

UNIT - 3

CEMENT

QUESTION	ANSWER

Any substance which acts as a binding agent for materials is called cement. Cement is a fine grey powder which has a very desirable adhering property and is used for construction purpose.

Classification of Cement :-

- ① Natural Cement:- The cement which is produced by calcining and pulverizing natural cement rocks consisting of argillaceous or clay and limestone, is known as natural cement. They do not impart sufficient strength, but they are cheaper.
- ② Pozzolana Cement:- Pozzolanic cement is the most ancient of the manufactured cements. It was first made from volcanic ash from mount Vesuvius situated around a place called Pozzoli in Italy. Volcanic ash consisting of oxides of calcium, iron and aluminium, when mixed with lime and heated, produces pozzolanic cement.
- (3) Slag Cement :- It is prepared from blast furnace slag and hydrated lime. It is then dried and finely pulverized. Slag cements are slow to harden, so an accelerator like clay, salt or caustic soda is sometimes added. They have lower strength.

- by calcining together limestone and calcareous raw materials.
- ④ Portland cement:- It is most important and valuable cementing material, used for constructional work. It was named because paste of cement will set water on setting and hardening resembles in colour and hardness to portland stone, a lime stone quarried in Dorset.

* Manufacture of Portland Cement:

Raw material for cement manufacture -
Following are the required for the manufacture of portland cement:-

- 1) Calcareous materials - This material supplies lime. The following kind of calcareous materials are:
 - (i) Lime stone (contains 65-80% CaCO_3) (ii) chalk,
 - (iii) Shale (iv) calcite etc.

Lime is the main constituent of cement. The properties of the lime should be properly maintained, because it makes the cement to expand and disintegrate.

- 2) Argillaceous materials: These materials supplies silica, iron oxide and alumina. The argillaceous material used are: (i) clay (ii) marl (iii) sand (iv) shale (v) blast furnace slag etc.

- Silica (SiO_2) - Imparts strength to cement
- Iron oxide - provide grey color strength and hardness

- Sulphur trioxide :- (in small amount) provide soundness and strength of to the cement
- Powdered Coal.
- Gypsum - ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to retard retard the setting action while transportation. In fact enhances the setting time of cement.

* Percentage composition of main constituents:-

Lime CaO = 60 to 67%	Sulphur trioxide SO_3 = 1-2%
Silica SiO_2 = 15 to 25%	Soda and Potash ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) = 0.5 - 1.31%
Alumina Al_2O_3 = 3 to 5%	
Fe_2O_3 = 0.5 to 6%	Magnesia MgO = 0.1 to 4%

* Manufacturing Process:-

The actual manufacturing process involve the following steps:-

- (i) Crushing , (ii) mixing , (iii) Burning , (iv) Grinding
(v) Packaging

These are two methods of manufacture of cement:-

- (1) Dry Process
- (2) Wet Process.

- (1) Dry Process: Dry process is quite similar to wet process with the only difference that no water is added to the material in grinding and thus no slurry is made. The process has advantage of low fuel cost.

- (2) Wet Process: The wet process is quite common and is universally employed for the manufacture of

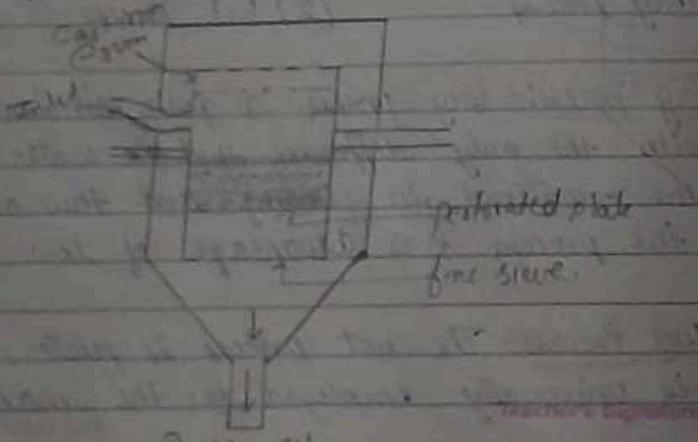
The muddy mixture formed after grinding
in presence of water is known as slurry.

portland cement. The process involves following steps-

- (i) **Crushing**- Raw material will be crushed by crushers, which reduces the size of raw material to an approximately $\frac{3}{4}$ inches.
- (ii) **Grinding**- The grinding of raw materials to be carried out in two stages. First by ball mills and then by tube mills. Material from ball mill to the tube mill is conveyed by means of screw conveyors. The material is mixed with 30-40% water before grinding.

(a) Ball Mill grinding-

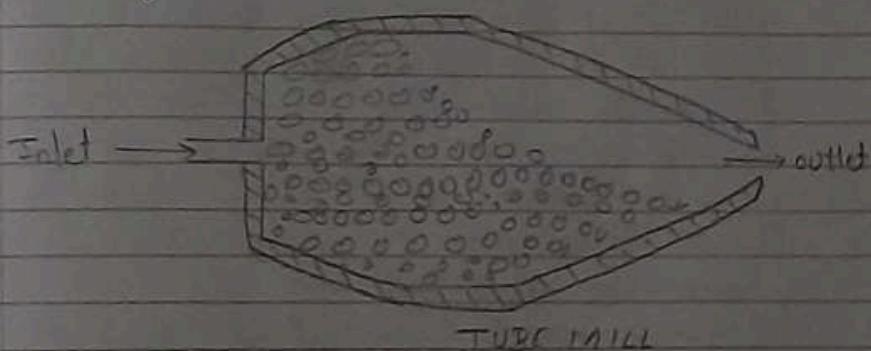
It consists of cast iron drums containing iron or steel balls of different sizes. Out passes through the perforated plate and falls on the fine sieve. The coarse particles are retained by the screen and return to the interior of the drum through an opening.



- The principle used in this mill is impact and shear produced by sliding tumbling and rolling of a large number of steel or flint balls or pebbles.

(b) Tube Mill grinding

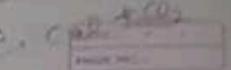
The tube mill is just like a ball mill but has a different shape. It is conical at the discharge end. In principle the tube mill is the same but it continually operates. On one side material is fed and from the other end the material comes out. The size of grinding depends upon the speed of feeding. After the grinding material passes through 1000 mesh sieve. The finer the particle the better is the quality of cement produced as the reacting particles when finer have got large surface area of contact.



(iii) storage of ground materials:-

The ground material containing 30-40% of water are stored in separate tanks equipped with agitators.

for - Raw material with plenty of water that mixture is known as slurry



mixture melts and forms little rounded pasty masses called as clinkers.



(ii) Correction tank:- when correction tank is full, a sample of material is taken out for analysis. If the slurry is not of the required composition, it is corrected by adding more of deficient raw materials.

(iv) Burning:- The slurry is transferred to rotary kiln where burning of raw materials take place and actual chemical changes take place.

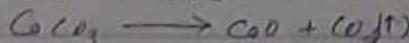
i) There are two types of kiln
1) Rotatory kiln 2) Vertical shaft kiln (Vsk)

ii) Rotatory kiln:

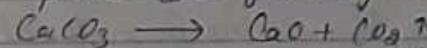
Rotatory kiln line
in (indirect injection
method)

(a) Drying zone:- Here the temperature is moderate ($100-500^{\circ}C$). This zone is known as drying zone because in this zone water is driven out of the slurry by means of hot gases.

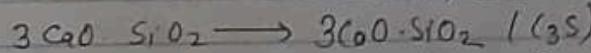
(b) Calcination zone:- Its temperature is about $1000^{\circ}C$ and it is the middle portion of the kiln here organic matter burns away. $CaCO_3$ decomposes into a Ca & CO_2 .



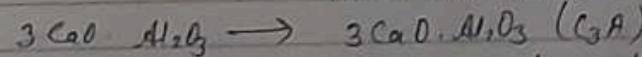
(c) Burning zone:- In this part temp is about $1400^{\circ}C$ - $1500^{\circ}C$. In this zone, mixture melts and forms little rounded pasty masses about the size of peas which are called Clinkers. Clinkers are greenish or black in colour. The main reactions taking place are following:-



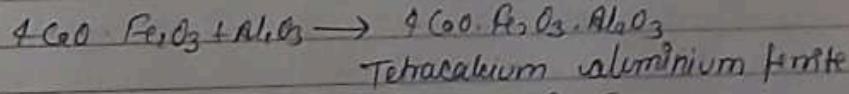
Dicalcium silicate



Tri calcium silicate



Tricalcium aluminate



Tetracalcium aluminium ferrite

Let, $C = CaO$, $A = Al_2O_3$, $F = Fe_2O_3$, $S = SiO_2$

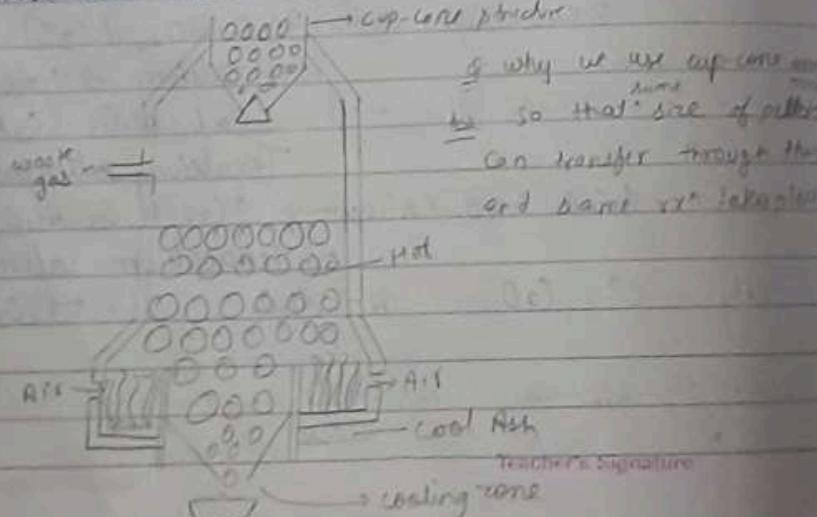
refractory bricks generally used for a number of reasons at any time.

The rotatory kiln is a long steel cylinder with length of 30-60 m and diameter 2-4 m. The kiln is slightly inclined downward towards the exit end. It can be rotated at a desired speed as it is mounted on rollers.

2) Vertical shaft kiln (V.S.K):

- It is used in mini scale plant.
 - Large chimney like tower lined with refractory bricks which is 35-75 ft in height and 10-12 ft in diameter.
 - There are two methods of preparation of pellets.
- (a) Black Meal Process: raw material + coal → grinding
→ +15% H_2O → pellets

- (b) Fuel Slurry Process: raw material are dry ground separately and coal is ground wet separately. These are then mixed into pellets.



Kiln can be divided into four zones:-

- Preheating (drying) zone
- Calcination zone
- Finishing / Burning zone
- Cooling zone - where clinkers are collected

* Advantages :-

- It utilizes pellets so no dust discharge into the atmosphere.
- Low melting constituents are not formed so no problem of clinker clogging to refractory lining.
- The plant is quite compact, so work on heat reuse.

Chemistry of Portland Cement:

The main composition of Portland cement is -

- (i) Tricalcium silicate (C_3S) - 45% responsible for developing ^{high} strength and rapid hardening. Strength Rate of hydration (ROH) = medium; setting time (ST) \approx 7 days.
Setting time: how much time is required by a particular composition for setting.

- (ii) Dicalcium silicate (C_2S) - 25% responsible for progressive increase in strength.
ROH = slower, ST = 28 days

- (iii) Tricalcium aluminate (C_3A) - 10% doesn't contribute in strength and resistance to chemical

attack cause initial stiffening and cracks due to volume changes so the lower form of C3A is preferred fast - quick fast - ST - 1 day

- (iv) Tetracalcium Aluminoferrite (C_4AFe) - It 10% it inactive does not contribute in strength.
RDS: slow, ST - 7 days
- Free lime + CaO , MgO , $CaSO_4$ no effect

Setting And Hardening of Portland Cement:

- when cement is mixed with water, hydration begins which results in gel and crystal product formation - Interlocking of the crystals binds the particles into a compact rock like material. The process of solidification involves:

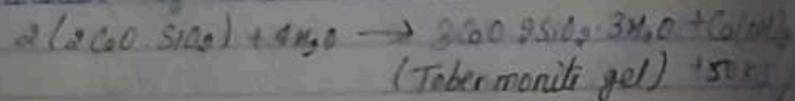
 - 1) Initial setting 2) Final setting 3) Hardening

Setting is just stiffening of the original cement paste while hardening is development of strength and toughness.

- 1) Initial setting - It is mainly due to the hydration of C_A (Tricalcium aluminate)



It's reaction is completed within 7 days
Hydration of dicalcium silicate

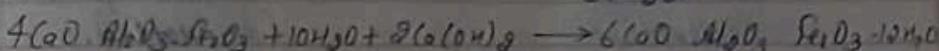
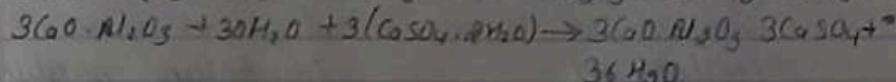
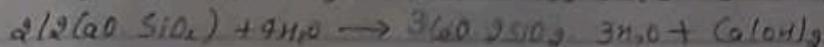
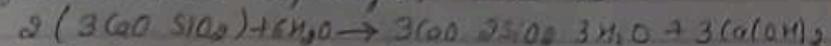


- Q: why we use Tobemanite gel?

- A: because -> (i) it has good adhesive property
(ii) it has very high surface area

(iii) Final setting: It takes place after few hours of mixing. After this mixture can't be moulded into any shape and mass attains stiffness

(iv) Hardening: After final setting of the solid cement material begins to gain strength. It depends on chemical composition combination of cement and water. The process of hardening continues with a great speed in the beginning afterwards speed is reduced and after dryness of cement it stops setting and hardening involves hydration and hydrolysis. These are -



Factors Affecting the rate of setting & hardening:

Gypsum is used as the retarder and is added at the mill before final grinding of the product. It has been found that 2% gypsum provides the most effective retarding action. The initial set of portland cement should be b/w 45 minutes and 10 hours.

