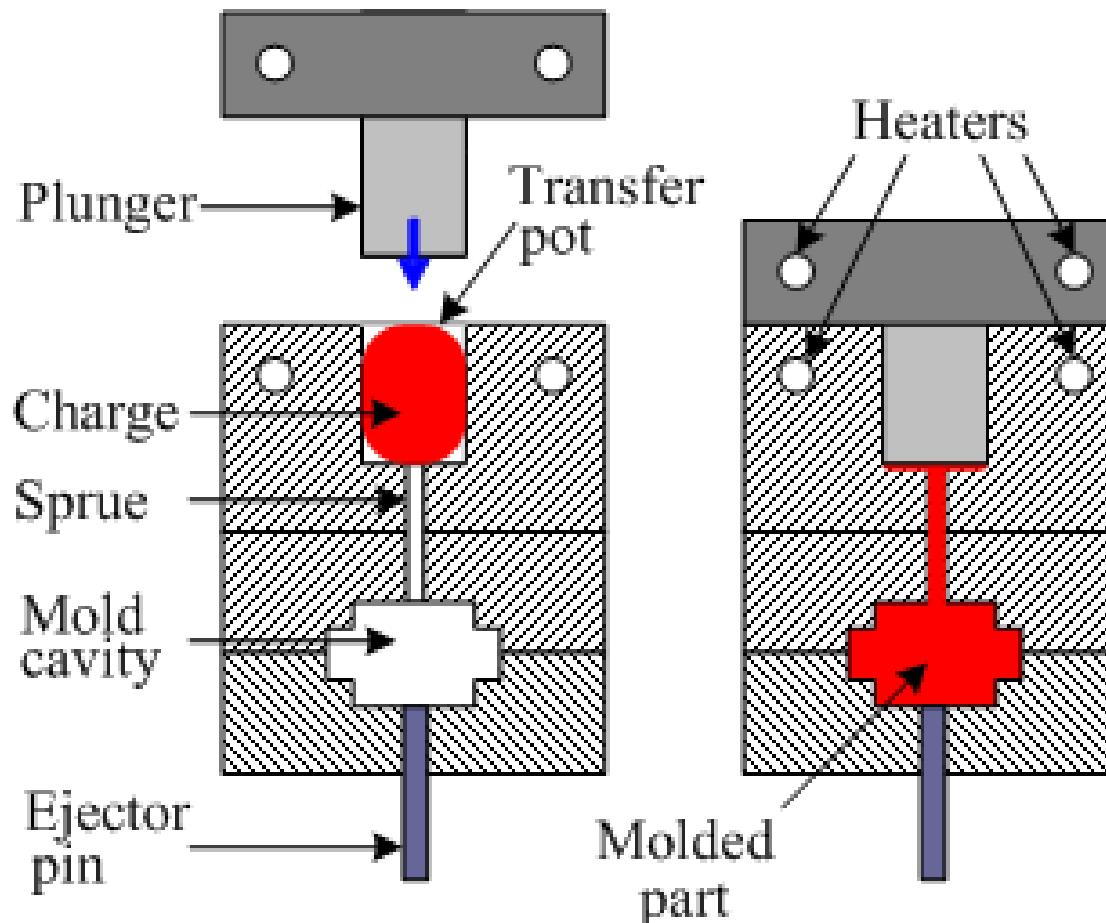
TS charge is loaded into a chamber immediately ahead of mold cavity, where it is heated; pressure is then applied to force soft polymer to flow into heated mold where it cures

Two variants:

Pot transfer molding - charge is injected from a "pot" through a vertical sprue channel into cavity

Plunger transfer molding – plunger injects charge from a heated well through channels into cavity.

Transfer Molding



Thermosets

www.substech.com

Extrusion Molding-

Thermoplastic granules are fed from a hopper by a rotating screw through a heated cylinder.

The **tapered shape of the screw** compacts the plastic as it becomes plasticized. This part of the process is similar to the heating and compacting stages in the injection moulding process. **The difference** being that the softened material is allowed to flow out through a die in a continuous stream

(**Extrusion moulding**) rather than be pumped intermittently in measured amounts into a mould.(**Injection moulding**)

The die which is fitted to the end of the extruder barrel determines the cross-section of the extrusion.

Widely used for thermoplastics and elastomers to mass produce items such as tubing, pipes, hose, structural shapes, sheet and film, continuous filaments, and coated electrical wire

Carried out as a **continuous process**; ***extrudate*** is then cut into desired lengths

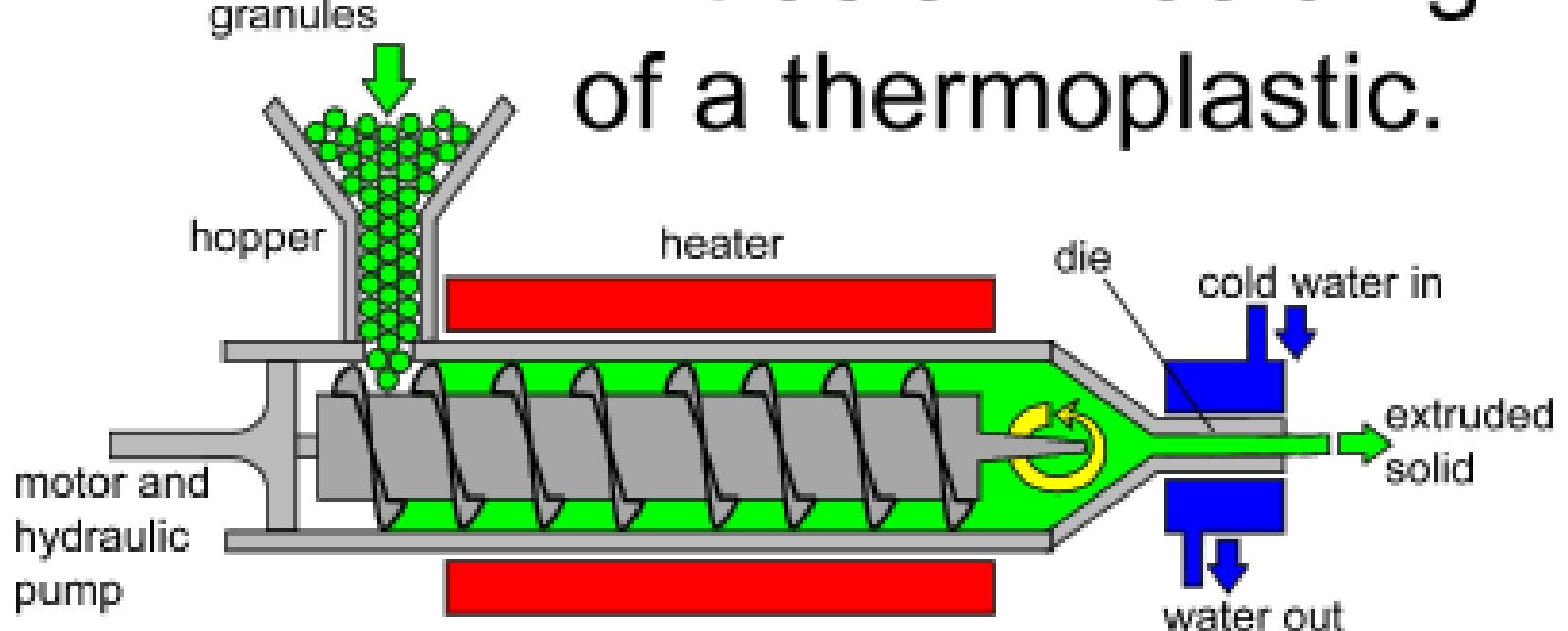
Extrusion

This process can be compared to squeezing toothpaste from a tube. It is a continuous

process used to produce both solid and hollow products that have a constant

cross-section. E.g. window frames, hose pipe, curtain track, garden trellis.

Extrusion Moulding of a thermoplastic.



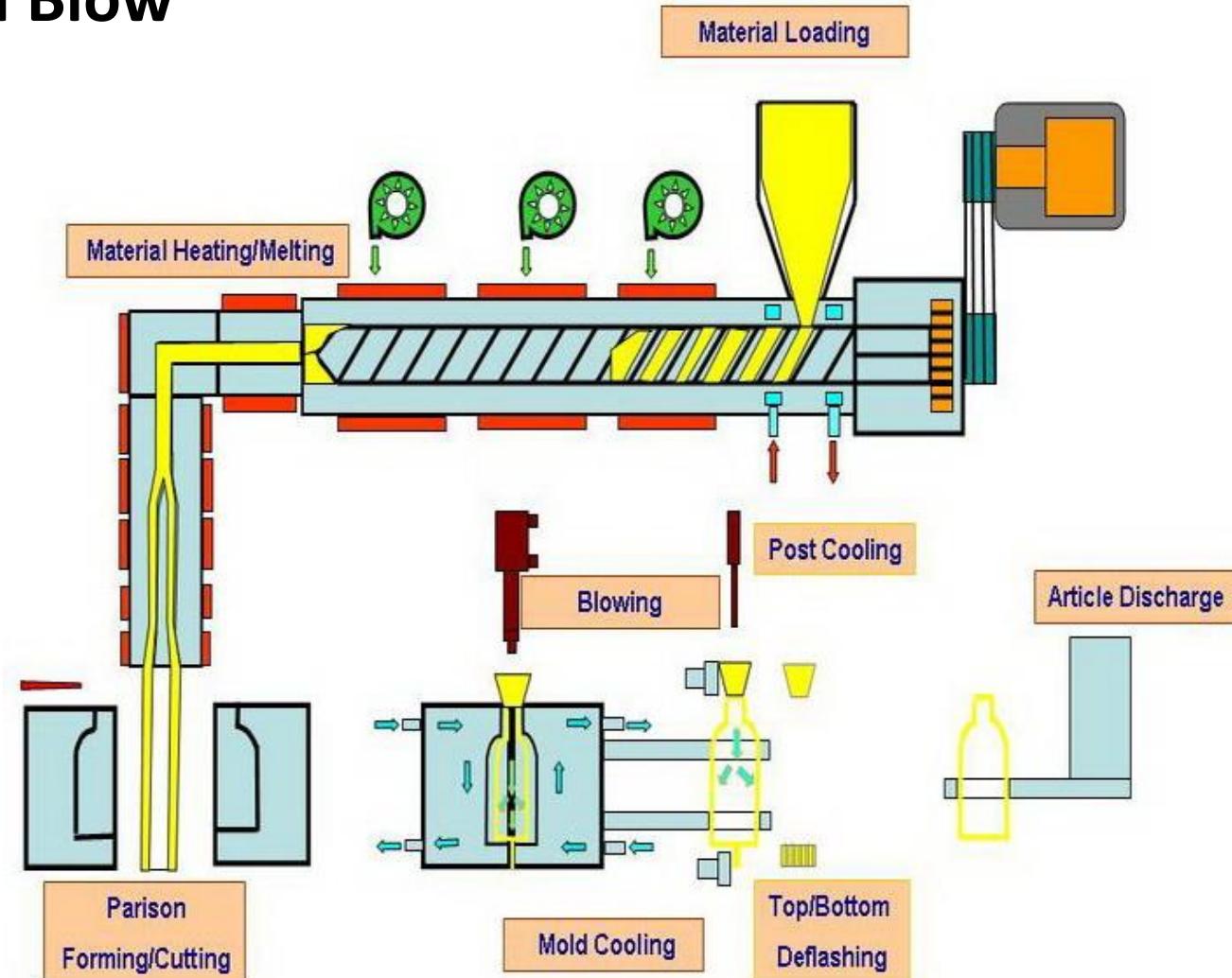
Thermoplastic

• *Horizontal*

<https://www.youtube.com/watch?v=Tp2Rdx69SSo>

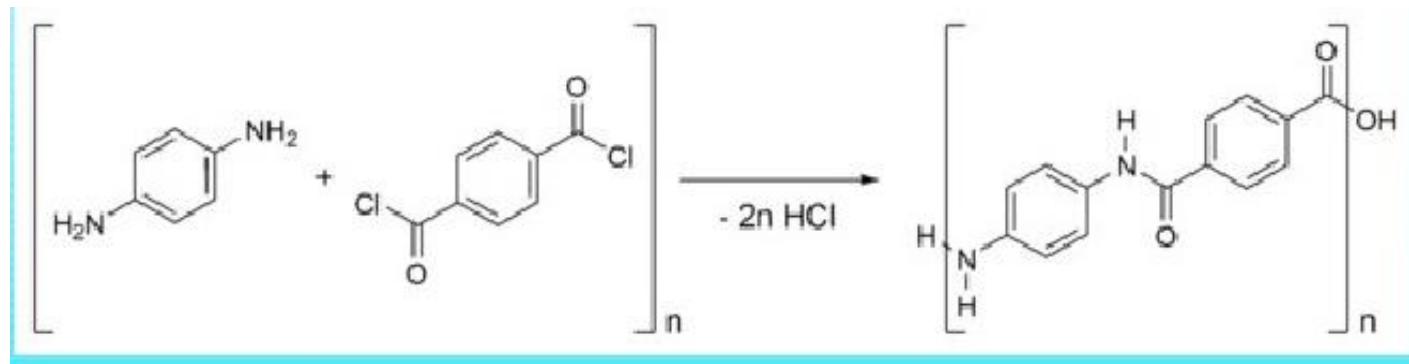
**Also called as
'Extrusion Blow
Molding'.**

