

# SURFACE CHEMISTRY

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## 1. ADSORPTION

Surface chemistry is that branch of chemistry which deals with the study of the phenomenon occurring at the surface or interface, i.e., at the boundary separating two bulk phases.

### 1.1 Introduction to Adsorption

Adsorption is a surface phenomenon. In this process, accumulation or concentration of a substance takes place at the surface or interface as compared to the bulk phases.

Hence **Adsorption** is defined as the phenomenon of existence of a substance in different concentrations at the surface of another substance than in the bulk phases.

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 solutions. The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**. The adsorption of gases on the surface of metals is called **occlusion**.

### 1.2 Difference between Adsorption and 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 them and this phenomenon is known as **sorption**.

### 1.3 Types of Adsorption

Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified as:

#### i) Physical adsorption (Physisorption)

In physical adsorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are of the weak Vander Waals' type. Since the forces of attraction are weak, the process of Physisorption can be easily reversed by heating or decreasing the pressure of the adsorbate (as in the case of gases).

#### ii) Chemical adsorption (Chemisorption)

In Chemisorption, the forces of attraction between the adsorbate and the adsorbent are very strong; the molecules of adsorbate form chemical bonds with the molecules of the adsorbent present in the surface.

The differences between Physisorption and Chemisorption are summarized in the below table.

Physisorption	Chemisorption
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(Physical adsorption)	(Chemical adsorption)
<ol style="list-style-type: none"> <li>Forces of attraction are van der Waals' forces.</li> <li>Depends on nature of gas. Easily liquefiable gases are adsorbed readily.</li> <li><math>\Delta_s</math> is always negative.</li> <li>Equilibrium is attained readily and it is reversible.</li> <li>Forms multimolecular layers on adsorbent surface.</li> <li>No compound formation takes place.</li> <li>This type of adsorption occurs at low temperature; It decreases with increase in temperature.</li> <li>Increase of pressure increases adsorption</li> </ol>	<p>Forces of attraction are chemical bond forces.</p> <p>Much more specific and depends upon the nature of the both the adsorbate and adsorbent.</p> <p><math>\Delta_s</math> is positive for endothermic.</p> <p>Equilibrium is attained slowly and mostly not reversible.</p> <p>Forms unimolecular layer.</p> <p>Surface compounds are formed.</p> <p>This type of adsorption first increases with increase of temperature. This effect is called activated adsorption.</p> <p>High pressure is favourable. Decrease of pressure does not cause desorption.</p>

### 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 20-40 kJ mol<sup>-1</sup>. Chemical adsorption, on the other hand involves strong chemical bond formation and the heat of chemisorptions is quite high, of the order of 80-400 kJ mol<sup>-1</sup>.

### 1.4 Adsorption of Gases on Solids

#### Factors affecting 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 (adsorbate):

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<sub>3</sub>, CH<sub>4</sub>HCl, Cl<sub>2</sub>, SO<sub>2</sub>, CO etc. are adsorbed more than permanent gases like H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> etc. Chemisorption is specific in nature. Therefore, only those gases will be adsorbed which form chemical bonds with it.

#### (ii) Nature of solid (adsorbent):

Activated charcoal is the most common adsorbent for easily liquefiable gases. Poisonous gases such as CH<sub>4</sub> and CO fall in this group. Therefore, it is used in gas

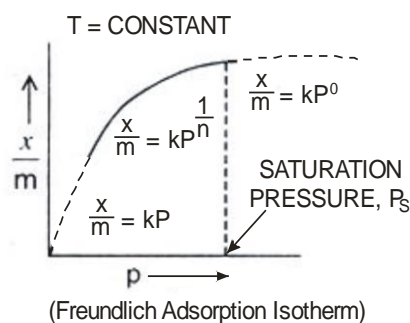
masks. Other gases such as  $O_2$ ,  $H_2$  and  $N_2$  adsorb more on metals such as Ni, Pt and Pd.

**(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 a solid, 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.



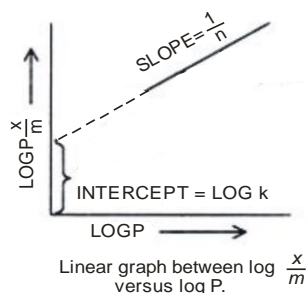
At a certain pressure the adsorption reaches a maximum value i.e. the adsorption becomes saturated and the corresponding pressure is called saturation pressure ( $P_s$ ). Beyond this pressure the adsorption remains constant. At low pressures,  $x/m$  varies linearly with  $p$

$$\therefore \frac{x}{m} \propto p^1$$

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

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

This is called **Freundlich adsorption isotherm**.



**Langmuir isotherm:** Freundlich isotherm fails at high pressure and only for physical adsorption. Langmuir isotherm is represented as

$$\frac{x}{m} = \frac{ap}{1 + bp} \quad (\text{a and b are constants})$$

At very high pressure, ( $bp \gg 1$ )

$$\frac{x}{m} = \frac{a}{b}$$

At very low pressure, ( $bp \ll 1$ )

$$\frac{x}{m} = ap$$

**Example:**

The following data were obtained for the adsorption of CO on 3g of charcoal at 0°C

Pressure, P (mm)	180	540
Volume of gas adsorbed, x (cc)	16.5	38.1

Reduced to S.T.P

Calculate the values of the constants k and n used in Freundlich equation.

**Solution:**

According to Freundlich adsorption isotherm equation,

$$\frac{x}{m} = k p^{(1/n)} \quad \text{or} \quad \log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Substituting the values of the two given sets, we get

$$\text{For 1}^{\text{st}} \text{ set: } \log \frac{16.5}{3} = \log k + \frac{1}{n} \log 180 \quad \dots \dots \dots \text{(i)}$$

$$\text{For 2}^{\text{nd}} \text{ set: } \log \frac{38.1}{3} = \log k + \frac{1}{n} \log 540 \quad \dots \dots \dots \text{(ii)}$$

Subtracting eqn (i) from (ii), we get

$$\log \frac{38.1}{16.5} = \frac{1}{n} \log \frac{540}{180}$$

$$\log 2.3091 = \frac{1}{n} \log 3 \quad \text{or } n = 1.31$$

Substituting the value of n in eqn (i), we get

$$\log 5.5 = \log k + \frac{1}{1.31} \log 180$$

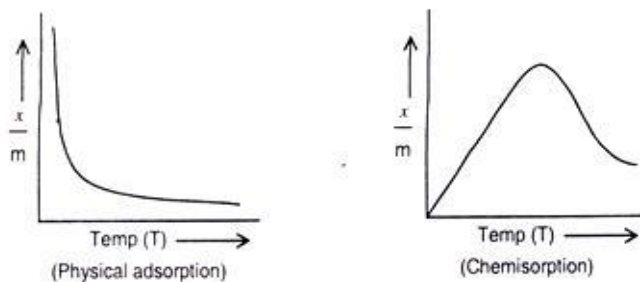
$$\text{or } 0.7404 = \log k + 1.7216$$

$$\log k = -0.9812$$

$$\therefore k = 0.1044 \text{ cm}^3 \text{ g}^{-1} \text{ (when pressure is in mm).}$$

**(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 case of physical adsorption, x/m decreases with increase in temperature. However, 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 chemisorptions require 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 inter-particle spaces will be too small to allow penetration of gas molecules.

#### Competing adsorption:

There is always a competition between different adsorbate to adsorb on the adsorbent. A strongly adsorbable 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.

### 1.5 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.

#### Factors affecting adsorption from solutions are:

1. Nature of the adsorbate and the adsorbent
2. Temperature: The adsorption decreases with increase of temperature.
3. Surface area of the adsorbent: the greater the surface area of the adsorbent, greater is the adsorption.
4. Concentration of the solute in the solution:

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

$$\frac{x}{m} = k C^{\frac{1}{n}} \text{ (Where } n > 1\text{)}$$

Taking logarithm, it becomes

$$\log x/m = \log k + 1/n \log C$$

this equation implies that a plot of  $\log(x/m)$  against  $\log C$  should be a straight line with slope  $1/n$  and intercept  $\log k$ .

This is applicable for small ranges of concentrations.

### 1.6 Applications of Adsorption

Some of the applications of adsorption are as follows:

- I. In Production of high vacuum: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.
  - II. Gas masks: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.
  - III. Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
  - IV. Removal of colouring matter from solutions: Animal charcoal removes colours of solutions by adsorbing coloured impurities.
  - V. Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of  $H_2SO_4$  by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
  - VI. Separation of inert gases: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
  - VII. 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 sugarcane juice in the manufacture of sugar.
  - VIII. Froth floatation process
  - IX. Adsorption indicators: Various dyes, which owe their use to adsorption, have been introduced as indicators particularly in precipitation titration. For example,  $KBr$  is easily titrated with  $AgNO_3$  using eosin as an indicator.
  - X. Chromatographic analysis: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.
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## 2. CATALYSIS

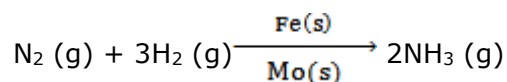
### 2.1 Introduction to Catalysis

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.

