UNIT-1 - Water & its treatment

- water quality parameters
  - colour
  - odour
  - turbidity
  - pH
  - Hardness
  - Alkalinity
  - TDS
  - COD
  - BOD
  - ~~Flo~~ fluoride
  - Arsenic

- Boiler feed water
  - Troubles ⇒
    1. Scale & sludge
    2. Priming & foaming
    3. caustic embrittlement
    4. Boiler corrosion

- water treatment
  - Municipal water treatment
  - Desalination of brackish water
  - Treatment of boiler feed water
    - Internal treatment
    - External treatment
      - Ion-exchange process
      - zeolite process

. — x — .

Boiler feed water ⇒

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

Boiler troubles ⇒

1. scale & sludge formation
2. Priming & foaming
3. caustic embrittlement
4. Boiler corrosion

1. scales & sludges ⇒

sludge : * Loose, & slimy precipitate, & non-adherent precipitate

* sludge forming substances

* $MgCO_3$, $MgCl_2$, $MgSO_4$ & $CaCl_2$

* Disadvantages

* Poor conductors of heat

* Boiler efficiency decreased.

* Prevention

* By using soft water

* By blow-down operation

scale : * Hard & adherent precipitate

* scale forming substances

* $Ca(HCO_3)_2$, $CaSO_4$, $Mg(OH)_2$

* Disadvantages

* Act as thermal insulator

* Lead to explosion

* prevention ↑ ($CaCO_3$ scale)
  * By using acids (HCl, H_2SO_4)
  * By internal & external treatment
  * By applying thermal shocks (brittle) scrapers, wirebrush etc...
    (At Initial stage)
  * By using EDTA for $CaSO_4$ scale

2. Priming & Foaming (carry over) ⇒

wet steam ⇒
* steam + droplets of water ⇒ wet steam
  ⇓
  some dissolved salts & suspended impurities
  Reason
  ↳ priming & foaming

Priming ⇒ * Process of production of wet steam
* Reason ⇒ * High steam velocity
  * High water level
  * sudden boiling of water
  * poor boiler design
* Prevention
  * By controlling of steam velocity
  * By keeping low water level
  * Good boiler design
  * By using treated water.

Foaming ⇒

* Formation of stable bubbles above the surface of water is called foaming.

* Reason ⇒ * Presence of oil & grease
* Presence of finely divided particles

* Prevention ⇒
* By adding coagulant (Sodium aluminate & Aluminium hydroxide)
* By adding anti-foaming agent (synthetic polyamide)

3. Caustic embrittlement (Intercrystalline cracking) ⇒

* Generally, boilerwater contains trace amount of Na_2CO_3. In high pressure boiler, this Na_2CO_3 undergoes decomposition to give NaOH.

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

* This NaOH enters into the minute cracks & crevices & convert the surrounding area as sodium ferrate.

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

* This sodium ferrate causes of brittlement of boiler parts like bands, joints, rivets etc...

Prevention ⇒

* By using sodium phosphate as softening agent instead of Na_2CO_3

* By adding tannin, lignin to block the cracks.

4. Boiler corrosion ⇒

* Reason 1. Dissolved oxygen
  2. Dissolved CO_2
  3. Dissolved salts.

1. Dissolved oxygen ⇒

* At high temperature, the dissolved oxygen attack the boiler material.

$Fe + 3H_2O + \overset{1.5}{}O_2 \rightarrow 2Fe(OH)_3 \downarrow$

$2Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \downarrow$

Prevention ⇒

1. By chemical method.
2. By mechanical method.

chemical method ⇒

1. By adding sodium sulphite

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

2. By adding Hydrazine. (Best method)

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

Mechanical method ⇒ (De-aerator)

* water is allowed to fall slowly on the perforated plates

* The sides of the tower are heated & a vacuum pump is also attached to it.

* Inside the tower high temperature & low pressure is maintained which reduce the dissolved oxygen content of water.

2. Dissolved carbon dioxide

* Dissolved CO_2 produces carbonic acid which is acidic & corrosive in nature.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

* CO_2 gas is also produced from the decomposition of $Ca(HCO_3)_2$ present in water.

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

Prevention ⇒

* By adding NH_4OH

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

* By de-aeration method.

3. Dissolved salts

* Salts like $MgCl_2$, $CaCl_2$ undergoes hydrolysis at high temperature to give HCl which corrodes the boiler

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

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

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

Prevention ⇒

* By adding alkali (base)

$HCl + NaOH \rightarrow NaCl + H_2O$

Municipal / Domestic water treatment ⇒

1. Municipal water treatment ⇒

Sources of water
↓
Screening
↓
Aeration → Sedimentation
↓
Sterilisation (or) Disinfection ← Filtration ← coagulation

1. Screening ⇒

* The process of removing floating material (leaves, wood pieces etc..) from water is known as Screening

* Raw water → Screen (holes) → water (free from floating materials)

2. Aeration

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

* To remove CO_2, H_2S, volatile impurities manganous salts & ferrous salts.

3. Sedimentation

* The process of removing suspended impurities from water is known as sedimentation.

* To remove 75%. suspended impurities

* water tank → 2-6 hours undisturbed → settle down at the bottom.

4. coagulation

* To remore finely divided clay, silic

* water → coagulants added { Alum $Al_2(SO_4)_3$ }

$Al_2(SO_4)_3$ ↓

$Al(OH)_3$ → settle down at the bottom

gelatinous precipitate

5. Filtration

* The process of removing bacteria, colour, taste, odour, and suspended particles is known as filtration.

water → Filter bed (fine sand, coarse sand & gravel)

↓

Thick top layer of fine sand scrapped off ← Rate of filtration decreases

↓

Replaced with clean sand

6. sterilisation / Disinfection

* The process of destroying harmful bacteria is known as sterilisation.

1. By using ozone ⇒

* ozone - powerful disinfectant

$O_3 \rightarrow O_2 + O$ ↳ * Nascent oxygen
* powerful oxidising agent

Disadvantages ⇒

* Costly * Not for large scale

* They cannot be stored for long time.

2. By using UV radiation

* This method mostly useful for sterilizing water in swimming pool.

Disadvantages ⇒
* costly * Turbid water cannot be treated.

3. By chlorination
1. By adding chlorine gas
2. By adding chloramine
* This is better disinfectant than chlorine.
* $Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$

2 : 1 ratio Chloramine.

3. By adding bleaching powder

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

$Cl_2 + H_2O \rightarrow HCl + HOCl$

HOCl + Bacteria → Bacterium killed.

Break point chlorination

* water contains bacteria, organic impurities, reducing substances, free ammonia. (Fe^{2+}, H_2S).
* To kill the bacteria, chlorine may be added to water directly as a gas or in the form of bleaching powder.

* When chlorine is added to water, the results obtained can be depicted graphically. This graph shows the relationship between the amount of chlorine added to water and the residual chlorine.

* Initially the applied chlorine is used to kill the bacteria and oxidises all the reducing substances present in water & there is no free residual chlorine.

* As the amount of applied chlorine increases, the amount of combined residual chlorine also increases. This is due to the formation of chloramine & other chloro compounds

* At one point, on further chlorination the oxidation of chloramine and other impurities starts and there is a fall in the combined chlorine content.

* The point at which combined residual chlorine decreases to a minimum point where oxidation of chloramines and other impurities complete and free residual chlorine begins to appear.

Desalination of Brackish water

Desalination ⇒

* The process of removing common salt from the water is known as desalination.

Brackish ~~taste~~ water ⇒

* The water containing dissolved salts with a peculiar salty (or) brackish taste is called brackish water.

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

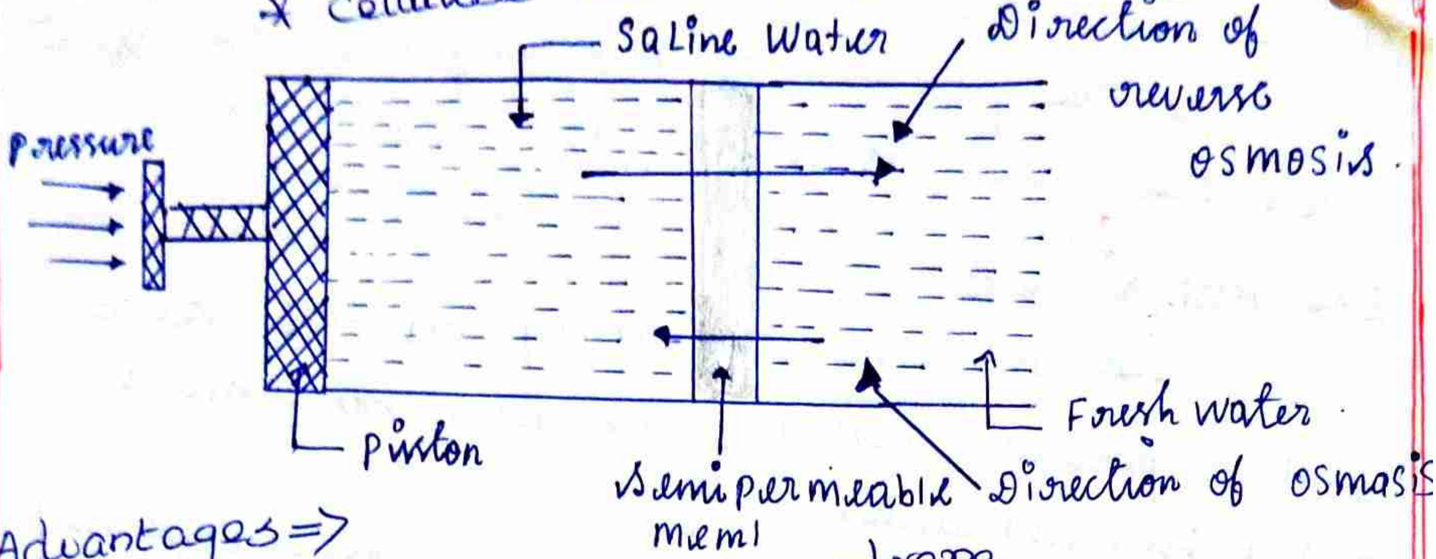
Reverse osmosis ⇒

* If two solutions of different concentrations are separated by a semi-permeable membrane, solvent flows from lower concentration region to higher concentration region. This process is called osmosis.

* If hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration region, the solvent flows from higher concentration region to lower concentration region. This process is called reverse osmosis. This process is also known as super filtration.

Membranes ⇒

* cellulose acetate, cellulose butyrate.



Advantages ⇒

* High lifetime of membrane
* Removes ionic, non-ionic & colloidal impurities.
* Low capital cost

Treatment of boiler feed water (or) softening of water (or) conditioning of water ⇒

* softening of water can be done by two methods
  1. Internal treatment
  2. External treatment

⇓

Ion-exchange process   Zeolite process

Internal treatment ⇒ Boiler compounds

External conditioning / treatment ⇒

* This method is used to remove hardness producing salts from the water.

Ion-exchange (or) Demineralisation process ⇒

* This method is used to remove almost all the ions (Cations & Anions).
* It is carried out by using ion-exchange resins.
* Resins are longchain, crosslinked, insoluble organic polymers with a microporous structure.
* Two types of resins → cation exchange resin
  → Anion exchange resin

cation exchanger ⇒

* It is represented by RH_2
* It has acidic functional group which
* It exchanges their cations with other cations of hard water.
* Example ⇒ sulphonated coal
  sulphonated polystyrene.

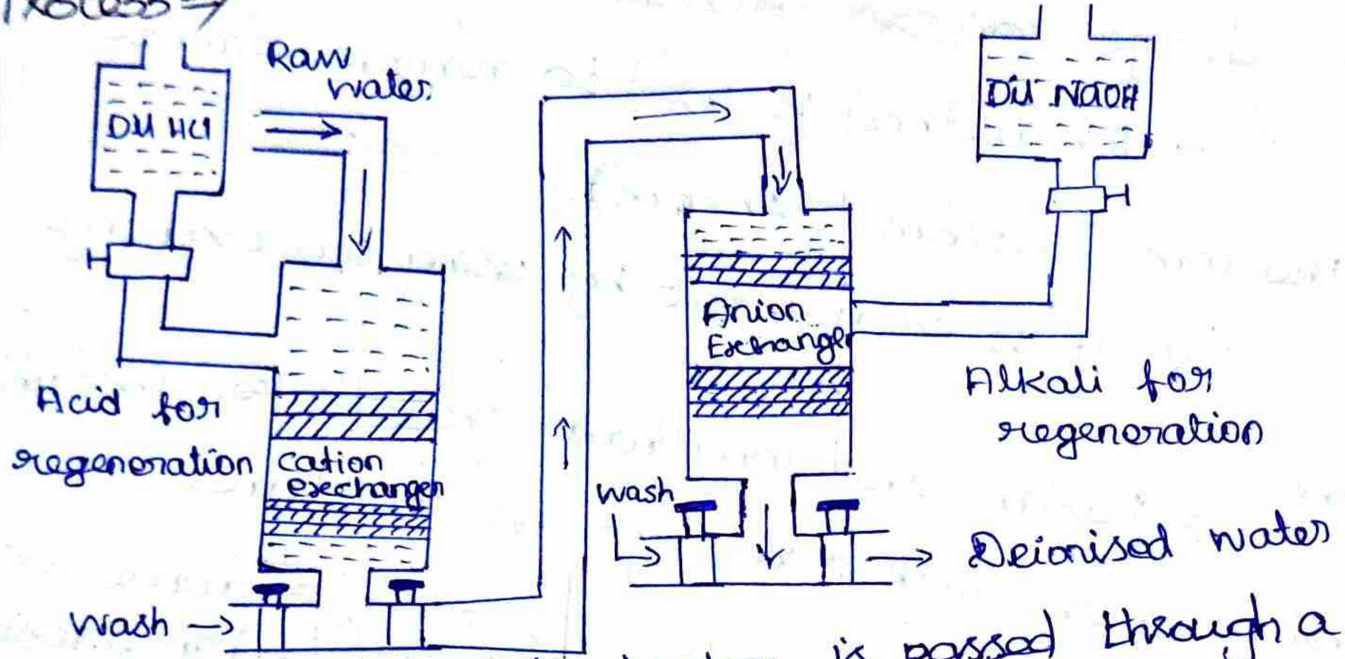
Anion exchanger ⇒

* It is represented by $R'(OH)_2$
* It has basic functional group which

exchanges their anions with other anions of hard water.

* Example ⇒ 1. Cross linked quaternary ammonium salts
2. Urea - Formaldehyde resin

Process ⇒



* At first, hardwater is passed through a cation exchange column

* Here all cations are absorbed $(Ca^{2+}, Mg^{2+}, K^+, Na^+)$

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

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

* The cation free water is then passed through an anion exchange column

* Here all anions $(Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-)$ are absorbed.

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

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

* Now the water is free from both cations & anions. This water is known as DM water (or) De-ionised water

Regeneration ⇒

* When the cation exchange resin gets exhausted, it can be regenerated by using dil HCl or H_2SO_4.

$RCa + 2HCl \rightarrow RH_2 + CaCl_2$

* similarly, anion exchange resin is regenerated by using dil. NaOH

$R'Cl_2 + 2NaOH \rightarrow R'(OH)_2 + 2NaCl.$

Advantages ⇒ * Highly acidic / alkaline water can be treated.

* water - low hardness (2 ppm).

Disadvantages ⇒ * water containing Fe, Mn & turbid water cannot be treated

* Expensive method.

Zeolite process

* Zeolite is hydrated sodium aluminosilicate

* General formula → $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$
$x = 2\text{-}10,\ y = 2\text{-}6$

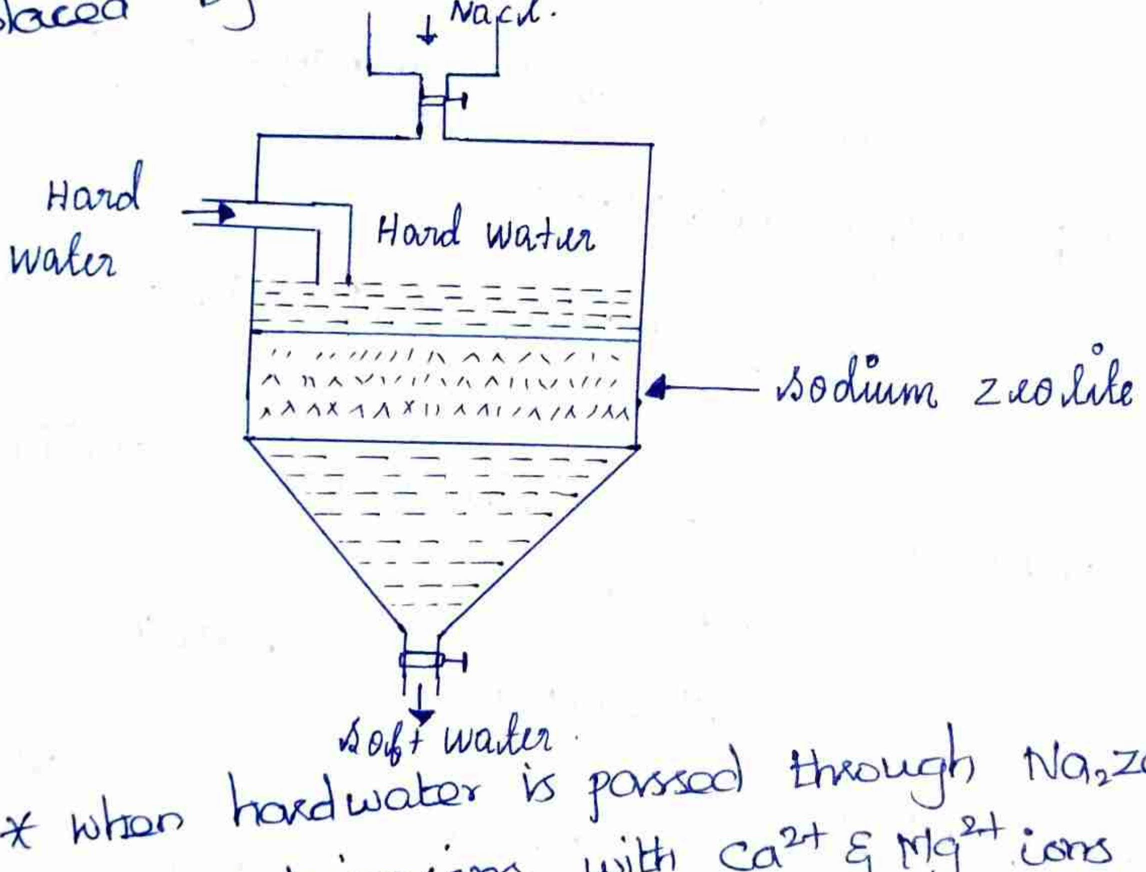
* Natural zeolite → Green sand & non-porous

* Synthetic zeolite → Permutit (porous & gel structure)

* Example for synthetic zeolite → Na_2Ze

* Here, sodium ions are loosely bonded & easily replaced by Ca^{2+} & Mg^{2+} ions present in water.

Process ⇒



* When hardwater is passed through Na_2Ze, it exchanges its sodium ions with Ca^{2+} & Mg^{2+} ions present in the hardwater.

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

$MgCl_2 + Na_2Ze \rightarrow MgZe + Na_2SO_4$

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

Regeneration ⇒

* When Na_2Ze gets exhausted, it can be regenerated by using 10% NaCl.

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$

Advantages ⇒

* water - low hardness (2 ppm)
* cheap method * No sludge is formed
* Equipment is compact. * Easy to operate.

Disadvantages ⇒

* Turbid water cannot be treated
* Acidic water cannot be treated.
* The softened water contains more dissolved salts. ↳ This leads to caustic embrittlement & boiler corrosion.
* Brackish water cannot be treated.

* water containing Fe & Mn cannot be treated.

Sources of water ⇒

* Rain * Rivers & lakes * wells & springs

* Sea water.

water treatment ⇒

* The process of removing all types of impurities from water & making it fit for domestic or industrial uses is called water treatment.

Types of impurities ⇒

* Physical impurities

* suspended impurities - sand, oil etc ↑ Turbidity

* colloidal impurities - silica, clay organic waste ↓ Taste, colour & odour

* chemical impurities

* Dissolved salts - Bicarbonates, sulphates & chlorides of Ca & Mg - Carbonates & bicarbonates of Na & K

* * Dissolved gases - CO_2, O_2 H_2S, SO_2 ↓ Make water acidic → corrosion

* Biological impurities.

* Fungi, bacteria, other micro organism ↓ diseases

water quality Parameters

* In order to decide treatment required or type of application, the water quality is very important parameter.

1. colour ⇒

* It is a shade given by organic or inorganic material

sources ⇒

* Algae, organic dyes - organic sources
* Fe, Mn, inorganic dyes. Inorganic sources

significance ⇒

* yellowish tinge > Indicates the presence of Cr & organic matter.
* yellowish red > Indicates the presence of iron
* Red-brown > Indicates the presence of peaty matter

Removal of colour ⇒

* By coagulation, settling, adsorption & filtration

Tastes & odours ⇒

Taste ⇒

* The sensation of flavour perceived in the mouth & throat on contact with a substance

Odour ⇒

* It is a smell (or) scent caused by one or more volatilized chemical compounds

Sources ⇒

* Organic sources - Algae.

* Inorganic sources - Mercaptans, amines & sulphides

Significance ⇒

* To identify valuable nutrient in the environment.

* Taste - enables the evaluation of foods for toxicity.

* Taste - helps us to decide what to eat.

Removal of taste & odour ⇒

* Organic taste & odours - Removed by activated carbon treatment.

* Inorganic tastes (H_2S or Iron) - Removed by oxidation, chlorination (or) precipitation

Turbidity & sediments ⇒

* It is the reduction of clarity of natural water.

Sources ⇒

* Inorganic Sources - clay, silt, silica, sulph

* organic sources - oil, fat, grease etc...

Problems ⇒

* water softening processes cannot be carried out

* Disinfection efficiency gets reduced.

Significance ⇒

* It changes the taste & odour of water

* It blocks light to aquatic plants & organism

* It reduces the growth rate of algae.

* It increases the temperature of water because suspended particles absorbs more heat.

Removal of turbidity ⇒

* Removed by sedimentation followed by

1) coagulation & filtering
2) coagulation & settling
3) coagulation, settling & filtering

pH ⇒

* It is defined as negative logarithm of hydrogen ion concentration.

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

  * For drinking water - pH = 6.5 to 8.5

  * For irrigation - pH = 6 to 9.

$0 \longrightarrow 7 \longrightarrow 14$

Acidic Neutral Basic

Significance ⇒

* Solubility can be determined
* Biological availability can be determined
* Acid rain.

Alkalinity ⇒

* It is one of the chemical properties of water which measure its acid-neutralising ability.

* OH^-, CO_3^{2-} & HCO_3^- → causing alkalinity

Sources ⇒

* Fertilizer, detergent, leather & paint.

Significance ⇒

* Very high alkalinity - Harmful to aquatic organism

* Caustic embrittlement.

Removal ⇒

* By adding calculated amount of Hcl

Total Dissolved Solids ⇒ TDS

* It is defined as the measure of all inorganic & organic substances present in water.

significance ⇒

* TDS level should not exceed more than 300 ppm

* If TDS level high (>1200), it affects the colour, odour & taste.

* scale formation in water pipes, heaters boilers & house hold appliances.

Fluoride ⇒

* surface water - low concentration of fluoride.

sources ⇒

* Fluoride containing minerals, domestic sewage.

significance ⇒

* 0.7-1.2 mg/lit → Public water supplies

* If fluoride concentration is low, it causes dental caries in children

* If fluoride concentration is high, it causes fluorosis.

Removal ⇒

* By precipitation (Aluminium salts in alkaline media)
* By using strongly basic anion exchange resin.
* By adsorption on activated carbon.

Arsenic ⇒

* It is a metallic element that forms a number of poisonous compounds.

Source ⇒

* Agriculture, Mining & industrial processes.

Significance ⇒

* Long term intake of arsenic compound contaminated water - skin, kidney & bladder cancer
* It also causes diabetes, hypertension & reproductive disorders.
* children - illness

Chemical oxygen Demand (COD) -

* It is defined as, the measure of amount of oxygen required to chemically oxidise all the oxidisable impurities present in the sewage using an

oxidising agent (acidified $K_2Cr_2O_7$)

Significance ⇒

* COD - used to measure pollutants in water waste water, & aqeous hazardous wastes.

* Biologically oxidisable & inert organic matter can be measured.

* It is used to measure pollut monitor water treatment plant efficiency.

Biological oxygen Demand (BOD ⇒

* It 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 ⇒

* BOD - used to calculate the amount of decomposable organic matter present in the sewage.

* If BOD less than 3ppm, pure water

* If BOD more than 4 ppm, polluted water.

* If

Hardness ⇒

* It is one of the chemical properties of water which does not produce lather with soap solution.