When the small particles of cement are mixed with water, they tend to form a layer of hydro-

and gel. In order to continue the reaction, water must diffuse or migrate through the everthickening of coating. Thus, the hardening of concrete is dependent upon both physical (diffusion) and chemical (hydration) processes which are speeded by a rise in temperature.

Physical changes occurring in setting, hardening, and ageing of cement can be shown as -

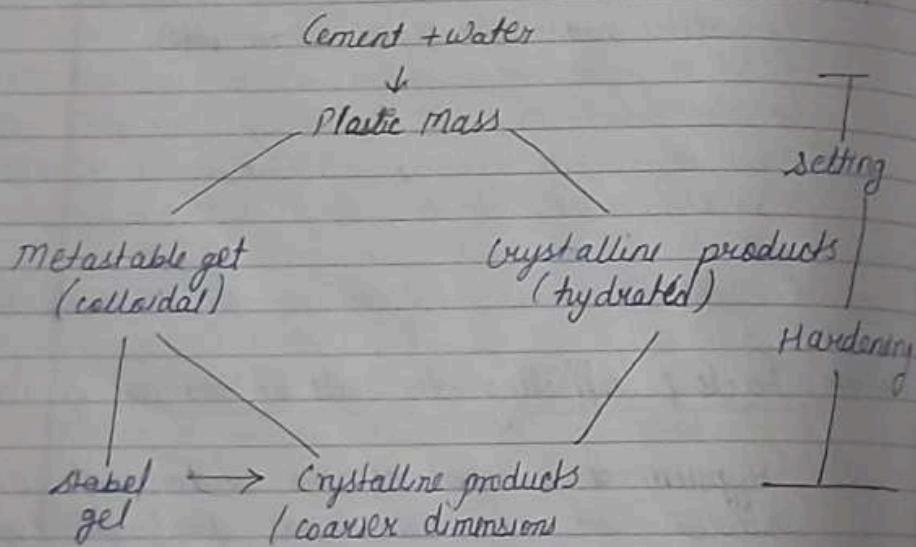
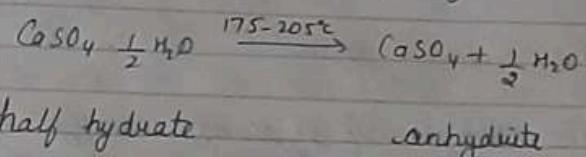
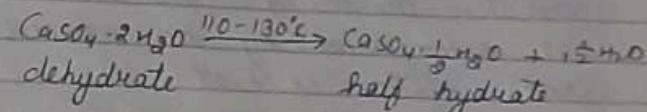


Fig: Schematic diagram of setting and hardening of cement.

Gypsum and Gypsum Products (Plaster of Paris):

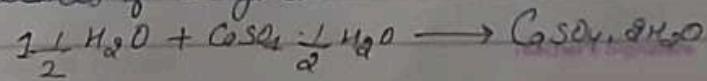
The raw material used for manufacture of plaster of paris ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) is a stony mineral known as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The dehydration of gypsum is a two-stage process.



The half hydrate is quite stable and is packaged in bags for use as an ingredient of plaster. The anhydrite tends to absorb water rapidly and gets converted to the half hydrate. If the anhydrite is overheated during calcining, it tends to become inert and lose its ability to harden.

* Hardening of gypsum:-

Gypsum is a peculiar substance in that the hydrate is less soluble in water than the half-hydrate. Thus, if the half-hydrate is mixed with water, it slowly reacts and precipitates needles of dehydrate.



Refractories

A number of factors affect the rate of initial mass of gypsum stiffening or setting of gypsum. For example, use of warm water (i.e. raising the temperature of plastic mass) sets it quickly without retarders. Setting occurs in about 10 minutes. The setting and hardening of gypsum are accompanied by an increase in volume and evolution of heat.

Properties of gypsum:-

The strength of gypsum usually varies between 50 and 150 kg/cm² although higher strengths are possible.

Gypsum is a good fire-resistant material having good insulating properties and thus it retards fire damage to wooden and steel framing when exposed to fire. The insulating properties of gypsum are impaired by loss of water of hydration.

* Definition:-

These are specially designed materials capable to withstand at extremely high temperature without being destroyed because of their high melting point. Refractory's retain their chemical and physical properties at the elevated (high) temperature.

* Classification of refractories:-

1. On the basis of fusion (melting) temp:
 - (i) Lower temp' refract (1600 - 1800°C) - Fire clay (to 1600°C)
 - (ii) High temp' refract (1800 - 2000°C) - Chromites
 - (iii) Super refract (2000°C to above) - Zircon

2. On the basis of chemical composition:-

- (i) Acid refractory:-
 - Made up of acidic oxides like SiO_2 and Al_2O_3
 - Easily attacked by basic substances e.g. silica & alumina that's why we can't use basic substances in acidic refractory.

(ii) Basic refractories-

- Made up of basic oxides like MgO , CaO
 - easily attacked by acidic substances e.g. Calcite (CaCO_3) that's why we can't use acidic substances in basic refractory

(3) On the basis of oxide content:-

- single oxide refractory - alumina, magnesia, zirconia
- mixed oxide refractory - zircon (ZrO_2), chrome (Cr_2O_3), FeO
- non oxide refractory - Borides, Carbides (SiC)

Properties of Refractories- (in shape)

- ① Refractoriness: It is the ability of a material to resist the high temp^r and heat without appreciable deformation or softening. It is measured as melting temp^r of material or softening temp^r of material.
- Higher the softening temp^r more valuable the refractory.
 - Pyrometric cones - refractory specimen of standard dimension (38 mm height and 19 mm triangular base) and composition.
- ## We made it in cone shape because if it melts then it is visible but in brick shape it doesn't visible. Thus, we made pyrometric cones in cone shape.



⇒ Pyrometric cones

• Measurement of Refractoriness:-

Pyrometric Cone equivalent (PCE) / Sugar cones

It is expressed in a relative measure called PCE. The test refractory in the form of a cone is kept alongside similar sized standard cones (sugar cones) and all are heated with uniform rate. The standard cones are assigned serial no. with increasing softening temperature. When the cone softens and destroys one of the standard cone refractory is also softer. The serial no. of the std. cone is noted and this no. is PCE of the test cone. For eg. silica refract has a PCE of 33 with the temp^r range of 1700-1750°C, which indicates that the silica refract can be used with operating temp^r 1700°C.

② Thermal expansion and contraction (Dimensional stability):

This is the effect of temp^r on size.

Expansion on heating decreases the furnace capacity. Repeated expansion and contraction may lead to wear and tear as well as breakage of the refractory material.

• Hence a good refractory material should have least possible thermal expansion & contraction.

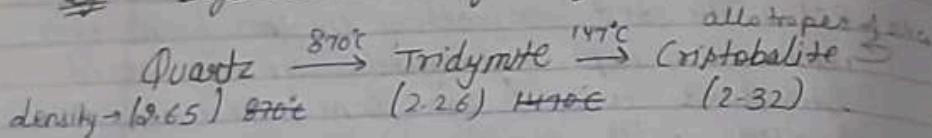
-:- Permanent expansion leads to transformation of one crystalline form to another low

Amorphous \rightarrow powdered form

$$[+ (\gamma) = v(\gamma)]$$

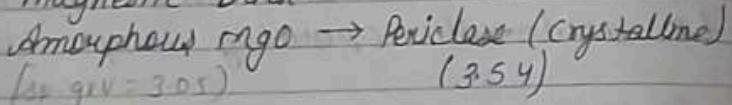
density form.

e.g. Crystalline transform of silica.



-/- Permanent Contraction:- Due to high temperature for long duration loss of fusible constituents & refract melt forms liquid which fills the pores of the refract body causing shrinkage or transformation of one crystalline form to another more dense form can also takes place.

e.g. Magnesite brick.



③ Load bearing Strength / Refractoriness Under Load (RUL):- (load bearing capacity at 1000°C temp.)

It is the resistance to compressive loads tension and shear stresses under high temperature. The refractory bricks must possess high mechanical strength.

- This is capacity of a refractory to bear the minimum possible load, without breaking or deforming. RUL is - H
- RUL is the temp. at which the deformation begins and at which at least 10% deformation sets in. Refractor

fire clay refractories \rightarrow mixed type insulation

$\text{Al}_2\text{O}_3 \text{, } \text{SiO}_2$

It is better than silica refractories b/c it has no thermal expansion coefficient.

Tunnel ovens

ness under load can be determined in two ways:-

- Rising Temp. test:- Here a load of 2 kg/cm² is applied and then temperature is raised to 1000°C at the rate of 150 per minute and then at the rate of 80°C per minute. The point of collapse is observed and curve for temp. against height of cone is drawn.
- Maintained Temp. Test:- In this test the amount of deformity is recorded at a constant temp. in a given time.
 - In this temp. & load are interdependent. If we increases the load then temp. is decreased to refractory can break.

④ Porosity:- porosity of a material is defined as the ratio of its pores volume to bulk volume.

- It decreases the strength.
- decreases the resistances to thermal shocks.
- Less porous porous refractory have the highest thermal conductivity.

⑤ Spalling resistance:- The breaking, cracking, peeling off or fracturing of a refractory bricks under high temp is known as spalling. Thermal spalling results from the

Glass

- * Definition: Glass is a fused mixture of silicates of sodium (monovalent cation) and calcium (divalent cation) which is a amorphous, hard, brittle, Transparent or translucent super cooled liquid having very high viscosity.
- * It has no sharp melting point due to its amorphous solid nature. When it is heated it gradually softens and can be moulded in any desired shape and a no. of articles can be made.

A glass may be represented as $mM_2O \cdot nNO \cdot 6SiO_2$ where m is monovalent alkali metal & n is bivalent metal and x or y are whole nos.
soda-lime glass $Na_2O \cdot CaO \cdot 6SiO_2$

Properties of Glass:

Physical Properties:

- * It is an amorphous non-crystalline transparent and water insoluble.
- * It is hard and has ^{no} sharp M.P
- * It is very brittle and cracks in an irregular fashion by mechanical jerks
- * It is insulator of heat and electricity.
- * Glass is highly sensitive to thermal shock. A glass article cut once cracks when heated suddenly or cooled from a hot state.
- * It can incorporate colouring material preserving transparency.

where the no. B pores are less
where the no. C pores are more
single or multi layered refractory nature
and (Silica refractory) 1700-1750
and (fire-clay refractory) low to medium

- uneven expansion or contraction in the refractory bricks due to rapid changes in temp.
- Spalling resistance order for some of the refractories is:

resistance for silica brick

silica carbide > fireclay bricks > magnesite
> silica bricks

④ Thermal Conductivity:- Refractoriness of low thermal conductivity reduce the heat loss while in some cases high thermal conductivity is desirable for effective heat transmission. (Eg: coke-oven batteries)
(Externally heated coke ovens)

Thermal conductivity (λ) = heat loss (W) / (internally)
electrical conductivity (always low for all substances)
Chemical characteristics (exception graphite)
Texture (refractory structure)
Permeability
Heat Capacity

→ It should be high for a good quality of a refractory

the material can pass through one another.

→ Permeability to air/burner resistance should be high.

→ no separation of crystalline products

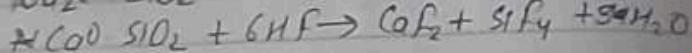
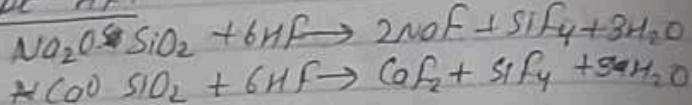
- Glass is vitrified product.
• "when glass is softened by heating and is kept as such for a long time, it appears to lose its transparency on account of the crystallization of the individual silicates. The phenomenon is called devitrification of glass." → transparency decreases

⇒ Chemical properties:-

ordinary glass is alkaline.

not attacked by oxidizing agents & water.

Readily attacked by alkalis, not by acids except HF.



When glass is fused it decomposes into alkali silicates and carbonate. If the resulting mass is cooled and treated with dil. HCl, silicic acid as well as chlorides of metals is formed.

Manufacturing of Glass:-

Raw materials:-

1) Silica (SiO_2):- silica is normally added as

fine particles of quartz or white silica. It should be free from impurities (like iron oxide, which acts as colouring agent).

2) Compounds of alkali metals:-

- Na_2O_3 (soda ash), NaNO_3 , Na_2SO_4 as a source of Na_2O to prepare soft glass.
- K_2O or NaNO_3 or potash feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}_2\text{O}_3$) used to glaze

6. modifiers-

7. Melting and refining agents:- These are used to promote refining for removal of gas bubble from the glass. e.g. Na_2SO_4 , Na_2SO_3 , NaCl , Arsenic oxide, CaF_2 .

8. Colouring and decolorising Agents-

Cr_2O_3 - green

CaO - Blue

V_2O_5 - Yellow green

CuO - Red. Fe_2O_3 - Brown

Decolorising agent - Se, Cerium oxide, neodymium oxide.

9. Opalising agents: They permit separation of crystals or droplets in the glass during working and given an opalescent appearance.
e.g.: - fluorides & calcium phosphate.

