Solutions

CMR INSTITUTE OF TECHNOLOGY

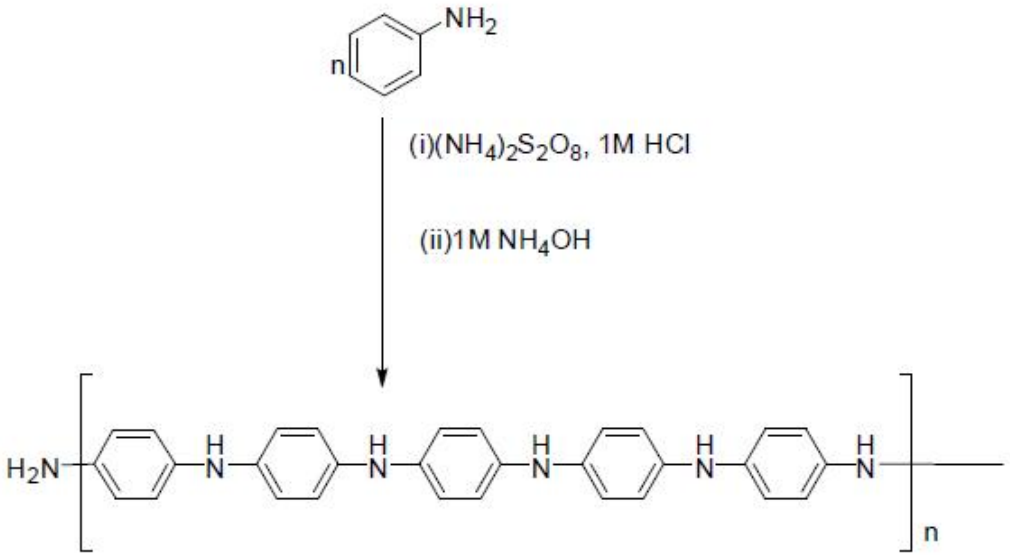
Sub:	**Engineering Chemistry**					Code:	15CHE22
Date:	31/05/2017	Duration:	90 mins	Max Marks:	50	Sem: II	Branch: All

Internal Assessment Test III – May 2017

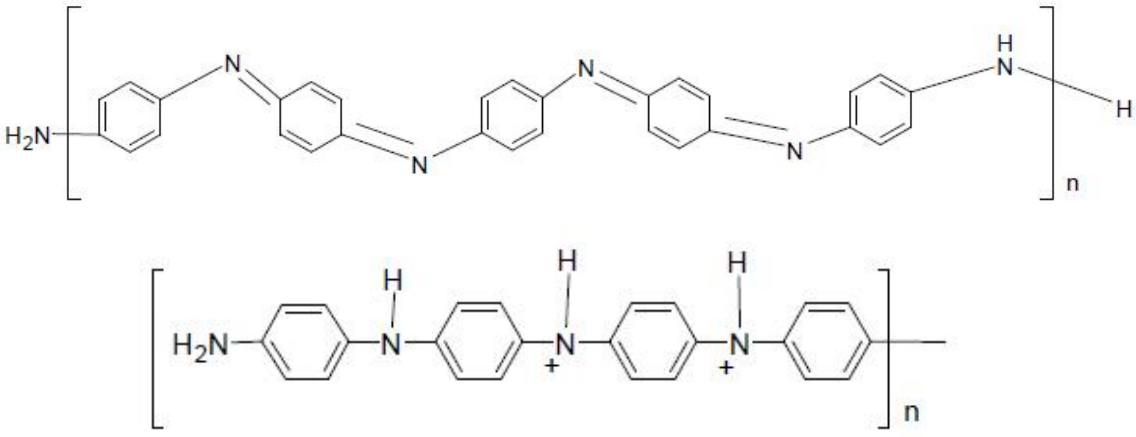
1. (a) What are conducting polymers? Discuss the mechanism of electronic conduction in polyaniline. (06 Marks) (CO5, L1, L2)

