

There are many properties of matter, which are related to their surface. Such properties become predominant if the substance is in finely divided form or its surface is rough. Under these conditions the surface area increases enormously and large amount of material is present in the surface. The surface related properties of matter are adsorption, colloidal state and emulsions.

1. ADSORPTION

Suppose we have a substance either in the liquid or solid form. Let us consider a molecule in the bulk of the substance. It experiences forces of attraction uniformly from all sides by neighbouring molecules. There is no net force acting on it. If we consider a molecule near its surface we find that such a molecule is not bonded to other molecules from all sides but has certain unutilised valencies, as there are no molecules above the surface. In order to satisfy the unutilised valencies, the molecules at the surface attract and retain other molecular species when the substance is brought in contact with them. The substance, which has different concentration at the surface than in the bulk of the adjoining phases, is said to be adsorbed. The phenomenon of existence of a substance in different concentrations at the surface of another substance than in the bulk phases is called adsorption.

The substance whose surface adsorbs molecular species of another substance is called adsorbent and the substance, which gets adsorbed, is called adsorbate. If the concentration of a substance at the surface of another substance is more than in the bulk of the adjoining phases, it is called ***positive adsorption***. If the concentration of a substance at the surface of another substance is less than in the bulk of the adjoining phases, it is called ***negative adsorption***. This type of adsorption takes place only in case of solutions. Adsorption can take place at a solid–gas surfaces; for example charcoal adsorbs colouring matter in solutions and is used to decolourise brown cane juice and colloidal aluminium hydroxide is used in the purification of water because of its adsorbing properties. Hence,

powdered charcoal and aluminium hydroxide are good adsorbents. Gases and liquids adsorbed on the surface of a solid are called adsorbates. It should be clearly understood that though adsorption is a surface phenomenon, the extent and firmness of adsorption are dependent to a great extent on the nature of the adsorbent and the adsorbate.

1.1 Difference Between Adsorption And Absorption

Adsorption is different from absorption. When a substance is uniformly distributed throughout the bulk of another substance, this shows that absorption has taken place. It occurs at the uniform rate throughout the body of the material. On the contrary, adsorption involves unequal distribution of the molecular species in the bulk and the surface. It is a surface phenomenon. It is rapid in the beginning and gradually slows down at the equilibrium. The forces involved in adsorption are either weak Vander Waal's forces or strong chemical bond forces.

In certain cases, both the adsorption and the absorption take place simultaneously and it is not easy to distinguish between them. Such substance is said to be sorbed and the phenomenon is known as *sorption*.

1.2 Types of Adsorption

Physisorption (Physical adsorption)	Chemisorption (Chemical adsorption)
1. Caused by intermolecular Vander Waal's forces.	Caused by chemical bond formation.
2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily.	Much more specific and depends upon the nature of the both the adsorbate and adsorbent.
3. Heat of adsorption is small (about 5 kcal per mol)	Very large (20 – 100 kcal per mol)
4. Reversible	Irreversible
5. Forms multimolecular layers on adsorbent surface.	Forms unimolecular layer.
6. Occurs at low temperature; decreases with increase in temperature.	Increases with increase of temperature.
7. Increase of pressure increases adsorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
8. Equilibrium is attained readily and it is reversible.	Equilibrium is attained slowly and mostly not reversible.

Enthalpy of adsorption:

The adsorption of one substance on the surface of another leads to the existence of new types of forces between them. Therefore, it is an exothermic process and is accompanied by the release of energy. The enthalpy or heat of adsorption is defined as the heat energy evolved when one mole of adsorbate is adsorbed on the surface of adsorbent. Since physical adsorption involves weak forces of attraction between the molecules of the adsorbent and the adsorbate, the heat of

physisorption is generally low, of the order of $20\text{--}40\text{ kJ mol}^{-1}$. Chemical adsorption, on the other hand involves strong chemical bond formation and the heat of chemisorption is quite high, of the order of $80\text{--}400\text{ kJ mol}^{-1}$.

1.3 Adsorption of Gases on Solids

The extent of adsorption of a gas on the surface of a solid depends on the following factors

- (i) Nature of gas (ii) Nature of solid (iii) Specific area of solid
(iv) Pressure of gas (v) Temperature (vi) Activation of solid

(i) Nature of gas:

Since physical adsorption is non specific in nature, any gas will be adsorbed on the surface of a solid to some extent or other. However, under any given conditions of temperature and pressure, easily liquefiable gases such as NH_3 , CH_4 , HCl , Cl_2 , SO_2 , CO etc. are adsorbed more than permanent gases like H_2 , O_2 , N_2 etc. Chemisorption is specific in nature. Therefore, only those gases will be adsorbed which form chemical bonds with it.

(ii) Nature of solid:

Activated charcoal is the most common adsorbent for easily liquefiable gases. Poisonous gases such as CH_4 and CO fall in this group. Therefore, it is used in gas masks. Other gases such as O_2 , H_2 and N_2 adsorb more on metals such as Ni , Pt and Pd .

(iii) Specific area of solid:

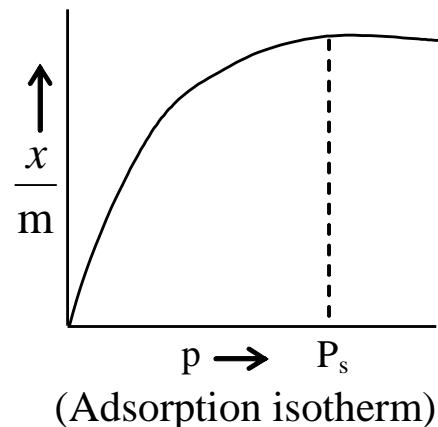
Specific area of an adsorbent is the surface area available for adsorption per gm of adsorbent. Greater the specific area of an adsorbent, greater will be the adsorption. The specific area of an adsorbent can be increased by making the surface rough. The pores must be large enough to allow penetrations of gas molecules.

(iv) Pressure of a gas:

As physical adsorption is reversible, it is accompanied by decrease in pressure. Therefore, it is expected that at a given temperature the extent of adsorption will

increase with the increase of pressure of the gas. The extent of adsorption is measured as x/m where m is the mass of adsorbent and x that of adsorbate. If the physical adsorption is limited to unimolecular layer, the plot of x/m vs equilibrium pressure at a constant temperature is as shown.

It is evident from the graph that at a certain pressure the adsorption reaches a maximum value i.e. the adsorption becomes saturated and the corresponding pressure is called saturation pressure (P_s). Beyond this pressure the adsorption remains constant.



At low pressures, x/m varies linearly with p

$$\therefore \frac{x}{m} \propto p^1 \text{ or } \frac{x}{m} = kp^1$$

At high pressures, $\frac{x}{m}$ is independent of p

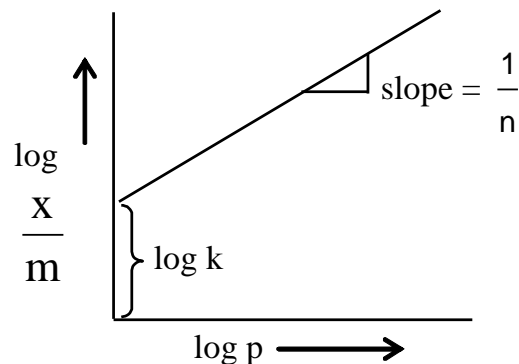
$$\therefore \frac{x}{m} \propto p^0 \text{ or } \frac{x}{m} = kp^0$$

At intermediate pressures, the variation of $\frac{x}{m}$ vs p can be expressed as $\frac{x}{m} \propto p^{\frac{1}{n}}$ where $n > 1$.

