

## Solutions

**CMR  
INSTITUTE OF  
TECHNOLOGY**



Sub:	<b>Engineering Chemistry</b>	Code:	<b>17CHE22</b>
Date: <u>21/05/2018</u>	Duration: <u>90</u> mins	Marks: <u>50</u>	Sem: <u>II</u>
			Branch: <u>All</u>

### Internal Assessment Test III

**1. (a) A polymer has the following composition 100 molecules of molecular mass 1000g/mol, 250 molecules of molecular mass 2500g/mol and 400 molecules of molecular mass 4000g/mol, Calculate the number and weight average molecular weight. (05 Marks) (CO1, L2)**

**Solution:**

$$M_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3}$$

Given,  $N_1=100$ ,  $N_2=250$ ,  $N_3=400$ ,  $M_1=1000\text{g/mol}$ ,  $M_2=2500\text{g/mol}$ ,  $M_3=4000\text{g/mol}$

$$M_n = [100(1000) + 250(2500) + 400(4000)] / 100 + 250 + 400$$

$$= 3100\text{g/mol}$$

$$M_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3}$$

$$M_w = [100(1000)^2 + 250(2500)^2 + 400(4000)^2] / 100(1000) + 250(2500) + 400(4000)$$

$$= 3467.74\text{g/mol}$$

**(b) What is Glass Transition temperature? Explain any two factors affecting Tg. (05 Marks) (CO1, L4)**

**Solution:** The temperature at which the polymer abruptly transforms from a glassy brittle state to a soft rubbery state is called glass transition temperature (Tg).

**(i) Flexibility:** Higher flexibility of polymer chain leads to higher segmental mobility and hence lower will be Tg. The different factors which lower chain flexibility of the polymer increases its Tg. Linear polymer chain made of C-C, C-O and C-N single bonds have higher degree of freedom of rotation and large chain flexibility; thus have low Tg. Presence of rigid structures in polymer chain such as aromatic or cyclic structure hinder freedom of rotation thus lowering of chain flexibility and increase in Tg.