A catalyst is a substance that increases the rate of a reaction by providing an alternate path of lower activation energy. Since catalysts are not consumed in a reaction, very small quantities of catalyst are required to enhance a reaction rate.

#### Promoters and Poisons

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



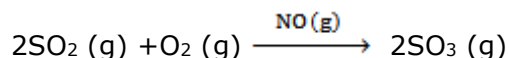
### 2.2 Characteristics of Catalytic Reactions

- The amount of catalyst and chemical composition at the end of the reaction remains unchanged; it may, however, undergo considerable change in physical form.
- A small quantity of the catalyst is capable of producing the desired effect.
- The action of a catalyst is specific to a large extent.
- The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.
- A catalyst does not alter the final state of equilibrium in a reversible reaction.

### 2.3 Types of Catalysts

**i) Positive catalysis:** If a catalyst increases the speed of reaction, it is called a positive catalyst and the phenomenon is called positive catalysis.

#### Examples:



Oxidation of  $\text{SO}_2$  in presence of NO or  $\text{V}_2\text{O}_5$  are examples of positive Catalysis.

**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:

Glycerol is used to slow down the decomposition of hydrogen peroxide. Oxidation of chloroform in presence alcohol is an example of negative catalysis.

**iii) Auto catalysis:** In this type of catalysis, the reaction product itself is the catalyst for that reaction.

#### Example:

Addition of a few crystals of  $\text{MnSO}_4$  greatly accelerates the reduction by oxalic acid of purple permanganate to the nearly colorless manganese (II). When no manganese

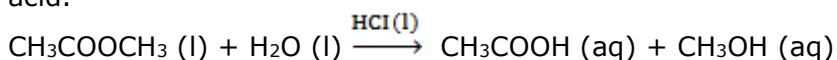


(II) ion is added, the reaction initially proceeds slowly, but the rate gradually increases because the product auto catalyzes the reaction.

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

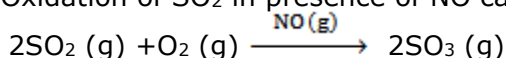
**Examples:**

1) Hydrolysis of methyl acetate is catalyzed by H<sup>+</sup> ions furnished by hydrochloric acid.



Both the reactants and the catalyst are in the same phase (Liquids).

2) Oxidation of SO<sub>2</sub> in presence of NO catalyst

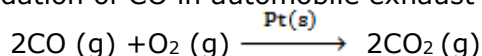


Both the reactants and the catalyst are in the same gaseous phase.

**v) Heterogeneous catalysis:** A catalytic process in which the catalyst and the reactants are in different phases is called heterogeneous catalysis. In heterogeneous catalysis the reaction starts at the surface of the solid catalyst hence this process is also called contact or surface catalysis.

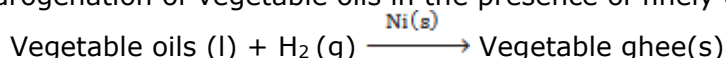
**Examples:**

1) Oxidation of CO in automobile exhaust by platinum catalyst



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

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



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

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

**Examples:**

- 1) 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.
- 2) The reduction of mercuric chloride (HgCl<sub>2</sub>) 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<sub>4</sub> and HgCl<sub>2</sub>, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of HgCl<sub>2</sub>.

## 2.4 Adsorption Theory of Heterogeneous Catalysis

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

exothermic process, the heat of adsorption is taken up by the surface of the catalyst, which is utilized in enhancing the rate of the reaction.

Another theory of heterogeneous catalysis is the **intermediate compound formation theory** which suggests that the reactants first combine with the catalyst to form an intermediate complex which decomposes to form the products and regenerates the catalyst.

The modern adsorption theory is the combination of the above two theories. According to this theory, there are free vacancies on the surface of solid catalyst.

The mechanism involves five steps:

- Diffusion of reactants to the surface of the catalyst.
- Adsorption of reactant molecules on the surface of the catalyst.
- Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate
- De-sorption 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.

## 2.5 Nature of Solid Catalysts

The nature of the solid catalyst has profound effects on heterogeneous catalytic reactions. Solid catalysts can be metals, semiconducting oxides and sulphides, insulating oxides and acids. These substances can be used in the pure form or in the form of mixtures. The catalysts can be crystalline, microcrystalline or amorphous.

Important features of solid catalysts:

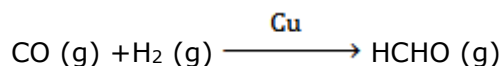
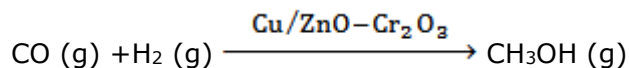
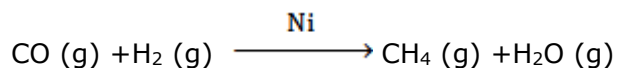
### 1. Activity:

The activity of a catalyst is its capacity to increase the speed of reaction. The reactant must adsorb reasonably strongly for the catalyst to be active but must not adsorb so strongly that they are immobilized and other reactants are left with no space on the catalyst surface adsorption. It has been found that for hydrogenation the catalytic activity increases as we go from group 5 metals to group 11 with maximum activity shown by group 7-9 elements of the periodic table.

### 2. Selectivity:

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.

For example, the reaction of CO with H<sub>2</sub> yields different products when different catalysts are used i.e,



### 3. Specificity:

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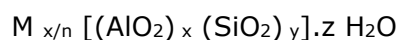
Action of a catalyst is highly specific (selective) in nature i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means a substance which acts as a catalyst in one reaction may fail to catalyze other reaction.

## 2.6 Shape - Selective Catalysis by Zeolites

The catalytic reaction that depends upon the structure of pores of the catalyst and the size of the reactant and product molecules is called shape/selective catalysis.

In such reactions, Zeolites are used as catalysts. Zeolites are good shape/selective catalysts because of their honeycomb-like structures. Zeolites are aluminosilicates i.e., three dimensional network silicates in which some silicon atoms are replaced by aluminium atoms. They are found in nature as well as synthesized for catalytic selectivity.

Zeolites are micro porous aluminosilicates of the general formula,



Where n is the charge of the metal cation,



z is the number of moles of water of hydration, which is highly variable.

Zeolites, before using as catalysts, are heated in vacuum so that the water of hydration is lost. As a result, zeolite becomes porous i.e., the cavities in the cage-like structure which were occupied by the water molecules become vacant. The size of the pores generally varies between 260 pm and 740 pm. Thus only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily.

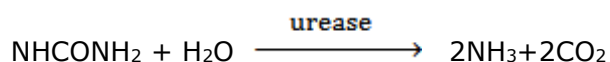
The reactions taking place in Zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the Zeolites. That is why these types of reactions are called 'shape-selective catalysis' reactions.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them so that a mixture of hydrocarbons is formed.

## 2.7 Enzyme Catalysis

Living organisms carry out thousands of chemical reactions which take place in dilute solution at ordinary temperature and pressure. For example they can use small molecules to assemble complex biopolymers such as proteins and DNA. Organisms can produce molecules that combat bacterial invaders. They can break down large, energy-rich molecules in many steps to extract chemical energy in small portions to drive their many activities.

Most of these reactions are catalyzed by biochemical catalysts called enzymes. Enzymes are proteins with high molar mass ranging from 15,000 to 1,000,000 g/mol. Enzymes are incredibly efficient catalysts. They increase rates by  $10^8$  to  $10^{20}$  times. Enzymes are also extremely specific: each reaction is generally catalyzed by a particular enzyme. Ureas, for example, catalyses only the hydrolysis of urea and none of the several thousand other enzymes present in the cell catalyses that reaction:



The remarkable specificity of enzymes results from the fact that each enzyme has a

specific, active site on its surface. When the reactant molecules, called the substrates of the reaction, bind at the active site, a chemical change is initiated. In most cases, substrates bind to the active site through intermolecular forces: H-bonds, dipole forces and other weak attractions.

### 2.7.1 Characteristics of Enzyme

The following characteristics are exhibited by enzyme catalysts:

1. **Highly efficient:** Enzymes are very efficient catalyst. They speed up the rate of a reaction by a factor of up to  $10^{20}$ .
2. **Highly specific nature:** Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyze more than one reaction.
3. **Small quantity:** Only small amounts of enzymes can be highly efficient.
4. **Highly active under optimum temperature:** The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalyzed reactions.
5. **Highly active under optimum pH:** The rate of an enzyme-catalyzed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.
6. **Enzyme activators (co-enzymes):** The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably. Activators are generally metal ions such as  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e.,  $\text{Na}^+$  ions are catalytically very active.
7. **Enzyme inhibitors and poisons:** Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

### 2.7.2 Mechanism of Enzyme Catalysis:

The most accepted mechanism of enzyme catalyzed reaction is known as Lock and Key mechanism. According to the lock-and-key model, when the 'key' (substrate) fits the 'lock' (active site), the chemical change begins. However, modern X-ray crystallographic and spectroscopic methods show that in many cases, the enzyme changes shape when the substrate lands at the active site. This induced-fit model of enzyme action pictures the substrate inducing the active site to adopt a perfect fit, rather than a rigidly shaped lock and key.

