Introduction

Definition of Adsorption and Related Terms :

(i) **Adsorption :** The phenomenon of increase in concentration at the surface due to molecular surface forces is known as adsorption.

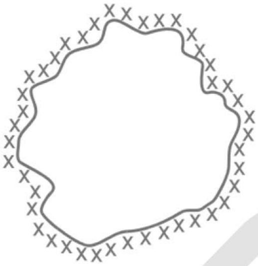
(ii) **Adsorbate :** The substances solids, gases or liquids which are adsorbed on the surface of adsorbent are called adsorbate.

(iii) **Adsorbent :** The solid or liquid substance on the surface of which adsorption takes place is called adsorbent.

Examples of adsorbents are **activated charcoal, Pt, Pd, Ni, Silica gel, gelatin, Al_2O_3, starch etc.**

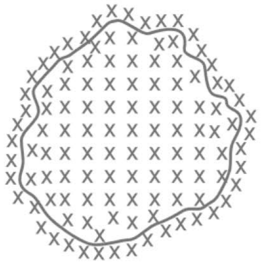
(iv) **Absorption :** When a substance is uniformly distributed throughout the body of a solid or liquid, the phenomenon is called absorption.

(v) **Sorption :** It may be defined as the process in which both adsorption and absorption take place simultaneously.



Adsorption

Absorption



Sorption

	Adsorption		Absorption
1.	It involve higher concentration of the gas or liquid at the surface of a substance.	**1.**	It involves uniform distribution of the molecular species throughout the bulk.
2.	It is rapid in the beginning and slows down near the equilibrium.	**2.**	It occurs at a uniform rate.
3.	It is a surface phenomenon.	**3.**	It occurs throughout the body of the material.
4.	It is a fast process.	**4.**	It is a slow process.

Mechanism of adsorption

Adsorption is due to the fact that the surface particles of the adsorbent are in different state than the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface, particles are not surrounded by atoms or molecules on all sides and hence they possess unbalanced or residual attractive forces.

(i) Adsorption is an exothermic process

so $\Delta H = -ve$

(ii) Freedom of movement of gas molecules decreases
so $\Delta S_{gas} = -ve$

(iii) Adsorption is a spontaneous process
so $\Delta G = -ve$ but $\Delta S_{total} > 0$

Examples.

1. $H_2O(g)$
- **Anhy. $CaCl_2 \rightarrow$ Absorption**
- **Silica gel $\rightarrow$ Adsorption**

2. $NH_3(g)$
- **$H_2O \rightarrow$ Absorption**
- **Charcoal $\rightarrow$ Adsorption**

3. Ink
- **Chalk $\rightarrow$ Absorption (water is absorbed)**
- **Chalk $\rightarrow$ Adsorption (ink is adsorbed)**

4. When Charcoal is mixed with Methylene blue then its blue colour is adsorbed (adsorption) by charcoal and the dye becomes colourless.

5. When the Magneson reagent (indicator used to detect present of Mg in solution) is mixed with white precipitate of $Mg(OH)_2$ blue colour is adsorbed by white precipitate (adsorption) of $Mg(OH)_2$.

6. When charcoal is mixed in yellow sugar solution, then yellow colour is adsorbed by charcoal and white coloured sugar solution is obtained (adsorption).

Types of Adsorption

Depending upon the nature of forces between molecules of adsorbate and adsorbent, adsorption is of two types.

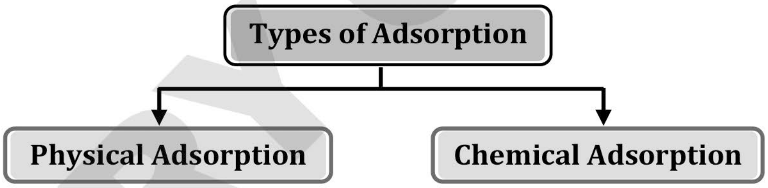
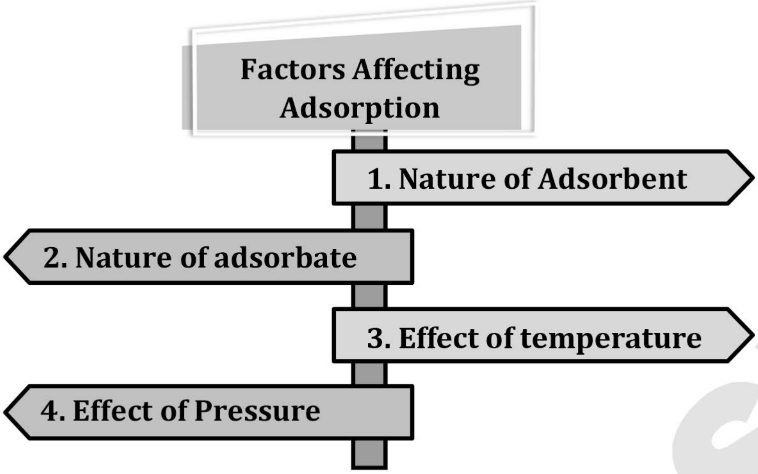


Table : Comparison of Physi-sorption and Chemi-sorption

	Physical Adsorption	Chemical Adsorption
1.	It is caused by intermolecular van der Waal's forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible	It is irreversible.
4.	Heat of adsorption is low (–20 to –40 kJ mol^{-1}).	Heat of adsorption is high (–80 to –240 kJ mol^{-1}).
5.	No appreciable activation energy is involved.	High activation energy is involved.
6.	It forms multimolecular layers on adsorbent surface under high pressure.	It forms unimolecular layer.
7.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
8.	It decreases with increase in temperature.	It first increases then decreases with temperature.

Factors Affecting Extent of Adsorption (x/m)



(i) Nature of adsorbent :

For Solids : Adsorption ∝ Surface area of adsorbent or free valency of the solid.

(ii) Nature of adsorbate:

For gases : Adsorption ∝ Critical temperature of gas (T_C)

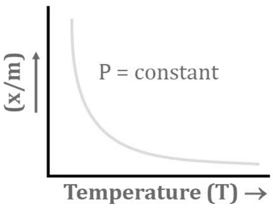
Volume of gases at N.T.P. adsorbed by 1 g of Charcoal.

Gas	H_2	N_2	CH_4	CO_2	HCl	NH_3	SO_2
Critical Temperature, Tc (K)	33	126	190	304	324	406	430
Volume adsorbed (mL)	4.7	8	16.2	48	72	181	380

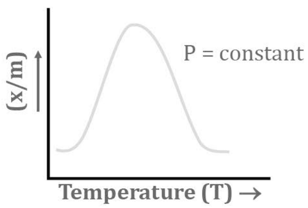
Critical temperature increases
Ease of liquefaction increase
Extent of adsorption increases

(iii) Effect of temperature : Adsorbate + Adsorbent ⇌ Adsorption; ΔH = –ve (exothermic process)

Normally adsorption decreases with temperature because adsorption is exothermic process. Physical adsorption shows regular decrease with temperature, but chemical adsorption first increases then decreases with temperature because it is specific, requires activation energy and in this process heat supplied may be used as its energy of activation.



Physical adsorption



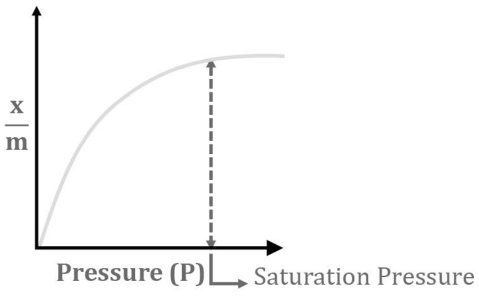
Chemical adsorption

(iv) Effect of Pressure : (Adsorption Isotherm)

The extent of the adsorption of a gas on a solid is generally expressed as $\frac{x}{m}$.

Where : x = Mass of adsorbate, m = Mass of adsorbent

Theoretically $\frac{x}{m} \alpha P$



Adsorption Isotherm

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

Freundlich adsorption isotherm : (Physical adsorption)

(i) Freundlich adsorption isotherm is obeyed by the adsorption where the adsorbate forms single layer on the surface of the adsorbent.

