

## B.Tech.

First Semester Examination, December-2010

### Engineering Chemistry (CH-101-F)

**Note :** Attempt five questions in all. All questions carry equal marks.

**Q. 1. (a) Define the terms phase and components with respect to phase rule.**

**Ans. Phase :** A phase is a chemically homogeneous, physically distinct and mechanically separable part of a system. It is denoted by P.

**Component :** The minimum number of chemical constituents taking part in equilibrium by means of which composition of each phase can be expressed either directly or by means of a chemical equation is known as component.

**Q. 1. (b) Give the concept of inhibitors in catalysis.**

**Ans.** Substances that reduce the action of catalysts. They are also referred to as negative catalysis. They act either by inactivating catalysts or by removing reaction intermediates such as free radicals. They may also modify selectivity in addition to rate.

**Q. 1. (c) State pour point.**

**Ans.** The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed conditions. It is a rough indication of the lowest temperature at which oil is readily pumpable.

The pour point can also be defined as the minimum temperature of a liquid particularly lubricant after which on decreasing the temperature, the liquid ceases to flow.

**Q. 1. (d) Differentiate between scale and sludge.**

**Ans.**

Sludge	Scale
(i) They are soft, loose and slimy precipitate floating in boiler.	(i) They are hard deposits adhering to the walls of boiler.
(ii) They can be removed easily.	(ii) They are very difficult to remove.
(iii) They are formed by substances like $\text{CaCl}_2$ , $\text{MgSO}_4$ , $\text{MgCl}_2$ etc.	(iii) They are formed by substances like $\text{CaSO}_4$ , $\text{Mg}(\text{OH})_2$ etc.
(iv) Less dangerous.	(iv) Very dangerous.

**Q. 1. (e) What is microbiological corrosion?**

**Ans.** Microbiological corrosion or microbiological corrosion, is the corrosion caused by or promoted by microorganisms, usually chemoautotrophs [organisms which obtain energy by the oxidation of electron donors in their environments]. It can apply to both metals & non-metallic materials.

**Q. 1. (f) Give important applications of PVC.**

**Ans. (i) Plasticized PVC** is used for making rain coats, table cloths, curtains, plastic coated clothes, soles for shoes.

**(ii) Unplasticized or Rigid PVC** is used for making sheets, safety helmets, floor coverings, refrigerator components etc. They have very high rigidity.

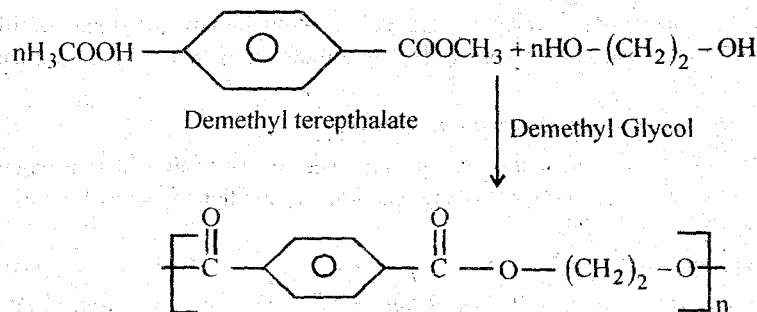
**Q. 1. (g) Define Beer's Law.**

**Ans. Beer Law :** It states that when a beam of monochromatic radiation is passed through a solution of an absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of incident radiation as well as the conc. of solution.

**Q. 1. (h) What is condensation polymerization, give example?**

**Ans. Condensation Polymers :** Polymers which are formed by the polymerisation of monomers with elimination of small molecules like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$  etc. are known as condensation polymers.

**Example :**



**Q. 1. (i) Give the principle of flame photometry.**

**Ans.** Flame photometry is used in inorganic chemical analysis to determine the concentration of certain metal ions. It is basically a flame test.

It works on the principle of detection of colours by a photometer (A device). The filters select the colours to be detected by photometer. The intensity of colours is quantified by photoelectric circuitry.

**Q. 1. (j) What is temporary hardness? How it can be removed?**

**Ans. Temporary Hardness** of water is due to the presence of bicarbonates of calcium, magnesium and heavy metals & carbonate of iron.

Temporary hardness can be removed by boiling.