Types of hardness ⇒

- Temporary hardness
- Permanent hardness

Temporary hardness ⇒ Carbonate hardness (or)
Alkaline hardness

*

* It is caused by $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$

Removal ⇒

* By boiling ($Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$)

* By adding lime ($Ca(OH)_2$)

$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$

Permanent hardness ⇒ Non-carbonate hardness (or) Non-alkaline hardness

* It is caused by { $MgCl_2$ $MgSO_4$ $CaCl_2$ $CaSO_4$ }

Removal ⇒

* By lime-soda process

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$

* By zeolite process

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

Significance ⇒

* Hardness is very important in industrial uses because it forms scale in boilers & pipe lines

* Hardness decreases metal toxicity because Ca^{2+} & Mg^{2+} help keep fish from absorbing metal into their blood. such as lead, arsenic. & cadmium

Internal conditioning (or) treatment

(or) Boiler compounds ⇒

* Some chemicals are directly added into the boiler to remove scale forming substance which were not completely removed in external treatment. These chemicals are called boiler compounds.

1. Phosphate conditioning ⇒

* This is used in high pressure boiler

* Na_3PO_4 is used to remove scale formin substance ($CaSO_4$)

* This Na_3PO_4 reacts with Ca^{2+} & Mg^{2+} salts to give sludges.

* The sludges are removed by blow-down operation.

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

3 types of Na_3PO_4 ⇒

* Na_3PO_4 (Too alkaline) - used for too acidic water.

* Na_2HPO_4 (weakly alkaline) - used for acidic water.

* NaH_2PO_4 (acidic) - used for alkaline water.

2. Colloidal conditioning ⇒

* This is used in low pressure boiler.

* Colloidal conditioning agents - Kerosene agar-agar, gelatin used to remove scale forming substances.

* These colloidal agent get coated over the scale forming substance & convert them into sludge.

* The sludge can be removed by blow down operation.

3. Sodium aluminate conditioning ⇒

* $NaAlO_2$ - used to remove scale forming substance.

* It undergoes hydrolysis to give $Al(OH)_3$ & NaOH.

* This NaOH precipitates Mg as $Mg(OH)_2$

* $Al(OH)_3$ & $Mg(OH)_2$ → gelatinous precipitate.

* They entrap finely divided silica solid & colloidal silica, & settled easily as sludges

* Then the sludges can be removed by

blow-down operation.

4. calgon conditioning ⇒

* calgon → sodium hexa meta phosphate

$Na_2[Na_4(PO_3)_6]$

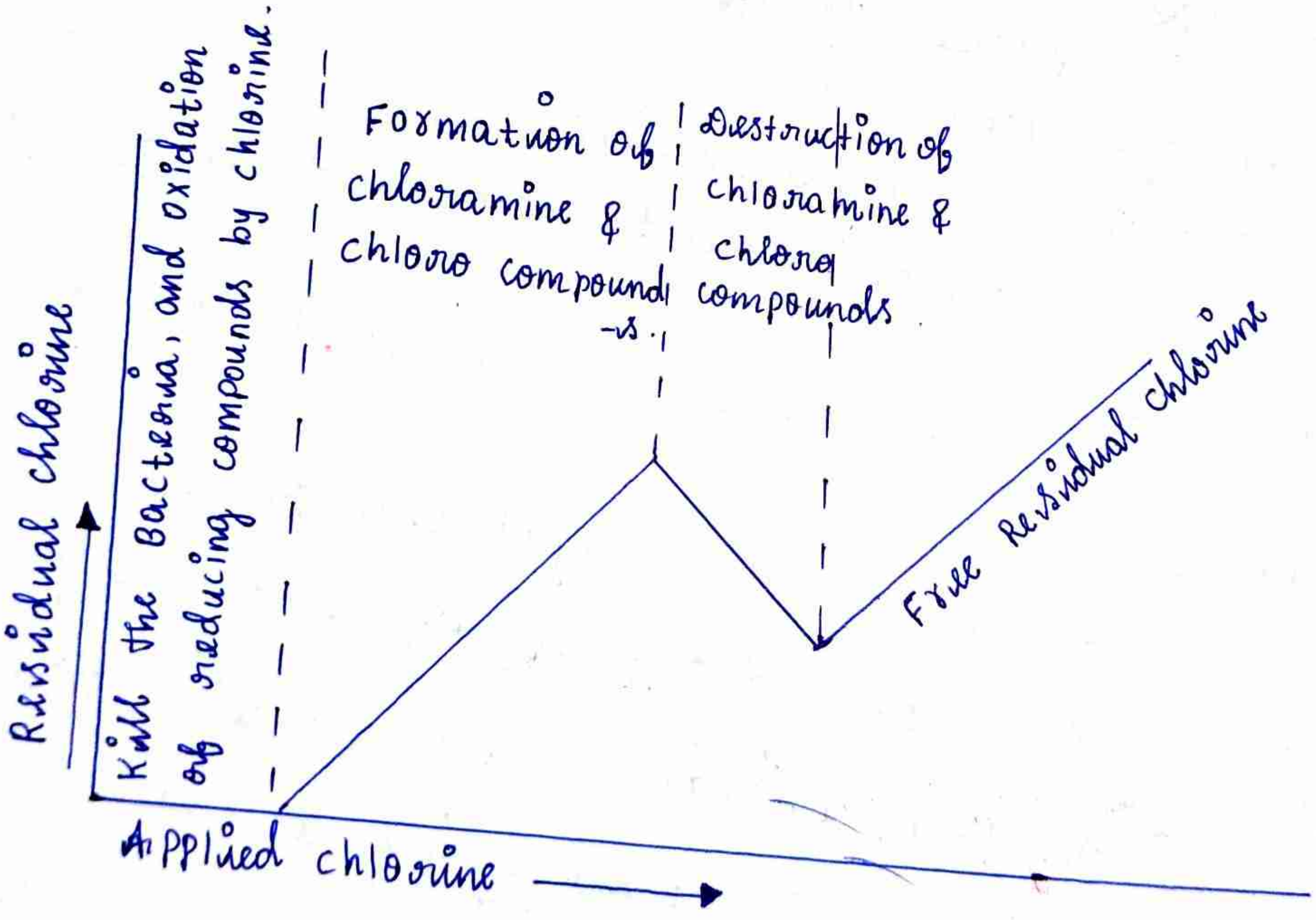
* This reacts with Ca^{2+} ions to form highly soluble complex. So there is no problem of sludge disposal.

* So calgon conditioning is the best method

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4.$$

— x —

Break point chlorination ⇒



Nano chemistry

UNIT-II

* Nano means 10^{-9}m

Nanochemistry ⇒

* combination of chemistry & nanoscience.

* "The study of chemical behaviours of very small particles of a substance"

* "study of chemistry at the nano-scale"

Difference between molecules, bulk materials & nano-particles ⇒

	Molecule	Bulk materials	Nano-particle
1.	collection of atoms	* collection of ~~few~~ 1000 molecules (less than 100 nm)	* collection of few molecules (less than 100nm
2.	size → picometer	* Micron size	* less than 100nm in diameter
3.	surface area →	* less	* High
4.	Hardness →	* less	* 5 times higher than bulk.
5.	strength →	* less	* 3 times "
6.		* constant physical properties	* size dependent properties

7. * Corrosion resistance	* Less	* High
8. Optical properties	-	* unexpected opti properties Ex⇒ ZnO - UV blocking property * Gold - Red colour
9. Melting point	* High Ex⇒ Gold bar - 1064°C	* low melting pt Ex⇒ Gold nano ⇓ 300°C
10. Sintering	* High temp	* low temp
11. Electrical properties	* Less	* 3 times higher than bulk.
12. Wear resistance	* Less	* 170 times "
13. Suspension	* Not possible	* possible - because of high surface area

Properties of Nanomaterials ⇒

1. Electrical properties

* Electrical conductivity decreases due to increased surface scattering.

* Ex → Polymeric fibre

* Nanocrystalline material → very good insulator because they save more energy

* Ex → Nickel-metal hydride - less frequent recharging

Optical properties

* optical properties of nanomaterials are different from bulk materials.

Reason ⇒

1) Quantum confinement of electrons
2) Surface plasma resonance.

Ex → colour of metallic nanoparticles may vary with their sizes.

3. Mechanical properties.

* Mechanical properties of nano materials are different from bulk materials

* Mechanical properties increased by adding nano-filler.

* Ex → Nano-crystalline carbides - stronger, harder, more wear & corrosion resistant

→ used in micro drills & spark plugs.

4. Magnetic properties

* Magnetic properties of nano material are different from bulk materials.

* Bulk → Ferro-magnetic

* Nano particles → super-paramagnetic

↓

Reason → large surface area

Size dependent properties

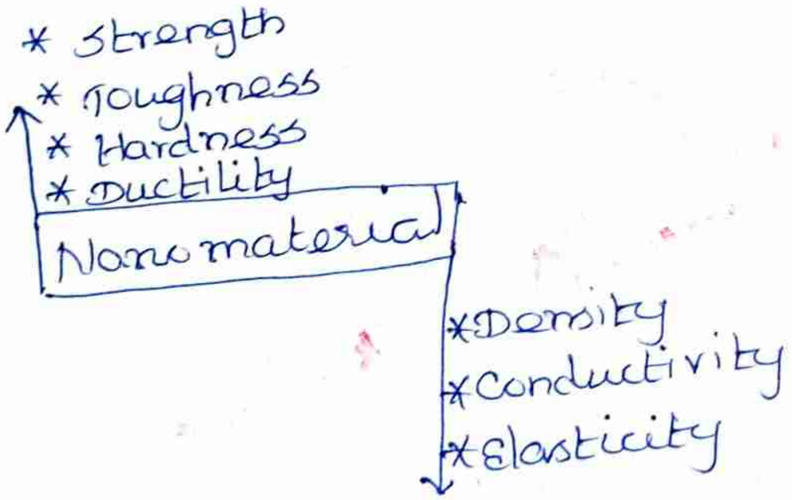
* Nanomaterials are composed of grains & grain boundaries. Nanometre size grains have only few thousands of atoms

* If we reduce the grain size, nearly all the properties like hardness, strength, ductility density, conductivity etc.. changed for nanomaterials.

* When we decrease the grain size, volume of grain boundaries increases. so density decreases

* The mechanical & chemical properties of nanomaterial can be changed due to defect dynamics.

* The elastic property of nanomaterial is decreased due to the presence of defects.



Types of Nano materials

1. Nanoparticles - 3 dimension
2. Nanoclusters - 0 dimension
3. Nanowire - 2 dimension
4. Nanorods - 2 dimension
5. Nanotubes - 2 dimension

Nano particle ⇒ (Smaller than crystal but bigger than molecule)

* Size ranges from 1-100 nm.

* 3-D structure

* Ex ⇒ TiO_2, Gold, silver, ZnO

uses ⇒

* TiO_2 - cosmetics because it absorbs UV rays

* Nano silver - catalyst in industries

* Medicine

* Nano silver - for making bone cement surgical instruments

Nano cluster ⇒

* Size - 0.1 to 10 nm

* 0-dimensional structure

* Among all nanomaterial, Nanocluster is the smallest sized nano material.

* In clusters, all the atoms are bound by metallic, covalent, ionic, hydrogen bond or

vander waals' force of attraction.

Magic number ⇒

* The number of atoms present in the clus-ters of critical sizes with higher stability, is known as magic number.

* The properties change with the number of constituent atoms, the type of element & the net charge on the cluster.

Properties ⇒

* Atomic cluster or molecular cluster are formed by nucleation of atoms or molecules.

* The reactivity of nano cluster are decreased due to their decrease in size.

* Low melting point due to high surface to volume ratio.

* Electronic structure is more confined than the bulk materials.

Applications ⇒

* catalyst * used in chemical sensors

* As light emitting diode in quantum computers.

Nanorods ⇒

* length to width ratio less than 20
* 2-D structure
* Ex ⇒ ZnO, CdS, Galluim nitride nanorods

Properties ⇒

* They have optical and electrical properties

Applications ⇒

* Display technologies * Micro mechanical switches.
* Major role in applied electric field, micro electromechanical systems
* Nanorod + Nobble metal nanoparticle ⇒ Theragnostic agents
* used in energy harvesting & light emitting devices
* used as cancer theropeutics

Nanowires ⇒

* length to width ratio greater than 20
* 2-D structure
* Diameter → 10 - 100 nm.

Example ⇒ * AU, Ni, Pt - Metallic nanowires

* Si, GaN - semiconductors
* SiO_2, TiO_2 - Insulator
*

Synthesis ⇒

1) Template-assisted synthesis

* simplest method

* Templates have very small cylindrical pores or voids. within the host material.

* The empty spaces are filled with the chosen material to form nanowires.

2) VLS (vapour-Liquid-solid) method

* Absorption of the source material from the gas phase into a liquid phase (catalyst).

* A nucleation event generates a solid precipitate, upon supersaturation of the liquid alloy

* This seed acts as site for further deposition of material.

Properties ⇒

* Low conductivity than bulk material.

* It shows distinct optical, chemical thermal & electrical properties

* silicon nanowire - Photoluminescence characteristics

es ⇒

- To prepare p-n junction & logic gates.
- In digital computing
- High density data storage
- To link small components into very small circuits

Nanotubes ⇒

- Diameter → 1 - 100 nm
- They have 2D structure.
- Organic (or) inorganic nanotubes.
- Ex ⇒ CNT, SNT, DNA nanotube, Boron nitride nanotube.

carbon nanotube ⇒ (CNT)

- Tubular forms of carbon
- when graphite sheets are rolled into a cylinder, their edges join to each other form CNT.
- Each carbon atom in the carbon nanotube is linked by covalent bond.
- The different ropes are hold together by weak vander walls forces.

structure (or) types of carbon nanotubes ⇒

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

Single walled nanotubes ⇒

* It has only one graphite tube.
* Diameter - 2nm & length - 100 μm

Properties ⇒

* Excellent conductor

Types of SWNT's ⇒

* Based on the orientation of hexagon lattice, It is divided into three types.

1. Arm-chair structure → The lines of hexagons are parallel to the axis of nanotube. * Metal
2. Zig-zag structure → The lines of carbon bonds are down the centre. * semiconductor
3. chiral nanotubes → It exhibits twist or spiral around the nanotube. * Semiconductor

Multi-walled nanotube ⇒

* It has multiple layers of graphite
* Both metallic & semiconducting

Properties

* Used to store fuels (Hydrogen & methane)

- High thermal conductivity & Kinetic properties

Uses ⇒

- Battery technology
- As catalyst in industries
- For protecting electronic equipments, it is used as light weight shielding materials
- For drug delivery
- It is used in composites, ICs
- Efficient catalyst for some chemical reactions.
- Good biosensor. So it is used to find many molecules present in the blood
- used in water softening process as a filter

Preparation of Nanomaterials

I. Top-down process (or) Physical (or) Hard method

II Bottom-up process (or) chemical (or) soft method

Synthesis of CNT ⇒

1. Pyrolysis of hydrocarbons
2. Laser evaporation

Pyrolysis ⇒

$$\text{Acetylene} \xrightarrow[\text{Fe-silica (or) Fe-graphite}]{700^\circ C} \text{CNT}$$

Laser evaporation ⇒

* At high temperature (1200°C), an intense laser beam is passed on graphite, sheet containing small amount of Co & Ni, in a quartz tube reactor.

* An inert gas (Ar (or) He) is passed simultaneously into the reactor to sweep the evaporated carbon atoms from the furnace.

* The evaporated carbon atoms condensed as carbon nanotubes on the colder copper collector.

Properties ⇒

* strong, & elastic flexibility

* It can withstand extreme strain in tension.

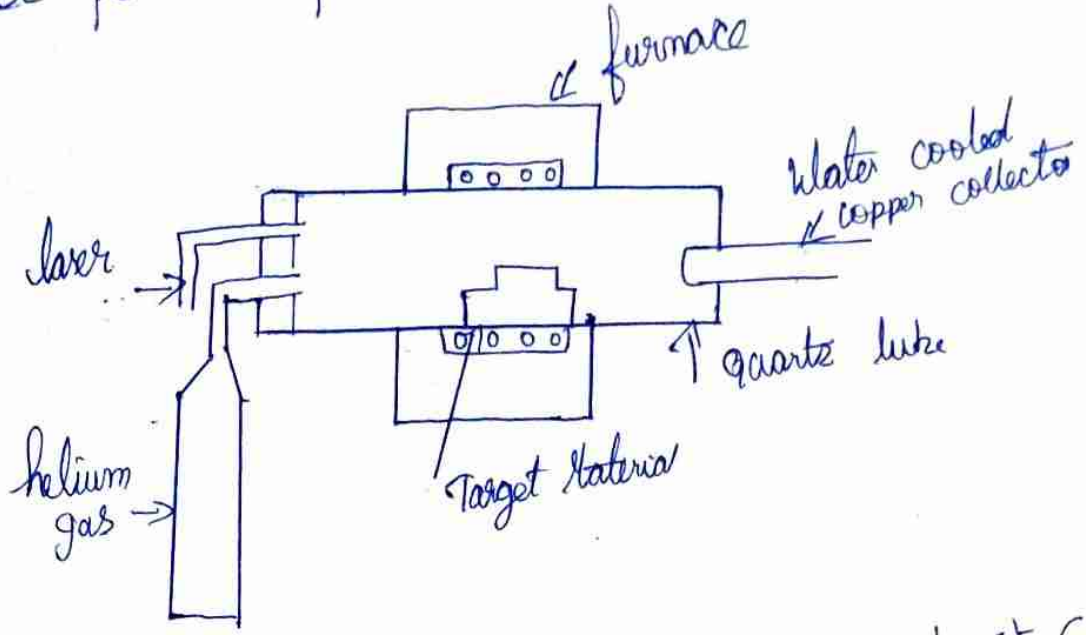
* It acts as metallic (or) semi conducting materials

Laser ablation

* Target - evaporated by high power laser pulse.

* Stoichiometry - not affected

* Ablation rate → The total mass ablated from the target per laser pulse



* Target material containing catalyst (Ni or Co) is vapourised by passing laser beam at high temp at 1200°c in a quartz tube reactor.

* Simultaneously, Inert gas (Ar, He) is passed into the reactor to sweep the evaporated particles from the furnace.

uses ⇒

* Diameter (10 - 20 nm) & 100 μm - nanotubes produced by this method.

substances
+
solvent catalyst

↓

coating solution

spin coating   spray coating   Dip coating

Gel → Aged gel → Amorphous film

↓

crystallized nano particle.

2. solvothermal process

- * solvent (High temperature - 100 - 1000°C)
- * Moderate to high pressure (1 - 10,000 atm)

zinc oxide ⇒

* zinc acetate dihydrate - dissolved in 2-propanol at 50°C.

* subsequently, the solution is cooled to 0°C & NaOH is added to precipitate ZnO. The solution is then heated to 65°C to allow ZnO growth.

* Finally capping agent is added to arrest the growth. The rod shaped ZnO nano-crystal obtai-ned

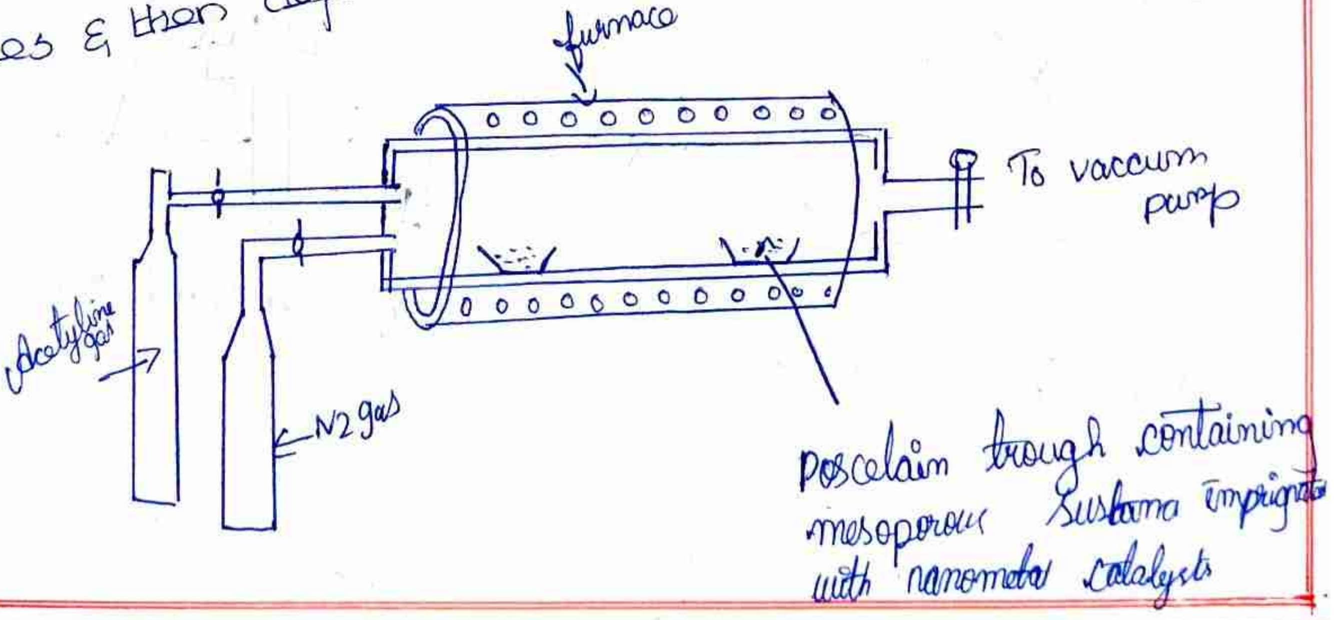
- ceramic particles & coating can be produced.
- silicon, carbon → Nanoparticle

Advantages ⇒

- very easy to operate
- Heat required - less
- Eco-friendly method
- stable product
- Economical process.

chemical vapour deposition (CVD) ⇒

- Gaseous molecules are converted into solid nanoparticles in the form of tubes, wires (or) thin films.
- Initially, solid materials → gaseous molecules & then deposited as nanomaterials.



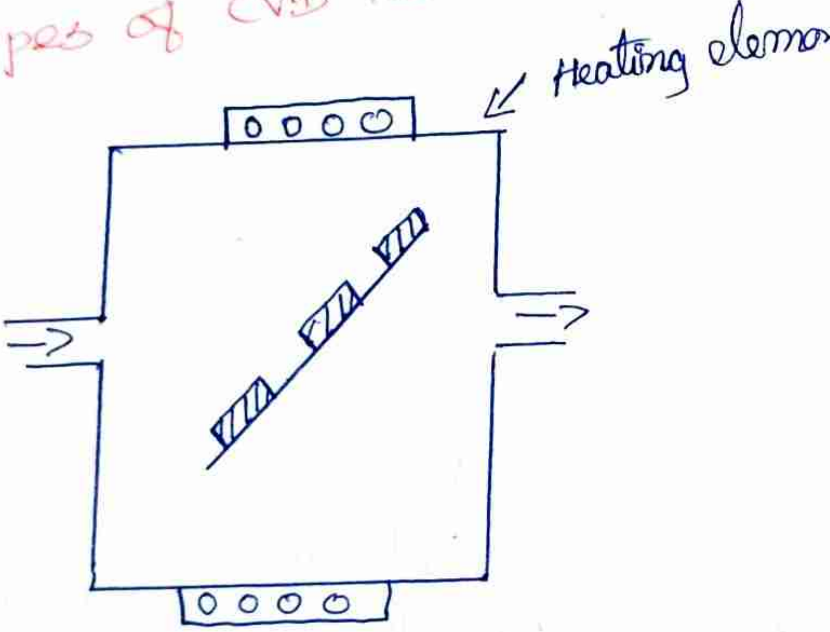
* The reactor consists of high temperat
vaccum furnace maintained at inert atmosphere.

* The solid substrate containing catalyst like Ni, Co, iron supported on a substrate material like silica, quarts is kept inside the furnace.

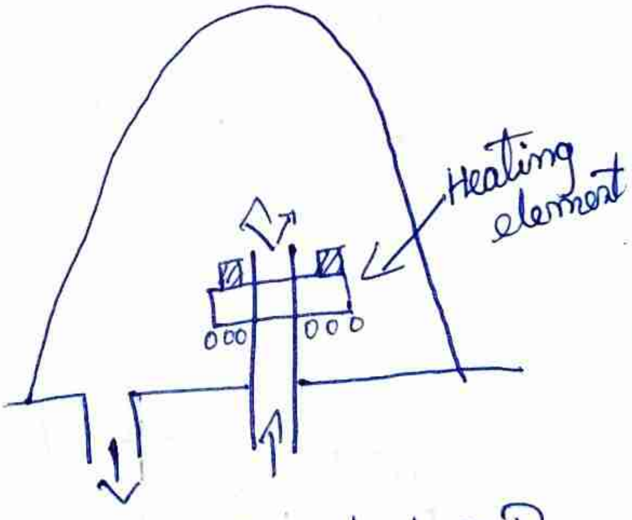
* The hydrocarbon cylinders (ethylene, acetylene & nitrogen cylinders are connected to the furnace.

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

Types of CVD reactor ⇒



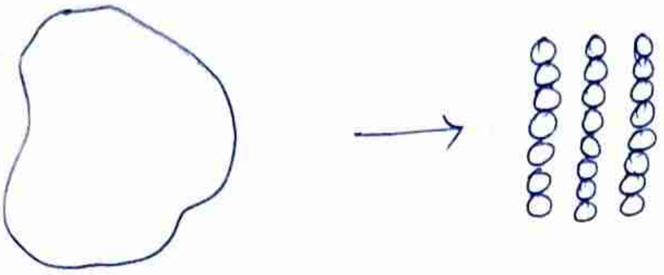
a) Hot Wall CDD



b) cold wall CVD

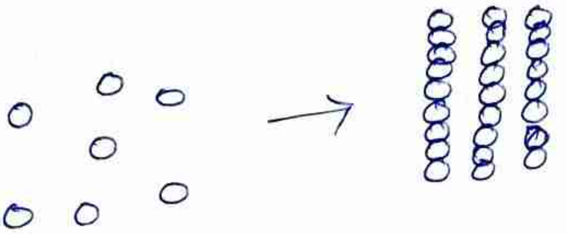
Top-down process

* conversion of bulk materials into smaller particles of nano structure.