$\boxed{\frac{x}{m} = kP^{\frac{1}{n}}}$ Freundlich adsorption isotherm equation; $n \geq 1$

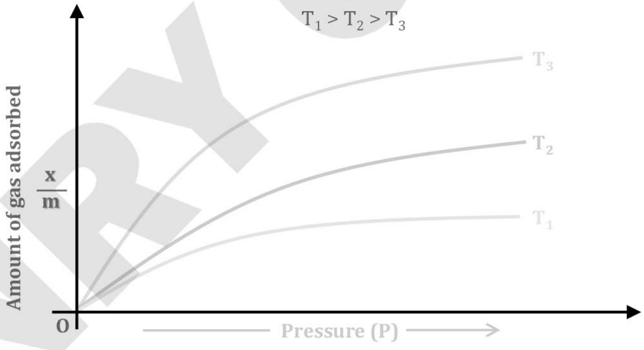
and in logarithmic form $\boxed{\log\frac{x}{m} = \log k + \frac{1}{n}\log P}$; $0 \leq \frac{1}{n} \leq 1$; in general $\frac{1}{n}$ is 0.1 to 0.5.

where x is the weight of the gas adsorbed by m g of the adsorbent at a pressure P, thus x/m represents the amount of gas adsorbed on the unit mass of adsorbent, k and n are constant at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating that the amount of the gas adsorbed does not increase as rapidly as the pressure.

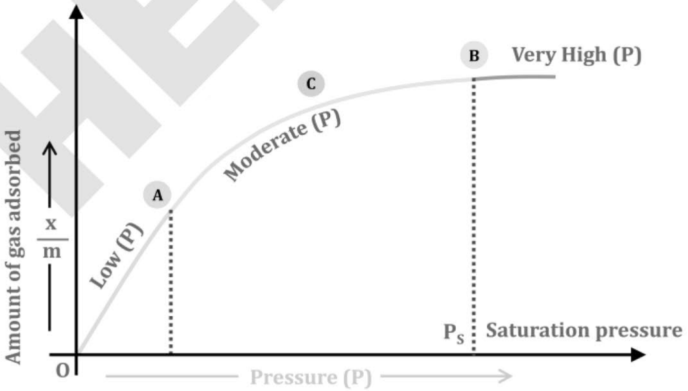
(ii) At low pressure, the extent of adsorption varies linearly with pressure $\frac{x}{m} \propto P$ ... (a)

(iii) At high pressure, it becomes independent of pressure. $\frac{x}{m} \propto P^0$ ... (b)

(iv) At moderate pressure, $\frac{x}{m}$ depends upon pressure raised to powers $\frac{x}{m} \propto P^{\frac{1}{n}}$ ... (c)



Freundlich adsorption isotherm plot of x/m against P



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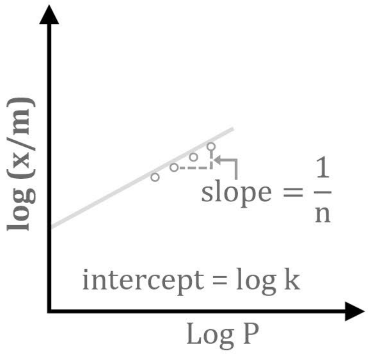


Plot of log x/m against log P for the adsorption of a gas on a solid

Adsorption in solutions (Liquid + Solid)

Ex. Dyes solution + Charcoal

$$\frac{x}{m} = kC^{\frac{1}{n}} \qquad [C = \text{concentration of liquid}]$$

Applications of Adsorption

1. Gas masks
2. Removal of colouring matter from solution
3. Separation of inert gases

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

(i) **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.

(ii) **Removal of colouring matter from solutions :** Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(iii) **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.

Golden Key Points

- Generally adsorption is exothermic process but an example of chemical adsorption is endothermic.
  Ex. Glass + $H_2(g) \rightleftharpoons$ Glass/$H_2(g)$; ΔH = Positive [Exception]
- Freundlich adsorption isotherm explains physical adsorption upto moderate pressure but fails at high pressure.
- Occulusion → Adsorption of gases on metal surface voids is called occlusion.

Colloidal Solution

Thomas Graham (1861) studied the process of diffusion of dissolved substances through a parchment paper or an animal membrane and divided the substances into two classes :-

(1) Crystalloid (2) Colloid

But this classification soon proved to be wrong since a crystalloid could behave as a colloid under different conditions and vice-versa.

For example: NaCl behaves as a crystalloid in aqueous medium and behaves as a colloid in benzene medium, whereas soap behaves as a typical colloid in water and behaves as a crystalloid in alcohol.

So new classification was given based on the size of solute particles.

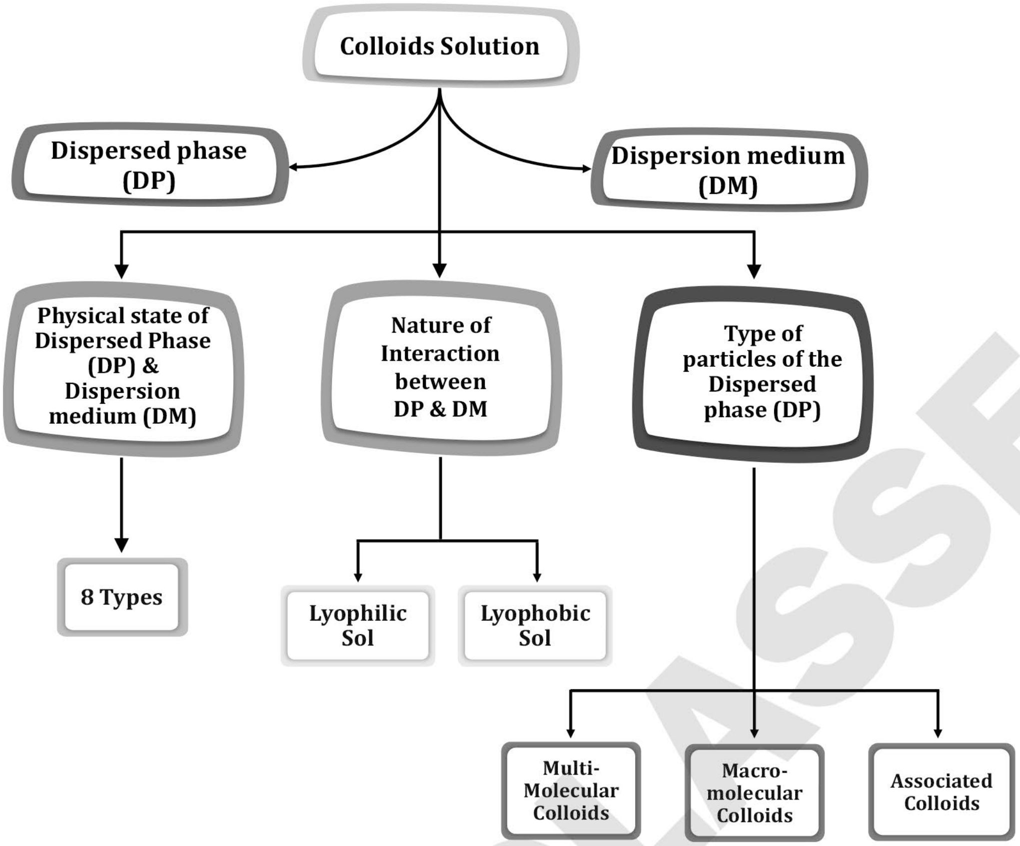
Table : Comparison of true solutions, colloids and suspension

S.No.	Property	True Solution or Crystalloid	Colloid	Suspension
1.	Particle size	< 1 nm	1 nm to 1000 nm	> 1000 nm
2.	Visibility	Not visible with any of the optical means	May be visible with ultramicroscope	Visible with naked eye
3.	Separation (a) With filter paper (b) With membranes (ultrafiltration)	Not possible Not possible	Not possible Possible	Possible Possible
4.	Diffusion	Diffuses rapidly	Diffuses very slowly	Does not diffuse
5.	Settling	Does not settle	Does not settle due to gravity But it may settle under Centrifuge	Settle due to gravity
6.	Nature	Homogenous	Heterogenous	Heterogeneous
7.	Tyndall effect & Brownian moment	Does not show	Shows	May or may not show

Types of Colloidal Solutions

A colloidal system is made of two phases. The substance distributed as the colloidal particles is called **Dispersed phase** or internal phase or the discontinuous phase. The continuous phase in which the colloidal particles are dispersed is called **dispersion medium**. For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.

