MOHAMED SATHAK A.J. COLLEGE OF ENGINEERING
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NOTES OF LESSON

CY3151- ENGINEERING CHEMISTRY

Unit-I Water and Its Treatment

Water

Water is an abundant, wonderful and very useful resource. Water plays a main role in the existence of human beings, animals and plants. It is also utilized in steam generation, coolant in power plants and chemical plants. It occupies a unique position in different industries like, steel, paper, textile, chemical etc. The main application of water is irrigation and in day today life activities.

Sources of Water

(i) Rain Water:

It is the purest form of natural water. But during the journey downwards to the surface through the atmosphere it dissolves gases like CO_2, NO_2, SO_2 and suspended solid particles.

(**ii) Surface Water:** (River, Lake and Ocean)

River water : It is mainly fed by rains and springs. It flows over the surface and dissolve the minerals like chlorides, sulfates, carbonates, bicarbonates of Na, Ca, Mg and Fe. River water also contains organic matter, produced by the decomposition of plants and small particles of sand and rock suspension.

Lake Water : It has more constant chemical composition. The quantity of organic matters is high. It contains fewer amounts of dissolved materials.

Sea Water/Ocean Water : It is the most impure form of water. Rivers bring the impurities to the sea. Continuous evaporation of sea water also increases the impurity. It is more saline in nature. Sea water contains about 3.5 percent of dissolved salts, principally sodium chloride NaCl (2.7%), and magnesium chloride and sulphate (0.6%).

(iii) Underground Water: (Wells and springs)

A part of rain water which falls on earth surface percolates through soil into the earth. During its downward journey, it dissolves a number of salts and meets a hard rock where it may be stored or come in the form of spring.

Impurities in Water

Classification of Impurities

Physical Impurities	1. Suspended Impurities 2. Colloidal Impurities	
Chemical Impurities	3. Dissolved Impurities	Dissolved Salts and Dissolved Gases
Biological Impurities	4. Biological Impurities	

Type	Source and Properties	Removal Methods
Suspended Impurities	Soil, sand, decayed plant and animal matter. Make the water turbid. Particle size is > 10000 A°	Filtration, Sedimentation, Settlement
Colloidal Impurities	Finely divided clay and silica, mud organic and inorganic particles. Particle size is 10 - 1000 A°	Coagulation followed by sedimentation, filtration. Coagulants $FeSO_4$, alum
Dissolved Impurities	Dissolved salts – Chlorides, sulphates, nitrates, bicarbonates, carbonates of Ca, Mg, Na, etc., Dissolved gases- CO_2, NO_2, SO_2	Chemical treatment. Deaeration method for gases
Biological Impurities	Algae, fungi, bacteria and small aquatic animals	Sterilization, Bleaching, Chlorination, Ozone treatment

Water Quality Parameters

Physical Parameter	**Chemical Parameter**
Colour	pH
Odour and Taste	Hardness
Turbidity	Alkalinity
Temperature	Fluoride
TDS	Arsenic
	BOD,COD

Physical Parameter

Colour

- Material from decayed organic matter (vegetation), inorganic matter such as soil, stones, rocks give colour to the water.
- Change in the appearance of water.

Organic Source: Algae, organic dyes.
Inorganic Source: Cr, Fe & Mn compounds and inorganic dyes from industries.
(Yellow- Cr; Red or Brown – Fe)
Removal Methods: Adsorption, Filtration, Settling

Taste & Odors

Taste and odour in water can be caused by foreign matter such as organic materials, inorganic compounds, and dissolved gases. These materials may come from natural, domestic, or agricultural sources.
Organic source: Algae, decaying vegetation
Inorganic Source: Mercaptans, amines & Sulphides

Removal Methods: Aeration, Chlorination, Activated Carbon treatment.

Turbidity

Turbidity is the cloudiness of water. It is the ability of the light to pass through the water. Caused mainly by suspended material, clay, silt, plankton, greases.

Disadvantages of turbidity:

- Aesthetically unacceptable
- It can increase the cost of water treatment.
- Hiding place for harmful microorganisms. Turbidity shields them from disinfection process.
- Affecting the life of aquatic organisms like egg, larva maturing.
- Suspended particles provide adsorption media for heavy metals such as mercury,
- Chromium, lead, cadmium, and many hazardous organic pollutants.
- Raises the water temperature (suspended particles absorb more heat). So decreases the concentration of dissolved oxygen.
- Turbidity is measured by instrument called Nephelometric turbidimeter and the unit for turbidity is NTU (Nephelometric Turbid Unit)

Removal Methods: Coagulation, Settling, Filtration.

Temperature

Temperature is measured by the unit degree Celsius (^oC). Temperature of the surface water is influenced by atmospheric conditions. Temperature of ground water is influenced by characteristics of bedrocks. Temperature raise will decrease the amount of dissolved oxygen (DO) in the water.

Total Dissolved Solids (TDS)

TDS stands for total dissolved solids, and represents the total concentration of dissolved substances in water. TDS is made up of inorganic salts such as calcium, magnesium, chlorides, sulfates, bicarbonates, etc, along with other inorganic compounds that easily dissolve in water. These dissolved solids not good for health and must be filtered out before intake. Water purifier with Reverse Osmosis (RO) technology is the best solution to treat water with high TDS. An RO water purifier doesn’t completely remove TDS, but reduces the level of TDS to make it palatable and consumable.

Total solid (TS) = Total dissolved solid (TDS) + Total suspended solid (TSS) (2)

Chemical Parameter

pH

pH is one of the most important parameters of water quality. It is defined as the negative logarithm of the hydrogen ion concentration. pH ranges from 0 to 14, 7 is the neutral. pH less than 7 indicates acidity, whereas a pH of greater than 7 indicates a basicity.

$$pH= -\log[H^+]$$

Pure water is neutral, with a pH close to 7.0 at 25°C. Safe ranges of pH for drinking water are from 6.5 to 8.5 for domestic use and living organisms.

- Most aquatic animals and plants have adapted to live in water with a specific pH even a slight change will affect them.
- A pH below 4 or above 10 will kill most fish.
- Heavy metals such as cadmium, lead, and chromium dissolve more easily in highly acidic water.

Alkalinity

The alkalinity of water is its acid-neutralizing capacity. Alkalinity of water is mainly caused by the presence of hydroxide ions (OH^-), bicarbonate ions (HCO_3^-), and carbonate ions (CO_3^{2-}), or a mixture of two of these ions in water. Alkalinity is determined by titration with a standard acid solution (H_2SO_4 of 0.02 N) using selective indicators (methyl orange or phenolphthalein).

- The high level of either acidity or alkalinity in water is the indication of industrial or chemical pollution.
- It is harmful for aquatic organisms
- Alkaline water cause corrosion in the boiler when used as boiler feed water.

Hardness

Hardness is the term used to express the properties of highly mineralized water. The dissolved minerals in water cause problems like scale deposits in hot water pipes and difficulty in producing lather with soap. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions cause the greatest portion of hardness in naturally occurring waters

Temporary Hardness (Carbonate Hardness/Alkaline Hardness) which is due to carbonates and bicarbonates can be removed by (i) boiling and (ii) treating with lime.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$$

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow + H_2O + CO_2$$

Permanent Hardness (Non-Carbonate Hardness/Non-Alkaline Hardness) which is remaining after boiling is caused mainly by sulfates and chlorides. It can be removed by (i) lime-soda process (ii) Zeolite process

$$CaCl_2 + Na_2CO_3 \xrightarrow{\Delta} CaCO_3 \downarrow + NaCl$$

$$CaSO_4 + Na_2Ze \xrightarrow{\Delta} CaZe \downarrow + Na_2SO_4 \downarrow$$

Fluoride

- A moderate amount of fluoride ions (F^-) in drinking water contributes to good dental health.
- About 1.0 mg/L is effective in preventing tooth decay, particularly in children.
- Excessive amounts of fluoride cause discoloured teeth, a condition known as dental fluorosis
- The maximum allowable levels of fluoride in public water supplies depend on local climate

Arsenic

- It is a metallic compound and forms number of poisonous compounds.
- Source: Natural deposits run off from agriculture, mining and industries.

Causes

- Long-term intake leads to skin cancer, diabetes, hypertension also affects bladder, kidney.
- Greater risk found in children.

Biological Oxygen Demand (Biochemical Oxygen Demand) (BOD)

- BOD is the amount of oxygen used by microorganisms (bacteria, yeasts and plankton) for the oxidation of organic matter.
- It is a measure of the degree of contamination and is expressed in mgO_2/L.
- It is a time-consuming biological process. The standard measurement is performed at 20°C for 5 days and is called BOD5.
- In general terms, the greater the pollution, the higher the BOD.

Chemical Oxygen Demand (COD)

- COD is the amount of oxygen required for the oxidation of all the oxidizable impurities present in the water by $K_2Cr_2O_7$ in acidic medium.
- This test only takes about 2 hours much less time compared to BOD test.
- The greater the pollution, the higher the COD.
- The main difference between BOD and COD is that, COD measures all organic and inorganic material, while BOD only measures organic material which can be biologically degraded.

Treatment of Water for Domestic Supply (or) Municipal Water treatment

Primary Treatment

Rivers and lakes are the most common sources of water used by municipalities. The water should be free from colloidal impurities, domestic sewages, industrial effluents and disease producing bacteria. Hence domestic supply of water involves the following stages in the purification processes.

Screening

It is a process of removing the floating materials like leaves, wood pieces, etc. from water. The impure water is allowed to pass through a screen, having large number of holes, which retains the floating materials and allows only the water to pass.

Aeration

The process of passing air to the water or mixing water with air is known as aeration. The main purpose of aeration is

(i) To remove gases like CO_2, H_2S and other impurities causing bad taste and odour to water.

(ii) To remove ferrous and manganous salts as insoluble ferric and manganic salts.

Sedimentation

It is a process of removing suspended impurities by allowing the water to stand undisturbed for 2-6 hours in a big tank. Most of the suspended particles settle down at the bottom, due to forces of gravity, and they are removed. Sedimentation removes only 75% of the suspended impurities.

Coagulation

Finely divided clay, silica, ete, do not settle down easily and hence cannot be removed by sedimentation. Such impurities are removed by coagulation method.

In this method certain chemicals, called coagulants, like alum, $Al_2(SO_4)_3$ etc. are added to water. When the $Al_2(SO_4)_3$, is added to water, it gets hydrolysed to form a gelatinous precipitate of $Al(OH)_3$, The gelatinous precipitate of $Al(OH)_3$, entraps the finely divided and colloidal impurities, settles to the bottom and can be removed easily.

Filtration

It is the process of removing bacteria, colour, taste, odour and suspended particles, etc. by passing the water through filter beds containing fine sand, coarse sand and gravel.
A typical sand filter is shown in the figure 1.1

The sand filter consists of a tank containing a thick top layer of fine sand followed by course sand, fine gravel and coarse gravel. When the water passes through the filtering medium, it flows through the various beds slowly. The rate of filtration decreases slowly due to the clogging of impurities in the pores of the sand bed. When the rate of filtration becomes very slow the filtration is stopped and the thick top layer of fine sand is removed and replaced with clean sand. Bacteria are partly removed by this process.

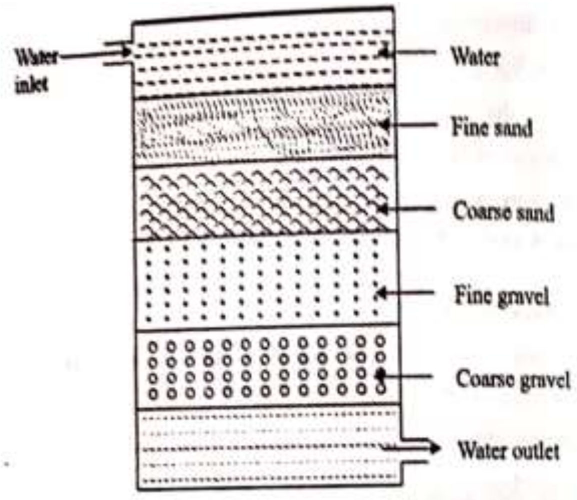


Fig 1.1 Sand Filtration

Sterilization (or) Disinfection

The processof destroying the harmful bacteria is known as sterilization (or) disinfection. The chemical used for this method is called disinfectants.

(i) By using Ozone

(ii) By using ultraviolet (UV) radiation

(iii) By Chlorination

(i) By using Ozone

Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen. The nascent oxygen is a powerful oxidising agent and kills the bacteria.

$$O_3 \longrightarrow O_2 + [O]$$

Disadvantages

- This process is costly and cannot be used in large scale
- Ozone is unstable and cannot be stored for long time.

(ii) By using ultraviolet (UV) radiation

UV rays are produced by passing electric current through mercury vapour lamp. This is particularly useful for sterilizing water in swimming pool.

Disadvantages

- This process is costly
- Turbid water cannot be disinfected.

(iii) By Chlorination

The process of adding chlorine to the water is called chlorination. It can be done by following methods.

- ***(a) By adding chlorine gas***

  Chlorine gas bubbled in the water it acts as a very good disinfectant.

- ***(b) By adding Chloramine***

  When chlorine and ammonia are mixed and chloramine is formed.

$$Cl_2 + NH_3 \longrightarrow \underset{\text{Chloramine}}{ClNH_2} + HCl$$

  Chloramine compounds decompose slowly to give chlorine. It is a better disinfectant than chlorine.

- ***(c) By adding bleaching powder***

  When bleaching powder is added to the water, it produces hypochlorous acid (HOCl). HOCl is a powerful germicide.

$$\underset{\text{Bleaching powder}}{CaOCl_2 + H_2O} \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow \underset{\text{Hypochlorous acid}}{HCl + HOCl}$$

$$\text{HOCl + Bacteria} \longrightarrow \text{Bacterias are killed}$$

Break Point Chlorination

Water contains the following impurities

(i) Bacterias

(ii) Organic impurities.

(iii) Reducing substances (Fe^{2+}, H_2S, etc.).

(iv) Free ammonia.

Chlorine added to water directly as a gas or in the form of bleaching powder. When chlorine is applied to water, the results obtained can be depicted graphically by the following Fig. 1.2. The graph shows the relationship between the amount of chlorine added to water and the residual chlorine.

It is observed from the graph that initially the applied chlorine is used to oxidise all the reducing substances present in the water and there is no free residual chlorine. (**upto A**)

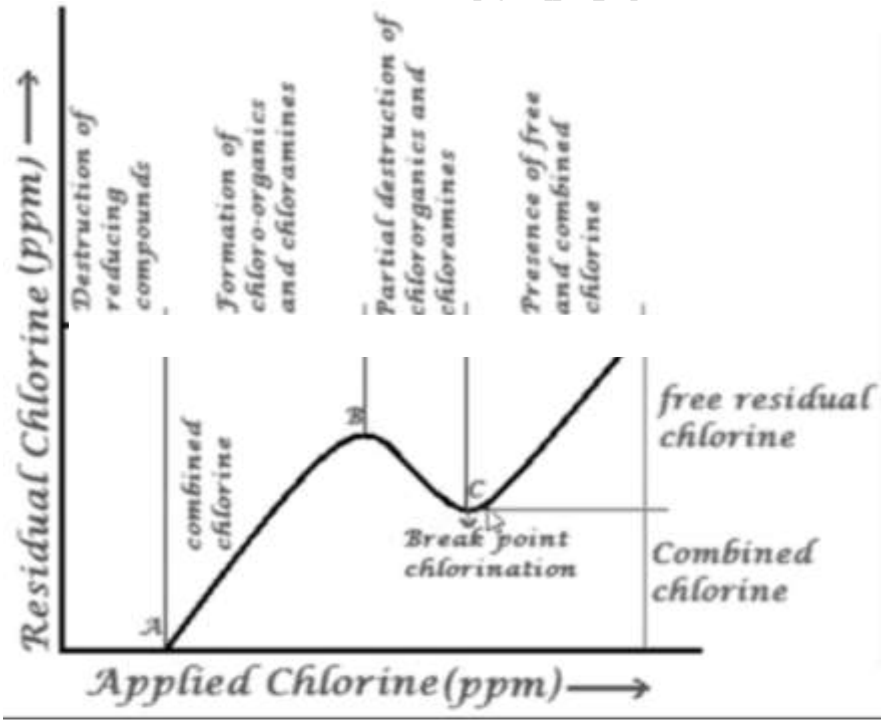


Fig 1.2 Break Point Chlorination

As the amount of applied chlorine increases, the amount of combined residual chlorine also increases. This is due to the formation of chloramine and other chloro organic compounds. (**A to B**)

At one point, on further chlorination, the oxidation of chloramines and other impurities starts and there is a fall in the combined chlorine content. **(B to C)** Partial destruction of chloro-organics and chloramines. Thus, the break point chlorination eliminates bacteria, all the reducing substances, organic substances responsible for the bad taste and odour, from the water.

Advantages

- Break point chlorination gives idea of amount of chlorine required for chlorination.
- Removes odour and colour in water.
- Destroys completely all the disease producing bacteria.
- Prevents if any growth of weeds in water.

Desalination of Brackish Water

The process of removing common salt (sodium chloride) from the water is known as desalination. The water containing dissolved salts with an abnormal salty (or) brackish taste is called brackish water.

Depending upon the quantity of dissolved solids, water is classified as

Fresh water: < 1000 ppm of dissolved solids
Brackish water: 1000-35,000 ppm of dissolved solids
Sea water: > 35,000 ppm of dissolved solids

Reverse Osmosis (RO)

Sea water and brackish water can be made available as drinking water through desalination process. Desalination is carried out by reverse osmosis.

When two solutions of different concentrations are separated by a semi-permeable membrane, solvent (water) flows from a region of lower concentration to higher concentration. This process is called osmosis and the driving force for this phenomenon is osmotic pressure.

If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration side, the solvent flow is reversed i.e., solvent flows from higher concentration to lower concentration. This process is called reverse osmosis (Fig. 1.3). Thus, in the process of reverse osmosis pure water is separated from salt water. This process is also known as super-filtration. The membranes used are cellulose acetate, cellulose butyrate, etc.

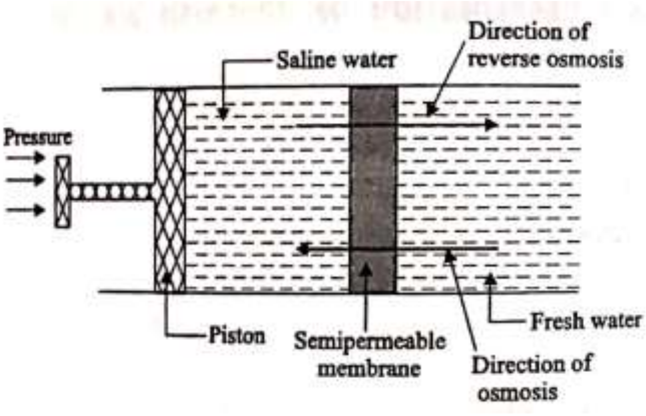


Fig 1.3 Reverse Osmosis

Advantages

- The life time of the membrane is high, and it can be replaced within few minutes.
- It removes ionic, non-ionic as well as colloidal impurities.
- It gives us clean and pure water by blocking all contaminants.
- The available RO systems are very compact, and it requires small space.
- Low capital and operating cost & high reliability

Disadvantages of Reverse Osmosis

- Sometimes reverse osmosis leads to clogging of the whole system
- Hard water can damage the system.

Boiler Feed Water

The water fed into the boiler for the production of steam is called boiler feed water. Boiler feed water should be free from turbidity, oil, dissolved gases, alkali and hardness causing substances.

Requirements for boiler water

- Free from hardness causing salts
- Free from suspended impurities
- Free from oil and greases
- Free from dissolved salts and gases
- Free from alkalinity

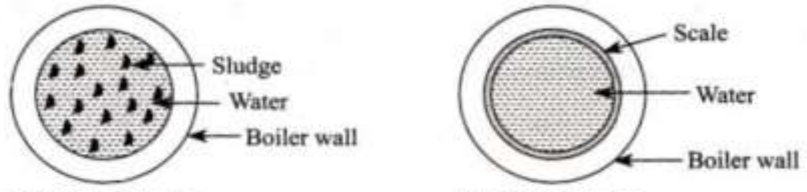
Boiler troubles (or) Disadvantages of using hard water in boilers

If hard water obtained from natural sources is fed directly into the boilers, the following troubles may arise.

1. Formation of Scales and Sludges in boilers
2. Priming and foaming (carry over)
3. Caustic embrittlement
4. Boiler corrosion

Formation of Scales and Sludges in boilers

Boilers are employed for the steam generation in power plants, where water is continuously heated to produce steam. As more and more water is removed in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place in two ways.



(a) Sludge in boiler (b) Scale in boiler

Fig 1.4 Formation of Scales and Sludges in boilers

Sludge

Sludge is a soft, loose and slimy precipitate formed within the boiler. The dissolved salts whose solubility is more in hot water and less in cold water produce sludges. Sludges are formed by the salts like $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$

Disadvantages of sludge

- Sludges are bad conductors of heat and results in the wastage of heat and fuel.
- Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings leading to the choking of the pipes.

Prevention

- By using softened water
- Blow down operation carried out frequently to prevent sludge formation.

Scale

Scales are hard, adhering precipitates formed on the inner walls of the boilers. Scales are stick very firmly on to the inner walls of the boiler. Scales are formed by the salts like $Ca(HCO_3)_2$, $Mg(OH)_2$, $CaSO_4$

Disadvantages of Scale

- Poor conductor of heat, so wastage of heat and fuels.
- Lowering of boiler safety is due to overheating of the boiler.
- Decrease in efficiency of the boiler due to scales deposit.
- Can lead to boiler explosion.

Prevention

- Using softened water.
- External and internal treatment
- By giving thermal shocks
- They can also be removed by scrapers and wire brush

Table 1.1 Comparison of Scales and Sludges

	Sludge	**Scale**
1	Sludge is a loose, slimy and non-adherent precipitate	Scale is a hard adherent coating
2	Sludges are formed by the salts like $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$	Scales are formed by the salts like $Ca(HCO_3)_2$, $CaSO_4$, $Mg(OH)_2$
3	Sludges are bad conductors of heat. Excess of sludge formation decreases the efficiency of boiler.	Scales acts as thermal insulators. It decreases the efficiency of boiler. Sometimes leads to the explosion.
4	*Prevention* • Sludge formation can be prevented by using softened water. • It can also be removed by blow-down operation. • It is a process of removing portion of concentrated salt water by fresh water frequently from the boiler.	• Scale formation can be prevented by using acids like HCl, H_2SO_4 • Scale formation can be removed by External treatment, Internal treatment • By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing. • They can also be removed by scrapers and wire brush

Priming and Foaming (Carry Over)

Priming

During the production of steam in the boiler, some droplets of liquid water are carried along with the steam. The process of producing wet steam is called priming. The steam with droplets of liquid water carry some dissolved salts and suspended impurities with them.

Causes	Prevention
a) Improper boiler design	a) Good boiler design
b) Sudden boiling of water	b) Maintain boiling temperature
c) High steam velocity	c) Controlling the steam velocity
d) High water level in the boiler	d) Fill the water up to low water level
e) Presence of dissolved salts in the water	e) By using treated water

Foaming

The formation of stable bubbles over the surface of water is called foaming. It leads to excess priming.

Causes	*Prevention*
a) Presence of oil and grease	a) Adding coagulants - sodium aluminate or aluminium hydroxide.
b) Presence of fine sludges	b) Adding anti foaming agents – synthetic polyamides.

Caustic embrittlement

It means inter crystalline cracking of boiler metal due to presence of alkaline water in the boiler. The boiler water containing Na_2CO_3 undergoes decomposition to give NaOH and CO_2.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

This NaOH flows into the cracks, bends, and joints and dissolves the iron metal of the boiler by converting to sodium ferroate. This causes embrittlement of boiler wall.

$$Fe + 2NaOH \longrightarrow \underset{\text{sodium ferroate}}{Na_2FeO_2 + H_2}$$

Prevention

- By maintaining the pH value of water and neutralization of alkali.
- By using softening reagents.

- By adding tannin or lignin or sodium sulphate which blocks the hair-cracks thereby preventing the flow of NaOH.

Boiler corrosion

It is the decay of boiler material by chemical or electrochemical attack on its environment. It is due to the presence of

a) Dissolved oxygen

b) Dissolved Carbon dioxide

c) Dissolved salts

Dissolved oxygen in water is mainly responsible for the boiler corrosion. Dissolved oxygen attacks the boiler material at higher temperature.

$$4Fe + 6\,H_2O + 3O_2 \longrightarrow 4\,Fe(OH)_3 \downarrow$$

Removal of dissolved oxygen

Dissolved oxygen can be removed by chemical or mechanical method.

Chemical method

Sodium sulphite, hydrazines are the chemicals used for removing dissolved oxygen. Hydrazine is an ideal compound for removing dissolved oxygen in the water since the products are water and N_2 gas

$$2\,Na_2SO_3 + O_2 \longrightarrow 2\,Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

Mechanical de-aeration

In this process water is allowed to fall slowly on the perforated plates fitted inside the tower. The sides of the towers are heated and a vacuum pump is attached to it. The high temperature and low pressure inside the tower reduces the amount of dissolved oxygen.

