CHAPTER 05

Surface Chemistry

- The process in which molecular species are accumulated at the surface rather than in the bulk of a solid or liquid is termed as **adsorption**. e.g. water vapours on silica gel; H₂, O₂, NH₃ on activated charcoal.
- **2.** Solids, particularly in finely divided state have large surface area, therefore metals in finely divided state acts as good adsorbents.
- **3.** Adsorption is an exothermic process i.e. ΔH of adsorption is always negative. Since, the molecules of the gas are held on the surface of the solid adsorbent hence, entropy decreases (because their freedom of movement become restricted), i.e. ΔS is negative.
- **4. Types of adsorption** The two types of adsorption of gases on solids are as follows:
 - The adsorption in which accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces is called physical adsorption or physisorption. It is also called van der Waals' adsorption. These types of adsorption show lack of specificity, depends on nature of adsorbate and are reversible in nature.
 - The adsorption in which gas molecules or atoms are held to solid surface by chemical bonds is called **chemical adsorption** or **chemisorption**. It is highly specific in nature and results in the formation of only monomolecular layer. This type of adsorption is irreversible and has more (–)ve value for ΔH .
- **5.** Adsorption isotherm is the curve that shows the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.
 - Freundlich gave the following relationship between *x/m* and *p* at particular temperature.

$$\frac{x}{m} = k p^{1/n} (n > 1)$$

where, m = mass of adsorbent,

x = mass of gas adsorbed on mass m, p = pressure, k and n = constant, n = integer

or $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$

• When log *x/m* is plotted (at *y*-axis) with log *p* (at *x*-axis), a straight line is obtained with slope 1/n and intercept on *y*-axis is equal to log *k*. (: y = mx + c)

6. Adsorption from Solution Phase

Following observation has been made in this case :

- Extent of adsorption decreases with increase in temperature and increases with an increase of surface area of the adsorbent.
- Extent of adsorption depends on the concentration of solute in the solution and on nature of the adsorbent and adsorbate.
- 7. A substance that changes the rate of a chemical reaction without itself undergoing any chemical change, is known as **catalyst** and the process is known as **catalysis**.

Catalysis can be divided into two groups. These are as follows :

 The phenomenon in which reactants and catalysts are present in the same phase (i.e. liquid or gas) is known as homogeneous catalysis.

- The phenomenon in which the reactants and catalysts are in the different phases, is known as heterogeneous catalysis.
- 8. Adsorption Theory of Heterogeneous Catalysis This theory explains the mechanism of heterogeneous catalysis.

The steps involved are as follows :

- Diffusion of reactants to the surface of the catalyst.
- Adsorption of reactant molecules on the surface of the catalyst.
- Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
- Desorption of reaction products from catalyst surface.
- Diffusion of reaction products away from catalyst surface.
- **9.** When the catalytic reaction depends upon the porous structure of catalyst, the size and shape of the reactant and of the product molecules, the reaction is known as **shape-selective catalysis**.

Zeolites are microporous aluminosilicates. General formula is $M_{x/n}[(AIO_2)_x(SiO_2)_y] \cdot zH_2O$. e.g. ZSM-5 converts alcohols directly into gasoline (or petrol a mixture of hydrocarbons) by dehydrating them.

- **10. Enzymes** are biochemical catalysts that catalyse the reactions occurring in living beings. These are highly specific in nature and work well only at a specific pH.
- **11.** A **colloid** is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

Colloids are classified on the basis of following criteria. On the basis of physical state of dispersed phase and dispersion medium.

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid Sol	Gemstone and coloured glasses
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Dust, smoke
Liquid	Solid	Gel	Jellies, butter, cheese
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, colud, insecticide spray
Gas	Solid	Soild sol	Charcoal, pumice stone
Gas	Liquid	Foam	Whipped cream, froth, soap lather

- On the basis of nature of interaction between dispersed phase and dispersion medium.
- (a) Colloidal sols directly formed by mixing substances like gum, gelatin, starch, rubber, etc. with a suitable liquid (the dispersion medium) are called lyophilic sols. These sols are also called reversible sols or protective colloids (as they protect lyophobic sols) from coagulation. These sols are quite stable and cannot be coagulated.

- (b) Substances like metals, their sulphides etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods. Such sols are called lyophobic sols. These sols are also called irreversible sols. Lyophobic sols need stabilising agents for their preservation.
- On the basis of type of particles of the dispersed phase.
- (a) Multimolecular colloids are formed by the aggregation of a large number of atoms or small molecules of a substance, when they aggregate together to form a species having size in the colloidal range, e.g. sulphur sol consists of particles containing a thousand or more of S₈ sulphur molecules.
- (b) Macromolecules, in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range, i.e. they are molecules of larger size of colloidal range. Such colloids are called

macromolecular colloids.

These colloids are guite stable and resemble with true solutions in many respects, e.g. naturally occurring macromolecules such as starch, cellulose. polymers, proteins and enzymes.

- (c) Some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.
- The formation of micelles takes place only above a • particular temperature, called **Kraft's temperature** (T_{κ}) and above a particular concentration, called Critical Micelle Concentration (CMC).

12. Preparation of Colloid

- · By chemical method $2H_2S + SO_2 \xrightarrow{Oxidation} 3S_2 + 2H_2O$ $2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{(Sol)} Reduction \rightarrow$ 2Au+3HCOOH+6HCI
- Bredig's Arc method involves dispersion as well as condensation. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.
- **Peptisation** is the process of converting freshly prepared precipitate into colloidal sol by shaking it with the dispersion medium in the presence of small amount of electrolyte. The electrolyte added is called the peptising agent.
- 13. Purification of Colloidal Solutions by diffusion through a suitable membrane is called **dialysis**. The apparatus used for this purpose is called **dialyser**.
- 14. Properties of Colloidal Solutions :
 - Colligative properties The value of colligative properties of colloids are of small order as compared to the true solutions.

- · When light falls on sol, it absorbs the light and scatter it. This phenomenon of scattering of light is called Tyndall effect. The illuminated path of light passing through the colloids is called **Tyndall cone**.
- Brownian movement The colloidal particles appear to be in a state of continuous *zig-zag* motion. This motion is called Brownian movement.
- 15. The process of settling of colloidal particles is called coagulation or precipitation of the sol. It is done by electrophoresis, boiling, mixing two oppositely charged sols or by addition of electrolytes.
- 16. Hardy-Schulze rule According to this rule, "greater the valence of the flocculating ion added, greater is its power to cause precipitation".

Flocculation value $\sim \frac{1}{\text{Coagulating power}}$

For example The order of coagulating power of the cations is

 $AI^{3+} > Ba^{2+} > Na^+$.

The order of coagulating power of the anions is $[Fe(CN)_{6}]^{4-} > PO_{4}^{3-} > SO_{4}^{2-} > CI^{-}.$

- 17. Emulsions are formed when both the dispersed phase and dispersion medium are liquids in a colloidal system. Two types of emulsions are:
 - Oil dispersed in water type Milk, vanishing cream.
 - Water dispersed in oil type Butter and cream.
- 18. It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to that one on clouds from an aeroplane.
- 19. Blood is an albuminoid suspended in water, which implies that blood is a colloid. Alum and FeCl_a solution stop bleeding due to coagulation.
- 20. Colloidal sol adsorbs one of its own ion from the solution preferentially and gets charged. This charge attracts ions of opposite charge from the solution and forms an electrical double layer. This is called Helmholtz electrical double layer.