$$\text{or } \frac{x}{m} = k p^{\frac{1}{n}}$$

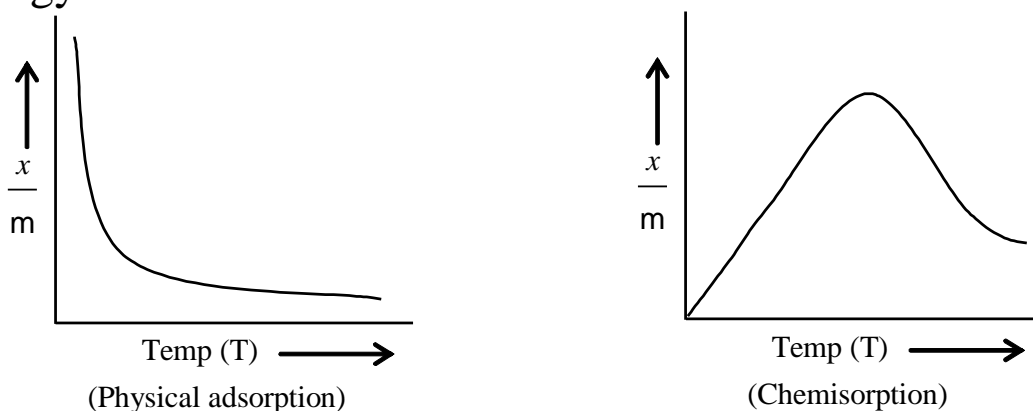
$$\text{or } \log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

This is called Freundlich adsorption isotherm.



(v) Temperature:

As adsorption is accompanied by release of heat energy, so in accordance with Le–Chatelier’s principle, the increase of temperature should decrease the extent of adsorption. This has indeed been found to be so. A plot of x/m vs temperature at constant pressure is called **adsorption isobar**. In the case of physical adsorption x/m decreases with increase of temperature whereas in the case of chemisorption, x/m initially increases with temperature and then decreases as shown below. The initial increase is due to the fact that chemisorption requires activation energy.



(vi) Activation of solid:

Activation of adsorbent means increasing its adsorbing power. This is increased by increasing specific area either by making the surface rough or by breaking the solid into smaller particles. But care must be taken so that particles do not become very small, otherwise the interparticle spaces will be too small to allow penetration of gas molecules.

Competing adsorption:

There is always a competition between different adsorbates to adsorb on the adsorbent.

A strongly absorbable substance can easily displace a weakly adsorbed substance.

For example, on the surface of activated charcoal, gases such as O_2 , N_2 etc. are already adsorbed. But when charcoal comes in contact with poisonous gases

such as CH_4 , CO which are strongly adsorbable, O_2 and N_2 get displaced. If a mix of gases is allowed to adsorb on a particular adsorbent, the strongly adsorbable adsorbate adsorbs to a greater extent than its partial pressure indicates. For example, moisture though present in small proportion in air is strongly adsorbed by silica gel. Charcoal adsorbs poisonous gases even though they are present in small concentration in air.

1.4 Adsorption From Solution

Some solids are capable of adsorbing certain solutes from the solution. This property is made use of in adsorbing colouring matter from solutions of organic substances. Raw cane juice is decolourised by activated charcoal. Similarly, charcoal adsorbs oxalic and acetic acid dyes from their aqueous solutions. Freundlich adsorption isotherm is also applicable to solutions by replacing the pressure term by the concentration (C) of adsorbates in solutions. The relationship is modified as follows

$$\frac{x}{m} = kC^{\frac{1}{n}}$$

Taking logarithm, it becomes

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

A graph between $\log \left(\frac{x}{m} \right)$ and $\log C$ is a straight line for small ranges of concentrations.

1.5 APPLICATIONS OF ADSORPTION

Some of the applications of adsorption are as follows:

(i) Activated charcoal is used in gas masks to remove poisonous gases such as carbon monoxide, methane etc. Animal charcoal is used to remove colouring matter from cane sugar juice in the manufacture of sugar.

- (ii) Ion exchange resin is used to remove hardness of water.
- (iii) Several organic compounds are purified by chromatographic adsorption.
- (iv) Silica gel is used for removing and controlling humidity.
- (v) The catalytic effect of a number of catalysts like spongy iron (in the manufacture of ammonia) and nickel, platinum or palladium (used in the reduction of unsaturated hydrocarbons) is based on the principle of adsorption.

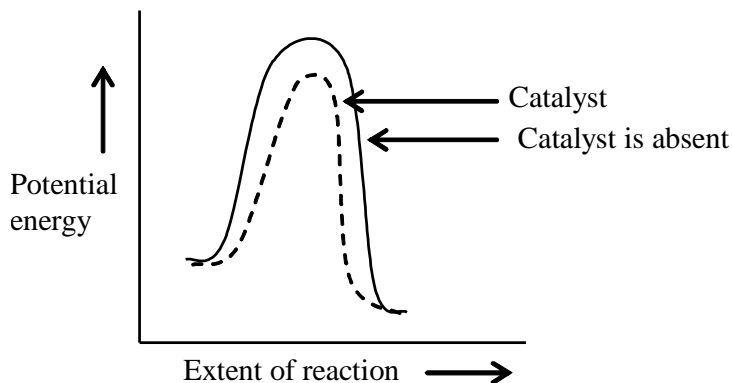
2. CATALYSIS

Catalysis is the phenomenon by which the rate of a reaction is altered (accelerated or retarded) by the presence of a substance, which itself remains unchanged chemically in the process. The substance altering the rate of the reaction is a catalyst.

2.1 Characteristics of Catalytic Reactions

The catalyst remains unchanged in amount and chemical composition at the end of the reaction; it may, however, undergo considerable change in physical form.

- (i) A small quantity of the catalyst is capable of producing the desired effect.
- (ii) The action of a catalyst is specific to a large extent. Thus, the decomposition of KClO_3 is catalysed by MnO_2 but not by platinum.
- (iii) The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.
- (iv) A catalyst does not alter the final state of equilibrium in a reversible reaction.
- (v) A certain minimum energy must be possessed by the reactants so that they may react and produce the products. This is called the **activation energy** (E_a) for the reaction. A catalyst is said to lower the activation energy and thus increase the rate of the reaction.

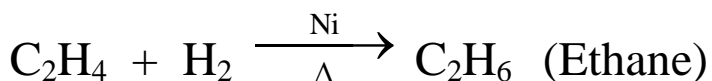


Thus, a catalyst increases the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalyzed reaction.

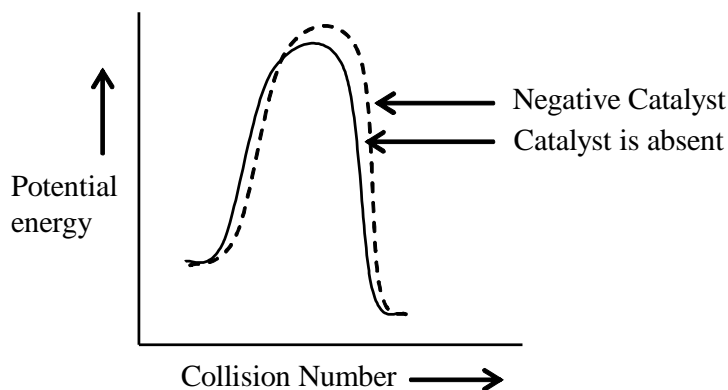
2.2 Types of Catalysis

(i) Positive catalysis: The catalyst increases the rate of a reaction.

Examples: $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3$ (Contact process)



(ii) Negative catalysis (Inhibitor or retarder): Chemical reactions are sometimes retarded by the presence of a foreign substance the substance is known as a negative catalyst.