Eg: Tg of polyethylene -110C

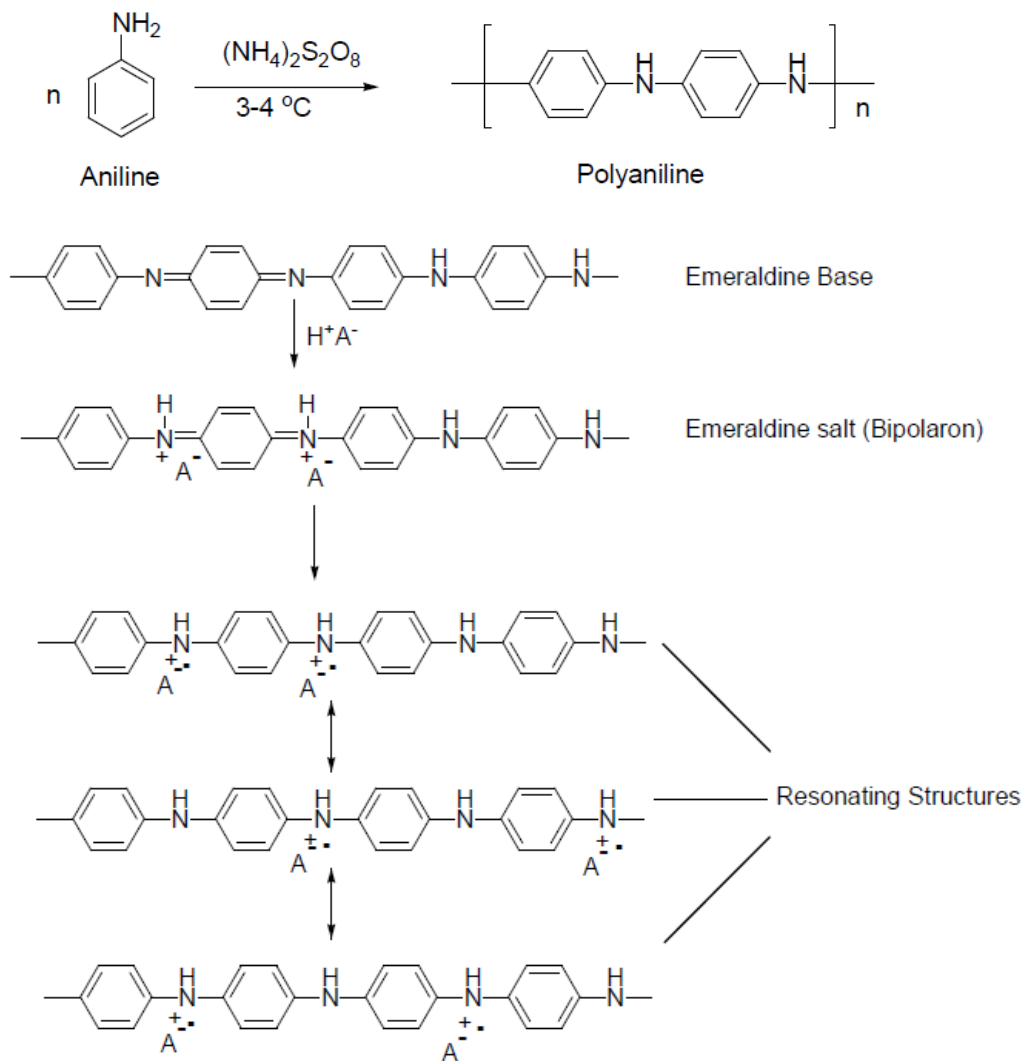
Tg of polystyrene 100C

**(ii) Branching and Cross linking:** A high density of branching brings the polymer chains closer, lowers the free volume, reduces the chain mobility and thus results in an increase in Tg. Small branching increases the chain volume through small chain ends, thereby increasing the chain mobility and decreasing the Tg. The presence of excessive hydrogen bonding also reduces the chain flexibility. When the chains are cross linked through covalent bonds, there is almost total immobility of the chain and segment. Thus Tg will be considerably more in this case.

Eg: Tg of polyethylene -110C, Polystyrene 100C and Polymethyl styrene 170C

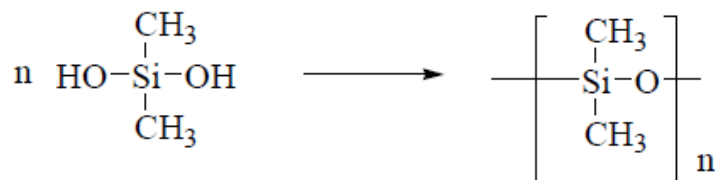
**2. (a) Explain the Mechanism of conduction of polyaniline. (05 Marks) (CO1, L3)**

**Solution:**



**(b) Describe the synthesis and applications of silicone rubber. (05 Marks) (CO1, L3)**

**Solution:** The monomer is dimethyl silanol which is unstable and immediately undergoes intermolecular condensation to give silicones.



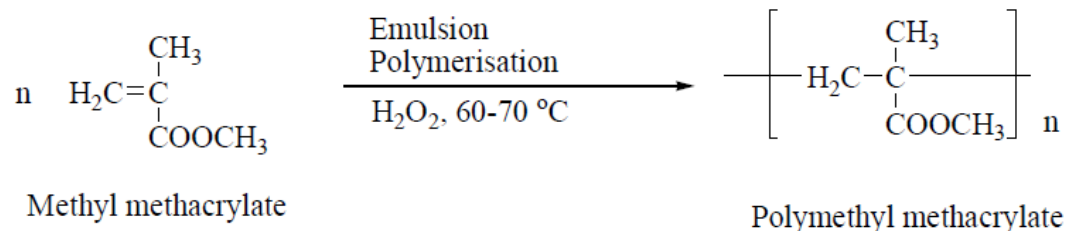
**Properties:**

1. Silicones have high thermal stability and can be heated in air to about 200C
2. They are water repellent and chemically inert.
3. They show good resistance to effect of weathering.

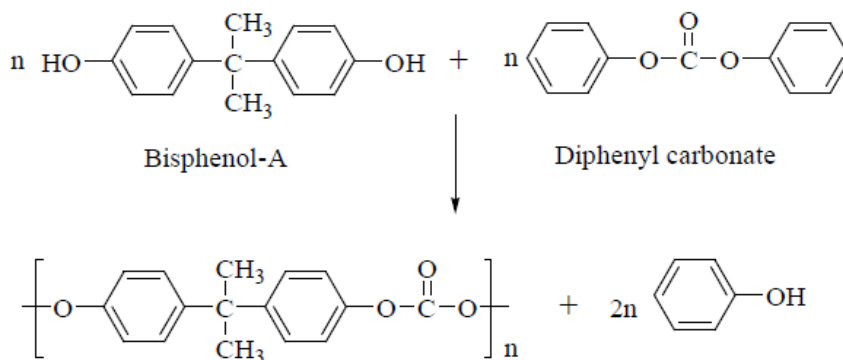
**Applications:**

1. They are used in making lubricants, used in gaskets, seals, wire and cable insulation.
2. In manufacturing tyres for fighter aircrafts.
3. In making artificial heart valve, transfusion tubings etc.

