Solutions

CMR INSTITUTE OF TECHNOLOGY

Sub:	**Engineering Chemistry**							Code:	17CHE12
Date:	18/11/2017	Duration:	90 mins	Max Marks:	50	Sem:	I	Branch:	All

Internal Assessment Test III – November 2017

1. (a) What are elastomers? Detail the synthesis and applications of elastomers taking silicone rubber as an example. (05 Marks) (CO105, L1,L3)

Solution: ELASTOMERS are high polymers which undergo very large elongation under stress, yet regain original dimension on release of stress. They have linear but highly coiled structure. eg. Natural rubber, synthetic rubbers like neoprene, butyl rubber etc.

Properties and uses

1. Silicones have high thermal stability and can be heated in air to about 2000C
2. They are also water repellant.
3. They are used in making lubricants, used in gaskets, seals, wire and cable insulation.

(b) Discuss scale and sludge formation taking place in boiler due to contaminated feed water. Mention their ill effects. (05 Marks) (CO106, L3)

Solution: Scale and Sludge formation: Water is heated under high temperature and high pressure inside the boiler. It gets evaporated to get steam and thus the impurities present in water get progressively concentrated, when impurities reach a saturation point it precipitates out.

If precipitate formed is hard, dense and adherent coating on the boiler surface, it is called as scale. On the other hand if the ppt formed with in the boiler are soft, loose, greasy silky ppt, it is known as sludge.

Scales: These are hard deposits which stick to inner wall/surface of the boiler and are difficult to remove. The composition of boiler scales varies over a wide range. However they may be broadly classified into 3 types.

1. Scales containing salts of Ca and Mg such as CaCO3, CaSO4 etc. These scales are characterized by their names such as carbonate scale, sulphate scales etc.

- Salt of Mg form scale due to the formation of $Mg(OH)_2$, which has low solubility.

  $Mg(HCO_3)_2 \qquad Mg(OH)_2 + 2CO_2$
- Calcium bicarbonate decomposed on heating produces calcium carbonate which has low solubility in water and hence forms scales

  $Ca(HCO_3)_2 \qquad CaCO_3 + CO2 + H2O$
- Solubility of CaSO4 decreases with increase in temperature. In boiler the temperature at the walls will be higher than in the interior. The $CaSO_4$ gets saturated in the water which is in contact with surface and it gets precipitated out in the form of scales.

2. Scales containing ferrous and ferric compounds such as oxides, carbonates and phosphates.

3. Silicate Scales: Silica react with Ca and Mg present in water to form silicates of calcium and magnesium. These silicates form hard and glassy scale on the inner surface of boiler.

Harmful effects of boiler scales:

1. Wastage of fuel: scales is a bad conductor of heat. It is like coating of insulating layer on metal surface. This leads to reduced rate of heat transfer and thus loss or wastage of fuel.

2. Lowering of boiler efficiency: Excessive scaling results clogging of boiler tubes or boiler parts may get chocked by deposition of scales. This may reduce the water circulation and thus efficiency of boiler.

3. Boiler explosion: Scales forms a coating on inner surface of boiler. On heating metal gets heated faster than scales as metal is a very good conductor of heat. This results in expansion ofmetal but scales do not expand much. Due to this, scales crack and water from inside the boiler comes in contact with hot metal and immediately forms steam. This steam exerts a pressure on the boiler wall which may crack under pressure and burst.

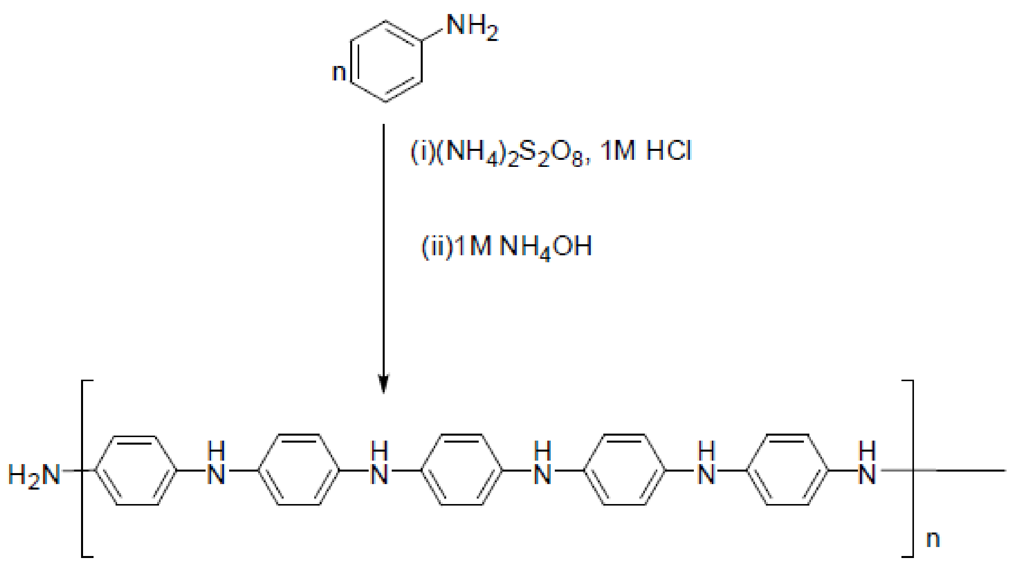
4. Loss of strength of boiler: Because of overheating boiler material gets softer and weaker and thus make boiler unsafe to use.