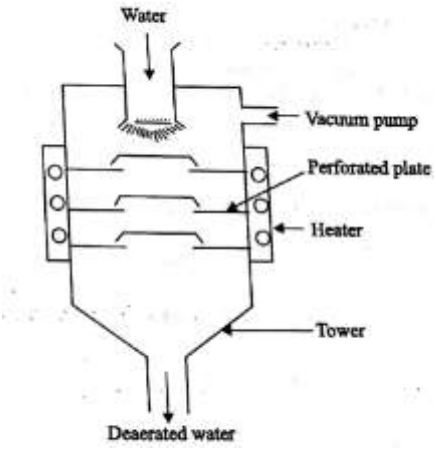


Fig 1.5. Mechanical de-aeration

Treatment of boiler feed water: Internal treatment

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into soluble compounds is called **internal treatment** of the boiler feed water. Internal treatment can be done following types.

a) Phosphate conditioning

The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

$$3CaCl_2 + 2\,Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$$

$$3MgSO_4 + 2\,Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$$

Generally three types of phosphates are used,

Na_3PO_4 – Trisodium phosphate – More alkaline & used for highly acidic water
Na_2HPO_4 – Disodium hydrogen phosphate – Less alkaline & used for slightly acidic water
NaH_2PO_4 – Sodium dihydrogen phosphate – More acidic & used for alkaline water

b) Colloidal conditioning

In low pressure boilers, scale formation can be prevented by adding colloidal conditioning agents like kerosene, tannin, agar-agar gel, gelatin, starch. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

c) Sodium Aluminate conditioning

In boiler water, sodium aluminate ($NaAlO_2$) undergoes hydrolysis to give gelatinous white precipitate of aluminium hydroxide and sodium hydroxide. The NaOH precipitates magnesium salts as gelatinous $Mg(OH)_2$. The gelatinous precipitates entrap the colloidal silica and finely divided solids and settled easily. This can be removed by blow down operation.

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3\downarrow + NaOH$$

$$2NaOH + MgCl_2 \longrightarrow Mg(OH)_2\downarrow + 2NaCl$$

d) Calgon conditioning

Calgon is sodium hexametaphosphate, $Na_2[Na_4(PO_3)_6]$. With calcium and magnesium ions, it forms a highly soluble complex and prevents scale and sludge formation. It is used for high and low pressure boilers.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow \underset{\text{soluble complex}}{Na_2\,[Ca_2(PO_3)_6]} + 2\,Na_2SO_4$$

Treatment of boiler feed water: External treatment

It involves the removal of hardness producing salts from the water before feed in to boiler. The external treatment can be done by two processes.

1. Demineralisation or Ion-exchange process.
2. Zeolite process.

Demineralisation or Ion-exchange process

In this process, both the cations and anions are completely removed. It is carried out by ion-exchange resins. Resins with acidic functional group are capable of exchanging H^+ ions with other cations. Resins with basic functional groups are capable of exchanging OH^- ions with other anions.

Cation Exchange Resins

Resins containing –COOH, $-SO_3H$ functional groups which responsible for exchanging their H^+ ions with other cations in the water. RH = Cation exchange resin.

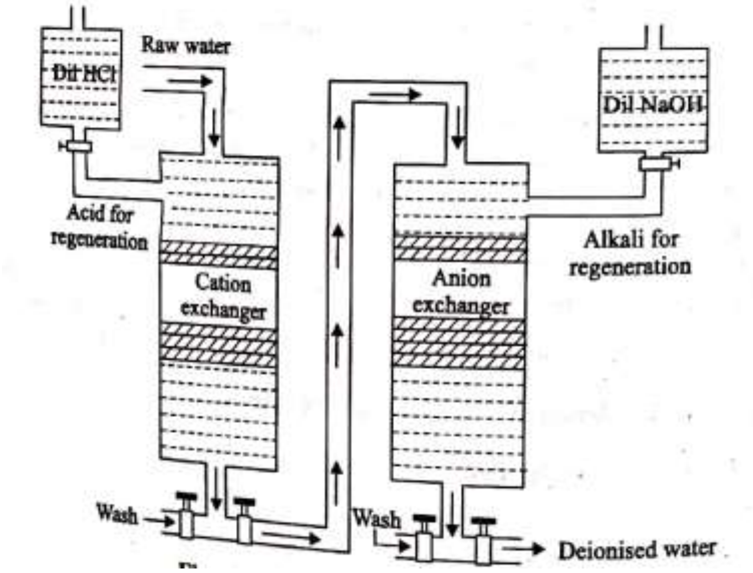
Example: Sulphonated coals, sulphonated poly-styrenes

$$2RH + CaCl_2 \longrightarrow R_2Ca + 2HCl$$

$$2RH + MgCl_2 \longrightarrow R_2Mg + 2HCl$$

$$2RH + CaSO_4 \longrightarrow R_2Ca + H_2SO_4$$

$$2RH + MgSO_4 \longrightarrow R_2Mg + H_2SO_4$$



Anion Exchange Resins

Resins containg NH_2^-, OH^- functional groups which responsible for exchanging their anions ions with anions in water.

Example: Urea-formaldehyde resin, cross-linked quaternary ammonium salts

$$ROH + HCl \longrightarrow RCl + H_2O$$

$$2ROH + H_2SO_4 \longrightarrow R_2SO_4 + 2H_2O$$

Process

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca^{+2} and Mg^{+2} ions and exchange equivalent amount of H^+ ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH^- ions. The water coming out from the exchanger is free from anions and cations. Thus water of zero hardness is obtained. This water is known as demineralised or deionised water.

Regeneration

When ion exchangers losses its capacity they are said to be exhausted. The exhausted cation exchanger is regenerated by passing dil. HCl or dil. H_2SO_4.

$$R_2Ca + 2HCl \longrightarrow 2RH + CaCl_2$$

$$R_2Mg + H_2SO_4 \longrightarrow 2RH + MgSO_4$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$RCl + NaOH \longrightarrow ROH + NaCl$$

Merits (or) Advantages of Ion-exchange process

- Very good for use in high pressure boilers also.
- Highly acidic or alkaline water can be treated.
- The residual hardness of treated water is very low (2 ppm).

Demerits (or) Disadvantages of Ion-exchange process

- The equipment is costly and more expensive chemicals are needed.
- Turbid water cannot be treated.
- Water containing Fe, Mn cannot be removed as they form complexes with resins.

Zeolite Process

Zeolites are naturally occurring hydrated sodium alumino silicate minerals ($Na_2O.Al_2O_3.xSiO_2.yH_2O$). Natural zeolites are in green colour and non-porous. The synthetic zeolite form is called permutit or boiling stone which is porous and gel like structure. It is represented by Na_2Ze.

Process

When hard water is passed through a bed of sodium zeolite, it exchanges its sodium ions with calcium and magnesium ions present in the hard water.

$$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2\,NaCl$$

$$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$$

$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2\,NaHCO_3$$

Regeneration

After some time Zeolite gets exhausted. The exhausted zeolite can be regenerated by treating with 10% solution of NaCl.

$$MgZe + 2\,NaCl \longrightarrow Na_2Ze + MgCl_2$$

$$CaZe + 2\,NaCl \longrightarrow Na_2Ze + CaCl_2$$

Advantages of Zeolite Process

- Hardness of the water obtained by this process is very low (1-2 ppm).
- The equipment is compact and occupies small space.
- It is a clean and rapid process.
- The operation is simple.
- It is a cheap method. The regenerated zeolite can be used again.
- There is no sludge formation during the process.

Advantages of Zeolite Process

- Turbid water cannot be treated, which blocks the zeolite's pore.
- Acidic water cannot be treated, which decomposes the zeolite structure.
- Water containing Fe, Mn salts cannot be treated.
- Brackish water cannot be treated.

Table 1.2 Differences between the zeolite process and ion-exchange (Demineralisation) process

S.No.	***Zeolite process***	***Ion-exchange process***
1	It exchanges only cations except Na+ ions.	It exchanges both anions and cations.
2	Acidic water cannot be treated.	Acidic water can be treated
3	Brackish water cannot be treated.	Brackish water can be treated
4	The treated water contains more dissolved salts.	The treated water does not contain any dissolved salts.
5	Soft water is produced	Demineralised water is produced
6	Water containing turbidity, Fe, Mn salts cannot be treated.	Water containing turbidity, Fe, Mn salts cannot be treated.

Unit - II - Nanochemistry

"There's is plenty of room at the bottom - New field of science" - Feynman's

Nano means a billionth (1×10^{-9}m). The study and control of phenomena and materials at length scales below 100 nm. Diameter of a single atom can vary from 0.1 to 0.5nm.

Terms Used in Nano:

Nanoscience (or) Nanochemistry: The study of phenomena and manipulation of materials at atomic, molecular and macro-molecular scales.

Nanotechnology: The design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.

Nanoparticles: The particles with grain size (diameter) less than 100nm. and obtained as colloids. These to remain single crystal and present on the surface of nanocrystals. Nanoparticles posses electronic behavior, governed by quantum, they are also called as quantum dots.

Nano materials: The materials having components with size less than 100 nm at least in one dimension.

Nanomaterials	Examples	Uses
* One dimension	Thin films & Coatings	Electronic device manufacture
* Two dimensions	Carbon nanotubes (CNTs) nanowires, Bio polymers	Novel mechanical and electrical properties for digital computing.
* Three dimensions	Nano particles, colloids Dendrimers, Quantum dots. Precipitates	Paints, displays, Catalyst, Batteries.

At nano scale → materials posses larger surface area.
→ Quantum effects can begin to dominate the property

Distinction between Molecules, Nanomaterials and Bulk materials

→ The size of nano particles are less than 100 nm in diameter, Molecules are in the range of picometers, but bulk materials are larger in micron size.

→ Molecule is a collection of atoms, nanoparticles are collection of few molecules that is less than 100 nm but bulk materials contains thousands of molecules.

→ Surface area of nanoparticles is more than the bulk materials.

→ Hardness of nanomaterials is five times more than the bulk materials.

→ Strength of nanomaterials is 3-10 times higher than the bulk materials.

→ Nanoparticles possesses size dependent properties but bulk materials possess constant physical properties.

→ Corrosion resistance is more than the bulk materials, hence localised corrosion in nanomaterials is stopped.

→ Behavior of bulk materials can be changed, but cannot enter inside the nanoparticles.

→ Due to its size, nanoparticles possess unexpected optical properties. Examples: Nanogold appears deep red to black whereas gold in bulk looks yellow.

→ Nanoparticles possesses lower melting point than the bulk materials. Example: Melting point of nanogold (2.5 nm) is 300°C, but bulk Gold possess 1064°C.

→ Sintering of nanoparticles takes place at lower temperature and in short time than the bulk materials.

→ Electrical properties, resistivity of nanoparticles are increased by three times.

→ Suspension of nanoparticles is possible due to high surface area, but bulk materials cannot.

→ The wear resistance of nanoparticles are 170 times higher than the bulk materials.

Comparison of Molecules, Nanomaterials and Bulk materials

S. NO	Properties	Molecules / Atom	Nanomaterials	Bulk materials
1.	Size of Constituting Particles.	Few Angstroms(Å) (10^{-10}m)	Angstrom to nano-meter(10^{-10} to 10^{-9}m)	Microns to higher.
2.	Number of Constituting particles.	One for Atom, Many for Molecules	Two to several thousands.	Infinite.
3.	Electronic structure	Confined	Confined	Continuous
4.	Geometric structure	Well-defined Structure and Predictable. Ex NaCl, HCl	Well-defined Structure and Predictable. Ex $(NaCl)_n$	crystal structures decide. Ex: Gold bar & Silver bar

Size dependent Properties:

All properties like hardness, strength, ductility, elastic modulus, melting point, density, thermal conductivity, thermal expansion co-efficient, diffusivity and so on, change for nanomaterials. The material behavior vary so significantly by a mere reduction in grain size. Nanostructured materials are composed of grains and grain boundaries. Nanometer-sized grains contain only a few thousands of atoms within each grain.

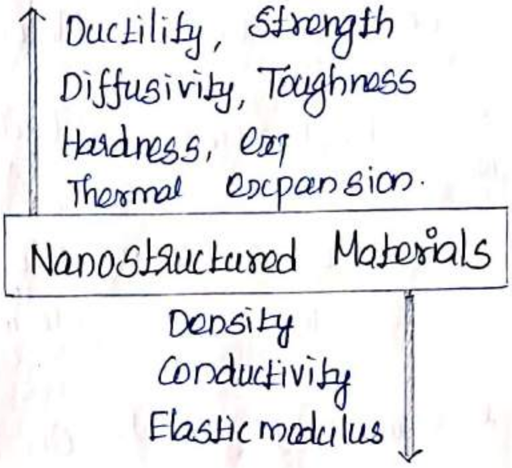
A large number of atoms reside at the grain boundaries. As the grain size decreases, there is a significant increase in the volume of of grain boundaries or interfaces.

The properties of materials are bound to be governed to a large extent by defect configurations, dynamics and interactions. Hence the mechanical and chemical properties of nanomaterials are significantly altered due to defect dynamics.

The elastic modulus of nanomaterials Can be significantly different from that of bulk alloys, due to the presence of increased fraction of defects.

examples: * Nanocrystalline ceramics are tougher and stronger than those with Coarse grains.

* Nano-sized metals exhibit significance increase in yield strength and the toughness decreases.



Property	Change in property in Comparison to bulk
Hardness	5 times increase
Strength	3–10 times increase
Wear resistance	170 times increase
Frictional coefficient	Reduced to half
Corrosion resistance	Reduced or localised corrosion is stopped
Magnetic Properties	Lower coercivity, Saturation magnetisation reduced by 5%.
Electrical Properties	Resistivity increased by 3 times
Hydrogen diffusion	Higher
Electrocatalytic properties	Improved electrocatalytic activities for hydrogen evolution.

Properties of Nano-Materials:

Melting points: Nanomaterials have a significantly lower melting point and appreciable reduced lattice constants. This is due to huge fraction of surface atoms in the total amount of atoms. As the grain size is reduced, the Melting Point is lowered.

Optical properties: Reduction of material dimensions has pronounced effects on the optical properties. Optical properties of nanomaterials are different from bulk forms. The change in optical properties is caused by two factors

i) The quantum confinement of electrons within the nano-particles increases the energy level spacing.
Example: The optical absorption peak of a semiconductor nanoparticles shifts to a short wavelength, due to an increased band gap.

ii) Surface plasma resonance, which is due to smaller size of nano-particles than the wavelength of incident radiation.
Example: The colour of metallic nano-particles may change with their sizes due to surface plasma resonance.

Magnetic properties: * Magnetic properties of nanomaterials are different from that of bulk materials. The shape and size of the nanoparticles are important for their magnetic properties The strength of a magnet is decided by its coercivity and saturation magnetization values.

* Ferromagnetic behavior of bulk materials disappear, when the particle size is reduced and transfers to super-paramagnetics. This is due to the huge surface area.

Mechanical properties: * Very less amount of defects observed in nano-materials are responsible for increased mechanical strength.

i) Mechanical properties of polymeric materials can be increased by the addition of nano-fillers.

ii) As nanomaterials are stronger, Harder and more wear resistant and corrosion resistant, they are used in spark plugs. Example: Nano-crystalline carbides are much stronger, Harder and wear resistant and are used in micro drills.

* Nanoscale multilayers made of metallic or ceramic materials exhibited Ultra high hardness.

Electrical properties:

i) Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, it can be increased, due to better ordering in micro-structure. Ex: Polymeric fibres.

ii) Nanocrystalline materials are used as very good separator plates in batteries, because they can hold more energy than the bulk materials.

Example: Ni-Metal hydride batteries made of nanocrystalline Ni and Metal hydride, require far less frequent recharging and last much longer.

Chemical properties:

Any heat treatment increases the diffusion of impurities, structural defects and dislocations and can be easily push them to the nearby surface. Increased perfection will have increased chemical properties.

Types of Nanomaterials:

Nano particle:

Definition: The term nanoparticle is generally used to refer a small particle with all three dimensions less than 100 nm. The term also includes subcategories such as nanopowders, nano clusters and nanocrystals.

Nanocluster is an amorphous/semicrystalline nanostructure with atleast one dimension being between 1-10 nm and a narrow size distribution.

Nano powder is an agglomeration of nanocrystalline nanostructural sub units with atleast one dimension less than 100 nm.

Properties of nanoparticles:

* Quantum confinement in semiconductor particles.

* Nanoparticles have a very high surface area to volume ratio.

* Sintering take place at low temperature.

* Evolution of superparamagnetism in magnetic materials.

* The large surface area to volume ratio also reduces the incipient melting temperature of nanoparticles.

* Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects. There is a significant shift in the optical absorption spectra towards the blue (shorter wavelength). as the particle size reduced.

* Surface plasmon resonance in certain metallic nano-particles.

Applications of nanoparticles:

* Colloidal gold has been successfully used as a therapy for Rheumatoid arthritis.

* Surface coating in biological application.

* Large variety of cosmetics and sunscreens are produced which contain nanoparticles for effective working.

* Nanoparticles can be manipulated to perform various specialized functions such as drug delivery, cancer treatment, imaging and sensing.

* Digital quantum batteries are storing energy and information in a novel way using nanoparticles and nanovacuum tube arrays that enhance the efficiency and fabricate low cost options.

* Nanosensor and nanorobots are used to monitor climate changes.

Nanoclusters:

Nanoclusters are fine aggregates of atoms or molecules. The size of which ranges from 0.1 to 10 nm. Of all the nanomaterials, nanoclusters are the smallest sized nanomaterials due to their close packing arrangement. Example: CdS, ZnO.

In nanocluster, all the atom are bound by forces like metallic, covalent, ionic, hydrogen bond or Vander Waals force of attraction.

Clusters of certain critical size are more stable than others. Nanoclusters consisting of up to a couple of hundred atoms, but larger aggregates, containing 10^3 or more atoms are called nanoparticles.

Magic Number - The number of atoms present in the clusters of criticle sizes with higher stability.

Nanoclusters can be distinguished from the nature of forces present between atoms. The property of clusters can vary with the number of constituent atoms, the type of element and the net charge of cluster.

Properties of nanoclusters:

* Atomic or Molecular clusters are formed by the nucleation of atoms or molecules respectively.
* Reactivity of nanoclusters are decreased due to their decrease in size.
* Melting point of nanoclusters are lower than the bulk due to high surface to volume ratio.
* Electronic structure of the nanocluster is more confined than the bulk materials.

Applications of nanoclusters:

→ Nanoclusters are used as catalyst in many reactions

→ It is used in nano based chemical sensors

→ It is used as a LED in quantum computers.

Nanorods:

Nanorod is two dimensional cylindrical solid material having an aspect ratio i.e., length to width ratio less than 20.

Examples: ZnO, CdS, Gallium nitride nanorods.

Synthesis of nanorods:

Nanorods are produced by direct chemical synthesis. A combination of ligands act as shape control agents and bond to different facets of the nanorods with different strength.

This allows different nanorods to grow at different rates producing an elongated objects. Many of the above nanorods are not manufactured due to lack of commercial demand.

Properties of nanorods:

→ Nanorods are two dimensional materials.

→ It exhibits optical and electrical properties.

Applications of nanorods:

→ Nanorods find application in display technologies.

→ It is used as cancer therapeutics.

→ It is used in energy harvesting and LED devices.

→ It is used in the manufacturing of micromechanical switches, applied electric field, micro electro mechanical system.

→ Nanrod with noble metal nanoparticles function as theragnostic agents.

Nanowires:

Nano wire is two dimensional cylindrical solid material having an aspect ratio ie., length to width ratio greater than 20. Diameter of the nanowire ranges from 10-100 nm.

Examples:

Metallic nanowires - Au, Ni, Pt Nanowire of Insulators - SiO_2, TiO_2

Molecular nanowires - DNA Nanowire of Semiconductors - InP, Si, GaN

Synthesis of nanowires:

1. Template-assisted synthesis - It is a simple way to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material and the empty spaces are filled with the chosen material to form nanowires.

2. Vapour - Liquid - Solid (VLS) method - It involves the absorption of the source material from the gas phase into a liquid phase of catalyst. Upon supersaturation of the liquid alloy, a nucleation event generates a solid precipitate of the source material. This seed serves as a preferred site for further deposition of material at the interface of the liquid droplet, promoting the elongation of the seed into a nanowire.

Properties of nanowires.

- Nanowires are two-dimensional material.
- Conductivity of a nanowire less than that of bulk materials
- It exhibits distinct optical, chemical, thermal and electrical properties due to this large surface area.
- Silicon nanowire shows strong photoluminescence characteristics.

Uses of nanowires:

* Nanowires are used for enhancing mechanical properties of Composites.

* Nanowires replace conventional copper wires used in Computers, televisions.

* It is also used to prepare active electronic Components such as P-n junction and logic gates.

* Semiconductor nanowire crossings are expected to play a important role in future of digital Computing.

* Nanowires find applications in high-density data storage eiether as magnetic read heads or as patterned storage media.

* It is also used to link tiny components into very small circuits.

Nanotubes:

Nanotubes are tube like structures with diameter of 1-100 nm and a length of few nm to microns. Nanotubes Consist of tiny cylinders of carbon and other materials like boron nitride. Nanotubes may be organic (or) inorganic.
Examples: Carbon nanotube, Silicon nanotube, DNA nanotube,
Boron nitride nanotube.

Carbon nanotubes (CNTs)

Carbon nanotube is a tubular form of Carbon with 1-3 nm diameter and a length of few nm to microns.

Generally carbon in the Solid phase exist in different allotropic forms like graphite, diamond, fullerene and nanotubes.

Carbon nanotubes are tubular forms of carbon. When graphite sheets are rolled into a cylinder, their edges join to each other form carbon nanotubes. Each atom in the carbon nanotube is linked by covalent bonds. But the number of nanotubes align into ropes and are held together by weak Vander walls forces

Structures(or) Types of carbon nanotubes:

Depending upon the way in which graphite sheets are rolled, two types of CNTs are formed

1. Single - walled nanotubes (SWNTs)
2. Multi - walled nanotubes (MWNTs)

1. Single-walled nanotubes (SWNTs)

SWNTs consist of one tube of graphite. It is one -atom thick having a diameter of 2nm and a length of 100µm. SWNTs are very important, because they exhibit important electrical properties. It is an excellent conductor.

Three kinds of nanotubes are resulted, based on the orientation of the hexagon lattice.

a) Arm-chair structures: The lines of hexagons are parallel to the axis of the nanotube.

b) Zig-Zag structures: The lines of carbon bonds are down the centre.

c) Chiral nanotubes: It exhibits twist or spiral around the nanotubes.

It has been confirmed that arm-chair carbon nanotubes are metallic while zig-zag and chiral nanotubes are semiconducting.

2. Multi-walled nanotubes (MWNTs)

MWNTs (nested nanotubes) consist of multiple layers of graphite rolled in on themselves to form a tube shape. It exhibits both metallic and semi conducting properties. It is used for storing fuels such as hydrogen and methane.

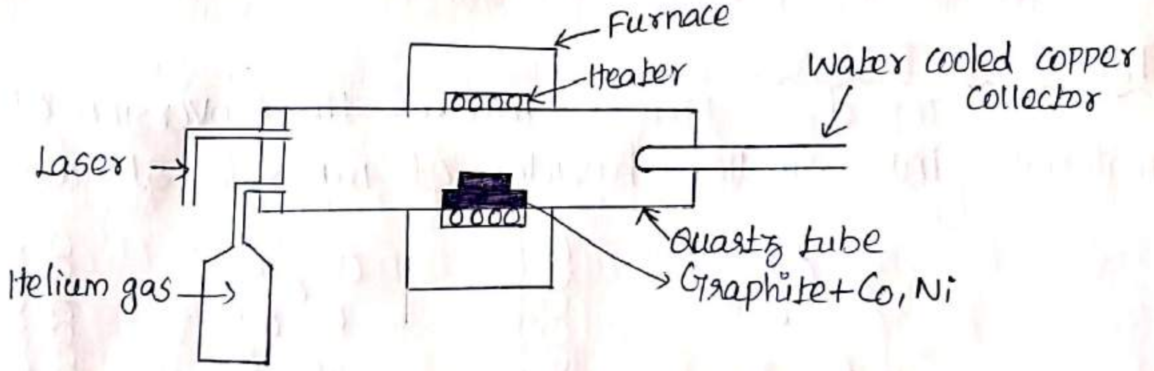
Synthesis of Carbon Nanotubes

Carbon nanotubes can be synthesized by the following methods.

1. Pyrolysis of hydrocarbons
2. Laser evaporation.

1. Pyrolysis: Carbon nanotubes are synthesized by the pyrolysis of hydrocarbons such as acetylene at about 700°C in the presence of Fe-silica or Fe-graphite catalyst under inert conditions.

2. Laser evaporation: It involves vapourization of graphite target, containing small amount of cobalt and nickel, by exposing it to an intense pulsed laser beam at higher temperature (1200°C) in a quartz tube reactor. An inert gas such as argon (or) helium is simultaneously allowed to pass into the reactor to sweep the evaporated carbon atoms from the furnace to the colder copper collector, on which they condense as carbon nanotubes.



Laser evaporation technique

Properties of CNTs:

→ CNTs are very strong, withstand extreme strain in tension and posses elastic flexibility.

→ The atoms in a nanotube are continuously vibrating back and forth.

→ It is highly conducting and behaves like metallic or semiconducting materials.

→ It has very high thermal conductivity and kinetic properties.

Uses of CNTs:

→ It is used in battery technology and in industries as catalyst.

→ It is also used as light weight shielding materials for protecting electronic equipments.

→ CNTs are used effectively inside the body for drug delivery.

