Chapter-05

Surface Chemistry

LECTURE-01

Introduction:

Surface chemistry deals with phenomena that occur at surfaces or interfaces. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. The bulk phases may be pure compounds or solutions. Many important phenomena, noticeable amongst these being corrosions, electrode processes, heterogeneous catalysis, dissolution, and crystallization occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work, and daily life situations. Some important features of surface chemistry are adsorption, catalysis, and colloids including emulsions and gels.

Adsorption:

(i) **The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption**. The surface of a solid tends to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk.

(ii) The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

(iii) Adsorption is essentially a surface phenomenon. Solids, particularly in a finely divided state, have a large surface area, and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in a finely divided state, etc. act as good adsorbents.

Adsorption in action:

(i) If a gas like O_2, H_2, CO, Cl_2, NH_3, or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.

(ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colorless. The molecules of the dye, thus, accumulate on the surface of the charcoal, i.e., are adsorbed.

(iii) An aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colorless as the coloring substances are absorbed by the charcoal.

(iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

(v) It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by adsorption.

(vi) The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

The distinction between Adsorption and Absorption:

Adsorption:

(i) In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent.

Ex: when a chalk stick is dipped in ink, the surface retains the color of the ink due to the adsorption of colored molecules. On breaking the chalk stick, it is found to be white from inside.

Ex: Water vapors are adsorbed by silica gel.

(ii) In other words, in adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent,

Absorption:

(i) In absorption, the substance is uniformly distributed throughout the bulk of the solid.

Ex: when a chalk stick is dipped in ink, the solvent of the ink goes deeper into the stick due to absorption.

Ex: Water vapors are absorbed by anhydrous calcium chloride.

(ii) In absorption, the concentration is uniform throughout the bulk of the solid. Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes. Therefore the phenomenon in which both adsorption and absorption can take place simultaneously is known as **Sorption.**

Mechanism of Adsorption:

(i) Adsorption arises because the surface particles of the adsorbent are not in the same environment as the particles inside the bulk.

(ii) Inside the adsorbent, all the forces acting between the particles are mutually balanced but on the surface, the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces.

(iii) These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.

(iv) The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

(v) Another important factor affecting adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is a decrease in surface energy which appears as heat.

(vi) Therefore, adsorption is an exothermic process. So ΔH of adsorption is always negative.

(vii) When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. As a result entropy of the gas decreases after adsorption, i.e., ΔS is negative.

(viii) Adsorption is thus accompanied by a decrease in enthalpy as well as a decrease in entropy of the system.

(ix) For a process to be spontaneous, ΔG must be negative, at constant temperature and pressure, i.e., there is a decrease in Gibbs energy. So $\Delta G = \Delta H - T\,\Delta S$

(x) ΔG can be negative if ΔH has sufficiently high negative and $-T\Delta S$ is positive.

(xi) Thus, for the spontaneity of the adsorption process, the combination of these two factors makes ΔG negative.

(xii) As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state, equilibrium is attained.

Types of Adsorption:

There are mainly two types of adsorption of gases on solids such as

(i) Physical adsorption or Physisorption (ii) Chemical adsorption or Chemisorption

(a) If an accumulation of gas on the surface of a solid occurs on account of weak Vander Waals'forces, the adsorption is termed as **physical adsorption or physisorption**.

(b) When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**.

(c) The chemical bonds may be covalent or ionic. Chemisorption involves high energy of activation. Sometimes these two processes occur simultaneously and it is not easy to identify the type of adsorption.

(iv) Physisorption occurs at low temperatures. So it may pass into chemisorption as the temperature is increased.

Ex: Dihydrogen is first adsorbed on nickel by Vander Waals' forces. Then molecules of hydrogen dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Characteristics of physisorption:

(i) Lack of specificity:

A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals' forces are universal.

(ii) Nature of adsorbate:

The amount of gas adsorbed by a solid depends on the nature of the gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as Vander Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).

(iii) Reversible nature:

Physical adsorption of a gas by a solid is generally reversible.

$$\text{Solid} + \text{Gas} \rightleftharpoons \text{Gas / Solid} + \text{Heat}$$

Thus, More gas is adsorbed when pressure is increased as the volume of the gas decreases (Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperatures and decreases with increasing temperature (Le-Chatelier's principle).

(iv) The surface area of adsorbent:

The extent of adsorption increases with the increase of the surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) Enthalpy of adsorption:

Physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20–40 kJ mol-1). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

Characteristics of chemisorption:

(i) High specificity:

Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate.

Ex: Oxygen is adsorbed on metals by oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

(ii) Irreversibility:

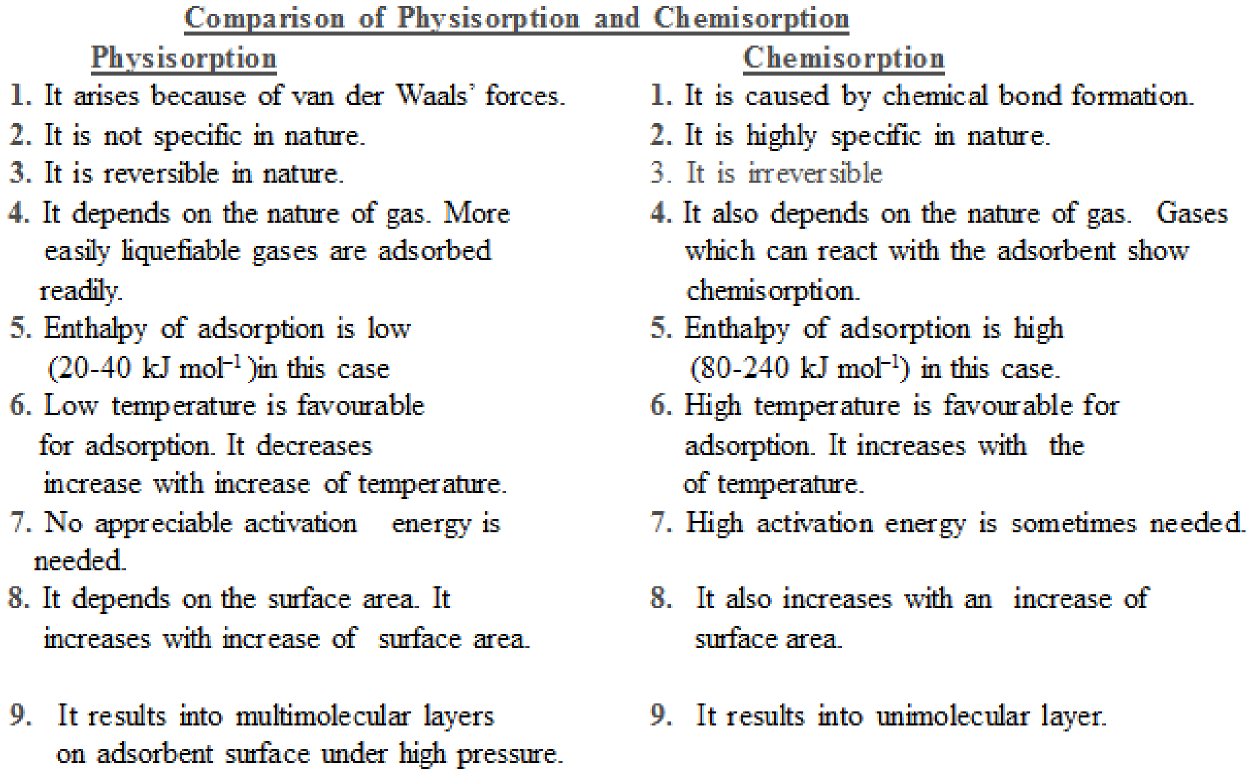
Chemisorption is usually irreversible. It is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption increases with the rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually, high pressure is also favorable for chemisorption.