Bottom-up process

* Building-up of material from the bottom by atom by atoms, molecule by molecule



1. Sol-Gel process
2. Solvothermal synthesis
3. Laser ablation
4. chemical vapour deposition
5. Electro deposition
6. Electrospinning

1. Sol-Gel process ⇒

* wet chemical technique

* used to produce metal oxides

* Monomer → colloidal solution (sol → precursor)

* Slowly colloidal solution forms gel-like system

a) sedimentation

* The solution is allowed to keep for sometime to occur sedimentation.

* Then remaining liquid should be poured.

b) centrifugation

* To increase the process of phase separation.

c) Drying & densification

* To remove the remaining liquid - by shrinkage & densification

d) Firing (or) crystallization

* To improve mechanical properties & structural stability

* sintering & densification done.

* The cell - Reference electrode, cathode & anode.

* All electrodes are connected with the battery through an voltmeter & dipped in an electrolyte.

* when the current is passed, the metal ions enters in the pores & gets reduced at the cathode.

Electrodeposition of Gold on silver ⇒

* Anode - Gold sheets
* cathode - silver plate
* Alumina template
* Electrolyte - $AuCl_3$

* when current is passed, Au^+ ions diffuse into the pores of alumina template & gets reduced at the cathode.

Advantages ⇒

* cheap method
* complex shaped objects can be coated
* uniform film or wire is obtained
* Metal nanowires (Ni, Co, Cu & Au) - can be prepared.

1. Hot-wall CVD

- Tubular form
- Indirect heating

2. Cold-wall CVD

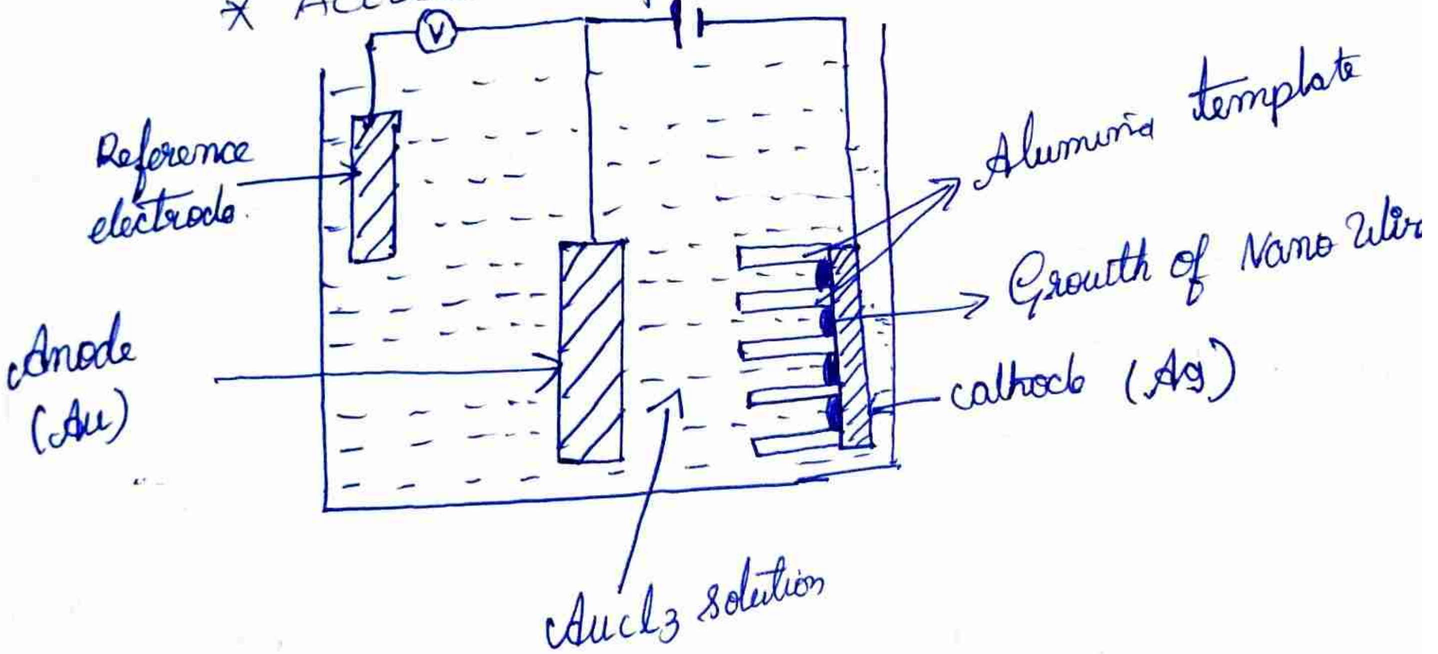
- Direct heating.

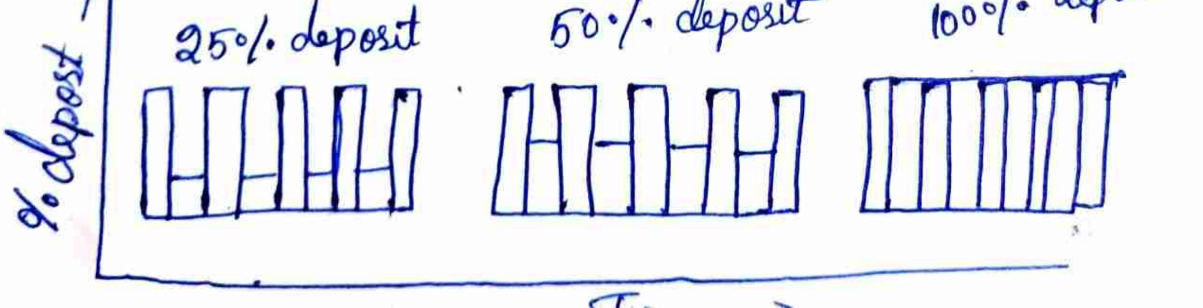
Advantages ⇒

- pure products
- Economical
- defect free product
- simple experiment

Electro-deposition (or) Electrochemical deposition ⇒

- Template assisted electro deposition
- Active template - cathode.





ocess ⇒

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

* A high voltage is applied to create an electric field between the needle tip & the collector, a charge accumulates at the liquid surface.

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

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

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

Applications ⇒

* It is used in diagnosis & treatment of diabetes

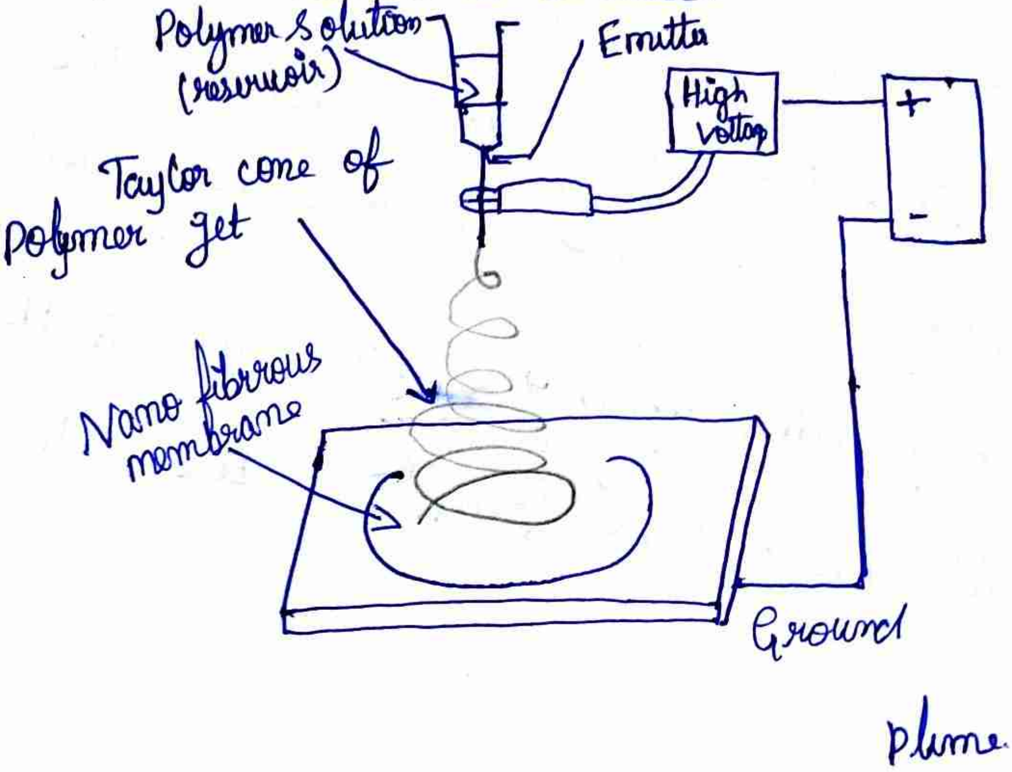
* In solar cell, fuel cell, super capacitors

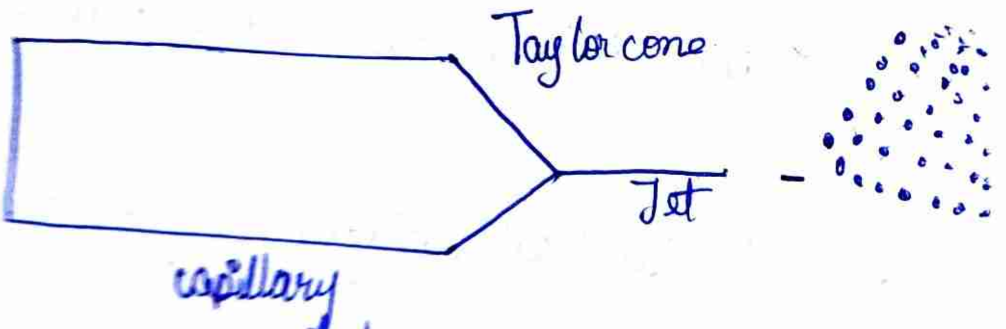
Electrospinning ⇒

* The ultrafine fibres are produced by charging and ejecting a polymer solution through a spinneret under high voltage electric field

Components ⇒

- * High voltage power supply
- * A polymer reservoir
- * A conductive needle,
- * A conductive collector





Electro spinning

Applications of Nanomaterials

* Nano material has unique chemical, physical & mechanical properties, so it can be used for various applications.

Medicine ⇒

1) Nano drug - cancer & TB therapy
2) chips - various chips
3) Nano-medibots - Anti cancer drug
4) Gold coated nanoshell - It converts light into heat & destruct tumours.
5) As sensor - various sensors
6) Protein analysis.
7) Blood Immuno assay - Gold nanoshell used
8) Imaging & therapy - Gold nanoshell used
9) Targeted drug delivery - slow & selective release of drug
10) Repair neurological damage.

Agriculture ⇒

1) Eco-friendly & green method → Improves fertilization process & plant growth.
2) To decrease the amount of harmful chemicals.
3) Nanosensor - To findout the diseases
4) Nano devices - Genetic engineering of plants.

5) To findout plant disease

6) Precision farming techniques - to improve crop yield.

7) Some nanomaterials - antimicrobial agent

8) Nano-particle based pesticides & herbicides

In Energy ⇒

1. Power generation
   * To run powerplant

2. Generating hydrogen from sea water
   * Electrolysis of hydrogen - using nickel selenide as a catalyst.

3. High efficiency light bulbs
   * Nano-engineered polymer matrix used for the production of high efficiency light bulbs.

4. Increasing the electricity in windmills.
   * stronger & lower weight blades
   * Nano-tubes - filled epoxy used

5. Generating electricity from waste heat
   * Nanotube sheets have been used to build thermocells that generates electricity

storing hydrogen for fuel cell powered cars

* Graphene layers are used.

7. Reducing power loss in electric transmission wires

* CNT wires are used.

8. Reducing the cost of solar cell

* Nanotech solar cells

9. Nano battery & fuel cell.

Electronics ⇒

* Quantum wires - high electrical conductivity
* Integrated memory circuits
* NONIFET - Nanoparticle organic Memory Field Effect Transistor - created by combining gold nanoparticles with organic molecule.
* Nanowires - to create transistors without p-n junctions
* Nano radios - CNT used
* MOSFET - Metal oxide semi conductor Field Effect Transistor - Act both as switches & amplifiers

* Nano catalyst . effective catalyst because

1. High surface area
2. Enhanced reactivity

1. water purification
   * Nanosilver catalyst

2. Bio-diesel production
   * KF/CaO → solid base nano catalyst

3. Fuel cell application
   * carbon-supported electro-catalyst

4. In drug delivery
   * CNT- drug delivery system.

5. Gold nanoparticles ⇒
   * Important catalyst in co-oxidation epoxidation of propylene, hydrogenation of unsaturated hydrocarbons.

6. Nanopowder silica catalyst (or) platinum nano particles - show strong catalyst for hydrolysation reactions.
7. Titania based nano catalyst - Photo catalysis
8. Nano-MgO - for dehydrogenation

Use

* used in textiles for smart clothing, protecting clothing & fire retardant fibres

* used in sensors (Gas sensors, chemical sensors & fluorescence sensors.

* In drug delivery, artificial blood vessel & wound dressing.

* e-spun fibres - filtration & thermal insulation.

UNIT III Phase rule

* Homogeneous reversible reactions studied by law of mass action

* Heterogeneous reversible reaction - Phase rule

* Gibbs willard 1874 - phase rule introduced.

Phase rule ⇒

* If the equilibrium between any number of phases is not influenced by gravity, electrical (or) magnetic forces but is influenced only by pressure, temperature & concentration, then the number of degree of freedom (F) is related to number of components (C) & number of phases (P) by the following phase rule equation

$$F = C - P + 2$$

Important definitions ⇒

Phase ⇒

* "Any homogeneous, physically distinct & mechanically separable portion of a system which is separated from other parts of the system by definite boundaries"

1) gaseous phase

* All gases are completely miscible &

* Example- Air (mixture of O_2, H_2, CO_2 etc

- single phase.

2) liquid phase

* The number of liquid phase - depends on the number of liquids present & their miscibilities

* Example - If two liquids are miscible - they will form one liquid phase & one vapour phase. * Alcohol - water.

* If two liquids are immiscible, they will form three phases (two liquid phase & one vapour phase) * Alcohol - water - oil

solid phase ⇒

* Every solid forms a separate phase

Example ⇒

* water system - 3 phases

* sugar solution in water.

component ⇒

* " The smallest number of independently variable constituents" & the composition of each

ase can be expressed in the form of a chemical equation"

Example ⇒

* water system - $\underset{(s)}{\text{Ice}} \rightleftharpoons \underset{(l)}{\text{water}} \rightleftharpoons \underset{(g)}{\text{vapour}}$

↓

one component

Degree of freedom (F) ⇒

* The minimum number of independent variable factors such as temperature, pressure & concentration which must be fixed in order to define the system completely"

* Example → water system - Non-variant

* F = 1 → univarient

* F = 2 → Bivarient

* F = 3 → Trivarient

Phase Diagram.

* A graph obtained by plotting one degree of freedom against another is called phase diagram.

Types of phase diagram ⇒

1. P-T diagram - For one component system
2. T-C diagram - For two component system

Uses of phase diagram ⇒

* To understand the properties of mate

* To study about low melting eutectic alloy.

One component system.

water system ⇒

* water exists in three possible phases namely solid, liquid & vapour.

* Three forms of equilibria

solid ⇌ Liquid
Liquid ⇌ vapour
solid ⇌ vapour.

* This phase diagram has curves, areas and triple point.

curve OA ⇒

* The curve OA - vapourisation curve.

* At any point on the curve, water & water vapour exist in equilibrium

* water ⇌ water vapour

* According to phase rule

$F = C - P + 2 = 1 - 2 + 2 = 1$ $\boxed{F = 1}$

* univarient

* The curve OA will extend upto the critical temperature (374°C). Beyond the critical temperature, only water vapour will exist, no water phase.

curve OB ⇒

* The curve OB - Sublimation curve

* At any point on the curve, Ice and vapour exist in equilibrium.

* Ice $\rightleftharpoons$ vapour.

* According to phase rule,

$F = C - P + 2 = 1 - 2 + 2 = 1$ $\boxed{F = 1}$

* univarient

* The curve OB will extend upto (-273°C) absolute zero temperature. Beyond this, no vapour will exist, only ice can be present.

curve OC ⇒

* The curve OC - melting point curve.

* At any point on the curve, Ice & water exist in equilibrium.

* Ice ⇌ water
* According to phase rule,

$F = C - P + 2 = 1 - 2 + 2 = 1$ $\boxed{F = 1}$

* univarient

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

Point 'O' ⇒ (Triple point)

* At this point, three curves OA, OB and OC meet at a point 'O'. Here, three phases namely solid, liquid and vapour are simultaneously at equilibrium.

* Ice ⇌ water ⇌ vapour.
* According to phase rule,

$F = C - P + 2 = 1 - 3 + 2 = 0$ $\boxed{F = 0}$

* Non-varient
* Temperature - 0.0075°C & pressure - 4.58 mm

Curve OB' ⇒ (Metastable equilibrium)

* The curve OB' - vapour pressure curve of super-cool water

* At any point on the curve, super cool water & vapour exist in equilibrium.

* super cool water ⇌ vapour.

* sometimes water can be cooled below 0°C without the formation of ice, this water is called super cooled water.

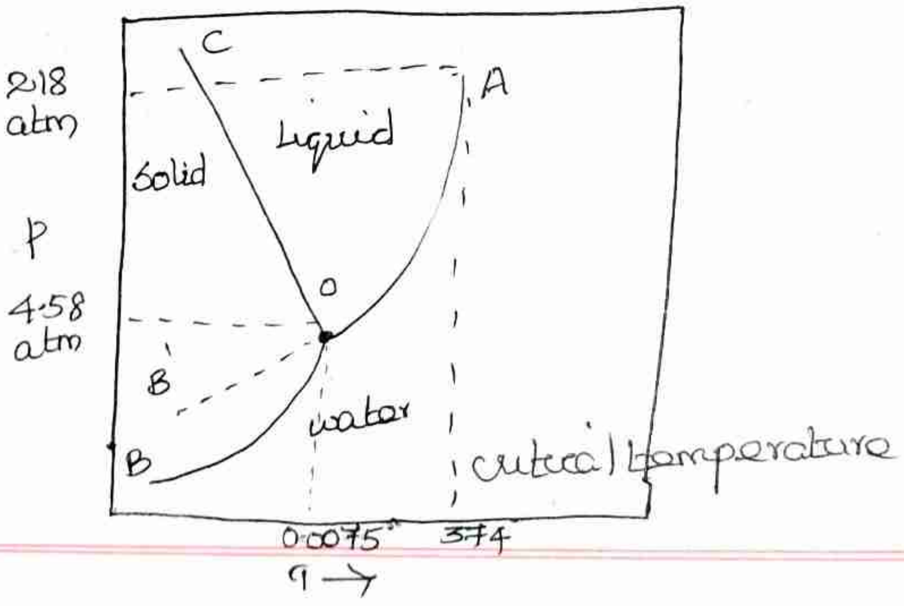
* It can be converted into solid ice by disturbance (or) seeding.

Areas ⇒

* AOC → water
* BOC → Ice
* AOB → vapour.
* Acc. to phase rule, F = C − P + 2

$F = 1 - 1 + 2 = 2$ $\boxed{F = 2}$

* Bivarient

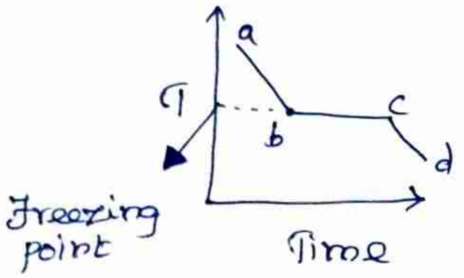


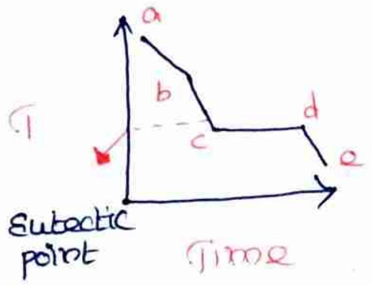
Thermal Analysis ⇒ (or) cooling curves ⇒

* Thermal analysis is a method in which cooling curves of various compositions are stud during solidification.

* The shape of curves can be determined by thermal analysis.

cooling curve for a pure solid ⇒





* A pure substance in the fused state is allowed to cool slowly & the temperature is noted at different time interval.

* Initially, the rate of cooling is continuous. when it reaches the point 'b', solid begins to appear.

* Solidification completes at the point 'c'

* At BC, solid ⇌ liquid melt

* Along the curve CD, temperature decreases.

oling curve for a mixture ⇒

* Two substance (A & B) in the fused state is allowed to slowly.

* Initially, the rate of cooling is continuous. When it reaches the point 'b', one solid (A or B) begins to appear.

* At C, second solid begins to solidify.

* Along the curve CD, temperature remains constant & it is called eutectic temperature.

* Along the curve de, de, temperature decreases.

Uses of cooling curves ⇒

* Melting point & eutectic temperature c

be noted.

* Percentage purity of the compounds can be noted.

* The behaviour of the compounds can be clearly understood.

* To find out the phase diagram of two component system.

Two component system

Reduced phase rule (or) condensed system ⇒

* The system in which only the solid & liquid phases are considered and the gas phase is ignored is called condensed system.

$\boxed{F' = C-P+1}$ → Reduced phase rule (or) condensed phase rule

Binary Alloy system

Lead silver system ⇒

* The system is studied at constant pressure, & the vapour phase is ignored

$\boxed{F' = C - P + 1}$ → Reduced phase rule

* It contains lines, areas & the eutectic point.

1. curve OA ⇒

* The curve OA → Freezing point curve of silver.

* Point A → Melting point of pure Ag ($961^\circ C$)

* The curve AO shows the melting point of Ag is decreased by the continuous addition of Pb.

* At any point on the curve, solid Ag & melt are in equilibrium

$$\text{Solid Ag} \rightleftharpoons \text{Melt}$$

* According to reduced phase rule

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \quad \boxed{F' = 1} \rightarrow \text{univariant}$$

2. curve BO ⇒

* The curve BO → Freezing point curve of Pb.

* Point B → Melting point of pure Pb.

* The curve BO shows the melting point of Pb is decreased by the continuous addition of Ag

* At any point on the curve, solid Pb & melt

are in equilibrium

Solid Pb $\rightleftharpoons$ Melt

* According to reduced phase rule

$F' = C - P + 1 = 2 - 2 + 1$ $\boxed{F' = 1}$ → univarient

3. Point 'O' Eutectic point ⇒

* The curves AO & BO meet at point 'O' at temperature 303°C

* Here, three phases are in equilibrium.

Solid Pb + Solid Ag $\rightleftharpoons$ Melt

* According to reduced phase rule

$F' = C - P + 1 = F' = 2 - 3 + 1$ $\boxed{F' = 0}$ → Non-variant

* The point 'O' → Eutectic point (or) temp

* Eutectic composition → 97.4% Pb + 2.6% Ag

Areas ⇒

* The area above the line AOB → single phase

$F' = C - P + 1 = 2 - 1 + 1$ $\boxed{F' = 2}$ → Bivarient

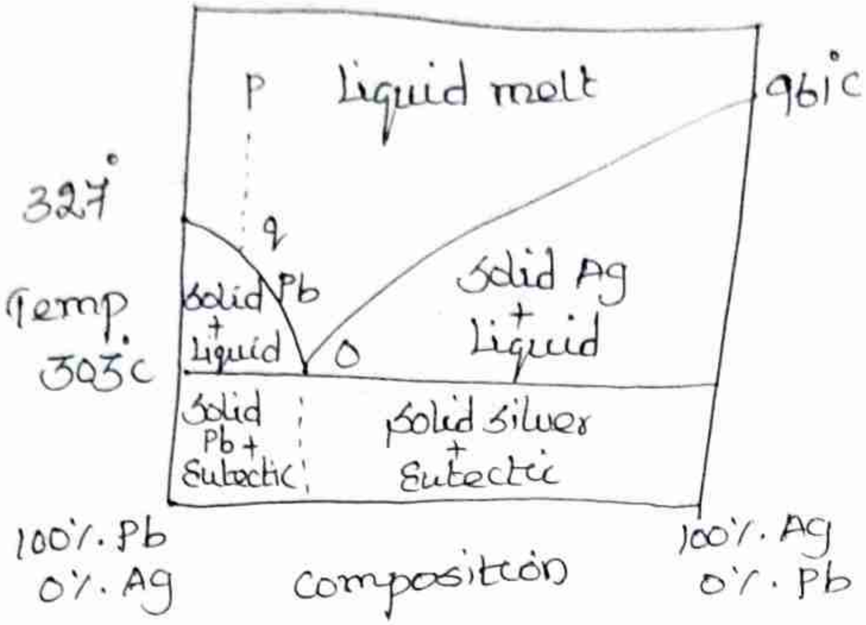
* So, temperature & composition have to be specified.

