

# Surface Chemistry

- Surface chemistry deals with the processes that occur at the surfaces.
- The surface is represented by separating the bulk phases by a hyphen or a slash. Example - The interface between a solid and a gas is represented by solid-gas or solid/gas.
- The examples of surface phenomenon are as follows: heterogeneous catalysis, corrosion, electrode processes, dissolution and crystallization.

## Adsorption

- It is a surface phenomenon.
- The accumulation of molecular species at the surface is known as adsorption.
- It is the tendency of a solid to attract and retain the molecules of the phase into contact.
- The molecules remain at the surface only and they do not go deeper into bulk.
- **Adsorbate** - The molecular species or the substance which accumulates on the surface is called adsorbate.
- **Adsorbent** - The material at which adsorbate accumulate is known as adsorbent.

### Adsorption in action-

- When a gas like  $H_2$ ,  $O_2$ ,  $CO$ ,  $Cl_2$  or  $NH_3$  is taken in a closed vessel. The vessel is containing powdered charcoal; it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal means get adsorbed at the surface.
- The water molecules adsorbed on the surface of the silica gel so air becomes dry in the presence of silica gel.
- When animal charcoal is added to a solution of an organic dye for example methylene blue; the solution is stirred briskly and filtered. After

filtration the colorless filtrate is obtained. The molecules of the dye get collected on the surface of the charcoal.

- When aqueous solution of raw sugar is passed through beds of animal charcoal it becomes colorless because the coloring substances are adsorbed by the charcoal.

The above examples show that adsorption is power of solid surface to hold gas or liquid molecules.

### Distinction between Adsorption and Absorption

1. In case of absorption the substance is uniformly distributed throughout the bulk of the solid. While in adsorption the substance is aggregate at the surface only and not in to the bulk of the adsorbent. Example: When we dip a piece of chalk in to the ink solution. The surface takes up the color of the ink due to adsorption of colored molecules whereas the solvent of the ink goes deeper inside the stick due to absorption. When we break the chalk, it is white from inside.
2. There is a difference between absorption and adsorption. For example, water vapors are adsorbed by silica-gel but absorbed by anhydrous  $\text{CaCl}_2$ .

### Mechanism of adsorption –

- The surface particles of the adsorbent are not surrounded by molecules of their kind so there are less attractive forces at the surface particles.
- The extent of adsorption increases with the increase in surface area per unit mass of the adsorbent at a given pressure and temperature.
- The decrease in residual forces of the surface occurs always during adsorption. Eventually there is decrease in surface energy which appears as heat. Thus, it is an exothermic process.

$$\Delta H = -ve$$

The entropy of gases decreases after adsorption.

$$\Delta S = -ve$$

$$\Delta G = -ve$$

For the spontaneity of a process, the thermodynamic requirement is that, at constant temperature and pressure,  $\Delta G$  should be negative. There is a decrease in Gibbs energy.

$$\Delta G = \Delta H - T \Delta S$$

- A spontaneous adsorption process is a combination of  $\Delta H$  and  $-T\Delta S$ . These two factors make  $\Delta G$  negative.
- As the adsorption proceeds  $\Delta H$  becomes less negative. Eventually,  $\Delta H$  become equal to  $T\Delta S$  and  $\Delta G$  become zero. At this state equilibrium is attained.

### Types of adsorptions -

- There are two types of adsorptions: Physisorption and chemisorption.

#### 1. Physisorption or physical adsorption-

If accumulation of gas on the surface of a solid occurs by weak van der Waals' forces, then the adsorption is known as physisorption.

##### Characteristics of physisorption

- a. **Lack of specificity:** An adsorbent does not show any preference for a particular gas because the van der Waals' forces are universal.
- b. **Surface area of adsorbent:** The extent of adsorption increase with the increase in surface area of the adsorbent. Fine metals and porous substances having large surface areas are good adsorbents.
- c. **Nature of adsorbate:** The amount of gas adsorbed by a solid relies upon nature of gas. Generally, easily liquefiable gases tend to adsorb more as van der Waals forces are stronger near the critical temperatures. For example: 1g of activated charcoal adsorbs more  $\text{SO}_2$  (critical temperature 630K), than  $\text{CH}_4$  (critical temperature 190K) which is still more than 4.5 mL of  $\text{H}_2$  (critical temperature 33K).
- d. **Enthalpy of adsorption:** Physical adsorption's enthalpy of adsorption is quite low, because the attraction between gas

molecules and solid surface is due to weak van der Waals forces. It is an exothermic process.

- e. **Reversible nature**: Physical adsorption of a gas by a solid is usually reversible.



A gas is adsorbed when pressure is increased as the volume of the gas decreases according to Le-Chatelier's principle. The gas can be removed by decreasing pressure. The adsorption process is exothermic so the physical adsorption occurs easily at low temperature and decreases with increasing the temperature.

## 2. Chemisorption or chemical adsorption-

- When the gas molecules are held to the solid surface by chemical bonds then adsorption is known as chemisorption.
- The chemical bonds can be ionic or covalent in nature.
- Chemisorption involves a high energy of activation. And it is known as activated adsorption.

### Characteristics of chemisorption

- a. **High specificity**: Chemisorption is highly specific. It occurs only when there is some possibility of chemical bonding between adsorbent and adsorbate. For example: O<sub>2</sub> is adsorbed on metals by the oxide formation and hydrogen is adsorbed by transition metals due to the hydride formation.
- b. **Surface area**: Chemisorption increase with increase in surface area of the adsorbent.
- c. **Irreversibility**: In chemisorption compound formation takes place. It is usually irreversible in nature. Chemisorption is an exothermic process but it is very slow at low temperatures on account of high energy of activation. Physisorption of a gas which is adsorbed at low temperature may change into chemisorption at a high temperature.
- d. **Enthalpy of adsorption**: Enthalpy of chemisorption is high as it involves the chemical bond formation.

Table: Comparison between Physisorption and Chemisorption

<b>Physisorption</b>	<b>Chemisorption</b>
It arises due to van der Waals forces.	It occurs due to chemical bond formation.
It is reversible in nature.	It is an irreversible process.
It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
It is not specific in nature.	It is highly specific.
Low temperature is favorable for adsorption. It decreases with increase in temperature.	High temperature is favorable for adsorption. It is directly proportional to the temperature.
It gives rise to multi-molecular layers on adsorbent surface under high pressure.	It results into unimolecular layer.
No appreciable activation energy is needed.	High activation energy is sometimes needed.
Enthalpy of adsorption is low (20-40 kJ mol <sup>-1</sup> ) in this case.	Enthalpy of adsorption is high (80-240 kJ mol <sup>-1</sup> ) in this case.

### Adsorption Isotherm –

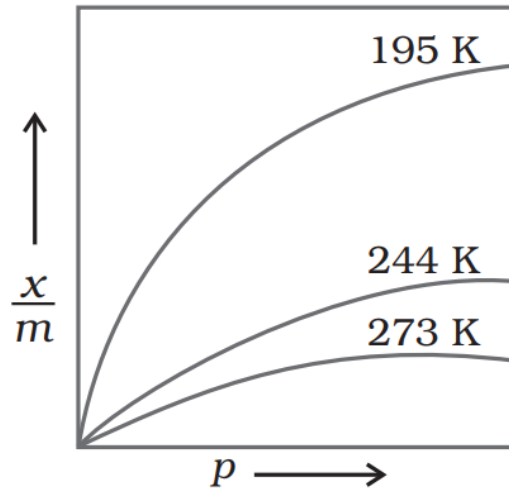


Figure: Adsorption isotherm

- The variation in the amount of gas adsorbed by an adsorbent with the pressure at constant temperature is expressed by means of a curve termed as adsorption isotherm.
- There are various type of adsorption isotherm like Freundlich, Langmuir and Tempkin isotherms.

