

SURFACE CHEMISTRY

Adsorption

Adsorption is due to the presence of **unbalanced forces**, believed to have developed either during crystallisation of solids or due to presence of unpaired, electrons or free valencies in solids having d-orbital. In liquids it is due to surface tension.

Difference between adsorption and absorption

Sr. No.	Adsorption	Absorption
1	Adsorption is a surface phenomenon. The adsorbing substance is called adsorbate and is only concentrated on the surface of adsorbent.	It is a bulk phenomenon. In absorption the substance penetrates into the bulk of the other substance.
2	The rate of adsorption is rapid to start with and its rate slowly decreases.	Absorption occurs at a uniform rate

The amount of heat evolved when one mole of an adsorbate gets adsorbed on the surface of an adsorbent is called molar **heat (enthalpy) of adsorption**.

Adsorption in Terms of Gibb's Helmholtz Equation

Adsorption is an exothermic reaction. Therefore, adsorption is accompanied by release of energy or ΔH is always negative and favours the process. Also adsorbate molecules get lesser opportunity to move about on the surface of adsorbent. Thus, entropy factor opposes the process. According to Gibb's Helmholtz equation,

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

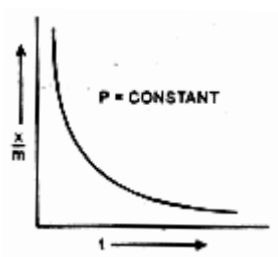
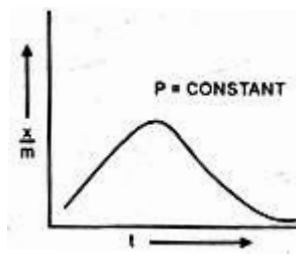
Since adsorption does actually take place, ΔH is greater than $T \Delta S \therefore \Delta G$ is negative. As the adsorption continues, the difference between the two opposing tendencies becomes lesser and lesser till they are equal i.e., $\Delta H = T \Delta S$ or $\Delta G = 0$. At this stage, equilibrium called **adsorption equilibrium** gets established and there is no net adsorption taking place at this stage.

Types of Adsorption

There are two types of adsorption.

- Physical adsorption (or Vander waal's adsorption) or physisorption.
- Chemisorption

Characteristics of Physical and Chemisorption

Physio-sorption	Chemisorption
1. Adsorption by weak vander waal's forces.	By chemical force (covalent or ionic bond)
2. Multimolecular layer may be formed	Unimolecular layer will be formed
3. Low heat of adsorption viz. about 20-40 kJ/mol	High heat of adsorption viz. about (200-400 kJ/mol)
4. Easily reversed	Not reversed
5. Molecular state of adsorbate on adsorbent is same. No surface compounds are found.	Molecular state may be different. Surface compounds are found.
6. Usually occurs rapidly at low temperature and decreases with increase in temperature. 	It occurs at high temperature initially but then decreases. 
7. It increases with pressure	Change in pressure will have less effect on chemisorptions
8. Not specific	Highly specific
9. Extent of adsorption depends on ease of liquefaction i.e. surface area, critical temperature, inversion temperature Vanderwaal's constant 'a', e.g. Adsorption of gases on charcoal	There is no relative between extent of adsorption and ease of liquefaction of gas. e.g. Adsorption of H_2 on Pt; decomposition of NH_3 in presence of tungsten, decomposition of Hl on gold (zero order)

Application of Adsorption

- In gas mask:

Finally divided coconut charcoal is used as gas masks for absorbing toxic gases like CH₄, CO, COCl₂. It is usually used for breathing in coal mines to adsorb poisonous gases.

2. In preserving Vacuum:

In Dewar flasks, activated charcoal is placed between the walls of the flask so that any gas which enters into annular space either due to glass imperfection or diffusion through glass is adsorbed.

3. As dehumidizer e.g silica gel

4. Fe(OH)₃ antidote adsorbent in Arsenic poisoning.

5. **In clarification of sugar:** Sugar decolorized by treating sugar solution with charcoal powder. The latter adsorbs the undesirable colours present.

6. **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H₂SO₄ by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

7. **In Chromatography:** The different chromatographic techniques such as adsorption, paper or column chromatography which are used for the purification and the separation of the substances available in small amounts, are based upon the theory of selective adsorption.

