CMR
INSTITUTE OF
TECHNOLOGY

Sub:	**Engineering Chemistry**						Code:	15CHE12
Date:	16/11/2016	Duration:	90 mins	Max Marks:	50	Sem: I (J,K,L,M,N,O)	Branch:	EC/EE/TE/CV

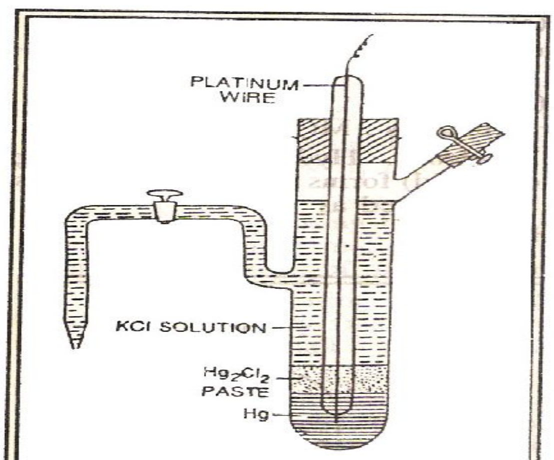
Improvement Test – November 2016

1(a) Describe the construction and working of a calomel electrode.

Calomel electrode

It is a metal **-metal insoluble salt electrode** is also called as secondary reference electrode.

Construction: Electrode consists of glass tube. The bottom of the glass tube is filled with pure mercury (Hg) on which a calomel paste (Hg + Hg_2Cl_2) is placed. The remaining part of the glass tube is filled with sat. or std KCl Solution. It also contains side tube serves as salt bridge and a platinum wire is dipped into the mercury so that it serves as electrical contact.



The calomel electrode.

Half cell representation: The calomel electrode is represented as, KCl /$HgCl_2$, Hg

Working:

(a). When it acts as anode(ox^n): $2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

(b). When it acts as cathode(Red): $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

The electrode potential of the calomel electrode is mainly depends on the concentration of KCl used,

Electrode potential is calculated using Nernst equation,

$$E = E^{\circ} - \frac{2.303RT \log[Cl^{-}]}{F}$$

For, 0.344V for [KCl] = 0.1N

0.281V for [KCl] = 1.0N

0.2422V for [KCl] = saturated KCl

(b) Explain the process of anodizing. Why is Al anodized?

Anodizing is a process in which a protective passive oxide film is artificially (chemically or electrochemically) produced on certain metals. It is also called as anodic oxidation process.

Process:

In this method base metal is made as anode, in an electrolytic bath of suitable composition and passing direct electric current. The most commonly used baths are chromic acid, sulfuric acid, phosphoric acid, oxalic acid etc and lead in general used as a cathode.

When we apply external EMF, at anode oxidation takes place ($Al \longrightarrow Al^{3+} + 3e^{-}$). The Al^{3+} gets combined with the oxygen and formed Al_2O_3 on the anode. This oxide layer is a porous. The strength and corrosion resistance of the anodized film can be increased by sealing, which involves dipping the metal in boiling water or steam or metal salt solution. This treatment changes porous alumina at the surface of the coating into monohydrate ($Al_2O_3.H_2O$), which occupies more volume thereby the pores are sealed. This coating provides good adherence for paints and dyes.

This process is carried out as follows:

The article is degreased, polished and connected to the anode. Steel or copper is made the cathode. The electrolyte consist of 5-10% chromic acid. the temperature of the bath is maintained at 35 ^{o}C. A potential is applied and gradually increased from 0-40 V during first 10 min. Anidizing is continued for 20 min at 40 V. After 20 min, the potential is increased to 50 V and held at this temp for 5 min. An opaque oxide layer is obtained.

