Unit
5

Surface Chemistry

Some of the most important chemicals are produced industrially by means of reactions that occur on the surfaces of solid catalysts.

Objectives

After studying this Unit, you will be able to

• describe interfacial phenomenon and its significance;

• define adsorption and classify it into physical and chemical adsorption;

• explain mechanism of adsorption;

• explain the factors controlling adsorption from gases and solutions on solids;

• explain adsorption results on the basis of Freundlich adsorption isotherms;

• appreciate the role of catalysts in industry;

• enumerate the nature of colloidal state;

• describe preparation, properties and purification of colloids;

• classify emulsions and describe their preparation and properties;

• describe the phenomenon of gel formation;

• list the uses of colloids.

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

In this Unit, you will be studying some important features of surface chemistry such as adsorption, catalysis and colloids including emulsions and gels.

5.1 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency 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. **The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption**. 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**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in 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 colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.

(iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed 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.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

5.1.1 Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while 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.

5.1.2 Mechanism of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. 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. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. 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.

5.1.3 Types of Adsorption

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption or physisorption**. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Some of the important characteristics of both types of adsorption are described below:

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 gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der 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. Thus,

$$Solid + Gas \rightleftharpoons Gas/Solid + Heat$$

More of 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 temperature and decreases with increasing temperature (Le-Chatelier's principle).

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

(v) *Enthalpy of adsorption:* No doubt, 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. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.

 (ii) *Irreversibility:* As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption 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 often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.

(iii) *Surface area:* Like physical adsorption, chemisorption also increases with increase of 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.

Table 5.1: 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 with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase 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 an increase of surface area.	8. It also depends on the surface area. It too 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.

5.1.4 Adsorption Isotherms

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

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

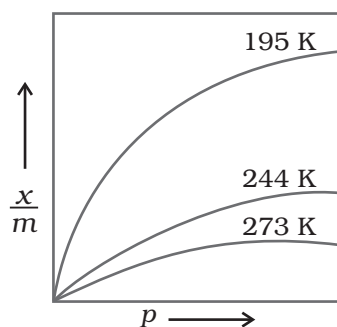$$\frac{x}{m} = k.p^{1/n} \ (n > 1) \qquad\qquad \dots (5.1)$$

Fig. 5.1: Adsorption isotherm

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 mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of eq. (5.1)

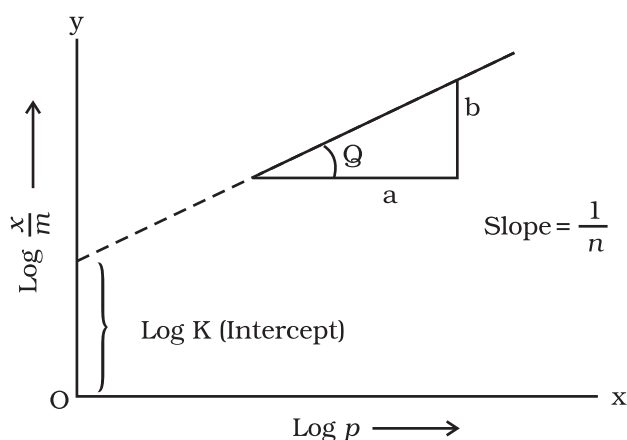$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad\qquad \dots (5.2)$$

Fig. 5.2: Freundlich isotherm

The validity of Freundlich isotherm can be verified by plotting $\log \frac{x}{m}$ on y-axis (ordinate) and $\log p$ on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the y-axis gives the value of $\log k$.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (5.2) holds good over a limited range of pressure.

When $\dfrac{1}{n} = 0, \dfrac{x}{m}$ = constant, the adsorption is independent of pressure.

When $\dfrac{1}{n} = 1, \dfrac{x}{m} = k\,p$, i.e. $\dfrac{x}{m} \propto p$, the adsorption varies directly with pressure.

Both the 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.

5.1.5 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 adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson reagent. The colour is due to 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 of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in 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 behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\dfrac{x}{m} = kC^{1/n} \qquad \qquad ...(5.3)$$

(C is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of the above equation, we have

$$\log \dfrac{x}{m} = \log k + \dfrac{1}{n}\,\log C \qquad \qquad ...(5.4)$$

Plotting $\log \dfrac{x}{m}$ against $\log C$ 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 give the value of x. Using the above equation, validity of Freundlich isotherm can be established.

5.1.6 Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

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

(iii) *Control of humidity*: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) *Removal of colouring matter from solutions*: Animal charcoal removes colours of solutions by adsorbing coloured 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 excellent examples of heterogeneous catalysis.