Vertical



<https://www.youtube.com/watch?v=xJtyn0vumQU>

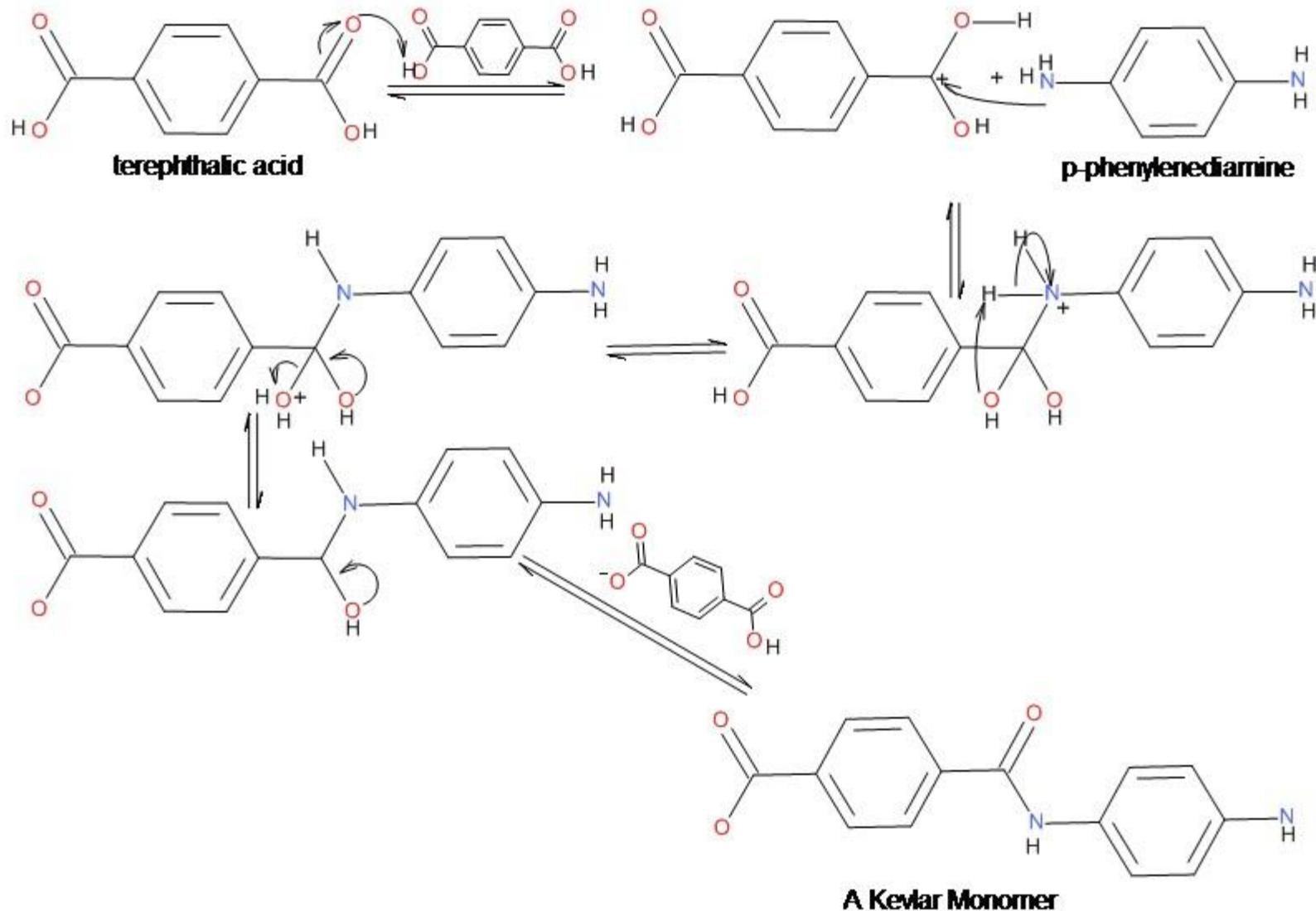
Synthesis of some important polymers- Kevlar



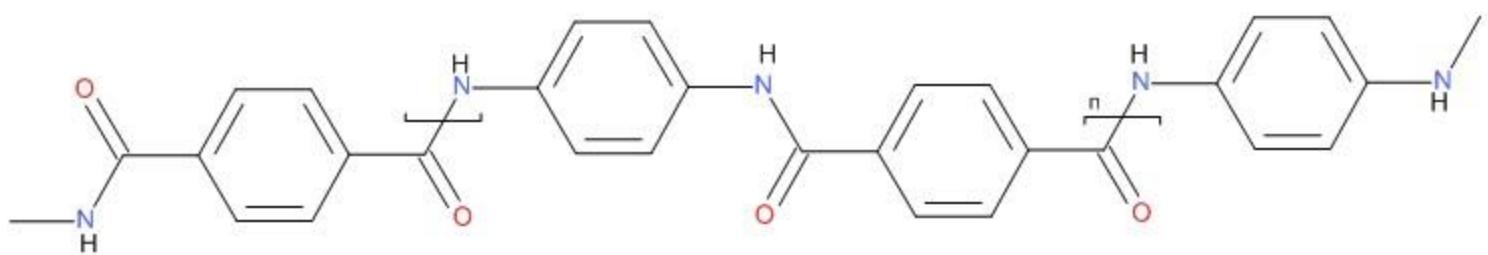
This is a amide co-polymer synthesized by condensation polymerisation of phenylene diamine and terphthaloyl chloride.

Terephthalic acid is used for manufacture of Kevlar but as terephthaloyl chloride is more active than the terephthalic acid, terephthalic aid is converted to terephthalic chloride which is used to manufacture Kevlar.

Condensation mechanism-



Polymerisation



Kevlar

Basic Information

- Kevlar is a high strength material first used in the 1970's.
- It has the iupac name poly(imino-p-phenyleneimino= terephthaloyl)
- Its molecular formula is [-CO-C₆H₄-CO-NH-C₆H₄-NH-]_n
- It is made up of the monomers 4-phenylene-diamine (*para*-phenylenediamine) and terephthaloyl chloride
- Kevlar's relative molecular mass is 238.241g.
- The glass transition temperature of kevlar is 170 degrees Celsius
- Kevlar is insoluble in water



Chemical Data

- Kevlar is made during a condensation reaction making hydrochloric acid as a by product.
- The production of Kevlar is extremely expensive due to the costs implicated with storing concentrated sulphuric acid.
- Kevlar when spun, has a relative density of 1.44 and has a tensile to weight ration of 5:1

- Kevlar is rarely used outdoors unprotected from sunlight as it suffers from ultra violet light degradation.
- Kevlar is very heat resistant and decomposes above 675K without melting.

Kevlar in Use

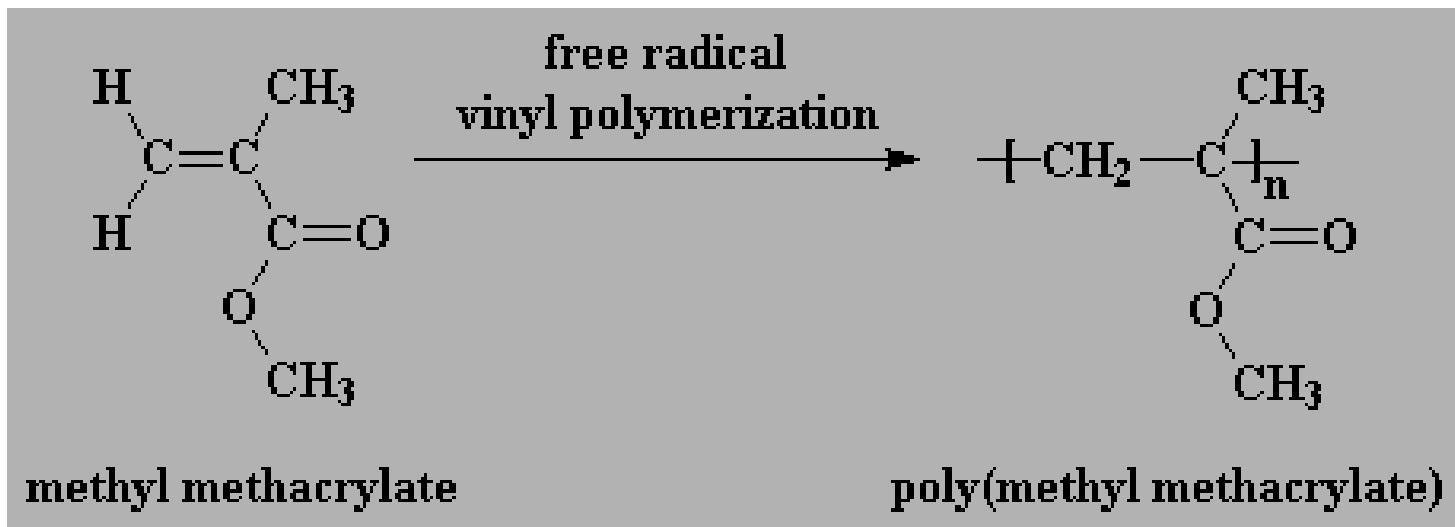


Good for its function

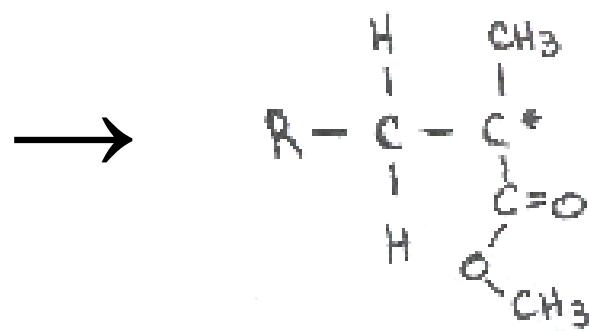
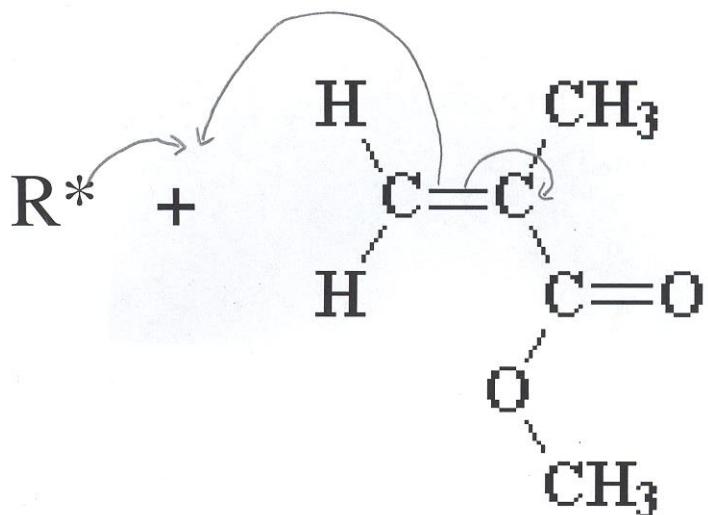
- Kevlar's physical hardness and tensile strength both make it very suitable for its function, in bulletproof vests, for example.
- Its hydrogen bonds give strength to the material, creating quite strong intermolecular bonds between kevlar molecules, giving it its strength and durability.

Polymethyl Methacrylate

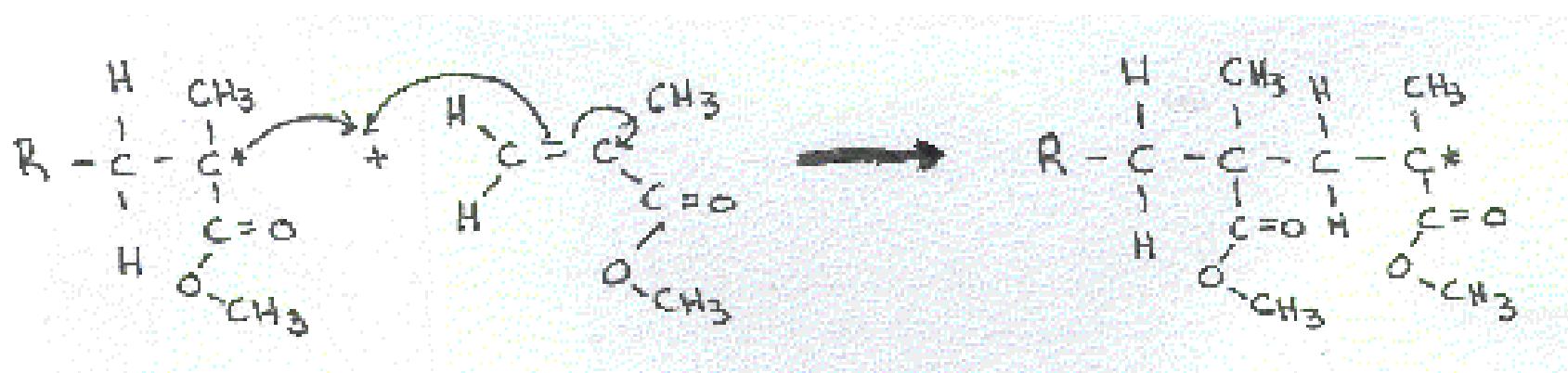
- PMMA is manufactured from Methyl methacrylate by addition polymerisation (Free Radical Polymerization).



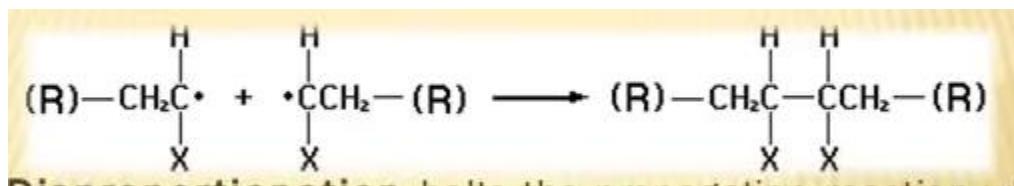
- Step 1 : Free radical (R^*) plus methyl methacrylate



Step 2 : Polymerization - MMA radical plus MMA :repeated many, many times

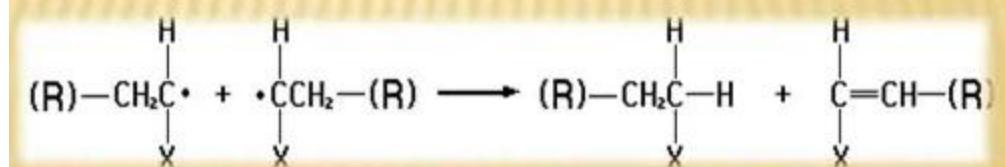


Step 3 : Termination – occurs when two radicals join



Disproportionation

Combination

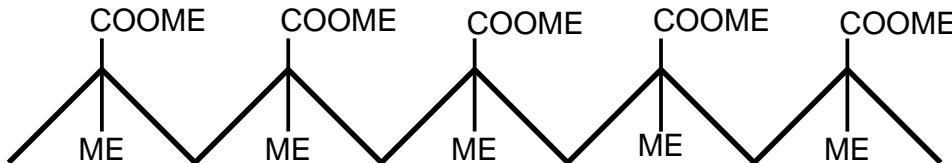


Catalysts

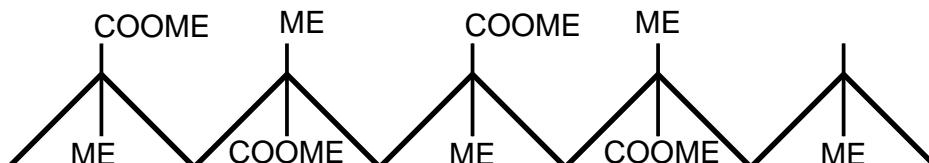
- Multiple catalysts can be used in production of PMMA. Some of these are:
 - Butyl Lithium
 - Highly active catalysts based on group 4 metallocenes
 - An aluminum system supported by salen ligands

Why Use Different Catalysts?

