UNIT- I

WATER AND ITS TREATMENT.

1. Introduction.

The main sources of water are

(i) Rain
(ii) Rivers and lakes (Surface water).
(iii) Wells and springs (underground water).
(iv) Sea water.

Types of impurities in water

The impurities present in the water may be broadly classified into three types.

Impurities

- Physical impurities
  - Suspended impurities
    - eg: sand, oil droplets, vegetable and animal Matter. impart turbidity to water
  - colloidal impurities
    - like finely divided silica, clay and organic waste products impart colour and taste to water.
- Chemical impurities
- Biological impurities
  - Like fungi, bacteria and other microorganisms cause deseases.

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Chemical impurities.

(a) Dissolved salts:

Bicarbonates, sulphates chlorides of Ca & Mg and carbonates, bicarbonates of Na and K. Make the water alkaline.

(b) Dissolved gases:

O_2, CO_2, H_2S, SO_2 make the water acidic so they accelerate the rate of corrosion.

Water Quality parameters:

1. colour:

(i) Colour is shade imparted by organic material which change the appearance of water.

(ii) The colour of natural water is mainly due to the presence of dissolved or colloidal organic or inorganic materials.

Sources:

Organic sources:

Algae, tannins, humic compounds Organic dyes, etc.,

Inorganic sources:

Fe and Mn compounds chemicals and inorganic dyes from various industries.

Sanitary Significance:

1) Dyeing, scouring and laundering.

2). Yellowish tinge: presence of 'cr' and organic matter.

Yellowish Red: Presence of iron

Red-brown: presence of peaty matter.

Removal of Colour:

Colour and colour producing materials are removed by coagulation, settling, adsorption and filtration.

2. Tastes and odours:

Taste:

Taste is the sensation of flavour perceived in the mouth and throat on contact with a substance.

odour:

odour is a smell caused by one or two volatilized chemical compounds that are genera found in low concentration.

Sources: Algae and decaying vegetation etc.
(organic)

Inorganic Sources: Mercaptans, amines, sulphides e

Significance:

1. Disagreeable odours and tastes are objectionable for various industrial processes such as food products, beverages, textiles paper, pulp. Most of the odours in natural waters are organic in nature, except H_2S.
2. Taste help us to decide what to eat and influences how efficiently we digest these foods.
3. Senses of smell and taste are vital is identification of valuable nutrients in the environment.
4. Taste enables the evaluation of foods for toxicity.

Removal of tastes and odours:

1. Organic tastes and odours may be removed by aeration (or) activated carbon treatment.
2. Inorganic tastes due to H_2S (or) Iron may be removed by chemical methods like oxidation, chlorination or precipitation.

3. Turbidity and sediments:

Turbidity is the reduction of clarity of natural water due to the presence of finely divided insoluble impurities suspended in water.

Sources:

Inorganic sources:

clay, silt, silica, ferric hydroxide, calcium carbonate, sulphur etc.

Organic sources:

Finely divided vegetable or animal matter, oils, fats, greases, micro-organisms etc.,

problems caused by Turbidity:

(i) presence of turbidity and sediments in boiler water and cooling water system cause problems.

(ii) water-softening processes cannot be carried out.

(iii) Due to deposition of these organic impurities, disinfection efficency gets reduced

Significance:

(i) ~~presence~~ Turbidity affects the taste and colour of drinking water.

(ii) As turbidity affects the disinfection process, it must be removed.

(iii) Turbidity have many negative effects aquatic life, it block light to aquatic plants, aquatic organisms.

(iv) Turbidity affects the growth rate of algae.

(V) It increases water temperature because Suspended particles absorbs more heat

Removal of Turbidity and sediments

Turbidity of water removed by sedimentation followed by,

(i) coagulation and filtering

(ii) coagulation and settling

(iii) coagulation, settling and filtering.

(eg)

1. Turbidity caused by suspended silt and mud is objectionable in boilers and in cooling-water systems.
2. It caused by colloidal or dissolved gases organic matter will interfere with water-Softening processes.

4. pH:

The hydrogen ion concentration is represented by the pH value, which is defined as

$$pH = -\log_{10}[H^+].$$

It is defined as negative logrithm of hydrogen ion conc. The pH ranges from 0-14 as

$$0 \longleftrightarrow 7 \longleftrightarrow 14$$

Acidic Neutral Basic

For drinking water pH = 6.5 to 8.5

For irrigation = 6.00 to 9.00

6. TDS:

TDS stands for Total dissolved solids. It is defined as the measure of all inorganic and organic substances present in water.

Significance:

(i) TDS impacts the salinity of water

(ii) TDS in water may not be ideal for your health and must be filtered out before intake

(iii) TDS higher than 300 ppm may not be potable as it can taste salty.

(iv) water with high level of TDS (>1200) impacts the color, odour and taste dramatically.

(v) water with high level of TDS may not be suitable due to excessive scaling caused by it in water pipes, heaters, boilers and household appliances.

7. Fluoride:

It is found in ground water as a result of dissolution from geologic formulations. Surface water generally contain much smaller concentration of fluoride.

Fluoride containing minerals : Fluorapatite ($Ca_{10}F_2(PO_4)_6$)
Cryolite (Na_3AlF_6)
igneous rocks containing fluorosilicate

Significance of pH:

1. It determines the solubility
2. It also determines the biological availability
3. A rise (or) fall is pH can indicate chemical pollution (or) acid rain. Many animals cannot live in water at a pH level below 5 (or) above 9.

5. Alkalinity:

Alkalinity of water is a measure of its acid - neutralising ability. The natural alkalinity in water is imparted by the hydroxides, carbonates and bicarbonates.

Sources:

Industries like fertilizer, detergent, leather and paint.

Significance:

1. Very high value of alkalinity are harmful to aquatic organisms.
2. Alkalinity in boiler feed water causes - caustic embrittlement of pipes.

Removal of Alkalinity:

Alkalinity in water, can be removed by adding limited amount of HCl.

contaminated domostic sewage, run-off from agricultural lands } Phosphate fertilizer

Sanitary significance:

1. Optimum fluoride concentration is in the range of 0.7 to 1.2 mg/lit.
2. Beneficial health effects have been observed where the fluoride levels are optimum.
3. If the fluoride conc. is low in drinking water it causes dental carries in children.
4. If the fluoride concentration is high it causes fluoresis.

Removal of fluoride:

1. Precipitation using aluminium salts in alkaline media.
2. Using strongly basic anion exchange resin.
3. By absorption on activated carbon.

8. Arsenic:

Arsenic is a metallic element that forms a number of poisonous compounds. It is found in nature at low levels, mostly in compounds with oxygen, chlorine and sulfur.

Source: Arsenic can get into drinking water from natural deposits (or) run off from agriculture, mining and industrial processes.

Significance:

(i) Long term intake of arsenic contaminated water leads to arsenic poisoning with cancer of skin, bladder, kidney.

(ii) It produces diabetes, hypertension and reproductive disorders.

(iii) children may be a greater risk of illness, when higher level of arsenic are present.

9. Chemical oxygen Demand (COD)

COD is defined as "the measure of amount of oxygen required to chemically oxidise all the oxidisable impurities present in the sewage using an exissing agent like acidified $K_2Cr_2O_7$.

Significance of COD:

(i) Determination of COD is carried out only in 3 hrs but determination of BOD is carried out after 5 day.

(ii) It measures both the biologically oxidisa and biologically inert organic matter.

(iii) COD test is used to monitor water treatment plant efficiency.

Types of Hardness:

Based on the types of dissolved salts present in water, it can be classified into two types.

1. Temporary hardness
2. Permanent hardness

1. Temporary hardness (or carbonate hardness) or Alkaline hardness.

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

(i) Boiling the water
(ii) adding lime to the water.

2. Permanent hardness (or Non-carbonate hardness (NCH)) (or) Non-alkaline hardness.

This is due to the presence of chlorides and sulphates of calcium and magnesium. It cannot be removed by boiling. But it can be removed by

i) Lime soda process
2) Zeolite process.

Significance of Hardness:

1. Hardness affects the amount of soap that is needed to produce foam (or) lather.

(iv) COD is used to measure pollutants in water, waste water and aqueous hazardous wastes.

(v) It provides an index to assess the effect of discharged waste water on the environment.

10. Biological oxygen Demand [BOD]:

BOD is defined as, the amount of free oxygen required by bacteria for the biological oxidation of the organic matter under aerobic conditions at 20°C for a period of 5 days.

Significance of BOD:

(i) It indicates the amount of decomposable organic matter present in the sewage.

(ii) It enables us to determine the degree of pollution at any time in the sewage stream.

(iii) Lesser the BOD, better is the quality of water (i.e) the water sample with BOD of less than 3 ppm is considered as pure water, whereas the water more than 4 ppm is considered as polluted water.

11. Hardness of water:

Hardness is the property (or) characteristics of water, which does not produce lather with soap.

2. Hardness is very important in industrial uses, because it forms scale in heat exchange equipment boilers and pipe lines.

3. Hardness mitigates metal toxicity because Ca^{2+} and Mg^{2+} help keep fish from absorbing metals such as lead, arsenic, cadmium into their blood stream.

Treatment of water for Domestic supply (or Municipal water treatment.

Sources of water

↓

Screening

↓

Aeration

↓

Sedimentation

↓

Coagulation

↓

Filteration

↓

Sterilisation (or Disinfection

Primary Treatment:

1. Screening:

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

2. Aeration:

The process of mixing water with air is known as aeration. The main process is

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

(ii) to remove ferrous and manganous salts [illegible] as insoluble ferric and manganic salts.

3. Sedimentation:

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

4. Coagulation:

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

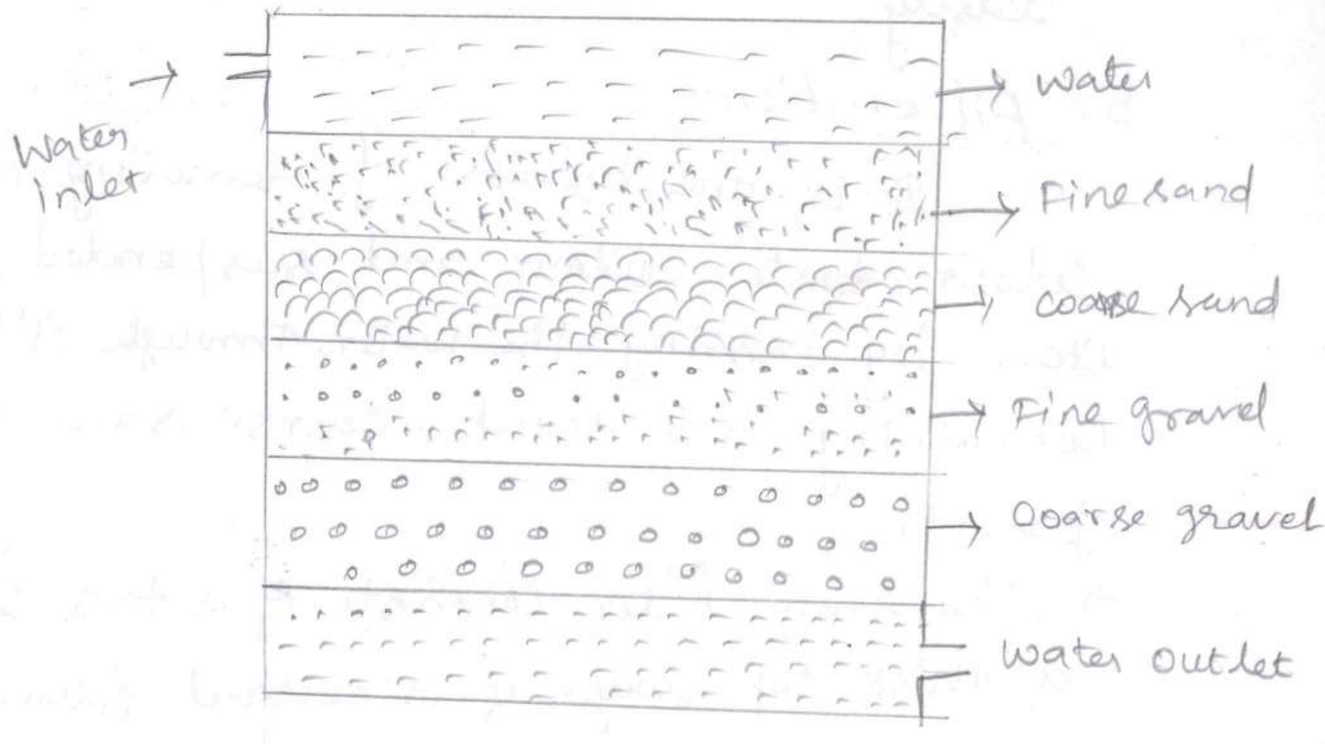
1. In this method chemicals, called Coagulants like alum, $Al_2(SO_4)_3$ etc.. added to water. when the $Al_2(SO_4)_3$ is added to water, it gets hydrolysed to form a gelatinous ppt of $Al(OH)_3$
2. The gelatinous ppt of $Al(OH)_3$ entraps the finely didived and colloidal impurities, settles to the bottom and can be removed easily.

5. Filteration:

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.

→ The sand filter consists of a tank containing a thick top layer of fine sand followed by coarse sand, fine gravel, coarse gravel.

- When the water passes through the filtering medium, it flows through the various beds slowly.
- The rate of filteration decreases slowly due to the clogging of impurities in the pores of the sand bed.
- When the rate of filteration becomes very slow, the filteration is stopped.
- Then the thick top layer of fine sand is scrapped off and replaced with clean sand.
- Bacterias are also partly removed by this process.



Sand Filter

Sterilisation (or) Disinfection:

The process of desroging the harmful bacterias is called as Sterilisation or disinfection. The chemicals used for this purpose are called disinfectants. It can be carried out by the following methods.

1. 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.

$O_3 \rightarrow O_2 + [O]$.

mono oxygen atm newly formed thing.

This nascent Oxygen is a powerful oxidising agent and kills the bacteria.

D. A. (Disadvantages).

(i) Costly and cannot be used in large scale.

(ii) Ozone is unstable and cannot be stored for long time.

2. By using UV radiation.

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

Disadvantages:

i) costly

(ii) Turbid water cannot be treated.

3. By chlorination:

The process of adding chlorine to water is called chlorination.

(i) By adding chlorine gas:

Chlorine gas can be bubbled in the water as a very good disinfectant.

(ii) By adding chloramine.

When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl.$$

chloramine decomposes slowly to give chlorine. It is a better disinfectant than chlorine.

(iii) By adding bleaching Powder.

When bleaching Powder is added to water, it produces hypochlorous acid, is a Powerful Germicide.

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

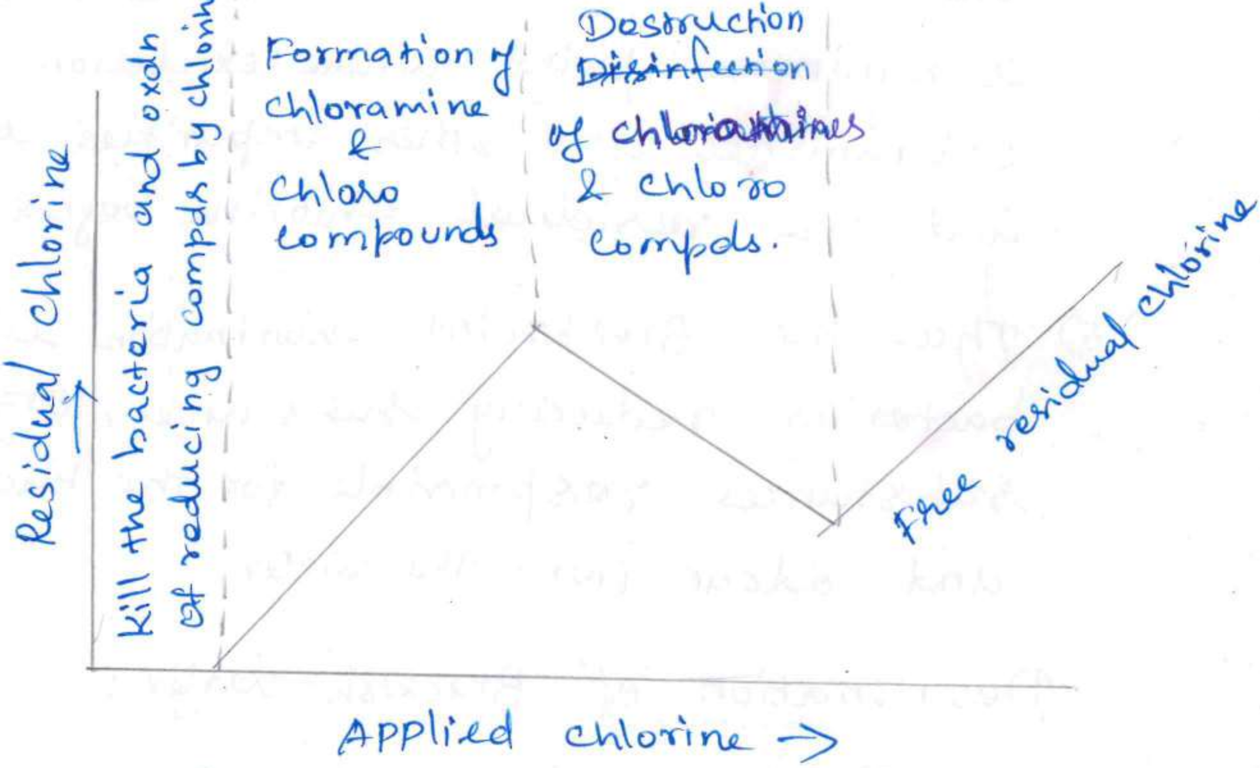
$$Cl_2 + H_2O \rightarrow \underset{\text{Hypochlorous acid}}{HOCl}$$

$$HOCl + \text{Bacteria} \rightarrow \text{Bacterias are killed}.$$

Break Point Chlorination

Water contains the following impurities.

(i) Bacteria
(ii) Organic impurities
(iii) Reducing Substances (Fe^{2+}, H_2S etc)
(iv) Free ammonia.



Break point chlorination.

Chlorine may be added to water directly as a gas or in the form of bleaching powder. When chlorine is applied to water, ~~the~~

1) Initially, the applied chlorine is used to kill the bacterias and oxidises all the reducing substances present in the water and there is no free residual chlorine.

2) As the amount of applied chlorine increases, the amount of combined residual chlorine also increases.

3) At one point, on further chlorination, the oxdn of chloramines and other impurities starts and there is a fall is the combined Chlorine content.

4) "Break Point chlorination is the point at which the combined residual chlorine decreases to a minimum point where oxidation of Chloramines and other impurities complete and free residual chlorine begins to appear".

5) Thus the Breakpoint chlorination eliminates bacterias, reducing substances, organic substances responsible for the bad taste and odour from the water.

Desalination of Brackish Water:

The process of removing common salt (NaCl) from the water is known as desalination.

Depending upon the quantity of dissolved Solids, water is graded as,

1. Fresh water - contains < 1000 PPm of dissolved solids
2. Brackish water - > 1000 but < 35,000 PPm of dissolved Solids
3. Sea water - > 35,000 PPm of dissolved solids.

Reverse osmosis (RO).

When two solutions of different concentrations are separated by a semi-permeable membrane, solvent (water) flows from a region of lower conc.. to higher conc.. This process is called. osmosis.

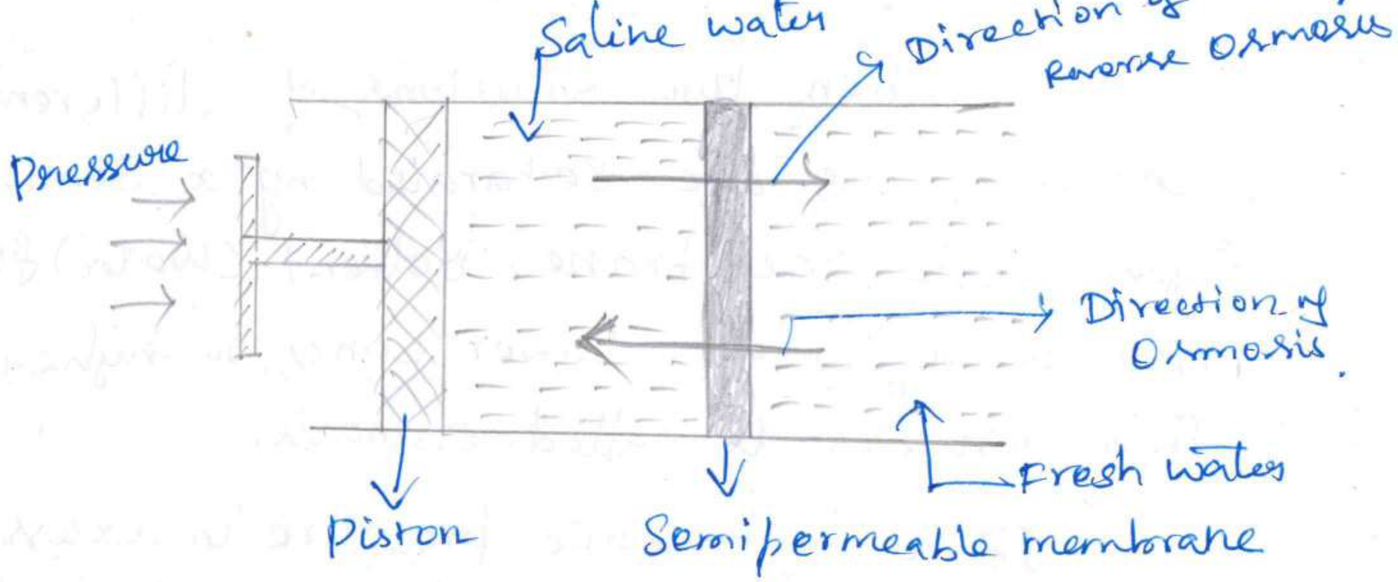
If a hydrostatic pressure in excess of osmotic pressure is applied on the higher conc.. side ; the solvent flow is reversed. (i.e) solvent flows from higher concentration to lower concentration. This process is called reverse osmosis. Thus in the process of reverse osmosis pure water is seperated from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

Advantages:

(i) Life time of membrane is high and it can be replace within few minutes.

(ii) It removes ionic, non ionic, colloidal impurities.

(iii) Due to low capital cost, simplicity, low operating, this process is used for converting sea water into drinking water.



Reverse osmosis.

Boiler feed water (or) Boiler Troubles:

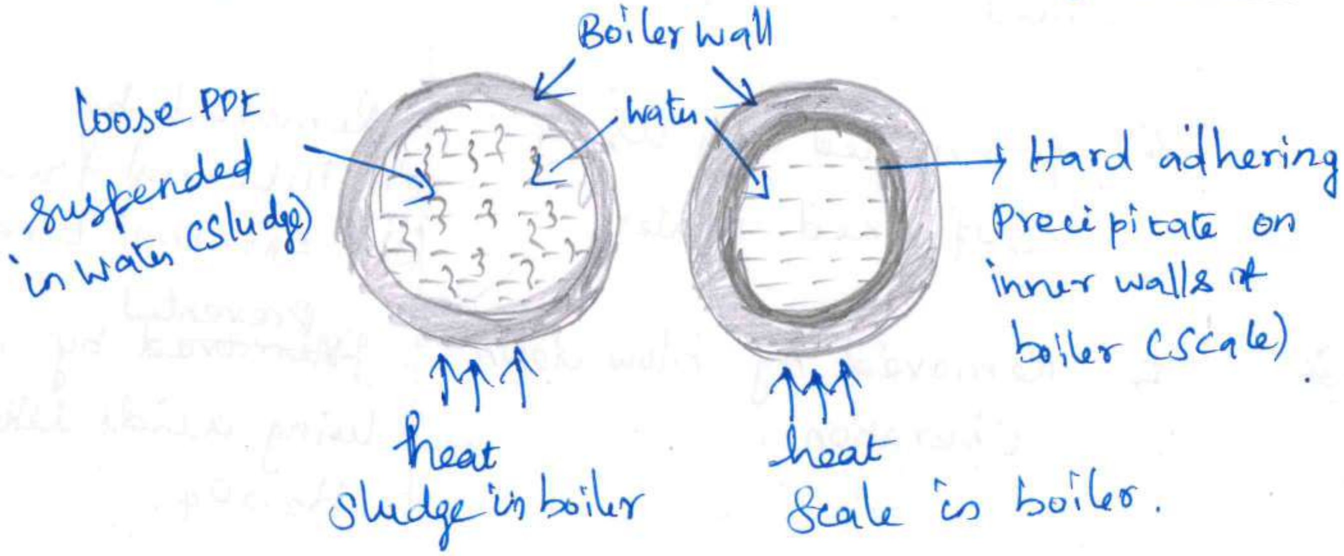
* The water fed into the boiler for the production of steam is called boiler feed water.

* Boiler feed water should be free from turbidity, oil, dissolved gases, alkali and hardness causing substances.

Boiler troubles (or) disadvantages of using hardwater in boilers.

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

1. Formation of Scales and Sludges in boilers



Sludge in boiler Scale in boiler.

When water is continuously converted into steam in boilers or heat exchangers, the conc.. of dissolved salts in water increases progressively. When it reaches their saturation point, they are thrown out in the form of precipitates on the inner walls of boiler (or) heat exchangers.

1. Sludge (loose deposit).
2. Scale (Hard deposit).

Comparison of scales and Sludges

Sludge	Scale.
1. loose, slimy, non-adherent PPt	1. hard adherent coating
2. Sludge forming substances are $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$ etc.	2. Scale forming substances are $Ca(HCO_3)_2$, $CaSO_4$, $Mg(OH)_2$.

3. Poor conductors of heat.	Thermal insulators.
4. Prevented by using Softened water	Removed by (i) internal treatment (ii) External treatment
5. Removed by blow-down Operation.	~~Removed~~ Prevented by dissolving using acids like HCl, H_2SO_4.
6. Blow down operation is a process of removing a portion of concentrated water by fresh water. Frequently from the boiling during steam production.	They can be removed by applying thermal shocks, scrapers, wire brush etc.,

Disadvantages of Scale formations

1. wastage of fuel

Thickness of Scale (unit)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150

2. Decrease in efficiency

3. Boiler explosion.

Prevention of Scale formation

1. At the initial stage scales can be removed using Scrapers, wire brush etc.,

2. If scales are brittle, they can be removed by thermal shocks.

3. By using suitable chemicals like dil. acids (for $CaCO_3$ scale), EDTA (for $CaSO_4$) with which they form suitable complexes.

4. If the scales are loosely adhering, they can be removed by frequent blow down operation.

2. Priming and Foaming (carry over)

Priming:

It is the process of production of wet steam.

Priming is caused by,

(i) High steam velocity
(ii) very high water level in the boiler
(iii) sudden boiling of water
(iv) very poor boiler design.

Prevention:

(i) controlling the velocity of steam
(ii) keeping the water level lower
(iii) Good boiler design
(iv) using treated water.

Foaming:

The formation of stable bubbles above the surface of water is called foaming. These bubbles are carried over by steam leading to excessive priming.

Caused by,

(I) presence of oil & grease

(ii) Presence of finely divided particles.

Prevention:

i) adding coagulants like sodium aluminate, aluminium hydroxide.

(ii) adding anti foaming agents like synthetic polyamides.

Caustic Embrittlement (intercrystalline cracking)

Boiler water usually contains a small proportion of Na_2CO_3. In high pressure boilers this Na_2CO_3 undergoes decomposition to give NaOH.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2.$$

This NaOH flows into the minute hair cracks and crevices, usualy present on the boiler material by capillary action and dissolves the surroundings area of iron as sodium ferroate

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2\uparrow$$

Prevention:

(i) using sodium phosphate as softening agent instead of Sodium carbonate.

(ii) By adding tannin, lignin to the boiler water which blocks the hair cracks.

Boiler corrosion:

It occurs due to the presence of

1. dissolved oxygen
2. dissolved CO_2
3. dissolved salts.

1. Dissolved O_2:

Dissolved oxygen in water is mainly responsible for the corrosion of boiler. The dissolved O_2 in water attacks the boiler Material at higher temp.

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

Removal of dissolved O_2:

It can be removed by Chemical (or) Mechanical methods.