* The area below the line AO, below the line BO & below the point 'O' → Two phases.

* According to reduced phase rule

$F' = 2 - 2 + 1 = \boxed{F' = 1} \rightarrow$ univarient

Diagram ⇒



pattinson's process ⇒

* Argentiferous lead - 0.1% Ag
* It is heated to a temperature above its melting point. So it has only liquid phase which is represented by 'p'
* Then it is allowed to cool. The temp falls down along the line 'pq'.
* As soon as the point 'q' is reached, Pb is crystallised out & the solution contain large amount of Ag.
* On further cooling, more and more pb

is separated along the Line 'BO'

* Here the percentage of Ag - 2.6%

Pattinson's process ⇒

* The process of raising the relative proportion of Ag in the alloy is known as pattinson's process.

uses of Eutectic system ⇒

* Suitable alloy composition can be predicted with the help of eutectic system.

* used in preparing solders, used for joining two metal pieces together.

Merits of phase rule ⇒

* Applicable to physical & chemical equilibria

* Different systems having the same degrees of freedom behave similarly.

* Convenient method of classifying the equilibrium states in terms of phases, components & degree of freedom.

Composite Materials

Introduction ⇒

* All engineering materials - outstanding characteristics & limitations.

* To meet stringent & specific requirements - composites developed.

Definition ⇒

* A material system - Two or more micro constituents which are mutually insoluble, differing in form (or) composition & forming distinct phases.

Need for composites ⇒

* Never undergoes corrosion & less fracture toughness.

* Need of power transmission along with data transmission is increasing, so composites are highly essential.

* Low weight * less fuel consumption & emission.

* Stronger & stiffer

Advantages ⇒

* High specific strength & lower specific gravity.

* Lower electrical conductivity & thermal expan

* Better corrosion & oxidation resistance.

* Even at high temp, maintain very good strength.

Constituents of composites ⇒

* Matrix phase (or) matrix resin

* Dispersed phase (or) Reinforcement

Matrix phase ⇒

* The continuous body constituent - covers the composite.

* May be metals, ceramics, polymers
  - Metal matrix composites (MMC)
  - Ceramic matrix composites (CMC)
  - Polymer matrix composites (PMC)

Liquid Resins ⇒

* Polymers used as adhesives, potting compounds, sealants in a liquid form called Liquid resins.

d. and other weather conditions

- * GRP → strongest & most resistive to deforming forces
- * CRP → 25% reduction in weight

Metal matrix composites ⇒

Properties ⇒

- * Extremely good thermal stability, high strength
- * MMC → Toughness, ductility
- * They can withstand at high temperature

Uses ⇒

- * Used in engine blades, combustion chambers
- * Al & Mg MMC's - automotive industry
- * Defence & automobile industry, biomedical & sports equipment industry.

Ceramic Matrix composites ⇒

Properties ⇒

- * They can be used at temperature above 1500°c because of their good corrosion resistance stability at elevated temperatures
- * At high temperature, good oxidation resistance.

4. Aramid FRP

Properties =>

* Ductility * Respond non catastrophically to compressive stresses.

Uses =>

* structural components in aircraft, helicopter parts.

5. Alumina FRP

Properties =>

* Good abrasion resistance, Dimensional stability

Uses =>

* Components of engine parts in automobiles
* components of turbine engine.

Advantages of FRP =>

* High strength to weight ratio than the metal
* 75% low weight than steel
* Capacitance & leakage current can be reduced
* Better corrosion resistance
* Excellent durability & fire resisting properties
* Ideal for outdoor installation because it is impervious to the effect of sunlight, heat

Types of composites.

polymer composites (or) Fibre reinforced polymer composite

preparation ⇒

* Prepared by bonding a fibre material with a resin matrix & curing by heat & pressure.

* Reinforcing agent → Glass, Graphite, alumina carbon, boron etc..

* Resin matrix → Polyesters, epoxy, phenolic silicone & polyamide polymer resins.

properties of FRP ⇒

* High yield strength,

* High mechanical properties

* High corrosion & heat resistance property.

Resins	Reason
1. Polyester resin	* very good strength & mechanical properties
2. Epoxy resin	* Good mechanical properties
3. silicone resins	* Excellent thermal & electrical properties
4. Phenolic resins	* To withstand high temp.
5. Thermoplastics (PET, polyamide)	* Repeatability & repairability

Types of FRP composites ⇒

1. Glass FRP

properties ⇒

* Low density, dielectric constants.

* High tensile strength, corrosion & chemical resistance, Non- flammability.

uses ⇒

* Automobile parts, storage tanks, plastic pipes

2. Boron FRP

properties ⇒

* Excellent stiffness & compressive strength.

* very difficult to prepare B-FRP

uses ⇒

* Horizontal & vertical tail in aeroplane

3. Carbon FRP.

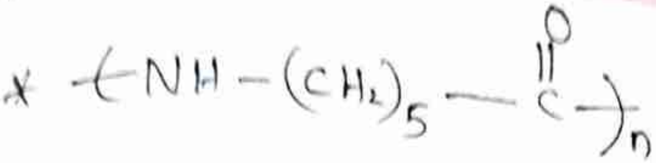
properties ⇒

* Light density * corrosion resistance

uses ⇒

* structural components of aircraft & helicopters, recreational equipments, sports materials etc..

ylon ⇒



* $-\!\!\left(NH-(CH_2)_5-\overset{\overset{O}{\|}}{C}-\right)_n$

* used as reinforcements for epoxide resin systems to give flexible laminates with high abrasion and chemical resistance.

* pure aromatic polyamide → Aramid

* prepared by spinning liquid crystal aramid oligomers (Kevlar).

* Nomex → Meta-linked poly-m-phenylene isophthalimide

* Kevlar → para-linked poly-p-phenylene phthalimide

* used as high performance fibres because of high tensile strength, stability at high temp.

* (-200 to 200°c) - Retaining mechanical prop-erties, excellent toughness

* Used in reinforcements, bullet proof clothing, race drivers, astronaut suits etc.

Particulates ⇒

* Small pieces of hard solid materials
* Metallic (Or) non-metallic

Effect ⇒

* Surface hardness gets increased
* wear & abrasion resistance increased
* shrinkage & friction reduced
* Electrical & thermal conductivities modified

Flakes ⇒

* very thin solid like material
* Ex ⇒ Mica flakes.
* Mica - Electrical and thermal insulating appliances

whiskers ⇒

* Thin strong fibre like material
* Ex → Graphite, silicon carbide, silicon nitride
* High elastic modulus, high degree of crystallinity
* High strength * costly

1) cotton fibre ⇒

* vegetable fibre * cellulose molecul

* Linear polymer of β-glucose.

* Dough moulding compounds (DMC).

* Decorative finish - Painted fabrics used.

2) wool fibre

* Animal protein fibre * α-aminoacids

* Elastic property - presence of hydrogen bond between various peptide chain.

3) silk

* Natural protein fibre (silkworm)

* Softness, strength, elongation

* Excellent insulator of heat

4) sisal

* low-cost fibrous material.

* Used in phenolic based dough moulding compounds.

5) Jute and coir.

* Low-cost fibrous material * used as woven cloth.

1) polyethylene terephthalate (PET) (or) Terylene Dacron ⇒

- Ethylene glycol + Terephthalic acid $\xrightarrow[\text{condensation}]{}$ PET.

- chemical and abrasion resistance.
- used in light weight woven fabrics.
- combined with glass fibres.

2) Poly propylene ⇒

- propylene $\xrightarrow[\text{polymerisation}]{}$ Polypropylene.

- Better hardness, strength, stiffness.
- used for making ropes, carpets, blankets hand bags etc...

3) Carbon fibre ⇒

- organic fibre $\xrightarrow[\text{inert atmosphere}]{\text{pyrolysis}}$ Carbon fibre

PAN ⇒

- $\left(CH_2 - \underset{\substack{| \\ CN}}{CH} \right)_n$ polyacrylonitrile
- uses ⇒ To make surfacing tissues

* Ex ⇒ Epoxy adhesives, polysulphides

ure reactions ⇒

* Formation of cross-linking in certain polymers is called cure reaction
* Done by curing agent
* Uncross-linked linear polymer - functional groups (or) double bonds. Also called pre-polymers.

Dispersed phase ⇒ or Reinforcement

* The structural constituent - decide the internal structure of composite.
* Ex ⇒ Fibres, particulates, flakes whiskers.

Reinforcement ⇒

* The process of improving the characteristics of the plastic matrix by adding reinforcing agents.
* May be organic & inoragonic.
* May be in the form of powder, flakes fibres.

Fibres ⇒

* They are long & thin filament of - polymer, metal (or) ceramics - (100:1) High length to diameter ratio.

* Fibre - rovings, cloth, chopped strands form

* High tensile strength, high stiffness

* Decrease overall density of composites.

1. Natural fibre ⇒ From naturally available sources
cotton, wool, silk, jute

2. Semi-synthetic fibre ⇒ From modifying the naturally occuring material
Rayon, cellulosic

3. synthetic fibre ⇒ From Laboratory processes
polyester fibre, polypropylene carbon fibre, glass fibre

4. Aramid fibre ⇒ Aromatic polyamide.
Kevlar.

matrixes used → Glass, ceramics, carbides
rides, oxides & borides

* Reinforcements → Al_2O_3, B, C, SiC & SiO_2

Hybrid composites

* New materials composed of a suitable polymer matrix reinforced with two different fibres

Types of hybrid composites ⇒

* structurally hybridized composites
* Materials hybridized in chemical bond
* Functionally hybridized composites.

Properties ⇒

* very good properties compared to their single fibre composites.
* superior mechanical and tribological properties.

uses ⇒

* used in light-weight transport
* used in light weight orthopedic components and sporting goods.
* used to make furniture like chair, table & bath tubs.

* used in railway coach interiors

* used to make plates & spoons.

* used in many of the interior & exterior applications

UNIT-IV → fuels & combustion

* fuel - combustible substance which consists of carbon as the main constituent.

* During combustion, C & H combine with O_2 with simultaneous liberation of heat.

Example → $C + O_2 \rightarrow CO_2$ · 94 Kcals

$2H_2 + O_2 \rightarrow 2H_2O$ 68.5 Kcals.

* The main source of fuel is coal & crude petroleum oil.

Requirements of a good fuel ⇒

* cheap & readily available * safe & economical for storage & transport. * should not undergo spontaneous combustion * High calorific value * moderate ignition temperature * combustion should be easy controllable. * low moisture content because the moisture content reduces the calorific value. * combustion product should not be harmful. * low - non - combustible matter (or) ash content.

classification of fuels ⇒

Based on occurance & physical state fuels are classified.

1. Based on occurance, fuels are classified into two types.

* Primary fuel ⇒ It occurs in nature as such.

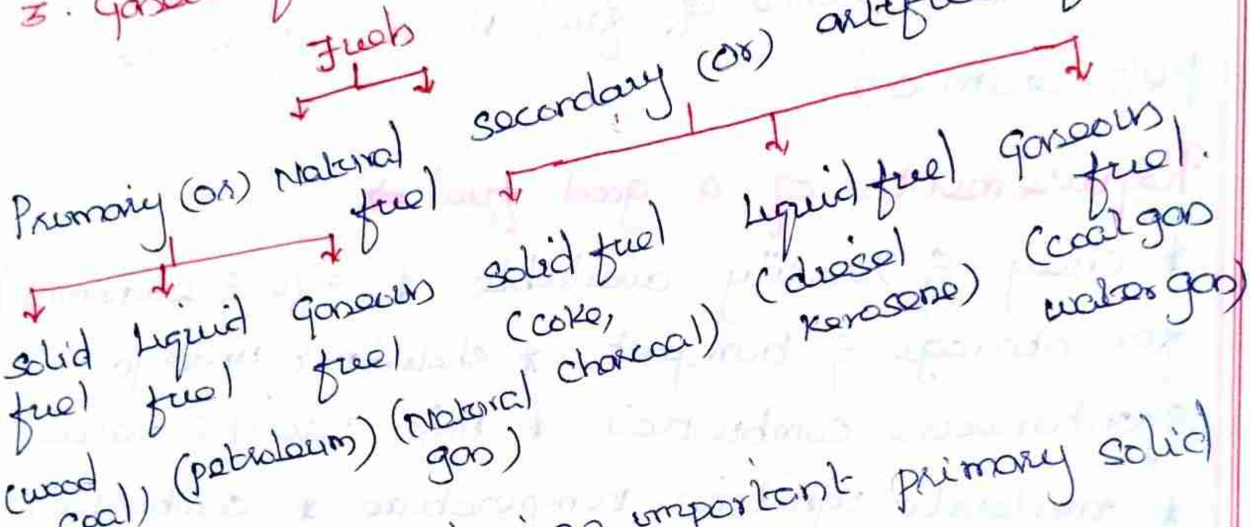
Example: coal, petroleum, Natural gas

Secondary fuel → It is derived from primary &

Example ⇒ coke, gasoline, coal gas

B. Based on their physical state both primary & secondary fuels may be sub-classified into types.

1. solid fuel: coal, coke.
2. Liquid fuel: gasoline, diesel.
3. Gaseous fuel: coal gas, natural gas.



Solid Fuel ⇒ * coal is an important primary solid fuel.

coalification (or) metamorphism ⇒ * coal is classified on the basis of its rank.

The rank of coal indicates its degree of maturity.

wood → Peat → Lignite → Bituminous coal → Anthracite

The progressive transformation of wood to anthracite results in

* Decrease in moisture * Decrease in volatile content * Decrease in hydrogen, oxygen, nitrogen & sulphur content * Increase in carbon content * Increase in hardness * Increase in calorific value

lysis of coal ⇒ * To check the quality of coal, analysis of coal is carried out.

Proximate Analysis ⇒

* Involves the determination of percentage of moisture content, volatile matter, ash content & fixed carbon in coal.

Moisture content ⇒

* About 1gm of powdered air dried coal sample is taken in a crucible. * It is heated at 100 - 105°C in an electric hot air oven for 1 hour. * The loss in weight of the sample is found out.

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

volatile matter ⇒

* After the analysis of moisture content, the crucible with residual coal sample is covered with a lid, * It is heated at 950 ± 20°C for 7 minutes in a muffle furnace. * The loss in weight of the sample is found out.

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

Ash content ⇒

* After the analysis of volatile matter, the crucible with residual coal sample is heated without lid. * It is heated at 700 ± 50°C for ½ an hour in a muffle furnace. The loss in weight of the sample is found out.

$$\% \text{ of ash content} = \frac{\text{weight of ash formed}}{\text{weight of air-dried coal}} \times 100$$

Fixed carbon ⇒

* calculated by substracting the sum of % of moisture, volatile & ash content from 100

= 100 - % of (moisture content + volatile matter + ash content)

Significance ⇒

1) Moisture content

* High percentage of moisture is undesirable because

i) it reduces the calorific value.

ii) it consumes more heat in the form of latent heat of evaporation & hence more heat is to be supplied to the coal.

iii) it increases the transport cost.

2) volatile matter & Ash content

ash content

* High percentage of volatile matter is undesirable because

i) it reduces the calorific value

ii) Ash causes hindrance to heat flow & produces clinkers, which blocks the air supply through the fuel.

iii) It increases the transporting, handling & storage costs.

iv) It involves additional cost in ash disposal.

3) Ash content volatile matter

High percentage of volatile matter is undesirable because

* it reduces the calorific value of coal.

* large proportion of fuel on heating will

still over as vapour. which escapes out unburnt

iii) coal with high percentage of volatile matter burns with a long flame with high smoke.

iv) coal containing high percentage of volatile matter do not coke well.

4) Fixed carbon

i) High percentage of fixed carbon is desirable because higher the percentage of fixed carbon in a coal, greater is its calorific value.

ii) the percentage of fixed carbon helps in designing the furnace and the shape of the fire-box

Ultimate Analysis ⇒

* Involves the determination of percentage of carbon and hydrogen content, nitrogen content sulphur content, ash content & oxygen content.

1. carbon & hydrogen content

A known amount of the coal sample is burnt in a current of O_2 in a combustion apparatus. The carbon & hydrogen present in the coal sample are converted into CO_2 & 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 & H_2O vapours are absorbed respectively in KOH & anhydrous $CaCl_2$ tubes of known weights.

* The increase in weight of KOH tube is due to the formation of CO_2 while increase in weight of $CaCl_2$ tube is due to the formation

of H_2O. From the weights of CO_2 & H_2O the % of carbon & hydrogen present in the can be calculated as follows.

$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

$CaCl_2 + 7H_2O \rightarrow CaCl_2 \cdot 7H_2O$

m = weight of the coal sample taken
x = increase in weight of KOH tube
y = increase in weight of $CaCl_2$ tube.

a) Percentage of carbon

$$\underset{12}{C} + O_2 \rightarrow \underset{44}{CO_2}$$

44 gms of CO_2 contains, 12 gms of carbon

$\therefore$ x gms of CO_2 contains $= \frac{12}{44} \times x$ gms of carbon

m gms of ~~CO_2~~ coal contains $= \frac{12}{44} \times x$ gms of carbon

$\therefore$ 100 gms of coal contains $= \frac{12}{44} \times \frac{x}{m} \times 100$ gms of carbon.

(or)

$$\%\text{ of carbon in coal} = \frac{\text{Increase in wt of KOH tube}}{\text{wt of coal sample}} \times \frac{12}{44} \times 100.$$

b) Percentage of hydrogen

$$\underset{2}{H_2} + \tfrac{1}{2}O_2 \rightarrow \underset{18}{H_2O}$$

18 gms of water contains 2 gms of hydrogen

$\therefore$ y gms of H_2O contains $= \frac{2}{18} \times y$ gms of hydrogen

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

$\therefore$ 100 gms of coal contains $= \frac{2}{18} \times \frac{y}{m} \times 100$ ''

(or)

$$\%\text{ of hydrogen in coal} = \frac{\text{Increase in wt of } CaCl_2 \text{ tube}}{\text{wt of coal sample}} \times \frac{2}{18} \times 100$$

Nitrogen content ⇒

* Kjeldahl's method is used to determine the nitrogen content. * A known amount of powdered coal sample is heated with con. H_2SO_4 in presence of K_2SO_4 (catalyst) in a long necked flask.

* Nitrogen in the coal is converted into ammonium sulphate and a clear solution is obtained.

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

* Then the clear solution is heated with excess of NaOH and the liberated NH_3 is distilled over & is absorbed in a known volume of standard N/10 HCl.

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$NH_3 + HCl \rightarrow NH_4Cl.$$

* The volume of unused N/10 HCl is determined by titrating it against standard N/10 NaOH.

* Thus, the amount of acid neutralised by liberated NH_3 from coal is determined. From this the percentage of nitrogen is calculated as follows

Calculation ⇒ Let, the weight of coal sample = m gm

Initial volume of N/10 HCl = V_1 ml.

Volume of unused N/10 HCl = V_2 ml.

∴ The acid neutralised by NH_3 = $V_1 - V_2$ ml.

We know that

1000ml of 1N HCl ≡ 1 mole of HCl ≡ 1 mole of NH_3

≡ 14 gms of N_2 (or 17 gms of NH_3)

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

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

100 gms of coal sample contains.

$= \frac{14 \times (V_1-V_2) \times N/10}{1000 \times 1} \times \frac{100}{m}$ gms of N_2

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

(or)

% of N_2 in coal = $\frac{1.4 \times \text{volume of acid consumed} \times N}{\text{wt of coal sample}}$

3. Sulphur content

* A known amount of coal sample is burnt completely in a bomb calorimeter. During this process, sulphur is converted into sulphate which is extracted with water.

* Then the extract is treated with $BaCl_2$ & sulphates are precipitated as $BaSO_4$. The precipitate is filtered, dried & weighed. From the weight of $BaSO_4$ obtained, the sulphur present in the coal is calculated as follows

Calculation ⇒ Let, the weight of coal = m gm

x = weight of $BaSO_4$

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

233 gms of $BaSO_4$ contains = 32 gms of sulphur.

∴ x gms of $BaSO_4$ contains = $\frac{32}{233} \times x$ gms of S

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

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

∴ % of sulphur in coal = $\frac{32}{233} \times \frac{x}{m} \times 100$

(or)

% of sulphur in coal = $\frac{32}{233} \times \frac{\text{wt. of } BaSO_4}{\text{wt of coal}} \times 100$.

4. Ash content

Determination of ash content is carried out as in proximate analysis.

5. oxygen content

% of oxygen in coal = 100 − % of (C+H+N+S+ash).

significance ⇒

1) carbon & hydrogen content.

- Higher the % of carbon & hydrogen, better is the quality of coal & higher is its calorific value
- The % of carbon is helpful in the classification of coal.
- Higher % of carbon in coal reduces the size of combustion chamber required.

2) Nitrogen content

- Nitrogen does not have any calorific value

& its presence in coal is undesirable.

* Good quality coal should have very little content

* Sulphur content

Though sulphur increases the calorific value, its presence in coal is undesirable because

i) the combustion products (SO_2, SO_3) are harmful and have corrosion effects on equipments.

ii) The coal containing sulphur is not suitable for the preparation of metallurgical coke as it affects the properties of the metal.

4. Oxygen content

i) lower the % of oxygen higher is its calorific value.

ii) As the oxygen content increases its moisture holding capacity increases & the calorific value of the fuel is reduced.

Proximate Analysis	Ultimate Analysis
* Determinations of physical constituents like moisture, volatile, ash and fixed carbon content in coal	* Determination of chemical constituents like carbon hydrogen, nitrogen & sulphur & oxygen content in coal.
* Approximate composition of the main constituents of coal.	* Exact composition of the elementary constituents of coal.

Carbonisation ⇒ "process of converting coal into coke is known as carbonisation".

Caking coal ⇒ when coals are heated strongly, the mass becomes soft, plastic & fuses to give a coherent mass. such type of coals are called caking coals.

Coking coal ⇒ If the mass produced is hard, porous and strong then the coals are called coking coals.

Thus, all caking coals are caking coals but all caking coals are not coking coals.

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 is called metallurgical coke.

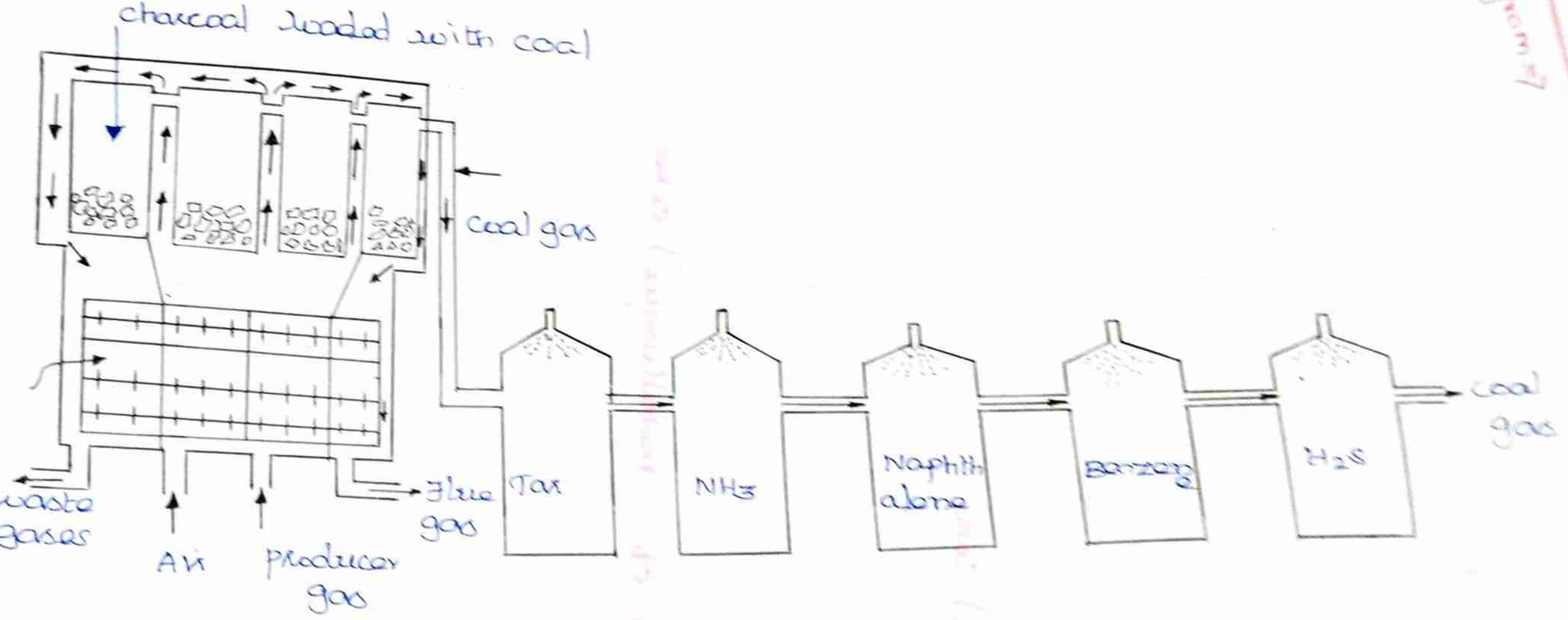
Manufacture of metallurgical coke:

* So many types of ovens used for the manufacture of metallurgical coke. But the important one is Otto-Hoffman's by product oven.