(vi) *Separation of inert gases*: Due to the difference in 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*: A number of drugs are used to kill germs by getting adsorbed on them.

(viii) *Froth floatation process*: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent (see Unit 6).

(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 colour at the end point.

(x) *Chromatographic analysis*: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

Intext Questions

5.1 Write any two characteristics of Chemisorption.

5.2 Why does physisorption decrease with the increase of temperature?

5.3 Why are powdered substances more effective adsorbents than their crystalline forms?

5.2 Catalysis

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

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
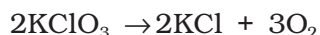
However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance.

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.

Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis. You have already studied about catalysts and its functioning in Section 4.5.

Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow[Mo(s)]{Fe(s)} 2NH_3(g)$$
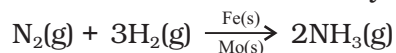
5.2.1 Homogeneous and Heterogeneous Catalysis

Catalysis can be broadly divided into two groups:
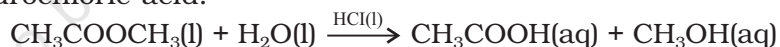
(a) Homogeneous catalysis

When the reactants products 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 sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.
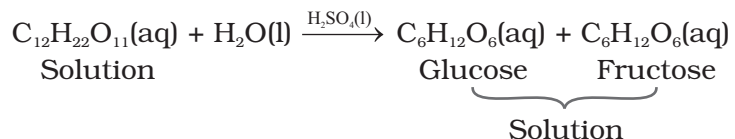
$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$
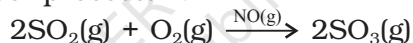
The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

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

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underset{\underset{\text{Solution}}{\underbrace{\text{Glucose} \qquad \text{Fructose}}}}{C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)}$$
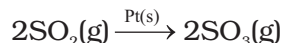
Both the reactants and the catalyst are in the same phase.

(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 sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$
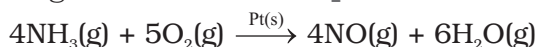
The reactant is in gaseous state while the catalyst is in the solid state.

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

$$N_2(g) + 3H_2(g) \xrightarrow{\text{Fe(s)}} 2NH_3(g)$$
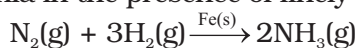
The reactants are in gaseous state while the catalyst is in the solid state.

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

$$4NH_3(g) + 5O_2(g) \xrightarrow{\text{Pt(s)}} 4NO(g) + 6H_2O(g)$$

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

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

$$\text{Vegetable oils(l)} + H_2(g) \xrightarrow{\text{Ni(s)}} \text{Vegetable ghee(s)}$$
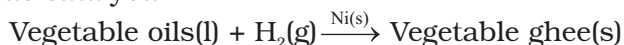
One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

5.2.2 Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The old theory, known as adsorption theory of catalysis, was that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction.

The catalytic action can be explained in terms of the intermediate compound formation, the theory of which you have already studied in Section 4.5.1

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

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

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

(iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate (Fig. 5.3).

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

(v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. 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
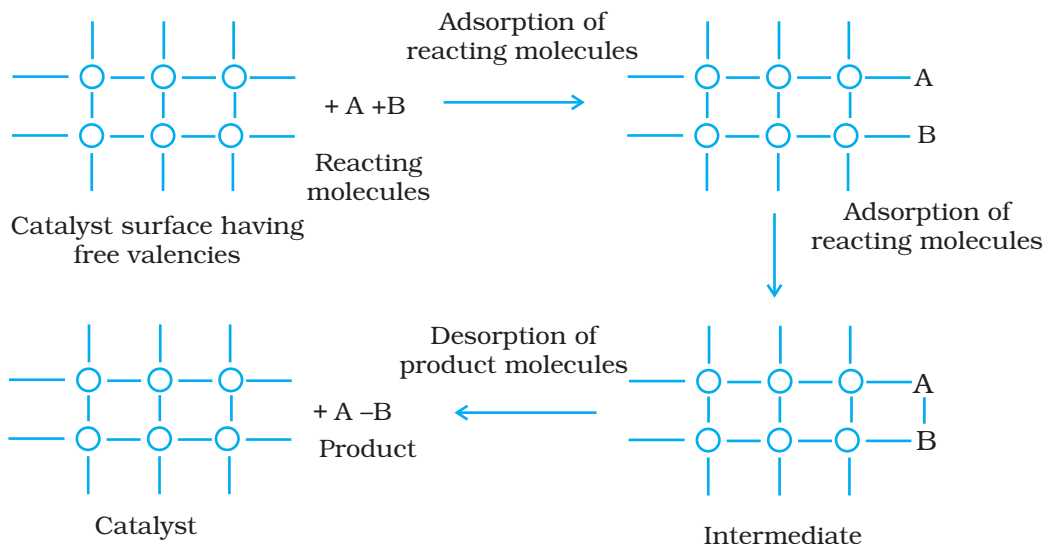
Fig. 5.3
Adsorption of reacting molecules, formation of intermediate and desorption of products

