

5

CHAPTER



SURFACE CHEMISTRY

- * Adsorption
- * Colloids
- * Catalysis
- * Emulsions

ADSORPTION

The surface chemistry deals with phenomena that occur at the surfaces or interfaces. The surface or interface is represented by separating the bulk phase by a hyphen or a slash. Important phenomena like electrode processes, dissolution, crystallisation and heterogeneous catalysis occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

4.1.1

Adsorption and absorption


Accumulation of molecular species at the surface of a solid is called adsorption


The surface of a solid and liquid is always in a state of strain or tension due to the presence of unbalanced forces on the surface. To satisfy these unbalanced forces, molecules of other substances accumulate on the surface. The phenomenon of accumulation of molecular species of a substance at the surface of solid or liquid is called adsorption. The substance whose molecular species accumulated at the surface is called adsorbate and the substance on whose surface accumulation occurs is called adsorbent. The adsorbent may be a solid or a liquid and the adsorbate may be a gas or liquid or solute in solutions.

If a gas like O_2 , NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, the pressure of the gas decreases due to the accumulation of gas molecules at the surface of the charcoal. In this case gas is adsorbate and charcoal is adsorbent.

If animal charcoal is added to a solution of organic dye like methylene blue and stirred well, solution becomes colourless due to the adsorption of organic dye on the animal charcoal.

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

Adsorption is essentially a surface phenomenon. This process will be more effective if the surface of the solid adsorbent is clean and free from the surface impurities. The process of removing impurities from the surface of the adsorbent and making the surface clean is called activation of the adsorbent. Charcoal is activated by heating it at 573K–1273K in vacuum or in the presence of an inert gas.

Adsorption is due to unbalanced or residual attractive forces on the surface. During adsorption, there is always a decrease in residual force of the surface which appears as heat. Therefore adsorption is an exothermic process. When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. This causes the decrease in entropy of gas after adsorption. So entropy of adsorption (ΔS) is always negative. For a process to be spontaneous, ΔG must be negative at constant temperature and pressure. Thus, in an adsorption process which is spontaneous, a


Adsorption is due to residual attractive forces on the surface


Absorption is bulk phenomenon

combination of ΔH and $-T\Delta S$ makes ΔG negative. As the adsorption proceeds, ΔH becomes equal to $T\Delta S$ and at this state equilibrium is attained.

Absorption is a bulk phenomenon. 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. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapour is absorbed by anhydrous calcium chloride, but it is adsorbed by silica gel as shown in Fig 5.1.

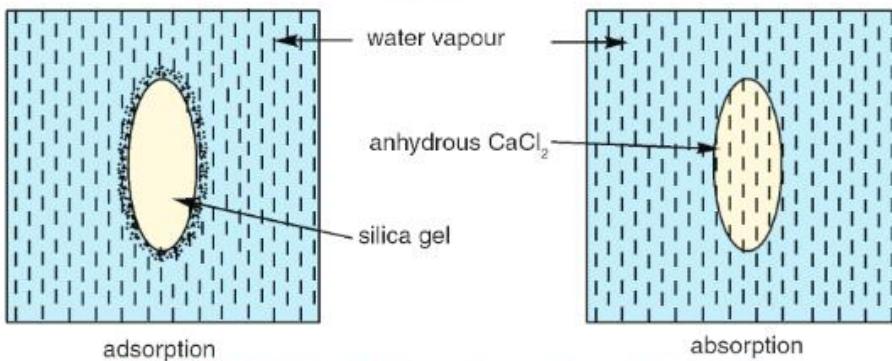


Fig 5.1 Distinction between adsorption and absorption

Sometimes both adsorption and absorption can take place simultaneously. It is called sorption. Sorption of a gas on metal is called occlusion. When hydrogen gas kept in contact with finely divided palladium metal, hydrogen gas is occluded on palladium. Reverse process of sorption is called desorption.

5.1.2

Types of adsorption

Adsorption of gases on solids are mainly of two types, based on the forces of attraction between adsorbate molecules and the surface of adsorbent. If the van der Waals forces are responsible for adsorption of adsorbate molecules on the surface of the adsorbent, then the adsorption is called physical adsorption or physisorption. Adsorption of hydrogen or oxygen or carbon dioxide on charcoal is an example of physisorption.

If a chemical bond is responsible for adsorption of adsorbate molecules on the surface of the adsorbent then the process is called chemical adsorption or chemisorption. The chemical bond may be ionic or covalent in nature. Adsorption of hydrogen on nickel is an example of chemisorption.

Hydrogen molecules are first adsorbed on nickel by van der Waals forces. The adsorbed hydrogen molecules dissociate to form hydrogen atoms. These atoms are held on the surface by chemisorption as shown in Fig 5.2.

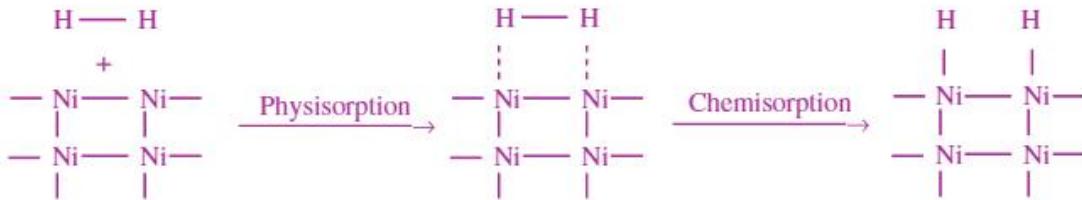


Fig 5.2 Chemisorption of hydrogen on nickel


**Chemisorption
needs activation
energy and is
called activated
adsorption**



Since the chemisorption needs activation energy, it is also referred as activated adsorption. Both physisorption and chemisorption are exothermic. The amount of heat evolved when one mole of an adsorbate is completely adsorbed on the surface of an adsorbent is called enthalpy of adsorption (ΔH_{ad}).

Physical adsorption lacks specificity. An adsorbent does not show any preference for a particular gas. The amount of gas adsorbed by a solid depends on the nature of gas. Generally gases with higher critical temperatures are readily adsorbed. Physisorption of a gas on a solid is generally reversible. It occurs rapidly at high pressure and low temperature. The extent of physisorption will be high, if the adsorbent has higher surface area. The enthalpy of activation as well as the enthalpy of physical adsorption are low.

Chemical adsorption is highly specific as chemisorption involves the formation of a chemical bond. It is usually irreversible. On account of high enthalpy of activation, chemical adsorption is slow. Usually high pressure and high temperature are favourable for chemical adsorption, but the effect of pressure is complex on chemisorption. The extent of chemisorption is increased with increase in the surface area of adsorbent. The extent of chemisorption is increased with increase in the surface area of adsorbent. Then enthalpy of chemisorption is high.

Enthalpy of adsorption is less for physisorption due to weak van der Waals forces but it is high for chemisorption due to strong chemical bond. Enthalpy of adsorption value is about $20\text{--}40 \text{ kJ mol}^{-1}$ for physisorption but it is about $80\text{--}300 \text{ kJ mol}^{-1}$ for chemisorption. Some more differences between physisorption and chemisorption are given in Table 5.1.

Table 5.1 Differences between physisorption and chemisorption

S.No.	Property	Physisorption	Chemisorption
1	Nature of adsorption	Adsorption is weak	Adsorption is strong
2	Ease of desorption	Easy since weak van der Waals forces are involved	Not easy since chemical forces are involved
3	Reversibility of process	Reversible and occurs rapidly	Irreversible and occurs slowly
4	Energy of activation	Insignificant and very low	Significant and relatively high
5	Specificity of adsorption	Not specific since it takes place on the surface of any solid	Highly specific since it takes place on specified surfaces only
6	Effect of temperature on adsorption	Extent of adsorption decreases with increase in temperature	Extent of adsorption increases with increase in temperature
7	Effect of pressure on adsorption	Increases with increase in pressure of adsorbate gas and finally attains a limiting value	Pressure of adsorbate gas has a negligible effect
8	Number of adsorbate layers formed	Usually multilayered	Only unilayered
9	Dependence on the nature of the adsorbate and the adsorbent	Depends on the nature of adsorbate gas only. Easily liquefiable gases are readily adsorbed	Depends on nature of adsorbate as well as adsorbent. No correlation can be given
10	Surface area of adsorbent	Increases with increase in surface area of adsorbent	Increases with increase in surface area of adsorbent

5.1.3**Factors effecting adsorption**

Excess of adsorption is more for easily liquifiable gases

Excess of physical adsorption increases with pressure

Amount of the gas adsorbed per unit mass of the adsorbent is called extent of adsorption. Usually it is expressed as x/m , where x is the mass of gas adsorbed and m is the mass of adsorbent. Extent of adsorption of gases on solids depends on the following factors.

a) **Surface area of the adsorbent :** Adsorption is a surface phenomenon. The extent of adsorption is directly proportional to the surface area of adsorbent. Finely divided metals and porous solids like charcoal, silica gel, etc., possess more surface area when compared with solid lumps. Thus they are good adsorbents.

b) **Nature of the gas :** Greater the critical temperature (T_c) of the gas, stronger is the van der Waals force of attraction between gas molecules. Thus gases with high critical temperature are easily liquified and are adsorbed to a greater extent. Gases like SO_2 , HCl , NH_3 , CO_2 , etc., have high critical temperature. They have high extent of adsorption when compared with permanent gases like H_2 , N_2 , O_2 , etc. For example, one gram of an activated charcoal adsorbs 400ml of SO_2 ($T_c = 430\text{K}$), 20ml of CH_4 ($T_c = 356\text{K}$) but 5ml of H_2 ($T_c = 253\text{K}$) only. Extent of adsorption depends on critical temperature in physisorption, but not in chemisorption.

c) **Effect of the pressure of gas :** Physisorption of a gas on solid adsorbent is a reversible process. After some time rate of adsorption and rate of desorption becomes equal. This is called equilibrium state. The pressure at this state is called equilibrium pressure (P). In the case of physisorption, the gas forms a monolayer at low pressure and multiple layers at high pressures. Hence in physisorption, extent of adsorption increases with increasing the equilibrium pressure.

It is observed that at low temperatures, the adsorption of a gas increases rapidly as the pressure is increased in very small values. The variation of adsorption of N_2 gas by one gram of charcoal at different temperatures is shown in Fig 5.3.