10. Cullet:- crushed glass from defective article.
It makes the melting easy.

Manufacturing steps:-

1. Melting of Raw materials: The raw materials are ground and mixed resulting homogenous mixture is known as "batch". It is carried out in furnaces. Glass furnaces are of two types -

(i) Pot furnace

recuperation

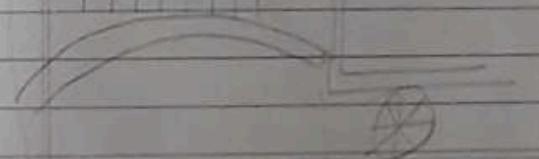
(ii) Tank furnace

regenerative

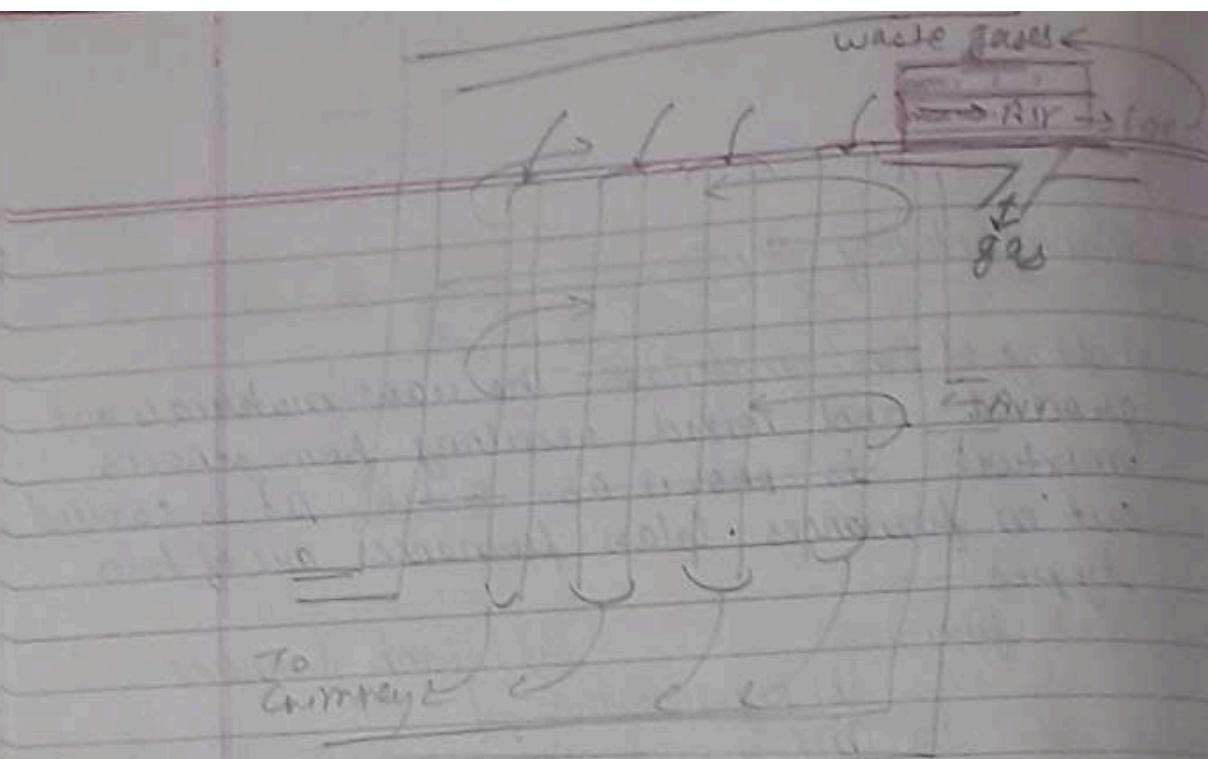
(a) Regeneration:- Utilization of the heat of waste gases for heating the incoming fuel gas and air for producing greater intensity flame (we use a checker box flame)

(b) Recuperation:- The incoming gases flow continuously in one direction only. (separate bellows are used)

checker box



Regenerator



Process of chemical Rxn for preparation of soft (soda glass).

- Below 700°C : Moisture and oxides of As, Sb, Pb and chlorides of Na, K

Acids and Bases

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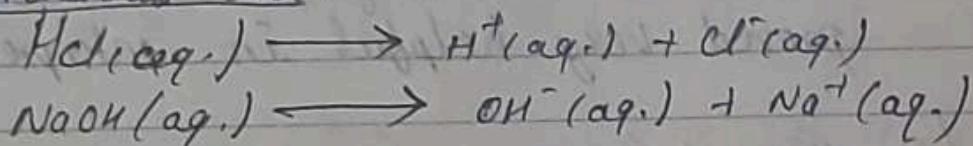
There are three concepts of acids and bases in current use. These three concepts are as follows-

- (a) Arrhenius Concept
- (b) Bronsted-Lowry Concept
- (c) Lewis concept.

(a) Arrhenius concept:-

According to this concept, an acid is a compound that releases H^+ ions in water, and a base is a compound that releases OH^- ions in water.

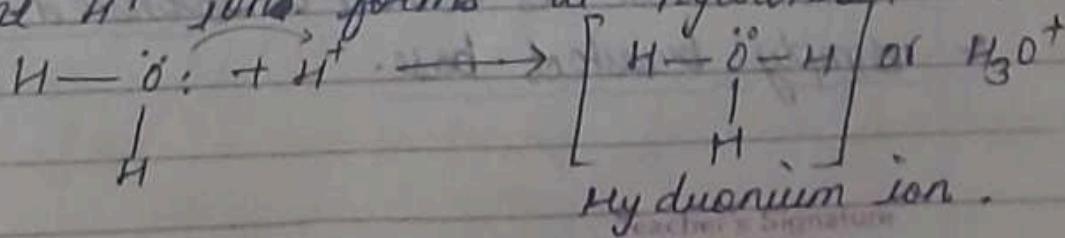
For example, HCl is an Arrhenius acid and NaOH is an Arrhenius base.



Limitations of Arrhenius Concept:-

It has the following limitations:-

- (i) Free H^+ and OH^- ions do not exist in water - The H^+ and OH^- ions produced by acids and bases respectively do not exist in water in the free state. They are associated with water molecules to form simple ions through hydrogen bonding. Thus the H^+ ions forms a hydronium ion.



Similarly, OH^- ion forms the complex H_3O_2^- .

- (i) Limited to water only - Arrhenius defined acids and bases as complex compounds producing H^+ and OH^- ions in water only. But a truly general concept of acids and bases should be appropriate to other solvents as well.
- (ii) Some bases do not contain OH^- . Arrhenius base is one that produces OH^- ions in water. Yet there are compounds like NH_3 and CO that are bases but contains no OH^- in their original formulation.
- Arrhenius model of acids and bases, no doubt, proved very helpful in interpreting their actions.

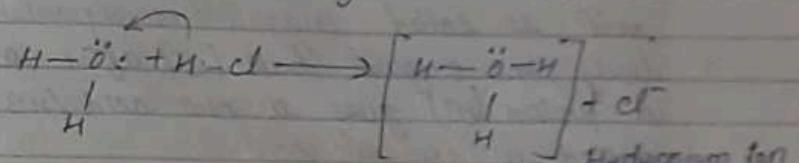
(B) Bronsted-Lowry Concept:

According to the theory, an acid is any molecule or ion that can donate a proton (H^+) & a base is any molecule or ion that can accept a proton. So that we can say that an acid is a proton donor while a base proton acceptor.

- In acid qualifying Bronsted-Lowry concept is termed as a Bronsted-Lowry acid or simply Bronsted acid and base is termed as Bronsted-Lowry base or simply Bronsted-base.

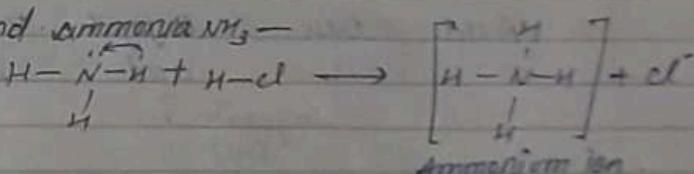
Examples of Bronsted acids and bases:-

- (i) HCl gas + H_2O : when dry HCl gas dissolves in water, each HCl molecule donates a proton to a water molecule to produce hydroxium ion.



HCl is a Bronsted acid and water accepts a proton is a Bronsted base.

- (ii) HCl and ammonia NH_3 :



Ammonium ion

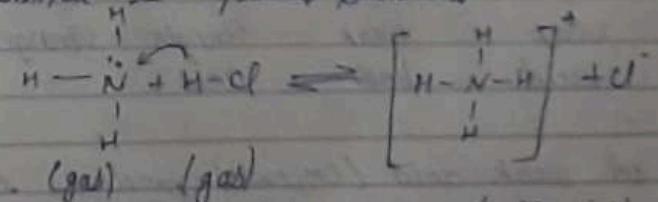
HCl \rightarrow Bronsted Lewis Acid

NH_3 \rightarrow Bronsted Lewis base.

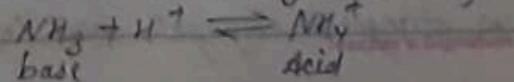
* Bronsted-Lowry concept is superior to Arrhenius Concept:

(i) Much wide scope.

(ii) Not limited to aqueous solutions.



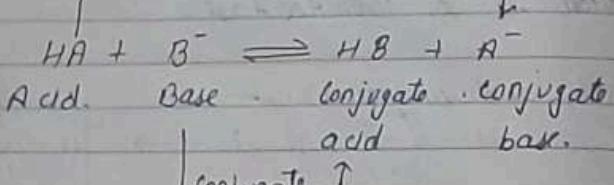
(iii) Release of H_2O not necessary to qualify a base.



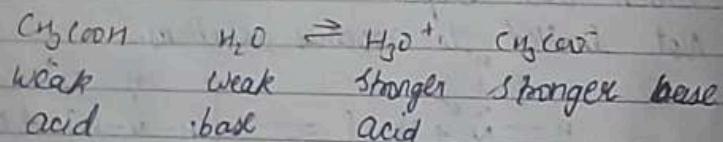
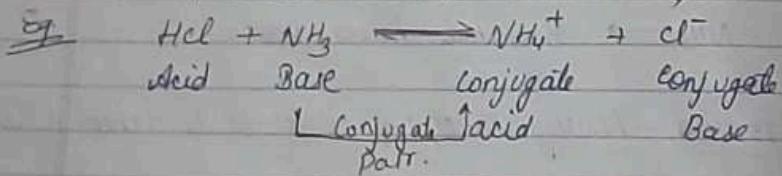
* Conjugate Acid-Base pairs-

In an acid-base rxn the acid (HA) gives up its proton (H^+) and produces a new base (A^-). The new base that is related to the original acid is called conjugate (meaning related) base. Similarly, the original base (B^-) after accepting a proton (H^+) gives a new acid (HB) which is called a conjugate acid.

Conjugate pairs



Conjugate pair ↓



weak acid (CH_3COOH) produces a strong conjugate base (CH_3COO^-); and a weaker base (H_2O) gives a stronger conjugate acid (H_3O^+).

Teacher's Signature

Since we conclude that:

- (a) A weak base has strong conjugate acid.
- (b) A weak acid has strong conjugate base.

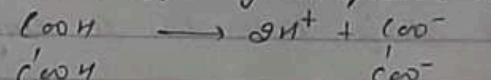
* Cases Classed of Brønsted Acids and Bases-

→ There are variety of Brønsted acids-

- (1) Monoprotic acids- which are capable of donating one proton only e.g;



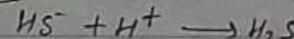
- (2) Polyprotic acid- which are capable of donating two or more protons e.g. H_2SO_4 , H_3PO_4 and carbonic acid (H_2CO_3), hydrosulphuric acid, etc.



Oxalic acid. oxalate ion

→ Similarly, there are Brønsted bases-

- (1) Monoprotic bases- which can accept one proton.



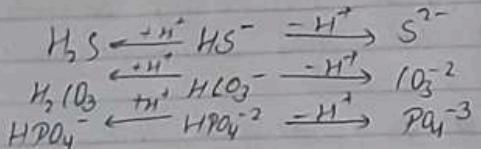
- (2) Polyprotic bases- which can accept two or more H protons.

e.g. anions of diprotic and triprotic acids.



- # Amphiprotic substances- molecules or ions that can behave both as Brønsted acids and bases are called Amphiprotic substances.

Listed below are some Amphotropic ions:-



* Strength of Brønsted Acids and bases:-

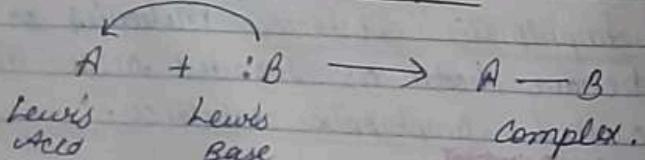
The strength of a Brønsted acid depends upon its tendency to donate a proton. The strength of a Brønsted base depends on its ability for accepting a proton.

A strong acid has a conjugate base & a strong base has a conjugate acid.

(c) Lewis Concept of Acids and Bases:-

According to this theory - an acid is an electron-pair acceptor and a base is an electron-pair donor.

Lewis pictured an acid and base as sharing the electron pair provided by base. This creates a covalent bond (or coordinate bond) b/w the Lewis acid and Lewis base. The resulting combination is called complex.

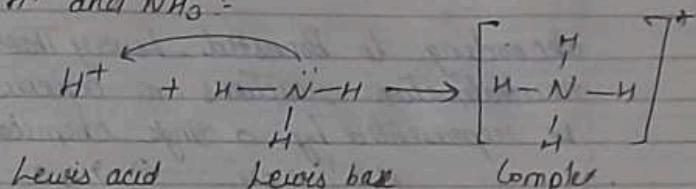


It may be noted that:-

- (i) all cations or molecules short of an electron-pair acts as Lewis acid.
- (ii) all anions or molecules having a lone electron-pair acts as Lewis base.

* Examples of Lewis reaction:-

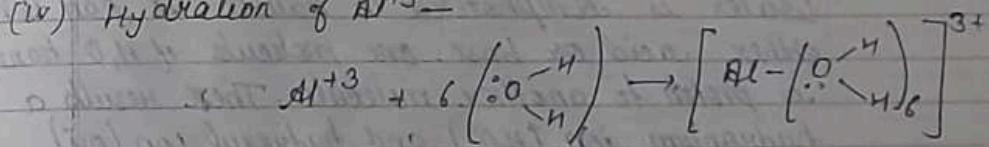
(i) Between H^+ and NH_3 :



(ii) Between H^+ & OH^-

(iii) B/w BF_3^+ and NH_3 .