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

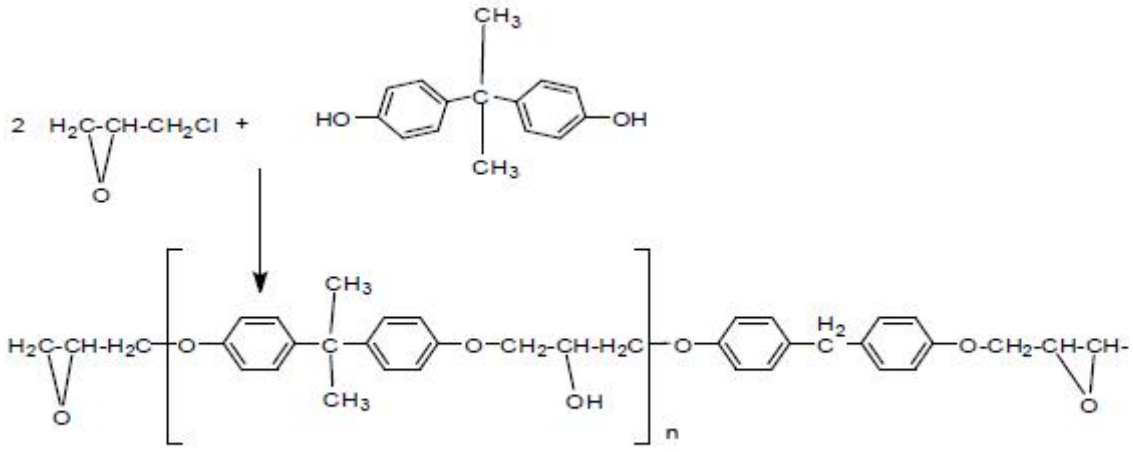
Mechanism :



The structure of emeraldine is given below *(after treatment with alkaline solution)*



(b) Explain the synthesis, properties and applications of epoxy resin. (04 Marks) (CO5, L3)
Solution:



probable structure of an epoxy resin

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

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

2. (a) In a COD experiment 25 mL of waste water was allowed to react with 10mL of $K_2Cr_2O_7$. The leftover $K_2Cr_2O_7$, after oxidizing the impurities, when titrated, required 11.5 mL of 0.025N FAS solution. In a blank titration, when 10mL of $K_2Cr_2O_7$ solution was directly titrated required 18.5mL of 0.025N FAS solution. Calculate COD of waste water. (05 Marks) (CO6, L3)

Solution: Given, V = 25 mL, b = 18.5 mL, a = 11.5mL, N_{FAS} = 0.025N

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

$$= 0.025 \text{ X } (18.5\text{-}11.5) \text{ X } 8000/\ 25 = 56 \text{ mg of } O_2 /dm^3$$

(b) What are elastomers? Discuss synthesis and applications of silicone rubber? (05 Marks) (CO5,L1,L2)

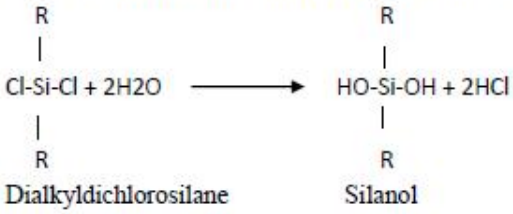
Solution: ELASTOMERS are high polymers which undergo very large elongation under stress, yet regain original dimension on release of stress. They have linear but highly coiled structure. eg. Natural rubber, synthetic rubbers like neoprene, butyl rubber etc.