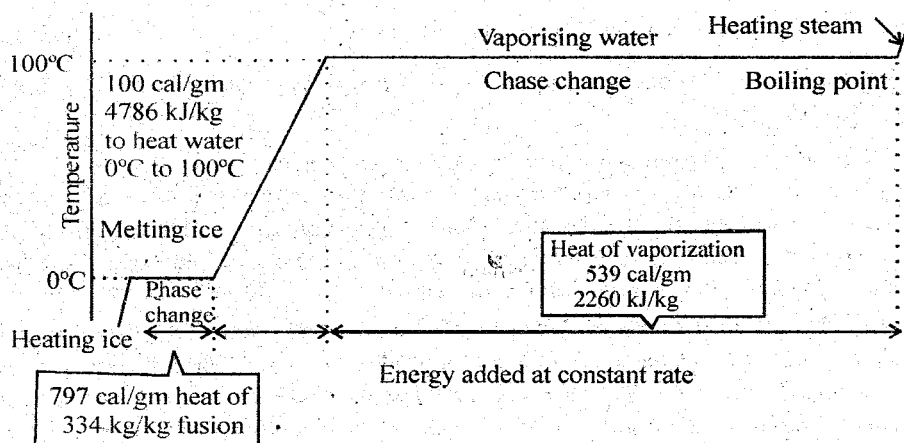
## Section-A

**Q. 2. (a) Draw and explain the composition temperature phase diagram of  $\text{Na}_2\text{SO}_4$  - water system and label it properly.**

**Ans.** Phase diagram in physical chemistry, engineering, mineralogy and materials science is a type of chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium. In mathematics and physics, "phase diagram" is used with a different meaning : a synonym for a phase space.

Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to lines that mark conditions under which multiple phases can coexist at equilibrium. Phase transitions occur along lines of equilibrium. Triple points are points on phase diagrams where lines of equilibrium intersect. Triple points mark conditions at which three different phases can coexist. For example, the water phase diagram has a triple point corresponding to the single temperature and pressure at which solid, liquid, and gaseous water can coexist in a stable equilibrium. The solidus is the temperature below which the substance is stable in the solid state. The liquidus is the temperature above which the substance is stable in a liquid state. There may be a gap between the solidus and liquidus; within the gap, the substance consists of a mixture of crystals and liquid.

Transitions between solid, liquid and gaseous phases typically involve large amounts of energy compared to the specific heat. If heat were added at a constant rate to a mass of ice to take it through its phase changes to liquid water and then to steam, the energies required to accomplish the phase changes (called the latent heat of fusion and latent heat of vaporization) would lead to plateaus in the temperature vs time graph. The graph below presumes that the pressure is one standard atmosphere.



**Q. 2. (b) Explain following with suitable examples :**

**(i) Poisoners in catalysis,**

**(ii) Enzymatic catalysis.**

**Ans. (i) Poisoners in Catalysis :** Substances that reduce the action of catalysts are called poisoners or poisons. But the process is irreversible. They are used when the particular product is required from a reactant which can undergo a number of reductions/reactions. So to stop a reaction midway which is catalysed, poisoners are used.

**Example :**

In the reduction of ethyne to ethene, the catalyst is palladium (Pd) partly poisoned with lead (II) acetate  $[Pb(CH_3COO)_2]$ . Without the deactivation of catalyst, the ethene produced will be further reduced to ethane.

**(ii) Enzymatic Catalysis :** Enzyme catalysis is the catalysis of chemical reactions by specialized proteins known as enzymes. Catalysis of biochemical reactions in the cell is vital due to the very low reaction rates of the uncatalysed reactions.

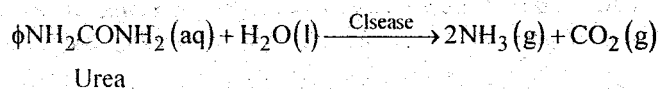
By providing an alternative reaction route & by stabilizing intermediates the enzyme reduces the energy required to reach the highest energy transition state of the reaction.

The reduction of activation energy ( $\epsilon_a$ ) increases the number of reactant molecules with enough energy to reach the activation energy & form the product.