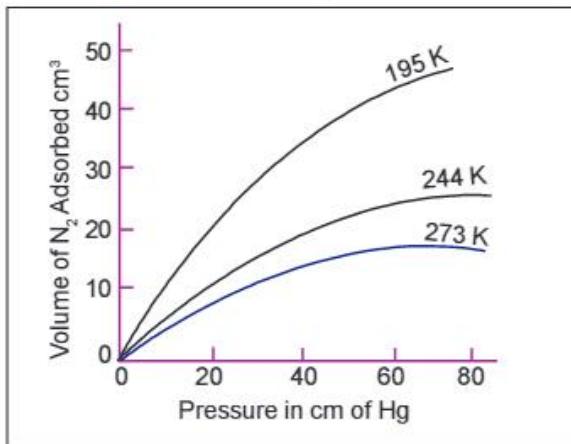


Fig 5.3 Variation of adsorption of nitrogen with pressure

The relation between the extent of adsorption (x/m) of the gas and the equilibrium pressure at constant temperature is called adsorption isotherm. This may be expressed in the form of equation or graphical curve. For physisorption, adsorption isotherm is given in Fig 5.4. There are two familiar adsorption isotherms: Freundlich isotherm and Langmuir isotherm.

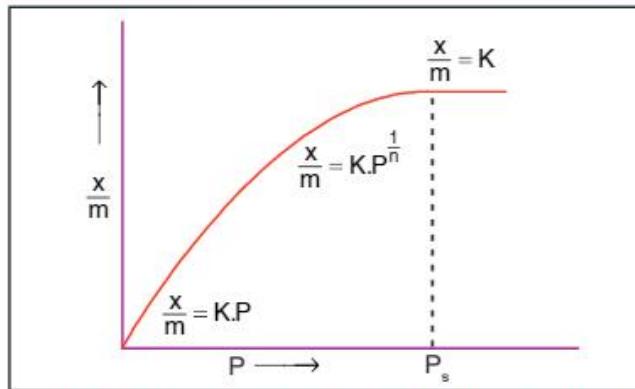


Fig 5.4 Adsorption isotherm for physisorption

Extent of adsorption (x/m) with pressure (P) is given in Freundlich isotherm as $(x/m) = K.P^{n^{-1}}$



Freundlich adsorption isotherm : Three observations can be made easily from isotherm of Fig 5.4. At low pressure, the graph is almost straight line. It indicates that x/m is directly proportional to the equilibrium pressure (P).

$$\frac{x}{m} \propto P \quad \text{or} \quad \frac{x}{m} = K.P, \text{ where } K \text{ is constant.}$$

At high pressure, the curve becomes straight line parallel to pressure axis. It indicates that at high pressure, x/m is independent of equilibrium pressure. The equilibrium pressure at which x/m remains constant is called saturation pressure (P_s).

$$\frac{x}{m} \propto P^0 \quad \text{or} \quad \frac{x}{m} = K.P^0 = \text{constant}$$

At intermediate range of pressures, x/m is directly proportional to the fractional power of the pressure. This relation is called Freundlich adsorption isotherm.

$$\frac{x}{m} \propto P^{\frac{1}{n}} \quad \text{or} \quad \frac{x}{m} = K.P^{\frac{1}{n}}$$

Here, K and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. $1/n$ is a fractional and its probable range is 0.1 to 0.5.

Logarithmic form of Freundlich adsorption isotherm is $\log(x/m) = (1/n) \log P + \log K$. The validity of Freundlich isotherm can be verified by plotting $\log(x/m)$ on Y-axis and $\log P$ on X-axis. If it comes to be a straight line, the Freundlich isotherm is valid. Freundlich isotherm is valid over a certain range of pressure only and it fails at high pressures. The slope of the straight line (Fig 5.5) gives the value of $1/n$, the Y-intercept gives the value of $\log K$.

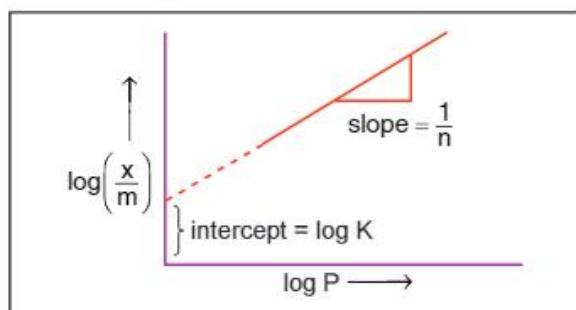


Fig 5.5 Freundlich adsorption isotherm

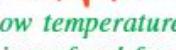

Quantitative theory of adsorption was given by Langmuir



Langmuir equation

$$\frac{x}{m} = \frac{ap}{1+bp}$$




Low temperature is preferred for physisorption and high temperature for chemisorption



Adsorption isobars are used to distinguish between physisorption and chemisorption


Langmuir adsorption isotherm: The first quantitative theory of adsorption was given by Langmuir. The main assumptions of the theory are given below.

a) The surface of solid adsorbent is homogeneous and has a fixed number of adsorption sites.

b) Each adsorption site can adsorb one gas molecule only. This means adsorption is confined to a monomolecular layer.

c) Adsorption is considered as an equilibrium process comprising of evaporation and condensation occurring simultaneously at a given temperature.

d) Rate of evaporation is directly proportional to the fraction of area of the surface covered by the adsorbed gas. If θ is the fraction of area covered,

$$\text{Rate of evaporation} \propto \theta \text{ (or)}$$

$$\text{Rate of evaporation} = K_d \cdot \theta, \text{ where } K_d \text{ is a constant.}$$

Rate of condensation is directly proportional to the product of the pressure of the gas (P) and the fraction of area uncovered, $(1 - \theta)$ by adsorbed gas.

$$\text{Rate of condensation} \propto P(1 - \theta) \text{ (or) rate of condensation} = K_a \cdot P(1 - \theta)$$

e) At equilibrium, rate of evaporation and condensation are equal. $\frac{x}{m} = \frac{ap}{1+bp}$

This is called Langmuir adsorption isotherm. The constants, a and b are temperature dependent and their values can be calculated from experimental data.

d) Effect of temperature : Generally physisorption takes place at low temperatures, while chemisorption takes place at high temperatures. At 463K, N₂ gas undergoes physisorption on iron metal but at 723K, iron nitride is formed due to chemisorption. As the temperature rises, physisorption may change into chemisorption or desorption may take place. Graphs showing the variation of extent of adsorption with temperature at constant pressure are called adsorption isobars (Fig 5.6) are useful to distinguish between adsorption isobars for physisorption and chemisorption.

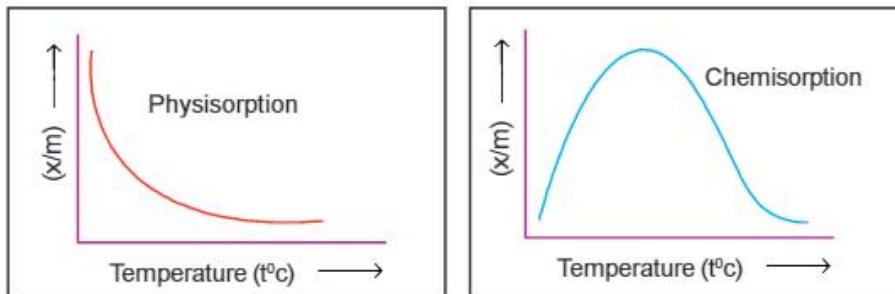


Fig 5.6 Adsorption isobars

The process of adsorption is exothermic and its reverse process desorption is endothermic. As per Le-Chatelier's principle, desorption is favourable at high temperature. Thus with an increase in the temperature, extent of adsorption decreases for physisorption. In case of chemisorption, extent of adsorption first increases, it reaches a maximum value and then decreases as the temperature is further increased. This behaviour is expected because like all chemical reactions, some activation energy is required for chemisorption.

5.1.4**Adsorption from solutions**

Porous and finely divided solids can adsorb solute from solutions also. For example, activated charcoal is used to remove coloured impurities from brown coloured sugar cane juice in the cane sugar industry. Freshly precipitated metal hydroxides are good adsorbents for dyestuffs in solution. For example, the precipitate of $Mg(OH)_2$ attains blue colour when it is precipitated in the presence of magneson reagent. The colour is due to adsorption of magneson.

When an aqueous solution of acetic acid is shaken with charcoal, the former is adsorbed on the latter. As a result the concentration of acetic acid in solution decreases and on the surface of charcoal increases. This is called positive adsorption. When a dilute solution of KCl is shaken with wood charcoal, the solvent from the solution is adsorbed by the adsorbent. As a result the concentration of the solute in the solution is greater than the initial concentration. This is called negative adsorption.

Adsorption of solute from the solutions follow the same principles as those laid down for the adsorption of gases by solids. The extent of adsorption is directly proportional to the surface area of the adsorbent.

The extent of adsorption is inversely proportional to the temperature of the solution. The extent of adsorption depends on the nature of the adsorbent and the adsorbate. The extent of adsorption depends on the concentration (C) of the solute in the solution.

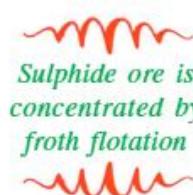
Freundlich adsorption isotherm for adsorption of solute from solution is $\frac{x}{m} = K.C^{1/n}$, where C is the equilibrium concentration of solute in the solution.

5.1.5**Applications**

Some of the important applications of adsorption are given below.

1. Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases like chlorine, carbon monoxide, etc.,
2. Silica and alumina gels are used as adsorbents for removing moisture and controlling humidity.
3. Many substances like vegetable oils, sugar cane juice, etc., are decolourised by removing the colouring matter with the help of adsorbents like activated charcoal, fresh metal hydroxides, fuller's earth, etc.
4. Activated charcoal is used to produce very high vacuum in a vessel evacuated by a vacuum pump.
5. Separation of noble gases in Dewar's method is based on adsorption phenomenon.
6. A number of drugs are used to kill germs by getting adsorbed on them.
7. Sulphide ore is concentrated by froth flotation process. In this process ore particles adsorb on the air bubbles.
8. Surfaces of certain precipitates such as silver halides have property of adsorbing some dyes like eosin, fluorescein, etc. As a result they produce a characteristic colour at the end point. These are used as adsorption indicators.
9. Chromatographic analysis is also based on adsorption phenomenon.
10. In heterogeneous catalysis adsorption of gaseous reactants on the solid surface of the catalysts increases the rate of reaction.

Extent of adsorption from solutions increases with increase in concentration



Sulphide ore is concentrated by froth flotation





P.5.1 Why does physisorption decrease with increase in temperature?



Physisorption is an exothermic process therefore it is favoured at low temperature with increase in temperature desorption takes place.



P.5.2 Critical temperature of SO_2 , N_2 , NH_3 and CH_4 are 430K, 126K, 406K and 356K. Arrange in the descending order of volume of these gases adsorbed per gram of charcoal.

Solution Extent of adsorption is directly proportional to critical temperature.