5. Expense of cleaning: Cleaning process of scale is very much expensive.

2. (a) Define conducting polymers. Also explain the mechanism of conduction in polyaniline. (06 Marks) (CO105, L1,L4)

Solution: Those polymers which can conduct electricity are known as conducting polymers. These organic polymers have conjugated backbone with alternating single and double carbon-carbon bonds. Example: Poly aniline

Mechanism :

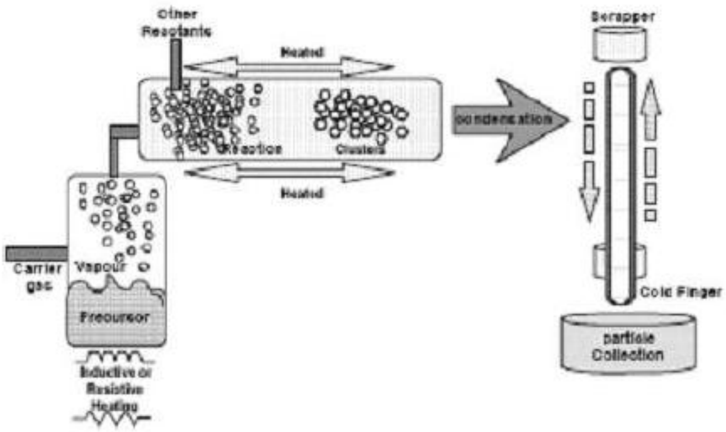


(b) Describe the chemical vapour condensation method of preparation of nanoparticles. (04 Marks) (CO105, L4)

Solution: In this method, the precursor material is vaporized, and the vapours are brought into contact with a hot surface of a reactor under supercritical conditions favouring nucleation of particles. The precursor material can be solid, liquid or gas at room temperature, but are delivered to the reactor as a vapour. In case of solids, they are sublimed by heating from an external source and for liquids and volatile solids dissolved in solvents, precursors are bubbled out using inert gas. Vapours decompose in the hot zone and form particles that agglomerate. They are further swept by inert gas onto the surface of a cold finger, where they get condensed. The particles are scrapped into a collector at regulated intervals. Due to high supersaturation that results in this method, it is typically used to synthesis NPs of metals in large scale. Metal NPs are produced by using their carbonyls and acetylacetonates as precursor materials. Examples are Fe(CO)5 for Fe; W(CO)6 for W; Cu and Ni acetylacetonates for their respective metal NPs.

Chemical vapour synthesis enables formation of doped or multicomponent nanoparticles. NCs of

Y2O3:Eu3+ are prepared from vapours of organometallic Y and Eu precursors mixed at required ratios. Encapsulated materials can also be prepared using this approach, such as NaCl encapsulated Si particles. The nanostructured material is prepared by reacting SiCl4 vapours with those of sodium in a heated furnace. The encapsulation prevents agglomeration of particles.



3. (a) How does an adhesive function? Illustrate on the synthesis and applications of epoxy resin. (05 Marks) (CO105, L4)

Solution: The function of an adhesive is to bind together two or more materials so that the resulting material can be used as a single piece. Adhesives are classified into natural and synthetic.

Natural adhesives - eg.Common gum and glue. Synthetic adhesives - eg.Resins.

Properties: 1. Excellent adhesion quality for various surfaces. 2. Highly resistant to water, solvents, acids and alkalies.

Applications: 1. Adhesive is used for lamination. 2. Adhesive is used as structural adhesive

(b) Define COD. In COD test 29.5 & 15.6 cm3 of 0.02 N FAS solution is required for blank and sample titration respectively. The volume of test sample used is 25 cm3. Calculate the COD of sample solution. (05 Marks) (CO106, L1,L4)

Solution: COD: It is defined as the amount of O2 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 $K_2Cr_2O_7$.