even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.
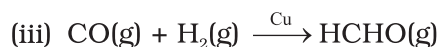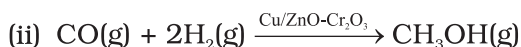
Important features of solid catalysts

(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 immobilised 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 (Class XI, Unit 3).

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$
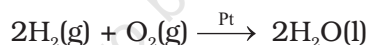
(b) Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product selectively, when under the same reaction conditions many products are possible. Selectivity of different catalysts for same reactants is different. For example, starting with H_2 and CO, and using different catalysts, we get different products.

(i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

(iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Thus, it can be inferred that the action of a catalyst is highly selective in nature. As a result a substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

5.2.3 Shape-Selective Catalysis by Zeolites

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.** Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous

aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. 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. They are found in nature as well as synthesised for catalytic selectivity.
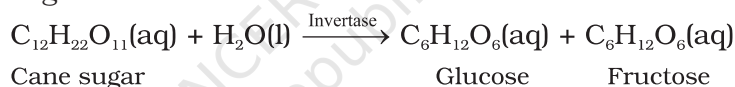
Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

5.2.4 Enzyme Catalysis

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts; catalyse numerous reactions, especially those connected with natural processes. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**.

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme-catalysed reactions:

(i) *Inversion of cane sugar*: The invertase enzyme converts cane sugar into glucose and fructose.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{Invertase} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$
Cane sugar $\qquad\qquad\qquad\qquad\qquad$ Glucose $\qquad$ Fructose

(ii) *Conversion of glucose into ethyl alcohol*: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6(aq) \xrightarrow{Zymase} 2C_2H_5OH(aq) + 2CO_2(g)$$
Glucose $\qquad\qquad$ Ethyl alcohol
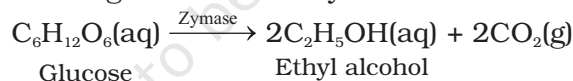
(iii) *Conversion of starch into maltose*: The diastase enzyme converts starch into maltose.

$$2(C_6H_{10}O_5)_n(aq) + nH_2O(l) \xrightarrow{Diastase} nC_{12}H_{22}O_{11}(aq)$$
Starch $\qquad\qquad\qquad\qquad\qquad$ Maltose
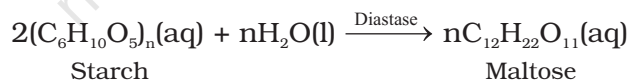
(iv) *Conversion of maltose into glucose*: The maltase enzyme converts maltose into glucose.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{Maltase} 2C_6H_{12}O_6(aq)$$
Maltose $\qquad\qquad\qquad\qquad$ Glucose
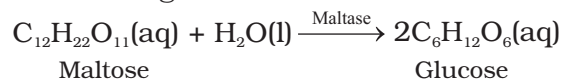
(v) *Decomposition of urea into ammonia and carbon dioxide*: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{Urease} 2NH_3(g) + CO_2(g)$$
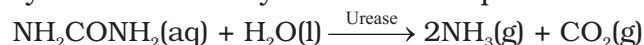
(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

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

Table 5.2 gives the summary of some important enzymatic reactions.

Table 5.2: Some Enzymatic Reactions

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

Characteristics of enzyme catalysis

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by 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 catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse 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. Human body temperature being 310 K is suited for enzyme-catalysed reactions.

(iv) *Highly active under optimum pH*: The rate of an enzyme-catalysed 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 are 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 completely 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 a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, -COOH, -SH, -OH, etc. These are actually the active