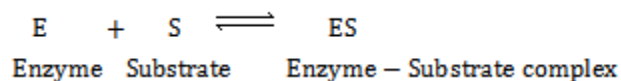
Lock and key mechanism of enzyme action:

- Formation of complex between enzyme and substrate (ES)
- Conversion of this complex to an enzyme-intermediate complex (EI)
- Further conversion to a complex between enzyme and product (EP)
- Dissociation of the enzyme - product complex, leaving the enzyme unchanged.

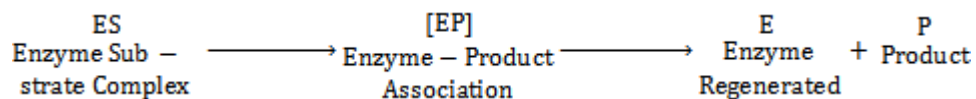
The enzyme catalyzed reactions take place in two steps as follows:

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1. Formation of enzyme-substrate complex.



2. Dissociation of enzyme-substrate complex to form the products.



The rate of formation of product depends upon the concentration of Enzyme and substrate.

## 2.8 Catalysts used in industries

The following are the Catalyst used in industries for various processes.

1. Haber's process for manufacture of ammonia  
**Catalyst:** Finely divided iron + Mo as promoter
2. Ostwald's process for manufacture of nitric acid  
**Catalyst:** Platinised asbestos
3. Lead chamber process for manufacture of  $\text{H}_2\text{SO}_4$   
**Catalyst:** Nitric oxide
4. Contact process for manufacture of  $\text{H}_2\text{SO}_4$   
**Catalyst:** Platinised asbestos or vanadium pentoxide
5. Deacon's process for manufacture of chlorine  
**Catalyst:** Cupric chloride
6. Bosch's process for manufacture of hydrogen  
**Catalyst:** Ferric oxide + chromic oxide as promoter
7. Synthesis of methanol  
**Catalyst:** Zinc oxide + chromic oxide as promoter
8. Hydrogenation of vegetable oils  
**Catalyst:** Finely divided Nickel

### 3. COLLOIDAL STATE

#### 3.1 Introduction to Colloidal State

While studying the diffusion of solutions through an animal membrane, **Thomas Graham** (1861) observed that certain substances such as sugar, urea, sodium chloride etc. in the dissolved state passed through the membrane, while the solutions of substances such as glue, gelatin, gum Arabic etc. did not. This observation led him to classify the soluble substances into two categories:

##### (i) Crystalloids

##### (ii) Colloids

According to Graham, crystalloids were those substances which could be obtained in crystalline form and whose solutions were able to pass through an animal membrane. On the other hand, colloids were those substances which were amorphous in nature and whose solutions were unable to pass through the membrane. However, it was soon realized that the classification of dissolved substances made by Graham was not tenable because certain substances could act both as crystalloids and colloids.

Later on it was found that the diffusibility of crystalloids and non-diffusibility of colloids through an animal membrane was due to the difference in the size of their particles. Crystalloids formed smaller particles in solutions and therefore passed through the membrane. On the other hand, colloids formed larger particles (larger than the dimensions of the pores of the membrane) in solutions and were unable to pass through the membrane.

On the basis of the size of particles, the systems containing dispersed particles can be divided into following three categories.

#### 1. True solutions

True solutions are homogeneous system and have the size of dispersed particles less than 1 nm, i.e.  $10^{-9}$ . The particles of solute present in a true solution are either single molecules or ions and are homogeneously distributed throughout the solutions. These particles are invisible and cannot be seen even with a microscope. Due to very small size of dispersed particles, true solutions pass through ordinary filter paper as well as through animal membranes. Sodium chloride, sugar, urea etc. form true solutions in water.

#### 2. Colloidal solutions

Colloidal solutions are heterogeneous systems and have the size of dispersed particles lying between 1 nm-1000 nm (i.e.  $10^{-9}$ - $10^{-6}$  m). The particles in a colloidal solution are thus larger particles and are referred to as colloidal particles. Although colloidal particles are larger in size but can be seen only with the help of an ultra microscope. Colloidal solutions can pass through ordinary filter paper but not through an animal membrane, Gum Arabic, gelatin, glue etc. form colloidal solutions when dispersed in water.

#### 3. Suspensions

Suspensions are also heterogeneous system and have still larger particles. The size of particles in a suspension is more than 1000 nm (i.e.,  $>10^{-6}$ m). These particles are either visible to naked eye or can be seen under a microscope. The suspensions neither pass through an animal membrane nor through an ordinary filter paper. Stirred muddy water is an example of suspensions.

Colloidal solutions are intermediate of true solutions and suspensions. Colloidal solutions are not only formed by certain specific substances as mentioned above but

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they can be obtained from any substance by subdividing or aggregating its particles in the size ranges 1 nm-1000 nm. Practically, all substances can be made to exist in colloidal form. Therefore instead of talking of colloidal solution, it would be more appropriate to talk of the colloidal state of matter.

The colloidal state of matter may be defined as follows:

The colloidal state matter is the state in which the size of the particles lies in between range are called **Colloidal systems**.

Table: Characteristics of True solutions, Colloidal solutions and Suspensions

S.No.	Property	True solution	Colloidal solution	Suspension
1.	Particle size	Less than 1 nm (i.e. $10^{-9}\text{m}$ )	Between 1 nm-1000nm (i.e. $10^{-9}\text{m}$ - $10^{-6}\text{m}$ )	Greater than 100nm (i.e. $10^{-6}\text{m}$ )
2.	Nature	Homogeneous	Heterogeneous	Heterogeneous
3.	Visibility of particles	Invisible	Visible under ultra-microscope	Visible to naked eye or under microscope
4.	Appearance	Transparent	Generally transparent but may show translucence	Opaque
5.	Filterability	Passes easily through ordinary filter paper as well as animal membranes	Passes easily through ordinary filter paper but not through animal membranes	Does not pass either through ordinary filter paper or through animal membranes.
6.	Setting of particles under gravity	Particles do not settle	Colloidal particles do not settle under gravity. However, they can be made to settle under high speed centrifugation	Particles settle on standing
7.	Diffusion of particles	Diffuses rapidly	Diffuses slowly	Does not diffuse
8.	Scattering of light by particles (Tyndall effect)	Does not scatter light	Scatters light and exhibits Tyndall effect	Tyndall effect may be exhibited

### 3.1.1 Dispersed phase and Dispersion medium

**Dispersed phase:** The substance present in the form of colloidal particles in a colloidal system constitutes the dispersed phase. Thus, the dispersed phase may be defined as the phase constituting the colloidal particles. For example, in a colloidal solution of ferric hydroxide in water, the ferric hydroxide particles are of colloidal size and constitute the dispersed phase.

**Dispersion medium:** The medium in which the colloidal particles are dispersed is called dispersion medium. For example, in the colloidal solution of ferric hydroxide in water, water is the dispersion medium.

### 3.2 Classification of colloids

Classification of colloids is based on the following three ways:

#### 3.2.1 Based on Physical State of Dispersed Phase and Dispersion medium

Depending upon the physical state of the dispersed phase and dispersion medium, eight types of colloidal systems are possible. These are described in the table given below:

**Types of Colloidal Systems**

S.No	Dispersed phase	Dispersion medium	Common name	Examples
1.	Solid	Solid	Solid sol	Gems, ruby glass, coloured glasses, pigmented plastics etc.
2.	Solid	Liquid	Sol	Gold sol, sulphur sol, ferric hydroxide sol, $As_2S_3$ sol, ink, most of the paints, starch dispersed in water, muddy water etc.
3.	Solid	Gas	Aerosol of solids	Smoke, dust etc.
4.	Liquid	Solid	Gel	Cheese, butter, boot polish, jellies etc.
5.	Liquid	Liquid	Emulsion	Milk, emulsified oils, medicines etc.
6.	Liquid	Gas	Aerosol of liquids	Fog, mist, clouds, Liquid sprays etc.
7.	Gas	Solid	Solid foam	Pumice stone, styrene foam, foam rubber etc.
8.	Gas	Liquid	Foam or Froth	Lemonade froth, soap lather, shaving cream foam etc.