→ It is used in composites, ICs, efficient catalysts for some chemical reactions.

→ It acts as a very good biosensor. Due to its chemical inertness carbon nanotubes are used to detect many molecules present in the blood.

→ It is also used in water softening process as a filter.

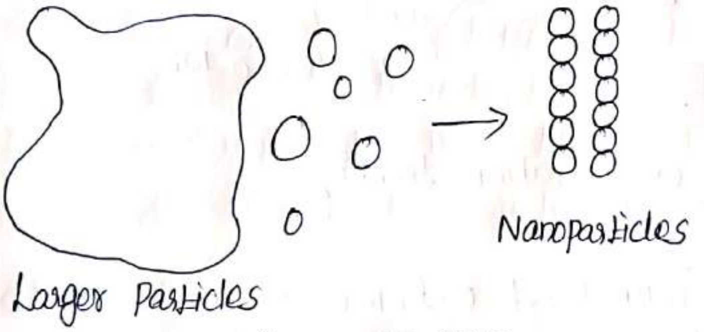
Preparation of Nanomaterials

The following two approaches are used for the synthesis of nanomaterials.

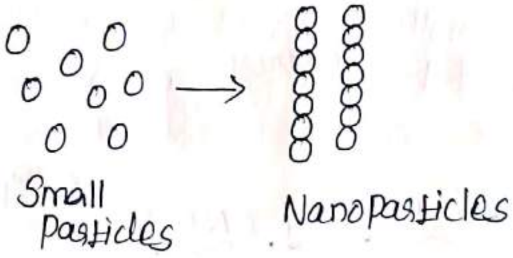
1. Top-down process or Physical or Hard methods
2. Bottom-up process or Chemical or Soft methods

Top-down process:

Top-down process involves the conversion of bulk materials into smaller particles of nanoscale structure.



Top-down Process



Bottom-up Process

Bottom-up Process:

Bottom-up process involves building-up of materials from the bottom by atom by atoms, molecule by molecule or cluster to the nanomaterials.

Sol-Gel process: Wet chemical technique or chemical Solution deposition:

The Sol-gel method for producing solid materials from Small molecules. It is used for the fabrication of metal oxides. It involves Conversion of monomer into a colloidal solution (Sol) that act as a precursor. This sol gradually evolves towards the formation of a gel-like system.

It involves the following steps. 1. Hydrolysis & Polycondensation, 2. Gelation, 3. Aging, 4. Drying, 5. Densification & 6. Crystallisation.

The Volume fraction of particles (particle density) may be Slow that a significant amount of fluid need to be removed for the gel-like properties to be recognized. It is done by two ways.

i) Sedimentation:

The solution is allowed to keep for some time for Sedimentation to occur and then pour off the remaining liquid.

ii) Centrifugation:

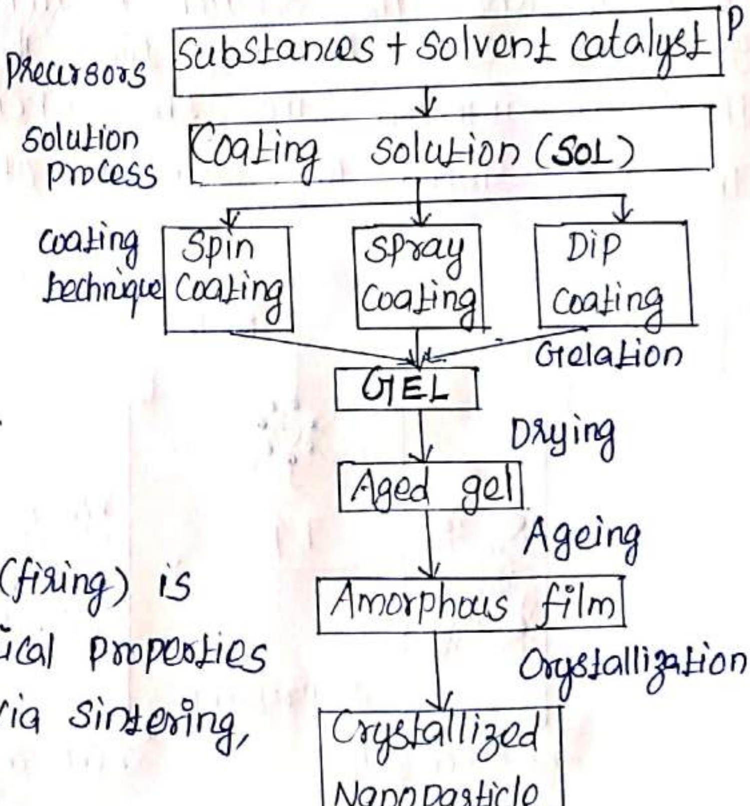
Centrifugation can also be used to accelerate the process of phase separation.

Drying and densification

Removal of the remaining liquid (solvent) is done by drying process, which accompanied by shrinkage and densification.

Firing (or) Crystallization

A thermal treatment (firing) is necessary to enhance mechanical properties and structural stability via sintering, densification.



Various steps of Sol-Gel process.

Solvothermal Synthesis:

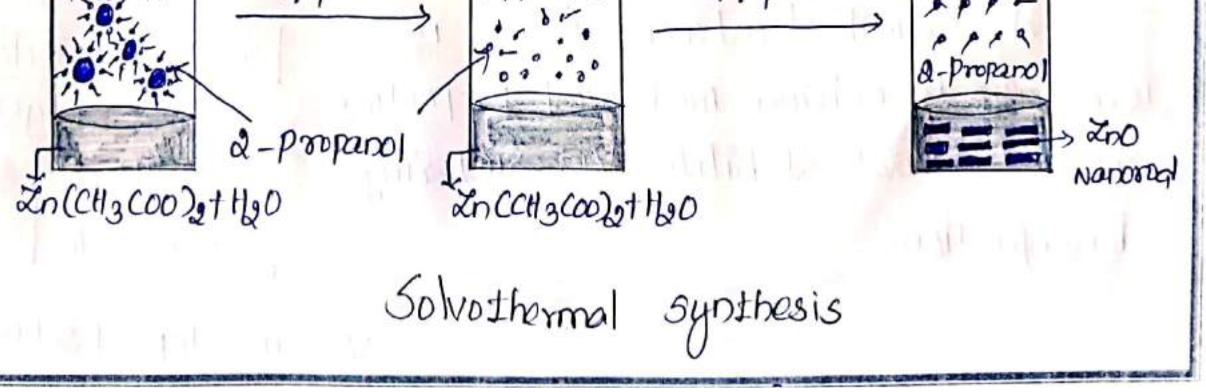
Solvothermal synthesis involves the use of solvent under high temperature (between 100°c to 1000°c) and moderate to high pressure (1 atm to 10,000 atm) that facilitate the interaction of precursors during synthesis.

Method: A solvent like ethanol, methanol, 2-propanol is mixed with certain metal precursors and the solution mixture is placed in an autoclave kept at relatively high temperature and pressure in an oven to carry out the crystal growth. The pressure generated in the vessel, due to the solvent vapour, elevates the boiling point of the solvent.

Example: Solvothermal synthesis of Zincoxide.

Solvothermal synthesis of zinc oxide:

Zinc acetate dihydrate is dissolved in 2-propanol at 50°c. Subsequently, the solution is cooled to 0°c and NaOH is added to precipitate ZnO. The solution is then heated to 65°C to allow ZnO growth for some period of time. Then a capping agent (1-dodecane thiol) is injected into the suspension to arrest the growth. The rod shaped Nanocrystal is obtained.



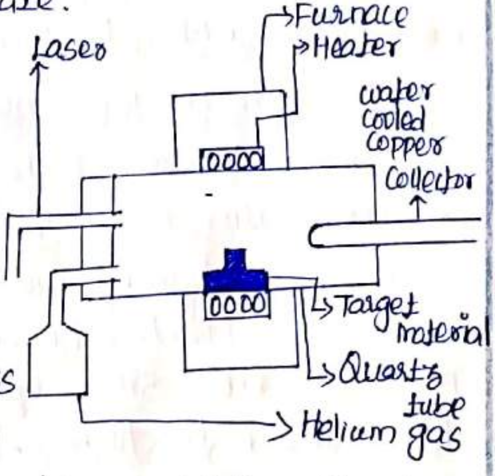
Solvothermal synthesis

Laser ablation:

In laser ablation technique, high-power laser pulse is used to evaporate the material from the target.

The stoichiometry of the material is protected in the interaction. The total mass ablated from the target per laser pulse is referred to as the ablation rate.

Vapourisation of target material containing small amount of catalyst (Ni or Co) by passing an intense pulsed laser beam at a higher temperature to about 120°c in a quartz tube reactor. Simultaneously an inert gas such as Argon, Helium is allowed to pass into the reactor to sweep the evaporated particles from the furnace to the colder collector.



Laser ablation Chamber

Uses:

- Nanotubes having a diameter of 10 to 20 nm and 100μm can be produced by this method.
- Ceramic particles and coating can be produced.
- Other materials like silicon, carbon can also be converted into nanoparticles by this method.

Advantages of laser ablation:

- It is very easy to operate.
- The amount of heat required is less.
- It is an eco-friendly method (No solvent used).
- The obtained product is stable.
- This process is economical.

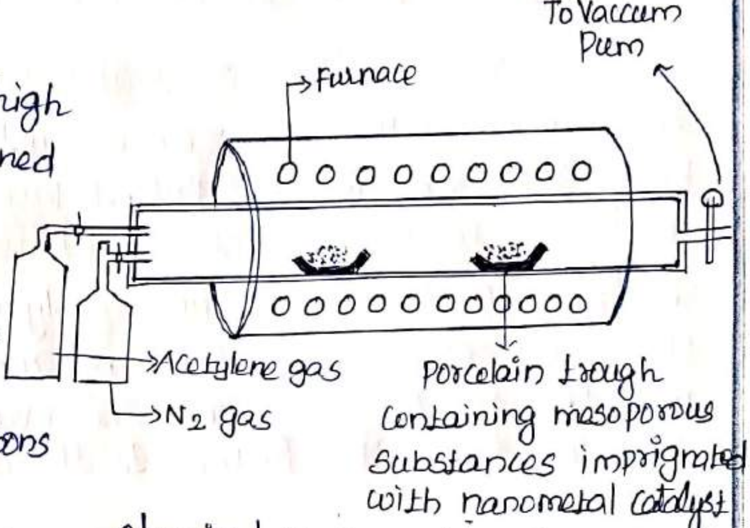
Chemical Vapour Deposition (CVD)

Conversion of gaseous molecules into solid nanomaterials in the form of tubes, wires or thin films.

Solid materials are converted into gaseous molecules and then deposited as nanomaterials.

Example: CNT Preparation.

The CVD reactor consists of a high temperature vacuum furnace maintained at inert atmosphere. The solid substance containing catalyst like Ni, Co, Fe supported on a substrate material like silica, quartz is kept inside the furnace. The hydrocarbons such as ethylene, acetylene and N_2 cylinders are connected to the furnace.



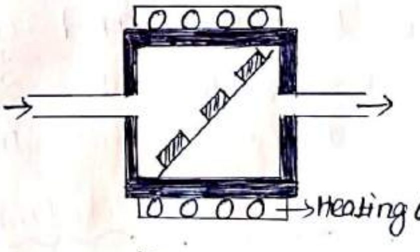
Chemical Vapour deposition.

Carbon atoms produced by the decomposition at 1000°c, condense on the cooler surface of the catalyst.

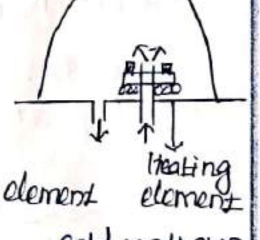
Types of CVD Reactor

Hot-wall CVD:

Hot-wall CVD reactors usually tubular in form. Heating is done by surrounding the reactor with resistance elements.



Hot-wall CVD



Cold wall CVD

Cold-wall CVD

In Cold-wall CVD reactors, substrates are directly heated inductively while chamber walls are air or water cooled.

Advantages of CVD:

* Nanomaterials, produced by this method, are highly pure, defect free and economical method.

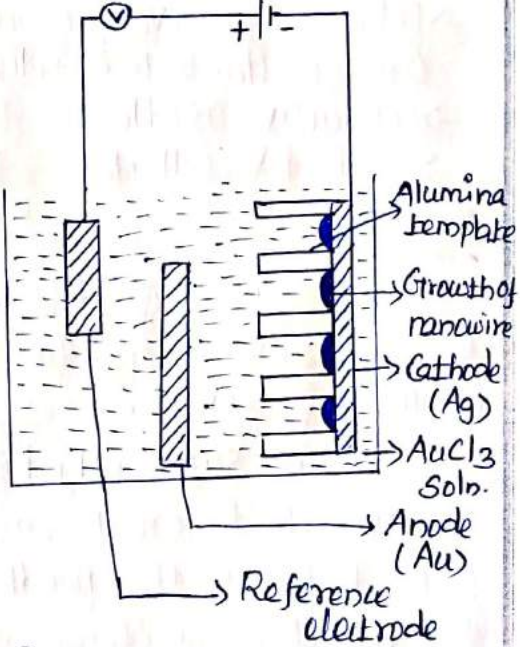
* Mass production in industry can be done without major difficulties.

Electrodeposition (or) Electrochemical deposition:

Electrodeposition is an electrochemical method in which ions from the solution are deposited at the surface of cathode. Template assisted electro-deposition is an important technique for synthesizing metallic nanoparticles with controlled shape & size. Array of nanostructured materials with specific arrangements can be prepared by this method using an active template as a cathode.

The cell consists of a reference electrode, specially designed cathode and anode.

All these electrodes are connected with the battery through an voltmeter and dipped in an electrolytic solution of a soluble metal as shown in figure.



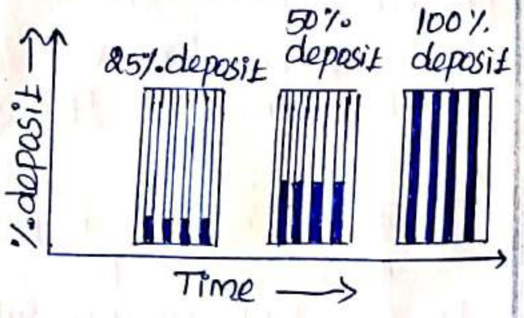
Process of electrodeposition

When the current passed through the electrodes of template, the metal ions from the solution enter into the pores and gets reduced at the cathode, resulting in the growth of nanowire inside the pores of the template.

Example: Electrodeposition of Gold on Silver

Nanostructured Gold Growth of nanowires or nanorods inside the pores of Alumina templates.

Au sheet - Anode
Ag plate - cathode
Array of Alumina template
AuCl$_3$ - electrolyte

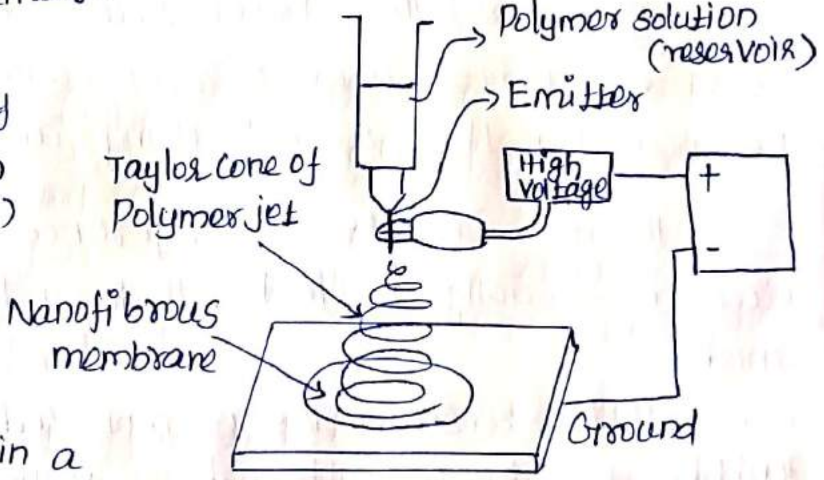


Advantages:

- → Relatively cheap and fast method.
- → Complex shaped objects can be coated
- → Film or wire obtained is uniform
- → Metal nanowires (Ni, Co, Cu, Au) can be fabricated.

Electrospinning:

Electrospinning is a method of producing ultrafine (in nm) fibres by charging and ejecting a polymer solution through a spinneret under a high-voltage electric field and to solidify or coagulate it to form a filament.



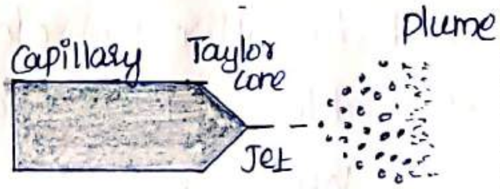
Components:

- →High voltage power supply
- →Polymer reservoir (maintain constant flow rate of solution)
- →Conductive needle,
- →Conductive collector

Process:

A polymer is dissolved in a suitable solvent and filled in the capillary reservoir.

When sufficiently high voltage is applied to create an electric field between the needle tip and the collector, a charge accumulates at the liquid surface.



Electrospinning

When the electrostatic repulsion is higher than the surface tension the liquid meniscus is deformed into conically shaped structure known as a Taylor cone.

Once Taylor cone is formed, the charged liquid-jet is ejected towards the collector.

Depending on the viscosity of the solution, solid fibre will be formed as the solvent evaporates.

Applications:

- It is used in diagnosis and treatment of diabetes.
- Electrospun fibres are used in energy storage devices such as solar cell, fuel cell and super capacitors.
- It is used in textiles for smart clothing, protecting clothing and fire retardant fibres.
- It is used in sensors (gas sensor, chemical sensor, fluorescence sensor)
- In Biomedical, used in drug delivery, Artificial blood vessel, wound dressing.
- e-spun fibres employed in filteration and thermal insulation.

Applications of Nanomaterials:

Nano technology finds significant impact on all most all the industries and all areas of society.

Medicine:

1. Nano drugs - Nanomaterials are used as drugs for cancer & TB therapy.
2. Laboratories on a chip - Nanotechnology is used in the production of laboratories on a chip.
3. Nano-medibots - Nanoparticles function as nano-medibots that release anti-cancer drug and treat cancer.
4. Gold-coated nanoshells - Converts light into heat, enabling the destruction of tumours
5. Gold nanoparticles as sensors - Gold nanoparticles undergo colour change during the transition of nanoparticles.
6. protein analysis - Protein analysis done by using nanomaterials
7. Gold nanoshells - It is used ~~as~~ for blood immuno assay and imaging, therapy.
8. Gold nanoparticles - Used as slow and selective release of drugs to the targetted organs
9. Repairing work - Used in partially repair neurological damage.

Agriculture:

→ Nanomaterials Prepared by eco-friendly and green method with plant extracts. for improving fertilization process, plant growth regulators.

→ Minimize the amount of harmful chemicals usage

→ Nano sensors used in crop protection for the identification of diseases and residues of agrochemicals.

→ Nanodevices used for genetic engineering of plants.

→ Nanomaterial used in plant disease diagnosis & postharvest - Management.

→ Nanomaterials used as antimicrobial agent, food packing, Pesticides, herbicides, to improve crop yields but not damage soil, water.

Energy:

Nanomaterials are used to improve the efficiency of energy generation (or) develop new methods to generate energy.

1. Power generation - Sun light, Concentrated on nanoparticles, Can produce steam with high energy efficiency.
2. Generating hydrogen from sea water - The use of a nanostructured thin film of Nickel selenide as a catalyst for the electrolysis of hydrogen from sea water.
3. Producing high efficiency light bulbs - Nano engineered Polymer matrix is used for Producing high efficiency light bulbs
4. Increasing the electricity generated by wind mills - Stronger lower weight blades, made from nano tubes filled epoxy, in wind mills increase the amount of electricity.
5. Generating electricity from waste heat - Sheets of nanotubes have been used to build thermocells.
6. Storing hydrogen for fuel cell powered cars - Graphene layers are used in fuel tank high amount of hydrogen storage.
7. Reducing power loss in electric transmission wires - Carbon nanotube wires help to reduce resistance in transmission grid.
8. Reducing the cost of solar cell - Nano tech solar cells are lower cost than the conventional solar cells.
9. Nanobattery and fuel cell - Nanomaterials used to increase efficiency.

Electronics:

* Quantum wire have high electrical Conductivity
* Integrated memory circuits as a effective devices
* Nanowires to build transistors without P-n junctions
* Nanoradios using carbon nano tubes.
* A transistor, NOMFET (Nanoparticle organic Memory Field effect Transistor) is created by combining Au nanoparticles with organic compounds
* MOSFET (Metal oxide semi conductor Field Effect transistors) performs both as switches and as amplifiers

Catalysis:

Nanoparticle catalysts are highly effective due to high surface area and enhanced reactivity.

1. Water purification - Nanosilver catalyst is highly efficient in controlling microbes in water.
2. Bio-diesel production:- Solid base nanocatalyst KF/CaO can be used for biodiesel production with yield more than 96%.
3. Fuel cell application: Carbon supported electro-catalysts play an important role in fuel cell.
4. In drug delivery :- carbon nanomaterials find more applications in biological fields. including drug delivery systems.
5. Gold nanoparticles: Au nanoparticles as catalyst in CO-oxidation, epoxidation of propylene, hydrogenation of unsaturated hydrocarbons.
6. Nanopowder silica catalyst (or) Pt nanoparticles exhibit very strong catalytic activity for hydrolysation reactions.
7. Titania- based nano catalysts are being increasing used in photocatalysis
8. Nanocrystalline MgO particles act as an effective catalyst for dehydrogenation.

x———x

PHASE RULE

Phase Rule

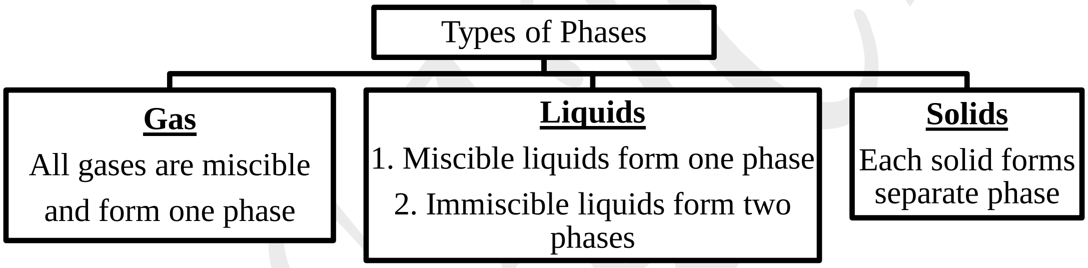
If a heterogeneous system in equilibrium is influenced by pressure, temperature and concentration and not influenced by electrical, magnetic and gravitational forces, then the degrees of freedom (F) is related to phases (P) and components (C) by the phase rule equation.

$$F = C - P + 2$$

DEFINITION OF TERMS USED

Phase (P):

Phase is any homogeneous, physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces. A phase may be a gas, liquid or solid.



Eg.1. Water system:

$$\text{Ice(s)} \rightleftharpoons \text{Water(l)} \rightleftharpoons \text{steam(g)}$$

It contains three phases. (One solid, one liquid and one gas)

Eg 2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

It contains three phases. (Two solids and one gas)

Components(C):

It is defined as the minimum number of molecular species in terms of which the composition of all phases may be expressed in the form of a chemical equation.

Eg.1. Water system:

$$\text{Ice(s)} \rightleftharpoons \text{Water(l)} \rightleftharpoons \text{steam(g)}$$

Component of all phases is H_2O. Hence C=1.

Eg 2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Composition of all three phases can be expressed in terms of two constituents.

Eg.:- $CaCO_3$ and CaO

Phase	$CaCO_3$	CaO	CO_2
Components	$CaCO_3 + 0CaO$	$0CaCO_3 + CaO$	$CaCO_3 – CaO$

Hence number of Components=2

Degree of freedom (F):

It is defined as the minimum number of independent variable factors such as temperature, pressure and composition, which must be fixed in order to define the system perfectly.

Eg.1 Ice(s) $\rightleftharpoons$ Water(l) $\rightleftharpoons$ steam(g)

P=3 and C=1

Then, F=C-P+2=1–3+2=0

Eg.2 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

C =2; and P =3

Then, F = C– P+2 = 2–3 +2 = 1

Merits of Phase of Rule

- It is applicable to both physical and chemical equilibria.
- It helps in deciding whether the given number of substances remains in equilibrium or not.
- It is a convenient method to classify the equilibrium states in terms of phases, components and degree of freedom.
- It is useful for understanding the heterogeneous equilibrium.
- It indicates that the different systems having the same degree of freedom behave in a similar manner.

Limitations of Phase Rule:

1. It takes into account only the variables like temperature, pressure and concentration.
2. The influence of factors such as electric, magnetic, gravitational force etc. are ignored.
3. It is applicable only to heterogeneous system in equilibrium.

PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against another.

Types of Phase Diagrams:

a) P-T diagram

If the temperature is plotted against pressure, the diagram is called P-T diagram

b) T-C diagram

If the temperature is plotted against composition, the diagram is called T-C diagram.