$$E + S \rightleftharpoons [E-S] \longrightarrow E + P$$

Active site

E + S → Enzyme (catalyst) | Substrate (reactants) | Enzyme-Substrate complex | Enzyme | Products
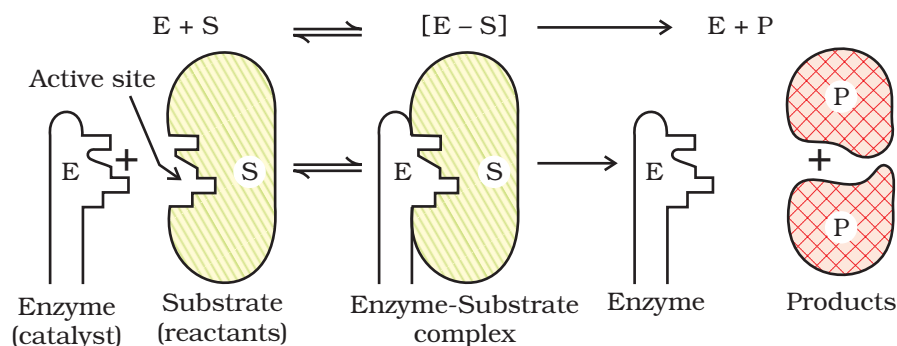
Fig. 5.4: Mechanism of enzyme catalysed reaction

centres 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. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

Step 1: Binding of enzyme to substrate to form an activated complex.
$$E + S \rightarrow ES^{\neq}$$

Step 2: Decomposition of the activated complex to form product.
$$ES^{\neq} \rightarrow E + P$$

5.2.5 Catalysts in Industry

Some of the important technical catalytic processes are listed in Table 5.3 to give an idea about the utility of catalysts in industries.

Table 5.3: Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573K.
3. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(l)$ oleum $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723K.

Intext Questions

5.4 In Haber's process, hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. The process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?

5.5 Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?

5.6 What is the role of desorption in the process of catalysis.

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5.3 Colloids

We have learnt in Unit 2 that solutions are homogeneous systems. We also know that sand in water when stirred gives a suspension, which slowly settles down with time. Between the two extremes of suspensions and solutions we come across a large group of systems called colloidal dispersions or simply colloids.

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

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm^2. If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60,000 cm^2 or 6 m^2. This enormous surface area leads to some special properties of colloids to be discussed later in this Unit.

5.4 Classification of Colloids

Colloids are classified on the basis of the following criteria:

(i) Physical state of dispersed phase and dispersion medium
(ii) Nature of interaction between dispersed phase and dispersion medium
(iii) Type of particles of the dispersed phase.

5.4.1 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. The examples of the various types of colloids along with their typical names are listed in Table 5.4.

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a

Table 5.4: Types of Colloidal Systems

Dispersed phase	Dispersion medium	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, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

liquid. Firefighting foams, used at emergency airplane landings are also colloidal systems. Most biological fluids are aqueous sols (solids dispersed in water). Within a typical cell, proteins and nucleic acids are colloidal-sized particles dispersed in an aqueous solution of ions and small molecules.

Out of the various types of colloids given in Table 5.4, the most common are **sols** (solids in liquids), **gels** (liquids in solids) and **emulsions** (liquids in liquids). However, in the present Unit, we shall take up discussion of the 'sols' and 'emulsions' only. Further, it may be mentioned that if the dispersion medium is water, the sol is called aquasol or hydrosol and if the dispersion medium is alcohol, it is called alcosol and so on.

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

Depending upon the nature of 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 liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called **reversible sols**. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.

(ii) *Lyophobic colloids*: The word 'lyophobic' means liquid-hating. 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 (as discussed later). 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. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called **irreversible sols**. Lyophobic sols need stabilising agents for their preservation.

5.4.3 Classification Based on Type of Particles of the Dispersed Phase, Multimolecular, Macromolecular and Associated Colloids

Depending upon the type of the particles of the dispersed phase, colloids are classified as: multimolecular, 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 size in the colloidal range (1–1000 nm). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

(ii) *Macromolecular colloids*: Macromolecules (Unit 15) in suitable solvents form solutions in which the size of the macromolecules

may be in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

(iii) *Associated colloids (Micelles)*: There are 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 temperature** (T_k) and above a particular concentration called **critical micelle concentration (CMC)**. On dilution, these colloids revert back 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

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as RCOO$^-$Na$^+$ (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 — 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).