(a) chemical method:

Sodium sulphite, hydrazine are some of the chemicals used for removing dissolved O_2.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

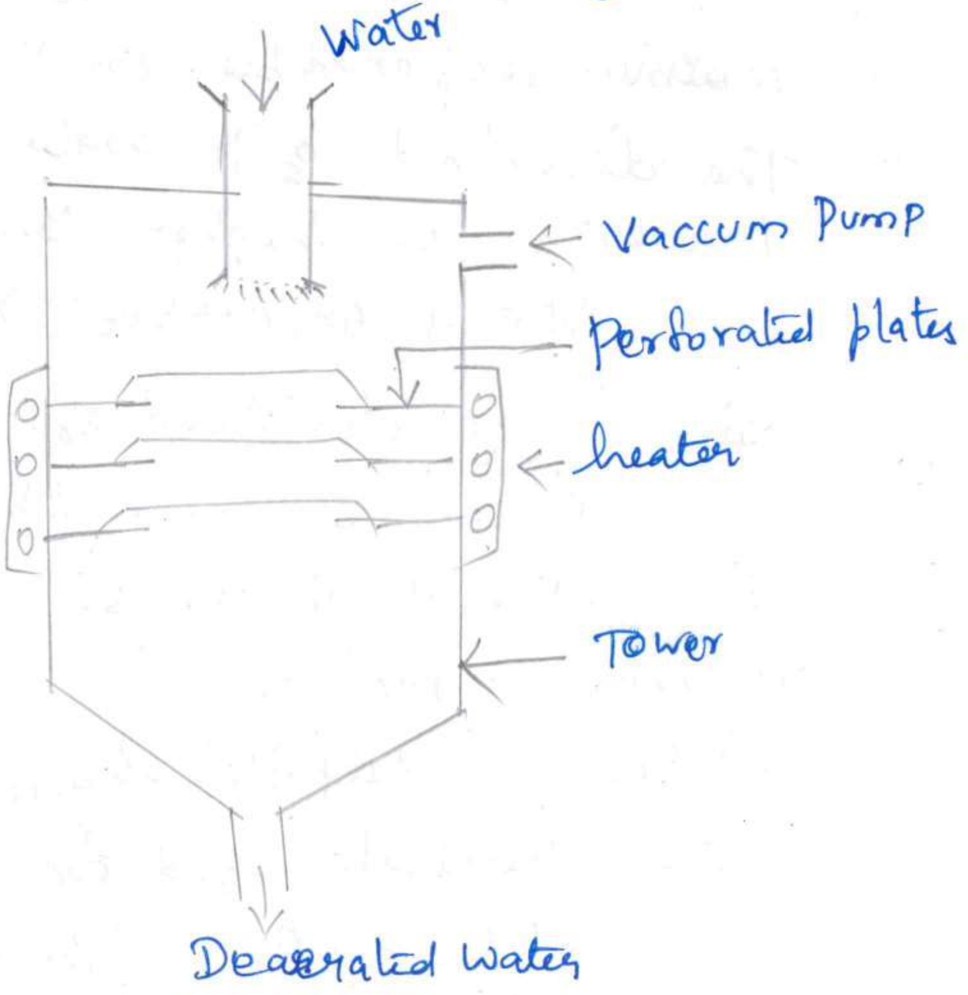
$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O.$$

Hydrazine is found to be an ideal component for measuring dissolved O_2 in the water. since the products are water and inert N_2 gas.

b) Mechanical - deaeration.

Dissolved O_2 can also be removed from water by mechanical deaeration.

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



Mechanical deaeration of water

2. Dissolved CO_2:

Dissolved CO_2 in water produce carbonic acid, which is acidic and corrosive is nature.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

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

Removal of D O_2:

1. By adding a calculated amount of NH_4OH into water.

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

2. By Mechanical de-aeration.

3. Dissolved $MgCl_2$:

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2\downarrow + 2HCl$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

Acids produced from dissolved salts are also mainly responsible for the corrosion of boilers. Salts undergoes hydrolysis of higher temp to give HCl, which corrodes boiler.

Removal of Acid: [Neutralization].

It can be avoided by the addition of alkali to the boiler water.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

TREATMENT OF BOILER FEED WATER.

WATER SOFTENING

CONTIONING METHODS

The process of removing hardness producing salts from water is known as softening (or conditioning of water.

There are two methods.

1. Internal treatment
2. External treatment.

Internal Treatment:

It involves the removal of scale forming substance, which were not completely removed in the external treatment, by adding chemicals directly into the boiler.

1. Phosphate Conditioning:

Scale formation can be avoided by adding sodium phosphate. It is used in high pressure boilers. The phosphate reacts with Ca^{2+} & Mg^{2+} salts to give soft sludges of Ca and Mg phosphates.

$$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4$$

Generally 3 types of phosphates are used.

a) Trisodium phosphate : Na_3PO_4 (too alkaline) – used for too acidic water.

b) Disodium phosphate : Na_2HPO_4 – weakly alkaline – used for weakly acidic water.

c) sodium dihydrogen phosphate:

NaH_2PO_4 - (acidic) - used for alkaline water.

colloidal conditioning:

Scale formation can be avoided by adding colloidal conditioning agents like kerosene, agar-agar, gelatin etc., It is used in low pressure boiler. These colloidal sustances get coated over the scale forming particles and convert them into non-adherent, loose ppt called sludge, which can be removed by blow-down operation.

3. Sodium aluminate conditioning:

Sodium aluminate, $NaAl_2O_2$ undergoes hydrolysis in boiler water to give gelatinous white precipitate of aluminium hydroxide and sodium hydroxide.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH.$$

This NaOH precipitates Magneisum as MgOH. The gelatinous ppts of sodium and magnesium hydroxide enrrap the colloidal silica and finely divided solids and settled easily. This can be removed easily by blow-down operation.

calgon conditioning:

calgon is sodium hexa meta phosphate $Na_2[Na_4(PO_3)_6]$. This substance interacts with calcium ions forming a highly soluble complex and thus prevents the precipitation of scale forming salt.

$$2\,caSO_4 + Na_2[Na_4(PO_3)_6] \rightarrow Na_2[ca_2(PO_3)_6] + 2Na_2SO_4$$

The complex $Na_2[ca_2(PO_3)_6]$ is soluble in water and there is no problem of sludge disposal. So calgon conditioning is better than phosphate conditioning.

External conditioning (or External Treatment-

It involves the removal of hardness producing salts from the water before feeding into the boiler.

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

I. Ion-exchange process: [Demineralisation process].

This process al removes almost all the ions both anion & cation present in hard water

Demineralisation process is carried out by using Ion-exchange resin, which are long chain insoluble organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties. The following two types of ion-exchange resins are used.

1. cation exchange resin (or cation exchanger
2. Anion exchange resin (or Anion exchanger.

1. Cation exchanger:

Resins containing acidic functional groups (−COOH, $-SO_3H$) are capable of exchanging their H^+ ions with other cations of hardwater. It is represented by RH_2.

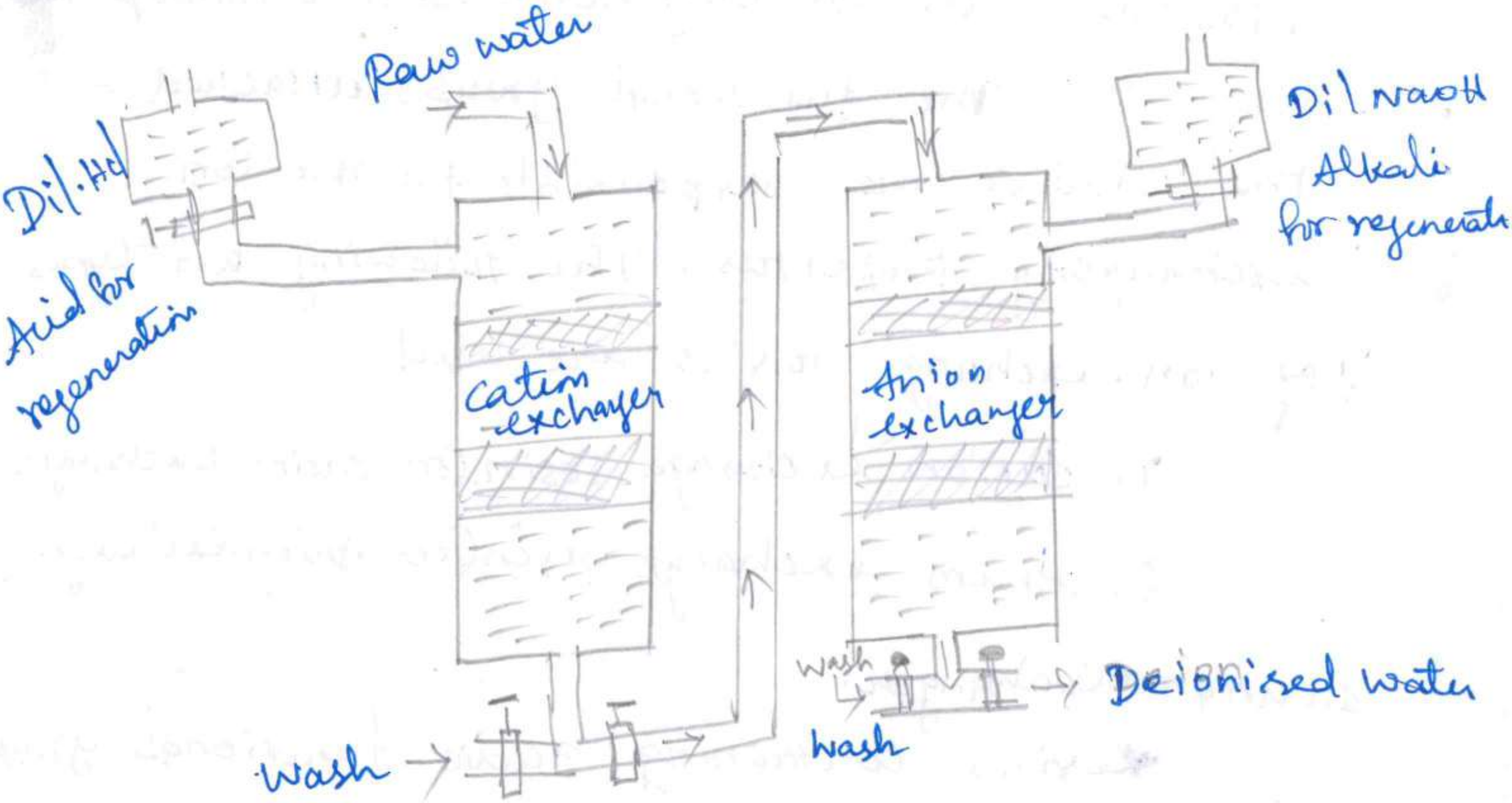
eg: Sulphonated coals, Sulphonated polystyrene.

$R-SO_3H$; $R-COOH \equiv RH_2$.

2. Anion Exchanger:

Resins containing basic functional groups ($-NH_2$, −OH) are capable of exchanging their anions of hard water. Anion exchange resin is represented as $R(OH)_2$.

eg: (i) cross-linked quarternary ammonium salt
(ii) Urea-formaldehyde resin
(iii) $R-NR_3OH$; $R-OH$, $R-NH_2 \equiv [R(OH)_2]$



Demineralisation Process.

The hard water first passed through a cation exchanger column. which absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} etc., present in the hard water.

$$RH_2 + CaCl_2 \rightarrow RCa + 2HCl$$

$$RH_2 + MgSO_4 \rightarrow RMg + H_2SO_4$$

$$RH + NaCl \rightarrow RNa + HCl.$$

This cation free water is then passed through a anion exchange column, which absorbs all the anions like Cl^-, SO_4^{2-}, HCO_3^- etc. Present in the water.

$$R'(OH)_2 + 2HCl \rightarrow R'Cl_2 + 2H_2O$$

$$R'(OH)_2 + H_2SO_4 \rightarrow R'SO_4 + 2H_2O$$

The water coming out of the anion exchanger is completely free from cations and anions. This water is known as demineralised or deionized water.

Regeneration

$$RCa + 2HCl \rightarrow RH_2 + CaCl_2$$

$$RNa + HCl \rightarrow RH + NaCl.$$

$$R^1Cl_2 + 2NaOH \rightarrow R^1(OH)_2 + 2NaCl$$

Advantages:

1. Highly acidic (or alkaline water can be treated by this process.

2. The water obtained by this process will have very low hardness (nearly 2 ppm).

Disadvantages:

1) Water containing turbidity, Fe and Mn cannot be treated, because turbidity reduces the output and Fe, Mn from stable compound with the resin

2) The equipment is costly and more expensive chemicals are needed.

Zeolite process (or Permutit process.

Zeolites are naturally occuring hydrated Sodium alumino silicates, Its general formula is $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ ($x=2-10$, $y=2-6$). The synthetic form is called Permutit. represented by Na_2Ze.

Process:

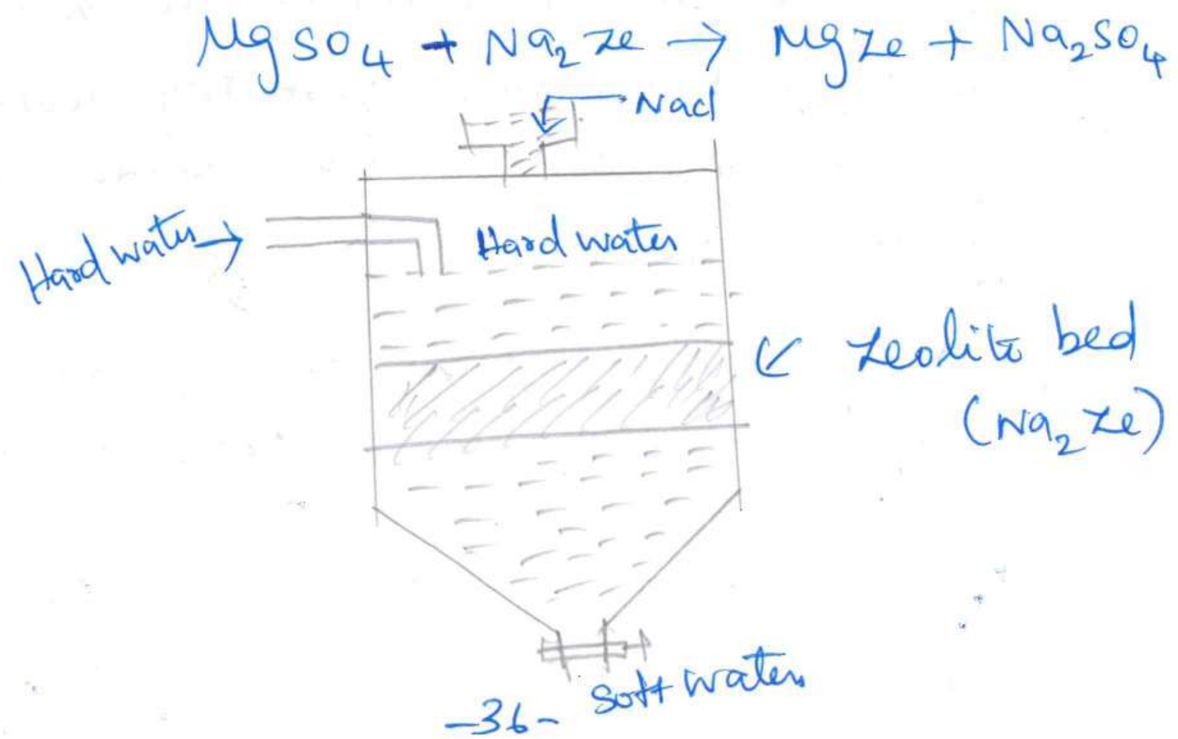
when hardwater is passed through a bed of sodium zeolite (Na_2Ze) kept in a cylinder it exchanges its sodium ions with Ca^{2+} and Mg^{2+} ions present in the hardwater to form calcium and magnesium zeolites.

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

$$Mg(HCO_3)_2 + Na_2Ze \rightarrow MgZe + 2NaHCO_3.$$

$$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$$

$$MgSO_4 + Na_2Ze \rightarrow MgZe + Na_2SO_4.$$



$$CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$$

$$MgCl_2 + Na_2Ze \rightarrow MgZe + 2NaCl$$

Regeneration. By treating with 10% NaCl

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2.$$

Advantages:

1. Obtained water will have 1-2 ppm of hardness
2. This method is cheap. b/c the regenerated Zeolite can be used again.
3. No sludge is formed.
4. Occupies small space (compact).
5. Operation is easy.

Disadvantages:

1. Turbid water cannot be treated
2. Acidic water cannot be treated
3. The softened water contains more dissolved sodium salts like $NaHCO_3$, Na_2CO_3. such water is boiled in boilers, CO_2 and NaOH is produced resulting in boiler corrosion, and caustic embrittlement.
4. Water containing Fe/Mn cannot be treated b/c regeneration is very difficult.

(v) cannot be used for brackish water.

b/c brackish water contains Na^+ - so the exchange rxn will not occur.

Difference b/w Zeolite and Demineralisation

Zeolite process	Demineralisation process.
1. It exchanges only cations	1. exchanges cation & anions.
2. Acidic water cannot be treated	2. Acidic water can be used.
3. The treated water contains relatively large amount of dissolved salts. which lead to Priming & foaming caustic embrittlement.	3. The treated water contain any dissolved salts. Hence there is no Priming and foaming
4. Water containing turbidity Fe, Mn cannot be treated	4. Water containing turbidity Fe, Mn cannot be treated.

UNIT-II

NANOCHEMISTRY

Introduction:

'Nano' means a billionth (1×10^{-9}m)

Nanoparticles:

Nanoparticles are from (1–50 nm).

Nano materials:

Nanomaterials are the materials having components with size less than 100 nm at least in one dimension.

- * Nanomaterials in one dimension, are layers such as a thin film ~~of~~ or surface coatings.
- * In two dimension, are tubes such as nanotubes and nanowires.
- * In three dimension, are particles like precipitates, colloids and quantum dots.

Nanochemistry (or) Nanoscience:

Study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales.

Nanotechnology:

Design, characterisation, production and applications of structures, systems and devices by controlling size and shape at 10^{-9}m scale or the single atomic level.

Distinction b/w nanoparticles and Bulk materials.

1. The size of nanoparticles are less than 100 nm in diameter, molecules are in the range of picometers, but bulk materials are larger in micron size.

2. Molecule is a collection of atoms.	2. NP is collection of few molecules (1-100) less than 100nm ~~but~~
3. Surface area is more	3. surface area is less.
4. Hardness is 5 times less than NM.	4. Hardness is 5 times more than the bulk materials.
5. Strength is lower than Lp.	5. Strength is 3-10 times more than the bulk materials.
6. Possess constant physical properties	6. Possesses size dependent properties
7. Corrosion rate is high	7. Corrosion resistance is high
8. Behaviour can be changed but cannot be enter inside the nano particles.	8. due to its size possesses unexpected optical properties.

eg: 1. Gold nanoparticles appear deep red to black color in soln.

2. ZnO NP' possesses superior UV blocking property compared to bulk material.

3. Absorbant of Solar radiation in photovoltaic cell containing NPs are higher than the film [bulk materials].

4. NPs possesses lower melting point than the bulk materials.

Important properties of Nanomaterials

1. Electrical properties

(i) Electrical conductivity decreases with a reduced dimension due to increased surface scattering.. However it can be increased, due to higher better ordering in micro structure.

eg. polymeric fibers.

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

eg: Ni - Metal hydride made of nanocrystalline nickel and metal hydride, require for less frequent recharging and [illegible] last must much longer.

2. Optical properties:

Reduction of material dimensions has pronounced effects on the optical properties.

eg: colour of metallic NPs may change with their sizes due to surface plasma resonance.

3. Mechanical properties:

The 'NM' have less defects compared to bulk materials, which increases the mechanical strength.

Eg: Nano-crystalline carbides are much stronger, harder and wear resistant and are used in micro drills.

4. Magnetic properties:

Ferro-magnetic behaviour of bulk materials disappear, when the particle size is reduced and transfers to super paramagnetics. This is due to the huge surface area.

Types of nanomaterials:

1. Nano particles
2. Nano clusters 0-dimension
3. Nanowire 1-D
4. Nano rods
5. Nanotubes 2D.

Nano particles:

The size of which ranges from 1-100nm. They have 3 dimensional structures.

eg. TiO_2, gold, silver, ZnO etc.

Applications:

1. TiO_2 is used in cosmetics as they are very good uv- absorber.
2. Nano-Ag are used as a catalyst in industries.
3. NP's are used in medicine.
4. Nano silver particles are used in making bone cement, surgical instruments etc.,

Nanoclusters:

These are fine aggregates of atoms or molecule. The size of which ranges from 0.1 to 10 nm. Of all the nanomaterials, nanoclusters are the smallest sized nano materials because of their close packing arrangement of atoms.

eg: CdS, ZnO etc.,

All the atoms, in nanocluster, are bound by forces like metallic, covalent, ionic, hydrogen bond or vannda waals force of attraction. clusters of certain critical size are more stable that others. Nano. clusters Growing of up to couple of 100 atoms, but larger aggregates containing 10^3 or more atoms are called nanoparticles.

Magic number:

It is the nos. of atom present in the clusters of critical sizes with higher stability

Nanorods:

Nano rod is two dimensional cylindrical solid material having [an aspect ratio (i.e) length to width ratio less than 20.

eg. ZnO, CdS, Gallium nitride nanorods.

Synthesis of nano rods:

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

Properties:

1. Nano rods are two-dimensional materials.
2. It exhibits optical & electrical properties

Applications:

1. Find applications in display technologies
2. Manufacturing of micro mechanics switches
3. Used in applied electric field. micro electro mechanical systems.
4. Used in energy harvesting and light emitting diodes.
5. Nanorods have used as cancer therapeutical

Nano wires:

It is two - dimensional cylindrical solid material having an aspect ratio. (i.e) length to width ratio greater than 20. Diameter of the nanowires ranges from 10 - 100nm.

eg: Different types of nanowires.

1. Metallic Nanowire — Au, Ni, Pt
2. Nanowires of Semiconductor — PbS, InP CdNi
3. Nanowires of insulators - SiO_2, TiO_2.
4. Molecular nano wire — DNA.

Synthesis of nanowire.

1. Template - assisted synthesis

It is a simple way to fabricate nanoclusters. 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. VLS (vapour - liquid - Solid) Method.

It involves the absorption of the source material from the gas phase into a liquid phase of catalyst. Upon super saturation of the liquid alloy, a nucleation event generates a solid ppt 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.

Uses of nanowires:

1. used for enhancing mechanical properties of composites.
2. To prepare active electronic components such as p-n junction and logic gates.
3. It replaces conventional copper wires used in computers, televisions.
4. used to link tiny components into very small circuits.
5. semiconductor nanowire play a vital role in future of digital computing.
6. It finds applns in high density data storage either as magnetic read heads or as patterned storage media.

Nano tubes:

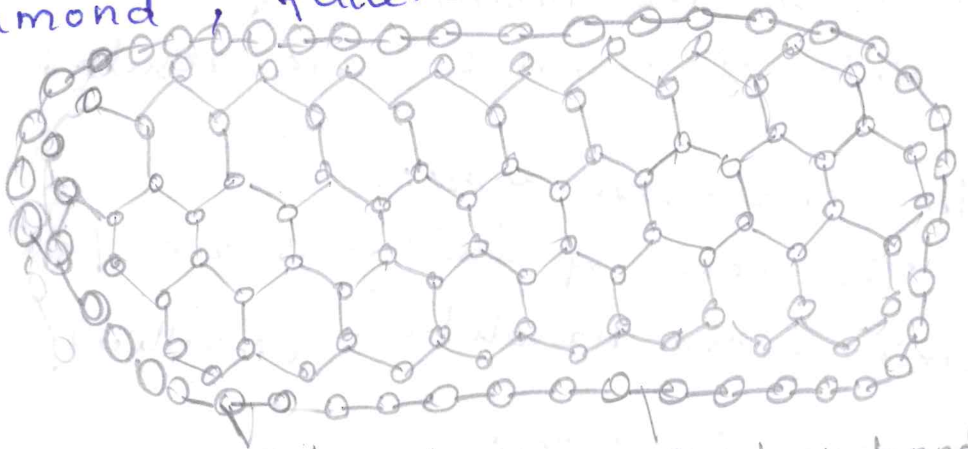
Nano tubes are tube like structures with diameter of 1-100 nm and a length of few nm to microns. Nanotubes consists of tiny cylinders of carbon and other materials like boron nitride. Nanotubes may be organic (or) inorganic.

eg: carbon nano tube
silican "
DNA "
Boron nitride "

1. CNTS (carbon nanotubes)

CNT 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 exits in different allotropic forms like graphite, diamond, fullerenece and nanotubes.



single walled carbon nanotubes.

CNTs are tubular forms of carbon. when graphite sheets are ~~tie~~ rolled into a cylinder, their edges join to each other form carbon nanotubes. Each carbon atom in the carbon nanotubes is linked by covalent bonds. But the number of NTs alighn into ropes and are held together by weak Wanderwaals forces.

Types (or) structures of CNT:

Depending upon the way in which graphites are rolled, two types of CNTs are formed.

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

SWNTS:

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

Based on the orientation of the hexagon lattice three kinds of Nanotubes are resulted.

(a) Arm - chair structure:

The lines of hexagons are parallel to the axis of the nanotube. (Metallic).

(b) Zig - Zag Structures:

The lines of carbon bonds are down the centre.

(c) chiral structures:

It exhibits twist or Spiral around the nanotube [semi conducting].

2. Multi walled nanotubes [MWNTs].

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

Synthesis of CNTs:

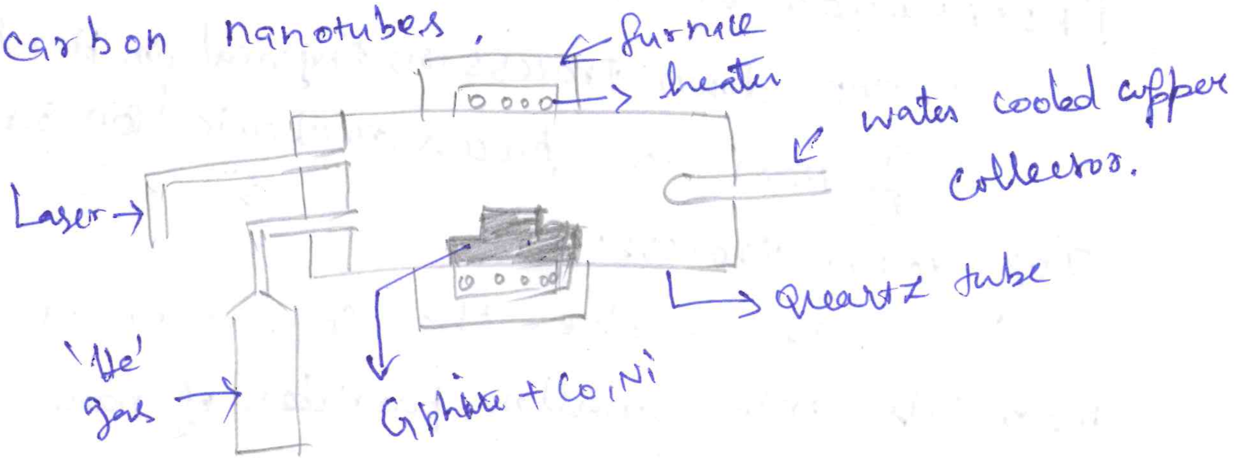
1. Pyrolysis of hydrocarbons.
2. Laser evaporation.

1. Pyrolysis:

CNTs are synthesised by the Pyrolysis of hydrocarbons such as acetylene at about 700°c in the presence of Fe-silica or Fe-graphite catalyst under inert condition.

2. Laser evaporation:

It involves vapourisation of graphite target, containing small amount of cobalt and nickel, by exposing it to an intensed pulsed laser beam at higher temp (1200°c) is a quartz tube reactors. An inert gas, 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.



Properties of CNTS

1. CNTS are very strong, withstand strain and posses elastic flexibility.
2. behaves like semiconducting materials.
3. It has very high thermal conductivity and kinetic properties.