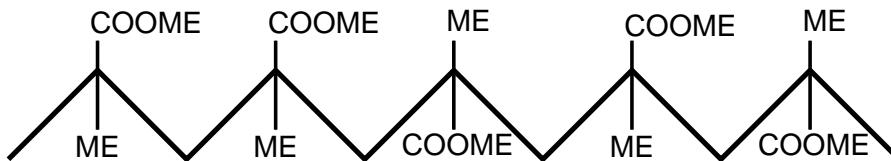
- Different catalysts result in different versions of the polymer
 - Variation is due to the placement of the ester (R-O-R) and methyl (CH_3) groups along the polymer backbone
- Isotactic – similar groups on same side of chain



- Syndiotactic – two groups alternate



- Atactic – displays no regular pattern



❖ Every other carbon in the chain is a stereocenter

Properties of PMMA

- Lighter than glass (density is about half that of glass)
- Shatter proof
- Softer and easier to scratch than glass (scratch resistant coatings may be applied)
- Transmits more light than glass (92% of visible light)
- Does not filter UV light (may be coated with UV film)
- More transparent than glass, so windows can be made thicker

Current uses for PMMA

- Include many uses similar to those for which it was first developed but include many things never imagined by the inventors! A partial list of the uses for PMMA includes:

- Safety glass such as Plexiglass and Lucite – uses range from windows for aquariums and under-water restaurants to safety shields at hockey rinks to skylights in your home to simple paperweights

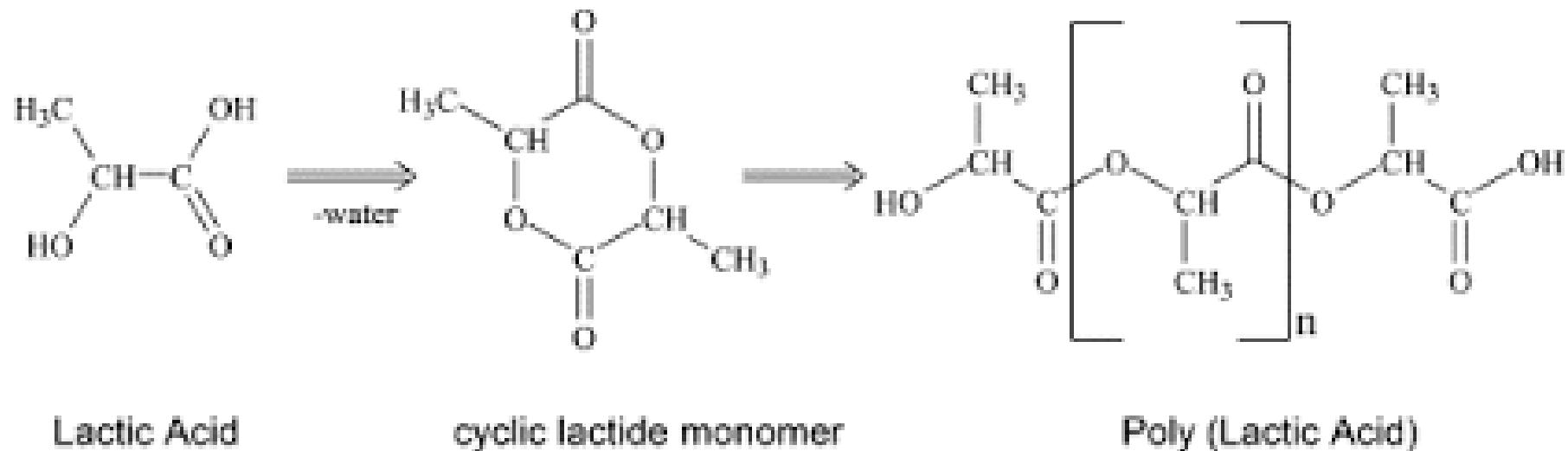


Medical Uses

- Used as bone cement for use in arthroplastic procedures of the hip, knee, and other joints for the fixation of polymer or metallic prosthetic implants to living bone
- Used in Pacemakers

What are characteristics of biomedical polymers?

PolyLactic acid (Bio-Degradable Polymer)



Condensation mechanism- Removal of water molecule

Polylactic acid, PLA is a [thermoplastic polyester](#) with backbone formula $(C_3H_4O_2)_n$ or $[-C(CH_3)HC(=O)O-]_n$, formally obtained by [condensation](#) of [lactic acid](#) $C(CH_3)(OH)HCOOH$ with loss of water. It can also be prepared by ring-opening polymerization of [lactide](#) $[-C(CH_3)HC(=O)O-]_2$, the cyclic dimer of the basic repeating unit. The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used. PLA has become a popular material due to it being economically produced from [renewable resources](#). The monomer is typically made from fermented plant starch such as from [corn](#), [cassava](#), [sugarcane](#) or [sugar beet pulp](#). In 2010, PLA had the second highest consumption volume of any [bioplastic](#) of the world. Its widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in [3D printing](#).

Properties-

PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a [glass transition](#) 60–65 °C, a [melting temperature](#) 130-180 °C, and a [Young's modulus](#) 2.7–16 GPa.

Heat-resistant PLA can withstand temperatures of 110 °C.

Several technologies such as [annealing](#), adding [nucleating](#) agents, forming composites with fibers or [nano-particles](#), chain extending and introducing crosslink structures have been used to enhance the mechanical properties of PLA polymers. Polylactic acid can be processed like most thermoplastics into [fiber](#) and film.

The high surface energy of PLA results in good printability, making it widely used in 3D printing. PLA is used as a feedstock material in desktop [fused filament fabrication](#) by [3D printers](#), such as [RepRap](#) printers. PLA objects can be fabricated by 3D printing, casting, [injection moulding](#), [extrusion](#), machining, and solvent welding.

PLA is soluble in a range of organic solvents like ethyl acetate. PLA is also soluble in hot [benzene](#), [tetrahydrofuran](#), and [dioxane](#).

PLA can be [solvent welded](#) using [dichloromethane](#). [Acetone](#) also softens the surface of PLA, making it sticky without dissolving it, for welding to another PLA surface.

Applications-

PLA is used in [disposable tableware](#), [cutlery](#), housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays. (However, PLA is not suitable for microwavable containers because of its low glass transition temperature.

It is used for compost bags, food packaging and loose-fill packaging material that is cast, injection molded, or spun.

In the form of a film, it shrinks upon heating, allowing it to be used in [shrink tunnels](#).

In the form of fibers, it is used for monofilament fishing line and netting.

In the form of [non-woven fabrics](#), it is used for [upholstery](#), disposable garments, [awnings](#), feminine hygiene products, and [diapers](#).

PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as [ABS](#). Such blends have good form stability and visual transparency, making them useful in low-end packaging applications.

PLA is used for automotive parts such as floor mats, panels, and covers.

PLA is used for vegetation and weed prevention. It is used for sandbags, planting pots, binding tape and ropes.

Applications in the field of Medicine-

PLA can degrade into innocuous lactic acid, so it is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh.

It breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. to the bone) as that area heals. PLA has high strength characteristics.

Thanks to its bio-compatibility and biodegradability, PLA has also found ample interest as a polymeric scaffold for drug delivery purposes.

The composite blend of various PLA with tricalcium phosphate (TCP) is used as scaffolds for bone engineering.

Poly-L-lactic acid (PLLA) is the main ingredient in Sculptra, a facial volume enhancer used for treating lipoatrophy of the cheeks.

PLLA is used to stimulate collagen synthesis in fibroblasts via foreign body reaction in the presence of macrophages. Macrophages act as a stimulant in secretion of cytokines and mediators such as TGF- β , which stimulate the fibroblast to secrete collagen into the surrounding tissue. Therefore, PLLA has potential applications in the dermatological studies

Degradation-

PLA is degraded abiotically by three mechanisms:[\[42\]](#)

1.Hydrolysis: The ester groups of the main chain are cleaved, thus reducing molecular weight.

2.Thermal degradation: A complex phenomenon leading to the appearance of different compounds such as lighter molecules and linear and cyclic oligomers with different *Mw*, and lactide.

3.Photodegradation: UV radiation induces degradation. This is a factor mainly where PLA is exposed to sunlight in its applications in [plasticulture](#), packaging containers and films.

PLA is effectively digested in hotter industrial composts, usually degrading best at temperatures of over 60°C.

PLA samples of various molecular weights were degraded into [methyl lactate](#) (a green solvent) by using a metal complex catalyst.

PLA can also be degraded by some bacteria, such as [Amycolatopsis](#) and [Saccharothrix](#). A purified protease from [Amycolatopsis](#) sp., [PLA depolymerase](#), can also degrade PLA.

Enzymes such as [pronase](#) and most effectively [proteinase K](#) from [Tritirachium album](#) degrade PLA.

Four possible end-of-life scenarios are the most common:

Recycling: which can be either chemical or mechanical. Currently, the SPI [resin identification code](#) 7 ("others") is applicable for PLA.



Composting: PLA is biodegradable under industrial composting conditions, starting with chemical hydrolysis process, followed by microbial digestion, to ultimately degrade the PLA. Under industrial composting conditions (58 °C), PLA can partly (about half) decompose into water and carbon dioxide in 60 days, after which the remainder decomposes much more slowly.

Incineration: PLA can be [incinerated](#) without producing chlorine-containing chemicals or heavy metals because it contains only [carbon](#), [oxygen](#), and [hydrogen](#) atoms. Since it does not contain chlorine it does not produce [dioxins](#) during incineration.

Landfill: the least preferable option is landfilling because PLA degrades very slowly in ambient temperatures, often as slowly as other plastics.

Polymers In Medicine

Cellophane

PGA, PLA, PLGA

Polydimethylsiloxane

Polyethylene and PMMA

Polytetrafluoroethylene

Polyurethane

What are they?

Substances other than food or drugs contained in therapeutic or diagnostic systems that are in contact with tissue or biological fluids.

Why use Biomaterials?

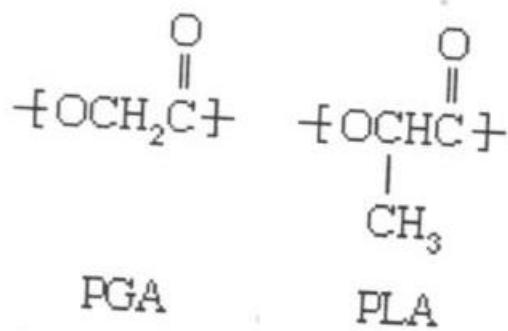
Improve patient's quality of life by replacing a defective body part with a substitute.

Physicians were limited to use off-the shelf supplies.

Novel biodegradable polymers and modified natural substances.

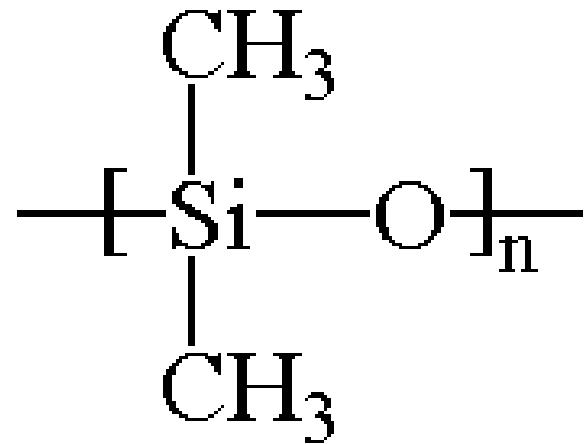
Applications of Biomaterials			
Polymer	Applications	Polymer	Applications
PDMS	Catheters, heart Valves	Polytetrafluoroethylene	Heart valves Vascular grafts Nerve repair
Polyurethane	ventricular assist Devices	Polyethylene	Catheters, hip prostheses
PGA, PLA, And PLGA	Drug delivery, devices	Polymethylmethacrylate (PMMA)	Fracture fixation
		Cellophane	Dialysis membranes

Polylactic acid, Polyglycolic acid



- Amorphous forms used in drug delivery systems
- Crystalline forms good for scaffolding, or sutures; stents, plastic surgery, plates rods, pins, screws.
- **Two essentials in scaffolding: high surface to volume ratio, highly porous**
 - Allows cells to easily proliferate for setup of pathways
 - Setup of pathways for nutrients

Polydimethylsiloxane



- “Silicon”
- Lubricants and Foaming agents
- Pacemakers and Vaccine Delivery systems

- Used in treatment of prostate carcinoma
- Small biodegradable pellets (188 m) injected into area of body where needed; heart valves, blood filters, vascular tubing, artificial heart.
- Smaller doses, less toxic effects for patient

PMMA

- Thermoplastics, exhibit moderate to high tensile strength with moderate elongation
- Used for Hip replacement and Fracture Fixation
- Annual procedures approaching 5 Million
- Metal alternatives have corrosive problems



PMMA disc over femoral window during the molding process

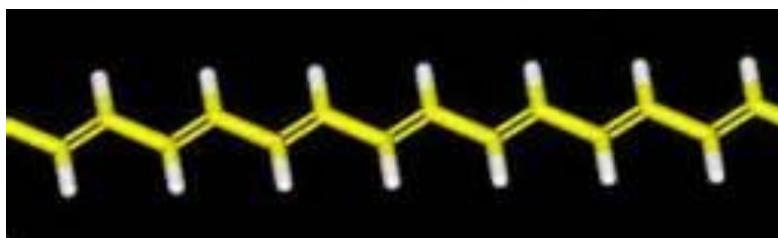
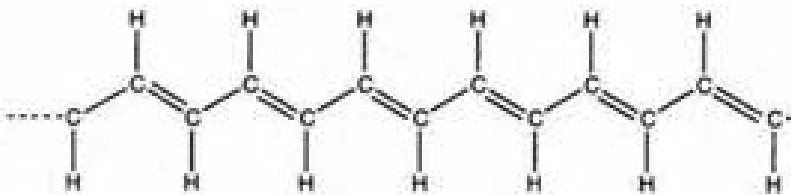


PMMA template after polymerization, showing molded plug

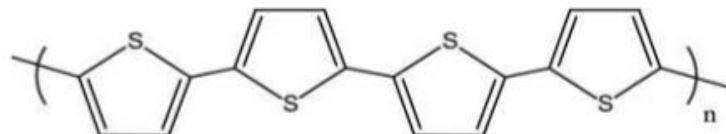
Conducting polymers

Intrinsically conducting polymers (ICPs) belong to a class of organic materials with unique electronic properties such as electric conductivity, electrochromism, and electroactivity. Conjugated electrons in the backbone of their macromolecules are responsible for these properties. Due to their high electrical properties, ICPs are intensively investigated for application in electronics, microelectronics, optoelectronics mainly for areas in aerospace and automobile industries. Among the most promising applications of the ICPs are corrosion protection, solid-state charge storage devices, electromagnetic screens, antistatic coatings and gas separation coatings. However, poor mechanical properties, environmental sensitivity, moderate stability of electrical properties with temperature significantly limit the industrial applicability of ICPs.