1. **Freundlich adsorption isotherm-**

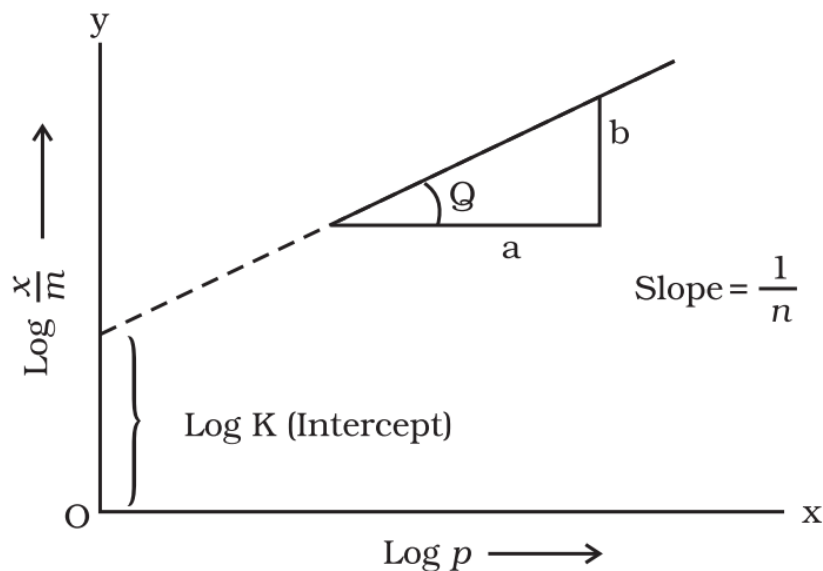


Figure: Freundlich isotherm

- He propounded a relationship between the quantity of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. The relation is as follows-

$$\frac{x}{m} = k \cdot p^{1/n}$$

Here x = mass of the gas adsorbed on adsorbent

m = mass of the adsorbent

p = pressure

k and n are constant depends upon temperature.

- A graph is plotted between mass of the gas adsorbed per gram of the adsorbent versus pressure.
- According to this curve at a fixed pressure there is a decrease in physical adsorption with increase in temperature. These curves approach saturation at high pressure.
- Taking log of above relation:

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

- The Freundlich isotherm's validity is verified by plotting a graph between  $\log x/m$  and  $\log p$ . If it comes to be a straight line then the Freundlich isotherm is valid.
- Slope =  $1/n$
- Intercept =  $\log k$
- Freundlich isotherm tells us the behavior of adsorption in an approximate manner.  $1/n = 0$  to  $1$ .
- When  $1/n = 0$ ,  $x/m$  is constant.
- When  $1/n = 1$ ,  $x/m = k p$ , i.e.  $x/m \propto p$ , the adsorption varies directly with the pressure.
- The experimental isotherms saturate at high pressure. This cannot be explained by Freundlich isotherm, means it fails at high pressure.

### Adsorption from solution phase

- Solids can adsorb solutes from solution too. Here are some examples:

1. When a solution of acetic acid and water is stirred with charcoal; some amount of the acid is adsorbed on the surface of charcoal thus the concentration of the acid decreased in the solution.
2. The precipitate of  $Mg(OH)_2$  gets blue colored when precipitated in presence of magneson reagent. The color is due to adsorption of magneson.
3. The litmus solution is shaken with charcoal it becomes colorless.

➤ In case of adsorption from solution phase-

- i. The extent of adsorption decrease with increase in temperature.

$$\text{Adsorption} \propto \frac{1}{\text{temperature}}$$

- ii. The extent of adsorption increase with increase in surface area of the adsorbent.

$$\text{Adsorption} \propto \text{Surface area}$$

- iii. The degree of adsorption relies upon the concentration of the solute in the solution.
- iv. The degree of adsorption relies upon the nature of the adsorbent and the adsorbate.

Freundlich's equation approximately describes the behaviour of adsorption from solution:

$$\frac{x}{m} = k.C^{1/n}$$

Here C= Equilibrium concentration

On taking log of above equation:

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

A graph of  $\log x/m$  versus  $\log C$  gives a straight line which validates the Freundlich isotherm.

### Application of Adsorption –

Here are some applications of adsorption as follows:

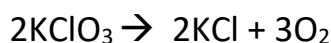


- **Production of high vacuum:** A high vacuum is created by adsorbing the remaining traces of air from a vessel by charcoal in vacuum pump.
- **Gas masks:** Gas mask which is made of activated charcoal or mixture of adsorbents. It is mostly used for breathing in coal mines to adsorb poisonous gases.
- **Separation of inert gases:** Since there is difference in degree of adsorption of gases by charcoal, separation of a mixture of noble gases can be done by adsorption on coconut charcoal at different temperatures.
- **Removal of colouring matter from solutions:** Animal charcoal removes colors of solutions by adsorbing the coloured impurities.
- **Control of humidity:** Aluminum or silica gels are used as adsorbents for removing moisture and controlling humidity.
- **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of a catalysts enhances the rate of reaction. For example: Manufacture of ammonia using iron as a catalyst, manufacture of  $\text{H}_2\text{SO}_4$  by contact process and use of finely divided Ni in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
- **In curing diseases:** Various drugs are used to kill germs by getting adsorbed on germs.
- **Froth floatation process:** Lower quality sulphides ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.
- **Adsorption indicators:** Surfaces of certain precipitates such as  $\text{AgX}$  (X-halide) have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic color at the end point.
- **Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption has numerous applications in analytical and industrial fields.

## Catalysis

- Berzelius propounded the term catalyst.

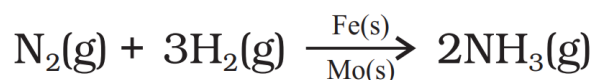
- Substances which speed up the rate of a chemical reaction and remain chemically and quantitatively unchanged at completion of the reaction are called catalysts. The phenomenon is known as catalysis.
- Potassium chlorate (KClO<sub>3</sub>) is when heated at 653-873K to decomposes slowly giving O<sub>2</sub>.



- By adding a little amount of manganese dioxide (MnO<sub>2</sub>) the temperature at which decomposition takes place becomes of lower range; which is 473-633K. The manganese dioxide remains unchanged after the reaction with respect to its composition and mass.

➤ **Promoters and poisons**

Promoters are substances which increase the activity of a catalyst while poisons decrease the activity of a catalyst. Example: In Haber's process for preparation of ammonia, molybdenum (Mo) acts as a promoter for iron; which is used as a catalyst.

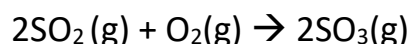


**Homogenous and heterogeneous catalysis** – Catalysis is categorized in to two classes:

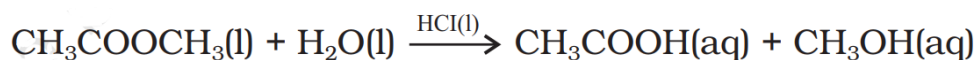
A. **Homogenous catalysis** - When the reactants products and the catalyst are in the same phase (liquid or gas), the process is said to be homogeneous catalysis. Example:

- Oxidation of sulphur dioxide (SO<sub>2</sub>) into sulphur trioxide (SO<sub>3</sub>) with O<sub>2</sub> in the presence of oxides of nitrogen as the catalyst in the lead chamber process. All reactants and products exist in the same phase.

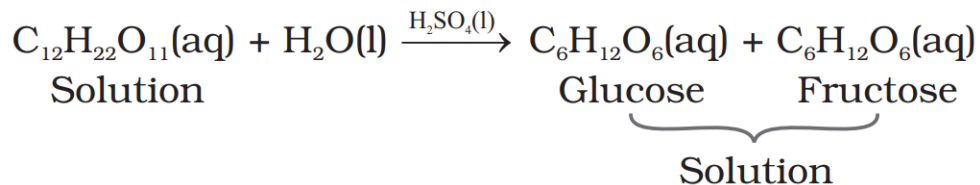
NO (g)



- Hydrolysis of methyl acetate is catalyzed by H<sup>+</sup> ions provided by hydrochloric acid.