Catalysis

Catalyst is a substance which changes the speed of a reaction, and usually, can be recovered completely unchanged at the end of a reaction. However it may take part in a reaction consumed in one step and regenerated in another. This phenomenon is known as **Catalysis**.

A substance is termed a positive catalyst or simply as catalyst if it accelerates the rate of chemical reaction. On the other hand, the added substance is termed as negative catalyst if it retards the rate of a chemical reaction.

Example of Negative Catalysts:

i) H₃PO₄ or acetanilide in the decomposition of H₂O₂.

ii) Alcohol in the oxidation of chloroform leading to the formation of phosgene.

iii) Tetraethyl lead or nickel carbonyl acting as antiknock material in internal combustion engines.

iv) Antifreezes like glycerol which retard the rusting of the machines.

Catalytic Promoters

There are certain substances which when added only in small quantity to a catalyst enhance its activity. This substance itself may not be catalyst. Such substances which enhance the activity of a catalyst are called catalytic promoters. E.g. Molybdenum is used as Promoter for Fe catalyst in Haber's process.

Catalytic Inhibitors or poisons

The rates of some reactions are reduced considerably by the presence of small amounts of other substances called **inhibitors**. The substance whose presence decreases or destroys the activity of a catalyst are called poison. **CO or H₂S in hydrogen gas** acts as a poison for Fe catalyst in Haber process.

Types of Catalysis

Broadly, two types of catalysis are known:

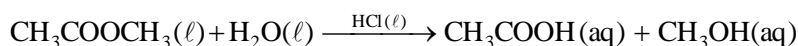
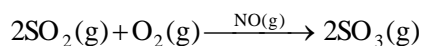
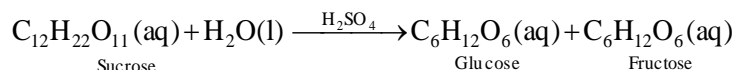
(a) Homogeneous catalysis

(b) Heterogeneous catalysis

(a) Homogeneous catalysis

If the catalyst is present in the **same phase as the reactants**, it is called a homogeneous catalyst and this type of catalysis is called homogeneous catalysis.

Ex:

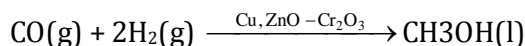


b) Heterogeneous catalysis:

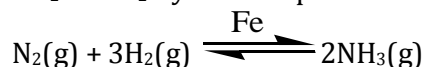
In this type of catalysis the catalyst is present in a different phase than that of the reactants. In heterogeneous catalysis, catalyst is generally a solid and the reactants are generally gases but sometimes liquid reactants are also used. It is also known as surface catalysis.

Ex:

i) Synthesis of methyl alcohol (CH₃OH) from CO and H₂ using a mixture of copper, ZnO and Cr₂O₃ as catalyst.



ii) Manufacture of ammonia from N₂ and H₂ by Haber's process using iron as catalyst.



Theories of Catalysis

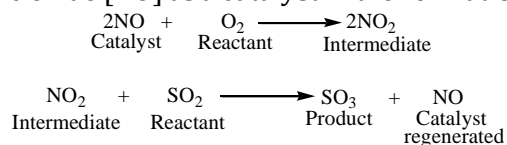
Intermediate Compound Formation Theory

This theory explains **homogeneous catalysis mainly**.

According to this theory, the catalyst combines with one of the reactants to give an intermediate compound. This compound intermediately 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 SO₃ is explained as follows:

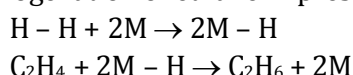


Adsorption Theory:

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:

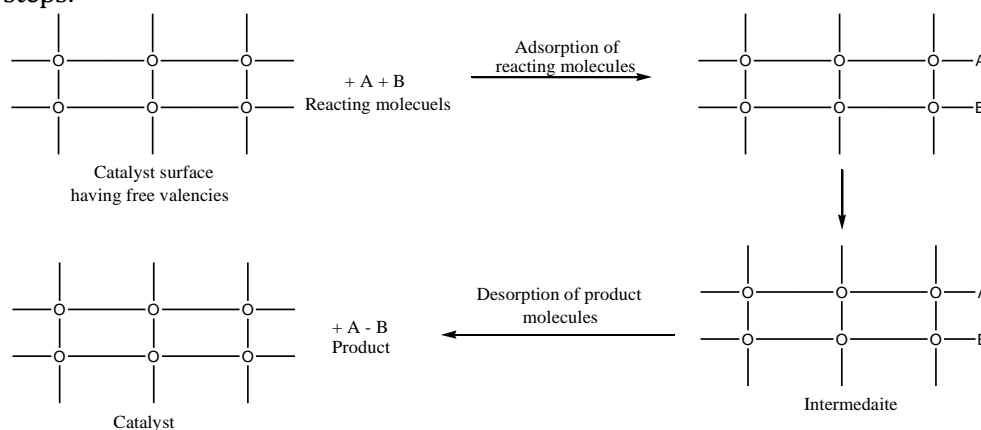
- (i) The reactant molecules are adsorbed on the surface of the catalyst at adjacent point. Adsorption leads to higher concentration of the adsorbed reactant on the surface of a catalyst.
- (ii) As adsorption is an exothermic process, the heat of adsorption provides the necessary activation energy for the chemical reaction to proceed and enhance rate of greater.
- (iii) 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 occurs at the surface of the catalyst at a much faster rate.

e.g. Hydrogenation of ethane in presence of Ni



Modern Adsorption Theory of Heterogeneous Catalysis

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



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

- i) Diffusion of reactants to the surface of the catalyst.
- ii) Adsorption of reactant molecules on the surface of the catalyst.
- iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
- iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.
- v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the basis for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving 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 effective even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.

General Characteristics of Catalytic Reactions

1. The catalyst is unchanged chemically at the end of the reaction:
2. Only a small quantity of the catalysts is generally needed:
3. The catalyst does not alter the position of equilibrium in a reversible reaction
4. The catalyst does not initiate the reaction

Important feature of solid catalysts

(a) Activity

It is ability of a catalyst to catalyse a process. The activity of a catalyst depends upon the strength of chemisorption to a large extent.

(b) Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with H₂ and CO using different catalysts we get different products.

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

Shape - Selective Catalysis by Zeolites

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

The catalysis that depends upon the **pore-structure of the catalyst and molecular sizes of reactants and product molecules** is called **shape selective catalysis**. e.g. **zeolites** are shape selective catalysts due to their honey-comb structure. ZSM-5 is used for converting methanol to gasoline.

Zeolites are micro-porous aluminosilicates of the general formula $M_{x/n} [(AlO_2)_x (SiO_2)_y] \cdot zH_2O$, where n is the charge on the metal cation M^{n+} which is usually Na^+ , K^+ or Ca^{2+} and z is the number of water molecules of hydration which are highly variable. They are three dimensional network silicates in which some silicon atoms are replaced by Al giving Al - O - Si frame work.

Enzymes

Thus, enzymes are defined as biological catalysts. Chemically, all enzymes are globular proteins with high molar mass ranging from 15,000 to 1,000,000g mol⁻¹ and form colloidal solution in water.

Properties of Enzymes: Some important properties of enzymes are:

(i) Specificity

Each enzyme catalyses only one chemical reaction.

(ii) Efficiency

Enzymes are very efficient catalysts. They speed up rate of a reaction by factors of upto 10²⁰.

(iii) Small quantity

Only small amounts of enzymes can be highly efficient.

(iv) Optimum temperature and pH

Enzyme catalysed reactions is maximum at particular pH called optimum pH, which is between 7.4 and temperature of 298-310K under one atmospheric pressure.

(v) Enzyme activators (Co-enzymes)

The activity of certain enzymes is increased in the presence of certain substances called co-enzymes. e.g. if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced. The activators are generally metal ions like Na^+ , Cu^{+2} , Mn^{+2} , Co^{+2}

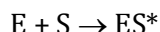
(vi) Influence of Inhibitors and poisons:

The action of enzymes is controlled by a number of mechanisms and are inhibited by certain organic molecules called **inhibitors**. **Ex drugs**

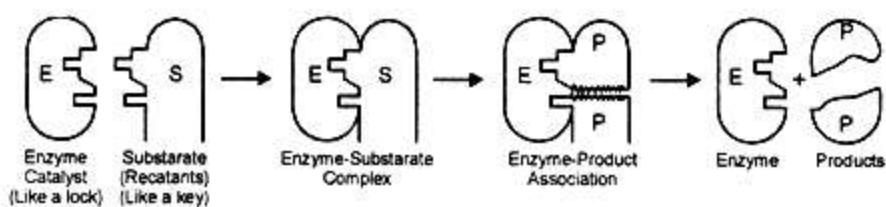
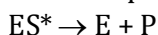
Mechanism of Enzyme Catalysis

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

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



Step 2: Decomposition of the activated complex to form product.