The RCOO$^-$ ions are, therefore, 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
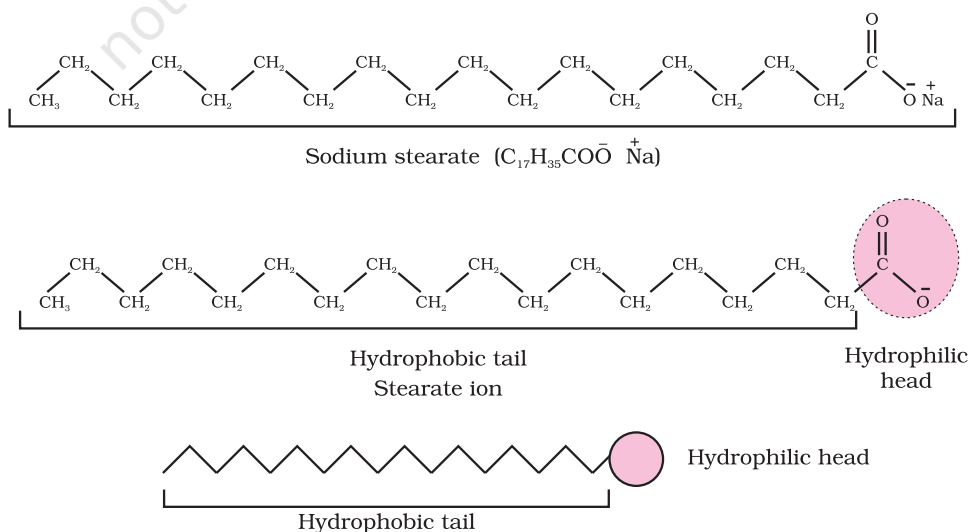

Sodium stearate ($C_{17}H_{35}$COO$^-$ Na$^+$)

Hydrophobic tail
Stearate ion

Hydrophilic head

Hydrophilic head

Hydrophobic tail

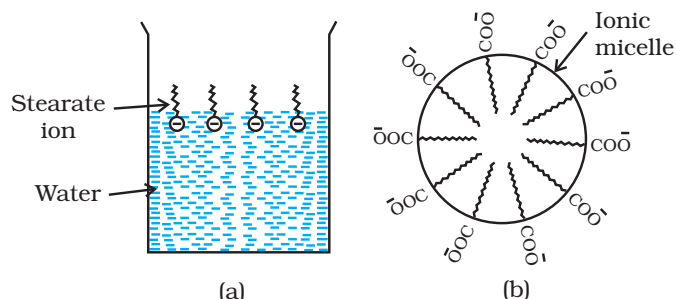*Fig. 5.5: Hydrophobic and hydrophilic parts of stearate ion*

Fig. 5.6: (a) Arrangement of stearate ions on the surface of water at low concentrations of soap
(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

shape with their hydrocarbon chains pointing towards the centre of the sphere with COO⁻ part remaining outward on the surface of the sphere. An aggregate thus formed is known as '**ionic micelle**'. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents, e.g., sodium laurylsulphate, $CH_3(CH_2)_{11}SO_4^- Na^+$, the polar group is $-SO_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

Cleansing action of soaps

It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon – like central core. The cleansing action of soap is due to the
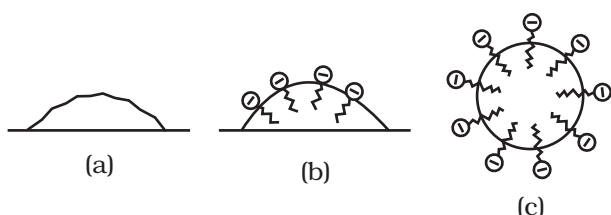

Fig. 5.7: (a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.7). 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 of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

5.4.4 Preparation of Colloids

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

(a) Chemical methods

Colloidal dispersions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.
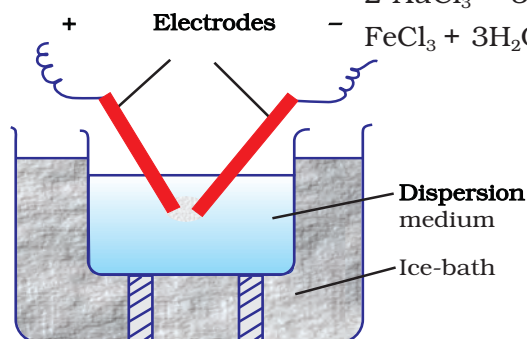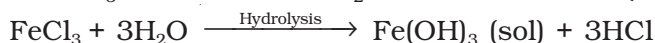
$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\ AuCl_3 + 3\ HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol) + 3HCl$$

(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, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 5.8). The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

Fig. 5.8: Bredig's Arc method

(c) Peptization

Peptization may be defined as the **process of converting a precipitate into colloidal sol** by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **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 charge on precipitates, which ultimately break up into smaller particles of the size of a colloid. You will learn about the phenomenon of development of charge on solid particles and their dispersion in Section 5.4.6 under the heading "Charge on collodial particles".