Depending on the dispersed phase or dispersion medium, colloidal solutions can be classified by 3 ways-



(A) Classification of Colloidal Systems Based on Dispersed Phase and Dispersion Medium

Dispersed phase	Dispersion medium	Type of Colloidal Solution	Example
Solid	Solid	Solid sol	Ruby glass (Gold dispersed in glass), Gem stones, Minerals
Solid	Liquid	Sol	Ink, Colloidal gold, Paints, Cell fluids, Silt
Solid	Gas	Aerosol	Dust, Soot in air, (Smoke)
Liquid	Solid	Gel	Cheese, Curd, Jellies, Boot polish, Opal
Liquid	Liquid	Emulsion	Milk, Hair cream, **Butter**, Cold Cream
Liquid	Gas	Aerosol	Fog, Mist, Clouds, Insecticide sprays
Gas	Solid	Solid Sol	Cork, Pumice stone, Foam rubber, Bread, Cake
Gas	Liquid	Foam	Whipped Cream, Shaving Cream, Soda water, Soap lather

A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular structure but colloidal solution is heterogeneous in nature.

Sol : If the colloidal system has the appearance of a fluid, then it is called a **Sol.** On the basis of dispersion medium different types of sols are possible.

S.N.	Dispersion medium	Name of solution
i.	Water	Hydrosol or aquasol
ii.	Benzene	Benzosol
iii.	Alcohol	Alcosol
iv.	Air	Aerosol

(B) Classification Based on Interaction Between Dispersed Phase and Dispersion Medium : Lyophilic sol and lyophobic sol

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (Solvent - loving). For example - dispersion of gelatin, starch, gum and proteins in water.

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions. Eg. : Metals and their sulphides

Comparison of Lyophilic and Lyophobic sols

S. No.	Property	Lyophilic sol (Emulsoid)	Lyophobic sol (suspensoid)
1	Preparation	Can be easily prepared by shaking or warming the substance with solvent.	Can not be prepared easily. Special methods are required.
2	Stability	Are more stable	Are less stable
3	Reversibility	Are reversible	Are irreversible
4	Viscocity	Viscosity is much higher than that of solvent	Viscosity is nearly same as that of the solvent
5	Surface tension	Surface tension is usually low	Surface tension is almost same as that of solvent
6	Hydration or solvation	These are highly solvated as the particle have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7	Charge	The particles have little charge or no charge at all	The particles carry a characteristic charge either positive or negative
8	Visibility	Particles can not be seen under microscope	Particles can be seen under microscope
9	Coagulation or precipitation	Not easily precipitated	Easily precipitated
10	Tyndall effect	Less Scattering	More Scattering
11	Migration in electric field	May or may not migrate as they may or may not carry charge	Migrate towards anode or cathode as these particles carry charge
12	General Example	**Mostly of organic nature** Example: Gelatin, Starch, Gum, Albumin & Cellulose Solution	**Mostly or Inorganic nature** Example: Transition metal salt like Gold, As etc.

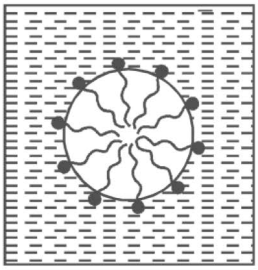
(C) On the Basis of Type of Dispersed Phase

Multi Molecular	Macro Molecular	Associated colloids
Formation by aggregation of large number of atoms is or smaller molecules of substance. Ex. → **Gold Sol (Au)** **Sulphur sol (S_8)**	In suitable solvents, macro-molecules form solutions in which the size of particles may be in colloidal range. Ex. → **Starch, Cellulose,** **Protein etc.**	These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles. Ex. → **Soap & Detergent**

Associated Colloids [Micelles]

Substances whose molecules aggregate to form particles of colloidal dimensions are called associated colloids. The molecules of soaps and detergents are usually smaller than the colloidal particles. However, in concentrated solutions, these molecules associate and form aggregates of colloidal size. These aggregates of soaps or detergent molecules are called Micelles. Soaps and detergents are strong electrolytes and give ions when dissolved in water

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} \rightarrow C_{17}H_{35}COO^- + Na^+$$



Solid Circle (•)
Represents
Polar group ($-COO^-Na^+$)
Wave line(~)
Represents
Non-Polar group (–R)

The negative ions aggregate to form a micelle of colloidal size. The negative ion has a long hydrocarbon chain and a polar group ($-COO^-$) at one end. In micelle formation, the long hydrocarbon chain (tail) which is insoluble in water is directed towards the center while the soluble polar head is on the surface in contact with water. The charge on the micelle is responsible for the stability of this system.

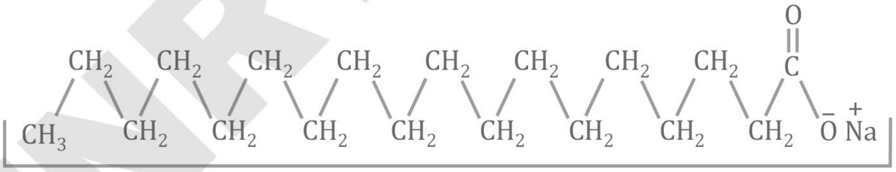
Critical Micelle concentration (CMC) :

The concentration above which associated colloids or Micelles are formed is called CMC.

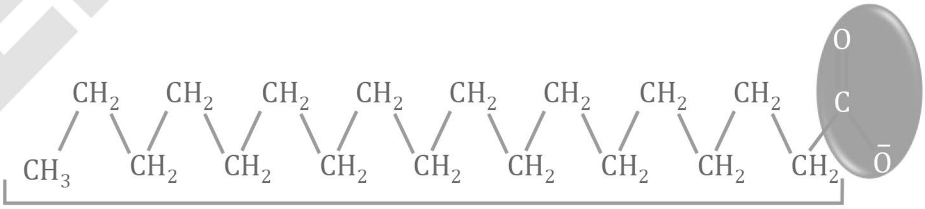
CMC of soap is 10^{-4} to 10^{-3} mol lit^{-1}.

These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

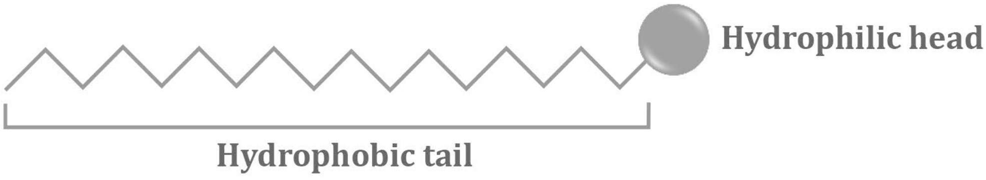
Kraft Temperature (T_K) : Temperature above which Micelles are formed.



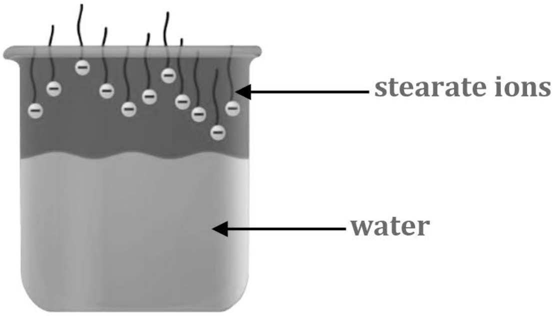
Sodium stearate ($C_{17}H_{35}\overset{-}{C}OO\overset{+}{N}a$)



Hydrophobic tail of stearate ion



Hydrophobic and hydrophilic parts of stearate ion



(a)

(a) Arrangement of stearate ions on the surface of water at low concentrations of soap

(b)

(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

Necessary and Sufficient Condition for Micelle Formation are:-

(a) Compounds must have hydrophobic part means long chain alkyl group.

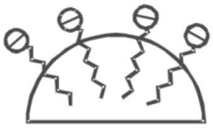
(b) Compounds must have hydrophilic part means $-SO_3^-, -COO^-, -\ddot{\underset{\cdot\cdot}{O}}-, -\overset{+}{N}R_3$ etc.

All these compounds which forms micelle are also known as surfactants. They are surface active agents which reduces surface tension.