(iv) Hydration of Al^{3+} -



• Three models for acid and bases

Model	Definition of acid	Definition of base
Arrhenius	H^+ producer	OH^- producer
Bronsted-Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	e-pair donor

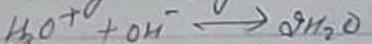
Advantages of Lewis Acid-

- (1) All the Brønsted-Lowry acid-base reactions are covered by the Lewis model.
- (2) Many reactions which do not involve transfer of proton are covered by Lewis theory.



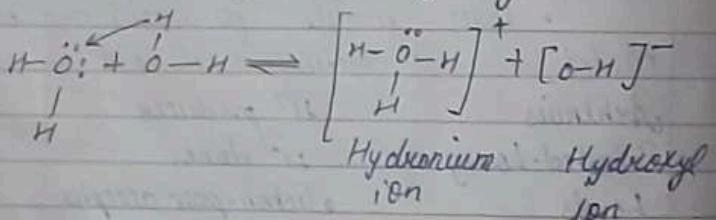
Neutralisation in Brønsted-Lowry Theory -

According to Brønsted-Lowry Theory, all acid-base neutralisation reactions in aqueous solution can be represented by a single chemical rxn -



Water can act both as an acid and a base-

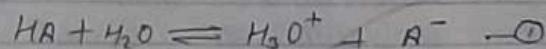
water is amphoteric in nature. It can behave either acid or base. One molecule of H_2O transfers a proton to another molecule. This results a hydronium ion (H_3O^+) and hydroxyl ion (OH^-).



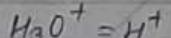
The above reaction in which water molecules interact to produce a hydronium ion and a OH^- ion is called auto-ionisation of water. It may be written as - $2H_2O \rightleftharpoons H_3O^+ + OH^-$.

* Relative Strength of acids -

The strength of an acid depends on its ability to transfer its proton (H^+) to a base to form its conjugate base. When a monoprotic acid (HA) dissolves in water, it transfers its proton to water to form hydronium ion (H_3O^+) and a conjugate base.



for simplifying
we take



thus we can write eq. reaction (1) as -



Applying the law of mass action to the acid dissociation equilibrium we can write -

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a is called acid dissociation constant.

- In dilute solution of the acid (HA) we note that concentration of liquid water remains constant.
- The strength of an acid is defined as the concentration of H^+ ions in its aqueous solution at a given temperature.

Therefore the value of K_a for a particular acid is a measure of its acid strength or acidity.

In any aqueous solution of a strong acid, practically all the original acid (HA) is dissociated and the value of K_a is large. On the other hand, a weak acid in aqueous solution is dissociated to a very small extent and the value of K_a is also small. Thus in general we can say that the value of acid dissociation constant is large for a strong acid while it is small for a weak acid.

* Calculation of Relative strength of weak acids from K_a .

We have seen that for an acid in aqueous solution we have, $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ and $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$.

Let c moles per litre be the concentration of the acid and α its degree of dissociation. Then,

$$[\text{H}^+] = c\alpha$$

$$[\text{A}^-] = c\alpha$$

$$[\text{HA}] = c(1-\alpha)$$

Substituting the values in the equilibrium expression we have - $K_a = \frac{c\alpha \times c\alpha}{c(1-\alpha)}$

$$= \frac{c\alpha^2}{(1-\alpha)}$$

For weak acids $1-\alpha \approx 1$. Therefore,

$$K_a = c\alpha^2$$

For two different acids 1 and 2, let the degree of dissociation be α_1 and α_2 and the dissociation constants k_1 and k_2 then

$$\text{for acid 1. } K_1 = c\alpha_1^2 \quad \text{--- ①}$$

$$\text{for acid 2. } K_2 = c\alpha_2^2 \quad \text{--- ②}$$

① ÷ ②, we get.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{k_1}{k_2}}$$

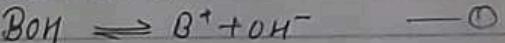
Since $[\text{H}^+]$ is a measure of acid strength and it depends on the degree of dissociation α , we can write.

$$\frac{\text{Strength of acid 1}}{\text{Strength of acid 2}} = \sqrt{\frac{k_1}{k_2}}$$

The ratio of $\sqrt{\frac{k_1}{k_2}}$ would give up the relative strengths of the acids.

Relative strength of bases:-

Let us consider a base BON whose dissociation can be represented as-



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BON}]} \quad \text{--- ②}$$

K_b is called base dissociation constant or base ionisation constant.

The strength of a base is defined as the conc. of OH^- ions in its aqueous soln at a given temp.

- Calculation of k_b

$$k_b = \frac{[\text{B}'][\text{OH}^-]}{[\text{BOH}]}$$

$$[\text{BOH}] = c(1-\alpha) \text{ mol/l}$$

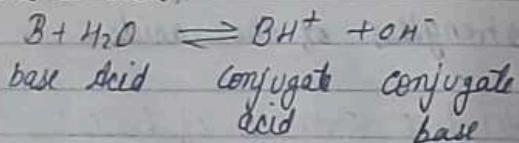
$$[\text{B}'] = c\alpha \text{ mol/l}$$

$$[\text{OH}^-] = c\alpha \text{ mol/l}$$

$$\text{so, } k_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)}$$

$$\left\{ k_b = \frac{\alpha^2 c}{(1-\alpha)} \right\}$$

- k_b for Brønsted bases:-



$$\left[k_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \right]$$

The pH of the solution:-

It is defined as negative of the base -10 log of H^+ concentration. Mathematically it may be expressed as-

$$\text{pH} = -\log [\text{H}^+]$$

where, $[\text{H}^+]$ is the concn of hydrogen ions in mol per lit.

Alternate form -

$$\text{pH} = \log \frac{1}{[\text{H}^+]}$$

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

pH is used as a general way to express other quantities

- Concentration of $[\text{OH}^-]$ ions in aqueous soln of a base is expressed as -

$$\text{p}[\text{OH}^-] = -\log [\text{OH}^-]$$

- Equilibrium constant for water is written as -

$$\text{pK}_w = -\log [\text{K}_w]$$

Measurement of pH

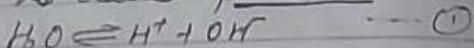
The pH of a given solution can be measured with the help of an apparatus called pH meter.

This consist of a voltmeter connected to two electrodes

- a standard potential electrode of known potential; and
- a special electrode enclosed in a glass membrane that allows migration of H^+ ion

pH scale:-

The scale on which pH values are computed is called pH scale.



$$K_w = \frac{[H^+][OH^-]}{[H_2O]} \quad \textcircled{2}$$

$$[H^+][OH^-] = K_w = \text{const} \quad \textcircled{3}$$

where K_w is known as water dissociation or water ionization constant.

K_w found experimentally is 10^{-14} .

The concⁿ of H^+ and OH^- ions in pure water is equal. By using eqⁿ ③

$$[H^+][OH^-] = \sqrt{K_w} = \sqrt{10^{-14}}$$

$$[H^+] = [OH^-] = 10^{-7} \text{ mol/l}$$

neutral solution

$$[H^+] = [OH^-]$$

acidic ..

$$[H^+] > [OH^-]$$

basic ..

$$[H^+] < [OH^-]$$

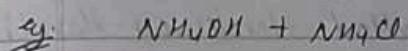
- All solutions having pH less than 7 are acidic and greater than 7 is basic.

:- Buffer Solution:-

A buffer solution is one which maintains the pH fairly constant even upon the addition of small amounts of acid or base.

In other words, buffer solution resists a change in its pH. Two common types of buffer are:-

- A weak acid together with a salt of the same acid with a strong base. These are called Acidic Buffers. e.g. $CH_3COOH + CH_3COONa$.
- A weak base and its salt with strong acid. These are called Basic Buffers.



* Calculation of the pH of Buffer solutions:-

The pH of an acid buffer can be calculated from the dissociation constant K_a , of the weak acid and the concⁿ of the acid and the salt used.

The dissociation expression of the weak acid, may be represented as -



$$K_a = \frac{[H^+][A^-]}{[HA]}$$



$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \quad \textcircled{1}$$

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad \textcircled{2}$$

Taking negative logs of both sides of eq ②,

$$-\log[H^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

$$-\log[H^+] = pK_a \text{ and } \log K_a = pK_a - \textcircled{2}$$

From eqⁿ ① we have,

$$pH = pK_a - \log \frac{[\text{acid}]}{[\text{salt}]} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

This relationship is called Henderson-Hasselbalch equation or simply Henderson eqⁿ.

Similarly, for basic buffer-

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Acid-Base Indicators: An acid-base indicator is an organic dye that signals the end-point by a visual change in colour.

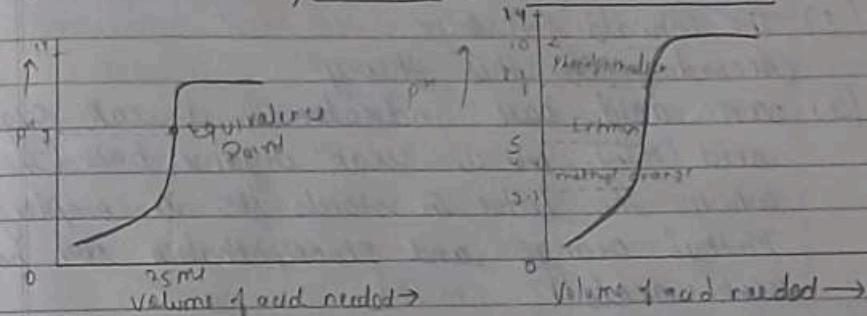
Phenolphthalein and methyl orange are two common examples of acid-base indicators. Phenolphthalein is pink in base solution and colourless in acid solution.

Thus phenolphthalein signals the end-point by a colour change from colourless to pH pink.

Similarly, methyl orange indicates the end-points by a color change from red (in acid) to yellow (in base).

pH curve and Indicator Range:

During an acid-base titration the pH of the solution in the receiver flask changes with the addition of the titrant from the burette. A plot of pH against the volume of the solution being added is known as pH curve or titration curve.



CHOICE OF A SUITABLE INDICATOR:

The choice of a suitable indicator for a particular acid-base titration depends on the nature of the acid and the base involved in the titration. We may have the titration of:

- a strong base with a strong acid
- a weak acid with a strong base
- a strong acid with a weak base
- a weak acid with the weak base.

Theories of acid-base Indicators:

An acid-base indicator is an organic substance used for the detection of equivalence point or neutral point in an acid-base titration. Two theories have been put forward to explain the indicator action in acid-base titration:-

- (1) The Ostwald's Theory
- (2) The quinonoid Theory.

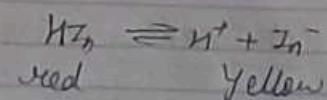
(1) The Ostwald's theory-

According to this theory:-

- (a) an acid-base indicator is a weak organic acid (HIn) or a weak organic base ($InOH$), where the letter In stands for a complex group. Methyl orange and phenolphthalein are both weak acids.
- (b) the unionised Indicator, HIn has a color diff from the In^- ions produced by the ionisation of the indicator in aqueous solution.
- (c) the degree of de-ionisation of the indicator determines the visible colour of the indicator solution.

How an Acid-base indicator works-

Let us explain the indicator action by taking example of methyl orange.



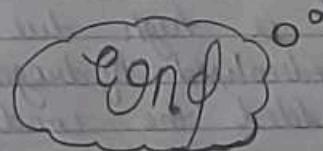
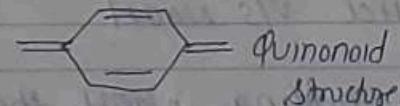
$$K_{In} = \frac{[In^-][H^+]}{[HIn]}$$

where, K_{In} is the dissociation constant of the indicator is called Indicator constant.

2) Quinonoid Theory:-

The quinonoid theory tell us the cause of colour change of an indicator in acid-base solutions. It lays down that:-

- (a) the unionised HIn molecule and the anion In^- are tautomeric forms of the indicator which is an organic dye.
- (b) One tautomeric form possesses the quinonoid structural unit it is called quinonoid form.



Conductometric Titration :-

- Basic principle of conductometric titration-

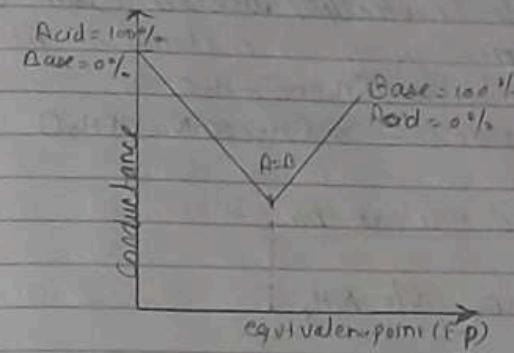
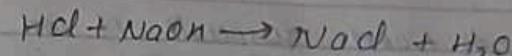
It is based on the fact that during the titration one of the ion is replaced by other ion. These two ions are different in their ionic conductivity. The equivalence (end point) point of the titration may be located graphically by plotting the change in the conductance as the function of volume of reagent added.

* There are four type of this titration:-

- 1) Strong Acid - Strong base-

Eg. HCl v/s NaOH

Before adding NaOH the conductance of HCl soln is high due to the highly mobilized hydrolyzed hydrogen ions. When NaOH is added the conductance falls (reduces) due to the replacement of H^+ ion with Na^+ ions. This decrement continues till the equivalence point. And at the equivalence point only NaCl will remain. After equivalence point the conductivity increases due to the presence of OH^- ion.