Given, V = 25 cm^3, b = 29.5 cm^3, a = 15.6 cm^3, N_{FAS} = 0.02N

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

$$= 0.02 \text{ X } (29.5-15.6) \text{ X } 8000/ 25 = 88.6 \text{ mg of } O_2 /dm^3$$

4. (a) Explain ion exchange process for softening of water. How is the exhausted resin regenerated in ion exchange process? (CO106, L4)

Solution:

The water obtained after this process is ions free and called as ion exchanged water or deionized (demineralized) water.

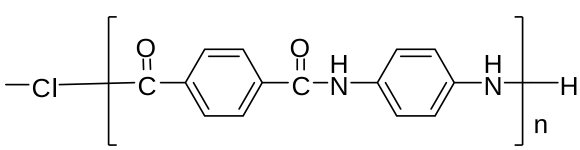
Regeneration of spent catalyst: After some time when the resins are exhausted and loose their capacity to exchange ions, they need to be regenerated again. Regeneration is the reversal of the reaction taking place for ion exchange.
The cation exchange resin is regenerated by flushing it with hydrochloric acid

$$RM + H^+ \longrightarrow RH + M^+$$

$$R_2M + 2H^+ \longrightarrow 2RH + M^{2+}$$

(b) What are polymer composites? Explain the synthesis and applications of Kevlar. (05 Marks) (CO105, L4)

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.
It is obtained by aramide fibers is coated with some resin matrix.
Aramide ex:



poly(paraphenylene terepthalamide)

It is an aromatic polyamide with the name poly(para-phenylene terephthalamide).
The linkage through para positions of the phenyl rings gives Kevlar a strong ability to stretch and hence its extra strength.

Properties and applications:

- It forms even better fibres than non-aromatic polyamides.
- It has high tensile strength and modulus than fibre glass.
- These are used for structures which require stiffness, high abrasion resistance and light weight.
- Applications include lightweight boat hulls, aircraft fuselage panels, pressure vessels, high performance race cars, bullet proof vests and puncture resistant bicycle tyres.

5. (a) With a neat sketch, explain the desalination of water by reverse osmosis method. (05 Marks) (CO106, L4)

Solution: 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).

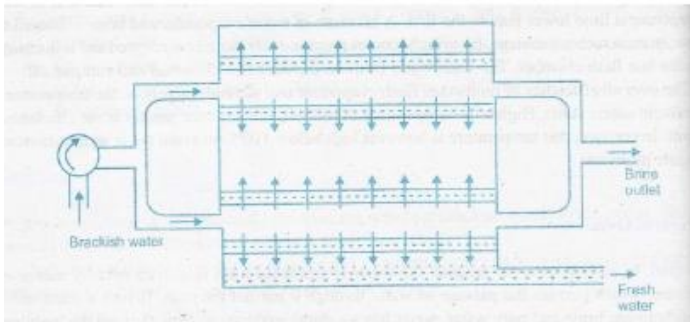
This natural process may be reversed by applying a pressure on the brine side higher than that of the osmotic pressure, and then fresh water tends to flow from brine into fresh water. Thus the process, which reverses the natural spontaneous osmosis, is called reverse osmosis. The greater

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. 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



(b) Explain precipitation technique as a suitable method to prepare nanomaterials. (05 Marks) (CO105, L4)

Solution: 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.

<u>Principle:</u> 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. Bulk precipitates of the size of µm to 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.

<u>Example and process:</u>

Preparation of nano-sized AgBr from $AgNO_3$ and NaBr solutions.

A double jet precipitation apparatus is used to prepare nanoparticles of AgBr by solution precipitation using equimolar $AgNO_3$ and NaBr solutions. 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 . The rate of reagent addition through fine tubes is controlled using a remote pump. AgNO3 is introduced above the inlet zone of the mixing device, while NaBr is added below. The solution concentration is kept high and the temperature of the system maintained at 70 ^{0}C. 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.

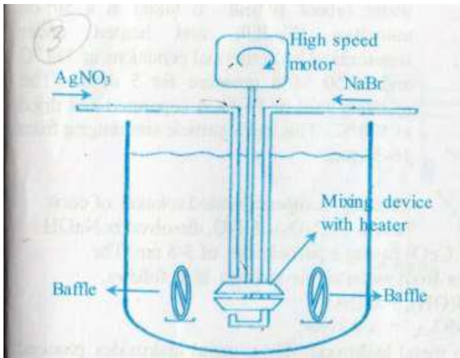


Fig. 9.8 *Controlled double jet precipitation* apparatus

6. (a) What are nanomaterials? Discuss how do surface & thermal properties of nanomaterials change with respect to their bulk. (05 Marks) (CO105, L3).