It is to be noted that the colloidal system of a gas into some other gas is not possible because a gas mixed with some other gas always forms a homogeneous gaseous solution. Since colloidal systems are heterogeneous, they cannot be obtained by dispersing a gas into some other gas.

Out of the various types of colloidal systems listed above, the most common are sols (solids dispersed in liquid), gels (liquids dispersed in solids) and emulsions (liquids dispersed in liquids).

Depending upon the nature of dispersion media, sols are usually given different names as follows:



Dispersion medium	Name of the sol
Water Alcohol Benzene Gases	Aquasol or Hydrosol Alcosols Benzosols Aerosol

### 3.2.2 Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the affinity of the dispersed phase for the dispersion medium, colloidal systems can be classified into following two categories.

- (i) Lyophilic sols                      (ii) Lyophobic sols

A brief description of these two types of sols is given below:

- 1. Lyophilic sols:** These term lyophilic means liquid-loving (i.e. solvent loving). Certain substances have an affinity for certain liquids and readily form colloidal dispersions with them. The substances which when mixed with a suitable liquid (dispersion medium) readily form colloidal solutions are called **lyophilic colloids** or **intrinsic colloids** and the sols thus formed are called lyophilic sols. When water is used as the dispersion medium, such colloids are termed as hydrophilic colloids and their colloidal dispersion in water are known as hydrophilic sols.

Arabic gum, gelatin, albumin, starch etc. are some common examples of lyophilic colloids. Gum sol, starch sol, sols of proteins in water, sols of polymers in organic solvents etc. is some examples of lyophilic sols.

Lyophilic sols are stable and do not get precipitated easily. In fact, they are self stabilized, i.e. they do not require any stabilizing agent to preserve them. An important characteristic of these sols is that if dispersed phase is separated from dispersion medium (say by evaporation), the dispersed phase can again be brought in the sol state simply by mixing it with the dispersion medium. This is why hydrophilic sols are also known as reversible sols.

- 2. Lyophobic sols:** The term lyophilic means liquid-hating (i.e. solvent-hating). The substances which do not pass much affinity for the dispersion medium and do not readily pass into the sol state when mixed with the medium are called hydrophobic colloids or extrinsic colloids. Their sols are prepared by using special techniques and they are referred to as hydrophobic sols. Sols of metals e.g. gold sol, platinum sol etc. and the sols of insoluble substances such as metal sulphides and oxides are some examples of lyophilic sols.

Lyophilic sols are relatively less stable as compared to lyophilic sols. They are easily precipitated (or coagulated) on addition of small amounts of electrolytes, by heating or agitation. Moreover, the precipitated dispersed phase cannot be brought back into the sol state by simply mixing it with the dispersion medium. This is why hydrophobic sols are also known as irreversible sols. The Lyophobic sols need stabilizing agents to keep them in the sol form for a longer time.

The important points of difference between the lyophilic sols and lyophobic sols are summarized in the table given below:

<b>S.No.</b>	<b>Property</b>	<b>Lyophilic sols</b>	<b>Lyophobic sols</b>
1.	Ease of preparation	Lyophilic sols can be prepared easily by simply shaking the lyophilic colloids with the dispersion medium	Lyophobic sols cannot be obtained simply by shaking the lyophobic colloids with the medium. They can be obtained only by using special techniques.
2.	Hydration	They are heavily hydrated.	They are not much hydrated.
3.	Stability	Due to hydration, they are quite stable and are not easily coagulated.	They are less stable and get coagulated by heating, by agitating or on addition of small amount of an electrolyte.
4.	Reversibility	Reversible	Irreversible
5.	Visibility	The dispersed particles are neither visible nor detected easily even under ultra-microscope.	The dispersed particles, though not visible can be detected easily under ultra microscope.
6.	Viscosity	The viscosity is much higher than that of the dispersion medium.	The viscosity is almost the same as that of the dispersion medium.
7.	Surface tension	The surface tension is usually lower than that of the dispersion medium	The surface tension is nearly the same as that of the dispersion medium.
8.	Charge on particles	The dispersed particles have little or no charge on them.	The dispersed particles carry a definite charge which is either positive or negative.
9.	Migration of particles in an electric field	The dispersed particles may migrate in either direction or may not migrate at all.	Depending upon the nature of charge present, the dispersed particles migrate in a particular direction.

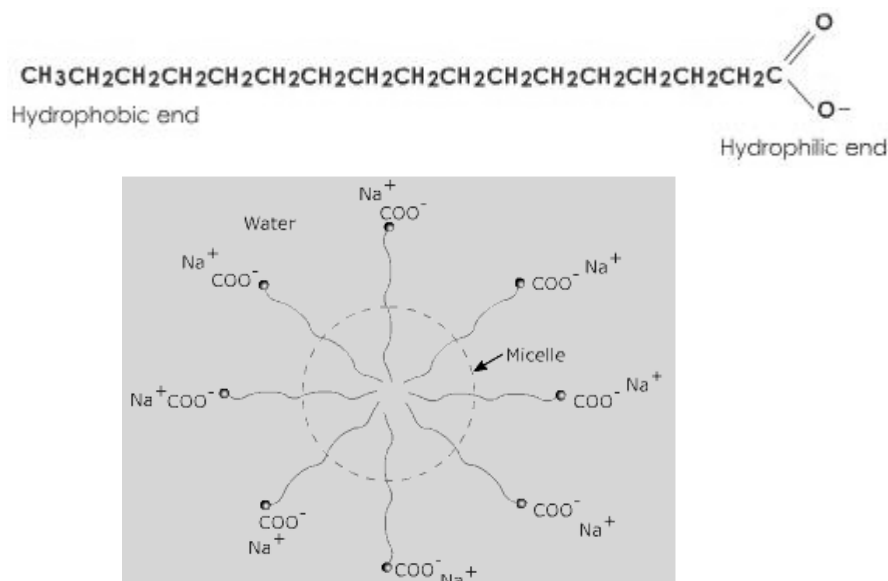
### 3.2.3 Based on Type of Particles of the Dispersed Phase

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

- (i) **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter  $< 1\text{nm}$ ). The species thus formed are called multimolecular colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of  $\text{S}_8$  sulphur molecules.
- (ii) **Macromolecular colloids:** Macromolecules in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.
- (iii) **Associated colloids (Micelles):** There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as associated colloids. The formation of micelles takes place only above a particular temperature called Kraft temperature ( $T_K$ ) and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is  $10^{-4}$  to  $10^{-3}$  mol  $\text{L}^{-1}$ . These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

#### Mechanism of Micelles formation:

Micelles are formed by specific molecules which have lyophilic as well as lyophobic ends. Ordinary soap which contains sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ) forms micelle in water. The stearate ion has a long hydrocarbon end that is hydrophobic (because it is non polar) and a polar carboxyl group ( $\text{COO}^-$ ) that is hydrophilic.



When the concentration of sodium stearate is below its CMC, then it behaves as a normal electrolyte and ionizes to give  $\text{Na}^+$  and  $\text{C}_{17}\text{H}_{35}\text{COO}^-$  ions. As the concentration exceeds the CMC, the hydrophobic end starts receding away from the solvent and approaches each other. However, the polar  $\text{COO}^-$  part interacts with water. This leads to the formation of a cluster having the dimensions of a colloid particle. In each cluster a large number of stearate groups clump together in a spherical manner such that the hydrocarbon parts interact with one another and the  $\text{COO}^-$  groups remains projected in water.

### 3.3 Preparation of Colloidal Solutions

Lyophilic colloids have a strong affinity for the dispersion medium and readily form a sol by bringing them into contact or by warming them with the medium. For example, sols of starch, gelatin, gum Arabic etc. can be prepared just by warming them with water. Similarly, a colloidal solution of cellulose nitrate can be prepared by dissolving it in an organic solvent such as ethyl alcohol. The product obtained is commercially called **collodion**.

Since lyophobic colloids practically have no affinity for the dispersion medium, they do not readily pass into the medium to form a colloidal solution. Hence special methods are required for the preparation of lyophobic sols. The methods used for the preparation of lyophobic sols can broadly be divided into the following two categories.