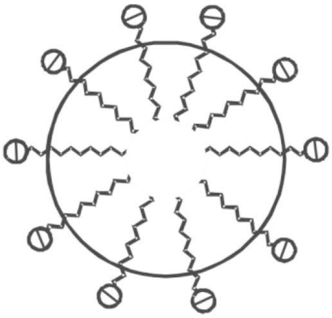
Cleansing Action of Soaps

The cleansing action of soap is due to fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of stearate ions in the oil droplet and hydrophilic part projects out of grease droplet like bristles. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

(a) Grease on cloth



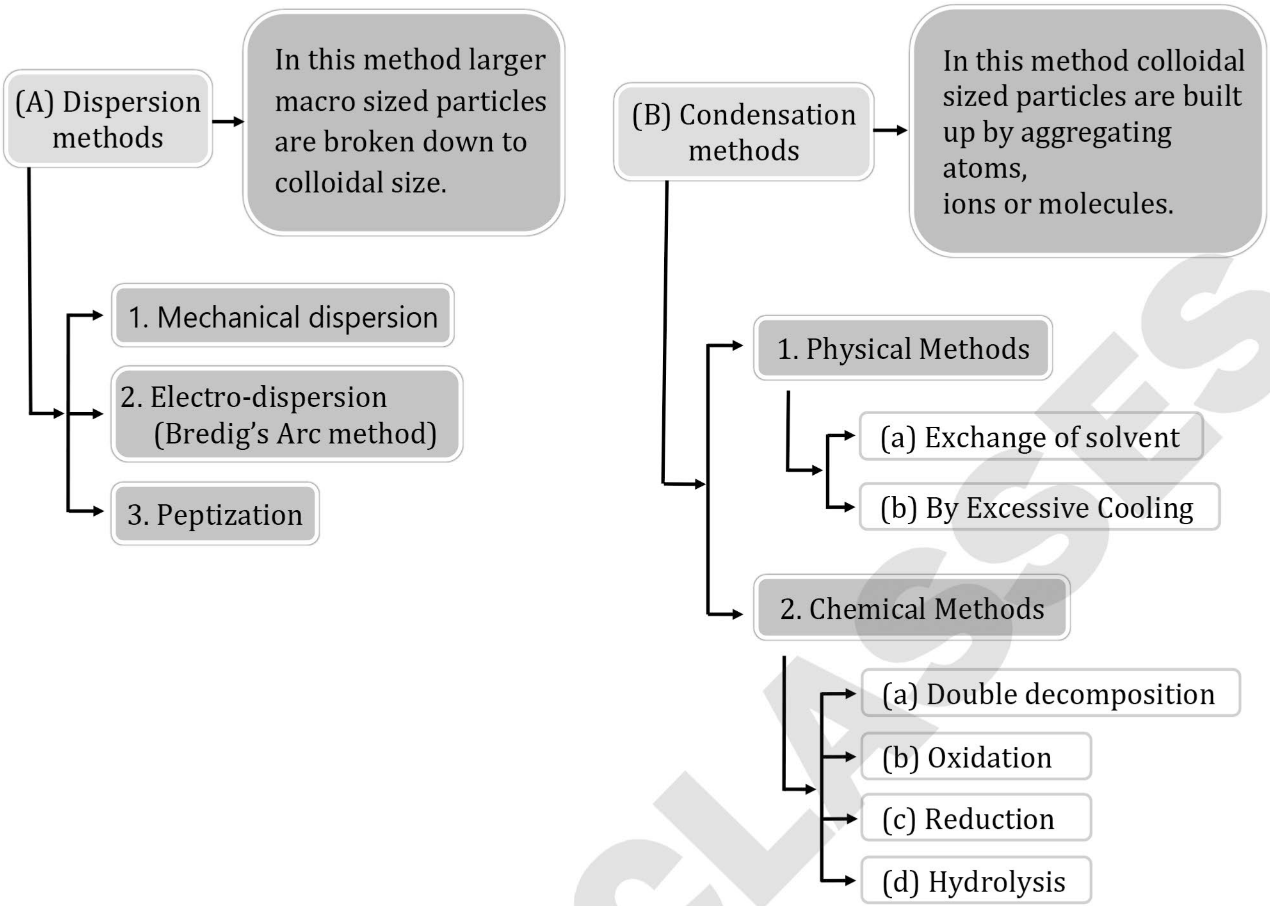
(b) Stearate ions arranging around grease droplet



(c) micelle formed

Methods of Preparation

Lyophilic sols may be prepared by simply warming the solid with liquid dispersion medium eg. starch with water. On the other hand lyophobic sols have to be prepared by special methods. These methods fall into two categories –



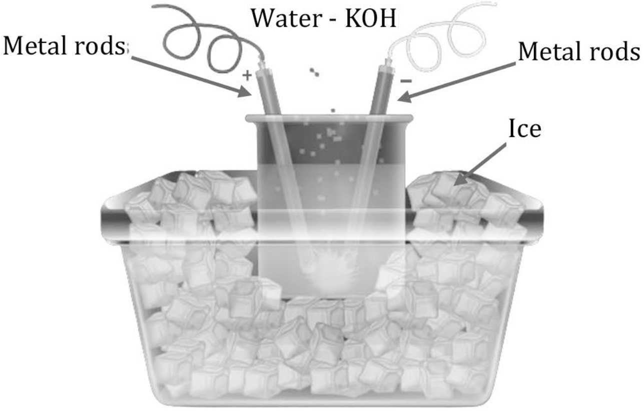
(A) Dispersion Methods.

(i) Mechanical dispersion : The substance to be dispersed is grinded as finely as possible and then shaken with the dispersion medium to form a suspension. This suspension is passed through colloidal mill where the suspended particles are broken to produce particles of colloidal size. Ex.: Ink, paints.

(ii) Electro-dispersion (Bredig's arc method) :

This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agent such as a trace of KOH. The water is cooled by immersing the container in a ice bath. The intense heat of the arc vaporizes some of the metal which condenses under cold water.

Ex. : Pt, Ag, Cu, Au, Pb Sol are prepared by this method.



Electro-dispersion

(iii) Peptization (Peptization is a opposite process of coagulation)

The process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used is called a **Peptizing agent.**

Few Examples of Sols obtained by Peptization :

(i) $AgI\downarrow + AgNO_3 \rightarrow [AgI]\ Ag^+ : NO_3^-$

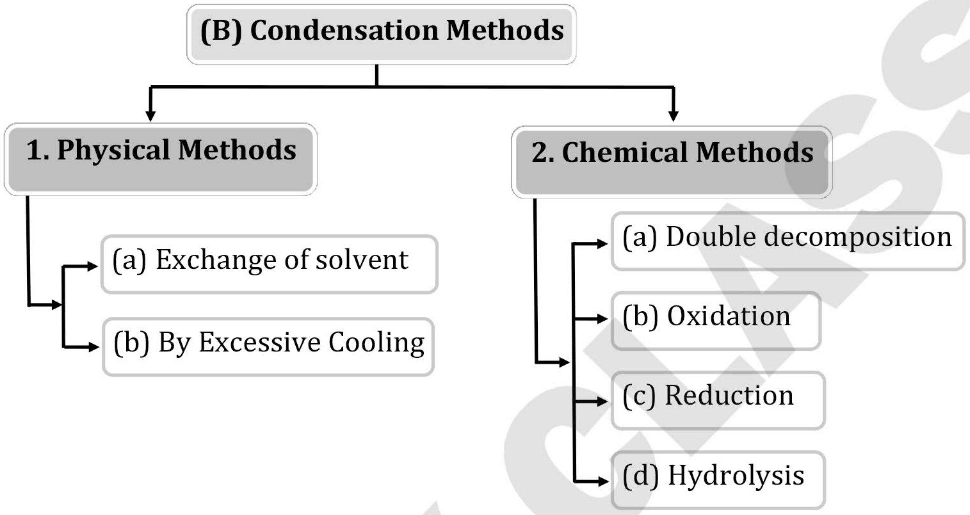
(ii) $AgI\downarrow + KI \rightarrow [AgI]\ I^- : K^+$

(iii) $Fe(OH)_3\downarrow + FeCl_3 \rightarrow [Fe(OH)_3]\ Fe^{3+} : 3Cl^-$

(iv) $Fe(OH)_3\downarrow + NaOH \rightarrow [Fe(OH)_3]\ OH^- : Na^+$

(v) $CdS\downarrow + H_2S \rightarrow [CdS]\ S^{2-} : 2H^+$

The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added-particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.



(B) Condensation methods

(1) Chemical methods : The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided. **Some familiar reactions used are :**

(a) Double decomposition : A 1% solution of arsenic oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, then a stream of H_2S is passed through the solution. This is continued till an intense yellow coloured solution is obtained.

$$\underset{}{As_2O_3} + \underset{\text{(excess)}}{3H_2S} \rightarrow \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O$$

(b) Oxidation : A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide or oxidising agent

Ex.: HNO_3, Br_2, Etc.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S\ (Sol)$$

Sulphur sol can also be obtained when H_2S is bubbled through an oxidising agent (bromine water or nitric acid)

(c) Reduction : Colloidal solutions of metals like gold, silver, platinum, lead etc. can be obtained when their salts solutions are acted upon by reducing agents.

$$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au(Sol)$$

(d) Hydrolysis : Colloidal solution of many metal hydroxides are prepared by this method. Ferric hydroxide sol is prepared by the hydrolysis of ferric chloride with boiling water.