**3. (a) Explain the synthesis and applications of: (a) PMMA and (b) Polycarbonate. (05 Marks)  
(CO2, L4)**

**Solution:****Applications:**

- (i) For making lenses, air craft windows, artificial eyes, TV screens, attractive sign boards etc.
- (ii) It is also used for making transparent bottles, tubes etc.
- (iii) It can be used as paints and adhesive.

**Applications**

1. They are used in making industrial safety glasses, because of optical clarity.
2. They are used in machinery hoses due to its resistance to abrasion and chemicals.

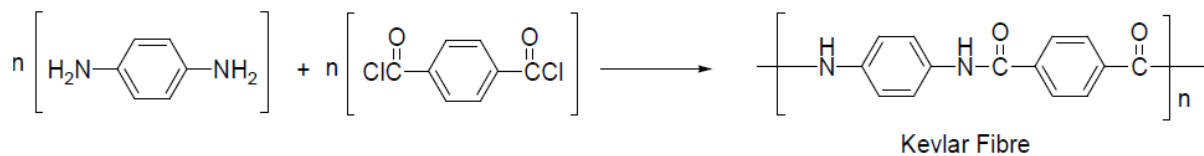
**(b) Define polymer composites. Explain the synthesis, properties and application of Kevlar. (05 Marks) (CO4, L2)**

**Solution:** The combination of two or more distinct components to form a new class of material suitable for structural applications is referred to as composite materials. When one of the components is a polymer, the resulting composite is called a polymer composite. Each component can however, retain its parent constituents, particularly in terms of mechanical properties. These polymer composites are obtained by bonding a fiber material with a polymer resin matrix under pressure and/or heat. The common fibre materials used in polymer composites are glass fibre, boron filament, carbon/graphite fibers or Kevlar. The common resin matrixes used are polyesters, epoxy, phenolic, silicon, vinyl derivatives and polyamides.

(a) Phenolic resins are used wherever resistance to high temperature is needed.

(b) Epoxy resins impart high mechanical properties.

(c) Silicon resins impart high excellent electrical and thermal properties.



**Properties:**

1. The linkage through para positions of the phenyl rings gives Kevlar a strong ability to stretch and hence its extra strength.
2. It has very light weight.
3. It has high tensile strength and modulus. (It forms even better fibres than non-aromatic polyamides).

**Applications:**

1. These are used for structures which require stiffness, high abrasion resistance and light weight.
2. Used in light weight boat hulls, aircraft panels and racer cars.
3. Used in bullet proof vests and puncture resistant bicycle tyres.

**4. (a) Define COD and BOD. In a COD test 29.5 cm<sup>3</sup> and 16.5 cm<sup>3</sup> of 0.05N FAS solution are required for blank and sample titration respectively. The volume of the test sample used is 25 cm<sup>3</sup>. Calculate the COD of the sample solution. (06 Marks) (CO4, L3)**

**Solution: BOD (Biological Oxygen Demand):** It is defined as the amount of oxygen required by microorganisms to oxidize the organic wastes present in one litre of waste water over a five-day period at 20C.

**COD (Chemical Oxygen Demand):** It is defined as the amount of O<sub>2</sub> consumed in the complete chemical oxidation of organic and inorganic wastes present in 1 litre of waste water by using strong oxidizing agent, such as acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Given, V = 25 mL, b = 29.5cm<sup>3</sup>, a = 16.5 cm<sup>3</sup>, N<sub>FAS</sub> = 0.05N

$$\text{COD of the sample} = \frac{N_{\text{FAS}} \times (b-a) \times 8 \text{ g dm}^{-3}}{V}$$

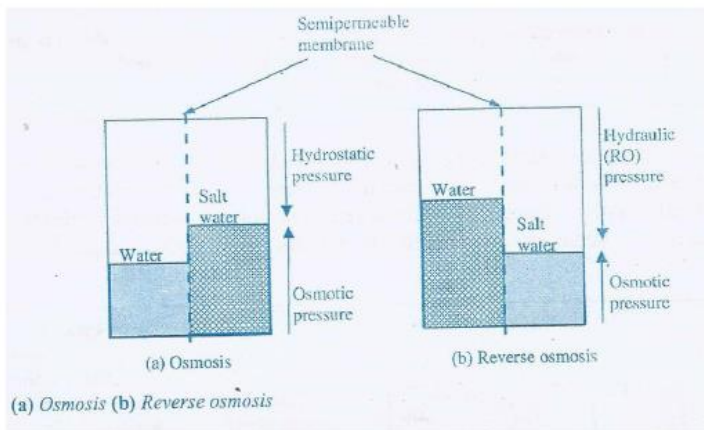
$$= 0.05 \times (29.5-16.5) \times 8000 / 25 = 208 \text{ mg of O}_2 / \text{dm}^3$$

**(b) What is desalination? Discuss the desalination of water by reverse osmosis. (04 Marks) (CO4, L2, L3)**

**Solution:** The process of partial or complete demineralization of highly saline water such as the sea water is referred to desalination. In partial demineralization, the amount of dissolved salts reduced to such a level, that water is rendered potable.