(iii) Surface area:

Like physical adsorption, chemisorption also increases with an increase in the surface area of the adsorbent.

(iv) Enthalpy of adsorption:

Enthalpy of chemisorption is high (80-240 kJ mol^{-1}) as it involves chemical bond formation.



Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	1. It is caused by chemical bond formation.
2. It is not specific in nature.	2. It is highly specific in nature.
3. It is reversible in nature.	3. It is irreversible
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol^{-1})in this case	5. Enthalpy of adsorption is high (80-240 kJ mol^{-1}) in this case.
6. Low temperature is favourable for adsorption. It decreases increase with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with increase of surface area.	8. It also increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	9. It results into unimolecular layer.

LECTURE-2

Factors affecting adsorption of gases on solids:

The following are the factors affecting adsorption of gases on solids.

(i) Surface area (ii) Nature of gas (iii) Temperature (iv) Pressure

(i) Surface area:

The extent of adsorption increases with the increase of the surface area of the adsorbent.

(ii) Nature of gas:

The amount of gas adsorbed by a solid depends on the nature of the gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed.

(iii) Temperature:

The magnitude of adsorption decreases with a rise in temperature.

(iv) Pressure:

At constant temperature, the adsorption of a gas increases with an increase in pressure.

Adsorption Isotherms:

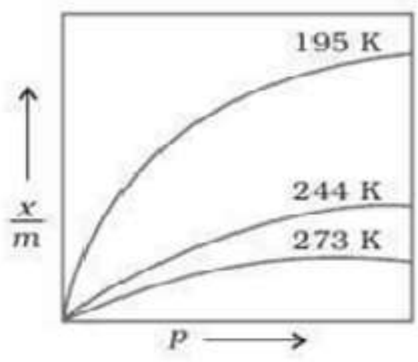
The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed using a curve termed as **adsorption isotherm**.

Freundlich adsorption isotherm:

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{x}{m} = kP^{\frac{1}{n}} (n > 1)$$

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where the mass of the gas adsorbed per gram of the adsorbent is plotted against pressure.



At low P, the graph is nearly straight and sloping. It can be represented by the equation as

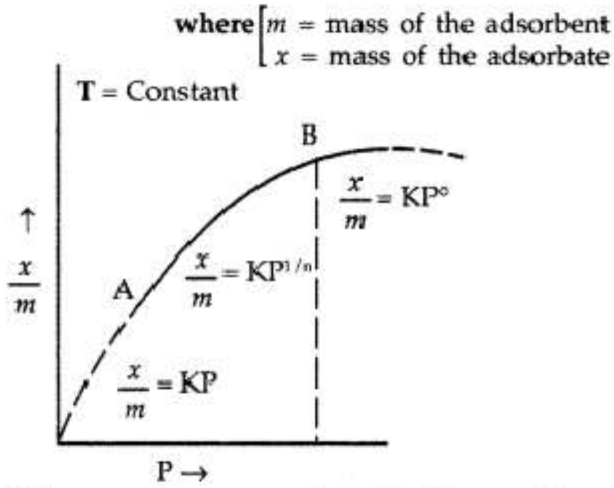
$$\frac{x}{m} \propto p^1 \quad or \quad \frac{x}{m} = kp^1 ---------(i)$$

At high P, x/m becomes independent of the value of P. It can be represented by the equation as

$$\frac{x}{m} \propto p^0 \quad or \quad \frac{x}{m} = kp^0 \text{ --------}(ii)$$

In the intermediate range of pressure, x/m will depend on Praised to powers between 1 and 0. Thua for a small range of pressure, the equation can be represented as

$$\frac{x}{m} \propto p^{\frac{1}{n}} \quad or \quad \frac{x}{m} = kp^{\frac{1}{n}} \text{ -------}(iii)$$



Variation of x/m with increase in pressure at constant temperature (Freundlich adsorption isotherm)

These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with an increase in temperature. These curves always seem to approach saturation at high pressure Taking the logarithm of eq-(iii)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \text{ ----------------}(iv)$$

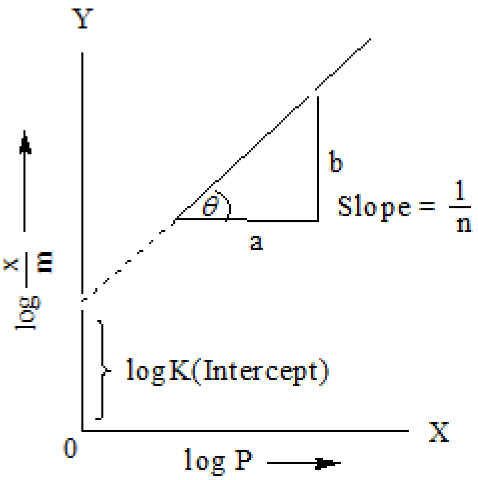
(a) The validity of Freundlich isotherm can be verified by plotting **log *x* /*m*** on the *y*-axis (ordinate) and **log p** on the x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid.