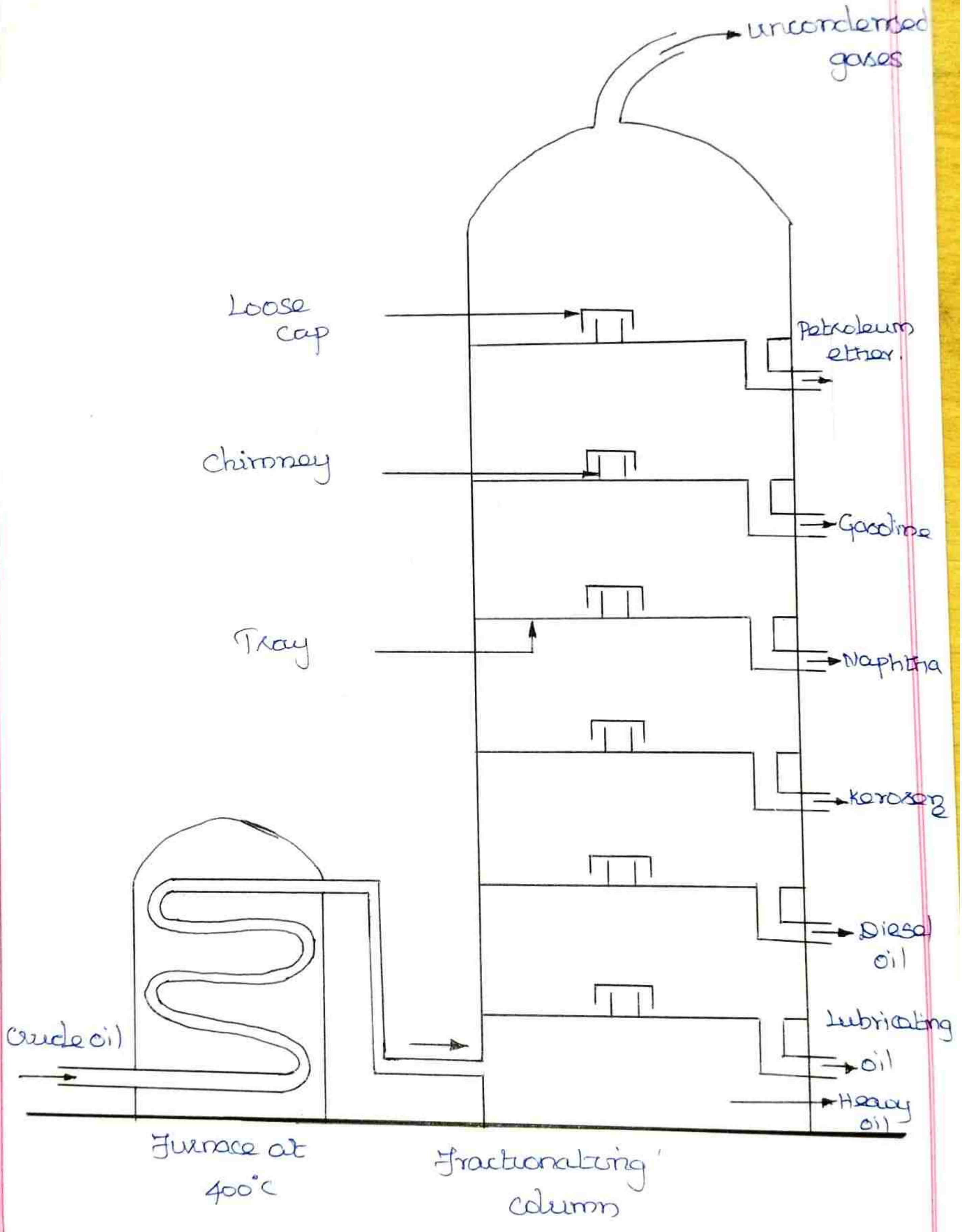
Method ⇒

* To increase the thermal efficiency of the carbonisation process & recover the valuable by products (coal gas, ammonia, benzol oil etc...)

Diagram :-


charcoal loaded with coal
coal gas
waste gases
Air
producer gas
flue gas
Tar
NH3
Naphthalene
Benzene
H2S
coal gas

ractional distillation of crude petroleum ⇒



synthetic petrol ⇒ The gasoline obtained from the fractional distillation of crude petroleum oil is called straight run petrol. As the use of gasoline is increased, the amount of straight run gasoline is not enough to meet the requirements of the present community. So we are in need of finding out a method of synthesizing petrol.

* coal contains 4.5% hydrogen compared to about 18% in petroleum. So coal is a hydrogen deficient compound.

* If coal is heated with hydrogen to high temp under high pressure, it is converted to gasoline.

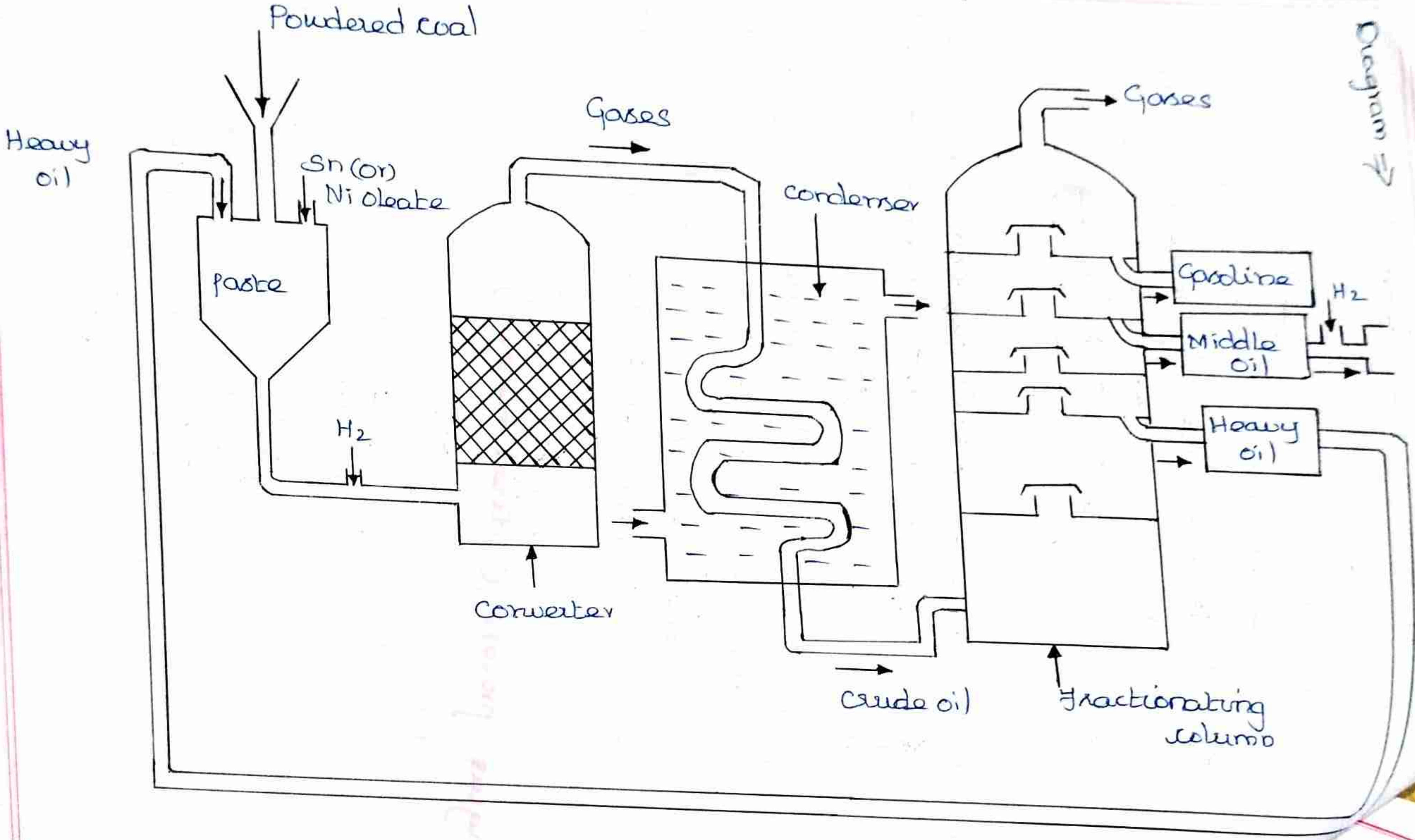
"The preparation of liquid fuel from solid fuel is called hydrogenation of coal (or) synthetic petrol".

Bergius process (direct method)

* This is the important method to prepare synthetic petrol.

* Finely powdered coal is made into a paste with heavy oil & 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 of 200-250 atm.

Diagram ⇒


Powdered coal
Heavy oil
Sn (or) Ni oleate
paste
H_2
Gases
Converter
condenser
Gases
Gasoline
H_2
Middle oil
Heavy oil
Crude oil
Fractionating column

Combustion of fuels

combustion ⇒ " Process of rapid exothermic oxidation in which a fuel burns in the presence of oxygen with the liberation of heat & light"

Aim of combustion ⇒ To get the maximum amount of heat from a combustible substance in the shortest time.

Example ⇒ $C+O_2 \rightarrow CO_2$, $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ } Exothermic Reaction.

calorific value ⇒ " Total amount of heat liberated, when a unit mass of fuel is burnt completely.

Units ⇒ calorie, Kilocalorie, British Thermal Unit centigrade Heat unit.

calorie ⇒ The amount of heat required to raise the temperature of 1 gram of water through 1°C.

Types of calorific value { Higher calorific value
Lower calorific value.

Higher (or) Gross calorific value ⇒ " Total amount of heat produced when a unit quantity of the fuel is completely burnt and the products of combustion are cooled to room temperature.

Lower / Net calorific value ⇒ " the net heat produced when a unit quantity of the fuel is burnt completely and the products 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

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

$\boxed{NCV = GCV - 0.09 H \times 587}$, where H = % H_2 in the fuel

Theoretical calculation of calorific value ⇒

Dulong's formula ⇒

$$GCV = \frac{1}{100}\{8080C + 34,500(H - O/8) + 2240S\} \text{ kcal/}$$

where C, H, O & S represent the % of the correspondin elements in the fuel.

$$NCV = \{HCV - \frac{9}{100}H \times 587\} \text{ kcal/kg}$$

Stoichiometric calculation of fuel air air ratio ⇒

- For efficient combustion, it is essential that the fuel must be brought into intimate contact with sufficient quantity of air.
- C, H, S, & O → combustible constituents
- N, CO_2 & Ash → Non-combustible constituents.

1) substances always combine in definite propor-tions which are determined by the molecular weights of the substances.

Example ⇒

a) combustion of carbon

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

12 parts by weight of carbon requires 32 parts by weight of O_2. (or) 1 part by volume of carbon requires 1 part by volume of O_2 for complete combustion.

∴ c parts by weight of carbon require

$$= \frac{32}{12} \times c \text{ parts by wt of } O_2.$$

b) combustion of hydrogen

$2H_2 + O_2 \rightarrow 2H_2O$

2×2 32 36 (By weight)

4 parts by weight of H_2 requie 32 parts by wt of O_2.

(or)

2 parts by volume of H_2 requie 1 part by volume of O_2.

∴ H parts by weight of hydrogen requie parts by weight of O_2

$= \frac{32 \times H}{4}$ parts by weight

Some of the hydrogen is present in the combined form with oxygen. This combined hydrogen does not take part in combustion reaction. ∴ the quantity of combined hydrogen must be deduced from the total hydrogen in the fuel.

$2H_2 + O_2 \rightarrow 2H_2O$

4 : 32

1 : 8

Now, 1 part by weight of H_2 combines with 8 parts by weight of O_2

So the available $H_2 = H - O/8$

∴ $(H - O/8)$ parts by weight of H_2 requires parts by weight of O_2

$= \frac{32 \times (H - O/8)}{4}$

2. Amount of O_2 required by the fuel will be given by substracting the amount of O_2 already present in the fuel from the total or theoritical amount of O_2 required by the fuel.

Net amount of O_2 required = Total amount of O_2 required - O_2 already pre in the

3. Air contains 21% of O_2 by volume and 23% of O_2 by weight. Hence from the amount of O_2 required by the fuel, the amount of air required can be calculated.

Minimum weight of air required $= \frac{100}{23} \times$ minimum O_2

Minimum volume of air required $= \frac{100}{21} \times$ minimum O_2.

4. Molecular mass of air is taken as 28.94 g/mol.

5. Density of air at NTP = 1.29 kg/m³.

6. 22.4 litres (22,400 ml) of any gas at NTP (0°C & 760 mm of Hg) has a mass equal to its 1 mole.

Thus, 22.4 litres of CO_2 at NTP will have a mass of 44g (44 is the molecular weight of CO_2)

7. Excess air for combustion

- very essential to supply excess air for complete combustion of the fuel.
- calculated from the theoritical amount of air as follows

$$= \frac{\text{Theoritical amount of air}}{100} \times (100 + \text{\% of Excess air})$$

Problems based on combustion reaction ⇒

I step → write the equation for the combustion reaction.

II step → From the equation calculate the amount of oxygen required for the elements or compounds present in the fuel.

III step → If oxygen is mentioned in the problem, substract the weight or volume of oxygen already present in the fuel from the total volume of O_2 required by the other elements or compounds.

IV step → Since N_2, CO_2 & H_2O are non-combustible. they do not require any oxygen (air). Ignore the values, if they are mentioned in the problem.

V step → Finally, calculate the amount of air required by the fuel by multiplying 100/21, (if volume %) with total amount of oxygen required, and 100/23 (if weight %) with total amount of oxygen required.

VI step → Excess amount of air for combustion

$$= \text{Theoretical air} \times \frac{100 + \%\ \text{of Excess air}}{100}$$

Ignition temperature ⇒

Defn ⇒ The lowest temperature to which the fuel must be heated, so that its starts burning smoothly.

- Ignition temperature of coal - 300°C
- liquid fuel - 200-450°C
- Gaseous fuel - 800°C

Spontaneous ignition temperature (SIT) ⇒

" The minimum temperature at which the fuel catches fire (ignites) spontaneously without external -heating

* If the ignition temperature of a fuel is low can catch fire very quickly. On the other hand if the ignition temperature is high, it is diffic to ignite the fuel.

Explosive range (or) limits of inflammability →

* All gaseous fuels have two limits called upperlimit and lower limit.

* Lower limit represents the smallest proportion of combustible gas.

* upper limit represents the largest proportion of combustible gas.

* The range covered by these limits is termed as explosive range of the fuels. For continuous burning the amount of fuel present in the fuel-air mixture should not go below the lower limit (or) above the upper limit.

Example → The explosive range of petrol is 2-4.5. This means that when the concentration of petrol vapour in petrol-air mixture is between 2 & 4.5 by volume, the mixture will burn on ignition.

* when the concentration of petrol vapour in petrol-air mixture is below 2% or above 4.5 (upper limit) by volume, the mixture will not burn on ignition.

Gas	Lower limit	upper limit
H_2	4	74 80
Acetylene	3	14
Natural gas	5	

fn ⇒ "Limiting composition of a gas-air mixture beyond which the mixture will not ignite & continue to burn"

Flue gas Analysis (Orsat method) ⇒

Flue gases ⇒ "Mixture of gases (CO_2, O_2 CO) coming out from the combustion chamber"

* The analysis of a flue gas would give an idea about the complete or incomplete combustion process. The analysis of flue gases is carried out by using Orsat's apparatus.

Description ⇒ * It has a long 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 this tube is connected with a graduated burette.

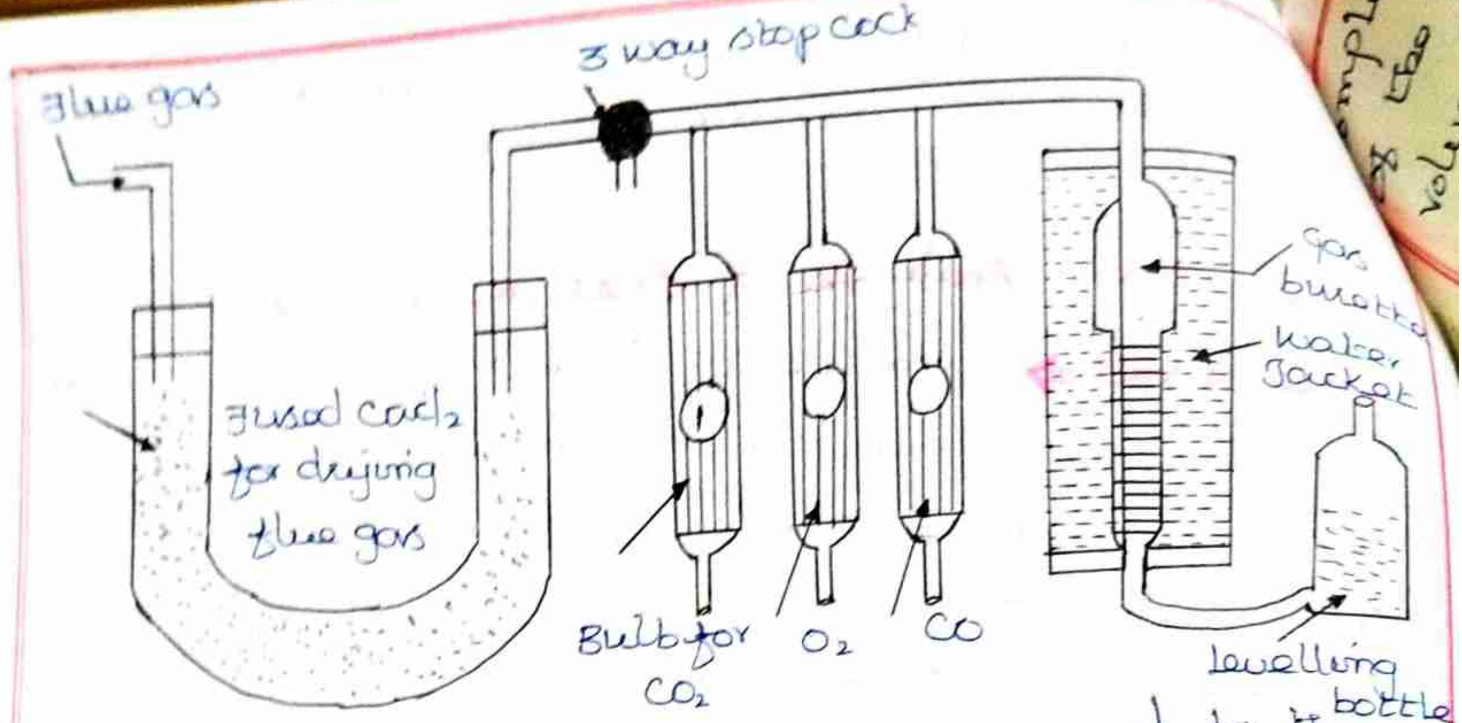
* The burette is surrounded by a water-jacket to maintain the temperature of gas constant.

* The lower end of the burette is connected to a water reservoir by a rubber tube.

* The level of water in the burette can be raised (or) lowered by raising (or) lowering the reservoir.

* The horizontal tube is also connected with three different absorption bulbs 1, 2 & 3 for absorbing CO_2, O_2 & CO.

* KOH absorbs only CO_2
* Alkaline pyrogallol solution absorbs CO_2 & O_2
* Ammoniacal cuprous chloride absorbs CO_2, O_2 & CO



working ⇒ * The 3-way stop cock is opened to the atmosphere & the reservoir is raised, till the burette is completely filled with water & air is excluded from the burette.

* Now, the 3-way stop cock is connected to the flue gas supply & the flue gas is sucked into the burette & the volume of flue gas is adjusted to 100 cc by raising & lowering the reservoir.

* Then the 3-way stop cock is closed.

a) Absorption of CO_2

* Bulb I stopper is opened & all the gas is passed into the bulb-I by raising the level of water in the burette.

* Then the gas enters into the bulb-I, where CO_2 present in the flue gas is absorbed by KOH.

* Again the gas is sent to the burette. This process is repeated for several times to ensure

plete absorption of CO_2. The decrease in volume of the flue gas in the burette indicates the volume of CO_2 in 100 cc of the flue gas.

b) Absorption of O_2

Bulb-2 stopper is opened. The O_2 present in the flue gas is completely absorbed by alkaline pyrogallol. The decrease in volume of flue gas in the burette indicates the volume of O_2 in 100 ml of the sample.

c) Absorption of CO

Bulb-3 stopper is opened. The CO_2 present in the flue gas is completely absorbed. The decrease in volume of flue gas in the burette indicates the volume of CO in 100 ml of the flue gas sample. The remaining gas in the burette after the absorption of CO_2, O_2 & CO is taken as nitrogen.

Significance of flue gas Analysis ⇒

- Gives an idea about the complete or incomplete combustion process of a fuel.
- If there is a presence of CO in flue gas, it indicates that incomplete combustion of fuel. It reveals the short supply of O_2.
- If there is a presence of O_2 in flue gas which ensures the complete combustion of fuel & excess supply of O_2.

Knocking

* A type of explosion * In an IC engine due to sudden pressure rise

causes ⇒

* Petrol engine → gasoline : air, 1:17

* sudden ignition of fuel - presence of unwanted impurities in fuel.

* Good gasoline - resist knocking

* straight chain paraffins > Branched chain paraffins > cycloparaffins > olefins > Aromatics

Improvement of antiknocking property ⇒

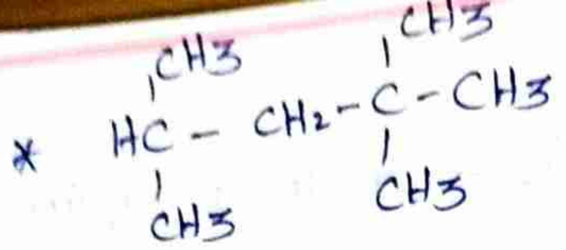
* By blending (High octane number + low octane number)

* By adding TEL * By adding aromatic Phosphates.

Octane number

* To express the knocking property of petrol

* n-heptane knocks very badly & Iso-octane - less knocking

* 

$\underset{CH_3}{\overset{CH_3}{HC}} - CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - CH_3$ Iso-octane (octane number-100)

* $CH_3-(CH_2)_5-CH_3$ n- heptane (octane number-0)

Leaded petrol ⇒

* Petrol + TEL → Leaded petrol

Mechanism of knocking ⇒

* TEL reduces the knocking tendency of hydrocarbon.

* Free radical mechanism - chain growth - explosion

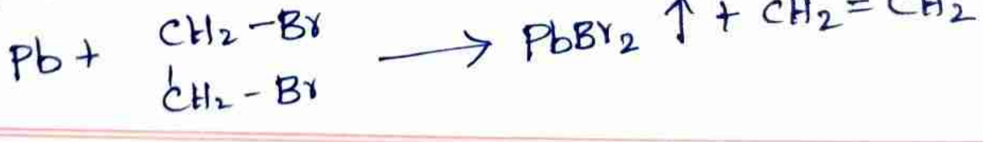
* If the chains are stopped before their growth, knocking will stop.

Disadvantages ⇒

* TEL - Lead oxide & metallic lead.

* This lead deposits on the spark plug & corrodes. To avoid this, ethylene dibromide is added.

* This ethylene dibromide, reacts with Pb & PbO to give volatile lead bromide. But this creates pollution. so aromatic phosphates are added.



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

oil ⇒

* Mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbon.

* calorific value - 11000 Kcal/kg

* Good fuel for diesel engine.

causes of knocking ⇒

* Initially air alone compressed & raises the temperature to 500°c. Then oil is sprayed & further raises the temperature & pressure.

* Ignition lag ⇒ The time between injection of fuel & its ignition is called ignition lag (or) delay

* Reason for delay → Time taken for vapourisation of oil.

* If the ignition lag is short, diesel knock will not occur.

Diesel Index ⇒

* The quality of diesel oil - diesel index number

$$\text{Diesel Index number} = \frac{\text{Specific gravity} \times \text{Aniline point in} \, {}^{\circ}\text{F}}{100}$$

Cetane number ⇒

* To express the knocking property of fuel.

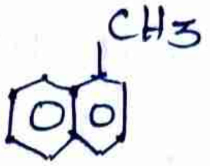
* Hexa decane - $C_{16}H_{34}$ - short ignition lag

* α-methyl naphthalene - long ignition lag

Definition ⇒

* The percentage of hexa decane present in a mixture of hexa decane and α-methyl naphthalene is called cetane number.

$CH_3-(CH_2)_{14}-CH_3$
n. cetane
(cetane number-100)



α-methyl naphthalene
(cetane number - 0)

* straight chain paraffins > cycloparaffins > olefins > Branched paraffins > Aromatics.

* Dopes ⇒ To improve cetane number
* Doping agent ⇒ Ethyl nitrate, Iso-amyl nitrate

Gasoline oil	Diesel oil
* C_5-C_9 Hydrocarbons	* C_{15}-C_{18} hydrocarbons
* Fuel for SI engine	* Fuel for CI engine
* octane number - to express knocking property	* cetane number - to express knocking property.
* Reason - premature ignition	* Reason - Ignition lag
* Antiknocking improved by TEL	* Antiknocking improved by doping with ethyl nitrate.

dvantages ⇒

* cheaper than petrol * Absorbs moisture

* Less emission of CO, hydrocarbon

Disadvantages ⇒

* Low calorific value than petrol, so specially designed engine is required

* Starting trouble - because of high surface tension

* corrosion - takes place

* The engine & carburetor need to be modified because less amount of O_2 needed for combustion.