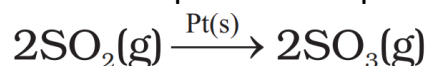


- c. Hydrolysis of sugar is catalysed by  $\text{H}^+$  ions provided by sulphuric acid.

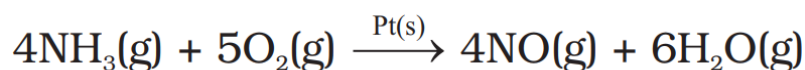


**B. Heterogeneous catalysis** – When reactants and catalyst are in different phases, it is known as heterogeneous catalysis. Examples:

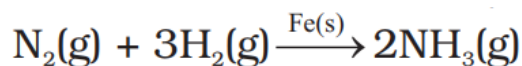
- a. Oxidation of  $\text{SO}_2$  into  $\text{SO}_3$  in the presence of platinum.



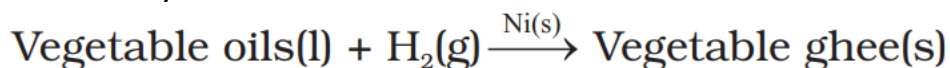
- b. Oxidation of ammonia into NO in the presence of platinum gauze in Ostwald's process.



- c. Combination between  $\text{N}_2$  and  $\text{H}_2$  to form ammonia in the presence of finely divided iron in Haber's process.



- d. Hydrogenation of vegetable oils in the presence of finely powdered nickel as catalyst.



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

### Adsorption theory of heterogeneous catalysis –

- This theory explains the mechanism of heterogeneous catalysis.
- According to old adsorption theory of catalysis the reactants in gaseous state or in liquid state, are adsorbed on the surface of solid catalyst. The rate of reaction increase with the increase in concentration of the reactants on the surface.
- Adsorption is an exothermic process and the heat of adsorption is

- The mechanism of this theory involves following steps:
  1. Diffusion of reactants at the surface of the catalyst.
  2. Adsorption of reactant molecules on the surface of the catalyst.
  3. Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.

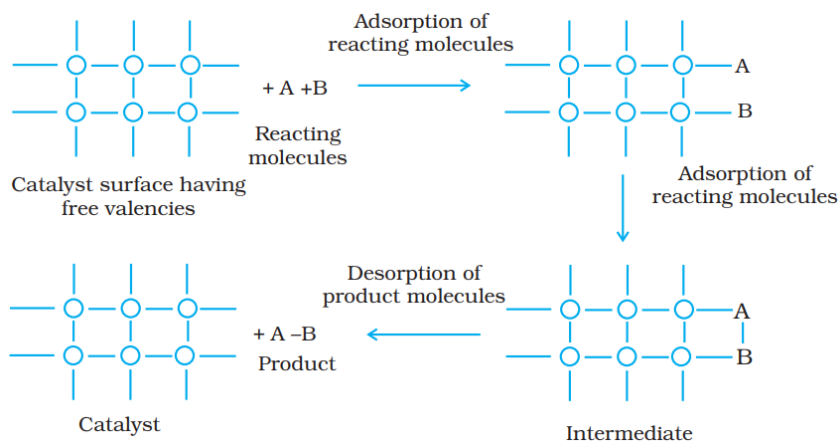


Figure: Adsorption of reacting molecules, formation of intermediate and desorption of products

4. Desorption of reaction products from the catalyst surface and making the surface available again for further reaction to occur.
5. The surface of the catalyst contains free valencies which provide the space for chemical forces of attraction. When a gas comes in contact with such a surface; gas molecules are held up there due to loose chemical combination. Different molecules are adsorbed alongside, they may react with each other and form new molecules. Thus formed molecules get evaporated to leave the surface for the fresh reactant molecules.

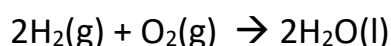
This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is very effective even in small quantities.

## Important features of solid catalysis

### (A) Activity –

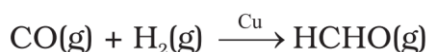
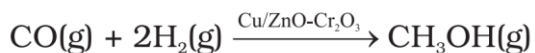
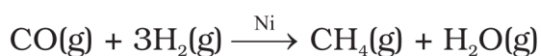
- The catalyst activity affected by the strength of chemisorption.
- The reactants must get adsorbed strongly on to the catalyst surface to become active. Reactant should not be adsorbed too strongly so it become immobilized and other reactants have no space left on the catalyst's surface to get adsorbed.
- In hydrogenation reaction the catalytic activity increases from Group 5 - 11.

Pt



### (B) Selectivity –

- The catalyst selectivity is catalyst's ability to direct a reaction to yield a particular product selectively; when under the same reaction conditions many products formation are possible.
- Selectivity of different catalysts for same reactants is different.
- For example here we have taken H<sub>2</sub> and CO and different catalysts:



- Thus we can conclude that the action of a catalyst is highly selective in nature.

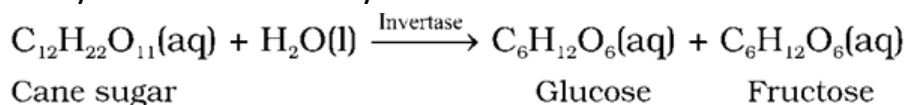
### Shape selective catalysis by Zeolites –

- Some catalytic reaction depends upon the structure of pore in catalyst and the size of the reactant and product molecules. These type of reactions are called shape-selective catalytic reactions and the process is called shape selective catalysis.
- Zeolites are good example of shape-selective catalysts because of their honeycomb-like structures. They are microporous aluminosilicates with 3d-network of silicates in which some silicon atoms are replaced by aluminium atoms providing Al–O–Si framework.

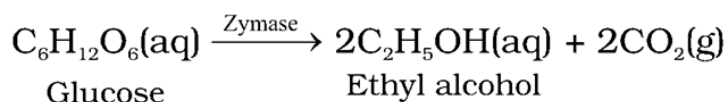
- The reactions taking place in zeolites depend not only upon size and shape of reactant and product molecules but also upon the pores and cavities of the zeolites.
- They can occur naturally as well as synthesized for catalytic selectivity.
- Zeolites are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization.
- An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline or petrol by dehydrating them to give a mixture of hydrocarbons.

### Enzyme catalysis –

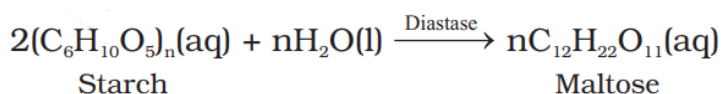
- Enzymes are complex nitrogenous organic compounds which are produced by living animals and plants.
- They are protein molecules with high molecular mass and they form colloidal solutions in water.
- They catalyze numerous reactions mainly those connected with natural processes.
- Numerous reactions that occur in the bodies of animals and plants to maintain the life process are mainly catalyzed by enzymes.
- The enzymes are identified as biochemical catalysts and the phenomenon is known as biochemical catalysis.
- The following are some of the examples of enzyme catalyzed reactions –
  1. Inversion of cane sugar: cane sugar converted into glucose and fructose by the invertase enzyme.



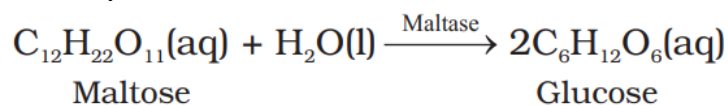
2. Conversion of glucose into ethyl alcohol: Glucose is converted into ethyl alcohol and CO<sub>2</sub> by the zymase enzyme.