**Example :**

$\phi$  trypsin

Trypsin is a serine protease that leaves protein substrates at lysine and arginine amino acid residues.



**Q. 3. (a) What is meant by homogeneous and heterogeneous catalysis? Explain giving suitable examples.**

**Ans. Homogeneous Catalysis :** The catalysts which function in the same phase as the reactants are k/a homogeneous catalysts and process is k/a homogeneous catalysis. They are typically dissolved in a solvent with the substrates.

An example of homogeneous catalysis involves the influence of  $H^+$  on the esterification of esters.

**Example :** Methyl acetate (e) from acetic acid (a) & methanol (l) is catalysed by  $H^+$  ions from HCl (l).

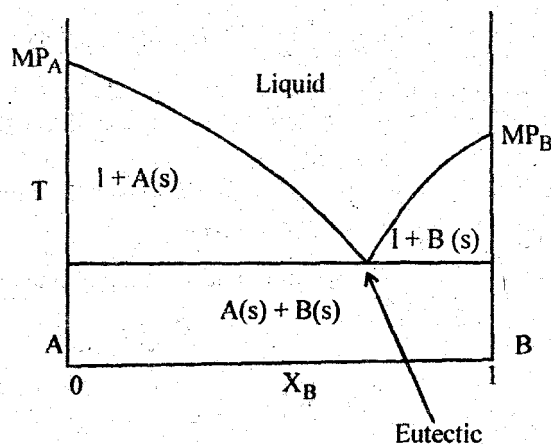
**Heterogeneous Catalysis :**

The catalysts that act in a different phase than the reactants are k/a heterogeneous catalysts & process is heterogeneous catalysis. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms are known for reactions on surfaces, depending on how the absorption takes place. The reaction rate depends on the surface area of catalyst (in case of solids). Smaller the catalyst particle size, larger the surface area, so faster will be the reaction.

**Example :** In Haber's process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto active sites on the iron particles. Once absorbed, the bonds within the reacting molecules are weakened and new bonds between the resulting fragments form in part due to close proximity. So, the triple bond in nitrogen is weakened and hydrogen and nitrogen combine.

**Q. 3. (b) Describe a method to determine eutectic point for a two component system by using cooling curve method.**

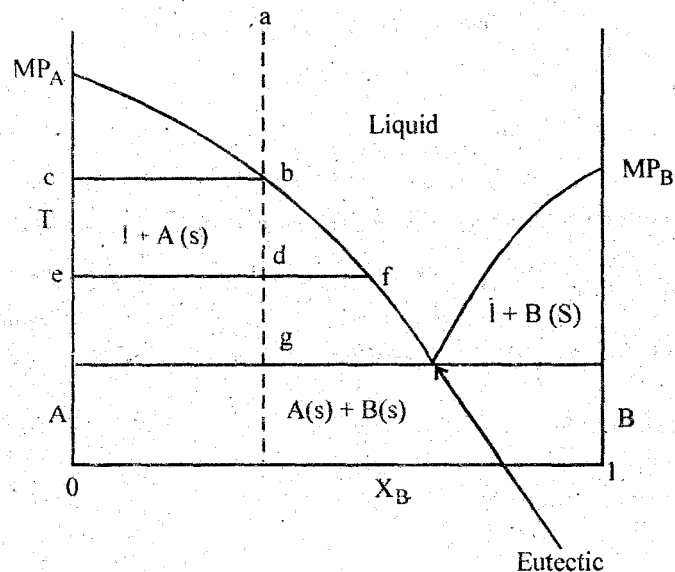
**Ans. Two-Component Cooling Curve :** Two-component boiling diagrams. These diagrams are descriptions of the state of the system on a graph of temperature versus composition (at constant pressure). At high temperatures the system is all in the gas (or vapor) phase. At the lower temperatures the system is in the liquid phase. In between these two situations there is a region where there are two phases (vapor and liquid) in equilibrium with each other. If we continue to cool the system we will eventually reach a temperature where one or both of the pure components will freeze. At temperatures at and below the melting points the phase diagram will look something like the following hypothetical phase diagram involving a substance "A" and a substance "B." In this diagram we are plotting temperature versus the mole fraction of substance B.