**Reverse Osmosis:**

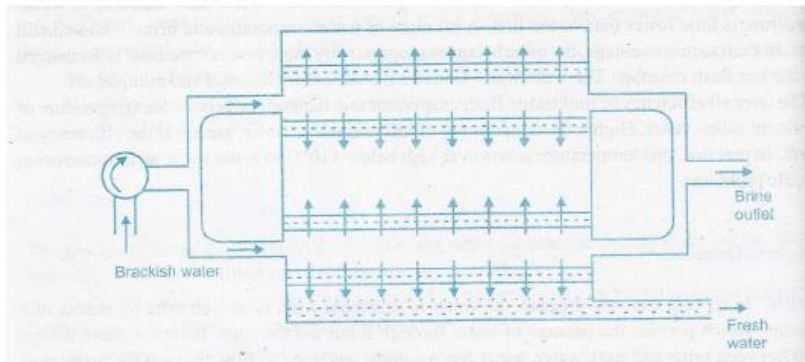
Osmosis is the physical movement of a solvent through a semi permeable membrane from lower concentration to higher concentration. When two aq. Solution of different concentration are separated by a semi-permeable membrane, water passes through the semipermeable membrane in the direction of more conc. solution as a result of osmotic pressure. (i.e. pressure exerted by this mass transfer is known as osmotic pressure).



This natural process may be reversed by applying a pressure on the brine side higher than that of the osmotic pressure, and then fresh water tends to flow from brine into fresh water. Thus the process, which reverses the natural spontaneous osmosis, is called reverse osmosis. The greater the pressure applied the more rapid is the diffusion.

Sea water exerts an O.P. of about 240 psi. Reverse osmosis can be effected by the use of pressure in the range of 410-510 psi.

**Process:** An R.O. unit is simple as shown in fig. given below.



**Fig: Reverse osmosis method of desalination**

A series of tubes made up of porous material is lined on the inside with extremely thin film of cellulose acetate semi-permeable membrane. These tubes are arranged in parallel array in fresh water.

Brackish water is pumped continuously at high pressure through these tubes. Water flows from brackish water into fresh water. The flow of water is proportional to applied pressure which in turn depends on the characteristics of the film. Greater the number of tubes, larger is the surface area and hence more production of fresh water. Concentrated brine and fresh water are withdrawn through their respective outlets.

**Advantages:**

1. The energy requirements are low.
2. Process is simple and continuous.
3. It involves no phase changes
4. Provides odorless, crystal clear water.
5. Easy to maintain

**Disadvantages:**

1. This method is not used on large scale production of fresh water
2. It is only successful in recovery of fresh water from brackish water

**5. (a) Describe ion exchange method for softening of water? How do you regenerate the resin in this method? (05 Marks) (CO4, L4)**

**Solution:**

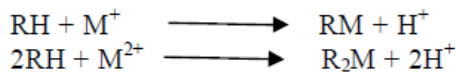
Water softening is the process of reducing the dissolved salts of Ca, Mg and Fe in water, thus reducing the hardness of water and making it soft.

In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin.

Ion exchange resin is a cross-linked organic polymer having some ionisable group. It may be of two types depending upon the nature of the ionisable group.

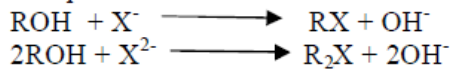
1. **Cation exchange resin or cation exchanger:** These resins have acidic group as the ionisable group such as  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{H}_2\text{PO}_3$  group. These resins contains replaceable hydrogen ( $\text{H}^+$ ) ion and they exchange cationic portion of salts with  $\text{H}^+$ .
2. **Anion exchange resin or anion exchanger:** These resins have basic group which are capable of exchanging their  $\text{OH}^-$  group with the anion present in water. They have group like  $-\text{NH}_2$ ,  $-\text{NHCH}_3$ ,  $-\text{OH}$  groups.

**Process:** In this process cations and anions are packed in separate column. Hard water is first passed through cation exchange resin where cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are removed from hard water by exchanging  $\text{H}^+$  ions as follows.