Examples

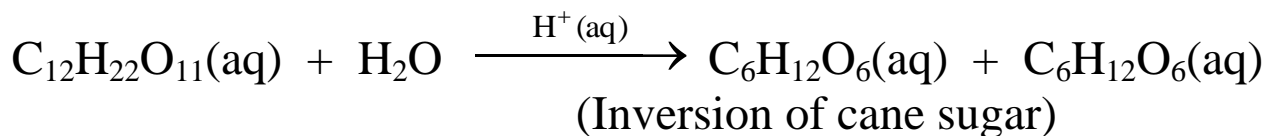
Alcohol, Acetanilide: Prevents oxidation of Na_2SO_3 by air

H_3PO_4 : Prevents decomposition of H_2O_2

(iii) Auto catalysis: In this type of catalysis, one of the product of the reaction catalyses the reaction. In the oxidation of oxalic acid by KMnO_4 , Mn^{2+} ion

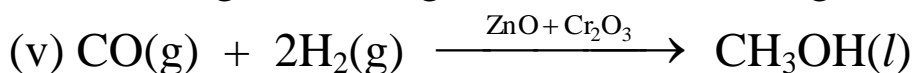
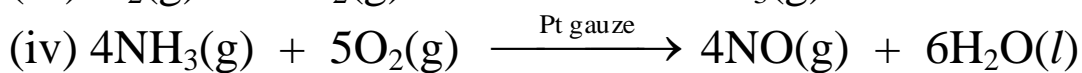
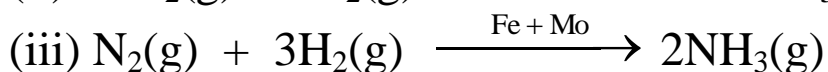
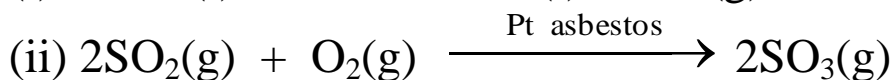
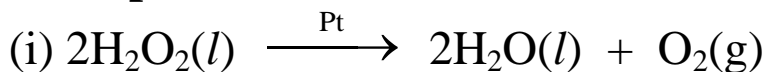
formed is known to accelerate the reaction. So, when KMnO_4 solution is run into warm solution of oxalic acid (+ dil. H_2SO_4), initially there is a time lag before decolourisation occurs; as more KMnO_4 is added, the decolourisation becomes almost instantaneous.

(iv) Homogeneous catalysis: A catalytic process in which the **catalyst is in the same phase as the reactant** is called homogeneous catalysis.



(v) Heterogeneous catalysis: A catalytic process in which the **catalyst and the reactants are in different phases** is called heterogeneous catalysis. This process is also called contact or surface catalysis.

Examples



(vi) Induced catalyst: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

Examples of induced catalysis:

(i) Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

(ii) The reduction of mercuric chloride (HgCl_2) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of KMnO_4 and HgCl_2 , both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of HgCl_2 .

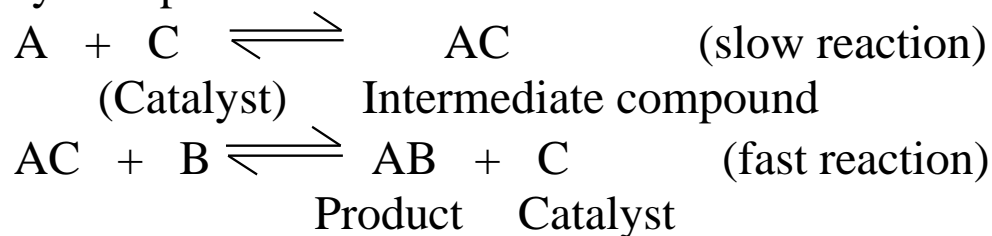
2.3 Theories of Catalysis

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. First theory, known as intermediate compound formation theory explains successfully the homogeneous catalysis. The second theory termed as adsorption theory explains the heterogeneous catalysis.

(i) Intermediate compound formation theory

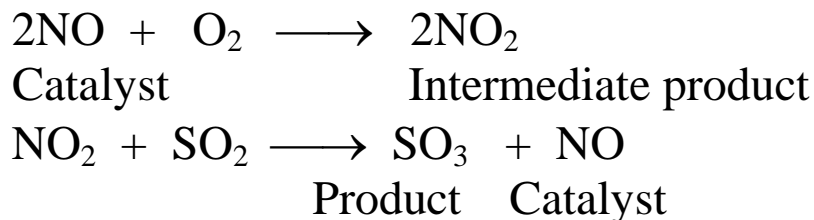
According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

Consider, a reaction of the type $\text{A} + \text{B} \xrightleftharpoons{\text{C}} \text{AB}$ which occurs in presence of a catalyst C, may take place as



$$\text{Rate} = k[\text{A}][\text{C}]$$

Many catalytic reactions can be explained on the basis of this theory. Consider the catalytic oxidation of SO_2 to SO_3 in the lead chamber process. This occurs as follows



This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. The scope of this theory is, however, limited, as the formation of intermediate compound is possible in the case of homogenous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons and action of finely divided catalysts.

(ii) Adsorption theory

This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when the catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the 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 up by the surface of the catalyst, which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

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

- (i) Diffusion of reactants to the surface of the catalyst.
- (ii) Some form of association between the catalyst surface and the reactants occurs. This is assumed to be adsorption.
- (iii) Occurrence of chemical reaction on the catalyst surface.
- (iv) De-sorption of reaction products away from the catalyst surface.
- (v) Diffusion of reaction products away from the catalyst surface.

3. COLLOIDAL STATE

Thomas Graham tried to classify solids into (i) crystalloids and (ii) colloids based on the diffusion of dissolved solids through parchment paper or animal membrane. Substances like common salt, urea, sugar etc., which readily pass through the membrane while in the dissolved state were called crystalloids while substances like starch, gelatin, gum Arabic etc. which in the dissolved state either do not pass through the membrane or pass through very slowly were called colloids. This classification was rejected because the same substance under one set of conditions behaved like a crystalloid and under other set of conditions behaved like a colloid. For example, NaCl in water behaves like a crystalloid but in benzene behaves like a colloid. Soap in water behaves like a colloid while in alcohol it behaves, like a crystalloid. Therefore, there is no separate class of substances called colloidal substance. It is just a state of matter into which every substance can be obtained by a suitable method. The nature of a substance whether crystalloid or colloid depends upon the size of the solute particles. When the size of solute particles lies between 1 nm to 100 nm it behaves like a colloid. If size of solute particles is greater than 100 nm, it exists as suspension and if particle size is less than 1 nm it exists as a true solution. Colloidal solution is heterogeneous in nature and always consists of at least two phases—namely disperse phase and dispersion medium. The component present in small proportion and consisting of particles of colloidal dimensions is called **disperse phase**. The medium in which colloidal particles are dispersed is called **dispersion medium**.

SURFACE CHEMISTRY

The two phases can be solid, liquid or gas. There are eight different types of colloidal solutions.

Disperse phase	Dispersion medium	Common name	Example
Solid	Solid	Solid sol.	Alloys
	Liquid	Sol	gold sol, paints
	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, table jellies, pearl
	Liquid	Emulsion	Milk, emulsified oils
	Gas	Liq. aerosol	Mist, fog, cloud
Gas	Solid	Solid foam	Pumice stone
	Liquid	Foam	Soap lather, whipped cream

If colloidal solution has fluid like appearance it is called **sol**. The dispersion medium in such cases is generally liquid. Depending upon the nature of medium, colloids are sometimes given special names. For example

Dispersion medium	Name of the sol
Water	Hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

3.1 Classification On The Basis Of Interaction Between Different Phases

Depending upon the nature of interaction between disperse phase and dispersion medium, colloids are classified as

LYOPHILIC COLLOIDS

In the case of lyophilic colloids, the disperse phase has great affinity for dispersion medium. In such cases the disperse phase does not easily get

precipitated and the colloids are quite stable. The solids obtained after evaporation of the medium can be easily brought back to the colloidal state by shaking the solids with the dispersion medium. Such colloids are thus **reversible**. Examples of lyophilic colloids are gum, gelatin, starch, proteins and certain polymers in organic solvents. If water is used as the dispersion medium, the colloid is called hydrophilic colloid.