Note that the freezing point of the solution decreases as we move away from either pure A or pure B. This is a phenomenon that we have discussed previously when we talked about freezing point depression in the

section on colligative properties.

Let's pick a point in the liquid region on the above diagram and cool the system at constant composition and pressure along the dotted line starting at point "a."



Going from point a to point b nothing much happens. We are just cooling the liquid (or melt). At point b, however, we begin to crystallize out some pure component A. When we cross the curved line at point b we are moving into a two phase region. On this diagram the two phases are pure component A and the liquid mixture. As we already know, in a two phase region we must track two different compositions so we draw a tie-line. In this case the tie-line runs from point b to point c. Where the tie-line intersects the closed curve at b indicates the composition of the liquid phase. In this diagram the other end of the tie-line intersects the edge of the diagram at pure solid A (point c). As we continue to cool the system the tie-lines track the composition of the liquid and solid phases. By the time we get to point d the left end of the tie-line (point e) still tracks the pure solid A. The right end of the tie-line tracks the liquid composition at point f. Notice that the liquid at point f is much richer in component B. This is because we have been removing component A from the solution by crystallizing it out.

When we reach point g the liquid has reached the eutectic composition. At this temperature and liquid composition both pure solid A and pure solid B will crystallize out together. In this phase diagram crystals of the two substances will be interspersed among each other. (The crystals may very well be microscopic so that the mixture looks homogeneous to the naked eye. In this case, the only way to tell that we have a mixture of two different crystals is to examine the solid under a microscope.) If we continue to remove heat from the mixture the system will remain at the eutectic temperature until all of the remaining liquid has solidified.

## Section-B

**Q. 4. (a) How is water softened by lime-soda process? Give the reactions involved in this process.**

**Ans.** Lime soda process is based upon the precipitation of soluble calcium & magnesium salts by addition of calculated amount of lime and soda.

Calcium ions are precipitated as calcium carbonates & magnesium as magnesium hydroxide. The  $\text{CaCO}_3$  &  $\text{Mg}(\text{OH})_2$  formed are then filtered off.

Line required, 
$$L = \frac{74}{100} \left[ \text{Temp. Ca}^{+2} + 2 \times \text{Temp. Mg}^{+2} + \text{Perm} \left( \text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3} \right) + \right. \\ \left. \text{CO}_2 + \text{H}^+ \left( \text{HCl or H}_2\text{SO}_4 \right) + \text{HCO}_3^- - \text{NaAlO}_2 \right]$$

Soda required,

$$S = \frac{106}{100} \left[ \text{Perm} \left[ \text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2} \right] + \text{H}^+ \left( \text{HCl} \right) - \text{HCO}_3^- \right]$$

**Q. 4. (b) 10 ml water sample requires 10 ml of EDTA. Calculate its hardness. 20 ml of  $\text{CaCl}_2$  solution, whose strength is equivalent to 1.75g of  $\text{CuCO}_3$  per litre, required 30 ml of EDTA solution.**

**Ans.**

**Q. 5. (a) Explain the advantages and disadvantages of the zeolite process for water softening.**

**Ans. Advantages :**

- (i) Hardness is almost completely removed and water of abt. 15 ppm of hardness is produced.
- (ii) The equipment used is compact.
- (iii) It requires less time for softening.
- (iv) Less skill is required for maintenance.
- (v) No danger of sludge formation.

**Disadvantages :**

- (i) Only cations  $\left( \text{Ca}^{+2}, \text{Mg}^{+2} \right)$  are replaced by sodium ions & not the acidic ions.
- (ii) Treated water contains more sodium salts than in lime-soda process.

**Q. 5. (b) Write short notes on :**

**(i) Ion Exchange Process**

**(ii) Sedimentation**

**Ans. (i) Ion Exchange Process :** Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials.

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are :

- (i)  $H^+$  (proton) and  $OH^-$  (hydroxide).
- (ii) Single charged monoatomic ions like  $Na^+$ ,  $K^+$ , or  $Cl^-$ .
- (iii) Double charged monoatomic ions like  $Ca^{2+}$  or  $Mg^{2+}$ .
- (iv) Polyatomic inorganic ions like  $SO_4^{2-}$  or  $PO_4^{3-}$ .
- (v) Organic bases, usually molecules containing the amino functional group  $NR_2H^+$ .
- (vi) Organic acids, often molecules containing  $-COO^-$  (carboxylic acid) functional groups.
- (vii) Biomolecules which can be ionized : amino acids, peptides, proteins, etc.