Bio-diesel

* Methyl esters of fatty acids → Bio-diesel

* Mono alkyl esters of long chain fatty acids derived from vegetable oils

Manufacture ⇒ Trans-esterification (or) alcoholysis

* If vegetable oils used directly, incomplete combustion & corrosion takes place

* To overcome the above problems, trans-esterification is carried out.

Power Alcohol

* Ethyl alcohol + petrol → Power alcohol

* To increase octane number, ethyl alcohol is added.

* Ethyl alcohol + diesel → E- diesel

Manufacture ⇒

I step ⇒ Manufacture of ethyl alcohol

* Fermentation of carbohydrates.

* $C_6H_{12}O_6 \xrightarrow{Yeast} 2C_2H_5OH + 2CO_2$

* Concentration of alcohol - increased by 97.6% by fractional distillation

II step ⇒ Conversion of ethyl alcohol into power alcohol

* 100% alcohol - by removing last traces of water from rectified spirit. It is done by

1. Alcohol is distilled with benzene
2. Alcohol is distilled in the presence of dehydrating agent.

Properties ⇒

* Low calorific value (7000 kcal/kg)

* High octane number (90)

* Good antiknocking property

* High compression ratio

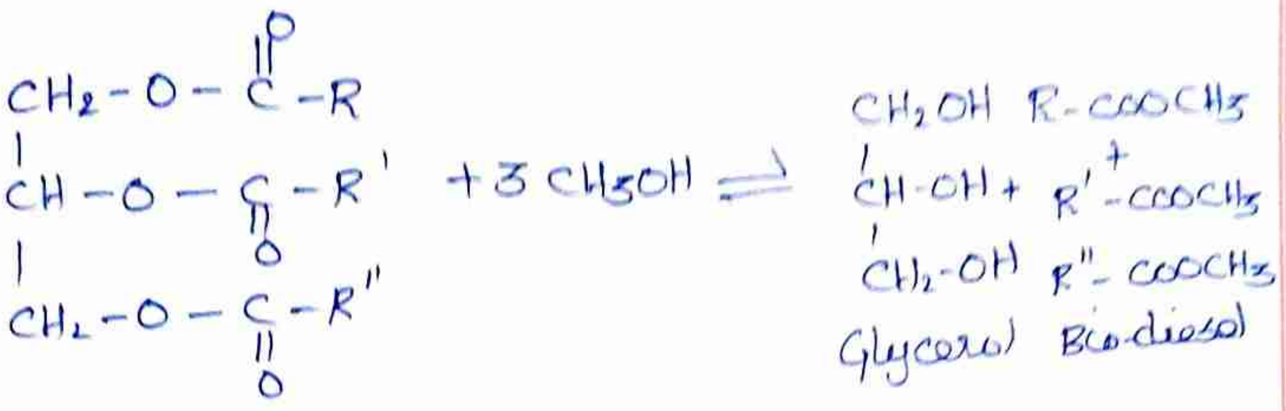
Uses ⇒

* Very good fuel for motors.

Alcoholysis - Displacement of alcohol from an by another alcohol

* vegetable oil + Methanol ⟶ Bio diesel

* Bio-diesel - blended with petroleum diesel



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

Advantages ⇒

* Bio-degradable * Prepared from renewable resources * Less gaseous pollutants

Disadvantages ⇒

* Gels in cold weather

* Hygroscopic - absorb water from atmosphere

* Horse-power of the engine decreased.

* Degrades & soften the rubber & plastics

* High percentage (10%) of NO_x emission

carbon Emission

efinition ⇒

* The release of carbon into the atmosphere

* Since green house gas emissions are often calculated as CO_2 equivalents, they are reffered to as "carbon emissions".

sources ⇒

* Burning of fossil fuels - coal, oil, natural gas

Reduction of carbon emission ⇒

* Reduced by reducing green house gas emission. It is done by

1. In industry
   - ⇒ Including energy efficiency
   - ⇒ Fuel switching
   - ⇒ combined heat & power
   - ⇒ use of renewable energy
2. Avoiding HFC's in refrigeration, air conditioning & foam blowing
3. In oil & gas production, the leakage of green house gases can be controlled by reducing pressure from pipelines

carbon Footprint

* Total amount of green house gases (CO_2 & CH_4) that are generated by our direct and indirect activities.

Individual carbon footprint ⇒

* smaller your carbon footprint → Better for the future

* Bigger your carbon footprint → Have bigger negative impact in environment

* The average carbon foot print for a person in united state - 16 tons.

* To avoid 2°c rise in global temperature, the average global carbon footprint per year needs to drop under 2 tons by 2050.

sources ⇒ * climate change * volcanos * Green house gases emitted from human activities * Transportation * Electricity generation * Industrial activities

How to lower carbon footprint ⇒

* By making small changes in our action

e can reduce carbon footprint.

* calculate your carbon footprint

* Drive less * Switch to an electric (or) hybrid car * switch to renewable energy * Get energy efficient appliances * unplug electrical devices when not in use.

* Eat less meat

* start a home garden * Adopt 4R approach

* Don't waste water

UNIT V Energy sources & storage devices

Introduction ⇒

* Energy - "capacity to do work"

* Types < conventional energy sources / Non - conventional energy sources

Stability of nucleus ⇒

* Actual mass of an isotope - less than the sum of the masses of protons, neutrons and electron

Definition ⇒

* "The difference between the calculated and experimental masses of nucleus"

* $\Delta m = \left\{ \begin{array}{c} \text{Total mass of} \\ p, n \text{ & } e^- \end{array} \right\} - \left\{ \begin{array}{c} \text{experimental} \\ \text{mass of the} \\ \text{nucleus} \end{array} \right\}$

Calculation of mass defect ⇒

* consider an isotope, atomic number = Z Mass number = A, If an atom contains Z proton, Z e^- & (A - Z) neutron

m_p = mass of proton

m_n = mass of neutron

m_e = mass of an e^-

∴ calculated mass of isotope

$M' = Zm_p + Zm_e + (A-Z)m_n$

$= Zm_H + (A-Z)m_n$

(where $m_p + m_e$ = mass of H atom, $= m_H$)

Let,

M = Actual experimental mass of the nucleus

$\Delta m = M' - M$ (or)

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

Problem ⇒

1. Calculate the mass defect of $^{40}_{20}Ca$, 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.

Solution ⇒

Mass defect (Δm) $= Zm_p + (A-Z)m_n - M$

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

$m_n = 1.0086$ amu, $M = 39.975$ amu

$\Delta m = (20 \times 1.0078 + 20 \times 1.0086 - 39.975)$

$= 0.353$ amu

Result ⇒

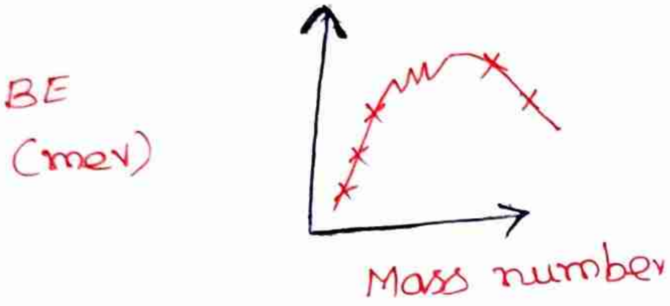
$\boxed{\Delta m = 0.353 \text{ amu}}$

Binding energy ⇒

"Energy released when a given number of protons & neutrons coalesce to form nucleus"

* Energy required to disrupt the nucleus into its constituent protons & neutrons.

Binding energy Vs Nuclear stability ⇒



* The stability of nucleus increases upto a mass number of 65 and decreases.

* Some subsidory peaks in the plot at $_2He^4$, $_6C^{12}$ & $_8O^{16}$.

* Reason: Equal number of protons & neutrons.

Calculation of B.E ⇒

$$E = \Delta mc^2 \qquad \mathcal{E} = \{ Zm_H + (A-Z)m_n - M \} \times c^2$$

$\mathcal{E}$ → Binding energy of the nucleus

Δm → Mass defect   c → Velocity of light

UNIT-IV Energy sources

Nuclear Energy ⇒ " Energy derived from nuclear fission (or) fusion reaction is called nuclear energy".

Ex ⇒ $_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{140} + {}_{36}Kr^{93} + 3\,{}_{0}n^{1} + E$.

Reason for loss of energy ⇒

* The energy released during fission reaction is due to loss in mass. The loss in mass is converted into energy according to Einstein equation

$$E = mc^2 \qquad (\because \Delta m = m - m')$$

c = velocity . E = Energy.

Disadvantages ⇒

* Radiation damage the cells in human body

* cancer, blindness, genetic disorder.

* sterility in young generation.

Advantages ⇒ * power generation * source of pure water * cancer treatment * To destroy micro-organism * pest control * To delay the ripening of fruits.

Nuclear Fission ⇒ " Process of splitting of heavier nucleus into two or more smaller nuclei with simultaneous liberation of large amount of energy.

Mechanism ⇒ $_{92}U^{235} + {}_{0}n^{1} \rightarrow \left[{}_{92}U^{236}\right] \rightarrow {}_{56}Ba^{140} + {}_{36}Kr^{93} + 3\,{}_{0}n^{1}$

Characteristics ⇒

* When a heavy nucleus is bombarded by a slow moving neutron, two (or) more smaller nuclei are formed.

* Two / more neutrons are formed * Large quantities of energy is formed.

* All the fission fragments are radioactive, giving β & γ- radiation.

* All the fission reactions are a self-propagating chain reaction.

* The chain reaction can be controlled by absorbing some neutrons.

* Every secondary neutron does not strike a nucleus because some neutrons may escape into air.

* The no of neutrons released in a single fission reaction is known as multiplication factor.

* Multiplication factor should be one for a nuclear reaction to continue.

Advantages ⇒

Nuclear Fission	Fossil fuel energy
* Small amount of fuel gives large amount of energy	* Large amount of fuel is required to give large amount of energy.
* Fuel is supplied only one time	* Fuel should be supplied continuously.

Disadvantages ⇒

Nuclear Fission	Fossil fuel energy
* Serious pollution	* Less pollution than nuclear fission
* Safe disposal of nuclear waste is essential	* No need to dispose safely.

Nuclear Fusion ⇒ " Process of combination of lighter nuclei into heavier nucleus, with simultaneous liberation of large amount of energy.

Example ⇒ Fusion occurs in the sun.

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

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

* The fusion reaction can start only when the atoms are heated to very high temperature. such a high temperature, required is produced by fission reaction.

* The combination of these nuclei is very difficult because all the nuclei are positively charged.

* To combine them, it should overcome the electrostatic repulsion. In fact, the hydrogen to helium fusion reaction in the sun occur at about 100 million degree centigrade.

* Thus, to start nuclear fusion reaction, high temperature is required. So this is called

thermonuclear reaction.

Example ⇒ Hydrogen bomb.

Disadvantages ⇒ we cannot use the energy derived from nuclear fusion, because no known material can withstand such a high temperature. Thus so we cannot design of thermonuclear fusion power plant.

characteristics ⇒ No limit on the amount of nuclear fusion that can occur.

* The distance between the nuclei should be one fermi. * Energy liberation four times higher than nuclear fission. * sufficient amount of kinetic energy should be given to start nuclear fusion reaction * only lighter nuclei can undergo nuclear fusion reaction.

Differences between nuclear fission & fusion ⇒

Nuclear Fission	Nuclear fusion.
* Process of breaking of heavy nucleus into small nuclei.	* Process of combination of lighter nuclei to heavy nucleus.
* Emits radioactive rays.	* Does not emit radioactive rays.
* Takes place at ordinary temperature.	* Takesplace at high temp
* The mass & atomic no of new element are lower than parent nucleus.	* The mass & atomic no of product are higher than starting element.
* Leads to chain reaction	* Does not lead to chain reaction
* Emits neutrons.	* Emits positrons.
* controlled easily	* cannot be controlled.

Nuclear chain reaction ⇒

In nuclear fission reaction, the neutrons emitted from the fission of U^{235} atom may hit another U^{235} nuclei and cause fission producing more neutrons & so on. Thus, a chain of self sustaining nuclear nuclear reactions will be set up with the release of large amount of energy. But the amount of energy released will be less than expected. Thus, the fission of U^{235} by slow moving neutrons is a chain reaction.

Reason for less energy ⇒

- Some neutrons may escape from the surrounding

(or)

- Neutrons may be absorbed by U^{238} which is present as impurity.

Definition ⇒

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

Criteria for nuclear chain reaction ⇒

- Sufficient amount of U^{235} must be present to capture the neutrons for a nuclear chain reaction to continue.

Critical mass ⇒ The amount of fissionable material required to continue the nuclear chain reaction is called critical mass.

- The critical mass of U^{235} 1 Kg - 100 kg.

a) Super critical mass : If the mass of the fissionable material (U^{235}) is more than the critical mass, it is called super critical mass.

b) Sub critical mass : If the mass of the fissionable material is smaller than the critical mass, it is called sub-critical mass.

Thus, the mass greater or lesser than the critical mass will stop the propagation of the chain reaction.

Example ⇒

When U^{235} is bombarded by a thermal neutron it undergoes the following reaction with the release of three neutrons.

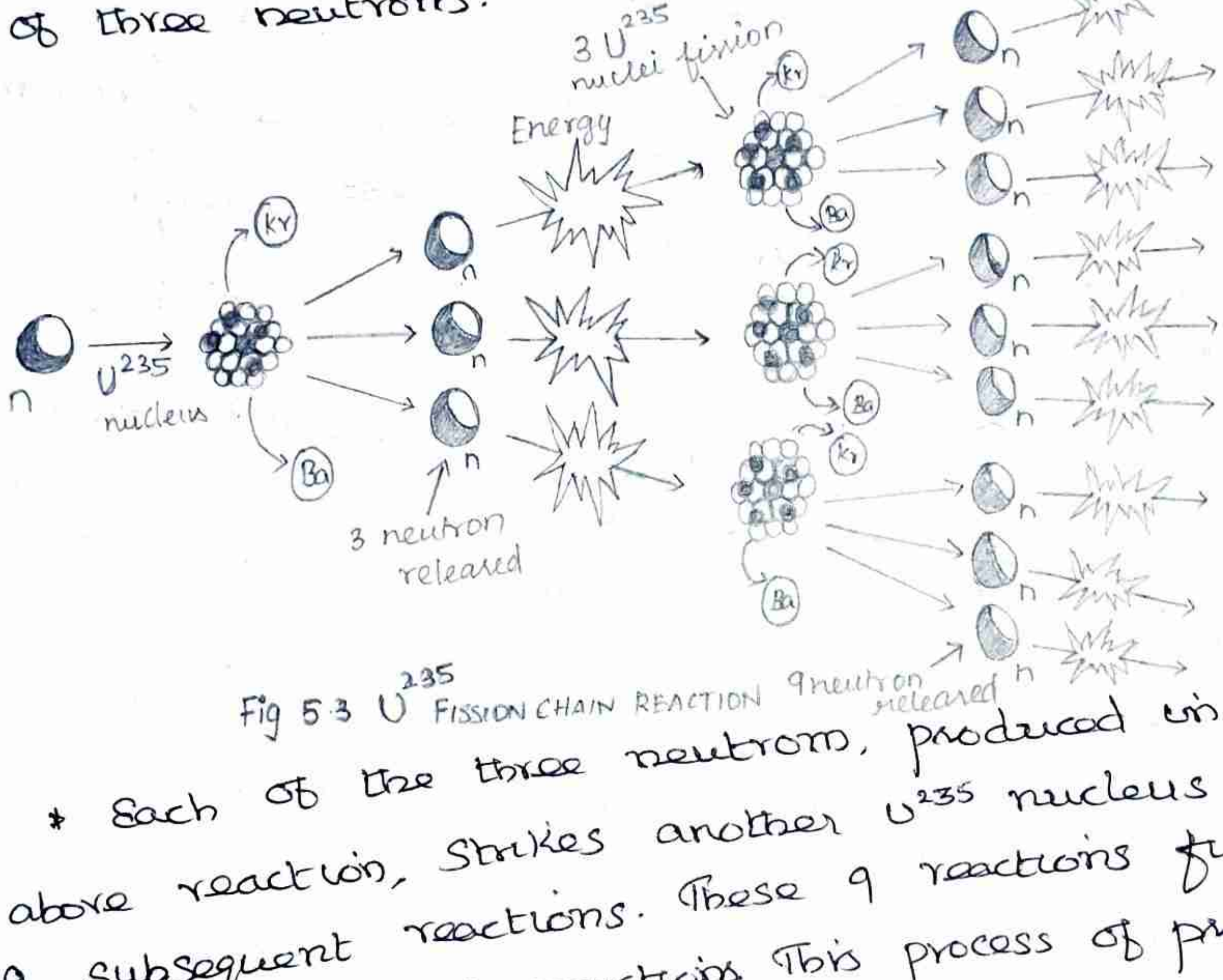


Fig 5.3 U^{235} FISSION CHAIN REACTION

* Each of the three neutrons, produced in the above reaction, strikes another U^{235} nucleus causing 9 subsequent reactions. These 9 reactions further give rise to 27 reactions. This process of propagation of the reaction by multiplication in threes at each fission is called chain reaction.

Types of nuclear fission reaction ⇒

* Uncontrolled nuclear fission reaction
* Controlled nuclear fission reaction.

* If a nuclear fission reaction is made to occur in an uncontrolled manner, then the energy released can be used for many destructive purposes.

Ex ⇒ Atom bomb.

* If a nuclear fission reaction is made to occur in a controlled manner, then the energy released can be used for many constructive purposes.

Ex ⇒ Nuclear reactor

Nuclear Reactor / pile

Defn ⇒ The equipment used to carryout fission reaction under controlled conditions is called a nuclear reactor.

Classification of nuclear reactors ⇒

Based on the type of neutron energy, fuel used, moderator and purpose, nuclear reactors may be classified in different ways.

1. Based on neutron energy & moderator

Thermal neutron reactors ⇒ In these reactors, nuclear fission reaction is brought out by slow moving neutrons. These are further classified into various types

a) Light water moderated reactors (LWR).

In this reactor, ordinary water is used as moderator & coolant.

* These are cheaper & simpler and have excellent safety & stability when compared to other nuclear reactor. These are further classified into

i) Boiling water reactor ii) pressurized water reactor iii) Super critical water reactors.

b) Heavy water moderated reactor (HWR)

Heavy water is used as moderator.

c) Graphite moderated reactors (GMR)

Graphite is used as moderator. These are further classified into a) Gas cooled reactors b) water cooled reactors.

2. Fast neutron reactors ⇒

In these reactors, nuclear fission reaction is brought out by unmoderated fast moving neutrons. These are generally cooled by liquid metal.

II) Based on fuel used

1. Burner; Nuclear fuel is burnt to produce heat or electrical energy.

2. Converter (or) Breeder type reactor.
fuel is reproduced.

III) Based on purpose

Based on the purpose for which type of reactor is operated, these are further classified into 1) power reactor 2) Breeder reactor c) Materials testing reactor.

Components of a nuclear reactor ⇒

1. fuel rods 2. control rods 3. Moderators. 4. coolants 5. Pressure vessel 6. protective shield 7. Turbine.

Fuel rods ⇒

The fissionable material used in the nuclear reactor is enriched U^{235}. The enriched fuel is used in the Reactor in the form of rods or strips.

Example ⇒ U^{235}, Pu^{239}.

Function ⇒ Produces heat energy & neutrons, that start nuclear chain reaction.

control rods ⇒ To control the fission reaction, movable rods, made of cadmium (or) boron, are suspended between fuel rods.

* These rods can be lowered or raised and control the fission reaction by absorbing excess neutrons.

* If the rods are deeply inserted inside the reactor they will absorb more neutrons & the reaction becomes very slow.

* If the rods are pushed outwards, they will absorb less neutrons & the reaction will be very fast.

$$ {}_{43}Cd^{113} + {}_{0}n^{1} \longrightarrow {}_{43}Cd^{114} + \gamma\text{-ray}. $$

Example ⇒ Cd^{113}, B^{10}

Function ⇒ It controls the nuclear chain reaction,

* Avoids the damage of reactors.

Moderator ⇒ The substances used to slow down the neutrons are called moderators.

* When the fast moving neutrons collide with moderator, they lose energy & gets slow down.

Example ⇒ H_2O, D_2O, Graphite, beryllium

Functions ⇒ The kinetic energy of fast moving neutrons (1 MeV) is reduced to slow neutrons (0.25e)

Coolants ⇒ Liquid coolant is circulated in the reactor core to absorb the heat.

* It enters the base of the reactor and leaves at the top. The heat carried by out-going liquid is used to produce steam.

Example ⇒ water, heavy water, liquid metal (Na, K) air (CO_2).

Function ⇒ It cools the fuel core.

Pressure vessel ⇒

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

Function ⇒ It can withstand the pressure as high as 200 kg/cm².

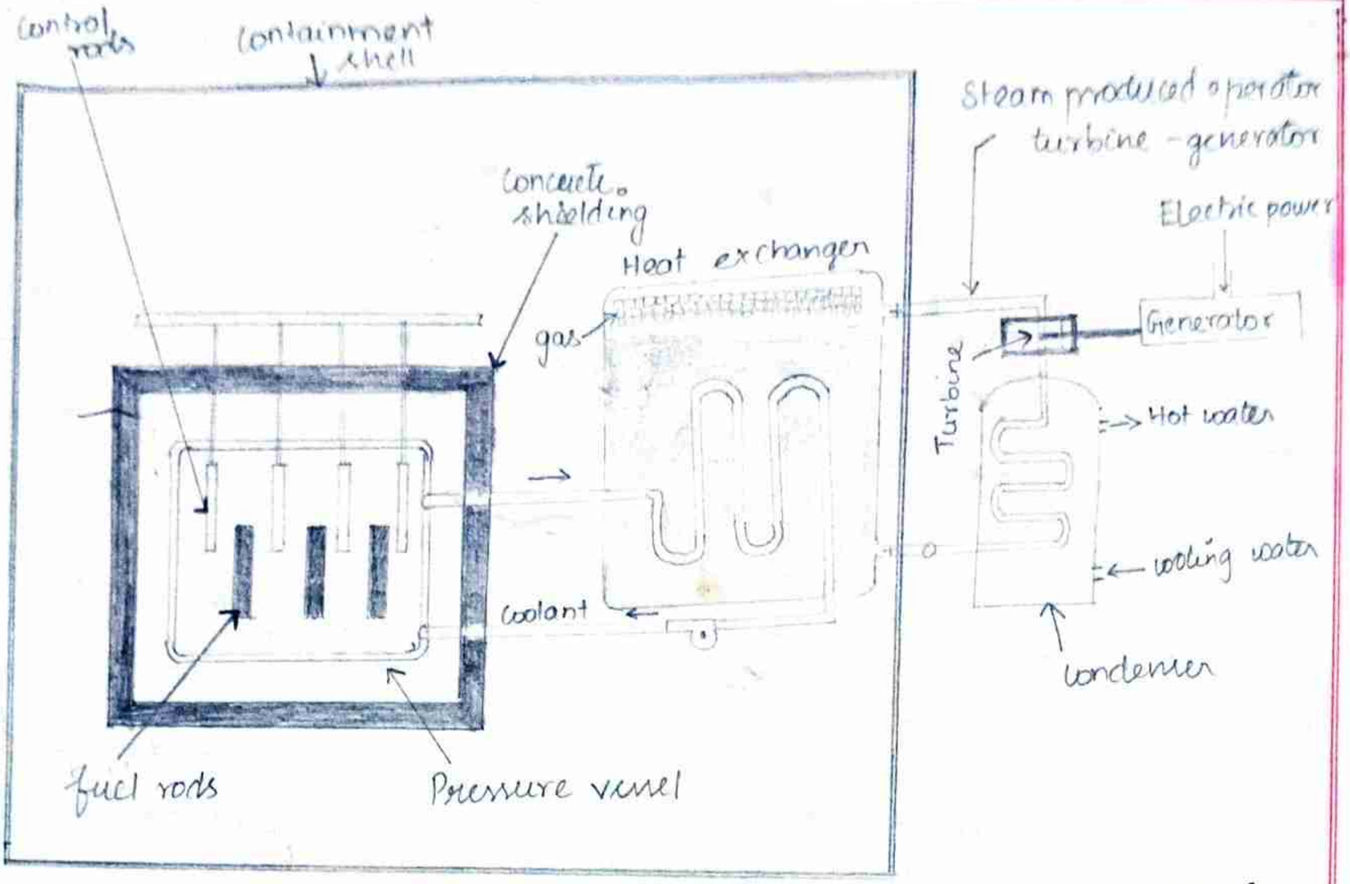
Protective shield ⇒ Nuclear reactor is covered by a thick concrete shield. (more than 10 m)

Function ⇒ The environment & operating personals are protected from destruction in case of leakage of radiation.