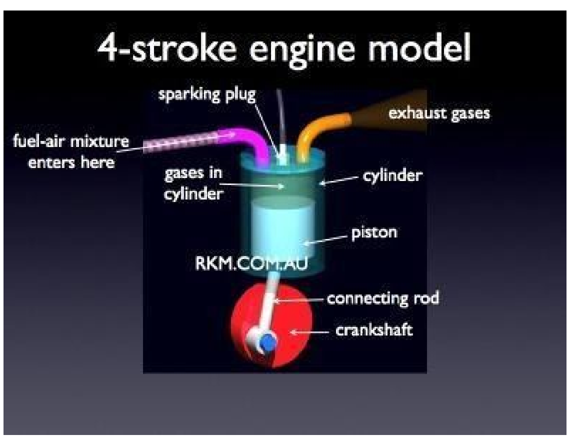
Al can passivates easily and because of its attractive finish and environmentally safe nature anodized aluminium is one of the most widely used industrial, commercial and domestic materials.

2(a) What is knocking? Write the mechanism of Petrol Knocking.

It is defined as the characteristic rattling, metallic sound produced due to thermal shock waves hitting the cylinder walls and piston during explosive combustion of gasoline in an internal combustion (IC) engine.

Petrol Knocking: Petrol engine is spark ignited engine. Gasoline is burnt to produce energy. Following things happen to petrol in an IC engine.

- Petrol is vaporised and vapour is mixed with air.
- The petrol air mixture is drawn into combustion chamber (Suction stroke).
- The petrol air mixture is compressed (Compression stroke).
- The mixture is ignited by a spark from spark plug and burnt.
- The gases produced by the combustion reaction expand.
- Expansion causes the piston to move i.e. kinetic energy is produced.
- When the flame front (after ignition) moves at optimum speed, fuel is burnt smoothly and completely.
- When the flame front moves slowly, products of initially burnt fuel, exert pressure on un- burnt fuel-air mixture. Due to build up of pressure, temperature will also increase.
- All the un-burnt fuel is ignited ahead of the flame front. This produces thermal shock waves (explosive combustion) which hit the cylinder walls and piston; resulting in a characteristic metallic sound called “knocking” or “pinking”. The probable reactions during normal combustion and knocking are presented below taking ethane as the fuel component.



Normal combustion: $C_2H_6 + 3\frac{1}{2}\ O_2 \longrightarrow 2CO_2 + 3H_2O$

Explosive combustion: $C_2H_6 + O_2 \longrightarrow CH_3-O-O-CH_3$ *(ethane peroxide)*

$CH_3-O-O-CH_3 \longrightarrow CH_3CHO + H_2O$ *(acetaldehyde)*

$CH_3CHO + 1\frac{1}{2}\ O_2 \longrightarrow HCHO + CO_2 + H_2O$ *(formaldehyde)*

$HCHO + O_2 \longrightarrow H_2O + CO_2$

(b) Describe how the following factors influence the nature of electrodeposits.

(i) Brightners

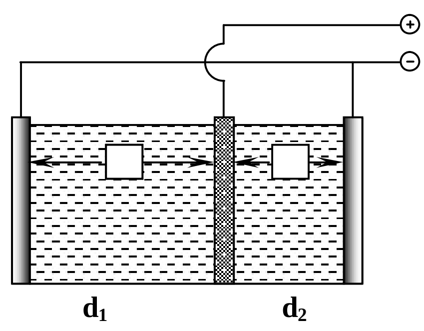
Brighteners are used to get fine grained, reflective, bright electrodeposits. When the grain size is less than the wave length of the light, it is known to give brightened appearance. Smaller grains are formed by promoting formations of larger number of crystal nuclei. Brighteners are known to work by adsorbance over nuclei, disallow the deposition / growth over existing nuclei. Thus, brighteners prompt the formation of fresh nuclei and produce microscopically fine deposits.

Examples: aromatic sulphones and sulphonates, thiourea, coumarin, etc.

(ii) Throwing power

Ability of the plating bath to give uniform deposits on the object surface irrespective of its size or shape is called throwing power.