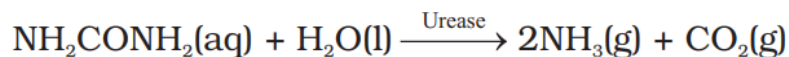
3. Conversion of starch into maltose: The diastase enzyme converts starch into maltose.



4. Conversion of maltose into glucose: Maltose is converted into glucose by an enzyme called maltase.



5. Decomposition of urea into ammonia and CO<sub>2</sub>: The enzyme urease catalyzes this reaction.



6. Conversion of milk into curd: It is an enzymatic reaction brought about by the lacto bacilli enzyme present in curd
7. The pepsin enzyme converts proteins into peptides in stomach while the pancreatic trypsin converts proteins into amino acids by hydrolysis in intestine.

Table: Some enzymatic Reactions

Enzyme	Source	Enzymatic reaction
<b>Invertase</b>	Yeast	Sucrose → Glucose and fructose
<b>Zymase</b>	Yeast	Glucose → Ethyl alcohol and CO <sub>2</sub>
<b>Diastase</b>	Malt	Starch → Maltose
<b>Maltase</b>	Yeast	Maltose → Glucose
<b>Urease</b>	Soyabean	Urea → Ammonia and CO <sub>2</sub>
<b>Pepsin</b>	Stomach	Proteins → Amino acids

### Characteristic of enzymes catalysis –

- Most highly efficient:** One molecule of an enzyme can transform one million molecules of the reactant per minute.
- Highly specific nature:** Each enzyme is specific for a given reaction. One catalyst cannot catalyze more than one reaction. Example: the urease enzyme catalyzes the hydrolysis of urea only. It cannot catalyze hydrolysis of any other amide.
- Highly active under optimum temperature:** The rate of an enzyme reaction becomes maximum at a specific temperature, called the optimum temperature. The optimum temperature range for enzymatic activity is around 298-310K. Human body temperature 310 K is suited for enzyme-catalyzed reactions.
- Highly active under optimum pH:** The rate of an enzyme-catalyzed reaction is maximum at a particular pH called optimum pH. It is between pH values 5-7.

5. **Increasing activity in presence of activators and co-enzymes:** The enzymatic activity is increased in presence of certain substances, which are known as co-enzymes. It has been observed that when a small non-protein or vitamin is present along with an enzyme, the catalytic activity is enhanced significantly. Activators are generally metal ions such as  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  etc. When these metal ions weakly bonded to enzyme molecules and increase their catalytic activity. Amylase in presence of sodium chloride i.e.,  $\text{Na}^+$  ions are catalytically very active.
6. **Influence of inhibitors and poisons:** enzymes are inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups of the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

### Mechanism of enzyme catalysis

- There are many cavities present on the surface of colloidal particles of enzymes.
- These cavities have characteristic shape and possess active groups. Active groups are like  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{SH}$ ,  $-\text{OH}$ , etc. on the surface of enzyme particles.
- The molecules of the reactant have complementary shape, fit into these cavities just like a key fits into a lock.
- On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

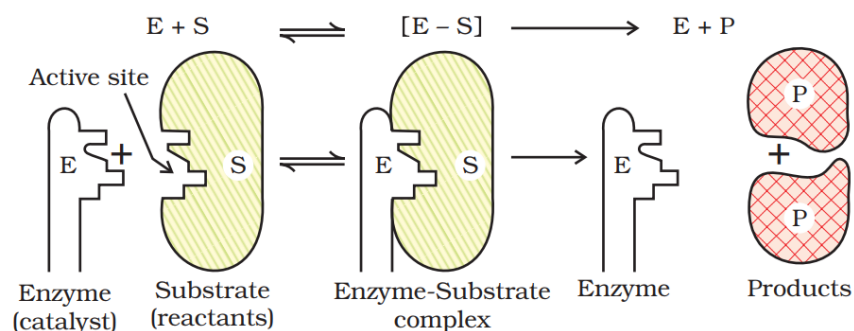
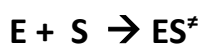


Figure: Mechanism of enzyme catalyzed reaction

- The enzyme-catalyzed reactions can be proceed in two following steps:

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





Step 2: Decomposition of activated complex give the product.



Table: some industrial catalytic processes

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

## Colloids –

- A colloid is a heterogeneous system in which one substance is dispersed as very fine particles in another substance called dispersion medium.
- Colloidal particles size range between 1 and 1000 nm.
- The essential difference between a solution and a colloid is particle size.
- Colloidal particles have an enormous surface area per unit mass due to their small size.

## Classification of colloids –

### 1. Classification based on Physical state of dispersed phase and dispersion medium

- Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, there are eight types of colloidal systems possible.
- Mixture of two gases is a homogeneous mixture and it is not a colloidal system.

Table: Types of colloidal systems

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

## 2. Classification on the basis of nature of interaction between dispersed phase and dispersion medium

- Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two classes - lyophilic and lyophobic.

### 1. Lyophilic colloids:

- The word lyophilic means liquid-loving.
- Colloidal sols made by mixing materials like gum, gelatin, starch, rubber, etc., with a suitable liquid are known as lyophilic sols.
- If the dispersion medium is separated from the dispersed phase by evaporation; the sol can be reconstituted by simply remixing with the dispersion medium; so these sols are known as reversible sols.
- These sols are quite stable and cannot be easily coagulated.

### 2. Lyophobic colloids:

- The word lyophobic means liquid-hating.
- When metals and their sulphides mixed with the dispersion medium, they do not form the colloidal sol.
- Their colloidal sols can be synthesized only by special methods.
- Such sols are called lyophobic sols. These sols are readily precipitated or coagulated by adding small amounts of electrolytes, by heating or by shaking and they are not stable.
- Once precipitated they do not give back the colloidal sol by simple addition of the dispersion medium. These sols are also called irreversible sols. Lyophobic sols can be persevered by adding stabilizing agents.

### 3. Classification based on the type of particles of the dispersed phase

- On the basis of the type of the particles of the dispersed phase, colloids are classified as: multi-molecular, macro-molecular and associated colloids.

#### 1. Multi-molecular colloids:

- When dissolved, a large number of atoms or molecules of a substance aggregate together to form species having size same as colloidal particle.
- The species thus formed are called multimolecular colloids. Example: a gold sol may contain particles of different sizes having large number of atoms.
- Sulphur sol consists of particles containing a thousand or more of  $S_8$  sulphur molecules.

#### 2. Macromolecular colloids:

- In suitable solvents macromolecules form solutions in which the size of the macromolecules might be in the colloidal particle range. Such systems are called macromolecular colloids.
- Natural macromolecules are starch, cellulose, proteins and enzymes.
- Man-made macromolecules are polystyrene, polythene, nylon, synthetic rubber, etc.

#### 3. Associated colloids (Micelles):

- These compounds at low concentrations behave as normal strong electrolytes and higher concentrations show colloidal behavior due to aggregation.
- The aggregated particles thus formed are called micelles. These are also called as associated colloids.
- The formation of micelles takes place only at a particular temperature called Kraft temperature ( $T_k$ ) and at a particular concentration called critical micelle concentration (CMC).
- On dilution, these colloids revert back to individual ions. Examples: soaps and detergents.
- The CMC value for soaps is  $10^{-4}$  to  $10^{-3}$  mol  $L^{-1}$ .
- These colloids have both lyophobic and lyophilic parts.