Where R is part of resin,  $\text{M}^+$  is monovalent ion like  $\text{Na}^+$  and  $\text{M}^{2+}$  is divalent ion like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ .

The cation free water is passed through another tank having anion exchanger, which absorbs all the ions present in water and leave behind the water molecules.



Where  $\text{X}^-$  and  $\text{X}^{2-}$  represent the anion such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$

Thus the cation and anion impurities in water are replaced by an equal number of  $\text{H}^+$  and  $\text{OH}^-$  ions

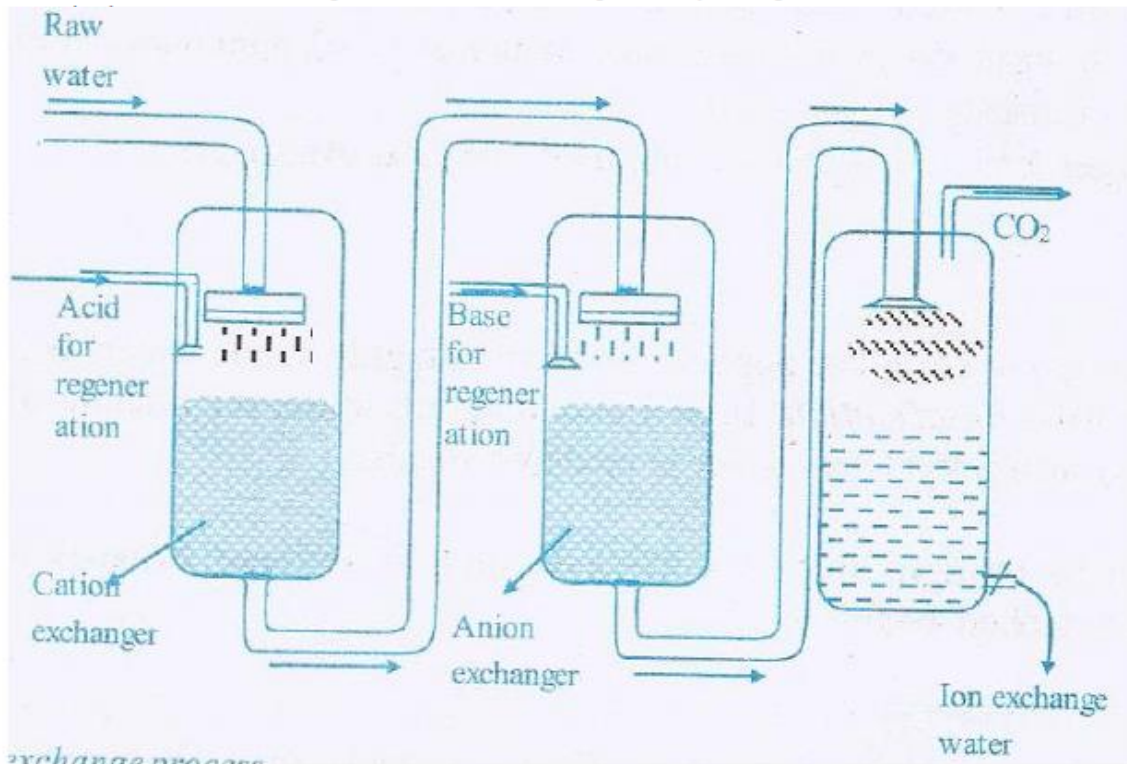


Fig. Ion Exchange process

**Regeneration of spent catalyst:** After some time when the resins are exhausted and lose their capacity to exchange ions, they need to be regenerated again. Regeneration is the reversal of the reaction taking place for ion exchange.

The cation exchange resin is regenerated by flushing it with hydrochloric acid



The anion exchange resin is regenerated by reacting it with sodium hydroxide.



**Advantage:**

1. Process is completed in few seconds.
2. Use of chemical is minimized.
3. Water of very high purity is obtained.
4. Apparatus is easy to set up and maintain.
5. Resins can be regenerated and can be reused over and over again.

**(b) What are nanomaterials? Explain any two size dependent properties of nanomaterials. (05 Marks) (CO4, L1, L4)**

**Solution:** Nanomaterials: are nano-sized materials having at least one physical dimension in the size range of 1-100 nm. They include nanoparticles, nanostructured materials, agglomerates and aggregates.