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

Light water nuclear power plant ⇒

In this, U^{235} fuel rods are submerged in water. Here the water acts as coolant & moderator.



working ⇒

* The fission reaction is controlled by inserting or removing the control rods (B^{10}) automatically from the spaces in between the fuel rods.

* The heat emitted by fission of U^{235} in the fuel core is absorbed by the coolant (light water).

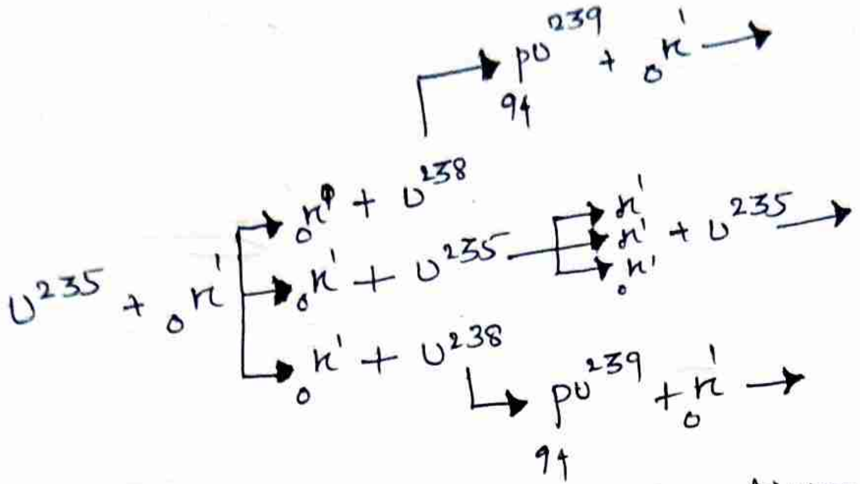
* Then the heated coolant goes to the heat exchanger containing sea water. Here, the heated coolant transfers their heat to sea water which is converted into steam. Then the steam drives the turbine generating electricity.

Breeder Reactor

Defn ⇒ The instrument used to convert non-fissionable material into fissionable material ($U^{238} \rightarrow U^{235}$)

* Breeder reactor breeds more no of fissionable material than it uses.

Example ⇒



* In breeder reactor, of the three neutrons emitted in the fission of U^{235}, only one is used to propogate the chain reaction.

* The other two are allowed to react with U^{238}. Thus, two fissionable atoms are produced for each atom of U^{235} consumed.

* ∴ Breeder reactor breeds more no of fission-able material than it uses. So, Pu^{239} is a man-made nuclear fuel & Secondary nuclear fuel.

Significance ⇒

* The non-fissionable nuclei (U^{238}, Th^{232}) are called fertile nuclei & converted into fissile nuclei.

* Fissionable nuclei such as U^{235}, Pu^{239} are called fissile nuclei.

Solar energy conversion ⇒

" Process of conversion of direct sunlight into more useful forms. This conversion takes place by two mechanism. 1) Thermal conversion 2) photo-conversion.

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

* solar energy is an important source for low temperature heat which is useful for heating buildings, water, & refrigeration.

Methods ⇒

1. solar heat collector 2. solar water heater.

Solar heat Collector ⇒

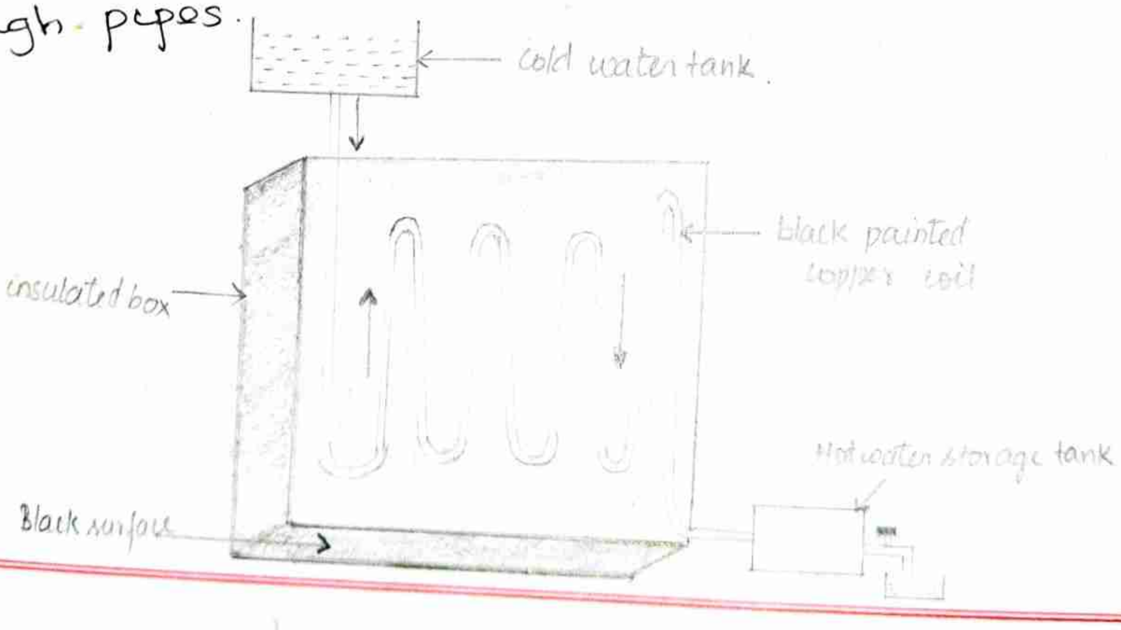
* solar heat collectors consist of natural material like stones, bricks (or) materials like glass, which can absorb heat during the day time & release it slowly at night.

uses ⇒ * used in cold places where houses are solar heat collectors. Kept in hot condition using

Solar water heater ⇒

* It consists of an insulated box inside of which is painted with black paint. It is also provided with a glass lid to receive & 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 & flows out into a storage tank. From the storage tank water is supplied through pipes.



Photoconversion ⇒

* conversion of light energy into electric energy directly by the photoelectric effect.

* When the energy of solar radiation falls on the surface of a metal, it is absorbed & used to excite and eject electrons from the surface. This ejected electrons move in a circuit and generate current.

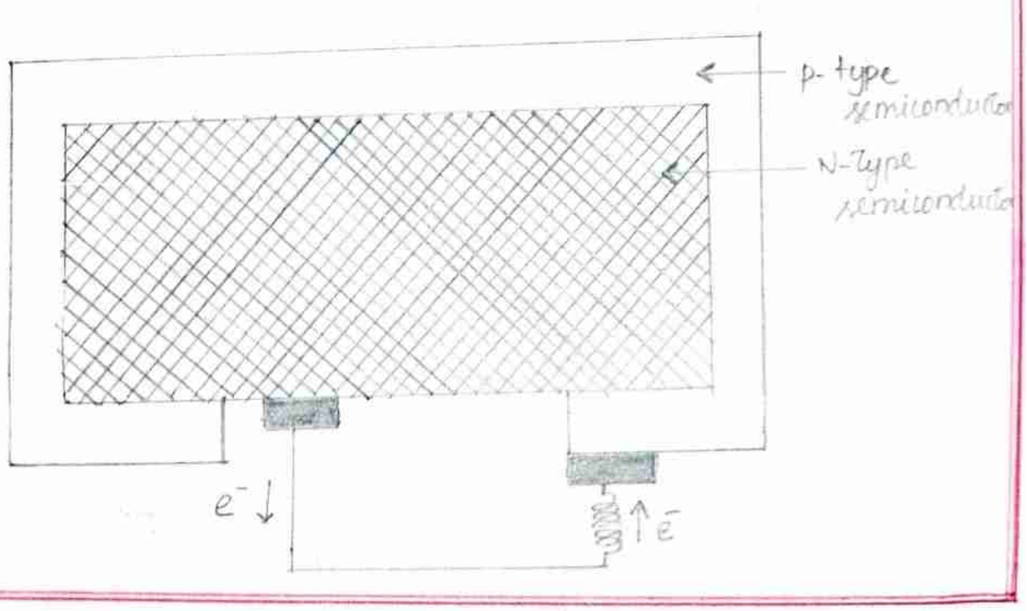
Methods ⇒ Photogalvanic cell.

Definition ⇒ It converts the solar energy directly into electrical energy.

Principle ⇒ * The basic principle is based on the Photovoltaic effect. When the solar rays fall on a two layer of semi conductor devices, a potential difference between the two layer is produced. This difference causes flow of e^-s & produces potential difference electricity.

Construction ⇒

Solar cell consist of a p-type semiconductor (si doped with B) and n-type semiconductor (si dopped with P). They are in close contact with each other.



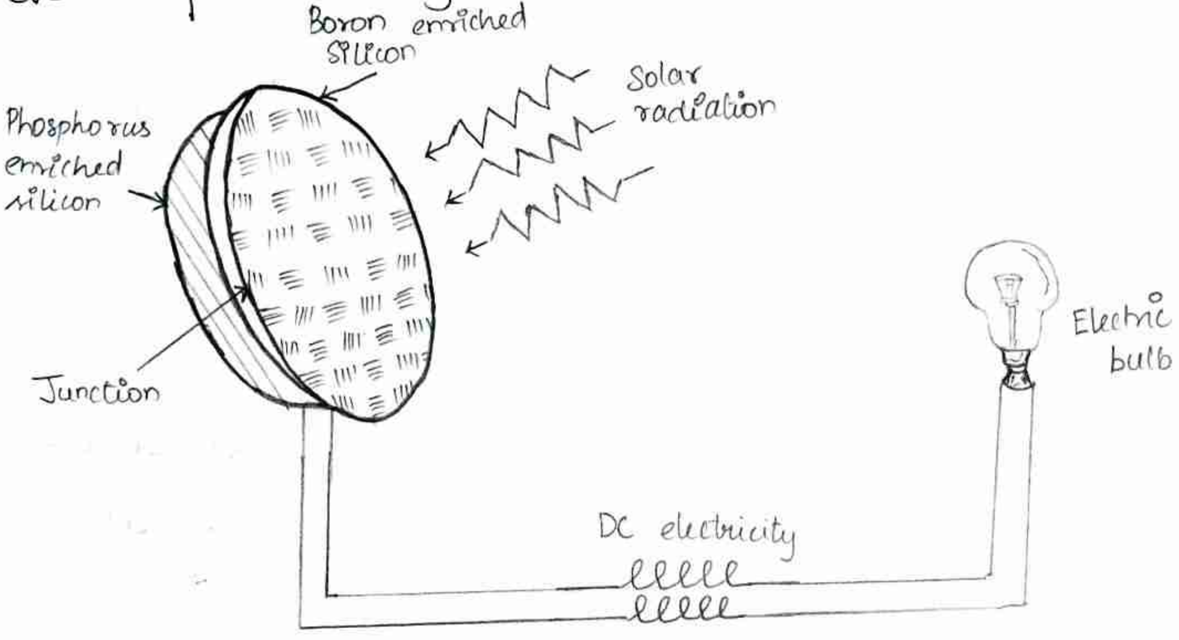
Working ⇒ When the Solar rays fall on the top layer of p-type semiconductor, the electrons from the valence band get promoted to the conduction band and cross p-n junction into n-type semiconductor.

* Thereby potential difference between two layers is created, which causes flow of electrons. Thus, when the p & n layers are connected to an external circuit, electrons flow from n-layers to p-layers and hence current is generated.

* The potential difference & hence current increases as more solar rays falls on the surface of the top layer.

Applications ⇒

1. Lighting purpose : Now-a-days, electrical street lights are replaced by solar street lights.



Solar cell (PV cell)

2. Solar pumps run by solar battery.

* When a large no 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..

* Also they are used in remote areas where conventional electricity is a problem.

* Solar cells are used in calculators, electronic watches, radios & TV's.

* Solar cells are superior to other type of cells because those are non-polluting & eco-friendly.

* Solar energy can be stored in Ni-cd & lead acid batteries.

* They are used to drive vehicles.

* Solar cells made of silicon are used as a source of electricity in space craft and satellites.

Advantages ⇒

* Solar cells are used in remote & isolated areas, forests & hilly regions.
* Maintenance cost is low.
* Noise & pollution free.
* Long life time
* They works at ambient temperature.
* They need not be recharged.

Disadvantages ⇒

* Capital cost is high
* Storage of solar energy is not possible
* Produces only DC voltage
* Solar energy is not

available throughout day & night.

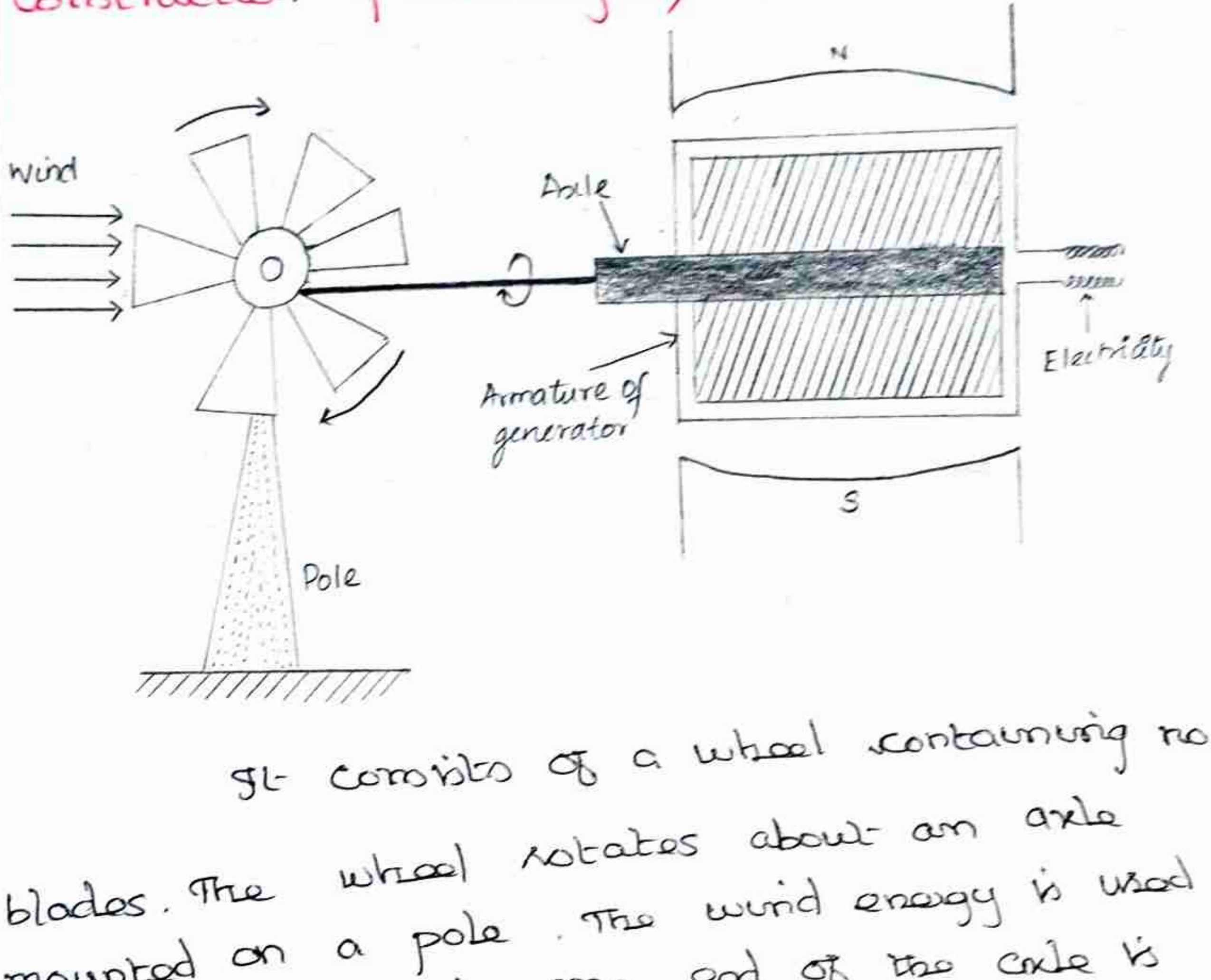
Wind Energy ⇒ Moving air is called wind. Energy derived from the force of wind is called wind energy. Kinetic energy of the wind is converted into mechanical energy.

Methods ⇒ * wind mill * wind form

windmill ⇒ It is a device used to convert wind energy into mechanical energy.

wind energy → kinetic energy → Mechanical energy → Electrical energy.

construction & working ⇒



It consists of a wheel containing no of blades. The wheel rotates about an axle mounted on a pole. The wind energy is used to rotate the wheel. One end of the axle is connected to the armature of a generator, which rotates between two poles of a strong magnet.

* Another end of the axle is connected to the shaft of the wind mill.
* When wind falls on the wheel of a wind mill, it rotates & generates electric current.
* Thus, the kinetic energy of the wind is converted into electric energy.

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 no of windmills are connected.
* Thus, the region where large no 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 larger scale.

Other methods ⇒ * sky sail, * ladder mill

* Sky wind power
* Kite ship
* sequoia automation
* Briza technologies

Advantages ⇒

* Does not produce any pollution
* Renewable
* very cheap & economic

Disadvantages ⇒

* Public resists for locating the wind farms in populated areas due to noise generated by the

machines.

* Loss of aesthetic appearance.
* wind farms located on the migratory routes of birds will cause hazards.
* wind turbines interfere with electromagnetic signal.
* wind energy is not sufficient to operate very heavy machine.

uses of wind energy ⇒

* wind energy is used to move sail boats in lakes, rivers & seas.
* It is used to operate water pumps
* It is used to run the flour mill to grind the grains.
* It is also used to produce electricity.

Batteries

* Battery is an electrochemical cell which converts chemical energy into electrical energy.

* The potential of the battery is related to free energy change (ΔG).

* In an electrochemical cell, the system does work by transfering electrical energy through an electric circuit. Thus, ΔG for a reaction is a measure of the maximum useful work, that can be obtained from a chemical reaction.

ΔG = maximum useful work, But

maximum useful work $= nFE$

* When a cell operates, work is done on the surroundings. $\Delta G = -nFE$ or $\Delta G < 0$

* Negative sign indicates decrease in free energy.

* One of the main uses of the galvanic cell is the production of portable electrical energy. These cells are known as batteries.

Battery ⇒
* An Arrangement of several electro-chemical cells which are connected in series

cell ⇒ Has only one anode & cathode

Battery ⇒ Has several anodes & cathodes

Requirements of a battery =)

- light weight and compact
- long life when it is in use or not in use.
- voltage should not change during its use.

Types of battery =>

a) Primary battery

- chemical reaction cannot be reversed.
- Can not be recharged & used again & again
- Ex => Dry cell, mercury cell.

b) Secondary battery

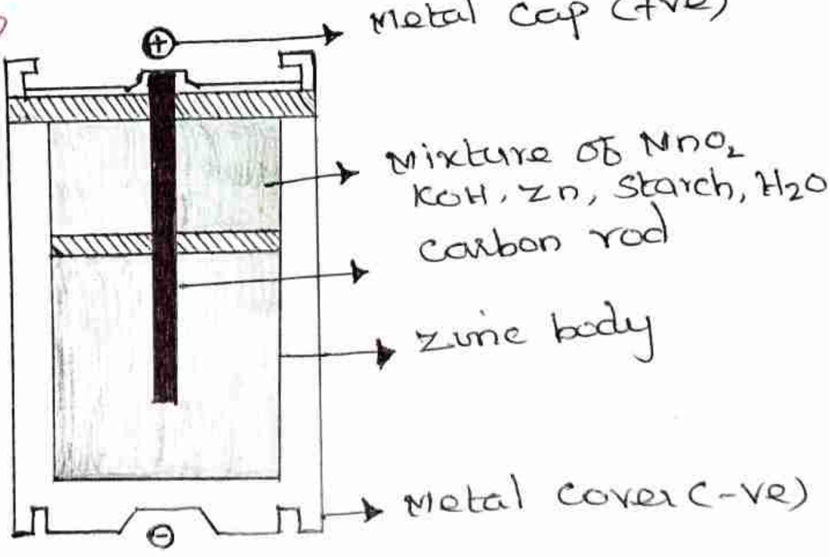
- chemical reaction can be reversed.
- can be recharged & used again & again
- Ex => NICAD, Lead-Acid battery

c) Flow battery

- Reactants, products and electrolytes are continuously passing through the cell. Here chemical energy is converted into electrical energy.

Ex => H_2-O_2 fuel cell, CH_3OH - O_2 fuel cell.

Alkaline battery =>



Alkaline battery ⇒

Electrode → Anode - Zinc body
cathode - Graphite

Electrolyte → powdered Zn, KOH & MnO_2

Emf → 1.5 V

cell reaction ⇒

At Anode : Zn is oxidised to Zn^{2+} by liberating electrons.

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$Zn^{2+} + 2OH^\ominus \rightarrow Zn(OH)_2$$
$$\overline{Zn + 2OH^\ominus \rightarrow Zn(OH)_2 + 2e^-}$$

At cathode ⇒ MnO_2 is reduced to Mn_2O_3 by accepting e's from the anode.

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^\ominus$$

overall cell reaction ⇒

At Anode ⇒ $Zn + \cancel{2OH^\ominus} \rightarrow Zn(OH)_2 + \cancel{2e^-}$

At Cathode ⇒ $2MnO_2 + H_2O + \cancel{2e^-} \rightarrow Mn_2O_3 + \cancel{2OH^\ominus}$

$$\overline{Zn + 2MnO_2 + H_2O \rightarrow Zn(OH)_2 + Mn_2O_3 + V}$$

Advantages ⇒

* Zn does not dissolve in basic medium

* longer life time than dry cell because no corrosion takes place

* constant voltage

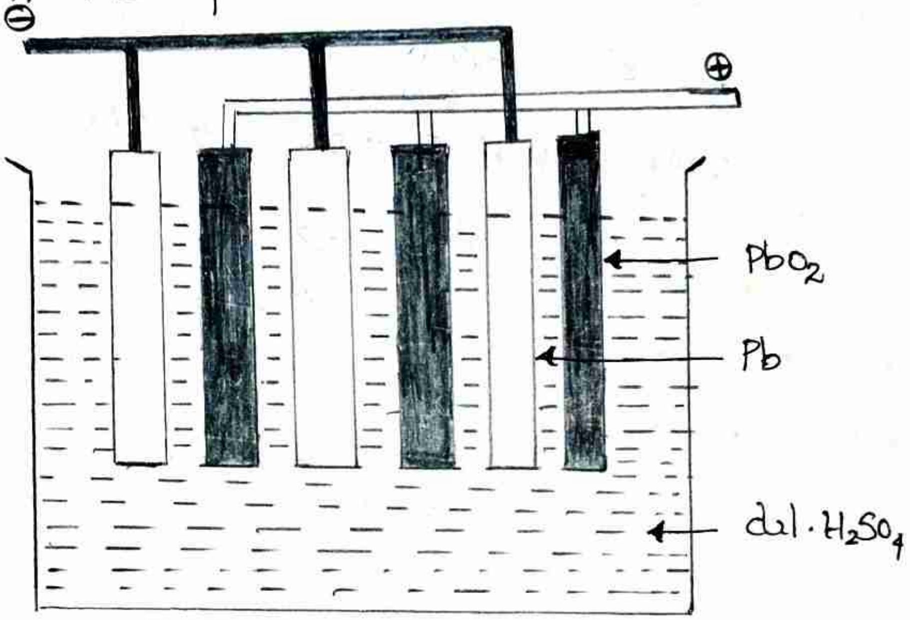
Lead storage cell (or) Lead Acid battery

- Secondary battery
- Act as electrolytic & electrochemical cell.
- When it is discharged, the cell may act as electrochemical cell.
- When it is recharged, the cell may act as electrolytic cell.
- Electrode
  - Anode - Pb
  - cathode - PbO_2
- Electrolyte → dil. H_2SO_4 (1.30 gm/ml)
- Emf → 6-12 V.

Cell representation ⇒

$Pb / PbSO_4 \parallel H_2SO_4 \parallel PbO_2 / PbSO_4$

Diagram ⇒



Working ⇒ Discharging

At Anode : Pb is oxidised to Pb^{2+} ions by liberating electrons.

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

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$

At cathode : PbO_2 is reduced to Pb^{2+} ions by accepting electrons from the anode.

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

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

$PbO_2 + 4H^+ + SO_4^{2-} \rightleftharpoons PbSO_4 + 2H_2O$

overall cell reaction ⇒

At Anode ⇒ $Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$

At cathode ⇒ $PbO_2 + 4H^+ + SO_4^{2-} \rightleftharpoons PbSO_4 + 2H_2O$

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightleftharpoons 2PbSO_4 + 2H_2O + \mathcal{E}$

(or)

$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O + \mathcal{E}$

Recharging ⇒ when current is applied in opposite direction, the cell reaction is reversed. ie cell can be recharged.

$2PbSO_4 + 2H_2O + \mathcal{E} \rightleftharpoons Pb + PbO_2 + 2H_2SO_4$

Advantages ⇒ High voltage * Low-self discharging rate * Act effectively at low temp.

Disadvantages ⇒

* Environmental pollution * Mechanical strain reduces battery capacity.

NICAD battery (or) Nickel- Cadmium battery

* Secondary battery * Act as electrolytic & electrochemical cell.

* When it is discharged, the cell may act as electrochemical cell

* When it is recharged, the cell may act as electrolytic cell.