(b) The slope of the straight line gives the value of 1/*n*. The intercept on the *y*-axis gives the value of log *k*.

(c) Freundlich isotherm approximately explains the behavior of adsorption. The factor 1/*n* can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (iv) holds good over a limited range of pressure.

(d) When $1/n = 0$, x/m = constant, the adsorption is independent of pressure. When $1/n = 1$ $x/m = k\,p$, i.e. $x/mp\ \alpha\ p$, the adsorption varies directly with pressure.

(e) Both conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.



Adsorption from Solution Phase:

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is absorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colorless. The precipitate of Mg $(OH)_2$ attains blue color when precipitated in presence of magneson reagent. The color is due to the adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.
(ii) The extent of adsorption increases with an increase in the surface area of the adsorbent.
(iii) The extent of adsorption depends on the concentration of the solute in the solution.
(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behavior of adsorption from solution by taking a concentration of the solution as

$$\frac{x}{m} = kC^{\frac{1}{n}} ---------(i)$$

[C=Equilibrium concentration, i.e., when adsorption is completed].

On taking the logarithm of the above equation, we have

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C ------(ii)$$

Plotting log *x/m* against logC a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations gives the value of *x*.

Applications of Adsorption:

(i) Production of high vacuum:

The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) Gas masks:

A gas mask (a device which consists of activated charcoal or a mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) Control of humidity:

Silica and aluminum gels are used as adsorbents for removing moisture and controlling humidity.

(iv) Removal of coloring matter from solutions:

Animal charcoal removes the colors of solutions by adsorbing colored impurities.

(v) Heterogeneous catalysis:

Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process, and use of finely divided nickel in the hydrogenation of oils are examples of heterogeneous catalysis.

(vi) Separation of inert gases:

Due to the difference in the degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) In curing diseases:

Several drugs are used to kill germs by getting adsorbed on them.

(viii) Froth floatation process:

Low-grade sulfide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.

(ix) Adsorption indicators:

Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic color at the endpoint.

(x) Chromatographic analysis:

Chromatographic analysis based on the phenomenon of adsorption finds several applications in analytical and industrial fields.

Catalysis:

The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius, in 1835. He suggested the term **catalyst** for such substances. Thus

The Substances, which can accelerate the rate of a chemical reaction and remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis.

Ex: Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873K.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much-accelerated rate. The added manganese dioxide remains unchanged concerning its mass and composition.

Promoters and poisons: **Promoters** are substances that enhance the activity of a catalyst while **poisons** decrease the activity of a catalyst. Ex: In Haber's process for the manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s),Mo(s)} 2NH_{3(g)}$$

Catalysis can be broadly divided into two groups:

Homogeneous and Heterogeneous Catalysis:

(a) Homogeneous catalysis:

When the reactants and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis. The following are some of the examples of homogeneous catalysis:

(i) Oxidation of sulfur dioxide into sulfur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} NO(g)\ 2SO_3(g)$$

The reactants, sulfur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

(ii) Hydrolysis of methyl acetate is catalyzed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and the catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalyzed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(l)} \xrightarrow{H_2SO_{4(l)}} \underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(aq)}}$$

Both the reactants and the catalyst are in the same phase.

b) Heterogeneous catalysis:

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below:

(i) Oxidation of sulfur dioxide into sulfur trioxide in the presence of Pt.

$$2SO_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

The reactant is in a gaseous state while the catalyst is in the solid-state.

(ii) The combination of dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

The reactants are in a gaseous state while the catalyst is in a solid-state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt(s)} 4NO_{(g)} + 6H_2O_{(g)}$$

The reactants are in a gaseous state while the catalyst is in a solid-state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as a catalyst.

$$\text{Vegetable oils(l)} + H_{2(g)} \xrightarrow{Ni(s)} \text{Vegetable ghee(s)}$$

One of the reactants is in the liquid state and the other in a gaseous state while the catalyst is in the solid-state.

Adsorption Theory of Heterogeneous Catalysis:

(i) This theory explains the mechanism of heterogeneous catalysis. The old theory, known as the adsorption theory of catalysis. According to this theory reactants in a gaseous state or solutions, are adsorbed on the surface of the solid catalyst.

(ii) The increase in the concentration of the reactants on the surface increases the rate of reaction.

(iii) Adsorption being an exothermic process, the heat of adsorption is utilized in enhancing the rate of the reaction.

(iv) The catalytic action can be explained in terms of the intermediate compound formation. The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localized on the surface of the catalyst.

The mechanism involves five steps:

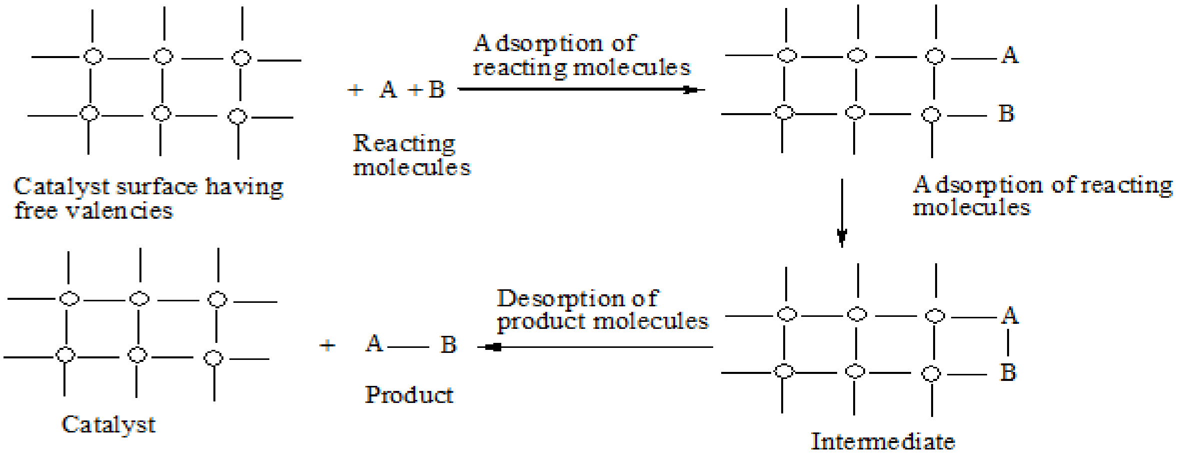
(a) Diffusion of reactants to the surface of the catalyst.