Order of extent of adsorption of the given gases is: $\text{SO}_2 > \text{NH}_3 > \text{CH}_4 > \text{N}_2$.



P.5.3 Per two gram of charcoal, a gas is adsorbed by 0.1g and 0.2g at 10 torr and 80 torr pressure respectively. Calculate the n value in Freundlich adsorption isotherm.

Solution
$$\frac{x}{m} = K \cdot P^{1/n} \quad (\text{or}) \quad \frac{x_1}{x_2} = \left(\frac{P_1}{P_2} \right)^{1/n} \Rightarrow \frac{0.1}{0.2} = \left(\frac{10}{80} \right)^{1/n} \quad (\text{or}) \quad \left(\frac{1}{2} \right)^1 = \left(\frac{1}{2} \right)^{3/n}$$

Therefore, the value of n is 3.



P.5.4 The coagulation of 100ml gold sol is completely prevented by adding 0.25g of starch to it before adding 10ml of 10% NaCl solution. Calculate the gold number of starch.

Solution 10ml of 10% NaCl solution is added to 100ml of gold sol. Thus, 1ml of 10% NaCl has been added to each 10ml of gold sol.

Weight of starch required for 100ml gold sol = 0.25g = 250mg.

Weight of starch and in 10 ml sol = 25 mg.

Gold number of starch = 25.

EXERCISE - 5.1.1

- Explain the terms “adsorption” and “absorption” with at least two examples. Give the differences between physical adsorption and chemical adsorption.
- Give an account of adsorption of gases by metals with examples.
- Write the characteristics of physical adsorption.
- Write the characteristics of chemisorption.
- Give an account of Freundlich adsorption isotherm.
- Why does physisorption decrease with the increase of temperature?
- Why are powdered substances more effective absorbents than their crystalline forms?
- Explain adsorption of solute from solutions with examples.

CATALYSIS

Berzelius introduced the term catalysis (Cata-wholly, lysis-to losen). Substances, which alter the rate of a chemical reaction and themselves remain chemically unchanged after the reaction, are known as catalysts. The phenomenon is known as catalysis. Positive catalyst increases the rate of reaction but negative catalyst decreases the rate of reaction. Reaction between hydrogen and oxygen to form water is very slow and it takes many years for the formation of considerable amount of water. But in the presence of platinum, water will be formed immediately. Platinum is positive catalyst for the formation of water.

Rate of decomposition of hydrogen peroxide is decreased in the presence of glycerol. So glycerol is negative catalyst for decomposition of hydrogen peroxide. Positive catalyst is commonly called catalyst and negative catalyst as inhibitor.

5.2.1

Characteristics of catalyst

A catalyst does not initiate a reaction. The pressure of a catalyst will only increase the rate of reaction.

A catalyst remains chemically unaffected at the end of the chemical reaction. Even though it enters at one step in the reaction mechanism, it is released back in another step of the reaction mechanism.

A catalyst is not consumed in the reaction. So a little amount of catalyst is generally sufficient to speed up a chemical reaction.

A catalyst does not effect the position of equilibrium in a reversible reaction. But it helps to attain the equilibrium quickly.

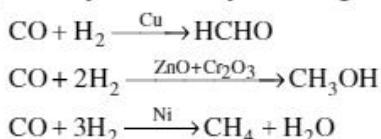
A catalyst generally functions under optimum conditions of temperature, pressure and pH.

Finely divided substances function as more effective catalysts than the coarsely divided substances. For example finely divided nickel functions as a good catalyst in hydrogenation of oils into fats.

A substance which increases the activity of catalyst but it self cannot act as catalyst is called promoter. For example, in Haber's process of manufacture of ammonia, molybdenum is the promoter for iron catalyst. In the manufacture of methanol from water gas, Cr_2O_3 is the promoter for ZnO catalyst.

A substance which decreases the activity of catalyst is called catalytic poison. For example, As_2O_3 acts as a catalytic poison for platinum catalyst in the preparation of sulphur trioxide from sulphur dioxide. H_2S functions as poison for iron catalyst, in the Haber's process and CO for platinum in the oxidation of hydrogen.

The action of catalysts in many instances is selective. For every reaction there may be a specific catalyst. Change of catalyst may give changed products.



Change of temperature may increase or decrease the catalytic activity of a substance. For example, the activity of metals and some metal oxides as catalysts increases with increase of temperature. But the activity of biological catalysts, enzymes, decreases with increasing the temperature.

5.2.2

Types of catalysis

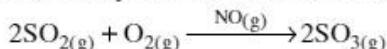
Reactants and catalyst are in the same phase for homogeneous catalysis.

Catalysis reactions are broadly divided into two types, homogeneous and heterogeneous catalysis reactions.

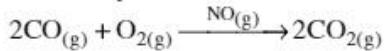
Homogeneous catalysis

The catalytic process in which the reactants and the catalyst are in same phase is known as homogeneous catalysis. Some examples are given below.

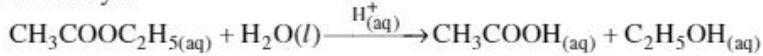
a) Oxidation of sulphur dioxide into sulphur trioxide in the presence of nitric oxide as catalyst in the lead chamber process.



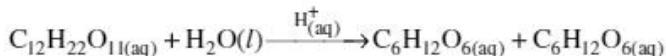
- b) Oxidation of carbon monoxide into carbon dioxide in the presence of nitric oxide as catalyst.



- c) Hydrolysis of ester into carboxylic acid and alcohol in the presence of a mineral acid as catalyst.



- d) Hydrolysis of sucrose into glucose and fructose in the presence of a mineral acid as catalyst.

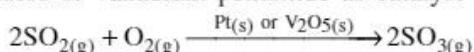


Here a) and b) are gas phase reactions and c) and d) are liquid phase reactions.

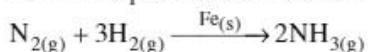
Heterogeneous catalysis

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

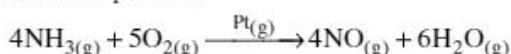
- a) Oxidation of sulphur dioxide to sulphur trioxide in the presence of platinised asbestos or vanadium pentoxide as catalyst in contact process.



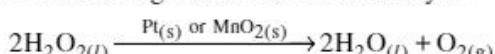
- b) In Habers process iron is used as catalyst in the synthesis of ammonia.



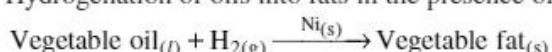
- c) Oxidation of ammonia into nitric oxide in the presence of platinum as catalyst in Ostwald's process.



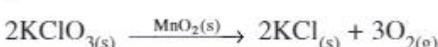
- d) Decomposition of hydrogen peroxide into water and oxygen in the presence of platinum or manganese dioxide as catalyst.



- e) Hydrogenation of oils into fats in the presence of finely divided nickel as catalyst.



- f) Decomposition of potassium chlorate in the presence of manganese dioxide as catalyst.



5.2.3

Theories of catalysis

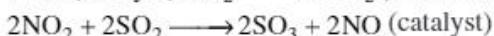
Homogeneous catalysis can be explained by intermediate compound theory

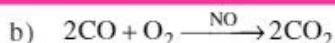
The action of catalyst is explained by two different theories. They are intermediate compound formation theory and adsorption theory.

Intermediate compound formation theory: Homogeneous catalysis can be explained generally by intermediate compound formation theory. Initially catalyst combines with one or more of the reactants to form an intermediate compound. The intermediate compound decomposes alone or in chemical reaction with other reactants to give the products and the catalyst. Some examples are given below.

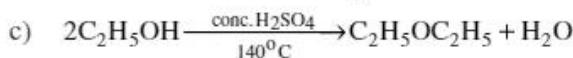
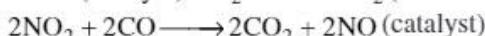
- a) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{NO}} 2\text{SO}_3$

The mechanism is : $2\text{NO} \text{ (catalyst)} + \text{O}_2 \longrightarrow 2\text{NO}_2 \text{ (intermediate)}$

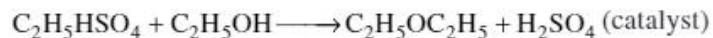
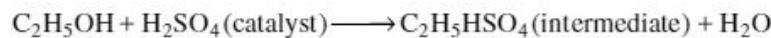




The mechanism is : $2\text{NO} (\text{catalyst}) + \text{O}_2 \longrightarrow 2\text{NO}_2 (\text{intermediate})$



The mechanism is :



Heterogeneous catalysis can be explained by adsorption theory

Adsorption theory : This theory explains the mechanism of heterogeneous catalysis. 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 mechanism involves five steps : Diffusion of reactants on to the surface of the catalyst. Adsorption of reactant molecules on the surface of the catalyst. Occurrence of chemical reaction on the surface of catalyst through formation of an intermediate. Desorption of reaction products from the catalyst surface and thereby making the surface available again for more reaction to occur. Diffusion of reaction products away from the catalyst's surface.

In a broad way, the process of hydrogenation of ethylene to ethane on nickel catalyst is represented schematically in Fig 5.7.

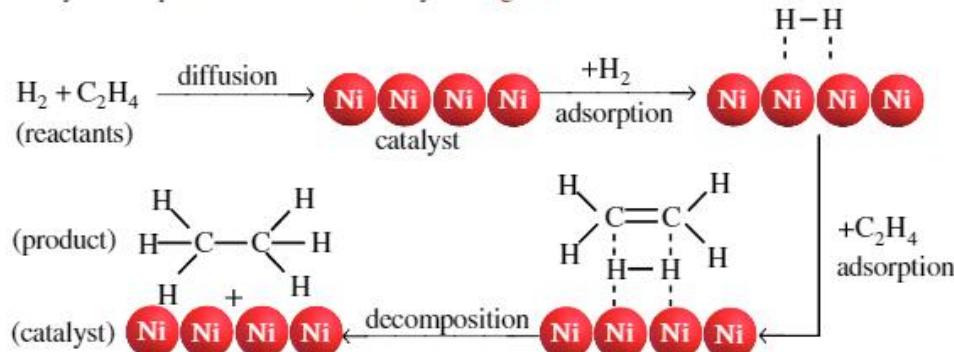
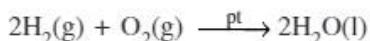


Fig 5.7 Mechanism of hydrogenation of ethylene in the presence of nickel catalyst

Activity and selectivity are important features of solid catalysis

Important features of solid catalysis are : (a) activity and (b) selectivity.

a) **Activity :** The activity of a catalyst depends up on 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



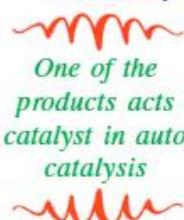
b) **Selectivity :** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with H_2 and CO , and using different catalysts, we get different products.