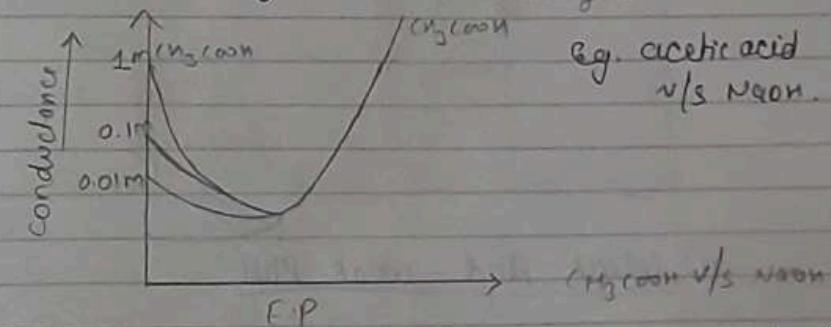


HCl v/s NaOH

- 2) Weak Acid - Strong Base:-

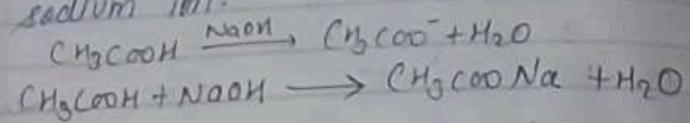
weak acid $HACOON$ releases H^+ slowly & conductance in starting is slow.

e.g. acetic acid v/s NaOH.



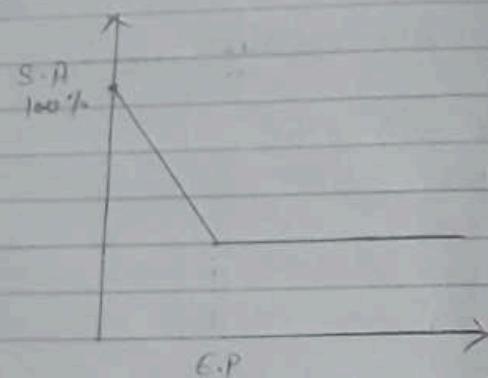
Initially the conductance is low due to the low conductivity of H^+ ions of acetic acid (weak acid). On the addition of NaOH the conductivity decreased due to the replacement of H^+ ion by Na^+ ion. The conductivity also decreased due to the common ion effect of acetic acid, acetate ions but soon conductivity increases on adding

NaOH. As NaOH dissociates H ion and undisociates (neutralise) acetate ion with sodium ion.



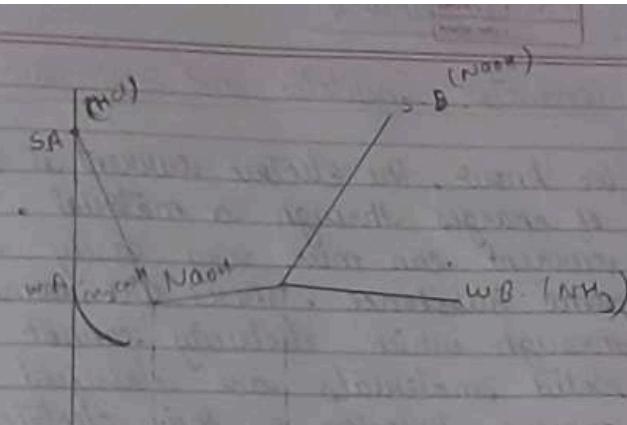
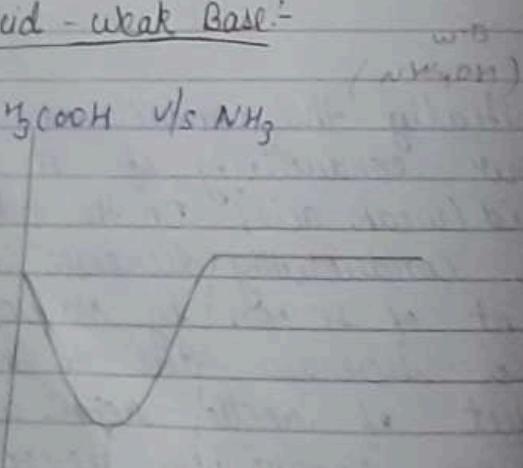
3) strong acid - weak base:

Eg:- H_2SO_4 v/s NH_3



4) Weak Acid - weak Base:

Eg:- CH_3COOH v/s NH_3



G₁ (end point) G₂ (end point)

(on combining all four)

Superconductor
Conductivity cell

Conductometric titration

n-type and p-type Semicon-

explain how does buffer solution works in
titrations

Acid and base buffers

Conductance and specific conductance

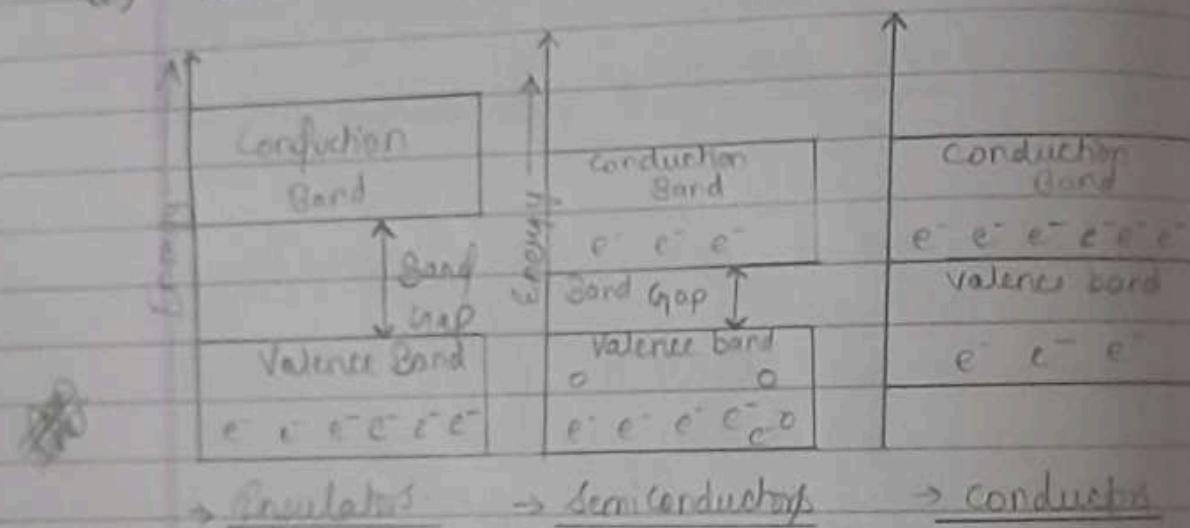
Conductors

Conductor, insulator and semiconductor-

We know, the electric current is the flow of charges through a material. This current can move very easily through some substance. There are some media through which electricity cannot move at all. Solid materials are classified into three groups depending on their electricity conduction.

(i) Conductor

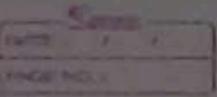
(ii) Insulator (iii) semi-conductor



UNIT-5

2/12/2021

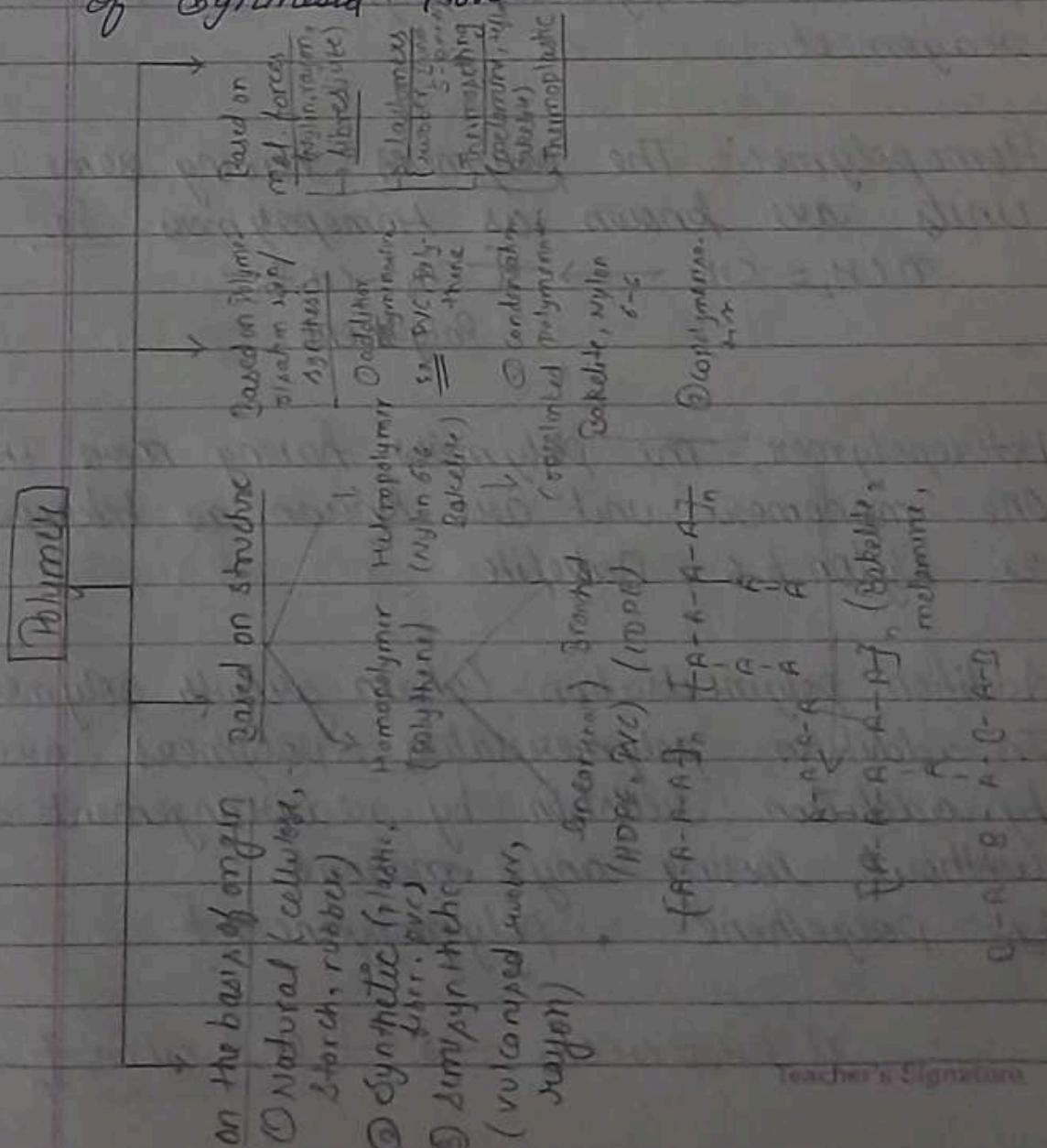
POLYMERS



Polymers are high molecular weight compounds composed of a large number of simple repeating units. These simple units have low molecular weight and known as monomers.

The word polymer derived from Greek word 'Poly' means many and 'mers' means unit.

The properties of polymers depends upon their configuration, degree of polymerization, mode of synthesis. Now -



Teacher's Signature

Natural Polymers:- These polymers are derived from plants and animals. Eg: protein, jute, cellulose, starch, rubber, latex, etc.

Synthetic Polymers:- These are synthesised in lab and manufactured according to the industrial need.
Eg: fibre, plastic, pvc.

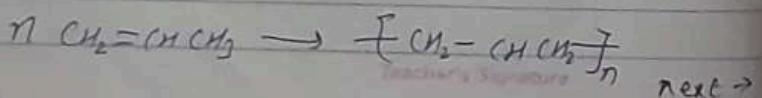
Semisynthetic polymers:- The natural polymers which are modified in lab according to the need are known as semisynthetic polymers. Eg: Buna-S, Buna-N, rayon, etc.

Homopolymer:- The polymers having same monomer units are known as homopolymers. Eg:
 $n \text{CH}_2=\text{CH}_2 \rightarrow -[\text{CH}_2-\text{CH}_2]_n$
Polythene

Heteropolymer:- The polymers having more than one monomer unit are known as heteropolymer.
Eg: Nylon 6-6, Bakelite

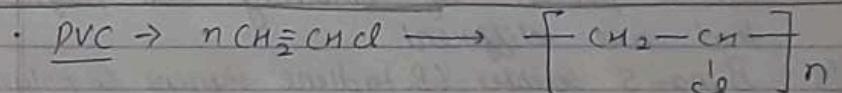
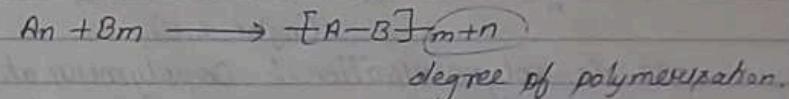
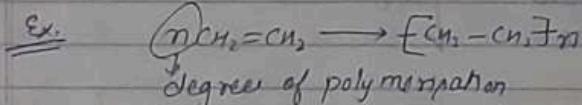
Addition polymerisation:- (chain growth polymerisation)
In addition polymerisation, polymers are formed by addition reaction by rearrangements of bonds without losing any molecule.

Eg: polyethene, polypropylene $\rightarrow -[-]$



Degree of Polymerisation:-

Degree of polymerisation is defined as the no. of monomeric units in a polymer.



→ Uses of polythene -
Used in plastic, plastic bags

→ Uses of polypropylene -
film wrap, carpet, etc.

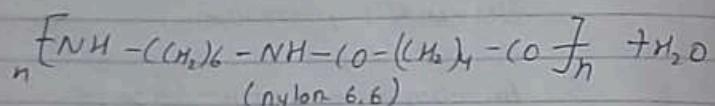
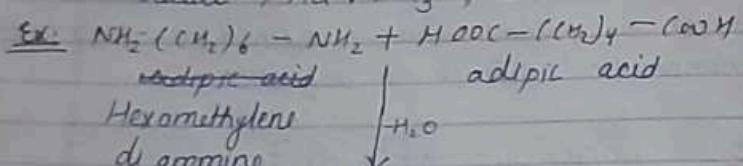
→ Uses of PVC -
pipes, sliding, flooring, etc.

→ Polystyrene $\rightarrow n \text{CH}_2=\text{CH}(\text{C}_6\text{H}_5) \rightarrow -[\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n$
used for making toys, cabinet, packaging material.