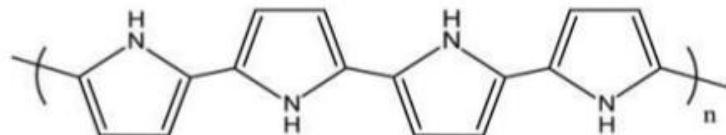
Polyacetylene



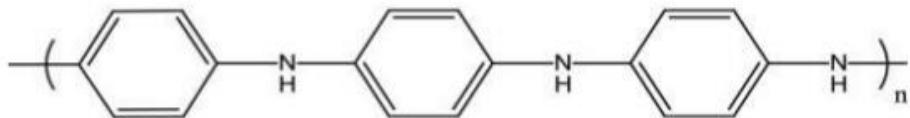
Few Common Conducting Polymers



polythiophene



polypyrrole



polyaniline

(DCP) Doped conducting polymer

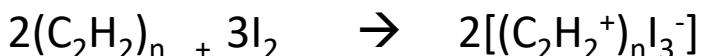
While the addition of a donor or an acceptor molecule to the polymer is called "**doping**", the reaction that takes place is actually a redox reaction.

- The first step is the formation of a cation (or anion) radical, which is called a soliton or a polaron.



- As synthesized conductive polymers exhibit very low conductivities. It is not until an electron is removed from the valence band (**p-doping**) or added to the conduction band (**n-doping**, which is far less common) does a conducting polymer become highly conductive.
- Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes. This movement of charge is what is actually responsible for electrical conductivity.

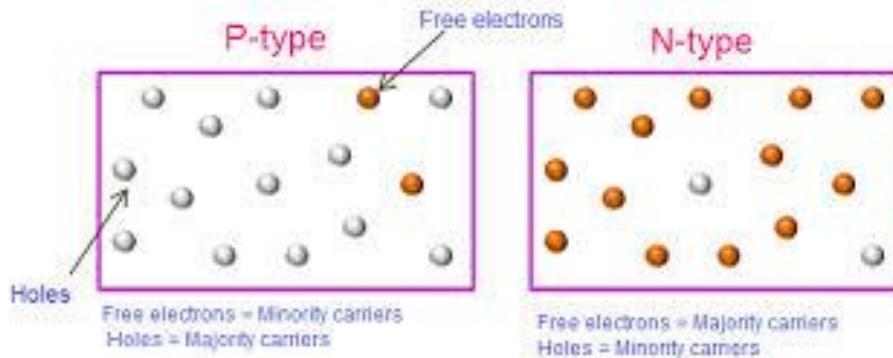
(i) Oxidation process (p-doping):



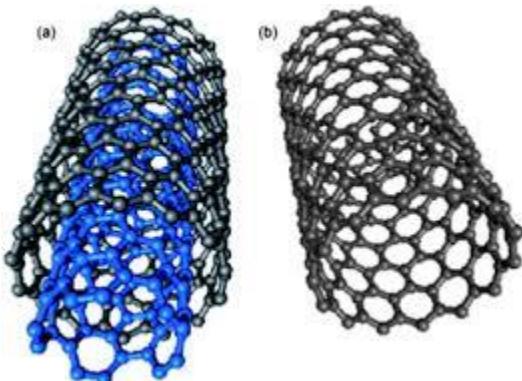
(i) Reduction process (n-doping):



The above reactions are most likely to occur saturated polym electrons, as they can be very easily removed from the polymeric chains to form polyion therefore, these are the types of polymers, which assume high conductivity on doping.



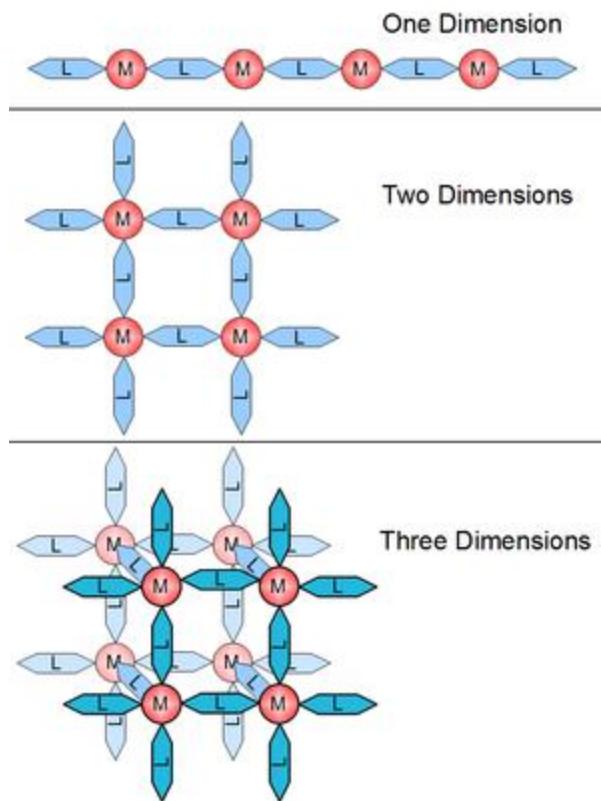
- *ECP*
- One type of extrinsically conducting polymer consists of a matrix of poly(ethene) with a percentage of **conducting carbon black** (a form of powdered graphite) incorporated (filled) in it. If the carbon black particles are close enough to be in contact with one another, the material conducts. If the particles are not in contact, it is an insulator. This means that the **degree of electrical conduction depends on temperature**. At high temperature, the poly(ethene) matrix expands and pulls the particles of carbon black away from each other, decreasing the conductivity. At lower temperatures the poly(ethene) contracts, the carbon black particles are closer and the material conducts well. This temperature dependence of conductivity leads to the use of this material in **self-regulating heater cable and PolySwitch*** re-settable circuit protection devices.



- Another type includes the blends
 - Extrinsically conductive polymers can involve a blend of conductive and nonconductive polymers.
- ***Co-ordinate Conjugate Polymers (CCP)-***
- A **coordination polymer** is an inorganic or organometallic polymer structure containing metal cation centers linked by organic ligands. More formally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.
- It can also be described as a polymer whose repeat units are coordination complexes. Coordination polymers contain the subclass coordination networks that are coordination compounds extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions. A subclass of these are the metal-organic frameworks, or MOFs, that are coordination networks with organic ligands containing potential voids.

Coordination polymers are relevant to many fields such as [organic](#) and [inorganic chemistry](#), [biochemistry](#), [materials science](#), [electrochemistry](#), and pharmacology, having many potential applications. This interdisciplinary nature has led to extensive study in the past few decades.

Coordination polymers can be classified in a number of different ways according to their structure and composition. One important classification is referred to as [dimensionality](#).



A structure can be determined to be one-, two- or three-dimensional, depending on the number of directions in space the array extends in. A one-dimensional structure extends in a straight line (along the x axis); a two-dimensional structure extends in a plane (two directions, x and y axes); and a three-dimensional structure extends in all three directions (x, y, and z axes). This is depicted in Figure

In most coordination polymers, a ligand (atom or group of atoms) will formally donate a lone pair of electrons to a metal cation and form a coordination complex via a Lewis acid/ base relationship (Lewis acids and bases). Coordination polymers are formed when a ligand has the ability to form multiple coordination bonds and act as a bridge between multiple metal centers.

Polymers in industry

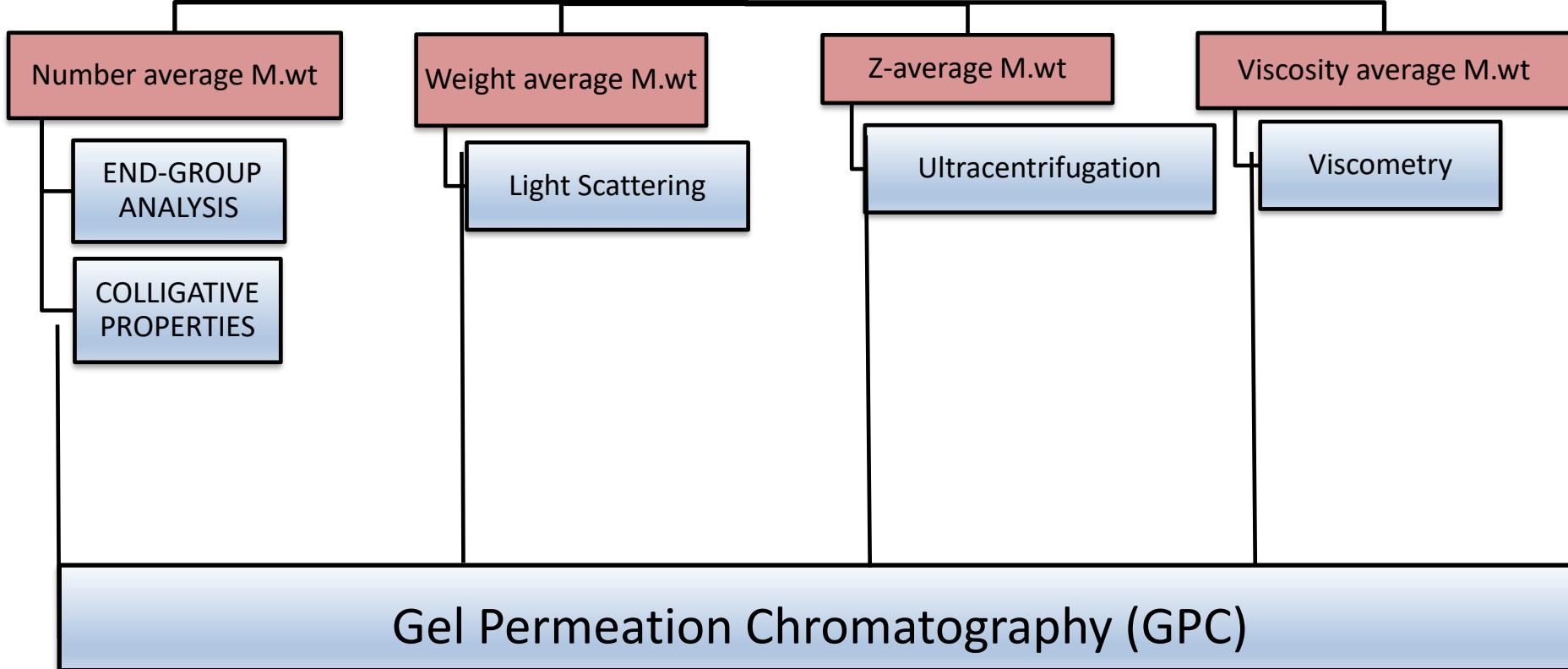
Type	Abbreviation	Typical Uses
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea-formaldehyde	UF	Similar to PF polymer; also treatment of textiles, coatings
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment
Epoxy	-	Protective coatings, adhesives, electrical and electronics applications, industrial flooring highway paving materials, composites
Melamine-formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware

Polymer Molecular weight and its Measurement methods

There are several reasons why we might want to measure polymer average molecular weight and its distribution:

1. The molecular weight and its distribution determine the **viscous and elastic properties** of the molten polymer. This affects **the processibility** of the melt and also the behavior of the resulting solid material. *For example*, a resin suitable for extrusion must have a high viscosity at low shear rates so that the extrudate maintains its integrity. To be suitable for injection molding, however, the same resin must have a low viscosity at high shear rates so that the injection pressure not be excessive.
2. The molecular weight of a polymer can determine its **applications**. *For example*, the resin used for making polycarbonate water bottles differs significantly in molecular weight from the polycarbonate that goes into compact disks.
3. Differences in molecular weight distribution also influence the polymer properties. As a consequence, two chemically similar polymers, processed identically, that have the **same molecular weight but different molecular-weight distributions** may result in products that show significantly **different shrinkages, tensile properties, and failure properties**. For this very important reason, it is advantageous to know the molecular weight and molecular-weight distribution of the polymers used.
4. Other situations where the molecular weight and its distribution directly influence results include **phase equilibrium and crystallization kinetics**.

M.wt Measurement Methods



NOTE: The choice of method for polymer molecular weight determination is influenced by factors such as: (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements.

Molecular Weight:

Molecular weight of a chemical compound can be defined, simply, as the sum of the atomic weights of each of the atoms in the molecule.

Examples:

Water (H_2O) is 2 H (1g) and one O (16g) = $2*(1) + 1*(16) = 18 \text{ g/mol}$

Methane CH_4 is 1 C (12g) and 4 H (1g) = $1*(12) + 4*(1) = 16 \text{ g/mole}$

Polyethylene $-(\text{C}_2\text{H}_4)-_{1000}$ = 2 C (12g) + 4H (1g) = $28\text{g/mole} * 1000 = 28,000 \text{ g/mole}$

Average Molecular Weight

Polymers are made up of many molecular weights or a distribution of chain lengths. In other other words, if one takes polyethylene as an example, this polymer may have chains of ethylene (C_2H_4) with different lengths; some longer than others.