### Mechanism of micelle formation

- In soap solutions soap is sodium or potassium salt of a higher fatty acids and may be represented as  $\text{RCOO}^-\text{Na}^+$  (like sodium stearate  $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ , it is a major component of many bar soaps).
- When dissolved in water, it dissociates into  $\text{RCOO}^-$  and  $\text{Na}^+$  ions.
- The  $\text{RCOO}^-$  ions consist of two parts —
  1. A long hydrocarbon chain R which is hydrophobic and non-polar.
  2. A polar group  $\text{COO}^-$  which is hydrophilic and polar.
- The  $\text{RCOO}^-$  ions are present on the surface with their  $\text{COO}^-$  groups in water and the hydrocarbon chains R staying away from it and remains at the surface.
- At critical micelle concentration the anions are aggregate to form a spherical shape with their hydrocarbon chains pointing towards the center of the sphere with  $\text{COO}^-$  part remaining outward on the surface of the sphere.
- An aggregate thus formed is known as ‘ionic micelle’. These micelles may contain 100 such ions. In case of detergents, like sodium lauryl-sulphate,  $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+$ , the polar group is  $-\text{SO}_4^-$  along with a long hydrocarbon chain.
- The mechanism of micelle formation is similar to the soaps.

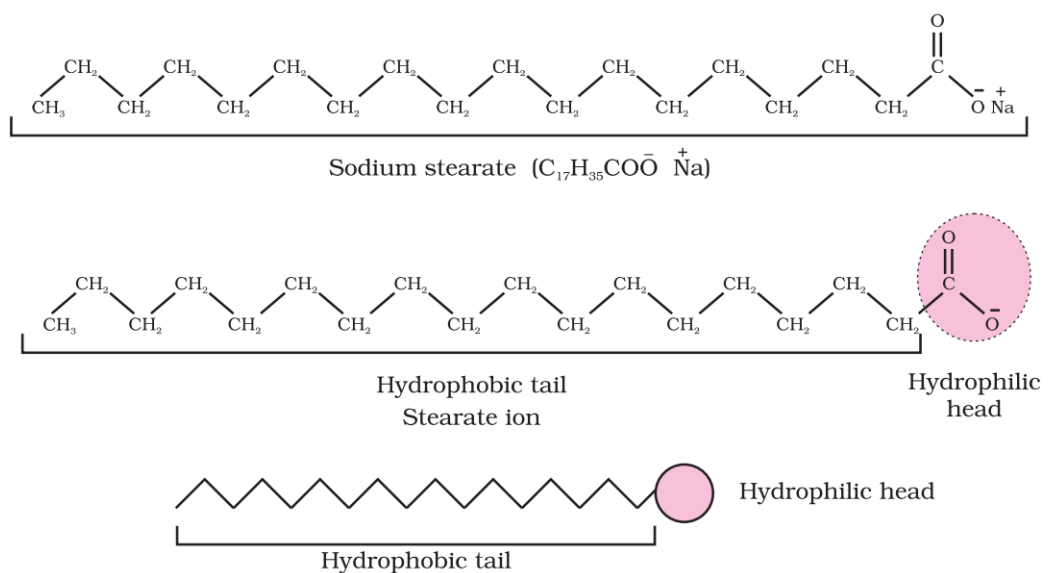


Figure: Hydrophobic and hydrophilic parts of stearate ion

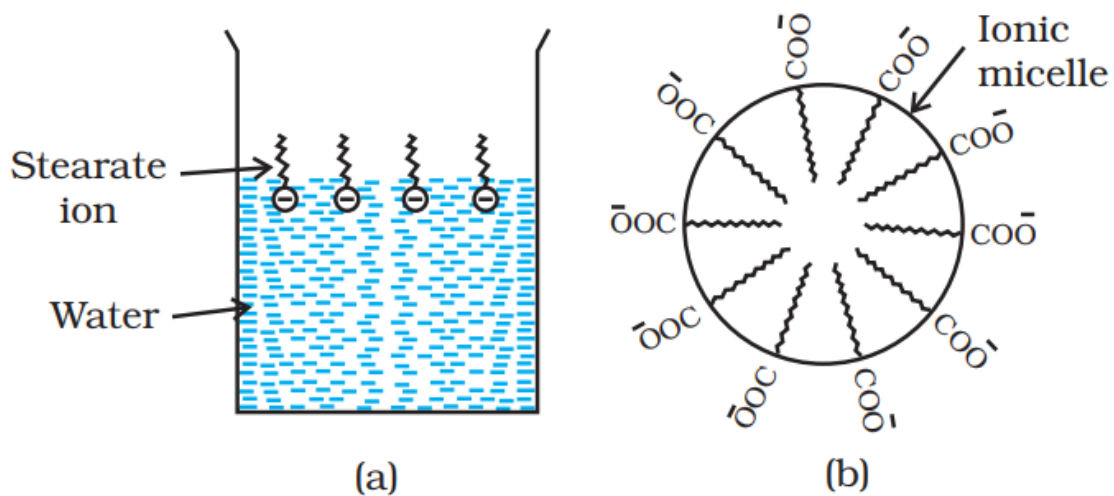


Figure: (a) The arrangement of stearate ions on the surface of water at low concentrations of soap (b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

### Cleaning actions of soaps –

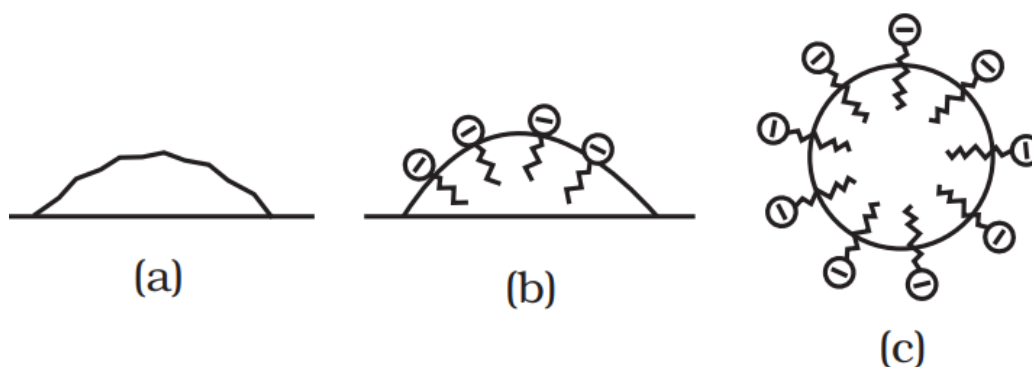


Figure: (a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

- A micelle consists of a hydrophobic hydrocarbon central core. Soap molecules form micelle around the oil droplet in such a manner that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles thus cleansing action of soap is done.
- The polar groups can interact with water and the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface.

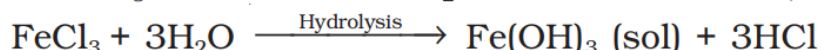
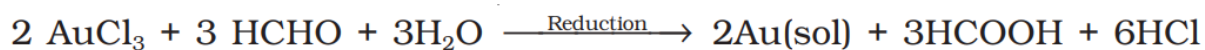
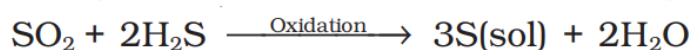
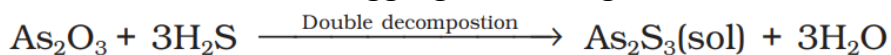
- Soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

## Preparation of colloids –

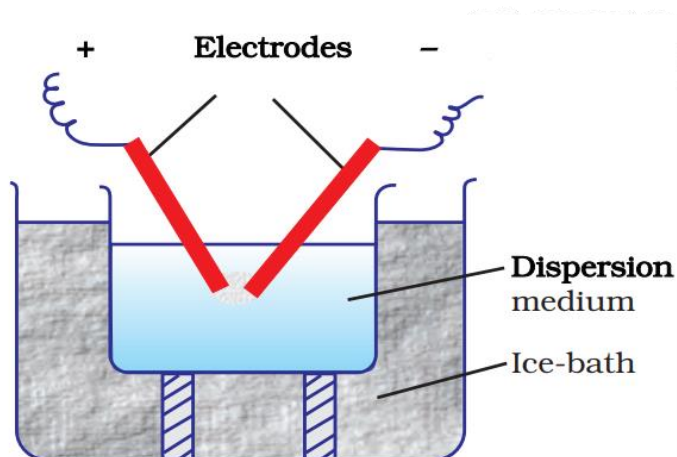
- There are few important methods for the preparation of colloids are as follows:

### 1. Chemical methods

- Colloidal dispersions can be prepared by chemical reactions leading to formation of molecules by double decomposition, reduction or hydrolysis oxidation.
- These molecules then aggregate leading to formation of sols.