USES OF PHASE DIAGRAM

a) The study of low melting eutectic alloys used in soldering can be carried out using phase diagram.

b) It is possible to predict whether eutectic alloy or solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

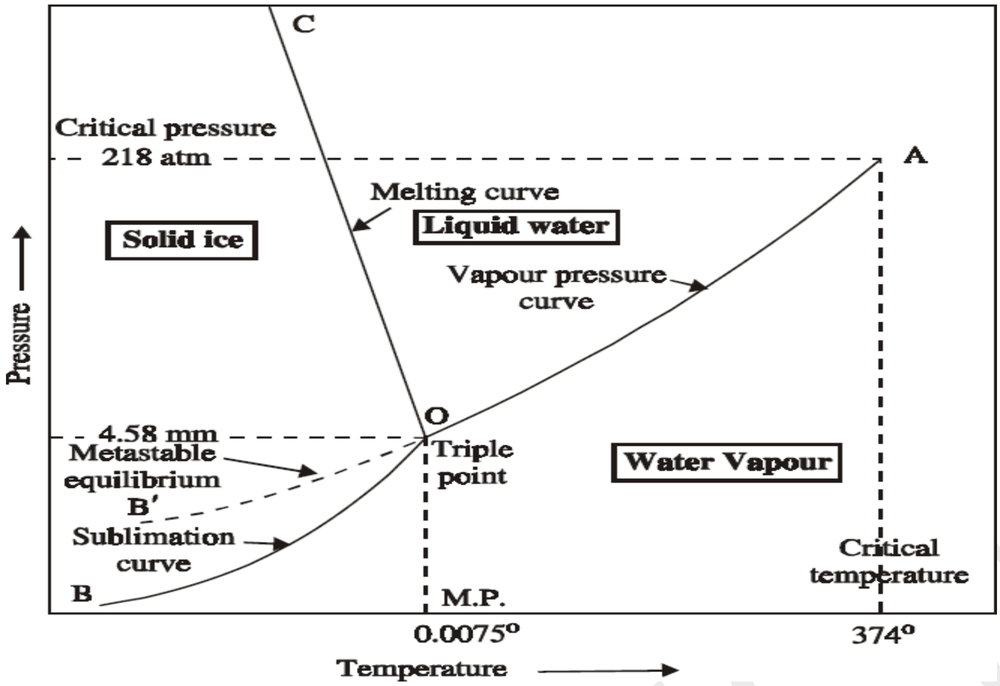
APPLICATIONS OF PHASE RULE TO ONE COMPONENT SYSTEM

WATER SYSTEM

Water exists in three possible phases namely solid, liquid and vapour.

$$\text{Ice(s)} \rightleftharpoons \text{Water(l)} \rightleftharpoons \text{Vapour(g)}$$

Here only one component (water) is present. Hence it is a one-component system.



1) Areas:

Area AOC – Liquid

Area BOC – Solid

Area BOA – Vapour

In the areas, C = 1; and P = 1

∴F = C–P+2 =1–1+2=2 It is bivariant.

They have two degrees of freedom. (i.e.) To specify a point in an area, we have to specify both the temperature and pressure.

2) Curves: OA,OB,OC

i) Curve OA: Vapourisation curve

The following equilibrium will exist.

Water (l) $\rightleftharpoons$ Vapour (g)

Here, C = 1; and P = 2

∴F = C–P+2 =1–2+2=1 It is univariant.

It extends up to 374°C (critical temperature) and 218.5 atm. (critical pressure). Beyond this, the equilibrium will disappear and vapour only will exist.

ii) Curve OB: Sublimation curve

The following equilibrium will exist.

Ice(s) $\rightleftharpoons$ Vapour(g)

Here, C = 1; and P = 2

∴F = C–P+2 =1–2+2=1 It is univariant

It extends up to –273°C. At this point, only solid ice will be present.

iii) Curve OC: Melting point curve

The following equilibrium will exist.

Ice(s) $\rightleftharpoons$ Water (l)

Here, C = 1; and P = 2

∴F = C–P+2 =1–2+2=1 It is univariant

The negative slope of the curve indicates that the melting point of ice is lowered with increase of pressure.

iv) Curve OB' : Metastable curve

It is the vapour pressure curve of super-cooled water. It represents the metastable system.

Super-cooled water $\rightleftharpoons$ Vapour

3) Point O:

The curves meet at point 'O'. All the three phases coexist at this point. Hence this point is known as triple point. It occurs at 0.0075°C and 4.58 mm.

$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{Vapour}_{(g)}$

Here, C = 1; and P = 3

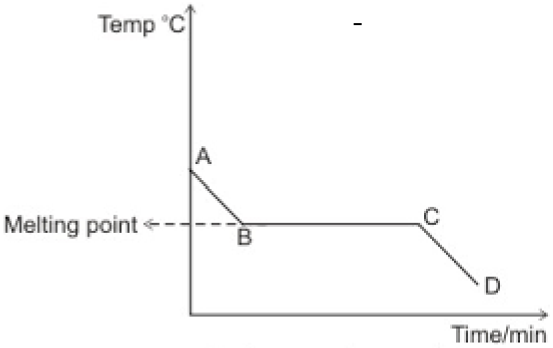
∴F = C–P+2 =1–3+2=0 It is invariant

THERMAL ANALYSIS (or) COOLING CURVE

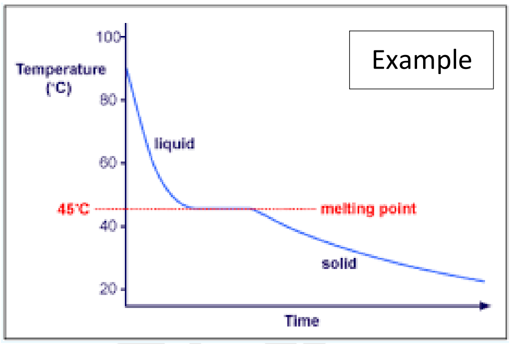
Thermal analysis is a study of the cooling curves of various compositions of a system during solidification. The shapes of the freezing point curves can be determined by thermal analysis.

Example 1: A pure substance

The pure substance in the fused state is allowed to cool slowly and the temperature is noted at different time intervals. A graph is drawn between temperature and time.

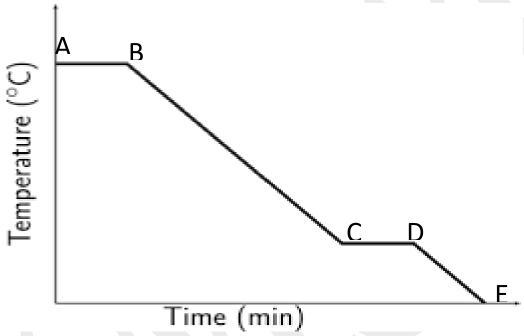


Cooling curve of a pure substance



Initially, the rate of cooling is continuous. . At point ‘b’, solid begins to appear. The temperature remains constant until all the liquid is solidified. The line ‘bc’ represents the equilibrium between the solid and the liquid. The corresponding temperature is the freezing point (or) melting point.

Example 2: Mixture of two substances



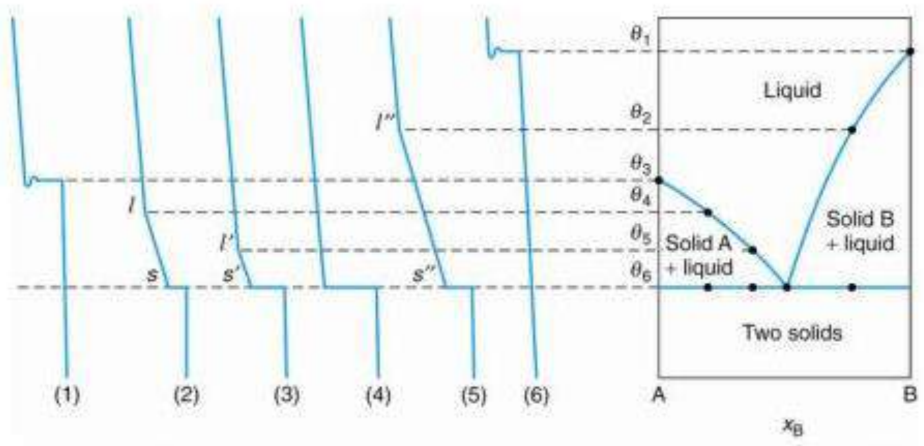
At point ‘B’ one substance A or B begins to solidify which is indicated by a break and the rate of cooling is different. On further cooling at the break point ‘C’ the second compound also begins to solidify. The temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture (line cd). At the point ‘D’ cooling of solid mass begins. The temperature corresponding to line CD gives the eutectic temperature.

The experiment is repeated for various compositions of A and B and various cooling curves are recorded. The phase diagram is constructed by plotting the freezing point against the composition.

USES OF THERMAL ANALYSIS:

1. Used to derive phase diagram of any two component system.
2. Used to determine the eutectic temperature.

3. Used to determine the percentage purity of the compounds.
4. **Used** to understand the behaviour of the compounds.



<u>TWO COMPONENT ALLOY SYSTEM</u>

REDUCED PHASE RULE OR CONDENCED SYSTEM

Solid-liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible. Hence, experiments are conducted under atmospheric pressure.

The system in which only the solid and liquid phases are present and the gas phase is ignored is called a condensed system. The phase rule becomes

$$F=C-P+1$$

This is called reduced (or) condensed phase rule.

Binary alloy system (or) Simple eutectic system

Eutectic system is a binary system consisting of two components which are completely miscible in liquid state but immiscible in the solid state. They do not react chemically. Of different mixtures of two components, the mixture having the lowest melting point is called eutectic mixture.

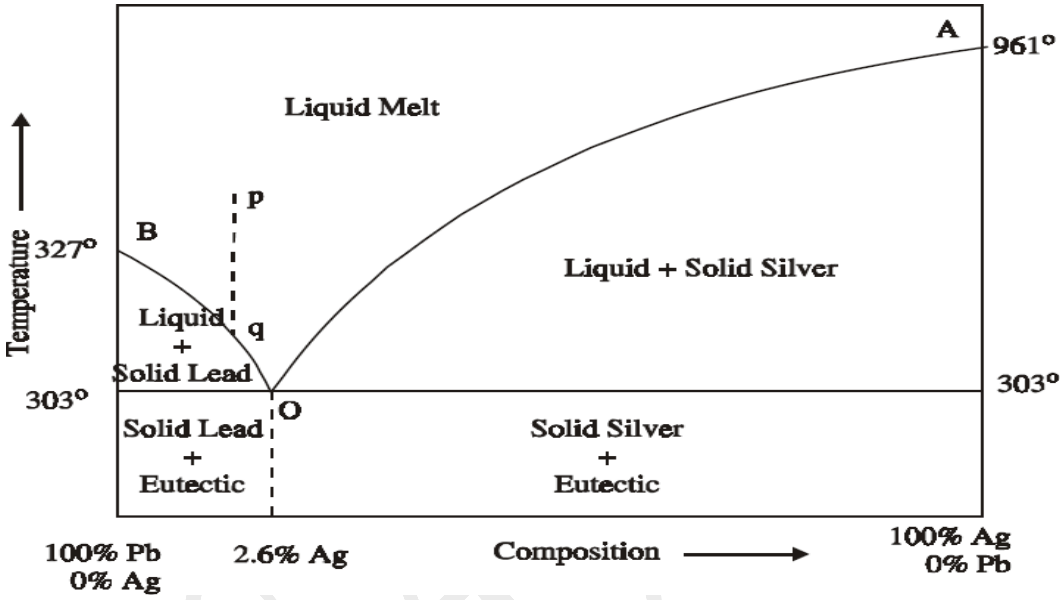
Eg. Pb-Ag system , Bi-Cd system

BINARY ALLOY SYSTEM (or) THE SIMPLE EUTECTIC SYSTEM

LEAD-SILVER SYSTEM

It is a two component system.. At constant pressure, the vapour phase is ignored and condensed phase rule is used.

Hence, $F=C-P+1$



(i) Curve AO

It is freezing point curve of silver. It indicates the depression of melting point of silver by the addition of lead. Point A is the melting point of pure Ag (961°C).The following equilibrium exits.

$$\text{Solid Ag (s)} \rightleftharpoons \text{Melt (l)}$$

Here, $P=2$; $C=2$: Hence, $F=C-P+1=2-2+1=1$; Univariant

(ii) Curve BO

It is freezing point curve of Pb. It indicates the depression of melting point of lead by the addition of silver. Point B is the melting point of pure Pb (327°C). The following equilibrium exits.

. $$\text{Solid Pb(s)} \rightleftharpoons \text{Melt (l)}$$

Here, $P=2$; $C=2$: Hence, $F = C-P+1 = 2-2+1=1$; Univariant

(iii) Point O (Eutectic point)

Curves AO and BO meet at Point O, where three phase are in equilibrium.

$$\text{Solid Pb(s)} + \text{Solid Ag(l)} \rightleftharpoons \text{Melt(l)}$$

Here P=3; C=2: Hence F=C–P+1=2–3+1=0 ;Non-variant

At point O, the composition of Pb is 97.4% and 2.6% of Ag. The temperature corresponding to point O (303°C) is eutectic temperature.

(iv) Areas

Area above line AOB contains solution of Pb and Ag.

Here P=1; C=2: Hence F=C–P+1=2–1+1=2 ; Bivariant

Application of Lead-Silver system:

Pattinson's process for the desilverisation of Argentiferous Lead:-

The process of increasing the composition of Ag in the alloy is known as Pattinson process.

Argentiferous Lead (small amount of silver≈ 0.1%)

↓ Heated above its melting point

System consist only the Liquid phase (point P)

↓ Cooling

Reaches the point q (Pb crystallised out containing increasing amount of Ag)

↓ Further cooling

More and more Pb separated along line BO

↓

Point O reached (% of Ag = 2.6%)

Uses

- Suitable alloy composition can be predicted.
- Used in preparing solders.

Composite Materials

Definition:-

A material system consisting a misture of two (or) more micro-constituents, which are mutually insoluble, differing in form (or) composition and forming distinct phase.

Need for composities :-

1. As composites never rust and have less fracture toughness than Metals.
2. To reduce maintenace cost.
3. It is essential because according to the needs, using different fibres and matrix, properties of composities can be modified.
4. In telecommunication industries need of power transmission along with data transmission is increasing so composites are highly essential
5. It is lower weight reduces fuel consumption and emission.
6. As Carbon fibre weights about 25% as much as steel and 70% as much as aluminium and is much stronger and stiffer than both materials, we need composites.

Advantages (or) characterstics

(i) They possess higher specific strength and lower specific gravity

(ii) They possess lower electrical conductivity and thermal expansion

(iii) They possess better creep, fatigue strength, corrosion and oxidation resistance.

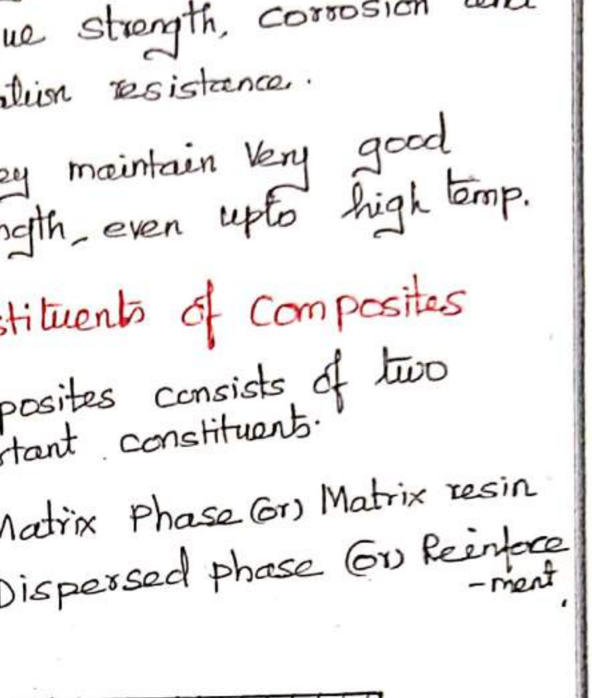
(iv) They maintain very good strength even upto high temp.

Constituents of Composites

Composites consists of two important constituents.

(i) Matrix Phase (or) Matrix resin

(ii) Dispersed phase (or) Reinforce-ment.



(i) Matrix phase

Matrix phase is the continuous body constituent, which enclose the compositie.

Matrix phase may be Metal, Ceramics, Polymers.

Composities using these matrix are knaon as

(i) Metal Matrix Composites (MMC)
(ii) Ceramic Matrix composities (CMC)
(iii) Polymer Matrix Composites (PMC)

Liquid Resins

Polymers used as adhesives, potting compounds, sealants, etc... in a liquid form are called as liquid resins.

Examples:-

Epoxy adhesives, Polysulphides

Dispersed Phase (or) Reinforcement

Dispersed phase is the structural constituent which determines the internal structure of composite.

Examples:-

Fibres, particulates, Flakes.

Reinforcement:-

* It is a process of improving the characteristics of the plastic matrix by adding reinforcing agents.

* The reinforcing agents may be organic (or) inorganic in nature

* They may be in the form of powder, flakes, fibres.

* These materials are characterised by high strength, excellent resistance to erosion, Corrosion.

1. Fibres

*Fibres are long and thin filament of any macromolecular substance such as polymer.

* The fibre can be used in variety of forms like continuous rovings, cloth, etc...

Characteristics of Fibre

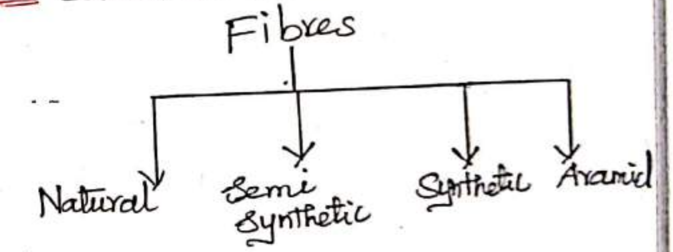
(i) Fibre possess high tensile strength
(ii) It possesses high stiffness.
(iii) It lowers overall density of composites.

Classification of Fibres

(i) Natural fibres:

These are derived from naturally available

Ex: cotton, wool, silk



(ii) Semi-Synthetic fibres:

These are produced by modifying the naturally occuring materials. Ex: Rayon, cellulosic.

(iii) Synthetic fibre:

These are produced exclusively by the laboratory processes.

Ex polyester, polypropylene

(iv) Aramid fibre:

These are aromatic polyamides.

(i) Important Natural Fibres

(a) Cotton fibres:

* cotton is a vegetable fibre and is made of cellulose molecule, which is a linear polymer of β-glucose.

* Cotton fibre provide a low cost fibrous reinforcements for the use in dough moulding compounds (DMC)

(b) Wool fibres:

* Wool is an animal protein fibre.

* It is also made up of α-amino acids.

* These amino acids are joined end-to-end in the form of peptide chains forming long chain molecules.

(c) Silk:

* Silk is a natural protein fibre produced by the insect, silk worm.

* It possesses all the desirable qualities of fibre such as softness, strength, elongation etc...

* It is an excellent insulator of heat.

(d) Sisal:

* Sisal is another low-cost fibrous material

* Which is also used in phenolic based dough moulding compounds.

(e) Jute and Coir:-

* They are also low-cost fibrous material for reinforcement for polyester resin.

(ii) Synthetic Fibres

(a) Poly propylene:

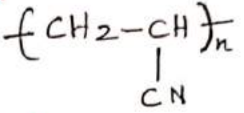
* It is obtained by polymerisation of propylene.

* These fibres possess better hardness strength, stiffness.

(b) Carbon fibres:

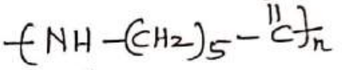
* It is continuous filament by the pyrolysis of organic fibres in an inert atmosphere such as Cellulose, PAN - Polyacrylonitrile

PAN



$$\left[CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} \right]_n$$

(C) Nylon

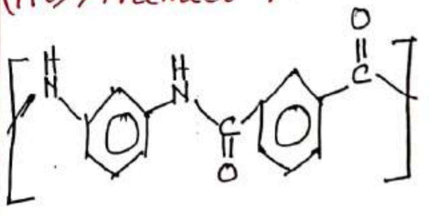


$$\left[NH - (CH_2)_5 - \overset{\displaystyle O}{\overset{\|}{C}} \right]_n$$

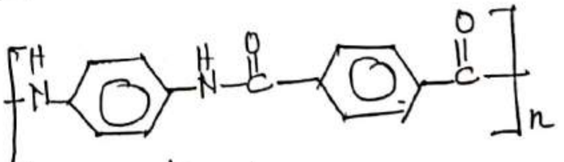
* Nylon fabrics are used as reinforcement for epoxide resin system to give flexible laminates with high impact.

* It is abrasion and chemical resistance.

(iii) Aramid Fibres



Nomex.



Kevalar

* The wholy aromatic polyamides are called as aramids.

* They are made by Spinning liquid crystal aramid oligomers (Kevlar)

2. Particulates:

* Particulates are small pieces of hard solid materials.

* They particles in a given matrix is random.

* They may be metallic (or) non-metallic.

* Generally distribution of particles in a given matrix is random, so the resulting composites are usually isotropic.

Effect of particulate in particulate composite:-

(i) Surface hardness gets increased.

(ii) Wear and abrasion resistance are increased.

(iii) performance at elevated temperature is improved.

(iv) Shrinkage and friction is reduced.

(v) Electrical and thermal conductivities are modified.

3. Flakes:

Flakes are very thin solid like materials.

Example: mica flake

* Flakes can be packed more efficiently than fibres (or) spherical particles.

* Flakes especially mica can be used in electrical and thermal insulating appliances.

4. Whiskers:-

Whiskers are thin strong fibre like material made by growing a crystal.

Example:- Graphite, silicon carbide

* They possess high elastic modulus and high degree of crystallinity.

* They possess exceptionally high strength.

* As it is costly and difficult to incorporate in matrix they find limited use in composite.

Types of composites

Fibre Reinforced polymer Composites:-

"A matrix of polymeric material that is reinforced by fibers (or) other reinforcing material"

Preparation:-

~~Disphar~~

$$\left.\begin{array}{c}\text{Matrix phase}\\+\\\text{Dispersed phase}\end{array}\right\}\xrightarrow[\text{Pressure}]{\text{Temp}}\text{Composites}$$

Matrix phase + Disperse phase $\xrightarrow[\text{Pressure}]{\text{Temperature}}$ Fibre Reinforced polymer [FRP]

Ex polyesters, Epoxy, phenolic silicone, polyamide

Ex Fibre, particulates Flakes

Characteristics (or) Properties of FRP :-

- It possess superior properties like higher yield strength.
- It possess high corrosion resistance and heat resistance.
- It is light weight, Dimensional stability
- It is low thermal conductivity, Low installed costs.

Types of FRP Composites

Glass-FRP:

Properties:-

- lower densities, dielectric constant
- Higher tensile strength & impact resistant
- Excellent corrosion resistance
- Excellent chemical resistance.

Application:

- It is used in Automobile parts storage tanks,
- It is used in plastic pipe, flourings.

Boron-FRP:

properties:-

- It is excellent stiffness and compressive strength
- Manufacturing of B-FRP is difficult.

Application :-

- It is used in Horizontal and vertical tail in aeroplane.
- It is used in stiffening spares, ribs.etc...

Carbon-FRP

properties:-

- It is lighter density, ~~excellent~~
- It is excellent resistance to corrosion.
- Retention of desired properties even at elevated temperature.

Application:-

- It is used in air craft and helicopters
- It is used as a sports material
- It is used in Antenna disc. solar panal.

Aramid FRP:-

properties:-

- They are metal-like ductile and respond non- catastrophically to compressive stresses.

Application;

- It is used as structural component in aircraft, helicopter parts.

Alumina-FRP:-

properties:-

- It is good abrasion resistance
- It is good dimentional stability.

Application:

- It is used in components of turbine engine.

Advantages of FRP :-

* polymer composite has very high strength to weight ratio than the Metal
* The weight of FRP is 75% lower than the weight of steel, so it improves performance, reduce energy need, simplifies handling.
* Using polymer composite devices both capacitance and leakage current can be reduced.
* FRP offers better corrosion resistance.
* FRP possesses excellent durability and fire resisting properties.
* It is ideal for outdoor installation, because it is impervious to the effect of sunlight, heat, cold and other weather conditions.
* Glass reinforced polymer are strongest and most resistive to deforming forces.

Metal Matrix Composites :-

properties :-

* It is extremely good thermal stability, high strength, good stiffness
* It is low specific weight
* It is high fracture toughness, ductility.
* They can withstand at high temperature in corrosive environment than polymer Composities.

Uses :-

* It is mainly used in engine parts.
* They are used in engine blades, combustion chambers.
* Al and Mg MMC are used in automotive industry.
* They improve fuel efficiency because of the weight reduction.
* It is used in biomedical and sports equipment industry.

Ceramic Matrix Composites:

properties:

* It is used at temperature above 1500°C
* It is good corrosion resistance
* ceramics provide necessary strength at high temperature.
* It is good oxidation resistance.

Uses:-

* They are used in re-entry thermal shields in space vehicles and tiles, pump seal, round rings.

Hybrid Composites

Hybrid composites are new class of materials composed of a suitable polymer matrix reinforced with two different fibres.

Types :-

1. structurally hybridized composities
2. Materials hybridized in chemical bond
3. Functionally hybridized composites.

Properties:-

- * Hybrid composites possess very good properties compared to their single fibre composites.
- * They possess strong, tough and higher impact resistance.
- * When hybrid composites are stressed in tension, failure does not occur suddenly.
- * They possess balanced strength and stiffness.
- * They also have balanced thermal distortion stability.
- * They exhibit superior mechanical and tribological properties than other composites.