- i) $\text{CO(g)} + 3\text{H}_2\text{(g)} \xrightarrow{\text{Ni}} \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$
- ii) $\text{CO(g)} + 2\text{H}_2\text{(g)} \xrightarrow{\text{Cu/ZnO-Ce}_2\text{O}_3} \text{CH}_3\text{OH(g)}$
- iii) $\text{CO(g)} + \text{H}_2\text{(g)} \xrightarrow{\text{Cu}} \text{HCHO(g)}$

Thus, it can be inferred that the action of a catalyst is highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means that a substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

5.2.4

Autocatalysis

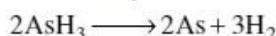


In some reactions, one of the products formed acts as catalyst and catalyses the reaction further. Such phenomenon is called autocatalysis and the catalyst is called auto catalyst. Autocatalysis reactions take place slowly initially but later they become fast due to the formation of the product which acts as catalyst. Some examples are given below.

- a) In the oxidation of oxalic acid by potassium permanganate in acidic medium, manganous ion (Mn^{2+}) formed functions as an autocatalyst.



- b) In the decomposition of arsine to arsenic and hydrogen, arsenic formed functions as an autocatalyst.



5.2.5

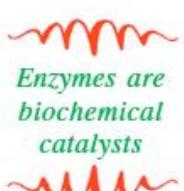
Shape-selective catalysis

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 honey comb-like structures.

Aluminosilicates are microporous with three dimensional network in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si frame work. Zeolites are 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.

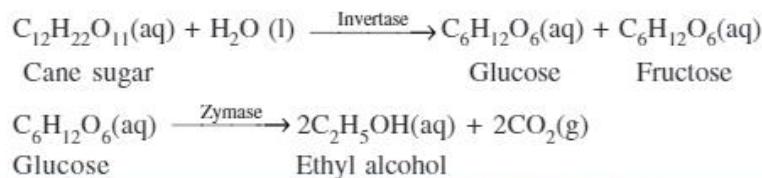
5.2.6

Enzyme catalysis

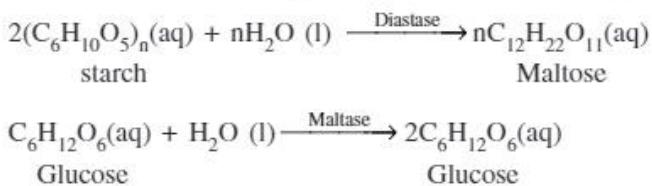


Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as biochemical catalysts and the phenomenon is known as biochemical catalysis. Some examples of enzyme catalysis reactions are given below and summarised in Table 5.2.

- a) In the manufacture of ethyl alcohol from molasses, invertase enzyme converts sucrose into glucose and fructose, zymase enzyme converts glucose into ethyl alcohol.



- b) In the manufacture of ethyl alcohol from starch, diastase enzyme converts starch into maltose and maltase enzyme converts maltose into glucose.




Urease enzyme catalyses the decomposition of urea


- c) The enzyme urease catalyses the decomposition of urea into ammonia and carbon dioxide.



- d) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.
e) Lacto bacilli enzyme present in curd converts milk into curd.
f) Amylase enzyme present in saliva of mouth converts starch into glucose.
g) Nitrogenase enzyme is found in the bacteria of the root nodules of leguminous plants such as peas and beans. It catalyse the conversion of N_2 from atmosphere to ammonia in the soil, called nitrogen fixation.

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


Enzyme is a highly specific and efficient catalyst


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

- a) Enzymes are highly specific in nature. One catalyst cannot catalyse more than one reaction.
b) Enzymes are highly efficient. One molecule of an enzyme may transform one million molecules of the reactants per minute.
c) Enzymes are highly active under optimum temperature and pH only. On either side of the optimum temperature, the enzyme activity decreases. For enzymatic activity optimum temperature range is 298–310K and optimum pH range is 5–7. Human body temperature being 310K is suited for enzyme catalysed reactions.
d) The enzymatic activity is increased in the presence of certain non-protein substances known as coenzymes.

e) 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 ions are catalytically very active.

f) 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 $-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$, $-\text{OH}$, etc. These are actually the active centres on the surface of enzyme particles. The molecules of the substrate (reactant), which have complementary shape, fit into these cavities just like a key fits into lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products. Mechanism of enzyme catalysis is represented schematically in Fig 5.8.

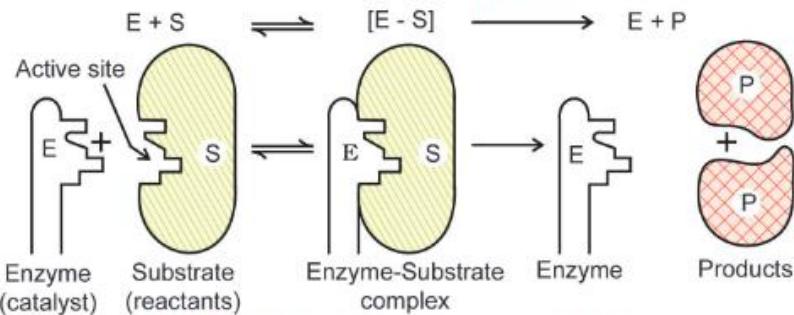


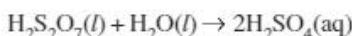
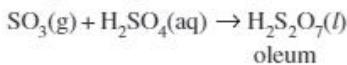
Fig 5.8 Mechanism of enzyme catalysis

In enzyme catalysed reactions first enzyme binds with substrate to form enzyme substrate activated complex. It decomposes to give enzyme and product.



P.5.5 Write the catalyst and equations of ostwald's process.

Solution Platinised asbestos is used as catalyst in ostwald's process at 573 K. The chemical equation in the process are : $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$



P.5.6 What role does adsorption play in heterogenous catalysis.

Solution In heterogenous catalysis, the molecules of the reactants are adsorbed on the surface of catalyst. The increased concentration of the reactants on the surface influences the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is taken by the reactant molecule to increase their chemical activity.



P.5.7 Why ester hydrolysis is slow in the beginning and becomes faster after some time ?

Solution In the hydrolysis of ester, carboxylic acid formed in the reaction acts as autocatalyst. Thus the reaction is slow in the beginning and becomes faster after some time due to the formation of acid which acts as catalyst.



P.5.8 Why is it necessary to remove CO when ammonia is obtained by Haber's process?

Solution CO forms iron pentacarbonyl complex with iron. CO is consumed in the reaction and acts as catalytic poison for iron. Thus it is necessary to remove CO from the reaction mixture.

EXERCISE - 5.1.2

- What is catalysis? How is catalysis classified? Give two examples for each.
- What are the characteristics of a catalyst?
- Explain homogeneous and heterogeneous catalysis. Give two examples for each. Give their mechanisms.
- Explain intermediate compound formation theory of catalysis with two examples.
- Explain the adsorption theory of catalysis with one example.
- Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?
- What is the role of desorption in the process of catalysis?

COLLOIDS

5.3.1

Colloids and true solutions

Colloidal solution is a heterogeneous solution with size of solute particle in the range $1m\mu$ to 1μ

Thomas Graham classified the soluble substances into two categories, crystalloids and colloids depending upon the rate of their diffusion through permeable membranes. Crystalloids are those substances which are in crystalline form and whose solutions diffuse rapidly through a vegetable or animal membrane. eg: sugar, urea, salts, acids, bases, etc.

Colloids are those substances which are generally amorphous and whose solutions diffuse slowly through a vegetable or animal membrane. eg: gelatin, albumin, starch, silicic acid, glue, gum arabic, etc. This classification of substances into crystalloids and colloids was proved unsatisfactory because a particular substance would be crystalloid in one solvent and a colloid in the other. For example, NaCl is crystalloid in water but colloid in benzene.

The term colloidal substance is replaced by colloidal state or colloidal solution. Thus colloid is not a type of substance but it is a state of a substance which depends upon its particle size in solution.

On the basis of particle size mixtures are classified into three types. These can be true solutions, suspensions and colloidal solutions. True solution is a homogeneous binary system in which the particle size of the solute is in the order of $m\mu$ or less. Sugar, urea, salts, acids, bases, etc., dissolved in water are examples for true solutions. Colloidal solution is a heterogeneous binary system in which the particle size of the solute is in the range of $1m\mu$ – 1μ . Starch, gelatin, glue, etc., dissolved in hot water are examples for colloidal solutions. Suspension is a heterogeneous system which contains small insoluble particles of size greater than 1μ . eg: sand in water, dirt in water, etc.,

Colloidal solution contains two phases. They are dispersed phase and dispersion medium. The phase which is dispersed in the other is called dispersed phase. It is also called internal phase or discontinuous phase. The phase in which the dispersion is done is called dispersion medium. It is also called external phase or the continuous phase. Some examples for colloidal solutions are given below.

Colloidal solution contains two phases


Cloud is a colloidal solution of water droplets dispersed in air


Blood is a colloidal solution of solid RBC in water

5.3.2

Classification of colloids


Aerosol is a colloidal solution in which medium is air


Gel is a liquid dispersed in a solid medium

- 1) Smoke is a colloidal solution of carbon particles dispersed in air. In smoke, dispersed phase is carbon (solid) and dispersion medium is air (gas).
- 2) Cloud is a colloidal solution of water droplets dispersed in air. In cloud, dispersed phase is water (liquid) and dispersion medium is air (gas).
- 3) Starch sol is a colloidal solution of starch particles dispersed in water. In starch solution dispersed phase is starch (solid) and dispersion medium is water (liquid).
- 4) Gold sol is a colloidal suspension of gold particles (dispersed phase), dispersed in water (dispersion medium). In gold sol dispersed phase is gold particles (solid) dispersion medium is water (liquid).
- 5) Milk is a colloidal solution of liquid fat droplets (dispersed phase) dispersed in water (dispersion medium).
- 6) Blood is a colloidal solution of solid albuminoid substances (dispersed phase) dispersed in water containing some salts and other substances (dispersion medium).

Classification based on the physical state: Based on the physical state of the dispersed phase and dispersion medium, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system.

A colloidal solution of a solid dispersed phase in liquid dispersion medium is generally referred to as 'sol'. If dispersion medium is air, the sol is called aerosol. If dispersion medium is water, the sol is called hydrosol or aquasol. Starch sol, gold sol, milk, etc., are examples of hydrosols. If dispersion medium is alcohol, the sol is called alcosol. The examples of the various types of colloids along with their typical names are listed in **Table 5.3**.