Mechanism of enzyme catalysed reaction

Colloidal State

Comparison of Suspensions Colloids and True Solutions

S.No.	Property	True Solution	Colloids	Suspension
(i)	Particle size	< 10Å	10Å to 10 ³ Å	> 10 ³ Å
(ii)	Visibility	Not visible with any of the optical means	Visible with ultramicroscope	Visible with naked eye
(iii)	Separation (a) with filter paper (b) with membranes	Not possible Not possible	Not possible Possible	Possible Possible
(iv)	Diffusion	Diffuses rapidly	Diffuses very slowly does not settle	Does not diffuse
(v)	Settling	Does not settle	but it may settle under Centrifuge	Settles under gravity
(vi)	Nature	Hemogeneous	heterogeneous	Heterogeneous

(vii)	Appearance	Clear	Generally clear	Opaque
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Colloids and their Classification

(i) Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending on the physical states of dispersed phase or dispersion medium, colloidal solutions are of eight types:

Dispersed phase	Dispersion Medium	(appearance)	Name	(e.g.) alloys
Solid	Solid	(solid)	Solid Sol	Coloured glasses, Pearl, Ruby, alloys, gems
Solid	Liquid	(liquid)	Sol	Ag, Sol, Au, Sol., S. Sol., Muddy water, gelatin in water, paint
Solid	Gas	(gas)	Aerosol	Smoke, dust, strom
Liquid	Liquid	(liquid)	Emulsion	Milk, medicines, oil water, blood
Liquid	Solid	(solid)	Gel	shampoo, jelly, cheese, butter , all fruits and veg, polish, curd
Liquid	Gas	(gas)	Aerosol of liquid	Cloud, fog, mist, spray
Gas	Liquid	(liquid)	Foam	Soap leather, whipped cream, shaving cream, soda water, froath
Gas	Solid	(solid)	Solid foam	Styrene foam, Foam rubber

A colloidal dispersion of **one gas in another is not possible** since the two gases would give a homogenous molecular structure.

(ii) Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

(a) Lyophilic Sols

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (solvent-linking). For example – dispersion of gelatin starch, gum and proteins in water. Such colloidal solutions can be easily prepared in water directly so called intrinsic colloids. These solutions are stable known as reversible colloids since the residue left on evaporating can be readily transferred back into colloidal state by adding water. These sols are quite stable and cannot be easily coagulated.

(b) Lyophobic Sols

Colloidal solution in which the dispersed phase has no affinity or attraction for the dispersion medium are called Lyophobic colloid (solvent hating) solutions. Colloidal solutions of metals which have negligible affinity for solvents are examples of this type. Lyophobic colloidal solutions are less stable. On evaporation of solvent the residue cannot be easily transferred back into colloidal state by ordinary mean hence also called extrinsic colloid. Therefore, lyophobic colloids are also called **irreversible colloids**. Lyophobic sols need stabilizing agents for their preservation. Such sols are readily precipitated on addition of small amount of electrolytes by heating or by shaking.

(iii) Classification Based on Type of Particles of the Dispersed Phase

Depending upon the type of the particles of the dispersed phase, colloids are classified as:

(a) Multimolecular Colloids:

On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter < 1 nm). The species thus formed are called **multimolecular** colloids. For example, a gold sol may contain particles of various sizes having many atoms. Sulphur sol consists of particles containing a thousand or more of S₈ sulphur molecules.

(b) Macromolecular Colloids

These are formed by macromolecules which have bigger size than the colloidal particle but as soon as they are put in suitable solvents, they get dissociated to form smaller particle of the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respects. Examples of naturally occurring macromolecules are starch, cellulose, proteins and enzymes; and those of man-made macromolecules are polythene, nylon, polystyrene, synthetic rubber, etc.

(c) Associated Colloids (Micelles)

There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called **micelles**. These are also known as **associated colloids**. The formation of micelles takes place only above a particular temperature called **kraft temperature (T_k)** and above a particular concentration called **critical micelle concentration (CMC)**. Surface active agents such as **soaps and synthetic detergents** belong to this class.