Uses:

1. It is used in light-weight transport structural components.
2. It is also used in light weight orthopedic components and sporting goods.
3. It is used to make furniture like chair, table and bath tubs.
4. It is used in railway coach interiors.
5. It is used as a plates and spoons.
6. It is mainly used in Automobile industry.

Uses (or) Merits of Phase rule

1. It is applicable to both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium state in terms of phase, component and degrees of freedom.
3. It indicates that the different system having the same degrees of freedom behave similarly.
4. It helps in deciding whether the given number of substance remain in equilibrium or not.

Limitations of Phase rule:-

1. Phase rule canbe applied only for the system in equilibrium
2. Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.
3. All the phases of the system must be present under the same conditions of pressure and temperature
4. Solid and liquid phases must not be in finely divided state, otherwise deviation occur.

UNIT-5

FUELS AND COMBUSTION

Introduction

Fuel is a combustible substance, containing carbon as the main constituent, which on burning gives large amount of heat. During combustion, carbon and hydrogen combine with oxygen with liberation of heat.

$$C+O_2 \rightarrow CO_2 + 94\text{kcals}$$

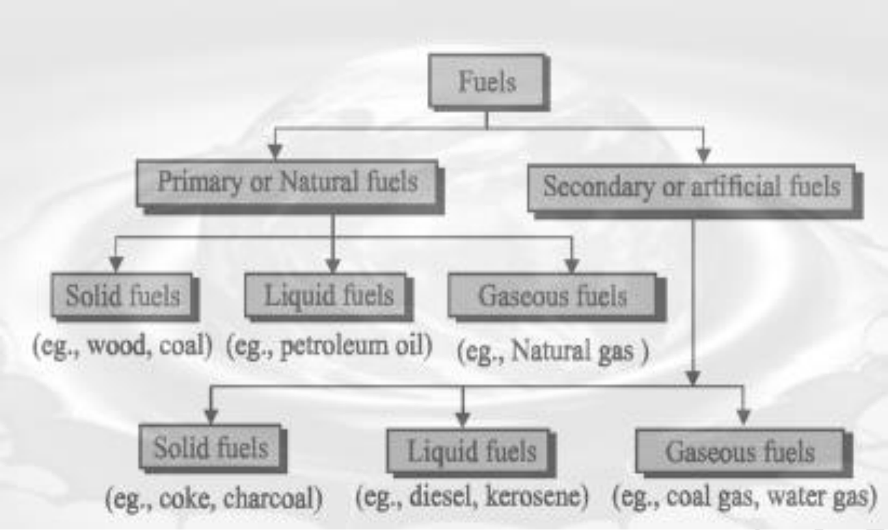
$$2H_2+ O_2 \rightarrow 2H_2O + 68.5\text{kcals}$$

Characteristics of a good fuel

1. It should be cheap and readily available.
2. It should be safe and economical for storage and transport.
3. It should not undergo spontaneous combustion.
4. It should have higher calorific value.
5. It should have moderate ignition temperature.
6. The combustion should be easily controllable.
7. It should have low moisture content, because the moisture content reduces the calorific value.
8. The products of combustion should not be harmful.
9. It should have low non combustible matter or ash content.

Classification of fuels

Fuels are classified on occurrence and physical states as follows



Calorific value

The calorific value of a fuel is the total amount of heat liberated, when a unit mass of fuel is burnt completely. Its units are kilocalorie or BTU (British Thermal unit).

Higher calorific value or Gross calorific value (G.C.V)

Gross calorific value (G.C.V) is the total amount of heat produced, when a unit quantity of the fuel is completely burnt and the products of combustion are cooled to room temperature.

Lower calorific value or Net calorific value (N.C.V)

Net calorific value (N.C.V) is defined as the net heat produced, when a unit quantity of the fuel is completely burnt and the products of combustion are allowed to escape.

The two are related as,

N.C.V = G.C.V − Latent heat of water produced

N.C.V = G.C.V – Mass of Hydrogen X 9 X latent heat of condensation of water vapour.

Dulong's formula for the Theoretical calculation of GCV and NCV.

GCV (or) HCV

$$= \boxed{\frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] \text{kcal/kg}}$$

$$\text{N C V (or) L C V} = \boxed{\left[\text{HCV} - \frac{9}{100} H \times 587\right] \text{kcal/kg}}$$

Calculation of GCV and NCV

1. **Calculate the net calorific value if the gross calorific value is 2550 kcal/kg and contains 6.5% H.**

NCV = GCV – [0.09H x 587] kcal/kg

= 2550 – [0.09 x 6.5 x 587]

NCV = 2206.6 kcal/kg.

2. **Calculate Gross and Net calorific values of a coal having the following composition.**

C = 80%; H = 7%; O = 3%; S = 3.5%; N = 2.5% and Ash = 4.4%

Solution

(i) GCV

GCV = 1/100{8080 x % of C + 34500 (% H - % O/ 8) + 2240 x % S}

= 1/100{8080 x 80 + 34500 (7- % 3/ 8) + 2240 x 3.5}

= 8080 x 80+345(7-0.375) + 2240x 3.5

= 6464 + 2285.6 + 78.4

= 8828kcals/kg.

(ii) NCV

$$\begin{aligned} NCV &= GCV - (0.09\,H \times 587) \\ &= 8828 - (0.09 \times 7 \times 587) \\ &= 8828 - 369.8 \\ &= \mathbf{8458.2 kcals/kg.} \end{aligned}$$

SOLID FUEL

Coal

Coal is an important primary solid fuel that has been formed as a result of alternation of vegetable matter under some favorable condition.

This process of alteration of vegetable matter to coal is called coalification.

Classification of coal

Coal is classified on the basis of its rank/ grade.

Wood →Peat → lignite → Bituminous coal → Anthracite

Analysis of coal

1.Proximate Analysis of Coal

Determination of % of

Moisture content | Volatile matter | Ash content | Fixed carbon

i) **Moisture content :**

$$\text{1 g of air-dried coal} \xrightarrow[\text{1 hr, electric hot-air oven}]{\Delta,\ 100 - 105^0c} \text{Loss in weight of coal is calculated}$$

$$\%\ \text{of Moisture in coal} = \frac{\text{Loss in weight of the coal}}{\text{Weight of air-dried coal}} \times 100$$

ii) **Volatile Matter :**

$$\text{Moisture removed coal} \xrightarrow[\text{covered with lid} \quad 950 \pm 20^0\text{c}]{\text{Muffle furnace, 7 min}} \text{Loss in weight of coal is noted}$$

$$\%\ \text{of volatile matter in coal} = \frac{\text{Loss in weight of the coal}}{\text{Weight of moisture free coal}} \times 100$$

iii) **Ash content :**

$$\begin{array}{c}\text{Moisture \& Volatile matter} \\ \text{removed coal}\end{array} \xrightarrow[\textbf{without}\text{ lid} \quad 700 \pm 50^0\text{c}]{\text{½ hr}} \text{Loss in weight of coal is noted}$$

$$\%\ \text{of ash content in coal} = \frac{\text{Loss in weight of the coal}}{\text{Weight of dried coal}} \times 100$$

iv) **Fixed Carbon :**

% of Fixed carbon in coal = 100 - % of (Moisture content + Volatile matter + Ash content)

Significance of Proximate Analysis

A good quality coal has **High calorific value.** For High calorific value, coal must contain

1. Low Moisture content
2. Low Volatile matter
3. Low Ash content
4. More Fixed Carbon

S.NO	CONTENTS	SIGNIFICANCE
1.	High Moisture	i) Reduces Calorific value of coal ii) Consumes more heat
2	High volatile matter	i) Reduces Calorific value of coal ii) Burns and produces high smoke
3	High Ash content	i) Reduces Calorific value of coal ii) Blocks the air supply through the fuel
4	More Fixed carbon	i) Greater calorific value ii) Helps in designing the furnace

2.Ultimate Analysis of Coal

Determination of % of

Carbon & Hydrogen　Nitrogen Sulphur　Ash　Oxygen

i) Carbon & Hydrogen content :

$$\text{A known amount of coal} \xrightarrow[\text{Combustion Apparatus}]{O_2} \text{Formation of } CO_2 \text{ \& } H_2O$$

Reactions :

$$C + O_2 \longrightarrow CO_2$$

$$H_2 + ½ O_2 \longrightarrow H_2O$$

KOH Tube :

- CO_2 vapour is absorbed
- Increase in weight of the KOH tube = Weight of CO_2

Anhydrous $CaCl_2$ Tube :

- H_2O vapour is absorbed
- Increase in weight of the $CaCl_2$ tube = Weight of H_2O

From the weight of CO_2 & H_2O, % of Carbon & Hydrogen is calculated.

$$\text{\% of Carbon in coal} = \frac{12 \times \text{Increase in weight of the KOH tube}}{44 \times \text{Weight of coal sample}} \times 100$$

$$\text{\% of Hydrogen in coal} = \frac{2 \times \text{Increase in weight of the } CaCl_2 \text{ tube}}{18 \times \text{Weight of coal sample}} \times 100$$

ii) **Nitrogen Content (Kjeldahl’s method) :**

Powdered Coal $\xrightarrow[K_2SO_4 \text{ Catalyst}]{\text{Con.}H_2SO_4,\ \Delta}$ Ammonium sulphate (clear solution)

$\downarrow$ NaOH

Neutralisation takes place $\xleftarrow{N/10 \text{ Std. HCl}}$ NH3

Reactions :

$2N + 3H_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$(NH4)_2SO_4 + 2NaOH \longrightarrow 2\,NH_3 + Na_2SO_4 + 2\,H_2O$

$NH_3 + HCl \longrightarrow NH_4Cl$

From the volume of HCl consumed,
% of Nitrogen is calculated.

$$\%\text{ of Nitrogen in coal} = \frac{14 \times \text{Volume of acid consumed} \times \text{Normality of acid}}{1000 \times \text{Weight of coal sample}} \times 100$$

i) Sulphur Content :

A known amount of coal $\xrightarrow[\text{Bomb calorimeter}]{\text{Burnt in}}$ Sulphate

$\downarrow$ Extracted with water

Extract

$\downarrow$ BaCl2

Filtered, dried & weighed $\longleftarrow$ BaSO4

From the weight of BaSO4, % of Sulphur is calculated.

$$\%\text{ of Sulphur in coal} = \frac{32 \times \text{Weight of BaSO4 tube}}{233 \times \text{Weight of coal sample}} \times 100$$

iv) **Ash content** :

$$\text{Moisture \& Volatile matter removed coal } \textbf{without} \text{ lid} \xrightarrow[700 \pm 50^{0}c]{\frac{1}{2}\ hr} \text{Loss in weight of coal is noted}$$

$$\%\ \text{of ash content in coal} = \frac{\text{Loss in weight of the coal}}{\text{Weight of dried coal}} \times 100$$

v) **Oxygen content :**

% of Oxygen in coal = 100 - % of (Carbon + Hydrogen + Sulphur+ Ash content)

Significance of Ultimate Analysis

A good quality coal has **High calorific value.** For High calorific value, coal must contain

1. High Carbon & Hydrogen content
2. Low Nitrogen content
3. Low Sulphur content
4. Low oxygen content

S.NO	**CONTENTS**	**SIGNIFICANCE**
1	High Carbon & Hydrogen	i) Increases calorific value of coal ii) Helps in the classification of coal
2	High Nitrogen	No calorific value

3	High Oxygen content	i) Low calorific value ii) Increases moisture holding capacity of coal
4	High Sulphur content	i) Increases calorific value ii) It produces SO_2 , SO_3 and corrosion takes place

Carbonisation

When coal is heated strongly in the absence of air, the volatile matter escapes out and a hard, strong, porous and coherent mass, called coke is formed. This process is called carbonization.

Types of carbonization

1. Low temperature carbonization (LTC)

   It is carried out 500 - 700°C. The coke formed is soft and mechanically less strength. The yield is 75 – 85%. The gaseous product formed has low calorific value.

2. High temperature carbonization (HTC)

   It is carried out 900 - 1200°C. The coke formed is hard and mechanically high strength. The yield is 65 – 75%. The gaseous product formed has high calorific value.

Metallurgical Coke

When bituminous coal is heated strongly in the absence air, the volatile matter removed and the mass becomes hard, strong, porous and coherent which is called Metallurgical Coke.

Characteristics / Requisites of metallurgical coke.

i) Purity : Low moisture, ash and sulphur contents in metallurgical coke

ii) High Porosity

iii) High Mechanical strength

iv) High Calorific value

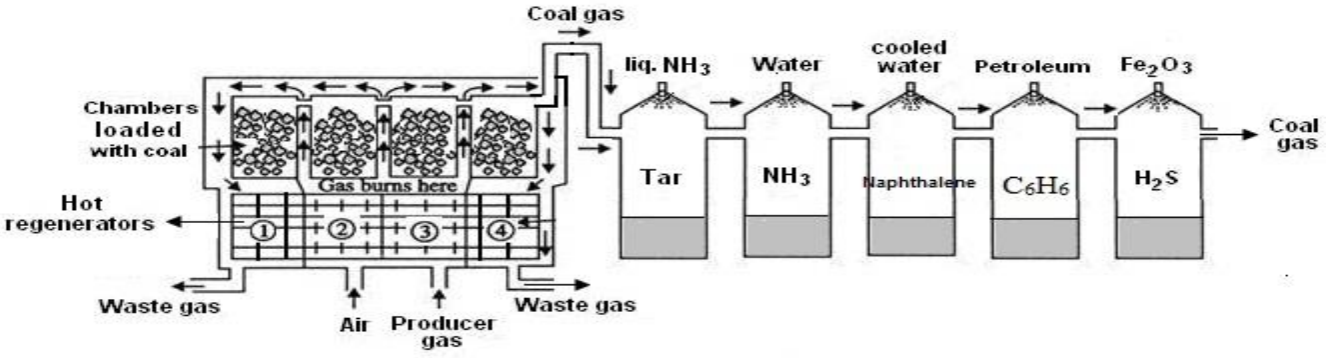
v) Easy combustibility

Manufacture of metallurgical coke by Otto-Hoffman's by-product oven method.

Otto-Hoffmann oven consists of a number of series of narrow silica chambers. Each chamber is provided with a charging hole at the top. The oven is provided with iron door at each end for discharging the coke.

Coal is charged into chambers and the doors are closed. The chambers are heated by a mixture of preheated air and producer gas at 1200^oC. The coal undergoes combustion and liberates waste gases. The heat of the waste gases are used for heat regeneration of oven before leaving the chamber. Therefore, heating of the oven is continued till the liberation of volatile gases is completed.

After 24 hours, the coke is removed from the oven and quenched with water. The yield of coke is about 75%. The valuable by- products like coal gas, tar, ammonia, H_2S, benzene etc., are recovered.



Recovery of by-products:

(i) *Tar:*

The flue gases are first passed through a tower in which liquor ammonia is

sprayed. Tar and dust get dissolved and collected in a tank below, which is heated by
steam coils to recover back the ammonia sprayed.

(ii) *Ammonia:*

The gases are then passed through another tower in which water is sprayed. Here ammonia gets converted to NH_4OH.

(iii) *Naphthalene*:

The gases are again passed through a tower, in which cooled water is sprayed.
Here naphthalene gets condensed.

(iv) *Benzene:*

The gases are passed through another tower, where petroleum is sprayed. Here benzene gets condensed to liquid.

(v) *Hydrogen Sulphide*:

The remaining gases are then passed through a purifier packed with moist Fe_2O_3. Here H_2S is retained.

The final gas left out is called coal gas which is used as a gaseous fuel.

Advantages of Otto Hoffman's process:

1. Valuable by products like ammonia, coal gas, naphthalene etc. are recovered.
2. The carbonization time is less.
3. Heating is done externally by producer gas.

II Liquid Fuels

Petroleum

Petroleum is naturally occurring liquid fuel of dark brown or black coloured viscous oil obtained under the earth's crust consisting a mixture of paraffinic, olefinic and aromatic hydrocarbons with small amount of inorganic compounds such as nitrogen, oxygen and sulphure.

Classification of Petroleum

It is classified into three types.

1. Paraffinic – base type of Petroleum
2. Naphthenic or asphaltic base type of Petroleum
3. Mixed base type of Petroleum.

Refining of petroleum or crude oil.

Crude oil : Mixture of oil, water and unwanted impurities.

Refining of crude oil consists of 3 steps.

Step 1: Removal of water impurities:

$$\text{Crude oil} \xrightarrow[\text{Flow between two highly charged electrodes}]{\textbf{Step-1}} \text{Separation of water by Cottrell‟s process}$$

$$\downarrow$$

$$\text{water removed crude oil}$$

Step 2: Removal of sulphur impurities:

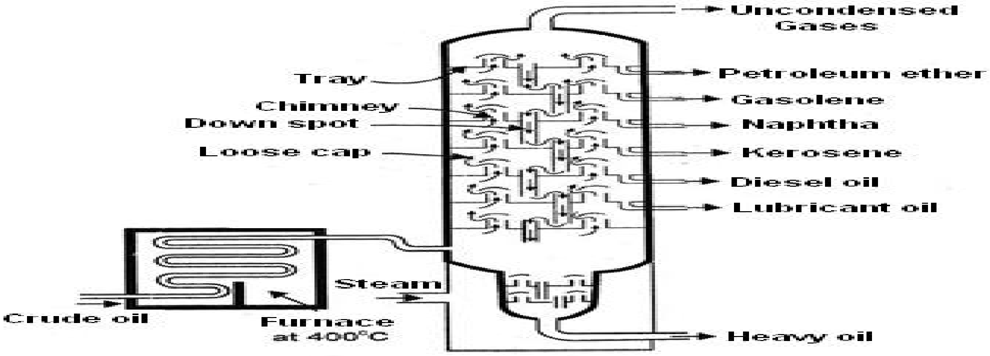
$$\text{water removed crude oil} \xrightarrow[\text{CuO}]{\textbf{Step - 2}} \text{CuS (removed)}$$

$$\downarrow$$

$$\text{Purified crude oil}$$

Step 3: Fractional distillation

After the removal of water and sulphur compounds, the purified crude oil is then heated to about 300° – 400℃ in an iron retort, where the volatile constituent of oil gets vapourised except the residue. The hot vapors are then passed into the bottom of a fractionating column. Fractions having **higher** boiling point condense at **lower** trays where fractions having **Lower** boiling point condense at **higher** trays. Various fractions obtained at different trays are given in table. The gasoline obtained by this fractional distillation is called ***straight-run gasoline*.**



S.No.	Fraction	Boiling range	Composition	Uses
1.	Uncondensed gases	Below 30℃	$C_1 – C_4$	As a fuel under the name of LPG.
2.	Petroleum ether	30 – 70℃	$C_5 – C_7$	As a solvent.
3.	Gasoline or petrol	40 – 120℃	$C_5 – C_9$	Fuel for internal combustion engines.
4.	Naphtha or solvent spirit	120 – 180℃	$C_9 – C_{10}$	As a solvent in paints and in dry cleaning.
5.	Kerosene oil	180 – 250℃	$C_{10} – C_{16}$	Fuel for stoves and jet engines.
6.	Diesel oil (or) fuel oil	250 – 320℃	$C_{15} – C_{18}$	Diesel engine fuel.
7.	Heavy oil	320 – 400℃	$C_{17} – C_{30}$	Fuel for ships and for production of gasoline by cracking.

Synthetic Petrol

The preparation of liquid fuels (petrol) from solid coal is called synthetic petrol. The process is named hydrogenation of coal.

Manufactured of synthetic petrol by Bergius process.

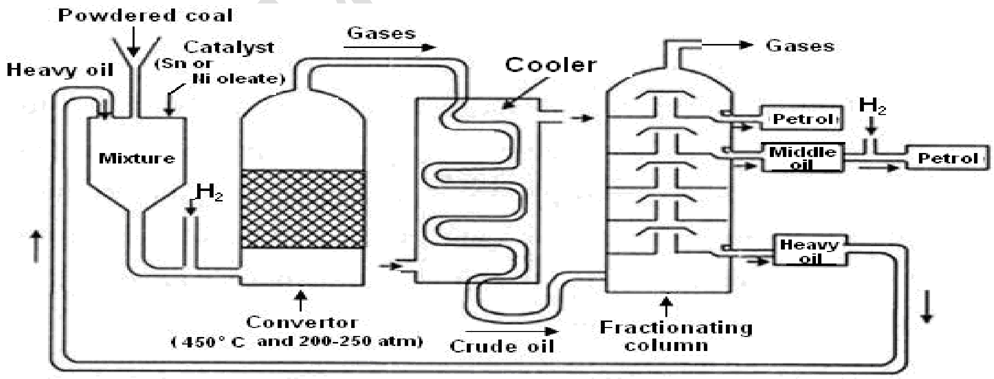
Coal - 4.5% hydrogen
Petroleum - 18% hydrogen

When compared to petroleum, coal is a hydrogen deficient compound. If coal is heated with hydrogen under high temperature and high pressure, solid coal will be converted into liquid fuel. It is called hydrogenation of coal and the liquid fuel obtained is called synthetic petrol.

Bergius process for manufacture of synthetic petrol:

In this method, the finely powdered coal is made into a paste with heavy oil and a powder of catalyst (tin or nickel oleate). This mixture is sent to a converter and heated with hydrogen gas at 450℃ under a pressure of 200 – 250 atm for about 1.5 hours.

During this process, hydrogen combines with coal to form saturated higher hydrocarbons, which decomposes at higher temperature to yield mixture of low boiling hydrocarbons.



The mixture is sent into the cooler, where the crude oil is obtained. The crude oil is then fractionated to get ***(i) Gasoline (or) Petrol (ii) Middle oil (iii) Heavy oil***

The middle oil is further hydrogenated in the vapour phase in the presence of solid catalyst to yield more petrol. The heavy oil is recycled for making paste with fresh coal dust. The yield of petrol is about 60% of the coal dust used.

Knocking

Knocking is a kind of explosion due to sudden pressure rise occurring in internal combustion engine. It can be reduced by adding TEL (Tetra Ethyl Lead).

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

Straight chain paraffins > branched chain paraffins (iso paraffins)> cycloparaffins (naphthalenes) > olefins > aromatics.

Leaded petrol:

When the petrol is mixed with Tetra ethyl lead (TEL), it is called leaded petrol.

<u>*Disadvantages of using TEL*</u>

TEL is converted to lead oxide and lead which is harmful to engine life.

It is reduced 1) by adding small amount of ethylene dibromide.

$$Pb + \begin{matrix} CH_2-Br \\ | \\ CH_2-Br \end{matrix} \longrightarrow PbBr_2\uparrow + CH_2=CH_2$$

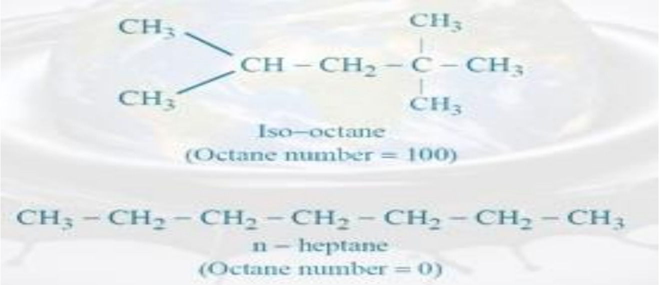
2) by using aromatic phosphates instead of TEL.

Diesel oil:

It is a high boiling fraction of crude oil between 250-320°C. It is a mixture of $C_{15} - C_{18}$ hydrocarbons. Its calorific value is 11000 Kcal/kg. It is used as good engine fuel.

Octane number

It is used to express the knocking property of petrol. Octane number is equal to the percentage of isooctane present in a mixture of n-heptane and isooctane.



Iso–octane

(Octane number = 100)

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

n – heptane

(Octane number = 0)

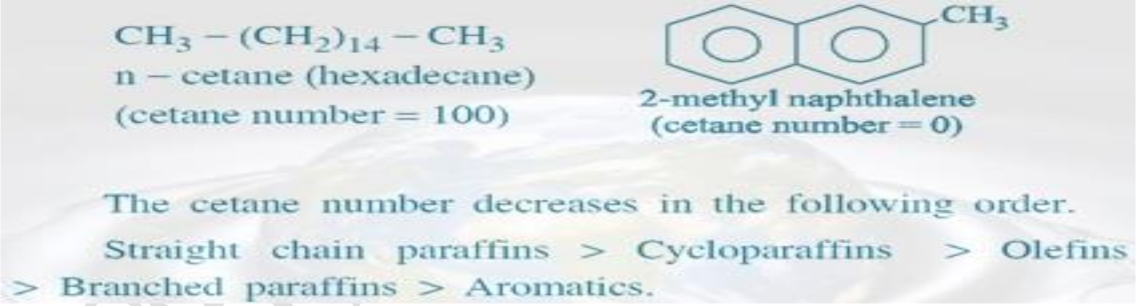
Improvement of Octane number:

i) By adding anti-knock agents like tetra ethyl lead or aromatic phosphates

ii) By mixing with petrol of higher octane number

Cetane number:

It is used to express the knocking property of diesel. Cetane number is the percentage of hexadecane (cetane) present in a mixture of hexadecane and 2-methyl naphthalene which has the same ignition lag as the fuel under test.



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

n – cetane (hexadecane)

(cetane number = 100)

2-methyl naphthalene

(cetane number = 0)

The cetane number decreases in the following order.

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

Improvement of cetane number:

Cetane value of diesel can be increased by adding dopes like ethyl nitrate, iso-amyl nitrate.