Throwing power is determined by use of Haring-Blum cell. The cell is a rectangular box made of PVC (polyvinyl chloride) with a provision to place two plate type cathodes at distances, d_1 & d_2 ($d_1 > d_2$) from the active anode kept in between the two as shown in the figure. Electroplating is carried out for certain length of time, anode gets dissolved and deposits on to two cathode surfaces facing the anode (opposite sides will be blocked for such deposition). Let the mass of metal deposited be m_1 & m_2 on cathodes which are at distances, d_1 and d_2 respectively.



mass of metal deposited = $\mathbf{m_1, m_2}$

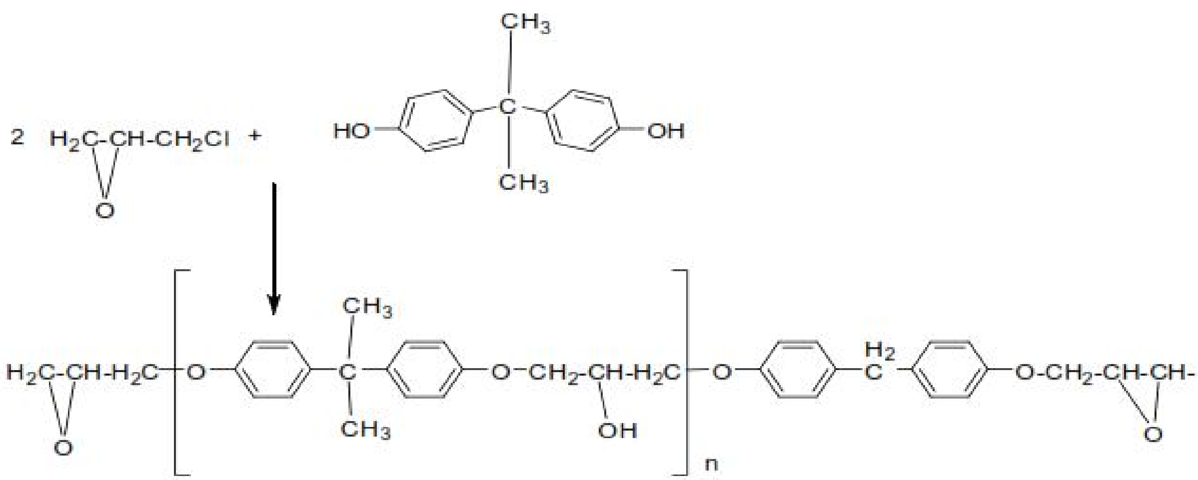
Suppose, $D = \frac{d_1}{d_2}$ and $M = \frac{m_2}{m_1}$. Percentage throwing power is calculated as

$$\% \text{ Throwing Power} = \frac{(D - M)100}{D + M - 2}$$

Throwing power of 100% represents uniform electrodeposition on to object surfaces, whereas, lower values represent as much uneven deposits.

3(a) What is adhesive? Explain the synthesis of epoxy resin and mention two applications of it.

Adhesive is defined as a polymeric substance used to bind together two or more materials so that the resulting material can be used as a single piece.



probable structure of an epoxy resin

APPLICATIONS:
(i)They are widely used as structural adhesives because of their excellent chemical resistant and good adhesion.
(ii) They are used for laminating materials.

(b) What is elastomer? Write synthesis, properties and applications of Silicon rubber.

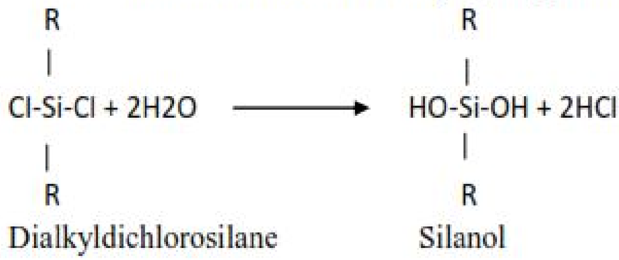
Elastomers are high polymers which undergo very large elongation under stress, yet regain original dimension on release of stress. They have linear but highly coiled structure.