Mechanism of Micelle Formation

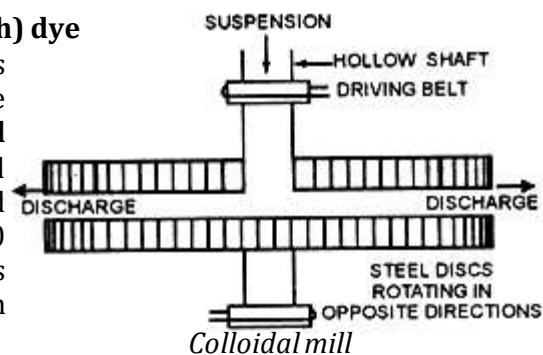
Note: The soaps and detergents form micelles in water only because of the presence of charge on their molecules. Micelles formation does not occur in solvent like ethyl alcohol since it is not as polar as soaps. That is why only water is used for the washing of dirty clothes.

Method of Preparation of Colloidal Solution

(a) Dispersion Method

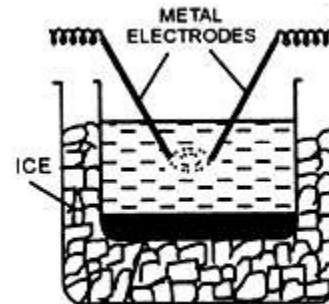
1. Mechanical dispersion (e.g. black ink, paint, varnish) dye

Solid material is first finely grounded by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into **the colloid mill**. The simplest form of colloid mill consist of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are grounded down to colloidal size and are then dispersed in liquid.

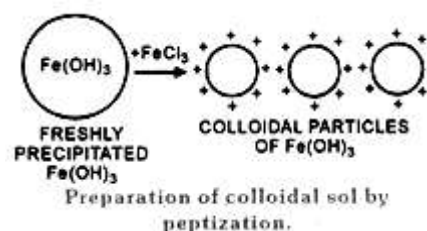


2. Electrical Dispersion (Bredig's arc Method) (e.g. metal sol.)

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.



Bredig's method



3. Peptization

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed **peptization**, the electrolyte used is called a **peptizing agent**. During Peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which cause electrostatic repulsion and ultimately break up into smaller particles of the size of a colloid.

Ex:

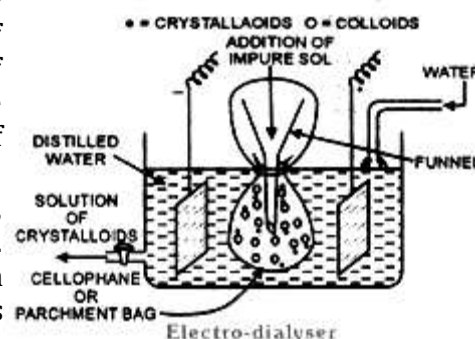
Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms, a dark raddish brown solution. Ferric chloride acts as a peptizing agent.

Purification of Colloidal Solutions

- **Dialysis:**

ialysis is a process of removing a dissolved substance (impurities) from a colloidal solution by means of diffusions through semipermeable which is a bag of suitable membrane containing colloidal solution to be purified, placed in a vessel (or continuous flow of water).

When potential difference is applied across the membrane, ions in the solution move faster towards opposite electrode. This process is called **electrodialysis**. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in figure. The ions present in the colloidal solution migrate out towards the oppositely charged electrodes.



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Ultra-filtration: Such filter are called ultrafilters. However, the pores of filter paper can be reduced in size by impregnating with colloidion solution to stop the flow of colloidal particles. **The usual colloidion is a 4 % solution of nitro-cellulose in a mixture of alcohol and ether.** An ultra-filter paper may be prepared by soaking the filter paper in a colloidal solution, hardening by formaldehyde and then finally drying it.

- **Ultracentrifugation:** In this method, the impure sol is taken in a tube which is placed in an ultracentrifuge. In this machine, the tube is rotated at a very high speed. As a result, the colloidal particles settle down at the bottom of the tube whereas the crystalloids and other soluble impurities remain in the solution. This solution is decanted off and the colloid particles are remixed with the dispersion medium to give the pure colloidal sol.