Out of various types of colloids listed in the Table, the most common colloids are:
 Sols (Solids dispersed in liquids),
 Gels (liquids dispersed in solids) and
 Emulsions (liquids dispersed in liquids)

Table 5.3 Types of colloidal systems

Dispersed phase	Dispersion medium	Type of colloid	Examples of the colloidal system
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids, starch solution, blood, gold sol
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair creams
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide, sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Classification based on the interaction between two phases : Based on the interaction between dispersed phase and dispersion medium, colloidal sols are divided into two types. They are lyophilic (solvent loving) and lyophobic (solvent hating). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic. The colloidal solutions, in which the particles of dispersed phase has great affinity for the dispersion medium are called lyophilic sols. Generally high molecular weight organic compounds such as starch, gelatin, glue, gum, proteins, rubber and certain polymers in water are lyophilic sols.

The colloidal solutions, in which the particles of dispersed phase have no affinity for the dispersion medium are called lyophobic sols. Lyophobic sols are obtained from inorganic materials such as metals like Ag and Au, metal hydroxides like Al(OH)_3 and Fe(OH)_3 , metal sulphides like As_2S_3 , etc. Smoke, cloud, gold sol, etc., are also lyophobic sols. Differences between lyophilic sols and lyophobic sols are given in the **Table 5.4**.

Table 5.4 Difference between lyophilic sols and lyophobic sols

Property	Lyophilic sols	Lyophobic sols
1. Preparation	Prepared easily by usual method	Prepared by special methods
2. Nature	These particle carry little or no charge	These particles carry positive or negative charge
3. Stability	Sols are more stable	Sols are less stable
4. Action of electrolytes	Cannot be easily precipitated	Sols are easily precipitated
5. Hydration (solvation)	These particle are weakly hydrated	These particle are weakly hydrated
6. Viscosity	Viscosity is much higher than that of the medium	Viscosity is about the same as that of the medium
7. Surface tension	Surface tension is generally lower than that of the medium	Surface tension is usually same as that of the medium
8. Visibility	Particles cannot be readily detected even under ultra microscope	Particles can be readily detected under ultra microscope
9. Reversibility	These sols are reversible	These sols are irreversible
10. Tyndall effect	Exhibit weak Tyndall effect	Exhibit Tyndall effect

Multimolecular, macromolecular and associated colloids have difference in particles of the dispersed phase

Classification based on type of particles of the dispersed phase: Depending upon the type of particles of the dispersed phase, colloids are classified as multimolecular, macromolecular and associated colloids.

On dissolution, a large number of atoms or molecules of the substance aggregate together to form species having the size in the colloidal range. The species thus formed are called multimolecular colloids. eg: gold sol, sulphur sol, etc. Gold sol contains particles of various sizes having many atoms. Sulphur sol contains particles containing thousands of S_8 sulphur molecules.

Macromolecules in suitable solvents form solutions in which the size of the macro-molecules may be in the colloidal range. Such heterogeneous systems are called macro-molecular colloids. These colloids are quite stable and resemble true solutions. Examples of naturally occurring macromolecules are starch, glucose, proteins and enzymes and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

5.3.3**Preparation of lyophobic colloids**

Lyophilic colloids can be prepared easily by shaking or warming the dispersed phase with dispersion medium. Lyophobic sols are prepared by special methods like dispersion methods and condensation methods. In dispersion methods, the substance in bulk is broken down into fine particles of colloidal dimension. Some dispersion methods are mechanical dispersion, electrical dispersion and peptization.

Mechanical dispersion : Solid material is first finely crushed by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The simplest form of colloidal mill consists of two metal discs held at a small distance as shown in Fig 5.9. Two discs revolve in opposite direction at a very high speed about 7000 revolutions per minute. The particles are ground down to colloidal size and are then dispersed in the liquid, containing a stabiliser. Colloidal graphite and printing ink are prepared by this method.

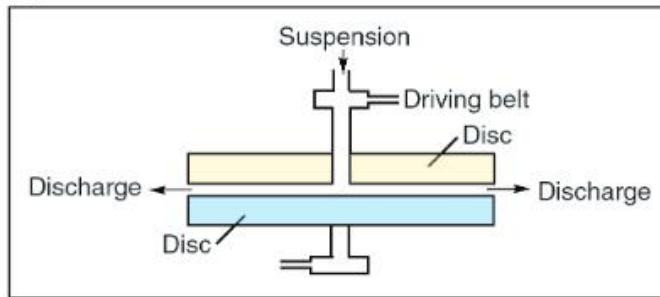


Fig 5.9 Colloidal mill

Electrical dispersion (Bredig's) arc method : This process involves dispersion as well as condensation. Colloidal sol of metals like gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metals immersed in water containing some stabilising agent such as caustic potash. The water is cooled by immersing the container in an ice bath. Schematic diagram of Bredig's arc method is given in the Fig 5.10. The intense heat of the arc vapourises some of the metal, which then condenses to form particles of colloidal size.

Peptisation: The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte is called peptisation. The electrolyte used for this purpose is called peptising agent.

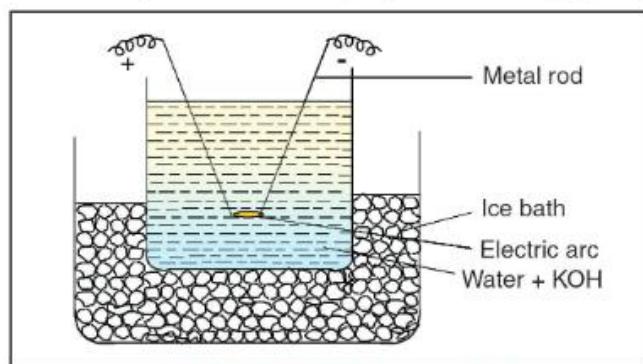


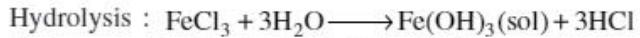
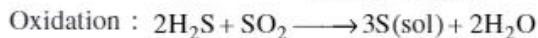
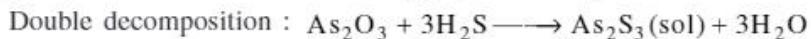
Fig 5.10 Bredig's arc method


Ferric hydroxide sol is prepared by treating ferric hydroxide precipitate with ferric chloride solution


During the peptisation, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitate, which ultimately breaks up into smaller particles of colloidal size. Ferric hydroxide sol is prepared by treating freshly precipitated ferric hydroxide with small amount of ferric chloride solution. Here ferric chloride solution acts as peptising agent.

In condensation methods, very small particles aggregate to form particles of colloidal dimensions. Chemical methods and exchange of solvents are examples for it. In some cases, a third substance is added to increase the stability of the solution.

Chemical methods: Colloidal solutions 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.



Exchange of solvent : Colloidal solution can be prepared by taking a solution of the substance in one solvent and transferring to another solvent in which the substance is relatively less soluble. A colloidal solution of sulphur is obtained by pouring a solution of alcoholic sulphur into water, due to low solubility of sulphur in water.

5.3.4

Purification of colloidal solutions


Dialysis is the process of separating a crystalloid from a colloid


Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these impurities to a requisite minimum. The process of reducing the concentration of impurities is called purification of colloids. Dialysis and ultrafiltration are important methods of purification of colloidal solutions.

Dialysis: This process is based upon the fact that the particles in true solution pass easily through the parchment membrane but colloidal particles do not. In this process the sol is placed in a parchment paper or cellophane bag which in turn is suspended in a tank through which distilled water is circulated continuously. The molecules and ions diffuse through the membrane into the outer water and pure sol behind. Thus dialysis may be defined as the process of separating a crystalloid from a colloid by diffusion through suitable membrane. The apparatus used for the purpose is known as dialyser.

The process of diffusion may be hastened by using hot water in hot dialysis. The process of dialysis can be quickened by applying electric field, provided the impurities are electrolytes. The process is known as electrodialysis. Under the influence of electric field, ions will migrate faster to the oppositely charged electrodes placed outside the bag and as shown Fig 5.11.

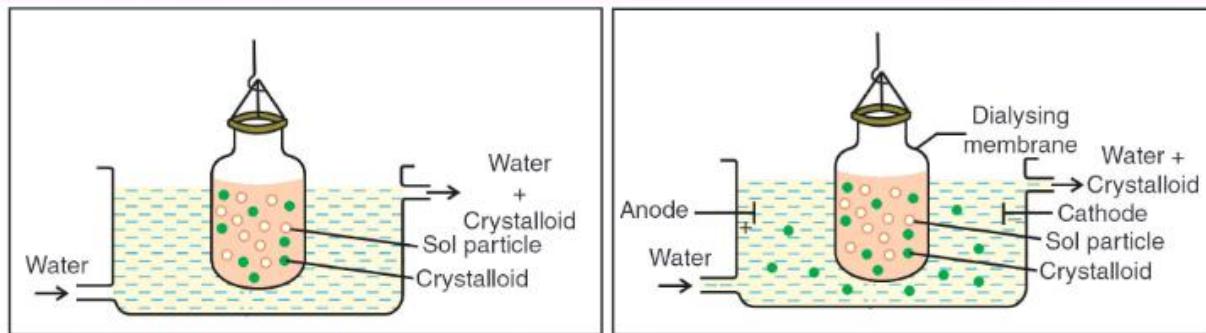


Fig 5.11 Ordinary dialyser and electrodialyser

Ultrafiltration is slow, but speeds up with pressure

Ultrafiltration: This process is based upon the fact that solvent and soluble impurities in the colloidal solution can pass through the pores of ultrafilter paper but not colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. Ordinary filter paper can be converted to ultrafilter paper by reducing the pore size. Ultrafilter paper made by soaking the ordinary filter paper in colloidion solution followed by hardening with formaldehyde and finally drying it. The usual colloidion is a 4% solution of nitrocellulose. By using ultrafilter paper colloidal particles are separated from rest of the solution. Ultrafiltration is a slow process and to speed up, pressure or suction is applied. The colloidal particles left on the ultrafilter paper are then stirred with fresh dispersion medium to get a pure colloidal solution.



P.5.9 How to save a patient suffering from kidney failure?

Solution

Blood is a colloidal solution.

In case of kidney failure, blood cannot be purified. Under such conditions, the blood is separated from dissolved toxic impurities by dialysis and reintroduced in the blood stream.

5.3.5

Properties of colloids

The values of colligative properties are less for colloidal solutions

Colligative properties: Colloidal particles are bigger aggregates. Thus, the number of particles in the colloidal solution is comparatively small as compared to true solution. The van't Hoff factor (i) for colloidal sols is very low ($<< 0.1$). Hence the values of colligative properties like lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure are less for colloidal solution, when compared with true solution of same concentration.