Synthesis

1. $SiCl_4$ on treatment with Grignard reagent gives dialkyl dichloro silane

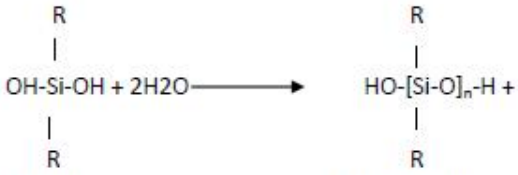
$$SiCl_4 + 2RMgI \longrightarrow \underset{\text{dialkyldichlorosilane}}{R_2SiCl_2} + 2Mg(I)Cl$$

2. These dichlorosilanes are readily hydrolyzed to give silanols.



Dialkyldichlorosilane Silanol

3.Silanol is unstable and immediately undergoes intermolecular condensation to give silicones.



Silanol Silicone rubber

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.

3. (a) What are the key parameters which effect boiler corrosion? Discuss their role and prevention with suitable reactions? (06 Marks) (CO6, L1, L2)

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_2
- Acid from the dissolved salts

1. **Corrosion due to Dissolved Oxygen:** When water containing O_2 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.

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \longrightarrow \underset{\text{(Rust)}}{2(Fe_2O_3.2H_2O)}$$

2. **Corrosion due to CO_2:** CO2 is present in the water either from the airor due to the presence of temporary hardness.

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 + 2CO_2$$

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

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

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

3. **Acids from the dissolved salts:** Minerals acids are produced by the hydrolysis of salts like $MgCl_2$, $FeCl_2$ present in boiler feed water.

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

This acid reacts with iron to form rust.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

1. Removal of 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 O_2 scavangers 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.
     $2\,Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$
   - In High pressure boilers the removal of oxygen is done by treatment with a very small amount of hydrazine.
     $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
     The reaction is complete in a few seconds and no trace of hydrazine remains as it is completely converted into nitrogen.

2. Removal of CO_2:

1. Mechanical removal can be done by deaeration.
2. Chemical removal can be done by treating with lime or NH_4OH

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

3. Removal of acidic impurities: Finally acidic impurities can be removed by treatment of water with alkaline NH_4OH.

(b) Describe the precipitation method of preparation of nanomaterial with an example. (04 Marks) (CO5, L3)

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.

Principle: 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.

Example and process:

Preparation of nano-sized AgBr from AgNO3 and NaBr solutions.

A double jet precipitation apparatus is used to prepare nanoparticles of AgBr by solution precipitation using equimolar AgNO3 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.

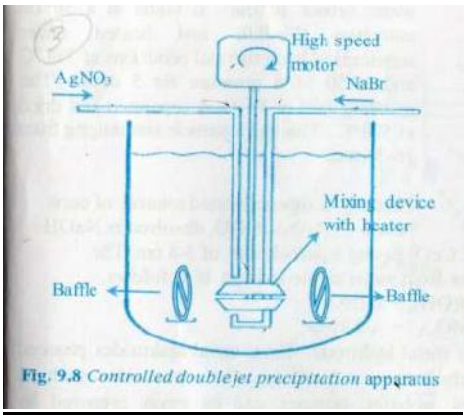
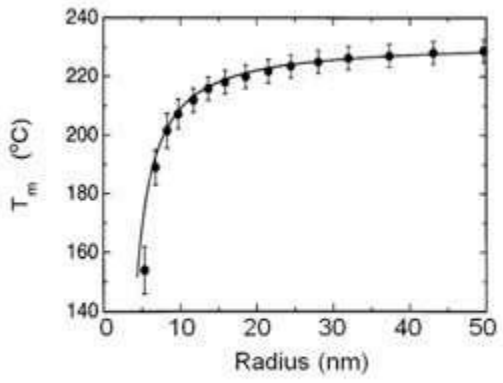


Fig. 9.8 *Controlled double jet precipitation* apparatus

4. (a) Discuss any three size dependent properties of nanomaterials. (06 Marks) (CO5, L3)

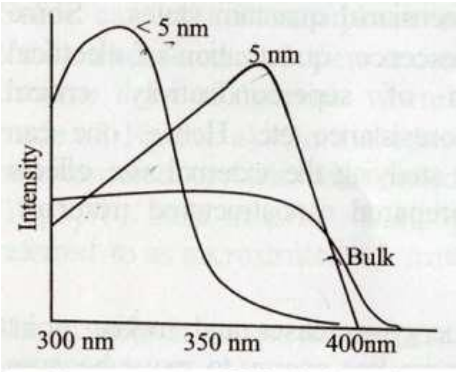
Solution:

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.