LYOPHOBIC COLLOIDS

In the case of lyophobic colloids, the disperse phase has little affinity for the dispersion medium. These sols are relatively less stable. They can be easily precipitated by addition of small amount of electrolyte. Once the sol. is precipitated, it cannot be easily brought back to the colloidal state. They are thus **irreversible**. Examples of lyophobic sols are gold sol and sulphur sol etc. If water is used as the dispersion medium the sol is called lyophobic colloid.

Differences between lyophobic and lyophilic sols:

Lyophobic sols	Lyophilic sols
1. Colloidal particles are electrically charged	Particles may or may not be charged
2. Stability is due to electrical charge	Stability is due to adsorption of dispersion medium
3. Viscosity is similar to that of the dispersion medium	Viscosity is much higher than that of the dispersion medium
4. Surface tension is similar to that of dispersion medium	Surface tension is often lower than that of the dispersion medium
5. Exhibit Tyndall effect	These do not exhibit Tyndall effect
6. The particles are easily detected by the microscope	The particles cannot be readily detected by the microscope
7. Small quantities of electrolyte cause precipitation	Small quantities of electrolyte have little effect, but high concentration

	causes coagulation
8. The particles migrate in one direction in the electric field	The particles may migrate in either direction or not at all in an electric field
9. Not prepared by direct mixing. Irreversible	Often prepared by direct mixing. Reversible

3.2 Classification on The Basis of Nature of Colloidal Particles

Depending upon the nature of colloidal particles, the colloidal solutions can be classified as

- (i) Multimolecular colloid
- (ii) Macromolecular colloid
- (iii) Associated colloid

(i) Multimolecular colloids

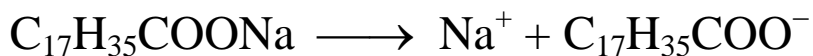
When on dissolution a large number of atoms or smaller molecules of a substance (with diameters less than 1 nm) aggregate together to form species having size in the colloidal range, the species thus formed are called multimolecular as colloids. For example, sulphur sol consists of colloidal particles, which are aggregates of S_8 molecules. A metal sol consists of particles of various sizes, which are clusters of several metal atoms. The atoms or molecules in each aggregate are held by Vander Waal's forces.

(ii) Macromolecular colloids

In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions i.e., (1–100 nm). They are polymers having very high molecular mass. They include natural polymers such as starch, proteins, cellulose and synthetic polymers such as polythene, polyester and nylon etc.

(iii) Associated colloids

This type of colloids includes substances, which behave as true solutions at low concentrations but become colloidal in nature at high concentrations due to the formation of aggregated particles called micelles. Soaps and detergents are examples of associated colloids. In aqueous solution sodium stearate (a kind of soap) ionises as



4. PREPARATION OF COLLOIDAL SOLUTIONS

Different type of methods is in use for the preparation of lyophobic and lyophilic sols.

4.1 Lyophobic Sols

The following two types of methods can prepare lyophobic sols.

(1) Condensation methods

(2) Dispersion methods

(1) Condensation methods

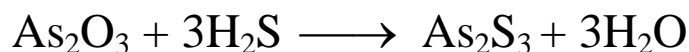
In these type of methods, particles of atomic or molecular size are induced to combine to form aggregates having colloidal dimensions. For this purpose, chemical as well as physical methods can be used.

(i) By chemical methods

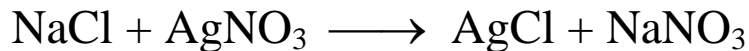
Colloidal solutions can be prepared by chemical reactions involving double decomposition, oxidation, reduction and hydrolysis.

(a) Double decomposition

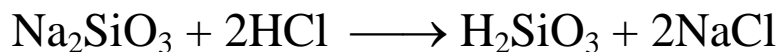
A colloidal solution of arsenious sulphide is obtained by passing hydrogen sulphide into solution of arsenious oxide in distilled water.



Sols of silver halide are obtained by mixing dilute solutions of silver salts and alkali metal halides in equivalent amounts.

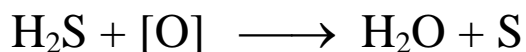
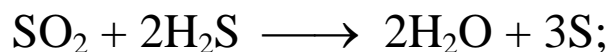


Silica gel sol is prepared by this method between dilute solutions of sodium silicate and HCl.



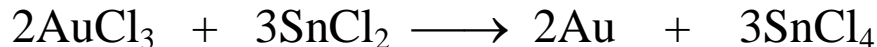
(b) Oxidation

A colloidal solution of sulphur can be prepared by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidising agent like bromine water or nitric acid.

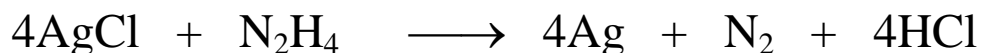


(c) Reduction

A colloidal solution of a metal like silver, gold or platinum can be prepared by the reduction of its salt solution with a suitable reducing agent such as stannous chloride, formaldehyde, hydrazine etc.



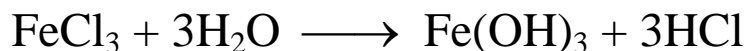
Gold sol



Silver sol

(d) Hydrolysis

By this method hydroxide sols of less electropositive metals like Fe, Al or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.



(ii) By Physical methods

(a) By exchange of solvent

In this method, although no chemical reaction is involved, it can be shown that when a relatively concentrated solution of a substance is added to a large volume of liquid in which it is sparingly soluble, particles of colloidal size result under suitable conditions. For example, the addition of an alcoholic solution of sulphur

to excess water causes the formation of colloidal sulphur, the sulphur being more insoluble in water than in alcohol.

(b) By excessive cooling

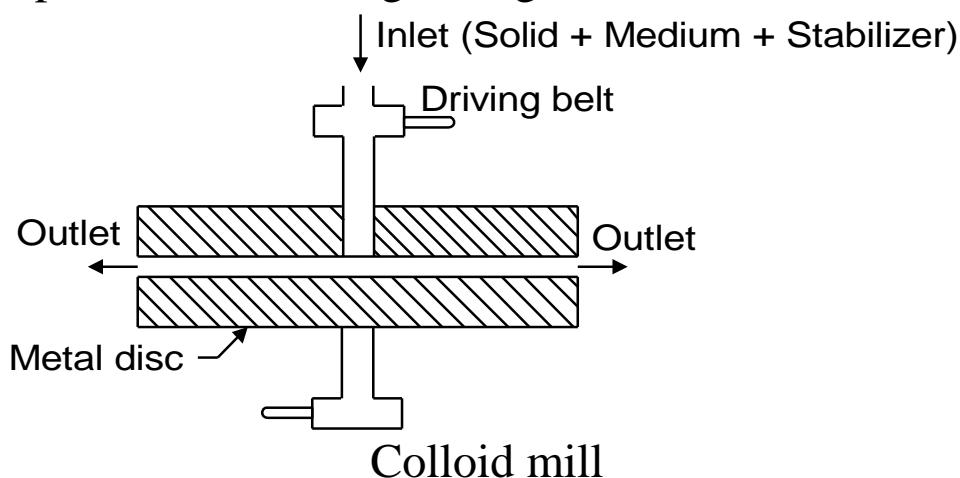
The colloidal solution of ice in an organic solvent such as chloroform or ether can be obtained by freezing a solution of water in the solvent. The molecules of water, which can no longer be held in solution separately combine to form particles of colloidal size.