Uses of CNTS

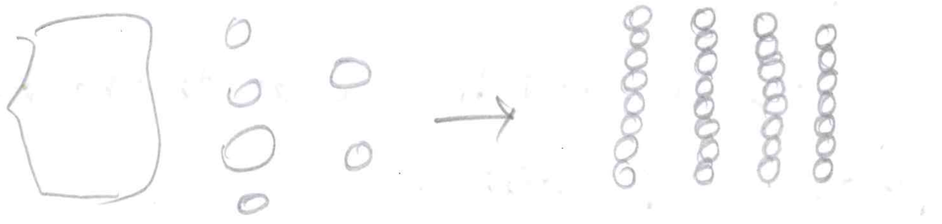
1. used in battery technology, and in industries as catalyst.
2. used as light weight shielding materials for protecting electronic equipments.
3. Used for drug delivery.
4. Composites, ICs.
5. used as catalyst for some chemical reactions.
6. water softening process, ~~as~~ CNT used as filter,
7. Acts as biosensor.

PREPARATION OF NANOMATERIALS

1. Top_down process (or) Physical (or) Hard ~~materials~~ Methods.
2. Bottom-down process (or) chemical (or) soft methods.

Top-down Process:

It involves the conversion of bulk materials into smaller particles of nano-scale structure.



Bottom-up process:

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

Important preparations.

1. Sol-gel process.

It involves the following steps.

1. Hydrolysis and Polycondensation
2. Gelation
3. Aging
4. Drying
5. Densification
6. crystallization.

Sedimentation:

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

(ii) centrifugation:

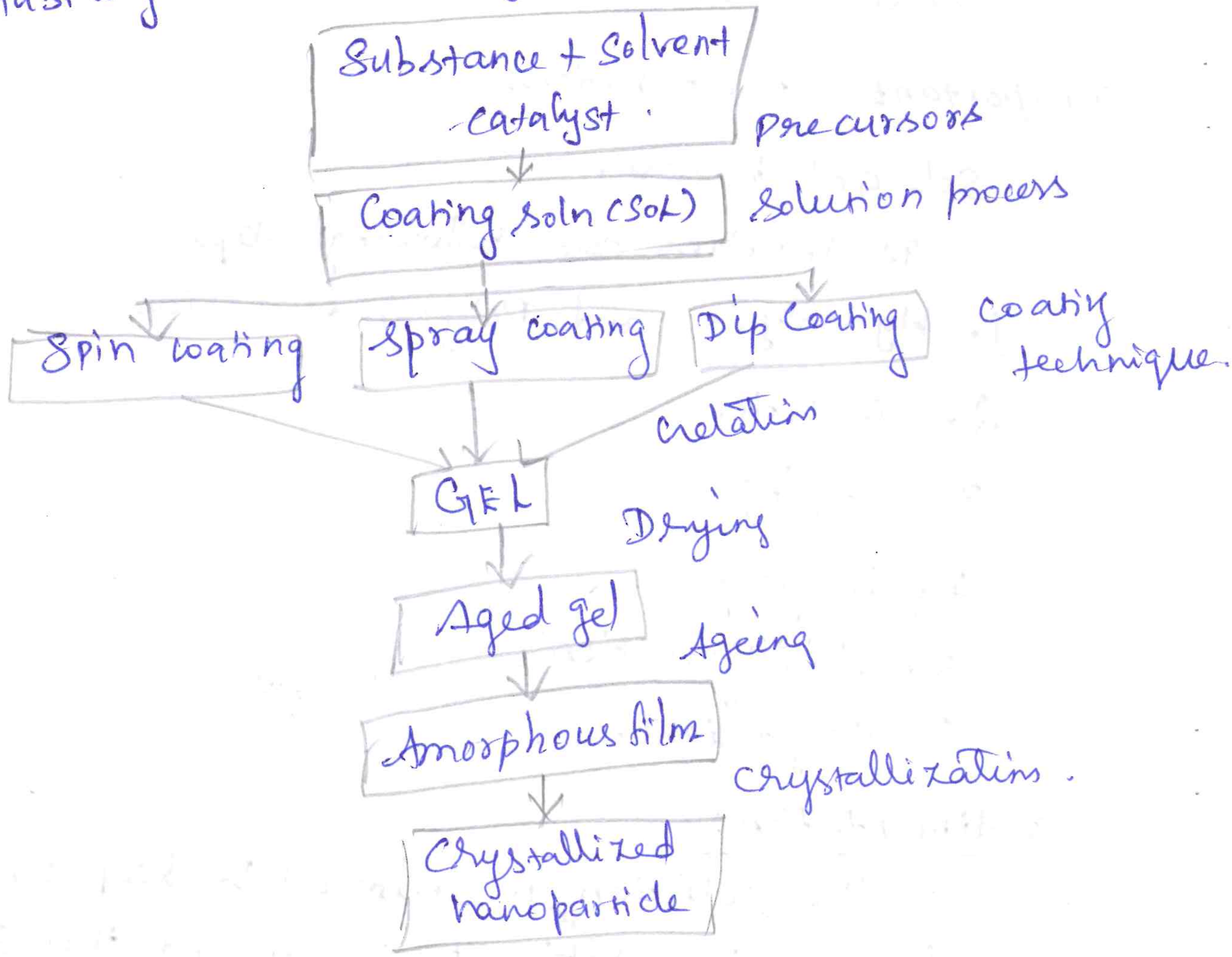
It is used to accelerate the process of phase separation.

(iii) Drying and densification.

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

(iv) Firing (or) crystallization:

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



various steps of sol-gel process.

Solvothermal synthesis:

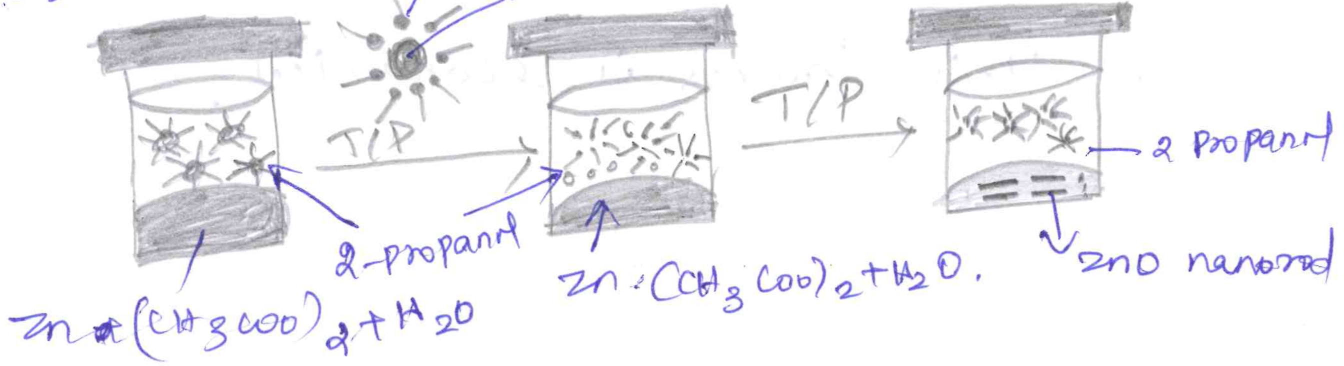
It involves the use of solvent under high temp (100°c to 1000°c) and moderate to high pressure (1 atm to 10,000 atm), that facilitate the interaction of precursors during synthesis.

Method:

A solvent like ethanol, methanol, 2-propanol is mixed with certain metal precursors and the soln mixture is placed in an auto clave 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.

eg: Solvothermal synthesis of ZnO.

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 soln is then heated to 65°c to allow ZnO growth for some period of time. Then a caping agent, (1-dodecane thiol) is injected into the suspension to arrest the growth. The rod shaped ZnO nano crystal is obtained.



Laser ablation:

This method involves vapourisation of target material containing small amount of catalyst (Ni or Co) by passing an intense pulsed laser beam at a high temp 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.

Uses:

1. Nanotubes having 10-20 nm and 100μm can be produced by this method.
2. Ceramic particles and coating can be produced.
3. Other materials like Si, C can be converted into NP.

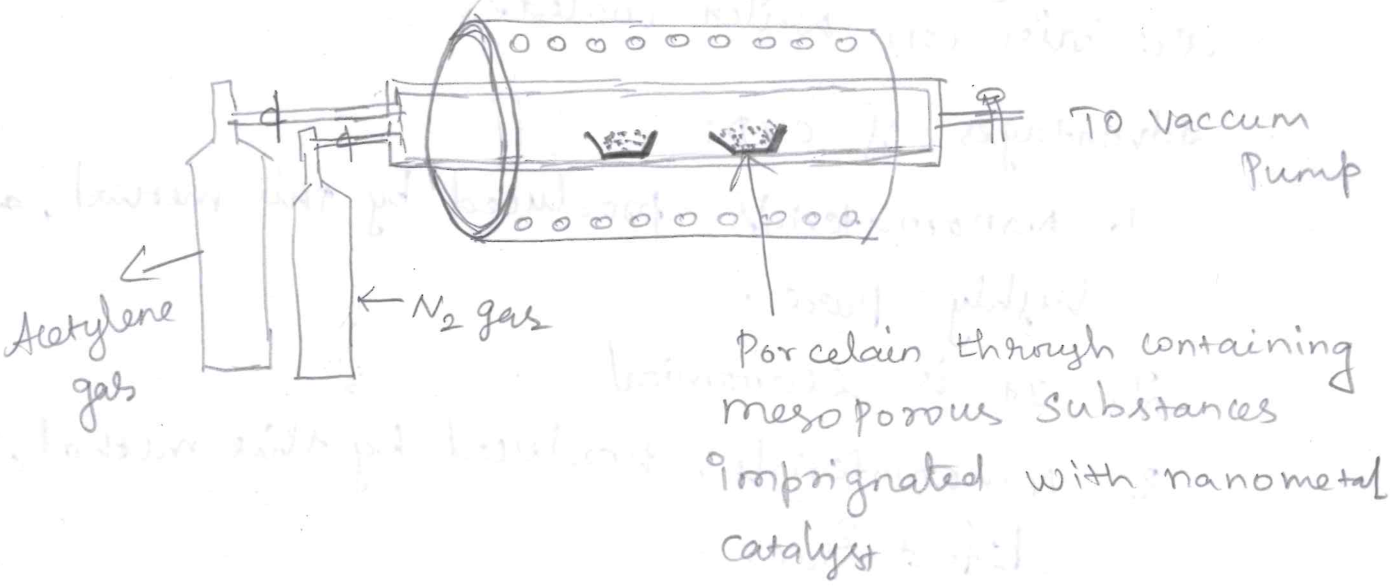
Advantages:

1. easy to operate
2. The amount of heat required is less.
3. ecofriendly i.e. No solvent is required.
4. product is stable
5. This process is economical.

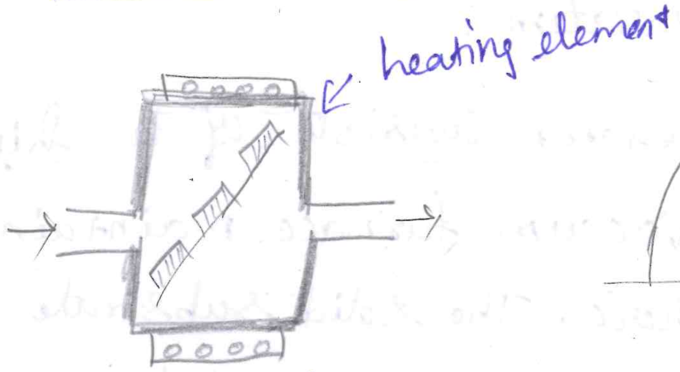
A. Chemical Vapour Deposition (CVD).

CNT Preparation.

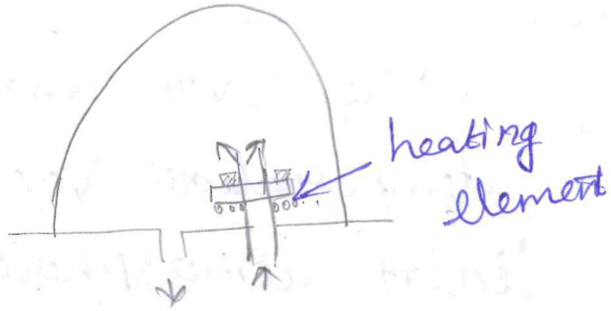
The CVD reactor consists of a higher temperature Vaccum furnace maintained at inert atmosphere. The solid substrate containing catalyst like Ni, Co, Fe supported on a substrate material like silica, quartz is kept inside the furnace. The hydrocarbons such as ethylene, acetylene and nitrogen cylinders are connected to the furnace. Carbon atoms produced by the decomposition at 1000°c, condense on the cooler Surface of the catalyst. As this Process is continuous, CNT is produced continuously.



Types of CVD Reactor:



Hot-wall CVD



Cold wall CVD

1. Hot-wall CVD

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

2. Cold-wall CVD

In cold wall CVD reactors substrates are directly heated inductively while chamber walls are air (or) water cooled.

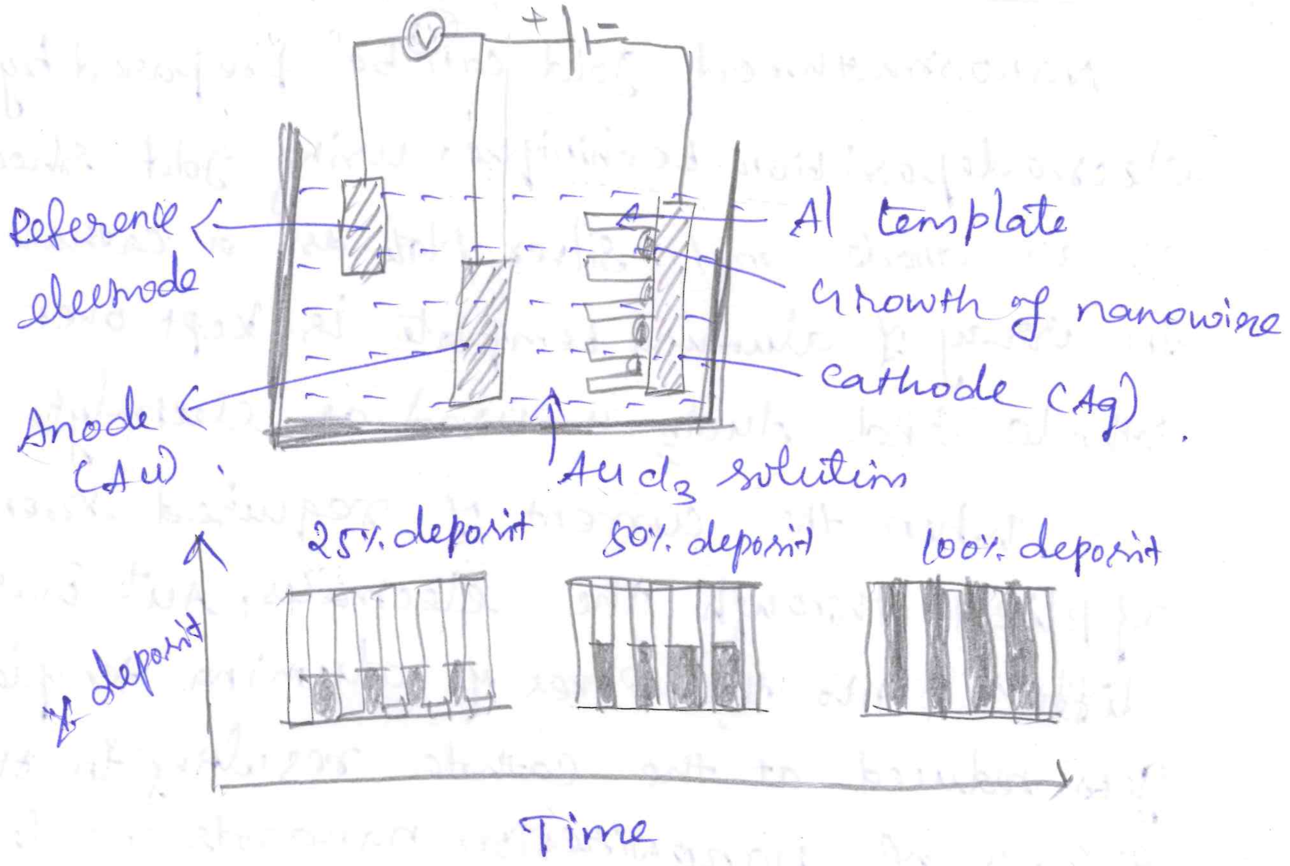
Advantages of CVD:

1. Nanomaterials, produced by this method, are highly pure.
2. It is economical
3. Nanomaterials, produced by this method, are defect free.
4. Mass Production can be done without Major difficulties.

5. Electro deposition (or) Electrochemical deposition

Electro deposition 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 synthesising metallic ~~nps~~ nanomaterials with controlled shape and size. Array of nano-structured materials with specific arrangements can be prepared by this method using an active template as cathode.

process of electro deposition:



Electro deposition method.

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

eg: Electrodeposition of Gold on silver

Nanostructured gold can be prepared by the electrodeposition techinique, using gold sheets as an anode and silver plate as a cathode. An array of alumina template is kept over the Cathode and $AuCl_3$ is used as electrolyte.

When the current of required strength is applied through the electrodes, Au^+ ions diffuce into the Pores of alumina templates and gets reduced at the cathode resulting in the growth of nanowires (or) nano rods inside the Pores of alumina template.

Advantages of Electro-deposition

1. cheap and fast
2. complex shaped objects can be coated
3. The film or wire obtained is uniform.
4. Metal nanowires including Ni, Co, Cu and Au can be fabricated by this method.

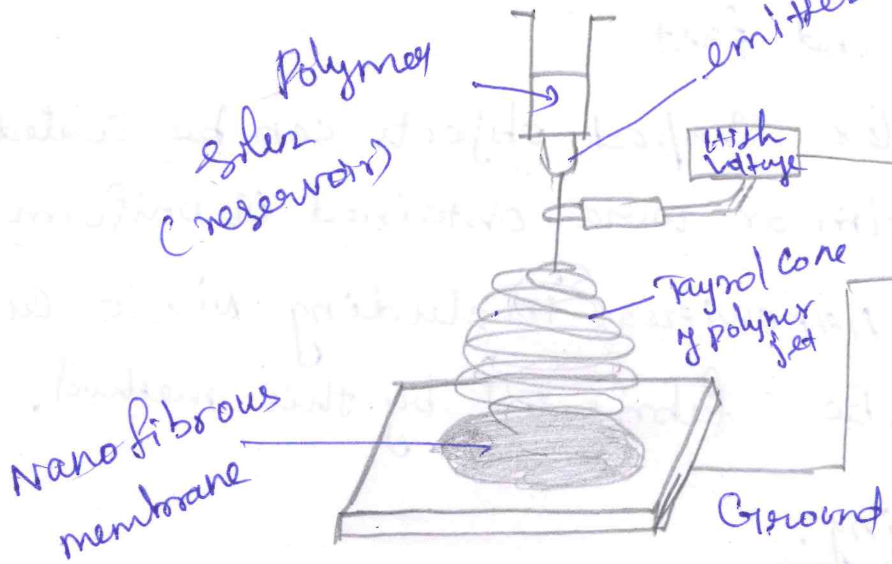
Electrospinning:

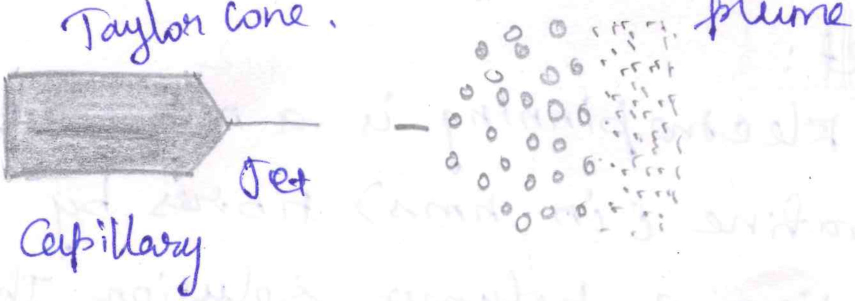
Def:

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

Components:

1. A high voltage power supply
2. A polymer reservoir that can maintain a constant flow rate of soln.
3. A conductive needle as polymer source connected to the high voltage power supply
4. A conductive collector (plane, drum, etc)





Process.

A Polymer is dissolved in a suitable solvent and is 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. When the electrostatic repulsion is higher than the surface tension the liquid meniscus is deformed into conically shaped structure known as Taylor cone. once the Taylor cone is formed, the charged liquid jet is ejected towards the collector. Depending upon the viscosity of the soln, solid fibre will be formed as the solvent

Applications:

1. It is used in diagnosis and treatment of diabetes
2. Electrospun fibres are used in ~~energy~~ energy storage devices such as, solar cell, fuel cell, super capacitors.
3. used in textiles for smart clothing, protecting clothing and fire retardant fibres.
4. Used in sensors like gas sensors, chemical sensors and fluorescence sensors.
5. In biomedical, it is used in drug delivery, artificial blood vessel and wound dressing.
6. e-spun fibres employed in a variety of applications such as filteration and thermal insulation.

Appln of Nanomaterials:

Medicine.

1. Nano drugs:: Nano materials are used as nano drugs for the cancer and TB therapy.
2. Laboratories on a chip:

Nano technology is used in the production of laboratories on a chip.

3. Nanomedibots:

Nano particles function as nanomedibots that release anti-cancer drug and treat cancer.

4. Gold coated nanoshells.

It converts light into heat enabling the destruction of tumours.

5. Gold nano particles as sensors:

Gold nano particles undergo colour change during the transition of nano particles.

6. Protein analysis:

Protein analysis can also be done using nanomaterials.

7. Gold nanoshells for blood immuno assay:

Gold nano shells are used for blood immuno assay.

8. Gold nanoshells in imaging

Optical properties of the gold nano shells are utilized for both imaging and therapy.

9. Targeted drug delivery using gold nano particles.

It involves slow and selective release of drugs to the targeted organs.

10. Repairing work: Nano technology is used to partially repair neurological damage.

II In Agriculture:

1. Nanomaterials prepared by eco-friendly and green method with plant extracts could increase agriculture potential for improving fertilization process, plant growth regulates.
2. They also minimize the amount of harmful chemicals that pollute the environment.
3. Nanosensors are used ~~in~~ crop protection for the identification of diseases and residues of agrochemicals.
4. Nanodevices are used for the genetic engineering of plants.
5. Nanomaterials are used in plant disease diagnostics.
6. It is also used in Postharvest management.
7. Precesion farming techniques might be used to further improve the crop yields but not damage soil and water.
8. Some nanomaterials are used as antimicrobial agents in food packing especially silver nanoparticles are in great interest.

9. Nano particle-based pesticides and herbicides are being explored for the application of antimicrobial agents to protect crops from various diseases.

IV In energy:

Nanomaterial are used in several applications 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, which can even be used as running power plants.

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 the sea.

3. producing high efficiency light bulbs.

Nano-engineered polymer matrix is used for the production of high efficiency light bulbs.

7. Titanium based nano ~~cryst~~ catalysts are being increasingly used in photo catalysis.

8. Nano crystalline MgO - Particles act as an effective catalyst for dehydrogenation.

UNIT - III

Phase Rule.

INTRODUCTION.

All the chemical reactions can be broadly classified into two types.

1. Irreversible reaction

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

2. Reversible Reaction

Homogeneous Reversible Rxn [Law of mass action

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

heterogeneous reversible Rxn [phase rule.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

gnb willard gibbs]

Phase rule:

If the eqbm between any number of Phases is not influenced by gravity, or electrical or magnetic forces but is influenced only by Pressure, temp and Concentration, no. of degree of freedom (F) of the systems is related to numbers of Components (C) and no. of Phases (P) by the following phase rule eqn..

$$\boxed{F = C - P + 2}$$

Definition of terms with examples

1. Phase (P)

Phase is defined as "any homogeneous physically distinct and mechanically separable portion of a system which is separated from other parts of the system by definite boundaries.

eg: (a) Gaseous phase (air).

All gases are completely miscible and there is no boundary between one gas and the other.

(b) Liquid phase:

The no. of liquid phases depends on the no. of liquids present and their miscibilities

Benzene-water ⇒ two liquid phase, one vapour phase.

Alcohol-water ⇒ one liquid phase / one vapour phase.

(c) Solid phase:

Decomposition of $CaCO_3$

$$CaCO_{3(s)} \rightleftharpoons \underset{(s)}{CaO} + CO_{2(g)}$$

In involves three phases $CaCO_{3(s)}$, $CaO_{(s)}$ and $CO_{2}(g)$.

(d) Ice$_{(s)}$ $\rightleftharpoons$ water$_{(l)}$ $\rightleftharpoons$ vapour$_{(g)}$

(e) A soln of a substance in a solvent consists of one phase only.

eg: sugar soln in water.

f) An emulsion of oil in water forms two phases.

g) $MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$. (Three phases).

h) Rhombic sulphur$_{(s)}$ $\rightarrow$ monoclinic sulphur$_{(s)}$

It form two phases

i) $\underset{(s)}{CaSO_4} + \underset{(l)}{5H_2O} \rightleftharpoons \underset{(s)}{CuSO_4 \cdot 5H_2O}$.

three phases: Component: 2.

2. <u>Component(C)</u>

Component is defined as, 'the smallest number of independently variable constituents by means of which the composition of each phase can be expressed in the form of a chemical equation

Examples:

(1) Ice$_{(s)}$ $\rightleftharpoons$ water$_{(l)}$ $\rightleftharpoons$ vapour$_{(g)}$ $\Rightarrow$ [Two component]

(2) Sulphur $\Rightarrow$ Rhombic $\rightleftharpoons$ monoclinic $\rightleftharpoons$ liquid $\rightleftharpoons$ vapour [one component]

(3) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Three phases, two component systems.

4) $Pcl_{5\,(s)} \rightarrow Pcl_{3\,(l)} + cl_{2\,(g)}$.

Three phases, Three component is two.

5) Aqueous solution of Nacl is a two component system. The constituents are Nacl & H_2O.

6) $CuSO_4 \cdot 5H_2O_{(s)} \rightleftharpoons CuSO_4 \cdot 3H_2O_{(s)} + 2H_2O_{(g)}$.

It is also a two component system.

7) $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$.

two phases; one component system

B/c when NH_3 & HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH_4Cl and hence the system will be one component system.

Degree of freedom (F).

Degree of freedom is defined as " the minimum number of independent variable factors such as temp, pressure and conc. which must be fixed in order to define the system completely.

if F=1 → univalent

F=2 → ~~bivalent~~ bivariant

F=3 → ~~trivalent~~ trivariant

F=0 ⇒ nonvariant.

eg) 1) $Ice_{(s)} \rightleftharpoons water_{(l)} \rightleftharpoons vapour_{(g)}$.

Phase = 3 ; Component = 1.

$F = C - P + 2 = 1 - 3 + 2 = 0$. Nonvariant

2) $water_{(l)} \rightleftharpoons watervapour_{(g)}$. [$F = 1 - 2 + 2$]

$F = 1$.

3) Gaseous mixture of N_2 & H_2.

$F = 2 - 2 + 2 = 2$ ⇒ Bivariant.

Phase diagram:

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

Types: 1. P–T 2. T–C.

1. P–T diagram:

If the Phase diagram is plotted between temperature against pressure, the diagram is called P–T diagram. It is used for one component systems.

2. T–C diagram: If the phase diagram drawn b/w temp Vs composition, the diagram is called T–C diagram. used for two component systems.