5.4.5 Purification of Colloidal Solutions

Colloidal solutions when prepared, generally contain 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 amount of impurities to a requisite minimum is known as purification of colloidal solution**. The purification of colloidal solution is carried out by the following mehods:
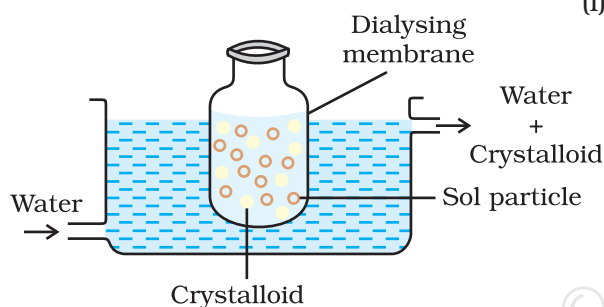
(i) *Dialysis*: **It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane**. Since particles (ions or smaller molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis. The apparatus used for this purpose is called **dialyser**. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing (Fig. 5.9). The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

Fig. 5.9: *Dialysis*

(ii) *Electro-dialysis*: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 5.10. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.
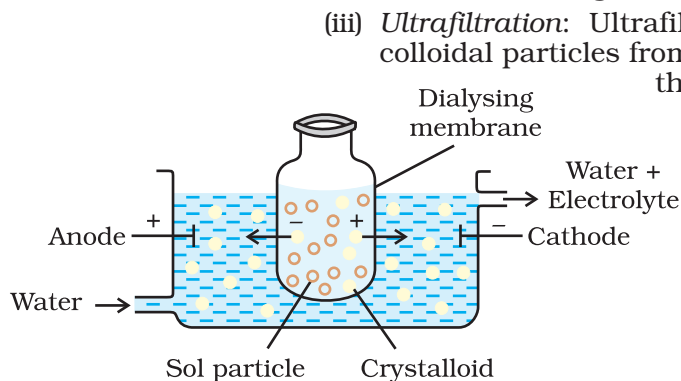
(iii) *Ultrafiltration*: Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with **collodion** solution to stop the flow of colloidal particles. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the

Fig. 5.10: *Electro-dialysis*

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 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 fresh dispersion medium (solvent) to get a pure colloidal solution.

5.4.6 Properties of Colloidal Solutions

Various properties exhibited by the colloidal solutions are described below:

(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 vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.
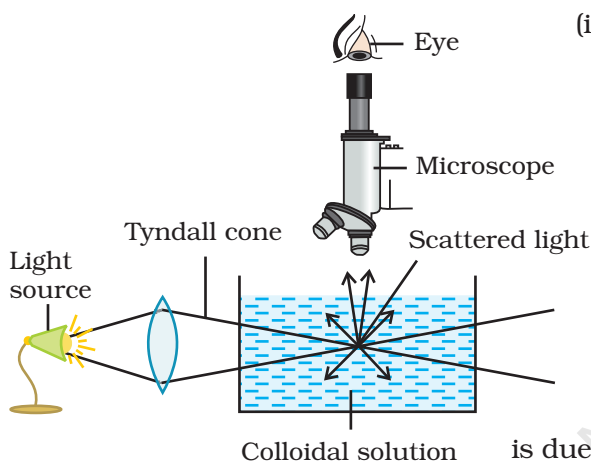

Fig. 5.11: Tyndall effect

(ii) *Tyndall effect*: If a homogeneous solution placed in dark is observed in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. Colloidal solutions viewed in the same way may also appear reasonably clear or translucent by the transmitted light but they show a mild to strong opalescence, when viewed at right angles to the passage of light, i.e., 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 **Tyndall effect**. The bright cone of the light is called **Tyndall cone** (Fig. 5.11). The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion.

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. 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.

Tyndall effect is used to distinguish between a colloidal and true solution. Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. 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 observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

(iii) *Colour*: The colour of 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 colour

of colloidal solution also changes with the manner in which 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. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.

(iv) *Brownian movement*: When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion was first observed by the British botanist, Robert Brown, and is known as Brownian movement (Fig. 5.12). This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion.
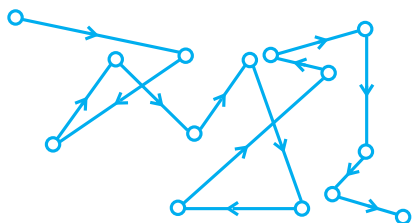

Fig. 5.12: Brownian movement

The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which 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. A list of some common sols with the nature of charge on their particles is given below:

Positively charged sols	Negatively charged sols
Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metals, e.g., copper, silver, gold sols.
Basic dye stuffs, e.g., methylene blue sol.	Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols.
Haemoglobin (blood)	Acid dye stuffs, e.g., eosin, congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

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 same charge prevent them from coalescing or aggregating when they come closer to one another.