(b) Adsorption of reactant molecules on the surface of the catalyst.

(c) The occurrence of chemical reaction on the catalyst's surface through the formation of an intermediate

(d) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

(e) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst has free valencies which provide the seat for chemical forces of attraction. When the gas comes in contact with such a surface, its molecules are held up there due to loose chemical combinations. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules. This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. However, it does not explain the action of catalytic promoters and catalytic poisons.



LECTURE-3

Important features of solid catalysts:

(a) **Activity**

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilized and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table.

(b) **Selectivity**

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product selectively. But under the same reaction conditions, many products are possible. The selectivity of different catalysts for the same reactants is different. Ex: H_2 and CO, form different products by using different catalysts. Thus, the action of a catalyst is highly selective. As a result, a substance that acts as a catalyst in one reaction may fail to catalyze another reaction.

Shape-Selective Catalysis by Zeolites:

(i) The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called **shape-selective catalysis.**

(ii) Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with a three-dimensional network of silicates in which some silicon atoms are replaced by aluminum atoms giving Al–O–Si framework.

(iii) The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites.

(iv) Zeolites are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohol directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

Enzyme Catalysis:

Enzymes are complex nitrogenous organic compounds that are produced by living plants and animals. They are protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts; catalyze numerous reactions, especially those connected with natural processes. Reactions that occur in the bodies of animals and plants to maintain the life process are catalyzed by enzymes. The enzymes are, thus, termed **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**. Many enzymes have been obtained in the pure crystalline state from living cells. However, the first enzyme was synthesized in the laboratory in 1969. The following are some of the examples of enzyme-catalyzed reactions:

(i) Inversion of cane sugar:

The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(l)} \xrightarrow{Invertase} \underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(aq)}}$$

(ii) Conversion of glucose into ethyl alcohol:

The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} \xrightarrow{\text{Zymase}} 2\underset{\text{Ethyl alcohol}}{C_2H_5OH_{(aq)}} + 2CO_{2(g)}$$

(iii) **Conversion of starch into maltose:**
The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_{n(aq)}} + nH_2O_{(l)} \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11(aq)}}$$

(iv) **Conversion of maltose into glucose:**
The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(aq)} \xrightarrow{\text{Maltase}} 2\underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}}$$

(v) **Decomposition of urea into ammonia and carbon dioxide:**
The enzyme urease catalyzes this decomposition.

$$NH_2CONH_{2(aq)} + H_2O_{(l)} \xrightarrow{Urease} 2NH_{3(g)} + CO_{2(g)}$$

(vi) **In stomach**:
The pepsin enzyme converts proteins into peptides while in the intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose Glucose and fructose
Zymase	Yeast	Glucose Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch Maltose
Maltase	Yeast	Maltose Glucose
Urease	Soyabean	Urea Ammonia and carbon dioxide
Pepsin	Stomach	Proteins Amino acids

(vii) **Conversion of milk into curd:**
It is an enzymatic reaction brought about by the lactobacilli enzyme present in curd.

Characteristics of enzyme catalysis:

Enzyme catalysis is unique in its efficiency and a high degree of specificity. The following characteristics are exhibited by the enzyme catalysts:

(i) **Most highly efficient:**
One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) **Highly specific nature:**
Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyze more than one reaction. For example, the enzyme urease catalyzes the hydrolysis of urea only. It does not catalyze the hydrolysis of any other amide.

(iii) **Highly active under optimum temperature:**
The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. The human body temperature is 310 K is suited for enzyme-catalyzed reactions.

(iv) **Highly active under optimum pH:**
The rate of an enzyme-catalyzed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.

(v) **Increasing activity in presence of activators and co-enzymes:**
The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably. Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e., Na^+ ions is catalytically very active.

(vi) **Influence of inhibitors and poisons:**
Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

Mechanism of enzyme catalysis:

There are several cavities present on the surface of colloidal particles of enzymes. These cavities are of a characteristic shape and contain active groups such as $-NH_2$, -COOH, -SH, -OH, etc. These are the active centers on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. The active groups, form an activated complex which then decomposes to yield the products.

$$E + S \rightleftharpoons [E\text{-}S] \longrightarrow E + P$$

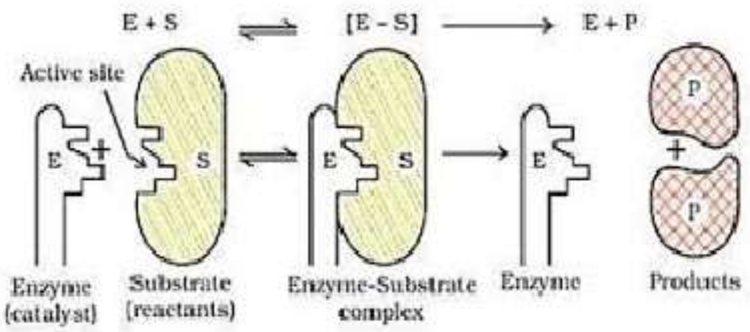
The enzyme-catalyzed reactions may be considered to proceed in two steps.

Step 1: Binding of the enzyme to substrate to form an activated complex.

$$E + S \rightarrow ES$$

Step 2: Decomposition of the activated complex to form the product.

$$ES \rightarrow E + P$$



Catalysts in Industry

(i) In Haber's process for the manufacture of ammonia, Finely divided iron, molybdenum as promoter used as a catalyst and is favorable at 200 bar pressure and 723-773K temperature. Nowadays, a mixture of iron oxide, potassium oxide, and alumina is used.

(ii) In Ostwald's process for the manufacture of nitric acid, Platinised asbestos is used as a catalyst. Temperature 573K is maintained.
(iii) In the Contact process for the manufacture of sulphuric acid, Platinised asbestos or vanadium pentoxide (V_2O_5) is used. Temperature 673-723K is maintained.