Uses of Phase diagram

1. It is possible to predict from the phase diagrams whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two Metals

2. Useful is understanding the properties of materials in the heterogeneous eqbm systems.

3. The study of the melting eutectic alloys used in soldering, can be carried out using phase diagram.

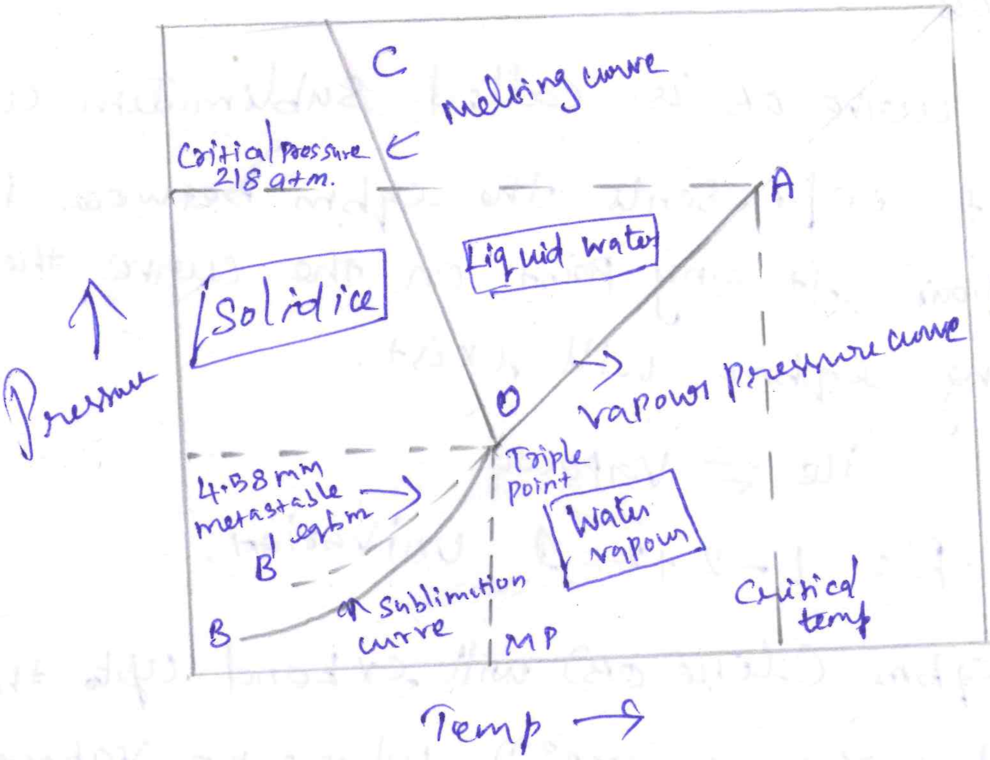
ONE COMPONENT SYSTEM :

WATER SYSTEM

Water exists in three possible phases namely solid, liquid and vapour. Hence there can be three forms of equilibria.

$$\text{Solid} \rightleftharpoons \text{liquid}$$
$$\text{Liquid} \rightleftharpoons \text{vapour}$$
$$\text{Solid} \rightleftharpoons \text{vapour}$$

This phase diagram contains curves, areas and triple point.



Curve OA:

The curve OA is called vapourisation curve It represents the eqm b/w water and vapour. At any point on the curve the following eqbm will exist.

$$\text{Water} \rightleftharpoons \text{water Vapour}.$$

$$F = C - P + 2$$
$$= 1 - 2 + 2 = 1. \text{ Univariant}$$

This eqbm (OA). will extend unpto the Critical temp (374°C). Beyond the critical temperature the eqbm will disappear only Water vapour will exist.

Curve OB:

The curve OB is called sublimation curve of ice. It represents the eqbm between ice and and vapour. At any point on the curve the following eqbm will exist.

$$\text{ice} \rightleftharpoons \text{vapour}.$$

$$F = 1 - 2 + 2 = 1 \text{ univariant}.$$

This eqbm (line OB) will extend upto the absolute zero (−273°c), where no vapour can be present and only ice will exist.

Curve OC:

The curve OC is called melting point curve of ice, it represents the eqbm between ice and water. At any point on the curve the following eqbm will exist.

$$\text{ice} \rightleftharpoons \text{water}$$

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

$F = 1$; univariant.

Point 'O' Triple Point

The three curves OA, OB and OC meet at a point 'O' where three phases namely solid, liquid and vapour are simultaneously at equilibrium.

This point is called triple point, at this point the following eqbm will exist,

$$\underset{(s)}{\text{ice}} \rightleftharpoons \underset{(l)}{\text{water}} \rightleftharpoons \underset{(g)}{\text{Vapour}}$$

$$F = C - P + 2 = 1 - 3 + 2 = 0.$$

Temp and pressure at the point 'O' are 0.0075°c and 4.58 mm respectively.

<u>Curve OB' : [Metastable eqbm].</u>

The curve OB' is called vapour pressure curve of the super-cool water or metastable equilibrium, where the following equilibrium will exist.

Super-cool water ⇌ vapour.

Sometimes water can be cooled below 0°c without the formation of ice, this water is called super-cooled water. Super cooled water is unstable and it can be converted into solid by "seeding" or by slight disturbance.

Areas:

Areas AOC, BOC, AOB represents water, ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temp and pressure. $F = C - P + 2 = 1 - 1 + 2 = 2.$

Bivariant

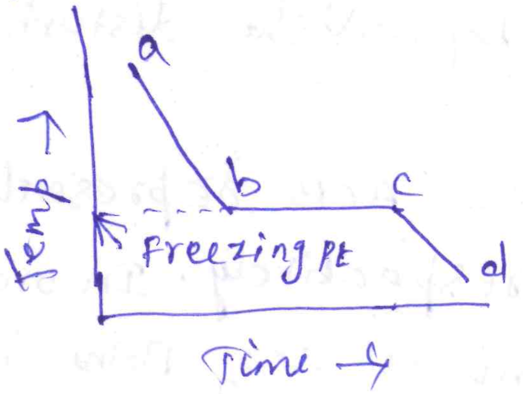
Experimental method of Construction of a simple eutectic - phase diagram.

Thermal analysis (or) cooling curves

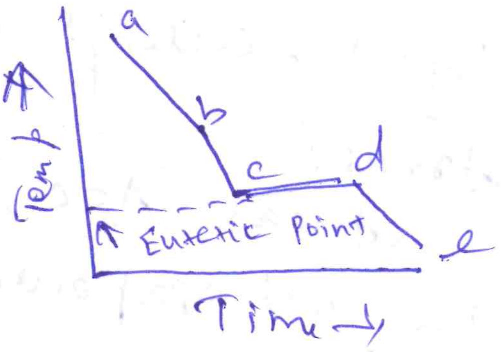
Thermal analysis is a method involving a study of the cooling curves of various compositions of a system during solidification. The Shapes of the freezing point curves for any system (involving Methods) can be determined by thermal analysis. The form of the cooling curve indicates the composition of the solid.

Cooling curve for a pure Solid

A Pure Substance in the fused state is allowed to cool slowly and the temp is noted at different time interval. These graph is plotted b/w temperature and time.



Cooling curve of Pure solid



Cooling curve of a mixture A & B.

Initially the rate of cooling is continuous. When it reaches the point 'b' solid begins to appear, now the temp remains constant until the liquid Melt is completely solidified. Solidification completes at the point 'c'. The horizontal line 'bc' represents the eqbm b/w the solid and liquid melt. After the point 'c' temp of the solid begins to decrease along the curve 'cd'.

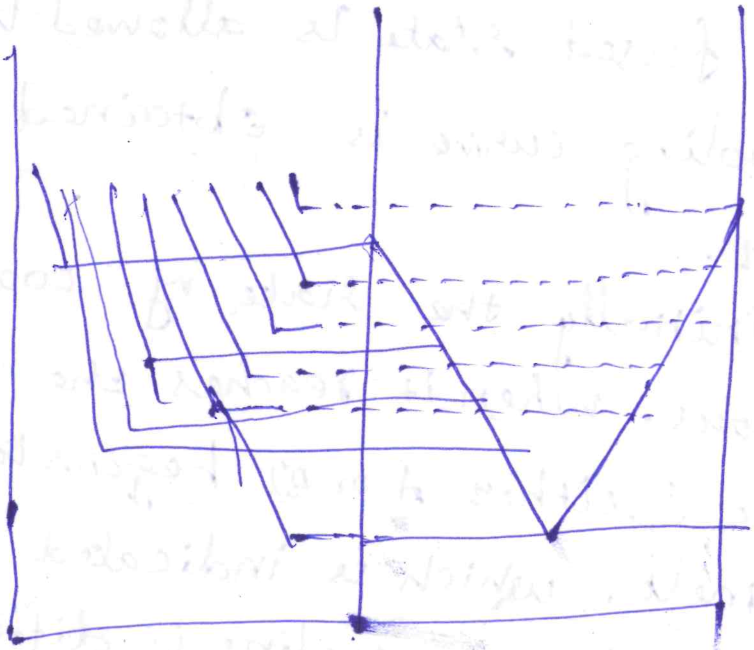
Cooling curve for a mixture

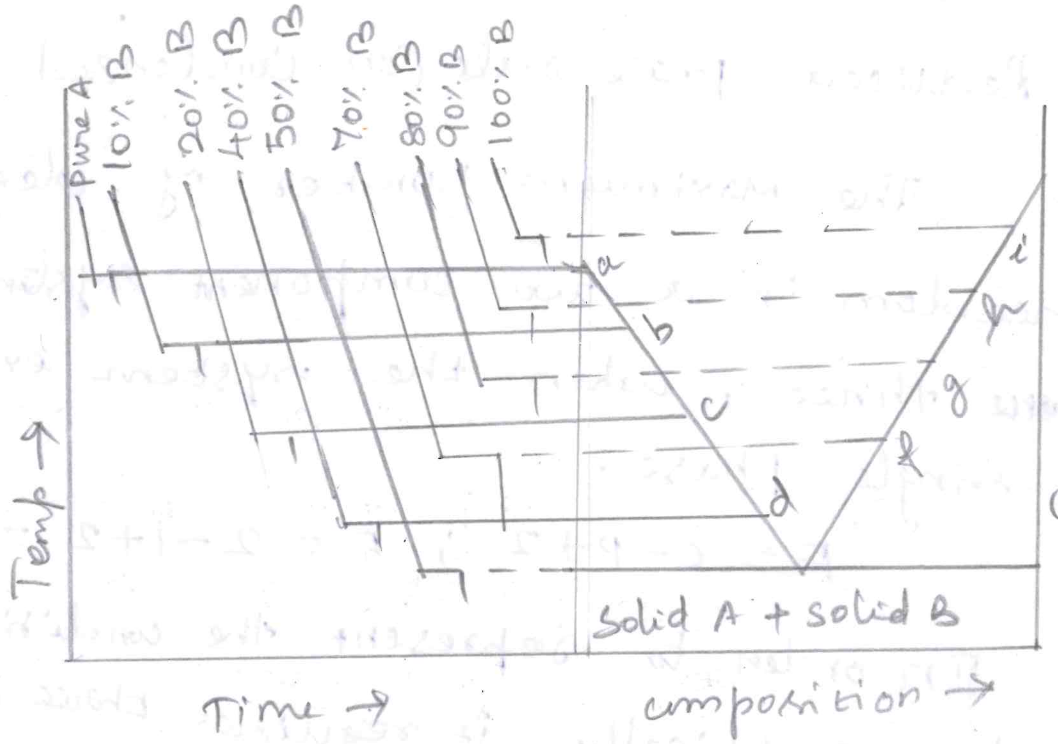
If a mixture of two substances (A & B) in the fused state is allowed to cool slowly, the cooling curve is obtained in a similar manner.

Initially the rate of cooling is continuous. When it reaches the Point 'b' one substance (either A or B) begins to solidify out of the melt, 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. Now the temp remains constant until the liquid melt is completely solidified.

which forms the eutectic mixture (line cd). After the break point 'd' cooling of solid mass begins. The temp of horizontal line of 'cd' gives the eutetic temperature.

The experiment is repeated for different compositions of A and B and the various cooling curves are recorded. From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temp in Y-axis.





cooling curve of various composition of two solids.

Uses of cooling curves

1. Melting point and eutetic temperature can be noted from the cooling curve.
2. percentage purity of the compds can be noted.
3. Behaviour of compds can be clearly understood
4. The composition corresponding to its freezing point yield the composition of the alloy.
5. The procedure of thermal analysis can be used to derive the phase diagrams of any two component system.

TWO COMPONENT SYSTEMS

Reduced phase rule (or) Condensed systems.

The Maximum number of degree of freedom in a two component systems will be ~~dcree~~ three, when the system exists as a single phase.

$F = C - P + 2$; $F = 2 - 1 + 2 = 3$.

In order to represent the conditions of eqbm graphically, it requires three co-ordinates namely P, T and C. This requires three dimensional diagram, which cannot be conveniently represented on paper. Therefore any two of the three variables must be chosen for graphical representation.

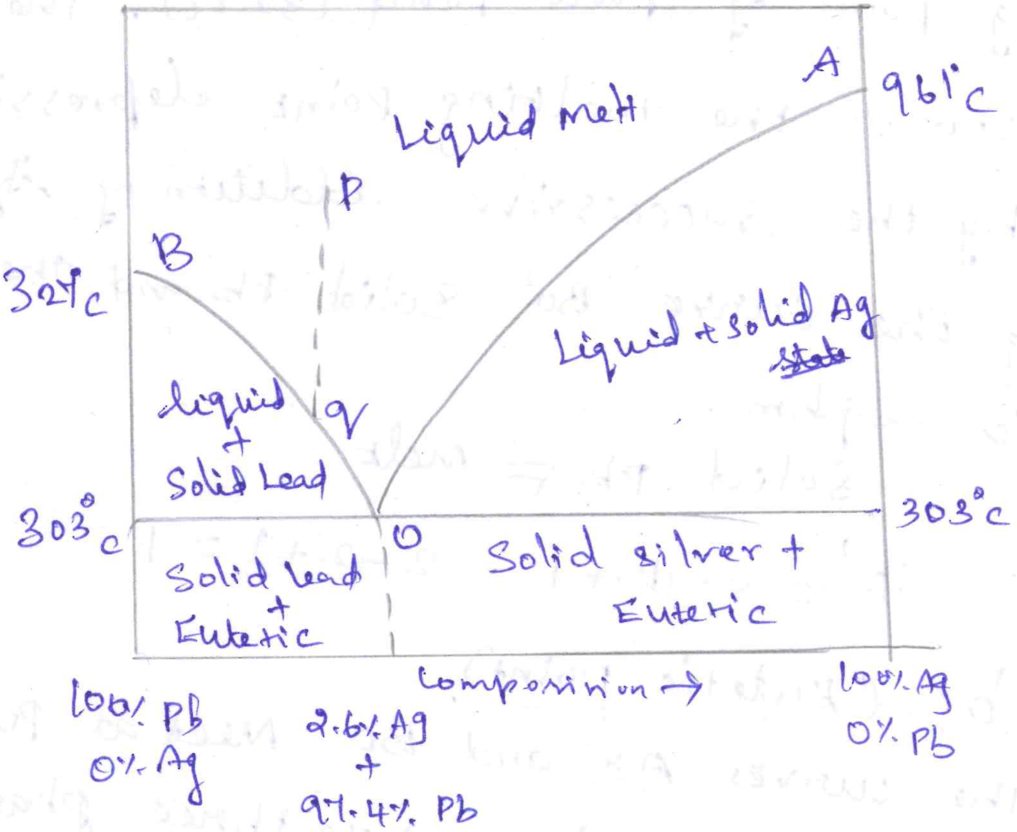
$$\boxed{F' = C - P + 1}.$$

eg: Binary Alloy system (or) The Simple Eutectic System:

Lead - silver system [Pb - Ag]

Solid Ag.

$F' = C - P + 1$



Curve AO:

The curve AO is known as freezing Point curve of silver. Point 'A' is the melting Point of pure Ag (961°c). The curve AO shows the melting Point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in eqbm.

Solid Ag ⇌ Melt

According to reduced phase rule eqn,

$F = C - P + 1 = 2 - 2 + 1 = 1$.

Curve BO: The curve BO is known as freezing point curve of Pb. Point B is the

Melting point of pure Lead (327°c). The curve Bo shows the melting point depression of 'Pb' by the successive addition of 'Ag'. Along the curve 'Bo' solid Pb and the melt are in eqbm.

Solid Pb ⇌ Melt

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

Point 'o' (Eutetic point).

The curves Ao and Bo Meet at Point 'o' at a temp of 303°c, where three phases (solid Ag, Solid Pb, liquid melt) are in eqbm.

solid Ag + Solid Pb ⇌ Melt.

$$F' = C - P + 1 = 2 - 3 + 1 \Rightarrow F' = 0$$

The system is non-Variant.

The Point 'o' is called eutetic point or Eutetic temperature and its corresponding composition 97.4% Pb + 2.6% Ag is called eutetic composition. Below this Point the eutetic compound and the metal solidify.

Areas:

The area above the line AOB has a single phase (molten pb + Ag).

$$F' = C - P + 1$$

$$= 2 - 1 + 1 = 2.$$

The system is bivariant.

Both the temp and composition have to be specified to define the system completely.

The area below the line AO (Solid Ag + Liquid melt) below the line BO (Solid Pb + liquid melt) and below the Point 'O' (Eutectic compd + Solid Ag (or) Solid Pb) have two phases and hence the system is univariant.

$$F' = C - P + 1 = 2 - 2 + 1 = 1.$$

The system is Univariant.

Application of Pattinson's process for the desilverisation of Argentiferous Lead.

The Argentiferous Lead, Consisting of a very small amount of Silver (0.1%) is heated to a temp above its melting Point, so that the system consisting of only the liquid phase represented by the Point 'p'. It is then allowed to cool. The temp falls down along the line pq. As soon as the point q is reached. Pb is crystallised out and the soln will Contain relatively increasing amount of Ag. On further cooling more and more Pb is separated along the line 'Bo' the mlt continues to be richer and richer in silver until the point 'o' is reached, where the percentage of Ag rises to 2.6%.

Thus the process of raising the relative proportion of Ag in the alloy is known as Pattinson's Process.

Uses of Eutectic system:

1. Suitably alloy composition can be predicted with the help of eutetic systems.

2. Eutetic systems are used in Preparing Solders used for joining two metal pieces together.

Uses of Phase rule:

1. It is applicable to both Physical and Chemical eqbm.
2. It is a convenient method of classifying the eqbm states in terms of phases, Components and degree of freedom.
3. It indicates that the different systems having the same degrees of freedom behave similarly.
4. It helps in deciding whether the given number of substances remain in eqbm or not.

Limitations of Phase Rule:

1. Phase rule can be applied only for the systems in eqbm.
2. only three variables like P, T, C are considered. but not electrical, magnetic, 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 deviations occur.

Composite Materials:

A composite material may be defined as " a material system consisting a mixture of two (or) more micro - constituents, which are mutually insoluble, different in form (or) composition and forming distinct phases".

Advantages:

1. Possess higher specific strength and lower specific gravity.
2. Possess lower electrical conductivity and thermal expansion.
3. better creep, fatique strength, corrosion and Oxdn resistance.
4. They maintain very good strength, even upto high temperature.

Constituents of Composites:

1. Matrix phase (or) matrix resin
2. Disappeared phase (or) Reinforcements.

Matrix phase (or) Matrix resin

1. Metal matrix composites (MMC)
2. Ceramic Matrix " (CMC)
3. Polymer matrix composites (~~CMC~~ PMC)

respectively.

Liquid resins:

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

eg: epoxy adhesives, Polysulphides are typical Commericially available adhesives.

Cure Reactions.

Formation of cross-linking in certain Polymers is known as cure reaction.

Dispersed Phase (or) Reinforcement.

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

eg. Fibres, Particulates, Flakes, whiskers.

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.

1. Fibres:

Fibres are long and thin filament of any macromolecular substance such as polymer, metal or ceramic having high length to diameter ratio at least 100:1. The fibre can be used in various of forms like continuous rovings, cloth, chopped strands etc.

Characteristics of fibre:

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

Classification of fibres

1. Natural fibre: Cotton, wool, silk, sisal, jute, coir
2. Semi synthetic: Rayon, cellulose
3. Synthetic fibre: Polyester, glass fibres, aramid fibers
4. Aramid fibres: aromatic polyamides. eg Kevlar

Important Natural Fibres:

(a) **cotton Fibres:** It is a vegetable fibre and is made of cellulose molecule, which is a linear polymer of β- glucose. used in Dough moulding Compounds (DMC). Mostly phenolic resin based moulding compounds.

(b) **wood fibre:** wool is a animal protein fibre. Like other proteins, wool 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. The elastic property of the wool fibre is due to the presence of hydrogen bond between various polypeptide chain.

(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. It has a bright lusture and it is an excellent insulator of heat, hence it is warm in winter and cool in summer.

(d) **Sisal:** Another low- cost fibrous material, which is also used in phenolic based dough moulding compounds.

Jute and coir: Low cost fibrous material for reinforcement for polyester resins. They can be used woven cloth (or) in yarn form the filament winding. ~~A varis~~ of objects like houses, building and fishing have been developed.

Synthetic fibres:

a. **PET** Polyethylene terephthalate (PET) ~~or~~ Terylene (or) Dacron.

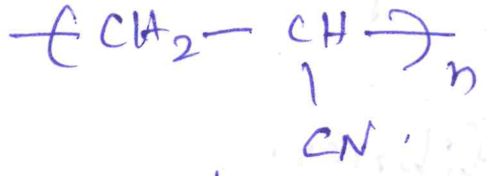
This fibre is used as surface tissues which can be ~~fa~~ used to provide improved chemical and abrasion resistance. They may be used in light weight woven fabrics. rarely used as the main reinforcement, even

b. **Poly propene:** It is obtained by polymerisation of propylene, ~~There fabrics used~~ on These fibres ~~fabri~~ possess better hardness, strength stiffness. These fibres are used in making ropes, carpets, blankets, hand bags, apparels etc.

Carbon fibre:

Carbon fibres are obtained as a continuous filament by the properties of organic fibres, in an inert atms which as cellulose, polyacrylonitrile (PAN).

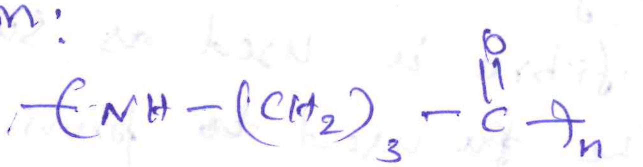
PAN =



$-\!\!\left(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)\!\!-_n$

Uses: conventional constructions (or light weight woven fabrics.

(d) Nylon:



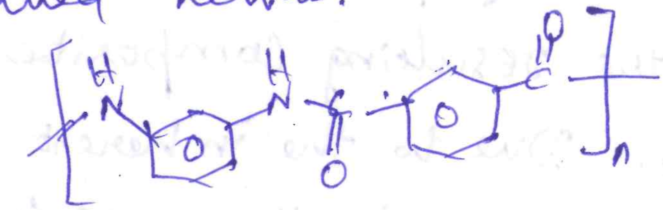
$-\!\!\left(NH-(CH_2)_3-\overset{\displaystyle O}{\overset{||}{C}}\right)\!\!-_n$

Nylon fabrics are used in reinforcements for epoxide resin systems to give flexible laminates with high impact abrasion and chemical resistance. They are sometimes combined with glass fibre reinforcements for specialized applications.

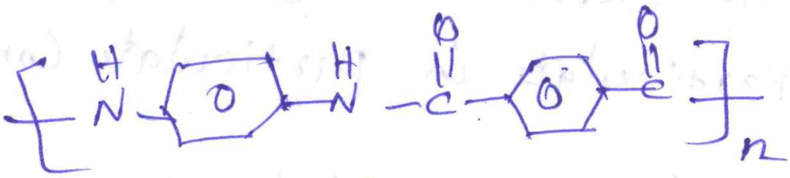
Aramid fibres:

Aromatic polyamides are called as aramids. They are made by spinning liquid crystals aramid oligomers (kevlar).

The meta-linked Poly-m-phenylene isophthalimide is called Nomex, where as Para-linked poly-p-phenylene phthalimide is called Kelvar.



Nomex.



Kevlar.

Properties:

These are used as high Performance fibers b/c of their high molecules, tensile strength, stability at high temperatures, wide temp range (−200 to 200°C) for retaining mechanical powperties, excellent toughness and impact resistance.

Uses:

in reinforcements, in tyres and bullet proof clothing, race drivers, astronaut suits etc.,

Particulates:

Particulates are small pieces of hard solid materials. They may be metallic (or) non-metallic. Generally distribution of particles in a given matrix is random, so the resulting composites are usually isotropic. Due to the inherent hardness, the particles in a composite cause constraints on the plastic deformation on the matrix.

Effect of Particulate in particulate Composites.

(i) Surface hardness gets increased

(ii) Wear & abrasion resistance are increased.

(iii) Performance at elevated temp is improved.

(iv) Shrinkage and friction is reduced.

(v) Electrical and thermal conductivities are modified.

Flakes:

Flakes are very thin solid materials.

eg. Mica Flakes.

1. They impart equal strength in all direction in a plane compared to fibres which reinforce unidirectionally one.

2. Packed more efficiently than fibre (or) Spherical Particles.

(iii) Flakes especially mica can be used in electrical and thermal insulating appliances.

Whiskers:

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

eg: Graphite, silicon carbide, silicon nitride.

1. Possess much higher strength.
2. Possess high elastic modulus and high degree of crystalinity.
3. They possess exceptionally high strength
4. As it is costly and ~~different~~ difficult to incorporate in matrix they find limited use in composite.

Types of composites.

Polymer composites or Fibre reinforced polymer composites.

Types of Composites

Polymer composites (or) Fibre Reinforced Polymer Composites.

Prepn

Fibre-reinforced plastics are produced by suitably bonding a fibre material with a resin matrix and curing them under pressure and heat. The main reinforcing agents used in FRP composites are glass, graphite, alumina, carbon, boron, etc., It can be in different forms such as short fibres, continuous filaments (or) woven fabrics.

The Resin matrix commonly used in FRP are Polyesters, epoxy, phenolic, silicone and polyamide polymer resins.

Resin	Reason.
1. Polyester resin	To provide very good strength and mechanical properties
2. Epoxy resin	impart good mechanical properties
3. Silicone resin	impart excellent thermal and electrical properties
4. Phenolic resin	withstand high temp
5. Thermoplastics (Polyamide, PET etc)	B/c of repeatability and repairability.

Types of FRP composites.

Name	properties	Applications.
1. Glass FRP	(1) lower densities, dielectric constants. 2) Higher tensile strength and impact resistance 3) Excellent corrosion resistance, chemical resistance, Non-flammability	Automobile parts, storage tank, Plastic pipes, fluorings, transportation industries etc.,
2. Boron FRP	1. Excellent stiffness and compressive strength 2. Manufacture is difficult.	Horizontal and vertical tail in Aeroplane, stiffening spares, ribs etc.
Carbon FRP	1. Lighter density 2. Excellent resistance to corrosion 3. Retention of desired properties even at elevated temperatures.	Structural components of aircraft and helicopters, Reachional equipments, Sports materials, Antanna disc, Solar pannel etc.,
Aramid FRP	Metal like ductile and respond non catastrophically to compressive stresses.	Structural component in aircraft, helicopter parts.
Alumina-FRP	Good abrasion resistance, creep resistance and dimensional stability.	Components of engine parts in automobile industry and components of turbine engine.

Advantages of Polymer composites.

1. Polymer composite has very high strength to weight ratio than the metal.

2. lower weight than the steel, so it improves performance, reduces energy need, simplifies handling.

3. ~~Ca~~ capacitance and leakage current can be reduced.

4. better corrosion resistance.

5. Excellent durability and fire resistance.

6. Ideal for outdoor installation, imperviious to the effect of sunlight, heat cold and other weather conditions.

7. GRP are stronger [glass fibre].

8. CRP [carbon fibre].
   in place of Aluminium sheet in traditional rudded are
   (i) 25% reduction in weight
   (ii) 95% reduction in components by combining parts and forming simpler moulded parts.

Metal Matrix composites.

Properties:

1. Exhibits extremely good thermal stability, high strength, good stiffness and low specific weight.
2. MMC possess fracture toughness, ductility and enhanced elevated temp.
3. Withstand elevated temperatures in corrosion environment than polymer composites.

Uses:

(i) MMCS are suitable alternatives with Al, Ti, Ni alloys as one of the matrix material and Al_2O_3, B_4C, SiC as one of the reinforcements.

(ii) They are used in engine blades, Combustion chambers etc.

(iii) Al and Mg MMCs are used in automotive industry.

(iv) they improve fuel efficiency b/c of the weight reduction.

(v) Used in biomedical and sports equipment industry.

Ceramic Matrix composites.

Properties:

1. CMCS are used at temp above 1500c, because of their good corrosion resistance, Stability at elevated temperatures and high Compressive strength.
2. Provide strength at high temp with good Oxidation resistance.
3. The matrixes used are glass, ceramics, carbides, nitrides, oxides and borides, the reinforcements are Al_2O_3, B, C, SiC, SiO_2.

Uses:

Used in Re-entry thermal shields in space vehicles and tiles, pump seal, round rings, brake linings etc.

Hybrid composites:

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

Types of Hybrid composites:

1. Structurally hybridized composites
2. Materials " "
3. Functionally " ".

Properties:

1. Possess strong, tough and higher impact resistance.
2. failure does not occur suddenly
3. Possess balanced strength and stiffness
4. Thermal distortion stability, reduced weight, improved fatigue resistance.
5. Superior mechanical and tribological properties than other composites.