The charge on the sol particles is due to one or more reasons, viz., due to electron capture by sol particles during electrodispersion of metals, due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer. Development of charge on sol particles by preferential adsorption of ions is described below.
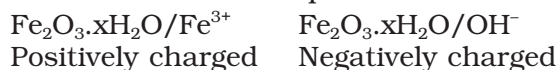
The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion

common to the colloidal particle usually takes place. This can be explained by taking the following examples:

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

$$AgI/I^- \qquad\qquad AgI/Ag^+$$
Negatively charged $\qquad$ Positively charged

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

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

Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.

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

The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. Fig. 5.13 depicts the formation of double layer. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers in the same manner as potential difference is developed in a capacitor. This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

If two particles of an insoluble material (precipitate) do not have double layers they can come close enough and attractive van der Waals forces pull them together. When particles possess double layer as shown in Fig. 5.13, the overall effect is that particles repel each other at large distances of separation. This repulsion prevents their close approach. They remain dispersed and colloid is stabilised.

The addition of more electrolytes to sol supresses the diffused double layer and reduces the zita potential. This decreases the electrostatic repulsion between particles to a large extent and colloid precipitates. That is why colloid is particularly sensitive to oppositely charged ions.

Fig. 5.13: Formation of double layer

(vi) *Electrophoresis*: The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When 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
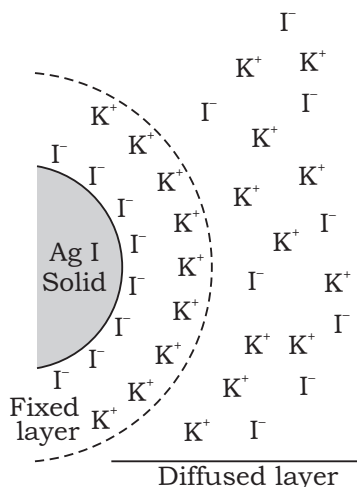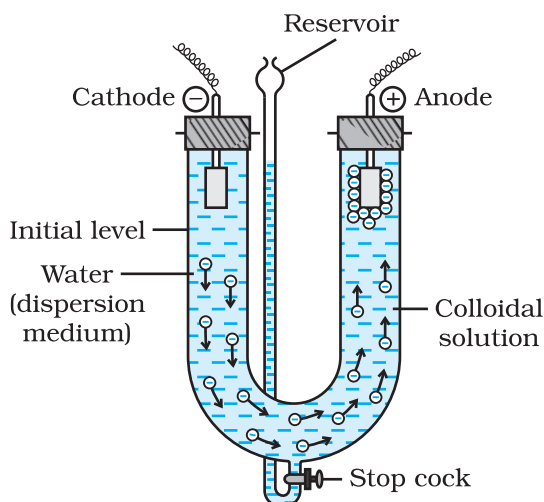
Fig. 5.14: Electrophoresis

particles move towards the anode. This can be demonstrated by the following experimental set-up (Fig. 5.14).

When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that 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, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

(iii) *By boiling*: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of 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*: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as 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: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

The minimum concentration of an electrolyte in millimoles per litre 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.

Coagulation of lyophilic sols

There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation 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 dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

Protection of colloids

Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

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 the latter from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.
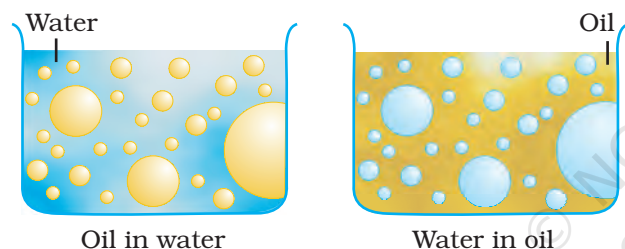
5.5 Emulsions

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. 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.
(i) Oil dispersed in water (O/W type) and
(ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsion are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream.

Water ⎯ Oil in water   Oil ⎯ Water in oil

Fig. 5.15: *Types of emulsions*

Emulsions of oil in water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called 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., and for W/O, 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 Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

5.6 Colloids Around Us

Most of the substances, we come across in our daily life, are colloids. The meals we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

Following are the interesting and noteworthy examples of colloids:

(i) *Blue colour of the sky*: Dust particles along with water suspended in 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 in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, 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 aeroplane.

(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 coagulation of blood forming a clot which stops further bleeding.