### 2. Electrical disintegration or Bredig's Arc method



**Figure: Bredig's arc method**

- This process involves dispersion as well as condensation.
- Colloidal sols of metals such as Ag, Au, Pt, etc., can be prepared by this method.
- In this method the electric arc is struck between electrodes of the metal immersed in the dispersion medium.

- The intense heat produced vaporizes the metal, which then condenses to form particles of colloidal size.

### **3. Peptization**

- It is a method of converting a precipitate into colloidal sol by mixing it with a dispersion medium in the presence of an electrolyte.
- The electrolyte used for this purpose is called peptizing agent.
- This method is applied to convert a freshly prepared precipitate into a colloidal sol.
- During the process of peptization the precipitate adsorbs on its surface one of the ions of electrolyte. This generates the development of –ve or +ve charge on precipitates, which ultimately break up into smaller particles of a colloidal size.

### **Purification of colloidal solutions –**

- The process used for reducing the amount of impurities to a requisite minimum is called purification of colloidal solution.
- The purification of colloidal solution is done by following methods:

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

- In this method dissolved substances are removed from a colloidal solution through a suitable membrane by diffusion. Since ions or smaller molecules in a true solution can pass through animal membrane or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis.
- The apparatus used for this purpose is called dialyzer. A suitable membrane-bag containing the colloidal solution is suspended in a vessel; through the vessel fresh water is continuously flowing.
- The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is obtained.

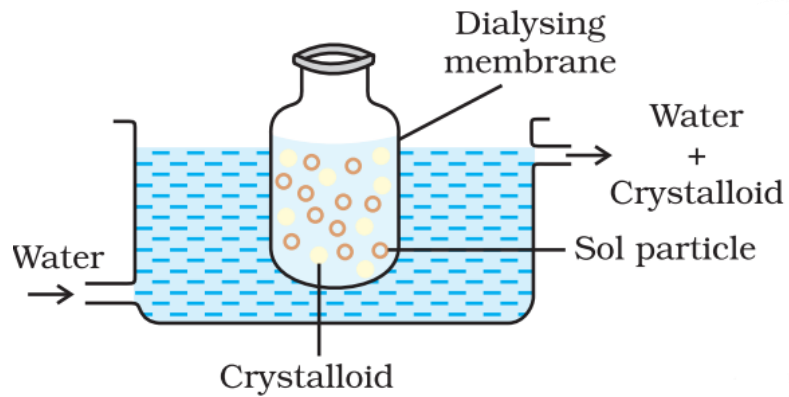


Figure: Dialysis

## 2. Electro-dialysis:

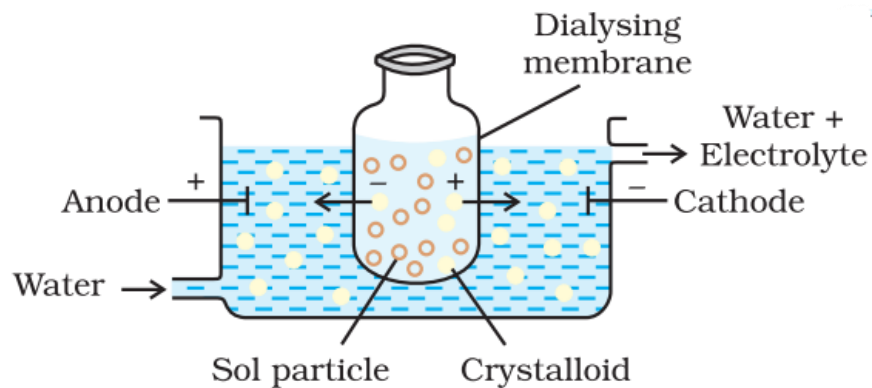


Figure: Electro-dialysis

- The dialysis is a very slow process. By applying an electric field it can be made faster in presence of an electrolyte, this process is called electro-dialysis.
- The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in to the compartment.
- The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

## 3. Ultrafiltration:

- Through this phenomenon the colloidal particles separated from the solvent and soluble solutes present in the colloidal solution by especially prepared filters.



- These filters are permeable to all substances except the colloidal particles.
- Due to the pores are too large colloidal particles can pass through ordinary filter paper.
- The pore size of a filter paper can be reduced by impregnating with collodion solution to stop the flow of colloidal particles.
- The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether.
- An ultra-filter paper can be prepared by soaking the filter paper in a collodion solution, hardening by formaldehyde and then finally drying it.
- The colloidal particles can be separated from rest of the materials by ultrafiltration. Ultrafiltration is a slow process. To speed up the process pressure or suction through pump is applied.
- The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium or solution to get a pure colloidal solution.

### **Properties of colloidal solutions –**

There are various properties shown by colloidal solutions which are as follows:

#### **1. Colligative properties:**

- The values of colligative properties like osmotic pressure, depression in freezing point, lowering in vapour pressure, and elevation in boiling point, etc. These are of small order as compared to values shown by true solutions at same concentrations.

#### **2. Tyndall effect:**

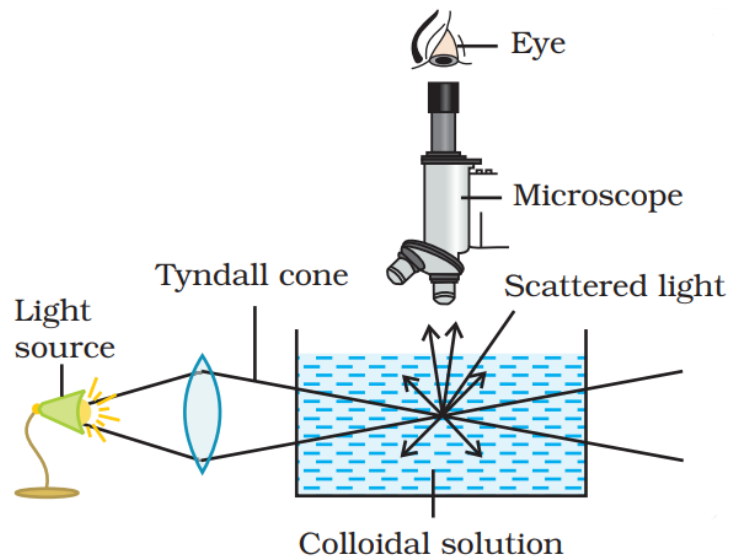


Figure: Tyndall effect

- This effect was first observed by Faraday and later studied in detail by Tyndall and it is termed as Tyndall effect.
- If we observe a homogeneous solution placed in dark in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of light beam, it appears completely dark.
- When colloidal solution viewed at right angles to the passage of light that is the path of the beam is illuminated by a bluish light.
- The bright cone of the light is called Tyndall cone.
- The Tyndall effect is produced due to scattering of light by colloidal particles in all directions in space. This scattering of light irradiates the beam path in the colloidal dispersion.
- Tyndall effect can be seen during the projection of a picture in the cinema hall due to scattering of light by dust and smoke particles present there.
- Tyndall effect is observed only when the following two conditions are satisfied –
  1. The diameter of the dispersed particles should not be lesser than the wavelength of light used.
  2. The refractive indices of the dispersed phase and the dispersion medium should be different in magnitude.