Example:

Polyethylene $-(\text{C}_2\text{H}_4)-_{1000}$ has some chains with 1001 repeating ethylene units, some with 1010 ethylene units, some with 999 repeating units, and some with 990 repeating units. The average number of repeating units or chain length is 1000 repeating ethylene units for a molecular weight of $28*1000$ or 28,000 g/mole .

Therefore, polymers must be represented by the value of average molecular weight.

- (4) Viscosity-average molecular weight (M_v) can be obtained, experimentally, from dilute-solution viscometer using Mark-Howink equation. The viscosity-average molecular weight falls between M_n and M_w depending upon whether the solvent is a good or poor solvent for the polymer. In the case of a good solvent, $M_v = M_w$.

- **Mark-Howink-Sakurada equation:**

$$[\eta] = K \bar{M}^a$$

$[\eta]$: intrinsic viscosity
 K, a : constant for specific polymer and solvent
 \bar{M} : average molecular weight

NOTES:

1. A measure of the breadth of the molecular-weight distribution is given by the ratios of molecular-weight averages. For this purpose, the most commonly used ratio is M_w/M_n , called the *polydispersity index* or *PDI*.

$$PDI = \frac{M_w}{M_n} > 1 ; \text{ polymers having } PDI = 1 \text{ are called monodisperse polymers}$$

2. Degree of Polymerization (*DP*): is the number of monomeric units in a macromolecule or **polymer** or oligomer (consists of a few repeating units Or *DP* is the number of repeat units).

$$DP_w = \frac{M_w}{M_0} , DP_n = \frac{M_n}{M_0} ; \text{ where } M_0 \text{ is the monomer molecular weight.}$$

Viscometry

A method that is widely used for routine molecular-weight determination is based on the determination of intrinsic viscosity, η , of a polymer in solution through measurements of solution viscosity.

The fundamental relationship between η and molecular-weight is given in Mark-Howink eq

$$[\eta] = KM^a$$

$[\eta]$: intrinsic viscosity
 K, a : constant for specific polymer and solvent
 M : average molecular weight

It is clear in the above equation that the value of intrinsic viscosity of the diluted polymer is needed to determine the molecular weight. To find the intrinsic viscosity, a series of experimental measurements and calculations have to be made. These steps are as follows:

1. The relative viscosity can be measured experimentally using a suitable viscometer:

Relative viscosity :

$$\eta_{\text{rel}} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

η : solution viscosity
 η_0 : solvent viscosity
 t : flow time of solution
 t_0 : flow time of solvent

2. The intrinsic viscosity can be calculated as shown below:

Relative viscosity

$$\eta_{rel} = \frac{t}{t_0}$$

Specific viscosity

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

Reduced viscosity

$$\eta_{red} = \frac{t - t_0}{t_0 * c} = \frac{\eta_{sp}}{c}$$

Inherent viscosity

$$\eta_{inh} = \ln \frac{t}{t_0} = \ln \frac{\eta_{rel}}{c}$$

Intrinsic viscosity

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{red})$$

$$[\eta]_K = \lim_{c \rightarrow 0} (\eta_{inh})$$

Red arrows: Parameter used for intrinsic viscosity determination for multi concentration measurements

Grey arrows: Parameter used for intrinsic viscosity determination for single concentration measurements

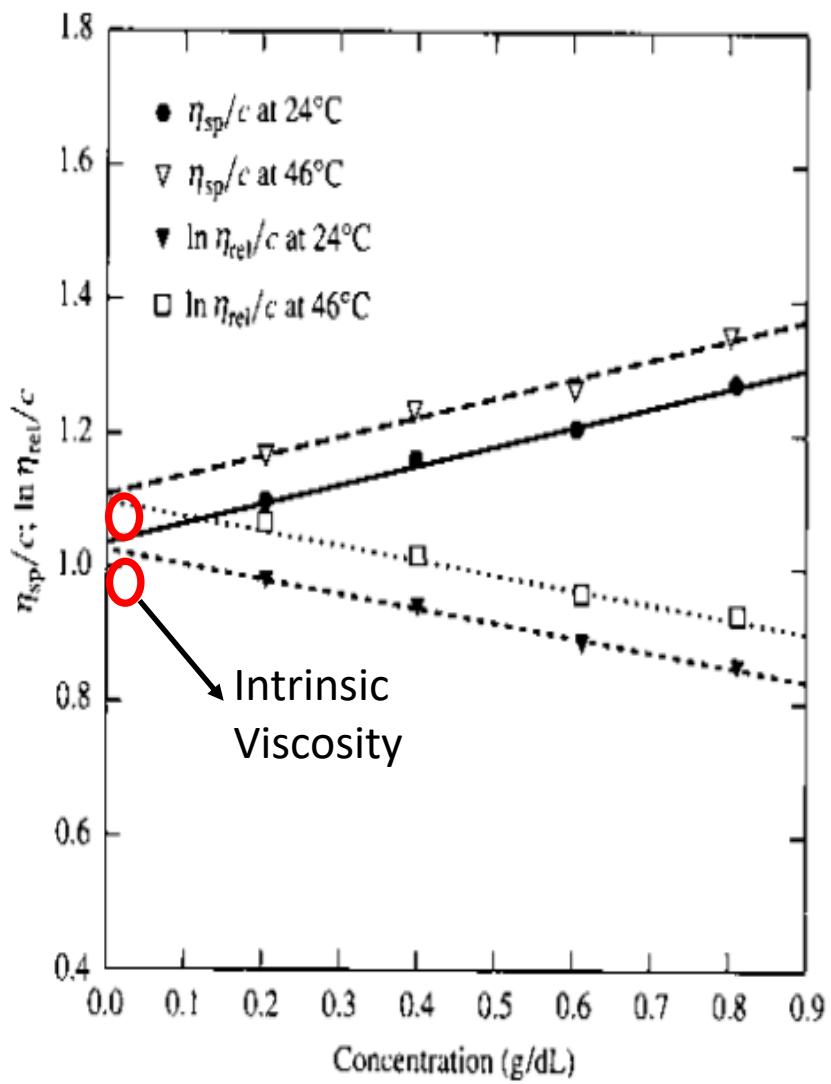


Fig. 1 Reduced viscosity and inherent viscosity of nylon 66 in 90% formic acid (Adapted from Ph.D thesis of R Walia, P. S., Chemical Engineering, West Virginia University, Morgantown, 1998).

Polymers

Dr. Druman Utekar

Definition

- Polymer is high molecular weight substance formed by joining a large number of small repeating units called as Monomers.
- In Greek language poly means many & mer means units
- Polymers form very important components in our daily life. The polymers are highly useful in domestic industrial & medical fields.

Examples

- Rubber
- Polyethene, $n\text{CH}_2=\text{CH}_2 \xrightarrow{\text{polymerization}} (\text{CH}_2 - \text{CH}_2)_n$
- Polypropylene
- Teflon

The following are the reasons for the extensive use of polymers.

- Most of the polymers are non-toxic & safe to use.
- They have low densities (light in weight) so transportation polymers will be easy.
- They possess good mechanical strength.
- These are resistant to corrosion and will not absorb moisture when exposed to the atmosphere.
- These can function as good thermal & electrical insulators.
- These can be moulded and fabricate easily.
- They possess aesthetic colors.

But the limitations for the use of polymers are

- Some polymers are combustible.
- The properties of polymers are time dependent
- Some of them cannot stand high temperature.

Classification of polymers

A) Based on source

B) Based on Physical State

Amorphous and semi crystalline

C) Based on Thermal Behavior or Response to Heat.-

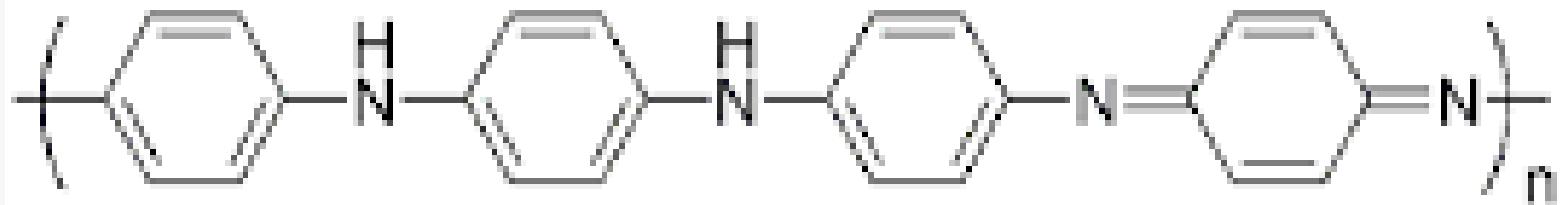
D) Based on end use.-Fibres, Plastics, Elastomers, Films, Paints, Adhesives

E) Based on Origin

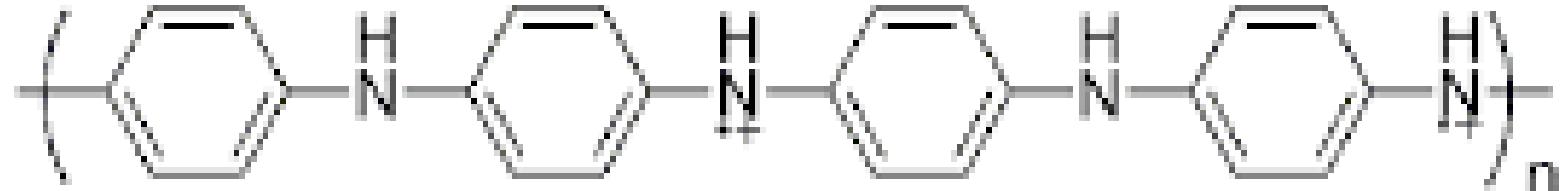
F) Based on Tacticity

Classification of polymers

- G) Based on Conductance
- H) Based on Environment Friendly Nature
- I) Based on the type of monomers
- J) Based on Number of Monomers
- K) Based on Chemical Nature
- L) Based on Growth Mechanism of Polymerization



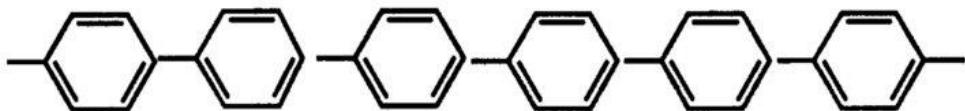
Polyaniline (Emeraldine Base)



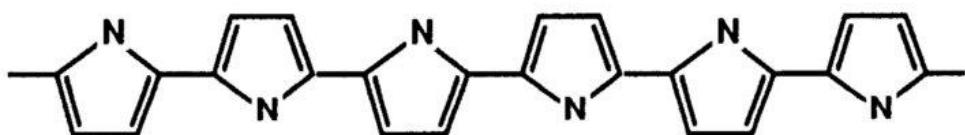
Polyaniline (Emeraldine Salt)



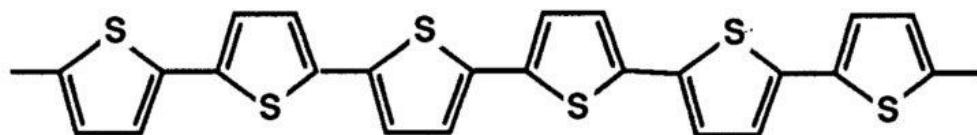
POLYACETYLENE



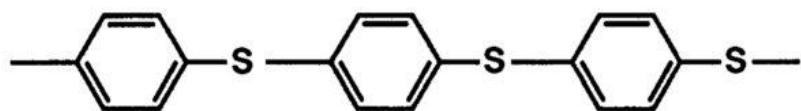
POLYPHENYLENE



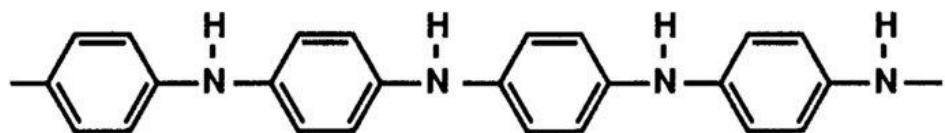
POLYPYRROLE



POLYTHIOPHENE



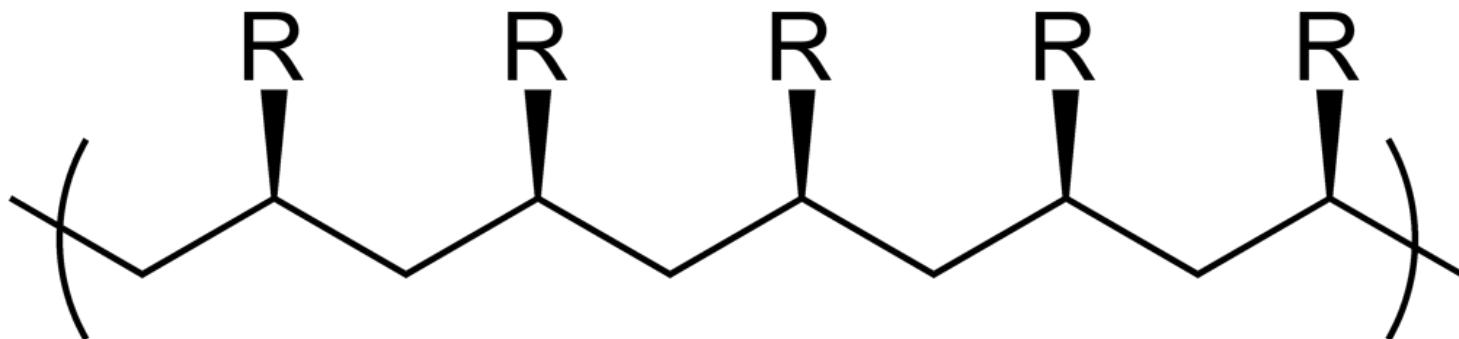
POLY(PHENYLENE-SULFIDE)



POLYANILINE

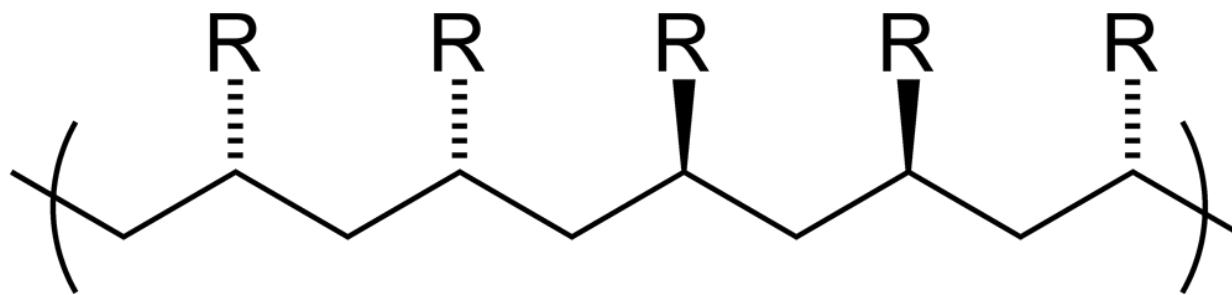
Based on Tacticity

- The arrangement of functional groups on carbon backbone of the polymer is called Tacticity.
 - It is mainly divided into 3 types.
- 1) **Isotactic polymers:** Those polymers in which the functional groups are arranged on the same side are called Isotactic polymers. E.g.: PVC

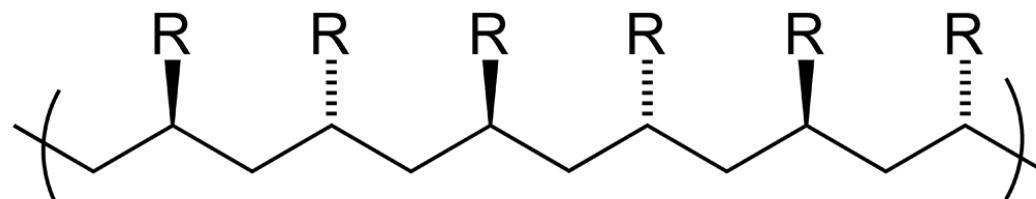


2) **Atactic polymers:** When there is no regular arrangement of functional groups on the back bone of the polymer chain these polymers are called atactic polymers.