#### A) Dispersion or Disintegration Methods

In these methods, the bigger particles of a substances are broken down to form smaller particles of colloidal dimensions thus obtained are stabilized by the addition of certain stabilizing agents. Some important dispersion methods are as follows:

- 1) Mechanical dispersion method:** In this method, the dispersion of the coarse material (whose colloidal solution is to be prepared) is carried out in a machine called colloid mill. It consists of two heavy steel discs separated by a little gap. The gap may be adjusted according to the particle size desired. The two discs rotate at high speed (about 8000 revolutions per minute) in the opposite direction. A suspension of the substance in water is introduced into the mill. The coarse particles present in the suspension are grinded to the particles of colloidal dimensions and get dispersed in water to form a sol. Finer dispersion can be obtained by adding an inert diluents which prevents the colloidal particles to grow in size. For example, glucose is used as diluents in the preparation of sulphur sol.
- 2) Electrical dispersion method (Bredig's arc method):** This method is used for the preparation of sols metals such as gold, silver, platinum etc. In this method, an electric arc is struck between the two electrodes of the metal (whose colloidal solution is to be prepared) immersed in the dispersion medium (say water). The dispersion medium is cooled by surrounding it with a freezing mixture. High temperature of the arc vaporizes some of the metal. The vapour condenses to the particles of colloidal size on cooling. The colloidal particles thus formed get dispersed in the medium to form a sol. of the metal.
- 3) Peptization:** In this method, a freshly prepared precipitate of the substance is made to pass into the colloidal state by the addition of a suitable electrolyte. The process of dispersing a freshly prepared precipitate into colloidal form by using a suitable electrolyte is called peptization. The electrolyte added is called peptizing agent.

**Examples:**

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- i) When a small amount of ferric chloride solution is added to the freshly precipitated ferric hydroxide, a reddish brown coloured colloidal solution of ferric hydroxide is obtained. This occurs due to the adsorption of  $\text{Fe}^{3+}$  ions over ferric hydroxide particles which causes them to disperse into the solution due to the electrostatic repulsions between the similarly charged particles.
- ii) When a freshly prepared precipitate of silver iodide is shaken with a dilute solution of silver nitrate, a colloidal solution of silver iodide is obtained.

## b) Condensation Methods (Aggregation Method):

In condensation methods, the smaller particles of the dispersed phase are aggregated to form larger particles of colloidal dimensions. Some important condensation methods are described below:

### 1. Chemical Methods:

Some chemical reactions may be used to aggregate smaller particles of atomic or ionic sizes to form large particles of colloidal dimensions. These reactions actually involve the formation of the dispersed phase as insoluble reaction products. Some important reactions leading to the formation of hydrophobic sols are as follows.

- i) **Oxidation:** Colloidal solution of sulphur can be prepared by oxidizing an aqueous solution of  $\text{H}_2\text{S}$  with a suitable oxidizing agent such as bromine water, nitric acid or  $\text{SO}_2$ .

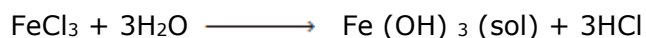


- ii) **Reduction:** Sols of gold, silver, platinum etc. can be obtained by the reduction of dilute solutions of their salts with a suitable reducing agent. For example, gold sol can be obtained by reducing a dilute aqueous solution of gold with stannous chloride.

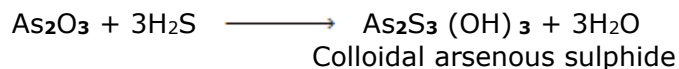


The gold sol thus obtained is called purple of Cassius.

- iii) **Hydrolysis:** Sols of ferric hydroxide and aluminium hydroxide can be prepared boiling the aqueous solution of the corresponding chlorides. For example,



- iv) **Double decomposition:** The sols of inorganic insoluble salts such as arsenous sulphide, silver halides etc. may be prepared by using double decomposition reaction. For example, arsenous sulphide sol can be prepared by passing  $\text{H}_2\text{S}$  gas through a dilute aqueous solution of arsenous oxide.



### 2. Physical Methods:

#### (i) Exchange of solvent:

This method involves the pouring of the true solution to another solvent in which the solute is insoluble but the solvent is completely miscible. An exchange of solvent gives the colloidal solution of the solute. The method may be used for the preparation of the sols of sulphur and phosphorus. For example, sulphur is soluble in alcohol but less soluble

in water. When an alcoholic solution of sulphur is poured into water, a colloidal solution of sulphur is obtained.

**(ii) By excessive cooling:**

A colloidal sol of ice in an organic solvent such as  $\text{CHCl}_3$  or ether is obtained by freezing a solution of water in the solvent. The molecules of water, which can no longer be held in solution separately come together to form particles of colloidal size.

### **3.4 Purification of Colloidal Solutions (Sols)**

A colloidal solution prepared by the above mentioned methods usually contains the impurities of electrolytes. The presence of electrolytes in smaller concentrations stabilizes a sol but their presence in large concentration tends to destabilize the colloidal solution. Therefore, it is necessary to purify colloidal solutions by removing the impurities of electrolytes present in them. Following methods are generally used for the purification of colloidal solutions (sols).

#### **1. Dialysis:**

The process of separating the impurity particles of true solution dimensions (crystalloids) from an impure sol by means of diffusion through a suitable membrane such as parchment paper or cellophane membrane is called dialysis.

The apparatus used in this method is called dialyzer. It consists of a bag made of parchment or cellophane. The bag is filled with the impure sol to be purified and is suspended in a tank through which pure water is circulated. The impurities of electrolytes present in the sol diffuse out of the bag leaving behind pure sol in the bag.

**Electro-dialysis:** Dialysis is a slow process. However, it can be expedited by applying an electric field. Under the influence of electric field, the impurity ions move faster to the oppositely charged electrodes and the process gets quickened. This process is referred to as electro-dialysis.

#### **2. Ultra-filtration:**

The pores of an ordinary filter paper are large enough to allow the passage of both impurity particles as well as colloidal particles. Therefore an ordinary filter paper cannot be used for removing the impurities of electrolytes from an impure sol. However, if the pore size of ordinary filter paper is reduced, it can be used for separating the impurities from impure sols. This is achieved by treating an ordinary filter paper with collodion or gelatin followed by its hardening by dipping it in formaldehyde solution. This treatment reduces the pore size and enables it to check the passage of colloidal particles through it. Filter papers thus obtained are called ultrafilters. Filtration through ultrafilters is called ultra-filtration.

In ultra filtration, the ultra-filter is supported over a wire mesh and the impure sol is poured over it. The impurity particles (electrolytes) pass through the ultra-filter while the larger colloidal particles are retained. The process is very slow. However, it can be expedited by applying pressure on sol side or by using a suction pump on the filtrate side. By using a series of graded ultrafilters, impurities of different size can easily be removed and it is even possible to separate colloidal particles of different size from one another.

#### **3. Ultra-Centrifugation:**

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Ultracentrifugation involves the separation of colloidal particles from the impurities by centrifugal force. The impure sol is taken in a tube and the tube is placed in an ultracentrifuge. The tube is rotated at high speeds. On account of this, the colloidal particles settle down at the bottom of the tube and the impurities remain in the solution. This solution is termed as centrifugate. The settled colloidal particles are removed from the tube and are mixed with an appropriate dispersing medium. Thus, the pure sol is obtained.

### 3.5 Properties of Colloidal Solutions

#### 3.5.1 General Physical Properties of Colloidal Solutions

The important physical properties of colloidal solutions are described below:

- (i) **Heterogeneity:** Colloidal solutions are heterogeneous in nature and consist of two phases-dispersed phase and dispersion medium.
- (ii) **Visibility of dispersed particles:** Although colloidal solutions are heterogeneous in nature, yet the dispersed particles present in them are not visible to the naked eye and they appear homogenous. This is because colloidal particles are too small to be visible to the naked eye.
- (iii) **Filtrability:** Due to very small size, the colloidal particles pass through an ordinary filter paper. However, they can be retained by animal membranes, cellophane membrane and ultra filters.
- (iv) **Stability:** Lyophilic sols in general and lyophobic sols in the absence of substantial concentrations of electrolytes are quite stable and the dispersed particles present in them do not settle down even on keeping. However, on standing for a long time, a few colloidal particles of comparatively larger size may get sedimented slowly.
- (v) **Colour:** The colour of a colloidal solution depends upon the size of colloidal particles present in it. Larger particles absorb the light of longer wavelength and therefore transmit light of shorter wavelength. For example, a silver sol having particles of size 150nm appears violet, whereas that having particles of size 60nm appears orange yellow.

#### 3.5.2 Colligative Properties of Colloidal Solutions

Colloidal solutions exhibit colligative properties, i.e., lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure in the same way as the true solutions of electrolytes and non-electrolytes do. However, the magnitudes of these properties for colloidal solutions are much smaller than those obtained for true solutions. This is because colloidal particles exist as aggregates. For a given mass of the substance, the number of colloidal particles present in the colloidal solution of the substance will be much less than the number of particles present in its true solutions. Since a colligative property depends upon the number of particles, a colloidal solution will exhibit much lower value of a colligative property as compared to that exhibited by a true solution having the same mass of the same substance.

As colloidal solutions have low values of colligative properties, it is quite difficult to measure them accurately. However, they exhibit measurable osmotic pressures. The osmotic pressures of colloidal solutions can be measured with a reasonable degree of accuracy. This property is used for the determination of the average molecular masses of the colloids.