Comparison / Difference between gasoline oil and diesel oil

S.No.	Petrol (Gasoline) oil	Diesel oil
1.	Low boiling fraction of petroleum, C_5 –C_9 hydrocarbons.	High boiling fraction of petroleum, C_{15} – C_{18} hydrocarbons.
2.	It is a fuel for Spark Ignition (SI) engine.	It is a fuel for Compression Ignition (CI) engine.
3.	Knocking tendency of petrol is measured in octane number or rating.	Knocking tendency of diesel is measured in cetane number or rating.
4.	Knocking is due to premature ignition.	Knocking is due to delay in the ignition.
5.	Anti-knocking is improved by the addition of Tetra Ethyl Lead (TEL).	Anti-knocking is improved by Ethyl nitrate.
6.	Higher amount of pollutants.	Lesser amount of pollutants.
7.	Consumption is more.	Consumption is less.
8	Thermal efficiency is low.	Thermal efficiency is high.

III Gaseous Fuels

CNG (Compressed Natural Gas):

When the natural gas is compressed under pressure of 1000 atm , it is called CNG.

Its calorific value is **1200 – 1400 Kcal/m^3**.

Properties of CNG:

(i) It is a light weight gas, cheapest and eco friendly

(ii) The ignition temperature is 540°C

(iii) Less expensive than petrol and diesel.

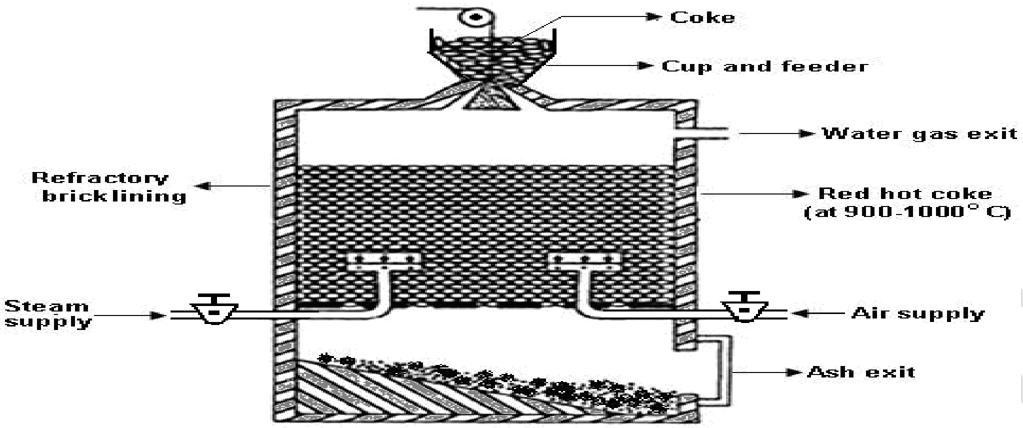
(iv) It produces less CO and hydrocarbon emission.

(v) For ignition, it requires more air.

Uses of CNG:

Used as an alternate to petrol and diesel for vehicles.

Advantages over other fuels:



Uses

1. Used in the synthesis of ammonia
2. Used to synthesis of gasoline.
3. Used in the manufacture of power alcohol
4. Used in the manufacture of carbureted water gas (water gas + oil gas)
5. A fuel gas.

Power alcohol:

When 10 % absolute ethyl alcohol is blended with petrol , it is called power alcohol. Its calorific value is **7000 Kcal./Kg**

Manufacture: It consists of 2 steps.

Step-I : Synthesis of ethyl alcohol

Ethyl alcohol is synthesized by fermentation of carbohydrates (sugar material).

Example: Fermentation of molasses with yeast generates alcohol.

$$\underset{\text{Glucose (Sugar)}}{C_6H_{12}O_6} \xrightarrow{\text{Yeast}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

It yields only above 20% alcohol. The concentration of alcohol can be increased up to 97.6% by fractional distillation. It yields rectified spirit.

Step-II : Synthesis of power alcohol

The last traces of water from rectified spirit is removed by distilling the alcohol with benzene or dehydrating agent. Then, 10 % absolute ethyl alcohol is blended with petrol to form power alcohol.

Properties:

1. Low calorific value 2. High octane number
2. 3. Good anti-knocking property
4. High compression ratio 5. Generates 10% more power than petrol

Uses: Very good fuel.

Advantages:

(i) Cheaper than petrol (ii) Biodegradable fuel

(iii) Minimum emission of greenhouse gases (iv) Decreases the damage of ozone layer (v) Burns more cleanly

Disadvantages of power alcohol:

(i) Production of ethanol requires significant energy and land.

(ii) Fuels with more than 10% ethanol may cause corrosion.

(iii) It requires specially designed engine. (iv) It causes starting trouble.

(v) It may undergo oxidation to give acetic acid, which corrodes engine part.

Biodiesel :

Biodiesel is the methyl esters of fatty acids derived from vegetable oils or animal fats.

Problems of using vegetable oil directly:

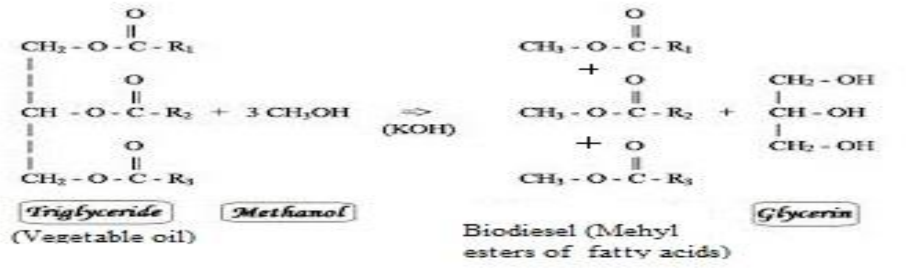
- Viscosity and molecular weight of vegetable oils are higher than diesel.

- Atomization is very poor, hence incomplete combustion.
- It causes deposit formation on engine.
- Misfire and ignition delay.

Manufacture: Trans-esterification or Alcoholysis

Biodiesel fuel is produced from a variety of crops like soya bean, mustard, flax, sunflower, palm oil, hemp, jatropha, rape seed, canola and animal fats.

Biodiesel is synthesized by trans-esterification of vegetable oil and fat by methanol in the presence of catalyst (NaOH, KOH) to give monomethyl esters of fatty acids and glycerin.



Uses:

It is a pure fuel. It can be used in existing diesel engines without modification.

Advantages:

(i) Biodegradable fuel (ii) Renewable fuel (iii) Less expensive (iv) Less toxic (v) Less smoke emissions (vi) Clean-burning fuel (vii) Best engine performance.

Disadvantages: (i) It requires energy to produce biodiesel (ii) It gels in cold weather (iii) It degrades and soften the rubber (iv) It absorbs the water from atmosphere (v) It decreases the horse power of engine.

hence 2.34 kg of O_2 supplied = (100/23) x 2.34 = 10.174kg of air.

The amount of air required by the
complete combustion of 100kg of fuel = 10.174 x 100 = **1017.4kg** of air.

IGNITION TEMPERATURE

It is the minimum temperature at which a fuel will burn smoothly.

Spontaneous Ignition Temperature (SIT)

It is the minimum temperature at which the fuel catches fire spontaneously without external heating.

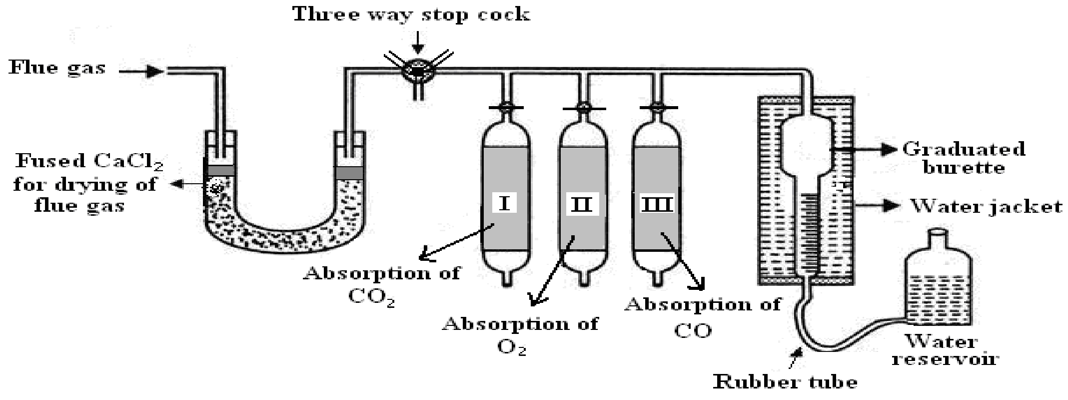
Explosive range

It is the range of composition of a gas-air mixture that will burn if an ignition source is introduced. Beyond which the gas - air mixture will not ignite and continue to burn.

e.g Natural gas – lower limit 5
- upper limit 14.

Flue gas analysis by Orsat apparatus method.

The mixture of gases (like CO_2, O_2, CO and N_2) coming out from the combustion chamber is called flue gas.



Principle :

This method is based on the absorption principle. The gases like CO_2 , O_2 and CO are absorbed by KOH, alkaline pyrogallol and ammoniacal cuprous chloride solutions respectively.

Significance :

i) It gives an idea about the complete combustion of fuel or not.

ii) If CO is high in the flue gas, it shows incomplete combustion of the fuel and

short supply of oxygen.

iii) If CO_2 and O_2 are high in the flue gas, it shows complete combustions of the fuel and excess supply of oxygen.

Description of Orsat's apparatus

- It consists of a horizontal tube having three way stop cock.
- One end of the tube is connected to a U- tube containing fused $CaCl_2$.
- Another end of the tube is connected to a graduated burette.
- The burette is surrounded by a water jacket.
- The lower end of the burette is connected by a water reservoir.
- The middle of the horizontal tube is connected with 3 bulbs (I, II and III) for

absorbing flue gases as follows:

i) Bulb I - KOH solution and it absorbs only CO_2

ii) Bulb II - alkaline pyrogallol solution and it absorbs only O_2

iii) Bulb III - ammoniacal cuprous chloride solution and it absorbs CO.

Working of Orsat apparatus:

- The three – way stop cock is opened.

- The burette is filled with water, by raising the water reservoir to remove air from the burette.
- Then, the flue gas is taken in the burette upto 100 cc by raising and lowering the reservoir.
- The three way stop cock is now closed.

Absorption of gases in bulbs

i) Absorption of CO_2

- The stopper of the bulb I is opened.
- The flue gas is allowed to pass into the bulb I.
- CO_2 present in flue gas is absorbed by KOH.
- It is repeated several times.
- The decrease in volume of burette indicates the volume of CO_2 .
- Now the stopper is closed.

ii) Absorption of O_2

- The stopper of the bulb II is opened.
- The flue gas is allowed to pass into the bulb II.
- O_2 present in flue gas is absorbed by alkaline pyrogallol.
- It is repeated several times.
- The decrease in volume of burette indicates the volume of O_2.
- Now the stopper is closed.

iii) Absorption of CO

- The stopper of the bulb III is opened.
- The flue gas is allowed to pass into the bulb III.
- CO present in flue gas is absorbed by ammoniacal cuprous chloride solution. It is repeated several times.

- The decrease in volume of burette indicates the volume of CO.
- Now the stopper is closed.

iv) Nitrogen

The remaining gas in the burette after the absorption of CO_2, O_2 and CO is nitrogen.

The % of N_2 in flue gas = [100 − (% of CO_2 + % of O_2 + % of CO)]

UNIT - 5

ENERGY SOURCES

INTRODUCTION

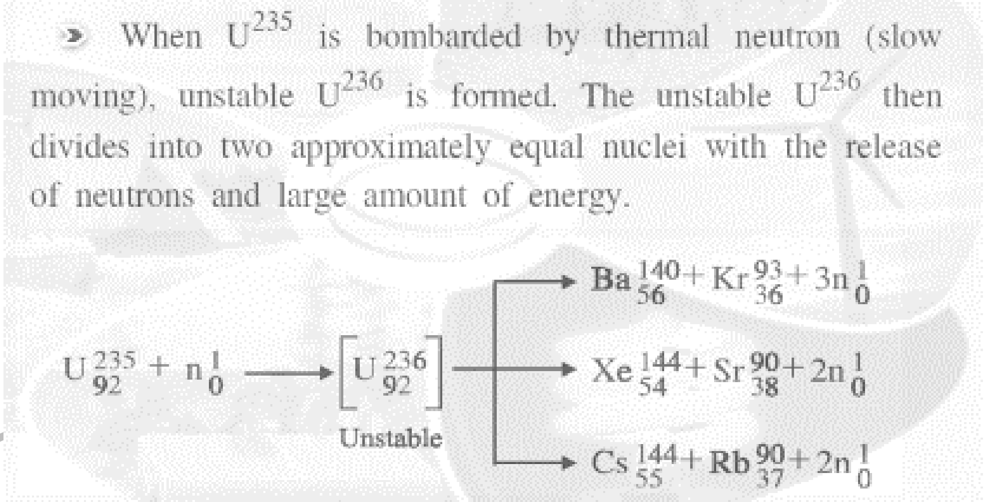
We mainly depend on the conventional sources of energy like coal, petroleum, gas, etc. These sources are limited in quantity and can be exhausted in future. To overcome this energy crisis, the renewable energy sources can be used.

NUCLEAR FISSION

Nuclear Fission is a process of splitting heavier nucleus into two or more smaller nuclei on bombardment by thermal neutrons with simultaneous liberation of large amount of energy.

$$ {}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{36}Kr^{92} + {}_{56}Ba^{141} + 3\ {}_{0}n^{1} + \text{energy} $$

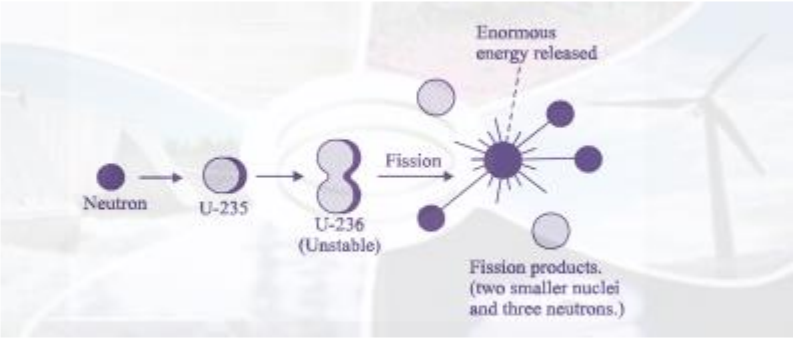
Mechanism of fission



- When U^{235} is bombarded by thermal neutron (slow moving), unstable U^{236} is formed. The unstable U^{236} then divides into two approximately equal nuclei with the release of neutrons and large amount of energy.

$$ U^{235}_{92} + n^{1}_{0} \longrightarrow \underset{\text{Unstable}}{\left[U^{236}_{92}\right]} \longrightarrow \begin{cases} Ba^{140}_{56} + Kr^{93}_{36} + 3n^{1}_{0} \\ Xe^{144}_{54} + Sr^{90}_{38} + 2n^{1}_{0} \\ Cs^{144}_{55} + Rb^{90}_{37} + 2n^{1}_{0} \end{cases} $$

Illustration of fission



Characteristics:

1. Heavy nucleus splits into two or more smaller nuclei.
2. Two or more neutrons are produced by each fission.
3. Large amount of energy is produced.
4. All the fission products are radioactive and emits β and γ rays.
5. The atomic weights of fission products ranges from about 70 to 160.
6. All fission reactions are self-propagating chain-reactions.
7. It can be controlled and maintained by control rods - nuclear reactor.
8. *Multiplication factor*:

It is the no of neutrons, resulting from a single fission. If it is less than 1 , chain reaction does not take place.

Classification of nuclear fission:

There are 2 types.

(i) Uncontrolled fission reaction:

If a nuclear fission reaction is made to occur in an uncontrolled manner, it is an uncontrolled nuclear fission.

Eg. Atom bomb

(ii) Controlled fission reaction:

If a nuclear fission reaction is made to occur in an controlled manner, it is an controlled nuclear fission.

Eg. Nuclear reactor

Advantages of nuclear fission energy:

- Nuclear energy requires very small amount of nuclear fuel
- Once the nuclear fission reaction starts, we get nuclear energy over a long period of time in a nuclear reactor.

Disadvantages of nuclear fission energy:

- It causes nuclear pollution.
- It causes genetic mutation.
- Safe disposal of nuclear waste is difficult.

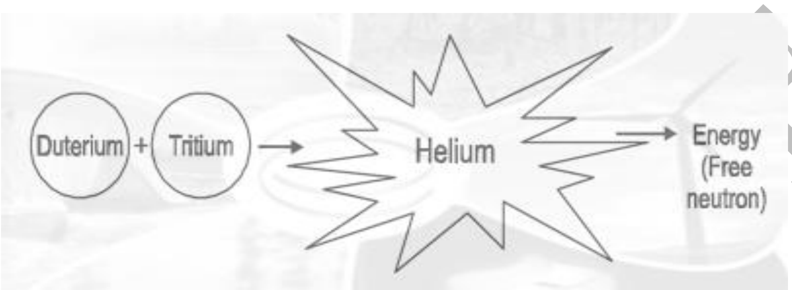
NUCLEAR FUSION

It is the process of combination of lighter nuclei into heavier nucleus with simultaneous liberation of large amount of energy.

(e.g) solar system

$_1H^2 + {}_1H^2 \rightarrow {}_2He^4 +$ Energy

$_1H^2 + {}_1H^3 \rightarrow {}_2He^4 + {}_0n^1$



The energy of stars and sun is arised from the fusion reactions in which hydrogen is converted into helium. The fusion reactions can start only when the atoms are heated to very high temperatures. Such a high temperature required is produced by fission reaction.

Eg. In hydrogen bomb, fusion occurs by the fission of atom bomb which acts as trigger.

Characteristics of nuclear fusion:

- There is no limit on the amount of nuclear fusion that can occur.
- It is possible only when the distance between the nuclei is of the order of one Fermi.
- The amount of energy in fusion is four times greater than fission.
- Sufficient amount of kinetic energy must be provided.
- Only lighter nuclei can undergo nuclear fusion reaction.

Disadvantages of fusion:

- Utilization of fusion energy is problem, because no known material can withstand at high temperature.
- It cannot be controlled easily.
- Design of thermonuclear fusion power plant is very difficult.

Difference between nuclear fission and fusion

S.NO	**NUCLEAR FISSION**	**NUCLEAR FUSION**
1.	It is the process of breaking of heavier nucleus into smaller nuclei	It is the process combination of smaller nuclei in to a heavy nucleus
2.	It emits radioactive rays	It does not emit rays
3.	It occurs at ordinary temperature	It occurs at high temperature
4.	The mass number and atomic number of new elements are lower than that of parent nucleus	The mass number and atomic number of product is higher than that of starting elements
5.	It gives chain reaction	It does not give chain reaction
6.	It emits neutron	It emits positrons
7.	It can be controlled	It cannot be controlled
	Eg: Atom bomb	Eg: Hydrogen bomb

NUCLEAR CHAIN REACTIONS

A fission reaction, where the neutrons from the previous step continue to propagate and repeat the reaction is called nuclear chain reaction.

Criteria for nuclear chain reaction:

1. For continuous nuclear chain reaction, sufficient amount of ${}_{92}U^{235}$ must be present to capture the neutrons. Otherwise neutrons will escape from the surface.

a) *Critical mass*:

The minimum amount of fissionable materials ${}_{92}U^{235}$ or Pu^{239} required to continue the nuclear chain reaction is called critical mass.

b) *Super- Critical mass* :

If the mass of the fissionable material ${}_{92}U^{235}$ is more than the critical mass, then it is called super- critical mass.

c) *Sub- Critical mass*:

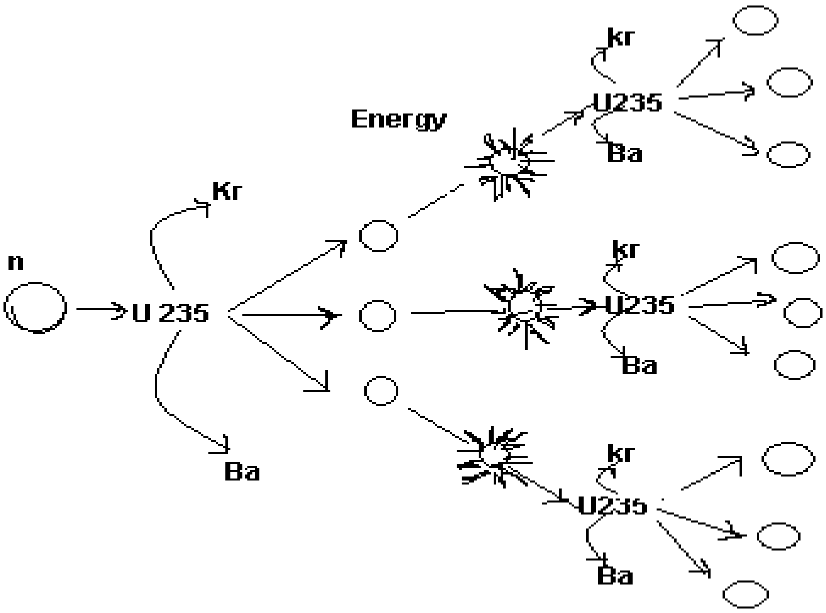
If the mass of the fissionable material $_{92}U^{235}$ is lesser than the critical mass, then it is called sub- critical mass.

2. The super or sub critical mass will hinder the propagation of the chain reaction.

Illustration of the Nuclear chain reaction:

When $_{92}U^{235}$ nucleus is bombarded by thermal neutron, it undergoes the reaction with release of three neutrons.

$$_{92}U^{235} + _{0}n^{1} \rightarrow _{36}Kr^{92} + _{56}Ba^{141} + 3\ _{0}n^{1} + \text{energy}$$



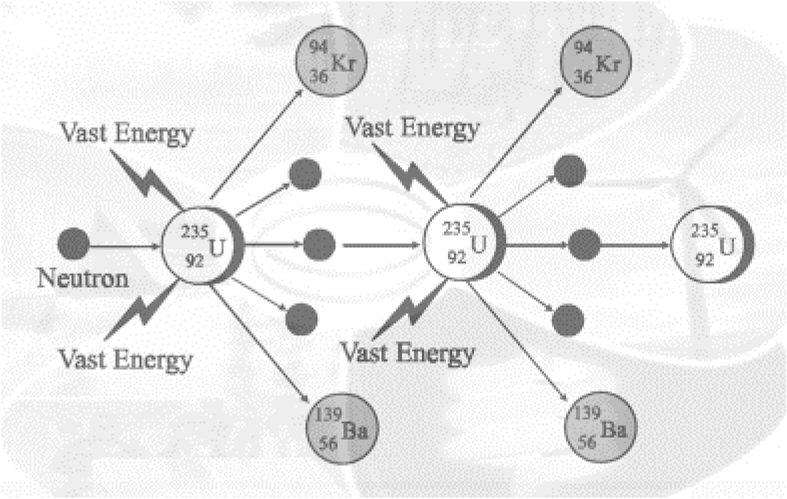
Each of the three neutrons, produced in the reaction, strikes another $_{92}U^{235}$ nucleus causing (3*3) 9 subsequent reactions. This is called chain reaction.

NUCLEAR ENERGY

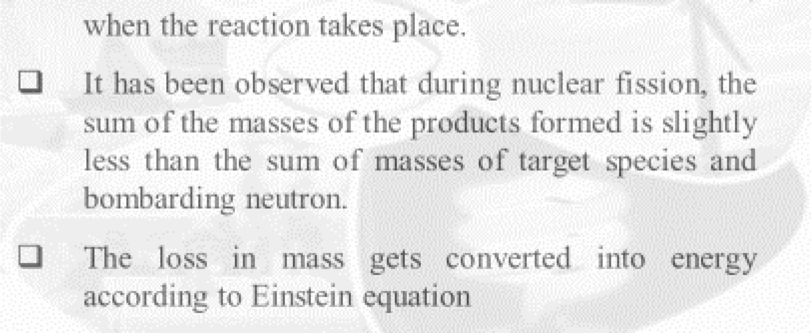
The energy released by nuclear reaction is called nuclear energy or nuclear energy.

Example:

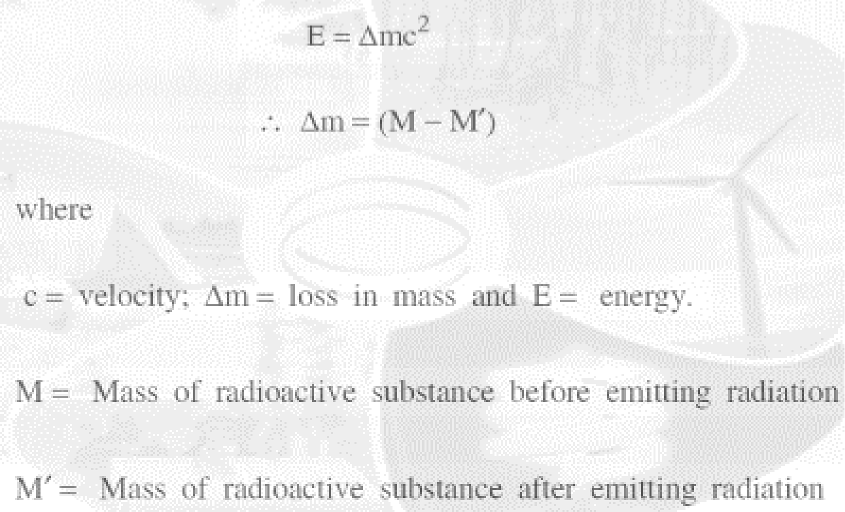
$$_{92}U^{235} + _{0}n1 \rightarrow _{36}Kr^{92} + _{56}Ba^{141} + 3\ _{0}n^{1} + \text{energy}$$



Causes of the release of nuclear energy:



- ☐ The enormous amount of energy released during the nuclear fission is due to the loss in some mass, when the reaction takes place.
- ☐ It has been observed that during nuclear fission, the sum of the masses of the products formed is slightly less than the sum of masses of target species and bombarding neutron.
- ☐ The loss in mass gets converted into energy according to Einstein equation



$$E = \Delta mc^2$$

$$\therefore \quad \Delta m = (M - M')$$

where

c = velocity; Δm = loss in mass and E = energy.