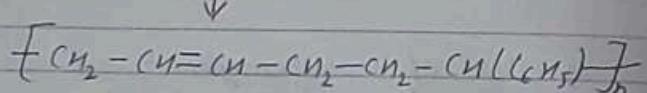
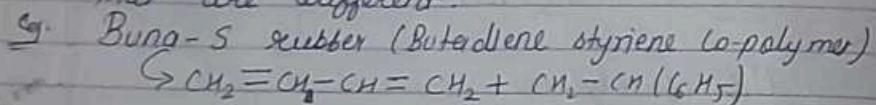
Condensation polymerisation (step wise polymerisation)-
Condensation polymerisation are kind of polymers formed through condensation reaction, losing

u example of condensation polymers & their uses

a molecule as a by product such as water molecule, H_2O , NH_3 , alcohol.



Co-polymerization :- Co-polymerization is defined as a process of combining two polymers that are different.



Fibres:- These are thread like structures obtained from natural sources as well as synthesized in the laboratory as per the requirement.
Ex: rayon, nylon, jute.

Elastomers:- They are thread like structures having high tensile strength. elastomers have low melting point.

Ex: rubbers, modified rubber, Buna-S, Buna-N.

V.S. Saravanan Maru,

Thermosetting:- Thermosetting polymers are formed by condensation polymerization. They consist 3D-network structures. The thermosetting polymers are linked by strong covalent bonds. They are hard, strong and brittle. They do not soften on heating and can't be remould. Thermosetting polymers posses high melting point.
Ex: Bakelite, melamine, Teflon

Thermoplastics:- Thermoplastics are composed by chain polymerization. They consist linear long chain polymers and held together by weak van der waal forces. In comparison to thermosettings, thermoplastics are soft, weak and less brittle. They posses low molecular weight & low melting point. They can be softened on heating and can be remoulded.
Ex: HDPE, nylon.

X [# Types of Polymerization :] X

[# Free Radical Reaction Mechanism :] X

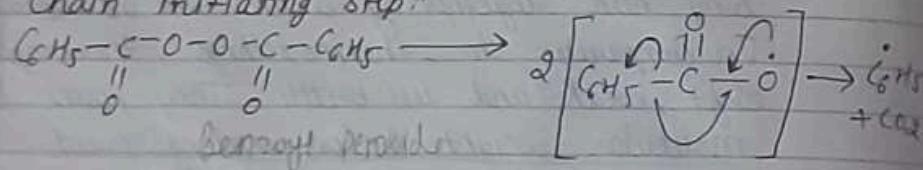
X [Chain initiating step :] X

- Types of polymerisation
- These steps are only for addition polymerisation.
- There are three types of polymerisation:-
- 1) free radical polymerisation (rxn)
 - 2) Cationic polymerisation rxn
 - 3) Anionic polymerisation rxn

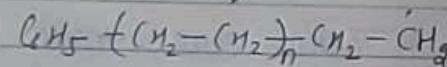
1) Free Radical:-

In free radical polymerisation free radical form during chain initiation step and a small molecule like H_2O or O_2 remove as a byproduct. This free radical reacts with a monomer (different / same) and form long chain free radical. This process is known as chain propagating step which further reacts with a free radical and form polymer at chain terminating step.

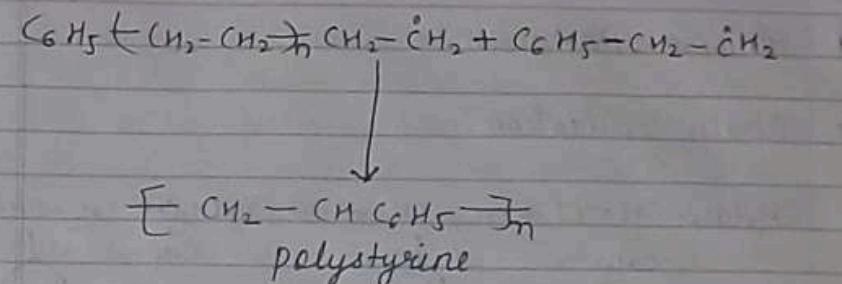
Chain initiating step:-



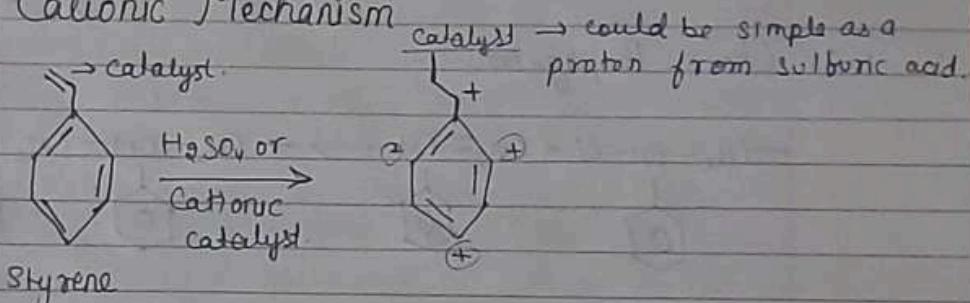
Chain propagating step:-



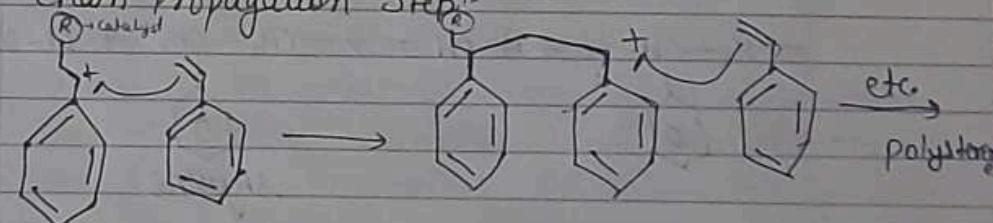
Chain terminating steps:-



2) Cationic Mechanism

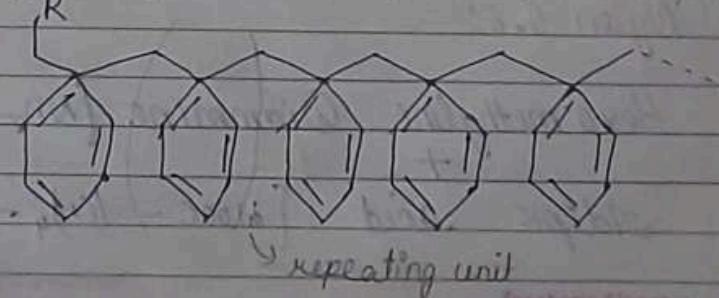


Chain propagation step:-



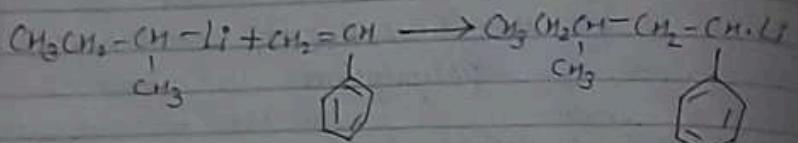
Chain termination:-

By adding a unit of last product polystyrene formed

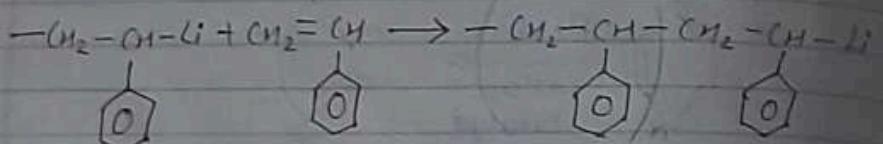


3) Anionic Polymerisation:-

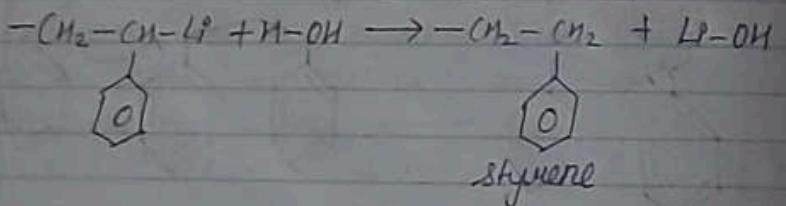
• Chain Initiation:-



• Chain Propagation:-



• Chain Termination step:-



* Synthesis, Properties and Uses of Polymers:-

1) Nylon 6,6:-

Hexamethylene Diamine $[\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2]$

Adipic acid $[\text{HOOC}-\text{(CH}_2)_4-\text{COOH}]$

→ Gom's form
→ GOM + IUPAC
water formaldehyde

$\text{C}=\overset{\text{H}_2}{\text{C}}-\text{C}=\text{C}$ → Isoprene
 $\text{C}=\overset{\text{H}_2}{\text{C}}-\text{C}=\text{C}$ → Neoprene

Buna-S → synthetic rubber

→ vulcanization of rubber

usage of sulphur to quality of rubber (1)

D) Properties & uses of polymers:-

- (i) PVC (ii) Nylon 6,6 (iii) Bakelite
- (iv) Neoprene (v) Buna-S (vi) Terylene
- (vii) polyethylene

(i) PVC ⇒ properties:-

strong rigid solid

(ii)-

pipes, siding, flooring

(ii) Nylon 6,6:- properties:-

- It has high abrasion resistance and high melting point.
- It has high tensile strength
- Very good resistance to photo degradation
- It has good advantage over industrial purpose products because it reduces moisture sensitivity in new products and has a high dimensional stability and mod.

→ It is amorphous solid

→ High soluble in boiling water

→ It is very difficult to dye but once dyed it has high colorfastness and less susceptible to fading

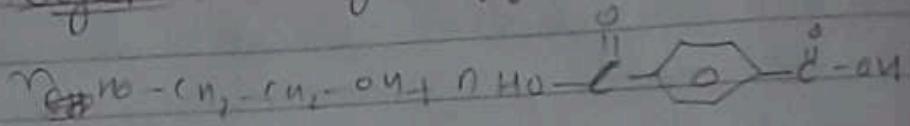
D) Neoprene → it has resistance to vegetable and mineral oil

D) It is used for manufacturing of conveyor belts, car seats, boxes

Date _____

Subject _____
Page No. _____

† Terylene: ethylene glycol + terephthalic acid



Properties \rightarrow very strong fibre and softer very little
loss strength not when wet
 \rightarrow elastic in nature and

Used Used in textile industry to make hard wear
Used for h. & laundry usage as a
automatic clothing vacuum packaging packaging
machine.

UNIT-2

Unit 2

Purification of Water & Softening of water:-

The treatment to remove or reduce hardness of water is termed as softening of water. It can be achieved by -

- 1) Removal of hardness causing Ca & Mg salts.
- 2) Conversion of these salts into soluble Na salts.
- 3) Use of electrical methods.

- There are 2 types of removal methods -
 - (i) External Treatment methods.
 - (ii) Internal Treatment methods.

(i) External Treatment methods:-

The external treatment is carried out before the entry of water into boiler. This prevents boiler troubles.

Now The main external treatments are -

- (a) Lime Soda Process
- (b) Zeolite process
- (c) Ion - exchange process

(ii) Internal Treatment methods:-

The treatment of water inside the boiler is known as internal treatment. It refers to the ~~conditioning~~ conditioning of water within the boiler using various chemicals. This is a corrective treatment method to remove those salts which are not removed

by external treatment. Different phosphates, carbonates, carbonates, colloidal & cationic are used in internal treatment.

(i) External treatment Method:-

(a) By adding Lime:- / Clarke's Process / Lime Soda Process:-

In this method, the basic principle is to convert all soluble hardness causing salts into insoluble precipitate by appropriate chemical treatment.

In this method, Calcium hydroxide (lime)

/ Sodium carbonate (Na_2CO_3) is added to the water. The reac's of lime & soda with various salts that in water are as follows:-

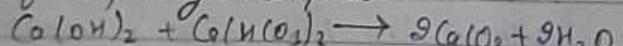
1. Removal of gases:-



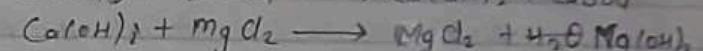
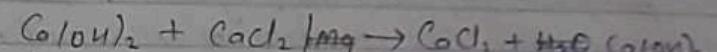
2. neutralization of free mineral acids:-



3. removal of temporary hardness:-



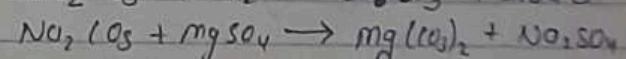
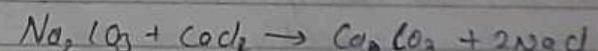
4. removal of permanent Hardness:-



5. removal of other salts:-



After the treatment of lime soda removed Ca hardness & hardness introduced due to the lime process.



There are two types of lime-soda (L-S) process:-

(i) Cold L-S

(ii) Hot L-S

(i) Cold L-S Process:-

In this method calculated quantities of lime soda are mixed with water at room temperature. The precipitate formed are very fine hence cannot be moved by filtration immediately. Normally it takes 24 hours for setting. To make setting faster coagulants like sodium aluminate, aluminium sulphate or alum are added.

These coagulants get hydrolysed to gelatinous precipitates of aluminium hydroxide which easily entrap the fine particles of solids and make them to settle down.



The residual hardness/hardness is generally 50-60 ppm.

⇒ There are 2 types of cold L-S Process-

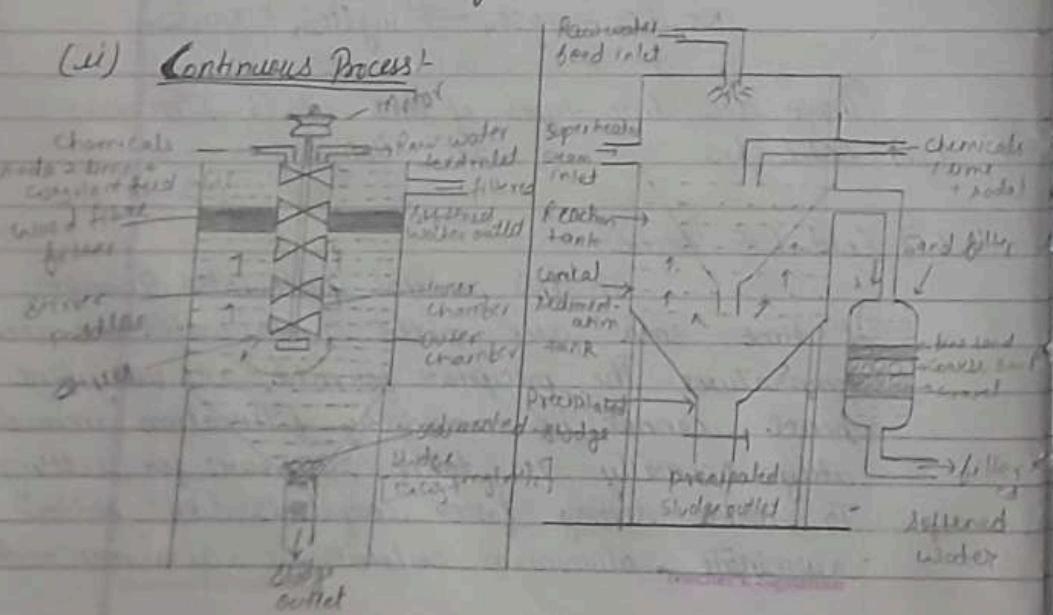
- (i) Batch Process
- (ii) Continuous Process

(i) Batch Process:-

This process is carried out in tanks.