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### 3.5.3 Mechanical Properties of Colloidal Solutions

#### a) Brownian movement

Colloidal particles present in a colloidal solution exhibit a very important property called Brownian movement. When a colloidal solution is viewed under an ultra microscope, the colloidal particles are seen continuously moving in a zigzag path. The property was discovered by a botanist Robert Brown in 1827, when he observed that pollen grains suspended in water exhibit random zigzag motion. After the name of the discoverer, the property was named as Brownian movement. It may be defined as follows.

The continuous zigzag movement of the colloidal particles in the dispersion medium in a colloidal solution is called Brownian movement.



Zig-zag or Brownian motion

**Cause of Brownian movement:** Brownian movement is due to the unequal bombardments of the moving molecules of dispersion medium on colloidal particles. The moving molecules of the dispersion medium continuously attack on colloidal particles from all sides and impart momentum to them. Since the chances of their collisions are unequal, the net driving force on a colloidal particle forces it to move a particular direction. As the particle moves in that direction, other molecules of the medium again collide with it and the particle changes its direction. The process continues. This results in a random zigzag movement of the colloidal particle.

The Brownian movement decreases with an increase in the size of colloidal particle. This is why suspensions do not exhibit this type of movement. Brownian movement plays an important role in imparting stability to a sol. This is because Brownian movement opposes the gravitational forces acting on colloidal particles and prevents them from getting settled down.

#### b) Diffusion

Colloidal particles like solutes in true solution diffuse from a region of higher concentration to that of lower concentration. Because of their bigger sizes colloidal particles move slowly and diffuse at a slower rate.

#### c) Sedimentation

Under the influence of gravity, colloids tend to settle down very slowly. This settling down rate is accelerated by ultra centrifugation.

### 3.5.4 Optical Properties of Colloidal Solutions

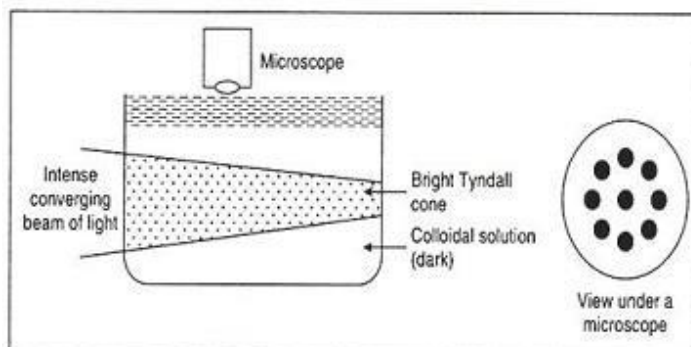
#### Optical Properties (Tyndall Effect)

When an intense converging beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light. This phenomenon is called Tyndall effect and the illuminated path is known as **Tyndall cone**. The phenomenon was

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first observed by Tyndall in 1869.



### Tyndall effect

The Tyndall effect is due to the scattering of light by colloidal particles. Since the dimensions of colloidal particles are comparable to the wavelength of ultraviolet and visible radiations, they scatter these radiations and get illuminated. Tyndall observed that the zone of scattered light is much larger than the particle itself. This is why colloidal particles look like bright spots when viewed with a microscope at right angles to the beam of light as shown in figure. Thus, Tyndall effect may be defined as the scattering of light by colloidal particles present in a colloidal solution.

Tyndall effect is not exhibited by true solutions. This is because the particles (ions or molecules) present in a true solution are too small to scatter light. Thus, Tyndall effect can be used to distinguish a colloidal solution from a true solution. The phenomenon has also been used to devise an instrument known as ultra microscope. The instrument is used for the detection of the particles of colloidal dimensions. Tyndall effect also establishes the fact that colloidal systems are heterogeneous in nature.

### 3.5.5 Electrical Properties of Colloidal Solutions

Some important electrical properties of colloidal solutions are as follows:

**(A) Presence of electrical charge on colloidal particles and stability of sols:** One of the most important properties of colloidal solutions is that colloidal particles possess a definite type of electrical charge. In a particular colloidal solution, all the colloidal particles carry the same type of charge, while the dispersion medium has an equal but opposite charge. Thus, the charge on colloidal particles is balanced by that of the dispersion medium and the colloidal solution as a whole is electrically neutral. For example, in a ferric hydroxide sol, the colloidal ferric hydroxide particles are positively charged, while the dispersion medium carries an equal and opposite negative charge.

The stability of a colloidal solution is mainly due to the presence of a particular type of charge on all the colloidal particles present in it. Due to the presence of similar and equal charges, the colloidal particles repel one another and are thus unable to combine together to form larger particles. This keeps them dispersed in the medium and the colloidal solution remains stable. This is why sol particles do not settle down even on standing for a long time.

Based on the nature of charge, the colloidal sols may be classified as positively charged and negatively charged sols. Some common examples of these sols are given below.

#### Positively charged sols:

Metallic hydroxide sols e.g.,  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ , etc.,  $\text{TiO}_2$  sol, haemoglobin, sols

of basic dyes such as methylene blue etc.

**Negatively charged sols:**

Metal sols e.g., Au, Ag, Cu, Pt etc. sols, metal sulphide sols e.g.,  $As_2S_3$ , CdS etc. sols; starch sol, sols of acid dyes such as Congo red etc.

**Origin of charge on colloidal particles:**

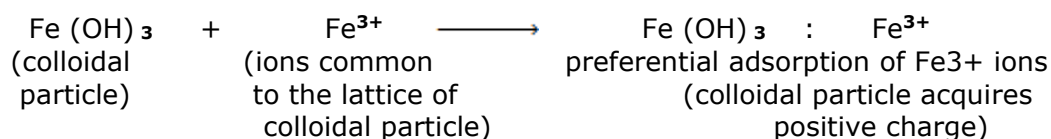
There are several views regarding the origin of charge on colloidal particles. According to these views, colloidal particles acquire charge due to the following reasons.

**(i) Due to dissociation of the adsorbed molecular electrolytes:** Colloidal particles have a strong tendency to adsorb reactant or product molecules. The molecules thus adsorbed on the surface of colloidal particles may undergo dissociation/ionization and may impart charge to them. For example, during the preparation of sulphide sols (e.g.,  $As_2S_3$  sol),  $H_2S$  molecules get adsorbed on colloidal particles.  $H_2S$  molecules thus adsorbed undergo ionization and release  $H^+$  ions into the medium. Consequently, colloidal particles are left with negative charge.

**(ii) Due to the dissociation of molecules forming colloidal aggregates:** The molecules responsible for the formation of aggregates of colloidal dimensions may themselves undergo dissociation/ionization resulting in the development of charge on the colloidal particles formed by their aggregation. For example, the soap molecules ( $RCOONa$ ) dissociate to give  $RCOO^-$  and  $Na^+$  ions.  $RCOO^-$  ions aggregate together to form micelles which carry negative charge as explained earlier.

**(iii) Due to preferential adsorption of ions from solutions:** The colloidal particles have a tendency to preferentially adsorb a particular type of ions from the solution. A colloidal particle usually adsorbs those ions which are in excess and are common to its own lattice. This preferential adsorption of a particular type of ions imparts a particular type of charge to colloidal particles.

For example, when a ferric hydroxide sol is prepared by the hydrolysis of ferric chloride in warm water, the colloidal particles of  $Fe(OH)_3$  formed have a tendency to adsorb preferentially the  $Fe^{3+}$  ions present in the solution. This is because  $Fe^{3+}$  ions are common to the lattice of  $Fe(OH)_3$  particle. The  $Fe^{3+}$  ions thus adsorbed impart positive charge to the colloidal particles present in the sol.



Similarly, during the preparation of  $AgCl$  sol using excess of  $KCl$  solution, the  $Cl^-$  ions are preferentially adsorbed and the colloidal particles acquire negative charge. However, if an excess of  $AgNO_3$  is used,  $Ag^+$  ions get preferentially adsorbed and the colloidal particles acquire positive charge.



(colloidal particle) (Silver ions present in excess in the solution) Preferential adsorption of  $\text{Ag}^+$  ions. (Colloidal particle acquires positive charge)

**(B) Electrophoresis:** Due to the presence of a particular type of electrical charge, the colloidal particles present in a colloidal dispersion move towards a particular electrode under the influence of an electric field. The direction of movement of the colloidal particles is decided by the nature of charge present on them. If the colloidal particles carry positive charge, they move towards cathode when subjected to an electric field and vice versa. The phenomenon is called electrophoresis and may be defined as:

The movement of colloidal particles towards a particular electrode under the influence of an electric field is called **electrophoresis**.

The phenomenon of electrophoresis clearly indicates that the colloidal particles carry a particular type of charge. The property can be used to find the nature of charge carried by colloidal particles in a colloidal dispersion. Electrophoresis is an important phenomenon and finds several applications in industry.