Tyndall effect: This is an optical property. If a homogeneous solution placed in dark is observed in the direction of light, it appears clear. If it is observed from a direction at right angle to the direction of light beam, it appears perfectly dark. If a colloidal solution placed in dark is observed in the direction of light, it appears reasonably clear or translucent by the transmitted light. If it is observed from a direction at right angle to the direction of light beam, an illuminated beam is observed.

This effect was first observed by Faraday and studied in detail by Tyndall. This is termed as Tyndall effect. The bright cone of the light is called Tyndall cone. The Tyndall cone is shown in Fig 5.12.

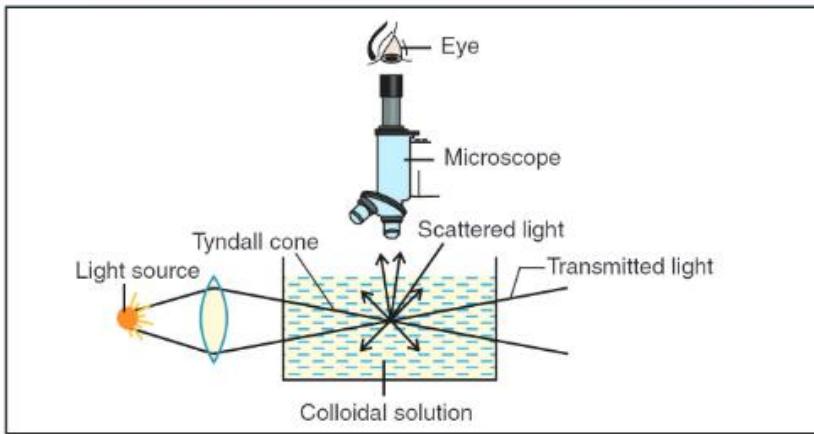


Fig 5.12 Tyndall cone

Tyndall effect due to scattering of light by particles of colloidal sol.

Finest gold sol is red. Gold sol is yellow with bigger gold particles

Continuous zig-zag motion of particles is called Brownian motion

The Tyndall effect is due to scattering of light by colloidal particles in all directions. Tyndall effect is observed only when the diameter of the dispersed particles is greater than the wavelength of the light used and the difference in refractive indices of two phases is very high. Lyophobic colloids satisfy both the conditions and hence exhibit Tyndall effect. Lyophilic sols do not satisfy the second condition and hence Tyndall effect is not observed. Zsigmondy constructed ultramicroscope based on Tyndall effect.

Colour: The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles, size and nature of the particles and the way the observer receives the light.

For example, milk and water mixture appears blue when viewed by the reflected light and looks red by the transmitted light. Finest gold sol is red in colour. As size of the particles increases, it becomes purple, then blue and finally golden yellow.

Brownian movement: This is a kinetic property of colloids. When colloidal particles are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous motion in zig-zag directions as indicated in Fig 5.13.

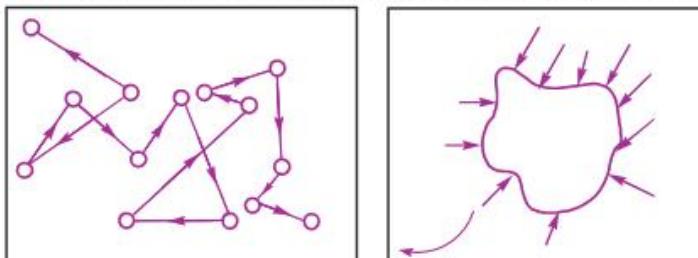


Fig 5.13 Movement of colloidal particles

This motion was first observed by Brown and hence is known as Brownian movement. This motion is independent on the nature of the colloid but depends on size of the particles and viscosity of solution. Smaller the size of particles and lesser the viscosity, faster is the motion. The motion becomes intense at high temperature. The brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. Brownian movement has a stirring effect which does not permit the particles to settle and thus makes sols stable.

Electrical properties: Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution. Some examples of positively and negatively charged sols are given in Table 5.5.

Table 5.5 Examples of charged sols

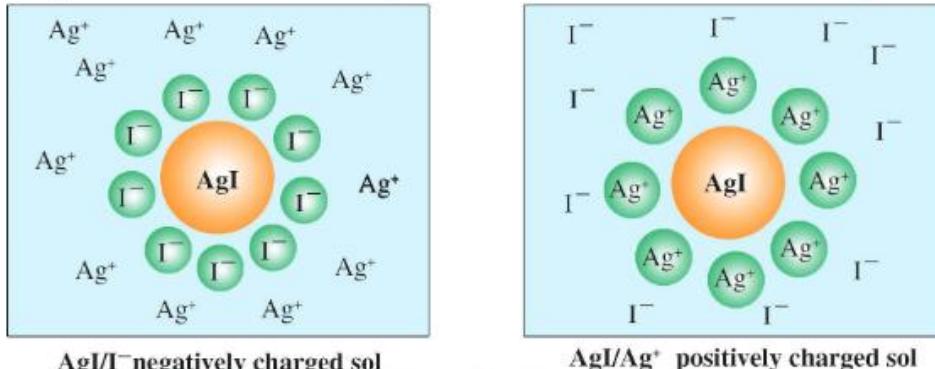
Positively charged sols	Negatively charged sols
Hydrated metallic oxides, like $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{CrO}_3 \cdot x\text{H}_2\text{O}$, etc.	Metals sols like copper sol, gold sol, etc.
Basic dye stuffs, like methylene blue sol.	Metallic sulphides, like As_2S_3 sol, CdS sol.
Haemoglobin	Acid dye stuffs, like eosin, congo red sols.
Oxide sol like TiO_2 sol.	Sols of starch, gum, gelatin, clay, etc.

The charge on
sol particles
may be due to
electron capture

The charge on the sol particles may be due to electron capture by sol particles during electrodispersion of metals or due to preferential adsorption of ions from the solution. 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.

When ferric chloride solution is added to hot water, a positively charged solution of hydrated ferric oxide is formed due to the adsorption of ferric ions. However, when ferric chloride solution is added to excess caustic soda solution, a negatively charged solution is obtained due to adsorption of hydroxyl ions.

When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when potassium iodide solution is added to silver nitrate solution, positively charged sol results due to adsorption of silver ions from dispersion medium. These are shown in Fig 5.14.

Fig 5.14 Negatively and positively charged AgI sols

Potential
difference in the
double layer is
called zeta
potential

A layer of positive or negative charge formed by selective adsorption on the surface of a colloidal particle is termed fixed layer. This layer attracts the counter ions from the medium forming a second layer called mobile layer or diffused layer. The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. The charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between the layers, called the zeta potential or electro kinetic potential.

The presence of similar charges on colloidal particles prevents them from coalescing or aggregating when they come closer to one another due to repulsion between them. Thus the charge of colloidal particles is responsible for the stability of colloidal solution.


Movement of colloidal particles under electrical potential is called electrophoresis


Electrophoresis: The existence of charge on colloidal particles is confirmed by electrophoresis experiment. When electrical potential is applied across two platinum electrodes dipped in a colloidal solution, the colloidal particles move towards the oppositely charged electrode. The movement of colloidal particles under an applied electric potential is called electrophoresis.

When the movement of colloidal particles is prevented by some suitable parchment membrane, the dispersion medium moves in an electric field. This phenomenon is termed electroosmosis. In negatively charged sols, sol particles carry negative charge and dispersion medium carries positive charge. In electrophoresis experiment sol particles move towards anode and medium moves towards cathode.

5.3.6

Coagulation


The process of settling of colloidal particles is called coagulation


The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If the charge is removed, the particles will come nearer to each other to form aggregates and settle down under the force of gravity. The process of settling of colloidal particles is called coagulation. This is also called flocculation or precipitation of the sol.

Coagulation of lyophobic sols

Electrophoresis: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated as shown in Fig 5.15.

Mutual coagulation: When two oppositely charged sols are mixed in almost equal proportions, sol particles neutralise their charges and get partially or completely precipitated. This type of coagulation is called mutual coagulation.

Boiling: When a sol is boiled, the absorbed layer is disturbed due 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.

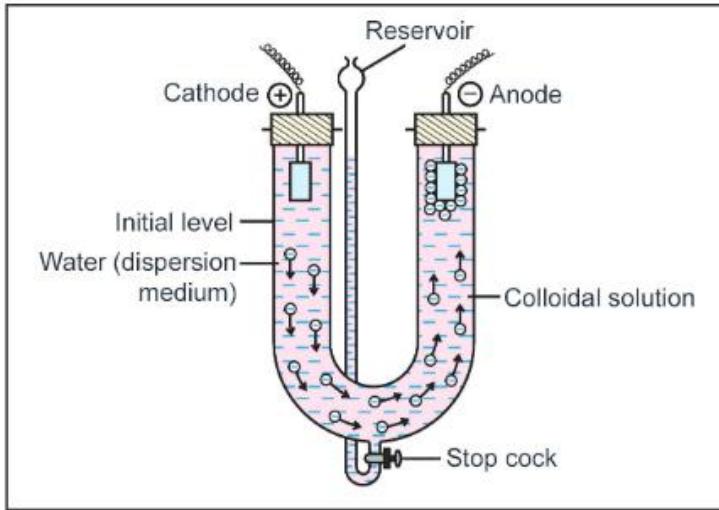


Fig 5.15 Coagulation of colloidal particles by electrophoresis

Persistent dialysis: On prolonged dialysis, traces of electrolyte in the sol are removed almost completely. The colloids become unstable and finally precipitated.

Addition of electrolytes: When excess of an electrolyte is added, the colloidal particles are precipitated. This is due to the fact that, the colloidal particles take up


Flocculating power of ion is more with ion of higher valency


oppositely charged ions from the electrolyte and neutralise their charge. 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.

Generally 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, flocculating power is in the order, $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$. Similarly, in coagulation of a positive sol, flocculating power is in the order, $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$.

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

Factors responsible for the stability of lyophilic sols are charge and extensive solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This can be done by adding an electrolyte and by adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sol, the dispersed particles are dehydrated. Even a small quantity of electrolyte can bring about coagulation.

Protection of colloids

Lyophilic sols are generally more stable than lyophobic sols, because lyophilic colloids are extensively solvated. 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 electrolyte. Lyophilic colloids used for this purpose are called protective colloids.

Zsigmondy introduced the term gold number to measure the protective power of different protective colloids. He defined the gold number as the minimum weight in milligrams of dry protective colloid to be added to 10ml of a standard gold sol to just prevent its coagulation by addition of 1ml of 10% NaCl solution.

Gold number of gelatin, haemoglobin, egg albumin and potato starch are respectively 0.005–0.01, 0.03–0.07, 0.1–0.2 and 25. Lesser the gold number, higher is the protective power. Thus, gelatin and starch have the maximum and minimum protective powers.