M = Mass of radioactive substance before emitting radiation

M′ = Mass of radioactive substance after emitting radiation

Hazards of using nuclear energy:

- Nuclear radiation can damage the structure of cells in human body.
- It causes diseases like cancer and blindness.
- It causes genetic disorder

- It causes sterility in young generation

Applications of nuclear energy:

- Used as eco-friendly energy resources
- Used for electricity generation
- The water discharged from the nuclear reactors is free from radiation and is clean enough to conserve animals
- Health care:

  Used in treatment of cancer.

  Eg. Radioactive isotopes
- Used for sterilization to destroy microorganism
- Used to control agricultural pests

NUCLEAR REACTOR

Nuclear reactor is a device used to produce electricity in which nuclear fission takes place in a controlled rate.

Components of a Nuclear Power Plant (Or) Light Water Nuclear Power Plant

1. Reactor core
2. Fuel elements
3. Moderator
4. Coolant
5. Control rod
6. Pressure vessel
7. Protective shield
8. Turbine

1. Reactor core

It consists of fuel elements, moderator, coolant and control rods.

(i) Fuel elements:

They are of fissile isotope . Used in the form of rods or strips.

Example: $_{92}U^{235}$, $_{94}Pu^{239}$

Functions:

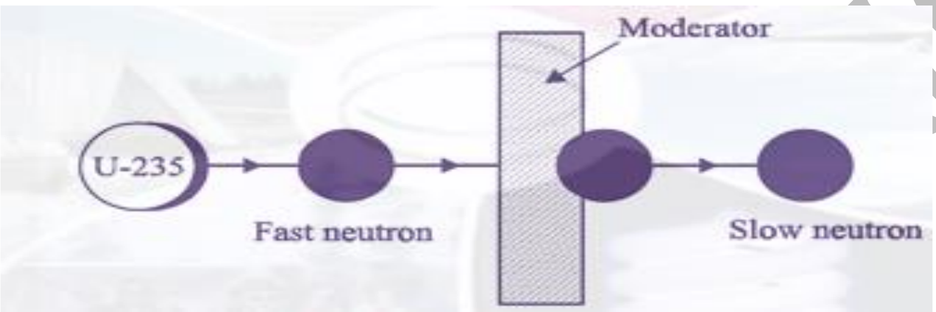
(i) It produces high heat energy.

(ii) It produces neutron for nuclear chain reaction.

(ii)Moderators:

These are used to convert the fast moving neutrons (1 MeV to 0.25 eV) into slow moving neutron by colliding with them.

Example: Ordinary water, Heavy water, Graphite, Beryllium



(iii) Coolants:

The heat produced inside the reactor is absorbed by the coolant. It is circulated, enters at the base and exit at the top.

Example: Ordinary Water, heavy water, liquid metal (Na, K), organic liquids.

(iv) Control rods (Movable rods) :

These are used to control the fission rate . It is suspended between fuel rods. If the rods are inserted inside, they will absorb more $_0n^1$, reaction becomes very slow. If the rods are raised, reaction becomes very fast.

Example: $_5 B^{10}$, $_{43}Cd^{113}$

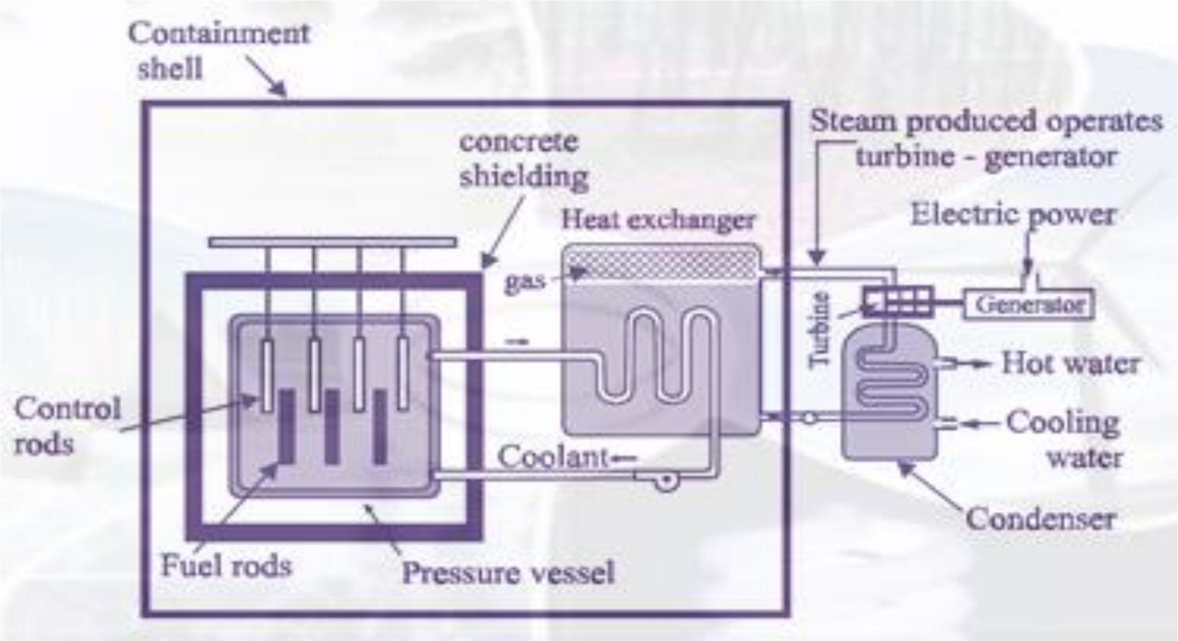
$$_{43}Cd^{113} + _0n^1 \rightarrow _{43}Cd^{114} + \gamma\text{-ray}$$

$$_5 B^{10} + _0n^1 \rightarrow _5 B^{11} + \gamma\text{-ray}$$

Functions:

(i) It controls the nuclear chain reaction.

(ii) It prevents the damage of the reactor.



2. Pressure vessel:

It encloses the core and also provides the entrance and exit passages for the coolant.

Function:

It withstands the pressure as high as 200 kg/cm^2 .

3. Protective shield:

It is a thick massive concrete shield of 10 m thickness, that encloses the nuclear reactor.

Function:

It prevents the γ-rays and harmful radiation.

4. Turbine:

In heat exchanger, the heat from the coolant is exchanged to sea water and produce steam at high pressure. It is used to rotate the turbine to produce electricity.

Working:

The U^{235} is bombarded with thermal $_0n^1$ produces fission products and three secondary neutrons which initiate nuclear chain reaction. It can be controlled by control rods (B^{10}). The heat produced during fission is absorbed by coolant (light water). The hot coolant (water at 300 ° C) then goes to the heat exchanger containing sea water. The coolant transfers heat to sea water which is converted into steam , the steam then drives the turbines to generate electricity.

Disadvantages:

(i) Nuclear reactor cause nuclear pollution to environment.

(ii) The radioactive fission products release harmful radiation for several 100 years.

(iii) It causes genetic mutation.

(iv) *Problem on Disposal of radioactive waste*

Disposal of radioactive waste is a problem. It causes radioactive pollution for several hundred years. The radioactive waste is packed in concrete barrels, which are buried in the sea.

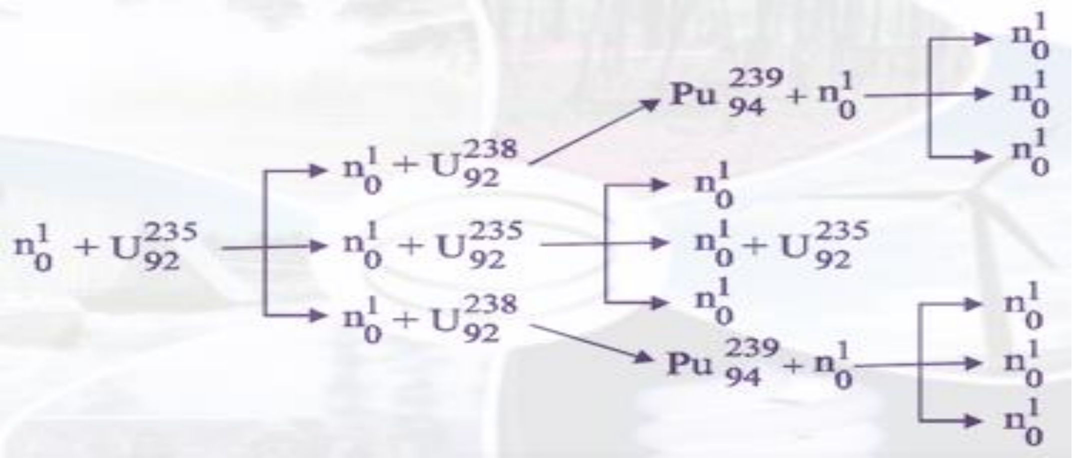
BREEDER REACTOR

Breeder reactor is a reactor which converts non-fissionable material (U^{238}, Th^{232}) into fissionable material (U^{235}, Pu^{239}). This reactor produces more fissionable material than it consumes.

Illustration

$$\underset{\text{Non –fissionable}}{{}_{92}U^{238}} + \underset{\text{(from fission)}}{{}_{0}n^{1}} \rightarrow \underset{\text{Fissionable}}{{}_{94}Pu^{239}} + 2\,e^{-}$$

$${}_{94}Pu^{239} + {}_{0}n^{1} \rightarrow \underbrace{{}_{38}Sr^{90} + {}_{56}Ba^{147}}_{\text{(fission products)}} + 3\,{}_{0}n^{1} + \text{energy}$$



Out of three neutrons emitted in the fission of $_{92}U^{235}$, only one is used in propagating the fission chain with U^{235}. The other two neutrons are allowed to react with $_{92}U^{238}$. Thus, two fissionable atoms of Pu^{239} are produced for each atom of U^{235} consumed. So breeder reactor produces more fissionable materials than it consumes.

Significance:

(i) The non-fissionable nucleides converted into fissile nucleides .

(ii) As regeneration of fissile nucleides, efficiency increases.

SOLAR ENERGY CONVERSION

Solar energy conversion is the process of conversion of direct sunlight into thermal energy and electrical energy.

Two methods:

1. Photo conversion
2. Thermal conversion

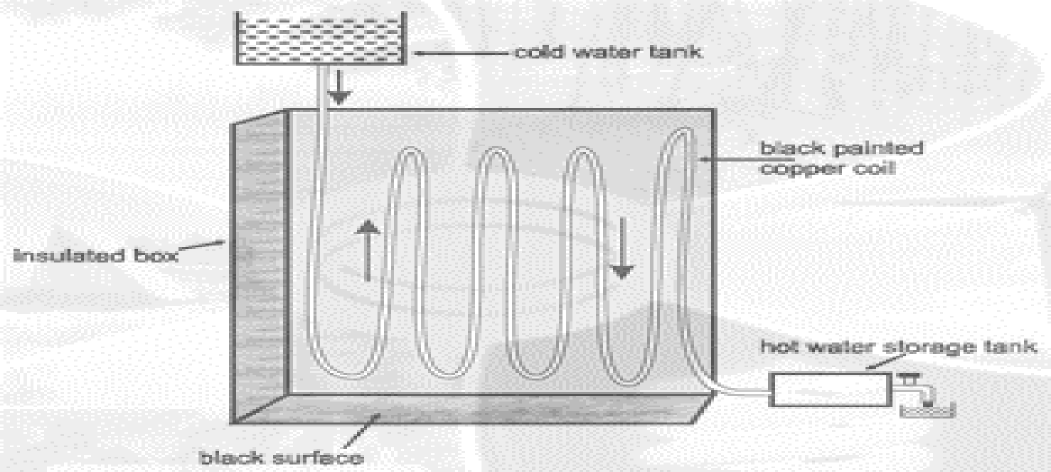
THERMAL CONVERSION OF SOLAR ENERGY

It involves absorption of thermal energy from sunlight in the form of IR radiation.

Eg.: Solar water heater, solar cooker, solar heat collector, etc.

1. *Solar water heater:*

It consists of an insulated box inside of which is painted with black paint. It is provided with a glass lid to receive and store solar heat. The water is allowed to flow inside the copper coil. The water gets heated up and flows out.



2. Solar heat collector:

It consists of natural materials like stones, bricks, glass which can absorb sun light during day time, and releases it slowly at night.

Uses:

It is used in cold places to keep houses in hot condition.

PHOTO CONVERSION OF SOLAR ENERGY

It involves conversion of solar energy into electrical energy by the photoelectric effect.

Solar energy → Electrical energy

Methods of photoconversion:

It can be made by photo galvanic cell or solar cell

SOLAR CELL OR PHOTOGALVANIC CELL:

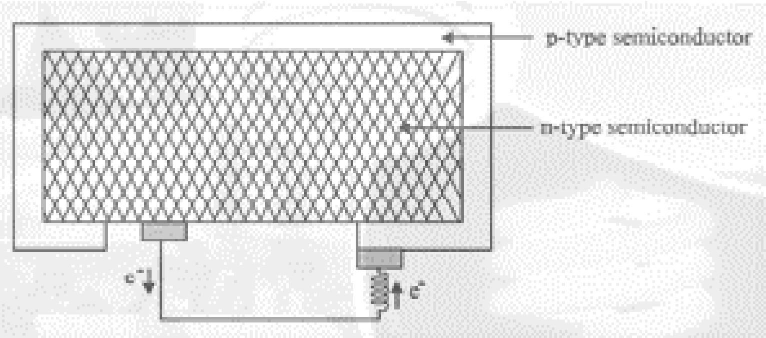
Solar cells or batteries are the devices that convert the solar energy into electrical energy.

Solar energy → Electrical energy

Principle:

It is based on PV effect, when the solar rays falls on a two layer of semiconductor devices, a potential difference between the two layer is produced. This potential difference causes flow of electrons and produces electricity.

Construction:



Solar cells consist of a p-type semiconductor (Si with B) and n-type semiconductor (Si with P). They are in close contact with each other.

Working:

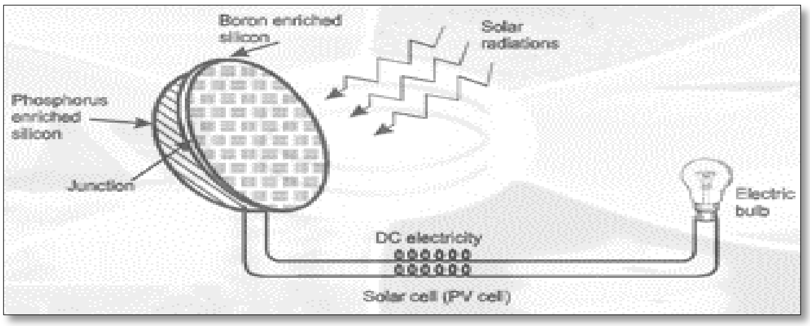
When solar rays fall on the top layer of p-type semiconductor, the electrons from the valence band get promoted to the conduction band and cross the p-n junction into n-type semiconductor. When the p and n layer are connected to an external circuit, electrons flow from n-layer to p-layer and hence current is generated.

SOLAR BATTERY:

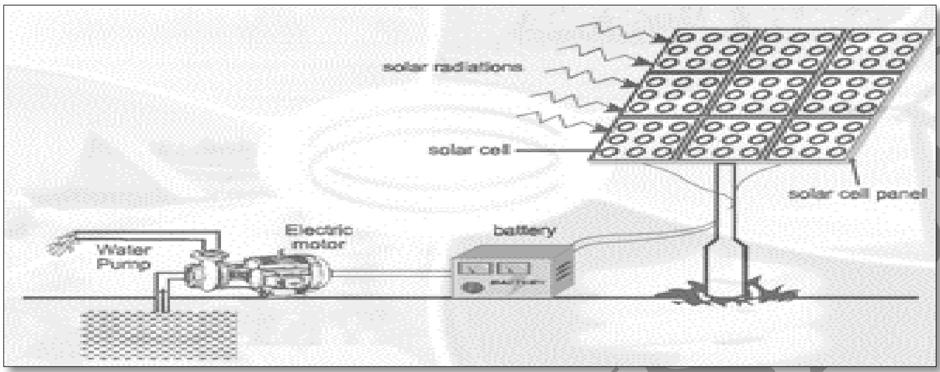
When large numbers of solar cells are connected in series, it forms a solar battery. Solar battery produces more electricity and run water pump, street light etc.

Uses:

1. Lighting purpose: Street lights are replaced by solar street light.



2. Water pumps run by solar battery.



3. Used in calculators, electronic watches, street lights, water pumps, radios & TVs.

4. Used to drive vehicles, space craft, satellites.

5. It can be stored in Ni-Cd and lead-acid batteries.

Advantages:

1. Pollution free energy
2. Eco friendly
3. Used in remote areas, forest and hilly regions
4. Maintenance cost is low
5. Long life time
6. It does not require recharge

Disadvantages:

1. The Solar energy is not available at night
2. The Solar power decreases during cloudy
3. It produces only DC voltage
4. High capital cost

Recent Development in solar cell materials

- *Crystalline Si*
- *Thin films*
- *Next generation Perovskite Solar Cells (PSCs)*
- *Solar paints*
- *Transparent solar windows*
- *Thermo radiative PV devices*

Crystalline silicon (c-Si)

Crystalline silicon is the most used (90% of the global PV market) semiconducting material in solar panels.

But, its efficiency is only 30%. So, solar cells with low-cost and high-efficiency materials are needed.

Ex: III – V multijunction materials: (efficiency > 30%)

Hybrid tandem III – V/Si solar cells: (efficiency > 30%)

Six-junction III – V solar cells under concentrated light: (efficiency > 47.1%)

Si-based bifacial technology: (efficiency is 11% more compared to standard panels)

Thin films

Due to their narrow design (light weight, flexibility and ease of installation) secondgeneration thin-film solar cells are growing as one of the most promising PV technologies.

This films are 350 times smaller light absorbing layers compared to standard Si panels.

Ex:

Cadmium-telluride (CdTe)

Amorphous silicon

Gallium – Arsenide (GaAs)

Copper – Indium – Gallium – Selenide (CIGS)

Of all, CIGS is the more efficient with efficiency upto 21%.

Perovskite solar cells

Among the next generation solar cells, hybrid metal halide perovskite solar cells (PSCs), play an important role due to their low price, thinner design, low temperature processing and excellent light absorption properties.

Ex: Combined pervoskite and S – PV materials shows a record efficiency of upto 28%

Solar paints

Solar paint is the another transformative technology. These can be coated over the polymer films.

Ex: Solar paint hydrogen generated energy from photovoltaic water splitting.

Quantum dots (Photovoltaic paint). Perovskite – based paints.

Transparent solar windows

They possess highly innovative applications. Their solar – to – electricity conversion efficiency is 10% more.

Thermoradiative PV devices (or) Reverse solar panels

They can generate electricity at night by utilizing the heat irradiated from the panels to the optically coupled deep space, which serves as a heat sink.

Wind Energy

- ✓ Energy generated from the force of wind is called wind energy
- ✓ It is stored in the form of electricity through wind mills.

Wind energy is harnessed by Wind Mills and Wind Farms

Windmills

- The device used to convert wind energy into electrical energy.

- The minimum speed of air required is 1.5km/h.
- It produce electricity of about 100kw.
- It consist of a wheel containing number of blades.
- The blades of the wind mill keep on rotating continuously due to the force of striking wind which produce electricity

Windfarms

- A large number of wind mills are linked in a definite pattern

- A large amount of electricity is produced.

Working of a wind mill

Working of a wind mill

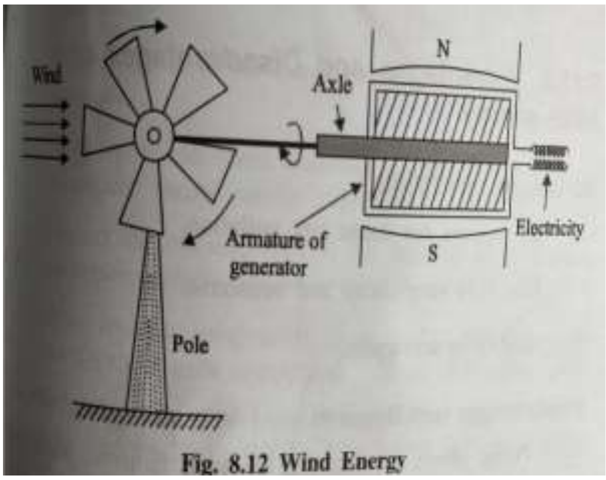


Fig. 8.12 Wind Energy

- It consists of a wheel containing number of blades.
- The wheel rotates about an axle mounted on a pole.
- The wind energy is used to rotate the wheel.
- One end of the axle is connected to the armature of a generator, which rotates between two poles of a strong magnet.
- Another end of the axle is connected to the shaft of the wind mill.
- When wind falls on the wheel of a wind mill, it rotates and electric current is produced.
- Thus, the kinetic energy of the wind is converted into electrical energy

Advantages

- Pollution free
- Renewable energy
- Very cheap
- Freely available

Disadvantages

- The direction of the wind is not predictable.
- It produces noise pollution.
- Wind turbines interfere with electromagnetic signals (TV, radio signal).
- It causes hazards to birds.

Uses

- It is used to produce large amount of electricity.
- Used to move sail boats in lakes, rivers and seas.
- Used to operate water pumps.
- Used to run the flour mill.

Other Methods To Harness The Wind Energy

- Sky sail
- Ladder mill
- Kite ship
- Sky wind power
- Briza technologies
- Sequoia automation

Geothermal energy

- Geothermal energy is the thermal energy present inside the Earth's crust in high temperature and pressure.
- It is a renewable energy source because heat is continuously produced inside the earth.
- Temperature of the earth increases at a rate of 20-75 ^{o}C per km, when we move down the earth surface.

Resources of Geothermal energy

- Geysers
- Hot springs
- Volcanoes
- Hot boiling mud pots
- Magma

Usage of geothermal energy can be classified into two types

Direct usage

The energy extracted is directly used without processing or converting it into any other form of energy which could be implied for other uses.

E.g : spas, springs, etc

Indirect usage

The energy extracted is processed, converted or transformed into an another form using turbines and generators, which could be used for other applications.

E.g; power plants, generators, turbines, etc.

The three types of power plants used to convert geothermal energy to electricity are,

- Dry steam power plant
- Flash steam power plant
- Binary cycle power plant

ADVANTAGES	DISADVANTAGES
▪ Available all the year around ▪ Doesn’t involve any combustion of fuel ▪ Independent of weather conditions Economically good alternative ▪ It is a sustainable source of energy ▪ Used for direct uses such as hot water bath, resorts, aquaculture, greenhouses	▪ It is not a widespread source of energy . ▪ Its installation costs more . ▪ It cant function when the steam runs out , which is the main source ▪ It may release harmful gases ▪ Natural calamities like earthquake , etc.. Can damage the system

BATTERIES AND FUEL CELLS

In the electrochemical cells, the chemical energy is converted into electrical energy. The cell potential is related to free energy change (ΔG).

ΔG = maximum useful work

$\Delta G = - nFE$ (or) $\Delta G < 0$

When cell operates, work is done on the surroundings (i.e. flow of electricity).

BATTERY

Battery is an electrochemical device containing 2 or more cells which converts chemical energy into electrical energy.

A Cell contains only one anode and cathode.

A battery contains several anodes and cathodes.

Requirements of a battery:

1. It should be light and compact
2. It should have long life
3. The voltage of battery should not vary

Types of battery:

It is classified into 3 types.

	1. Primary or Irreversible battery	**2. Secondary or Reversible battery**	**3. Flow or Fuel battery**
1	Non-rechargeable battery	Rechargeable battery	Fuel cells are the galvanic cells in which chemical energy of fuel is directly converted into electrical energy. Reactants are continuously passing through the cell.
2	Electrode reactions cannot be reversed.	Electrode reactions can be reversed by passing external current.	Eg: H_2-O_2 fuel cell
3.	Discarded after use.	Used over and over again.	
4.	Eg: Dry cell, Alkaline battery	Eg: Lead acid, Nicad, Lithium batteries.	

IMPORTANT PRIMATRY BATTERY

DRY CELL (OR) LECLANCHE'S CELL

It is a primary cell, which works without fluid component.