**(i) Catalytic activity:** Nanomaterials have high surface to volume ratio and so exhibit good catalytic activity. For example, nano-structured metal clusters (Pd clusters) show improved catalytic properties for hydrogenation. Such clusters are integral part of cortex catalysts (heterogeneous type), where the active catalytic material is supported on solid oxide surface. These catalysts have improved life time and better catalytic activity. Nanomaterials can be used to construct efficient electrodes for fuel cells and in enantioselective catalysis where chiral modifiers are immobilised on the surface of metal particles.

**(ii) Crystal structure:** The crystal structures of micro-sized and nano-sized materials of the same chemical composition, are however different in most cases. Eg: Y<sub>2</sub>O<sub>3</sub> is monoclinic at nano-dimensions while in bulk it has a cubic symmetry. Conventional ZrO<sub>2</sub> is monoclinic, while in nanoscale it has tetragonal symmetry.

**6. (a) Explain the synthesis of nanomaterials by Sol-gel process and precipitation method. (06 Marks) (CO6, L3).**

**Solution:**

**(i) Sol-Gel:**



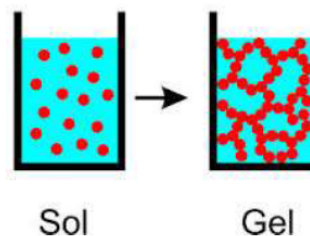
This is a colloidal process in which dispersions have two phases, a dispersed phase with particles having colloidal dimensions ( $< \mu\text{m}$ ) and a dispersion medium. The process can be used to obtain metal and metal oxide nanocrystals with controlled particle sizes.

Sols are solid particles formed by hydrolysis of metal precursors and are dispersed in the solution medium. The commonly used metal precursors are their (i) alkoxides  $[\text{M}(\text{OR})_n]$  and (ii) salts (MX), and

should have the tendency to form gels. Examples of  $\text{M}(\text{OR})_n$ , where  $-\text{OR}$  is an alkoxide group, may be methoxides, ethoxides, propoxides of Al, Fe, Ti, Zn, and salts like  $\text{FeCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Zn}(\text{NO})_3$  etc.

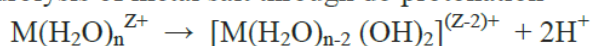
For nanomaterial synthesis, the process involves:

- (i) Hydrolysis of precursors
- (ii) Condensation and polycondensation to form particles
- (iii) Allowing gelation to occur (ageing)
- (iv) Drying of gel to obtain solid material, followed by its sintering to form nanoparticles

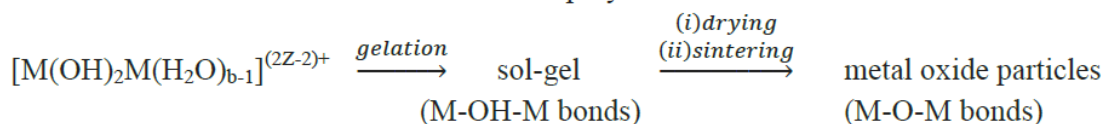
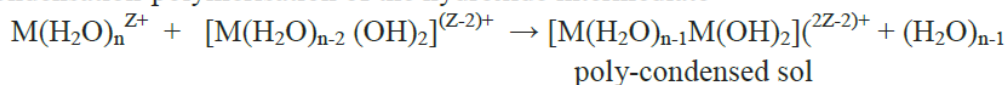


The important reactions in the process:

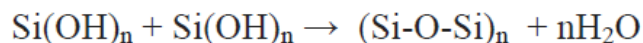
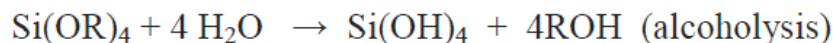
- (i) Hydrolysis of metal salt through de-protonation



- (ii) Condensation-polymerisation of the hydroxide intermediate



When an alkoxide is used, the important reactions are:



The material can be used to prepare nanocrystals, films and fibres.

## (ii) Precipitation Method:

The method employs mixing of reagents to get an insoluble material as a precipitate. For preparation of nanosized particles by this method, the reagents to be mixed are introduced at critical supersaturation limit. For example, when  $\text{AgNO}_3$  is mixed with  $\text{NaCl}$ , a precipitate of  $\text{AgCl}$  is formed. White  $\text{BaSO}_4$  precipitate is formed when  $\text{BaCl}_2$  is mixed with  $\text{H}_2\text{SO}_4$ .

The process involves (i) nucleation and (ii) growth of nuclei to form a particle. During nucleation few molecules come together and aggregate to form several nuclei. In the growth phase, smaller precipitates dissolve and get deposited on the bigger ones. This is Ostwald's ripening.