Uses:

1. It is used in light-weight transport structural components.
2. light weight orthopedic components and sporting goods.
3. To make furniture like chairs, table and bath tubes.
4. Used in railway coach interiors.
5. utensils like spoon, plates etc.
6. Automobile industry. for interior and exterior applications.

UNIT-IV

FUELS

Fuel is a combustible substance, containing carbon as the main constituent, which on burning gives large amount of heat.

During the process of combustion of a fuel, the atoms of carbon, hydrogen etc combine with oxygen with simultaneous liberation of heat.

$$C + O_2 \rightarrow CO_2 + 94 \text{ k cals.}$$

$$2H_2 + O_2 \rightarrow 2H_2O + 68.5 \text{ K cals.}$$

Requirements of Good fuel

1. It should be cheap and readily available.
2. Safe and economical for storage and transport.
3. Should not undergo spontaneous combustion.
4. Should have higher calorific value.
5. Should have moderate ignition temp
6. combustion should be easily controllable.
7. Should have low moisture content.
8. Products of Combustion should not be harmful.
9. Should have low non-Combustible matter or ash content.

Classification of fuels

I Based on occurence:

1. Primary fuels: occurs in nature as such. eg. coal, petroleum, natural gas.
2. Secondary fuel: Derived from primary fuel eg. coke, gasoline, coal gas.

II Based on their physical state:

1. Solid fuel ⇒ coal, coke
2. liquid fuel ⇒ gasoline (petrol), Diesel.
3. Gaseous fuel ⇒ Coal gas, natural gas.

Solid Fuels.

Coal:

Important primary fuel, formed as a result of alteration of vegetable matter under some favourable conditions.

Coalification (or) Metamorphism:

The process of conversion of vegetable matter to anthracite is called Coalification or metamorphism of coal.

Classification of coal:

Wood → Peat → Lignite → Bituminous Coal → Anthracite.

The progressive transformation of wood to anthracite results in,

decrease in moisture, volatile, H_2, O_2, N_2 and Sulphur content. Increase in 'C' content, hardness and calorific value.

Analysis of coal:

Proximate analysis

1. Moisture content:

About 1gm of powdered air-dried coal sample is taken in a crucible, and is heated ~~at~~ 100 - 105°c in an electric hot-air oven for 1 hr. The loss in weight of the sample is found out and the % of moisture is ~~fome~~. calculated.

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

2. Volatile matter:

After the analysis of Moisture content the crusible with residual coal sample is covered with a lid and is heated at 950 ± 20°c for 7 mts in a muffle furnace.

$$\% \text{ of Volatile matter} = \frac{\text{loss in wt of the coal}}{\text{wt of air-dried coal}} \times 100$$

% of Ash Content = $\frac{}{\text{Wt of air-dried coal}} \times 100$.

4. Fixed Carbon :

% of Fixed Carbon = 100 − % of [Moisture content + Volatile + ash]

Importance of Proximate Analysis:

1. Moisture

- It reduces the calorific value of coal
- It consumes more heat
- increases transport cost.

2. Volatile matter :

- reduced calorific value

- it increasing transporting, handling and storage cost.

4. Fixed Carbon.

- High % of Fixed carbon is desirable b/c higher the percentage of fixed carbon to a coal, greater calorific value.
- helps to design a furnace and the shape of the fire box.

ULTIMATE ANALYSIS

1. carbon and Hydrogen content
2. nitrogen content
3. Sulphur Content
4. ash Content
5. oxygen Content

1. 'C' and 'H' content :

A known amount of the coal sample is burnt in a current of O_2 in a Combustion apparatus. The 'C' & 'H' present in the coal sample. are Converted to CO_2 and H_2O respectively.

$$C + O_2 \rightarrow CO_2 \uparrow$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \uparrow.$$

The liberated CO_2 and H_2O vapours are absorbed respectively in KOH and anhydrous $CaCl_2$

* helps to design a furnace and the shape of the fire box.

ULTIMATE ANALYSIS

1. carbon and Hydrogen content
2. nitrogen content
3. Sulphur Content
4. ash Content
5. oxygen Content

1. 'C' and 'H' content :

A known amount of the coal sample is burnt in a current of O_2 in a combustion apparatus. The 'C' & 'H' present in the coal sample. are

b) % of 'H'.

$$H_2 + \frac{1}{2}O_2 \rightarrow \underset{[18]}{H_2O}$$

2.

18 gms of water contains 2gm of 'H'.

∴ y gm of H_2O " = $\frac{y \times 2}{18}$ gm of 'H'

m gm of coal contains = $\frac{2 \times y}{18}$ gms of 'H'.

100 gms of " " = $\frac{2 \times y}{18} \times \frac{100}{m}$

$$\% \text{ of 'H'} = \frac{\text{Increase in wt of CaCl}_2\text{ tube}}{\text{wt of coal sample taken}} \times \frac{2}{18} \times 100$$

Nitrogen Content:

It is carried out by kjeldhal's method. A known amt of powdered coal sample is heated with con. H_2SO_4 in presence of K_2SO_4 in a ~~tweng~~ long necked flask. 'N' in the coal is converted into ammonium sulphate and a clear soln is obtained.

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

The clear soln is heated with excess of NaOH and the liberated ammonia is distilled over and is absorbed in a known volum of std N/10 HCl.

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2$$

$$NH_3 + HCl \rightarrow NH_4Cl$$

The volume of unused $N/10$ HCl is then determined by titrating it against standard $N/10$ NaOH. Thus the amt of acid neutralised by liberated ammonia from coal is determined. From this the percentage of nitrogen is calculated as follows.

Let the wt of the coal sample taken = m gms

initial volume of $N/10$ HCl $= V_1$ ml

volume of unused $N/10$ HCl $= V_2$ ml

∴ The acid neutralised by ammonia $= (V_1 - V_2)$ ml

We know that,

1000 ml of 1 N HCl = 1 mole of HCl = 1 mole of NH_3.

$[\because HCl + NH_3 \rightarrow NH_4Cl]$.
1 mole 1 mole.

14 gm of N_2 (or 17 gm of NH_3].

$$\therefore (V_1 - V_2) \text{ ml of } N/10 \text{ HCl} = \frac{14 \times (V_1 - V_2) \times N/10}{1000 \times 1N}$$

'm' gm of coal sample contains

$$= \frac{14 \times (V_1 - V_2) \times N/10}{1000 \times 1} \text{ gms of } N_2$$

100 gm of coal sample contains

$$= \frac{14 \times (V_1 - V_2) \times N/10}{} \times \frac{100}{m} \text{ gms of } N_2$$

$$\% \ N_2 \text{ in coal} = \frac{14 \times \text{vol of acid consumed} \times \text{Normality}}{1000 \times \text{wt of coal sample}} \times 100$$

3. Sulphur content:

A known amount of coal sample is burnt completely in a bomb calorimeter. During this process 'S' is converted into sulphate, which is extracted with water. The extract is then treated with $BaCl_2$ solution so that sulphates are precipitated as $BaSO_4$. The ppt is filtered, dried and weighed. From the wt of $BaSO_4$ obtained, the sulphur present in the coal is calculated as follows.

Let, the wt of coal sample = m gms

Wt of $BaSO_4$ obtained = x gms.

$$\underset{32}{S} + 2O_2 \rightarrow SO_4^{2-} \xrightarrow{BaCl_2} \underset{233}{BaSO_4}\downarrow$$

233 gms of $BaSO_4$ contains 32 gm of 'S'

$\therefore$ x gm of $BaSO_4$ contains $= \frac{32 \times x}{233}$ gms of S'

m gms of coal sample contains $= \frac{32 \times x}{233}$ gm of S'

100 gms of coal sample " $= \frac{32 \times x}{233} \times \frac{100}{m}$ gms of 'S'

% of 's' in coal $= \frac{32 \times x}{233 \times m} \times 100$.

(or)

% of 's' in coal $= \frac{32 \times \text{Wt of } BaSO_4 \text{ obtained}}{233 \times \text{wt of Coal sample}} \times 100$.

4. Ash content:

It is carried out as in proximate Analysis.

5. Oxygen content:

% of 'O_2' in Coal = 100 − % of (C + H + N + S + ash).

Importance of ultimate Analysis:

'C' & 'H' contents:

(i) Higher the % of 'C' & 'H' better is the quality of coal and calorific value.

(ii) % of 'C' is helpful in the classification of Co

(iii) Reduce the size of combustion chamber required.

Nitrogen content:

1) does not have any calorific value, its presence in coal is undesirable

2. Sulphur content: (Presence is undesirable)

(i) combustion pdts of sulphur SO_2 and SO_3 are harmful and have corrosive effects on equipments.

(ii) Not suitable for the preparation of Metallurgical coke, it affects the Metals.

4. oxygen content :

(i) Lower the % of O_2 higher is its C.V.

(ii) As the O_2 content increases, its moisture holding capacity increases, and the calorific value of the fuel is reduced.

Difference b/w Proximate & Ultimate Analysis

Proximate Analysis	Ultimate Analysis.
1) It involves determination of physical constituents like Moisture, volatile, ash fixed carbon content in coal	1) involves the determination chemical constituents like O_2, S, N_2, H_2.
2) It gives approximate comparison of the main constituents of coal	2) It gives the exact composition of the elementary constituents of coal.

Carbonisation :

The process of converting coal into coke is known as carbonisation.

Caking and Coking Coals :

When coals are heated strongly, the mass becomes soft, plastic and fuses to give a coherent mass. Such type of coals are called caking coals.

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METALLURGICAL COKE

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

Characteristics of good Metallurgical coke

1. Purity
2. Porosity
3. Strength
4. Calorific value
5. Combustibility
6. Reactivity
7. Cost.

Manufacture:

Otto-Hoff mann's by-product oven.

1. The oven consists of a number of silica chamber is about 10-12 m long, 3-4m height and 0.4 – 0.45 m wide. 2. Each chamber is provided with a charging hole at the top. It is provided with a gas off take valve and iron door at each end for discharging coke.

3. Coal is introduced into the silica chamber and the chambers are closed, heated ~~by~~ to 1200°C

4. The air and gas are preheated by sending them through 2nd and 3rd hot regenerators. Hot flue gases produced during combustion are allowed to pass through 1st and 4th regenerators until the temp. has been raised to 1000°C.

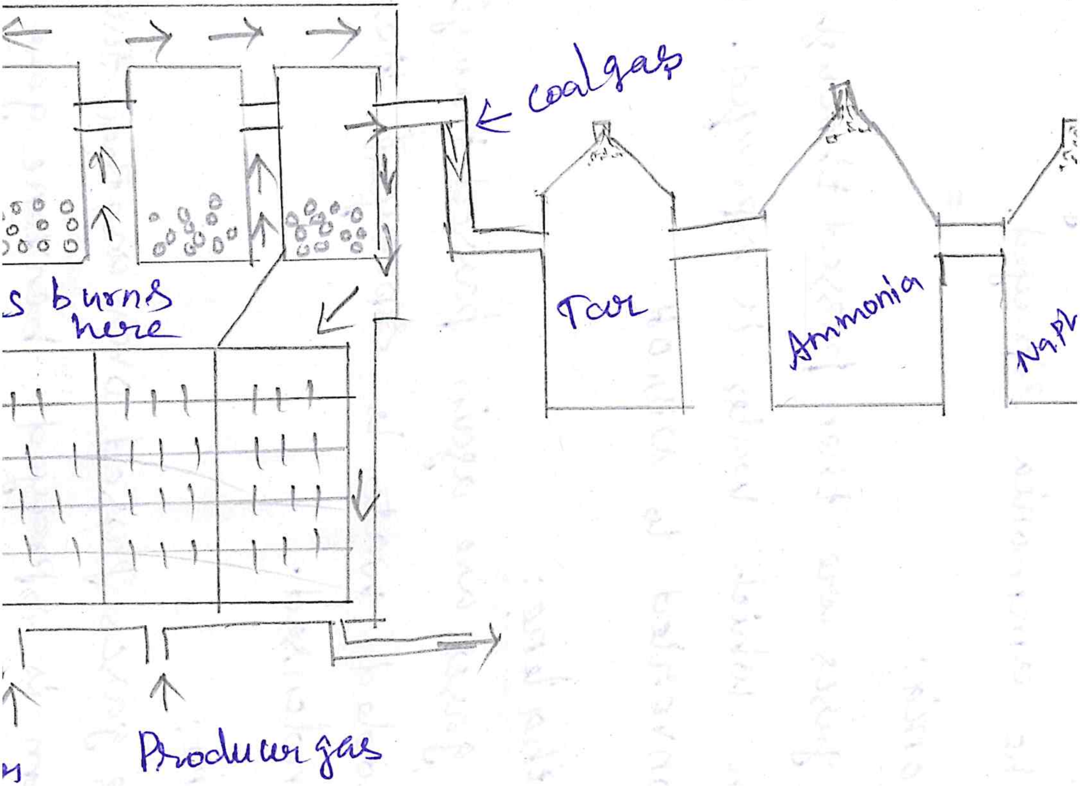
5. While 1st and 4th regenerators are being heated by hot flue gases, the 2nd & 3rd regenerators are used for heating the incoming air and gas mixture.

6. For economical heating, the direction of inlet gases and flue gases are changed frequently, is known as regenerative systems of heat economy.

7. When the process is complete, the coke is removed and quenched with water.

8. Time taken is about 12-20 hrs, Yield 70%.

9. The valuable by pdts like tar, NH_3, H_2S and benzol can be recovered from coal gas.



Otto-Hoffmann's by Pdt oven.

Recovery of by-Products

1. Tar :

The coal gases are first passed through a tower in which liquor ammonia is sprayed. Tar & dust get dissolved and collected in a tank below, which is heated by steam coils to recover back the ammonia sprayed.

2. Ammonia:

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

3. Naphthalene:

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

4. Benzene:

The gases passed over another tower, where Petroleum is sprayed. benzene gets condensed to liquid.

5. Hydrogen sulphide:

The remaining gases are passed through a purifier packed with moist Fe_2O_3. Here H_2S is retained. The final gas left out is pure coal gas, which is used as a gaseous fuel.

Advantages

1. valuable by products are recovered.
2. Carbonisation time is less.
3. Heating is done by Producer gas.

Liquid Fuels:

Petroleum or crude oil is naturally occuring liquid fuel. It is a dark brown or black coloured viscous oil found deep in earth crust.

Crude oil is a mixture of paraffinic, olefinic, aromatic hydrocarbons with small amounts of organic compounds like N, O, S.

C ⇒ 80 – 87%. H ⇒ 11 – 15%, S → 0.1 – 3.5,

N + O ⇒ 0.1 – 0.5%.

Classification

1. Paraffinic - Base type crude oil

It contains saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ with a smaller amount of naphthalenes and aromatics.

2. Naphthalene (or) Asphaltic base type crude oil

It contains cyclopaaffins or naphthalenes with a smaller amount of paraffinics and aromatics.

separating the crude oil into various fractions having different boiling Points is called Refining of Petroleum.

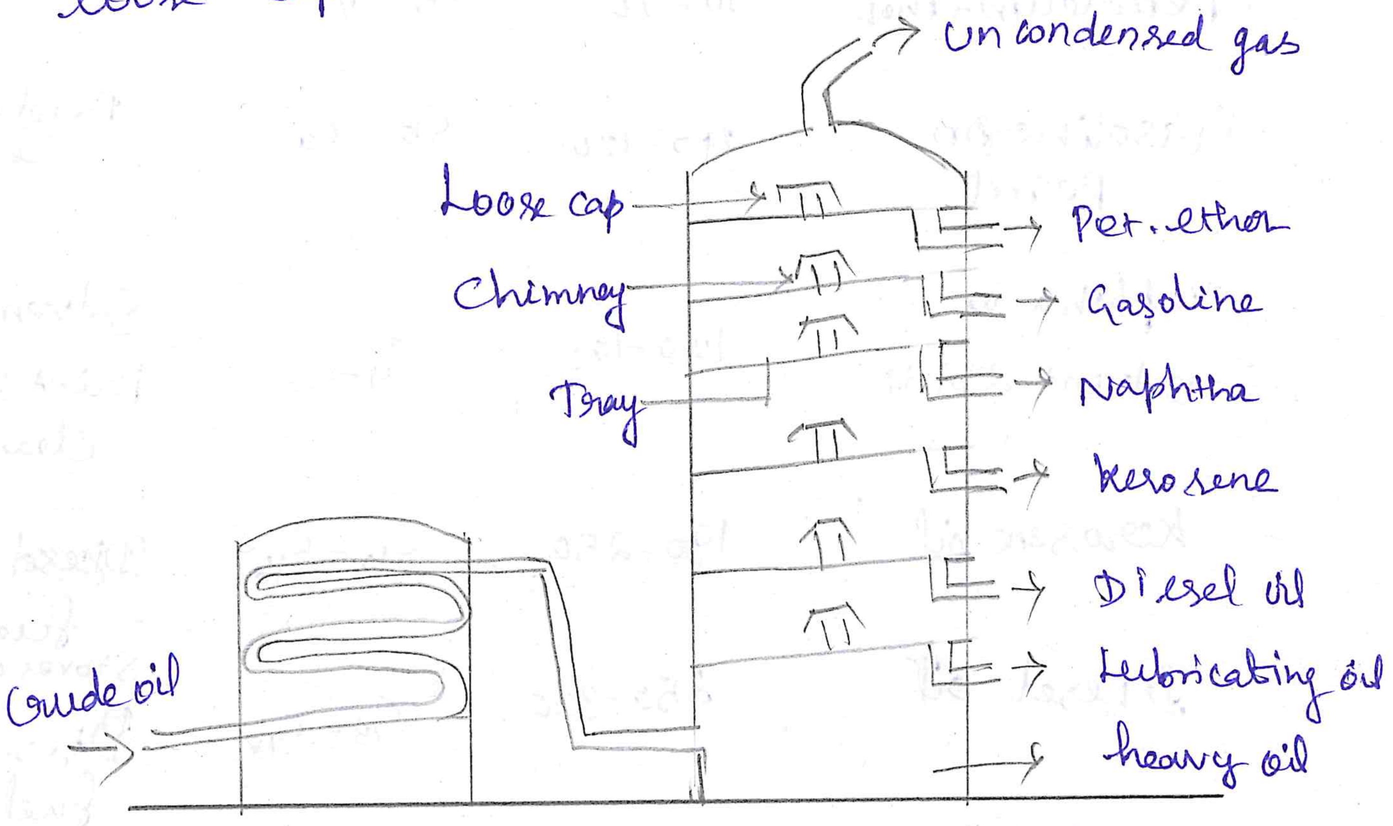
Step 1: Separation of water (Cottrell's process).

Crude oil is allowed to flow b/w two highly charged electrodes. where colloidal water droplets combine to form large drops, which is then separated out from the oil.

Step 2: Removal of harmful Sulphur compds

By treating the crude oil with copper oxide. The copper sulphide formed is separated

The fractionating column is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap.



Furnace at 400°c   Fractionating column

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

Name of the fraction	Boiling Range °c	Range of 'C' atoms	Uses
Uncondensed gas	Below 30	$C_1 - C_4$	Fuel (LPG).
Petroleum-ether	30-70	$C_5 - C_7$	Solvent
Gasoline (or) Petrol	40-120	$C_5 - C_9$	Fuel (I.C engine).
Naphtha or Solvent spirit	120-180	$C_9 - C_{10}$	Solvent in Paint & dry cleaning
Kerosene oil	180-250	$C_{10} - C_{16}$	~~Diesel engine~~ fuel for Stoves and Jet
Diesel oil	250-320	$C_{13} - C_{18}$	Diesel engine fuel.
Heavy oil	320-400	$C_{17} - C_{30}$	Fuel for ship and for production of gasoline by cracking

Name of the fraction	Uses
Lubricating oils	As Lubricants
Vaseline	Medicine and cosmetics
Grease	Lubricant.
Paraffin wax	candles, boot polishes.
Pitch at above 400°c	Making roads, water proof roofin

Synthetic Petrol:

Hydrogenation of Coal (or Manufacture of synthetic petrol.

The preparation of liquid fuels from Solid coal is called hydrogenation of coal (or Synthetic petrol.

Bergius process [direct Method]

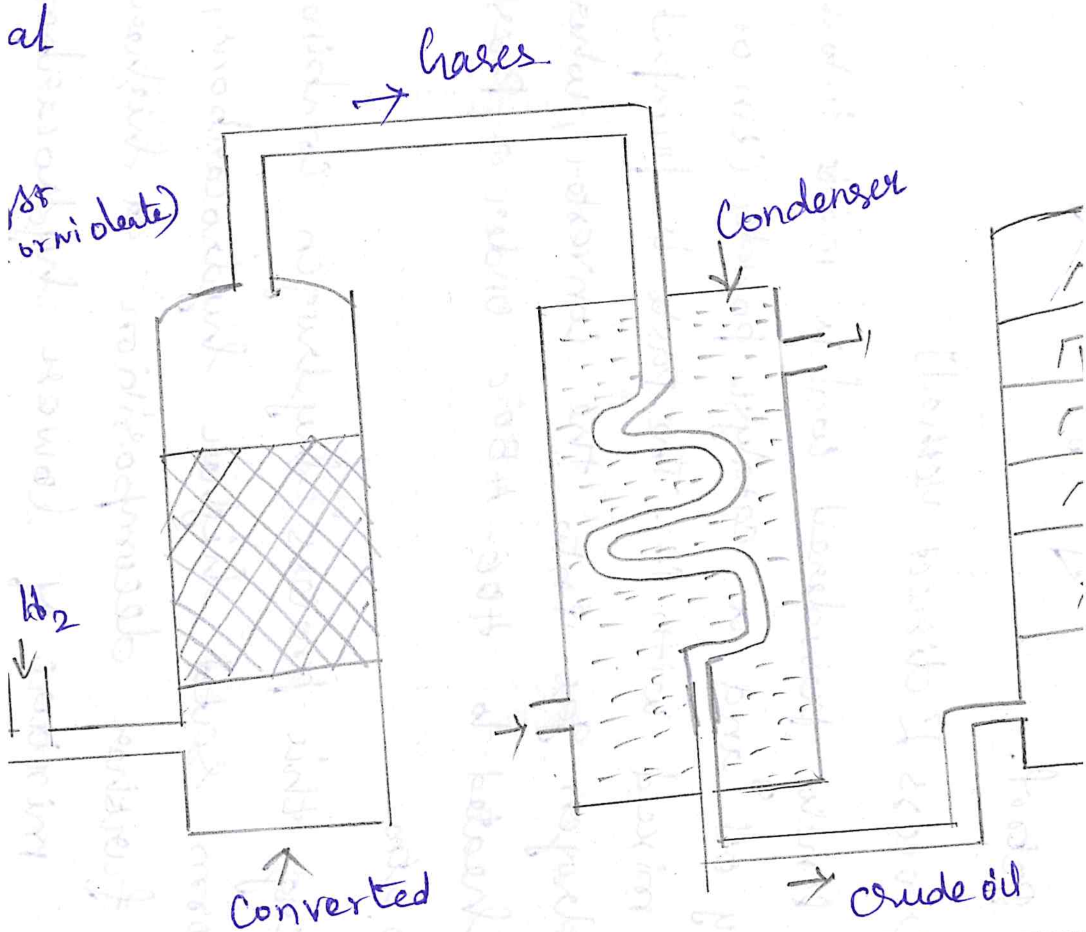
The finely powdered coal is made into a paste with heavy oil and a catalyst powder (tin or nickel oleate) is mixed with it. The paste is pumped along with hydrogen gas into the converter, where the paste is heated to 400-450°c under a pressure 200-250 atm.

During this process hydrogen combines with coal to form satd higher hydrocarbons, which undergo further decomposition at higher temp to yield mixture of lower hydrocarbons. Then led to a condense, where the crude oil is obtained.

The crude oil then fractionated to yield

(i) Gasoline (ii) Middle (iii) Heavy oil.

The middle oil is further hydrogenated to yield gasol
The heavy oil is recycled for making paste with fresh coal. Yield of gasoline is 60%..



Bergius Process

Knocking:

Knocking is a kind of explosion due to rapid pressure rise occuring in an Ic engine.

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

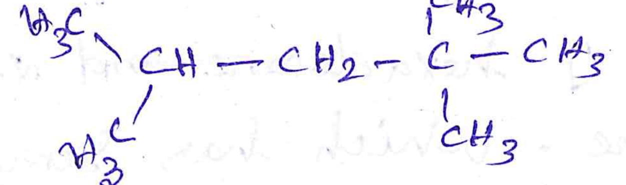
Straight chain paraffins > Branched chain Paraffin > cycloparaffins > olefines > Aromatics

Improvement of antiknock characteristics

1. Blending petrol of high octane number with petrol of low octane number.
2. By adding antiknock agents lik Tetra ethyl Lead
3. Aromatic phosphates are used as antiknock agent because it avoids Lead pollution.

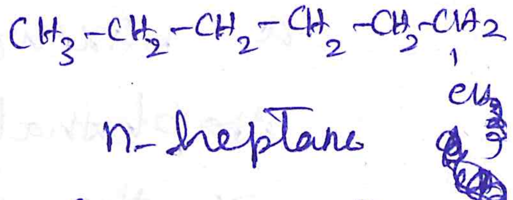
OCTANE NUMBER (or) OCTANE RATING

Thus, octane number is defined as "the ~~[illegible]~~ Percentage of iso-octane present in a Mixture of isooctane and n-heptane.



iso octane

(octane no = 100).



$CH_3-CH_2-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH_2}$

n-heptane

(octane no = 0)

Leaded Petrol (Anti-knock Agent).

The petrol containing tetra ethyl lead is called leaded petrol.

Diesel oil:

It is a fraction obtained b/w 250-320°c during fractional distillation of petroleum. It is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons Its calorific value is about 11000 kcal/kg. It is used as a very good diesel engine fuel.

Ignition lag:

The combustion of a fuel is a diesel engine is not instantaneous and the time b/w injection of the fuel and its ignition is called ignition lag or ignition delay.

Diesel index:

$$\text{Diesel index Number} = \frac{\text{Specific gravity (API)} \times \text{Aniline pt in } ^\circ F}{100}.$$

CETANE NUMBER OR CETANE RATING

The Percentage of hexa decane present in a mixture of hexadecane and α-methyl Naphthalene, which has same ignition lag as the fuel under test.

olefins > branched paraffin > Aromatics

The cetane no... of diesel oil can be increased by adding additives called dopes.

eg: Ethyl nitrate, iso-amyl nitrate.

Comparison of Petrol & Diesel.

PETROL	DIESEL
1. Low boiling fraction of petroleum contains $C_5 - C_9$ hydrocarbons.	High boiling fraction of petroleum contains $C_{15} - C_{18}$ hydrocarbons.
2. Fuel for SI engine	Fuel for CI engine
3. Knocking tendency is measured in octane Rating	Knocking tendency is measured in Cetane Rating
4. Knocking is due to	knocking is due to

Manufacture of Ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2C_2H_5OH + 2CO_2.$$

Glucose (Sugar).

Ethyl alcohol can be synthesised by fermentation of Carbohydrates

Conversion of ethyl alcohol into Power alcohol

water ~~from~~ in rectified spirit (97.6%)

can be removed by.

1) distilled with benzene. When benzene passes over with a portion of alcohol and water, it leaves behind power alcohol.

Uses:

1. It is used as a Very good fuel, in Motors.

Advantages:

1. Cheaper than petrol
2. If any moisture is present, Power alcohol absorb it.
3. As C_2H_5OH Contains oxygen atoms, complete Combustion occurs, So emission of CO, hydro-carbon, Particulates are reduced.

Disadvantages.

1. Calorific value is lower than petrol
2. Specially designed engine is required.
3. output power is reduced upto 35%.
4. Due to its high surface tension atomization of Power alcohol is difficult. So it causes Starting trouble.
5. It may undergo oxidation, to give acetic acid, which corrodes engine part.
6. As it contains oxygen atoms, the amount of air required for combustion is less therefore the engine and carburetor need to be modified.