(2) Dispersion methods

In these methods, large particles of a substance are broken into particles of colloidal dimensions in the presence of dispersion medium. Since the sols formed in this manner are unstable, they are stabilised by adding suitable stabilizers. Some of the methods employed for carrying out the dispersion are described as follows.

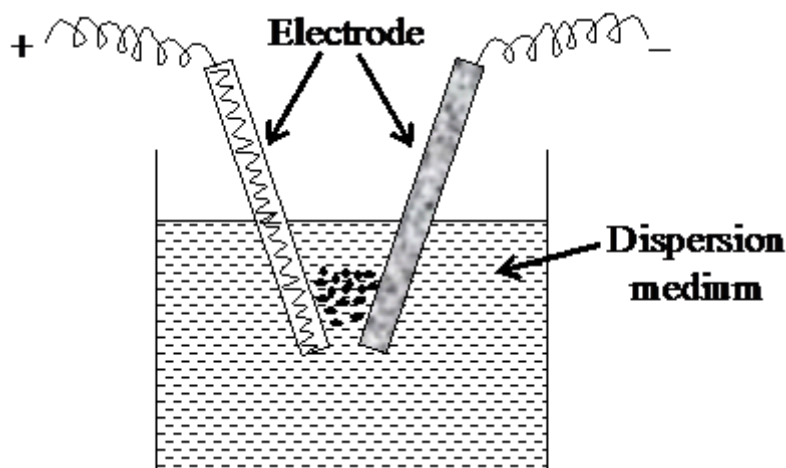
(a) Mechanical dispersions

Many substances can be reduced to colloidal size in a “colloidal mill” consisting of a series of discs rotating in opposite directions with only a small gap between them at the rate of 10,000 rpm. The dispersion medium together with the substance to be dispersed and a stabilizer is passed through the mill and after sometime, a colloidal solution results. The protective material stabilises the sol and prevents the particles from coagulating.



(b) Electrical disintegration or Bredig's arc method

This process involves dispersion as well as condensation. Colloidal solutions of metals such as gold, silver, copper, platinum etc., can be prepared by this method. In this method electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourizes some of the metal, which then condenses to form particles of colloidal size. A slight trace of electrolyte stabilises the sols formed.



(c) Peptization

This is a process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is generally applied to convert fresh precipitate into colloidal solutions because such precipitates are simply aggregates of colloidal particles held by weak forces.

Cause of peptization

During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of precipitate. This causes the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions. For example, when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent) it adsorbs Fe^{3+} ions and thereby split into colloidal particles of the type $[\text{Fe}(\text{OH})_3]\text{Fe}^{3+}$. Similarly, a precipitate of AgCl on shaking

with dilute solution of AgNO_3 adsorbs Ag^+ ion and get peptised to colloidal particles of the type $[\text{AgCl}]\text{Ag}^+$. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptised by ethanol. The colloidal solution of cellulose nitrate in ethanol is called 'collodion'.

(d) Washing Methods

It is common experience in analytical chemistry that a precipitate tends to pass through the filter paper while being washed free from electrolytes. It is probable that the electrolytes have caused the primary colloidal particles to form a precipitate and their removal may result in a return to the colloidal state.

4.2 Lyophilic Sols

Such type of sols is quite stable and can be easily prepared by shaking the dispersed phase in dispersion medium. A few examples of lyophilic sols are gelatin, gum, starch, egg albumin etc.

5. PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions obtained by any one of the methods described above contain impurities in the form of electrolytes or other soluble substances. These impurities have to be removed as they may destabilise the sol. The following methods are commonly used to purify a colloidal solution.

5.1 Dialysis

By this method soluble impurities are removed from colloidal solution by taking colloidal solution in a bag made of semipermeable membrane like parchment paper or cellophane and dipping it in water. The molecular and ionic impurities being small in size pass through the pores of semipermeable membrane. The colloidal particles are large enough so that they cannot pass through the pores.

Movement of the ions through the membrane can be expedited by the application of electric field through the two electrodes. This method is called *electrodialysis*.

5.2 Ultra Filtration

In this method, colloidal solutions are purified by carrying out filtration through special type of graded filter papers called ultra-filters. These filter-papers are made from ordinary filter paper by impregnating them with colloidal particles. These filter papers allow the electrolytes to pass through them but not the colloidal particles. The ultra-filtration is generally a slow process and can be hastened by the application of suction.

5.3 Ultra Centrifugation

In this method, the colloidal solution is placed in a high speed ultracentrifuge. On centrifuging, the colloidal particles settle down. The impurities remain in the dispersion medium and are removed by decantation. The settled colloidal particles are shaken with water containing peptizing agent to form the colloidal solution again.

6. PROPERTIES OF COLLOIDAL SOLUTIONS

The characteristic properties of colloidal solutions are as given below.

6.1 Heterogeneous Nature

A colloidal solution is heterogeneous in nature. It consists of two phases, namely the dispersed phase and the dispersion medium.

6.2 Colligative Properties

A colloidal solution has very small value of mole fraction of dispersed phase due to high average molecular mass of the colloidal particles. As a result, all the

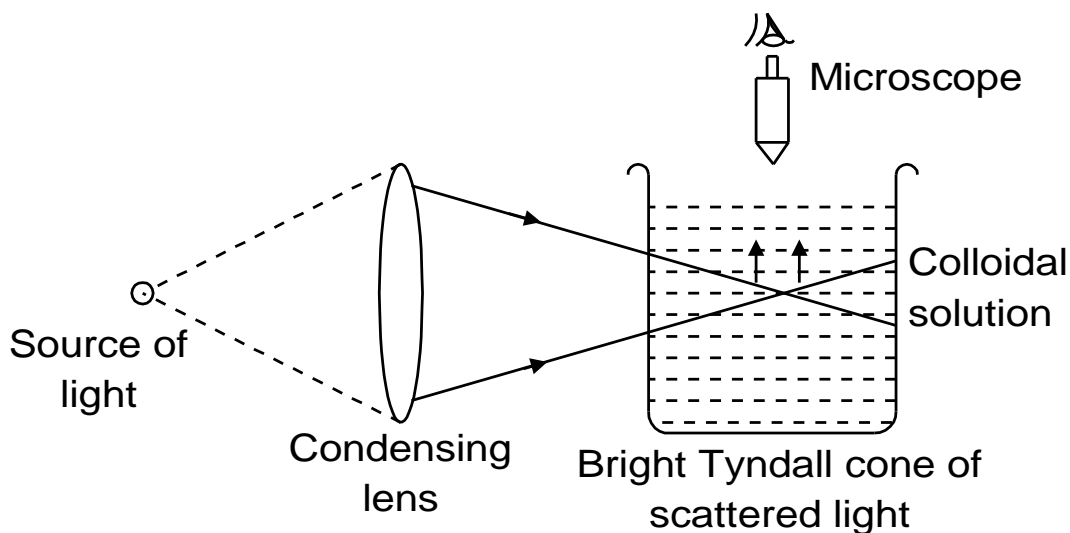
colligative properties of a colloidal solution have quite low values when compared to true solution having same concentration. However, the low osmotic pressure of a colloidal solution is measurable and can be used to determine the molecular weight of colloidal particles.

6.3 Filterability

The size of solute particles is smaller than the pore size of filter paper and therefore, they can readily pass through a filter paper. Colloidal particles, however cannot pass through ultra filters, parchment paper or animal membrane.

6.4 Tyndall Effect

When a strong beam of light is passed through a colloidal solution placed in a dark place, the path of light gets illuminated as a bluish light. This is known as Tyndall effect and is caused by the scattering of blue part of light by the colloidal particles. The scattering is caused if the size of particles is of the order of wavelength of light. The same effect is not observed when the light is passed through a true solution as the size of solute particles is too small to cause any scattering.