Solution: Nanomaterials are nano-sized materials having atleast one physical dimension in the size range of 1-100 nm. They include nanoparticles, nanostructured materials, agglomerates and aggregates and should have very narrow size-distribution.

Surface Property: 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.

Thermal properties: As size decreases, the surface energy of the crystals increases and their melting point decreases. This occurs because, the surface atoms in nano-sized crystals are in contact with fewer atoms of the substance and so require less energy to diffuse. For example, 3 mm CdSe nanocrystals (NCs) melts at 700 K compared to bulk CdSe, whose melting point is 1678 K.

(b) Explain activated sludge method of sewage treatment. How will you purify water further for removing heavy metals? (05 Marks) (CO106, L4)

Solution:

- 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.

For purifying water from heavy metals, it can be treated with S^{2-} ions (eg. H_2S treatment) and can be removed as insoluble sulphides.

7. (a) Explain the determination of dissolved oxygen in water by iodometric method. (06 Marks) (CO106, L4)

Solution: The measurements of the amount of oxygen actually dissolved in a water sample are of great importance as the oxygen content is important for many biological and chemical processes. DO test is used to control the amount of oxygen in boiler feed water by physical, chemical and mechanical methods.

Principle:

The principle involved in the determination of dissolved oxygen is, “In alkaline medium, the dissolved oxygen in water oxidizes KI and an equivalent amount of iodine is liberated. The liberated iodine is titrated against a standard sodium thiosulphate solution using starch as an indicator. However since dissolved oxygen in water is in molecular form and is not capable of reaction with KI. Hence an oxygen carrier such as Mn(OH)2 is required. The DO present in water sample oxidizes divalent manganese to tetravalent manganese. The basic manganic oxide formed acts as oxygen carrier to enable the dissolved oxygen in molecular form to take part in the reaction. Upon acidification, tetravalent manganese reverts to divalent state with the liberation of nascent oxygen, which oxidizes KI to I2. The liberated iodine is titrated against standard sodium thiosulphate solution using starch as indicator.

Procedure:

Pipette out 300 cm^3 of water sample into a clean glass stoppered bottle. Add 3 cm^3 of manganous sulphate solution dipping the pipette below the surface of water. Add 3 cm^3 of alkaline potassium iodide solution. Stopper the bottle and shake well and allow the precipitate to settle down. Now add 1 cm^3 of concentrated sulphuric acid slowly and mix well until the precipitate dissolves completely and get a clear solution. Pipette out known volume (v mL) of this solution into a clean conical flask and slowly titrate against std. sodium thiosulphate solution using starch as an indicator near the end point. The end point is indicated by disappearance of blue colour. Record the volume of sodium thiosulphate solution used.

(b)

Write a note on carbon nanotube. Mention two of its important applications. (04 Marks) (CO105, L4)

Solution: CNTs are allotropes of carbon with a tubular structure, having diameter of nanometer order, but length in micrometers. They can be visualized as the folding of a single layer of graphite sheet (also referred to as graphene) into a tubular structure. If there is a single sheet folded into a cylindrical structure, it is called as single wall carbon nanotube (SWCNT). If there are multiple sheets forming concentric layers, such structures are multi walled carbon nanotubes (MWCNT). MWCNTs have outer diameters ranging from 2 to 25 nm. CNTs have C atoms in sp2 hybridized state with a C-C bond length of 1.44 Å. They have densities between 1.2 to 2.0 less than that of diamond (3.5) and graphite (2.26). They have their ends open or closed, the ends being closed by semi-circular fullerene that act as caps.

Synthesis**:** One of the methods widely used for preparing CNTs is chemical vapour deposition (CVD) technique. In this process, thermal decomposition of a hydrocarbon (HC) is achieved in the presence of a
metal catalyst. The hydrocarbon vapours are passed over a catalyst (Fe, Co, Ni or Pt) kept in a tubular furnace at high temperatures. Depending on the HC precursor, the decomposition temperature used is in the range of 600-1200 0C. An inert gas is also passed for 15-60 mts. CNTs grow on the catalyst surface and are collected after cooling the furnace. Methane, ethylene, acetylene, CO, benzene (liquid), camphor and naphthalene (solid) are some of the precursors used for growing CNTs. Gaseous precursors are introduced directly into the furnace, while liquid precursors are purged by passing the inert gas. Vapors of the precursors are allowed to come into contact with the catalysts, which is usually coated on a substrate material. Hydrocarbon decomposition takes place on the metal surface, and the type of the CNT formed depends on the particle size of catalyst metal-cluster on the substrate surface.

More properties

- They behave as semiconductors, and their resistivity features can be changed on doping.
- CNTs are stronger than steel, and harder than diamond.

- Their thermal conductivity is higher than diamond
- The electrical conductivity is greater than copper.