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$

The hydroxide sol of Cr and Al can also be prepared by this method.

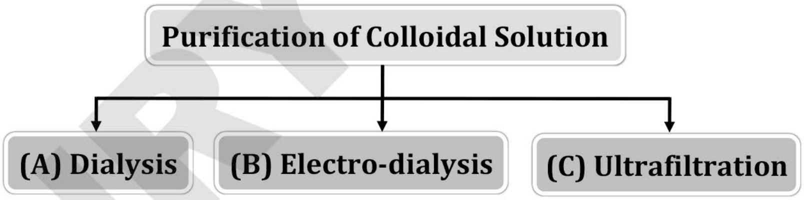
(2) Physical Methods :

(a) By exchange of solvent : when a true solution is mixed with an excess of some other solvent in which the solute is insoluble but solvent is soluble, a colloidal sol is formed. For eg. when a solution of sulphur in alcohol is mixed in excess of water, a colloidal sol of sulphur is formed.

(b) By excessive cooling : Molecules of certain substances condense together to form particles of colloidal size.

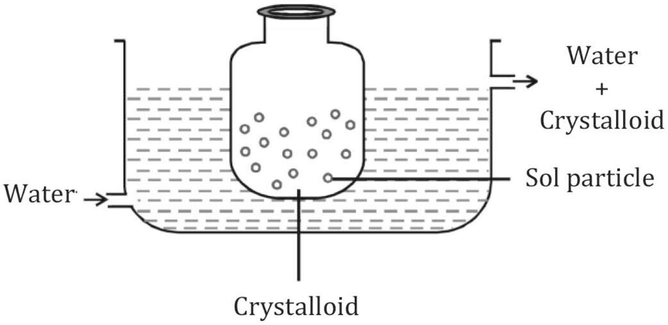
For Example : Colloidal sol of ice in an organic solvent like ether or chloroform may be prepared by freezing the mixture of water and the solvent.

Purification of Colloidal Solution



(a) Dialysis :

(i) The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis.



(ii) Its principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

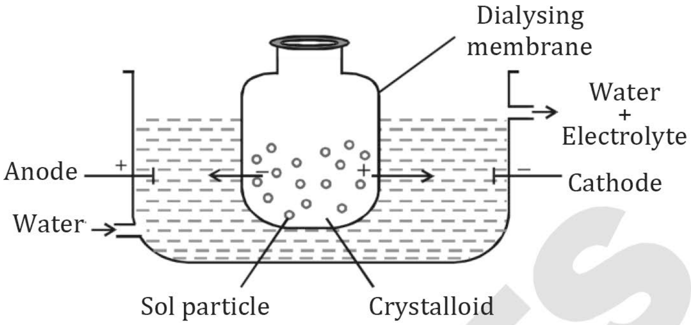
(iii) The impurities slowly diffuse out of the bag leaving behind pure colloidal solution

(iv) The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag.

(v) Prolonged dialysis can cause the colloid to coagulate.

(b) Electrodialysis

Process of dialysis can be made faster by applying an electric field if the dissolved substances in the impure colloidal solution is only an electrolyte.



(c) Ultrafiltration :

(i) Sol particles directly pass through ordinary filter paper because their pores are larger than the size of sol particles.

(ii) If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin or collodion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ultrafilter and the process of separating colloids by using ultra-filters is known as ultrafiltration.

(iii) Collodion is a 4% solution of nitro cellulose in mixture of alcohol and ether.

Properties of Colloidal Solutions

(a) Heterogenous : Colloidal particles in a solution differ in sizes and are not homogeneously distributed through out the solution.

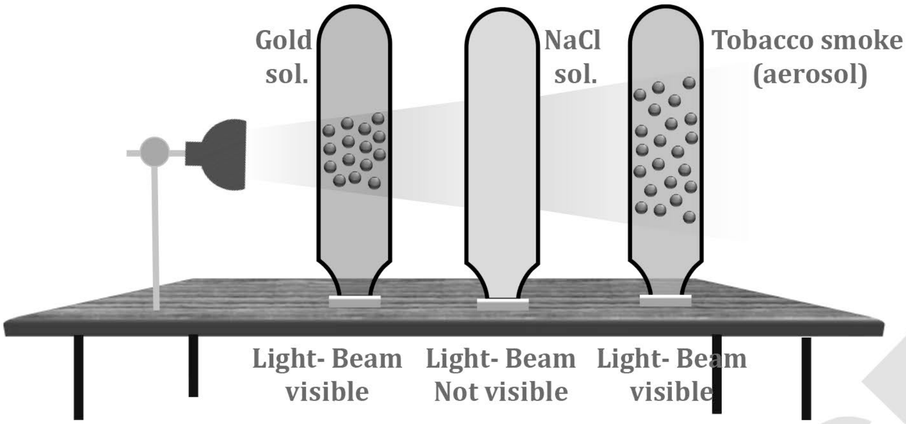
(b) Filterability : Colloidal particles pass through an ordinary filter paper but do not pass through parchment and other fine membranes.

(c) Surface tension and viscosity : For Lyophobic sols, surface tension and viscosity are not very different from those of the medium, as there is very slight interaction between the suspended particles and the medium. On the other hand Lyophilic sols show a high degree of solvation of the particles and therefore, the properties of the medium are modified. Thus, the viscosity is much higher for the sol than for the medium. Furthermore the surface tension of the sol is lower than that of pure medium.

(d) Colour : The colour of colloidal solution depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and the nature of particles. For example the colour of silver sol changes with the particle (suspended) diameter in solution the colour of colloidal solution also change with the manner in which the observer receives the light. For ex. mixture of milk and water appears blue when viewed by reflected light but red when viewed by transmitted light. finest gold sol is red in colour as size of particle increases it appears purple then blue and finally golden.

(e) Colligative properties : These properties depend on the number of solute particles in solution. In case of colloidal solutions, colloidal particles are the aggregates of ions or molecules and when compared to true solutions or normal solutions, the total no. of particles of solute in solution are very less due to large size and hence these solutions exhibit colligative properties to lesser extent.

(f) Visibility : Colloidal particles can not be seen with naked eyes or with the help of microscope. Colloidal particles, however scatter light and become visible as bright spots in a dark background when seen through a ultramicroscope. In 1903, Zsigmondy devised a microscope which is based on the principle of scattering of light by sol particles. A strong beam of light is focussed by a series of lenses in a vessel containing the sol. The colloidal solution is observed at right angle to the beam of light.



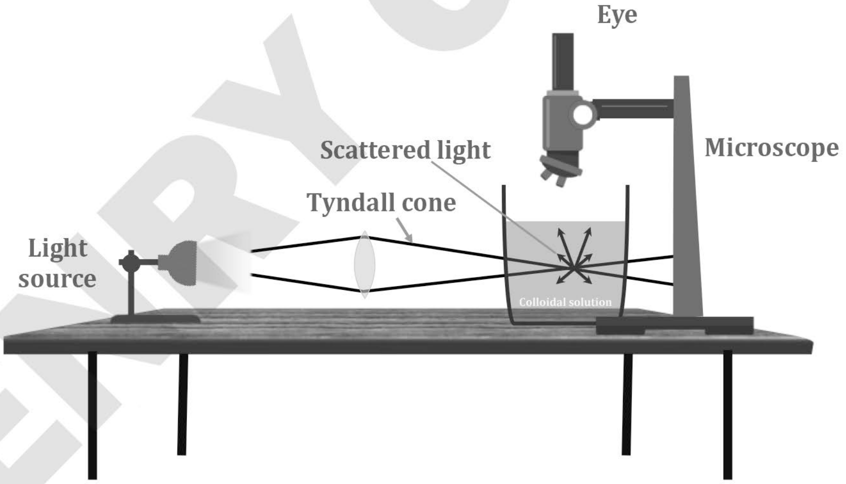
(g) Optical properties (Sols exhibits Tyndall effect) :

When a beam of light is passed through a sol and viewed at right angles, the path of the light shows up as a hazy beam of cone (illuminated path of bluish light). This was first observed by Faraday and later by Tyndall and is known as Tyndall effect. The same phenomenon is observed when a beam of sunlight enters a dark room through a small slit. When light is focussed on a sol and observed perpendicular to the beam of light rays, a cone is seen which is called Tyndall cone.