- Tyndall effect is used to distinguish between a colloidal and true solution.
- In 1903 Zsigmondy used Tyndall effect to set up an apparatus known as ultramicroscope.
- An intense beam of light is concentrated on the colloidal solution which is contained in a glass vessel. The focus of the light is observed with a microscope at right angles to the beam.
- Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope only observes the light scattered by colloidal particles.

### 3. Colour:

- The color of colloidal solution depends on the wavelength of light scattered by the dispersed particles.
- The wavelength of light depends on size and nature of particles.
- The color of colloidal solution also changes with the manner in which the observer receives the light.
- Example: a mixture of water and milk looks blue when viewed by the reflected light and red when seen by the transmitted light.
- Fine gold sol is red in color, as the size of particles increases; it appears purple, then blue and finally golden.

### 4. Brownian movement:

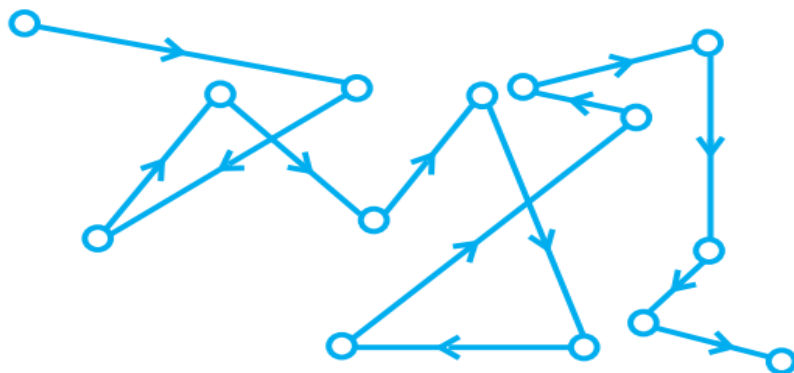


Figure: Brownian movement

- This movement was first observed by the British botanist Robert Brown and named as Brownian movement

- When colloidal solutions are observed from a ultramicroscope the colloidal particles seem to be in a state of continuous zig-zag motion.
- This motion is independent of the nature of the colloid but depends on the particle size and viscosity of the solution.
- Smaller the size and lesser the viscosity and faster is the motion.
- There is a bombardment of the particles by the molecules of the dispersion medium.
- The Brownian movement has a stirring effect which does not permit the particles to settle and responsible for the stability of sols.

### 5. Charge on colloidal particles:

- Colloidal particles carry an electric charge.
- The nature of this charge is the same on all the particles in a given colloidal solution and it can be either positive or negative.
- A table of few common sols with the nature of charge present on their particles are given below:

Positively charged sols	Negatively charged sols
Hydrated metallic oxides, Examples: $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	Metals, example: copper, silver, gold sols.
Basic dye stuffs, Examples: Methylene blue sol.	Metallic sulphides, Examples: $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , CdS sols.
Haemoglobin (blood)	Acid dye stuffs, e.g. eosin, congo red sols.
Oxides, examples: $\text{TiO}_2$ sol.	Sols of starch, gum, gelatin, clay, charcoal.

- The charge on the sol particles is due to one or more reasons that is due to electron capture by sol particles during electro-dispersion of metals, due to preferential adsorption of ions from solution or because of formation of electrical double layer.

- Development of charge on sol particles by preferential adsorption of ions can be explained by these following examples:
  1. When highly diluted solution of  $\text{AgNO}_3$  is added to highly diluted KI solution, the precipitated AgI adsorbs iodide ions from the dispersion medium and negatively charged colloidal sol results. When KI solution is added to  $\text{AgNO}_3$  solution, positively charged sol results due to adsorption of  $\text{Ag}^+$  ions from dispersion medium.

**$\text{AgI/I}^-$**   
Negatively charged

**$\text{AgI/Ag}^+$**   
Positively charged

2. When  $\text{FeCl}_3$  is added to the excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of  $\text{Fe}^{3+}$  ions. When  $\text{FeCl}_3$  is added to NaOH solution a negatively charged sol is obtained with adsorption of  $\text{OH}^-$  ions.

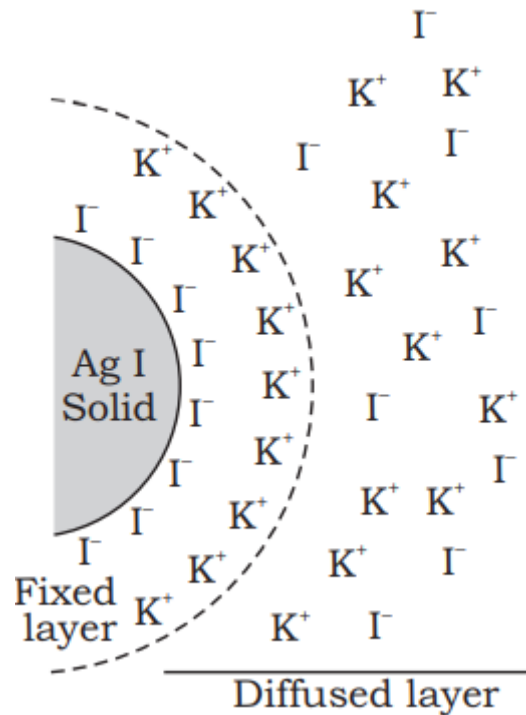
**$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O/Fe}^{3+}$**   
Positively charged

**$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O/OH}^-$**   
Negatively charged

- The first layer attracts counter ions from the medium forming a second layer as shown below:

**$\text{AgI/I}^- \text{K}^+ \quad \text{AgI/Ag}^+ \text{I}^-$**

- If two oppositely charged layers combine around the colloidal particle then this arrangement is called **Helmholtz electrical double layer**.



**Figure: Formation of double layer**

- The first layer of ions is termed as fixed layer as it is firmly held and the second layer is mobile so it is termed as diffused layer.
- The charges of opposite signs on the fixed and diffused parts generate a difference in potential between these layers.
- **Zeta potential** is potential difference between fixed layer and the diffused layer of opposite charges.
- If two particles of an insoluble material do not have double layers they can come close enough and attractive van der Waals forces pull them together.
- In double layer particles repel each other at large distances of separation. This repulsion prevents their close approach. They remain dispersed and colloid is stabilized.

## 6. Electrophoresis:

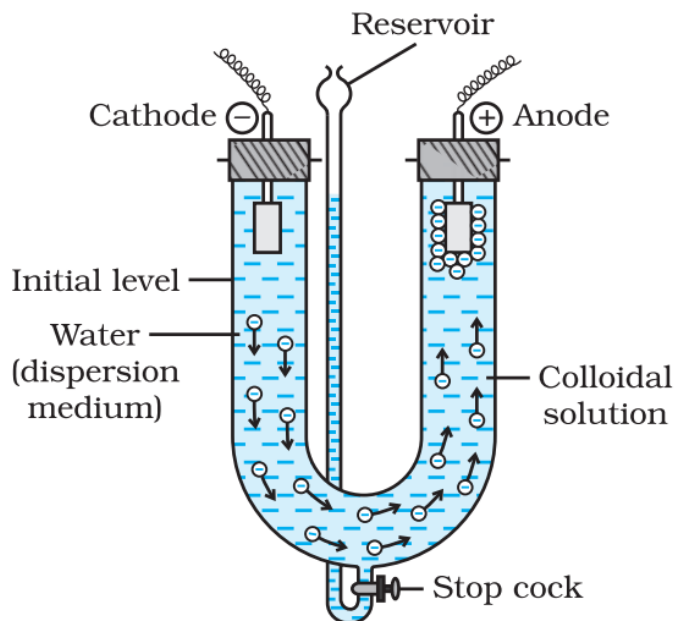


Figure: Electrophoresis

- Colloidal particles are charged and it is confirmed by electrophoresis.
- When electric potential is applied through the two platinum electrodes dipped in a colloidal solution, the colloidal particles move towards the electrodes.
- The movement of colloidal particles under the influence of an applied electric potential is called electrophoresis.
- Positively charged particles move towards cathode while the negatively charged particles move towards anode.