6.5 Visibility

Colloidal particles are too small to be seen with naked eye. But they become visible as bright spots against dark background when viewed through an ultramicroscope due to scattering of light caused by them.

6.6 Mechanical Properties

Brownian movement:

If the scattered light is viewed from the top, through a microscope, points of light originating from the individual colloidal particles can be seen. The colloidal particles of a colloidal solution when viewed through an ultramicroscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and hence known as Brownian movement. It is caused by the uneven impacts of the particles of the dispersion medium on the colloidal particles. As the size of the particles increases, the probability of uneven impacts decreases and the Brownian movement becomes slow. When the dispersed particles acquire the dimensions of suspension, no Brownian movement is observed.

Diffusion:

Colloidal particles like solute particles of a true solution diffuse from a region of higher concentration to that of lower concentration. However, colloidal particles diffuse at a slower rate due to their large size and high molecular mass.

Sedimentation:

The colloidal particles tend to settle down very slowly under the influence of gravity.

The sedimentation or the rate of settling down can be increased by ultracentrifuge.

6.7 Electrophoresis or Cataphoresis

The particles of the colloidal solution carry same type of charge, either positive or negative. The dispersion medium carries an equal and opposite charge. The colloidal solutions as a whole are electrically neutral. The origin of electrical charge on colloidal particles could be due to frictional electrification, electron captures or preferential adsorption of ions from solutions depending on the method used for the preparation of colloidal solutions. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form aggregates. This makes a colloidal solution stable and the colloidal particles do not settle down

Some of the common positively and negatively charged colloids are given below:

Positively charged Sol:

$\text{Fe}(\text{OH})_3$ sol, $\text{Cr}(\text{OH})_3$ sol, $\text{Al}(\text{OH})_3$ sol, $\text{Ca}(\text{OH})_2$, TiO_2 , dyes like methylene blue and haemoglobin.

Negatively charged Sol:

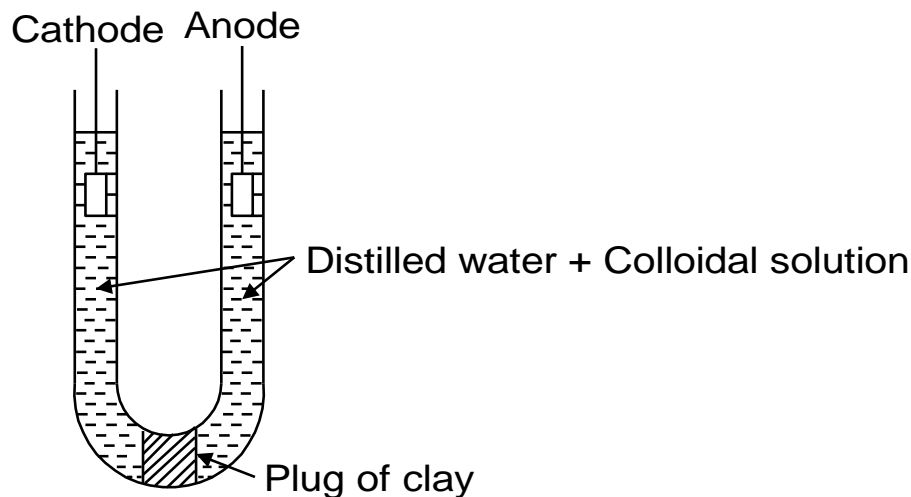
As_2S_3 sol, Sb_2S_3 sol, CdS sol, Au sol, Cu sol, Ag sol and acid dyes like congo red.

The existence of charge is shown by passing electric current through two electrodes when all the colloidal particles move towards the same electrode either cathode or anode. Positively charged colloidal particles move towards negatively charged cathode whereas negatively charged colloidal particles move towards positively charged anode. The movement of colloidal particles under the influence of electric field is called electrophoresis or cataphoresis.

Electro-osmosis:

If the dispersed phase is prevented from moving, the application of an EMF will, however result in movement of the dispersion medium. This is the basis of the phenomenon of *electro-osmosis* i.e., the passage of dispersion medium of a colloid through a porous diaphragm under the influence of an applied electric

field. This can be demonstrated in the following way. In the figure below, the plug of clay provides stationary negatively charged colloidal particles.



Electro-osmosis

Water, in contact with clay, must therefore carry a positive charge. Under the influence of an electric field, water will be found to move towards the cathode.

7. COAGULATION OF COLLOIDAL SOLUTIONS

A colloidal solution is stabilised by small amount of an electrolyte. But if the electrolyte is present in higher concentration, then the ions combine with colloidal particles and neutralise them. Once discharged, the colloidal particles unite together to form bigger particles and hence the coagulation takes place. The precipitation of a colloidal solution through induced aggregation by the addition of a suitable electrolyte is called coagulation or flocculation.

Certain minimum concentration of an electrolyte is needed to cause coagulation of a particular sol. *The minimum amount of an electrolyte (in millimoles) that must be added to one litre of a colloidal solution so as to cause its complete coagulation is called coagulation or flocculation value of the electrolyte.*

The coagulation value of an electrolyte varies from electrolyte to electrolyte. Hardy and Schulze studied the coagulation behaviour of various electrolytes and

presented their observations in the form of *Hardy–Schulze rule*, which states that:

- (i) The ions carrying charge opposite to that of sol particles are effective in causing the coagulation of the sol.
- (ii) Coagulating power of an electrolyte is directly proportional to the valency of the ions causing coagulation.

Thus, for the coagulation of negatively charged sols such as As_2S_3 , Al^{3+} ions are more effective than Ba^{2+} ions, which are more effective than Na^+ ions. In the same way, for the coagulation of positively charged sols such as $\text{Fe}(\text{OH})_3$, PO_4^{3-} ions are more effective than SO_4^{2-} ions which are more effective than Cl^- ions.

Other methods used to cause coagulation of colloidal solution are as follows:

(i) BY MUTUAL PRECIPITATION:

When two oppositely charged sol such as $\text{Cr}(\text{OH})_3$ and Sb_2S_3 are mixed in equimolar proportion, they neutralise each other and get coagulated.

(ii) BY ELECTROPHORESIS:

During electrophoresis of a sol, the colloidal particles move towards oppositely charged electrode. The particles touch the electrode, lose charge and get coagulated.

(iii) BY REPEATED DIALYSIS:

The stability of a sol is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by repeated dialysis, the sol will get coagulated.

(iv) BY HEATING:

Even simple heating may coagulate the sol.

PROTECTIVE COLLOIDS–GOLD NUMBER:

Lyophilic sols are reversible and are practically not affected by the electrolytes. Even if coagulated due to evaporation of dispersion medium, they can easily be brought back to colloidal solutions simply by shaking with some quantity of dispersion medium. Lyophobic sols, on the other hand are irreversible and are highly sensitive to the presence of electrolytes. They can be easily coagulated by

the addition of electrolytes beyond a certain minimum concentration. Once coagulated they cannot be revived back to colloidal solutions. However, addition of a small amount of lyophilic sol to a lyophobic sol, the former exerts a protecting influence on the latter against coagulation by electrolyte. For example, a gold sol or a silver sol protected by gelatin, gum–arabic or egg albumin, may not be coagulated easily. Different lyophilic sols exert protective influence to different extent. The protecting power of a protective colloid is expressed in terms of **Gold number** defined as below:

The number of milligram of the protective colloid that just prevents coagulation of 10 ml of standard gold sol when 1 ml of 10% solution of NaCl is added to it is called Gold number of the protective colloid.