Tyndall effect can be observed only when following two conditions can be satisfied.

(i) Diameter of dispersed particle is not much smaller than wavelength of light used.

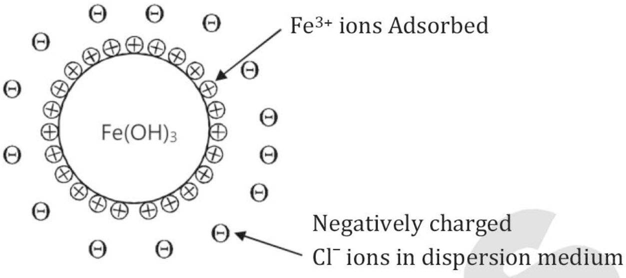
(ii) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.



(h) Kinetic properties : When a sol is examined with an ultramicroscope, the suspended particles are seen as shining of light. By following an individual particle, it is observed that the particle is in a state of continuous motion in zigzag path. The continuous rapid zigzag motion of a colloidal particle in the dispersion medium is called "Brownian movement or motion" (first observed by British botanist Robert Brown).

The Brownian movement has been explained to be due to the unbalanced bombardments of the colloidal particles by the molecules of dispersion medium.

(i) **Charge on colloidal particles :** Colloidal particles always carry an electric charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the solution.



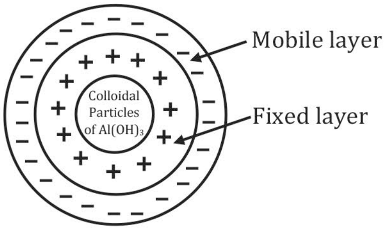
Representation of $Fe(OH)_3$ sol.

	Positively charged		**Negatively charged**
1.	Metallic hydroxides $Cr(OH)_3$, $Al(OH)_3$ & $Fe(OH)_3$ and hydrated metallic oxides $Al_2O_3.xH_2O$, $CrO_3.xH_2O$	1.	Metallic sulphides like As_2S_3, Sb_2S_3, CdS
2.	Basic dye in acidic medium stuff like: Methylene blue sol	2.	Acid dye in basic medium stuff like: Congo red sols
3.	Proteins in (acidic medium)	3.	Metal – Au, Ag, Cu, Pt etc.
4.	**Hemoglobin (Hb)**	4.	Proteins in (basic medium), Sols of starch, gum, gelatin, clay & charcoal

NOTE: Blood is a naturally occurring negatively charged colloid but Hemoglobin (Hb) is a positively charged colloid.

Electrical Double Layer

The combination of the two layers of +ve and –ve charges around the sol particle is called **Helmholtz double layer**. According to modern view, the first layer of ions is firmly held and is termed as **Fixed layer** or **Compact layer** while the second layer is mobile which is termed as **Diffused layer**



The diffused layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. The potential difference between the fixed layer and the diffused layer of opposite charge is called **Electrokinetic Potential** or **Zeta Potential**.

(j) **Electrophoresis :** If electric potential is applied across two platinum electrodes dipped in a colloidal solution, the colloidal particles move towards one or the other electrode, due to charge on them. The movement of sol particles under an applied electric potential is called "Electrophoresis". Depending upon the direction of movement of particles towards cathode or anode electrophoresis can be called "Cataphoresis' or 'Anaphoresis'. **Electrophoresis provides an experimental proof to show that the colloidal particles are charged particles.**

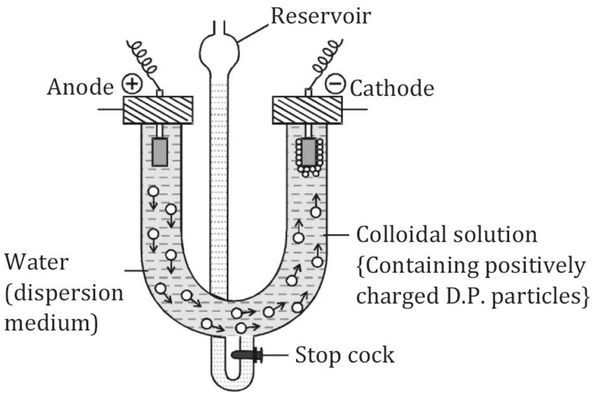


Fig.: Electrophoresis

(k) Electro osmosis : The medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movement of dispersion medium under the influence of applied potential is known as 'Electro-osmosis'. (In presence of plasma membrane)

(l) Coagulation or Precipitation : We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles. The repulsion forces between the charged particles do not allow them to settle. If somehow, the charge is removed there is nothing to keep the particles apart from each other. In such cases they aggregate or flocculate and settle down under the action of gravity. The flocculation and settling down of the dispersed phase particles is called coagulation or precipitation. The precipitation can be brought about in five ways–

Coagulation of lyophobic sol

- 1. By addition of electrolyte
- 2. By electrophoresis
- 3. By mixing two oppositely charged sols
- 4. By boiling
- 5. By repeated dialysis

(1) By addition of electrolytes : When an electrolyte is added in excess to a sol, then the electrolyte furnishes both the type of ions in solution. The oppositely charged ions get adsorbed on the surface of colloidal particles. This causes neutralization and the size mass of colloidal particle increases and it becomes a suspended particle. Due to greater volume and greater mass these suspended particles settle down and coagulate. The ion responsible for neutralization of charge on the particle is called the flocculating ion.

Hardy Schulze Rule : This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its coagulating power. Thus for the precipitation of As_2S_3 sol (–ve) the precipitating power of Al^{3+}, Ba^{2+}, and Na^+ ions is in the order

$Al^{3+} > Ba^{2+} > Na^+$

Similarly for precipitating $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{-3}$, SO_4^{2-} and Cl^- ions is in the order

$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$

The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in two hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

(2) By electrophoresis - During electrophoresis the charged sol particles migrate towards the electrode of opposite sign where they deposit their charge and then get coagulated (As neutral particles can aggregate and change to suspension particles.)

(3) **By mixing two oppositely charged sols -** The coagulation of two sols of opposite charge can be effected by mixing them eg. $Fe(OH)_3$ (positive sol) and Arsenic sulphide (negative sol) when mixed neutralize each other, join and coagulate.

(4) **By boiling -** Sols such as sulphur and silver halides dispersed in water get coagulated when boiled due to increased collisions between sol particles and water molecules, which removes the adsorbed charged layer from the sol and therefore the sol particles settle down.

(5) **By repeated dialysis -** When dialysis is repeated again and again then colloidal solution gets coagulated.

Coagulation of Lyophilic Sols :

Lyophilic sols are stable due to less charge and high solvation of the colloidal particles. When these two factors are removed, a lyophillic sol can be coagulated.

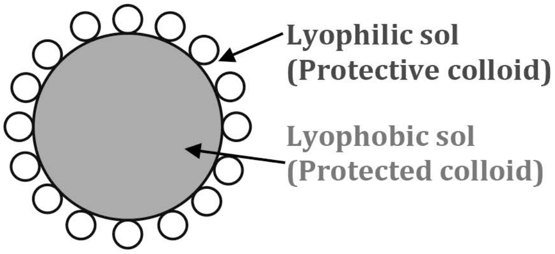
This is done (i) By adding electrolyte (ii) By adding suitable solvent.

When solvents such as alcohol and acetone are added to hydrophilic sol, the dehydration of dispersed phase occurs. Under this condition a small quantity of electrolyte can bring about coagulation.

Protection or Protective Action :

Lyophobic sols are readily precipitated by adding small amounts of electrolytes. However, these sols are often stabilized by the addition of lyophilic sols.

The property of lyophilic sols to prevent the precipitation or coagulation of a lyophobic sol is called protection. The lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a protective colloid. lyophilic sols form a thin layer around lyophobic sol or around the ions furnished by electrolyte and therefore the coagulation can not take place (as the size does not increase much). **Gelatin, Albumin, Gum Arabia, Potato Starch** are some of the examples of **Protective colloids.** The lyophilic colloids differ in their protective power. The protective power is measured in terms of gold number.



[Protection of lyophobic sol]

"Gold number" introduced by Zsigmondy. The number of **milligrams** of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophilic colloid).

The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.