## 7. Coagulation or precipitation:

- Coagulation involves the settling of colloidal particles of sol.
- It can be done by following ways:
  - (a) **By electrophoresis:**
    - The colloidal particles flow towards oppositely charged electrodes. On electrodes they get discharged and eventually get precipitated.
  - (b) **By mixing two oppositely charged sols:**
    - When oppositely charged sols are mixed in equal amount; they neutralize each other's charges and get precipitated.

- The mixing of the hydrated ferric oxide (+ve sol) and the arsenious sulphide (-ve sol); results in the precipitated forms. This type of coagulation is called as mutual coagulation.

(c) **By boiling:**

- After boiling a sol, the adsorbed layer get disturbed due to increased collisions with the molecules of dispersion medium.
- This reduces the charge on the particles and leads to settling down in the form of a precipitate.

(d) **By persistent dialysis:**

- On long dialysis, traces of the electrolyte present in the sol are removed totally and the colloids become unstable which eventually coagulate.

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

- When excess of an electrolyte is added to the sol, colloidal particles are precipitated.
- The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralization leading to the coagulation.
- The coagulating ion is responsible for the neutralization of charge on the particles. A negative ion causes the precipitation of positively charged sol and vice versa.

❖ **Hardy-Schulze rule** - The greater the valence of the flocculating ion added, the greater is its power to cause the precipitation. This is known as Hardy-Schulze rule.

❖ In the coagulation of a negative sol, the order of flocculating power is as follows:



❖ Similarly, in the coagulation of a positive sol, the order of flocculating power is as follows:



❖ The coagulating value is the minimum concentration of an electrolyte in mill moles per liter, which is required to precipitate a sol in two hours.



The coagulating power of an ion is inversely proportional to the amount of electrolyte to cause the precipitation.

### Coagulation of lyophilic sols:

- There are two factors responsible for the stability of lyophilic sols. These factors include the charge present and solvation of the colloidal particles.
- On removal of these two factors, a lyophilic sol can be coagulated.
- Coagulation is done
  - (i) By adding an electrolyte
  - (ii) By adding a suitable solvent.
- When solvents such as alcohol and acetone are added to hydrophilic sols; the dehydration of dispersed phase occurs. At this stage a small quantity of electrolyte can bring about coagulation.

### Protection of colloids

- Lyophobic sols are less stable than Lyophilic sols. Lyophilic colloids possess a unique property of protecting lyophobic colloids.
- When a lyophilic sol is mixed with lyophobic sol. The lyophilic particles surround the lyophobic particles and thus protect the later one from electrolytes.
- Lyophilic colloids used for this purpose are called protective colloids.

### Emulsions –

- These are liquid-liquid colloidal systems, means the dispersion of finely divided droplets in to another liquid.
- If two partially miscible liquids are stirred together in a beaker, a coarse dispersion of one liquid in to the other is obtained which is known as **emulsion**.
- Usually one of the two liquids is water. There are two types of emulsions.
  - (i) Oil dispersed in water (O/W type)
  - (ii) Water dispersed in oil (W/O type)

- Water (H<sub>2</sub>O) acts as dispersion medium In the first system. Examples: milk and vanishing cream. In milk liquid fat is dispersed in water. In the second system, oil is the dispersion medium.
- Common examples: butter and cream.
- Emulsions of oil in water are unstable, they separate into two layers. For stabilization of an emulsion, a third component called emulsifying agent is generally added.
- The emulsifying agent makes an interfacial film between the medium and suspended particles.
- The principal emulsifying agents for O/W emulsions are gums, proteins, natural and synthetic soaps, etc. and for W/O the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.
- Emulsions can be diluted by adding dispersion medium.
- They too exhibit Brownian movement and Tindal effect.
- By heating, freezing, centrifuging, etc. emulsions can be broken into liquids constituent.

### Colloids around us:

Following are the examples of colloids –

1. **Blue color of the sky:**

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

2. **Food articles:**

Milk, butter, halwa, ice creams, fruit juices, etc. are all colloids.

3. **Soils:**

Fertile soils are colloidal in nature. Humus present in soil acts as a protective colloid. Due to this colloidal nature, soils adsorb moisture and nourishing materials.

4. **Fog, mist and rain:**

- When air contains dust particles, it is cooled below its dew-point, the moisture from the air condenses on the surfaces of dust particles forming fine droplets. These droplets are colloidal in nature and continue to float in air in the form of mist / fog.

- Clouds are aerosols; which are small droplets of water suspended in air. Due to condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain.
- The rainfall occurs when two oppositely charged clouds meet. Artificial rain is produced by throwing the electrified sand or by spraying a sol which have opposite charge to the one on clouds.

#### 5. **Blood:**

It is a colloidal solution of albuminoidal substances. The alum and ferric chloride solution make a clot of blood which stops further bleeding. It is due to coagulation of blood corpuscles.

#### 6. **Formation of delta:**

River water is a colloidal solution of clay. Sea water contains a number of electrolytes. A point where river meets the sea, the electrolytes present in sea water coagulate the colloidal solution of clay and the formation of delta take place.

### Applications of colloids:

Colloids are widely used in the industry. Some examples are discussed below:

#### 1. **Electrical precipitation of smoke:**

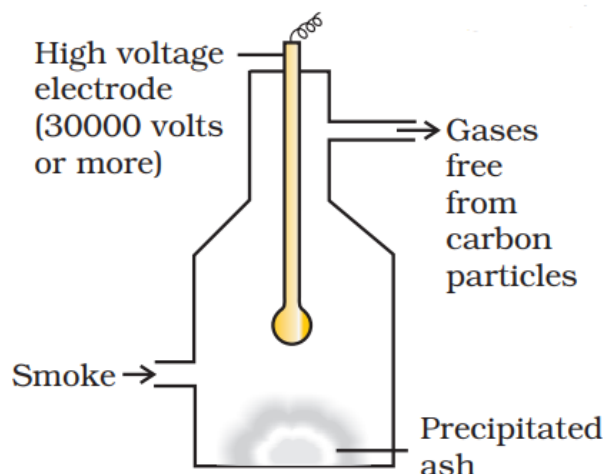


Figure: Cottrell smoke precipitator

- Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in the air.
- Before the smoke comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles.
- The particles when touch these plates lose their charge and settle down on the chamber floor. The precipitator is called cottrell precipitator.

## 2. Purification of drinking water:

- The water of natural sources is contaminated by suspended impurities. For the coagulation of the suspended impurities potassium alum is generally used.

## 3. Medicines:

- Most of the medicines are colloidal in nature. Example: argyrol is a Ag-sol which is used as an eye lotion.
- Colloidal antimony is used to cure kalaazar. Colloidal Au is used for intramuscular injection.
- Milk of magnesia; it is an emulsion and it is used for stomach disorders. Colloidal medicines are much effective because they have large surface area due to which they are easily assimilated.

## 4. Tanning:

- Animal hides are colloidal in nature.
- It has positively charged particles, when it is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. As a results in the hardening of leather. This process is termed as tanning. Cr-salts are used in place of tannin.

## 5. Photographic plates and films:

- Photographic films are made by coating the glass or celluloid film from an emulsion which is a light sensitive compound AgBr dissolved in gelatin.

## 6. Rubber industry:

- A colloidal solution of negatively charged rubber particles is known as latex. Rubber is produced by coagulation of latex.

7. **Industrial products:** Paints, inks, cement, synthetic plastics, rubber, graphite lubricants, etc. are all colloidal solutions.