Synthesis

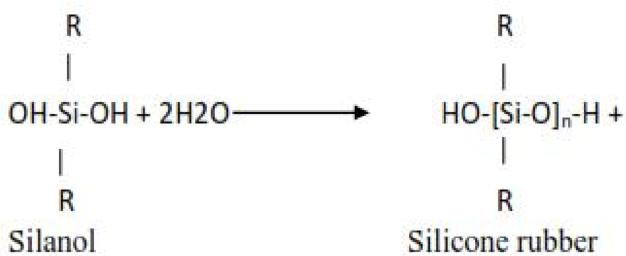
1. $SiCl_4$ on treatment with Grignard reagent gives dialkyl dichloro silane

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

2. These dichlorosilanes are readily hydrolyzed to give silanols.



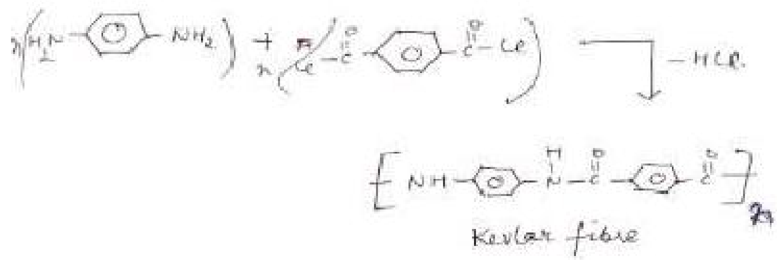
3.Silanol is unstable and immediately undergoes intermolecular condensation to give silicones.



Properties:
1. Silicones have high thermal stability and can be heated in air to about 200
C
2. They are also water repellant.
Uses:
They are used in making lubricants, used in gaskets, seals, wire and cable insulation.

4(a) What is polymer composite? Discuss synthesis of Kevlar and mention two applications of it.

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.



Applications: (i) Used in lightweight boat hulls. (ii) Used in high performance race cars, bullet proof vests and puncture resistant bicycle tyres.

(b) Discuss ion exchange method for softening of hard water. Explain with the help of a neat sketch. How is the exhausted resin regenerated in ion exchange method?

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.

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

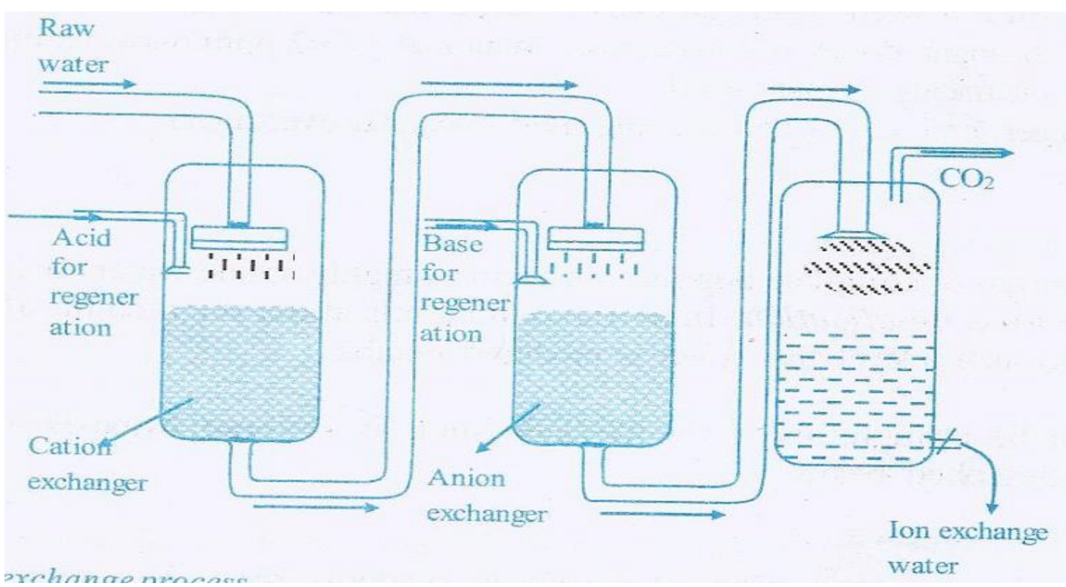
Where R is part of resin, M+ is monovalent ion like Na+ and M2+ is divalent ion like Ca2+, Mg2+.

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.



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

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

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

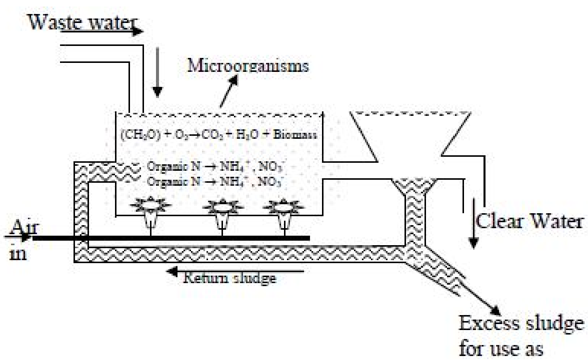
The anion exchange resin is regenerated by reacting it with sodium hydroxide.