**(C) Electro-osmosis:** When the movement of colloidal particles under the influence of the applied electric field is checked with the help of a suitable membrane (semi-permeable membrane), the dispersion medium moves in a direction opposite to the direction in which the colloidal particles would have otherwise moved. This phenomenon is called electro-osmosis and may be defined as:

The movement of dispersion medium under the influence of an electric field in the situation when the movement of colloidal particles is prevented with the help of a suitable membrane is called **electro-osmosis**.

**(D) Coagulation or flocculation:** The stability of a sol is due to the charge present on the colloidal particles. Due to similar charges, colloidal particles repel one another and are unable to combine together to form larger particles. However, if the charge on colloidal particles is destroyed, they are free to come nearer and grow in size. When the particles become sufficiently large, they get precipitated. This phenomenon is termed as coagulation or flocculation. The coagulation of colloidal solution can be achieved by the addition of an electrolyte. It is to be noted that a small amount of electrolyte is necessary for the stability of a sol because the ions of the electrolyte get adsorbed on colloidal particles and impart them some charge. However, when an electrolyte is added in substantial amount the positively charged ions of the electrolyte neutralize the charge on colloidal particles and compel the sol to get coagulated. Coagulation may be defined as

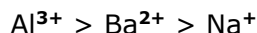
The phenomenon involving the precipitation of a colloidal solution on addition of an electrolyte is called **coagulation or flocculation**.

**Hardy-Schulze rule:** The coagulation capacity of an electrolyte depends upon the valence of ion responsible for causing coagulation. As we have seen above, the ion responsible for causing coagulation is the one which carries charge opposite to that present on colloidal particles. For example, a positively charged sol gets coagulated by the negatively charged ions of the added electrolyte. From a study of the coagulation behavior of various electrolytes towards a particular sol, Hardy and Schulze suggested a general rule known as Hardy-Schulze rule. The rule can be stated as follows.

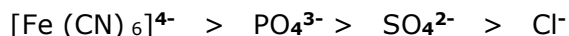
**The greater is the valence of the oppositely charged ion of the electrolyte added to a colloidal solution, the faster is the coagulation of the colloidal solution.**

Thus, higher the charge on oppositely charged ion greater is its coagulating power. For example, the coagulation power of different cations for coagulating a negatively charged sol

of  $\text{As}_2\text{S}_3$  follows the order.



Similarly, for the coagulation of a positively charged sol such as  $\text{Fe}(\text{OH})_3$ , the coagulating power of different anions follows the order.



**Flocculation value:** The coagulating power of an electrolyte is usually expressed in terms of its flocculation value which may be defined as follows.

*The minimum concentration (in millimoles per litre) of an electrolyte required to cause the coagulation of a sol is called the flocculation value of the electrolyte.*

The flocculation values (in millimoles per litre) for the coagulation of negatively charged  $\text{As}_2\text{S}_3$  sol and positively charged  $\text{Fe}(\text{OH})_3$  sol are given in the Table below.

**Table: Flocculation Values of Some Common Electrolytes**

For Negatively charged $\text{As}_2\text{S}_3$ Sol			For Positively charged $\text{Fe}(\text{OH})_3$ Sol		
Electrolyte	Flocculating ion	Flocculation value (millimoles/litre)	Electrolyte	Flocculating ion	Flocculation value (millimoles/litre)
NaCl	$\text{Na}^+$	52	KBr	$\text{Br}^-$	138
KCl	$\text{K}^+$	50	HCl	$\text{Cl}^-$	132
HCl	$\text{H}^+$	30	$\text{KNO}_3$	$\text{NO}_3^-$	132
$\text{MgCl}_2$	$\text{Mg}^{2+}$	0.72	$\text{K}_2\text{CrO}_4$	$\text{CrO}_4^{2-}$	0.315
$\text{BaCl}_2$	$\text{Ba}^{2+}$	0.69	$\text{K}_2\text{SO}_4$	$\text{SO}_4^{2-}$	0.210
$\text{ZnCl}_2$	$\text{Zn}^{2+}$	0.68	$\text{K}_2\text{C}_2\text{O}_4$	$\text{C}_2\text{O}_4^{2-}$	0.238
$\text{AlCl}_3$	$\text{Al}^{3+}$	0.093	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$[\text{Fe}(\text{CN})_6]^{3-}$	0.096

It is to be noted that a smaller flocculation value indicates the greater coagulating power of the electrolyte. Thus,

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

Some other methods for causing coagulation: The most commonly used method for causing coagulation in a colloidal solution is the addition of an electrolyte as described above. However, the coagulation of colloidal solution can also be achieved by any of the following methods.

**(a) By electrophoresis:** In electrophoresis, the charged colloidal particles migrate to the oppositely charged electrode and get discharged. This results in the coagulation of the colloidal solution.

**(b) By mixing two oppositely sols:** When two sols carrying opposite charges are mixed together in suitable proportions, the colloidal particles of one sol neutralize the charge present on the particles of the other sol and both get coagulated.

**(c) By persistent dialysis:** We have already seen that a small amount of electrolyte is essential to make a sol stable. When a sol is subjected to persistent dialysis, the traces of electrolyte also pass out through the membrane. In the absence of electrolyte, sol becomes unstable and gets coagulated.

(d) **By heating:** Even by simple heating may coagulate the sol.

### 3.6 Protective Colloids and Gold Number

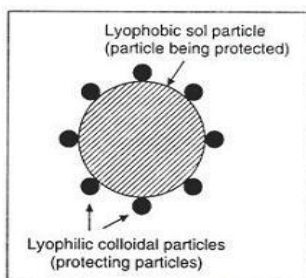
Lyophobic sols such as those of metals (e.g. Au, Ag, Pt etc.) are not very stable in the sense that they get easily coagulated (precipitated) in the presence of an electrolyte. This poses a big problem in their storage and usage. Contrary to this, lyophilic sols are much more stable and do not get coagulated easily under similar conditions.

It has been observed that in the presence of certain lyophilic colloids such as gum Arabic, gelatin, starch etc. the hydrophobic sols acquire greater stability towards coagulation, i.e. they get protected and do not get coagulated easily when an electrolyte is added.

The process of protecting a lyophobic sol from being coagulated (precipitated) on addition of an electrolyte by the use of a lyophilic colloids is called protection and the lyophilic colloid used for purpose is called a protective colloid.

For example, the addition of gelatin (a lyophilic colloid) to a gold sol (lyophobic sol) protects the latter from being coagulated on addition of sodium chloride solution.

The exact mechanism of protection is not very clearly understood. However, it is believed that the lyophilic colloid particles get adsorbed on the surface of the colloid particles present in the lyophobic sol. The adsorbed lyophilic particles thus form an envelope around the lyophobic sol particles and protect them from the action of electrolytes.



#### Protective action of lyophilic colloid particles

**Gold Number:** The protective power a lyophilic colloid is usually expressed in terms of a number called gold number introduced by Zsigmondy (1901). It may be defined as follows:

The gold number of a protective colloid is its minimum amount in milligrams which is just sufficient to prevent the coagulation of 10 ml of a gold sol on the addition of 1 mL of 10% sodium chloride solution.

It is to be noted that the smaller the value of gold number, the greater is the protective power of the protective colloid. The gold numbers of a few protective colloids are given in the table below:

**Gold Number of Some Protective Colloids**

Protective (Lyophilic) Colloid	Gold Number
Gum Arabic	0.10-0.15
Gelatin	0.005-0.01
Casein	0.01-0.02
Haemoglobin	0.03-0.07
Egg albumin	0.08-0.10
Sodium Oleate	0.4
Dextrin	6-20
Starch	20.25

**Example:**

For the coagulation of 100 ml of arsenous sulphide sol, 5ml of 1M NaCl is required. What is the flocculation value of NaCl?

**Solution:**

5ml of 1M NaCl contains NaCl =  $\frac{1}{1000} \times 5 \text{ moles} = 5 \text{ millimoles}$

Thus, 100ml of  $\text{As}_2\text{S}_3$  sol require NaCl for complete coagulation=5 millimoles

$\therefore$  1000 ml of the sol require NaCl for complete coagulation=50 millimoles

$\therefore$  Flocculation value of NaCl = 50

**3.7 Emulsions**

The liquid-liquid colloidal dispersions are called emulsions. The colloidal dispersion of two immiscible liquids in which one liquid acts as the dispersion medium and the other as dispersed phase is called **an emulsion**.

**Types of emulsion:** Depending upon the nature of dispersed phase, emulsions can be classified into following two types:

- (i) **Oil-in-water (O/W) type emulsions:** In oil-in-water emulsions, oil acts as the dispersed phase while water acts as the dispersion medium. The most common example of oil in water type emulsion is milk which consists of liquid fat globules dispersed in water.
- (ii) **Water-in-oil (W/O) type emulsions:** In water-in-oil type emulsions, water acts as the dispersed phase, whereas oil acts as the dispersion medium. This type of emulsions is also referred to as oil emulsions. Cod liver oil emulsion is a typical example of this type of emulsions in which water is dispersed in cod liver oil.