Thus, smaller the gold number of a protective colloid, greater will be its protecting power. The gold numbers of a few protective colloids are given below:

Potato starch	:	25
Egg albumin	:	0.15 – 0.25
Gum Arabic	:	0.15 – 0.25
Haemoglobin	:	0.03
Gelatin	:	0.006

8. GELS

Certain colloidal systems have the property of setting to a semi solid, jelly–like form when they are present at high concentration. Such a process is called gellation and the colloidal systems with jelly–like form are called gels. Gelatin, gum Arabic, agar and processed cheese are the examples of gels. Gels possess rigid structure formed due to interlocking of particles of disperse phase and create a loose framework. The particles of dispersion medium are trapped into the loose framework. The degree of rigidity varies from substance to substance. When gels are allowed to stand for a long time, they give out small quantity of

trapped liquid, which accumulates on the surface. This is called *syneresis* or *weeping*.

9. APPLICATIONS OF COLLOIDS

Colloidal particles of a colloidal solution carry either positive or negative charge, which makes them good conductors. This property of colloids is made use of in several applications. Some of the applications are given below:

9.1 Rubber Plating

This involves electro-deposition of negatively charged rubber particles from rubber sol on handles of different tools, rubber gloves etc.

9.2 Sewage Disposal

The sewage water contains impurities, which have colloidal dimensions, carry charge and therefore, do not settle down. These particles can be removed by electrophoresis. The sewage water is passed through a tunnel fitted with two electrodes. A high potential difference is applied when all the colloidal particles move to the oppositely charged electrodes, get neutralised and are coagulated.

9.3 Cottrell Smoke Precipitator

A number of industries release large quantity of smoke into the air causing air pollution.

The smoke contains unburnt colloidal carbon particles. It can be made free of colloidal particles by installing cottrell precipitator in the chimney of an industrial unit releasing smoke. It consists of two metal rods charged to high potential difference of the order of 30,000 V. The carbon particles get deposited and finally precipitated down while the gases free from carbon particles leave the chimney.

9.4 Artificial Rain

Clouds consist of colloidal water particles dispersed in air. They carry charge. When oppositely charged colloidal particles are sprayed over clouds, the water particles get neutralised and are coagulated into bigger water drops causing artificial rain.

9.5 Purification of Water

Colloidal particles present in impure water can be coagulated by adding small amount of potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. The ionic species furnished by alum cause coagulation of colloidal impurities.

9.6 Formation of Delta

The muddy river water contains colloidal particles of sand and clay, which carry negative charge. The sea water, on the other hand contains positive ions such as Na^+ , Mg^{2+} and Ca^{2+} . As the river water meets seawater, these ions discharge the sand or clay particles, which are precipitated as *delta*.

9.7 Foods

Milk is an emulsion of butterfat in water protected by a protein, casein. Salad dressing, gelatin desserts, fruit jellies and whipped cream are other examples. Bread, bun, cake are dispersion of air in baked dough.

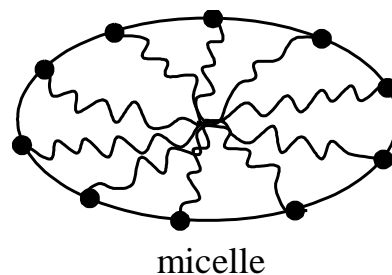
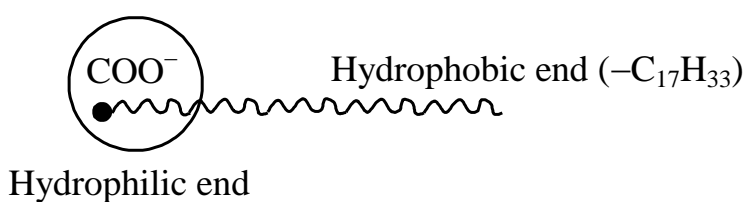
9.8 Medicines

Medicines in finely divided colloidal form are more effective and are easily absorbed in our system. Many ointments such as skin ointment, lotion, creams and antibiotics such as penicillin and streptomycin are produced in colloidal form.

10. ASSOCIATED COLLOIDS

Soaps and detergents form true solutions in water when their concentration is low. However, at high concentration, they form colloidal solutions, in which colloidal particles are formed by agglomeration of large number of soap or detergent molecules. These type of colloids are called associated colloids and the agglomerated colloidal particles are called micelles. The formation of micelles takes place above a certain concentration called critical micellization concentration (CMC). Each micelle system has a specific value of CMC.

The soap and detergent molecules have a hydrophobic group at one end and a hydrophilic group at the other end. Such type of molecules are called surfactant molecules. Sodium oleate ($\text{C}_{17}\text{H}_{33}\text{COO}^-\text{Na}^+$) is a typical example of soap. The long hydrocarbon part of oleate anion is the hydrophobic end while $-\text{COO}^-$ part is the hydrophilic end. The CMC value of sodium oleate is 3×10^{-3} M. When the concentration exceeds CMC, the hydrophobic parts of $\text{C}_{17}\text{H}_{33}\text{COO}^-$ anions are repelled by solvent molecules and are compelled to come close to each other. The lyophilic part i.e. COO^- ions spreads out due to attraction by the solvent molecules forming micelles, which are of colloidal dimensions.



Cleansing action of soap

A soap molecule contains a non polar hydrophobic group and a polar hydrophilic group. The dirt is held on to the surface of clothes by the oil or grease, which is present there. Since grease or oil is not soluble in water, the dirt particles cannot be removed simply by washing the clothes with water. When soap is applied, the non polar hydrophobic end dissolves the oil or grease. While

the polar -COO^- groups remain dissolved in water. In this way each oil droplet is surrounded by negatively charged -COO^- groups and hence cannot coalesce. These oil droplets containing dirt can be washed away with water.

11. EMULSIONS

Emulsions are the colloidal solutions in which both the disperse phase and the dispersion medium are liquids.

11.1 Types of Emulsions

There are two types of emulsions.

1. Oil in water type emulsions

In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. For example milk, vanishing cream etc.

2. Water in oil type emulsions

In this type of emulsions water is the dispersed phase and oil is the dispersion medium. For example butter, cod liver oil, cold cream etc.

11.2 Identification of Emulsions

The following tests can be employed to distinguish between the two types of emulsions.

1. Dye test:

An oil soluble dye is added to the given emulsion. If the background becomes coloured, the emulsion is water in oil type and if the tiny droplets become coloured, the emulsion is oil in water type.

2. Dilution test:

If the emulsion can be diluted with water, this indicates that the emulsion is oil in water type. In case the emulsion cannot be diluted with water, it is water in oil type.

11.3 PREPARATION OF EMULSIONS

Emulsion can be prepared by mixing oil and water and shaking them vigorously in the presence of small quantity of a substance known as emulsifying agent or emulsifier. It is essential to add emulsifier in order to prepare stable emulsions. Such emulsions have properties, which resemble somewhat those of lyophilic sols e.g. high viscosity, relatively high concentrations and stability to electrolytes. An excess of electrolyte may salt out the emulsifier and so cause instability. Emulsifying agents fall roughly into three categories.

(i) These are either, the long chain compounds with polar groups, such as the soaps and long chain sulphonic acids and sulphates, all of which produce a considerable decrease in the oil–water interfacial tension. When olive oil and water are shaken together, very little emulsification occurs, but the addition of a small amount of NaOH results in the formation of a stable emulsion. The sodium soap formed by hydrolysis acts as the emulsifier. It appears that certain optimum concentration of emulsifier is required to obtain stable emulsions. Any concentration of the emulsifier more or less than this does not cause effective stabilisation.

(ii) There are substances of a lyophilic nature such as proteins, e.g. casein in milk and gums.