* Electrode ⇉ Anode - Cd
  Cathode - NiO_2 (paste form)

* Electrolyte → KOH

* Emf → 1.4 V

cell representation ⇒

$Cd \mid Cd(OH)_2 \parallel KOH \parallel NiO_2 \mid Ni(OH)_2$

working ⇒ Discharging

At Anode : cadmium is oxidised to Cd^{2+} ions by liberating electrons.

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

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2$$

$$Cd + 2OH^- \rightleftharpoons Cd(OH)_2 + 2e^-$$

At cathode : NiO_2 is reduced to Ni^{2+} ions by accepting electrons from the anode.

$NiO_2 + 2H_2O + 2e^- \rightarrow Ni^{2+} + 4OH^-$

$Ni^{2+} + 2OH^{\ominus} \rightarrow Ni(OH)_2$

$NiO_2 + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2 + 2OH^-$

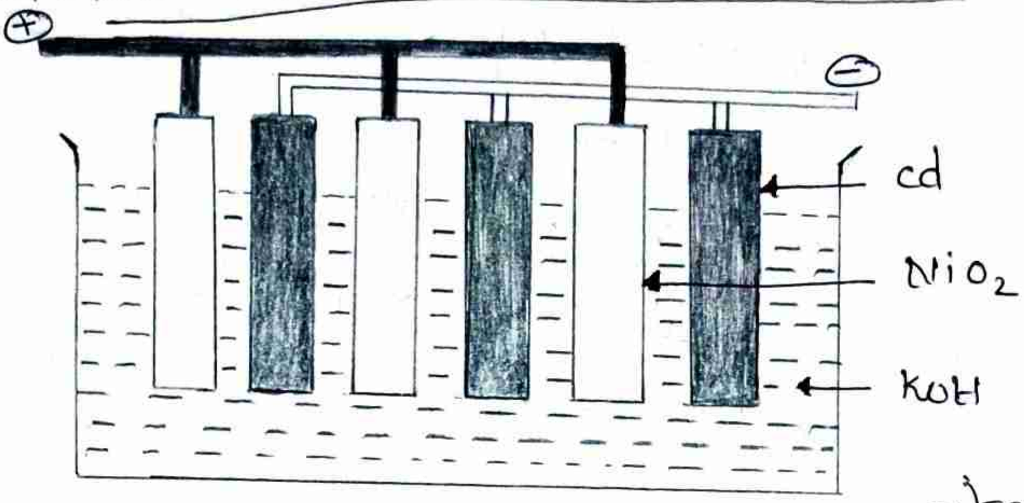
Overall cell reaction ⇒

At Anode : $Cd + \cancel{2OH^{\ominus}} \rightleftharpoons Cd(OH)_2 + \cancel{2e^-}$

At cathode: $NiO_2 + 2H_2O + \cancel{2e^-} \rightleftharpoons Ni(OH)_2 + \cancel{2OH^{\ominus}}$

~~Cd + 2H2O~~ $Cd + 2H_2O \rightleftharpoons Ni(OH)_2 + Cd(OH)_2 + E$

Diagram ⇒



Recharging ⇒ when current is applied in opposite direction, the cell reaction is reversed, ie the cell can be reversed. As a result, Cd gets deposited on anode & NiO_2 on the cathode.

$Cd(OH)_2 + Ni(OH)_2 + E \rightleftharpoons Cd + NiO_2 + 2H_2O$.

Advantages ⇒ * smaller & lighter

* Longer life time than lead acid battery
* packed in a sealed container, like a dry cell.

Disadvantage ⇒

* costly than lead acid battery

uses ⇒

* calculators, electronic flash units, transistors & cordless appliances.

Lithium Battery

- It is a solid state battery because solid electrolyte is used.
- Anode → Lithium, cathode → TiO_2
- Electrolyte → polymer (solid)
- Emf → 3V.

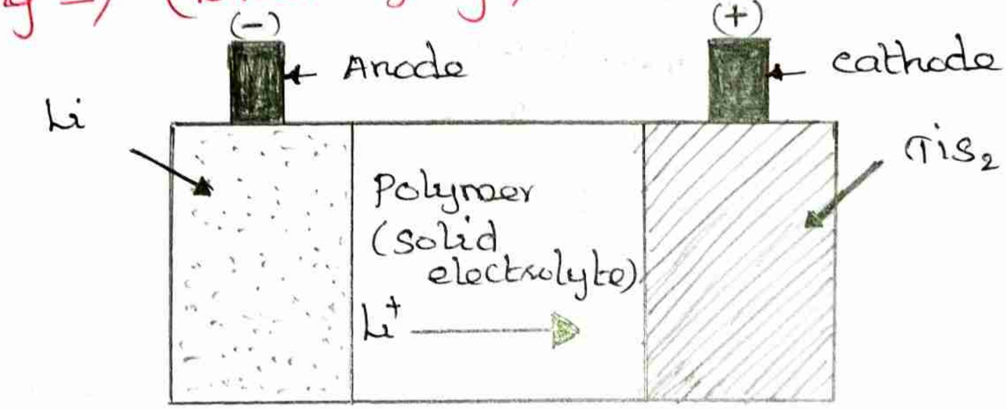
Construction ⇒

- Anode is made up of Lithium & cathode is made up of TiS_2

Electrolyte is solid polymer

-
- The cathode has the ability to accept both e⁻s & ions while electrolyte allows only ions but not e⁻s.

working ⇒ (Discharging)



At Anode : Lithium is oxidised to Lithium ions by releasing electrons.

$$Li \rightleftharpoons Li^+ + e^-$$

At cathode : TiS_2 is reduced by accepting e⁻s from the anode.

$$TiS_2 + e^- \rightleftharpoons TiS_2^-$$

overall cell reaction ⇒

$$Li + TiS_2 \rightleftharpoons \underbrace{Li^+ + TiS_2^-}_{LiTiS_2} + E$$

Recharging ⇒

$$E + LiTiS_2 \rightleftharpoons Li + TiS_2$$

when current is applied in opposite direction the cell reaction is reversed ie the cell can be recharged.

Advantages ⇒ It is the cell of future. why?

- * It produces high voltage (3V)
- * only 7 gm is enough to produce 1 mole of e's.
- * Li has higher E° value ∴ it generates higher voltage than other cells.
- * No risk of leakage from the battery because all constituents are solid.
- * It can be made in a variety of shapes & sizes.

Disadvantage ⇒

- * costly.

uses ⇒

calculators, watches, cameras, mobile phones Laptop etc...

Lithium - Sulphur battery

* secondary battery * Electrode ⟨ Anode - Li
cathode - Graphite

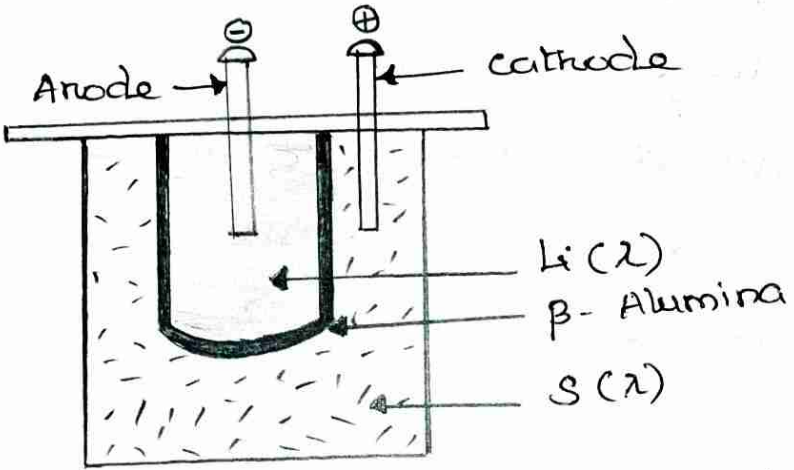
Electrolyte - β- Alumina.

Emf - 3V

Construction ⇒

- Anode is made up of Lithium
- cathode is made up of graphite.
- Electrolyte is β- Alumina which allows only $Li^{\oplus}$ ions but not big - polysulphide ions.
- Electrolyte prevents the direct contact between lithium & sulphur.
- cathode is dipped in liquid sulphur which act as electron acceptor.
- This battery should be operated in high temp because Li & S are in molten state.

Diagram ⇒



working ⇒ (Discharging)

At Anode: Lithium is oxidised to Li^+ ions by releasing electrons.

$$2Li \rightleftharpoons 2Li^+ + 2e^-$$

At cathode: sulphur accepts electrons from the anode.

†

$S + 2e^- \rightleftharpoons S^{2-}$

Over all cell reaction ⇒

At Anode : $2Li \rightleftharpoons 2Li^+ + 2e^-$

At cathode : $S + 2e^- \rightleftharpoons S^{2-}$

$2Li + S \rightleftharpoons 2Li^+ + S^{2-} + E$

Advantages ⇒

* Light weight * high energy density * used in electric cars.

Fuel cell

* It is an electrochemical cell which converts chemical energy into electrical energy without combustion.

Fuel + O_2 → oxidation product + Energ

Ex⇒ $H_2 - O_2$ fuel cell, $CH_3OH - O_2$ fuel cell.

Hydrogen oxygen fuel cell ⇒

* Simplest cell in which fuel (H_2) & oxidise (O_2) & liquid electrolyte are passed continu-ously.

* Electrode < Anode, cathode } compressed carbon containing Pt, Pd, Ag.

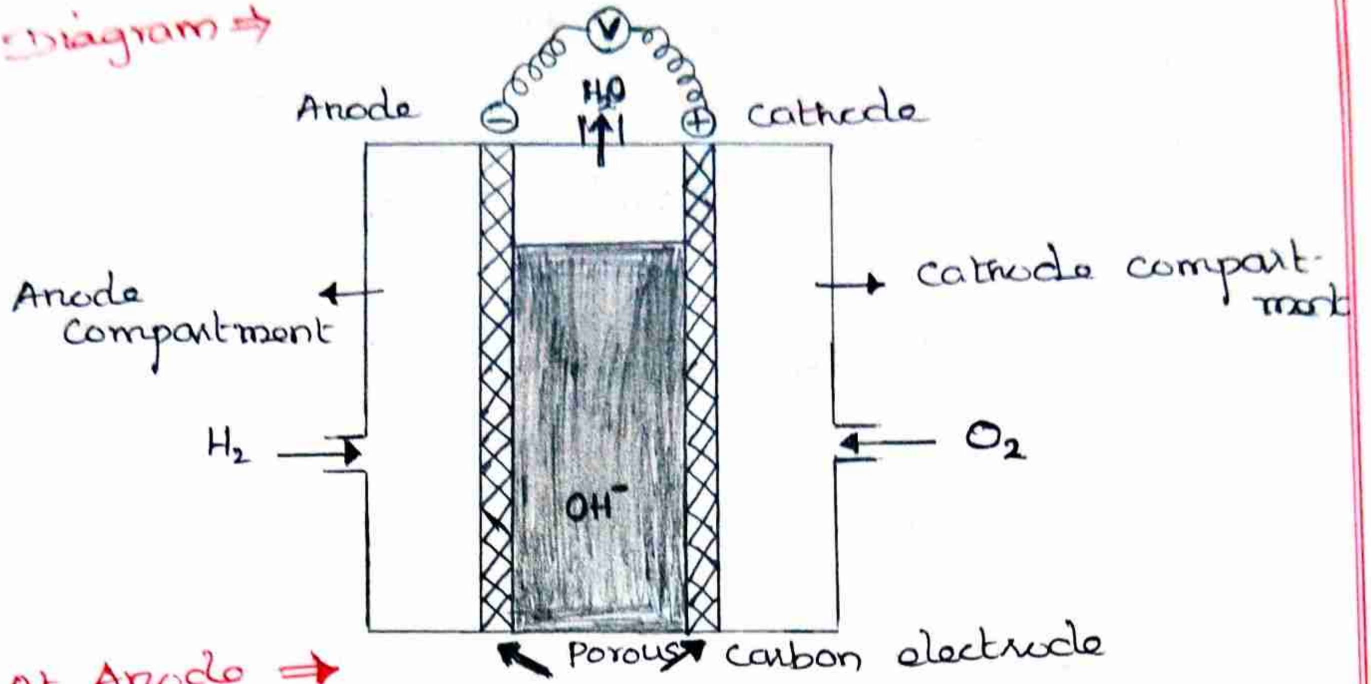
* Electrolyte - 25% KOH / NaOH

* Emf - 0.8 - 1V

working ⇒ * H_2 is bubbled through the anode compartment where it is oxidised

* oxygen is bubbled through the cathode compartment where it is reduced.

Diagram ⇒



At Anode ⇒

$2H_2 \rightarrow 4H^+ + 4e^-$

$4H^+ + 4OH^- \rightarrow 4H_2O$

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

At cathode ⇒

$O_2 + 4e^- \rightarrow 2O^{2-}$

$2O^{2-} + 2H_2O \rightarrow 4OH^-$

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

Over all cell reaction ⇒

At Anode ⇒ $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

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

$2H_2 + O_2 \rightarrow 2H_2O + 8.$

Advantages ⇒ * Pollution free * produces current & water.

Disadvantages ⇒

* costly electrodes * storage & handling of H_2 gas is dangerous * cannot store electric energy as other cells do.

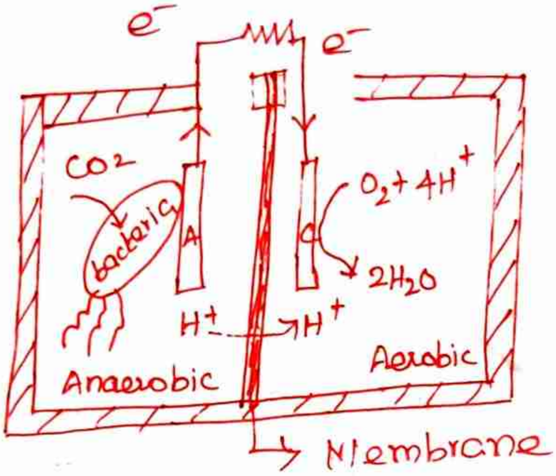
Uses ⇒ * Auxiliary energy source in space vehicles, submarines, military vehicles.

* The oxidation product (H_2O) is proved to be a valuable fresh water, by the astronauts.

Microbial Fuel cells (MFCs)

* Device - converts chemical energy to electrical energy by the action of micro-organism under anaerobic conditions

* Bio electricity is generated by the oxidation of organic waste and renewable biomass using bacteria.



Principle ⇒

* MFC's - Electrochemical cell using bioanode or bio-cathode

* Membrane separates the anode & cathode compartment.

* The e^-s produced during combustion oxidation are directly transferred to the cathode.

* The charge balance is maintained by the ionic movement inside the cell

* Organic electron donors that is oxidized to produce CO_2, protons & electrons.

* The cathode reaction uses O_2 as electron acceptor.

Components ⇒

* Anode compartment ↓ Microbes suspended under anaerobic conditions
* cathode compartment ↓ Electron acceptor (O_2)

Permeable membrane ⇒

* The compartments are separated by permeable cation-specific membrane.

working ⇒

* If electrodes are connected, anode oxidation takesplace on organic waste & electrons released from the process are transferred to the anode.
* From the anode these electrons are directed to the cathode across an external circuit.
* For every electron, a proton is transported across the membrane to the cathode.
* At last, oxygen present at the cathode recombines with hydrogen & electron to produce water.

Electric vehicles

* The vehicles powered by electric power is called electric vehicles.

* Also referred to as battery electric vehicles.

* Instead of an IC engine, electric motor is used.

* No exhaust gases * Low running cost.

working principle ⇒

* By plugging into a charge point and taking electricity

* Store electricity in rechargeable battery
* Feel lighter to drive
* Faster than traditional fuel engine.

Step 1 ⇒

* Controller takes & regulates electrical energy from

Step 2 ⇒

* Then the inverter sends electrical energy to the motor.

Step 3 ⇒

* Motor → electrical energy into mechanical energy

Step IV ⇒

* Rotation of the motor - vehicle moves

Step V ⇒

* When the brakes are pressed, the motor becomes an alternator & produces power → sent back to the battery.

Components ⇒

* Battery - Gives electricity to pow the vehicle.

* Charge point - To connect the vehicle to an external power supply

* DC converter - High voltage DC power → Low voltage DC power.

* Electric motor - Drives the vehicle's wheels

* Onboard charger - AC electricity to DC - To charge the battery

* Power electronics controller - Controls flow of electrical energy from battery to motor.

* Thermal system - To maintain the proper operating temperature range

* Transmission - Transfer mechanical power from the motor to drive the wheels.

Plug-in electric vehicles ⇒ Any vehicle that can be recharged from any external source of electricity such as wall sockets, rechargeable battery packs are called plug-in electric vehicles.

Types ⇒

* Battery electric vehicles / pure electric vehicles / fully electric vehicles

* Hybrid type vehicles
1) Hybrid electric vehicle
2) Plug-in Hybrid Electric vehicle

Battery Electric vehicle ⇒

* vehicles powered by battery * charged by plugging the vehicle into the charging equipment.

* Driving ranges from 150 - 300 miles.

* Not having Internal combustion Engine.

Hybrid type vehicle ⇒

1. Hybrid Electric vehicle (HEV)

* Internal combustion engine & an electric motor

* ICE - gets energy from fuel & motor gets electricity from batteries.

* The gasoline engine & electric motor simultaneously rotate the transmission which drives the wheels

* Batteries in HEC - only charged by ICE

2. Plug-in Hybrid Electric vehicle (PHEV)

* Powered by gasoline & rechargeable battery pack. * charged up with electricity * Also recharged by ICE

* It operates on electricity until their battery pack is depleted.

* Once the battery is empty, the engine takes over & the vehicle operates as a conventional non-plug in hybrid vehicle (gasoline)

Fuel cell Electric vehicles ⇒

* chemical energy → Directly electrical energy * It generates electricity on the vehicle itself.

Advantages ⇒

* Reduces emission * Energy efficient
* High performance & low maintenance
* Fuelled for very low price * Easy to recharge.

Disadvantages ⇒

* Travel only less distance * Long time to echarge * More expensive & battery packs may eed to be replaced. * Initial investment is high.

* Fuelling station still in the developing stage

Applications⇒

- River & deep water environments where it is difficult to use batteries.
- Carbon rich waste water converted into methane gas
- Used as convenient biosensor for waste water streams.
- Used in space, especially to operate remotely operated vehicles.

Super capacitor

- An electronic device - store large amount of electric charge. They store 10-100 times more energy per unit volume and deliver charge much faster than batteries.
- They use electrostatic double-layer capacitance

Design of super capacitor⇒

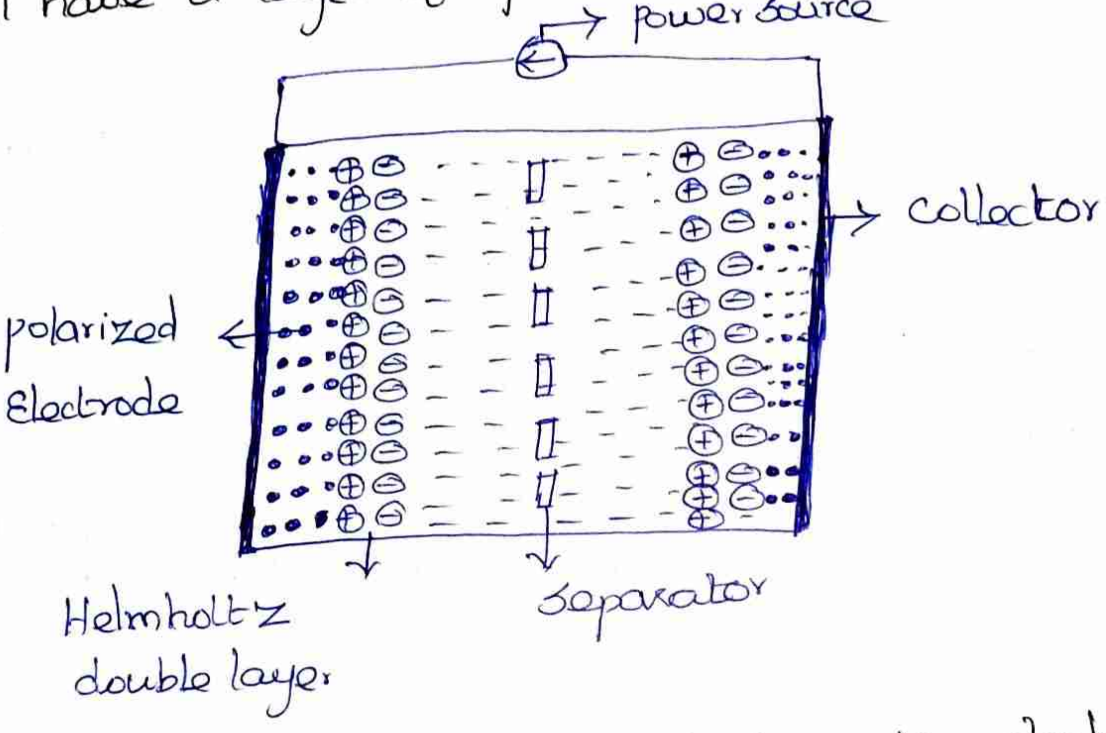
- Two electrodes - made from metal coated with a porous substance - powdery activated carbon
- Electrodes are separated by an ion-permeable membrane & dipped in an electrolyte
- Electrolyte connecting both the electrodes

Working ⇒

* When the electrodes are connected to the power source, ions in the electrolyte form electric double layers (Helmholtz electrical double layer).

* For example, positively polarized electrodes will have a layer of negative ions at the electrode electrolyte interface.

* Similarly, ~~positively~~ negatively polarized electrodes will have a layer of positive ions.



* This electric field polarizes the dielectric, so its molecules lineup in the opposite direction & reduce its strength.

* It means that it stores more electrical energy at an electrode-electrolyte interface.

Recent developments in solar cell materials

* A typical solar cell consists of semiconducting materials such as p and n-type silicon.

* In order to achieve maximum solar to electricity efficiency, innovative solar energy materials at low cost, are being used.

Types of highly investigated solar cell materials ⇒

* crystalline si * Thin films * solar paints
* Transparent solar windows * Thermoradiative PV devices * solar distillation

1. crystalline silicon (c-si)

* Most used semiconducting material in solar panels
* Efficiency - only 30%
* Example ⇒ III-V multijunction materials
* Hybrid tandem III-V/si solar cells
* six-junction III-V solar cells under concentrated light
* si-based bifacial technology

2. Thin films

* Due to their narrow design, second generation thin-film solar cells are growing as one of

mint)

the most promising PV technologies.

* Thin films are 350 times smaller light absorbing layers compared to standard Si-panels.

Examples ⇒

- * Cadmium-telluride (Cd-Te)
- * Amorphous silicon
- * Gallium-arsenide (GaAs)
- * Copper-Indium-Gallium-selenide (CIGS)

↓

More effecient

3. Perovskite Solar cells

* Hybrid metal halide perovskite solar cells (PSC's) play an important role due to their low price, thinner design, low temperature processing and excellent light absorption properties.

Examples ⇒

* combined perovskite & Si-PV materials shows a record efficiency upto 28%.

4. Solar paints ⇒

* They can be coated over the polymer films

Examples ⇒

* Solar paint hydrogen generates energy from Photovoltaic water splitting

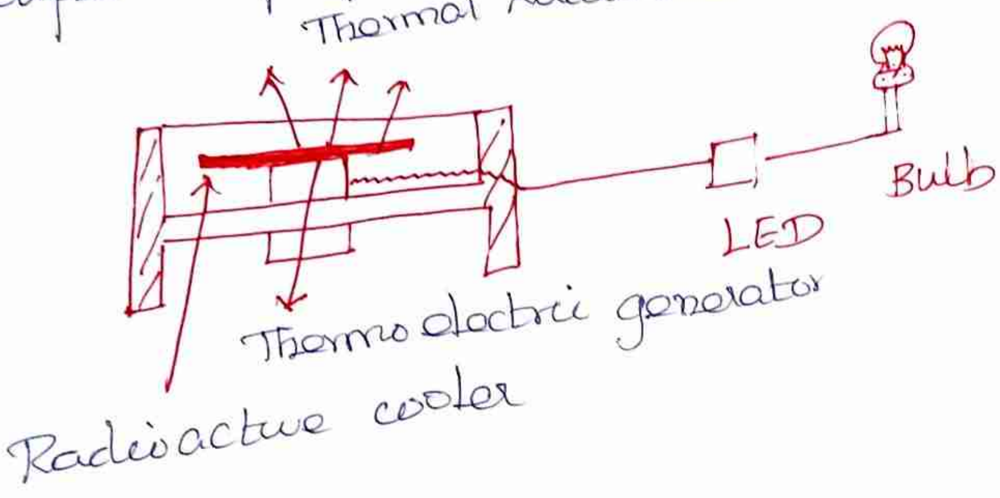
- Quantum dots (Photovoltaic paint)
- perovskite - based paints

5. Transparent solar windows

- They have highly innovative applications
- Their solar to electricity conversion efficiency is 10% more.

6. Thermoradiative PV devices (or) Reverse solar panel

- Generate electricity at night by using the heat irradiated from the panels to the optically coupled deep space, which acts as a heat sink.



7. Solar distillation

- It can harvest solar energy while using the dissipated heat from panels to purify water
- An integrated membrane distillation is also attached.