LECTURE 04

COLLOIDAL STATE

Thomas Graham divided the soluble substances into two types such as (i) Crystalloids (ii) Colloids. The crystalline substances like common salt, sugar, urea, etc dissolved in water and can pass through the animal membrane are called crystalloids and non-crystalline substances like starch, gum, glue, etc in the dissolved state cannot pass through the membrane are called colloids. Crystalloids form a true solution. But a crystalloid was found to behave as a colloid under different conditions. Ex: NaCl behaves as a crystalloid when dissolved in water but behaves as a colloid when dissolved in benzene. So a clear cut difference doesn't exist between crystalloids and colloids. The essential difference between a solution and a colloid is that of particle size. In a solution, the constituent particles are ions or small molecules. In a colloid, the constituent particles (Dispersed phase) are macromolecules like protein or synthetic polymer or an aggregate of many atoms, ions, or molecules. The colloids form bigger particles that cannot pass through the membrane. The dimension of colloidal particles lies in-between the dimension of particles of suspension and true solution. The dimension of colloidal particles lies in between 10^{-9} to 10^{-6} m or 1nm to 1000nm or $10A^0$ to $1000A^0$.

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

Classification of Colloids

Colloids are classified based on the following criteria:
(i) The physical state of the dispersed phase and the dispersion medium
(ii) Nature of interaction between the dispersed phase and the dispersion medium
(iii) Type of particles of the dispersed phase.

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Classification Based on Physical State of Dispersed Phase and Dispersion Medium:

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids, or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system.

Types of Colloidal Systems

D.P	D.M	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream

Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Out of the various types of colloids given the most common are **sols** (solids in liquids), **gels** (Liquids in solids) and **emulsions** (liquids in liquids). If the dispersion medium is water, the sol is called aqua sol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

Classification Based on the Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of the interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

(i) Lyophilic colloids:

The word 'lyophilic' means solvent-loving. The colloids in which particles of the dispersed phase and dispersion medium are strongly attracted is known as Lyophilic colloid. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. These sols are also called **reversible sols**. Because of the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. Furthermore, these sols are quite stable and cannot be easily coagulated.

(ii) Lyophobic colloids:

The word 'lyophobic' means solvent-hating. The colloids in which particles of the dispersed phase are weakly attracted by the dispersion medium is known as Lyophobic colloid. Substances like metals, their sulfides, 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 readily precipitated or coagulated on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable. These sols are also called **irreversible sols**. Because, if they are precipitated, they do not give back the colloidal sol by the simple addition of the dispersion medium. Thus Lyophobic sols need stabilizing agents for their preservation.

Classification Based on Type of Particles of the Dispersed Phase:

Depending upon the type of the particles of the dispersed phase, colloids are classified as multi molecular, macromolecular, and associated colloids.

(i) Multimolecular colloids:

On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having the size in the colloidal range (1–1000 nm) are called multimolecular colloids.

Ex: A gold sol may contain particles of various sizes having many atoms. Sulfur sol consists of particles containing a thousand or more of S_8 sulfur molecules.

(ii) Macromolecular colloids:

When the substances having macromolecules or having large molecular mass are dissolved in a suitable liquid, to form a solution having the size of particles in the

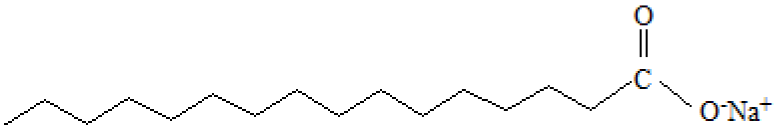
colloidal range then it is known as Macromolecular colloid. These colloids are quite stable and resemble true solutions in many respects.
Ex: starch, cellulose, proteins, and enzymes, etc are naturally occurring macromolecules. polythene, nylon, polystyrene, synthetic rubber, etc. are man-made macromolecules.

(iii) **Associated colloids (Micelles):**

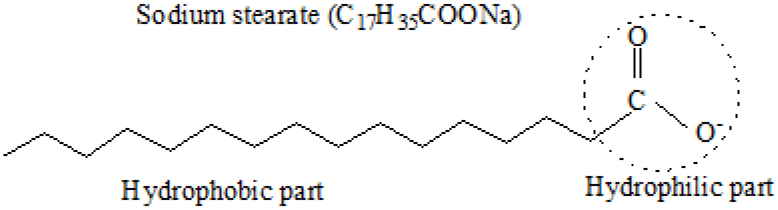
The substances which when dissolved in a medium at higher concentrations exhibit colloidal state properties due to the formation of aggregated particles are called associated colloids.
However, the substances which when dissolved in a medium at low concentrations behave as normal strong electrolytes. The aggregated particles thus formed are also called **micelles**. The formation of micelles takes place only above a particular temperature called **Kraft temperature** (**Tk**) and above a particular concentration called **critical micelle concentration** (**CMC**). On dilution, these colloids revert to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

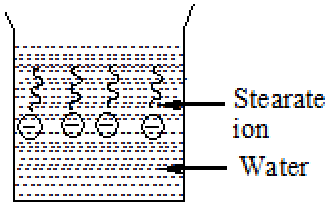
Mechanism of micelle formation:

Soap is sodium or potassium salt of higher fatty acid and may be represented as $RCOONa^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^-$ and Na^+ ions. The $RCOO^-$ ions, however, consist of two parts such as a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water-repelling), and a polar group COO^- (also called polar-ionic 'head'), which is hydrophilic (water-loving).

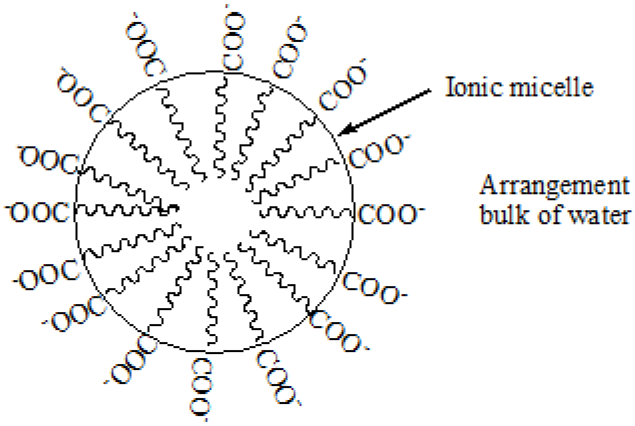


Sodium stearate ($C_{17}H_{35}COONa$)





Arrangement of stearate ion on the surface of water at low conc. of soap.