(iii) Insoluble powders for example, basic sulphates of iron, copper or nickel, finely divided lead sulphate and ferric oxide and lamp black stabilise a number of emulsions. The soaps of alkali metals favour the formation of oil in water emulsions, but those of the alkaline earth metals and of zinc, iron and aluminium give water in oil emulsions. Similarly, the basic sulphates stabilise oil in water emulsions whereas opposite type is formed when finely divided carbon is the emulsifying agent.

11.4 Application of Emulsions

Some of the important applications of emulsions are as given below:

1. In medicines

A number of pharmaceutical preparations are emulsions. These are oil in water type emulsion, which are easily acted upon by the digestive juices in the stomach.

2. In Metallurgical Operations

The sulphide ores are concentrated by froth flotation process, which involves the treatment of crushed ore with emulsion of pine oil.

12. SOME SOLVED EXAMPLES

Illustration 1.

The coagulation of 100 cm^3 of gold solution is completely prevented by addition of 0.25 g of starch to it before adding 10 ml of 10% NaCl solution. The gold number of starch is

- (a) 0.025 (b) 0.25
(c) 2.5 (d) 25

Solution:

Gold number of starch is the milligrams of starch added to 10 ml of standard gold sol just to prevent coagulation of Au sol when 1 mL of 10% NaCl is added to it. 10 mL of 10% NaCl is added to 100 mL of gold sol. In other words 1 mL of 10% NaCl is added to 10 mL of gold sol.

Quantity of starch added to 10 mL of gold sol = 25 mg

\therefore Gold number of starch = 25.

\therefore (d)

Illustration 2.

For adsorption of a gas on a solid, the plot of $\log x/m$ vs $\log P$ is linear with slope equal to: (n being a whole number)

- (a) k (b) $\log k$
(c) n (d) $1/n$

Solution:

For adsorption of a gas on the surface of a solid, the extent of adsorption (x/m) varies with P as given below:

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

where n is a whole number

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P.$$

Plot of $\log \frac{x}{m}$ vs $\log P$ is linear with a slope of $(1/n)$.

(d)

Illustration 3.

For the coagulation of 100 mL of As_2S_3 sol, 5 mL of 1 M NaCl is required. The flocculation value of NaCl is

(a) 50

(b) 5

(c) 47.6

(d) None of these

Solution:

Millimoles of NaCl added = 5

Volume of the sol containing NaCl solution = 100 mL.

Flocculation value is the amount of electrolyte (in millimoles) that must be added to 1 L of the colloidal solution so as to bring about complete coagulation.

$$\text{Flocculation value of NaCl} = \frac{5 \times 1000}{100} = 50 \text{ m mol L}^{-1}.$$

\therefore (a)

Illustration 4.

Which of the following colloid can be prepared by electrical dispersion as well as reduction method?

(a) Sulphur

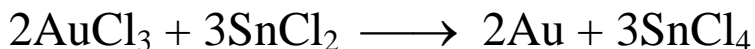
(b) Ferric hydroxide

(c) Arsenious sulphide

(d) Gold

Solution:

Of the given four options, only gold sol can be prepared by electrical dispersion method i.e., Bredig's arc method as well as reduction method when AuCl_3 is reduced by SnCl_2



(d)

Illustration 5.

Silver iodide is used for producing artificial rains because silver iodide

- (a) is easy to spray at high altitude (b) is insoluble in water
(c) has crystal structure similar to ice (d) is easy to synthesize

Solution:

Silver iodide is used for producing artificial rains because it has crystal structure similar to ice. When AgI is sprayed over clouds, it causes water droplets of clouds to coalesce to form bigger water drops and induce rains.

(c)

Illustration 6.

The particles of a particular colloidal solution of arsenic trisulphide (As_2S_3) are negatively charged. Which 0.0005 M solution of the following salts would be most effective in coagulating this colloidal solution, KCl, MgCl_2 , AlCl_3 or Na_3PO_4 ? Explain.

Solution:

Since As_2S_3 is a negatively charged colloidal sol, hence positively charged ion will cause its coagulation. By Hardy–Schulze rule “greater the charge on ion, greater the coagulating power to coagulate oppositely charged colloidal sol”, hence out of K^+ , Mg^{2+} , Al^{3+} and Na^+ , Al^{3+} would be most effective in coagulating this colloidal solution.

Illustration 7.

A sample of charcoal weighing 6 g was brought into contact with a gas contained in a vessel of one litre capacity at 27°C . The pressure of the gas was found to fall from 700 to 400 mm of Hg. Calculate the volume of the gas (reduced to STP) that is adsorbed per gram of the adsorbent under the condition of the experiment (density of charcoal sample is 1.5 g cm^{-3}).

Solution:

The adsorption is taking place in a closed vessel, thus when pressure falls there is correspondingly increase in volume and to keep volume constant, excess of the volume of the gas would be adsorbed.

Using $P_1V_1 = P_2V_2$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{700 \times 1000}{400} = 1750 \text{ ml}$$

Actual volume of the flask = 1000 – volume of charcoal

$$= 1000 - \frac{6}{1.50} = 996 \text{ ml}$$

Volume of the gas adsorbed = 1750 – 996 = 754 ml

Volume of the gas adsorbed per gram of charcoal = $\frac{754}{6} = 125.67 \text{ ml g}^{-1}$

Volume of the gas adsorbed per gram at STP $\left(\text{using } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \right)$

$$= \frac{125.67 \times 400 \times 273}{300 \times 760} = 60.19 \text{ ml g}^{-1}.$$

Illustration 8.

In the lower layer of the atmosphere, there is a great deal of dust. When the weather is fine, it is possible to see the magnificent red colour of the setting sun. What has this observation to do with colloids?

Solution:

Dust in the atmosphere is often colloidal. When the sun is low down on the horizon, light from it has to pass through a great deal of dust to reach our eyes. The blue part of the light is scattered away from our eyes. We see the red part of the spectrum, which remains. Red sunsets are the result of Tyndall effect on a large scale.

Illustration 9.

1 g of active charcoal is taken and its surface area is $3.01 \times 10^2 \text{ m}^2/\text{g}$. It adsorbs 100 ml of 0.5 M CH_3COOH in a single layer. After adsorption, its molarity becomes 0.49M. Find the surface area of the charcoal covered by one molecule of acetic acid.

Solution:

$$\text{Surface area} = 3.01 \times 10^2 \times 1 = 3.01 \times 10^2 \text{ m}^2$$

$$\text{Number of CH}_3\text{COOH molecules} = 0.001 \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$$

$$\begin{aligned}\text{Surface area of one molecule} &= \frac{3.01 \times 10^2}{6.023 \times 10^{20}} = 0.5 \times 10^{-18} \\ &= 5 \times 10^{-19} \text{ m}^2\end{aligned}$$

Illustration 10.

A solution of palmitic acid ($M = 256 \text{ g mol}^{-1}$) in benzene contains 4.24 g of acid per dm^3 . When this solution is dropped on a water surface the benzene evaporates and the palmitic acid forms a monomolecular film of the solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area covered by one palmitic acid molecule may be taken to be 0.21 nm^2 .

Solution:

Let the volume of palmitic acid solution required to cover the desired area of 500 cm^2 be $V \text{ ml}$.

$$\begin{aligned}\text{Number of molecules of palmitic acid in } V \text{ ml} &= \frac{4.24 \times V \times 6.023 \times 10^{23}}{1000 \times 256} \\ &= 9.976 \times 10^{18} \times V\end{aligned}$$

$$\begin{aligned}\text{The area covered by these molecules} &= 9.976 \times 10^{18} \times V \times 0.21 \times 10^{-14} \text{ cm}^2 \\ &= 2.095 \times 10^4 \times V \text{ cm}^2\end{aligned}$$

But this area is equal to 500 cm^2

$$\therefore 2.095 \times 10^4 \times V = 500$$

$$\text{or } V = 0.024 \text{ ml.}$$