(v) *Soils*: Fertile soils are colloidal in nature 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. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

Applications of colloids

Colloids are widely used in the industry. Following are some examples:

(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 Cottrell precipitator (Fig.5.16).
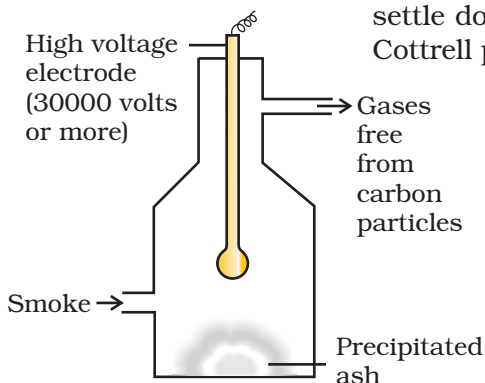

High voltage electrode (30000 volts or more)
Gases free from carbon particles
Smoke →
Precipitated ash

Fig. 5.16: 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 in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. 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 large surface area and are therefore easily assimilated.

(iv) *Tanning*: Animal hides are colloidal in nature. 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) *Cleansing action of soaps and detergents*: This has already been described in Section 5.4.3.

(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.

Intext Questions

5.7 What modification can you suggest in the Hardy Schulze law?

5.8 Why is it essential to wash the precipitate with water before estimating it quantitatively?

Summary

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a solid resulting into a higher concentration on the surface than in the bulk. The substance adsorbed is known as **adsorbate** and the substance on which adsorption takes place is called **adsorbent.** In physisorption, adsorbate is held to the adsorbent by weak van der Waals forces, and in chemisorption, adsorbate is held to the adsorbent by strong chemical bond. Almost all solids adsorb gases. The extent of adsorption of a gas on a solid depends upon nature of gas, nature of solid, surface area of the solid, pressure of gas and temperature of gas. The relationship between the extent of adsorption (x/m) and pressure of the gas at constant temperature is known as **adsorption isotherm**.

A **catalyst** is a substance which enhances the rate of a chemical reaction without itself getting used up in the reaction. The phenomenon using catalyst is known as **catalysis**. In homogeneous catalysis, the catalyst is in the same phase as are the reactants, and in heterogeneous catalysis the catalyst is in a different phase from that of the reactants.

Colloidal solutions are intermediate between true solutions and suspensions. The size of the colloidal particles range from 1 to 1000 nm. A colloidal system consists of two phases - the dispersed phase and the dispersion medium. Colloidal systems are classified in three ways depending upon (i) physical states of the dispersed phase and dispersion medium (ii) nature of interaction between the dispersed phase and dispersion medium and (iii) nature of particles of dispersed phase. The colloidal systems show interesting optical, mechanical and electrical properties. The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as **coagulation. Emulsions** are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of: (i) **oil in water type** and (ii) **water in oil type.** The process of making emulsion is known as **emulsification.** To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers. Colloids find several applications in industry as well as in daily life.

Exercises

5.1 Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.

5.2 What is the difference between physisorption and chemisorption?

5.3 Give reason why a finely divided substance is more effective as an adsorbent.

5.4 What are the factors which influence the adsorption of a gas on a solid?

5.5 What is an adsorption isotherm? Describe Freundlich adsorption isotherm.

5.6 What do you understand by activation of adsorbent? How is it achieved?

5.7 What role does adsorption play in heterogeneous catalysis?

5.8 Why is adsorption always exothermic ?

5.9 How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

5.10 Discuss the effect of pressure and temperature on the adsorption of gases on solids.

5.11 What are lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated ?

5.12 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?

5.13 What are enzymes ? Write in brief the mechanism of enzyme catalysis.

5.14 How are colloids classified on the basis of
(i) physical states of components
(ii) nature of dispersed phase and
(iii) interaction between dispersed phase and dispersion medium?

5.15 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?

5.16 What are emulsions? What are their different types? Give example of each type.

5.17 How do emulsifires stabilise emulsion? Name two emulsifiers.

5.18 Action of soap is due to emulsification and micelle formation. Comment.

5.19 Give four examples of heterogeneous catalysis.

5.20 What do you mean by activity and selectivity of catalysts?

5.21 Describe some features of catalysis by zeolites.

5.22 What is shape selective catalysis?

5.23 Explain the following terms:
(i) Electrophoresis (ii) Coagulation (iii) Dialysis (iv) Tyndall effect.

5.24 Give four uses of emulsions.

5.25 What are micelles? Give an example of a micellers system.

5.26 Explain the terms with suitable examples:
(i) Alcosol (ii) Aerosol (iii) Hydrosol.

5.27 Comment on the statement that "colloid is not a substance but a state of substance".