Variation in melting points with particle size for Sn particles

Optical properties: Optical properties are connected with the electronic structure. A change in crystal size brings about changes in electronic structure and bandgap (electrons are more restricted in movement in nano-sized particles) leading to changes in absorption or luminescence behavior of the material. Example: Bulk gold appears yellow in colour, whereas nanosized Au appears red. In ZnO, the luminescence spectra shows blue-shift as particle size reduces. ie. The wavelength of the emitted light shifts towards lower wavelengths.



Luminiscence spectra of ZnO with change in particle size. Wavelength of PL shifts towards lower wavelengths (blue shift) with size.

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_2O_3 is monoclinic at nano-dimensions while in bulk it has a cubic symmetry. Conventional ZrO_2 is monoclinic, while in nanoscale it has tetragonal symmetry.

(b) Explain treatment of sewage by activated sludge process. (04 Marks) (CO6, L3)

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.

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.

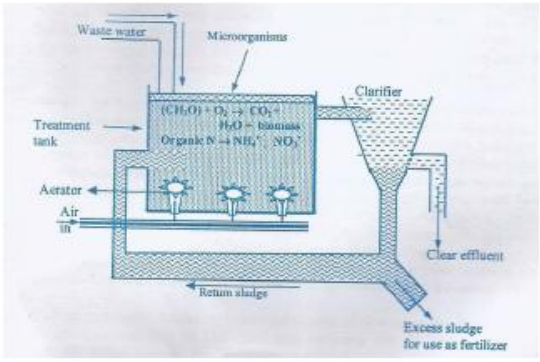


Fig. *Activated sludge process*

5. (a) Write a note on fullerenes and mention its applications. (05 Marks) (CO5, L1)

Solution: 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 icosahedrons structure with 20 hexagonal and 12 pentagonal rings forming the symmetry.

Buckminister Fullerene - C60

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.

Applications:

- Superconductivity is discovered in alkali doped fullerites at moderately high temperatures.
- Superconducting critical temperature (Tc) of doped fullerites increases with curvature of fullerenes cages, ie. as cluster size is reduced from C60 to C36, C28 and C20, their Tc increases.
- The index of refraction for fullerenes is 2.2 at 600 nm and they have a resistivity of 1014 Ω/m.
- They function as catalysts in organic reactions.
- They are used in biomedical field.

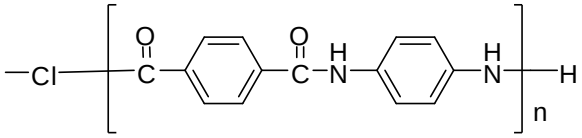
(b) What are polymer composites? Explain the synthesis, properties and applications of Kevlar fibre. (05 Marks) (CO5, L1, L3)

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.

6. (a) Explain ion exchange process for water softening. How the exhausted resin regenerates in ion exchange process? (05 Marks) (CO6, L3)

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 $-SO_3H$, -COOH, $-H_2PO_3$ group. These resins contains replaceable hydrogen (H+) ion and they exchange cationic portion of salts with H+.
2. **Anion exchange resin or anion exchanger:** These resins have basic group which are capable of exchanging their OH- group with the anion present in water. They have group like $-NH_2$, $-NHCH_3$, -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 Ca^{2+}, Mg^{2+} are removed from hard water by exchanging H+ ions as follows.

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

Where R is part of resin, M+ is monovalent ion like Na+ and M2+ is divalent ion like Ca2+, Mg2+.