The **smaller the gold number** of a protective lyophilic colloid, **greater is its protection power.**

Gold Number of some hydrophilic colloids

Lyophilic colloid	Gold Number
Gelatin	0.005 – 0.01
Egg albumen	0.08 – 0.1
Gum arabic	0.10 – 0.15
Potato – starch	25

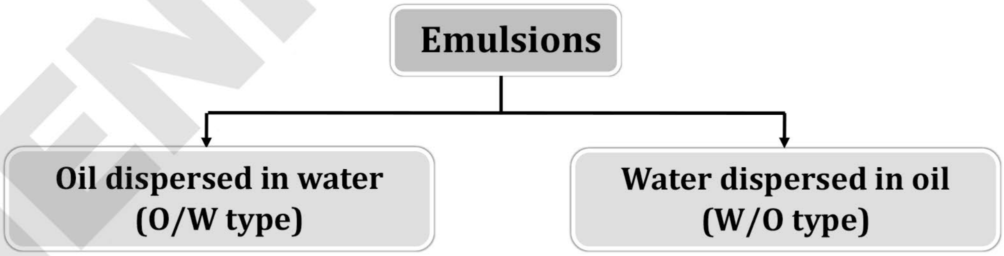
$$\boxed{\textbf{Gold Number} = 10 \times \frac{\textbf{Mass of lyophillic sol (mg)}}{\textbf{Volume of lyophobic sol (mL)}}}$$

$$\text{Protection Capacity } \alpha \ \frac{\mathbf{1}}{\mathbf{(Gold\ number)}}$$

Gelatin and starch have the maximum and minimum protective powers respectively.

Emulsions

Emulsions are liquid-liquid colloidal system. They are of two types –



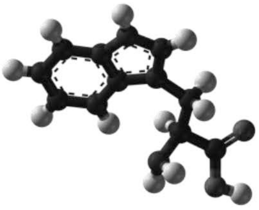
(i) Oil dispersed in water (O/W type) (ii) Water dispersed in oil (W/O type)

In the first type water acts as a dispersion medium. Examples of this type of emulsions are **milk** and **vanishing cream**. In milk, liquid fat is dispersed in water.

Milk

Vanishing cream

Soaps



Proteins

Butter

Cod liver oil

In the second system, oil acts as dispersion medium. Common examples of this type are **butter**, **cold cream**, **cod liver oil** etc.

Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For stabilization of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal emulsifying agents for o/w emulsions are **proteins, gums, soaps** etc. For w/o emulsion the principal emulsifying agents are **heavy metal salts of fatty acids, long chain alcohol, lamp black etc**.

Lamp black

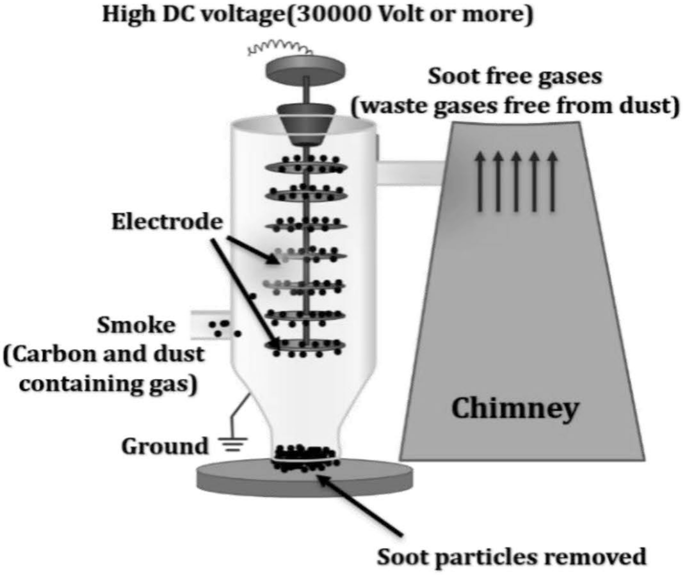
Applications of Colloids

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

Application of colloids

- 1. electrical Precipitation of smoke
- 2. Purification of drinking water
- 3. Medicines
- 4. Training
- 5. Cleansing action of soaps and

(i) Electrical precipitation of smoke : Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.



(ii) **Purification of drinking water:** The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) **Medicines :** Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.

(iv) **Tanning :** Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

(v) **Cleansing action of soaps and detergents :** This has already been described.

Golden Key Points

- Colloidal solution of graphite in water is called **"Aquadag"** while that in **Oil** is called **Oildag**.
- Gold solution in water is called **Purple of cassius**.

Catalyst and Catalysis

Substances which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as catalyst and the phenomenon is known as catalysis.

Catalysis can be broadly divided into two groups

(A) **Homogeneous catalysis :** When the reactants and the catalyst are in the same phase (i.e. liquid or gas), the process is said to be homogeneous catalysis.

Example :

(i) Lead chamber process : Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(g)} 2SO_{3(g)}$$

(ii) Inversion of cane sugar : In aqueous solution, it is catalysed by dilute acid (hydrogen ions)

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(\ell)} \xrightarrow{H_2SO_4\,(aq)} C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6\ (aq)}$$

(iii) Hydrolysis of methyl acetate is catalysed by H^+ ion furnished by hydrochloric acid

$$CH_3COOCH_{3(\ell)} + H_2O_{(\ell)} \xrightarrow{HCl(l)} CH_3COOH_{(aq)} + CH_3OH_{(aq)}$$

(B) **Surface catalysis or heterogeneous catalysis.** The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis .

Example :

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

(ii) Haber process for NH_3

$$N_{2(g)} + 3H_{2(g)} \xrightarrow[Mo(s)]{Fe(s)} 2NH_{3(g)}$$

(iii) Decomposition of H_2O_2

$$2H_2O_{2(\ell)} \xrightarrow{Pt(s)} 2H_2O_{(\ell)} + O_{2(g)}$$

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

$$\textbf{Vegetable oil}_{(l)} + H_{2(g)} \xrightarrow{Ni(s)} \textbf{Vegetable ghee}_{(s)}$$

(v) Synthesis of CH_3OH

$$CO_{(g)} + 2H_{2(g)} \xrightarrow[ZnO\text{-}Cr_2O_3]{Cu} CH_3OH_{(l)}$$

Some Other Related Terms

- Promoters
- Inhibitors
- Catalytic poison
- Autocatalysts
- Induced catalyst
- General characteristics of catalysts
- Theories of catalysis
- Catalysts in Industry
- Zeolites (Shape selective catalyst)

(a) **Promoters :** Those substances which do not themselves act as catalysts but their presence increases the activity of catalyst are called catalytic promoters.

Example : In Haber process for the synthesis of ammonia, Fe is catalyst while molybdenum (Mo) acts as a promoter $N_{2(g)} + 3H_{2(g)} \underset{Mo(promoter)}{\overset{Fe(catalyst)}{\rightleftharpoons}} 2NH_{3(g)}$

(b) **Inhibitors :** The substance which decreases the rate of chemical reaction is called inhibitor. It increases the activation energy for the reaction.

Example :

$$Na_2SO_3 + \frac{1}{2}O_2 \xrightarrow{C_2H_5OH} Na_2SO_4$$

$$C_6H_5CHO + \frac{1}{2}O_2 \xrightarrow{\text{Diphenylamine}} C_6H_5COOH$$

- H_3PO_4, glycerol and acetamide decrease the rate of decomposition of hydrogen peroxide.

(c) **Catalytic poison :** The substance whose presence decreases or destroys the activity of a catalyst is called catalytic poison.

Example :

Carbon monoxide or H_2S act as poison for Fe catalyst in Haber process for manufacture of NH_3.

As_2O_3 acts as poison for Pt asbestos in contact process for H_2SO_4.

(d) **Autocatalysts :**

When one of the product of the reaction begin to act as a catalyst, it is called auto catalyst.

Example :

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons \underset{\text{(Autocatalyst)}}{CH_3COOH} + C_2H_5OH$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow \underset{\text{(Autocatalyst)}}{2MnSO_4} + K_2SO_4 + 10CO_2 + 8H_2O$$

In the initial stage the reaction is slow but as soon as the product come into existence the reaction rate increases.

(e) Induced catalyst :

When a chemical reaction enhance, the rate of another chemical reaction it is called induced catalysis.

Example :

Sodium arsenite solution is not oxidised by air if however, air is passed through a mixture of Na_3AsO_3 & Na_2SO_3, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus influences the oxidation of sodium arsenite.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 \qquad Na_3AsO_3 + \frac{1}{2}O_2 \longrightarrow Na_3AsO_4$$

(f) General characteristics of catalysts :

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

(ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.