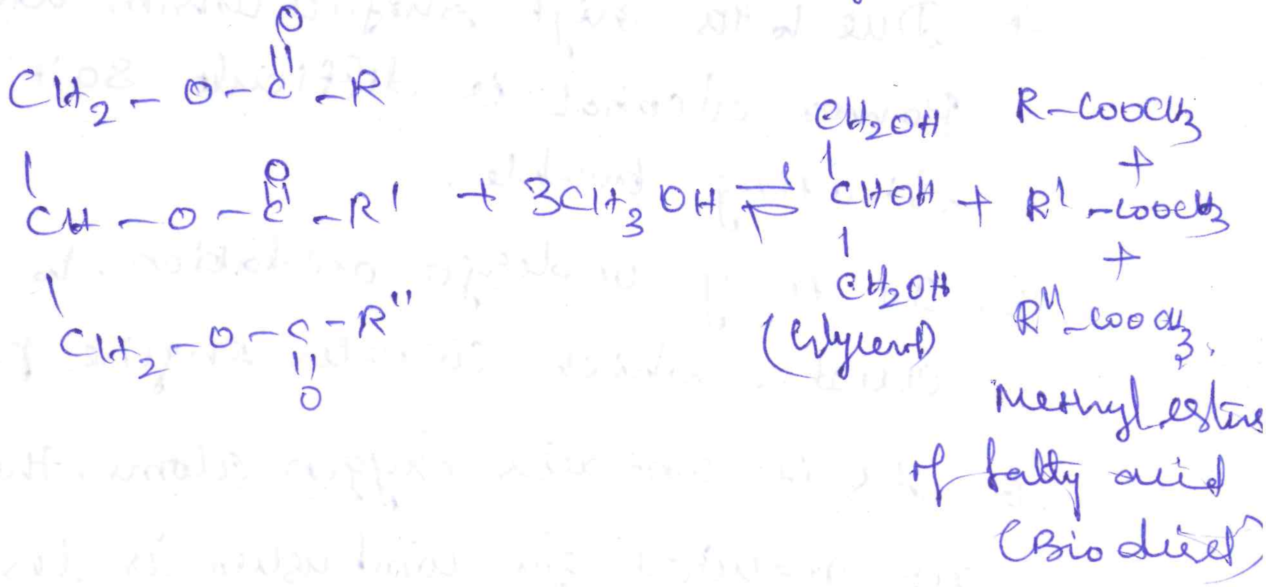
Bio-Diesel:

Problems in using vegetable oils directly

1. Viscosity of vegetable oils are high, atomization is very poor and hence inefficient mixing of oil with air leads to incomplete combustion.
2. Oxdn and thermal polymerisation causes deposit formation.
3. Their high viscosity causes misfire and ignition delay.
4. Specially designed engines are required.

Manufacture:

Trans-esterification (or) alcoholysis



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH_2-O-\underset{O}{\underset{\|}{C}}-R'' \end{array} + 3CH_3OH \rightleftharpoons \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{(Glycerol)} \end{array} + \begin{array}{l} R-COOCH_3 \\ + \\ R'-COOCH_3 \\ + \\ R''-COOCH_3 \end{array}$$

Advantages:

1. Bio-diesel is biodegradable
2. Prepared from renewable resources
3. gaseous pollutants are lesser
4. Prepared from various vegetable oils.
5. Best engine performance, less smoke emission are achieved.

dis advantages:

1. Bio-diesel gels in cold weather
2. hygroscopic is nature
3. degrades and soften the rubber and plastics.
4. about 10% higher nitrogen-oxide (NO_2) emission.

Combustion of Fuels

Combustion is a process of rapid exothermi oxidation, in which a fuel burns in the presence of oxygen with the evolution of heat and light.

$C + O_2 \rightarrow CO_2$ Exothermic

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ Exothermic

Large quantity of heat given out

Calorific value:

The total amount of heat liberated when a unit mass of fuel is burnt completely.

Units of Calorific Value

1. calorie
2. kilocaloric
3. British thermal unit (BTU)
4. Centigrade heat unit (CHU).

Calorie: It is defined as the amout of heat required to raise the temp of 1 gram of water through 1°C (15 to 16°C).

Higher (or) Gross calorific value (GCV).

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 temp.

Lower calorific value (NCV).
(Net).

The net heat produced, when a heate unit quantity of the fuel is completely burnt and the product of combustion are allowed to escape.

NCV = GCV – Latent heat of condensation of water vapour produced.

= GCV – Mass of Hydrogen × 9 × Latent heat of condensation of water vapour

$H_2 + O \rightarrow H_2O$

H_2	O	H_2O
2gm	16gm	18 gms.
1	8	9

1 Part by weight of H_2 produces 9 Parts by wt of H_2O. The latent heat of steam is 587 cal/gm

Thus, $NCV = GCV - \frac{9}{100} H \times 587$

$= GCV - 0.09 H \times 587$

where, $H = \%$ of H_2 in the fuel.

problems based on calorific value

1. Calculate the gross and net calorific values of Coal having the following compositions, C = 85%, H = 8%, S = 1%, N = 2% ash = 4% Latent heat of steam = 587 Cal/gm

$$GCV = \frac{1}{100}\left[8080 \times \%C + 34500\left[\%H - \frac{\%O}{8}\right] + 2240 \times \%S\right] \text{ Kcal/kg}$$

$$= \frac{1}{100}\left[8080 \times 85 \times 34500\left[8 - \frac{0}{8}\right) + 2240 \times 1\right] \text{ Kcal/kg}$$

$$= \frac{1}{100}\left[6{,}86{,}800 + 2{,}76{,}000 + 2240\right] \text{ kcal/kg}$$

$$= 1/100\left[9{,}65{,}040\right] \text{ Kcal/kg}$$

$$= 9650.4 \text{ kcal/kg.}$$

(ii) $$NCV = GCV - \frac{9}{100} H \times 587 \text{ Kcal/kg.}$$

$$= 9650.4 - \frac{9}{100} \times 8 \times 587 \text{ kcal/kg.}$$

$$= 9650.4 - 422.64$$

$$= 9227.70 \text{ kcal/kg.}$$

2. Calculate GCV and NCV of a coal sample having the following composition C=80%, H=7%, O=3%, S=3.5%, N=2.5% ash 4.4%.

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

$= \frac{1}{100}\left[8080 \times 80 + 34500\left(7 - \frac{3}{8}\right) + 2240 \times 3.5\right]$

$= \left[8080 \times 0.80 + 345\,(7 - 0.375) + 22.40 \times 3.5\right]$

$= 6464 + 2285.6 + 78.4$

$= 8828.0$ K.cal/kg.

ii) $NCV = GCV - 0.09H \times 587$

$= 8828 - (0.09 \times 7 \times 587)$

$= 8828 - 369.8$

$= 8458.2$ k cal/kg.

3) On analysis, a coal sample has the following composition by weight; C=85%, O=3% S=0.5%, ash=3%. NCV was found to be 8400 Kcal/kg. Calculate the percentage of hydrogen and gross calorific value of coal.

$GCV = [NCV + 0.09H \times 587]$

$= 8400 + 0.09H \times 587$

$= 8400 + 52.8H$. — ①

$GCV = \frac{1}{100}\left[8080 \times 85 + 34500\left(H - \frac{3}{8}\right) + 2240 \times 0.5\right]$

$= \frac{1}{100}\left[686800 + 34500H - 12937.5 + 1120\right]$.

$= 6868 + 345H - 129.4 + 11.2]$.

$= 6{,}749.8 + 345H$ kcal/kg. — ②.

② is substituted is ①

$GCV = [NCV + 0.09H \times 587]$ kcal/kg

34m $= 8400 + 0.09H \times 587$

$6749.8 = 8400 + 52.8H$.

$6749.8 + 345H = 8400 + 52.8H$.

$345H - 52.8H = 8400 - 6749.8$

$292.2H = 1650.2$

$H = \frac{1650.2}{292.2}$

$H = 5.647$.

$\% \text{ of } H = 5.647$.

$\therefore GCV = 8400 + 52.8 \times 5.647$
$= 8698.16$ kcal/kg.

4. Calculate the net and gross calorific value of a coal sample having following compositions

$C = 82\%$, $H = 8\%$, $O = 5\%$, $N = 14\%$, ash $= 3.6\%$

$\boxed{S = 0}$.

$$GCV = \frac{1}{100}\left[8080 \times 82 + 34500\left[8 - \frac{5}{8}\right] + 0\right]$$

$$= \frac{1}{100}\left[862560 + 254437.5\right].$$

$$= 9169.98 \text{ kcal/kg.}$$

$$NCV = GCV - \frac{9}{100} H \times 587.$$

$$= 9169.98 - \frac{9}{100} \times 8 \times 587$$

$$= 8747.34 \text{ kcal/kg.}$$

5. Calculate the gross and net calorific value of a fuel having following compositions 82% C, 8% H, 5% O, 2.5% S, 1.4% N and 2.1% ash.

$$GCV = \frac{1}{100}\left[8080 \times 82 + 34500\left(8 - \frac{5}{8}\right) + 2240 \times 2.8\right]$$

$$= \frac{1}{100}\left[922597\right]$$

$$= 9225.97 \text{ kcal/kg}$$

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

$$= 9225.97 - 0.09 \times 8 \times 587].$$

$$\simeq 8803.3 \text{ kcal/kg.}$$

A coal sample has 80% 'C', 9% H, 6% S remaining ash. Calculate GCV & NCV

$$GCV = \frac{1}{100}\left[8080 \times 80 + 34500\left(9 - \frac{0}{8}\right) + 2240 \times 6\right]$$

$$= \frac{1}{100}\left[64{,}6400 + 3{,}10{,}500 + 13440\right].$$

$$= \frac{1}{100}\left[9{,}70{,}340\right].$$

$$= 9{,}703.4 \text{ Kcal/kg.}$$

$$LCV = GCV - \frac{9}{100} H \times 587$$

$$= 9703.4 - \frac{9}{100} \times 9 \times 587$$

$$= 9703.4 - 475.47.$$

$$= 9227.93 \text{ kcal/kg.}$$

Ignition temperature (IT).

The lowest temperatures to which the fuel must be heated, so that it starts burning smoothly.

For coal − 300°c.

In liquids fuels the ignition temp is called flash point, ranges from 200−450°c. For gaseous fuel, 800°c.

Spontaneous ignition Temperature (SIT).

The minimum temp at which the fuel Catches fire (ignites) spontaneously without external heating.

Flue gas Analysis: (ORSAT METHOD).

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

Description of Orsat's apparatus

It consists of a horizontal tube. At one end of this tube, U-tube containing fused $CaCl_2$ is connected through 3-way stop cock. The other end of the tube is connected with a graduated burette. The burette is surrounded by a water jacket to keep the temperature of gas constant. The lower end of the burette is connected to a water reservoir by means of a rubber tube. The horizontal tube is also connected with three different absorption bulbs 1, 2, 3 for absorbing CO_2, O_2 and CO.

Working:

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

Absorption of CO_2

The stopper of the absorption bulb-1, containing KOH solution, is opened and all the gas is passed into the bulb-1 by raising the level of water in the burette. The gas enters into the bub-1, where CO_2 present in the flue gas is absorbed by KOH.

The gas is again sent into the burette. This process is repeated several times to ensure complete absorption of CO_2. The decrease in volume of the flue gas in the burette indicates the volume of CO_2 in 100cc of the flue gas.

Absorption of O_2:

Stop-cock of the bulb-1 is closed and stop cock of bulb-2 is opened. The gas is again sent into the absorption bulb-2, where O_2 present in the flue gas is absorbed by alkaline pyrogallol. The decrease in volume of the flue gas in the burette indicates the volume of O_2.

Absorption of CO:

Now stop-cock of bulb-2 is closed and stop-cock of bulb-3 is opened. The remaining gas is sent into the absorption bulb-3. where CO present in the flue gas is absorbed by ammoniacal cuprous chloride. The decrease in volume of the flue gas in the burette indicates the volume of CO. The remaining gas in the burette after the absorption of CO_2, O_2 & CO is taken as nitrogen.

Significance:

1. It gives an idea about the complete or incomplete combustion process.

2. If flue gas contains more CO, it indicates that incomplete combustion and short supply of O_2.

3. If the flue gas contain considerable amount of O_2, it indicates that complete combustion is occuring and also it indicates that the excess of O_2 is supplied.

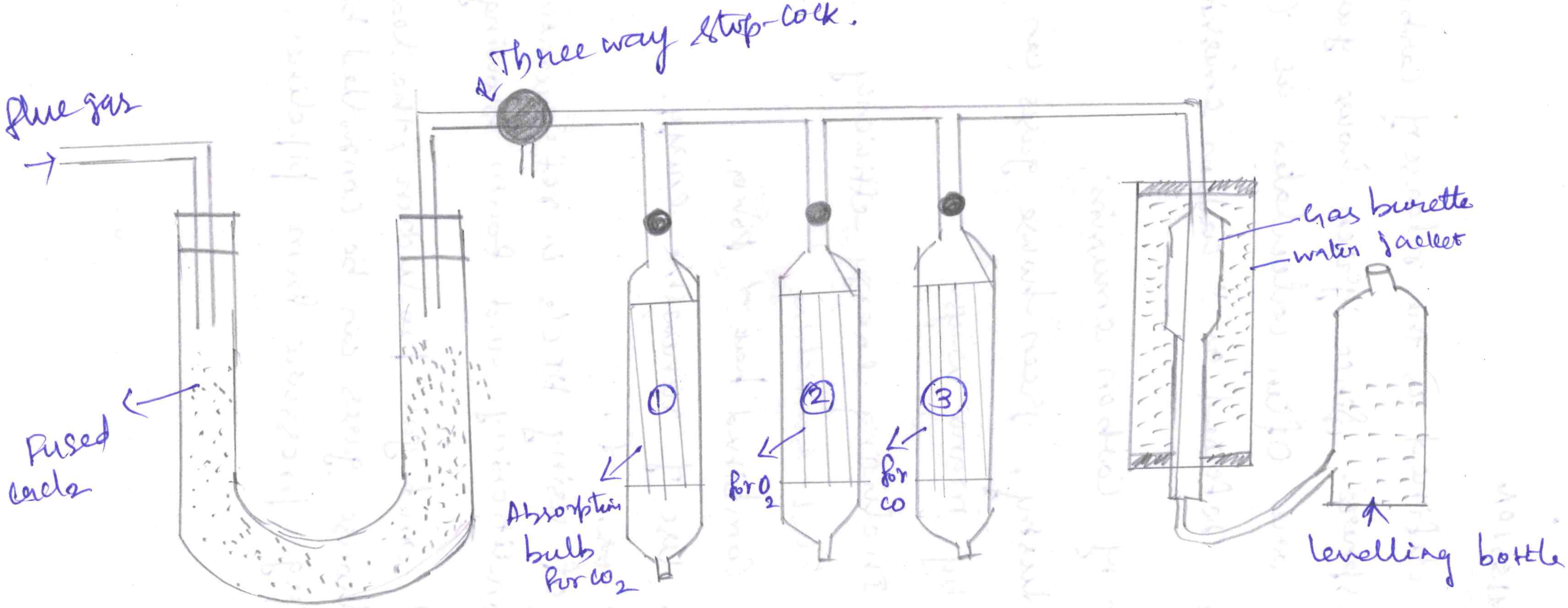
Precautions:

1. The reagents in the absorption bulb 1,2 and 3 should be brought to the etched Marked level one by one by raising and lowering reservoir bottle.

2. All the air from the reservoir bottle is expelled to atmosphere by lifting the reservoir bottle.

3. It is essential that CO_2, O_2 and CO are absorbed in the order only.

4. As the CO content in flue gas is very small, it should be measured carefully.


Three way Stop-cock.
flue gas
Fused cacl2
①
②
③
Absorption bulb for CO2
for O2
for CO
Gas burette
water jacket
levelling bottle

CARBON EMISSION

It is defined as the release of Carbon into the atmosphere. Since green house gas emissions are often calculated as "CO_2-equivalen" they are referred as "carbon emission".

Reduction of Carbon emission:

1. In industry, green house gases can be reduced by many ways.
    1. Including energy efficiency
    2. Fuel switching
    3. Combined heat and power.
    4. Use of renewable energy.
    5. [illegible]
2. Avoid of using HFC's in refrigeration, air conditioning and foam blowing
3. In oil and gas production, the leakage of green house gases can be controlled by reducing pressure from pipelines.

CARBON FOOTPRINT

It is the total amount of green house gases (including CO_2 and CH_4) that are generated by our direct and indirect activities.

Individual carbon footprint

It is the sum total of their direct and indirect carbon emissions over the course of a year.

(i.e) smaller your carbon foot print => better for future.

Bigger your carbon footprint => Higher negative impact in environment.

Sources of carbon footprint:

1) climate change
2) Natural process like vulcanes
3) Green house gases emitted from human activities
4) Pollution released by human beings doing human things.
5) Transportation accounted ~~by~~ for about 28% of total economy.
6) Electricity generation accounted for about 28%
7) Industrial activities 22%.
8) Heating and cooling in homes and business contribute 11%..

How to lower carbon footprint.

1. Calculate your carbon footprint.
2. Drive less.
3. Swith to an electric (or) hybrid car.
4. Travel smart
5. Switch to renewable energy
6. Consider solar panels.
7. Make your home more efficient.
8. Turn your thermostat just 2 degrees cooler in winter and 2 degrees warmer in summer.
9. Get energy efficient appliances.
10. ~~Upgrading~~ unplug electrical devices when not in use.
11. Buy locally - sourced food.
12. Start a home garden.
13. Eat less meat
14. Don't waste water
15. Reduce, reuse, recycle.

UNIT-V

ENERGY SOURCES

Mass defect:

It has been found that the actual mass of an isotope is always less than the sum of the masses of the protons, neutrons and electron from which it is formed.

Definition:

The difference between the Calulated and experimental massos of nucleus is called Mass defect, Δm.

$$\Delta m = \left[\begin{array}{c}\text{Total mass of the} \\ \text{protons, neutron} \\ \text{and electron}\end{array}\right] - \left[\begin{array}{c}\text{Experimental mass} \\ \text{of the nucleus}\end{array}\right]$$

Calculation of Mass defect:

Consider an isotope,

Its atomic number = Z
Mass number = A

$$_{Z}X^{A} \quad A - \text{Mass number}$$

Atomic number.

no. of protons = no. of electrons = Atomic no.

no. of neutron = Mass number − Atomic number

Let, M = Actual experimental mass of the nucleus.

Mass defect (Δm) = $M' - M$.

$$\Delta m = Zm_H + (A-Z) M_n - M.$$

Problems

1. Calculate the mass defect of ${}_{20}Ca^{40}$, which has atomic mass of 39.975 amu. The mass of proton is 1.0078 amu and the mass of neutron is 1.0086 amu

$$\Delta m = Zm_H + (A-Z) m_n - M.$$

'Ca' has 20 protons and 20 ~~electrons~~ neutrons.

$Z = 20$, $(A-Z) = 20$, $m_H = 1.0078$ amu

$M_n = 1.0086$ amu, $M = 39.975$ amu.

$$\Delta m = [20m_p + 20m_n - M] \quad (\because m_n = \text{Neglected})$$

$$= [20 \times 1.0078 + 20 \times 1.0086 - 30975]$$

$$= 120.156 + 20.172 - 39.9751].$$

$$= 40.328 - 39.975$$

$$= 0.353 \text{ amu}.$$

2. Calculate the mass defect of $_2He^4$, If its experimentally determined mass is 4.00390 amu. The masses of a proton, an electron and a neutron are 1.007825, 0.0005852 and 1.008668 amu respectively.

Soln:

Mass defect (Δm) of 'He' atom $= [2m_p + 2m_e + 2m_n - M]$

$_2He^4$ atom is composed of 2 protons, 2 electrons and 2 neutrons.

Gn $m_p = 1.007825$ amu, $m_e = 0.0005852$,

$m_n = 1.008668$ amu.

$$\therefore \Delta m = [2 \times 1.007825 + 2 \times 0.0005852 + 2 \times 1.008668 - 4.00390].$$

$$= 4.0341064 - 4.00390$$

$$= 0.0302964 \text{ amu}.$$

3. Mass of Hydrogen and neutron are 1.008 amu and 1.0072 amu respectively. If experimentally determined mass of sodium atom ($_{11}Na^{23}$) is 23.009 amu. Calculate Mass defect.

$$\Delta m = [11 \times m_H + 12\, m_n - M].$$

$_{11}Na^{23}$ is composed of 11 'H' atoms and 12 neutrons.

④

Gn m_p (or) $m_n = 1.008$ amu, $m_n = 1.0072$ amu.

$M = 23.0092$.

$\therefore \Delta m = [11 \times 1.008 + 12 \times 1.0072 - 23.0092]$

$= 0.1652$ ~~atm~~ amu.

---

4. calculate the mass defect of α-particle. Given that the mass of proton = 1.00758, $m_n = 1.00897$ amu, and mass of helium nucleus = 4.00820 amu

Δm of α-particle $= [2m_p + 2m_p - M$.

An α-particle is composed of 2 protons & 2 electrons

Ans. $m_p = 1.00758$ amu.

$m_n = 1.0097$ amu.

$M = 4.00820$ amu.

$\Delta m = [2 \times 1.00758 + 2 \times 1.00897 -$

$($ 4.00820

$= 0.02490$ amu.

5. Calculate the mass defect of the following fission reaction.

$$_{92}U^{235} + {}_0n^1 \longrightarrow {}_{36}Kr^{95} + {}_{57}Ba^{139} + 2\,{}_0n^1$$

Given that atomic mass of $U^{235} = 235.124$ amu

$Kr^{95} = 94.945$ amu ; $Ba^{139} = 138.954$ amu ; $_0n^1 = 1.0099$ amu

$$\Delta m = \text{Atomic mass of } [U + n - (Kr + Ba + 2n)]$$

$$= [235.124 + 1.0099 - (94.945 + 138.954 + 2 \times 1.0099)]$$

$$= [236.1339 - (233.899 + 2.0198)]$$

$$= 236.1339 - 235.9188$$

$$= 0.2151 \text{ amu}$$

Binding energy:

Binding energy is defined as the Energy released when a given number of protons and neutrons coalsce (unite) to form nucleus.

It is the energy required to disrupt the nucleus into its constituents protons and neutrons.

Binding Energy Vs Nuclear stability

A plot of Binding energy per nucleon against mass number for different elements gives the following graph.

Plot of Binding energy Vs Mass number

Calculation of binding Energy:

$$E = \Delta m c^2$$

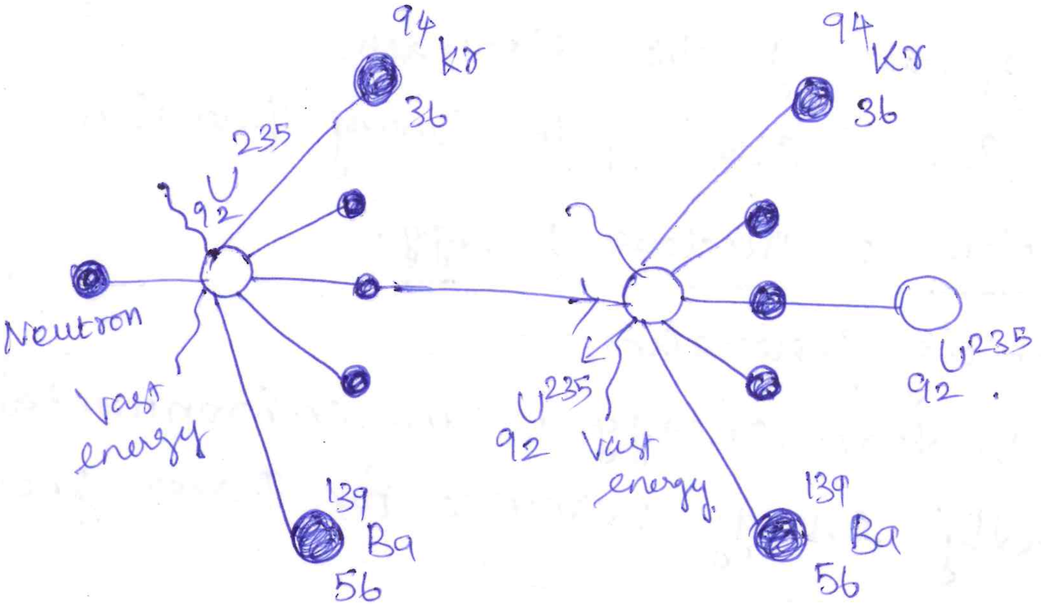
$$E = [Zm_H + (A-Z)m_n - M] \times c^2.$$

Where E = Binding energy of the nucleus
Δm = Mass defect
c = velocity of light (3×10^8 m/s)

NUCLEAR ENERGY:

The energy released by the nuclear fission or nuclear fusion is called nuclear energy.

the fission of U^{235} or P^{239} occurs simultaneously producing enarmous amount of energy in the form of heat and radiation.



Nuclear Energy.

$$E = \Delta m c^2 .$$

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

where, c = velocity,

Δm = loss in mass

E = Energy

M = Mass of radioactive substance before emitting radiation.

M' = Mass of radioactive substance after emitting radiation.

Hazards of using Nuclear Energy.

(i) The Nuclear radiation can damage the structure of cells is the human body.

(ii) causes diseases like cancer and blindness.

(iii) causes genetic disorder

(iv) causes sterility in young generation.

Applications of nuclear Energy.

1. Electricity generation.

Nuclear energy is an environmental friendly energy resource for power generation.

2. Source of pure water:

The water discharged from nuclear reactors is free from radiation and is clean enough to conserve animals and aquatic animals.

3. Health care:

Radioactive isotopes find use in treatment of cancer by radiotherapy. It is also used for sterilization to destroy micro-organisms.

4. Agriculture:

Used to control agricultural pests.

Nuclear radiation delays ripening of fruits.

Nuclear Reactor (Pile).

The arrangement or experimental equipment used to carry out fission reaction under controlled condition is called a nuclear reactor.

Light water Nuclear-Power plant

Definition:

Light-water nuclear powerplant is the one in which U^{235} fuel rods are submerged in water. Here the water acts as coolant and moderator.

Components of a light water nuclear Power plant

1. Fuel rods

The fissionable materials used in nuclear reactor is enriched U^{235} rods or strips.

eg. U^{235}, Pu^{239}

Fn: It produces heat energy and neutrons, that starts nuclear chain reaction.

2. Control rods:

These are movable rods, made of Cd (or) B are, suspended between fuel rods.

If the rods are deeply inserted inside the reactor, they will absorb more neutrons and the reaction becomes very slow. If the rods are pushed outwards, they will absorb less number of neutrons and the reaction will be very fast.

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

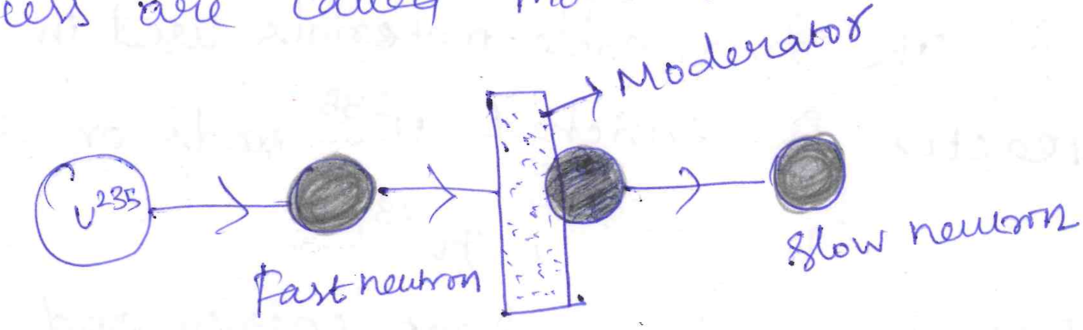
$$_5B^{10} + {}_0n^1 \rightarrow {}_5B^{11} + \gamma\text{-ray}.$$

eg. Cd^{113}, B^{10}.

Fn: It controls the nuclear chain reaction and avoids the damage of the reactors.

3. Moderators:

The substance used to slow down the process are called moderators.



Function:

When the fast moving neutrons collide with moderator they loss energy and gets slow down.

Eg: ordinary water, heavy water, graphite, Beryllium.

Fn: The kinetic energy of the moving neutrons (1 meV) is reduced in slow reactions. (0.25eV

4. Coolants:

- It absorbs heat produced during fission.
- circulated in the reaction core.
- It enters at base and leaves at top.
- The heat carried by out-going liquid is used to produce steam.

eg:- Water, heavy water, liquid Metal (Na or K) air (CO_2).

Fn: It cools fuel core.

5. Pressure Vessel

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

Fn: It withstand the pressure, 200 kg/cm^2.