Bulk precipitates of the size of  $\mu\text{m}$  to  $\text{mm}$  are generally formed when saturation concentration is reached and in absence of a controlled reaction. For nano-sized particles, the reagents are mixed at critical supersaturation limit, beyond which nucleation begins.

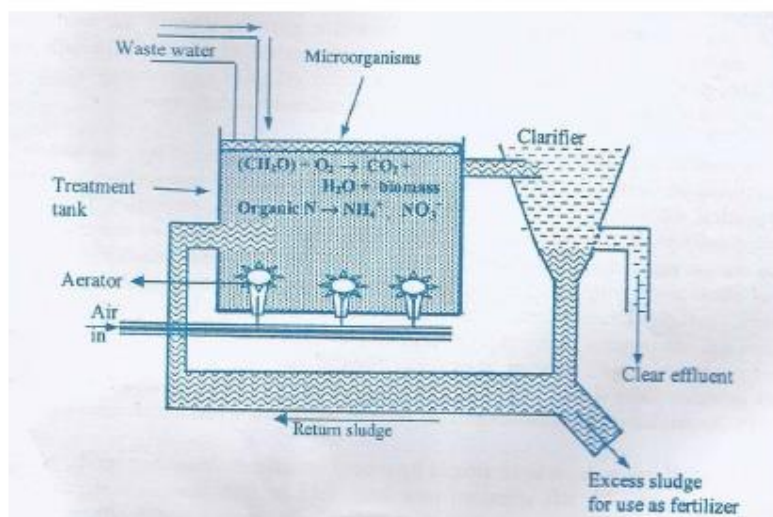
*Preparation of nano-sized AgBr from  $\text{AgNO}_3$  and NaBr solutions:* A double jet precipitation apparatus is used to prepare nanoparticles of AgBr by solution precipitation using equimolar  $\text{AgNO}_3$  and NaBr solutions. The apparatus allows to regulate particle concentration, temperature, rate of reagent addition and mode of mixing for the reaction.

The reagents are introduced through fine tubes into the apparatus in regulated pulses and a mixing device is used that is attached to a high speed motor shaft and rotates at controlled speed of 2000 rpm. The rate of reagent addition through fine tubes is controlled using a remote pump. One of the reagents (0.01 M  $\text{AgNO}_3$ ) is introduced above the inlet zone of the mixing device, while NaBr (0.01 M) is added below. The solution concentration is kept high ( $> 0.5$  M) and the temperature of the system maintained at  $70^\circ\text{C}$ . Baffles are present around the mixing device that inhibits the vertical rotation of the contents in the vessel.

At high rates of reagent addition, supersaturation is obtained at the introduction point leading to high nucleation rate for the particle formation. Supersaturation is relieved by stirring at regulated speed and the resulting emulsion will have particles of 7-60 nm AgBr. The use of capping agents and re-dispersion will stabilize the prepared nanoparticles.

## (b) Explain the activated sludge treatment of sewage water. (04 Marks) (CO4, L2)

**Solution:**



**Fig. Activated sludge process**

**(b) Secondary(Biological) treatment (Activated sludge process).**

- The waste water after the primary treatment is allowed to flow into large tanks where biological treatment is carried out.
- *Activated sludge* containing microorganisms (from a previous operation) is sprayed over the water. The microorganisms present in the sludge form a thin layer and thrive on the organic wastes in the sewage.
- Air is passed vigorously from the centre of the tank in order to bring good contact between the organic wastes and bacteria in presence of air and sunlight. Under these conditions, aerobic oxidation of organic matter occurs.
- The sludge formed is removed by settling or filtration. A part of the sludge is reused and the rest is used as fertilizer.
- The residual water is chlorinated to remove bacteria and finally discharged into running water or used for watering plants. The activated sludge process operates at 90-95 % efficiency of BOD treatment.

If the treated water contains a high concentration of phosphates, heavy metal ions, colloidal impurities and non-degradable organic compounds, the water is subjected to tertiary treatment.

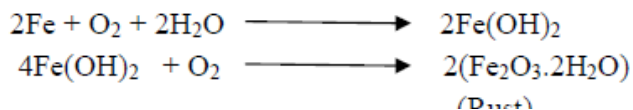
**7. (a) Discuss the boiler corrosion and its control. (06 Marks) (CO5, L4)**

**Solution:**

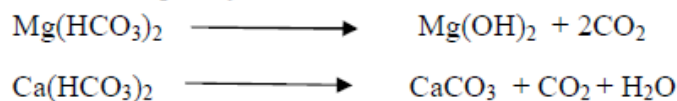
**Boiler Corrosion:** It is the most serious problem created by the use of unsuitable water in boiler. It is largely due to presence of

- Dissolved Oxygen
- Dissolved CO<sub>2</sub>
- Acid from the dissolved salts

1. **Corrosion due to Dissolved Oxygen:** When water containing O<sub>2</sub> is heated (350-450 °C) in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler material and forms rust.