Properties of Colloidal Solution

- **Colour:**

The colour of hydrophobic sol 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. The colour of colloidal solution also changes with the manner in which the observer receives the light.

For example, a mixture of milk and water appears blue when viewed by reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour, as the size of particles increases, it appears purple, then blue and finally golden. When light emitted by the setting sun passes through the blanket of dust, the blue part of the light is scattered away from our eyes and at the same time the red colour is seen. This sun appears red while setting.

- **Optical Properties: Tyndall effect**

The path of the light shows up a hazy beam of cone. This was first observed by Faraday and later by Tyndall and is known as **Tyndall effect**. It may be defined as the scattering of light by the colloidal particles in a colloidal sol. The bright cone of the light is called "**Tyndall cone**". The Tyndall effect is due to the fact that the colloidal particles absorb light and scatter it in all directions in a colloidal dispersion. Tyndall effect is observed only when the following two conditions are satisfied

- (i) The diameter of the dispersed particles is not much smaller than the wavelength of light used.
- (ii) The refractive index of dispersed phase & the dispersion medium differ greatly in magnitude.

Some examples of Tyndall effect are:

- (i) Blue colour of sky and sea water.
- (ii) Visibility of tails of comets.
- (iii) Twinkling of stars.

- **Kinetic Properties: (Brownian Movement)**

The continuous rapid zig-zag motion of a colloidal particle in the dispersion medium is called "**Brownian movement**" (first observed by British botanist Robert Brown).



The Brownian movement has been explained to be due to the unbalanced bombardments of the particles by the molecules of **dispersion medium**. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is **responsible for the stability of sols**.

- **Charge on Colloidal Particles:**

Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of +ve or -ve ions. When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

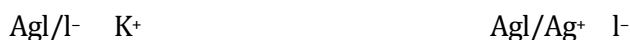
- (a) When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to AgNO_3 solution, positively charged sol results due to adsorption of Ag^+ ions from dispersion medium.



- (b) If FeCl_3 is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH^- ions.



Having acquired a positive or a negative charge by selective adsorption on the surface of a colloidal particle as stated above, this layer attracts counter ions from the medium forming a second layer, as shown below.



The combination of the two layers of opposite charges around the colloidal particle is called **Helmholtz electrical double layer**.

This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

The presence of equal and similar charges on colloidal particle is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coagulating or aggregating when they come closer to one another.

Electrical Properties:

- (a) **Stability of colloidal sols - Electrical charge on colloidal particles:** The dispersed phase particles carry either +ve and -ve charge and dispersion medium has an equal and opposite charge. The particles repel one another and hence do not coagulate, thus making the colloid stable.

(b) **Cataphoresis or Electrophoresis** is the movement of colloidal particles either towards cathode or anode, depending on their charge, under the influence of an electric field. Electrophoresis is used to determine nature of charge

Positive sol. Sol $\text{Fe}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, basic dye stuffs (methylene blue, methyl violet, Haemoglobin).

Negative Sol. Metal & sulphides: CdS , As_2S_3 , Cu , Ag , Pt and dyes (congo red, Prussian blue, silicic acid, gum, charcoal).

(c) **Electro Osmosis:**

The movement of dispersion medium under the influence of applied potential is known as "Electro-osmosis."

(d) **Coagulation or flocculation: [Process of setting of colloidal particle]**

The flocculation and setting down of the discharged sol particles is called coagulation or the precipitation and can be brought about in following ways:

- | | |
|---|--------------------------|
| (a) By addition of electrolyte. | (b) By electrophoresis |
| (c) By mixing two oppositely charged sols. (mutual precipitation) | |
| (d) By boiling | (e) Persistent dialysis. |

(a) **By Addition of Electrolytes:**

When an electrolyte is added in excess to a sol, the electrolyte furnishes both types of ions in solution. The oppositely charged ions get adsorbed on the surface of colloidal particles. This causes neutralization and thereby the size and mass of colloidal particle increases and it becomes a suspension particle. Due to greater volume and greater mass these suspension particles settle down i.e., they coagulate. The ion responsible for neutralization of charge on the particle is called **flocculating ion**.