Required amount of coagulant is added to ^{settling} water to settle down the ppt. It usually takes 2 hours for the ppt to settle down completely.

(ii) Continuous Process:-



Water to be treated and calculated quantity of lime-soda and coagulant are fed through the top the inner circular chamber fitted with rotating shafts having paddles. As the water flows down, there is mixing and due to the various chemical reactions taking place in this process, softening is achieved. The softened water rises upwards through the outer coaxial chamber. The solid sludge formed settles into the bottom conical portion of the outer chamber. The softened water is passed through a filtering medium to ensure complete removal of sludge. Filtered soft water flows out continuously through the outlet at the top. From the bottom, sludge is periodically removed.

(ii) Hot lime - Soda Process:-

This process is operated at higher temperature (90-100°C) which has several advantages:-

- (i) The reaction rate is increased and the softening reactions are completed in about 15 mins.
- (ii) Sludge settles faster and the addition of coagulants is not required.
- (iii) Dissolved gases like CO₂ are expelled.
- (iv) Viscosity is decreased and so filtration is faster.

Advantages of Lime Soda:-

- Less amount of coagulants are required.
- Rate of reaction increases with increase of Temp.
- The process is completed rapidly in 15 mins.
- Precipitate formed are larger & heavier and settled fast more rapidly.
- The process can be operated in the plant of small size / scale.

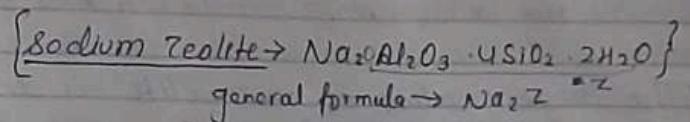
Disadvantages:-

- This process cannot be used for domestic purpose.
- This process is not suitable for many industries like Textile & paper industries.
- Spilled and careful supervision is required for efficient and economical operations.

Diff. b/w Hot L-S & Cold L-S:-

Cold L-S	Hot L-S
1. Rxn is slow.	Rxn is fast.
2. Filtration is slow.	At high temp., viscosity of water is reduced, so filtration is fast.
3. Use of coagulants is essential	No coagulants are needed
4. Lime consumption is high	less lime is consumed.
5. Steam is not used.	Steam is used.
6. The time taken is few hours	Here, time taken is few mins.
7. The residual hardness of water is 50-60 ppm	The residual hardness is 17-34 ppm

(b) Zeolite Process:-



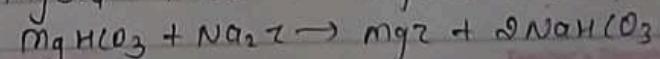
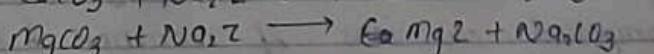
This process removes both temp. & permanent hardness of water. The chemical formula of sodium zeolite is - $\text{Na}_2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. This process is also known as permute process.

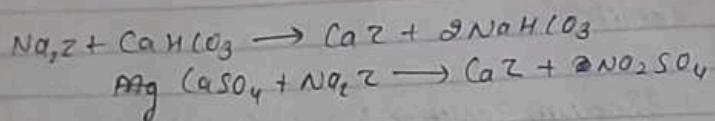
- Zeolites are of 2 types -

(i) Natural Zeolite :- These are non-porous & derived from green sand by washing, heating and treated with NaOH.

(ii) Synthetic Zeolite :- They can be prepared by heating Sodium silicate, Aluminium sulphate & Sodium Aluminate. It is a gel like structure. Synthetic Zeolite possessed high exchange capacity in comparison to natural zeolite.

- The following rxns are involved in Zeolite process of water treatment:-





The regeneration of geo-zeolite is carried out by washing of zeolite filter with brine solution (saturated salt of NaCl) & converted into sodium zeolite for reuse.



* Advantages :-

- Hardness of water is almost completely removed and water of 10 ppm of hardness is obtained.
- Equipment occupies small space.
- There is no/less chances to form sludge.
- Process automatically adjust itself for the variation of hardness of incoming water.

* Limitations :-

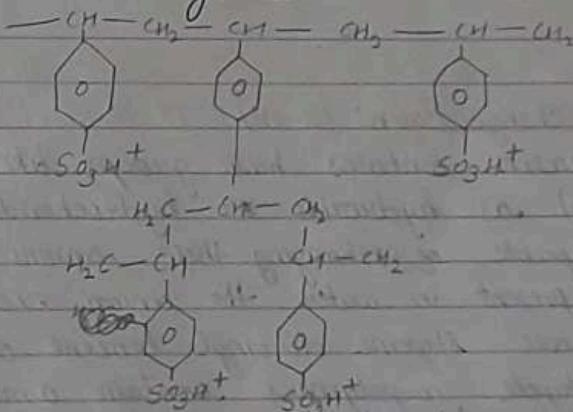
- Water should be free from turbidity otherwise turbidity clog the zeolite filters. Thereby, making it inactive.
- If the hard water contains coloured compounds or ions of manganese & iron, they must be removed first. Otherwise it can react with zeolite.

Mineral acids, if present in water destroys the zeolite. Therefore, they must be removed first before the entering of water to zeolite filter.

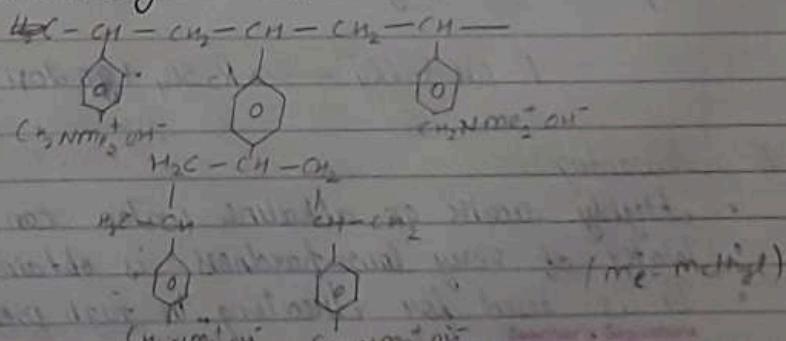
(c) Ion-Exchange Method:-

The process of ion-exchange is the property of material to exchange an ion in its structure for an ion in solution.

Cation exchange resin:-



Anion exchange resin:-



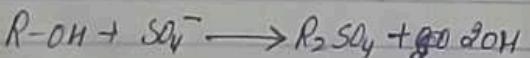
Cation Exchange resin: (R-H)

The resins used for this purpose are organic & insoluble cross-linked polymers of styrene di-vinyl benzene. These resins contain some acidic group like COOH , SO_3H , etc which are capable of exchanging their H-ions. These styrene di-vinyl benzene co-polymers on sulphuration or carboxylation obtain capability to exchange their Hydrogen ions with other cations present in water.



Anion Exchange Resin: (R-OH)

These resins contain basic groups like $\text{NH}_2 = \text{NHH}_2$ (azo group) as hydroxides or hydrochlorides which are capable of exchanging their anions with other anions present in water. The anion exchange resins are styrene di-vinyl benzene or amino formaldehyde co-polymers contain amino group on reaction / heating with NaOH these become capable of exchange their OH ions.



Advantages:-

- Highly acidic or alkaline water can be softer.
- Water of very low hardness is obtained.
- It is used for treating in high pressure boiler water.

Disadvantages:-

- Expensive chemicals & costly equipment is required.
- Water should be turbidity free. If the turbidity is above 10 ppm it has to be removed first otherwise filters will clog.

Boiler & its Troubles:-

Water used for steam raising should be free from impurities which can otherwise give rise to certain troubles in Boiler. The total destruction of several large power houses has ultimately been traced due to the use of unsuitable water which caused explosion of the boilers. In the treatment of boiler water, complete removal of impurities is not aimed, rather only those impurities are eliminated or kept within certain limits which lead to objectional phenomenon in the boilers. The major boiler troubles due to use of unsuitable water may be classified into following four categories:-

1. (a) Priming
2. Corrosion
3. Cyclic embrittlement and
4. Scale & sludge formation.

(a) Priming:- When steam is produced rapidly in the boilers, some very small droplets of water are carried out along with the steam. This process is called priming. The steam with very small water droplets are called "wet steam".

(b) foaming:- The formations of small and stable bubbles on the surface of boiler which do not break off easily. The foaming is caused by due to presence of oil and alkalis in boiler water. The oils and alkalis greatly lower the surface tension of water and thus increase the foaming tendency of water.

It can be avoided by-

- 1) The addition of anti-foaming agents like castor oil
- 2) the removal of foaming agent (oil) from boiler water.

• Priming is caused by-

- 1) the presence of large amount of dissolved salts
- 2) high steam velocities.
- 3) sudden boiling
- 4) improper boiler design.

• Priming can be avoided by-

- 1) controlling rapid change in steaming velocities.
- 2) proper design of boilers.
- 3) ensuring efficient softening.

(c) carryover:- The phenomenon of carrying of water along with impurities by steam is called carry over. This is mainly due to priming and foaming, usually both occurs together.

2) corrosion:- (Boiler Corrosion)-

Boiler corrosion is 'decay' or 'disintegration' of boiler body material by either chemical or, electrochemical reaction with its environment.

Reasons of boiler corrosion -

- Dissolved oxygen
- Carbon dioxide
- mineral acids.

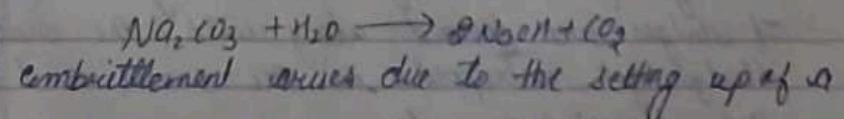
Disadvantages:-

- 1) Shortening of boiler life.
- 2) Leakage of joints and rivets.
- 3) Increase cost of repairs and maintenance.

3). Caustic embrittlement:-

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2 . The NaOH produced makes the boiler water "caustic".



Prevention:-

It can be prevented by -

- i) by using sodium phosphate as softening reagent instead of Na_2CO_3 in external treatment of boiled water
- ii) by adding lignin or tannin to boiler water that blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution in these areas

i) Scales & sludge formation :-

If the precipitation takes place in the form of loose & slimy layer precipitate, it is known as sludge.

If the precipitation takes place in the form of a hard, adhering crust/coating on the inner walls of the boiler, is known as scale.

Sludge - It is soft, loose and slimy precipitate formed with boiler. It is formed by the substance that have greater solubility values in hot water than in cold water. e.g. MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 , etc.

Disadvantages -

- 1) Sludges are poor conductor of heat, hence there is wastage of portion of the heat generated
- 2) If sludges are formed along with the scales, then sludge get entrapped in the scales and both get deposited as scales.

- 3) Excessive sludge formation disturbs the working of the boiler.

Preventive measure -

- 1) By using softened water.

By frequently blow-down operation (drawing off a portion of the concentrated water)

- Scales - The scales are difficult to remove, even with the help of hammers.

Formation -

- 1) Decomposition of CaCO_3
- 2) Deposition of CaSO_4
- 3) Hydrolysis of magnesium salts.
- 4) Presence of silica

Disadvantages -

- 1) wastage of fuel.
- 2) Lowering of boiler safety.
- 3) Decrease in efficiency
- 4) Danger of explosion.

Removal of scales -

- If scales are loosely adhering they can be removed by sea scraper or piece of wood or wire brush.
- If scales are brittle they can be removed by thermal shocks i.e. heating the boiler and suddenly cool down.

Prevention:-
} external treatment
Internal treatment

(ii) Internal treatment method:-

Following methods are used in internal treatment-

- Appropriate chemicals are added to precipitate the scale forming impurities in the form of sludge which can be removed by blow-down operation.
 - The problem causing reactions are converted into highly soluble compounds which will stay in dissolved form in the boiler water without causing any deposition.
- The internal treatment methods are generally followed by Blow-Down operations so that accumulated sludge is removed. The important treatments are-
- (i) Carbonate Conditioning :- This method can be used in low pressure boilers. Any scale forming salts like CaSO_4 is precipitated in the form of carbonate by adding Na_2CO_3 .



These loose precipitate of CaCO_3 can be removed by Blow Down operations.

- (ii) Colloidal conditioning : In low pressure boilers scale formation can be avoided by adding some organic substances like kerosene, tannin and agar-agar powder which get coated over the scale forming precipitate, thereby forming a non-sticky loose slimy deposition (sludge) which can be easily removed by blow Down operation.

(iii) Phosphate conditioning :- (Na_2PO_4)

In high pressure boilers scale formation can be avoided by adding sodium phosphate which reacts with scale forming substances and converted into easily removable soft sludge.

The phosphate used for this process should be adjusted to the pH 9.5 to 10.5.

(iv) Treatment with Sodium Aluminate (NaAlO_2) :-

When NaAlO_2 is added to the boiler water it gets hydrolysed and form loose precipitate which easily trap any fine suspended particles and colloidal impurities such as - Spice and oil and converted into sludge which will easily removed bly by Blow - Down operations.