2. **Corrosion due to CO<sub>2</sub>:** CO<sub>2</sub> is present in the water either from the air or due to the presence of temporary hardness.



It dissolves in water to produce carbonic acid which is slightly acidic in nature and cause corrosion.



3. **Acids from the dissolved salts:** Minerals acids are produced by the hydrolysis of salts like  $\text{MgCl}_2$ ,  $\text{FeCl}_2$  present in boiler feed water.



This acid reacts with iron to form rust.



**Electrochemical processes:** Impurities or stains in the metal constituting the boiler are responsible for electrochemical processes leading to corrosion. The impurities or the stains in the metal act as electrodes and thus a number of electrolytic cells are set up.

**Control of boiler corrosion:** It can be controlled by removing  $\text{O}_2$ ,  $\text{CO}_2$ , or any impurities from the feed water.

**1. Removal of  $\text{O}_2$ :**

1. First it is removed by deaeration. Removal of dissolved gases from boiler feed water is called deaeration. Several types of deaerator are available for this purpose.
2. Deoxygenation can also be carried by using chemicals such  $\text{O}_2$  scavengers to the boiling water.

- In low pressure boilers, the removal of oxygen is effected by adding a 3-5% solution of sodium sulphite to boiling water.



- In High pressure boilers the removal of oxygen is done by treatment with a very small amount of hydrazine.



The reaction is complete in a few seconds and no trace of hydrazine remains as it is completely converted into nitrogen.

**2. Removal of  $\text{CO}_2$ :**

1. Mechanical removal can be done by deaeration.
2. Chemical removal can be done by treating with lime or  $\text{NH}_4\text{OH}$



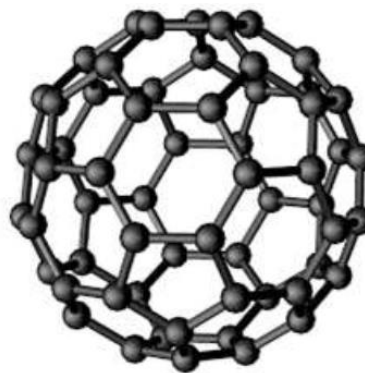
**3. Removal of acidic impurities:** Finally acidic impurities can be removed by treatment of water with alkaline  $\text{NH}_4\text{OH}$ .

**(b) Write a note on fullerenes. (04 Marks) (CO4, L2)**

**Solution:**

## 1. Fullerenes

Fullerenes are clusters made of carbon and are zero dimensional solids. They are allotropes of carbon with the formula C-60 and have 60 C atoms arranged spherically. They are also called Bucky balls and have truncated icosahedron structure with 20 hexagonal and 12 pentagonal rings forming the symmetry.



**Buckminster Fullerene - C60**

Fullerenes have particle size of 2 nm, density of  $1.65\text{g/cm}^3$  and sublimes at 800K.

The carbon atoms are  $sp^2$  hybridised, each carbon being bonded to three others in this material. Accordingly, there are two C-C bond lengths in fullerenes, the hexagonal bonds are shorter than pentagonal bonds.

They behave as soft electrophile and readily accept electrons during reactions. C60 structure can be easily hydrogenated, methylated and fluorinated. They form exohedral complexes in which an atom or group is attached to the outside of the cage, as well as endohedral complexes in which an atom is trapped inside the cage structure.

**Synthesis:** Fullerenes are prepared by creating an electric arc between two carbon or graphite electrodes in an inert gas atmosphere, when a black powder in the form of soot is produced. 10% of the soot is made up of C-60. They can be extracted from the soot by solvation in small amounts of toluene. After extraction, solvent is removed using a rotary evaporator, leaving behind a solid mixture of mostly C-60 with small amounts of larger fullerenes.

Bucky balls having more number of C atoms such as, 70, 76, 78, 84 etc arranged spherically have been isolated.

**More properties:**

- Superconductivity is discovered in alkali doped fullerites at moderately high temperatures.
- Superconducting critical temperature ( $T_c$ ) of doped fullerites increases with curvature of fullerenes cages, i.e. as cluster size is reduced from C60 to C36, C28 and C20, their  $T_c$  increases.
- The index of refraction for fullerenes is 2.2 at 600 nm and they have a resistivity of  $10^{14}\ \Omega\cdot\text{m}$ .
- They function as catalysts in organic reactions.