E.g.: PVC (Poly Vinyl chloride)



- **Syndiotactic Polymers:** The polymers with alternate arrangement of functional groups are called syndiotactic polymers for e.g.: PVC

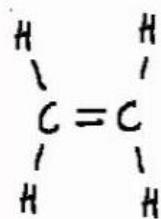


Difference between condensation and addition polymerisation:-

	Condensation polymerisation		Addition polymerisation
(1)	It is also known as step growth polymerisation	(1)	It is also known as chain growth polymerization
(2)	It takes place in monomers having reactive functional groups	(2)	It takes place only in monomers having multiple bonds.
(3)	It takes place with elimination of simple molecule like H_2O , NH_3 , HCl etc.,	(3)	It takes place without elimination of simple molecule.
(4)	Repeat units of monomers are different	(4)	Repeat units & monomers are same.
(5)	The polymer is formed in gradual steps	(5)	Reaction is fast and polymer is formed at once.
(6)	The molecular mass of polymer increases throughout the reaction	(6)	There is very little change in the molecular mass throughout the reaction
(7)	Product obtained may be thermosetting/thermoplastic	(7)	Product obtained are thermoplastic
(8)	E.g.: Bakelite, polyester ,polyamides etc.,	(8)	E.g:-Polyethylene, PVC, poly styrene.

Addition polymers

Monomer

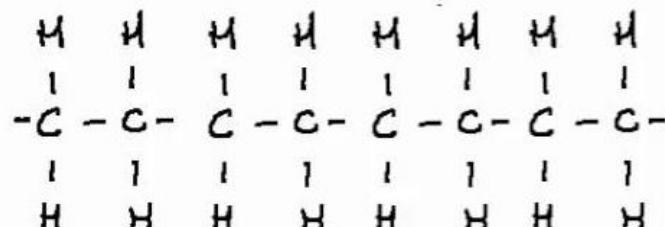


high pressure



catalyst

Polymer

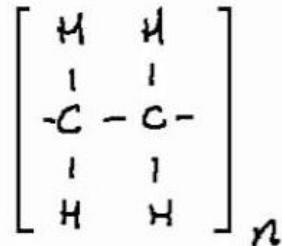
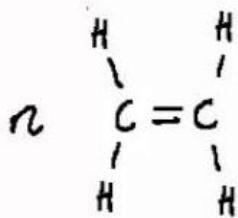


et^o

1. conc. H_2SO_4

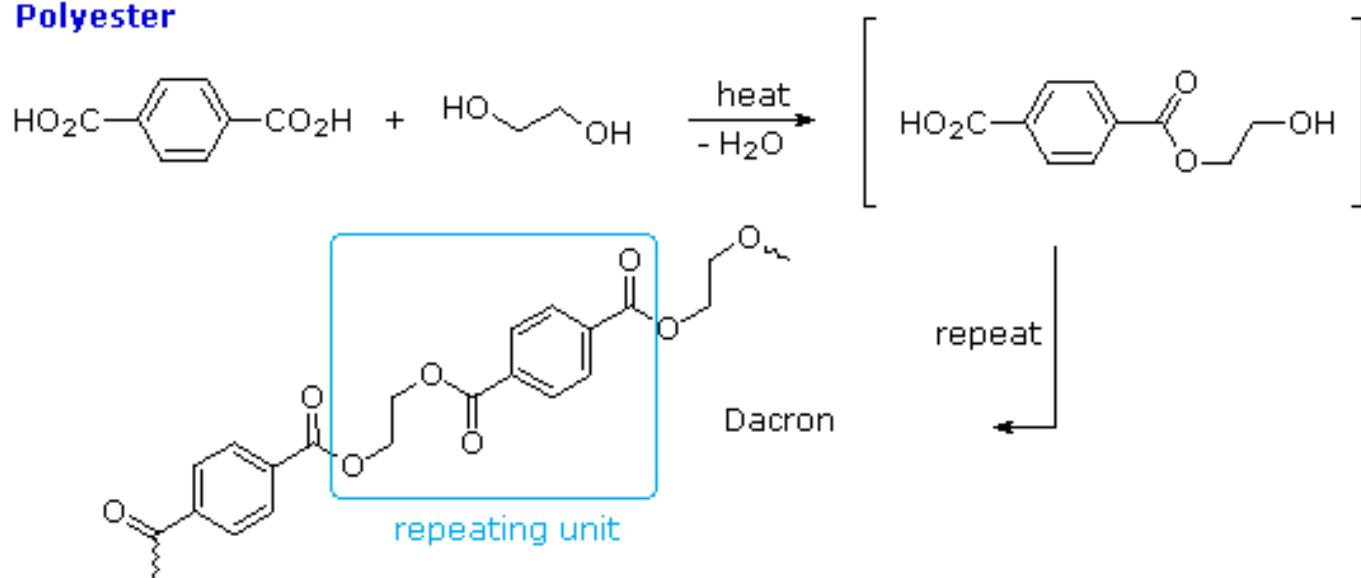
2. peroxide free
radicals

polymer units

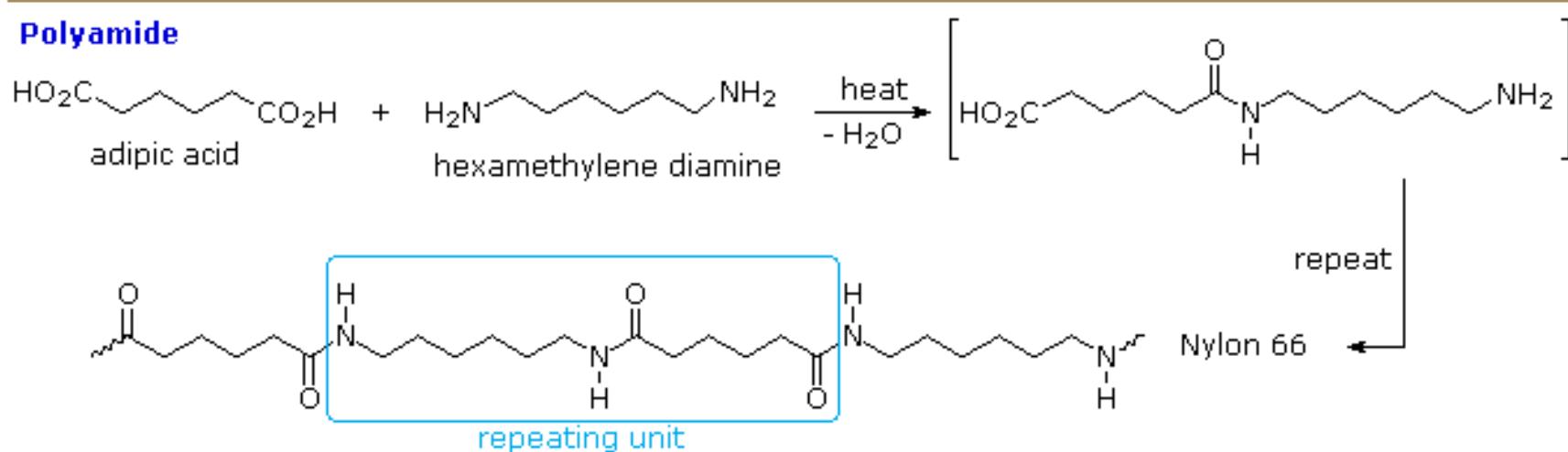


Examples of Condensation Polymers

Polyester



Polyamide



Difference between thermoplastic & thermosetting resins:-

Thermoplastic resins (or) Polymers		Thermosetting resins	
(1)	These are produced by addition polymerization	(1)	These are produced by condensation polymerization.
(2)	The resins are made of long chains attached by weak Vander Waal's force of attraction	(2)	The resins have three dimensional network structure connected bonds.
(3)	On heating they soften and on cooling become stiff chemical nature won't change.	(3)	On heating they become stiff & hard. No change on cooling. Chemical nature changes.
(4)	They can be remoulded	(4)	They cannot be remoulded because once set means they are permanently set
(5)	Scrap (waste product) can be used	(5)	Scrap cannot be used
(6)	The resins are soft, weak and less brittle	(6)	The resins are usually hard, strong tough & more brittle
(7)	These are easily soluble in some organic substances E.g.: PVC, polyethylene etc.,	(7)	Resins are not soluble in organic Solvents E.g.: Nylon, Bakelite etc.,
(8)	Contain long chain polymer with no cross linkage.	(8)	They have 3D network structure.

Molecular Mass of Polymer

- The molecular mass of polymer is an important property of polymer because many important properties are influenced by molecular mass. Polymers with higher molecular mass are tougher and more resistant. Their viscosities and softening temperature are also higher. Thus polymers with molecular mass are often required for particular purposes.
- Molecular mass of polymer is not a fixed or constant value like organic compound. Their molecular mass is controlled by polymerization reaction, which in turn depend upon availability of functional group, charge carrier, life time of charge carriers. Because of random nature of growth process, the product of polymerization process is mixture of chains of different length.
- Hence polymers are poly disperse mixture of various molecular mass polymers. Therefore molecular mass of polymers is average molecular mass.

Average molecular mass of polymers can be expressed in following ways

- ---
- 1. Number Average Molecular Mass (M_n)
- 2. Weight Average Molecular Mass (M_w)
- 3. Z-Average Molecular Mass (M_z)
- 4. Viscosity average Molecular Mass (M_v)

Methods for determining the molecular weights of polymer

- A) **Primary or Absolute methods**, which are capable of determining molecular weights from first principles like colligative property measurements(Which gives Mn) , light scattering measurements (which gives Mw)
- B) **Secondary or relative methods**, Which require calibration with samples of known molar mass. Examples Viscosity measurements which gives Mv.

Number average Molecular Mass (M_n)

In this number of molecules are involved in the molecular weight measurements. Hence the molecular weight is obtained by colligative property measurements and known as number average molecular weight.

Let us consider N₁, N₂, N₃.... be the number of molecules of polymer in a sample solution. And M₁, M₂, M₃ ...be the their molecular weight then Number average molecular weight is given by

$$\overline{M_n} = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i} = \frac{\sum_{i=1}^N w_i}{\sum_{i=1}^N w_i / M_i}$$

Polymer solution of polyethene	Number of molecules	Their molecular weight
Sample has	100 N ₁	150 M ₁
	200 N ₂	200 M ₂
	300 N ₃	300 M ₃

Weight Average molecular Weight

- Let us consider N₁, N₂, N₃..... be the number of molecules of polymer in a sample solution.
- And M₁, M₂, M₃ ...be the their molecular weight
- And W₁, W₂, W₃ ...be the their weight(mass) then Weight average molecular weight is given by

$$\overline{M_w} = \frac{\sum_{i=1}^N N_i M_i^2}{\sum_{i=1}^N N_i M_i} = \frac{\sum_{i=1}^N w_i M_i}{\sum_{i=1}^N w_i}$$

Polymer solution of polyethene	Molecular weight	Their weight
Sample has	100	15g
	200	20g
	300	30g

Z-average molecular Weight

Let us consider N₁, N₂, N₃.... be the number of molecules of polymer in a sample solution.

And M₁, M₂, M₃ ...be the their molecular weight, then Z-average molecular weight is given by

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

Viscosity-average molecular weight (M_v)

- viscosity, like light scattering, is greater for the larger-sized polymer molecules than the smaller ones, and is much closer to M_w than M_n

$$\overline{M}_v = \left[\sum_{i=1}^{\infty} w_i M_i^a \right]^{1/a} = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{a+1}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{1/a}$$

*w = weight fraction
N = number of moles
M = molecular weight
a = A constant*

- When $a = 1$, $M_v = M_w$, usually $a \sim 0.5-0.9$
- a is a measure of the hydrodynamic volume of the polymer
- varies with polymer, solvent and temperature

Mark-Houwink equation

- Mark-Houwink equation is valid for **broad** molecular weight distribution:

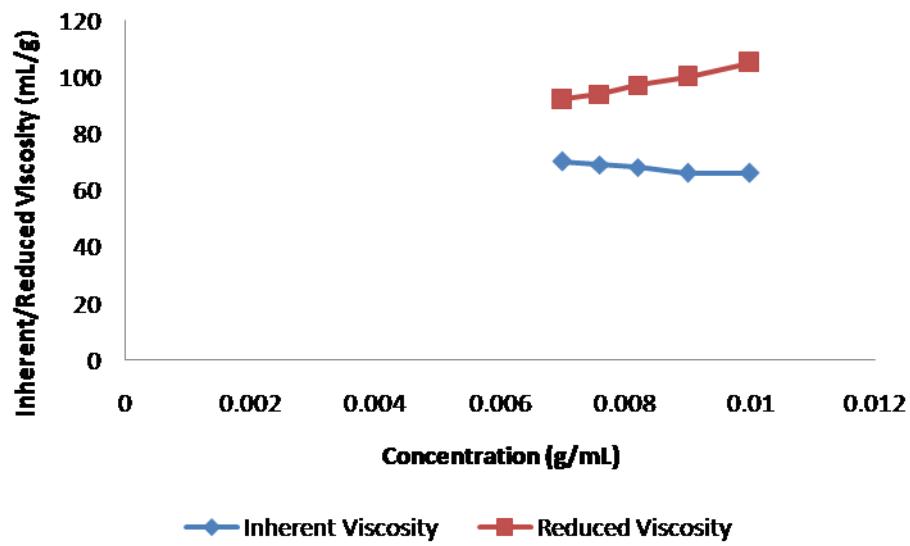
$$[\eta] = K_m \bar{M}_v^a$$

$[\eta]$ = intrinsic viscosity

\bar{M}_v = viscosity average molecular weight

K_m, a = constants for particular polymer-solvent combination

For flexible polymer chains a is 0.5 - 0.8, for stiff and rod like chains a is 2.0.