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.

$$ROH + X^{-} \longrightarrow RX + OH^{-}$$
$$2ROH + X^{2-} \longrightarrow R_2X + 2OH^{-}$$

Where X- and X2- represent the anion such as Cl^{-}, NO_3^{-}, SO_4^{2-}

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

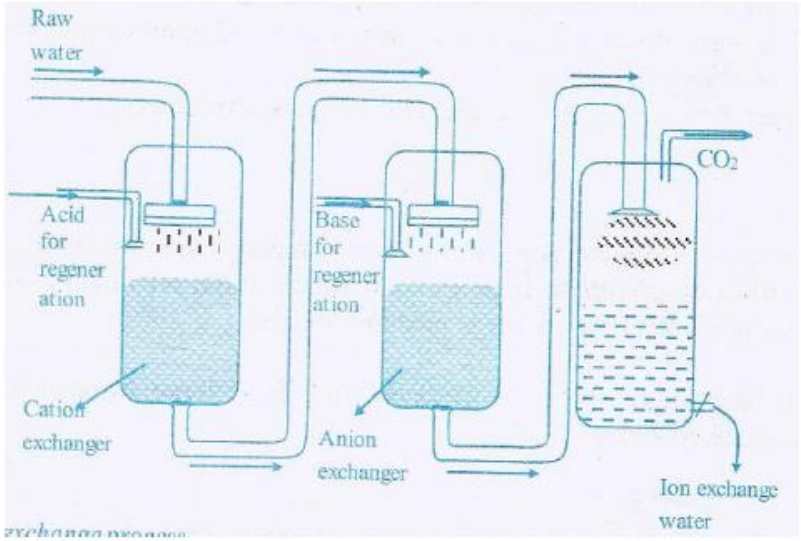


Fig. Ion Exchange process

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

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

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

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

$$RX + OH^- \longrightarrow ROH + X^-$$

$$R_2X + 2OH^- \longrightarrow 2ROH + X^{2-}$$

(b) Explain synthesis of nanomaterials by Sol-Gel method. (05 Marks) (CO5, L1, L3)

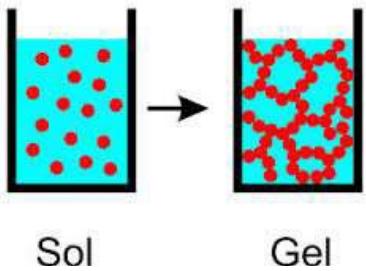
Solution:

This is a colloidal process in which dispersions have two phases, a dispersed phase with particles having colloidal dimensions (< μm) 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 [M(OR)n]and (ii) salts (MX), and should have the tendency to form gels.

Examples of M(OR)n, where –OR is an alkoxide group, may be methoxides, ethoxides, propoxides of Al, Fe, Ti, Zn, and salts like FeCl3, MnCl2, AlCl3, Zn(NO)3 etc.

Process:

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

$$M(H_2O)_n^{Z+} \rightarrow [M(H_2O)_{n-2}(OH)_2]^{(Z-2)+} + 2H^+$$

(ii) Condensation-polymerisation of the hydroxide intermediate

$$M(H_2O)_n^{Z+} + [M(H_2O)_{n-2}(OH)_2]^{(Z-2)+} \rightarrow [M(H_2O)_{n-1}M(OH)_2]^{(2Z-2)+} + (H_2O)_{n-1}$$

poly-condensed sol

$$[M(OH)_2M(H_2O)_{b-1}]^{(2Z-2)+} \xrightarrow{gelation} \text{sol-gel} \xrightarrow{(i)drying\ (ii)sintering} \text{metal oxide particles}$$

(M-OH-M bonds) (M-O-M bonds)

When an alkoxide is used, the important reactions are:

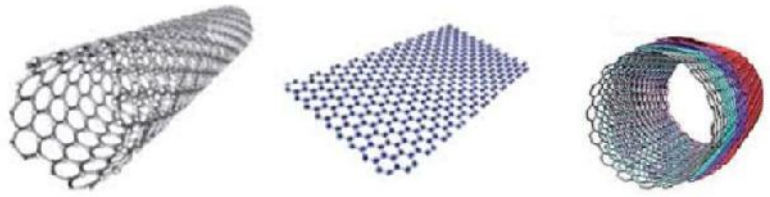
$$Si(OR)_4 + 4\,H_2O \rightarrow Si(OH)_4 + 4ROH \quad \text{(alcoholysis)}$$

$$Si(OH)_n + Si(OH)_n \rightarrow (Si\text{-}O\text{-}Si)_n + nH_2O$$

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

7. (a) What is carbon nanotube? Mention its method of preparation, properties and applications . (05 Marks) (CO5, L2)

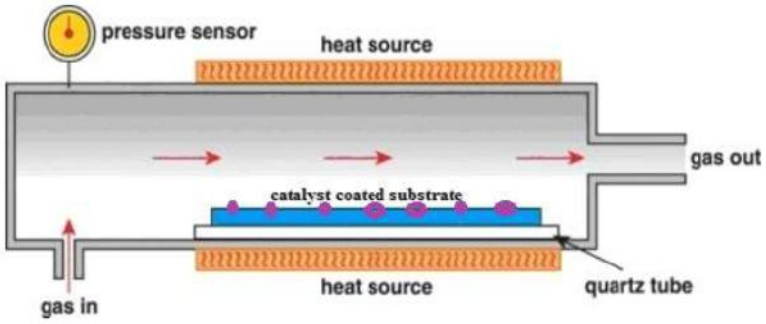
Solution: CNTs are allotropes of carbon with a tubular structure, having diameter of nanometer order, but length in micrometers. They can be visualized as the folding of a single layer of graphite sheet (also referred to as graphene) into a tubular structure. If there is a single sheet folded into a 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.



Carbon nanotube (CNT) Graphene Multiwalled nanotube

***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.

(b) Discuss the desalination of sea water by electrodialysis method. (05 Marks) (CO6, L3)

Solution:

Passage of an electric current through a solution of salt results in migration of cations towards the cathode and anions towards the anode. The use of semi permeable cation or anion exchange membrane in an electrolytic vessel permits the passage of only cations or anions respectively in the solution. This is the principle of desalination of water by electrolysis.

An electrodialyzer consists of a chamber carrying a series of compartments fitted with closely spaced alternate cation (C) and anion (A) exchange semi permeable membranes between the electrodes. An electrodialyzer unit will have 200 to 1000 compartments. The feed water is taken in the dialyzer and the electrodes are connected to a source of an electric current.

The anions pass through the anion permeable membrane towards the anode. However, these ions do not pass through the next membrane which is permeable only to cations. Similarly the cations moving in the other direction will pass through the cation exchange membrane but not the next. These anions and cations collect in the alternate chambers; the water in these is enriched with salt while that in the other compartments is desalinated.

Micro porous sieves provided near the electrodes prevent the reentry of any deposit, which might have been formed on the electrodes, into the feed water. The enriched and desalinated waters are withdrawn separately. The former is rejected and the desalinated water is recycled to further reduce the salt content.

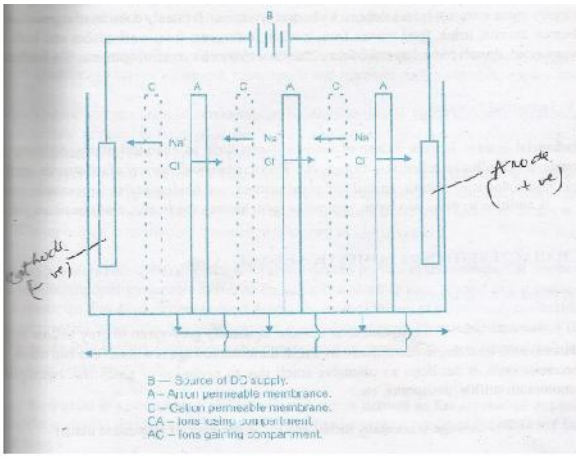


Fig. Electrodialyzer