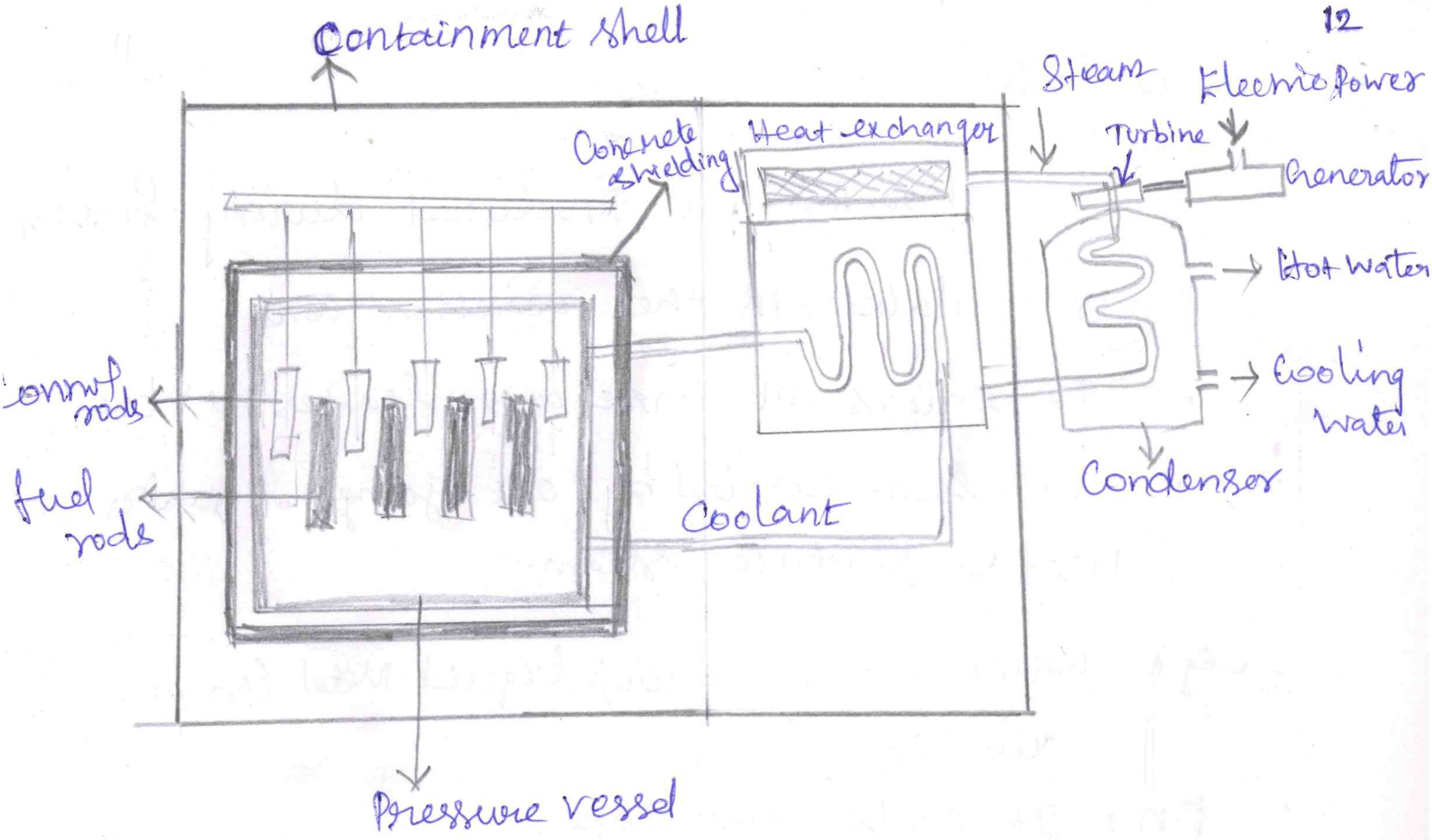
6. Protective Shield:

The nuclear reactor is enclosed in a thick massive concrete shield. (> 10m thick).

Fn: The environment and operating personnels are protected from destruction in case of leakage of radiation.

7. Turbine:

The steam generated in the heat exchanger is used to operate a steam turbine, which drives a generator to produce electricity.



8. Working:

- The fission reaction is controlled by inserting or removing the control rods of B^{10} automatically from the spaces in between the fuel rods.
- The heat emitted by fission of U^{235} is absorbed by coolant.
- The heated Coolant (water at 300°c) then goes to the heat exchanger containing sea water.
- Coolant transfers heat to sea water, which is converted to steam.
- The steam drives the turbines, generates electricity.

Pollution:

Nuclear Power plant will cause a serious damage to environment.

Problem on disposal of reactor waste

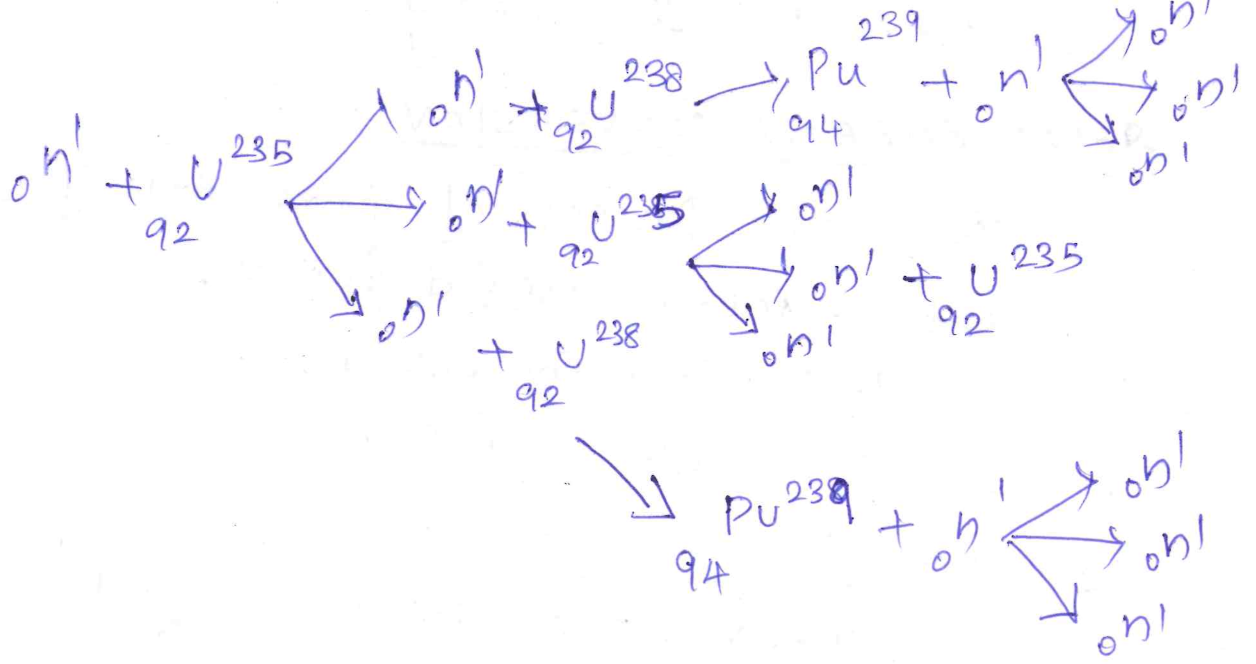
* The fission products Ba^{139} and Kr^{92} are themselves radioactive. They emit dangerous radiation for several hundred years.
* So the waste is packed in concrete barelles, which are burried deep in the sea. Salt water will not allow the radiation to come out.

BREEDER REACTOR:

Breeder reactor is the one which converts non-fissionable material (U^{238}, Th^{232}) into fissionable material (U^{235}, Pu^{239}).

$$_{92}U^{238} + {}_0n^1 \longrightarrow {}_{94}Pu^{239} + 2e^-$$

$$_{94}Pu^{239} + {}_0n^1 \longrightarrow \text{Fission Pdts} + 3\,{}_0n^1.$$



In breeder reactor, of the three neutrons emitted in the fission of U^{235} only one is used in propagating the fission chain with U^{235}. The other two are allowed to react with U^{238}. Thus, two fissionable atoms of Pu^{239} are produced for each atom of U^{235} consumed. Therefore the breeder reactor produces more fissionable material than it uses. Hence Pu^{239} is a man made nuclear fuel and is known as secondary nuclear fuel.

Significance:

1. fertile nucleides, are converted into fissile nucleides.
2. regeneration of fissile nucleides takes place its efficiency is more.

SOLAR ENERGY CONVERSION:

It is the process of conversion of direct sunlight to more useful forms.

1. Thermal conversion
2. Photo conversion

Thermal conversion:

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

Methods of thermal Conversion

1. Solar heat Collectors
2. Solar water heater

1. Solar heat collectors:

It consist of natural material like stones, bricks, glass which can absorb heat during day time and release it slowly at night.

Uses:

* used in Cold Places

2. Solar water heater:

* It consists of an ~~industrial~~ insulated box with black Point.
* It is also provided with a glass lid to receive and store solar heat.
* Inside the box it has black painted copper coil, through which cold water is allowed to flow in.
* which gets heated up and flows out into a storage tank.
* From the storage tank water is then supplied through the pipes.

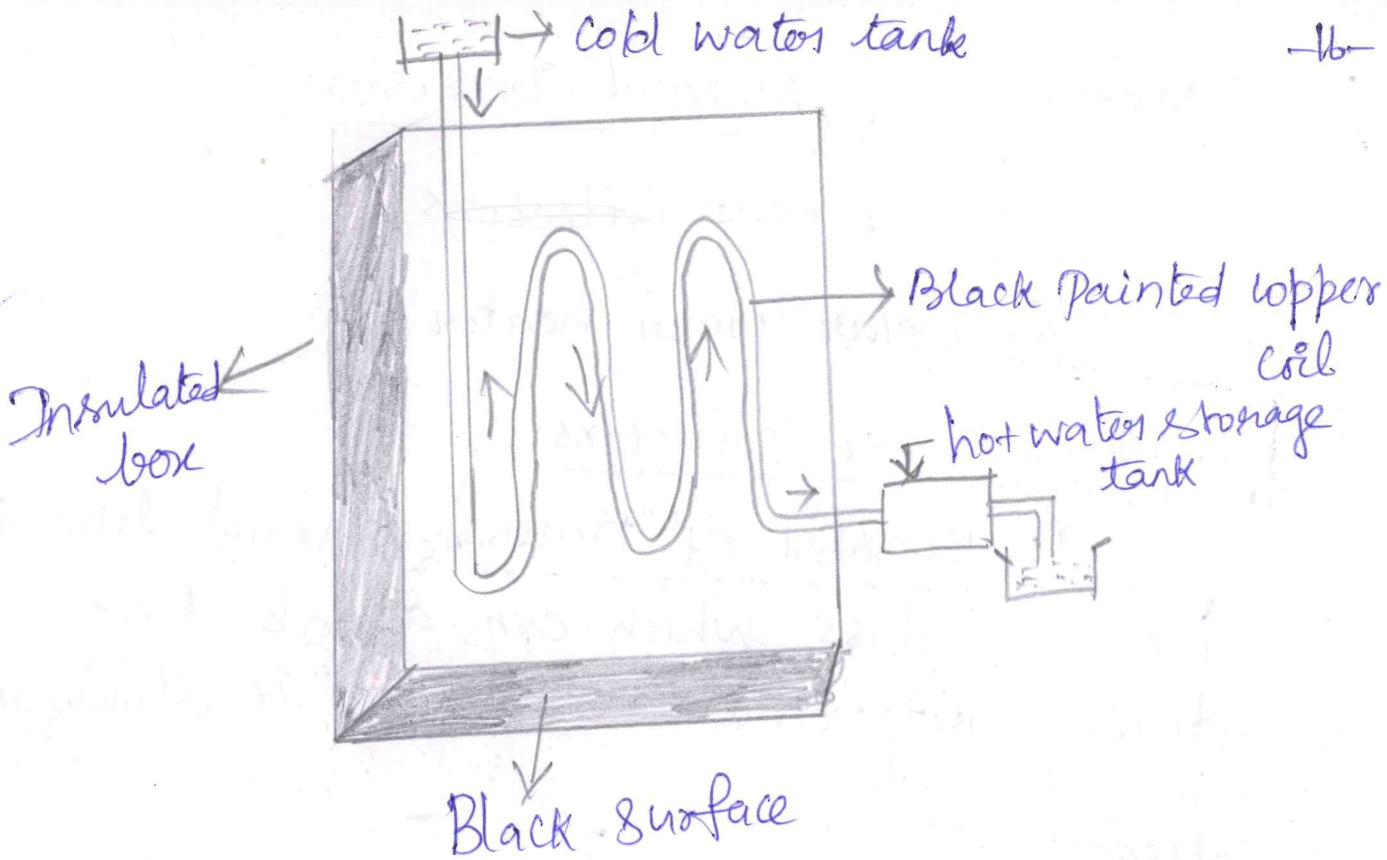


Photo conversion:

It involves conversion of light energy directly into electrical energy by the Photo electric effect.

Methods:

Photogalvanic cell (or) solar cell.

SOLAR CELL: [Photogalvanic cell]

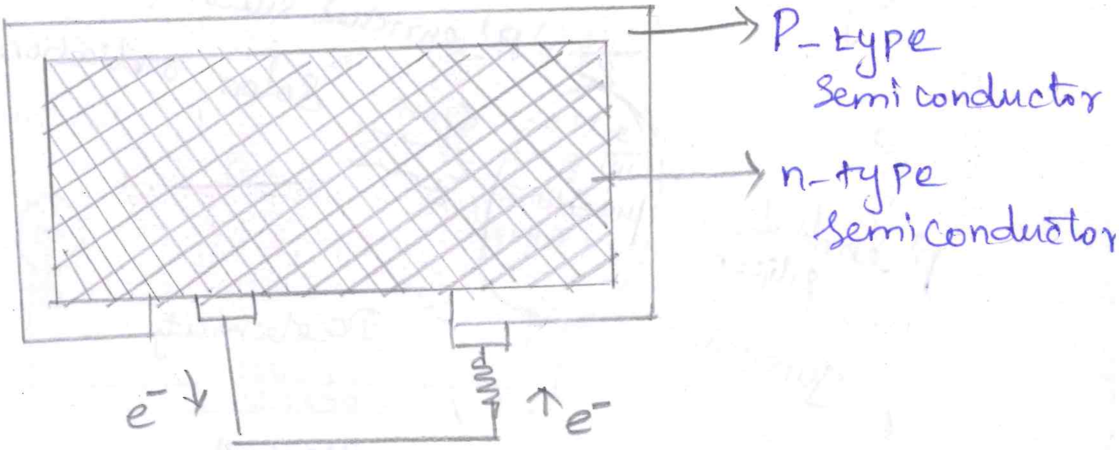
Solar cell is the one which converts the Solar energy (obtained from sun) directly into electrical energy.

Principle:

It is based on the Photovoltaic effect (PV) when the solar rays fall on a two layer of semi-conductor devices, a Potential difference b/w the two layer is Produced. This causes flow of electrons and Produces electricity.

Construction:

Solar cells consists of a p-type semi conductor (such as Si doped with B) and n-type Semiconductor (Si doped with P). They are in close contact with each other.



Solar cell.

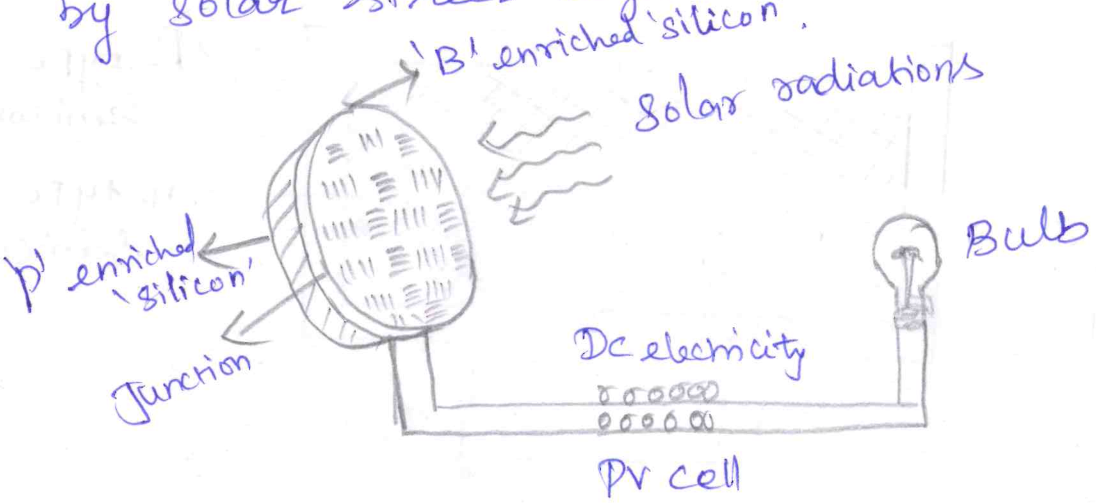
Working:

When the 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 semi conductor. There by potential difference b/w two layers is created, which causes flow of electron (i.e) electric current. Thus when 'p' and 'n' layers are connected to an external circuit, electrons flow from n-layer to P-layer and hence current is generated.

Applications of solar cells

1. Lighting Purpose:

Solar cells can be used for lighting Purpose. Now a days electrical street lights are replaced by solar street lights.



2. Solar pumps run by solar battery.

When a large number of solar cells are connected in series it form a solar battery. Solar battery produces more electricity which is enough to run, water pump, street light, etc., They are used in remote areas, where conventional electricity Suppy is a problem.

3. Solar cells are used in calculators, watches, radios and TVs, vehicles.
4. They are non-Polluting and eco-friendly.
5. Solar energy can be stored in Ni-cd batteries and Lead-acid batteries.
6. Solar cells made of silicon, used as a source of electricity in space craft and satellites.

Advantages and disadvantages of solar cells

Advantages (or) Merits

1. used in remote and isolated area, forests and hilly region.
2. Maintenance cost is low.
3. Noise and Pollution free
4. They operate at ambient temperature.
5. They need not be recharged.

Disadvantages:

1. capital cost is high
2. Storage of Solar energy is not possible.
3. It produces only DC voltage.
4. Not available throughout day and night.

Types of highly investigated solar cell materials.

The following semiconducting materials are used

1. crystalline Si
2. Thin films
3. Next generation perovskite solar cells (PSCs)
4. Solar Paints.
5. Transparent Solar windows
6. Thermo radiative PV devices
7. Solar distillation.

WIND ENERGY:

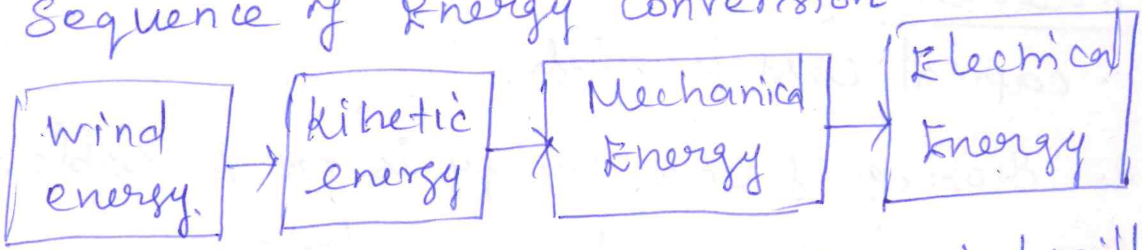
Moving air is called wind. Energy recovered from the force of wind is called wind energy. Kinetic energy of the wind is converted into Mechanical energy.

Methods of harnessing wind energy.

1. Wind mill

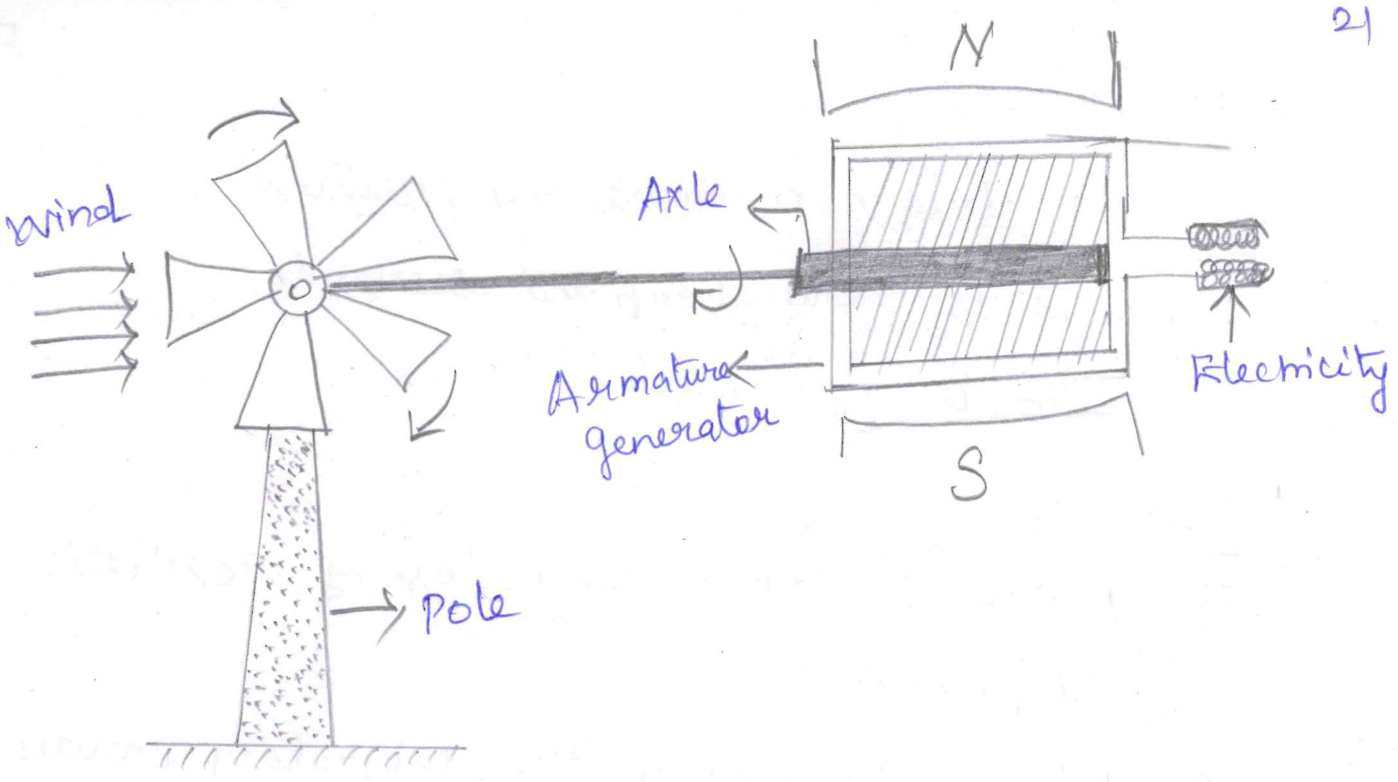
It is a device used to convert wind energy into Mechanical energy.

Sequence of Energy conversion



Construction and working of a wind mill.

- ✱. It consists of a wheel with number of blades.
- ✱. The wheel rotate an axle mounted on a pole.
- ✱. One end of the axle is connected to the armature of a generator, which rotates b/w two poles (North and South 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.
- ✱ The kinetic Energy of the wind is converted into electric energy.



2. Wind farm:

The electricity produced by a single wind mill is very small, which cannot be used for Commercial purpose. TO produce electricity on a large scale, a large number of wind mills are connected.

Thus, the region where large number of wind mills are erected to produce electricity is called wind energy farm. The small amount of electricity produced by each generator connected to each wind mill is combined to get electricity on a large scale.

3. Other Methods.

1. Sky sail
2. Laddermill.
3. kite ship
4. Sky wind Power
5. Briza technologies
6. Sequoia automation

Merits:

1) It does not cause any pollution.
2) It is very cheap and economic
3) It is renewable.

Demerits

1. Noise Pollution and loss of aesthetic appearance.
2. When located on the migratory routes of birds will cause hazards.
3. Wind turbines interfere with electromagnetic signals (TV, radio signals).
4. Wind energy is not sufficient to operate very heavy machine.

Uses:

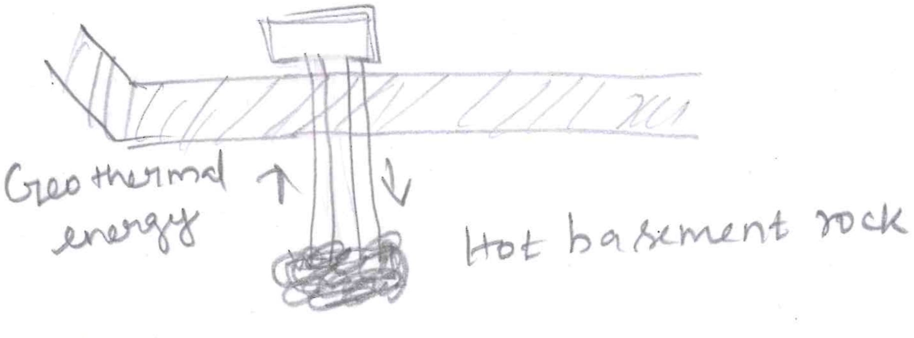
1. Wind energy is used to move the sail boats in lakes, rivers and seas.
2. Used to operate water Pumps.
3. Used to run the flour mill to grind the grai
4. Used to Produced Electricity.

Geo - Thermal Energy:

Temperature of the earth increases at a rate of 20-75°c per km, when we move down the earth surface. High pressure steam fields exist below the earth's surface in many places, "The Energy harnessed from the high temperature present inside the earth is called geothermal energy".

1. Natural geysers

In some places; the hot water (or) steam comes out of the ground through cracks naturally in the form of natural geysers.



2. Artificial geysers:

We can artificially drill a hole upto the hot region and by sending a pipe in it, we can make the hot water or steam to rush out through the pipe with high pressure.

Thus the hot water (or) steam coming out from the natural (or) artificial geysers is allowed to rotate the turbine to produce Electricity.

Significance of geothermal energy.

1. Power generation level is higher for geo-thermal than for solar and wind energies
2. Geothermal power plants can be brought on line more quickly than most other energy sources.
3. GTE is effectively and efficiently used for direct uses such as hot water bath, resorts, aquaculture, greenhouses.

UNIT - V.

BATTERIES

Battery:

A battery is an arrangement of several electrochemical cells connected in series, that can be used as a source of direct electric current.

A cell: It contains only one anode and cathode

A Battery: It contains several anodes and cathodes.

Requirements of a Battery

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. The voltage of battery should not vary appreciably during its use.

Types of Battery:

1. Primary Battery (or) Primary cells (or) Non-reversible Battery.

In these cells, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy.

The reactions occur only once and after use they become dead. They are not chargeable.

eg: Dry cell, mercury cell.

2. Secondary Battery (or) Secondary cells (or) Reversible battery

In these cells, the electrode reactions can be reversed by passing an external electrical energy. They can be recharged by passing electric current and used again and again. These are also called Storage cells (or) Accumulators.

eg: Lead acid storage cell,
Nickel- cadmium cell.

3. Flow battery (or) Fuel cells

In these cells, the reactants, products and electrolytes are continuously passing through the cell. Here chemical energy gets converted into electrical energy.

eg. H_2-O_2 fuel cell.

PRIMARY BATTERY

Dry cell (or) Leclanche's cell

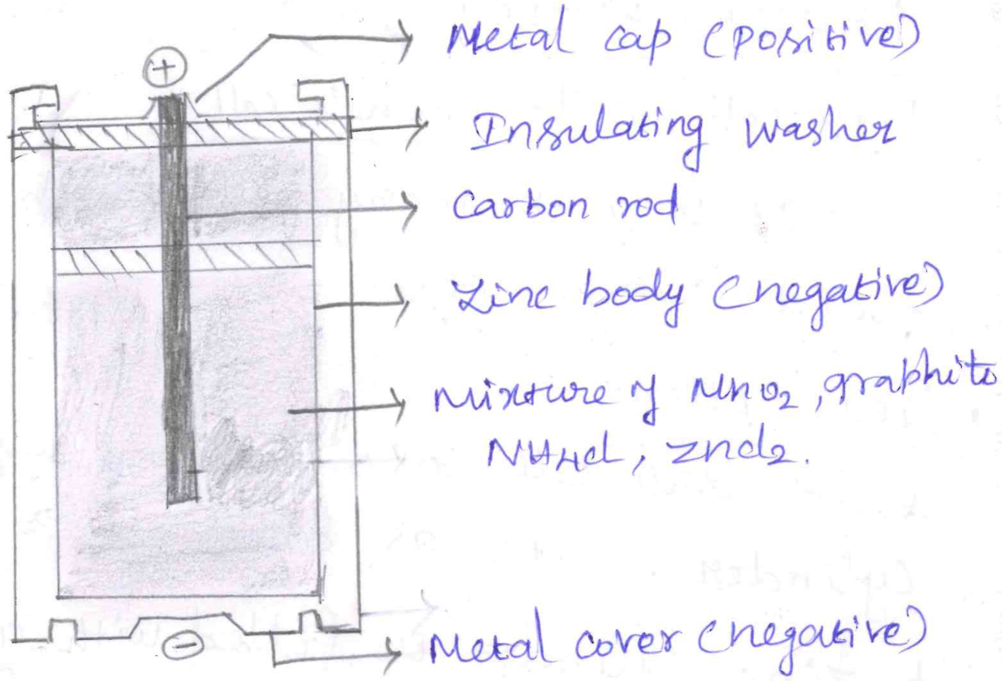
It is a primary cell, which works without fluid component.