Ion exchange is a reversible process and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions.

**(ii) Sedimentation :** Sedimentation is the tendency for particles in suspension to settle out of the fluid in which they are entrained and come to rest against a barrier. This is due to their motion through the fluid in response to forces acting on them : these forces can be due to gravity, centrifugal acceleration or electromagnetism.

Sedimentation is the termination of settling process (falling of suspended particles through the liquid.).

Sedimentation may pertain to objects of various sizes, ranging from suspensions of dust & pollen particles to cellular suspensions to solutions of single molecules such as proteins & peptides.

In chemistry, sedimentation is basically used to measure the size of large molecules (macromolecules). Where the force of gravity is augmented with centrifugal force in a centrifugal.

## Section-C

**Q. 6. (a) Give an account of the properties of lubricating oils.**

**Ans.** A lubricant is a substance introduced between two moving surfaces to reduce the friction between them, improving efficiency & reducing wear. It may also have the function of dissolving or transporting foreign particles & of distributing heat.

The largest application of lubricant, in form of motor oil, is to protect internal combustion engines. So, they must not catch fire easily.

Lubricants such as 2-cycle oil are added to fuels like gasoline which has low lubricity.

Lubricants have properties depending on the purpose for which they are to be used.

**For Example :**

**Cooking :**

- (i) As oils & fats in frying pass. So, they must contain no such harmful chemicals that might affect human body i.e., they must be non-toxic & chemically inert.
- (ii) Baking to prevent food sticking.

**Bio-medical Application on Humans :**

**Example :** Lubricants for artificial joints.

Lubricants must be smooth & must not affect any part of human body. They must not interfere & with reactions going on in the body, so must be chemically inert.

**In Medicinary :**

**Example :** Ultrasound examination.

Easy to use, cheap & easily available. Must not affect radiations.

**Q. 6. (b) Explain the mechanism of the following :**

**(i) Dry Corrosion**

**(ii) Lubrication.**

**Ans. (i) Dry Corrosion :** Type of corrosion that mainly occurs through direct chemical action of an oxidising gas.

**Example :** Oxygen, sulphur, halogens etc. in absence of a liquid or electrolyte at ambient or elevated temperature.

Dry corrosion is also known as high temperature corrosion.

**Example :** Attack of steel furnace by gases at high temperature.

Dry corrosion is a serious problem in industry such as aircraft, automobile, chemical, electrical, power generation, gas turbine, rocket engines, furnace etc. Where high temp. is encountered.

**(ii) Lubrication :** Lubrication is the process or technique employed to reduce wear of one or both surfaces in close proximity and moving relative to each another, by interposing a substance called lubricant between the surfaces to carry or to help carry the load (pressure generated) between the opposing surfaces. The interposed lubricant film can be a solid, (e.g. graphite,  $\text{MoS}_2$ ) a solid/liquid dispersion, a liquid, a liquid-liquid dispersion gasses exceptionally a gas.

**The Mechanism of Lubrication :** As the load increases on the contacting surfaces three distinct situations can be observed with respect to the mode of lubrication, which are called regimes of lubrication :

- (i) Fluid film lubrication is the lubrication regime in which through viscous forces the load is fully supported by the lubricant within the space or gap between the parts in motion relative to one another (the lubricated conjunction) and solid-solid contact is avoided
- (ii) Hydrostatic lubrication is when an external pressure is applied to the lubricant in the bearing, to maintain the fluid lubricant film where it would otherwise be squeezed out.
- (iii) Hydrodynamic lubrication is where the motion of the contacting surfaces and the exact design of the bearing is used to pump lubricant around the bearing to maintain the lubricating film. This design of bearing may wear when started or stopped, as the lubricant film breaks down.
- (iv) **Elastohydrodynamic Lubrication :** The opposing surfaces are separated but there occurs some interaction between the raised solid features called asperities, and there is an elastic deformation on the contacting surface enlarging the load bearing area whereby the viscous resistance of the lubricant becomes capable of supporting the load.
- (v) **Boundary Lubrication (Also Called Boundary Film Lubrication) :** The bodies come into closer contact at their asperities; the heat developed by the local pressures causes a condition which is called stick-slip and some asperities break off. At the elevated temperature and pressure conditions chemically reactive constituents of the lubricant react with the contact surface forming a highly resistant tenacious layer, or film on the moving solid surfaces (boundary film) which is capable of supporting the load and major wear or breakdown is avoided. Boundary lubrication is also defined as that regime in which the load is carried by the surface asperities rather than by the lubricant.