- Coagulation or flocculation is the process of bringing colloidal particles closer so that they aggregate to form larger particle that precipitate and settle down or float on the surface. It is usually done by addition of an electrolyte. Effective ions or electrolyte are those which carry charge opposite to colloids.
- **Hardy - Schulze rule** states that "greater is the valency of the oppositely charged ion of electrolyte being added, faster is the coagulation: e.g. for a negatively charged sol, the order is: $\text{Al}^{3+} > \text{Ba}^{2+} > \text{K}^+$, for a positively charged sol the order is: $\text{Fe}(\text{CN})_6^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$
- Coagulating value is the **minimum amount of electrolyte in milli moles** required to coagulate a 1 lit of solution of sol in two hours. The smaller the quantity needed, the higher will be the coagulating power of anion.

(b) **By Electrophoresis:**

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

(c) **By Mixing Two Oppositely Charged Sols:**

The mutual coagulation of two sols of opposite charge can be effected by mixing them. For e.g. $\text{Fe}(\text{OH})_3$ (positive sol) and Arsenious sulphide (negative sol) when mixed join and coagulate.

(d) **By Boiling**

Sols such as sulphur and silver halides disperse in water, get coagulated when boiled, due to increased collisions between sol particles and water molecules, which remove the adsorbed layer from the sol and therefore the sol particles settle down.

(e) **Persistent dialysis:**

The stability of a colloidal sol is due to presence of a small amount of the electrolyte. On prolonged dialysis, the electrolyte is completely removed. As a result, the colloidal sol becomes unstable and gets coagulated.

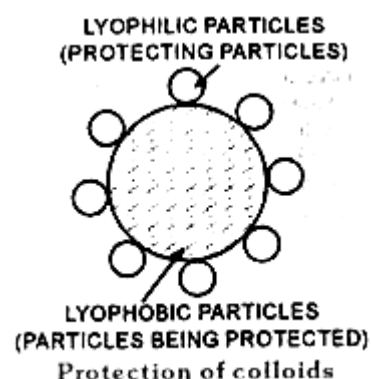
Coagulation of Lyophilic Sols:

Lyophilic sols are stable due to **charge and solvation** of the colloidal particles. When these two factors are removed, a lyophilic 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 of Colloids:

- Lyophilic sols are more stable than lyophobic sols hence they are used as protective colloids to increase the stability of lyophobic sols, e.g. addition of gums, gelatin etc. to certain metal sols. These sols are called **Protective colloids**.
- Protective action of lyophilic sols is explained due to formation of a thin layer around the lyophobic sol particles, thus preventing them from coming closer.



Emulsions

Emulsion is a colloidal system involving one liquid dispersed in another, provided both are immiscible. Some commonly known emulsions are Milk, butter, milk cream, cold cream, vanishing cream, etc. There are many drugs and medicines which are also in the form of emulsions e.g. various ointments, cod liver oil etc.

- **Types of emulsions:**

Depending upon the type of proportions in which these constituents are present, emulsion have been classified into two types.

1. **Oil in water emulsions** (O/W) are those in which oil is the dispersed phase and water is the dispersion medium. Milk is a common example in which liquid fats are dispersed in water. Similarly, if a few drops of nitrobenzene (oil) is added to water, an emulsion results. Varnishing cream is another example of this type.
2. **Water in oil emulsions** (W/O) are those in which water is the dispersed phase and oil is the dispersion medium, Butter is an example of water in oil emulsion in which water is dispersed in oil. Cod liver oil and cream are the other examples of these emulsions.

- **Emulsifier and Emulsifying Agents**

An emulsifier or emulsifying agent is a substance which helps in stabilizing an emulsion of oil and water and, thus, prevents them from getting apart. The commonly used emulsifying agents for O/W emulsion are soaps, detergents, lyphilic colloids, proteins, gums and agar etc. & for W/O emulsion are heavy metal salt of long chain fatty acids etc. The preparation of emulsion in the presence of an emulsifier is known **emulsification**. The role of an emulsifier in stabilizing an emulsion can be explained as :

Gels

- These are colloidal systems where liquids are the dispersed phase and solids act as dispersion medium, e.g. curd, cheese etc. When a warm solution of gelatin is cooled it sets to a semisolid mass which is gel. This process is called **gelation**.