Description:

- A dry cell consists of a zinc cylinder, acts as anode.
- zinc cylinder is filled with an electrolyte consisting of NH_4Cl, $ZnCl_2$ and MnO_2, in the form of paste using starch and water.
- A carbon rod (graphite) acts as cathode, is immersed in electrolyte in the centre of the cell.
- zinc cylinder has an outer insulation of card board case.
- During use, the zinc cylinder gets consumed and at the end, it will develop holes which are responsible for leakages.

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 reaction:

At anode: $Zn \rightarrow Zn^{2+} + 2e^-$

At Cathode: $NH_{4(aq)}^{+} + MnO_{2(s)} + 2e^- \rightarrow MnO(OH)^- + NH_3$

Overall reaction: $Zn + NH_{4(aq)}^{+} + MnO_{2(s)} \rightarrow Zn^{2+} + MnO(OH)^- + NH_3$

In cathode reaction, Mn is is reduced from +4 oxidation state to +3 oxidation state. The liberation of NH_3 gas, which disrupts the current flow, is prevented by a reaction of $NH_{3(g)}$ with Zn^{2+} (from $ZnCl_2$).

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

The voltage of Leclanche's cell = 1.5V.

Uses:

It is used in transistor radios, calculators, Flash lights, torches etc.,

Disadvantages:

1. This dry cell does not have an indefinite life b/c NH_4Cl being acidic corrodes the zinc container, even if it is not used.
2. when current is drawn rapidly from it, products build up on the electrodes, so voltage drop occurs.

IMPORTANT SECONDARY BATTERIES

Lead - Acid Storage cell.

Storage cell

It can operate both as a voltaic cell and as an electrolytic cell. when it acts as a voltaic cell, it supplies electrical energy and becomes run down. when it is recharged, the cell operates as an electrolytic cell.

Description:

1. A Lead-acid storage cell consists of a 3-6 Voltaic cells connected in series to get 6-12V. Battery.
2. In each cell anode is made up of Lead, the Cathode is made up of PbO_2.
3. A no.. of lead plates (anodes) are connected in parallel and a no.. of PbO_2 Plates (cathodes) are also connected in parallel.

4. various plates are separated from the adjacent one by insulators like rubber or glass fibre.

5. The entire combinations is immersed in dil. H_2SO_4 (38% by mass) having a density of 1.30 (gm / ml).

The cell represented as;

$$Pb / PbSO_4 \| H_2SO_{4(aq)} | PbO_2 | Pb$$

Working:

When the Lead-acid battery operates, the following reaction occurs,

At anode:

Lead is oxidised to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble $PbSO_4$.

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} PbSO_{4(s)} + 2e^-$$

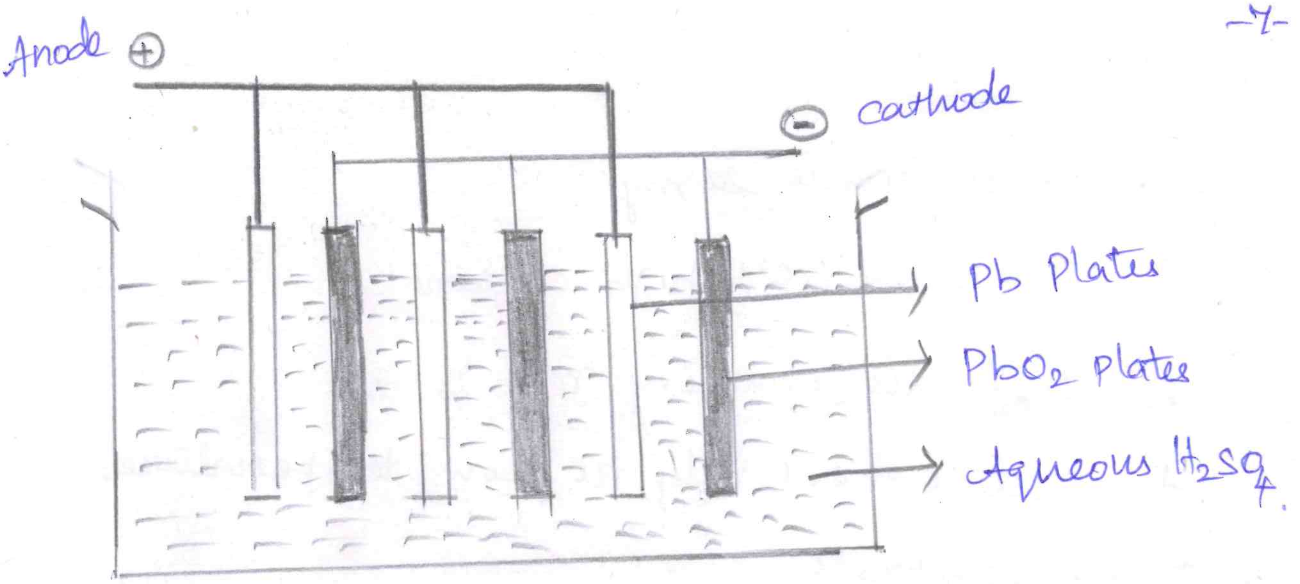
At cathode:

PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble $PbSO_4$.

$$PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^- \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} PbSO_{4(s)} + 2H_2O$$

overall rxn:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O + \text{Energy}.$$



From the above cell reaction it is clear that, $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is ~~used~~ ~~used~~ used up. As a result the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/ml. So the battery needs recharging.

Recharging the Battery :

The cell can be recharged by passing electric current in the opposite direction. The electrode reaction gets reversed. As a result Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases.

The net reaction during charging,

$$2PbSO_{4(s)} + 2H_2O + \text{Energy} \rightleftharpoons Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$$

Advantages:

1. It is made easily
2. produces very high current
3. self dis-charging rate is low
4. acts effectively at low temperature.

Disadvantages:

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

Uses:

1. Used in automobiles like cars, buses, trucks etc.,
2. Used in gas engines ignition, telephone exchangers, hospitals, Power stations etc.,

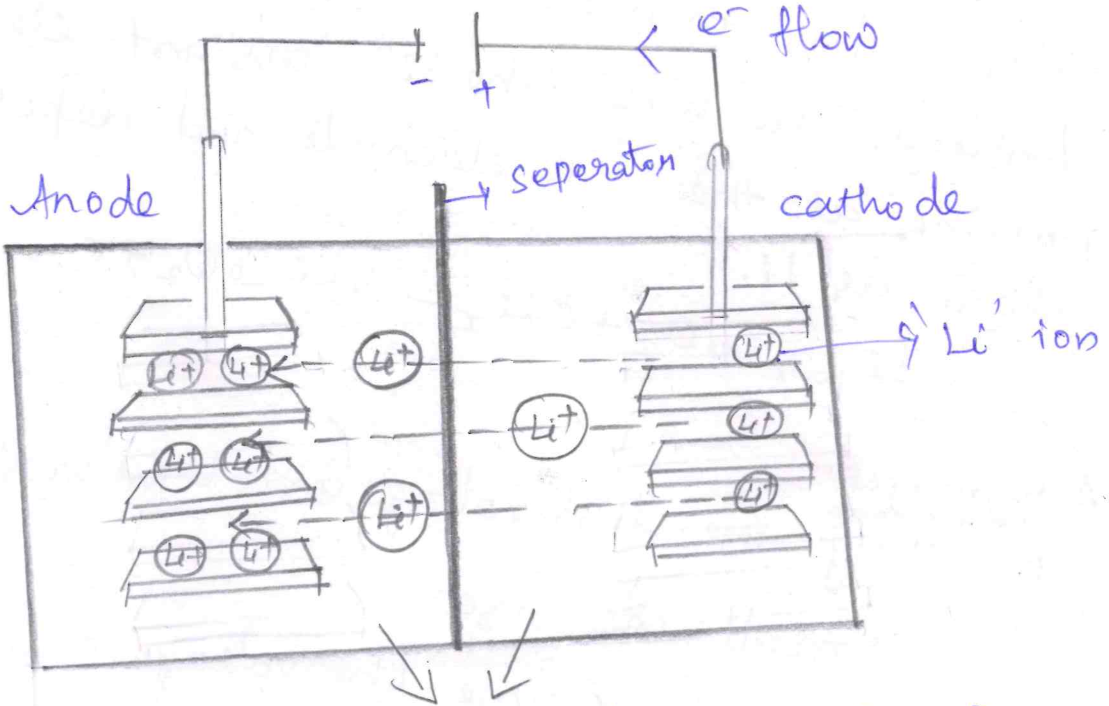
Lithium-ion Battery

It is a secondary battery. The movement of lithium ions are responsible for charging and discharging. It has,

- +ve electrode (lithium-metal oxide)
- -ve electrode (Porous carbon)
- An electrolyte (Polymer gel)

Construction:

- ★ the Positive electrode is typically made from a layers of chemical compound called Li-Co oxide. ($LiCoO_2$).
- ★ The -ve electrode is made of layers of Porous carbon (graphite).
- ★ Both the electrodes are dipped in a polymer gel (electrolyte) and separated by a separator, which is a perforated plastic, and allows the $Li^{(+)}$ ions to Pass through



Electrolyte (gel polymer)

Working:

Charging:

During charging, Li^+ ions flow from the Positive electrode ($LiCoO_2$) to the negative electrode (graphite) through the Electrolyte

Electrons flow from the +ve electrode to the negative electrode through the wire. The e^-s and Li^+ ions combine at the -ve electrode and deposit there as Li.

$$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + CLi_x$$

Discharging:

During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the +ve electrode. Electrons also flow from the -ve to +ve electrode through the wire. The Li^+ ions and electrons combine at the +ve electrode and deposit there as Li.

$$Li_{1-x}CoO_2 + CLi_x \rightarrow LiCoO_2 + C.$$

Advantages:

1. They are high voltage and light weight batteries
2. small in size
3. Produces 3 time the voltage of Ni-cd battery.

Uses:

It is used in cell phone, note Pc, Portable LED TV, semiconductor driven audio, etc.,

Electric Vehicles

Electric vehicles are the vehicles that are powered on electric power. They have an electric motor instead of an internal combustion engine.

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 wheels.

* Electric vehicles accelerate faster than the traditional fuel engines. So they feel lighter to drive.

Various steps of working.

Step 1:

Controller takes and regulates electrical energy from battery to inverter.

Step 2:

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

Step 3:

The motor Converts electrical energy into Mechanical energy (rotation)

Step IV:

Rotation of the motor 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.

Component of EV:

1. Battery:
   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 engine, motor etc.,

8. Transmission:

It transfers Mechanical Power from the motor to drive the wheels.

Plug-in electric vehicles:

1. Battery Electric vehicles (BEVs) (or) Pure electric vehicles (or) fully electric vehicles.
2. Hybrid type vehicles.
   - (a) Hybrid Electric Vehicle (HEV)
   - (b) Plug in hybrid electric Vehicles (PHEVs)

1. Battery Electric Vehicles (BEV).

These are the vehicles powered by a battery. These batteries can be charged by plugging the vehicle into the charging equipment driving ranges from 150 – 300 miles. This type of Vehicles do not have an ICE.

Hybrid type vehicles:

(a) Hybrid Electric Vehicle (HEV)

It has both an Internal combustion Engine [ICE] and an electric motor. In this type of electric cars; ICE gets energy from fuel. while the motor gets electricity from batteries. It offers a mixture of battery and gasoline powers.

The gasoline engine and electric motor simultaneously rotate the transmission, which drives the wheels. Batteries in HEC can only be charged by ICE by the motion of the wheels. The battery cannot be recharged from outside the system.

(b) Plug-in hybrid Electric Vehicle (PHEV)

This type of electric cars are powered by a conventional fuel and by a rechargeable battery park. This can be charged by plugging into an electrical plug. It can be recharged by ICE.

It operates on electricity until their battery pack to depleted. Once the battery is empty, the engine takes over and the vehicle operates as a conventional non-plug-in hybrid (gasoline) vehicle.

Fuel cell Electric vehicles

Herea chemical energy of the fuel is converted directly into electric energy. The main advantage of this vehicle is, it generates electricity, required to run their vehicle, on the vehicle itself.

Advantages:

1) Electric cars are energy efficient
2) It reduces emission
3) Performance is high and has low maintenance
4) It can be fuelled by for very low price.
5) It is more convinient and easy to recharge.

Disadvantages:

1) Electric cars can travel less distance,
2) Takes longer time to refuel.
3) More expensive.
4) Electric fuelling stations are still in the developing stages.
5) Initial investment is high.

Fuel cells

Def:

Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity without combustion.

Fuel + oxygen ⟶ oxidation products + Electricity

eg. $H_2 - O_2$ fuel cell.

Fuel Battery:

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

$H_2 - O_2$ fuel cell:

Description:

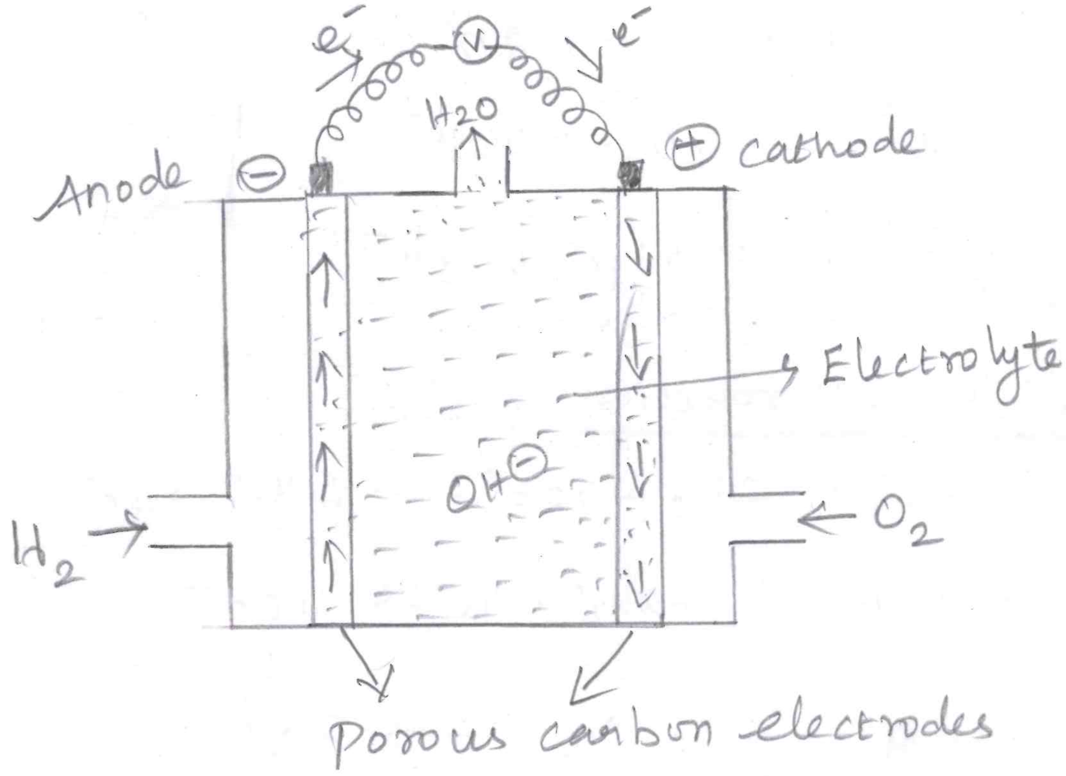
* It consists of two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon with catalyst Pt, pd, Ag.

* In between two electrodes an electrolytic solution such as 25% KOH or NaOH is filled.

* The two electrodes are connected through the volt meter.

Working

Hydrogen is bubbled through the anode compartment, where it is oxidised. The oxygen is bubbled through the cathode compartment, where it is reduced.



Various reactions

At anode:

Hydrogen gas, passed through the anode, is oxidised with the liberation of electrons which then combine with hydroxide ions to form water.

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \longrightarrow 2H_2O$$

Over all reaction at anode.

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

At cathode:

The electrons, produced at the anode, pass through the external wire to the cathode where it is absorbed by oxygen and water to produce hydroxide ions.

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

$$2O^{2-} + 2H_2O \rightarrow 4OH^-$$

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

Over all cell reaction

At anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

At cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

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

emf of the cell = 0.8 to 1.0V.

Applications:

1. $H_2 - O_2$ cells are used as auxiliary energy source in space vehicles, submarines or other military-vehicles.

2. The product of water is proved to be a valuable source of fresh water by the astronauts.

Advantages of $H_2 - O_2$ fuel cell

1. emits only water vapour and no other harmful chemicals to the environment.
2. Efficiency is more than 75%.
3. As hydrogen is the lighetest element, it can be transported easily from one place to another.
4. causes less noise pollution.

Limitations

1. Hydrogen gas is explosive
2. expensive to carry out
3. difficult to compress into liquid form.
4. Hydrogen is not present as it is but always present in combined form with either oxygen or some other element, so it must be separated first.

Advantages and disadvantages of fuel cells.

Advantages:

1. efficient, take less time for operation
2. Pollution free technique.
3. Produces electric current directly from the reaction of fuel and an oxidiser.
4. Produces drinking water.

Disadvantages of fuel cells

1. Fuel cells can not store electric energy as other cells do.
2. Electrodes are expensive and short lived.
3. Storage and handling of hydrogen gas is dangerous.

Microbial Fuel cells (MFCS).

It is a fuel cell device that converts chemical energy to electrical energy by the action of micro-organisms under aerobic condition.

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

Construction :

* MFCs are type of electrochemical cells, constructed using either bioanode and (or) a bio cathode.
* A membrane separates the compartments of the anode and the cathode.
* The electrons produced during oxidation are transferred directly to the cathode.

- * The charge balance of the system is maintained by the ionic movement inside the cell.

- * organic electron donors, that is oxidised to produce CO_2, protons and electrons are used in most MFCs.

- * The cathode reaction uses a variety of electron acceptors, mostly oxygen.

Components

(i) Anodic compartment:

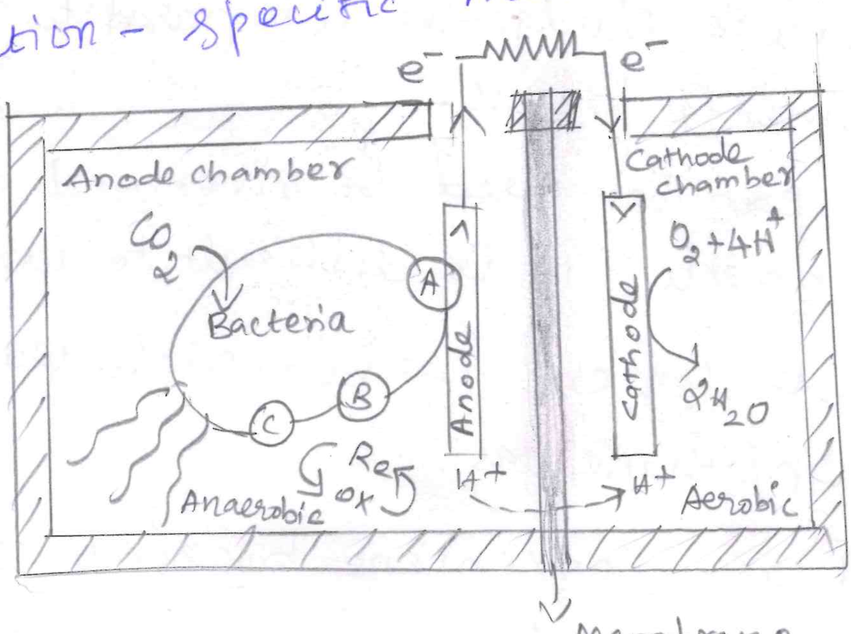
It consists of microbes suspended under anaerobic conditions in the anolyte.

(ii) cathodic compartment:

It consists of electron acceptor (oxygen).

Permeable membrane:

Anionic and cationic compartments are separated by a selectively permeable, cation - specific membrane.



Working:

* when both electrodes are connected, anode oxidation occurs on organic waste (biomass) and electrons released from the process are transferred to the anode. It can be accomplished by the electron mediators.

* From the anode these electrons are directed to the cathode across an external circuit.

* For every electron conducted, a proton is transported across the membrane to the cathode.

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

Applications:

1. In waste water treatment, MFCs, generate less excess sludge as compared to the aerobic treatment process.
2. MFCS can be used in river and deep-water environments, it is difficult to use batteries
3. Used to convert carbon rich waste water into methane gas.
4. Used as convenient biosensor for waste water streams.

5. Used in space, to operate remotely operated vehicles.

6. MFC's play an important role in the field of microbiology, soil chemistry and electrical engineering.

7. Commercial soil based MFC kits are available for the purchase on the wed and in toy stores.

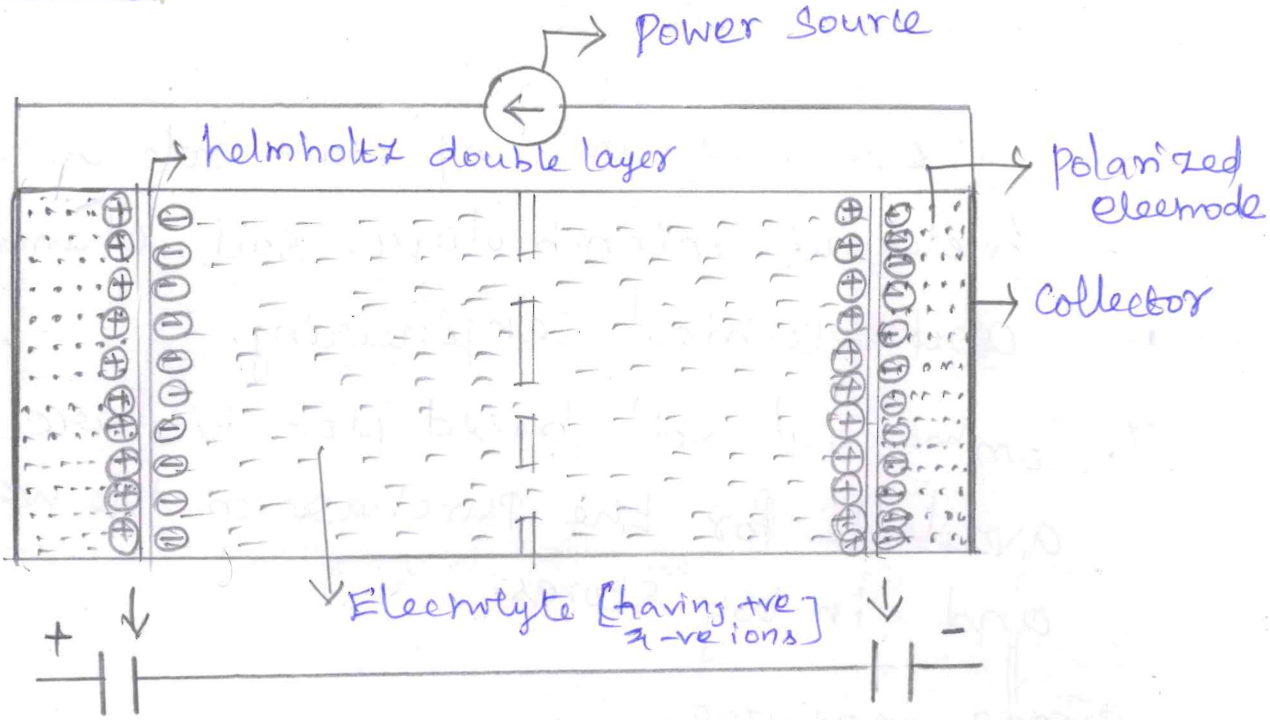
SUPER CAPACITOR

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

Design of Super Capacitor

It consists of two electrodes (made from metal coated with a porous substance like powdery activated carbon), separated by an ion-permeable membrane and dipped in an electrolyte, containing positive and negative ions connecting both the electrodes.

Working:



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

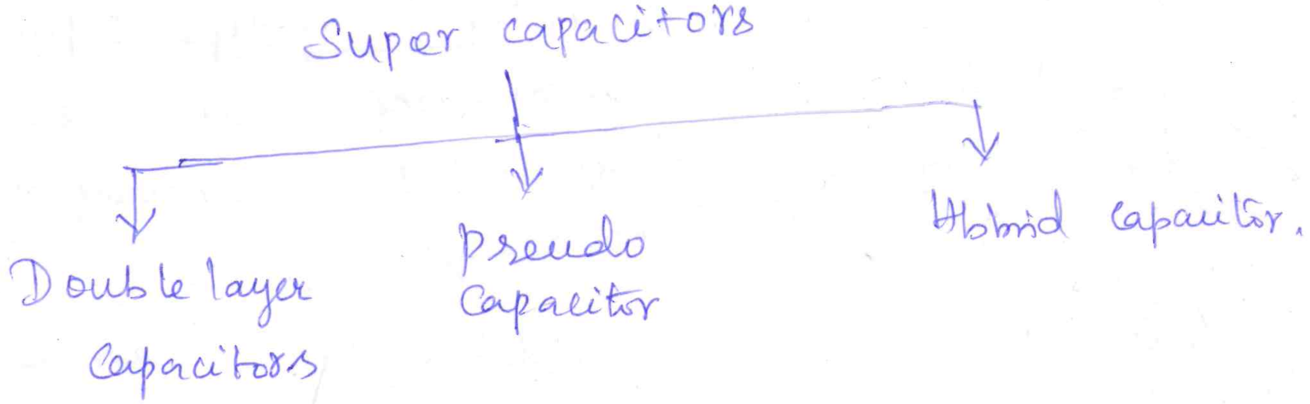
For example, +vely polarised electrodes will have a layer of -ve ions at the electrode / electrolyte interface.

Similarly, -vely polarised electrodes will have a layer of +ve ions at the electrode / electrolyte interface.

This electric field polarises the dielectric, so its molecules line up in the opposite direction to the field and reduce its strength. It means that it stores more electrical energy at an electrode-electrolyte interface.

Types of Super capacitors:

1. Double layer capacitors
2. Pseudo capacitors
3. Hybrid capacitors



1. Double layer capacitor:

It consists of two electrodes separator and electrolyte. The electrolyte is the mixture of positive ions and negative ions dissolved in water. The two electrodes are seperated by a seperator.

2. Pseudo capacitors:

It starts electrical energy by electron change transfer between electrode and electrolyte. This can be done by redox reaction.

3. Hybrid capacitors:

It is developed by using techniques of double layer capacitors and Pseudo capacitance and Pseudo capacitance is achieved.

Difference b/w battery, capacitor and super Capacitor.

Battery	Capacitor	Super capacitor.
Can store large amount of charge	cannot store large amount of charge.	can store large amount of charge
cannot deliver the charge very quickly	Can deliver the charge quickly	Can deliver the charge quickly.

Advantages

1. It is highly safe
2. Life time is very high (10 to 20 years).
3. It can be cycled millions of time
4. can be charged in seconds
5. It provides high power density and high load currents.
6. Its performance is excellent even at low temperature (-40°c).

Disadvantages:

1. cost per watt is high
2. It cannot be used as source for continuous power supply.
3. If higher voltage is required, the cells must be connected in series
4. High self discharge, it is higher than most batteries.

Applications:

1. voltage stabilization in start/stop system
2. Energy harvesting
3. Kitchen appliances
4. Regenerative braking system
5. consumer electronics
6. wind energy.
7. Utility meters
8. Remote Power for sensors, LEDs, switches
9. Energy efficiency and frequency regulation.