**Q. 7. (a) Why additives are used in lubricants? Give some examples.**

**Ans.** Lubricants are substances (often liquid) introduced between two moving surfaces to reduce the



friction between them, improving efficiency and reducing wear. Typically lubricants contain 90% base oil & less than 10% additives. As the name suggests, additives are substances added in small amounts to something in order to improve it.

Additives in lubricants :

- (i) Reduce friction & wear.
- (ii) Increase viscosity.
- (iii) Improve viscosity index.
- (iv) Resist oxidation.
- (v) Prevent aging.
- (vi) Control contamination etc.

A large number of additives are used to impart performance characteristics to lubricants. Main families of additives are :

- |  |                                   |
|--|-----------------------------------|
| (i) Antioxidants                       | (ii) Detergent & anti-wear        |
| (iii) Metal deactivators               | (iv) Corrosion & rust inhibitors  |
| (v) Friction modifiers                 | (vi) Extreme pressure controllers |
| (vii) Anti-foaming agents              | (viii) Viscosity index improvers  |
| (ix) Demulsifying + emulsifying agents | (x) Complexing agents, etc.       |

**Q. 7. (b) Write short notes on the following :**

- (i) **Soil Corrosion**
- (ii) **Stress Corrosion.**

**Ans. (i) Soil Corrosion :** Dry soil is not corrosive. It becomes so by virtue of water content & related water soluble salts which allow it to function as an electrolyte. In that case, we are dealing with an immersion condition exactly similar to that encountered in corrosion by water.

Just how corrosive a soil may be to a specific material depends upon the :

- (i) Specific constituents in the soil.
- (ii) Degree of aeration.
- (iii) Acidity or pH value.
- (iv) Electrical conductivity
- (v) Moisture & salt content
- (vi) Bacteria & microorganisms
- (vii) Soil texture.

**(ii) Stress Corrosion :** Stress corrosion is evidenced when the metal strength loss resulting from the combined stress and corrosion is greater than the effects of stress & corrosion acting separately. The magnitude of combined effect is a measure of the susceptibility of the material to stress corrosion.

It is evidenced as cracks appearing in material giving appearance of brittleness. The cracks may follow intergranular paths which grow at relatively slow velocities. If the load is constant during the period of crack growth, the cracks will reach a critical size to result in material failure. It does not usually occur in conditions in which metal suffers from serious general corrosion. It is therefore often not noticed resulting in fracture without warning.

## Section-D

**Q. 8. (a) What are silicones? Discuss their important properties and uses.**

**Ans.** Silicones are polymers that include silicon together with carbon, hydrogen, oxygen & other chemical elements.

**Properties :**

- (i) Good electrical insulation.
- (ii) Thermally stable.
- (iii) Repel water & form watertight seals.
- (iv) Excellent resistance to corrosion & none & UV light .
- (v) Non-sticky.
- (vi) Low chemical reactivity.
- (vii) Low toxicity.
- (viii) High gas permeability.

**Uses :**

- (i) **Coatings :** Non-sticky, hydrophobic coating.
- (ii) Cookware
- (iii) **Medicine :**  
Toys.

**Q. 8. (b) Explain the principle of IR spectroscopy. What is the importance of finger print region in this techniques?**

**Ans.** Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately  $14000 - 4000 \text{ cm}^{-1}$  ( $0.8 - 2.5 \mu\text{m}$  wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately  $4000 - 400 \text{ cm}^{-1}$  ( $2.5 - 25 \mu\text{m}$ ) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately  $400 - 10 \text{ cm}^{-1}$  ( $25 - 1000 \mu\text{m}$ ) lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

**Principle of IR Spectroscopy :** IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation