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

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

5(a) Discuss activated sludge process in sewage treatment.

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.

(b) Describe boiler corrosion due to dissolved O_2 , CO_2 and $MgCl_2$

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

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

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

   $2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$

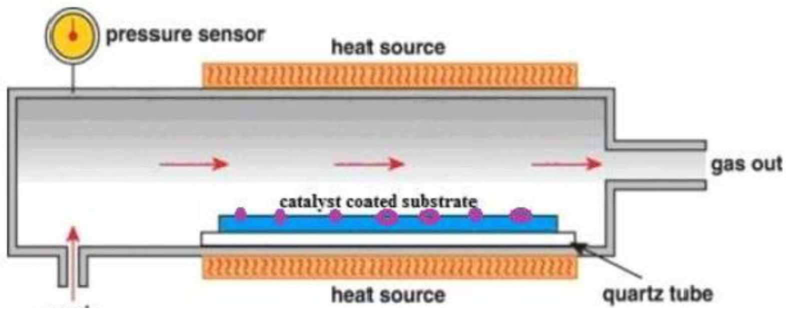
3. Removal of acidic impurities: Finally acidic impurities can be removed by treatment of water with alkaline NH_4OH.

6(a) What are carbon nanotubes? Write the synthesis , properties and uses of carbon nanotubes.

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.

***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 ^{0}C. 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 bubbling the inert gas. Vapours 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.

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.

Applications:

1. In drug delivery
2. In catalysis
3. In sensors
4. For cancer treatment
5. For tissue regeneration

(b) Explain the synthesis of nanomaterials by sol-gel method.

Principle:

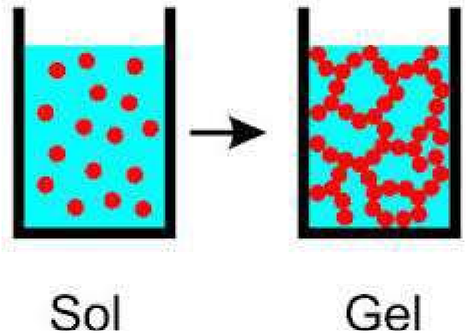
This is a colloidal process in which dispersions have two phases, a dispersed phase with particles having colloidal dimensions (< µm) and a dispersion medium. The process can be used to obtain metal and metal oxide nanocrystals with controlled particle sizes. Sols are solid particles formed by hydrolysis 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

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

(ii) Condensation-polymerisation of the hydroxide intermediate

$M(H_2O)n^{Z+} + [M(H_2O)n\text{-}2\ (OH)2]^{(Z-2)+} \rightarrow [M(H_2O)n\text{-}1M(OH)2]^{(2Z-2)+} + (H_2O)n\text{-}1$
poly-condensed sol

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

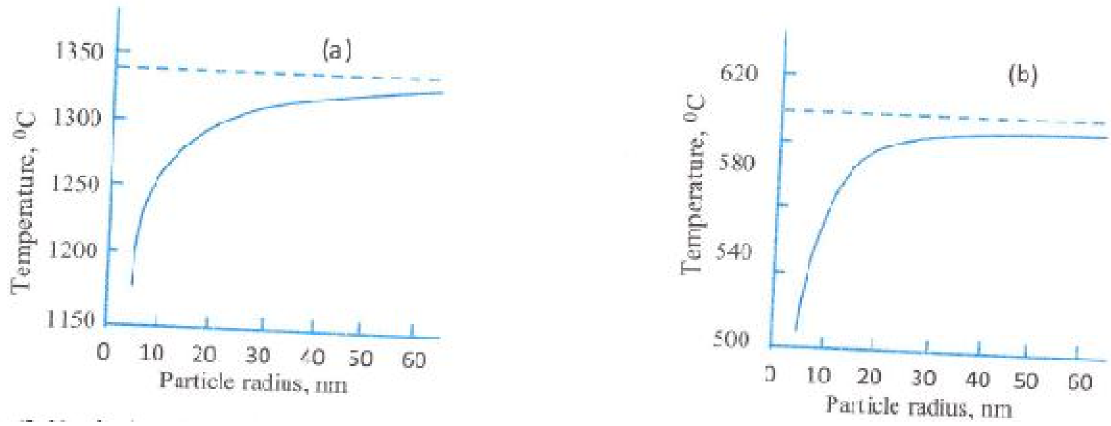
When an alkoxide is used, the important reactions are:

$Si(OR)4 + 4\ H_2O \rightarrow Si(OH)4 + 4ROH$ (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 are nano materials? Discuss three size dependent properties of nano materials.

Nano materials are the materials of nano scale dimension. Naoscale refers to 1-100nm.

a) Thermal properties : As size decreases surface energy increases and melting point decreases. This is due to the fact that surface atoms require less energy to move because they are in contact with fewer atoms of the substance. Eg. 3 mm CdSe nanocrystal metals at 700 K compared to bulk CdSe at 1678 K. Fig. 9.2 shows the variation in melting point with particle size of (a) gold, Au (b) lead, Pb.



Optical properties: Optical properties are connected with electronic structure. A change in zone structure leads to a change in absorption and luminescence spectra. Bulk gold appears yellow in color whereas nanosized gold appears red in color. The particles are so small that electrons are not free to move about as in bulk gold. Because of this restriction in movement, the particles react differently with light.. Nanostructured *semiconductors* are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots used in infrared optoelectronic devices. In ZnO, the luminescence spectra shows a blue shift, that is as the particle size reduces, the wavelength of the emitted light shifts towards lower wavelengths (Fig 9.3). Nanostructured semiconductors are used as window layers in solar cells.

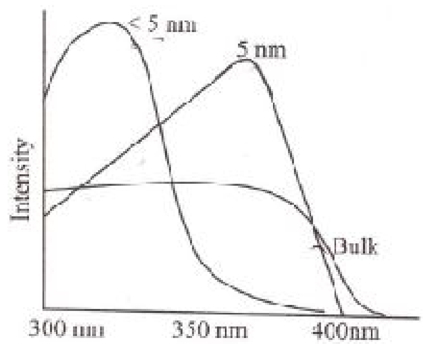


Fig.9. 3 *Luminiscence spectra of ZnO with change in particle size. Wavelength of luminescence shifts towards lower wavelengths (blue shift) with size.*

Mechanical properties: At nanoscale dimensions, the surface and interfacial forces in materials become dominant. Then forces like strain, adhesion and capillary forces exceed their normal magnitudes prevailing at macroscopic length scales. This inturn causes changes in physical properties like ductility, malleability and plasticity of the material.

Eg: (i) Cu shows reduced Young's modulus in the nanostate.
(ii) Nanophase ceramics are more ductile at elevated temperatures as compared to the coarse grained ceramics.

Magnetic effect: In bulk solids, magnetism is determined by the orientation of magnetic domains,separated by grain boundary. In nanophase, domain sizes are small that they correspond with grain boundaries which are also disordered. Nanoparticles have electronic structures with discrete states (morelike extended atomic structures) giving rise to special magnetic properties such as superparamagnetism.Magnetic nanocrystals and composites find application in high density information storage and sensors.

(b) Define COD. 25 cm3 of sewage water was refluxed with 10 cm3 of 0.25 N K2Cr2O7 in Conc. H2SO4 medium.The un-reacted K2Cr2O7 needed 6.1 cm3 of 0.1N FAS. 10 cm3 of 0.25 N K2Cr2O7 when titrated under same condition required 28.2 cm3 of 0.1N FAS. Calculate the COD.

COD is defined as the amount of oxygen consumed in the chemical oxidation of organic and inorganic wastes present in 1L of waste water.

Given , V = 25 cm^3, b = 28.2 cm^3 , a = 6.1 cm^3 , N_{FAS} = 0.1N

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

= 0.1 X (28.2-6.1) X 8000/ 25 = 707.2 mg of O_2 / L