(iii) A catalyst does not initiate a reaction.

(iv) When a catalyst is a solid, it is usually more efficient when used in finely divided form.

(v) Generally catalyst does not change the nature of products.

(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to decrease time to achive the equilibrium state or position of equilibrium.

(vii) Catalysts are generally specific in nature.

(viii) Catalyst can change rate constant of the reaction.

(ix) Catalysts participate in mechanism of reaction.

(x) Catalyst does not change enthalpy of reaction, free energy and entropy because they are state function.

(g) Theories of catalysis

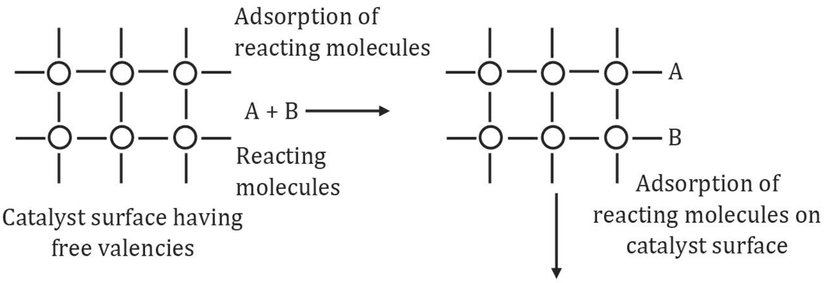
(I) Intermediate compound formation theory : This theory explains homogeneous catalysis mainly. According to this theroy, the catalyst combines with one of the reactants to give an intermediate compound. This intermediate compound reacts with the other reactants and gives the product and regenerates the catalyst in its original form.

Thus the reactants do not directly combine with each other, instead they react through the catalyst which provides an alternative pathway which involves lesser energy of activation.

For example: The function of nitric oxide [NO] as a catalyst in the formation of SO_3 is explained as follows.

$2NO$ + O_2 $\rightarrow$ $2NO_2$;
(Catalyst) (reactant) (Intermediate)
NO_2 + SO_2 $\xrightarrow[\text{reaction}]{\text{fast}}$ SO_3 + NO
(intermediate) (reactant) (product) (catalyst regenerated)

(II) Adsorption theory : This theory explains the heterogeneous catalysis. The role of a solid catalyst in enhancing the reaction rate is explained on the basis of this theory in the following steps.



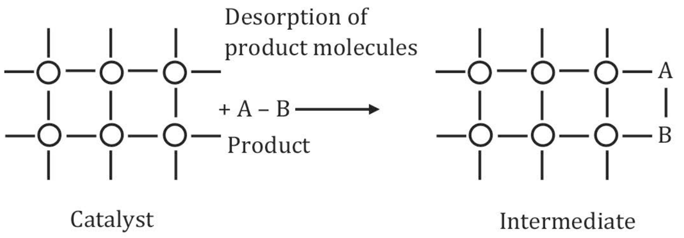


Fig.: Adsorption of reacting molecules, formation of intermediate and desorption of products

(i) The reactant molecules are adsorbed on the surface of the catalyst at adjacent points. Adsorption leads to higher concentration of the adsorbed reactant on the surface of a catalyst.

(ii) As adsorption is an exothermic process, the heat of adsorption provides the necessary activation energy for the chemical reaction to proceed.

(iii) The adsorbed reactant molecules are tied on the solid surface of the catalyst. The bonds between the atoms of chemisorbed reactant molecules are weakened. The reactant molecules of sufficient energy combine together and with the surface of the catalyst to form surface activated complex.

This adsorbed activated complex is decomposed to form products at a definite faster rate.

(iv) The product molecules rapidly leave the catalyst surface to make room for the other reactant molecules to get adsorbed. Thus the chemical combination between reactant molecules goes on at the surface of the catalyst at a much faster rate.

(h) **Catalysts in Industry :** Some of the important processes and their catalyst are given in below.

Industrial process	Catalyst used
Perparation of O_2 from $KClO_3$ (Homogeneous)	MnO_2
Haber's process for ammonia (Heterogeneous)	Fe : Mo as promotor
Ostwald's process for HNO_3 from NH_3 (Heterogeneous)	Pt Gauge
Chamber process for H_2SO_4 (Homogeneous)	Nitric oxide (NO) gas
Contact process for H_2SO_4 (Heterogeneous)	V_2O_5
Deacon's process for manufacture of Cl_2(Heterogeneous)	$CuCl_2$
Bosch process for H_2 (Heterogeneous)	$Fe_2O_3 + Cr_2O_3$ (promotor)
Manufacture of vegetable ghee (Heterogeneous)	Ni, Pt, Pd
Hydrolysis of ester (Homogeneous)	Aq. H_2SO_4/H^+
Aldol condensation of aldehyde (Homogeneous)	OH^-
Enolisation of ketone (Homogeneous)	H^+ or OH^-
Cracking of hydrocarbon (Heterogeneous)	Zeolites
Decomposition of O_3	'Cl' atom
$2CO + O_2 \rightarrow 2CO_2$	'NO'

(i) Zeolites (Shape selective catalyst) :

(i) The calatytic reaction that depends upon the pore structure of the catalyst & the size of the reactant is called shape selective catalysis. The pore size is generally in range 260-740 pm.

Ex. → Zeolite (honey comb – like structure).

Formula of Zeolite is $Na_{x/n}$ $[(AlO_2)_x(SiO_2)_y]$ z H_2O

(ii) Zeolite is also called sodium alumino silicate, water softner & cationic exchanger (Exchange only cation from hard water).

(iii) Zeolite is 3D silicate.

(iv) Zeolite, before using as catalyst are heated in vacuum so that the water of hydration is lost and as a result Zeolite becomes porous.

***Application of Zeolite :**

Normally used in petro chemical industries for cracking of hydrocarbon & isomerisation.

$**R – OH \xrightarrow{ZSM-5}$ gasoline (Petrol)

Enzyme Catalysis

(i) Enzymes are complex nitrogenous organic compounds which are produced from living plants and animals.

(ii) They are actually protein molecules of high molecular mass and form colloidal solutions in water.

(iii) They catalyse biochemical reactions.

Reactions catalyzed by enzymes :

	Enzyme	**Source**	**Reaction**
(i)	Invertase	Yeast	Sucrose → Glucose and Fructose
(ii)	Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
(iii)	Diastase	Malt	Starch → Maltose
(iv)	Maltase	Yeast	Maltose → Glucose
(v)	Urease	Soyabean	Urea → Ammonia and CO_2
(vi)	Pepsin	Stomach	Proteins → Amino acid

Characteristics of Enzyme Catalysis :

(i) **Highly efficient :** One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) **Highly specific nature :** One catalyst cannot catalyse more than one reaction.

(iii) Highly active under optimum temperature (298 K to 310 K)

(iv) Highly active under optimum pH (5 to 7)

(v) Increasing activity in presence of cofactor (Na^+, Mn^{2+}, Co^{2+}, Cu^{2+} etc.) and co-enzymes

Mechanism of enzyme catalysis (key lock theory) : There are number of active centres of definite shape present on the surface of colloidal particles of enzymes. The molecules of the reactant (substrate), which have complementary shape fit into these cavities just like a key fits into a lock. On account of the presence of active groups an activated complex is formed which then decomposes to yield the product.

Enzyme Substrate Activated complex Enzyme Products

$$E + S \rightleftharpoons [E – S] \rightarrow E + P$$

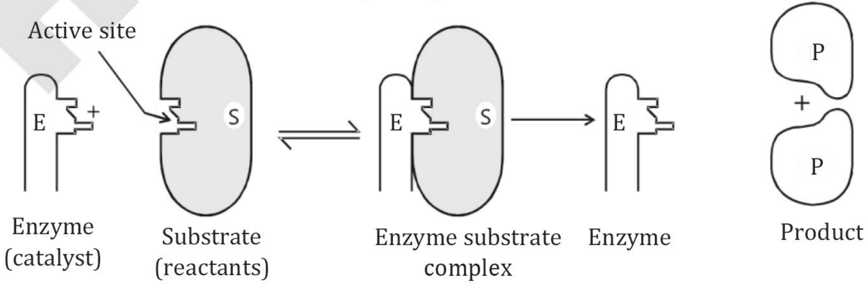


Fig : Mechanism of enzyme catalysed reaction