Applications of Colloidal System

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

1. **Medicines** in colloidal form can be easily adsorbed by body tissues & hence are more effective e.g. colloidal antimony is used in curing kalaazar, argyrols is a silver sol used as an eye lotion. Colloidal gold is used for intramuscular injection Neutralization of excess acidity by $\text{Al}(\text{OH})_3$, Milk of magnesia, an emulsion, is used for stomach disorders, colloidal sulphur – germ killer, kalolin used to remove toxins from intestine. Cod liver oil is emulsion of oil in water. Some ointment, antibiotics, Penicillin, streptomycin are produced in colloidal form. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.
2. **Food:** Gelatin in ice-cream. It preserve smoothness and prevent ice crystals formation, protein, milk, cheese are colloids, fruits, jelly, cream, bread is dispersion of air in baked dough.
4. **Purification of water by alums:** Water from rivers or lakes are sometimes used for domestic and industrial purpose after purification. The water from lake or river is turbid due to the presence of fine clay particles which are negatively charged. These can be removed by adding potash alum or aluminium sulphate. Al^{3+} ions from potash alum o aluminium sulphate neutralize the negative charge on clay particles. This causes the coagulation of clay particles which settle down leaving water which is clear of further treatment.
5. **Stoppage of bleeding from a fresh cut:** The bleeding from a fresh cut can be immediately stopped by applying a concentrated solution of ferric chloride or potash alum. Blood consists of colloidal particles of haemoglobins which carry positive charge on them. When ferric chloride or alum is applied on the cut these colloidal particles get their positive charge neutralized by the anions available from these substances in solution. In the absence of the charge, they get coagulated and the bleeding stops.
6. **Delta formation:** Formation of delta due to coagulation of colloidal particles of river water by sea salt. The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand, contains positive ions such as Na^+ , Mg^{2+} and Ca^{++} . As the river water meets sea water, these ions discharge the sand or clay particles which are precipitated as delta.
7. **Photographic plates and films:** Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.
8. **Fog, mist and rain.** In extremely cold weather, the temperature is very low. The water droplets (moisture) present in air condense on the surface of the dust particles that are suspended. Since these are colloidal in nature, they float in air in the form of mist or fog or extremely low, these colloidal droplets grow in size. They become bigger and bigger and when atmosphere is not in a position to hold them, they come down as rain.

In the winter season, the atmosphere generally becomes very foggy and visibility is quite poor. This leads to lot of inconvenience for vehicular movement and result in major accidents. Farmers are in the habit of burning husk in the open fields. This results in the release of unburnt carbon particles in the atmosphere. The water droplets condense on them and they appear as fog. But actually this is **smog** and not **fog** and is extremely injurious to health. This can lead to asthma, lung as well as throat cancer. It is very essential to educate our farmer community about these harzards.

9. **Purification of Blood:** Blood is a colloidal solution. It contains toxic waste products such as urea and uric acid which pass through the membrane while colloidal sized particles of blood proteins hemoglobin are retained. Kidney failure, therefore, leads to death due to accumulation of poisonous waste products in the blood. Blood is purified by dialysis.
10. **Chemical warfare: (Smoke screen):** 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 lead through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contract 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. Colloidal dispersions of certain substance, like TiO_2 (as dispersed phase) in air (as the dispersion medium) are used a smoke screens in warfare for the purpose of concealment. The dispersed phase particles (i.e. TiO_2) being very heavy rapidly drops down in the form of a curtain of drizzling whiteness.
11. **Artificial rain:** Tiny water droplets in clouds are electrically charged. In any cloud all such water particles carry the same charge. Artificial rain can be caused by spraying oppositely charged dust or fine sand or precipitates like AgI (which has a crystal structure similar to ice and as such particles of AgI can act as nuclei for precipitation) on to a cloud. Even certain salts in the form of fine particles can be sprayed. The neutralization of charge results in coagulation of water droplets or rain. Cloud-brust—a natural disaster resulting in a very heavy down pour over a very short time is believed to occur due to the mutual discharge of oppositely charged clouds.
12. **Cleaning Action of Soaps and Detergents:** Dust and dirt particles on clothes are colloidal in nature. Soaps being sodium salts of higher fatty acids coagulate them which become suspension particles called micelle and roll out due to greater volume and greater mass.
13. **Rubber Industry:** Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of Latex. Rubber is electroplated on metals when they act as anode.
14. **Tanning:** Process of hardening of leather is called tanning. Tannin obtained from plants is negatively charged sol and animal hides are also sol containing positively charged particle. Mutual coagulation results in hardening of leather.