Description:

Anode : Zn

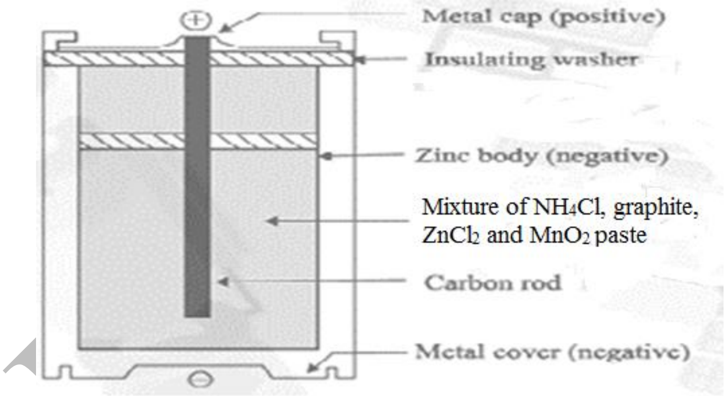
Cathode : Carbon rod (graphite)

Electrolyte : NH_4Cl, $ZnCl_2$ and MnO_2 paste

Voltage : 1.5 V

It consists of a zinc cylinder which acts as anode. The zinc cylinder is filled with in the electrolytic mixture of NH_4Cl, $ZnCl_2$ and MnO_2 paste. The carbon rod is immersed in the electrolyte in the Centre of the cell. During use, the zinc cylinder gets consumed and at the end, it will develop holes which are responsible for leakages.

Construction and Working:



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

Cell reactions:

At anode:

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

At cathode:

$$NH_4^+{}_{(aq)} + MnO_{2(s)} + 2e^- \rightarrow MnO(OH)^- + NH_3$$

Overall reaction:

$$Zn + NH_4^+{}_{(aq)} + MnO_{2(s)} \rightarrow Zn^{2+} + MnO(OH)^- + NH_3$$

The liberation of NH_3 gas disrupts the current flow and is prevented by the following reaction.

$$2\ NH_3 + ZnCl_2 \rightarrow [Zn(NH_3)_2]Cl_{2(s)}$$

Advantages:

*1) C*orrosion of Zn occurs

2) Zinc dissolves readily in basic medium

3) *No* Long life time

4) While using, voltage drop occurs; because the products are build up on the electrodes.

Uses:

Used in torches, toys, flash lights, calculator, transistor radios, etc.

IMPORTANT SECONDARY BATTERY

LEAD-ACID BATTERY OR LEAD ACCUMULATORS

Lead-acid battery is a secondary battery. When it acts as voltaic cell, it supplies electrical energy and run down. When it is recharged, it acts as an electrolytic cell.

Description:

Anode : Pb

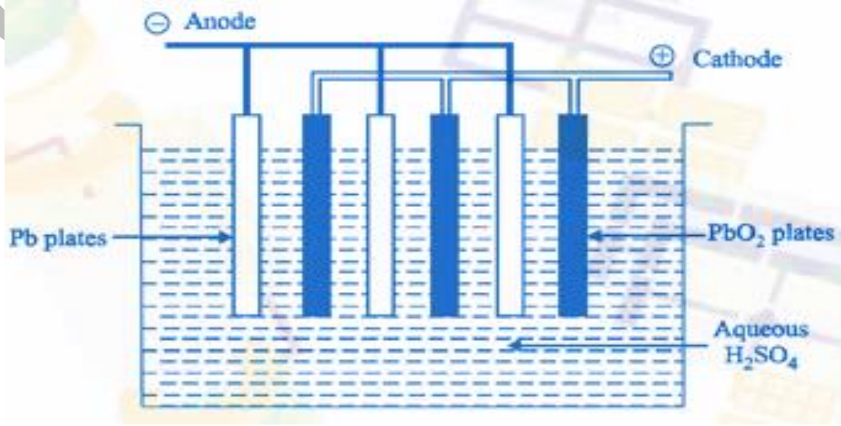
Cathode : PbO_2

Electrolyte : 20% Dil.H_2SO_4 (density 1.20 gm/ml)

Voltage : 2.0 V

Representation : $Pb \mid PbSO_4 \mid\mid H_2SO_{4(aq)} \mid PbO_2 \mid Pb$

Construction and working:



A lead storage battery consists of 3 or 6 voltaic cell. A number of anode and cathode plates are connected in series. Plates are separated from adjacent ones by insulators like rubber. This arrangement is immersed in dil. H_2SO_4.

***Working (On discharging)*:**

At anode :

Lead is oxidized to Pb^{2+} ions.

$$Pb_{(s)} + SO_4^{2-} \rightarrow PbSO_{4\,(s)} + 2e^-$$

At cathode:

PbO_2 is reduced to Pb^{2+} ions.

$$PbO_{2(s)} + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$

Overall reaction:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\longleftrightarrow}} 2PbSO_4 + 2H_2O + \text{Energy}$$

On discharging, $PbSO_4$ is deposited at both the electrodes and H_2SO_4 is consumed. So concentration of H_2SO_4 decreases gradually.

On Recharging:

The cell is recharged by applying electricity externally.

At anode :

$$PbSO_{4\,(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}$$

At cathode:

$$PbSO_4 + 2H_2O \rightarrow PbO_{2(s)} + SO_4^{2-} + 4H^+ + 2e^-$$

Overall reaction:

$$2PbSO_4 + 2H_2O + \text{Energy} \underset{\text{discharging}}{\overset{\text{charging}}{\longleftrightarrow}} Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4$$

Advantages of lead acid batteries:

1. It is made easily
2. It produces very high current
3. The self discharging rate is low
4. It also acts effectively at low temperature

Disadvantages:

1. Recycling of this battery causes environmental hazards
2. Mechanical strain and normal bumping reduces battery capacity

Applications:

1) Used in automobiles.

2) Used in UPS Systems and research centres etc.

3) Used in marketing areas etc.

4) Used in security and alarm systems.

5) Used in telephones, mines, hospitals, power plants.

IMPORTANT SECONDARY BATTERY

LITHIUM-ION BATTERIES (OR) LITHIUM-ION CELLS

Lithium-ion battery is a secondary solid state battery. The movement of Li ions are responsible for discharging or charging.

Construction:

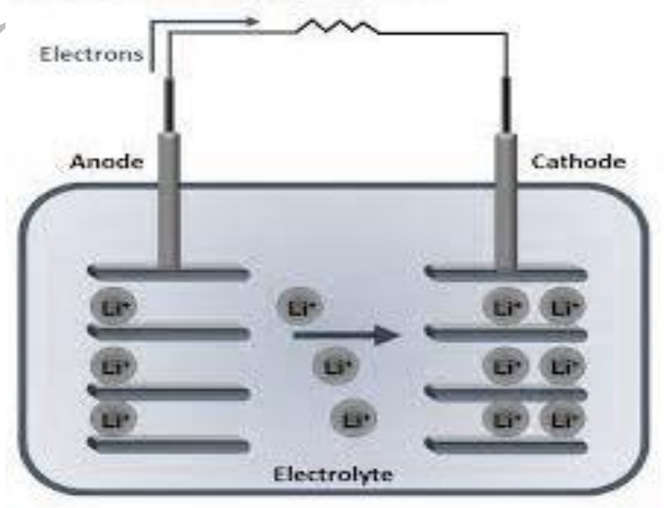
Anode (Negative current collector) : Li metal – Layers of porous Carbon

Cathode (Positive current collector) : $LiCoO_2$

Electrolyte : $LiAsF_6$ or $LiPF_6$

Separator : Polypropylene

Voltage : 3.0 V



Lithium ion battery is made up of an anode, cathode, separator, electrolyte, and two current collectors (positive and negative). The anode and cathode store the lithium.

Working (On discharging the current):

Lithium is oxidized to Li^+ ions with release of electrons. Li^+ ions move from anode to cathode and electrons pass through the external circuit connecting anode and cathode. The cathode receives both Li^+ ions and electrons.

Cell reactions

At anode: $Li \rightarrow Li^+ + e^-$

At cathode: $Li^+ + e^- + LiCoO_2 \rightarrow Li_xCoO_2$

Overall reaction: $Li + LiCoO_2 \rightarrow Li_xCoO_2$

Working (On charging the battery):

When plugging in the device, the opposite happens: Lithium ions are released by the cathode and received by the anode.

Overall reaction: $Li_xCoO_2 \rightarrow Li + LiCoO_2$

Advantages :

1) Lithium ion battery is a light weight battery and higher energy density.
2) It generates a higher voltage than other types of cells.
3) It has none of memory effect.
4) It produces three times the voltage of Ni-Cd batteries.
5) It can be made in variety of size and shapes.

Disadvantages:

More expensive than all other batteries.

Uses:

Used in cell phone, note PC, Portable LCD TV, Safety and Security Devices, camera, memory batteries, transistors etc.

FUEL CELLS

Fuel cell is a device which converts chemical energy of the fuel directly into electrical energy without combustion.

Fuel + Oxygen → Oxidation products + Electricity

Examples: Hydrogen-Oxygen fuel cell,
Methanol-Oxygen fuel cell,
Propane-Oxygen fuel cell.

Fuel Battery:

When a large number of fuel cells are connected in series, it forms fuel battery.

HYDROGEN - OXYGEN (H_2 - O_2) FUEL CELL

It is the simplest and most successful fuel cell. In this cell, fuel, oxidizer and electrolyte are simultaneously passed through the cell.

Description:

Fuel = Hydrogen

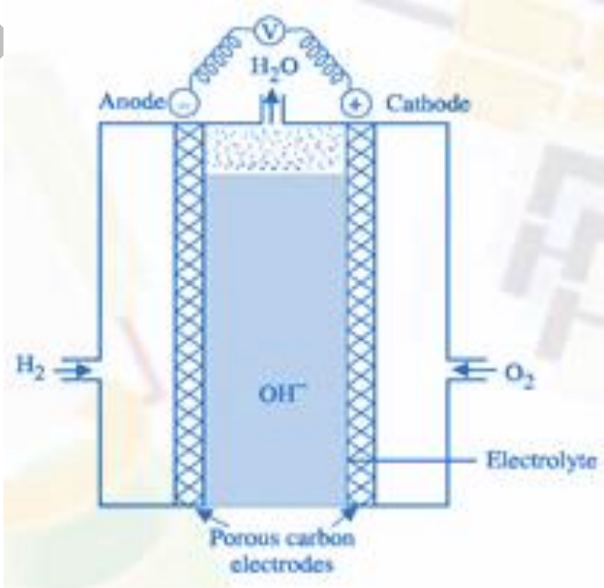
Oxidizer = Oxygen

Electrolyte = 25% KOH or NaOH

Electrodes (anode & cathode) = Porous compressed carbon containing small amount of catalyst (Pt, Pd, Ag and Ni)

Voltage = 1.0 V

Construction:



Working (Discharging):

Pure Hydrogen is bubbled through the anodic compartment where it is oxidized. The oxidizer (oxygen) is bubbled through the cathodic compartment, where it is reduced.

Cell reactions

At anode: Hydrogen molecules are oxidized to form water.

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

At cathode:

The electrons from anode are absorbed by oxygen and produces hydroxide ions.

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

Overall reaction:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O + \text{Electricity}$$

Applications:

1) It is used in space vehicles, submarines or other military-vehicles.

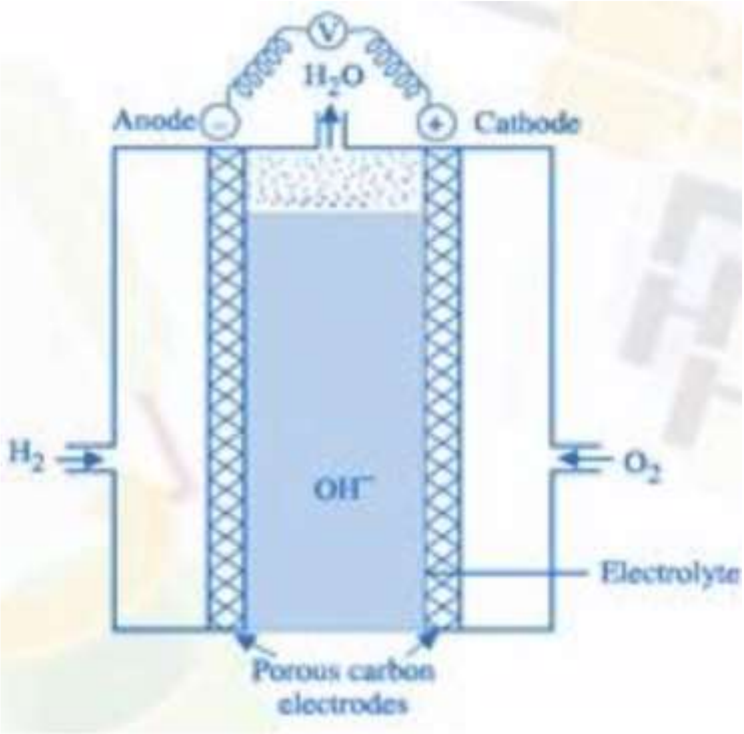
2) The product water is 100% pure.

Advantages:

1) No noise pollution and no thermal pollution
2) More efficiency and take less time for operation.
3) Highly reliable
4) Eco friendly
5) It produces 100% pure water

Disadvantages:

1. Fuel cells cannot store electric energy as other cells do
2. It is very expensive
3. Hydrogen gas is an explosive
4. It is difficult to compress the hydrogen gas into liquid form
5. Storage and handling of hydrogen gas is dangerous.



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Microbial Fuel Cells (MFCs)

Microbial fuel cell is a device that converts chemical energy to electrical energy by the action of micro-organisms under anaerobic conditions.

Bioelectricity is generated by the oxidation of organic waste and renewable biomass using bacteria.

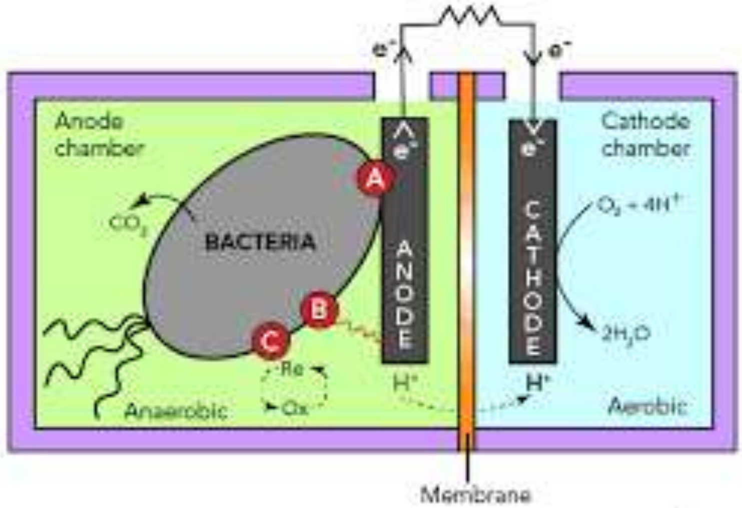
Construction:

MFC are type of electrochemical cell constructed using either bio cathode or bio anode. A membrane separates both cathode and anode compartments. The electron produced during oxidation is transferred directly to the cathode. The organic electron donor that is oxidized to produce CO2, proton and electron are used in most MFC.

Cathode uses variety of electron acceptor mostly oxygen

Anode Compartment: Microbes suspended under anaerobic conditions in the analyte

Cathode: Graphite, carbon paper
Membrane/ Separators: Separates Anode and Cathode
Limits the Oxygen diffusion from cathode to anode



Working principle

- When both electrode connected active biocatalyst in the anode oxidizes the organic substrates and produces electrons and protons.

- The protons are conducted to the cathode through membrane, and the electrons are reached through the external circuit.

- Finally oxygen present at the cathode recombines with hydrogen and electron to produce water.

Applications of Microbial Fuel Cell

- Microbial fuel cell (MFC) can generate electricity from bio waste and organic matter
- MFCs, generate less sludge as compared to the aerobic waste water treatment process
- MFCs used in river, deep-water environments and space (remotely operated vehicles)
- MFCs are used to convert carbon rich wastewater into methane gas
- MFCs are used as convenient biosensor for wastewater streams
- MFCs play an important role in the field of microbiology, soil chemistry and electrical engineering
- Many commercial soil based MFC kits are available as an education tool

Super Capacitor

Super capacitor is an electronic device that store large amount of electric energy. They store 10-100 times more energy per unit volume and deliver much faster than batteries.

Ordinary capacitor uses conventional dielectric storage, but super capacitor uses electrostatic double layer capacitance (EDLC) for storage

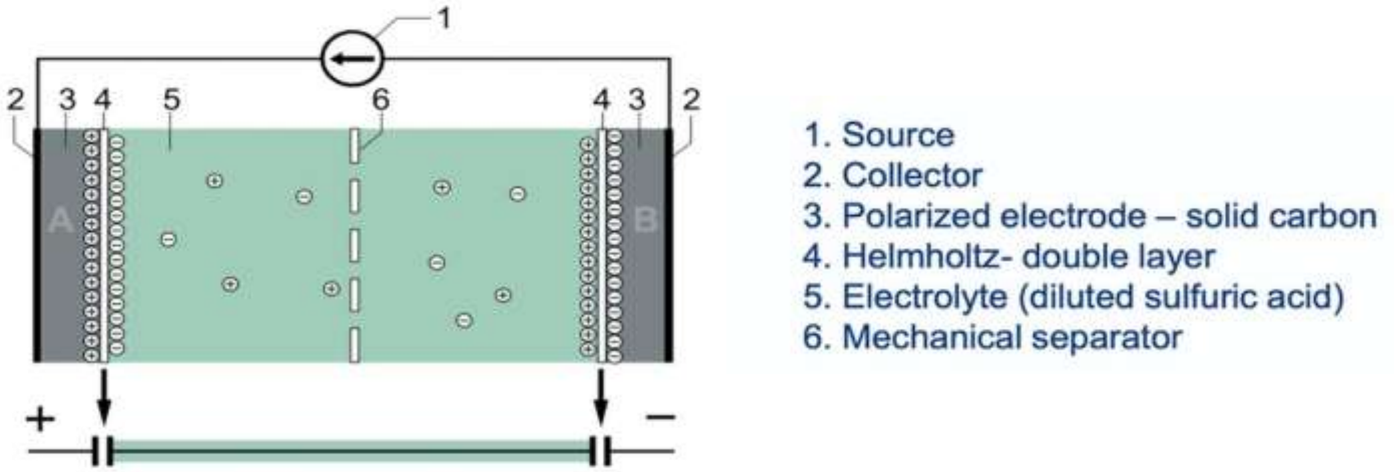
Principle

The basic principle of super capacitor is to store electrical energy through the electric double layer capacitance formed by the charge separation on the interface between the electrode and electrolyte.

Design & Working

Super capacitor consists of two electrodes made up of metal coated with porous substance like activated carbon.

The electrodes are separated by ion permeable membrane (separator) and dipped in electrolyte having positive and negative ions



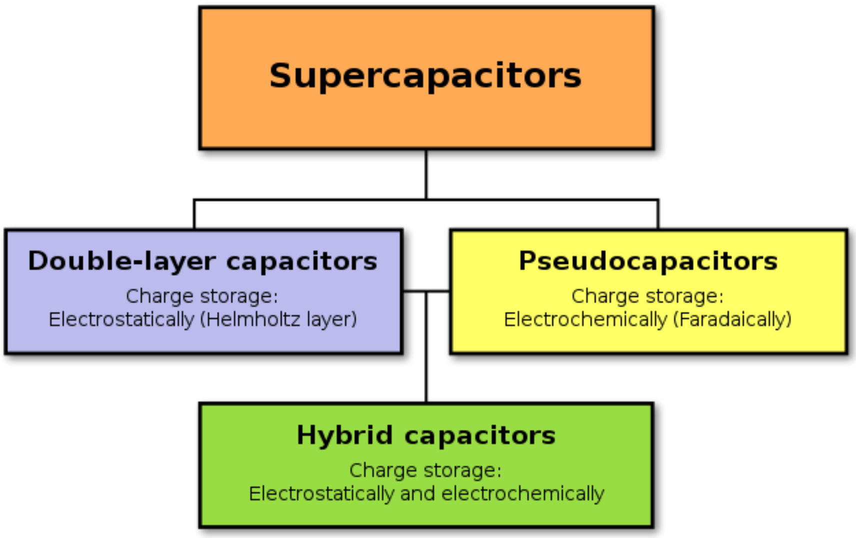
Working

When the electrodes are connected to the power source, ions in the electrolyte form electric double layers (Helmholtz electrical double layer) of opposite polarity to the electrodes polarity, creating an electric field between them.

- For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrolyte interface.
- Similarly negatively polarised electrodes will have a layer of positive ions at the electrode/electrolyte interface.
- This electric field polarizes the dielectric that stores more electrical energy at an electrode-electrolyte interface

Classified into 3 types:

- Double-layer capacitors
- Psuedo-capacitors
- Hybrid capacitors



1. Double layer capacitors

Charge Storage: Electrostatically (Helmholtz double layer)

2. Pseudo capacitors

Charge Storage: Electrochemically. This can be done by redox reaction.

3. Hybrid capacitors

Charge Storage: Electrostatically & Electrochemically

Advantages

- Highly safe
- Long life time (10-20 years)
- It can be cycled millions of time.
- Provides high power density and high load currents
- Good performance even at low temperature
- It can be charged in seconds.

Disadvantages

- Cost per watt is high
- High self-discharge that batteries
- It cannot be used as source for continuous power supply

Applications:

Super capacitors are used in many power management applications like,

- Voltage stabilization in start/stop system
- Consumer electronics
- Utility meters
- Remote power for sensors, LEDs, switches.
- Energy harvesting.
- Kitchen appliances.
- Wind energy.

ELECTRIC VEHICLE

- An electric vehicle (EV) is a vehicle that uses one or more electric motors for propulsion
- It can be powered by a power system with electricity from external source or by battery

- They have electric motor instead of Internal Combustion Engine (ICE)

Working Principle

Electric vehicles work by plugging into a charge point and taking electricity from the grid. They store electricity in rechargeable battery that power on electric motor, which rotates the wheels. Electric vehicles accelerate faster than the traditional fuel engines. So they feel lighter to drive.

Various steps of working

Step I: Controller takes and regulates electrical energy from battery to inverter.

Step II: The inverter then sends a certain amount of electrical energy to the motor.

Step III: The motor converts electrical energy into mechanical energy (rotation).

Step IV: Rotation of the motor rotor rotates the transmission, so the wheels turn and then the vehicle moves.

Step V: When the brakes are pressed, the motor becomes an alternator and produces power, which is sent back to the battery

Components

1. **Battery:** It provides electricity to power the vehicles.

2. **Charge port:** It allows the vehicle to connect to an external power supply to recharge the battery.

3. **DC/DC converter:** It converts higher voltage DC power from battery to lower voltage DC power.

4. Electric motor: It drives the vehicle's wheels.

5. Onboard charger: It converts AC electricity to DC power for charging the battery.

6. Power electronics controller: It controls the flow of electrical energy from battery to motor and controls the speed.

7. Thermal system (cooling): It maintains the proper operating temperature range of the engine, motor etc.

8. Transmission: It transfers mechanical power from the motor to drive the wheels.

Types of Electric Vehicles

- ✓ Battery Electric Vehicle (BEV
- ✓ Hybrid Electric Vehicle (HEV)
- ✓ Plug-in Hybrid Electric Vehicle (PHEV)
- ✓ Fuel Cell Electric Vehicle (FCEV)

Battery Electric Vehicle (BEV)

- It runs entirely on a battery do not have an ICE.
- Energy stored in a large battery pack that is charged by plugging into the electricity grid.
- The battery pack provides power to one or more electric motors to run the electric car.
- Its typical driving ranges from 150-300 miles

Example Volkswagen e-Golf, Tesla Model 3, BMW i3

Hybrid Electric Vehicle (HEV)

- ✓ HEVs have both an Internal Combustion Engine ICE and an electric motor.
- ✓ The engine gets energy from fuel, and the motor gets electricity from batteries.
- ✓ Both the engine and electric motor can turn the transmission at the same time, which drives the wheels.
- ✓ The batteries in HEV can only charged by the ICE, motion of the wheels or combination of both.
- ✓ The battery cannot be recharged from outside of the system.

Examples of HEV:

Honda Civic Hybrid, Toyota Prius Hybrid, Toyota Camry Hybrid.

Plug-in Hybrid Electric Vehicle (PHEV)

- ✓ PHEVs are powered by gasoline or bio-diesel and by a rechargeable battery pack.
- ✓ The battery can be charged up with electricity by plugging into an electrical outlet or electric vehicle charging station (EVCS).
- ✓ It operates on electricity until the battery is depleted.
- ✓ Then the engine takes over and the vehicle operates as a conventional gasoline vehicle PHEVs can run in at least 2 modes:
  (i) All-electric Mode (ii) Hybrid Mode

Examples of PHEV:

Mercedes GLE550e, Mini Cooper SE Countryman, Audi A3 E-Tron

Fuel Cell Electric Vehicle (FCEV)

- FCEVs employ ‘fuel cell technology’ to generate the electricity to run the vehicle.
- The chemical energy of the fuel is converted directly into electric energy.
- The FCEV generates the electricity required to run this vehicle on the vehicle itself.
- FCEVs are also known as Zero-Emission Vehicles.

Examples

Toyota Mirai, River simple Rasa, Hyundai Tucson FCEV, Honda Clarity Fuel Cell, Hyundai Nexo.

Advantages

- Electric vehicles are energy efficient
- It reduces emissions
- It requires less maintenance
- Environmental friendly
- Saving lots of money on fueling the car than gasoline vehicles

Disadvantages

- Electric vehicles cannot travel as far
- Fueling takes longer
- Electric vehicles are expensive
- Batteries need rare materials
- There aren’t enough charging points