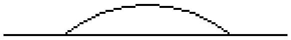


Arrangement of stearate ion in side the bulk of water at critical micelle conc.of soap.

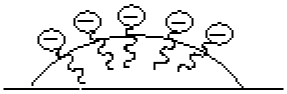
The $RCOO^-$ ions are, present on the surface with their COO^- groups in water and the hydrocarbon
chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the center of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as '**ionic micelle**'. Similarly, in the case of detergents, e.g., sodium lauryl sulfate, $CH_3(CH_2)_{11}SO_4^-Na^+$, the polar group is SO_4^{2-} along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is the same as that of soaps.

The cleansing action of soaps:

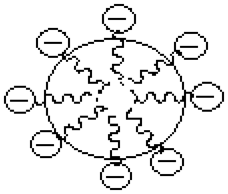
The cleansing action of soap is because soap molecules form micelle around the oil droplet in such a way that the hydrophobic part of the stearate ions is in the oil droplet and the hydrophilic part projects out of the grease droplet like the bristles.



Grease on cloth



Stearate ions arranging around the grease droplet



Grease droplet surrounded by stearate ions (micelle formed)

Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away from oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

Preparation of Colloids:

A few important methods for the preparation of colloids are as follows:

(a) Chemical methods:

(i) **Double decomposition:**

$$As_2O_3 + 3H_2S \rightarrow As_2S_3(sol) + 3H_2O$$

(ii) **Oxidation:**

$$SO_2 + 2H_2S \rightarrow 3S(sol) + 2H_2O$$

(iii) **Reduction:**

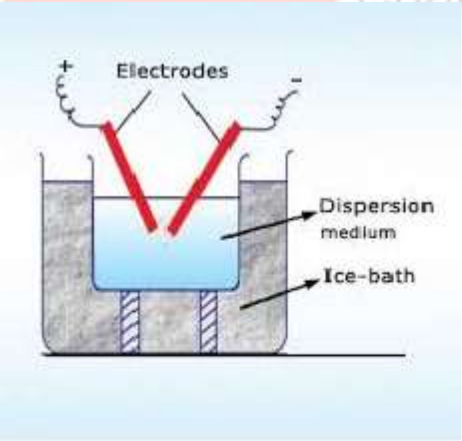
$$2\,AuCl_3 + 3\,HCHO + 3H_2O \rightarrow 2Au(sol) + 3HCOOH + 6HCl$$

(iv) **Hydrolysis:**

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3\ (sol) + 3HCl$$

(b) Electrical disintegration or Bredig's Arc method:

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, an 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.



(c) Peptization:

Peptization may be defined as the **process of converting a precipitate into a colloidal sol** by shaking it with a dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called a **peptizing agent**. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charges on precipitates, which ultimately break up into smaller particles of the size of a colloid.

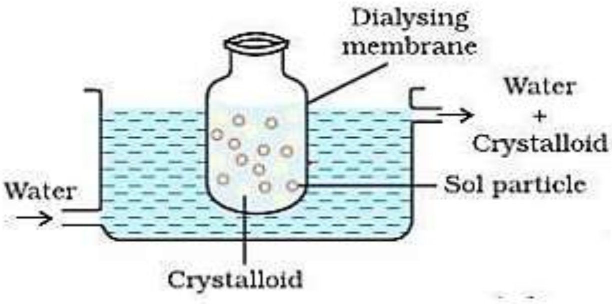
LECTURE-05

Purification of Colloidal Solutions:

Colloidal solutions when prepared, generally contain an excessive amount of electrolytes and some other soluble impurities. While the presence of traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. **The process used for reducing the number of impurities to a requisite minimum is known as the purification of a colloidal solution**. This can be carried out by the following methods.

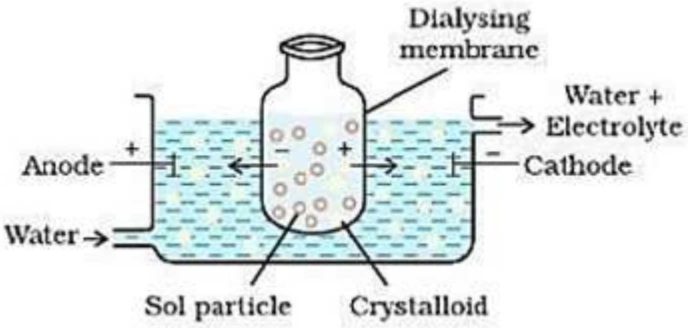
(i) Dialysis:

The process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane is known as Dialysis. The particles (ions of smaller molecules) in a true solution can pass through the animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles. Thus these are used as a membrane for dialysis. The apparatus used for this purpose is called a **dialyzer**. A bag of suitable membranes containing the colloidal solution is suspended in a vessel through which freshwater is continuously flowing. The molecules and ions diffuse through the membrane into the outer water and the pure colloidal solution is left behind.



(ii) Electro-dialysis:

Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane fitted with electrodes while pure water is taken outside. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.



(iii) **Ultrafiltration:**

Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with a **collodion** solution to stop the flow of colloidal particles. The usual collodion is a 4% solution of nitrocellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a collodion

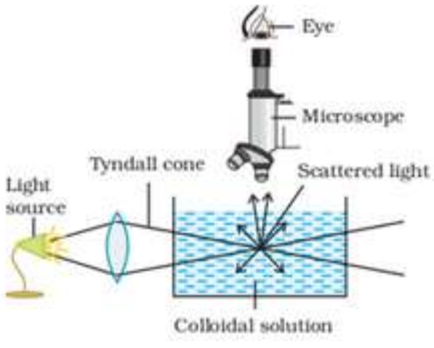
solution, hardening by formaldehyde, and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from the rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with a fresh dispersion medium (solvent) to get a pure colloidal solution.

Properties of Colloidal Solutions:

(i) **Colligative properties:**

Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapor pressure, and depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at the same concentrations.