Compounding of Plastics

- In order to impart certain definite properties to the finished products, resins are compounded with certain other substances. The process is called as compounding of plastics.

1. Binders or Resins

- The product of polymerization is called resins and this forms the major portion of the body of plastics.
- It is the binder, which holds the different constituents together.
- Thermosetting resins are usually, supplied as linear – polymers of comparatively low molecular weight, because at this stage they are fusible and hence, mouldable.
- The conversion of this fusible form into cross-linked infusible form takes place, during moulding itself, in presence of catalysts etc.
- A binder may compose of 30-100%.
- The binders used may be natural or synthetic or cellulose derivatives.

2. Fillers

- Fillers are generally added to thermosetting plastics to increase elasticity and crack resistance.
- Fillers improve thermal stability, strength, non combustibility, water resistance, electrical insulation properties & external appearance.
- E.g.: Mica(Hardness), cotton(Shock resistance) , carbon(electrical conductivity) black, graphite, BaSO₄ etc. Asbestos (Heat resistance)

3. Plasticizers

- Plasticizers are substances added to enhance the plasticity of the material and to reduce the cracking on the surface.
- Plasticizers are added to the plastics to increase the flexibility & toughness. Plasticizers also increase the flow property of the plastics.
- Commonly used plasticizers are vegetable oils, camphor, esters of steric, oleic acid, tributyl phosphate, triphenyl phosphate etc.

4. Dyes and Pigments

- These are added to impart the desired colour to the plastics and give decorative effect.
- e.g.: -Inorganic Pigments: Lead chromate (yellow), ferro cyanide (blue)
- Organic Pigments: Alizarin Red, Indigo Dye, Azo dyes.

5. Lubricants

- Includes Oils, waxes and soaps.
- They help in easy moulding and glossy finish to final product.
- The lubricant prevent the plastic materials from sticking to the mould.

6. Catalysts

- They are added to plastics to accelerate polymerizations reaction.
- ZnCl₂, CaO, ammonia, benzoyl peroxides

7. Stabilizers

- They are added to improve thermal stability during processing. Eg. Polymers of vinyl chloride show a tendency to undergo decomposition at moulding temperatures. So during their moulding heat stabilizers are added.
- i) Opaque moulding stabilizers: Salts of lead, like white lead, lead chromate, red lead, lead silicate etc.
- ii) Transparent Moulding stabilizers: Stearates of Lead, chromium and barium.

- In addition small quantitates of antioxidants, antiseptics, fungicides, flame retardants etc. are added as ingredient of plastics.

FABRICATION OF PLASTICS

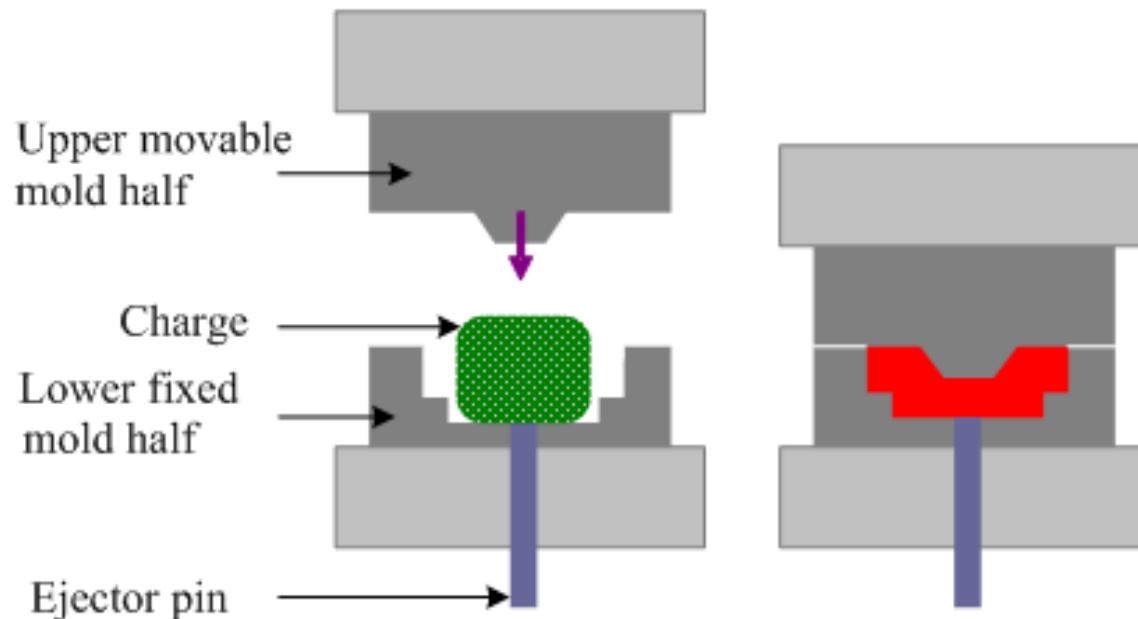
- Giving any desired shape to the plastics (granules or powders) by using mould under the application of heat and pressure.
- A proper method is to be selected depending on the shape and type of resin used.
- Methods involves partial melting of resinous mass by heating.
- In case of thermo-plasts molten resin is introduced in die/mould and desired shape could be achieved by compression and further cooling.
- In case of thermo-sets partially polymerized mass or raw materials are introduced in the die/mould, which further cured at high temperature in the mould itself to achieve desired shape.
 1. In case of thermoplasts, curing is done at room temperature (low temperature)
 2. In case of thermosets, curing is done at high temperature to obtain desired cross-linking

TYPES OF FABRICATION

- [I] Compression Molding (Suitable for Thermosets / Thermoplasts)
- [II] Injection Molding (Suitable for Thermoplasts)
- [III] Transfer Molding (Suitable for Thermosets)
- [IV] Extrusion Molding (Suitable for Thermoplasts)

COMPRESSION MOULDING

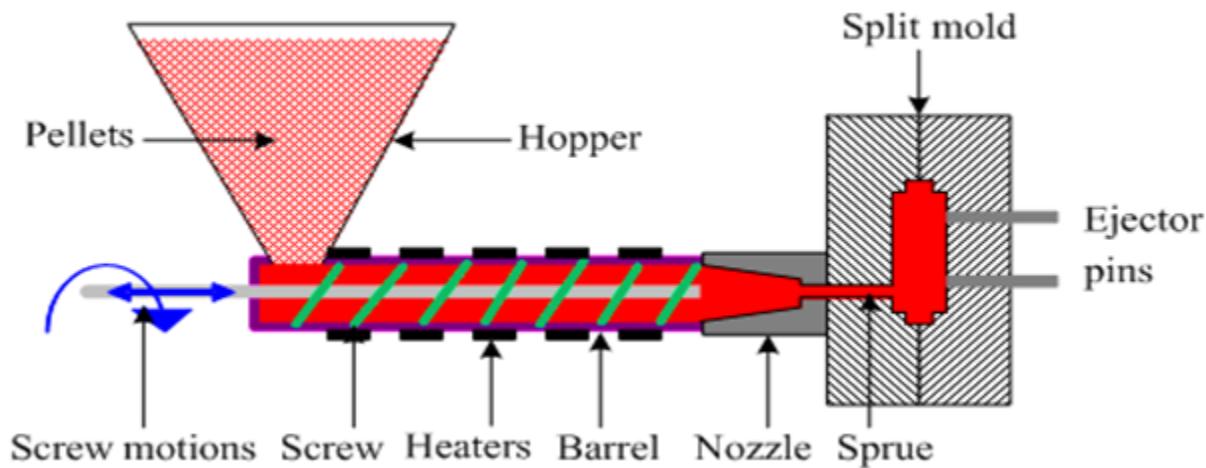
1. Common and oldest method for molding thermosetting / thermoplastic materials
2. Compression of raw materials or soften resinous mass is done in the mould /die under heat and pressure



COMPRESSION MOULDING

1. Predetermined quantity of raw materials is introduced carefully in the mould, further compressed by hydraulic pressure (2000 to 10000 psi)
2. Molten or soften resinous mass gets filled in the cavity of mould.
3. Curing is done by heating (Thermosetting) or by cooling (Thermoplastics)
4. Finally moulded article is separated from the mould by opening the mould apart.
5. Applications : Electric switch boxes, Ash trays, cabinets for radio, television, computers etc.

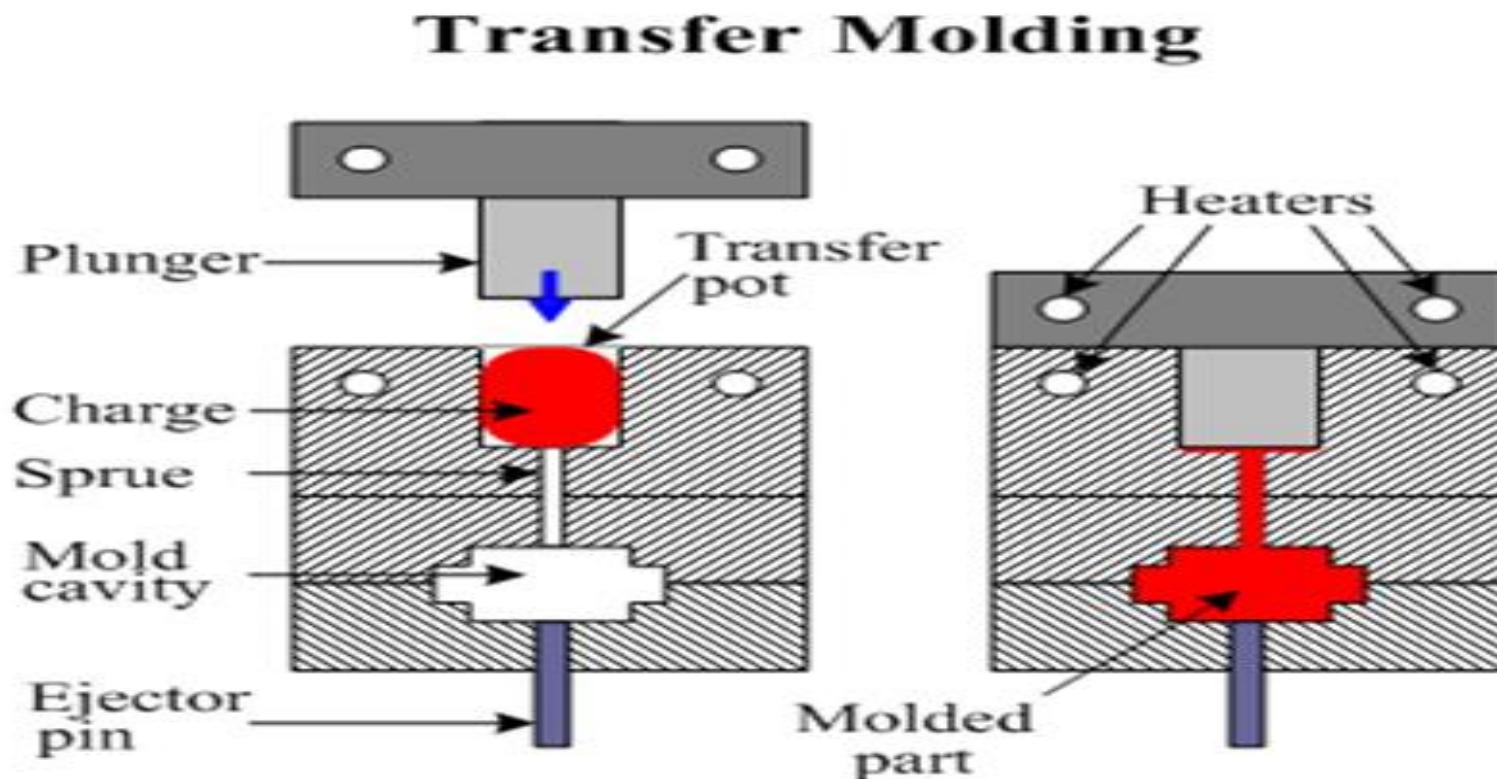
INJECTION MOULDING



INJECTION MOULDING

- This method is especially used for thermoplastic materials
- Powder or granular resin is heated in a cylinder and injected at a controlled rate in a mould with the help of piston plunger or screw.
- Piston plunger or screw is used to force the material in mould.
- Pressure up to 2000 kg/cm² (100 psi) is used
- Once the article is formed mould is cooled and half mould is opened to remove the finished article.
- Disadvantage of the method is formation of air bubbles or cavities in the articles
- Applications: Smaller but large volume articles such as, pen caps, bottle caps, cups, containers, mechanical parts