**Preparation of emulsions:** Emulsions are usually prepared by vigorously mixing the two liquids by using either a high speed mixing machine or by using ultrasonic vibrators. The process of making an emulsion is known as **emulsification**. Since the two liquids used for the preparation of an emulsion are completely immiscible, a stabilizing substance, known as **emulsifying agent or emulsifier** is required to stabilize the resulting emulsion. The emulsifier is added along with the component liquids. In the absence of emulsifying agent, the dispersed phase particles of colloidal size combine together resulting in the breaking up

of emulsion into two separate layers. Some of the important emulsifying agents are soaps, detergents, proteins, gums and agar. Among these, soaps and detergents are most commonly used emulsifiers.

**Role of emulsifier:** The emulsifiers for a protective film around the oil droplets dispersed in water. This prevents them to come closer and to coalesce, i.e. to combine together. Thus, the emulsion gets stabilized. For example, let us consider the role of soap which acts as an emulsifier for an oil-in-water emulsion. When soap is added to an o/w emulsion, the soap molecule ( $\text{RCOO}^-\text{Na}^+$ ) arrange themselves in such a way that the polar end groups dip in water whereas the hydrocarbon chains dip in oil droplet as shown in the figure below. Thus soap molecules get concentrated over the surface of the oil droplet and form a protective film. This decreases the interfacial between oil and water and the emulsion gets stabilized.

**Identification of emulsion type:** The type to which an emulsion belongs can be known as any of the following tests.

**(i) Dilution test:** This test is carried out by adding a few drops of water to the given emulsion. If the added water mixes freely with the emulsion, the emulsion is of oil-in-water (o/w) type. In case the added water does not mix up with the emulsion, the given emulsion is of water-in-oil (w/o) type. The experiment can also be carried out by adding a few drops of oil instead of water. If the added oil gets mixed up, the emulsion is of water-in-oil type.

**(ii) Conductivity test:** This test involves the addition of a small amount of electrolyte to the emulsion under the examination followed by the measurement of its conductance. If the conductance increases, the emulsion is of oil-in-water type. In case, there is no appreciable change in the conductance, the emulsion is of water-in-oil type.

**(iii) Dye test:** In this test, a small amount of an oil-soluble dye is added to the emulsion. If the emulsion becomes coloured, it is of water-in-oil type. If no change in colour is observed, the emulsion is of oil-in-water type.

### Properties of emulsions:

1. The size of the dispersed droplets in emulsions may be somewhat larger as compared to the size of dispersed particles in sols. Still, emulsions are colloidal systems and exhibit all the properties exhibited by colloidal solutions e.g. Brownian movement, Tyndall effect, electrophoresis, coagulation etc.
2. Emulsions can be broken into their constituent liquids by physical methods such as heating, freezing, centrifuging etc. or by destroying the emulsifying agent by a suitable chemical method. The process of breaking an emulsion to yield the constituent liquids is called demulsification.
3. Emulsions can be diluted by adding any amount of the dispersion medium, i.e., water for o/w emulsions and oils for w/o emulsions. The dispersed phase added into the emulsion forms a separate layer.

**Applications of emulsions:** Emulsions are very useful systems and find a number of applications. Some important applications of emulsions are given below.

**(i)** A large number of pharmaceuticals are prepared in the form of lotions, creams and ointments which are emulsions of oil-in-water or water-in-oil type and are easily absorbed by the body. Similarly, many cosmetics are also sold as emulsions. Several oily drugs are also prepared as emulsions to facilitate their absorption.

**(ii)** The concentration of sulphide one by froth floatation process involves the treatment

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of finely pulverized one with an oil emulsion. When air is bubbled in the mixture, the ore particles present in the emulsion are carried to the surface in the form of foam and may be collected.

**(iii)** Emulsifying properties of soaps and detergents are used in washing clothes, crockery etc. Soaps and detergents emulsify the greasy dirt and carry it away in the water used for washing.

**(iv)** Digestion of fats in the intestine is facilitated by emulsification. A small amount of fat reacts with the alkaline solution of the intestine to form sodium soap. The sodium soap thus formed emulsifies the rest of the fat. This helps digestive enzymes to carry out their functions in a better way and the fats get digested easily.

### 3.8 Applications of Colloids

Colloids play a very important role in nature, in our daily life and in industry. Some of the important applications of colloids are discussed below.

- 1. Food stuffs and medicines:** Many of food stuffs are colloidal in nature. Milk, butter, whipped cream, fruit jellies; ice cream, bread etc. are all colloidal in nature. For example, milk is an emulsion of butter fat in water, stabilized by milk protein (casein). Ice cream is a dispersion of colloidal ice particles in cream. Similarly, bread consists of air dispersed in baked dough.

Colloidal medicines are more effective and are easily absorbed by the body system. Therefore a large number of pharmaceutical preparations are emulsions. Halibut-liver oil, cod-liver oil, skin ointments etc. are emulsions. Antibiotics such as penicillin, streptomycin are usually injected in the body in colloidal form. Several metal sols are also used as medicines.

- 2. Purification of water:** In water works, water is usually purified by the addition of certain electrolytes such as potash alum, aluminium sulphate etc. This involves the phenomenon of coagulation. The impure water usually contains dispersed colloidal particles which cannot be removed by filtration. When potash alum is added to impure water, the negatively charged colloidal particles of impurities get coagulated by the action of  $Al^{3+}$  ions furnished by the alum and can be removed by filtration or decantation.
- 3. Sewage disposal:** Sewage water contains particles of dirt, mud etc. which are colloidal in nature and carry some electrical charge. These particles may be removed by using the phenomenon of electrophoresis. The sewage water is passed through a tunnel fitted with metallic electrodes and maintained at a high potential difference. The colloidal particles present in the sewage water migrate to the oppositely charged electrodes and get coagulated; the rubbish matter obtained on account of the coagulation of colloidal dirt particles may be used as manure.
- 4. Smoke precipitation:** Smoke is colloidal system and consists of electrically charged colloidal particles of carbon dispersed in air. As smoke is a big source of pollution. It is always desirable to precipitate it, i.e., to remove colloidal carbon particles present in it. The removal of colloidal carbon particles from smoke can be effected by using the phenomenon of electrophoresis. This is achieved in an apparatus called Cottrell precipitator.

Smoke is allowed to pass through a chamber having a number of metal plates attached to a metal wire connected to a source of high potential (20,000 to 70,000V). The electrically charged colloidal particles of carbon and dust get discharged when



come in contact with the oppositely charged plates and fall down to the bottom. The clean hot air leaves the precipitator from an exit near the top.

5. **Artificial rain:** Clouds are colloidal systems and consist of water vapour mixed with dust particles. The water molecules present in a cloud develop some electrical charge. Therefore, clouds can be made to rain by neutralizing the charge present on colloidal particles (water molecules). This type of rain is called artificial rain and may be carried out by spraying oppositely charged colloidal dust or sand particles over a cloud. This neutralizes the charge on water molecules and compels them to get coagulated, i.e. to rain.
  6. **Rubber industry:** Latex obtained from rubber trees is an emulsion consisting of a dispersion of negatively charged rubber particles in water. In order to obtain rubber from latex, the latter is boiled when rubber particles get coagulated. The coagulated mass is vulcanized and sold as natural rubber. Rubber-plated articles can be prepared directly from latex by electrically depositing the negatively charged rubber particles over the article to be rubber-plated by making the article an anode in the rubber-plating bath.
  7. **Leather tanning:** During the tanning of leather, the positively charged colloidal particles of raw skin and hides are coagulated by the negatively charged tanning materials which include tannin and compounds of aluminium and chromium. On soaking hides in the solutions of tanning materials, the coagulation of negatively charged tanning materials takes place in the pores of hides and the latter get hardened.
  8. **Cleansing action of soaps:** Soaps solution is colloidal in nature and removes dirt and oil from clothes by forming water soluble emulsion as explained earlier.
  9. **Smoke screen:** In chemical warfare, smoke screens are generally used to hide the movement of troops. Smoke screens are the colloidal dispersions of very fine particles of titanium oxide in air.
  10. **Blue colour of the sky:** The sky is the empty space around earth and as such has no colour. It appears blue due to the scattering of light by the colloidal dust particles present in air (Tyndall effect).
  11. **Preparation of Nano-materials:** Nano-materials which are used as catalyst are prepared by using reverse micelles.
  12. **Building roads:** Now a day, roads are built asphalt emulsified in water. This technique does not require the necessity of melting the asphalt.
  13. **Metallurgical operations:** Several metal ores are concentrated by froth floatation process. This process involves the treatment of the pulverized ore in emulsion of pine oil.
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