(ii) When a convergent beam of light is passed through a colloidal solution using a convex `lens then the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as the **Tyndall effect**. The bright cone of the light which is observed is called the **Tyndall cone.**



Tyndall effect

The Tyndall effect is because colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of the beam in the colloidal dispersion. The Tyndall effect can be observed during the projection of a picture in the cinema hall due to the scattering of light by dust and smoke particles present there. The Tyndall effect is observed only when the following two conditions are satisfied.

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude. The Tyndall effect is used to distinguish between a colloidal and a true solution. Zsigmondy, in 1903, used an ultramicroscope to study the Tyndal effect. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observes the light scattered by them. Thus, the ultramicroscope does not provide any information about the size and shape of colloidal particles.

(iii) **<u>Colour:</u>**

The color of the colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The color of the colloidal solution also changes with how the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. The finest gold sol is red; as the size of particles increases, it appears purple, then blue, and finally golden.

(iv) **<u>Brownian movement:</u>**

When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion. This motion was first observed by the British botanist, Robert Brown, and is known as the Brownian movement.

This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of the solution. The smaller the size and lesser the viscosity, the faster is the motion. The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect that does not permit the particles to settle and thus, is responsible for the stability of sols.

(v) **Charge on colloidal particles:**

Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative. The charge on the sol particles is due to

(i) Electron capture by sol particles during electro dispersion of metals.

(ii) Preferential adsorption of ions from solution or due to formulation of the electrical double layer. Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

Ex: When silver nitrate solution is added to the potassium iodide solution, the precipitated AgI adsorbs iodide ions from the dispersion medium and negatively charged colloidal sol results. However, when the KI solution is added to the $AgNO_3$ solution, positively charged sol results due to the adsorption of Ag^+ ions from the dispersion medium.

AgI/I^- (negatively charged) AgI/Ag^+ (Positively charged

Ex: If $FeCl_3$ is added to an excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to the adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH^- ions.

$Fe_2O_3.xH_2O/Fe^{3+}$	$Fe_2O_3.xH_2O/OH^-$
Positively charged	Negatively charged

The layer of positive or a negative charge that appeared by selective adsorption on the surface of a colloidal particle attracts counter ions from the medium forming a second layer.

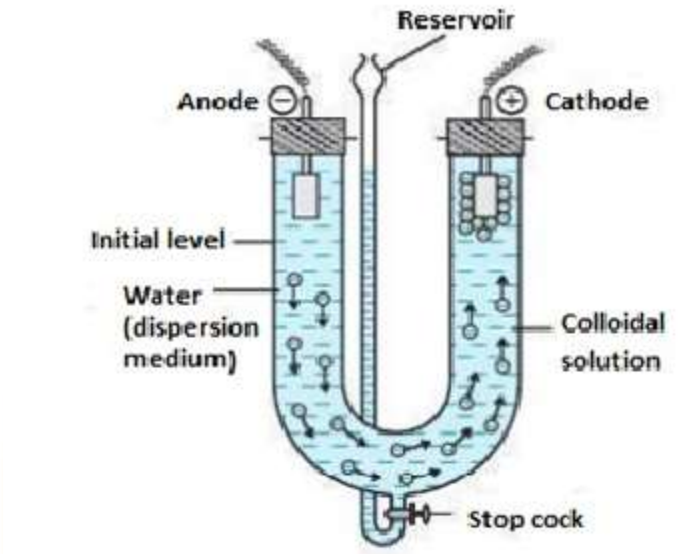
$AgI/I^- K^+$ AgI/Ag^+I^-

The combination of the two layers of opposite charges around the colloidal particle is called a **Helmholtz electrical double layer**. The first layer of ions is firmly held and is termed as a fixed layer while the second layer is mobile which is termed as a diffused layer. The charges of opposite signs on the fixed and diffused parts of the double layer result in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution because the repulsive forces between charged particles having the same charge prevent them from aggregating when they come closer to one another.

(vi) **Electrophoresis:**

The existence of charge on colloidal particles is confirmed by the electrophoresis experiment. When an electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. The movement of colloidal particles under an applied electric potential is called **electrophoresis.** Positively charged particles move towards the cathode while negatively charged particles move towards the anode.



During electrophoresis, if the movement of particles is prevented by some suitable means, then the dispersion medium begins to move in an electric field. This phenomenon is termed **electroosmosis**.

(vii) Coagulation or precipitation:

The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity. **The process of settling of colloidal particles is called coagulation or precipitation of the sol**. The coagulation of the lyophobic sols can be carried out in the following ways:

(i) By electrophoresis:

The colloidal particles move towards oppositely charged electrodes, get discharged, and precipitated.

(ii) By mixing two oppositely charged sols:

Oppositely charged sols when mixed in almost equal proportions, neutralize their charges and get partially or completely precipitated. This type of coagulation is called **mutual coagulation.**

Ex: Mixing of hydrated ferric oxide (+ve sol) and arsenious sulfide (–ve sol) neutralize to each other to form a precipitate.

(iii) By boiling:

When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of the dispersion medium. This reduces the charge on the particles and ultimately leads to settling down in the form of a precipitate.

(iv) By persistent dialysis:

On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.

(v) **By addition of electrolytes:**

(a) When an excess of an electrolyte is added, the colloidal particles are precipitated. It is due to the interaction of colloids with the opposite charge of ions. The neutralization results in coagulation.

(b) *The ion* responsible for the neutralization of charge on the particles is called the **coagulating ion or agent.** A negative ion causes the precipitation of positively charged sol and vice versa.

(c) It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its coagulating power. This is known as the **Hardy-Schulze rule**. In the coagulation of a negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{2+} > Na^{+}$

Similarly, in the coagulation of a positive sol, the flocculating power is in the order: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

(d) The minimum concentration of an electrolyte in millimoles per liter required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

LECTURE-06

Coagulation of lyophilic sols:

Two factors are responsible for the stability of lyophilic sols. These factors are the charge and salvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated.

This is done (i) by adding an electrolyte and (ii) by adding a suitable solvent.

When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of the dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

Protection of colloids:

(i) Lyophilic sols are more stable than lyophobic sols. This is because lyophilic colloids are extensively solvated.

(ii) Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

Emulsions:

(i) These are liquid-liquid colloidal systems, i.e., if one liquid is dispersed in another liquid then the colloid formed is known as an emulsion. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called emulsion. Generally, one of the two liquids is water. There are two types of emulsions.