TRANSFER MOULDING



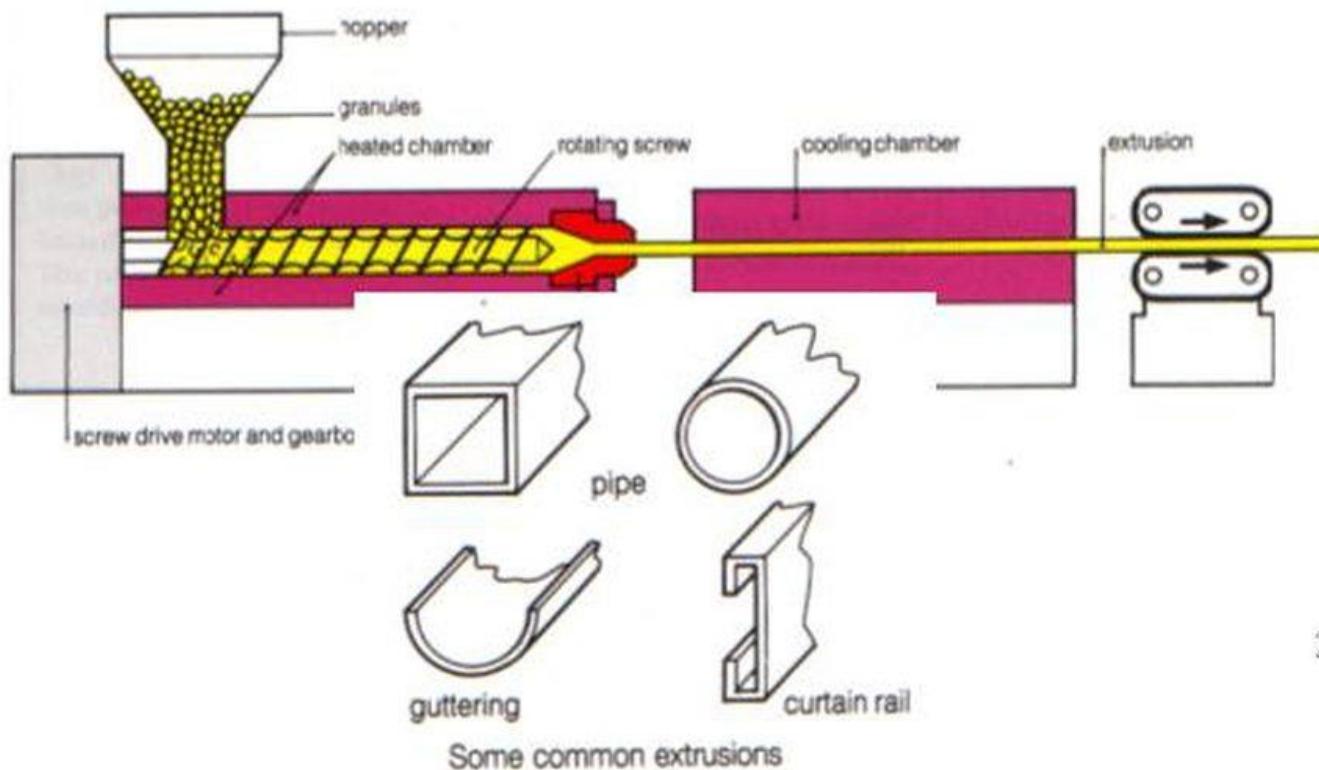
TRANSFER MOULDING

- The method combines features of both Compression Molding (hydraulic pressing of molding materials - thermosets) and Injection Molding (ram-plunger and filling the mold through a sprue).
- The method is used especially for molding thermosetting resins (thermosets)
- Products with relatively intricate designs could be fabricated with this method
- Powdered raw materials are heated at certain low temperature to soften and then introduced through an orifice or sprue in the mould
- Then it is cured in the mould at high temperature for certain time
- Finally the moulded article is removed by separation of mould

Advantages:

- Articles with intricate shapes could be designed
- Aerospace and automobile parts, car body, helmets
- The articles produced are blister free
- Fine wires and glass fibers can be inserted in the mould
- Even thick pieces can be cured completely and uniformly

Extrusion Molding

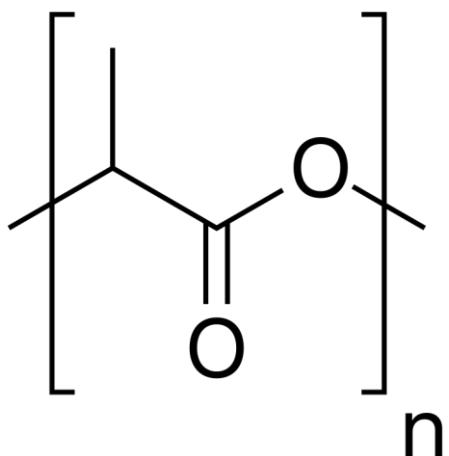


Extrusion Moulding

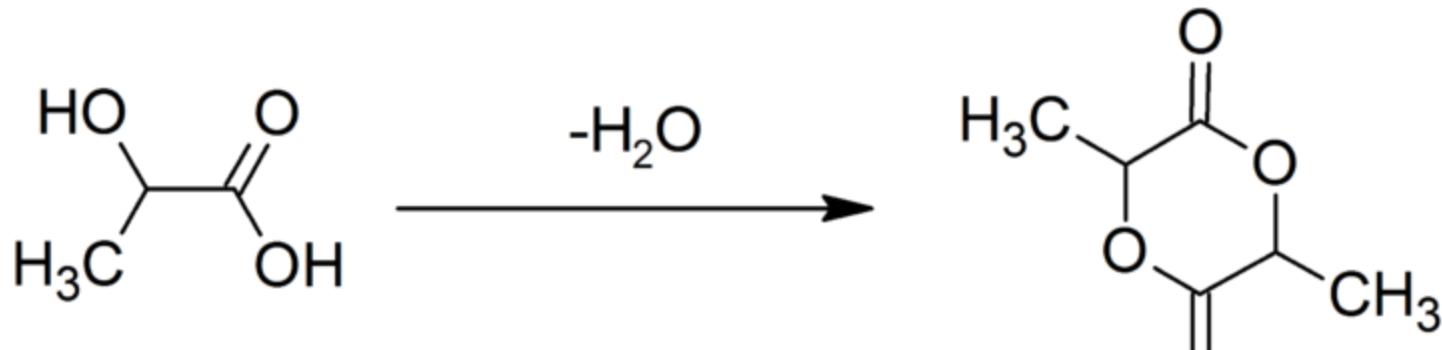
- Whenever continuous molding of material like wires, cables, and sheets is required extrusion molding is used. The thermoplastic materials are molded by this method. They undergo continuous molding to form articles of uniform cross section. In this method, the thermoplastic material are heated to plastic condition and pushed by means of screw conveyor in to a mould cavity having required outer shape of articles to be manufactured. Here the plastic mass gets cooled due to atmospheric exposure. A long conveyor carries away the cooled products continuously.

Biodegradable polymers-Polylactic acid

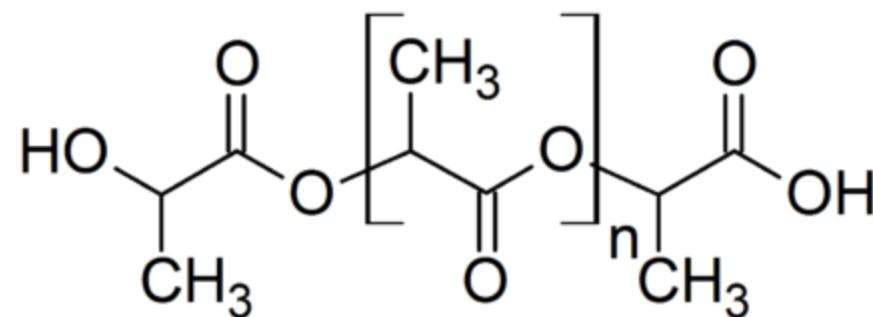
- Polylactic acid, also known as poly(lactic acid) or polylactide (abbreviation PLA) is a thermoplastic polyester with backbone formula $(C_3H_4O_2)_n$ or $[-C(CH_3)HC(=O)O-]_n$, formally obtained by condensation of lactic acid $C(CH_3)(OH)HCOOH$ with loss of water (hence its name). It can also be prepared by ring-opening polymerization of lactide $[-C(CH_3)HC(=O)O-]_2$, the cyclic dimer of the basic repeating unit.



- Synthesis
- The monomer is typically made from fermented plant starch such as from corn, cassava, sugarcane or sugar beet pulp.
- Several industrial routes afford usable (i.e. high molecular weight) PLA. Two main monomers are used: lactic acid, and the cyclic di-ester, lactide. The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts (typically tin octoate) in solution or as a suspension. The metal-catalyzed reaction tends to cause racemization of the PLA, reducing its stereoregularity compared to the starting material (usually corn starch).[7]
- The direct condensation of lactic acid monomers can also be used to produce PLA. This process needs to be carried out at less than 200 °C; above that temperature, the entropically favored lactide monomer is generated. This reaction generates one equivalent of water for every condensation (esterification) step. The condensation reaction is reversible and subject to equilibrium, so removal of water is required to generate high molecular weight species. Water removal by application of a vacuum or by azeotropic distillation is required to drive the reaction toward polycondensation. Molecular weights of 130 kDa can be obtained this way. Even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt. Carboxylic acid and alcohol end groups are thus concentrated in the amorphous region of the solid polymer, and so they can react. Molecular weights of 128–152 kDa are obtainable thus.



- H₂O



Properties

- PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a glass transition 60–65 °C, a melting temperature 130-180 °C, and a Young's modulus 2.7–16 GPa.[13][14][15] Heat-resistant PLA can withstand temperatures of 110 °C.[16] The basic mechanical properties of PLA are between those of polystyrene and PET.[13] The melting temperature of PLLA can be increased by 40–50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity. The temperature stability is maximised when a 1:1 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement. In the latter case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate[citation needed]. Biodegradation of PDLA is slower than for PLA due to the higher crystallinity of PDLA[citation needed]. The flexural modulus of PLA is higher than polystyrene and PLA has good heat sealability.
- Racemic PLA and pure PLLA have low glass transition temperatures, making them undesirable because of low strength and melting point. A stereocomplex of PDLA and PLLA has a higher glass transition temperature, lending it more mechanical strength.

Uses

- Consumer goods
- PLA is used in a large variety of consumer products such as disposable tableware, cutlery, housings for kitchen appliances and electronics such as laptops and handheld devices, and microwavable trays. (However, PLA is not suitable for microwavable containers because of its low glass transition temperature.) It is used for compost bags, food packaging and loose-fill packaging material that is cast, injection molded, or spun.[35] In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels. In the form of fibers, it is used for monofilament fishing line and netting. In the form of nonwoven fabrics, it is used for upholstery, disposable garments, awnings, feminine hygiene products, and diapers.
- PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as ABS. Such blends have good form stability and visual transparency, making them useful in low-end packaging applications.
- PLA is used for automotive parts such as floor mats, panels, and covers. Its heat resistance and durability are inferior to the widely used polypropylene (PP), but its properties are improved by means such as capping of the end groups to reduce hydrolysis.[35]

- Agricultural
- In the form of fibers, PLA is used for monofilament fishing line and netting for vegetation and weed prevention. It is used for sandbags, planting pots, binding tape and ropes .[35]
- Medical
- PLA can degrade into innocuous lactic acid, so it is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh.[35] Depending on the exact type used, it breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. to the bone) as that area heals. The strength characteristics of PLA and PLLA implants are well documented.

Equitable Access To Water

Shounak B Shelke
FY B.Tech (COMPS)



Data Collection and Analysis

AI can analyze this data to identify trends, predict potential issues, and optimize water distribution

AI can help address the challenges of equitable access to water by analyzing data to identify trends, predict potential issues, and optimize water distribution in the following ways:

- **Identifying trends:** AI can be used to identify trends in water use, such as which areas are using the most water, which times of day water use is highest, and how water use is changing over time. This information can be used to develop policies and programs to promote water conservation and ensure that everyone has access to the water they need.
- **Predicting potential issues:** AI can be used to predict potential water issues, such as droughts, floods, and water quality problems. This information can be used to develop early warning systems and take steps to mitigate the impacts of these events.

- **Optimizing water distribution:** AI can be used to optimize water distribution networks to ensure that everyone has access to water, even during periods of high demand. This can involve adjusting water pressure, routing water around blockages, and identifying areas where new infrastructure is needed.
- By analyzing water data, AI can help us to identify trends, predict potential issues, optimize water distribution, and better understand the root causes of inequity. This information can be used to develop policies and programs that ensure that everyone has access to the water they need.

How the data given by AI can be used in Equitable Access to Water:

- **Identify areas where equitable access to water is lacking:** The data can be used to identify areas where people do not have access to a sufficient quantity of safe, affordable, and accessible water. This information can be used to prioritize investments in water infrastructure and services in these areas.
- **Track progress towards equitable access to water:** The data can be used to track progress towards equitable access to water over time. This information can be used to identify what is working and what needs to be improved.
- **Understand the factors that contribute to inequitable access to water:** The data can be used to understand the factors that contribute to inequitable access to water, such as poverty, race, ethnicity, gender, and disability. This information can be used to develop policies and programs to address these root causes of inequity.

Examples

- **Map the distribution of water resources and infrastructure:** The data can be used to create maps that show the distribution of water resources and infrastructure. This can be used to identify areas where there is a need for new infrastructure or improvements to existing infrastructure.
- **Analyze water quality data:** The data can be used to analyze water quality data to identify areas where water quality is a concern. This information can be used to develop policies and programs to improve water quality and protect public health.
- **Compare water use and access across different groups:** The data can be used to compare water use and access across different groups, such as different income groups, racial and ethnic groups, and genders. This information can be used to identify groups that are disproportionately affected by inequitable access to water.

- **Track progress towards Sustainable Development Goal (SDG) 6.1:** The data can be used to track progress towards SDG 6.1, which calls for universal and equitable access to safe and affordable drinking water for all by 2030. This information can be used to hold governments and other stakeholders accountable for their commitments to achieving equitable access to water.

As AI technology continues to develop, we can expect to see even more innovative and effective ways to use AI to ensure that everyone has access to the water they need.

Real-life examples of ‘How AI is being used to address the challenges of equitable access to water around the world’:

- In Cape Town, South Africa, AI is being used to predict water demand and develop water conservation plans. This has helped to reduce water consumption and avoid water shortages.
- In India, AI is being used to monitor water quality and identify areas where there is a risk of water contamination. This information is being used to develop early warning systems and take steps to protect public health.
- In the United States, AI is being used to develop water distribution plans that prioritize access to water for vulnerable populations. This is helping to ensure that everyone has access to the water they need, even during periods of high demand.



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Thank You!