(v) Calgon conditioning : $\left[\text{Na}_2[\text{Na}_4(\text{PO}_3)_6] \right]$

This involved sodium hexa meta phosphate to boiler water. It prevents the scale and sludge formation by forming soluble complex.

WATER

* Hardness of Water:-

Hard water - which does not produce lather with soap but give precipitate with soap.

Soft water - which produce lather with soap.

- Hardness of water is due to presence of soluble salt of calcium, magnesium and other heavy metals in water.
- The scum or precipitate is due to the formation of insoluble soaps of Ca & Mg ions react with soap.

* Types of Hardness:

⇒ Temporary Hardness: Temporary hardness is caused by presence of dissolved bicarbonates of Ca & Mg.

→ This can be removed by boiling.



⇒ Permanent Hardness: It is due to presence of chlorides, & sulphates of dissolved Ca, mg, Fe and other heavy metals. The salts responsible for permanent hardening are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$.

→ This can't be removed by boiling.

→ These are also known as non-carbonate or non-alkaline hardness.

$$\text{Temp. Hardness} + \text{Permanent Hard.} = \text{Total Hardness}$$

→ Although Hardness of water is never present in the form of CaCO_3 as it is insoluble in water hardness of water is conveniently expressed in terms of equivalents of CaCO_3

→ The hardness is expressed in terms of equivalent to CaCO_3

→ The reason for choosing CaCO_3 as standard for express in hardness is ease in calculations on its molecular weight is exactly 100.

& CaCO_3 is most insoluble salt

* Units of Hardness:

1. Parts per million: Parts of CaCO_3 equivalent hardness per 10^6 parts of water.

$1 \text{ ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness}$
in 10^6 parts of water

2. Milligrams per litre: No. of milligrams of CaCO_3 equivalent hardness present in 1 lit. of water.

$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness tnt in 1L water}$

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

$$[1 \text{ mg/L}] = [\text{ppm}] / [1 \text{ mg of } \text{CaCO}_3 \text{ eq. per } 10^6 \text{ mg of H}_2\text{O}]$$

3. Clarke's degree: (${}^{\circ}\text{Cl}$)

${}^{\circ}\text{Cl} = 1 \text{ grain of } \text{CaCO}_3 \text{ eq. hardness per gallon of water}$
= 1 part of CaCO_3 of hardness per 70,000 parts

4. Degree French: (${}^{\circ}\text{Fr}$)

${}^{\circ}\text{Fr} = 1 \text{ part in the parts of } \text{CaCO}_3 \text{ eq. hardness}$
per 10^5 parts of water.

Millequivalents per litre:

No. of milli eq. of hardness
tnt per litre.

$$1 \text{ m.eq./L} = 1 \text{ meq of } \text{CaCO}_3 \text{ per litre of water}$$

$$= 10^3 \times 50 \text{ mg of } \text{CaCO}_3 / \text{litre}$$

$$= 50 \text{ mg/L of } \text{CaCO}_3 = 50 \text{ ppm}$$

Relation b/w Various units of Hardness:-

Units	ppm	mg/L	${}^{\circ}\text{Fr}$	${}^{\circ}\text{Cl}$
ppm	1	1	0.1	0.07
mg/L	1	1	0.1	0.07
${}^{\circ}\text{Fr}$	10	10	1	0.7
${}^{\circ}\text{Cl}$	14.3	14.3	1.43	1

Water:

water, a substance composed of the chemical elements hydrogen and oxygen. The existing state of water are gaseous, liquid and solid.

• Types of water impurities:

Physical impurities

Biological impurities

Chemical impurities

Physical impurities: physical impurities in water indicates the presence of suspended or colloidal insoluble matter including coarse particles (mud, sand, clay, etc.)

Biological impurities: Biological impurities are organic and inorganic particles defined as impurities resulting from living matter

Chemical impurities: chemical impurities inside a confined amount of liquid.

⇒ How to remove temporary hardness of water?
Temporary hardness of water can be removed by using calcium hydroxide, as calcium hydroxide converts bicarbonates to insoluble carbonates which can be removed by filtration.

⇒ How to remove permanent hardness of water?
Permanent hardness of water can be removed using a water softener, or ion exchange column.
Other method permanent hardness removal is RO (Reverse osmosis method)

Difference b/w Hard & Soft Water:

Hard water

Water which do not form leather with soap rapidly but forms a white cloud is called hard water

It contains dissolved Ca & Mg salt in it.

In hard water cleaning, quality of soap does not decrease, quality of soap is decreased. A large amount of soap is wasted.

Soft water

Water which foams easily with soap is called a soft water

It does not contain dissolved salts of Ca & Mg.

In soft water, cleaning quality of soap does not decrease, soap is not wasted.

Determination of Hardness of Water:

The hardness of water may be determined by the following methods:

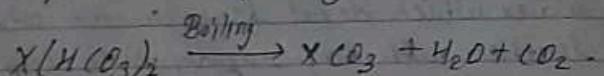
(i) O' Hearn's method

(ii) Soap titration method (Clark's method)

(iii) EDTA method (complexeometric method)

(i) O' Hearn's method:

Temporary hardness of a sample can be found out by determining alkalinity of water before boiling of water after boiling. The difference b/w the readings will represent temporary hardness.



bicarbonate in this is the unknown volume of water

sample is titrated against standard HCl

using methyl orange as an indicator

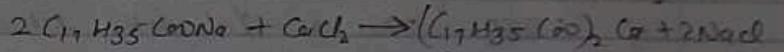
(ii) Soap titration method-

When a sample of hard water

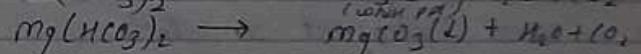
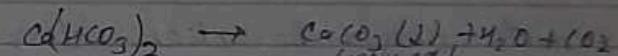
consisting of chlorides, sulphates of Ca & Mg and other heavy metals is treated or boiled with an excess amount of sodium carbonate, total hardness is removed by precipitation carbonates of Ca & Mg.

(iii) Permanent hardness can be calculated by this method. This method depends upon the fact that when soap is added to hard water the Ca & Mg ions in hard water reacts with soap and form insoluble compound which is known as scum or ppt.

Permanent Hardness:



Temporary Hardness:



In this method, known st water sample is titrated against standard soap solution and leather or scum is formed at the end point of the titration.

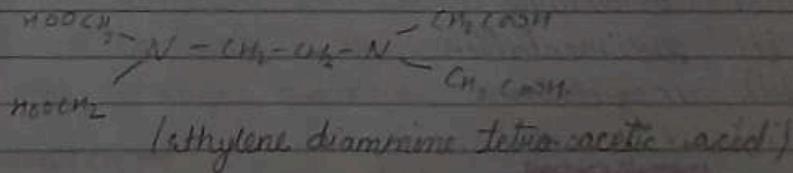
Some formulae

$$\text{Hardness} = \frac{\text{Volume of soap used} \times 50 \times 1000 \times \text{Normality of HCl}}{\text{Volume of water sample}}$$

(iii) EDTA method:-

The hardness of water can be also be determined by using EDTA method. It dissolves in water with great difficulty but its disodium salt dissolve in water quickly and completely. It is hexa dentate ligand.

Structure of EDTA-



* This method is based on complexometric reaction of Ca & Mg with sodium salt of EDTA. This is Volumetric titration method.

Essential requirements for drinkable water / qualities of drinkable water:-

- Water should be clean, clear and odourless and pleasant to taste.
- Turbidity (opaque) should not be greater than 10 ppm.
- It should be free from harmful gases.
- It should be free from poisonous metals like Pb, Hg, Arsenic, Cr.
- The pH of water should be 7.0 to 8.5
- Total dissolved solids and hardness should be less than 500 ppm.
- Fluoride should be less than 1.5 ppm.
- Sulphates & chlorides should be less than 250 ppm.
- It should be free from pathogens.

Purification of drinkable water:-

These are various steps in the process of purification of water from river to water treatment plants

- (i) Screening
- (ii) sedimentation
- (iii) coagulation
- (iv) filtration
- (v) Disinfection

Screening:-

The raw water is passed through screens / filters having holes where floating material stuck into these holes and rest of the water passes in a diff. chamber.

Sedimentation:-

When the water is turbid and contains dispersed particles and metals, preliminary (basic) sedimentation is generally preferred. In which coarse suspended particles are removed and it becomes easier for further treatment.

The sedimentation is of 2 types-

- Plain sedimentation
- Sedimentation with Coagulation (coagulation)
- Plane sedimentation:-

It is the process in which retention of water requires for a certain period of from 1 day to 10 days or as per requirements in a tank. This water transfers very slowly into another tank and solid particles present in water remains at the base.

Coagulation:-

In plain sedimentation fine particles like clay or colloidal impurities will not settle down under ordinary conditions as their

Settling velocity and particle size are very small and need more time to retention which is not possible. Therefore, it is necessary to add some chemicals to settle down these small particles. These coagulants are mainly-

- (i) Alum - $[K_2SO_4 \cdot Al_2(SO_4)_3] \cdot 24H_2O$ (potash alum)
- (ii) Sodium aluminate ($NaAlO_2$)
- (iii) Ferrous sulphate ($FeSO_4$)

By adding these chemicals impurities or fine particles get settle down as the ppt or in the form of diff. hydroxides.

Filtration:-

Now, precipitate will filter with diff. filters so clear water is obtained. There are several different types of filters mainly divided in 2 categories depending upon the condition of water-

- ① Gravity and sand filter
- ② Pressure filter

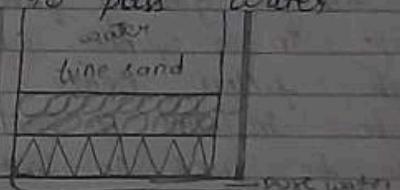
Disinfection:-

Water for drinking purpose is still not safe, even after screening, sedimentation, coagulation and filtration, because there is still presence of disease producing microorganisms and pathogens.

Therefore water is used for drinkable drinking purpose, must be free from such microorganism.

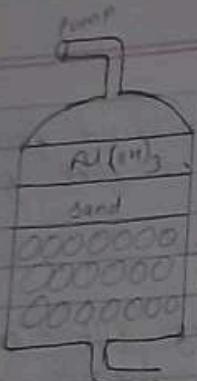
- * Types of Filtration:-
- Gravity filter-

Gravity filtration is carried out in a large rectangular tank consist of coarse medium which retains solid particles but allow to pass water.



Several different forms of filter media are available. Common filter contains fine sand at the top then coarse sand and then gravels at the bottom. Water from the sedimentation tank enters in at the top of the filter and passes throughout the layers and take in out from bottom. In gravity filters water passes through these layer at an atmospheric pressure due to gravity.

- Pressure filter:



These have same type of arrangement of filters as as gravity filter. The filter material is kept in a cylinder and water is forced through filters under pressure. These filters can be installed in water supply line or can be used in industrial water cooling units.

Disinfection - (remaining part)

The disinfection of water can be carried out by:-

- (i) Chlorination Method
- (ii) Bleaching Powder Method (CaOCl_2)
- (iii) Ozoneysis
- (iv) Boiling (H_2O_2)
- (v) Chloroammine treatment

(i) chlorination:-

Chlorine is the most commonly used disinfectant in water treatment. Chlorine may be added directly as gas or in

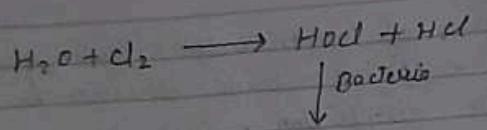
the form of concentrated solution. Correct dose and sufficient time should be ensure for effective disinfection. chlorine is react with water & forms hypochlorous acid which is very powerful germicide. This acid reacts with cell wall of pathogens and form hypochlorite (HOCl) which destroy the walls resultant to death of the pathogens.

Advantages of chlorination:-

- At low concentration, cl is very effective
- The rate of chlorine disinfection is satisfactory when water is treated from few hours to days.
- Cl residue remains in water which provide additional safety and preventing re-growth of bacteria.
- It is very effective and economical.
- It can be used at high temp^o and low temp^o.
- It does not introduce salt impurities in water.

Disadvantages of chlorination:-

- The main disadvantage is toxicity of material.
- Excess of chlorine produces unpleasant taste, odour, also produces irritation on skin and mucous membranes.
- It is less effective at higher pH and more effective at low pH.



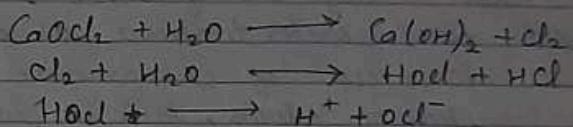
Break point chlorination:

Black Break point chlorination may be defined as the chlorination of water to such an extent that not only pathogens but also other organic impurities in water are destroyed → addition of chlorine in such an extent that ensure complete destruction of organic compounds which gives color, unpleasant odour, bad taste or well as diseases causing pathogen. It is also termed as free residual chlorine.

(ii) Treatment of Bleaching Powder:

Chlorine may be added in water in form of Bleaching powder (Ca(OCl)_2) which gives Calcium hydroxide. The OCl^- ions ruptures the cell membrane (destroy)

on oxidation and destroy disease producing pathogens.



→ Disadvantages:-

- It enhances the hardness in water.
- On storage CaOCl_2 may be react with atmospheric moisture and breakdown.
- Excess of CaOCl_2 creates skin irritation, bad taste and odour in water.

(iii) Ozonolysis:-

The ozone is highly unstable and harmless gas and an excellent disinfectant. It gives nascent oxygen which is very powerful oxidizing agent and kills all disease causing pathogens.

Advantages:-

- Excess of ozone is not harmful.
- It releases O_2 in water.
- It removes colour, odour and bad taste of water.

Disadvantage:-

- It is very expensive method. Hence it can't be used for municipal based water treatment.

(iv) Chloramine method:- (NH_2Cl)
It is an excellent bactericidal disinfectant. Now-a-days use of NH_2Cl increase in municipal based water treatment as a disinfectant because excess use of chloramine does not create unpleasant odours, taste in water. Also it is more stable -