(a) Oil dispersed in water (O/W type) and (b) Water dispersed in oil (W/O type).

(a) **Oil dispersed in water (O/W type)**

In this system, water acts as a dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilization of an emulsion, a third component called an emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc.,

(b) Water dispersed in oil (W/O type).

In this system, oil acts as a dispersion medium. Common examples of this type are butter and cream. The principal emulsifying agents for W/O are heavy metal salts of fatty acids, long-chain alcohols, lampblack, etc. Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed forms a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show the Brownian movement and the Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

Colloids Around Us

(i) The blue color of the sky:

Dust particles along with water suspended in the air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) Fog, mist, and rain:

When a large mass of air containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal continue to float in the air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in the air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet. It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an airplane.

(iii) Food articles:

Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) Blood:

It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to the coagulation of blood-forming a clot which stops further bleeding.

(v) Soils:

Fertile soils are colloidal in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

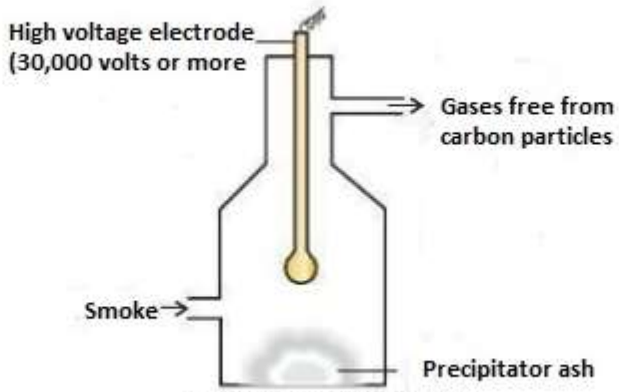
(vi) Formation of delta:

River water is a colloidal solution of clay. Seawater contains several electrolytes. When river water meets the seawater, the electrolytes present in seawater coagulate the colloidal solution of clay resulting in its deposition with the formation of the delta.

Applications of colloids

(i) Electrical precipitation of smoke:

Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called the Cottrell precipitator.



Cottrell Smoke precipitator

(ii) **Purification of drinking water:**

The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) **Medicines:**

Most of the medicines are colloidal. For example, Argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kala-azar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have a large surface area and are therefore easily assimilated.

(iv) **Tanning:**

Animal hides are colloidal. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

(v) **The cleansing action of soaps and detergents:**

It has been described in page-16.

(vi) **Photographic plates and films:**

Photographic plates or films are prepared by coating an emulsion of the light-sensitive silver bromide in gelatin over glass plates or celluloid films.

(vii) **Rubber industry:**

Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(viii) **Industrial products:**

Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions.

LECT-1: Answer the following questions:

1. Write any two characteristics of Chemisorption.
2. Why does physisorption decrease with the increase in temperature?
3. Why are powdered substances more effective adsorbents than their crystalline forms?
4. Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.
5. What is the difference between physisorption and chemisorption?
6. Give the reason why a finely divided substance is more effective as an adsorbent.
7. What are the factors which influence the adsorption of a gas on a solid?
8. What do you understand by the activation of adsorbent? How is it achieved?
9. Why is adsorption always exothermic?

LECT-2: Answer the following questions:

1. What are the factors which influence the adsorption of a gas on a solid?
2. What is an adsorption isotherm? Describe Freundlich adsorption isotherm.
3. What role does adsorption play in heterogeneous catalysis?
4. Discuss the effect of pressure and temperature on the adsorption of gases on solids.
5. Give four examples of heterogeneous catalysis.
6. How does Freundlich isotherm explain the behavior of adsorption?
7. Write the applications of adsorption.
8. Discuss the mechanism of adsorption.

LECT-3: Answer the following questions:

1. What are enzymes? Write in brief the mechanism of enzyme catalysis.
2. In Haber's process, hydrogen is obtained by reacting methane with steam in presence of NiO as a catalyst. The process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?
3. Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?
4. What is the role of desorption in the process of catalysis?
5. What do you mean by activity and selectivity of catalysts?
6. Describe some features of catalysis by zeolites.
7. What is shape-selective catalysis?
8. Write the important characteristics of enzyme catalysis.

LECT-4: Answer the following questions:

1. How are the colloidal solutions classified based on physical states of the dispersed phase and dispersion medium?
2. What are lyophilic and lyophobic sols? Give one example of each type.
3. What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?
4. How are colloids classified based on
   (i) Physical states of components (ii) nature of dispersed phase and
   (iii) Interaction between the dispersed phase and dispersion medium?
5. Explain the terms with suitable examples:
   (i) Alcohol (ii) Aerosol (iii) Hydrosol.
6. Comment on the statement that "colloid is not a substance but a state of substance".
7. Define the terms (i) Kraft temperature (ii) CMC
8. Discuss the mechanism of micelle formation.
9. Explain the cleansing action of soap.

10. What are peptization and peptizing agent? Explain.
11. How can you prepare colloids of gold by Bredig's arc method?
12. Write with an equation how will you prepare the following colloids:

LECT-5: Answer the following questions:

1. What are micelles? Give an example of a micelle system.
2 Explain the following terms:
(i) Electrophoresis (ii) Coagulation (iii) Dialysis (iv) Tyndall effect.
3. Explain what is observed
(i) When a beam of light is passed through a colloidal sol.
(ii) An electrolyte, NaCl is added to hydrated ferric oxide sol.
(iii) Electric current is passed through a colloidal sol?
4. Explain (i) Electro-dialysis (ii) Ultrafiltration
5. Why colligative properties of colloids are comparatively small as compared to the true solution?
6. Why colloidal solutions are colored?
7. Explain the terms (i) electrokinetic potential with example.
(ii) Coagulation (ii) Mutual coagulation (iii) Hardy-schulze rule.
8. Write the order of coagulating power of following ions:
(i) $[Fe(CN)_6]^{4-}$, PO_4^{3-}, SO_4^{2-}, Cl^- (ii) Al^{3+} , Ba^{2+} , Na^+

LECT-6: Answer the following questions:

1. What are micelles? Give an example of a micelle system.
2. What are emulsions? What are their different types? Give an example of each type.
3. How do emulsifiers stabilize emulsion? Name two emulsifiers.
4. The action of soap is due to emulsification and micelle formation. Comment.