Gelatin has lower gold number and has higher protective power


5.3.7

Colloids around us

Most of the substances, we came across in our daily life, are colloids. Some important examples are given here.

1. Blue colour of the sky and sea water : Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us. Blue colour of sea water is also due to the similar reason.

2. Fog, mist and rain : When a large mass of air containing dust particles, is cooled below its dew point, the moisture from the air condenses forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog.


Artificial rain can be caused by spraying a charged sol into the clouds.



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 charged sol to the clouds from an aeroplane.

3. Blood: Blood is a negative colloid. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot.

4. Soils: Fertile soils are colloidal in nature in which humus act as a protective colloid on account of colloidal nature, soils adsorb moisture and nourishing materials.

5. Formation of delta: River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea, electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with formation of delta.

5.3.8

Applications of colloids

1. 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 passed 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 in Cottrell precipitator (Fig 5.16).

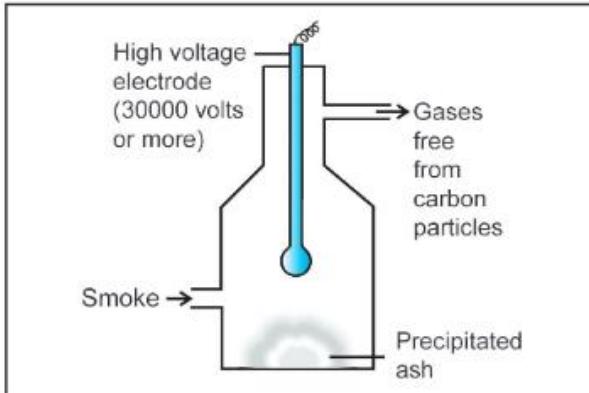


Fig 5.16 Cottrell smoke precipitator


Alum is used for purification of drinking water



2. Purification of drinking water: The water obtained from natural sources contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water pure and fit for drinking purposes.

3. 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 is used for stomach disorders. Colloidal medicines have large surface area and are easily assimilated.

4. Tanning: Animal hides are colloidal in nature. Hides possess positively charged particles and tannin contains negatively charged colloidal particles. When a hide is soaked in tannin, mutual coagulation takes place. This results in the hardening of leather. This process is called tanning. Chromium salts are also used in place of tannin.

5. Other application : Colloidal sols find applications in cleansing action of soaps in the preparation of photographic celluloid films in the industrial products like paints, inks, graphite, lubricants, synthetic plastics, cement, etc.



P.5.10 Why are hydrophobic sols easily coagulated?

Solution Hydrophobic sols are unstable. The charge on colloidal particles can be removed easily on addition of small amount of electrolytes (or) by heating (or) by shaking due to which particles become neutral and approach nearer to each other to form aggregates and settle down.



P.5.11 Tyndall effect is observed during the projection in a cinema theatre. Why?

Solution During the projection of picture, light travels from projector to the screen. This light is scattered by the dust and smoke particles. Hence, Tyndall effect is observed.



P.5.12 Is it possible to know the size and shape of colloidal particles by using ultramicroscope?

Solution With the ultramicroscope we can see only the light scattered by the colloidal particles, but not actual colloidal particle. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.



P.5.13 For coagulation of 10ml of a positive sol, the volumes of 1M each NaCl , Na_2SO_4 , Na_3PO_4 and $\text{Na}_4[\text{Fe}(\text{CN})_6]$ required separately are P, Q, R and S ml respectively. Arrange P, Q, R and S in the descending order.

Solution For coagulation of a positive sol, negative ions are required. As per Hardy-Schulze rule greater the valence of the flocculating ions, greater is the flocculating power and lesser volume is required.

Thus the correct order of the volume of solutions is: $P > Q > R > S$.



P.5.14 Ferric chloride forms both positively and negatively charged sols. Explain.

Solution When FeCl_3 is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of ferric ions. $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{Fe}^{3+}$ is a positively charged sol.

When FeCl_3 is added to alkali solution, a negatively charged sol of ferric oxide is formed due to adsorption of hydroxyl ions. $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}/\text{OH}^-$ is a negatively charged sol.



P.5.15 One gram of charcoal adsorbs 100ml of 0.5M CH_3COOH to form a monolayer and thereby the molarity of acidic acid is reduced to 0.49M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid (surface area of charcoal is $3.01 \times 10^2 \text{ m}^2/\text{g}$).

Solution Number of moles of acetic acid before the adsorption = $0.5 \times \frac{100}{1000} = 0.05$.

Number of moles of acetic acid after the adsorption = $0.49 \times \frac{100}{1000} = 0.049$.

Number of moles of acetic acid adsorbed = $0.05 - 0.049 = 0.001$.

Number of molecules of acetic acid adsorbed = $0.001 \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$.

Surface area of the charcoal occupied by each acetic acid molecule = $\frac{3.01 \times 10^2}{6.023 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$.



P.5.16 Gold numbers of four protective colloids A, B, C and D are 0.5, 0.01, 0.1 and 0.005 respectively. Arrange them in the correct order of their protective power.

Solution Lesser the value of gold number, higher will be the protective power.

The correct order of protective power is: $D > B > C > A$.



P.5.17 Comment on artificial rain.

Solution It is possible to cause artificial rain by throwing electrified sand or spraying a solution carrying charge opposite to the one on clouds from an aeroplane.



P.5.18 It is essential to wash a precipitate with water before its quantitative estimation. Why?

Solution During precipitation, preferential adsorption of common ion takes place from solutions. This will give error in estimating precipitate quantitatively.

Hence precipitate is washed to desorb the excess ions adsorbed to the precipitate.



P.5.19 For the coagulation of 100ml of arsenious sulphide solution, 5ml of 1M NaCl is required. Calculate the flocculation value.

Solution Number of millimoles of electrolyte NaCl required to coagulate 100ml of sol = $1 \times 5 = 5$.

$$\text{Number of millimoles of electrolyte required to coagulate 1000 ml of sol} = 5 \times \frac{1000}{100} = 50.$$

The minimum number of moles of electrolyte per litre required to cause precipitation is called flocculation value. Flocculating value of NaCl is 50 millimole L⁻¹.

EXERCISE - 5.1.3

- Give the differences between ‘colloidal solutions’ and ‘true solutions’.
- Explain the terms dispersed phase and dispersion medium with reference to smoke, cloud, blood, gold sol, starch sol and milk.
- Distinguish between lyophilic and lyophobic sols.
- Write the chemical methods of preparing lyophobic colloids.
- What are protective colloids? Define and explain gold number.
- Explain the terms dialysis and electrodialysis.
- Explain Tyndall effect and Brownian movement.
- What is coagulation? Explain with suitable examples.
- State and discuss Hardy Schulze rule.
- Demonstrate the electrophoresis experiment.
- Why is it essential to wash the precipitate with water before estimating it quantitatively?
- Mention four colloids around us. Discuss their significance.
- Write some important applications of colloids.

EMULSIONS

A dispersion of finely divided liquid droplets in another liquid dispersion medium is called emulsion. In emulsions, one liquid is water and the other liquid is immiscible with water. The immiscible liquid is referred to as ‘oil’. When a mixture of water and oil is shaken thoroughly an emulsion is formed.

5.4.1

Types of emulsions

Emulsions are classified into two types based on the nature and proportions of the two liquids mixed. They are oil in water type (O/W) and water in oil type (W/O). In an oil in water type emulsion, dispersed phase is oil and the dispersion medium is water. e.g.: milk, vanishing cream, etc. In a water in oil type emulsion, dispersed phase is water and the dispersion medium is oil. e.g.: butter, cold cream, stiff grease, cod liver oil, etc.

Emulsions are unstable. If the emulsion is kept for some time, the droplets of the dispersed phase get aggregated and separate as a separate layer. So another substance is added to the emulsion to keep it stable. The third substance added in small amounts to an emulsion to keep the emulsion stable is called emulsifier or emulsifying agent. The emulsifier forms a thin layer around the droplets of dispersed phase and decreases the interfacial tension between two liquids. Thus emulsion becomes stable.



The principal emulsifying agent for O/W emulsions are proteins, gums, natural and synthetic soaps and for W/O, heavy metal salts of fatty acids, long chain alcohols, lamp black, etc. Milk contains natural emulsifier caesin. Egg albumin emulsifies olive oil in water emulsion, solid HgI_2 emulsifies water in benzene and soap emulsifies kerosene in water emulsion.

The dispersed phase droplets in emulsions are often negatively charged and can be precipitated by electrolytes. Emulsions show Brownian movement and Tyndall effect. They can be diluted with any amount of dispersion medium. But when dispersed phase liquid is added to emulsion, it forms a separate layer. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

5.4.2

Micelles



Aqueous solution of soaps or detergents at low concentrations behaves as true solution, but at higher concentrations behaves as colloidal solution due to the formation of aggregates. The aggregated particles thus formed are called micelles or associated colloid. 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). For soaps, the CMC is 10^{-4} to 10^{-3} mole L $^{-1}$.

Mechanism of micelle formation: Soap is sodium or potassium salt of a higher fatty acids, eg: sodium stearate, $C_{17}H_{35}COO^-Na^+$. When sodium stearate is dissolved in water, it dissociates into stearate ion, $C_{17}H_{35}COO^-$ and sodium ion, Na^+ .

The stearate ion has non-polar alkyl group which is hydrophobic at one end and polar carboxylate ion, which is hydrophilic, at other end. Stearate ion is shown in Fig 5.17.

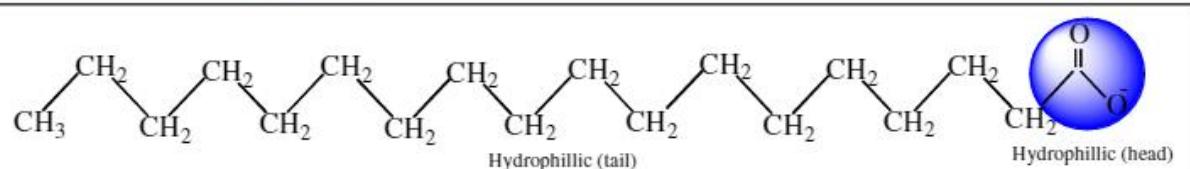


Fig 5.17 Stearate ion

The stearate ions are, therefore, present on the surface of water with their polar group in water and non polar group staying away from it. But at CMC, the stearate ions are pulled into the bulk of the solution and aggregate to form a colloidal size spherical particle. In this 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 and it contains hundreds of soap anions. The micelle can be defined as a colloidal sized particle formed in water by the association of simple molecules, each having a hydrophilic end and hydrophobic end. Formation of ionic micelle is shown in Fig 5.18.



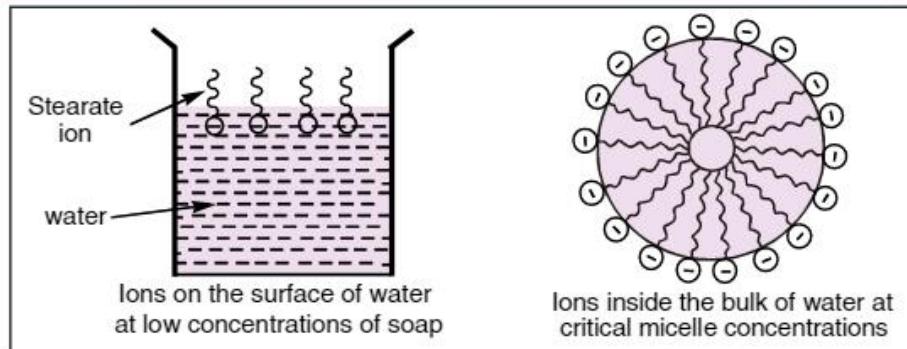


Fig 5.18 Formation of ionic micelle of stearate

Similarly, in case of detergents, eg: sodium laurylsulphate $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$, the polar group is $-\text{SO}_4^-$ along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

Cleaning action of soap : Solid clothes contain grease or fat adhered to the cloth. This is known as dirt. In the cleaning process of clothes, this dirt or grease forms an emulsion with water used for cleaning. But this emulsion is not stable and hence unless it is stabilised it cannot be removed from the cloth in the cleaning process.

When soap is applied, micelle is formed around the grease droplet in such a way that hydrophobic part of the stearate ion is in the grease droplet and hydrophilic part projects out of the grease droplet. Since the polar group can interact with water, the grease droplet surrounded by stearate ions is now pulled into water and removed from the dirty surface. Thus soap helps in emulsification of grease and washing away of it. The negatively charged sheath around the globules prevents them from coming together and forming aggregates. The schematic diagram of cleaning is shown in Fig 5.19.

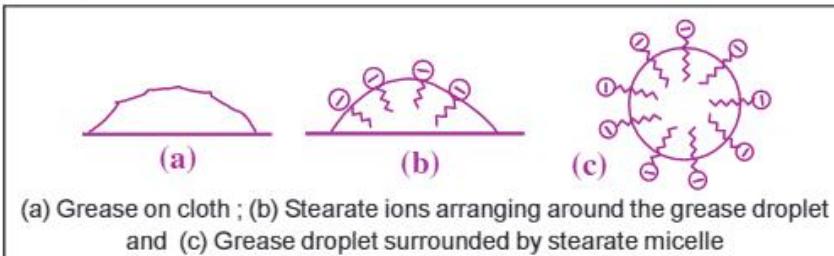


Fig 5.19 Mechanism of cleaning action of soap

5.4.3

Applications of emulsions

Emulsions are useful in washing process of clothes and cleaning of crockery. In the digestion of fats in intestines emulsions are used. The fat in the intestines form soap with alkali of the intestines. This converts the remaining fat into emulsion and stabilises it. Emulsions are used in the preparation of lotions, creams, and ointments in pharmaceuticals and cosmetics.

In the concentration of sulphide ores by froth flotation process, ethylxanthate acts as emulsifier and forms a stable emulsion of pine oil in water. Photographic plates and films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films. Rubber is obtained by coagulation of latex. Latex is an emulsion of polyisoprene droplets in water.

Deemulsification of cream gives butter

Cream is converted into butter by deemulsification process called churning. Oil water emulsion from oil wells broken to get oil. Emulsion formation or deemulsification are also used in the exploration of oil.



P.5.20 Write the difference in the size of stearate anion and stearate micelle.

Solution Stearate anion is a normal ion. Its size is in the order of 10^{-10}m .

Stearate micelle is formed by the aggregation of few hundreds of stearate anions leading to an associated colloid. The size of anionic micelle formed is in the order of 10^{-8}m .



P.5.21 What is deemulsification?

Solution Deemulsification is a reversal process of emulsion formation. The W/O type emulsion will break to give oil and water during deemulsification process.



P.5.22 Why gelatin is added to ice cream?

Solution Ice cream is an oil in water type emulsion. Gelatin is added to stabilise it.

EXERCISE - 5.1.4

- What are emulsions and how are they classified? Give examples.
- What is a micelle? Give an example of micelle formation.
- Explain the phenomenon of cleaning of clothes by using detergents and soaps.
- How are emulsions useful in digestion?



- Adsorption is a surface phenomenon but absorption is a bulk phenomenon.
- Adsorption is due to unbalanced molecular forces or valence forces. For adsorption, ΔH is $-ve$, ΔS is $-ve$, and ΔG is $-ve$.
- Physisorption is favourable at low temperature and high pressure. Chemisorption is favourable at high temperature.
- Extent of adsorption of a gas on charcoal is directly proportional to its critical temperature.
- Freundlich adsorption isotherm is, $x/m = K.P^{1/n}$. K and n are constants and depend on the nature of the adsorbent and gas.
- With increasing the temperature extent of chemisorption increases first, it reaches a maximum value and then decreases.
- Catalytic poison decrease the activity of catalyst. eg: As_2O_3 is a catalytic poison for platinum catalyst in contact process.
- Homogeneous catalysis can be explained by intermediate compound formation theory and heterogeneous catalysis can be explained by adsorption theory.
- Colloidal solution is heterogeneous binary system in which the size of particles is in the range of $1\text{m}\mu - 1\mu$.

CHEMISTRY IID

10. Liquid in liquid type colloids are called emulsions, liquid in solid type colloids are called gels.
11. High molecular weight organic compounds in water are lyophilic sols. Low molecular weight inorganic substances in water form lyophobic sols.
12. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by Bredig's arc method.
13. The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte is called peptization.
14. Colloids are purified by dialysis and ultrafiltration.
15. Tyndall effect is due to scattering of light by colloidal particles. Sky is blue in colour due to the scattering of blue light by dust particles in it.
16. The zig-zag motion of colloidal particles is called Brownian movement. It is due to unbalanced bombardment of colloidal particles by the molecules of dispersion medium.
17. Greater the valence of the flocculating ion added, greater is its power to cause precipitation.
18. Lyophilic sols are used as protective colloids.
19. A dispersion of finely divided liquid droplets in another liquid dispersion medium is called emulsion.
20. Soaps and detergents form micelles at the temperature greater than Kraft temperature and at the concentration greater than critical micelle concentration.
21. In washing process of clothes, soap functions as emulsifier for water dirt emulsion.
22. Emulsions are useful in washing of clothes, cleaning of crockery, preparation of creams and in pharmaceuticals.

EXERCISE - 5.2

1. Adsorption is accompanied with decrease in entropy, but the process is spontaneous. Explain.
2. How to distinguish between physisorption and chemisorption with the help of graphs.
3. For the coagulation of 100ml of a positive sol 10ml of 1M sodium chloride is required. Calculate the flocculation value. (Ans : 100)
4. How to distinguish lyophilic and lyophobic colloids with tyndall effect?
5. How to prepare negative and positive aluminium hydroxide sols?
6. Which property can be used to distinguish colloidal solution and true solution?
7. Colloidal sulphur exhibits Brownian movement, while a solution of sulphur in CS_2 does not. Why?
8. The charge of colloidal particles is responsible for the stability of sols. Explain.
9. A negatively charged solution is obtained when ferric chloride is added to caustic soda solution. Explain.
10. Why the colour of gold sol changes with the size of gold particles?

11. Rate of fruit fermentation increases with time. Why?
12. The decolourisation of permanganate with oxalate is initially slow, but gains momentum after some time. Why?
13. How the colloids are classified on the basis of type of particles in dispersed phase?
14. Explain the purification of colloids by dialysis and ultrafiltration.
15. Arrange the following substances in order of increasing ability to coagulate i) negatively charged sol and ii) a positively charged sol: X) ZnSO_4 , Y) AlCl_3 and Z) Na_3PO_4 .
 (Ans: In case of negative sol Y > X > Z, in case of positive sol Z > X > Y)
16. A catalyst lowered the energy of activation by 25 kJ mol^{-1} . How many times, the rate of reaction increases?
 (Ans : 2.4×10^4 times)
17. Why the reaction between nitric acid and copper is slow in the beginning but fast after some time?
18. During the micelle formation how the enthalpy, entropy and Gibbes energy changes?
19. Gold number of gelatin is 0.01. Calculate the weight of gelatin to be added to 50ml of gold sol to stop coagulation when 5ml of 10% NaCl added.
 (Ans : 0.05mg)
20. The surface area of activated charcoal is $10^3 \text{ m}^2 \text{ g}^{-1}$. If effective surface area of ammonia molecule is 0.129 nm^2 and complete monolayer coverage is assumed, how much ammonia at STP could be adsorbed on 10g of charcoal?
 (Ans : 2896 cm^3)
21. 20% surface sites have adsorbed N_2 . On heating N_2 gas is evolved from sites and were collected at 25°C and 0.001 atm in a container of volume 2.46 cm^3 . Density of surfaces sites is $6 \times 10^4 \text{ cm}^{-2}$ and surface area is 10^3 cm^2 . Find the number of surface sites occupied per molecule of N_2 .
 (Ans : 2)
22. A molecule of nitrogen occupies $1.62 \times 10^{-19} \text{ m}^2$. The volume of nitrogen at 0°C and 1.013 atm required to cover a sample of silica gel with unimolecular layer is $129 \text{ cm}^3 \text{ g}^{-1}$ of gel. Calculate the surface area per gram of gel?
 (Ans : $5.7 \times 10^2 \text{ m}^2$)
23. 0.1M AlCl_3 solution is more effective than 0.1M NaCl solution in coagulating arsenious sulphide sol while 0.1M AlCl_3 is less effective than 0.1M Na_3PO_4 solution in coagulating ferric oxide sol. Why?
24. For coagulation of 20ml of a negative sol X ml of 1M NaCl, Y ml of 1M BaCl_2 and Z ml of AlCl_3 are required separately. What is the order of X, Y and Z values?
 (Ans : X > Y > Z)
25. One gram of a protective colloid 'X' is to be added to 200ml of gold sol to prevent coagulation of it when 20ml of 10% NaCl is added. Calculate the gold number of protective colloid 'X'.
 (Ans : 50)
26. Soap forms a true solution at lower concentration, but forms a colloidal solution at higher concentrations. Explain.
27. Soap does not work properly in aqueous solutions with acidic pH values. Why?
28. What is de-emulsification process? How is it performed?

